

BOOK OF ABSTRACTS



**23rd European Conference
on Thermophysical Properties**

June 21 to June 24, 2026



TOPICS

- Transport properties
- Thermodynamic properties
- Thermophysical properties
- Advanced Experimental Techniques
- Advanced Materials Design and Characterisation
- Thermodynamic modelling for sustainable processes



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Plenary Lectures



Made to Measure: High-Precision Measurements of the Speed of Sound in Fluids

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Measurements of the speed of sound in a homogeneous fluid provide a rich source of thermodynamic information. In metrology, such measurements carried out in a monatomic gas with an uncertainty on the order of 1 ppm were used to establish the value of the Boltzmann constant prior to the revision of the SI system of units in 2018 [1]. A similar approach can be used for primary thermometry [2]. More generally, sound-speed measurements are used to access the thermodynamic properties of pure fluids and mixtures for the purposes of parameterizing, testing or optimizing thermodynamic models.

Two general approaches have emerged to permit measurements of low uncertainty over very wide ranges of conditions. Low-frequency acoustic resonators are ideally suited to measurements in gases up to moderate densities. These instruments are supported by an acoustic model that captures the physics of the system in detail, including key aspects such as visco-thermal boundary layers and coupling of gas and wall vibration. With such methods, relative uncertainties of below 0.01% can be achieved in a wide range of conditions [3]. Meanwhile, ultrasonic pulsed methods are ideally suited to measurements in liquids and dense supercritical fluids. The dual-path pulse-echo method in particular has been highly developed for such measurements [4].

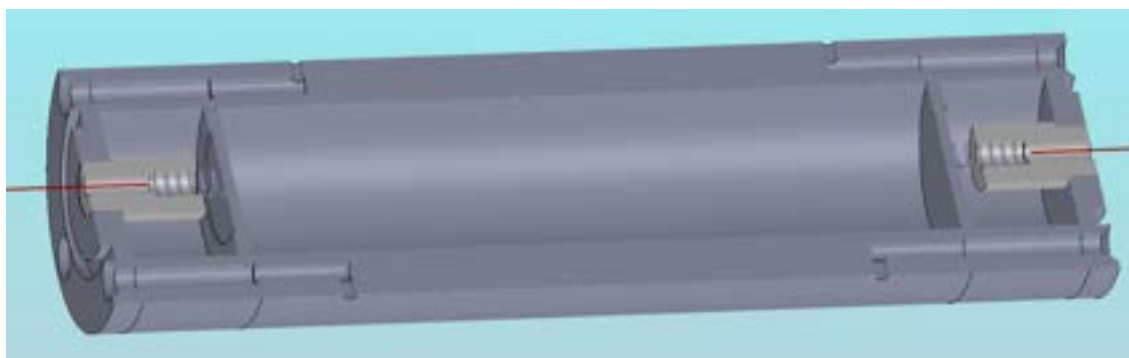


Figure 1. Cylindrical acoustic resonator for sound-speed measurements in compressed gases.

Currently, there is significant new interest in hydrogen and other light substances at extreme conditions. The thermodynamic properties of pure hydrogen are less well studied than those of other important industrial fluids and technological interests extend up to pressures of 100 MPa in the gas phase [5] and down to temperatures of 20 K for the liquid. This range of conditions presents significant measurement challenges the resolution of which will be described.

Significant references

1. J. Fischer, et al., *Metrologia* vol. 55, (2018) R1-20.
2. M.R. Moldover, R.M. Gavioso, J.B. Mehl, L. Pitre, M. de Podesta, J.T. Zhang, *Metrologia* vol. 51 (2014) R1-19.
3. M.R. Moldover, K.A. Gillis, J.J. Hurly, J.B. Mehl, J. Wilhelm, in *Experimental Methods in the Physical Sciences*, ed. by M. Levy, H.E. Bass, R. Stern (Academic Press, 2001), 377–427.
4. K. Meier, S. Kabelac, *Rev. Sci. Instrum.* 77, (2006) 123903.
5. T.-T.-G. Nguyen, C. Wedler, S. Pohl, D. Penn, R. Span, J.P.M. Trusler, M. Thol, *J. Chem. Thermodyn.* Vol. 198, (2024) 107341.

25 years of PC-SAFT - the journey towards modeling complex molecules

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PC-SAFT (Perturbed-Chain Statistical Associating Fluid Theory) was proposed in 2001 as an extension of SAFT-type models with the particular focus on modeling polymer systems. We took advantage of the physical background of SAFT and its ability to model the formation of H-bonds in associating systems. To model long-chain molecules, we replaced the hard-sphere reference by a hard-chain reference. The latter did not only remarkably improve the modeling results for polymers but for non-spherical molecules in general and is widely used today. Since then, PC-SAFT was further extended by several research groups to account for the impact of polarity (PCP-SAFT), to describe electrolytes (ePC-SAFT), polymeric networks, and even polyelectrolytes (pePC-SAFT).

These model developments allowed for also extending the range of applications and this will be the main focus of this talk. The journey started from modeling phase equilibria related to the production, purification and recycling of polymers, which was then extended to model the swelling of polymer networks and hydrogels. The latter are swollen by water or aqueous mixtures of biological relevant molecules which brought us to modeling a whole bunch of those molecules, such as organic osmolytes, amino acids or pharmaceutical compounds. The talk will illustrate applications of PC-SAFT to those systems covering all types of phase equilibria (VLE, LLE, and SLE) and even reaction equilibria. Accounting for activity coefficients using PC-SAFT for example allowed predicting the influence of solvent(s) and electrolytes on both yield and kinetics of (bio)chemical reactions.

Recent research of our group focuses on using PC-SAFT as an in-silico tool for process and product design related to the production, purification, and formulation of active pharmaceutical ingredients (APIs). APIs usually are crystalline solids and only very little soluble in aqueous media. To improve their bioavailability, APIs can be stabilized in their amorphous form in complex mixtures based on lipids or polymers, so-called formulations. The talk illustrates that thermodynamic predictions based on PC-SAFT can remarkably reduce the experimental effort for identify promising excipients, even including surfactants, and allow for reliable predictions of formulation stability during production and storage and of their release behavior in the human body.



Role of Cryogenic H₂, CO₂, and CH₄ in Decarbonised Energy Systems: Challenges and Opportunities

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As advanced economies seek to decarbonise, clean hydrogen has been identified as a missing link that can help solve the major challenges of storing renewable power and enabling the cost-effective supply of low-carbon energy. However, this is not the first time hydrogen has been promoted as the key to transitioning our energy system and prudence about over-hyped claims and projections is warranted. While there are important differences between the present opportunities for hydrogen and those of the past, key challenges remain. Recently, the imperative of energy security has revealed that natural gas will play a sustained role in the global energy supply and trade for many decades to come. This means that a new international trade in the capture, transport, use and storage of CO₂ will become increasingly important if decarbonisation objectives are to be met.

A common feature of the three primary molecules, H₂, CH₄ and CO₂, central to future energy and decarbonisation supply chains is the need to store, transport and handle them as cryogenic liquids. The associated engineering challenges vary with each fluid, given their significantly different temperature and pressure ranges, likely impurities, and the technical maturity of the associated liquefaction and storage systems. However, there are many commonalities and opportunities for concepts proven by the well-established LNG industry to be tested for decarbonisation applications. The takeaway idea from this lecture is how technologies and lessons from the LNG industry are central to the development of future CO₂ and hydrogen supply chains.

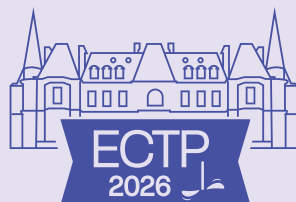
Oral Presentations



1.1

Transport properties

Viscosity Modelling



Influence of the Conformal State Point and Binary Interaction Parameters on ECS Viscosity Predictions for Asymmetric Mixtures

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The prediction of transport properties such as viscosity and thermal conductivity is essential for the design, optimization, and safety of industrial processes. In contrast to thermodynamic properties, transport properties are comparatively poorly described, particularly for mixtures containing long-chain or strongly asymmetric components, where limited experimental data exists. As a result, predictive models play a crucial role in determining the behavior of transport properties of mixtures. Among these, the Extended Corresponding States (ECS) approach is one of the most widely applied models.

Originally introduced by Ely and Hanley [1], the ECS model has been continuously refined, with recent implementations reported by Chichester and Huber [2] and Huber [3]. It is based on the corresponding states principle and makes use of the conformal state point (CSP), at which the residual contribution of a chosen reference fluid is evaluated and subsequently scaled to the mixture property via a correction factor. The accuracy of the ECS prediction therefore strongly depends on the determination of the CSP as well as on possible binary interaction parameters. While the method performs well for mixtures made up of similar components, its application to the aforementioned systems is considerably more challenging.

This work investigates the challenges associated with determining the CSP and evaluates its influence on ECS predictions. Using asymmetric mixtures of CO₂ + *n*-alkanes as representative test systems, the impact of the CSP variation on viscosity predictions is analyzed and compared with experimental data. Furthermore, the study demonstrates how the binary interaction parameters within the correction factor can improve the model performance, particularly for systems with high asymmetry. The findings highlight both the limitations of current ECS implementations and potential pathways for enhancing their predictive accuracy.

Acknowledgment

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References

1. J. F. Ely, H. J. M. Hanley, *Prediction of transport properties. 1. Viscosity of fluids and mixtures*, Ind. Eng. Chem. Fundamen., 20(4):323-332, 1981.
2. J. C. Chichester, M. L. Huber, *Documentation and assessment of the transport property model for mixtures implemented in NIST REFPROP (version 8.0)*, NIST Internal Report 6650, 2008.
3. M. L. Huber, *Models for viscosity, thermal conductivity, and surface tension of selected pure fluids as implemented in REFPROP v10.0*, NIST Internal Report 8209, 2018.

Effective Thermophysical Constants of Thousands of Fluids. II: Lennard-Jones and residual entropy scaling parameters for viscosity

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In our previous work [1], we compiled, examined, and fitted the critical constants (critical temperature, critical pressure, critical density) and acentric factors of 1422 pure fluids, based primarily on three sources: NIST REFPROP 10.0, NIST ThermoData Engine 10, and the Dortmund Data Bank 2023. That study represented the first part of a series aimed at determining effective thermophysical constants for thousands of fluids to enable reliable calculations of key thermophysical properties (including density, phase equilibria, heat capacity, entropy, enthalpy, viscosity, and thermal conductivity) over wide pressure and temperature ranges. The present work constitutes the second part of the series and focuses on the determination of Lennard–Jones (L-J) parameters and residual entropy scaling (RES) parameters for viscosity. The L-J parameters (the molecular diameter σ and the potential well depth ϵ/k_B) are used to compute dilute-gas viscosity via Chapman–Enskog theory. Effective values of σ and ϵ/k_B were obtained either by anchoring to REFPROP 10.0 calculations or by estimating them using new correlations linked to critical constants. The RES framework correlates residual viscosity with residual entropy, and in this work we adopt a recently developed two-parameter RES correlation from our forthcoming study. The two RES parameters were determined either by fitting to experimental viscosity data compiled from the TDE and DDB databases or, for fluids without available data, by estimating them using symbolic-regression correlations based solely on critical constants. As in our previous work, the quality of all effective constants was rigorously assessed, providing guidance for future experimental studies. The resulting parameters will be implemented in the OilMixProp software for practical applications.

Acknowledgement

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Significant references

1. X. Yang and M. Richter, *J. Chem. Eng. Data*, vol. 70 (2025), pp. 2911-2946

A prediction of viscosity for helium-methane binary system based on entropy scaling of viscosity

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1. Objectives

The primary objective of this study is to develop a reliable and thermodynamically consistent model for predicting the viscosity η of the helium-methane binary system across wide ranges of temperature, pressure, and composition. Viscosity data for this mixture remains scarce. This work aims to leverage the theoretical framework of entropy scaling of viscosity to address this data gap and establish a robust correlation superior to conventional empirical models.

2. Methodology

The methodology is based on the principle of entropy scaling[1,2], which posits that the reduced viscosity η^* is a unique function of the residual (or excess) entropy S_{ex} . The relationship is typically expressed as:

$$\eta^* = \eta \cdot f(\rho, T) = g(S_{ex}) \quad (1.1)$$

where $f(\rho, T)$ is a characteristic scaling factor.

To implement this, the highly accurate Helmholtz Equation of State (HEoS) was first employed to calculate the necessary thermodynamic properties, including density ρ and the residual entropy S_{ex} , for the He-CH₄ mixture across the target P - T - x space. The pure component scaling parameters for He and CH₄ were established using available experimental data. These parameters were subsequently extended to the binary system by applying a generalized, composition-dependent mixing rule for the residual entropy, allowing the model to accurately predict mixture viscosity without extensive mixture-specific experimental fitting.

3. Results

The developed entropy scaling model successfully correlated the viscosity data, demonstrating excellent agreement with the available experimental data for both pure components and the He-CH₄ mixture. The calculated values typically fell within an average absolute deviation (AAD) of 2% of the experimental mixture viscosities. Crucially, the model successfully predicted viscosity values in regions where experimental data is completely non-existent, particularly in the high-pressure and low-composition CH₄ regimes. The scaling function proved highly effective and robust, exhibiting a nearly universal relationship between the reduced viscosity and residual entropy across all tested compositions and conditions, validating the applicability of the entropy scaling concept to this complex binary system.

4. Conclusions

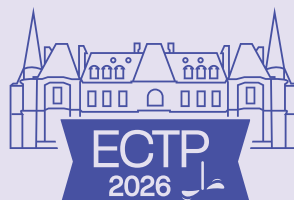
This study confirms the effectiveness of the entropy scaling principle as a powerful and accurate predictive tool for the viscosity of the He-CH₄ binary system. The resulting model provides a thermodynamically consistent, broad-range correlation that significantly expands the availability of reliable viscosity data for this mixture. This model is essential for accurate fluid dynamics simulations and is highly valuable for engineering applications in fields such as natural gas processing, cryogenic transport, and heat transfer design.

Significant references

1. Yang X, Xiao X, May EF, Bell IH. Entropy Scaling of Viscosity—III: Application to Refrigerants and Their Mixtures. J Chem Eng Data 2021;66:1385–98.
2. Bell IH. Entropy Scaling of Viscosity—II: Predictive Scheme for Normal Alkanes. J Chem Eng Data 2020;65:5606–16.

1.2

Transport properties Theory and Modelling



Towards a fundamental theory for transport properties of complex molecules

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Thermodynamic perturbation theory provides a powerful framework for linking the molecular-level description of fluids to their macroscopic thermodynamic properties at equilibrium. While further improvements are needed, the theory already delivers reliable predictions across a wide range of systems and has been successfully extended to complex molecular architectures such as chains and rings, as well as to sophisticated interactions including polar forces, quantum effects, and other important physical phenomena. However, a comparable theoretical framework for transport properties such as thermal conductivities, viscosities, and diffusion coefficients, that directly connects molecular information to macroscopic behavior across a broad range of conditions remains elusive. Such a framework could be considered the “holy grail” of transport property modeling.

State-of-the-art methodologies for calculating transport properties remain largely correlative in nature¹ and are neither grounded in molecular information nor predictive. An exception exists for simple fluids at infinite dilution, where kinetic theory enables highly accurate calculations of transport properties based solely on pair interactions. For certain cases, such as hydrogen at 20 K, kinetic theory is even considered to be more reliable and precise than experimental data.² However, extending kinetic theory to liquid-like densities has proven exceptionally challenging. In the mid-1960s, it was discovered that incorporating many-particle, correlated interactions caused the Enskog solutions of the Boltzmann equation to diverge. Although efforts to extend Enskog theory into the liquid regime were largely abandoned after this, research continued at moderate densities, where interactions are assumed to remain binary and uncorrelated. We argue that extending kinetic theory into the liquid-phase domain has received far too little attention over the past six decades, and we will share recent progress toward overcoming this limitation.

The Revised Enskog Theory (RET) extends classical kinetic theory to moderately dense fluids. Motivated by the success of Mie potentials in capturing the behavior of real fluids at equilibrium, we have developed a RET for Mie fluids.³ This approach successfully predicts transport properties up to the critical density, using pair potential parameters determined from equilibrium properties. By deriving physically meaningful transport lengths for energy and momentum transfer and incorporating them consistently into the theoretical framework, we have further extended RET to describe liquid-like densities at elevated temperatures.⁴ Our recent results indicate that a similar extension into the low-temperature liquid regime may soon be within reach. Ultimately, the goal is to develop a fundamental theory capable of predicting transport properties of fluid mixtures solely from molecular interaction data. We hope that the results may encourage renewed attention to kinetic theory as an underexploited foundation for modeling transport phenomena.

References

1. J.S. Løken, V.G. Jervell, M. Hammer, B. Hafskjold, T.T. Trinh, Ø. Wilhelmsen. *Fluid Phase Equilibria* 114584, (2025)
2. J.B. Mehl, M.L. Huber, and A. H. Harvey. *Int J. of Thermophysics* 31.4, 740-755, (2010)
3. V.G. Jervell and Ø. Wilhelmsen. *The Journal of Chemical Physics* 158.22 (2023)
4. V.G. Jervell and Ø. Wilhelmsen. *The Journal of Chemical Physics* 161.23 (2024)

Aqueous Hydroxide and Hydronium Diffusion-coefficients and Lifetimes Revealed by the Differences Between Experimental and Simulated Electrical Conductivity

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Grotthuss transfer (i.e. proton hopping), is the phenomenon that governs the transport of hydroxide and hydronium in aqueous systems¹. While most ions in water diffuse through vehicular transport (transport caused by Brownian motion of nonreacting molecular species), hydroxide and hydronium diffuse by structural transport as well (transport caused by chemical reactions). Because of this enhanced ion diffusion the electrical conductivity of hydroxide and hydronium mixtures is heightened as well. This makes aqueous KOH, NaOH, and HCl mixtures especially relevant for industrial applications where minimizing conductive losses through an electrolyte is critical. Grotthuss transfer has mostly been modelled with *ab initio* techniques, or with machine learned interatomic potentials. These methods are computationally expensive and cumbersome to set up. We propose a much simpler, entirely new method, utilizing our understanding of the limitations of classical forcefields.

We show that vehicular transport can be captured accurately with classical MD simulations and the structural transport component can be expressed with a biased random walk². Our method estimates the characteristics of this biased random walk from the difference between electrical conductivity computed with classical molecular dynamics (MD) simulations and experimental measurements. We have tested our method by simulating aqueous KOH, NaOH and HCl for a wide range (0-18 mol_{salt}/kg_{water} for KOH and NaOH, 0-10 mol_{salt}/kg_{water} for HCl) at 25 and 60 degrees Celsius. Simulation results show excellent agreement for ion lifetimes, self-diffusion coefficients, and the temperature dependence for the system density, viscosity, and self-diffusion coefficients of water and the nonreacting ions.

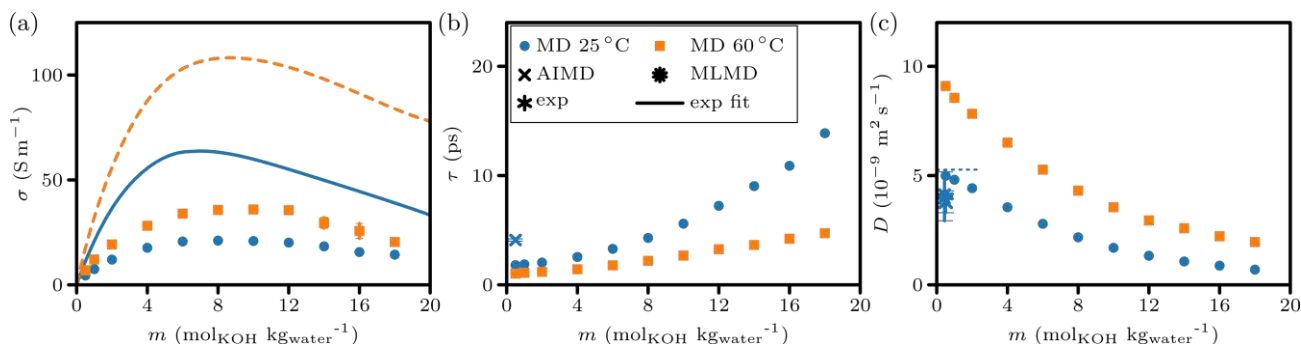


Figure 1. (a) Electrical conductivity, (b) hydroxide lifetimes, (c) and hydroxide self-diffusion coefficients of aqueous potassium hydroxide depending on the concentration at 25 and 60 °C. (a) Differences between the experimental fit and the MD simulation results are used to determine the characteristics of the biased random walk. (b) Hydroxide lifetimes increases with concentration and decreases with temperature. (c) Hydroxide self-diffusion coefficients at 0.5 mol/kg is equal to experimental results at infinite dilution, and close to both AIMD and MLMD results.

Significant references

- (1) Marx, D. Proton Transfer 200 Years after von Grotthuss: Insights from Ab Initio Simulations. *ChemPhysChem* **2006**, 7 (9), 1848–1870. <https://doi.org/10.1002/cphc.200600128>.
- (2) Fischer, S. A.; Dunlap, B. I.; Gunlycke, D. Correlated Dynamics in Aqueous Proton Diffusion. *Chem. Sci.* **2018**, 9 (35), 7126–7132. <https://doi.org/10.1039/C8SC01253A>.

Extending revised Enskog theory to liquid-like densities: Understanding collisional transfer of momentum and energy

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Since the 1920's, Chapman-Enskog theory has been widely used for the prediction of transport properties of dilute gases. However, at elevated densities the transfer of energy and momentum from one molecule to the next during a collision becomes a non-negligible mode of transport. This "collisional transport" of energy and momentum is captured by revised Enskog theory (RET), allowing the prediction of the viscosity, thermal conductivity, diffusion coefficients, and thermal diffusion coefficients of fluid mixtures at densities far exceeding the dilute gas state. Several previous works have investigated the residual transport properties predicted by RET, usually describing them through some form of excluded volume, which is captured by a temperature-dependent, empirically determined "core volume" of the molecules involved.

By considering the dynamics of momentum and energy exchange in binary encounters, we have found that the residual viscosity and thermal conductivity can be accurately predicted by two distinct "transfer lengths" that describe the transfer of momentum and energy between colliding molecules. Furthermore, we have derived expressions for the transfer lengths that can be evaluated directly from molecular interaction potentials. Additionally, the transfer lengths can be inferred from experimental transport property data. Combining RET with transfer lengths computed using accurate ab-initio potentials, the residual viscosity and thermal conductivity of several pure fluids and mixtures is accurately predicted up to liquid-like densities, as shown for argon in Figure 1.

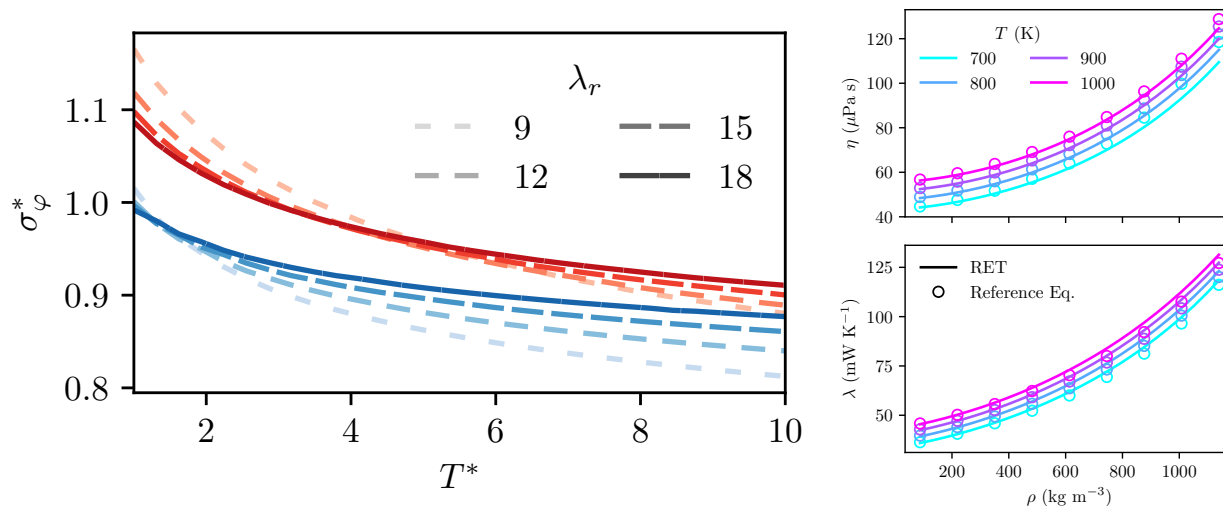


Figure 1. Left: The momentum transfer length (blue) and energy transfer length (red) of Mie fluids with different repulsive exponents as a function of temperature. Right: The viscosity (top) and thermal conductivity (bottom) of argon predicted by RET (lines) and computed from reference correlations (circles).

Acknowledgment

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Significant references

1. V. G. Jervell and Ø. Wilhelmsen, *J. Chem. Phys.*, vol. 158 (2023)
2. V. G. Jervell and Ø. Wilhelmsen, *J. Chem. Phys.*, vol. 161 (2024)

Viscosity, thermal conductivity and self-diffusion coefficient of the Lennard-Jones spline fluid: Evaluation of theories for a short-ranged potential

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The Lennard-Jones/spline (LJ/s) pair potential is truncated and splined such that the potential and its first derivative continuously approach 0 at $r^* \approx 1.74\sigma$, making it short-ranged. Extending previous work on the thermodynamic properties on the LJ/s fluid [1], we here present a systematic study on its transport properties [2]. To obtain the shear viscosity, thermal conductivity, and self-diffusion coefficient of the LJ/s fluid, both equilibrium and non-equilibrium molecular dynamics techniques were applied for states in the range $0.1 \leq \rho^* \leq 0.8$ and $0.7 \leq T^* \leq 10$. Four theoretical models were evaluated by comparing with simulation data. Both residual entropy scaling (RES) and extended corresponding state (ECS) theory with Argon as reference fluid proved capable of accurately describing the transport coefficients of the LJ/s fluid across the studied density-range. We also present a novel theory called “corresponding entropic states” (CES), which combines the concepts of entropy scaling and corresponding states. CES showed a comparable level of accuracy to RES and ECS, without any regression parameters. Revised Enskog theory (RET), a first-principles theory based on kinetic theory, yielded promising results for gaseous and near-critical densities. More work is needed to increase the accuracy of RET for denser fluids and for lower temperatures.

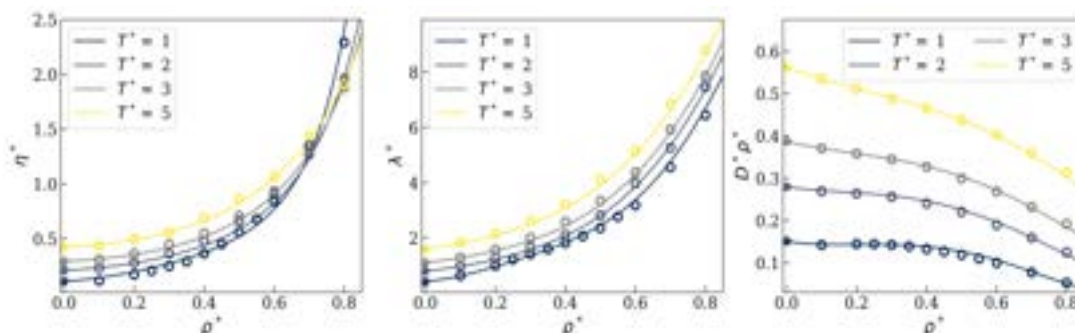


Figure 1. The presented RES model (lines), compared to molecular dynamics data (points) of the viscosity η^* , thermal conductivity λ^* and self-diffusion coefficient D^* of the LJ/s fluid.

Acknowledgment

The authors acknowledge funding from the Research Council of Norway (RCN), the Center of Excellence Funding Scheme, Project No. 262644, PoreLab, and the European Research Council (ERC) under the European Union’s Horizon Europe research and innovation program (grant agreement No. 101115669).

Significant references

1. B. Hafskjold, K.P. Travis, A.B. Hass, M. Hammer, A. Aasen, and Ø. Wilhelmsen, *Molecular Physics*, vol. 117 (2019), pp. 3754-3769.
2. J.S. Løken, V.G. Jervell, M. Hammer, B. Hafskjold, T.T. Trinh, and Ø. Wilhelmsen, *Fluid Phase Equilibria*, vol. 601 (2025).

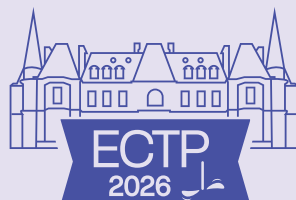
1.3

Transport properties

Mass Diffusivity

Measurement and

Data-Driven Modelling



Definitions and Preferred Symbols for Mass Diffusion Coefficients in Multicomponent Fluid Mixtures Including Electrolytes

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Diffusive mass transfer plays an important role in many engineering fields. For the design of processes and apparatuses, diffusive mass fluxes must often be determined, which requires knowledge of the associated transport property, the diffusion coefficient. Although the underlying theories date back to the 19th century, there is no consensus in the literature on which diffusivity, such as mutual, self-, or tracer diffusion coefficient, has to be used to characterize diffusive mass transport. Furthermore, numerous terms are in circulation for the same diffusion coefficient type, such as mass, Fick, mutual, binary, or interdiffusion coefficient. To address this issue, the International Union of Pure and Applied Chemistry (IUPAC) has initiated a research project with the aim to develop a consistent definition of diffusive mass transport in multicomponent mixtures, including electrolytes, and to give a recommendation for the terminology of the associated diffusion coefficients.

In this contribution, the definitions for mass diffusion coefficients in multicomponent fluid mixtures are presented on the basis of the related IUPAC report.¹ For this, the fundamentals of the description of molecular diffusion in non-electrolyte and electrolyte systems at constant temperature and pressure and in the absence of external fields are detailed. On the basis of Fick's law and the theory of Maxwell and Stefan, the description of diffusive fluxes is given in commonly used reference frames and a recommendation for the terminology of the associated diffusion coefficients is given. For non-electrolyte systems, the fluxes are stated for a general n -component mixture and the transformation of the diffusion coefficients between the different reference frames is detailed. In addition, the transformation of the component order for multicomponent mixtures is discussed. For binary electrolyte mixtures, the influence of the electroneutrality condition on the diffusive mass transport is discussed for systems consisting of either a molecular solvent and a dissolved electrolyte component or of two electrolyte components sharing a common ion.

Acknowledgment

This contribution was prepared in the framework of IUPAC project 2014-010-1-100. The authors gratefully acknowledge funding of the Erlangen Graduate School in Advanced Optical Technologies (SAOT) by the Bavarian State Ministry for Science and Art.

Significant references

1. T. Klein, C.J. Kankanamge, T.M. Koller, M.H. Rausch, A.P. Fröba, M.J. Assael, W.A. Wakeham, G. Guevara-Carrion, and J. Vrabec, *Pure and Applied Chemistry*, vol. 97 (2025), pp. 689-713

Fick Diffusion Coefficients in Blowing-Agent-Loaded Polymer Melts by Dynamic Light Scattering and Molecular Dynamics Simulation

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To produce thermoplastic foams by physical foam extrusion, a blowing agent is dissolved in the polymer melt and, upon extrusion through a die, bubble growth is induced. As the melt temperature T decreases, bubble growth stagnates and the final foam morphology is fixed during the solidification of the polymer. For the design and optimization of such processes and the produced foam products, a reliable modeling of the bubble growth in polymer melts at process-relevant conditions is necessary, which requires accurate data for the Fick or mutual diffusion coefficient D_{11} characterizing the mass transport of the dissolved blowing agent from the bulk to the interface of formed gas bubbles.

For the development of a fundamental understanding of mass transport in blowing-agent-loaded polymer melts, the investigation of mixtures based on well-defined polymer species is essential. Therefore, in this work, a comprehensive characterization of well-defined and nearly monodisperse polystyrene (PS) oligomers of varying molecular masses M , i.e., polymer chain lengths with dissolved nitrogen (N_2), carbon dioxide (CO_2), or 1,1,1,2-tetrafluoroethane ($R134a$) is performed. For this, D_{11} is accessed by dynamic light scattering (DLS) experiments and equilibrium molecular dynamics (EMD) simulations performed at temperatures T up to 533 K and pressures p corresponding to blowing agent mass fractions w_{solute} of $w_{N_2} \leq 0.5\%$ and (w_{CO_2} or w_{R134a}) $\leq 4\%$.^{1,2} In this context, a new force field was developed for EMD simulations of PS, which can accurately predict the properties of PS as a function of M as demonstrated by the comparison with density data from the literature. From the investigations performed, comprehensive structure-property relationships are derived. For the first time, a characteristic asymptotic behavior of D_{11} as a function of the polymer chain length is demonstrated at sufficiently large M . In the studied range of T and p , a w_{solute} -independent behavior of D_{11} is identified. Such behavior is usually only observed in ideal mixtures and could be explained for the nonideal mixtures at hand by separate analysis of the molecular dynamics and the fluid structure accessed in EMD simulations. Furthermore, an agreement of D_{11} and the self-diffusion coefficient D_1 of the blowing agent is demonstrated for the studied mixtures, which results from the identified nonideal mixture behavior as the present systems cannot be considered to be at infinite dilution.

Acknowledgment

This work was supported financially by the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG) via the Project-ID 510591037. The authors gratefully acknowledge funding of the Erlangen Graduate School in Advanced Optical Technologies (SAOT) by the Bavarian State Ministry for Science and Art as well as the scientific support and HPC resources provided by the Erlangen National High Performance Computing Center (NHR@FAU) of the Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU) under the NHR project AOTTP-DFG25-1. NHR funding is provided by federal and Bavarian state authorities. NHR@FAU hardware is partially funded by the German Research Foundation (DFG) – 440719683.

Significant references

1. P.S. Schmidt, C.J. Kankanamge, J. Klose, J.H. Jander, N. Vergadou, I.G. Economou, T. Klein, and A.P. Fröba, *Macromolecules* vol. 58 (2025), pp. 10238–10252.
2. P.S. Schmidt, J.H. Jander, F. Alhadi, M. Ratka, C. Bonten, T. Klein, and A.P. Fröba, *International Journal of Thermophysics* vol. 45 (2024), pp. 128:1–13.

A Machine Learning Approach to Predict the Self-Diffusivity of the Lennard-Jones Fluid

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The self-diffusivity of simple gases (e.g., CO₂, CH₄, etc.) is encountered in a plethora of industrial and environmentally-related processes and applications. Typically, when the measurement/estimation of a thermodynamic or transport property is required, the following three major routes are usually followed: (i) Conducting experimental measurements, (ii) developing theoretical/semi-empirical models, and (iii) performing molecular simulations such as molecular dynamics (MD) or Monte Carlo (MC).

In recent years an alternative approach has emerged, based on the utilization of Machine Learning (ML) methods. However, in order to create a reliable Machine Learning (ML) tool extensive experimental or computational data are required for the tool calibration. The case of the Lennard-Jones (LJ) fluid is an excellent candidate for testing different ML models for self-diffusivity predictions since a significant amount of computational data (MD) are available. Following our recent work [1], the purpose of the current study is twofold: (a) To conduct an extensive literature review for available values of self-diffusivities of the LJ fluid, and (b) To create a ML model based on the collected computational data achieving self-diffusivity results of high accuracy. To this extend, several classic Machine Learning methods such as Support Vector Machine (SVM), k-Nearest Neighbor (k-NN), Random Forest (RF), and ensemble ML as well, are compared in order to find the most suitable method for creating a robust prediction tool for describing accurately the self-diffusivity of the model LJ fluid.

Significant references

1. G. Gravanis, S. Papadopoulou, S. Voutetakis, K. Diamantaras, and I.N. Tsimpanogiannis, *Fluid Phase Equilib.*, vol. 592 (2025), 114325.

Physically Consistent Prediction of Diffusion Coefficients with Machine Learning

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Diffusion coefficients are essential for modeling a wide range of natural and engineering processes. However, due to the complexity of their experimental determination, available data are remarkably scarce, highlighting the need for reliable predictive methods. In recent years, machine learning (ML) models have emerged as alternatives to traditional semi-empirical approaches for predicting diffusion coefficients [1-3]. While these models can achieve higher predictive accuracy, they are typically limited to specific solvent classes or systems with existing data. Furthermore, they frequently violate fundamental physical constraints, e.g., that diffusion coefficients increase with temperature.

In this work, we present a framework of hybrid models for the physically consistent prediction of self-diffusion and mutual diffusion coefficients in liquid systems containing any number of components as a function of temperature and concentration based on the molecular structure of the components. The approach integrates neural networks with physical models, namely the Stokes-Einstein and Vignes equations, to preserve physical interpretability and consistency. By employing deep-set architectures [4], permutation invariance among components and consistency across compositions is ensured.

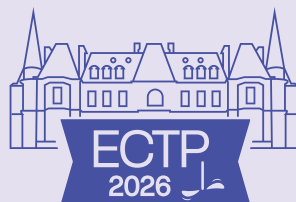
Despite being trained on the limited available experimental diffusion data, the models demonstrate excellent predictive accuracy for unseen components and mixtures, significantly outperforming established models in predicting diffusion coefficients at both infinite dilution and finite concentrations. The approach requires only the structural formula of the pure components (provided as SMILES) and the pure-component viscosities as input, giving it an unprecedented scope of applicability.

Significant references

1. O. Großmann, D. Bellaire, N. Hayer, F. Jirasek, and H. Hasse, *Digit. Discov.*, vol. 1 (2022), pp. 886–897.
2. A. Abbasi and R. Eslamloueyan, *Chemom. Intell. Lab. Syst.*, vol. 132 (2014), pp. 39–51.
3. J.P.S. Aniceto, B. Zêzere, and C.M. Silva, *J. Mol. Liq.*, vol. 405 (2024), art. 125009.
4. M. Zaheer, S. Kottur, S. Ravanbakhsh, B. Póczos, R. Salakhutdinov, and A.J. Smola, *Adv. Neural Inf. Process. Syst.* 30 (2017).

1.4

Transport properties Measurement and Modelling of Materials Emissivity



Emissivity Assessment of Sandblasted Surfaces: Decoupling Roughness and Surface Chemistry Effects

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The emissivity of metallic surfaces is influenced by several parameters, including surface roughness and surface chemistry [1]. Among the texturing processes used to generate roughness, sandblasting is employed either to enhance surface emissivity, for instance in nuclear applications where radiative cooling is a safety concern [2], or to produce isotropic roughness for validating emissivity models [3]. However, sandblasting induces significant chemical modification of the surface through the embedding of abrasive particles (typically alumina-based, Al_2O_3). This work aims to decouple the topographical and chemical effects on the emissivity of sandblasted titanium surfaces. Fifteen samples were sandblasted by varying the particle diameter and pressure, yielding a broad roughness spectrum ranging from $R_a = 0.5$ to $4.5 \mu m$, representing a nine-fold increase, while maintaining similar morphology. Normal spectral emissivity was measured using an integrating sphere. The results demonstrate that it is possible to separate the contributions of topography and chemistry, with the evolution of emissivity remaining consistent with the alumina percentages measured on the surface.

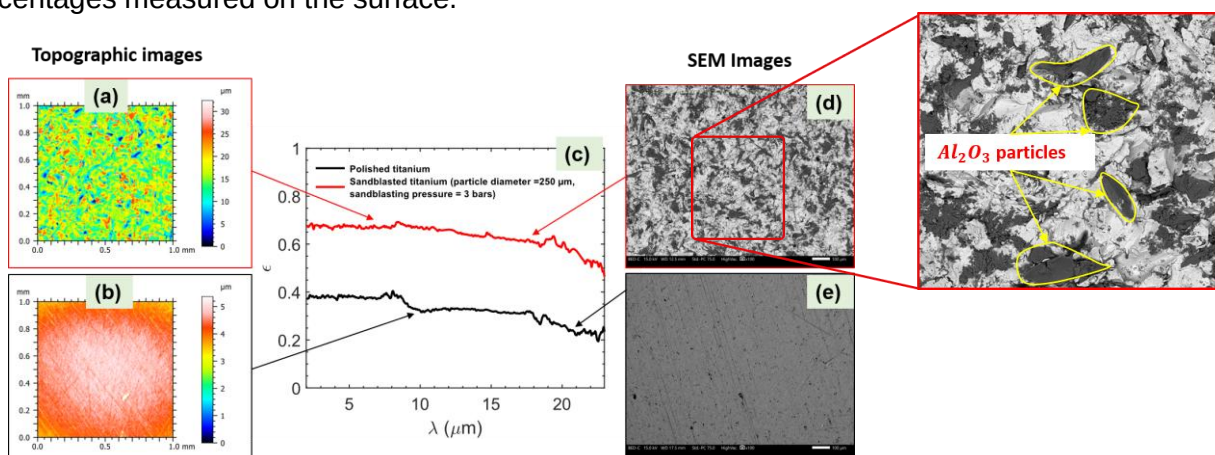


Figure 1. (a) topographic image of sandblasted titanium, (b) topographic image of polished titanium, (c) Normal spectral emissivity of polished and sandblasted titanium, (d) SEM image in BEC of sandblasted titanium, (e) SEM image in BEC of polished titanium.

Acknowledgment

The authors gratefully acknowledge financial support from the Carnot Institute ARTS and the French National Research Agency (ANR-23-CE10-0017).

Significant references

- [1] L. Del Campo *et al.*, « Emissivity measurements on aeronautical alloys », *J. Alloys Compd.*, vol. 489, n° 2, p. 482- 487, janv. 2010, doi: 10.1016/j.jallcom.2009.09.091.
- [2] T. Hunnewell *et al.*, « Total Hemispherical Emissivity of SS 316L with Simulated Very High Temperature Reactor Surface Conditions », *Nucl. Technol.*, vol. 198, p. 293- 305, juin 2017, doi: 10.1080/00295450.2017.1311120.
- [3] J. Hu, Z. Liu, J. Zhao, et B. Wang, « Prediction of Isotropic Rough Surface Directional Spectral Emissivity with Surface-Morphology-Dependent Modelling », *Metals*, vol. 13, n° 10, p. 1679, sept. 2023, doi: 10.3390/met13101679.

Influence of the spectral emissivity of refractories on the energy performance of industrial furnaces : Measurement and Modeling

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Our research focuses on the decarbonisation of high-temperature industrial processes. By combining experimental characterisation and numerical simulation, we seek to evaluate the impact of the emissivity of refractory materials on the energy performance of an aluminium remelting furnace equipped with natural gas oxy-fuel burners. The originality of the study lies in the explicit consideration of the spectral dependence of the emissivity of the walls and combustion gases in the calculation of radiative transfers.

On the experimental side, the CEMHTI's FTIR spectroscopy characterisation bench [1] was used to measure the normal spectral emissivity of the oxide materials constituting the furnace, over a temperature range up to 2500 K. This device makes it possible to accurately determine the evolution of emissivity spectra as a function of temperature and wavelength, which are essential data for realistic modeling of radiative transfers.

At the same time, numerical simulations integrating coupled heat transfer – conduction, convection and radiation – [2] between the heat source, the walls and the load in the combustion chamber were carried out. Based on the Monte Carlo method formulated in path spaces, they were performed in a complex geometry representative of an industrial furnace. The aim was to assess the influence of wall emissivity on the distribution of radiative flux and on the energy efficiency of the system.

This work paves the way for the joint optimisation of refractory material selection and furnace thermal design, with a view to reduce energy consumption and associated greenhouse gas emissions.

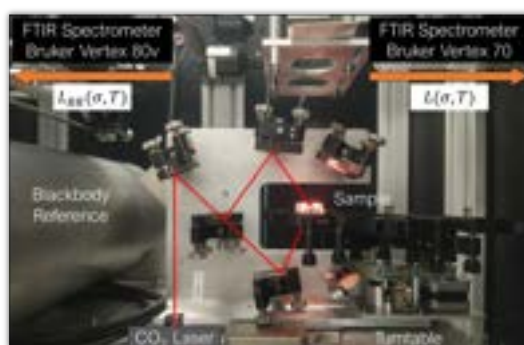


Figure 1. CEMHTI device for direct measurement of normal spectral emissivity at high temperatures.

Acknowledgment

This work is being carried out within the framework of the CANOPEE joint laboratory (CEMHTI, LEMTA, Saint-Gobain) and is funded by CNRS-MITI.

Significant references

1. D. De Sousa Meneses, P. Melin, L. del Campo, L. Cosson and P. Echegut, *Infrared Phys. Technol.*, vol. 69 (2015), pp. 96–101.
2. J. M. Tregan, J.-L. Amestoy, M. Bati, J.-J. Bézian, S. Blanco, L. Brunel, et al., *PLoS ONE*, vol. 18 (2023), pp. e0283681.



Performance Assessment of a Selective-Emissivity Roof Coating for Industrial Buildings

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This paper investigates the application of a selective-emissivity coating on the roof of an industrial warehouse and evaluates its impact on both energy consumption and indoor thermal comfort. The coating features a multilayer structure composed of an aluminum substrate, a SiO₂ middle layer, and a TiO₂ top layer, engineered to enhance solar reflectance and optimize thermal emissivity. A laboratory-based characterization was first conducted to determine the thermophysical properties of the multilayer coating, including its optical and thermal performance parameters. These measured properties were then used as inputs for dynamic energy simulations aimed at quantifying the resulting variations in cooling demand and indoor temperature profiles. Results indicate a substantial reduction in heat gains through the roof and an improvement in comfort metrics during summer conditions, confirming the effectiveness of selective-emissivity coatings as a cost-efficient passive strategy for industrial building envelopes. The study provides insights into the integration of advanced surface technologies in large-scale facilities and outlines directions for future performance optimization.

Emissivity Characterisation of Engineering Materials and Thermographic Phosphors within ThermoSI

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Reliable, traceable surface temperature measurement is a key enabler for advanced manufacturing, energy-efficient industrial processes and autonomous process control. Conventional surface thermometry, based on contact probes or thermal imaging, often suffers from large and poorly quantified uncertainties due to unknown emissivity and reflected radiation. The ThermoSI project within the European Partnership on Metrology addresses these issues by developing traceable in-situ thermometry solutions, including quantitative thermal imaging supported by thermographic phosphors, practical Johnson noise thermometry and AI-enabled self-validating temperature measurements.

One of the project tasks underpins quantitative thermal imaging by providing traceable emissivity data for key engineering materials and thermographic phosphors. Quantitative use of thermal imagers and phosphor coated reference spots requires knowledge of the spectral, angular and hemispherical emissivity of both the substrate and the phosphor coating over relevant temperature and spectral ranges. However, emissivity is notoriously difficult to measure with sufficiently low uncertainty, and independent methods are needed for validation.

A broad set of industrially relevant materials was investigated, including four representative engineering substrates (steels, aluminum, Inconel and titanium alloys), which served as the basis for a systematic emissivity study. Each material was examined in three configurations: the bare substrate, substrate with binder and substrate with a binder and MFG ($\text{Mg}_4\text{GeO}_{5.5}\text{F:Mn}$) phosphor mix (coating). Emissivity measurements were carried out using the Emissivity Measurement in Air Facility (EMAF) of PTB [1-2] over the temperature range 20 °C to 500 °C. A subset of samples was also measured in vacuum at -40 °C by means of the Reduced Background Calibration Facility 2 (RBCF2) [3]. The measurements include spectral, directional and hemispherical emissivity and were complemented by investigations of sample-to-sample variation as well as coating uniformity across different regions of the surface. In addition, the ageing behavior of the coated samples was studied through repeated thermal cycling (20 °C, 200 °C, 500 °C and back to 20 °C).

The resulting emissivity dataset provides a reliable foundation for quantitative thermal imaging and for the use of the phosphor-based thermometry technique in industrial environments. These reference data for key engineering materials, which will be made openly available via the Zenodo repository, represent a crucial resource for improving surface temperature measurements under realistic and demanding operating conditions. They will support the development and validation of reliable non-contact thermometry approaches across a wide range of advanced manufacturing applications.

Acknowledgment

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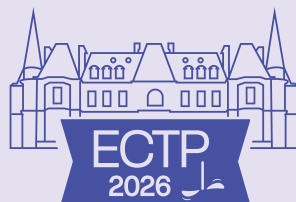
Significant references

1. C. Monte, J. Hollandt, High-Temperatures – High-Pressures, 39, 151-164, 2010
2. C. Monte, J. Hollandt, Metrologia, 47, 172-181, 2010, doi: 10.1088/0026-1394/47/2/S14
3. A. Adibekyan, et al., Int J Thermophys. 38, 89, 2017, doi:10.1007/s10765-017-2212-z

1.5

Transport properties

High Thermal Conductivity Materials



Experimental Study on High thermal conductivity UV-curable resin by the Transient Hot-wire Method

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In recent years, advancements in edge AI technologies have increased the demand for high-performance semiconductors capable of performing AI processing in real time on end devices. Consequently, semiconductor devices have become increasingly miniaturized and highly integrated, resulting in higher heat generation density within the chips. Enhancing thermal dissipation has therefore become an urgent challenge, particularly for interposers that connect chips to substrates, which are required to simultaneously exhibit high thermal conductivity and electrical insulation. Among potential materials, UV-curable resins offer high design flexibility and good microfabrication capability, making them suitable for 3D printing and promising candidates for next-generation interposers. However, their low intrinsic thermal conductivity remains a property that requires improvement. The objective of this study is to enhance the thermal conductivity of UV-curable resins and to precisely measure their thermal conductivities.

In this study, polyethylene glycol diacrylate (PEGDA), a UV-curable resin, was selected as the matrix material. PEGDA resins were enhanced in thermal conductivity by adding thermally conductive fillers such as aluminum nitride (AlN). The thermal conductivities of these composite resins were then measured using our transient hot-wire method. In our method, a step current is supplied to a thin metal wire, and the transient temperature change is measured. The diameter of the wire is 30 μm , and the metal wire is coated with parylene for electrical insulation. Since the wire is very thin and the measurement time is very short, our method achieves high measurement accuracy of 0.7%. To investigate the influence of filler loading on thermal performance, composite samples with different filler contents were prepared and evaluated.

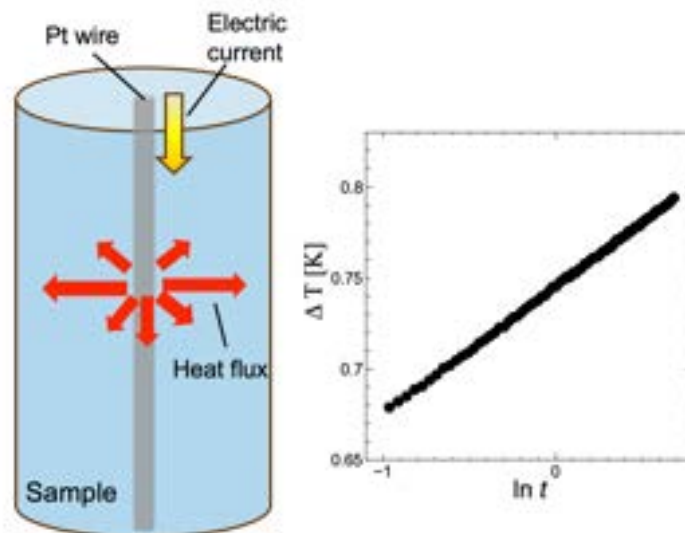


Fig. 1 Principle of the transient hot-wire method

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Study on Heat Flux Sensors Sensitivity under Various Conditions

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Heat flux sensors are effective tools for determining heat flux density and its flow direction [1]. They are widely used in thermal management and energy efficiency applications. Among various types of heat flux sensors, contact-type flat-plate sensors are the most commonly employed.

Reliable heat flux values can be obtained when the sensor is sandwiched between a hot plate and a cold plate. In fact, these sensors are typically calibrated by the steady-state method, most commonly the Guarded Hot Plate method [2, 3]. In practical applications, the sensor is usually placed on an object to measure heat flux from the object to the surrounding atmosphere. Under these conditions, the sensor detects the total heat flux, which consists of conductive, convective, and radiative heat transfer. It is difficult to separate these components, and their ratios can easily change depending on environmental conditions. This may lead to reliability issues in practical measurements.

To address this problem, we developed an apparatus to investigate the properties of heat flux sensors under different environmental conditions. The setup includes a 200 mm square hot plate inside a vacuum chamber, composed of aluminum plates and a film heater, ensuring good temperature uniformity. Heat flux sensors and T-type thermocouples were placed on both surfaces of the hot plate. Changes in temperature and sensor output voltage were measured in air and vacuum under various power levels supplied to the heater. Additionally, the effect of surface coverage with different tapes was examined under stable power conditions in air. The findings provide valuable insights into the environmental dependence of heat flux sensor performance and contribute to improving measurement accuracy for practical applications.

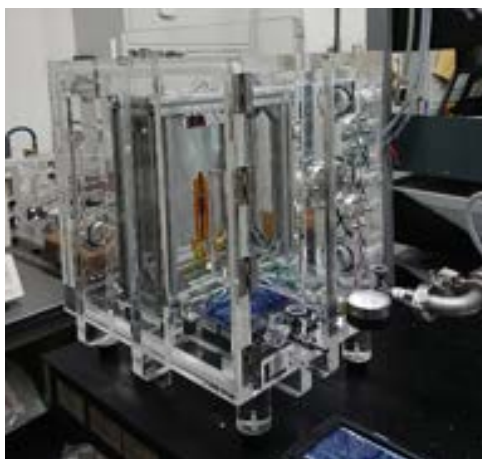


Figure 1. Developed apparatus for check of apparent sensitivity of heat flux sensors

Significant references

1. Sadao Sumigama, *Introduction to Heat Sensors: Principles, Structures, and Applications*, Keigaku Publishing, 1984. (in Japanese)
2. ISO 8302 : 1991 Thermal insulation–Determination of steady-state thermal resistance and related properties–Guarded hot plate apparatus.
3. M. Akoshima, N. Yamada, Establishment of the heat flux standard, Proceedings of 36th Japan Symposium on Thermophysical Properties (2015) D133. (in Japanese)

Microfabrication of High-Thermal-Conductivity Composite Resins by Two-photon 3D Printing

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The continued increase in device integration and power output has resulted in higher heat densities that compromise operational stability, representing a key barrier to the deployment of advanced technologies such as edge AI. To address this challenge, highly detailed thermal management of the interposer, which is the intermediate conductor plate in semiconductors, is required.

Furthermore, two-photon 3D printing techniques are gaining attention as methods for fabricating novel microdevices. This technology achieves polymerization reactions only near focus by concentrating high-fluence, ultra-short laser pulses, resulting in high spatial resolution. Moreover, the UV-curable resin material offers excellent electrical properties, lightness, and cost-effectiveness.

However, its low thermal conductivity limits the range of thermal conductivity control, which is a critical weakness.

Therefore, this study aims to fabricate microstructures that simultaneously achieve high spatial resolution and high thermal conductivity by the two-photon 3D printing on composite resin materials containing highly thermally conductive nanofillers. Generally, nanofillers that combine both high thermal conductivity and electrical insulation exhibit low optical transmittance, leading to substantial laser attenuation. As a result, layered fabrication using the two-photon 3D printing, which requires high-fluence laser focusing, has been difficult to achieve.

To address this issue, a new two-photon 3D printing approach, as shown in Fig. 1, is proposed. To control the gap between the substrate and the optical window to several micrometers, two automated stages were introduced, and a new fabrication mechanism compatible with them was created. This presentation evaluates the microstructures fabricated using the proposed method and discusses the validity of this approach.

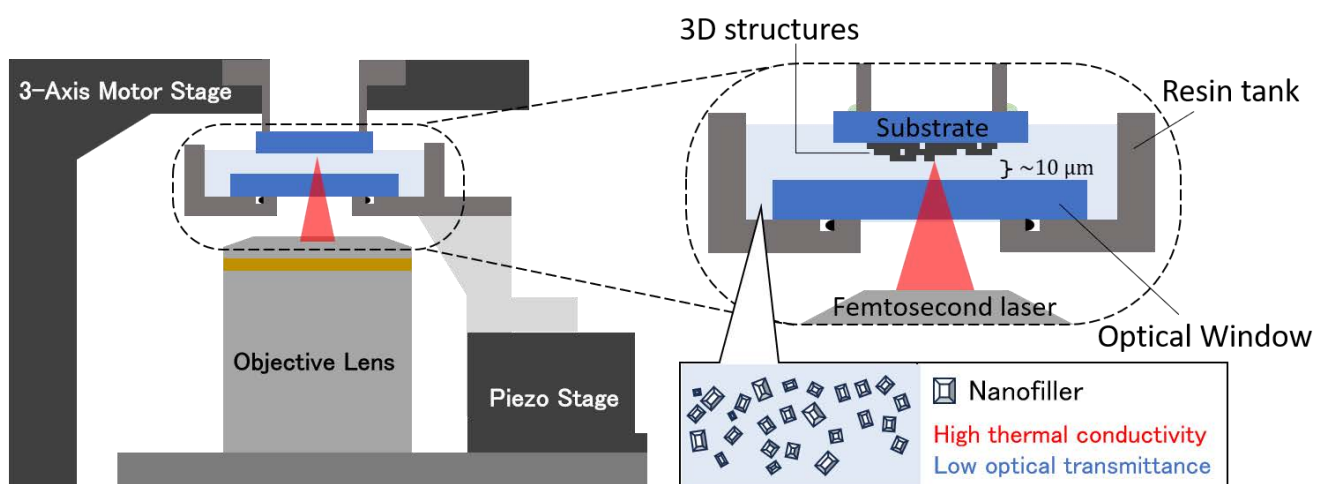


Fig. 1 Outline of the Proposed Fabrication Method

Acknowledgment

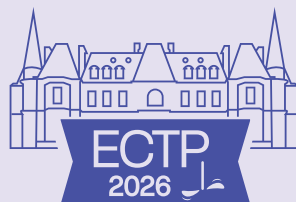
This work was partially supported by JSPS KAKENHI Grant Number 25K01177.

1.6

Transport properties

Mass Diffusivity

Measurement



Measurement of Diffusion Coefficients in Complex Fluids, Including Molecular and Particulate Systems, by Dynamic Light Scattering

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At present, the most frequent application of dynamic light scattering (DLS) is the study of collective diffusion coefficients for the characterization of macromolecular or particle size and size distribution. In this regard, the application of DLS to the bulk of fluids can be found, for example, for aerosols, colloidal dispersions, polymer solutions, and solutions and dispersions of biological macromolecules. In contrast to the situation regarding the application of DLS to study size, morphology, and structure of various systems, there are currently only a few research groups worldwide that use DLS to determine thermophysical properties. A fundamental advantage of DLS is that it allows for the determination of transport properties without applying any macroscopic gradient. DLS analyzes the dynamics of microscopic statistical fluctuations which can be related to various diffusive processes and, thus, to the transport properties to be measured. This is possible as according to Onsager's regression hypothesis, on a statistical average, the behavior of microscopic fluctuations is governed by the very same transport equations that are valid for macroscopic systems.

The present contribution reviews research activities mainly carried out over the last ten years at the Institute of Advanced Optical Technologies – Thermophysical Properties (AOT-TP) of the Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU) applying DLS to measure diffusion coefficients and, in some cases, to simultaneously determine the thermal diffusivity in complex fluids and particulate systems. Measurement examples are presented for a large variety of fluid mixtures and particulate systems, which represent, besides model or reference systems, especially systems relevant for process and energy technology. For the model systems, limitations of the method regarding the thermodynamic state and the accuracy will be discussed. For example, the study of an equimolar methane–propane mixture examines the resolvability and separability of mutual and thermal diffusivity in different fluid regions including the critical region.¹ The systematic investigation of liquids with dissolved gases^{2,3} contributes to the identification of structure-property relationships for the development of an empirical correlation that represents the mass diffusivity within about $\pm 10\%$.⁴ Technically relevant mixtures of liquids with dissolved gases studied are liquid organic hydrogen carriers (LOHCs) with hydrogen⁵ as well as polymer melts with blowing agents, e.g., nitrogen, carbon dioxide, or 1,1,1,2-tetrafluoroethane.⁶ A special class of systems are electrolytes which are of technological importance, e.g., for metal ion batteries⁷ or for underground hydrogen storage.⁸ They contain multiple species which can be represented in a binary mixture consisting of two salts by up to four different ions. Here, the dissociation and clustering of ions can influence the molecular mass transport, as it is evidenced by a combination of DLS and molecular dynamics simulations.⁷ Based on aqueous polyethylene glycol (PEG) solutions, which can be understood as both molecular and particulate systems, dispersions of very small spherical nanoparticles are studied.⁹ The results from DLS show that monodisperse PEGs are suitable model systems for studying the diffusion behavior of bimodal and also multimodal particulate systems. In the context of thermophysical property research, the analysis of particle diffusion coefficients in combination with the Stokes-Einstein equation can, in principle, provide information on the dynamic viscosity of the solvent, as documented for various pure ionic liquids and their mixtures with dissolved carbon dioxide.¹⁰ For the latter system, even the simultaneous determination of mutual diffusivity and particle diffusion coefficient is demonstrated. This is also possible for polyol-based microemulsions containing micelles swollen with carbon dioxide, which can be understood as spherical particles.¹¹ For these technical systems, which serve for the production of polyurethane foams, the micelle size that correlates with the pore size in the foam can be analyzed by DLS via the determination of the micelle diffusion coefficient under process-relevant conditions. In anisotropic particulate systems, in addition to the translational diffusion coefficient, the rotational particle diffusion coefficient is accessible, which in turn enables the characterization of the particle morphology.¹² Recent research activities for

particulate systems demonstrated also the applicability of DLS for the characterization of the particle aggregation kinetics in process technology by studying particle diffusion coefficients in evaporating single droplets.¹³ Moreover, it has been shown that DLS can be applied for studying particle diffusion coefficients not only in free media, but also under the influence of confinement in porous materials without using any refractive index matching fluid.¹⁴

Acknowledgment

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Significant references

1. M. Piszko, C. Giraudet, and A.P. Fröba, Diffusivities of an Equimolar Methane–Propane Mixture Across the Two-Phase Region by Dynamic Light Scattering, *Int. J. Thermophys.*, vol. 41 (2020), article 102.
2. C.J. Kankanamge, P. Damp, T.M. Koller, M.H. Rausch, D. Krug, W. Schröder, T. Klein, and A.P. Fröba, Thermal and Mutual Diffusivities in Binary Mixtures of Alkanes with Dissolved Gases by Dynamic Light Scattering (DLS), *Fluid Phase Equilib.*, vol. 596 (2025), article 114429.
3. T. Klein, M. Piszko, M. Lang, J. Mehler, P.S. Schulz, M.H. Rausch, C. Giraudet, T.M. Koller, and A.P. Fröba, Diffusivities in Binary Mixtures of [AMIM][NTf₂] Ionic Liquids with the Dissolved Gases H₂, He, N₂, CO, CO₂, or Kr Close to Infinite Dilution. *J. Chem. Eng. Data*, vol. 65 (2020), pp. 4116–4129.
4. F.D. Lenahan, M. Piszko, T. Klein, and A.P. Fröba, Prediction of Fick Diffusion Coefficients in Binary Mixtures of Liquids with Dissolved Gases at Infinite Dilution—A Review, *J. Chem. Eng. Data*, vol. 69 (2024), pp. 692–702.
5. F.E. Berger Bioucas, M. Piszko, M. Kerscher, P. Preuster, M.H. Rausch, T.M. Koller, P. Wasserscheid, and A.P. Fröba, Thermal Conductivity of Hydrocarbon Liquid Organic Hydrogen Carrier Systems: Measurement and Prediction, *J. Chem. Eng. Data*, vol. 65 (2020), pp. 5003–5017.
6. P.S. Schmidt, C.J. Kankanamge, J. Klose, J.H. Jander, N. Vergadou, I.G. Economou, T. Klein, and A.P. Fröba, Fick Diffusion Coefficients of Polystyrene Oligomers with Dissolved Blowing Agents by Dynamic Light Scattering and Molecular Dynamics Simulations, *Macromolecules*, vol. 58 (2025), pp. 10238–10252.
7. C.J. Kankanamge, T. Zhan, Z. Zhang, T. Klein, and A.P. Fröba, Influence of the Molecular Characteristics of the Solvent and the Solute Cation on Diffusive Mass Transport in Binary Electrolyte Mixtures by Dynamic Light Scattering and Molecular Dynamics Simulations, *J. Electrochem. Soc.*, vol. 171 (2024), article 110533.
8. M. Piszko, P.S. Schmidt, M.H. Rausch, and A.P. Fröba, Diffusivities in Water or Aqueous Solutions of Sodium Chloride with Dissolved Hydrogen and Methane by Dynamic Light Scattering, *Int. J. Hydrogen Energy*, vol. 68 (2024), pp. 499–510.
9. W. Wu, M. Supper, M.H. Rausch, M. Kaspereit, and A.P. Fröba, Mutual Diffusivities of Binary Mixtures of Water and Poly(ethylene) Glycol from Heterodyne Dynamic Light Scattering, *Int. J. Thermophys.*, vol. 43 (2022), article 177.
10. S. Bi, T.M. Koller, M.H. Rausch, P. Wasserscheid, and A.P. Fröba, Dynamic Viscosity of Tetracyanoborate- and Tricyanomethanide-Based Ionic Liquids by Dynamic Light Scattering, *Ind. Eng. Chem. Res.*, vol. 54 (2015), pp. 3071–3081.
11. M.S.G. Knoll, C. Giraudet, C.J. Hahn, M.H. Rausch, and A.P. Fröba, Simultaneous Study of Molecular and Micelle Diffusion in a Technical Microemulsion System by Dynamic Light Scattering, *J. Colloid Interf. Sci.*, vol. 544 (2019), pp. 144–154.
12. W. Wu, P.K. Chittam, F. Meißner, C. Damm, W. Peukert, and A.P. Fröba, Determination of Translational and Rotational Diffusivities of Anisotropic Nanoparticles by Heterodyne Polarized and Depolarized Dynamic Light scattering, *J. Phys. Chem. C*, vol. 128 (2024), pp. 9116–9129.
13. W. Wu, D.H. Panduro Vela, A. Bück, and A.P. Fröba, Characterization of Nanofluids in Evaporating Droplets by Dynamic Light Scattering, *Measurement*, vol. 220 (2023), article 113321.



14. W. Wu, J. Cui, U. Sultan, L. Gromotka, P. Margaretti, C. Damm, J. Harting, N. Vogel, W. Peukert, A. Inayat, and A.P. Fröba, Diffusion of Gold Nanoparticles in Porous Silica Monoliths Determined by Dynamic Light Scattering, *J. Colloid Interface Sci.*, vol. 641 (2023), pp. 251–264.

Characterization of Particle Diffusion Under Confined Conditions by Using Dynamic Light Scattering (DLS)

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For the design and optimization of particulate products, as it is the key objective and long-term vision of the Collaborative Research Centre 1411 (SFB 1411) at FAU, a fundamental understanding of particle diffusion characterized by the particle diffusivity D is necessary. In this context, the dependency of D on various aspects such as particle morphology, including the diameter d_p , concentration, surface characteristics, and properties of the base fluid has to be understood. Information on D is not only necessary in free media, but also in the presence of confinement as it is given, e.g., in complex porous materials used for particle chromatography. For a reliable determination of D in free media and under confined conditions, photon correlation spectroscopy (PCS) techniques, i.e., dynamic light scattering (DLS) and differential dynamic microscopy (DDM) are developed at AOT-TP,^{1,2} which are based on the temporal analysis of the scattered light from fluctuations in the particle number density in dispersions at macroscopic thermodynamic equilibrium. So far, at AOT-TP, a slowing down of D was revealed studying dispersions of gold nanoparticles confined in complex structures in form of inverse opals³ as well as porous silica monoliths.⁴ This work focuses on the characterization of particle diffusion under confined conditions in a model system with reduced degree of complexity to develop a fundamental understanding of particle diffusion under confinement. For this, D was studied by DLS in a thin dispersion layer confined in a newly developed wedge-shaped sample cell, which allows the systematic and well-defined variation of the confinement characteristics such as the confinement size L and the surface properties of the confining walls. Applying different scattering geometries, particle diffusion was probed considering the direction of particle motion with respect to the confining geometry. Here, the long-ranged nature of hydrodynamic particle-wall interactions slowing down particle diffusion parallel to the walls with decreasing $L \gg d_p$ was resolved experimentally for the first time, whereas diffusion perpendicular to the walls was found to be influenced only in the near-contact regime at $L \approx d_p$. From the accessed diffusivities, a simple geometric relationship describing particle diffusion with respect to the confining walls was derived. Furthermore, it was demonstrated that particle diffusion under confinement is governed by the relative confinement L/d_p and influenced by hydrophobic properties of the walls.

Acknowledgment

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Significant references

1. W. Wu, M.S.G. Knoll, C. Giraudet, M.H. Rausch, and A.P. Fröba, *Applied Optics*, vol. 62 (2023), pp. 8007–8017.
2. W. Wu, P.K. Chittem, F. Meißner, C. Damm, W. Peukert, and A.P. Fröba, *Journal of Physical Chemistry C*, vol. 128 (2024), pp. 9116–9129.
3. C. Giraudet, M.S.G. Knoll, Y. Galvan, S. Süß, D. Segets, N. Vogel, M.H. Rausch, and A.P. Fröba, *Transport in Porous Media*, vol. 131 (2020), pp. 723–737.
4. W. Wu, J. Cui, U. Sultan, L. Gromotka, P. Malgaretti, C. Damm, J. Harting, N. Vogel, W. Peukert, A. Inayat, and A.P. Fröba, *Journal of Colloid and Interface Science*, vol. 641 (2023), pp. 251–264.



Prediction of Diffusion Coefficients for High-Pressure Binary Gas Mixtures

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A framework was established to predict both Maxwell-Stefan and Fick diffusion coefficients for binary gas mixtures by combining kinetic theory with thermodynamic-factor correction. Thermodynamic factors were calculated using an analytical equation-of-state-based framework that incorporates both cubic equations of state and Helmholtz-energy-based models, enabling application over a wide range of temperatures, pressures, and mixture compositions, including systems relevant to natural gas, LNG, ammonia, and hydrogen storage. Pulsed gradient spin echo nuclear magnetic resonance (PGSE-NMR) was used to determine the composition-dependent intra-diffusion coefficients of the individual components [1], which were then converted to Maxwell-Stefan diffusion coefficients using the Darken relation. Experiment measurements for methane-hydrogen binary gas mixtures at 301.15 K and pressures of 60, 100, and 150 bar were compared with prediction results, showing good agreement with mean absolute differences of 6.8%, 5.3%, and 4.3%, respectively. Larger deviations were observed in the hydrogen-rich region. The proposed framework provides a practical method for predicting diffusion coefficients in high-pressure binary gas mixtures and clarifies the respective roles of kinetic-theory prediction and thermodynamic correction.

Significant references

1. Kobeissi, S., et al., *Measurements of intra-diffusion coefficients for gaseous binary mixtures*. Chemical Engineering Science, 2025. **303**.

Influence of α -Helical Content on the Thermodiffusion of Apomyoglobin

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Apo-myoglobin (Apo-Mb) is an extensively studied model system for investigating protein folding due to its distinct stable native, partially folded molten globule (MG), and unfolded states at acidic pH [1]. This study examines the impact of structural conformational changes on the thermodiffusive behavior of Apo-Mb using the infrared thermal diffusion forced Rayleigh scattering (TDFRS) technique [2]. The conformational states were modulated by varying pH and buffer conditions, with their structural changes confirmed via circular dichroism (CD) spectroscopy. The α -helical content decreased with decreasing pH. The thermodiffusion parameter $\Delta S_T(\Delta T)$, a measure of the temperature sensitivity of the Soret coefficient S_T , also showed a decrease, which is typically related to a decreasing hydrophilicity of the solute. Additionally, the buffer composition significantly influenced the thermodiffusive behavior: phosphate buffer promoted Apo-Mb aggregation through electrostatic screening, whereas acetate buffer favored Apo-Mb solubilization. Microsecond-long discrete protonation state constant pH molecular dynamics (CpHMD) simulations support the experimentally observed, pH- and buffer-dependent changes in α -helical content and highlight the differences in protein-buffer interactions for phosphate buffer versus acetate buffer. In conclusion, a strong correlation was observed between the thermodiffusion parameter $\Delta S_T(\Delta T)$ and the α -helical content, with $\Delta S_T(\Delta T)$ increasing alongside hydrophilicity and α -helical content (Fig. 1). These findings highlight the role of structural conformation and buffer environment in modulating the thermodiffusive properties of proteins.

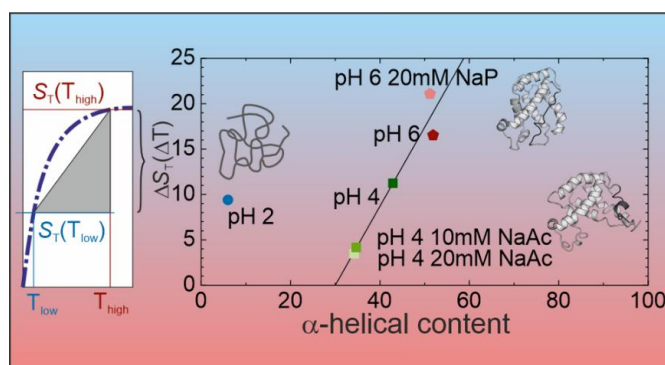


Figure 1. $\Delta S_T(\Delta T)$ decreases with decrease in hydrophilicity and α -helical content of the protein

Significant references

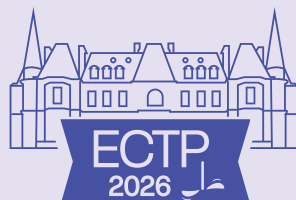
1. A.M. Stadler et al., *Phys. Chem. Chem. Phys.*, vol. 18 (2016), pp. 21527-21538.
2. B.A. Rudani et al., *Langmuir*, vol. 41 (2025), pp. 28322-28334.

1.7

Transport properties

Thermal Diffusivity

Measurement



A technical guide on high temperature thermal diffusivity measurements by the laser flash method

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The laser-flash method [1] is the most accurate metrological approach for measuring the thermal diffusivity of solid materials in a large temperature range. In nuclear, aeronautic, defense or space industries, the knowledge of thermal diffusivity at high temperature is of paramount importance for predicting the thermal behavior of advanced materials in real conditions and for defining their critical performance limitations at extreme temperatures (up to 3000 °C).

Measurement practices in the laboratories for determining the thermal diffusivity of solid materials are in many cases based on national or international standards. However, the most important standards related to this topic, such as ISO 18755 (2022), ISO 19629 (2018), EN 821-2 (1997), ISO 22007-4 (2024) and ASTM E1461-13 (2022), describe the general methodology to be applied to measure the thermal diffusivity according to the laser flash method, without giving specific recommendations for measurements performed at high temperatures.

It was therefore decided within the Best Practice Working Group of the Technical Committee for Thermometry from EURAMET (the European Association of National Metrology Institutes) to write a specific guide describing the basic technical requirements for performing thermal diffusivity measurements of solid materials at high temperature (between 500 °C and 3000 °C) by applying the laser flash method. This document has been produced on the basis of the results of the European project Hi-TRACE in order to enhance the equivalence and mutual recognition of high temperature thermal diffusivity measurement results obtained by laboratories. It is made freely available on the EURAMET website (<https://www.euramet.org/publications-media-centre/technical-guides>).

This presentation outlines the EURAMET Technical Guide No 5 “High temperature thermal diffusivity measurements by the laser flash method”. It presents recommended requirements for performing reliable and accurate thermal diffusivity measurements at high temperature, regarding especially: the laser flash apparatus, the preparation of the test, the calibration and measurement procedures [2, 3], the data analysis and the measurements uncertainty assessment [4].

Significant references

1. W. J. Parker, R. J. Jenkins, C. P. Butler, and G. L. Abbott, Flash Method of Determining Thermal Diffusivity, Heat Capacity, and Thermal Conductivity, *Journal of Applied Physics* 32, 1679 (1961).
2. G. Failleau, N. Fleurence, O. Beaumont, R. Razouk, J. Hameury and B. Hay, “Metal-carbon eutectic high temperature fixed points for in-situ calibration of radiation thermometers”, *High Temp.-High Press.* 50, 149 (2021).
3. M. Akoshima, B. Hay, B., M. Neda and M. Grelard, Experimental Verification to Obtain Intrinsic Thermal Diffusivity by Laser-Flash Method. *Int J Thermophys* 34, 778-791 (2013).
4. B. Hay, O. Beaumont, G. Failleau, N. Fleurence, M. Grelard, R. Razouk, G. Davée, J. Hameury, Uncertainty Assessment for Very High Temperature Thermal Diffusivity Measurements on Molybdenum, Tungsten and Isotropic Graphite. *Int J Thermophys* 43, 2 (2022).

Refinement of the Extended Pulse Technique for the Measurement of the Thermal Diffusivity of Solids

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In an earlier paper [1], the theory of a pulse technique for the measurement of the thermal diffusivity of solids was set out. In addition, a prototype instrument was designed in accordance with the theory of the device to ensure the minimum perturbation of the state of a sample from equilibrium and yet achieve a low uncertainty in the thermal diffusivity [1,2]. In that first version of the instrument, the temperature rise of the back face of a sample in response to an LED light pulse of finite duration at the front face, was detected using a micro-thermocouple whose bead was pressed into contact with the back face. It was demonstrated that the instrument conformed to the theory of it remarkably well and that, over a time period from 100 ms to 10 s, the theory precisely described the temporal evolution of the temperature at the center of the back face of the sample, once allowance was made for the perturbation caused by the characteristics of the thermocouple. These measurements were made at ambient temperature, using LED pulse strength to produce an easily analyzable rear face temperature rise between 1 and 4 C.

In this paper we present improvements to both the theory of the instrument and also its practical realization, allowing the use of a different, non-contact temperature measurement on the back face of the sample, and extending to elevated temperatures. To that end the theory has been extended to incorporate not just heat losses from the front a rear face but also from the circumferential surface of the solid sample. Numerical tests with the theory show that for the current instrument at moderate temperatures the heat losses from the periphery have a negligible effect upon the temperature at the center of the back face. It transpires that the positioning of the thermocouple at the exact center of the back face is not important. As a corollary of this finding, it was possible to replace the thermocouple detector with a non-contact, optical thermometric system that views a circular region of the back face. Such a thermometric system is available in the form of a thermopile, and it has now been incorporated into the instrument. The response of the thermopile selected was better than 5ms to 80 % of the maximum signal, three times faster than the original micro-thermocouple. Of course, it detects the average temperature rise of the sample over the area it views so that the theory can readily be employed to evaluate that average as a function of time.

It will be shown that the agreement between the theoretical predictions of the evolution of the temperature at the back face of samples for several materials are coincident with experimental observations over several orders of magnitude of time and that the derived values of the thermal diffusivity of standard materials are entirely consistent with those generally accepted, within the mutual experimental uncertainty. These findings bring within sight the possibility to achieve uncertainty in the measurement of the thermal diffusivity of solids of a few parts in a thousand under favorable conditions and substantiate the applicability of high-performance power LED sources in place of lasers.

1 W.A. Wakeham, P.S. Gaal, Z.D. Withrow and D.S. Gaal, *Int. J. Thermophys.*, vol. 46:25 (2025) <https://doi.org/10.1007/s10765-025-03504-w>

2 P.S. Gaal, Z.D. Schott and W.A. Wakeham, *Proc. International Thermal Conductivity Conference* (2024), In Press.

On the measurement of the in-plane thermal diffusivity: Data analysis in thin foils experiments

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The thermal diffusivity of materials is a key parameter to evaluate the thermal behavior of industrial components. Several methods are available to estimate the diffusivity, using different measurement techniques [1]. Amongst them, recently a photothermal technique has been developed for the case of thin foils [2].

This work further investigates some analytical solutions of the two-dimensional heat conduction differential equation for the geometry of a thin foil. The foil is made of a homogeneous material and is so thin that variations in temperature across it are negligible. On the contrary, on the surface of the foil, the temperature variation can be made considerable by delivering a localized heat pulse. It can be captured by a sequence of IR images. The model is then applied to some photothermal experimental setups, as depicted in Figure 1.

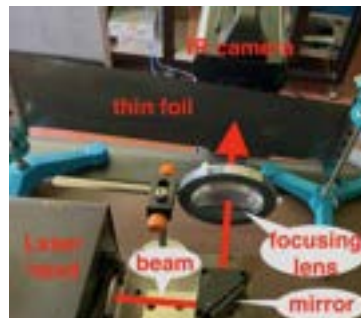


Figure 1. Experimental layout.

The analysis of thermal data leads to the estimation of the thermal diffusivity. In this work, the post-processing technique is discussed, with a focus on the challenges of error analysis.

Significant references

1. R. Kumar, R. Gupta, *Infrared Physics and Technology*, (2025), 150, art. no. 106037
2. P. Bison, G. Ferrarini, S. Rossi, *XXVII AIPT Meeting*, (2024), pp 154

Accurate In-Plane Thermal Diffusivity Characterization of Low-Diffusivity Materials by Flash Method

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Since its introduction in the 1960s [1], the Laser Flash Analysis (LFA) technique has become a standard for determining thermal diffusivity, typically in the through-plane direction. However, in-plane characterization is critical for anisotropic materials and thin isotropic samples with high thermal diffusivity, where through-plane measurements are not feasible due to rapid heat propagation. Although LFA models for in-plane thermal diffusivity analysis are available [2], reducing the influence of the sample holder remains a key limitation for accurate in-plane measurements.

To address this issue, we have developed innovative solutions to overcome this barrier. First, we redesigned our metal sample holder for in-plane measurements to minimize contact between sample and sample holder and replaced the construction material to polymer, whose thermal diffusivity is over ten times lower. Results obtained demonstrate a significant reduction in the sample holder influence, enabling accurate characterization of materials with in-plane diffusivity below 2 mm²/s (Figure 1).

Following a different approach, we developed a multi-slit sample holder, which, combined with an analytical solution for heat diffusion based on a two-dimensional Green's function and the mirror image method, allows characterization of thermal diffusivity along a specific in-plane direction [4]. Preliminary results confirm the feasibility of this approach, opening new possibilities for measuring thermal diffusivity in different in-plane directions, even for low-diffusivity materials.

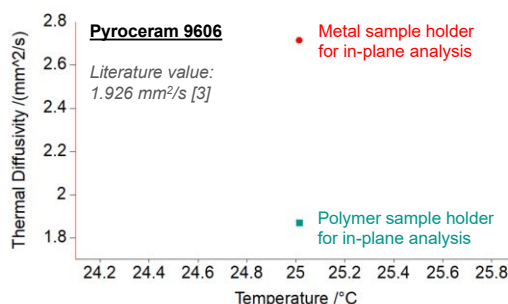


Figure 1. Results of in-plane analysis obtained with the original metal holder and the redesigned polymer holder for a low-thermal-diffusivity material

Acknowledgment

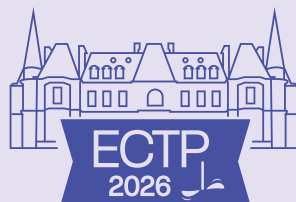
This research was partially carried out under the “Innovative Thermoelectric Conversion Technology Applicable as an Independent Power Source for Sensors.” project of the Future Society Creation Program of the Japan Science and Technology Agency (JST)

Significant references

1. W.J. Parker, R.J. Jenkins, C.P. Butler, and G.L. Abbott, *J. Appl. Phys.*, vol. 32 (1961), pp. 1679-1684.
2. T. Baba, T. Baba, Y. Ishibashi, and Y. Shinoda, *The 38th Japan Symposium on Thermophysical Properties*, Nov. 2017, Tsukuba, Japan, 135-137
3. D. Salmon, G. Roebben, A. Lamberty, and R. Brandt, EUR 21764 EN. 2007. JRC30964, *European Commission*, Brussels, Belgium.
4. Y. Shinoda, T. Baba, T. Baba, T. Mori, and Y. Ishibashi, *The 46th Japan Symposium on Thermophysical Properties*, Oct. 2025, Saga, Japan.

1.8

Transport properties Thermal Conductivity and Diffusivity measurement



Thermal conductivity of multi-component mixtures for natural gas

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Natural gas is one of the most important primary energy sources, accounting for almost one-fourth of the world's primary energy consumption. Accurately measuring the thermal conductivity of natural gas is critical for efficiency, safety, and economics across the energy sector. This key thermophysical property is essential for designing and optimizing equipment like heat exchangers and pipelines, ensuring maximum energy efficiency in gas processing and transport. It is also vital for safety, enabling precise prediction of heat flow and temperature distribution in pipelines and storage systems, which helps prevent accidents.

In this work, a new experimental system has been developed for low-temperature thermal conductivity measurement based on transient single hot wire method. The diameter and length of the platinum wire were 30μm and 30mm, respectively. The wire was fixed to two platinum rods with a diameter of 1mm. The experimental apparatus was made of stainless steel and sealed by welding. The apparatus was verified using propane, and the experimental data showed good agreement with the literature. The thermal conductivity of multi-component mixtures for natural gas with temperature ranging from 120 to 350K and pressures up to 15 MPa were obtained. A new correlation of the thermal conductivity of natural gas has been derived.

European inter-laboratory comparison on thermal diffusivity measurements of high conductive materials by the laser flash method

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An inter-laboratory comparison on thermal diffusivity measurements of high conductive materials is organized for the first time within EURAMET, the European Association of National Metrology Institutes. One of the main tasks of EURAMET is to coordinate at the European level the uniformity and comparability of measurements as well as their traceability to the International System of Units (SI). Inter-laboratory comparisons between National Metrology Institutes (NMIs) and Designated Institutes (DIs) are thus carried out to find common understanding about measurement and data analysis procedures, to assess measurement uncertainties and to estimate the measurement capabilities of the involved participant institutes.

Three NMIs and one DI participate in this international comparison: LNE, NPL, NMIJ and VINČA. It is organized in a “star” mode in which specimen sets are provided by the pilot laboratory (LNE) and send out to all the participants at the same time. This enables to limit the overall duration of the comparison and the risks of specimens loss or damage. The disk-shaped specimens needed are machined from the same blocks of materials in order to reduce any potential scattering of results between participants due to inhomogeneity effects. The homogeneity of the sets of specimens is studied by the pilot laboratory before launching the comparison process by measuring thermal diffusivity at 23 °C on all specimens.

Each participant measures the thermal diffusivity of three materials (two metallic materials and one isotropic graphite) between 23 °C and 1400 °C by applying the laser flash method [1]. In order to examine potential aging effect, each specimen is tested during two successive thermal cycles in the investigated temperature range, with a last thermal diffusivity measurement at 23 °C after the second run. The intrinsic thermal diffusivity value at the test temperature is estimated by applying an extrapolation procedure [2] enabling to correct the measured apparent thermal diffusivity from the influence of the laser pulse energy.

This paper gives a description of the comparison process (features of the devices involved, selection of the materials and definition of the protocol) and reports the preliminary results obtained along with the associated measurement uncertainties [3].

Significant references

1. W. J. Parker, R. J. Jenkins, C. P. Butler, and G. L. Abbott, Flash Method of Determining Thermal Diffusivity, Heat Capacity, and Thermal Conductivity, *Journal of Applied Physics* 32, 1679 (1961).
2. M. Akoshima, B. Hay, B., M. Neda and M. Grelard, Experimental Verification to Obtain Intrinsic Thermal Diffusivity by Laser-Flash Method. *Int J Thermophys* 34, 778-791 (2013).
3. B. Hay, O. Beaumont, G. Failleau, N. Fleurence, M. Grelard, R. Razouk, G. Davée, J. Hameury, Uncertainty Assessment for Very High Temperature Thermal Diffusivity Measurements on Molybdenum, Tungsten and Isotropic Graphite. *Int J Thermophys* 43, 2 (2022).

New Data on the Heat Capacity, Thermal Conductivity and Viscosity of the $\text{Li}_2\text{CO}_3\text{--Na}_2\text{CO}_3\text{--K}_2\text{CO}_3$ Molten Eutectic

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A project was started in Lisbon to measure thermal, chemical and thermophysical stability of a Li-Na-K-carbonate eutectic mixture. The salt was prepared from pure reagent precursors (Li_2CO_3 , Na_2CO_3 , K_2CO_3), and the mixing involved melting, solidification, and drying. Existing methods for their preparation (at room temperature, obtaining a solid composite of nanoparticles in the solid salt followed by melting at higher temperatures or temperatures above the melting point of base salt eutectic mixture) will be discussed. Thermal conductivity (transient hot-strip), viscosity (oscillating cup technique) melting points, and heat capacity (DSC) were the techniques chosen for the measurement. New data was obtained in the temperature range from the melting point ($\sim 400^\circ\text{C}$) to 650°C . Uncertainties achieved will be discussed.

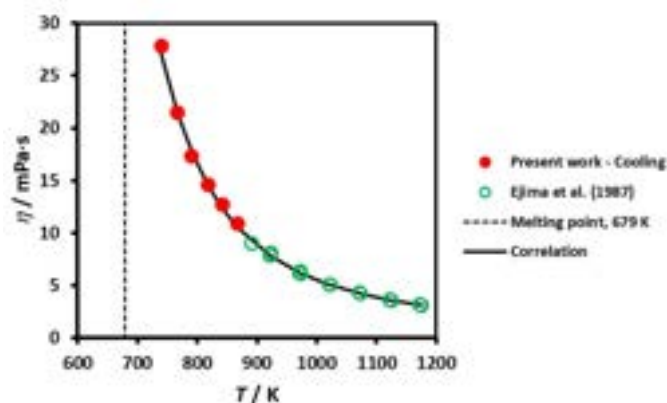


Figure 1. The viscosity of $\text{Li}_2\text{CO}_3\text{--Na}_2\text{CO}_3\text{--K}_2\text{CO}_3$ Molten Eutectic

Acknowledgment

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Significant references

- [1] C.A. Nieto de Castro, M.J.V. Lourenço, *Energies*, vol. 13 (2020), 99.
- [2] C.S.G.P. Queirós, M.J.V. Lourenço, S. I. Vieira, J.M. Serra and C.A. Nieto de Castro, *Rev. Sci. Instruments*, vol. 87 (2016), 065105.
- [3] V.B. Nunes, F.J.V. Santos, C.A. Nieto de Castro, *Int. J. Thermophys.* 1998, 19, 427-435.
- [4] T. Ejima, Y. Sato, T. Yamamura, K. Tamal, M. Hasebe, M.S. Bohn, G.J. Janz, *J. Chem. Eng. Data* vol. 32 (1987), 180-182.

Thermal Conductivity of $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$ and $[\text{C}_6\text{mim}][\text{N}(\text{CN})_2]$ Mixtures with H_2O . Understanding Structural Effects.

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In the current work we report the thermal conductivity for pure $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$ and $[\text{C}_6\text{mim}][\text{N}(\text{CN})_2]$ and for its aqueous mixtures, in the whole composition range, from 283 K to 343 K, for $P = 0.1$ MPa and analyse the effect of the cation alkyl chain length in the thermal conductivity of the pure n-3-alkyl-1-methylimidazolium dicyanamide ($n=2,4,6$) and in the structure of the aqueous mixtures, complementing previous studies on the effect of the cation on the structure of these mixtures.

The thermal conductivity was measured with the TPSYS02 thermal conductivity measurement system, employing a TP08 non-steady-state probe based on the transient hot-wire method (THW) and manufactured by Hukseflux Thermal Sensors B.V. Before the measurements, the system was validated with pure water, and the data have a relative expanded uncertainty $U_r = 0.02$.

The thermal conductivity of pure ionic liquids and their aqueous mixtures cannot be semi-theoretically estimated using the Bridgman and Filaments model at present, as shown by molecular modelling.

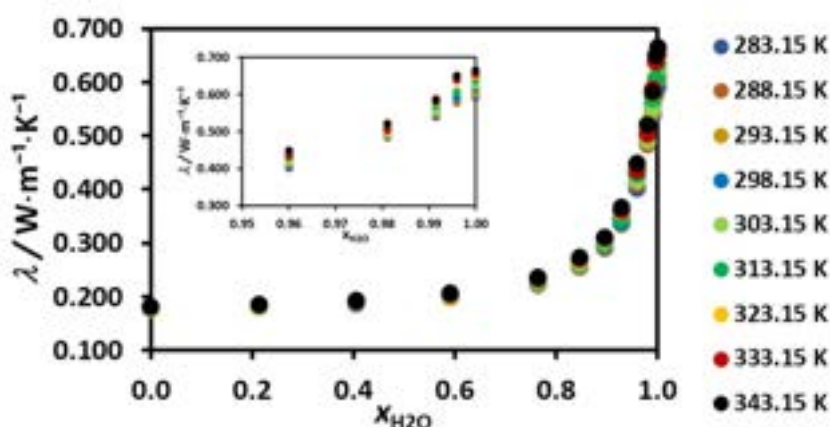


Figure 1. The thermal conductivity of the aqueous system of $[\text{C}_6\text{mim}][\text{N}(\text{CN})_2]$ as a function of the mole fraction of water, for the different temperatures studied. The indent shows the behavior for $0.95 < x_w < 1$.

Acknowledgment

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Significant references

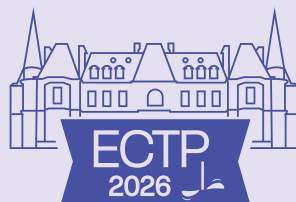
1. F.E.B. Bioucas, C.S.G.P. Queirós, D. Lozano-Martín, M. Ferreira, X. Paredes, A.F. Santos, F.J.V. Santos, M.L.M. Lopes, M. I. Lampreia, M.J.V. Lourenço, C. A. Nieto de Castro and K. Massonne. *Ind. Eng. Chem. Res.* vol. 61(5) (2022), pp. 2280–2305.
2. C.A. Nieto de Castro, A. Lamas, C. Magendran, R.M. Almeida, X. Paredes, Â.F. Santos, I.M.S. Lampreia, F.J.V. Santos, M.J.V. Lourenço. *J. Chem. Eng. Data*, vol. 69 (8), (2024), pp.2713–2734.
3. Rafael M. Almeida, Maria José V. Lourenço, Carlos Nieto de Castro. *J. Mol. Liq.*, vol. 397 (2024), 124123.
4. Rafael M. Almeida, Elitsa Gadeva, Ângela Santos, Rita Pacheco, Maria José V. Lourenço, Carlos A. Nieto de Castro. *J. Mol. Liq.*, vol. 436 (2025), 128270.

1.9

Transport properties

Thermal Conductivity

Measurement



Investigating Thermal Conductivity Anisotropy in Wurtzite Semiconductors: AlN, GaN, ZnO, ZnS

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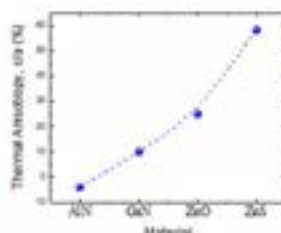
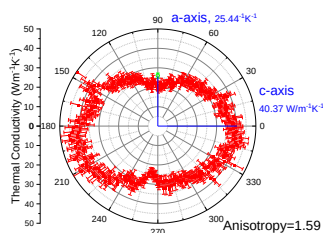
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Wurtzite-structured III-nitride (AlN, GaN) and II-oxide (ZnO) semiconductors are foundational materials for next-generation devices. They offer exceptional performance in high-power electronics, UV/blue lasers, and robust sensing applications due to their wide bandgaps, high breakdown fields, and outstanding thermal stability. Meanwhile, wurtzite ZnS holds significant promise for visible-light optoelectronics. While these applications critically rely on efficient thermal management, there remains a significant lack of consensus and consistent experimental data regarding their intrinsic thermal anisotropy. Specifically, previous studies often lack systematic investigation across different crystallographic planes, hindering the precise thermal design required for optimal device performance. To address the limitations of conventional thermometry—which struggles to provide reliable, non-destructive, and orientation-specific thermal conductivity data on the same sample—this work employs two novel, recently developed, and patented experimental methodologies (licensed by **Linseis Messgeräte GmbH**). These are suitable for investigating thermal conductivity along in-plane directions, thereby providing direct access to thermal anisotropy. We systematically investigated the thermal properties along the primary m-, a-, and c-crystallographic planes of these wurtzite semiconductors using Anisotropic Thermoreflectance Thermometry¹ (ATT) and Beam-Offset Thermoreflectance.² A key development in this approach is the use of a 1-dimensional heat source, which offers several advantages for probing heat transport along selected crystallographic orientations. Employing these techniques, we determine the complete thermal conductivity tensor for each wurtzite material. To provide a fundamental understanding of the observed heat transfer, the experimental results are complemented by an analysis of their acoustic vibrational properties, achieved through Raman and Brillouin scattering measurements conducted on the same samples. Furthermore, we conducted *ab initio* calculations to model the phonon dispersion and scattering mechanisms that govern the thermal anisotropy. The resulting data resolve long-standing inconsistencies and provide the precise parameters necessary for thermal modeling. **Figure 1** displays an example of our findings regarding the thermal anisotropy ratio at room temperature, as well as an angular-dependent thermal conductivity polar map for ZnS. This work delivers a complete experimental and theoretical framework essential for maximizing the thermal performance of next-generation wurtzite-based power and optoelectronic devices.



1. Pérez, L. A., Xu, K., Wagner, M. R., Döring, B., Perevedentsev, A., Goñi, A. R., Campoy-Quiles, M., Alonso, M. I. & Reparaz, J. Review Of Scientific Instruments, vol. (93), (2022). 034902.
2. Xu, K., Guo, J., Raciti, G., Goni, A. R., Alonso, M. I., Borrisé, X., Zardo, I., Campoy-Quiles, M. & Reparaz, J. S., International Journal Of Heat And Mass Transfer, vol. 214, (2023), 124376.

On The Effect Of Heater Heat Capacity On Thermal Conductivity Components Estimation Of Composite Materials When Using The Plane Source Method

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The orthotropic behaviour of unidirectional fibre-reinforced composites is fully described by the out-of-plane thermal conductivity k_x (in the perpendicular-to-fibre direction) and the in-plane thermal conductivity k_y (in the along-fibre direction). The plane-source method [1] is a promising transient method to estimate simultaneously both these conductivity components. In particular, the experimental device here investigated consists of a flexible, thin electrical heater put in contact with two identical, larger samples of composite material. Additionally, temperature measurements involved in the estimation procedure may be obtained from the unheated surface of the sample through non-contact measuring techniques. For this reason the sample backside is subjected to free convection with the surrounding air.

In this work the effect of the heater heat capacity on the estimates of the unknown parameters (i.e., k_x , k_y and the heat transfer coefficient h at the sample backside) is investigated when the tested sample is a fibre-reinforced-polymer (FRP) composite, and the Gauss-Newton method [2] for parameter estimation is used. For this purpose temperature measurements are simulated through a 3D FEM model, including both the heater and the insulating material around all the lateral boundaries of the experimental set-up. Random errors are then added to the numerical model results to simulate real temperature measurements. On the contrary, the thermal model describing the behaviour of the sample, completely neglects the presence of the heater. In fact, it considers only a 2D slab (sample) partially heated at one boundary, and exposed to free convection at the other one. Note that the exact analytical solution is already available in the literature [3, 4]. Then, the heater heat capacity effects are taken into account by applying the approximation error model (AEM) [5] to correct the original thermal model (reduced model).

Results show that, although the heater thickness is very small, its heat capacity significantly the estimates, even when it is less than 10% of the sample heat capacity (see Table 1). As shown in this table, the AEM can improve the estimates of all the unknown parameters by compensating the modelling errors related to the heater thermal inertia.

Table 1. Effect of the heater thermal inertia on the estimated parameters.

Parameter	Exact values	Heater neglected	Δ [%]	With AEM	Δ [%]
k_x [W/m°C]	0.6	0.2717	-54.7	0.6183	3.0
k_y [W/m°C]	0.7	0.7166	2.4	0.6875	-1.8
h [W/m ² °C]	4	6.2727	56.8	4.0129	0.3

Significant references

1. G. D'Alessandro and F. de Monte, *Heat Transf. Eng.*, vol. 43, no. 3-5 (2022), pp. 257-269.
2. J.V. Beck and K.J. Arnold, *Parameter Estimation in Engineering and Science*. New York, NY, USA, Wiley, 1977.
3. G. D'Alessandro, *Int. J. Heat Mass Transf.*, vol. 246 (2025), 127019.
4. R. McMasters, F. de Monte and J. Beck, *ASME J. Heat Transf.*, vol. 141 no.7 (2019), 071301.
5. C.C. Pacheco, H.R.B. Orlando, M.J. Colaço and G.S. Dulikravich, *Numer. Heat Transf. Part A*, vol. 68 (2015), pp. 1198–1219.

Thermal Conductivity Prediction Model Based on Hidden Scale Invariance

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This work introduced the critical parameters and acentric factor into the reduced thermal conductivity. The relationship between reduced thermal conductivity and reduced density was scaled into an exponential-linear superposition form. A predictive model for the thermal conductivity is constructed based on hidden scale invariance. A comprehensive dataset comprising 66,187 experimental data points for 123 pure fluids and 14,447 data points for 150 mixtures was compiled from approximately 600 references, primarily sourced from the NIST ThermoData Engine (TDE) database version 10.1. As a result, the proposed model achieves average absolute relative deviations (AARD) of 3.0% for pure fluids and 4.7% for mixtures. The model contains only three fitting parameters for each fluid. For mixtures, it requires only the weighted average of the pure fluid parameters, with no need for additional interaction parameters.

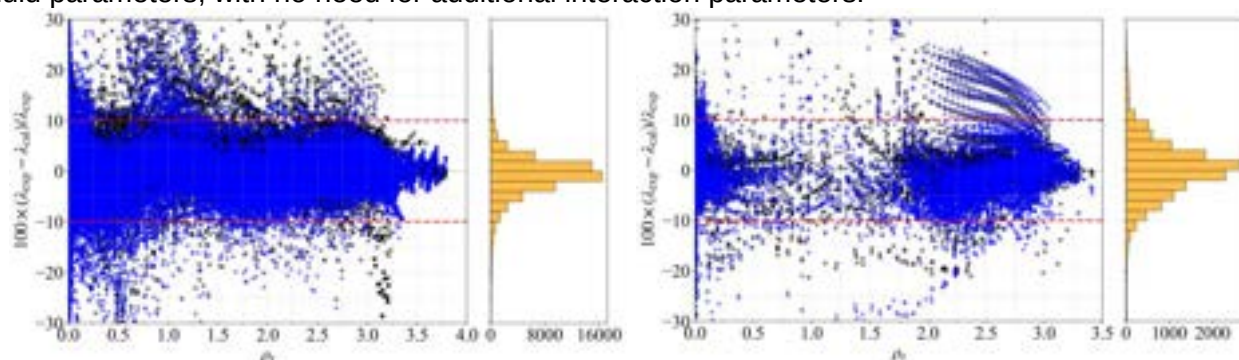


Figure 1. Relative deviations of 123 pure fluids (left) and 150 mixtures (right) from the calculated values λ_{cal} by the model in this work (●) and by the REFPROP 10.0 recommended model (■). The histogram on the right side only displays the deviation distribution of this work.

Table 1. Summary of experimental data for pure fluids and mixtures.

		Types	N_{tot}	N_{use}	N_{lim}	N_{dev}
pure fluids	total	123	66187	63661	1505	1021
	N/N_{tot}			96.2%	2.3%	1.5%
mixture	total	150	14447	13687	454	306
	N/N_{tot}			94.7%	3.1%	2.1%

N_{tot} : total number of experimental data; N_{use} : number of adopted data; N_{lim} filters out data points that exceed the limits of the reference equation of state in REFPROP 10.0; N_{dev} filters out data points that deviate from the model by more than 30%.

Acknowledgment

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Significant references

1. X. Wang, H. Guo, X. Dong, Y. Zhao, X. Yang, M. Gong, Liquid thermodynamic-transport property coupling: Linking thermal conductivity to density using hidden scale invariance, *Phys. Fluids*, 38(1) (2026).
2. Z. Li, Y. Duan, X. Yang, Linking Thermal Conductivity to Equations of State Using the Residual Entropy Scaling Theory, *Ind. Eng. Chem. Res.*, 63(42) (2024) 18160-18175.

Liquid Viscosity Measurements for 3,3,3-Trifluoropropene (R1243zf) and its Binary Mixtures with 1,1,1,2-Tetrafluoroethane (R134a) at Pressures up to 40 MPa

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The global phase-out of high global warming potential (GWP) refrigerants has prompted the development of low GWP alternatives, with a focus on hydrofluoroolefins (HFOs). This study presents experimental liquid viscosity measurements for pure 3,3,3-trifluoroprop-1-ene (R1243zf) and its binary mixtures with 1,1,1,2-tetrafluoroethane (R134a). R1243zf, a promising low GWP refrigerant (GWP = 0.29) with zero ozone depletion potential (ODP), has gained attention due to its favorable thermophysical properties and potential for use in refrigeration systems, as demonstrated by previous research on its vapor-liquid equilibrium (VLE) and other transport properties. Recent studies suggest that R1243zf/R134a mixtures are an ideal alternative to R410A in existing precision air conditioning systems. Viscosity is a crucial property for refrigerants, influencing heat transfer efficiency and compressor performance in refrigeration cycles. The liquid viscosities of R1243zf and its binary mixtures with R134a were measured using the vibrating-wire viscometer at temperatures ranging from (253 to 373) K and pressures up to 40 MPa. The combined expanded relative uncertainty ($k = 2$) of viscosity measurements was estimated to be 2.0%. The experimental data were compared with predictions from existing models. Additionally, the effect of pressure and temperature on viscosity was analyzed to provide insights into the operational performance of these mixtures under realistic working conditions.

2.1

Thermodynamic Properties

Density Measurement



Gravimetric Density Measurements: Gold Standard or Yesterday's News?

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Gravimetric density measurements based on the magnetic-suspension balance (MSB) have, in many cases, provided the most reliable and internally consistent fluid-density data available and underpin some of the most accurate reference equations of state. A recent review of four decades of MSB-based densimetry highlights both the outstanding performance and the limited global dissemination of such instruments [1]. Only a small number of MSB-based densimeters exist worldwide, and new developments have been rare, as evidenced in the past decade [2-4]. Moreover, obtaining reference-quality data with MSB-based densimeters requires substantial experimental expertise; e.g., systematic effects such as the force-transmission error must be carefully analyzed, quantified, and corrected to achieve the highest level of accuracy [5]. Nevertheless, MSB-based densimetry remains one of the most advanced thermophysical property measurement techniques available today.

In contrast, simpler commercial techniques – most prominently vibrating-tube densimeters – have gained ground because of their convenience, despite apparent limitations in the gas phase. At the same time, the need to provide transparent and defensible uncertainty statements in thermophysical property measurements persists; although GUM-based methodologies have long been the accepted standard, their complexity often leads to them being overlooked. Consequently, approaches that are easier to apply while remaining fully GUM-consistent – such as the recently introduced Sensitivity Analysis Method [6] – provide a reliable basis for robust and defensible uncertainty evaluations.

This plenary lecture will confront the central question: Is high-accuracy gravimetric densimetry still the “gold standard”, or is it becoming “yesterday's news”? Beyond this, the talk will also consider whether MSB-based technology will continue to play a meaningful role in the characterization of substances relevant to the energy transition – such as cryogenic energy carriers or fluids used in CCUS – or whether its future will be mainly restricted to national metrology institutes and carefully selected reference-data applications. Ultimately, the advantages and limitations of MSB-based densimetry will be contrasted with the practical appeal – and pitfalls – of alternative commercial methods.

Significant references

1. X. Yang, R. Kleinrahm, M. O. McLinden, M. Richter, *Int. J. Thermophys.*, vol. 44 (2023), 169.
2. X. Yang, M. Richter, Z. Wang, Z. Li, *J. Chem. Thermodyn.*, vol. 91 (2015), 17.
3. M. Richter, R. Kleinrahm, R. Lentner, R. Span, *J. Chem. Thermodyn.*, vol. 93 (2016), 205.
4. L. Bernardini, R. Kleinrahm, M. O. McLinden, M. Richter, *Int. J. Thermophys.*, vol. 45 (2024), 49.
5. R. Kleinrahm, X. Yang, M. O. McLinden, M. Richter, *Adsorption*, 25 (2019), 457.
6. L. Bernardini, M. O. McLinden, X. Yang, M. Richter, *Int. J. Thermophys.*, vol. 45 (2024), 164.

Dew-Point Density Measurements of Gas Mixtures with Low Uncertainty

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The development of predictive thermodynamic models is essential to enhance the efficient design of technical systems that reduce energy consumption and minimize environmental impact. Such models rely on high-quality experimental data with low uncertainties. Among such data, dew-point properties of gas mixtures are particularly important, yet difficult to measure due to phase-transition effects that can distort results. Addressing these challenges requires advanced experimental techniques in combination with robust datasets and uncertainty analysis methods.

State-of-the-art density and dew-point density measurements typically rely on Magnetic Suspension Balances^[1]. Although widely used, these instruments face limitations when applied to pure gases and gas mixtures because of sorption effects, especially near the dew line. Adsorption on the surfaces of immersed objects affects weight readings and derived densities, while selective adsorption of the less volatile component(s) on the apparatus's internal surfaces alters mixture composition. These effects increase measurement uncertainty, making improved experimental methods essential for generating reliable data and advancing thermodynamic modeling.

The Four-Sinker Densimeter (FSD)^[2] was developed to improve dew-point density measurements by simultaneously determining fluid density and adsorption loads, allowing partial correction of sorption effects. In this work, we present density and adsorption measurements for binary CO₂-hydrocarbon mixtures obtained with the FSD. The results are compared to previous state-of-the-art data, and a preliminary dew-point density analysis is provided. Since gravimetric systems alone cannot fully characterize the adsorbed phase, the measurements are complemented with Molecular Dynamics Simulations, which provide insights into selective adsorption and the density of the adsorbed phase^[3]. Together, these approaches form the basis for developing a correction model for dew-point density determination with low uncertainty.

Overall, we demonstrate that accurate dew-point densities measurements of gas mixtures constitute an interdisciplinary challenge that requires improved gravimetric techniques, high-accuracy calibration, accessible uncertainty analysis frameworks, and molecular-level modeling to properly characterize adsorption phenomena.

Acknowledgment

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Significant references

1. X. Yang, R. Kleinrahm, M. O. McLinden, and M. Richter, *Int. J. Thermophys.*, vol. 44.11 (2023), p. 169.
2. L. Bernardini, R. Kleinrahm, K. Moritz, M. O. McLinden, and M. Richter, *Int. J. Thermophys.*, vol. 45.49 (2024).
3. M. Sekulla, Linking Experiments and Molecular Simulations: A Way to Accurate Dew-Point Densities, *PhD Thesis* (2025).

Liquid Density of R1132(E) Measured by a Vibrating-Tube Densimeter

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To support the development of next-generation environmentally friendly refrigerants under strengthening global regulations on hydrofluorocarbons (HFCs), this study investigates the liquid density of the low-GWP hydrofluoroolefin (HFO) refrigerant R1132(E). Reliable liquid density data are essential for developing accurate equations of state (EOS), which are vital for the design and simulation of refrigeration and air-conditioning systems. Liquid density measurements were conducted using a vibrating-tube densimeter (Anton Paar DMA HPM) over temperatures from 273 to 353 K and pressures up to approximately 10 MPa. Figure 1 shows a schematic of the apparatus, which consisted of the densimeter in a thermostatic chamber, a platinum resistance thermometer, and a quartz pressure transducer. Temperature and pressure were stabilized to ± 0.01 K and ± 0.01 MPa before data acquisition. To convert oscillation period data into density, two types of calibration equations were constructed. In this study, a calibration procedure that employs water and R1336mzz(Z) as reference substances is referred to as a two-reference calibration, whereas a procedure that employs water, R1336mzz(Z), and vacuum—incorporating vacuum oscillation data to expand the density range and improve accuracy—is referred to as a three-reference calibration.

The two-reference calibration exhibited increasing deviations in the high-temperature and low-density region, yielding an average absolute deviation (AAD) of 0.63% and a maximum deviation of 2.5%. In contrast, the three-reference calibration significantly improved accuracy, with an AAD of 0.21% and a maximum deviation of 0.64%. Figure 2 presents the relative deviations. The measured densities also showed good agreement with values calculated using the Helmholtz-energy-based EOS developed by Akasaka and Lemmon [1]. The inclusion of vacuum-state oscillation data extended the calibration range beyond the densities of the reference fluids, enabling reliable measurements even near the saturation line. Comparison with constant-volume literature data confirmed that the three-reference calibration provides accuracy comparable to that technique [2]. These results demonstrate that the improved calibration approach enables high-precision liquid density measurements for R1132(E) over a wide thermodynamic range, supporting the development of next-generation low-GWP refrigerants.

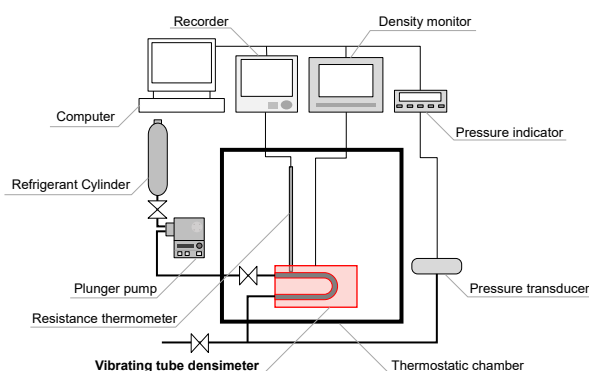


Figure 1. Schematic of density measurement apparatus.

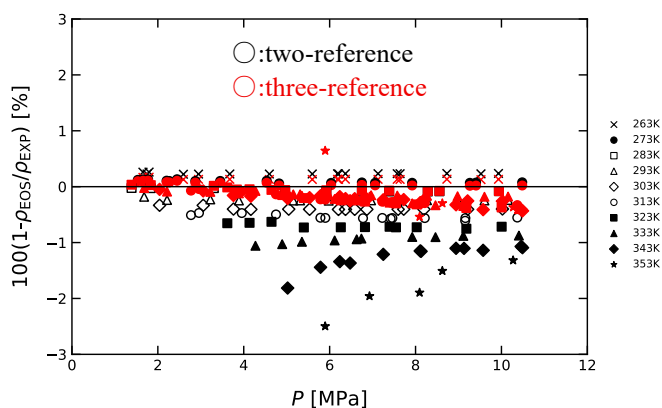


Figure 2. Relative deviations between the measured and calculated R1132(E) values.

Acknowledgment

The authors would like to express their sincere appreciation to Daikin Industries, Ltd. for providing the refrigerant sample used in this study.

Significant references

1. R. Akasaka and E. W. Lemmon, *Int. J. Thermophys.*, vol. 45 (2024), 174.
2. N. Sakoda, U. A. Perera, K. Thu, and Y. Higashi, *Int. J. Refrig.*, vol. 140 (2022), pp. 166–171.

Novel Measurement Protocol for LNG Density at Cryogenic Conditions Using a Vibrating-Tube Densimeter

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In line with the European Green Deal, the EU has set a legally binding target to reduce greenhouse gas emissions by at least 55% by 2030 relative to 1990 levels. To achieve this, increased use of liquefied energy gases is essential, with LNG thermodynamic properties identified as a research priority. The currently accepted LNG density uncertainty of 0.45% ($k = 2$) limits industrial practice. Reducing in-field uncertainties below 0.3% ($k = 2$) demands rigorous control of sampling and vaporization biases, enabling traceable and rapid cryogenic density measurements.

In this context, a commercial high-pressure vibrating-tube densimeter (VTD) is set up to perform low-flow LNG density measurements over the temperature range from 100 K to 140 K and at pressures up to 10 MPa. Previous work by von Preetzmann *et al.* [1] demonstrated the feasibility of using a VTD at temperatures down to 100 K. However, the vacuum oscillation period was found to increase significantly during thermal and pressure cycling, resulting in a persistent vacuum drift. This continuous change in the vacuum characteristics of the VTD impaired the applicability of established calibration models [2,3], reducing accuracy and substantially increasing experimental effort.

Against this background, we propose a new measurement protocol involving sequential state-point calibrations with He and N₂ at identical (T, p) conditions, followed by validation of the calibration parameters using CH₄. The calibrated densimeter is then applied to measure the densities of at least four ternary or quaternary LNG mixtures. This protocol aims to mitigate the impact of vacuum drift on experimental uncertainty while simultaneously simplifying the overall measurement procedure. The resulting densities are compared with EOS-LNG predictions [4] implemented in TREND 6.0 [5]. For validation, reference data for the identical LNG sample mixtures, measured with a cryogenic single-sinker magnetic-suspension densimeter [6] and reported in the GPA Research Report RR-254: *Thermodynamics of Liquefied Natural Gas (LNG)* [7], are used.

Acknowledgment

The authors gratefully acknowledge financial support from the CryoMet project (*Metrology for reliable liquefied energy gases measurement*, Project Number: 24GRD07).

Significant references

1. N. Von Preetzmann, D. Zipplies, R. Span, and M. Richter, *Int. J. Thermophysics.*, vol. 45 (2024), p. 72.
2. S.L. Outcalt and M.O. McLinden, *Ind. Eng. Chem. Res.*, vol. 46 (2007), pp. 8264–8269.
3. E.F. May, W.J. Tay, M. Nania, A. Aleji, S. Al-Ghafri, and J.P.M. Trusler, *Rev. Sci. Instrum.*, vol. 85 (2014), p. 095111.
4. M. Thol, M. Richter, E.F. May, E.W. Lemmon, and R. Span, *J. Phys. Chem. Ref. Data*, vol. 48 (2019), p. 033102.
5. R. Span, R. Beckmüller, A. Jäger, E. Mickoleit, T. Neumann, S. Pohl, B. Semrau, and M. Thol, *TREND. Thermodynamic Reference and Engineering Data 6.0*, Ruhr-Universität Bochum, Bochum (2022).
6. M. Richter, R. Kleinrahm, R. Lentner, and R. Span, *J. Chem. Thermodyn.*, vol. 93 (2016), pp. 205–221.
7. M. Richter, E.F. May, P. Eckmann, S.A. Al-Ghafri, and R. Kleinrahm, *Research Report RR-254 Thermodynamics of Liquefied Natural Gas (LNG)* (2024).

2.2

Thermodynamic Properties

Data-Driven Modelling



Unlocking molecular equations of state for process design with large-scale parametrization and data-driven extrapolation

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Vapor-liquid equilibria (VLE) are the workhorse of process engineering as they are crucial to model absorption and distillation processes which make up a significant share of the overall space, costs, and energy requirements of any given chemical or pharmaceutical production.¹ Small errors in the prediction of VLEs for multicomponent mixtures can – in the worst case – lead to significantly altered requirements for the separation process. In particular, it is crucial to know the presence of azeotropes as early as possible in the design of a separation sequence to avoid costly redesigns at later stages.

In the process industry g^E models (mostly NRTL and UNIQUAC) have been established as reliable tools for the calculation of VLEs. However, they are by design not suitable to model systems at higher pressures. A more comprehensive modeling approach is provided by equations of state, of which the family of cubic equations of state reached the highest adoption in industrial practice. Again, we face shortcomings with cubic equations of state, mostly around the choice of suitable mixing rules for a given system, and the modeling of systems containing hydrogen bonds. This leaves molecular equations of state like the SAFT family, which explicitly account for intermolecular interactions – including hydrogen bonds – to extrapolate well for a large space of chemicals. However, adoption has been slow due to the comparatively high complexity and computational demands.

In this work, we overcome the conventional computational limitations associated with molecular equations of state by using state-of-the-art computational tools like implicit automatic differentiation to parametrize the PC-SAFT equation of state² for the most comprehensive set of binary systems – close to 8000 – so far.³ The resulting binary interaction parameters are used to train neural network models in order to extrapolate to mixtures for which no experimental data is available as robustly as possible.

The resulting parametrization provides reliable VLE predictions for millions of binary systems and all their combinations in multicomponent mixtures. With this contribution, we aim to pave the way towards a stronger adoption of molecular equations of state in process design and thereby bring the molecular insights required for the design of a future sustainable chemical industry closer to the people who will engineer this transition.

Acknowledgment

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Significant references

1. D. Sholl, R. Lively, *Nature*, vol. 532 (2016), pp. 435-437.
2. T. Esper, G. Bauer, P. Rehner, and J. Gross, *Ind. Eng. Chem. Res.*, vol. 62 (2023), pp. 15300-15310.
3. P. Rehner, A. Bardow, J. Gross, *Int. J. Thermophys.*, vol. 44 (2023), pp. 179.

Machine Learning and Molecular Representations: Key Challenges in Data-Driven Thermodynamic Property Prediction

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The accurate prediction of thermodynamic and thermochemical properties remains a central challenge in chemical engineering, with direct implications for reaction kinetics, process design, and molecular innovation. Traditional computational methods—such as group contribution (GC), quantum chemistry (QC), and Monte Carlo simulations—have historically supported this effort, yet each faces practical limitations, including lack of generalizability, high computational cost, and sensitivity to modeling assumptions. As machine learning (ML) continues to advance, it offers a compelling alternative capable of learning complex structure–property relationships directly from data.

A critical but often underestimated factor in ML-based molecular property prediction is the choice and reliability of molecular representation. Recent studies show that engineered descriptors, string-based encodings, and learned graph representations can all yield competitive results, but their performance heavily depends on the stability, reproducibility, and chemical fidelity of the upstream data pipeline. Small variations in molecular geometry, descriptor generation software, or input formats can propagate significant errors into final predictions, even when robust ML algorithms and rigorous model development practices are applied.

This integrated work examines the methodological challenges associated with molecular representation and highlights their consequences through a case study on the prediction of gas-phase standard enthalpy and entropy of formation. The analysis outlines the strengths and limitations of state-of-the-art representation strategies—ranging from descriptors used in traditional QSPR approaches to graph neural network (GNN) architectures—and emphasizes how representation choices can profoundly influence model robustness and reproducibility. By showcasing the sensitivity of ML predictions to upstream computational steps, the study underscores the need for transparent and standardized workflows that ensure consistency in molecular data preparation.

Overall, the study reinforces the progress in ML-based thermodynamic property prediction depends not only on algorithmic advances but also on addressing the foundational challenges of molecular representation, ensuring that data-driven models remain trustworthy, generalizable, and suitable for engineering applications.

Acknowledgment

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Significant references

1. C. Trinh, Y. Tbatou, S. Lasala, O. Herbinet, and D. Meimaroglou, *Processes*, vol. 11 (2023), p. 3325.
2. C. Trinh, S. Lasala, O. Herbinet, and D. Meimaroglou, *Algorithms*, vol. 16 (2023), p. 573.
3. E. Heid, K. Greenman, Y. Chung, S. Li, D. Graff, F. Vermeire, H. Wu, W. Green, and C. McGill, *Journal of Chemical Information and Modeling*, vol. 64 (2023), p. 9.

Symbolic Regression for Shared Expressions: A single Saturation Pressure Model for over 20 Substances

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In process and energy engineering, the understanding of thermophysical properties, especially the phase-change behavior, is crucial. Classical modeling approaches for thermodynamic properties are time-consuming and often rely heavily on expert knowledge. Symbolic regression offers a promising alternative by enabling faster and more flexible model development. To support this, the symbolic regression tool Thermodynamics-informed Symbolic Regression (TiSR) [1] is being developed, which has already demonstrated its capability in our previous work [2]. TiSR aims to combine a symbolic regression core with features explicitly implemented for thermodynamic property modeling, including handling strongly scattered experimental data, different residual pre- and post-processing options, and the incorporation of domain- and problem-specific prior knowledge.

One of these features is the ability to develop shared expressions. By using a fixed mathematical structure with varying parameter sets, shared expressions can model many substances with a single expression. These types of expressions generalize better across substances and require fewer data points per individual substance for satisfactory fitting results. The structural and, in some cases, even the parameter optimization for shared expressions is often suboptimal, as parameter optimization is non-trivial and structural optimization (apart from trial-and-error) is still emerging. Therefore, despite their benefits, shared expressions are heavily underused.

Here, we demonstrate the potential of TiSR to develop a single mathematical expression for sublimation, melting, and vapor pressure (saturation pressure) for more than 20 substances. The resulting expression contains parameters valid for all substances and phases (global parameters), phase-specific parameters, and only one parameter for each substance/phase combination. This method drastically reduces the number of specific parameters required to model the saturation pressure, and thereby the number of required data points per substance. The new method will be evaluated against classical methods, and its associated uncertainty will be discussed.

Acknowledgment

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Significant references

1. V. Martinek, O. Frotscher, M. Richter, and R. Herzog, Zenodo (2025). <https://doi.org/10.5281/zenodo.15100641>
2. O. Frotscher, V. Martinek, R. Fingerhut, X. Yang, J. Vrabec, R. Herzog, and M. Richter, *Int. J. Thermophysics*, vol. 44 (2023), 105. <https://doi.org/10.1007/s10765-023-03197-z>

Machine-Learning-Guided Measurement and Modeling of Thermodynamic Properties: Symbolic Regression, Optimal Experimental Design, and a New Setup for LLE Characterization

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In process and energy engineering, it is crucial to understand the behavior of thermodynamic properties. Thermodynamic equations of state (EOS) are commonly used to incorporate these properties into process simulations and performance analyses. To accelerate EOS development, especially for mixtures, we present an approach that efficiently integrates data acquisition with physically informed modeling. This integrated workflow combines the software tool Thermodynamics-informed Symbolic Regression (TiSR) [1], developed within our ongoing project, with optimal experimental design (OED) to minimize the required experimental effort. The project establishes an iterative cycle in which symbolic regression generates candidate EOS, OED identifies the most informative next measurements, and the expanded data set feeds back into model refinement. This approach has already demonstrated significant reductions in measurement effort for density data [2].

In this work, the methodology is extended to fluid mixtures exhibiting liquid–liquid equilibria (LLE), which introduce additional challenges due to composition-dependent behavior and higher experimental cost. A new measurement setup for LLE characterization is introduced, combining (1) Raman spectroscopy for in situ analysis of phase compositions and (2) a vibrating-tube densimeter for in situ density determination. The setup is designed to enable accurate phase identification and composition analysis, providing high-quality data suitable for EOS development and for the validation of classical and machine-learning-based models. Initial experimental studies focus on the benchmark system water + isobutanol. In future work, OED-guided experiments will be used to conduct time- and cost-efficient experiments, emphasizing the incorporation of experiment-specific cost functions that reflect trade-offs associated with variations in temperature, pressure, and composition. The resulting LLE and density data will support the development of application-specific EOS and binary departure functions, leveraging TiSR's ability to impose thermodynamic shape constraints and ultimately enabling physically consistent and computationally efficient models.

Acknowledgment

This work was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) within the priority program SPP 2331 - Machine Learning in Chemical Engineering - project no. 466528284.

Significant references

1. V. Martinek, O. Frotscher, M. Richter, and R. Herzog, Zenodo (2025). <https://doi.org/10.5281/zenodo.15100641>
2. O. Frotscher, V. Martinek, R. Fingerhut, X. Yang, J. Vrabec, R. Herzog, and M. Richter, *Int. J. Thermophysics*, vol. 44 (2023), 105. <https://doi.org/10.1007/s10765-023-03197-z>

2.3

Thermodynamic Properties

Theory and Data-Driven Modelling



A new thermodynamic function for binary mixtures: the co-molar volume

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The objective of this work was to relate partial molar volumes of binary liquid mixtures to the intrinsic (Voronoi) volumes [1]. The purpose is to gain better understanding of the physical meaning of partial molar volumes in terms of the actual volumes occupied by the molecules. The intrinsic volumes are direct measures of the physical volumes occupied by the two components and they give information about the structure of mixtures more directly than do partial molar volumes [2]. Inspired by analysis of co-moving velocity in immiscible two-phase flow in porous media [3], we develop relevant theory and perform computer simulations to test the theory. Partial molar volumes were computed by molecular dynamics simulations for three different binary mixtures of Lennard-Jones/spline particles. For the same mixtures, we also computed intrinsic volumes by Voronoi tessellation. The two kinds of volumes are connected by a single new thermodynamic variable - the co-molar volume v_m - thus bringing intrinsic volumes into thermodynamics. The connection is given by $v_1 = \hat{v}_1 - x_2 v_m$ and $v_2 = \hat{v}_2 + x_1 v_m$ where v_i and $\hat{v}_i$ are the intrinsic volume and partial molar volume, respectively, of component i and x_i is the mole fraction of component i . Partial molar and intrinsic volumes are shown as function of composition in Figure 1. The connection is closed with a near-linear relation between v_m and $w = \hat{v}_1 - \hat{v}_2$ as shown in Figure 2.

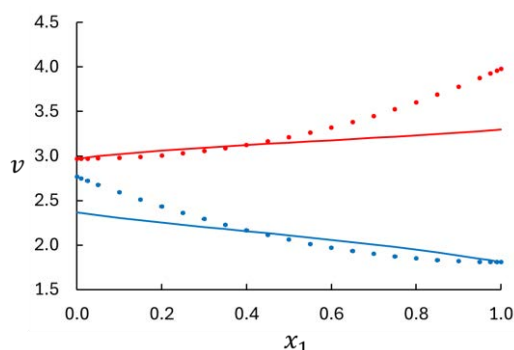


Figure 1. Partial molar volumes (dots) and intrinsic volumes (lines) as function of mole fraction of component 1. Blue and red symbols represent component 1 and 2, respectively.

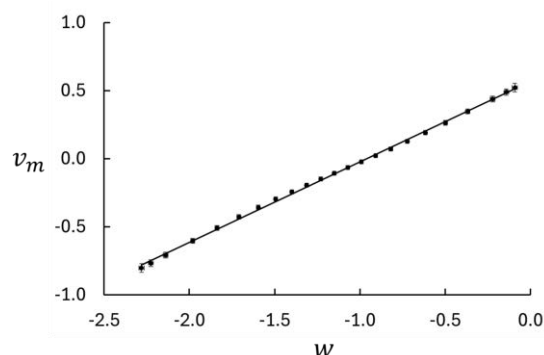


Figure 2. Co-molar volume v_m as a function of partial molar volume difference w .

Acknowledgment

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Significant references

1. K. P. Olsen, B. Hafskjold, A. Lervik, and A. Hansen, *J. Chem. Phys.*, vol. 163 (2025), 184504.
2. A. Nichiporenko, E. D. Kadtsyn, and N. N. Medvedev, *J. Molecular Liquids* vol. 423 (2025), 127005.
3. S. Roy, H. Pedersen, S. Sinha, and A. Hansen, *Transport in Porous Media*, vol. 143, (2022)69-102.

A Stochastic Helmholtz Equation of State Mixture Model with Quantified Model Errors

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The simulation and optimization of thermodynamic cycles and machines require adequate knowledge of the working fluids in use. In order to fulfil the rising needs for efficient and ecological appropriate machines, the use of mixtures with suitable properties in the desired working regimes is under discussion.

Thus, a proper knowledge of their thermophysical properties is of interest. Therefore, typically Helmholtz Equations of State (HEOS) are used. For mixtures, the Helmholtz energy is calculated using mixing models with adjustable interaction parameters. As the data used for calibration is subject to uncertainty, the inferred parameters are also uncertain. Furthermore, often no or only little data is available, hence simplified mixing models are used.

The distribution of interaction parameters can be estimated from noisy data using for instance Markov Chain Monte Carlo methods as used in [1] and shown in Figure 1. However, the quantified uncertainty in that work was only based on measurement noise. Different uncertainties and errors such as simplifications in the mixing model, uncertainties of the underlying HEOS or deviations due to a set convergence limit of the flash algorithm were not taken into account in the fit to Vapor-Liquid-Equilibrium (VLE) data. These errors can be summarized as model error [2] and can be calculated by appropriately assessing the remaining mismatch between data and the stochastic HEOS model. In this work a Bayesian approach to quantify model error will be presented. The method and resulting uncertainties will be illustrated for different working fluid mixtures and the impact of the uncertainties on property predictions and VLE properties will be visualized.

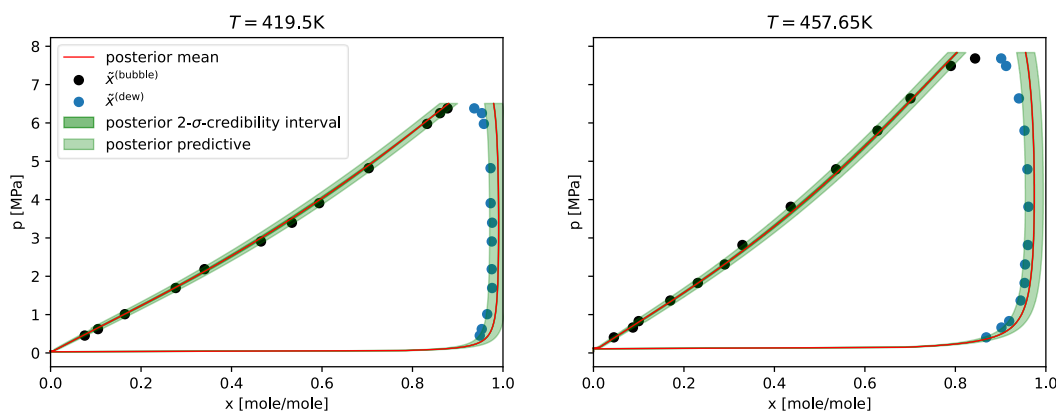


Figure 1. Posterior Predictive for the vapor-liquid equilibria of a propane-dodecane mixture at $T = 419.15K$ and $T = 457.65K$ [1]

Acknowledgment

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Significant references

1. L. Schnelting, B. B. Bederna, G. Raabe, U. Römer and C. Thomas, *38th Int. Conf. on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems*, Paris, July 2025.
2. K. Sargsyan, X. Huan and H. N. Najm, *Int. J. Uncertainty Quantification*, vol. 9, no. 4, pp. 365–394, 2019.

Thermodynamic Property Model Based on Physics-informed Neural Network (PINN) and Chaos Theory

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Establishing an equation of state (EoS) with accuracy, universality, and simplicity is the ideal objective in the research of thermodynamic property models. Machine learning technology is growing rapidly and has achieved significant success in applications. There are two primary research approaches for the application of machine learning in predicting thermodynamic properties. One involves integrating machine learning directly into the thermodynamic property models, such as the PC-SAFT EoSs or activity coefficient models, resulting in a clear mathematical function. Another one focuses on leveraging knowledge of thermodynamic consistency to create a black box model using machine learning. Here, we will construct a black-box model for thermodynamic properties of n-alkane based on the physics-informed neural network (PINN) framework,[1] which utilizes structured prior information to create both data-efficient and physically robust learners. The training and validation dataset comprises various experimental thermodynamic properties from TDE,[2] as well as calculation results from the Helmholtz energy EoSs included in REFPROP 10.0.[3] The input parameters contain the microscopic features: atom, the number of each atom, molecule special structure, bond parameters, dipole moment etc.; the group contribution features; the macroscopic features: the phase state (temperature, density or pressure), acentric factor, critical temperature and density, molar mass etc.; and the chaos features for normalizing properties from different fluids. We performed the uncertainty analysis of those input parameters to decisively identify and eliminate quantities with high sensitivity, which ensures the reliability and accuracy of our model. In addition to data bias, the loss function will incorporate constraints on thermodynamic consistency and isotropic line tends as part of the thermodynamic information in the PINN framework. Ultimately, a black box model for the thermodynamic properties of n-alkane was developed based on PINN, along with a method for evaluating the model.

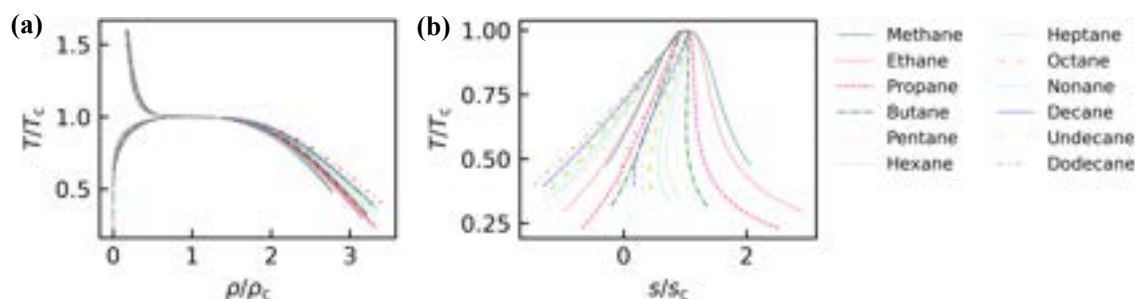


Figure 1. The saturation curves for n-alkanes from C1 to C12, C16, and C22 in the reduced temperature versus the reduced density (a) and versus the reduced entropy (b).

Acknowledgment

This work was supported by the Hundred Talents Program of the Chinese Academy of Sciences.

Significant references

1. M. Raissi, P. Perdikaris, and G. E. Karniadakis, *J. Comput. Phys.*, vol. 378 (2019), pp. 686–707.
2. V. Diky, C. D. Muzny, A. Y. Smolyanitsky, et al. ThermoData Engine (TDE) Version 10.1 (Pure Compounds, Binary Mixtures, Ternary Mixtures, and Chemical Reactions): NIST Standard Reference Database 103b, 2016.
3. E. W. Lemmon, I. H. Bell, M. L. Huber, and M. O. McLinden, NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties-REFPROP, Version 10.0, National Institute of Standards and Technology. Standard Reference Data Program, Gaithersburg 2018.

Fundamental Reverse van der Waals Equation of State

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It has been almost one and a half centuries since the van der Waals equation of state (vdW EoS) was first published. The vdW EoS was the first model to describe the liquid-vapor phase transition, unifying both states at a critical point.

Another significant 19th-century development was the Dieterici EoS, the first model to effectively introduce an exponential term to improve the fluid's critical-compressibility performance. The vdW EoS and the Dieterici EoS can be considered the base for today's EoS used in wide industrial applications. While the vdW EoS represents the origin of all cubic EoS, the Dieterici EoS, the first model incorporating an exponential term, can be considered the precursor of the Benedict–Webb–Rubin EoS and the subsequent multiparametric empirical reference EoS.

A frequently observed problem with some modern reference EoS is the occurrence of multiple roots along pVT isotherms, as shown in Fig. 1. This not only leads to additional, unphysical roots when densities are calculated for given pressures, but also renders the resulting densities inconsistent with the fundamental Gibbs theory. That is, the phase equilibrium between the physically consistent roots cannot be established by a global support tangent plane between the coexisting phases, as required in Gibbs theory.

In this work, we modify the original van der Waals EoS, yielding a semi-cubic volume dependency. The key modification is to replace the hard-sphere interaction in the van der Waals model with a soft-sphere interaction. By introducing this simple modification, the accuracy of the original van der Waals model is greatly improved (Fig. 2), while preserving key fundamental thermodynamic properties, such as a thermodynamically stable van der Waals loop (Fig. 3). The modified van der Waals EoS is close to the original EOS in its mathematical structure. Still, its constants can be empirically parametrized to a degree of accuracy competitive with that of multiparametric reference EoS, while preserving its consistency with the fundamental Gibbs theory. In general, the Reverse van der Waals EoS can deliver performance comparable to empirical models, such as the multiparametric EoS, or to statistical models, such as the SAFT models. In addition, given the van der Waals loop stability of the proposed EoS, it can also be used to model additional essential properties, such as interfacial tension and nucleation theories.

The proposed model is called Reverse van der Waals EoS because the pressure EoS is derived from the Helmholtz free energy rather than by integrating the EoS to obtain the Helmholtz potential.

Furthermore, simple one-fluid mixing rules have been derived, providing a good representation of thermodynamic properties, including vapor–liquid equilibria, for several industrially relevant mixtures.

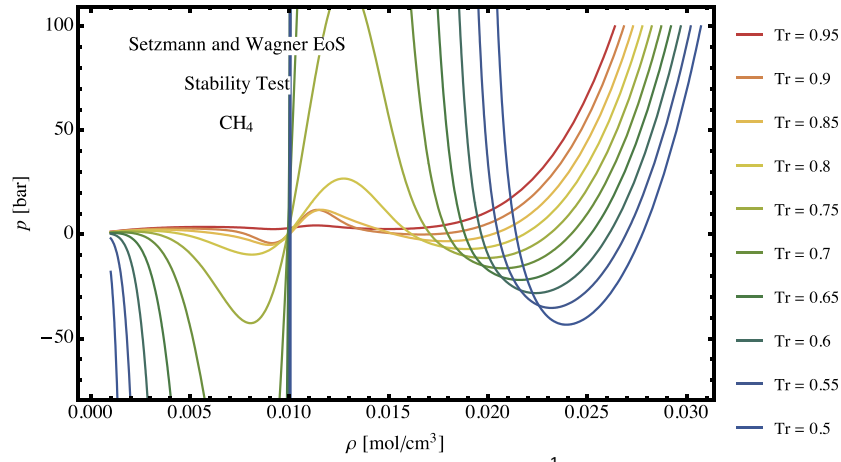


Figure 1. Isotherms for the Setzmann and Wagner¹ reference EOS for methane.

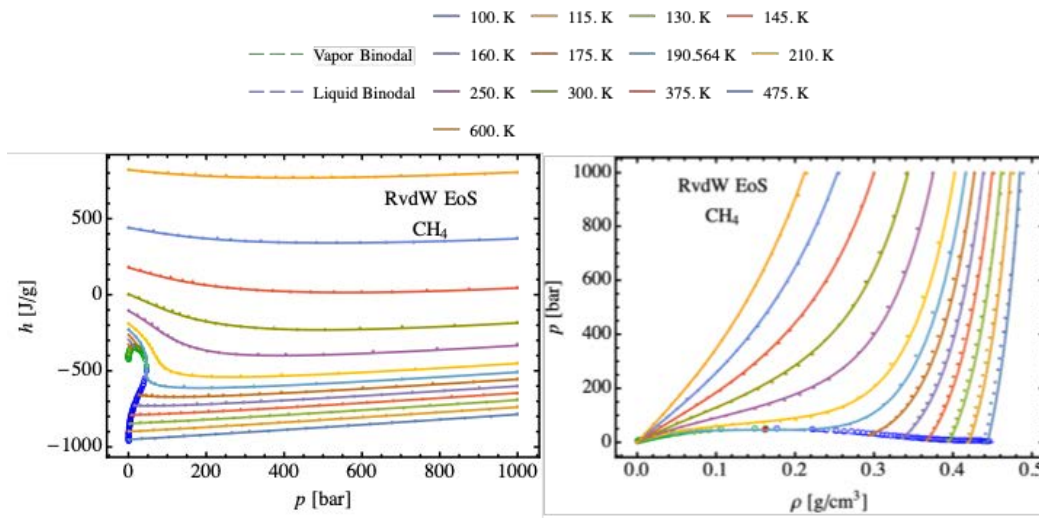


Figure 2. Enthalpy and density of methane performance using this work's EOS for methane.

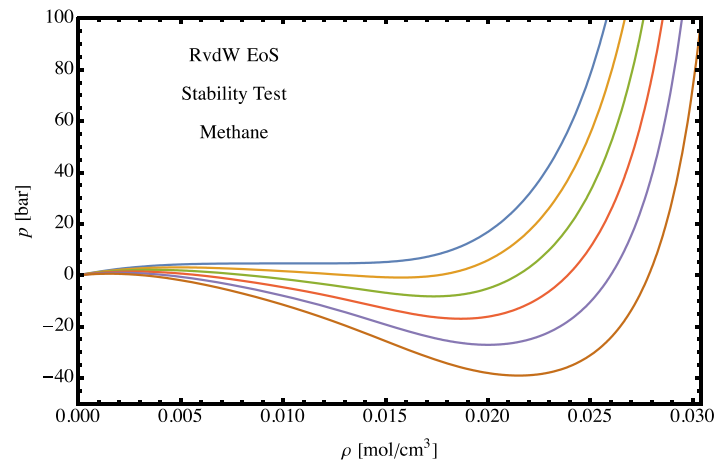


Figure 3. Stability of this work, EOS for methane.

References

1. U. Setzmann, W. Wagner, *J. Phys. Chem. Ref. Data*, vol. 20-6 (1991), pp. 1061-1151.

2.4

Thermodynamic Properties

CO₂-Based Mixtures



High-Pressure Equilibrium and Transport Behaviour of CO₂ + Cyclohexanol + Toluene Ternary Mixtures

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Understanding the equilibrium and transport properties of CO₂-solvent systems is essential for modelling high-pressure separation, extraction, and storage processes. We investigate the thermophysical behaviour of the ternary system CO₂ + cyclohexanol + toluene in the range 293.15 to 353.15 K and up to 30 MPa, combining high-pressure experiments with molecular dynamics simulations (MDS). Density, phase behaviour, Henry's law constants, and diffusivity were investigated.

The system exhibits liquid-liquid immiscibility at CO₂ mole fraction above 0.6 mol/mol, corresponding to type III phase behaviour [1]. Density increases with CO₂ concentration at lower temperatures, but decreases at higher temperatures (cf. Figure 1), with MDS reproducing within 1.7% deviation. Henry's law constant increases with temperature, reaching a maximum around 533 K, demonstrating the temperature dependence of solubility.

MDS reveals a complex diffusion behaviour, characterised by four Fick diffusion coefficients: D_{11} and D_{22} , driving primary solute fluxes, and D_{12} and D_{21} describing cross-coupled fluxes. At fixed CO₂ composition, D_{11} decreases with pressure, but increases with temperature and CO₂ concentration (cf. Figure 1), reflecting the competing effects of pressure and temperature.

This dataset provides high-quality reference data for modelling high-pressure CO₂-solvent mixtures and supports the development of predictive models for multicomponent diffusion in separation, reaction, and CCUS-related applications.

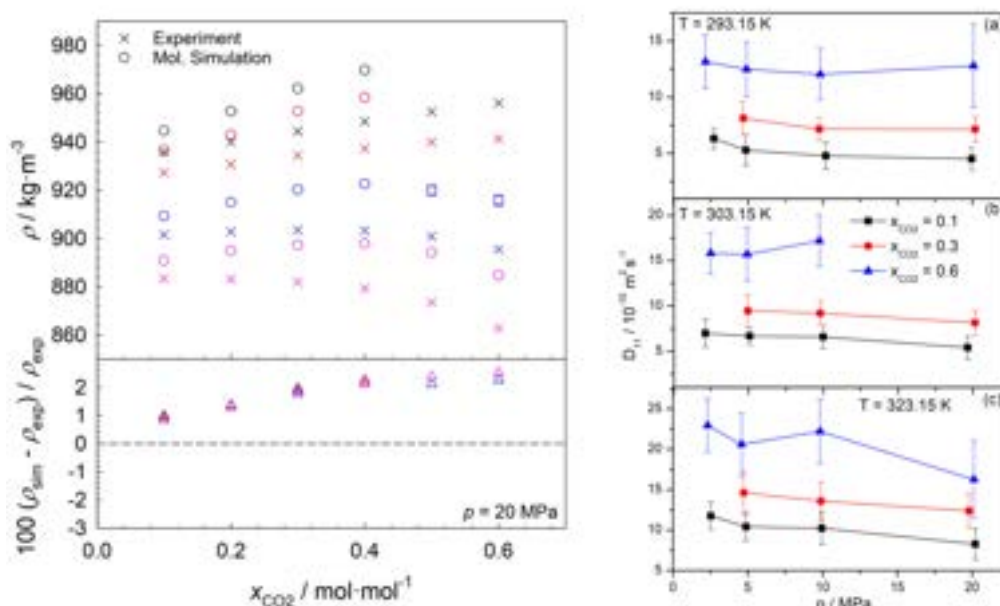


Figure 1. Left: Density of the ternary CO₂ mixture at $p = 20$ MPa. Right: Fick diffusion coefficient (in molar reference frame) of CO₂ D_{11} in the ternary mixture at $T = 293.15$ to 323.15 K

Acknowledgment

Supported by E2S UPPA Hub, CO2ES Chair, Investissements d'Avenir, ANR, and BMBF WindHPC.

Significant reference

1. H. Imuetinyan, D. Saric, JP. Bazile, C. Giraudet, G. Guevara-Carrion, JL. Daridon, J. Vrabec, and F. Croccolo, J. Chem. Eng. Data (2025), 70, 4, 1638–1651.

High-pressure phase behavior of the CO₂ + 2,6,10,14-tetramethylpentadecane system: experimental investigation

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The phase behavior of several binary systems containing CO₂ and a branched alkane were studied in the past [1]. However, among these investigated mixtures, only two involved a heavy branched alkane: squalane (C₃₀H₆₂) and 2,2,4,4,6,8,8-heptamethylnonane (C₁₆H₃₄) [2]. Such heavy compounds in mixture with CO₂ may present complex phase behavior including discontinuous critical curves between the pure components and liquid-liquid phase splitting.

In this work, the binary system CO₂ + 2,6,10,14-tetramethylpentadecane (C₁₉H₄₀; CAS 1921-70-6; pristane) was studied to supplement the existing database for such asymmetric mixtures. An optical high-pressure cell (with two sapphire windows and a piston) and a synthetic method were used to visually measure fluid phase transitions from 293 K to 363 K and at pressures up to 216 bar.

14 different mixtures with mole fractions of carbon dioxide ranging from 0.20 to 0.98 were studied to obtain a good overview of the system phase behavior. The experimental measurements reveal the occurrence of vapor-liquid, liquid-liquid and vapor-liquid-liquid phase transitions (see Fig. 1).

As expected, the phase diagram presents a liquid-liquid immiscible region and a three-phase (LLV) line. This LLV line goes from temperatures below 293 K up to an UCEP located somewhere between 308 K and 313 K. It is very likely that this system behaves as a type III binary system [3]. At 298 K, a barotropic inversion [4] between the two liquid phases in equilibrium was observed and filmed.

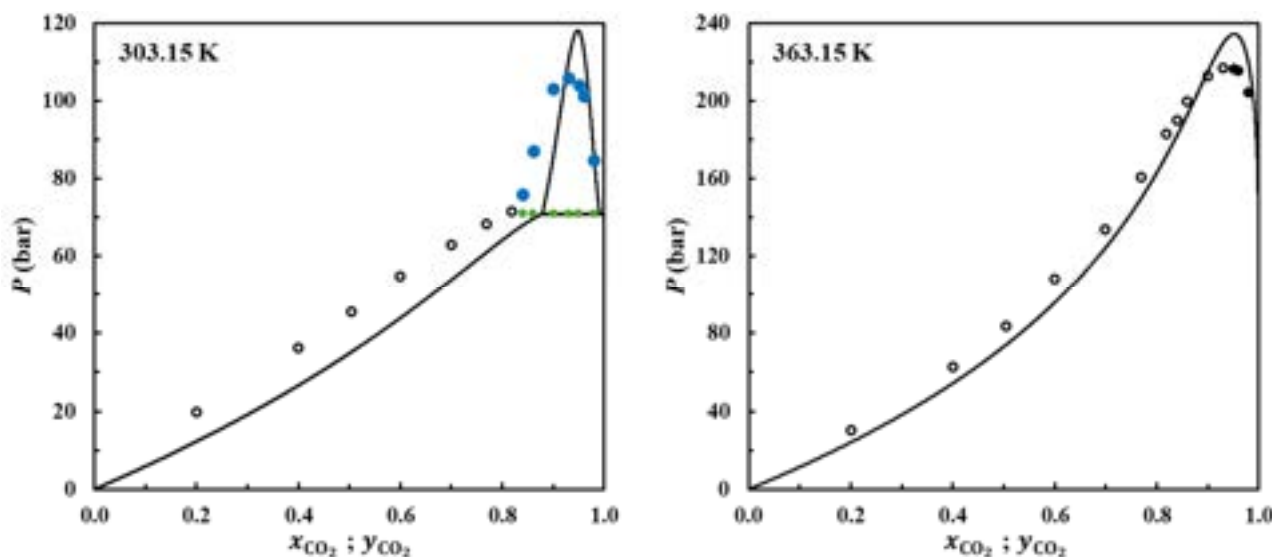


Figure 1. Isothermal phase equilibria of the system CO₂ + 2,6,10,14-tetramethylpentadecane. Experimental points measured in this work: ○ = bubble point, ● = fluid→liquid-liquid, ● = liquid-liquid→liquid-liquid-vapor, ● = dew point. Solid curves: Peng-Robinson equation of state ($k_{ij} = 0.051$).

Significant references

1. J.P. Bazile, J.L. Daridon, J.N. Jaubert, K. Abou-Alfa, and S. Vitu, *Int. J. Thermophysics*, vol. 46 (2025), 107.
2. J.F. Romero Yanes, F. Montel, and J.L. Daridon, *J. Supercrit. Fluids*, vol. 189 (2022), 105721.
3. P.H. van Konynenburg and R.L. Scott, *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.*, vol. 298 (1980), 495-540.
4. S.E. Quinones-Cisneros, *Fluid Phase Equilib.*, vol. 134 (1997), 103-112.

Isothermal Vapor-Liquid Equilibrium of Binary CO₂ and C₃O₈ Containing Mixtures and Classical Cubic Models of Equation of State

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The objective of the present work is to provide the reliable experimental VLE data for supercritical (SC) CO₂ and SC C₃H₈-containing binary mixtures and to evaluate the predictive capability of classical cubic equations of state (EoS). VLE measurements at high temperatures and pressures were performed using a static-analytic apparatus with gravimetric phase sampling as detailed in our earlier publications [1-3]. A unique feature of this method is the separate, sequential sampling of liquid and vapor phases under their respective equilibrium (P, T) conditions. The method offers four key advantages: (1) Minimal phase equilibrium disturbance: the sampler's annular design prevents phase mixing during extraction; separation occurs entirely within the sampler; (2) Superior thermal control: temperature regulation (copper jacket and insulation) ensures uniform heating and stable temperature control within < 0.05 K across the cell; (3) Large-volume sampling: 117 cm³ cell volume enables 4.1 cm³ samples, improving concentration accuracy (especially vapor phase) and enabling detection of subtle phase behavior, including critical opalescence (visual observation); (4) Thermodynamic consistency: sequential sampling under distinct (P, T) states ensures data thermodynamically consistency, critical for modeling and correlation. The combined expanded uncertainty at 95% confidence ($k=2$) are: $U(T)=0.15$ K (absolute); $U_r(P) = 0.0022$ (relative); and $U_r(z) = 0.030$ (relative, i.e., 3%), where $z = x$ or y . Measured VLE data for selected binary C₃H₈ + pyridine mixture are depicted in Fig. 1 together with the values predicted from cubic EoS. The values of the critical parameters (x_c, T_c, P_c) of C₃H₈ + pyridine mixture derived from the measured isothermal VLE data using the criterion of phase identity ($x=y$) are given in Table 1 and plotted in Fig. 1 (right) along with vapor pressure curves of the pure components and the reported critical curve data by Brunner [4].

The predictive performance of three theoretically based cubic models of EoS, namely PC-SAFT and CP-PC-SAFT, with universal system-independent binary parameters k_{12} , was assessed against the measured VLE data, as well as available critical, liquid-liquid equilibrium (LLE), and excess enthalpy data for the mixture. The results demonstrate that CP-PC-SAFT provides superior overall reliability compared with both PC-SAFT approaches. The accuracies of CP-PC-SAFT, PC-SAFT and Peng-Robinson (PR) EoS models in predicting the pure compound properties and the measured VLE data were studied. It was found that PR yields the less accurate results, while the over-all accuracies of both SAFT approaches are comparable. At the same time, the advantage of PC-SAFT in predicting the near-critical VLE can be explained by its overestimation of the pure compound critical temperatures and pressures. In this study the over-all robustness and reliability of three theoretically-based approaches applied with universal system-independent k_{12} values are examined, namely CP-PC-SAFT and PC-SAFT with the sets of molecular parameters. Examination of the critical data in this system available in the entire temperature range indicates that thanks to its rigorous obeying the pure compound critical data, CP-PC-SAFT is supposed to yield more accurate predictions of VLE at the temperatures higher than considered in the current study. Besides that, it was demonstrated that CP-PC-SAFT is superior in predicting the critical and available LLE data. It was also found that despite its more advanced theoretical background, PC-SAFT is characterized by the worst performance in predicting the considered data with the universal system-independent k_{12} value and exhibits unsatisfactorily over-all robustness and reliability.

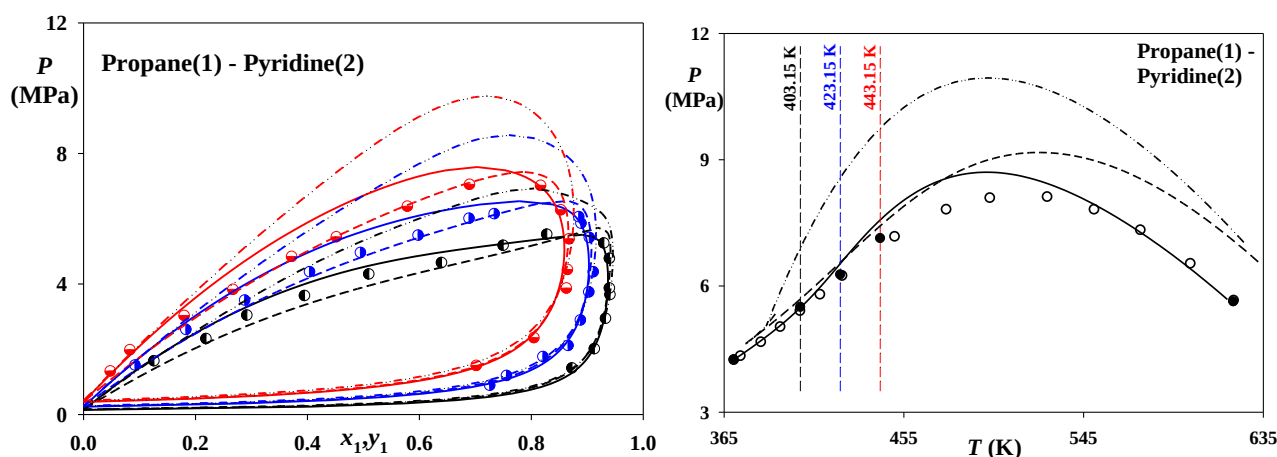


Figure 1. Measured and predicted isothermal VLE data in the system C_3H_8 – pyridine. **Left:** ● – 403.15 K, ○ – 423.15 K, ○ – 443.15 K. Solid lines – predictions of CP-PC-SAFT with $k_{12}=0.023$, dashed lines – of PC-SAFT with $k_{12}=0.017$, dotted-dotted-dashed lines – of PC-SAFT with $k_{12}=0.011$. Right (P_c – T_c projection of the critical line): ●–this work; ○ –reported by Brunner [4].

The critical parameters were estimated using an EoS and compared with those obtained from the VLE measurements (see Figure 1, right) and reported data by Brunner [4]. The reliability of the derived critical parameters was confirmed by direct visual observation of the liquid–gas meniscus in the optical cell. The critical curve of the C_3H_8 + pyridine mixture in the P_c – T_c projection originates from the critical point of pyridine, passes through a pressure maximum around 515 K and 8.2 MPa (as also reported by Brunner [4]), and terminates at the critical point of pure C_3H_8 . As shown in Figure 1 (right), the critical curve of C_3H_8 + pyridine is continuous (unlike the C_2H_6 + pyridine system [4]), smoothly connecting the critical points of both pure components. This corresponds to a Type - I phase diagram. The present critical point data for C_3H_8 + pyridine agree well with those of Brunner [4], with deviations in critical pressure within 0.5–1.5%. This excellent agreement further confirms the reliability and thermodynamic consistency of the present VLE measurements.

Table 1. Critical parameters of the binary C_3H_8 + pyridine mixture.

x / mole fraction of pyridine	T_c / K	P_c / MPa
0.00	369.89	4.2512
0.114 0.02	403.15 0.2	5.501 0.05
0.184 0.03	423.15 0.2	6.270 0.06
0.258 0.01	443.15 0.2	7.135 0.05
1.00	620.00 0.2	5.630 0.01

Acknowledgment

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References

1. V.F. Khairutdinov, I.Sh. Khabriev, T.R. Akhmetzyanov, L.Yu. Yarullin, F.R. Gabitov, I. Polishuk, and I.M. Abdulagatov, *J. Supercrit. Fluids*, vol. 203 (2023), 106060.
2. V.F. Khairutdinov, F.M. Gumerov, I.Sh. Khabriev, T.R. Akhmetzyanov, I.Z. Salikhov, I. Polishuk, and I.M. Abdulagatov, *Fluid Phase Equilib.*, vol. 564 (2023), 113615.
3. V.F. Khairutdinov, I.Sh. Khabriev, T.R. Akhmetzyanov, A.U. Aetov, I. Polishuk, and I.M. Abdulagatov, *Ind. Eng. Chem. Res.*, vol. 62 (2023), pp. 22103–22114.
4. E. Brunner, *J. Chem. Thermodyn.*, vol. 19 (1987), pp. 823–835.

Thermophysical Property Calculation Model for CO₂-based Mixtures Using the Crossover Volume-Translation SRK Equation of State

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The supercritical CO₂ (sCO₂) Brayton cycle system has attracted considerable attention due to its high efficiency, compact structure, and excellent adaptability to various heat sources. To further improve sCO₂ cycle performance, one promising approach is employing CO₂-based mixtures as working fluids. Accurate thermophysical property descriptions are essential for applying these mixtures. In this study, binary mixtures including CO₂/N₂, CO₂/R1234yf, and CO₂/H₂O were investigated. By adopting the Kiselev crossover method, crossover volume-translation SRK (CVTSRK) equations of state were established for pure fluids and CO₂-based mixtures. Additionally, new correlations for the binary interaction parameters were proposed, based on highly interpretable machine learning methods. These equations were applied to calculating thermophysical properties, such as single-phase $p\rho T(x)$ properties. The CVTSRK equations significantly enhance calculation accuracy in the near-critical region, provide reliable predictions of saturation properties for pure fluids, and reproduce critical parameters precisely. The developed models describe $p\rho T(x)$ properties accurately for both pure fluids and mixtures from subcritical to supercritical regions. The average absolute relative deviations in density calculations for CO₂-based mixtures remain within 2.6%. Furthermore, the models demonstrate stable and reliable extrapolation behavior under high-temperature conditions.

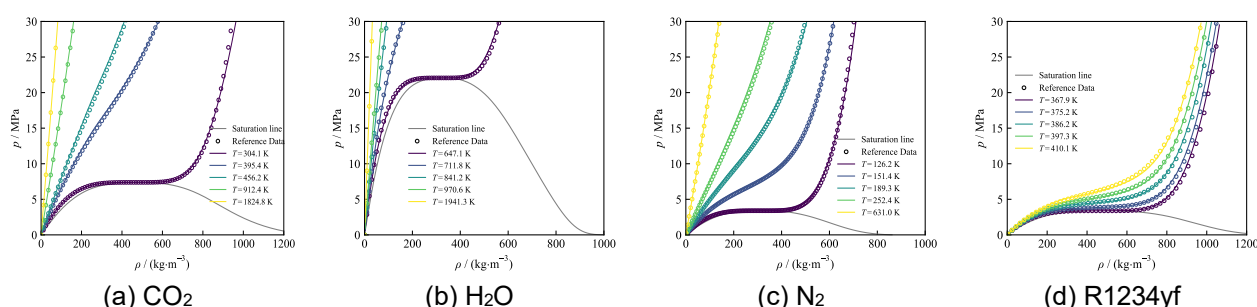


Figure 1. Calculation of $p\rho T$ property along isotherms using the CVTSRK equation of state

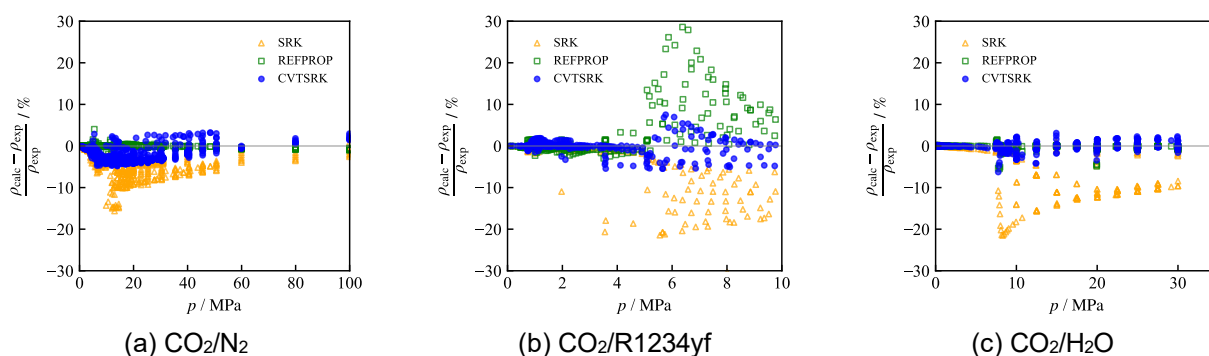


Figure 2. Relative deviations of calculated density from experimental data for CO₂-based mixtures

Acknowledgment

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Significant references

1. M. J. Martin, *Ind. Eng. Chem.*, vol. 59 (1967), pp. 34–52.
2. S. B. Kiselev, *Fluid Phase Equilibria*, vol. 147 (1998), pp. 7–23.

2.5

Thermodynamic Properties

Pure Compounds Modelling



New Fundamental Equation of State for Triethylene glycol

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Triethylene glycol (TEG) is widely used in industrial drying and gas dehydration processes [1]. Since complete separation of fluid mixtures is not possible, TEG can also be found in the emission of industrial plants. In carbon capture and storage systems, such impurities become relevant when CO₂ is transported through tanks or pipelines [2]. This is a key research focus in the COREu project, which aims to build a Europe-wide CO₂ transport network.

Impurities like TEG may form a second, highly concentrated and potentially corrosive liquid phase in the presence of water [2]. To avoid material degradation and ensure safe operation, it is necessary to determine the maximum TEG concentration that does not induce phase separation under typical transport pressures and temperatures. Such estimates are usually made with thermodynamic models, which must be as accurate as possible.

To accurately describe CO₂-rich mixtures including TEG, equations of state for pure components and their binary combinations are required. In this work, a new equation of state for TEG, explicit in the Helmholtz energy, is developed as a foundation for future mixture models. The Helmholtz-energy formulation not only enables the prediction of phase equilibria but also the calculation of homogenous thermodynamic properties such as density, heat capacities, and speed of sound through its derivatives. The model extends the EOS-CG 2021 [3] framework by introducing a dedicated multiparameter representation for pure TEG. Parameter optimization is performed with a multiparameter fitting algorithm, allowing the model to accurately reproduce available experimental data while maintaining physically consistent behavior even outside measured conditions [4,5]. The TEG model provides the basis for future mixture descriptions, for example for TEG+CO₂ or TEG+water systems, and contributes to establishing impurity limits to ensure safe CO₂ transport.

Acknowledgment

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Significant references

1. S. Gupta, Natural Gas: Extraction to End Use. BoD – Books on Demand, 2012.
2. D. Turunawarasu, P. S. C. Farias, A. Saidi, A. Amir, E. Luna-Ortiz, Solubility of TEG, MEG, and MeOH in CO₂: Improving CPA EoS modelling for CCS transport applications. *Fluid Phase Equilibria*, vol. 602 (2025), 114628.
3. T. Neumann, S. Herrig, I. H. Bell, R. Beckmüller, E. W. Lemmon, M. Thol, and R. Span, EOS-CG-2021: A Mixture Model for the Calculation of Thermodynamic Properties of CCS Mixtures. *International Journal of Thermophysics*, vol. 44 (2023), art. 178.
4. E. W. Lemmon, R. T. Jacobsen, A New Functional Form and New Fitting Techniques for Equations of State with Application to Pentafluoroethane (HFC-125). *Journal of Physical and Chemical Reference Data*, vol. 34, no. 1 (2005), pp. 69-108.
5. Personal communication with E. W. Lemmon, Advanced Fitting Algorithm, 2025.

Two distinct 4-parameter cubic equations tailored to reference thermodynamic property formulation. Application to argon, propane, and water.

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In this work we aim at equations of state (EOSs) which approach the accuracy of multiparameter (MP) EOSs but retain the single van der Waals loop naturally found for cubic EOSs. Single van der Waals loop is needed for modeling phase interfaces and for a new model of mixtures [1]. We test two forms of cubic EOSs: Generalized 4-parameter Cubic (G4C) EOS [2], and a newly developed Double Positive Root Cubic (DPRC) EOS. Both have 4 temperature-dependent parameters, which are fitted to the second virial coefficient and properties at density along a “sew-on line” (Fig. 1): pressure, compressibility, and Gibbs energy. G4C EOS represents a generalization of common cubic EOSs. DPRC EOS was found as the best form by studying the general 5-parameter cubic EOS. DPRC EOS employs a different repulsion term. The data were generated from reference MP EOSs. For the tested fluids – argon, propane, and water – both cubic EOSs accurately represent large parts of the vapor, liquid, and supercritical regions; DPRC EOS performs better. In the critical region, the EOSs show the mean-field behavior; consequently, their critical point is located at higher temperature than the physical one. It was found that cubic EOSs cannot reproduce negative values of the third virial coefficient at low reduced temperatures and, in the liquid region, show a too large curvature of pressure vs. density isotherms.

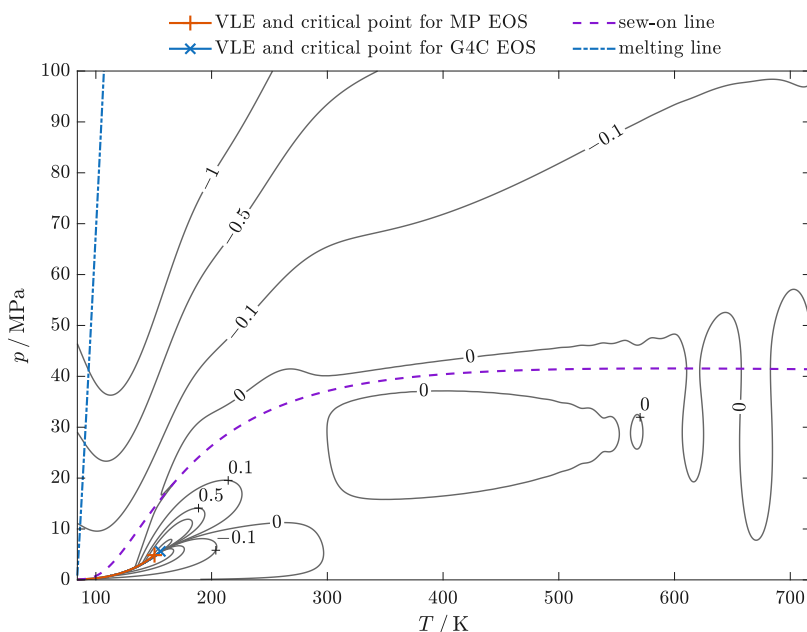


Figure 1. Percentual difference of densities obtained with the G4C EOS for argon from MP EOS [3].

Acknowledgment

We gratefully acknowledge funding from the Czech Science Foundation under project No. GA22-28869S and from the Czech Academy of Sciences under project No. RVO:61388998.

Significant references

1. J. Hrubý, *Int. J. Thermophys.*, vol. 44 (2023), 130.
2. J. Hrubý, A. Blahut, *Int. J. Thermophys.* vol. 46 (2025), 19.
3. C. Tegeler, R. Span, W. Wagner, *J. Phys. Chem. Ref. Data*, 28 (1999), 779.

Theoretical modeling of solid, liquid, and gas phases of water

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Thermodynamics sharply distinguishes water from common simple substances such as argon or methane. One of water's crystalline phases, ice Ih, is less dense than its coexisting liquid, implying an unusual negative slope of the freezing line in the pressure-temperature p - T plane. Likewise unusual is the behavior of the liquid phase. Thus, in contrast to the general case, the density ρ of liquid water decreases as T is lowered below a temperature of maximum density TMD(ρ), with TMD ≈ 277 K at $p \approx 1$ bar. The pattern of behavior gets even rarer as T is further lowered down below the freezing point while metastably maintaining the sample as a supercooled liquid, with thermodynamic response functions such as the isothermal compressibility κ_T exhibiting sharp rises [1].

Molecular simulation has taught us that a most plausible explanation of the intriguing behavior of liquid and supercooled water is the very existence of a second, liquid-liquid critical point with coordinates $T_c \approx 200$ K and $p_c \approx 1200$ bar according to the latest estimates [2,3]. The experimental evidence supporting this is growing [4-7].

A theoretical approach to the overall picture calls, in the first instance, for a description at the coarse-grained level of the one early provided by van der Waals for simple fluids. This demands describing water's solid, liquid, and gas phases as well as the transitions between them and the associated metastable states. Altogether, these requirements raise a stringent test for theory and, as far as we are aware, a statistical-mechanical prototype meeting all of them does not exist yet.

Here we approach this water's theoretical puzzle by suitably devising Ising-like models contemplating a gas phase, two liquid phases, and two solid phases. On working out the models at a mean-field level, we do find that they exhibit a liquid-liquid transition that terminates at a critical point and is metastable with respect to the solid phase.

Acknowledgment

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Significant references

1. R. J. Speedy and C. A. Angell, *J. Chem. Phys.*, vol. 65 (1976), pp. 851-858.
2. J. C. Palmer, P. H. Poole, F. Sciortino, and P. G. Debenedetti, *Chem. Rev.*, vol. 118 (2018), pp. 9129-9151.
3. F. Sciortino, Y. Zhai, S. L. Bore, and F. Paesani, *Nat. Phys.* vol.21 (2025), pp. 480-485.
4. L. Kringle, W. A. Thomley, B. D. Kay, and G. A. Kimmel, *Science*, vol. 369 (2020), pp. 1490-1492.
5. K. H. Kim et al., *Science*, vol. 370 (2020), pp. 978-982.
6. K. Amann-Winkel et al., *Nat. Commun.*, vol. 14 (2023), 442.
7. R. Tyburski et al., *Nat. Phys.* (2025), early access.

Measurements and modelling of pure solids for solubility predictions

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Impurities in unprocessed natural gas are typically removed to avoid the formation of solids during subsequent liquefied natural gas (LNG) production. Many of these impurities often have triple point temperatures higher than the liquefaction temperature of natural gas, and so they may freeze-out even if they are only present at concentrations as low as the parts-per-million (ppm) level. Unwanted solid formation can lead to blockages in cryogenic heat exchange equipment, causing significant safety and economic problems for plant operators. Despite this challenge, accurately predicting the conditions at which these solids form in LNG mixtures remains difficult, primarily due to the lack of reliable thermodynamic models, especially for the solid phase.

Commonly, the fugacity of a solid phase is calculated using the Classical approach [1], the Poynting factor method or with an equation of state (EOS). An EOS offers the highest accuracy but requires extensive thermodynamic data for the pure solid, such as molar volumes, heat capacities, and phase transition properties. The Poynting factor method can also provide good accuracy but relies on sublimation pressure and molar volume data, which may not be available for some impurities. The Classical approach only requires (at a minimum) the location of the triple point and the enthalpy of fusion; it can be refined further using parameters derived from the melting curve. The trade-off for this simplicity is lower accuracy, especially at conditions far from the triple point. In this work, we demonstrate the application of all three approaches, using hydrogen sulfide and n-decane as representative examples.

The available thermodynamic properties of H₂S were compiled and used to develop a solid Helmholtz EOS for phase I of H₂S based on the quasi-harmonic approximation. The EOS is valid for temperatures from (126.2 to 580.0) K and pressures up to 12 GPa, and can represent the available data for the isobaric heat capacity within 2.5%, and the molar volume within 2.3% along the sublimation curve (increasing to 4.8% at higher pressures). When combined with the existing fluid-phase model [2], the new EOS reproduces the experimental sublimation and melting pressures, as well as the heats of fusion, with average fractional deviations of 4.5%, 17.9%, and 0.12%, respectively. The large deviations in the melting pressures arise primarily from inconsistencies among the available experimental datasets.

However, sufficient data are not available for all solids. The Classical approach and the Poynting factor method can therefore be used as approximations for such components. For example, in the case of n-decane, a heavy hydrocarbon representative of straight-chain alkane impurities in natural gas, neither melting curve nor sublimation curve data are available. In this work, a total of 20 melting temperatures of pure n-decane were measured using optical microscopy at pressures up to 20 MPa. The enthalpies of fusion and sublimation were also determined using a cryogenic differential scanning calorimeter (DSC). These data were subsequently employed to construct the Classical approach and the Poynting factor method for n-decane. Finally, we then discuss the estimated accuracy of each of these approaches and their suitability. Ultimately, this work should help LNG plant operators better characterize the process conditions under which H₂S and n-decane may cause a freeze-out risk.

Acknowledgment

This work was funded by the Gas Processors Association and the Future Energy Exports Cooperative Research Centre.

Significant references

1. J. M. Prausnitz, R. N. Lichtenthaler, and E. G. de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, Pearson Education (1998).
2. E. W. Lemmon and R. Span, *Journal of Chemical & Engineering Data*, vol. 51 (2006), pp. 785-850.

2.6

Thermodynamic Properties

Hydrogen Modelling



Cryogenic Thermophysical Properties of Hydrogen from Molecular Dynamics with a Feynman–Hibbs–Corrected Mie Potential

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Cryogenic hydrogen holds a significant potential to participate decarbonising the industry, notably as a fuel for zero-carbon aviation therefore accurate cryogenic property data for parahydrogen in particular are essential for reliable modelling and design, yet experimental measurements remain sparse and uncertain across the liquid–vapour domain. Although the Feynman–Hibbs-corrected Mie (Mie–FH) potential has been previously applied in Monte Carlo simulations [1], and its implementation in molecular dynamics (MD) would enable to extract transport properties in addition to phase equilibria properties, such MD extraction has not been reported. This work establishes a quantum-corrected MD framework for parahydrogen using the Mie–FH potential to predict vapour–liquid equilibrium (VLE), thermodynamic, and transport properties relevant to cryogenic applications. Two-phase coexistence simulations reproduced the saturation curve with good agreement to reference data, confirming the suitability of the Mie–FH1 model for phase behaviour in MD. At 20 K and 2 bar, in the saturated-liquid region, the model reproduced density, self-diffusion and dynamic viscosity within 5–25% of reference values, yielding $\rho = 68.9 \text{ kg.m}^{-3}$, $D_{\text{self}} = 8.75 \cdot 10^{-9} \text{ m}^2.\text{s}^{-1}$ and $\mu = 1.3 \cdot 10^{-5} \text{ Pa.s}$. Thermal conductivity was determined through a short-timescale relaxation approach adapted from Hubman’s methodology [2], obtaining $\kappa = 0.12 \text{ W.m}^{-1}.\text{K}^{-1}$ at the same conditions, consistent with the $0.10 \text{ W.m}^{-1}.\text{K}^{-1}$ reference within uncertainty. These results demonstrate that Mie–FH-based MD provides physically meaningful predictions of VLE and key thermophysical properties of parahydrogen, offering a complementary data source when experimental values are limited or uncertain. These simulations could be used to augment existing experimental dataset by assessing the accuracy of existing interpolations.

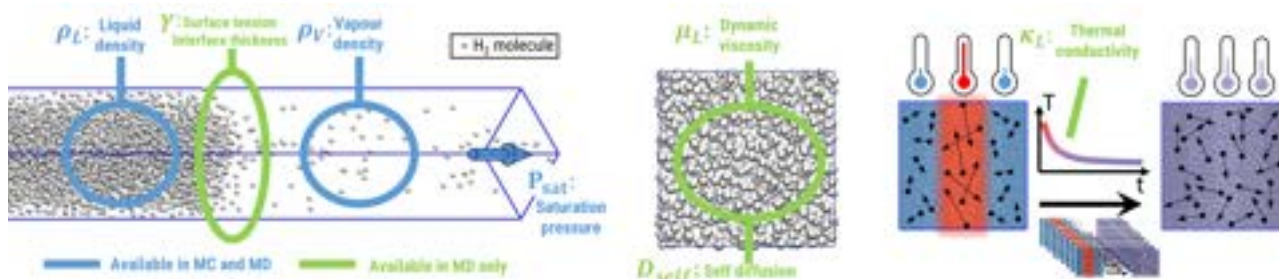


Figure 1. Molecular dynamics simulations and extracted properties: VLE (saturation and interface properties), single phase (viscosity and diffusion) and single phase thermal relaxations (thermal conductivity)

Acknowledgment

We gratefully acknowledge the University of Bath, GKN Aerospace and EPSRC for funding this PhD research within ZENITH (Project Reference: EP/X025403/1).

Significant references

1. A. Aasen et al., *Equation of state and force fields for Feynman-Hibbs-corrected Mie fluids. I. Application to pure helium, neon, hydrogen, and deuterium*, *Journal of Chemical Physics* 151 (6 Aug. 2019)
2. A. Hubman and F. Merzel, *Determination of thermal conductivities in liquids by identifying heat transport in nonequilibrium MD simulations*, *Journal of Molecular Liquids* 370 (Jan. 2023), p. 120916.



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Calculation of Thermodynamic Properties of Hydrogen by Path Integral Monte Carlo Simulations Using *Ab Initio* Potentials

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With hydrogen expected to play an important role in the transition of the energy supply system to renewable technologies, comprehensive and accurate thermodynamic property data is essential. Here, computational approaches can complement experimental methods, which is especially beneficial at low temperatures below the boiling point of liquid nitrogen, where experiments become difficult and costly.

However, the accurate theoretical prediction of thermodynamic properties of fluids consisting of atoms and molecules with small mass such as hydrogen requires the consideration of quantum effects of the nuclei. Path integral simulations, based on Feynman's formulation of quantum mechanics, provide a method to treat nuclei quantum-mechanically within a classical simulation without uncontrolled approximations. Based on our path-integral simulation framework [1,2], we are able to calculate all relevant thermodynamic properties including the density, speed of sound, and Joule–Thomson coefficient fully incorporating quantum effects based on highly accurate *ab initio* potentials for pairwise and nonadditive three-body interactions [3,4]. We perform simulations for hydrogen at selected state points in regions of the phase diagram with high-quality experimental data to validate our approach and additionally make predictions in regions of the phase diagram where experimental data is scarce. We observe good agreement with the available experimental data, which emphasizes the complementary benefits of theoretical approaches.

Acknowledgment

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Significant references

1. P. Marienhagen and K. Meier, *J. Chem. Phys.*, vol. 161 (2024), 224110.
2. P. Marienhagen and K. Meier, *J. Chem. Phys.*, vol. 163 (2025), 074116.
3. K. Patkowski, W. Cencek, P. Jankowski, K. Szalewicz, J.B. Mehl, G. Garberoglio, and A.H. Harvey, *J. Chem. Phys.*, vol. 129 (2009), 094304.
4. P. Marienhagen, G. Garberoglio, and R. Hellmann, *in preparation*.

2.7

Thermodynamic Properties

Phase and Chemical Equilibria



Algorithms for chemical and phase equilibrium calculations

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Advances in applied thermodynamics rest on three pillars: experimentation, theoretical modeling, and computation. Among various computational tasks, phase equilibrium calculations play a central role in process analyses and simulation. Both phase equilibrium and chemical equilibrium are governed by the same criteria established by Josiah W. Gibbs. Nevertheless, computational algorithms for chemical equilibrium calculations have not matured to the same extent as those for phase equilibrium. Moreover, different disciplines have developed distinct yet somewhat related approaches for computing chemical equilibrium.

This talk discusses methods for calculating simultaneous chemical and phase equilibrium. Recent developments in non-stoichiometric methods, especially RAND-type methods,^[1,2] will be reviewed. We show that the RAND family of methods provides a robust and efficient framework for solving multiphase reaction equilibrium problems. These methods are not limited to the classical isothermal flash; they can also be extended to other flash specifications^[3] and to saturation point calculations.^[4] Applications to CCS-related systems will also be presented.^[5]

In addition to general chemical equilibrium problems, we review the implicit incorporation of chemical equilibrium within thermodynamic models. Besides SAFT-type models, COSMO-based activity coefficient models such as COSMO-RS and COSMO-SAC also fall into this category. In fact, the self-consistency equation in COSMO-based models can be derived by minimizing the system energy associated with pairwise segment interactions, yielding a form analogous to the Wertheim term in SAFT-type models.^[6] On this basis, an optimization-based second-order solution procedure can be formulated for COSMO-based models, offering the possibility of coupling COSMO-based models with existing phase equilibrium calculation routines.

Significant references

1. D. Paterson, W. Yan, M.L. Michelsen, E.H. Stenby, SPE Journal, vol. 23 (2018), pp. 535-549.
2. C. Tsanas, E.H. Stenby, W. Yan, Ind. Eng. Chem. Res., vol. 56 (2017), pp. 11983-11995.
3. F. Medeiros, E.H. Stenby, W. Yan, AIChE J., vol. 67 (2020), e17050.
4. F. Medeiros, E.H. Stenby, W. Yan, Chem. Eng. Sci. vol. 247 (2021), 116911.
5. F. Medeiros, E.H. Stenby, W. Yan, Advances in Water Resources, vol. 152 (2021), 103918.
6. W. Yan, Chem. Eng. Sci., vol. 300 (2024), 120652.

A Robust Algorithm for Generating Pressure–Temperature Phase Diagrams with Solid–Liquid–Vapor Equilibrium

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Solid formation in cryogenic applications such as liquefied natural gas (LNG) poses significant operational risks and requires reliable prediction of solid–fluid equilibrium (SFE). However, complete pressure–temperature (P–T) diagrams that include vapor (V), liquid (L), and solid (S) phases, as well as their coexisting phases (e.g., SV, SL, SLV), are rarely available outside specialized proprietary software.

This work presents a robust algorithm for generating full P–T phase diagrams for systems exhibiting solid, liquid, and vapor phases, including their equilibrium boundaries. The method is built on a cubic equation of state (e.g., the Yang–Frotscher–Richter [1]) for fluid phases together with a classical solid-phase fugacity model. Basic vapor–liquid equilibrium (VLE) is obtained using two-phase Rachford–Rice calculations, whereas equilibrium involving solid phases (SV, SL, and SLV) is handled using the approach of Baker et al [2]. Phase boundaries, such as deposition, freezing, complete-freezing, dew, and bubble lines, are traced using a bisection scheme to determine the transition points between adjacent phases without solving the full equilibrium system analytically.

The algorithm generates complete P–T diagrams within a few tens of seconds on a standard desktop PC. An example diagram for a CO₂ + CH₄ + N₂ mixture is shown in Figure 1. The method demonstrates strong numerical robustness, with remaining challenges occurring only under extreme conditions such as very low temperatures or near the critical point – areas currently under further development. Because liquid–liquid phase separation in asymmetric systems, such as oil–refrigerant mixtures, is also an essential and industrially relevant phenomenon, extending the framework to full Solid–Liquid–Liquid–Vapor Equilibrium capabilities is part of ongoing work.

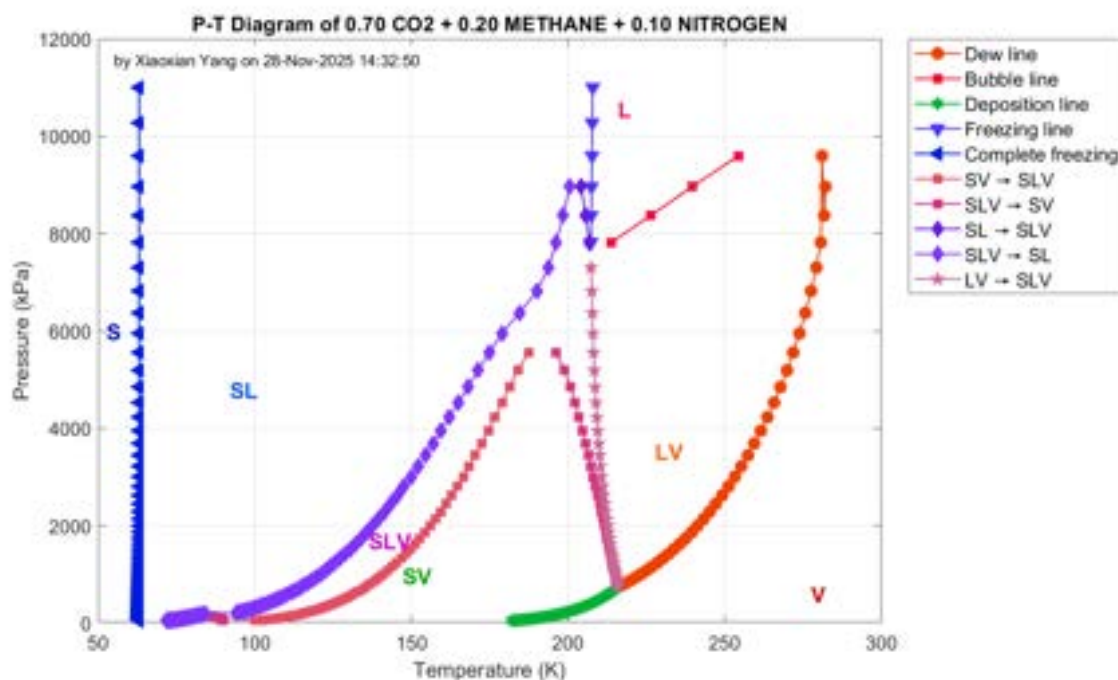


Figure 1. Pressure-temperature phase diagram of a CO₂ + CH₄ + N₂ mixture (in mole fraction)

Significant references

1. X. Yang, O. Frotscher, and M. Richter, *Int J Thermophys* **46**, 29 (2025).
2. C. J. Baker, J. H. Oakley, D. Rowland, T. J. Hughes, Z. M. Aman, and E. F. May, *Energy Fuels* **32**, 255 (2018).

Inconsistencies in Entropy for the Reaction of Ammonium Carbamate ($\text{NH}_2\text{COONH}_4$) to CO_2 and NH_3 Determined by Equilibrium Measurements and Calorimetry

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Obtaining the equilibrium constant, K_{eq} or its equivalent $\Delta_r G^\circ$, is the first step in understanding the chemistry of a reaction. The equilibrium constant can be determined directly or indirectly through calorimetric measurements of $\Delta_r H^\circ$ and $\Delta_r S^\circ$, which is obtained from the integral of C_p/T as a function of T . The equivalence of the two pathways to evaluate K_{eq} is based on the fact that ΔG , ΔH , and ΔS are state functions. However, enthalpies and entropies determined by equilibrium and by calorimetric methods often disagree. The disagreement has usually been attributed to experimental error, but it is possible that the equilibrium measurements and calorimetric measurements may not be measuring the same thing. The purpose of this paper is to determine if there are indeed differences in the thermodynamic functions determined from equilibrium measurements and from calorimetry. The equilibrium reaction of ammonium carbamate, $\text{NH}_2\text{COONH}_4$, to form CO_2 (g) and NH_3 (g) was chosen to test this hypothesis because the thermodynamic functions can be easily calculated using existing equilibrium pressure data and independently from calorimetric measurements of the enthalpy of reaction and the absolute entropy of ammonium carbamate calculated from heat capacity data. The difference in $\Delta_r H^\circ$ calculated from equilibrium measurements and from calorimetry are within the experimental uncertainty, but the difference in $\Delta_r S^\circ$ is $> 7\%$, which is significantly greater than the experimental uncertainty of 1% . Thus, we conclude the disagreement in $\Delta_r G^\circ$ arises from differences in $\Delta_r S^\circ$.

Solubility prediction and molecular modeling of pharmaceutical compounds and solvents with SAFT- Mie

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The prediction of the solid–liquid equilibrium solubility of pharmaceutical compounds is a major challenge for the pharmaceutical industry and solvent selection. We extend the SAFT- Mie group-contribution equation of state [1] to predict the phase behavior and solubility of several pharmaceutical compounds, including aspirin, salicylic acid, paracetamol, therapeutic deep eutectic solvents, and mefenamic acid [2], in a range of solvents.

Literature data for the vapor–liquid equilibria, density, and enthalpy of mixing are used to characterize the new group interactions of SAFT- Mie, with solubility data used to characterize new group-group interactions only in cases in which there are no other experimental data available. The transferability and predictive accuracy of the new models are assessed by comparing the theoretical predictions with available experimental solubility data.

Very good agreement with the experimental data is obtained for the systems considered, as can be seen in Figure 1 for the solubility of aspirin in 23 pure solvent systems. Our comparison includes water, alkanes, alcohols, ketones, esters, and aromatic compounds as families of solvents. The approach is also applied to the solubility prediction in mixed solvents.

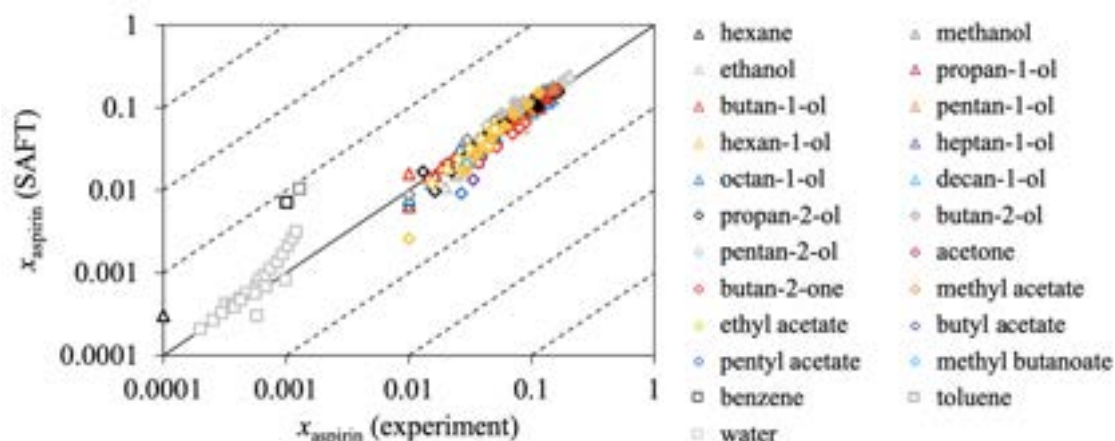


Figure 1. Parity plot for the solubility of aspirin in a range of solvents, at atmospheric pressure, comparing SAFT- Mie predictions and experimental data.

Significant references

1. V. Papaioannou, T. Lafitte, C. Avendaño, C. S. Adjiman, G. Jackson, E. A. Müller, A. Galindo, *J. Chem. Phys.*, vol. 140 (2014), pp. 054107.
2. S. A. Febra, T. Bernet, C. Mack, J. McGinty, I. I. Onyemelukwe, S. J. Urwin, J. Sefcik, J. H. ter Horst, C. S. Adjiman, G. Jackson, A. Galindo, *Fluid Phase Equilib.*, vol. 540 (2021), pp. 113002.

3.1

Thermophysical Properties

Organic Hydrogen Carriers



Experimental Investigation of Liquid Density and PC-SAFT Equation of State for Liquid Organic Hydrogen Carrier (LOHC) H₀-NEC/H₁₂-NEC

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The escalating depletion of fossil fuels and concerns over global warming have driven the transition toward hydrogen as a clean energy vector. However, its low volumetric density under ambient conditions necessitates advanced storage solutions [1]. *N*-heterocyclic liquid organic hydrogen carriers (LOHCs) are particularly attractive owing to their reversible hydrogenation/dehydrogenation, favorable thermodynamics and moderate operating temperatures. *N*-ethylcarbazole (H₀-NEC) stands out with a gravimetric hydrogen storage capacity of 5.79 wt%, positioning it as a leading candidate [2]. But its high melting point of 343 K results in solidification at ambient temperatures to limit applications especially in mobile systems. Blending H₀-NEC with dodecahydro-*N*-ethylcarbazole (H₁₂-NEC) can effectively depresses the melting point and ensures liquidity across a wide temperature range. Accurate thermophysical properties are vital for assessing the viability of H₀-NEC/H₁₂-NEC system and facilitating process engineering. Liquid density plays a pivotal role, as it governs volumetric hydrogen storage capacity, impacts storage vessel design and system mass in mobile applications, and provides essential inputs for thermodynamic modeling, heat/mass transfer and fluid dynamics simulations. Unfortunately, their liquid densities of H₀-NEC/H₁₂-NEC have not been reported over the wide thermodynamic conditions.

In this present study, liquid densities of binary mixtures ($x\text{H}_0\text{-NEC} + (1-x)\text{H}_{12}\text{-NEC}$) were measured by using a vibrating-tube densimeter at temperatures from 293.15 to 453.15 K and pressures up to 20 MPa. The combined expanded uncertainties ($k = 2$) of temperature, pressure and density were estimated to be 16 mK, 0.062 MPa and 0.6 kg·m⁻³, respectively. Based on these available datasets and Constantinou-Gani method, PC-SAFT EoSs of H₀-NEC/H₁₂-NEC have been developed to successfully predict liquid densities and isobaric heat capacities. Furthermore, derived thermodynamic properties and hydrogen storage capacities have been determined by theoretical models, which would be utilized to explore the microscopic interactions, process optimization and compositional screening.

Acknowledgment

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Significant references

1. J.L. Wong, J.J. Chew, B.T. Wong, et al. Catalysis Science & Technology 15 (2025) 4063-4084.
2. K. Stark, V.N. Emel'yanenko, A.A. Zhabina, et al. Industrial & Engineering Chemistry Research 54 (2015) 7953-7966.

Fick Diffusivity, Thermal Diffusivity, Thermal Conductivity, Density, and Mixture Composition of the Liquid Organic Hydrogen Carrier System Based on γ -Butyrolactone and 1,4-Butanediol

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The storage of hydrogen (H_2), which is believed to be one of the main energy carriers of the future, by pressurization or cryogenic liquefaction poses several challenges. One promising alternative technology that is to some extent already in use relies on liquid organic hydrogen carrier (LOHC) systems. Since many of the more or less established LOHC systems involve hydrocarbon pairs of aromatic and aliphatic nature as hydrogen-lean and hydrogen-rich molecules with the associated environmental issues, the currently discussed LOHC system based on γ -butyrolactone (GBL) and 1,4-butanediol (BDO) may be a game-changer in this respect. In addition to their biodegradability, these substances are already produced on large scales for reasonable prices and require relatively mild conditions of up to about 450 K for hydrogenation and dehydrogenation reactions employing rather cheap copper-based catalysts. A current drawback is, however, that thermophysical property data needed for efficient process design are scarce and generally lacking at process-relevant conditions including the presence of GBL/BDO mixtures and dissolved H_2 at elevated pressures. The present work aims to improve this situation by studying the transport properties thermal conductivity λ , thermal diffusivity a , and mutual diffusivity D as well as density ρ for the LOHC system based on GBL and BDO. λ and ρ were measured at a pressure p of 0.1 MPa with a guarded parallel-plate instrument and vibrating-tube densimeters at temperatures T of up to (353.15 and 473.15) K. a and D were investigated simultaneously by dynamic light scattering (DLS) from the liquid bulk of the fluid at macroscopic thermodynamic equilibrium without the need of imposing external gradients that could perturb the measurements, e.g., by inducing convective effects. In the DLS experiments, the presence of dissolved H_2 was additionally considered, where ranges of $T = (298.15\text{--}473.15)$ K and $p = (0.1\text{--}10)$ MPa were covered. It could be shown that dissolved H_2 does not influence a significantly and that due to the low H_2 solubility, the diffusion of H_2 in the liquid bulk is independent of its concentration. Furthermore, polarization-difference Raman spectroscopy (PDRS) was successfully calibrated for the optical determination of the LOHC-compound composition in the liquid phase and, thus, for the degree of hydrogenation. This helps to detect any corresponding changes during the DLS measurements and may be applied for process monitoring in the future. Together with visual inspections and frequent check measurements, the application of PDRS in parallel to DLS was also part of the considerable effort to validate the experimental data of the GBL/BDO system that exhibits an onset of changes in sample composition at elevated temperatures.

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Viscosity, Interfacial Tension, and Hydrogen Solubility for the Liquid Organic Hydrogen Carrier System Based on γ -Butyrolactone and 1,4-Butanediol

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Liquid organic hydrogen carriers (LOHCs) are regarded as promising media for the safe and efficient storage and transport of hydrogen (H_2). In this respect, a new LOHC system based on γ -butyrolactone (GBL) and 1,4-butanediol (BDO) is currently discussed since it can be processed under rather mild reaction conditions and exhibits beneficial biodegradability. For the design and optimization of hydrogenation and dehydrogenation processes, accurate thermophysical property data for this LOHC system are required. This includes the need of knowledge on the influences of the fluid composition and of physically dissolved H_2 under process-relevant conditions. So far, such information is scarcely available and limited to the pure LOHC compounds.

This work summarizes the results from recent research activities on the determination of the dynamic viscosity η , interfacial tension σ , and hydrogen solubility x_{H_2} for GBL, BDO, and their binary mixtures with GBL amount fractions of $x_{GBL} = (0.25, 0.50, \text{ and } 0.75)$ at temperatures T up to 473 K. Surface light scattering (SLS) was applied for the simultaneous measurement of η and σ , while capillary viscometry (CV) and pendant drop (PD) experiments were used to complement the data for the two pure LOHC compounds and their corresponding binary mixtures from SLS at a pressure p of 0.1 MPa. Further SLS and PD measurements conducted under H_2 atmospheres at p up to 10 MPa and T of (323, 348, and 373) K helped to evaluate the corresponding influence on η and σ . Here, it could be shown that the presence of H_2 resulting in total pressures of up to 10 MPa tends to reduce σ by up to approximately 5% compared to the values at 0.1 MPa, while a slight corresponding increase of η was observed for pure BDO and the BDO-rich mixture. In the same ranges of T and p , the isochoric-saturation method (ISM) combined with a vibrating-tube instrument gave access to x_{H_2} and the respective liquid density ρ . In this connection, it was found that the generally very low H_2 solubility is lower in the binary GBL/BDO mixtures than in the pure LOHC constituents. While polarization-difference Raman spectroscopy could be applied successfully for monitoring the degree of hydrogenation in form of x_{BDO} in SLS and ISM experiments, its calibration with respect to x_{H_2} at the ISM setup has proven to be challenging owing to the very low H_2 solubility. Another critical aspect within this study is the limited T stability of the samples, which partially varies between the individual LOHC-compound compositions and experimental boundary conditions. Therefore, the ranges of validity of the measured thermophysical property data had to be evaluated carefully. The finally obtained datasets provide reliable information for the assessment of the suitability of the GBL/BDO pair as a LOHC system and for facilitating the process design in the related H_2 storage applications.

Acknowledgment

This work was funded by the Bavarian Ministry of Economic Affairs, Regional Development and Energy as well as by the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG) under project number 524349465. The authors acknowledge funding of the Erlangen Graduate School in Advanced Optical Technologies by the Bavarian State Ministry for Science and Art.

3.2

Thermophysical Properties

H_2 and H_2 -Containing Mixtures I



Exploring the properties, behaviour, and challenges of cryogenic hydrogen

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Recent interest in cryogenic hydrogen is largely being driven by the global effort to decarbonize energy systems, where hydrogen has the potential to serve as a versatile, zero-emission energy carrier. Yet, despite many decades of research motivated by wide ranging applications, from high-energy physics through to biomedical imaging, space exploration, and as an energy commodity, our understanding of cryogenic hydrogen is incomplete and ability to accurately predict its behavior is insufficient. The fundamental challenge arises from molecular hydrogen naturally occurring as a mixture of *ortho* and *para* isomers, with an equilibrium composition that is strongly dependent on temperature, and conversion between isomers requiring a nominally forbidden nuclear-spin-state transition with large conversion enthalpy.

In this talk, I will provide an overview of our current experimental endeavors to investigate the properties and behavior of cryogenic hydrogen. This includes extending the range of dielectric property data for hydrogen at low temperature, which has revealed shortcomings in current hydrogen property models; quantifying the kinetics of hydrogen isomer conversion, in the presence of catalysts and adsorbents; studying the freezeout behavior of impurities in cryogenic hydrogen and their effect on conversion; and measuring sound speed and VLE for cryogenic mixed refrigerants, to evaluate models used in hydrogen liquefaction process design. This has required the development of novel measurement techniques to measure hydrogen isomer composition, based on Raman spectroscopy and microwave resonant cavities, and new high-pressure cryogenic apparatus to facilitate this research.

Acknowledgment

This work is supported by the Australian Research Council and the Future Energy Exports CRC.

Significant references

1. F. Luther, G.M. Sellner, M. Richter, and P.L. Stanwix, "Inherent single-point calibration for quantitative Raman analysis of *ortho-para*hydrogen composition", *International Journal Hydrogen Energy*, vol. 102 (2025), pp. 778-789.
2. G.M. Sellner, M.G. Hopkins, M. Goryachev, L.D. Tenardi, E.F. May, and P.L. Stanwix, "Measuring Hydrogen *ortho-para* Composition with a Microwave Cavity Resonator", *PRX Energy (accepted)*, (2026).

Experimental Investigation of Hydrogen-Brine Interfacial Tension: Influence of Salinity, Cation Species, and pH

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1. INTRODUCTION

With global hydrogen demand rapidly increasing, natural hydrogen - molecular hydrogen generated and accumulated in subsurface environments - has emerged as a promising low-carbon and potentially cost-effective alternative to hydrogen derived from fossil fuels. The effective development of such resources requires a detailed understanding of multiphase flow in porous reservoirs, including the role of interfacial tension (IFT) between hydrogen gas and reservoir brines, which controls hydrogen migration, trapping, and release from rock matrices. However, available IFT data for H₂-brine systems remain inconsistent and largely limited to NaCl solutions. This work presents a systematic experimental study of the IFT between hydrogen and brines containing different chloride salts (NaCl, KCl, CaCl₂, and MgCl₂) over a wide range of subsurface-relevant conditions, complemented by an investigation into pH effects in H₂-CaCl_{2(aq)} systems via the addition of Ca(OH)₂ or HCl.

2. APPARATUS & METHODOLOGY

Measurements were performed using a custom-designed high-pressure pendant-drop apparatus operating up to 30 MPa and 423 K. The apparatus consisted of a high-pressure, high-temperature titanium view cell closed at both end with sapphire windows, two precision syringe pumps for independent controls of gas and liquid injections and a high-resolution CCD camera for droplet imaging. Brine molalities were varied up to 5 molal for monovalent salts (NaCl and KCl) and up to 3 molal for divalent salts (CaCl₂, and MgCl₂). Droplet profiles were analysed using axisymmetric drop-shape analysis (ADSA) based on the Young-Laplace equation.

3. RESULTS & DISCUSSION

The results show that IFT decreases with increasing temperature and pressure, but increases with salinity, exhibiting clear cation-specific effects: divalent cations (Ca²⁺, Mg²⁺) yield systematically higher IFT values than monovalent (Na⁺, K⁺) salts at same brine molality. When plotting IFT values against Cl⁻ molality at constant temperatures, a near-linear relationship was observed across all four tested temperatures and for all brine types. These results enabled the development of a preliminary universal empirical model to estimate IFT in H₂-chloride brine binary system as a function of temperature, pressure and chloride molality, which can be applied in future reservoir-scale simulations of natural hydrogen production and storage processes.

4. CONCLUSION

This study provides the first comprehensive dataset of IFT in H₂-chloride brine binary systems encompassing multiple cation types and pH variations under reservoir-relevant conditions. The findings confirm clear trends with respect to temperature, pressure, and salinity, and demonstrate the feasibility of using simple empirical relationships for IFT estimation. These insights are critical for improving the accuracy of multiphase flow models in natural hydrogen reservoirs and can support the broader development of hydrogen exploration, production and sub-surface storage strategies.

ACKNOWLEDGMENT

The authors gratefully acknowledge the financial support for this project from Shell Research Ltd.

Density and isobaric heat capacity measurements for hydrogen-gas mixtures

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As hydrogen emerges as a new energy carrier, its transport and storage increasingly involve conditions where hydrogen mixes with other fluids, forming hydrogen-containing mixtures that can significantly influence system behavior. For example, hydrogen may be blended with natural gas during pipeline transport or may encounter residual petroleum components in subsurface storage formations. As a result, reliable thermophysical property data for these mixtures are essential for the safe and efficient design, modelling, and operation of hydrogen transport and storage systems.

This experimental study investigates the density and isobaric heat capacity of selected hydrogen-containing mixtures under conditions directly relevant to current and emerging hydrogen infrastructure. High-pressure measurements were conducted for mixtures including $\text{H}_2\text{-N}_2$, $\text{H}_2\text{-CH}_4$, and $\text{H}_2\text{-CO}_2$ across a broad range of hydrogen compositions, temperatures from 263.15 to 413.15 K, and pressures from 1 to 50 MPa. The resulting data were compared with values reported in previous experimental studies and with predictions from cubic and non-cubic equations of state. These new measurements provide important reference data to support model development, calibration, and validation for hydrogen transport and storage applications.

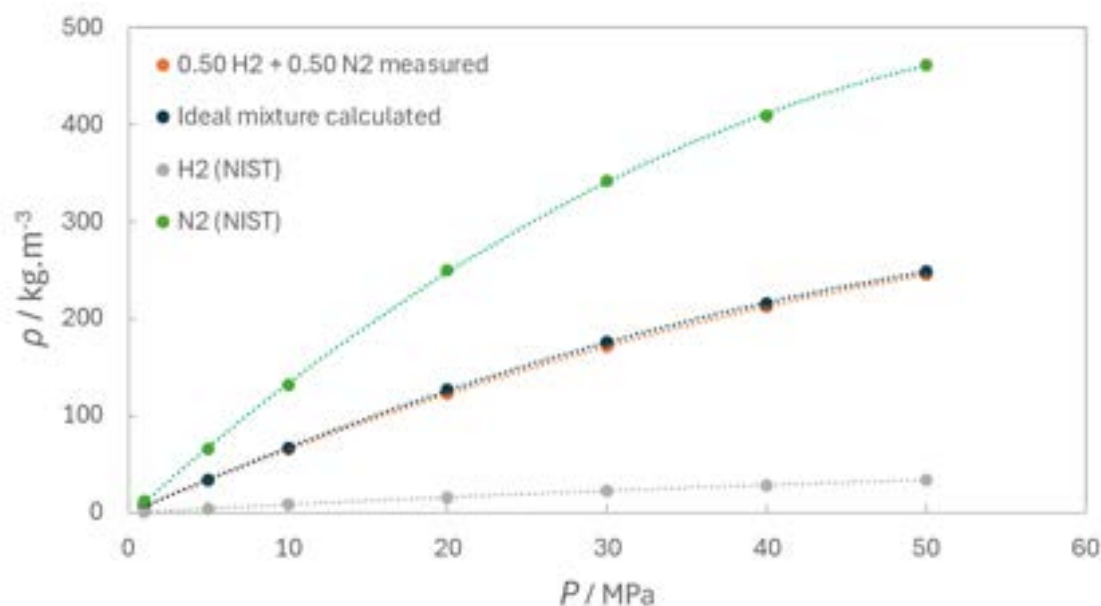


Figure 1. Experimental (P-ρ) measurements for the (0.50 H_2 + 0.50 N_2) mixture at 263.15 K and comparison with ideal-mixture behavior

Acknowledgment

The authors gratefully acknowledge funding from Equinor Energy ASA.

Significant references

1. D. Lozano-Martín, A. Moreau, and C.R. Chamorro, *Renewable Energy*, vol. 198 (2022), pp. 1398-1429.
2. R. Hernández-Gómez, D. Tuma, A. Gómez-Hernández, and C.R. Chamorro, *Journal of Chemical and Engineering Data*, vol. 62 (2017), pp. 4310-4326.

Experimental Validation of the Revised Dielectric Model for Hydrogen at Cryogenic Conditions

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In the global shift towards clean energy alternatives, hydrogen has emerged as a promising candidate due to its low environmental impact and high energy density, particularly in liquid form. This has driven the demand for high-precision sensor technologies capable of quantifying hydrogen properties for efficient and safe process monitoring, especially at the cryogenic conditions that hydrogen liquefaction requires. Dielectric permittivity, in particular, offers strong potential for cryogenic, online, and non-invasive hydrogen analysis and spin isomer (*ortho-para*) compositional measurement, as demonstrated in a previous work.¹ However, further development of such technology is limited by the accuracy of the existing predictive models for hydrogen's dielectric behaviour at low temperature. Recent theoretical developments have yielded a revised model that more rigorously describes hydrogen's dielectric behaviour, including vast improvement in representing *ortho*- and *para*-hydrogen mixtures, particularly in the cryogenic regime.² Yet, due to the scarcity of experimental data available, the low temperature performance of this model cannot currently be appropriately validated.

Presented in this work is the design and implementation of a dedicated experimental apparatus for dielectric constant measurements of hydrogen. The conditions covered are those at which there is limited or non-existent experimental data, namely, non-equilibrium *ortho-para* hydrogen mixtures at temperatures between (20 and 80) K and pressure up to 15 MPa. Dielectric constant measurements will be performed with a quasi-spherical microwave cavity resonator, capable of dielectric constant measurements with an expected uncertainty³ on the order of 0.1 ppm. The system incorporates an isomer-conversion system employing a well-characterised catalyst for *ortho-para* hydrogen mixture preparation, coupled with independent Raman spectroscopy for quantifying composition.

The resulting dataset will allow a rigorous evaluation of the revised dielectric model across cryogenic temperatures and elevated pressures. More broadly, this experimental capability provides a dedicated foundation for future dielectric model development and underpins progress toward accurate thermophysical property prediction and robust cryogenic sensing.

Significant references

1. G.M. Sellner, M.G. Hopkins, M. Goryachev, L.D. Tenardi, E.F. May, and P.L. Stanwix, *to be published (PRX Energy)*, (2025).
2. G.M. Sellner, A.H. Harvey, L. Incerti, P.L. Stanwix, and E.F. May, *27th International Conference on Chemical Thermodynamics*, S03 (2025).
3. E.F. May, M.R. Moldover, and J.W. Schmidt, *Molecular Physics*, vol. 107 (2009), pp. 1577-1585.

3.3

Thermophysical Properties Liquid Metals



Experimental and numerical study of liquid metals viscosity. Gravity effects study and microgravity exploration

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Thermophysical properties knowledge is a key challenge to develop new alloys and manufacturing processes. However, high temperatures and complex measurements make it a challenging task. Aerodynamic levitation gives the advantages of contactless measurements, decoupled heating, and the possibility to levitate many kinds of materials. But for surface tension [1-3] and viscosity [2] determination, many problems remain, like vibrational mode degeneracies and gravity effects.

This communication presents a complete finite element numerical modelling solving both CFD and moving mesh is developed and presented, focusing on vibrational modes degeneracies, and gives recommendations in the analysis of experimental results. For viscosity determination, the effect of gravity is quantified thanks to the numerical model. Outlooks are given to treat the problematic behavior of liquid metal submitted to the gravity effect.

The experimental methods developed at IRDL laboratory, both on ground and microgravity, will be presented. Specifically, the problems encountered on ground will be displayed, and the first attempt of a new kind of parabolic flights apparatus will be presented.

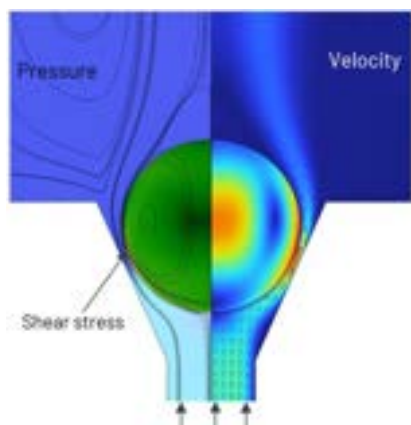


Figure 1. Multiphysics modeling of the experiment.

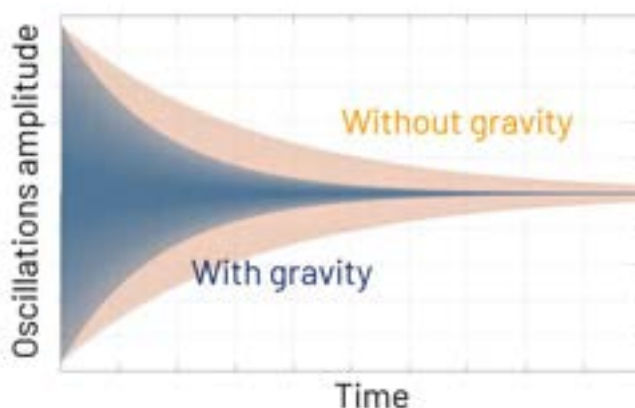


Figure 2. Effects of gravity (numerical results).

Acknowledgment

This work was funded by the French research agency ANR-23-CE08-0004, French space agency CNES with the Camélide project and the IRDL laboratory.

Significant references

- [1] Klapczynski et al. Surface tension measurements of liquid pure iron and 304L stainless steel under different gas mixtures . Journal of Molecular Liquids, vol. 350, (2022), p. 118558.
- [2] Pierre et al. Gravity impact on viscosity measurements by aerodynamic levitation . High Temperatures-High Pressures, vol. 53, no 3, (2024)
- [3] Le Maux et al. Sub-Second Surface Tension Measurement of Steels Containing Manganese in Aerodynamic Levitation . International Journal of Thermophysics, vol. 45, no 11, (2024), p. 162.

Electrical Conductivity of Iron Oxide Containing Oxide Melt

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As the global drive towards achieving carbon neutrality accelerates, the steel industry is experiencing substantial transformations. Innovative processes, such as Molten Oxide Electrolysis (MOE), are being developed to mitigate CO₂ emissions by substituting fossil fuels with electricity. Nevertheless, the electrical properties of molten slags—integral for process regulation—remain insufficiently understood. This investigation examines the alternating current (AC) electrical behavior of iron oxide-rich molten slags utilizing a four-terminal measurement technique based on the van der Pauw-Ohta method [1,2]. Measurements were performed at temperatures ranging from 1400 °C to 1600 °C under assorted atmospheric conditions. The findings indicate that electrical conductivity increases with temperature and iron oxide content, likely attributable to decreased network polymerization and increased mobility of cations, as exemplified in Figure 1. The discussion will also encompass the reactance and impedance characteristics depicted through Bode and Nyquist plots.

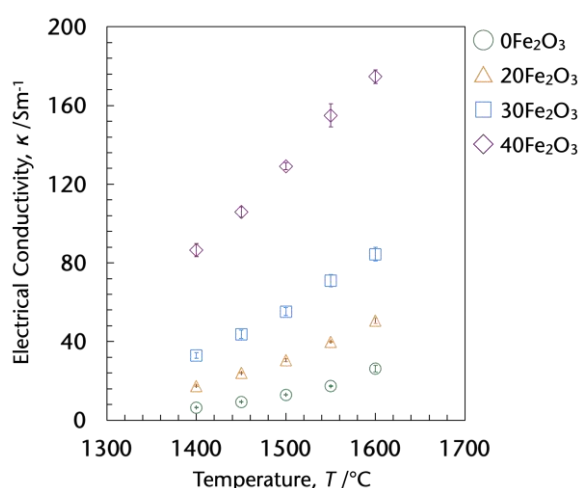


Figure 1. Electrical conductivity of iron oxide containing CaO-SiO₂-Al₂O₃ molten oxide.
Fe₂O₃ = 0-40mass%, CaO/SiO₂ = 1.0, Al₂O₃ = 20mass%.

Significant references

1. L.J. van der Pauw, Philips Res. Rep, vol. 13 (1958), pp. 1-9.
2. Y. Ota, A. Miyanaga, K. Morinaga, and T. Yanagase, Jpn. Inst. Met., vol. 45 (1981), pp. 1036.

Measurement of the density of liquid metals in aerodynamic levitation at high pressure and high temperature

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Measuring the density of liquid metals at very high temperatures is a real experimental challenge. Conventional contact methods often lead to sample contamination, while evaporation of metals limits the maximum measurement temperature even with levitation methods and affects the accuracy of the results [1]. The objective of this study is to determine the density of liquid metals near their boiling point, while minimizing evaporation losses. This approach is of particular interest for industrial applications such as laser welding where these temperatures are reached. The experiment is based on the aerodynamic levitation of a metal drop of approximately 2 mm of diameter in a helium flow. Heating is provided by a laser, while the behaviour of the drop is recorded using a high-speed camera [2]. A specific high-pressure measurement device is designed to limit evaporation and enable precise control of thermodynamic conditions. The obtained results make possible to determine linear laws of density variation with temperature for temperatures above 2 400 K. In addition, measurements taken under high pressure make possible to exceed the usual temperature limits [3], reaching up to 3 100 K. This work thus constitutes the first reliable experimental data in this temperature range. These results highlight the reliability of high-pressure aerodynamic levitation as a technique for investigating liquid metals and open up promising prospects for the analysis of materials close to their boiling point with a highly reduced evaporation.

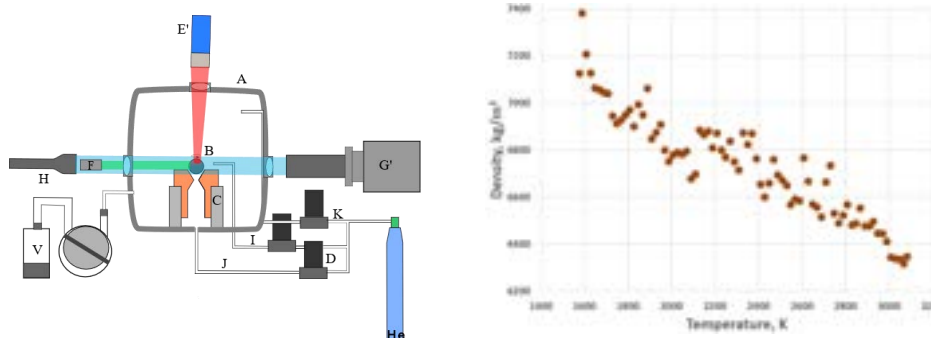


Figure 1. Schematic of the aerodynamic levitation setup (left) and evolution of the density of iron as a function of temperature at 92 bar (right). The main components are: (A) sealed chamber, (B) sample, (C) levitation nozzle, (D) flow meter, (E') 300 W laser, (F) two-colour pyrometer, (G') high-speed camera, (V) vacuum pump.

Acknowledgment

Thanks to the French National Research Agency (ANR-23-CE08-0004) for its financial support for this work.

Significant references

- [1] V. Klapczynski *et al.*, « Temperature and time dependence of manganese evaporation in liquid steels. Multiphysics modelling and experimental confrontation », *Scr. Mater.*, vol. 221, p. 114944, déc. 2022, doi: 10.1016/j.scriptamat.2022.114944.
- [2] D. Le Maux, M. Courtois, T. Pierre, B. Lamien, et P. Le Masson, « Density measurement of liquid 22MnB5 by aerodynamic levitation », *Rev. Sci. Instrum.*, vol. 90, n° 7, p. 074904, juill. 2019, doi: 10.1063/1.5089620.
- [3] Y. Shimoyama *et al.*, « Density of Fe-3.5 wt% C liquid at high pressure and temperature and the effect of carbon on the density of the molten iron », *Phys. Earth Planet. Inter.*, vol. 224, p. 77- 82, nov. 2013, doi: 10.1016/j.pepi.2013.08.003.

Fast surface tension measurement of liquid iron and 304L steel using an aerodynamic levitation apparatus and a new multi-bursts excitation

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Liquid metals play a central role in processes such as additive manufacturing, casting, and welding, where accurate control of surface tension is essential. This work introduces a fast, fully contactless method to determine the surface tension of liquid metals using the oscillating drop technique under aerodynamic levitation [1,2]. Long exposure time of materials at high temperature leads to problematic evaporation [3]. Here, a new kind of acoustic excitation is applied, followed by an analysis of the free vibration stage over a very short time (< 2 s). This protocol improves the precision of resonance frequency determination while limiting evaporation. A combined FFT (Fast Fourier Transform) and a temporal spectrogram analysis enables tracking of the temporal evolution of the $l = 2$ oscillation mode. This time resolved analysis highlights the frequency splitting caused by deformation or rotation of the droplet. A more reliable resonance frequency is identified through a weighted combination of degenerate peaks. Measurements performed on high-purity iron (99.95%) between 1500 °C and 2200 °C show good agreement with published data and are extended to a 304L stainless steel of interest for industry. The proposed method, faster and contamination-free, provides a reliable tool for high-temperature surface tension characterisation of liquid metals with a controlled evaporation over time.

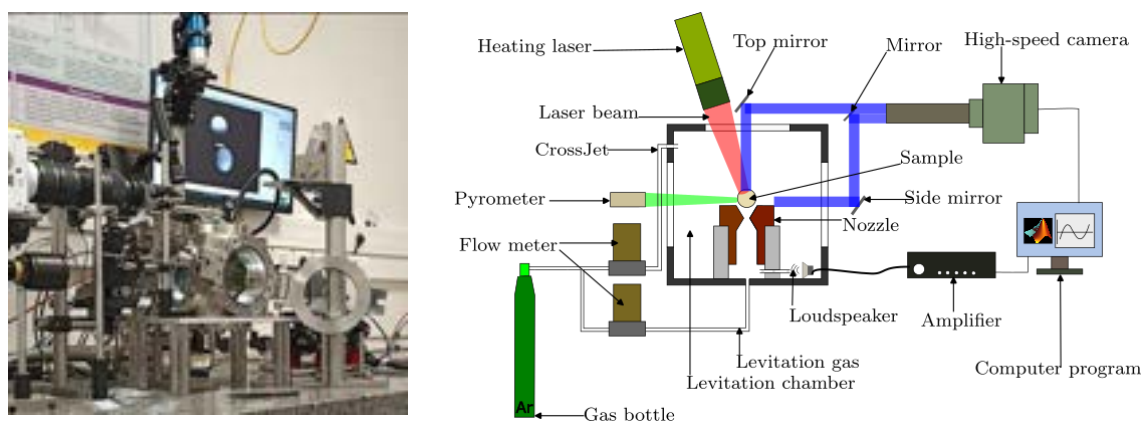


Figure 1. Experimental setup of aerodynamic levitated oscillating droplet.

Acknowledgment

This work is funded by the French National Agency (ANR) through the CaraMeLL project (Characterisation of Liquid Metals by Levitation at High Pressure and High Temperature) ANR-23-CE08-0004.

Significant references

- [1] V. Klapczynski, D. Le Maux, M. Courtois, E. Bertrand, and P. Paillard, Surface tension measurements of liquid pure iron and 304L stainless steel under different gas mixtures, *Journal of Molecular Liquids* **350**, 118558 (2022).
- [2] D. Le Maux, V. Klapczynski, M. Courtois, T. Pierre, and P. Le Masson, Surface tension of liquid Fe, Nb and 304L SS and effect of drop mass in aerodynamic levitation, *J Mater Sci* **57**, 12094 (2022).
- [3] V. Klapczynski, M. Courtois, R. Meillour, E. Bertrand, D. L. Maux, M. Carin, T. Pierre, P. L. Masson, and P. Paillard, Temperature and time dependence of manganese evaporation in liquid steels. Multiphysics modelling and experimental confrontation, *Scripta Materialia* **221**, 114944 (2022).

3.4

Thermophysical Properties Refrigerants I



Thermophysical Properties for the Development of Next-Generation Refrigerants

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Everchanging regulations are driving the search for new refrigerants for a variety of applications. New refrigerants must satisfy GWP, toxicity, and flammability constraints while providing efficient performance for their intended application. Screening studies [1,2] have demonstrated that the number of options for new refrigerant molecules remains limited, and this has motivated the exploration of refrigerant blends that balance GWP, flammability, and performance.

Here we present an approach that combines property measurements with the measurement and/or estimation of flammability and cycle performance to screen refrigerant blends for a particular application.

The first step for any proposed refrigerant blend is the collection of any available literature data for the binary constituents and the evaluation of those data and the adequacy of the available pure-fluid EOS and mixture models. If further data are required, vapor-liquid equilibria (VLE) for each are measured first. These data are used to fit the single mixture interaction parameter γ_T , as described by Bell[3]. This mixture model is then incorporated into a cycle simulation to provide estimated performance characteristics for the blend. The flammability is tested following standard protocols or estimated by the method of Linteris et al.[4]. If both the performance characteristics and the flammability results are favorable further measurements and modeling are carried out.

The goal of this second phase of measurements is to generate a complete mixture model for the refrigerant blend. This involves measurements of the speed of sound and density over wide ranges of temperature and pressure. While VLE and density data are the most important in EOS fitting, the speed of sound is a critical input to better describe derivative properties. We measure speed of sound because of the simplicity of the technique and higher accuracy compared to other properties, such as heat capacity, that would generate similar, so-called “thermal” data. These data are fitted to develop additional mixture interaction parameters and, possibly, a departure function. The model is then used with a more detailed cycle simulation to more critically assess the blend’s performance in the target application.

In our approach, only the binary constituents of a multicomponent mixture are considered. This traditional approach to modeling multicomponent mixtures was recently confirmed by Al-Barghouti et al.[5] for speed of sound. They compared experimental speed of sound data for four ternary refrigerant blends to mixture models that incorporated interaction parameters that were only fit to thermodynamic data for their binary constituents. They demonstrated that pure fluid equations of state (EOS) with binary interaction parameters can be extended to reliably predict the properties of multicomponent mixtures

We will present examples of the above approach based on recent projects in our group at NIST.

Significant references

1. M.O. McLinden, J.S. Brown, R. Brignoli, A.F. Kazakov, and P.A. Domanski, *Nature Comm.*, **8** (2017), 14476.
2. P.A. Domanski and M.O. McLinden, *Int. J. Refrig.*, **178** (2025), 410-417.
3. I.H. Bell, *J. Chem. Eng. Data*, **70** (2025), 1173-1181.
4. G.T. Linteris, I.H. Bell, and M.O. McLinden, *Int. J. Refrig.*, **104** (2019), 144–150.
5. K.S. Al-Barghouti, K.N. Avery, I.H. Bell, and A.J. Rowane, *Int. J. Thermophys.*, **46** (2025), 173.

Parametrization in PC-SAFT Framework for Accurately Describing Second-Order Derivative Properties of Hydrofluoroalkene (HFO) systems

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Hydrofluoroolefins (HFOs) and some low-GWP hydrofluorocarbons (HFCs), which are named environmentally friendly refrigerants, serve as highly-potential working fluids in low-temperature thermal energy utilization systems like organic Rankine cycles, thermal batteries, and heat pumps. Accurate characterization of thermodynamic properties, especially the caloric properties of sound speed and heat capacity in a wide temperature and pressure range is central to describing the energetic behavior of working fluids. The statistical associating fluid theory equation of state (SAFT EoS) balances accuracy and physicality, ensuring reliable thermodynamic analyses of new working fluids over a wide parameter range in energy systems. However, the recent SAFT EoSs have not fully considered the reliable characterization of second-order derivative properties like sound speed and heat capacity.

This work aims to achieve accurate description of phase equilibrium, density, and derivative properties of HFOs using PC-SAFT framework with concise computation and fewer parameters. Considering multiple types of polar and non-polar working fluids of HFOs and their mixtures, the PC-SAFT base model was tried to be combined with dipole terms, simplified association terms[1], new universal constants[2], and variable soft pulsation range parameters [3] for suitable parameterization method in characterizing the thermodynamic derivative properties of HFO. Firstly, the pure fluid parameters were fitted based on experimental data or dedicated EoS calculations. Then, a physics-embedding machine-learning method of Symbol Regression[4] was developed to explore the quantitative relationship between fluid parameters (m , σ , ϵ) with basic thermophysical parameters and molecular configuration parameters, assisting in improving parameter rationality and availability for less-knowledge fluids. In the future, we plan to take the parameter laws presented in similar studies of alkanes and alcohols as reference, to further explore the methods for decomposing HFO molecules into universal first-order and second-order atomic groups, and achieve the extrapolation calculation of HFO-series parameters, ensuring the engineering usability of the SAFT EoS in novel energy systems.

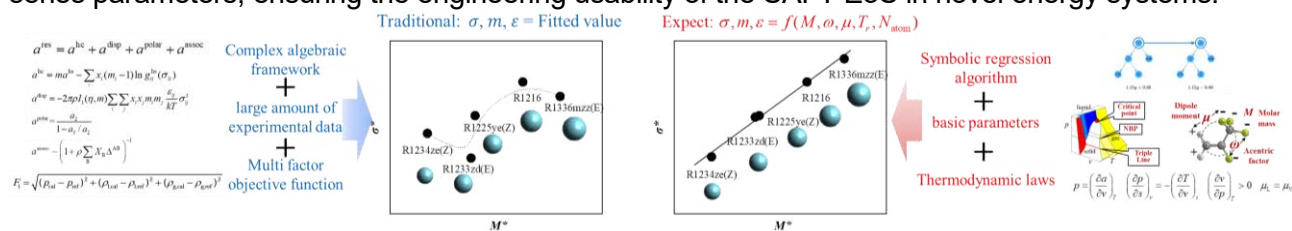


Figure 1. Method for obtaining SAFT EoS parameters conforming to molecular characteristics.

Acknowledgment

The authors acknowledge financial support from the National Research and Development Program of China (Nos. 2023YFB4102503) and the Creative Seed Fund of Shanxi Research Institute for Clean Energy, Tsinghua University.

Significant references

1. X. Liang, K. Thomsen, W. Yan, G. M. Kontogeorgis, Prediction of the vapor–liquid equilibria and speed of sound in binary systems of 1-alkanols and n-alkanes with the simplified PC-SAFT equation of state, *Fluid Phase Equilibria* 360 (2013) 222-232.
2. X. Liang, G. M. Kontogeorgis, New variant of the universal constants in the perturbed chain-statistical associating fluid theory equation of state, *Industrial & Engineering Chemistry Research* 54 (4) (2015) 1373-1384.
3. F. Yang, A. I. A. Pádua, Variable-Range PC-SAFT Parametrization for Accurate Modeling of Caloric Properties, Critical Temperature, and Critical Pressure: Normal Alkanes and Hydrogen, *Industrial & Engineering Chemistry Research* 64 (18) (2025) 9385-9395.
4. X. Peng, Y. Tan, L. Xu, Z. Yang, Y. Duan, Explicit-model exploring framework integrating thermodynamic principles and interpretable machine learning in predicting gaseous speed of sound, *Energy* 318 (2025) 134806.

Quantum Study for Global Warming Potentials of HFO-1243yc

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Using quantum-chemical calculations, we independently evaluated the atmospheric lifetime and radiative efficiency to estimate the global warming potential (GWP) of R1243yc, for which no literature values are currently available. Figure 1 compares the absorption spectra of R1243yc with those of the conventional refrigerant R1234yf. While the overall spectral shapes are similar, R1243yc exhibits a reduced absorption cross-section. Figure 2 presents the energy diagram for the addition reaction with OH radicals. The calculations show that this reaction proceeds downhill with a low activation barrier. The resulting GWP value is 0.002, which is lower than the value predicted by McLinden et al.¹

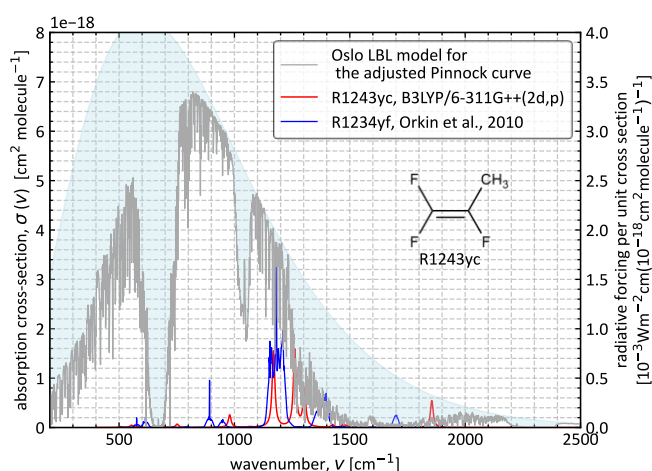


Figure 1. Absorption spectra of R1243yc and R1234yf.

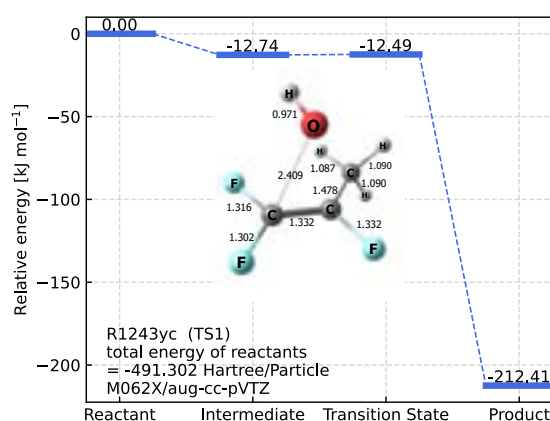


Figure 2. Energy diagram of OH radical addition to R1243yc

Acknowledgment

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Significant references

1. M.O., McLinden, A. F., Kazakov, J. S., Brown, P. A., Domanski, *Int. J. Refrig.* 38, (2014) 80-92.

Extending the Vapor–Liquid Equilibrium Study of the Propane–n-Pentane System for Refrigeration: New Measurements at Low Temperatures

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Introduction

The vapor–liquid equilibrium (VLE) of the propane–n-pentane system has been extensively studied for oil and gas applications at moderate to high temperatures (50–200°C) and elevated pressures. Demand for natural hydrocarbon refrigerants has recently increased due to their environmental benefits: these fluids are non-toxic, non-ozone-depleting, and exhibit low global warming potential, making them among the most climate-friendly and cost-effective options for cooling and heat pump applications. To assess the reliability of existing thermodynamic models under heat pump operating conditions, new experimental VLE data for propane–n-pentane were obtained at temperatures down to 20°C using static analytical apparatus. Two experimental setups were employed: one at the Centre for Energy Environment Processes (CEEP), Mines Paris – PSL, in Fontainebleau, France, and a newly constructed unit at Politecnico di Milano designed for low-temperature and low-pressure measurements down to 0.1 bar.

Results and discussion

The experimental campaign was carried out by sampling the vapor and liquid phase compositions of propane–n-pentane along three isotherms at 20, 40, and 60°C. The measured VLE data were compared with values calculated using the NIST REFPROP v10.0 database. The experimental vapor and liquid compositions show good agreement with the reference model across all investigated pressure and composition ranges as shown in fig. 1. This result not only confirms the accuracy of the equation of state implemented in REFPROP but also supports the validity of the underlying historical datasets, in particular the high-pressure data of Vejrosta et al. [3] acquired at 63°C. The higher-temperature measurements at 60°C thus provide an experimental bridge to these literature data, whereas the new measurements at 20 and 40°C represent previously unpublished VLE data that extend the validation of the REFPROP mixture model into the low-temperature range relevant for heat pump operation. Additional measurements at lower temperatures are planned to further characterize the system in the range relevant for heat pump operation.

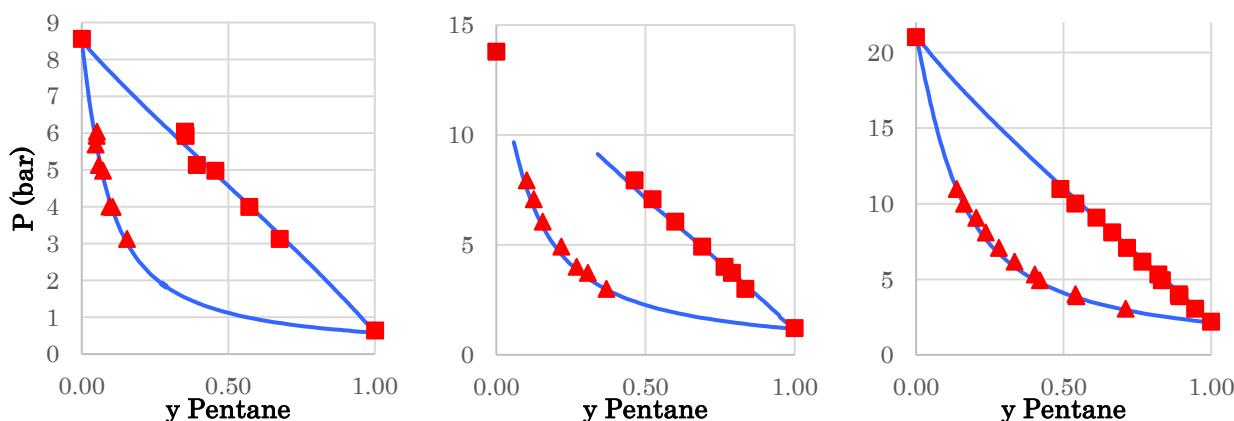


Figure 1. Pressure versus pentane mole fraction for the propane–n-pentane mixture: experimental data (red symbols) and NIST REFPROP calculated values (solid lines) at 20°C (left), 40°C (center), and 60°C (right).

Significant references

1. Sage, B. H., & Lacey, W. N. (1940). Phase Equilibria in Hydrocarbon Systems Propane–n-Pentane System1. *Industrial & Engineering Chemistry*, 32(7), 992-996.
2. Reamer, H. H., Sage, B. H., & Lacey, W. N. (1950). Phase Equilibria in Hydrocarbon Systems:

- Volumetric and Phase Behavior of the Propane–n-Pentane System. *Industrial & Engineering Chemistry*, 42(3), 534–539.
3. Vejrosta, J., & Wichterle, I. (1974). The propane-pentane system at high pressures. *Collection of Czechoslovak Chemical Communications*, 39(5), 1246-1248.
 4. Lemmon, E. W., Bell, I. H., Huber, M. L., & McLinden, M. O. (2018). NIST standard reference database 23: reference fluid thermodynamic and transport properties-REFPROP, Version 10.0, National Institute of Standards and Technology. *Standard Reference Data Program, Gaithersburg*, 45-46.
 5. Palm, B. (2008). Hydrocarbons as refrigerants in small heat pump and refrigeration systems—a review. *International journal of refrigeration*, 31(4), 552-563.
 6. Goni, M. U., Burgass, R., Chapoy, A., & Ahmadi, P. (2023). Experimental Vapor–Liquid Equilibrium (p, T, x) Data for Binary Systems of Propane (1) in n-Decane, n-Undecane, n-Dodecane, and n-Tridecane (2). *Journal of Chemical & Engineering Data*, 68(12), 3328-3337.
 7. Lemmon, E. W., McLinden, M. O., & Wagner, W. (2009). Thermodynamic properties of propane. III. A reference equation of state for temperatures from the melting line to 650 K and pressures up to 1000 MPa. *Journal of Chemical & Engineering Data*, 54(12), 3141-3180.

3.5

Thermophysical Properties

Complex Liquids I



Chemical stability of ionic liquids for high temperature MeOH synthesis at 513 K

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The direct hydrogenation of CO₂ to methanol is a promising route for carbon valorization, offering a sustainable pathway to reduce emissions while producing high-value chemicals. Although favorable kinetics are achieved near 513 K, the single-pass methanol yield conversions is typically limited to 10–20% due to thermodynamic constraints [1]. Ionic-liquid-assisted trickle-bed reactors have been proposed as a means to enhance yield conversion by selectively absorbing methanol in situ and thereby shifting equilibrium toward higher yields. However, the feasibility of such processes depends critically on the chemical stability of the ionic liquid under reaction conditions. At elevated temperatures, and particularly in the presence of water and protic species such as methanol, several ionic liquid (IL) families may undergo hydrolytic or nucleophilic degradation, especially those containing fluoroorganic groups or strongly basic anions [2].

This work experimentally assesses the chemical stability of ionic liquids pre-selected by COSMO-RS for high temperature CO₂-to-methanol production. IL–methanol–water mixtures were heated isovolumetrically at 513 K for extended periods in pressure autoclave reactor-lined reactors. Samples were analyzed by ¹H and ¹³C NMR spectroscopy before and after exposure, providing a preliminary assessment to identify the most stable ILs under reaction conditions. Additionally, combined with other analyses, these studies help elucidating possible degradation and assess the suitability of candidate ILs for continuous operation at high temperature.

The results deliver essential stability benchmarks for IL-based reactor concepts and inform the development of viable, energy-efficient process intensification strategies for CO₂ hydrogenation to methanol within a circular-economy framework.

Acknowledgment

This work was developed within the scope of the project CICECO Aveiro Institute of Materials, UID/50011/2025 (DOI 10.54499/UID/50011/2025) & LA/P/0006/2020 (DOI 10.54499/LA/P/0006/2020), financed by national funds through the FCT/MCTES (PIDDAC). This study also received financial support from Illimited project, financed by Horizon Europe agreement n° 101192964.

Significant references

1. M. Bukhtiyarova, T. Lunkenbein, K. Kähler, and R. Schlögl, “Methanol Synthesis from Industrial CO₂ Sources: A Contribution to Chemical Energy Conversion,” *Catal Letters*, vol. 147, no. 2, pp. 416–427, Feb. 2017, doi: 10.1007/s10562-016-1960-x.
2. M. G. Freire, C. M. S. S. Neves, I. M. Marrucho, J. A. P. Coutinho, and A. M. Fernandes, “Hydrolysis of tetrafluoroborate and hexafluorophosphate counter ions in imidazolium-based ionic liquids,” *Journal of Physical Chemistry A*, vol. 114, no. 11, pp. 3744–3749, Mar. 2010, doi: 10.1021/jp903292n.

Detailed comparison between the Group Contribution models available in the literature for estimating the density of ionic liquids over a wide temperature and pressure range

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A comprehensive evaluation was conducted on eight group contribution models to assess their ability to predict the P – ρ – T behavior of ionic liquids. This study aimed not only to analyze the accuracy of each model in estimating ionic liquid densities but also to offer practical guidance for their use in process engineering. The evaluation methodology was based on three main criteria: accuracy, the flexibility of their functional groups, and their capacity to describe the great variety of cations and anions available in our databank. To facilitate this assessment, we developed a robust database containing 17,663 experimental data points of 201 different ionic liquids organized into 9 cation families, distributed over a large temperature (217.58 – 473.15 K) and pressure (0.0865 – 300.00 MPa) ranges. The most significant result of this study was the percentage distribution of the average relative deviation (%ARD) obtained for all models, as depicted in Figure 1. The models proposed by Paduszyński and Domańska [1] (“PDO” model) and by Evangelista et al. [2] (“GCL” model) generated the most estimates whose deviations are in the range [0.0–1.0%], which 86% of the data estimated by the “PDO” model fell within this range; meanwhile for the “GCL” model, 65% of the predictions fell within this range. We conclude that the “PDO” model was the most accurate among all those studied, since it generates the lowest average absolute relative deviation (%AARD) value for the entire database (%AARD = 0.63%). However, the “GCL” model is the only estimation method whose functional groups can describe ionic liquids and molecular substances, making this model the only one suitable for estimating the density of mixtures of ionic liquids and molecular organic compounds.

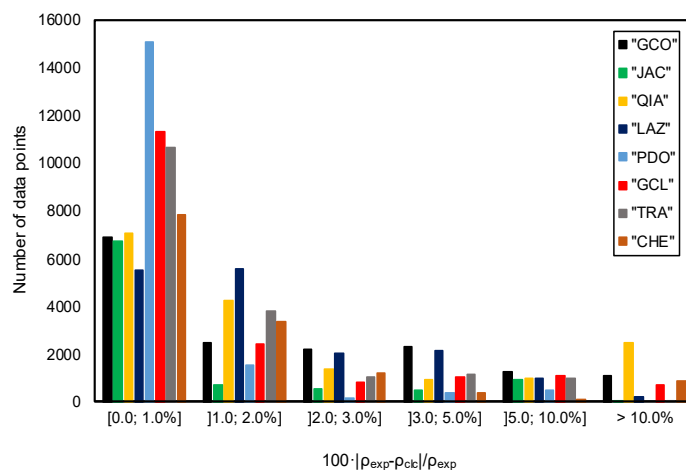


Figure 1. %ARD distribution for all models.

Significant references

1. K. Paduszyński, U. Domańska, *Industrial & Engineering Chemistry Research*, vol. 61 (2012), pp. 5340-5350.
2. N.S. Evangelista, F.R. do Carmo, R.S. de Santiago-Aguiar, H.B. de Sant'Ana, *Industrial & Engineering Chemistry Research*, vol. 53 (2014), pp. 9506-9512.

Influence of Different Gases and Molecular Catalysts on the Interfacial Tension and Viscosity of Ionic Liquids

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Ionic liquids (ILs) are promising working fluids for various fields of chemical and energy engineering. One application area is catalysis, where Supported Ionic Liquid Phase (SILP) systems are employed for industrially relevant reactions such as hydrogenation and hydroformylation. In SILP systems, a thin IL film containing a dissolved molecular catalyst is coated onto the surface of a porous solid support, providing a large surface area for the gaseous reactants and products dissolved in the liquid phase. A new paradigm in SILP technology aims to achieve strong surface enrichment of the catalyst, thereby promoting reactions preferentially at the gas-liquid interface. To design and optimize SILP systems, it is essential to understand their thermophysical properties under process-relevant conditions. However, data on the interfacial tension and viscosity as key properties for the description of interfacial phenomena like wetting and that of moment transport are often lacking.

In this contribution, we present the effects of dissolved gases and molecular catalysts on the interfacial tension and viscosity of ILs relevant to SILP systems. To characterize the gas-liquid interface at macroscopic thermodynamic equilibrium, surface light scattering (SLS) and the pendant-drop (PD) method are combined in a single experimental setup. By analyzing the same sample under identical conditions, the interfacial tension obtained by the PD method is used to determine the viscosity by SLS for fluids of relatively high viscosity such as ILs. The influence of representative gases in the form of hydrogen (H₂) and carbon dioxide (CO₂) of low and high solubility in ILs on both macroscopic properties is demonstrated for different imidazolium-based ILs at temperatures from (303 to 353) K and pressures up to 10 MPa.^{1,2} In a subsequent step, the system complexity is further increased by introducing commonly used molecular catalysts, specifically platinum (Pt) or Rh (rhodium)-based complexes.³ The measurement results for interfacial tension and viscosity are rationalized with the help of calculations obtained from molecular dynamics (MD) simulations and are correlated with experiments on the catalytic performance within a continuous pool reactor.

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Significant references

1. Z. Zhai, T. M. Koller, *J. Mol. Liq.*, vol. 377 (2023), 121491.
2. Z. Zhai, G. Hantal, A. Cherian, A. Bergen, J. Chu, C. R. Wick, K. Meyer, A. Smith, T. M. Koller, *Int. J. Hydrogen Energy*, vol. 72 (2024), pp. 1091-1104.
3. K. Antara, D. Hemmeter, Z. Zhai, D. Kremitzl, F. Maier, T. M. Koller, H.-P. Steinrück, M. Haumann, *ChemCatChem*, vol.16 (2024), e202400574.

Analysis of the Influence of the Cation Alkyl Chain on the Structure and Properties of Aqueous Mixtures of $[C_n\text{mim}][C(\text{CN})_3]$ ($n=2,4,6$)

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Chemical process design requires accurate values of the thermophysical properties of liquids to ensure quality in investment, operation, and safety. Ionic liquids, as potential replacements for currently used chemicals with mandatory requirements from European and International agencies in both current and future chemical processes, generate a wide range of mixtures. These mixtures necessitate efforts to develop reliable prediction and estimation methods, given the difficulty of measuring all properties of all known systems.

In our laboratory, we have conducted a systematic study of the properties of $[C_n\text{mim}][X]$ ionic liquid mixtures with water, measuring properties that provide molecular insights into the structure of the mixtures, combined with molecular simulation and spectroscopic information. The purpose of this contribution is to report new data for ionic liquids where $X = C(\text{CN})_3$, including properties such as density, speed of sound, and refractive index, across the entire composition range, for temperatures between 283 K and 343 K at 0.1 MPa. Immiscibility of $[C_4\text{mim}][C(\text{CN})_3]$ and $[C_6\text{mim}][C(\text{CN})_3]$ with water was observed for $x_w > 0.84$ and $x_w > 0.71$, respectively, showing strong repulsive forces between the water molecules and the anions/cations of the ionic liquid, forcing phase separation.

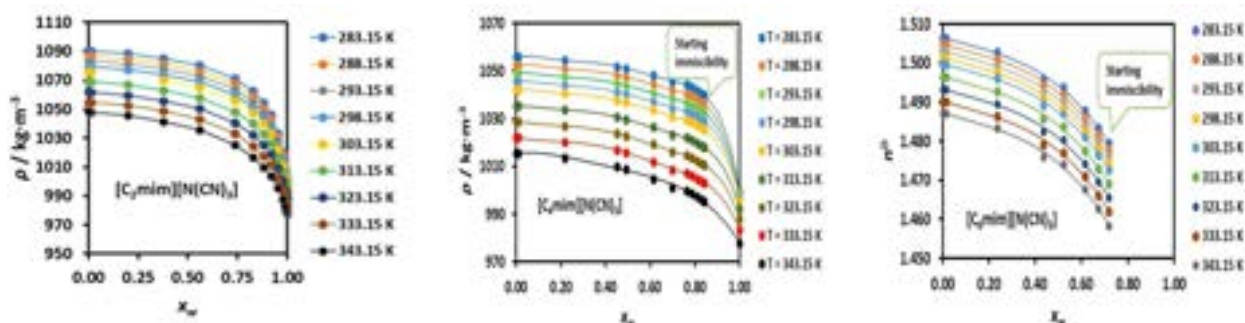


Figure 1. Some examples of properties variation with the mole fraction of water.

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Significant references

1. C.S.G.P. Queirós, X. Paredes, T.F.S. Avelino, D.E.N. Bastos, M. Ferreira, F.J.V. Santos, A.F. Santos, M.L.M. Lopes, M.J.V. Lourenço, H. Pereira and C.A. Nieto de Castro. *J. Mol. Liq.*, vol.297 (2020), pp. 111925.
2. F.E.B. Biucas, C.S.G.P. Queirós, D. Lozano-Martín, M. Ferreira, X. Paredes, A.F. Santos, F.J.V. Santos, M.L.M. Lopes, M. I. Lampreia, M.J.V. Lourenço, C. A. Nieto de Castro and K. Massonne. *Ind. Eng. Chem. Res.* vol. 61(5) (2022), pp. 2280–2305.
3. C.A. Nieto de Castro, A. Lamas, C. Magendran, R.M. Almeida, X. Paredes, Â.F. Santos, I.M.S. Lampreia, F.J.V. Santos, M.J.V. Lourenço. *J. Chem. Eng. Data*, vol. 69 (8), (2024), pp.2713–2734.

3.6

Thermophysical Properties

High-Temperature Materials I



The joint direct pulse heating facilities – measurement of thermophysical properties of solid and liquid metals and alloys from RT to above 4000 K

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Direct pulse heating is a well-known transient method for the measurement of thermophysical properties of high temperature electroconductive materials. Its fast, non-stationary regime of work allows experimental conditions at which testing materials do not undergo undesired chemical and mechanical changes that usually occurred in stationary techniques at high temperatures [1].

Several research laboratories around the world developed different experimental setups for the application of the direct pulse heating method. One of the most important characteristic of those setups is the heating rate of the sample under test, which defines how fast the measurements are. Thus, for example, the setups with the heating rate order of magnitude 10^3 K/s or 10^6 K/s perform within the millisecond or microsecond measurement range, respectively.

One millisecond pulse heating apparatus was developed and still is in use at the VINČA Institute in the range from room temperature up to 2600 K [2-3]. On the other hand, one very fast pulse heating setup having a heating rate of 10^8 K/s, was developed at TU Graz [4-5]. That facility was designed for measurements at very high temperatures, typically for investigating the materials liquid range, from melting temperature up to far into their liquid phase. It had been in continuous use and improvement for more than 4 decades till 2022, when G. Pottlacher, due to his retirement, offered his setup as a donation to N. Milošević. The complete fast experimental facility had been uninstalled, sealed and transferred to Institute VINČA at the end of 2022.

After the corresponding reconstruction, the new experimental space at VINČA, aimed to host both millisecond and fast microsecond direct pulse heating setups, was ready at the end of 2024. Reinstallation of the fast experimental setup in this space was first finished in 2025 and initial testing started in the second half of the same year. This presentation gives a short description of the joint facilities and retrospective of the fast facility transfer and reinstallation. Besides, it shows first measurement results obtained by the fast setup on three high temperature reference materials, molybdenum, tantalum and tungsten, which give very good agreement to data collected at TU Graz, before the transfer.

Significant references

1. A. Cezairliyan, Pulse calorimetry, in "Compendium of Thermophysical Property Measurement Methods, Volume 1 - Survey of Measurement Techniques", Eds. Maglič, K.D., Cezairliyan A., Peletsky, V.E., Plenum Press (1984), pp. 643-668
2. A.S. Dobrosavljević and K.D. Maglič, in "Advanced Course in Measurement Techniques in Heat and Mass Transfer", Hemisphere, Washington DC, USA, (1985), pp. 411-420
3. N.D. Milošević, *J. Thermal Analys. Calorim.*, vol. 147 (2022), pp. 4935-4943
4. E. Kaschnitz, G. Pottlacher and H. Jäger, *Int. J. Thermophys.*, vol. 13 (1992), pp. 699-710
5. G. Pottlacher, K. Aziz and A. Schmon, *High Temp. High Press.*, vol. 41 (2012), pp. 377-394

A Shadowgraph-Based Approach for Measuring Thermal Expansion of Ultra-High-Temperature Solids under Pulsed-Current Heating

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Refractory metals require accurate thermal expansion data at ultra-high temperatures to predict thermally induced stresses in aerospace and energy systems. Shadowgraphy, which detects length changes non-contactly from collimated-light silhouettes, is well suited for measurements approaching the melting point. Although liquid-phase measurements above 3000 K have been demonstrated using ultrafast current heating of ultrathin specimens [1,2], solid-phase implementations employing thermocouple-welded strip samples have been practically limited to ~2000 K because of thermocouple temperature tolerance and radiation-induced contrast loss [3].

To address these limitations, we have developed a new measurement approach that combines high-speed shadowgraph imaging with pulsed-current resistive heating [4]. The method uses a 405-nm backlight with bandpass filtering to preserve silhouette contrast under strong thermal radiation, while a welded Type-C thermocouple provides synchronized transient temperature tracking (Fig. 1). In proof-of-concept measurements on a niobium strip in high vacuum, both specimen length and temperature evolution were successfully captured beyond 2000 K, and the extracted thermal expansion behavior agreed with literature values within the estimated combined standard uncertainty of the method (below ~2%).

In this work, we describe the industrial motivation for high-temperature expansion metrology, outline the system architecture and optical design, and present an overview of the trial experiments. We also discuss approaches to establishing measurement traceability and improving uncertainty evaluation at ultra-high temperatures.

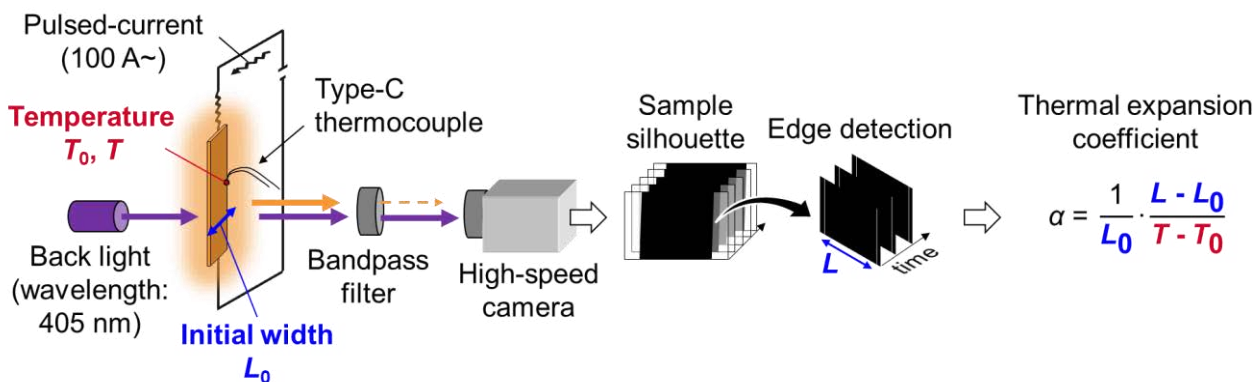


Figure 1. Conceptual schematic diagram to determine thermal expansion coefficients for a metal sample using setup based on high-speed shadowgraph imaging and Type-C thermocouple under pulsed-current.

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Significant references

1. T. Hüpf, C. Cagran, B. Wilthan, and G. Pottlacher, *J. Phys. Condens. Matter* **21**, 125701 (2009).
2. T. Hüpf and G. Pottlacher, *High Temp. High Press.* **40**(3), 271 (2011).
3. H. Watanabe and Y. Yamashita, *32nd Japan Symp. Thermophys. Prop.*, A108, 30 (2011).
4. I. Oriokasa and H. Watanabe, *Int. J. Thermophys.*, **46**(166) (2025).

Determination of Effective Radiative and Optical Properties of a Heterogeneous Fibrous Material by Homogenization

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High-temperature insulating materials feature complex heterogeneous microstructures combining fibers, binders, and opacifying particles, which significantly influence radiative heat transfer and overall thermal performance. In many industrial applications, including atmospheric re-entry systems and high-temperature furnace linings, these materials are assembled in multilayer configurations. Modeling the full heterogeneous structure of each layer is computationally prohibitive, an effective alternative is to represent each layer by an equivalent homogeneous medium described by effective radiative properties: the absorption coefficient κ , the scattering coefficient σ , and the Henyey-Greenstein asymmetry factor g , together with the effective optical properties: the refractive index n and the extinction coefficient k .

This work presents a methodology for determining all five effective properties using Monte Carlo Ray Tracing (MCRT) applied to a numerically generated 3D microstructure of MAFTEC 96, a commercially available alumina fiber-based insulation (96 kg/m³, ~96% porosity). The spectral complex refractive indices of the mullite fiber micro-constituents are first identified by coupling MCRT to a Levenberg-Marquardt optimization driven by integrating sphere measurements of reflectance and transmittance [1]. The five effective properties are then extracted directly from the ray trajectory statistics, without any supplementary inversion step.

The MCRT results are compared with two independent homogenization methods driven by the same integrating sphere data: the Modified Two-Flux Approximation (MTFA) [2], which yields κ and the transport scattering coefficient σ_{tr} , and the Inverse Adding-Doubling (IAD) method [3], applied here for the first time to a heterogeneous fibrous material. The systematic comparison shows that the retrieved κ and σ are sensitive to the assumed n and g , confirming that MCRT, as the only method that determines all five properties self-consistently.

Significant references

1. C. Daoût, O. Rozenbaum, D. De Sousa Meneses, and D. Rochais, Int. J. Heat Mass Transf. vol. 223 (2024) pp. 125-272.
2. L. Dombrovsky, J. Randrianalisoa, and D. Baillis, J. Opt. Soc. Am. A, vol. 23 (2006) pp. 91–98.
3. S.A. Prahl, M.J.C. van Gemert, and A.J. Welch, Appl. Opt., vol. 32 (1993) pp. 559–568.

3.7

Thermophysical Properties Electrolyte Solutions



Bridging Experiments, Simulations, and Data Science to Decode Salt Effects on the Solubility of Biomolecules

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Electrolyte solutions are the natural environment of biomolecules and are recognised as crucial to the regulation of their structure, function and physico-chemical behaviour, playing a central role in relevant biochemical processes.¹ Yet the quantitative description of ion-specific effects on their solubility remains an evident challenge in thermophysical chemistry. Despite decades of experimental measurements and the insights from the Hofmeister series, inconsistencies across datasets and the lack of a unified molecular interpretation continue to limit predictive capability.

This work presents a comprehensive framework for understanding the effects of salts on the solubility of amino acids and small peptides, integrating systematic experimental measurements, molecular dynamics simulations, and modern data-driven modelling. Solubility data for amino acids with different polarities and functionalities, as well as glycine derivatives, are examined in aqueous solutions containing mono-, di-, and trivalent ions spanning the Hofmeister series.² The results reveal distinct and ion-charge-dependent mechanisms governing salting-in and salting-out phenomena, highlighting the dominant role of specific ion-functional group interactions (Figure 1a) rather than bulk water structuring.³

To address long-standing inconsistencies in the literature, Gaussian Process modelling is employed⁴ to critically assess and reconcile solubility data (Figure 1b), enabling the identification of unreliable measurements and the rational prioritisation of new experiments. By bridging thermodynamic measurements, molecular-level interpretation, and statistical learning, this work establishes a robust thermophysical foundation for ion-specific effects in biomolecular systems and outlines a path toward predictive models for biological, pharmaceutical, and biotechnological applications.

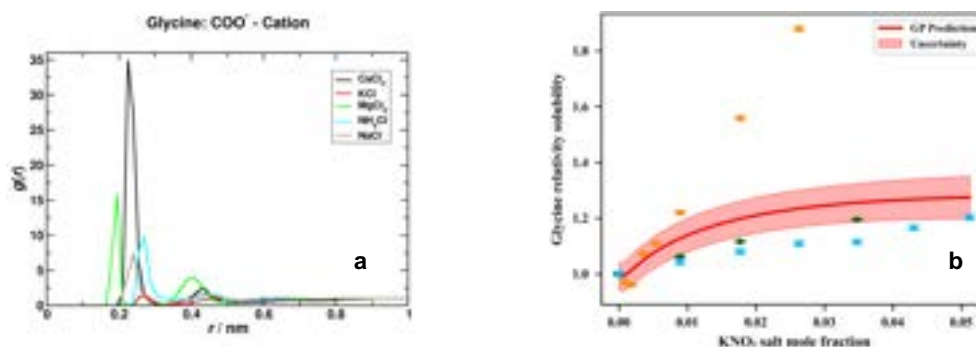


Figure 1. (a) Radial distribution functions of the cations around the COO⁻ group of glycine; (b) Gaussian Process model (red line) for the relative solubility of glycine in KNO₃ aqueous solution at 298.2 K.

Acknowledgment

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Significant references

1. P. Jungwirth, and B. Winter, *Annu. Rev. Phys. Chem.*, vol. 59 (2008), pp. 343-366.
2. M. Aliyeva, P. Brandão, J.R.B. Gomes, J.A.P. Coutinho, O. Ferreira, and S.P. Pinho, *Ind. Eng. Chem. Res.*, vol. 61 (2022), pp. 5620-5631.
3. L.I.N. Tomé, C.S.R. Sousa, J.R.B. Gomes, O. Ferreira, J.A.P. Coutinho, and S.P. Pinho, *RSC Adv.*, vol. 5 (2015), pp. 15024-15034.
4. C. Piske, P.G. Leite, M.A.R. Martins, O. Ferreira, J.A. P. Coutinho, D.O. Abranches, S.P. Pinho, *J. Sol. Chem.*, in press.

A Hybrid Model for Predicting Activities in Aqueous Electrolyte Solutions

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Mean ionic activity coefficients and osmotic coefficients are important properties for modeling many processes in industry and nature. Established activity coefficient models, such as those of Pitzer [1] or Bromley [2], require fitting to experimental data for each individual electrolyte and thus cannot predict properties for unstudied systems. However, since experimental data are generally scarce, this reliance on electrolyte-specific fitting severely limits their applicability. While some predictive approaches exist [2,3,4], they are typically limited in scope and rely on additional ion-specific descriptors, which are not always available.

Recently, matrix completion methods (MCMs) have been introduced for predicting the thermodynamic properties of mixtures [5,6]. These methods leverage the structure existing in binary mixture data, which can be organized in matrix form, where rows and columns correspond to individual components. Predicting missing entries, i.e., properties of unstudied combinations, then becomes a matrix completion problem.

In this work, we extend the MCM approach to electrolytes. Specifically, a hybrid model is presented that combines the Bromley model with an MCM. The MCM is employed to predict the electrolyte-specific parameters of the Bromley model, which are arranged in a matrix with cations and anions as rows and columns, respectively. Due to the lack of experimental data, the initial parameter matrix is only sparsely occupied, and the task of the MCM is to fill it up. This hybridization exploits the physical interpretability of Bromley's framework while leveraging the generalization capabilities of matrix completion. The hybrid model was trained end-to-end on experimental data for mean ionic activity coefficients and osmotic coefficients of aqueous solutions of 366 electrolytes at 298 K from the Dortmund Data Bank. As output, we obtain a completed matrix of Bromley parameters for 55 cations and 56 anions, enabling consistent prediction of concentration-dependent activities in aqueous solutions of 3080 electrolytes at 298 K, 2714 of which were previously unstudied, representing an increase in accessible systems by almost one order of magnitude compared to the experimental data. Our approach substantially extends the applicability of the Bromley model while maintaining high predictive accuracy, as demonstrated through evaluations on electrolytes excluded from model training.

Significant references

1. K. S. Pitzer, G. Mayorga, *J. Phys. Chem.* 77 (1973) 2300-2308.
2. L. A. Bromley, *AIChE J.* 19 (1973) 313-320.
3. J. Li, H.-M. Polka, J. Gmehling, *Fluid Phase Equilib.* 94 (1994) 89-114.
4. M. C. Simoes, K. J. Hughes, D. B. Ingham, L. Ma, M. Pourkashanian, *J. Chem. Eng. Data* 61 (2016) 2536-2554.
5. F. Jirasek, R. A. S. Alves, J. Damay, R. A. Vandermeulen, R. Bamler, M. Bortz, S. Mandt, M. Kloft, H. Hasse, *J. Phys. Chem. Lett.* 11 (2020) 981-985.
6. M. Kohns, P. Zittlau, F. Jirasek, *Fluid Phase Equilib.* 597 (2025) 114454.

Associative electrolyte PC-SAFT: Thermodynamic properties of aqueous, non-aqueous, and mixed solvent electrolyte solutions

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Electrolyte solutions are important in many industrial processes. However, modeling thermodynamic properties of electrolytes is challenging. Most theories have been developed for aqueous solutions and are not applicable when a different solvent is used. In this work, we study the associative electrolyte PC-SAFT (aePC-SAFT) model for aqueous, non-aqueous, and mixed-solvent electrolyte solutions. The model is similar to the ePPC-SAFT model [1-4], but with the mean spherical approximation theory replaced with the Debye–Hückel (DH) term [5], and the multipolar and non-additive hard sphere terms removed. Thus, the aePC-SAFT has a simpler formulation compared to ePPC-SAFT. The new model is different from other versions of electrolyte PC-SAFT, in that the association term is used for ion-solvent and ion-ion short-range interactions, i.e., the association term is used for hydrogen bonding of solvent molecules, solvation effects of solvent molecules around ions, and ion pairing between cations and anions. Figure 1 shows a schematic representation of the contributions in the aePC-SAFT model. The rationale for this treatment will be presented. The model has been parameterized using critically evaluated experimental data. Highly accurate ion-specific parameters have been obtained. The performance of the model is discussed and compared to ePPC-SAFT for aqueous, non-aqueous, and mixed-solvent solutions of alkali halide electrolytes. Efforts have been made to improve the model's accuracy at high molality, especially for the extremely large activity coefficients of lithium salts.

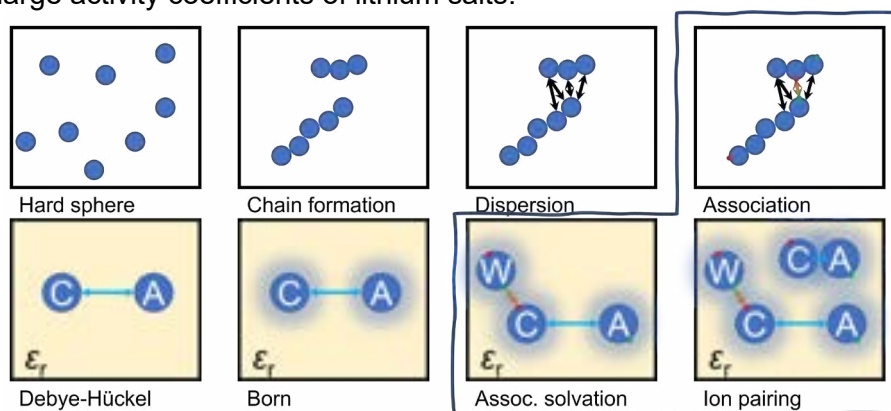


Figure 1. Schematic representation of the aePC-SAFT model contributions.

Acknowledgment

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Significant references

1. F. Yang, T. D. Ngo, J.S. Roa Pinto, G. M. Kontogeorgis, and J. C. de Hemptinne. Fluid Phase Equilib., vol. 570 (2023), pp. 113778.
2. F. Yang, G. M. Kontogeorgis, J. C. de Hemptinne. Fluid Phase Equilib., vol. 573 (2023), pp. 113853.
3. F. Yang, G. M. Kontogeorgis, J. C. de Hemptinne. Fluid Phase Equilib., vol. 583 (2024), pp. 114103.
4. F. Yang, A. Raeispour Shirazi, J. S. Roa Pinto, G. M. Kontogeorgis, and J. C. de Hemptinne. Ind. Eng. Chem. Res., vol. 63 (2024), pp. 12999-13015.
5. P. Debye and E. Hückel. Phys. Z., vol. 24 (1923), pp. 185-206.

Diffusivities in Electrolyte Mixtures by Dynamic Light Scattering and Molecular Dynamics Simulations

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Research at the Institute of Advanced Optical Technologies – Thermophysical Properties studies the influence of molecular characteristics of the solutes and solvents and of mixture composition on mass diffusivities in binary and ternary electrolyte systems. For this, dynamic light scattering (DLS) experiments and molecular dynamics (MD) simulations are utilized to access diffusion coefficients at temperatures from (293 to 423) K over a broad composition range extending to the vicinity of the solubility limit.^{1,2} Reliable data for Fick diffusion coefficients are determined by DLS and used to validate MD simulations, which in turn allow an insight into the fluid structure and the development of structure-property relationships and prediction models.³

The binary electrolyte mixtures, which are the focus of the present contribution, consist of different salts dissolved in either a non-electrolyte solvent or an ionic liquid sharing a common ion with the salt. Although these systems involve three distinct species, the diffusive mass transport is characterized through a single Fick diffusion coefficient D_{11} , due to the electroneutrality condition, which couples the movement of the charged ions. With the help of DLS, D_{11} can be obtained at saturation conditions by studying microscopic fluctuations in concentration. To obtain D_{11} by MD simulations, the Maxwell-Stefan diffusion coefficient $\bar{D}_{12}$ and the thermodynamic factor Γ_{11} are accessed and combined via $D_{11} = \bar{D}_{12} \cdot \Gamma_{11}$.

The results of the present study have shown that the dissociation of solute molecules into anions and cations greatly influences D_{11} .^{2,4} When the dissociation of electrolyte solutes is limited, which is indicated by a low dielectric constant of the solvent, the formation of large ion clusters occurs, subsequently decreasing D_{11} . The dissociation behavior is quantified by calculating solvation or coordination numbers by MD simulations and Raman spectroscopy. Concentration-dependent investigations indicate that D_{11} decreases strongly with increasing salt amount fraction x_{salt} . For the first time, this behavior of D_{11} could be related to the transition from solvent-separated ion-pairs (SSI) over contact ion-pairs (CIP) to ion aggregates (AGG) with increasing x_{salt} . By decoupling D_{11} into $\bar{D}_{12}$ and Γ_{11} by MD simulations, the different fluid structures in form of SSI, CIP, and AGG were found to be reflected mainly in Γ_{11} . The latter increases from a value of 1 at infinite dilution to values up to 13.5 with increasing x_{salt} as long as SSI prevail. With further increasing x_{salt} when CIP and AGG are formed, Γ_{11} decreases significantly which explains the decrease in D_{11} .

Acknowledgment

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Significant references

1. C.J. Kankanamge, T. Zhan, M. Piszko, T. Klein, and A.P. Fröba, *Electrochimica Acta*, vol. 462 (2023), article 142637.
2. C.J. Kankanamge, T. Zhan, Z. Zhang, T. Klein, and A.P. Fröba, *Journal of the Electrochemical Society*, vol. 171 (2024), article 110533.
3. C.J. Kankanamge, A.I. Diaz Zosel, T. Klein, and A.P. Fröba, *International Journal of Thermophysics*, vol. 46 (2025), article 142.
4. C.J. Kankanamge, T. Klein, and A.P. Fröba, *Journal of Chemical and Engineering Data*, vol. 70 (2025), pp. 1300-1311.

3.8

Thermophysical Properties Hydrocarbon Mixtures



Shape-selectivity effects of zeolites on hydroisomerization of long-chain alkanes

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Linear regression (LR) is used to predict thermochemical properties of alkanes at temperatures (0–1000) K to study chemical reaction equilibria inside zeolites. The thermochemical properties of C1 until C10 isomers reported by Scott are used as training data sets in the LR model which is used to predict these properties for alkanes longer than C10 isomers. Second-order groups are used as independent variables which account for the interactions between the neighboring groups of atoms. This model accurately predicts Gibbs free energies, enthalpies, Gibbs free energies of formation, and enthalpies of formation for alkanes which exceeds the chemical accuracy of 1 kcal/mol and outperforms the group contribution methods developed by Benson et al., Joback and Reid, and Constantinou and Gani. Predictions from our model are used to compute the reaction equilibrium distribution of hydroisomerization of C10 and C14 isomers in MTW-type zeolite. Calculation of reaction equilibrium distribution inside zeolites also requires Henry coefficients of the isomers which can be computed using classical force field-based molecular simulations using the RASPA2 software for which we created an automated workflow. The reaction equilibrium distribution for C10 isomers obtained using the LR model and the training data set for this model are in very good agreement. The tools developed in this study will enable the computational study of hydroisomerization of long-chain alkanes (>C10).

Significant references

1. **Prediction of Thermochemical Properties of Long-Chain Alkanes using Linear Regression: Applications to Hydroisomerization**
S. Sharma, J.J. Sleijfer, J. op de Beek, S. van der Zeeuw, D. Zorzos, S. Lasala, M.S. Rigutto, E. Zuidema, U. Agarwal, R. Baur, S. Calero, D. Dubbeldam, T.J.H. Vlugt
J. Phys. Chem. B, 2024, 128, 9619-9629
2. **Machine Learning-Based Predictions of Henry Coefficients for Long Chain Alkanes in One Dimensional Zeolites: Application to Hydroisomerization**
S. Sharma, P. Yang, Y. Liu, K. Rossi, P. Bai, M.S. Rigutto, E. Zuidema, U. Agarwal, R. Baur, S. Calero, D. Dubbeldam, T.J.H. Vlugt
J. Phys. Chem. C, 2025, 128, 18234-18249.

Thermophysical properties of sustainable liquid fuels

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The transport sector remains heavily dependent on fossil fuels [1], making the transition to sustainable liquid alternatives critical for reducing carbon emissions, particularly in hard to electrify applications such as aviation, motorsport, and heavy-duty transport [2]. A key barrier to adoption is the limited availability of high fidelity thermophysical property data, which are essential for engine design, fuel optimisation, and emissions modelling [3]. This study combines systematic experimental measurements with advanced modelling to address this gap. A well characterized five-component surrogate system was developed to represent complex fuels within a multicomponent Helmholtz energy framework. Real fuels can be mapped onto this reduced representation by measuring select properties and incorporating compositional data from gas chromatography. Experimental campaigns covered six surrogate mixtures, designed to mimic E10 and E20 gasoline blends, alongside seven commercial gasoline samples. Density and viscosity were measured between 0–40 °C and up to 70 MPa using a bespoke vibrating tube–vibrating wire apparatus, while specific heat capacity, thermal conductivity, and surface tension were determined at atmospheric pressure using flow calorimetry, transient hot-wire, and pendant drop methods, respectively. Vapor pressure was measured over the range 20–100 °C using a recirculating still, and enthalpy of vaporization was obtained from differential scanning calorimetry and vapor pressure correlations. The resulting dataset, validated with quantified uncertainties, demonstrates that surrogate mixtures capture the key thermophysical behaviour of real fuels, with measured densities (620–860 kg·m⁻³) and viscosities (4–6 mPa·s) at 20 °C, 0.1 MPa consistent with commercial gasoline. To extend predictive capability, a two-stage modelling framework was developed. First, surrogate mixtures were optimized to reproduce measured properties. Second, machine learning models, pre-trained on REFPROP-generated data, were fine-tuned using experimental results to correct systematic biases. Gradient boosting models achieved near-zero deviations for density, heat capacity, vapor pressure, and enthalpy of vaporization, outperforming random forest regressors. Parallel work focuses on refining REFPROP through optimization of binary interaction parameters using speed of sound and VLE data. This integrated framework combined validated experiments, surrogate formulation, and machine learning corrections providing a robust platform for rapid property prediction and screening of sustainable fuels. It advances both fundamental understanding and practical fuel design, accelerating the transition to low-carbon transport.

Significant references

1. H. Ritchie, P. Rosado and M. Roser, Fossil fuels, Our World in Data.
2. P. Cazzola, F. Gerard, M. Gerner, M. Gibbs and K. Young, Research for TRAN Committee: Assessment of the potential of sustainable fuels in transport.
3. M. J. Assael, Energy and Environment 2001, 162-178.

Investigation on the predictability of LKP and LKP-SJT binary interaction parameters for asymmetric *n*-alkane mixtures

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The presented work is motivated by the loss mechanisms of two-phase surge and gap flows in oil-injected rotary-type positive displacement compressors, used for the compression of refrigerants in various applications. Based on the simplified assumption that long-chain *n*-alkanes can be assumed as oil equivalents, thermodynamic properties of strongly asymmetric binary *n*-alkane mixtures were modelled with both the Lee-Kesler-Plöcker (LKP) [1,2] equation of state (EOS) and its recent modification LKP-SJT [3,4].

Previous optimizations of the LKP binary interaction coefficient k_{ij} against experimental data of density and vapor-liquid equilibria were extended to more binary *n*-alkane mixtures. Figure 1 illustrates the noticeable dependency of k_{ij} against the difference in critical temperature of the interaction partners. Since critical parameters and the acentric factor of simple molecules as *n*-alkanes can be estimated by empirical approaches or neural networks, this behavior of k_{ij} allows a more predictive utilization of both the LKP and LKP-SJT for these mixtures and probably also for other chain molecules. This is particularly important for poorly measured asymmetric mixtures. The results will contribute to a wider availability of resilient and predictive EOS for simulations of refrigeration applications.

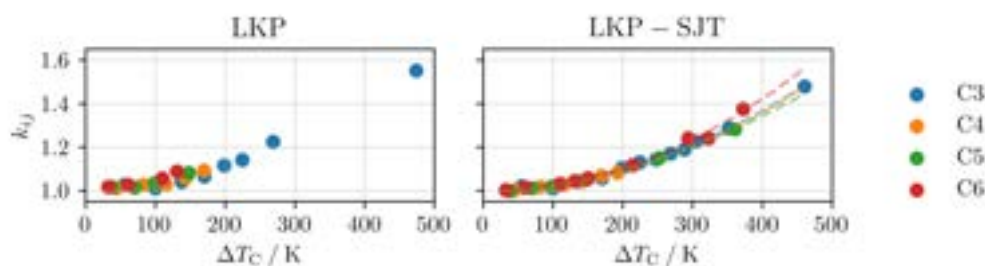


Figure 1. Dependency of the bubble point optimized LKP and LKP-SJT binary interaction parameter of mixtures of propane (C3), *n*-butane (C4), *n*-pentane (C5) and *n*-hexane (C6) with *n*-alkanes against their difference in critical temperature.

Acknowledgment

This work was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) within the Research Unit FOR 5595 Archimedes (Oil-refrigerant multiphase flows in gaps with moving boundaries - Novel microscopic and macroscopic approaches for experiment, modeling, and simulation) - Project number 510921053.

Significant references

1. B.I. Lee and M.G. Kesler. "A generalized thermodynamic correlation based on three-parameter corresponding states." *AIChE J.*, vol. 21, pp. 510-527, 1975.
2. U. Plöcker, H. Knapp, J. Prausnitz. "Calculation of high-pressure vapor-liquid equilibria from a corresponding-states correlation with emphasis on asymmetric mixtures." *Ind. Eng. Chem. Proc. Des. Dev.*, vol. 17, pp. 324-332, 1978.
3. F. Sabozin, A. Jäger, M. Thol, Enhancement of the Lee-Kesler-Plöcker equation of state for calculating thermodynamic properties of long-chain alkanes. *Int. J. Thermophys.*, vol. 45, p. 69, 2024.
4. F. Sabozin, M.F. Schneegans, A. Jäger, M. Thol. "Improving the LKP-SJT Equation of State: Application to Alkanes, Carbon Dioxide, and Their Mixtures." *Int. J. Thermophys.*, vol. 46, p. 54, 2025.

In pursuit of the high-pressure liquid-vapor and liquid-solid equilibria of asymmetric mixture

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Several mixtures that mimic the phase behavior of reservoir fluids have been studied in the literature. Most of these studies involve mixing a linear alkane with a gas (CO₂ or a light hydrocarbon such as methane)[1][2]. The complexity of the phase transition type increases not only with the hydrocarbon chain length but also with the chemical nature of the heavy components. Despite the large amount of data available in the literature, there is still a lack of information and understanding regarding mixtures that contain heavy hydrocarbons outside the alkane family but that are present in reservoir fluids in significant amounts, such as aromatic and polyaromatic compounds like *o*-terphenyl (C₁₈H₁₄, CAS 84-15-1). Medeiros *et al.* (2025)[3] investigated a highly asymmetric synthetic mixture composed of *o*-terphenyl + 2,2,4,4,6,8,8-heptamethylnonane + dodecylcyclohexane with light components, reporting an interesting retrograde behavior in the solid-liquid locus caused by gas addition. To better understand this behavior, the high-pressure phase transitions of two pseudo-binary liquid + gas systems composed of (pentadecane + *o*-terphenyl) + methane were investigated in this work. The liquid systems differ in global composition: BM1 ($x_{C15} = 0.4$ and $x_{\text{terphenyl}} = 0.6$) and BM2 ($x_{C15} = 0.6$ and $x_{\text{terphenyl}} = 0.4$). Phase transition measurements were performed for various global methane mole fractions using a classical high-pressure variable-volume equilibrium cell with full visual access to the mixture by following isothermal and isobaric procedures to delimitate phase boundaries. Experimental observations revealed both vapor-liquid and solid-liquid phase transitions within the investigated temperature range. The BM1 + CH₄ mixtures exhibited lower bubble-point pressures than the BM2 + CH₄ mixtures, indicating a lower methane solubility in the *o*-terphenyl-rich mixture. Regarding the high-pressure solid-liquid locus, BM1 exhibited a solid-liquid transition at lower temperatures compared to BM2 as given in Figure 1, which can be attributed to the solvent contribution of pentadecane in the mixture. Moreover, a solid-liquid-vapor point was identified by the intersection of the solid-liquid and vapor-liquid loci, revealing a retrograde behavior along the solid-liquid-vapor line. This result demonstrates the influence of methane addition on the solid-liquid equilibrium transition temperature.

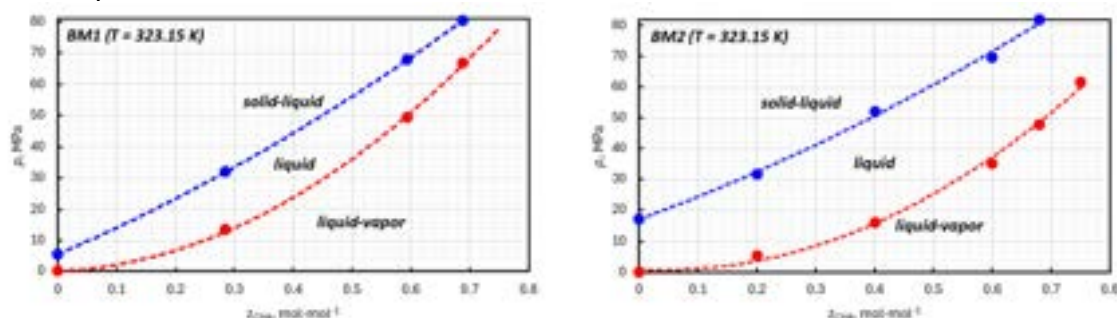


Figure 1. Isothermal pressure-composition (p - z_{CH_4}) BM1 and BM2 with methane at $T = 323.15$ K: solid-liquid equilibrium (blue dot, ●) and liquid-vapor equilibrium (red dot, ●).

Significant references

1. R. Dohrn, S. Peper, C. Secuianu, and J. M. S. Fonseca. *Fluid Phase Equilibria*, vol 579 (2024), pp. 113978.
2. H. Dantas Medeiros, M. F. L. da Costa, F. X. Feitosa, and H. B. de Sant'Ana. *Fluid Phase Equilibria*, vol 591 (2025), pp.114310.
3. H. Dantas Medeiros, J. P. Bazile, F. X. Feitosa, H. B. de Sant'Ana, and J. L. Daridon. *The Journal of Supercritical Fluids*, vol 219 (2025), pp. 106519.

3.9

Thermophysical Properties

H_2 and H_2 -Containing Mixtures II



From Molecular Insights to Subsurface Energy: How Thermophysical Properties of Fluids Advance Hydrogen and Gas Storage

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Underground storage of energy carriers and CO₂ requires reliable quantification of thermophysical properties, including both equilibrium and transport properties, of fluids under a wide range of pressures, temperatures, and confinement conditions. In this talk, we will present a multiscale panel of recent contributions from our team illustrating how molecular simulations, laboratory experiments, and thermodynamic and continuum-scale modeling can be combined to improve the understanding of fluid thermophysical behavior and reduce key uncertainties relevant to subsurface hydrogen and gas storage.

In the context of Underground Hydrogen Storage (UHS), we will report experimental measurements of hydrogen solubility and diffusivity in brines performed under controlled conditions representative of storage formations. These measurements are complemented by extensive Monte Carlo and Molecular Dynamics simulations, which provide microscopic insight into dissolution and transport mechanisms, as well as into the influence of pressure, temperature, and salinity [1,2]. Molecular simulations are further used to assess the impact of confinement and mineralogy, with a particular focus on hydrogen diffusion in water-saturated illite, representative of sealing and low-permeability formations [3]. To facilitate the use of these results at larger scales, physically based models are developed that capture the dominant controlling parameters and are subsequently integrated into reservoir-scale simulations of UHS, enabling improved predictions of hydrogen migration, losses, and overall storage performance [4].

Beyond hydrogen, we will address aspects relevant to natural gas storage and containment. Using molecular simulations, we have investigated aqueous diffusion-driven isotope fractionation of benzene, a trace compound that may be present in natural gas, and showing its lack of bias to biodegradation assessments in gas storage aquifers [5]. Finally, we will illustrate how a combined experimental, molecular, and thermodynamic approach captures non-ideal behavior in high-pressure supercritical mixtures, exemplified by CO₂ + n-alkane systems, where molecular clustering effects help rationalize observed volumetric and acoustic responses relevant to subsurface processes [6].

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Significant references

1. Kerkache, H., H. Hoang, P. Cézac, G. Galliéro, and S. Chabab, *J. Mol. Liq.*, 400 (2024), 124497.
2. Kerkache, H., H. Hoang, T. K. N. Nguyen, A. Geoffroy-Neveux, C. Nieto-Draghi, P. Cézac, S. Chabab, and G. Galliéro, *Int. J. Hydrogen Energy*, 128 (2025), pp. 279–290.
3. Kerkache, H., H. Hoang, N. Van Phuoc, S. Chabab, and G. Galliero, *Int. J. Hydrogen Energy*, 168 (2025), pp. 151033.
4. Ahmed, E., B. Amaziane, S. Chabab, S. D. Santacreu, G. Galliéro, O. M. yner, and X. Raynaud, *Int. J. Hydrogen Energy*, 168 (2025), pp. 150947.
5. Enrico, M., I. Le Hécho, H. Carrier, G. Galliéro, A. Petit, and R. Vermorel, *Geochim. Cosmochim. Acta*, 391 (2025), pp. 96–105.
6. Hamani, A. W. S., H. Hoang, T. Q. Q. Viet, J.-L. Daridon, and G. Galliéro, *J. Supercrit. Fluids*, 164 (2020), pp. 104890.

Transport Properties of Binary Gas Mixtures of H₂ with N₂, O₂, CO₂, H₂S, and H₂O from First Principles

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Hydrogen and its mixtures with other gases are expected to play a key role in the transition to renewable energy sources, which requires reliable thermophysical property data. In this work, we provide highly accurate values for the binary diffusion coefficients and shear viscosities of binary gas mixtures of hydrogen with nitrogen, oxygen, carbon dioxide, hydrogen sulfide, and water vapor at temperatures of up to 2000 K. This is accomplished by a first-principles approach, in which we use third-order kinetic theory and combine different schemes for treating the binary collision dynamics, such as full classical trajectories [1–3], the quantum-mechanical infinite-order sudden approximation [4], and the classical Mason–Monchick approximation [5]. All intermolecular interactions are described by highly accurate *ab initio* potentials, see, e.g., refs. [6–8]. The resulting transport property values are in excellent agreement, typically within a few tenths of a percent, with the most reliable experimental data and can be regarded as reference values.

Acknowledgment

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Significant references

1. E. Bich, J.B. Mehl, R. Hellmann, and V. Vesovic, in *Experimental Thermodynamics Volume IX: Advances in Transport Properties of Fluids*, edited by M.J. Assael, A.R.H. Goodwin, V. Vesovic, and W.A. Wakeham (The Royal Society of Chemistry, Cambridge, 2014), chap. 7, pp. 226-252.
2. E.L. Heck and A.S. Dickinson, *Comput. Phys. Commun.*, vol. 95 (1996), pp. 190-220.
3. A.S. Dickinson, R. Hellmann, E. Bich, and E. Vogel, *Phys. Chem. Chem. Phys.*, vol. 9 (2007), pp. 2836-2843.
4. G.A. Parker and R.T. Pack, *J. Chem. Phys.*, vol. 68 (1978), pp. 1585-1601.
5. L. Monchick and E.A. Mason, *J. Chem. Phys.*, vol. 35 (1961), pp. 1676-1697.
6. R. Hellmann and E. Bich, *Int. J. Thermophys.*, vol. 46 (2025), article 67.
7. R. Hellmann, *J. Chem. Phys.*, vol. 159 (2023), article 104303.
8. K. Patkowski, W. Cencek, P. Jankowski, K. Szalewicz, J.B. Mehl, G. Garberoglio, and A.H. Harvey, *J. Chem. Phys.*, vol. 129 (2008), article 094304.

Physics-informed Neural Network for Thermodynamically Consistent Modelling of Carbon dioxide-Hydrogen Mixtures in Underground Storage Applications

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Underground Hydrogen Storage (UHSP) in porous media stands as a pivotal solution for balancing the intermittency of renewable energy; its economic and environmental viability relies heavily on the selection of an effective cushion gas. While cushion gas is essential for maintaining reservoir pressure and ensuring deliverability, identifying carbon dioxide (CO₂) as a primary candidate offers a transformative dual advantage: it operationalises large-scale energy storage while simultaneously sequestering carbon, thereby directly addressing decarbonisation targets through the synergy of UHSP and Carbon Capture and Storage (CCS).

However, the deployment of CO₂ as a cushion gas introduces complex thermodynamic challenges, particularly within the mixing zone where the working gas (H₂) and cushion gas interact.[1] The significant disparity in thermophysical properties (including density and viscosity) between these species governs critical reservoir phenomena such as gravity segregation and viscous fingering. [Fig. 1] Consequently, mixture density modelling across reservoir conditions and various compositional ranges is paramount for reliable reservoir simulation. Cubic equations of state (CEoS), as a standard, fast and widely used tool in reservoir simulators, often requires extensive manual tuning to minimise deviations in this highly non-ideal region.

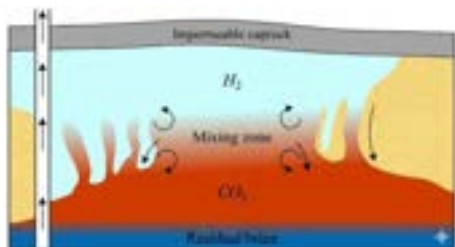


Figure 1. Mixing zone CO₂ as cushion gas and stored H₂ at the reservoir (fingering phenomena)

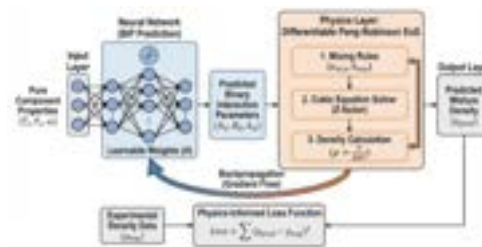


Figure 2. Architecture of the Physics-Informed Neural Network for binary mixture density prediction

To address this, we propose a novel Physics-informed Neural Network (PINN) framework that enforces thermodynamic consistency through a structured, multi-layered architecture. Our approach integrates hidden layers designed to optimise temperature-dependent binary interaction parameters based on pure component critical properties, which is coupled end-to-end with a differentiable Peng-Robinson equation of state (PR-EoS) layer. Unlike traditional black-box models, this architecture optimises parameters by minimising the error in the predicted physical density. Validated against a comprehensive high-quality dataset gathered from recent literature, our model demonstrates superior consistency and generalisation capabilities across reservoir conditions. [Fig. 2]

In conclusion, by integrating artificial intelligence with classical thermodynamics, we can significantly accelerate the parameter fitting procedure while ensuring strict adherence to physical laws. This work provides reservoir engineers with a robust, automated, and high-fidelity tool for simulating density-driven flow behaviours in CO₂-cushion systems, effectively bridging the gap between data-driven efficiency and physics-based reliability in the energy transition industry.

Significant references

1. Heinemann, N. *et al.* Enabling large-scale hydrogen storage in porous media – the scientific challenges. *Energy Environ Sci* 14, 853–864 (2021).

Measuring and modelling of dew points of water and hydrogen enriched natural gas

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For gas transport through pipelines and gas applications at industrial sites, it is important to know the relation between water content and dew or frost points of natural gases. So far, the calculation method that is commonly used in the European gas industry is based on a modified Peng-Robinson equation of state. The data of Oellrich et al. [1], which were used for the adjustment of the parameters of this equation, were very limited with regard to temperature, pressure, and composition ranges. Thus, these ranges were extended by new experiments. Furthermore, humid hydrogen and hydrogen-enriched natural gas are only sparsely investigated. Since hydrogen is playing an increasingly important role in the planned decarbonization of the gas sector, new experiments were carried out in order to fill this data gap.

In this paper, the potential but also the limitations of the employed measurement methods – see Fig. 1 – are presented. Recent experimental measurements are shown and compared to the experimental data of Oellrich et al [1]. In these comparisons, a discussion regarding the stable equilibrium is essential. An initial version of a new calculation method for applications in industry will also be presented. For that different models are compared and evaluated in the relation of a mixed hydrate model [2] and a new mixing model for hydrogen and water.

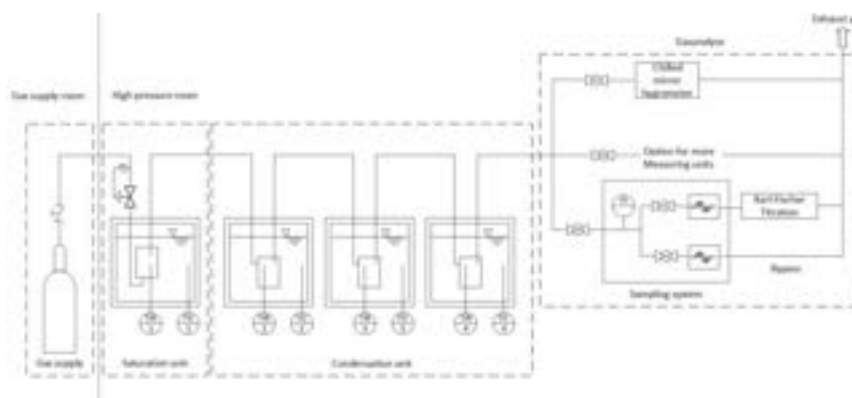


Figure 1. Scheme of the measuring apparatus

Acknowledgment

This work is funded by the German Technical and Scientific Association for Gas and Water (DVGW, registered association) – funding code G 202132 – HyWaBe.

Significant references

1. L. R. Oellrich, GERG- Water Correlation (GERG Technical Monograph TM 14): Relationship Between Water Content and Water Dew Point Keeping in Consideration the Gas Composition in the Field of Natural Gas (VDI Verlag GmbH, Düsseldorf, 2001).
2. S. Hielscher, V. Vins, A. Jäger, J. Hruby, C. Breitkopf, R. Span, A new approach to model mixed hydrates (Fluid Phase Equilibria, 2018).

3.10

Thermophysical Properties

Fluids for CCUS Applications I



Thermophysical Properties of CCUS Fluids in the Vicinity of the Critical Point and Widom Line

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Near the Widom line, Carbon Capture and Storage (CCS) fluids, primarily carbon dioxide (CO_2) and its mixtures, display pronounced anomalies in their thermophysical behaviour. This region marks a transitional zone where the fluid undergoes rapid shifts between liquid-like and gas-like states, driven by subtle changes in temperature and pressure. As a result, key properties such as speed of sound, heat capacity, isothermal compressibility, and density exhibit sharp peaks or large variations. These fluctuations are closely linked to the underlying molecular structure and critical phenomena, making the Widom line an area of significant interest for optimising CCS processes. Understanding these property changes is essential for accurate modelling, efficient design of transport and storage systems, and ensuring the stability and safety of operations.

In this communication, we present experimental methodologies, specialised equipment, and thermodynamic modelling approaches employed to investigate CO_2 -rich systems in the vicinity of the Widom line. Measurements of viscosity, density, and speed of sound were performed and benchmarked against predictions from a viscosity correlation and the Multi-Fluid Helmholtz Energy Approximation equation of state.

Our findings reveal that existing models exhibit significant deviations in this near-critical region compared to their performance at conditions farther from the Widom line, underscoring the need for improved formulations to accurately capture anomalous thermophysical behaviour.

Performance Analysis of Modified Apparatus for Liquid CO₂ Boil-off Study with Liquid Nitrogen

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Cryogenic storage and transport of liquefied gases are critical to emerging energy systems, including carbon capture and storage applications. During storage, unavoidable heat ingress leads to vapour generation, vessel pressurisation, and product loss [1], with the resulting boil-off behaviour strongly influenced by vessel geometry and initial liquid loading (ILL). Future cryogenic transport systems are expected to employ cylindrical vessels with high aspect ratios, motivating the need for experimental data obtained under representative geometric conditions. In this work, liquid nitrogen is used to commission and validate a modified high-aspect-ratio boil-off gas cell prior to liquid CO₂ experiments. The experimental apparatus consists of a stainless-steel cylindrical vessel housed within a vacuum-jacketed cryostat, equipped with 20 internal resistance temperature detectors distributed along the vessel height to capture vertical thermal gradients. Controlled heat ingress is imposed using external polyimide thermofoil heaters, while vessel pressure and boil-off flow rate are measured using calibrated pressure transducers and mass flow meters. Experiments were conducted at initial liquid loadings of 26%, 37%, and 75%, allowing systematic assessment of ullage volume effects under identical boundary conditions.

Results show that the steady boil-off rate increases with increasing initial liquid loading due to the larger wetted surface area available for heat transfer. In contrast, the vessel pressurisation rate during the self-pressurisation phase is highest at low liquid loadings, where the reduced thermal mass of the liquid and larger vapour volume promotes rapid vapour heating. Thermal stratification develops in all cases, with earlier collapse observed at lower liquid loadings, leading to more abrupt transitions to venting behaviour. These findings demonstrate the strong coupling between initial liquid loading, thermal stratification, pressurisation, and boil-off dynamics in high-aspect-ratio cryogenic vessels. The results validate the experimental platform for subsequent liquid CO₂ studies and provide relevant thermophysical insight for the design and operation of cryogenic storage and transport systems.

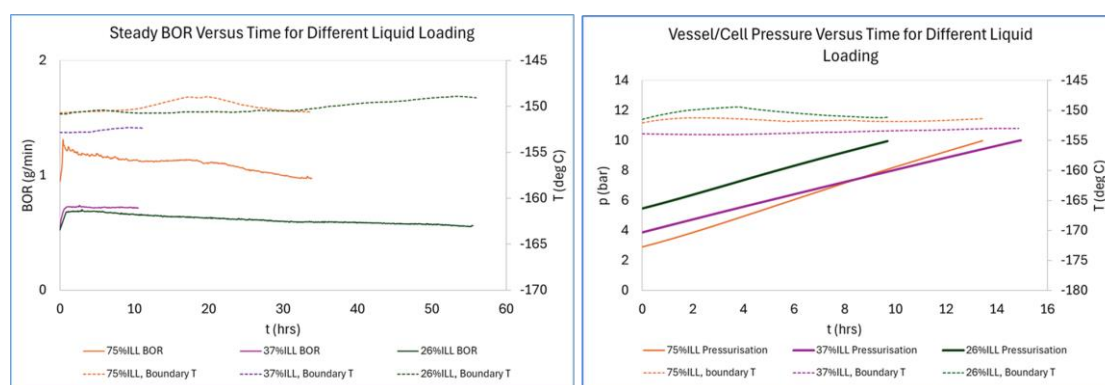


Figure 1. Evolution of boil-off rate and vessel pressure for liquid nitrogen at different initial liquid loadings in a high-aspect-ratio cryogenic vessel.

Acknowledgment

This work was supported by The University of Western Australia and FEnEx CRC.

Significant reference

1. F. Perez, S. Z.S. Al Ghafri, L. Gallagher, A. Siahvashi, Y. Ryu, S. Kim, S. Gyu Kim, M. L. Johns, E. F. May, *Energy*, vol. 222 (2021), pp. 119853.

Impurity Effects on VLE and Prediction Assessment in a CO₂-Rich System for CCUS

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Carbon dioxide (CO₂) is a major greenhouse gas, and its mitigation requires reliable thermodynamic data for CCUS applications. A CO₂-rich mixture (CO₂ 97.89%, N₂ 2.00%, Ar 0.10%, CH₄ 0.01% mol/mol) was investigated to expand the limited experimental data available for such systems¹. The objective is to evaluate the performance of the commercial software to predict the behavior of CO₂-rich mixtures. Experimental bubble and dew points were measured using a synthetic method² between 278–302 K in a PVT cell with a sliding piston. Phase transitions were detected visually—through the appearance of an interface—and graphically, by a change in the slope of the P–V curve during new-phase nucleation. Predictions from Multiflash-CPA (Infochem) and REFPROP were compared with the measurements (Figure 1). The analysis showed that, at lower temperatures, Multiflash provides good accuracy for bubble-point calculations; however, above approximately 288 K, REFPROP shows superior performance. For dew-point predictions, both models exhibited small deviations, reaching up to 4%. Overall, both Multiflash-CPA and REFPROP presented satisfactory agreement with the experimental results, supporting their applicability for the thermodynamic modeling of CO₂-rich mixtures in CCUS processes.

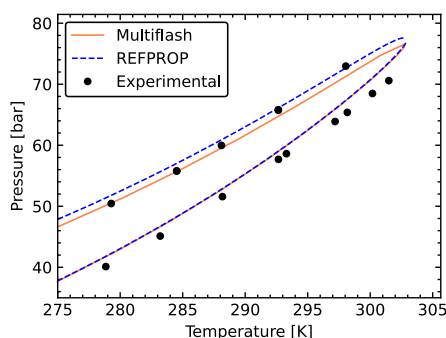


Figure 1. Experimental data vs. predicted VLE data.

Acknowledgment

The authors gratefully acknowledge the financial support provided by Petrobras and by the Human Resources Training Program (PRH).

Significant references

1. Vitali, M.; Leporini, M.; Masi, O.; Speranza, A.; Corvaro, F.; Marchetti, B. Net Zero Flow Assurance - Validation of Various Equations of State for the Prediction of VLE and Density of CO₂-Rich Mixtures for CCUS Applications. *International Journal of Greenhouse Gas Control* 2023, 125, 103877. <https://doi.org/10.1016/J.IJGGC.2023.103877>.
2. Dohrn, R.; Fonseca, J. M. S.; Peper, S. Experimental Methods for Phase Equilibria at High Pressures. *Annu Rev Chem Biomol Eng* 2012, 3 (Volume 3, 2012), 343–367. <https://doi.org/10.1146/ANNUREV-CHEMBIOENG-062011-081008/CITE/REFWORKS>.

Unveiling the Widom Region of Supercritical CO₂ through Non-Equilibrium Fluctuations

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Commonly, the supercritical phase is depicted as neither gas nor liquid, with properties that smoothly transition between the two phases. Supercritical fluids can combine high density, like liquids and low viscosity, like gases which can prove useful in industrial applications, e.g. CO₂ storage. However, real fluids are rarely at equilibrium due to the presence of property inhomogeneities. Here [1], we investigated supercritical CO₂ by analysing non-equilibrium density fluctuations, offering new insights into its behavior within the the Widom area. When the supercritical fluid is stressed by a thermal gradient, non-equilibrium fluctuations occur at all scales [2] and are amplified by the presence of the macroscopic gradient, especially within the Widom region, where density variations are large. The fluctuation dynamics becomes propagative in the intermediate scattering function (ISF) witnessing density stratification within the fluid. Closer to the critical point, properties vary strongly, with non-linear density profiles (cf. Fig. 1) and additional propagative modes indicate large thermodynamic fluctuations. The supercritical state is thus investigated by probing many temperatures in one single experiment providing evidence of the fluid stratification in a quasi-liquid and a quasi-gas phases, separated by a transition zone where fluid properties vary strongly.

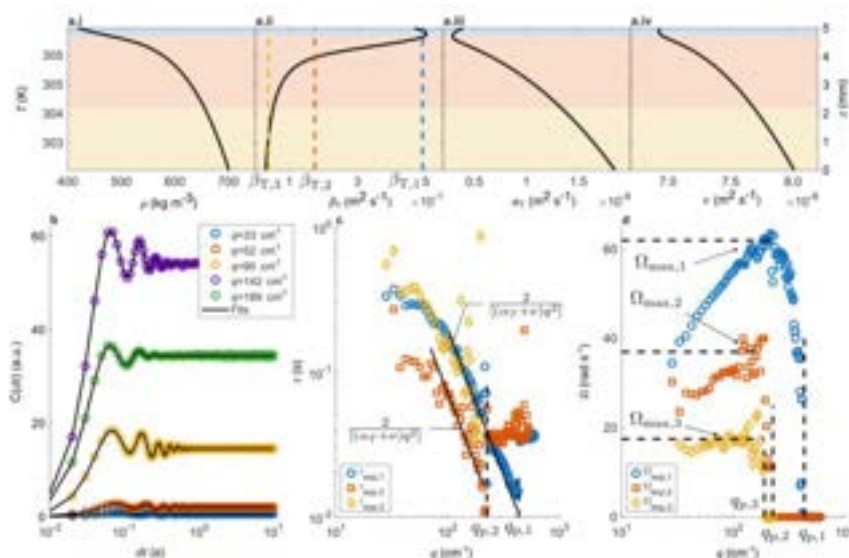


Figure 1. (Top panel) Thermodynamic properties of the fluid at $p = 7.7$ MPa, $T_{\text{mean}} = 32.86$ °C, $\Delta T = 4$ K. (Bottom panel) left – structure functions of the nonequilibrium fluctuations for five different wave numbers; middle – time decays of the density fluctuations as a function of the wave number; right - Brunt-Vaisälä frequency Ω of the density fluctuations.

Acknowledgment

Funded by the Investissements d'Avenir French Program (No. ANR161DEX0002), with partial support from CNES through GdR 2799 MF.

Significant reference

1. <https://arxiv.org/abs/2511.05588>
2. J. M. Ortiz de Zárate and J. V. Sengers, Hydrodynamic Fluctuations in Fluids and Fluid Mixtures. Elsevier, Amsterdam (2006)

3.11

Thermophysical Properties

H₂ and H₂–Containing Mixtures III



Speed-of-Sound and Raman Spectroscopy of Hydrogen Spin-Isomer Mixtures

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There is great and growing interest in hydrogen within the transition to net-zero greenhouse gas emissions. The changing role sees a shift away from hydrogen primarily being consumed soon after it was produced, typically travelling only a short distance and remaining above ambient temperature, towards long-distance transport and large-scale seasonal storage. Here, high densities are preferable, thus hydrogen may be compressed at ambient temperature to pressures of up to 100 MPa or condensed at temperatures around 20 K. The latter case is accompanied by a significant change in the composition of the hydrogen spin-isomer mixture and, by extension, its properties. The conversion between ortho- and para-hydrogen is a slow process in the absence of a catalyst, which renders non-equilibrium states accessible and industrially relevant.

Effective design of processes involving hydrogen, and their supporting infrastructure, requires an accurate understanding of the thermophysical properties across a broad range of conditions. Existing models are limited in their accuracy as there are currently insufficient data present in the open literature [1], especially when considering the influence of spin-isomer composition. Speed-of-sound, as a property that may be measured with low uncertainty, provides a route not only to more accurate models but also to determination of the spin-isomer composition. This capability has been demonstrated in the literature for gaseous hydrogen at near ambient temperatures [2] and is of interest for cryogenic applications, such as in the CryoMet project on metrology for liquefied energy gases.

Measurements of the speed-of-sound in hydrogen have been made using an acoustic resonator system derived from one previously used for measurements of normal hydrogen [3]. Hydrogen was passed over IONEX catalyst at 77 K to produce an approximately equimolar ortho/para-hydrogen mixture and allowed to undergo natural conversion to the equilibrium composition at various constant temperatures and pressures. This change was observed as a gradual shift in the speed-of-sound. Results were compared with Raman spectroscopy measurements with a high-pressure sapphire-window cell and a single-point calibration [4].

This Raman cell has since been transferred to a newly constructed cryogenic measurement apparatus for speed-of-sound measurements in liquid and supercritical hydrogen using steady-state (cylindrical resonator) and transient (dual-path pulse echo) techniques. The data produced will serve to support model development and allow for the evaluation of speed-of-sound techniques as an alternative to Raman spectroscopy for spin-isomer measurements at temperatures down to 15 K and pressures up to 20 MPa.

This work was supported in part by grants from the UK Engineering and Physical Sciences Research Council, Shell Research Ltd, and the European Partnership on Metrology.

Significant references

1. J. W. Leachman, R. T. Jacobsen, S. G. Penoncello, and E. W. Lemmon, *J. Phys. Chem. Ref. Data*, vol. 38 (2009), pp. 721–748.
2. S. Eisenhut, C. Haberstroh, *Int. J. Hydrog. Energy*, vol. 92 (2024), pp. 312–323.
3. T. Nguyen, C. Wedler, S. Pohl, D. Penn, R. Span, J.P.M. Trusler, M. Thol, *J. Chem. Thermodynamics*, vol. 198 (2024) 107341, pp. 1–19.
4. F. Luther, G.M. Sellner, M. Richter, P.L. Stanwix, *Int. J. Hydrog. Energy*, vol. 102 (2025), pp. 778–789.

Design of a Low-Temperature Cryostat System and Acoustic Resonator for Precise Speed-of-Sound Measurements in H₂ and Other Light Gases

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Hydrogen plays a key role in energy technologies; however, its thermodynamic properties at cryogenic conditions remain poorly characterised. Existing experimental data, mostly produced prior to the 1980s, are limited in both temperature and pressure range and do not adequately describe the compressed liquid and supercritical regions [1]. Reliable data are essential not only for improving thermodynamic models but also for ensuring safety and efficiency in hydrogen production, storage, and transport systems, where flow dynamics are critically dependent on sound speed. The present work aims to provide high-accuracy speed-of-sound data to support the refinement of hydrogen equations of state.

A cryogenic measurement facility was designed and constructed to perform speed-of-sound measurements over the temperature range of (15 to 100) K at pressures up to 20 MPa. The system integrates a low-temperature cryostat with advanced temperature control (± 1 mK stability in the measurement volume) and a high-precision aluminium acoustic resonator. The resonator employs a cylindrical geometry, selected for its design flexibility, reduced hydrogen inventory, and safety advantages, while ensuring accurate determination of resonance frequencies at the high sound speeds characteristic of hydrogen [2]. The resonator is mounted nodally within a CuCrZr pressure vessel to reduce vibrational coupling and reduce measurement uncertainty. A dual path pulse-echo device is also being commissioned for measurements at high densities and to provide comparisons. The facility incorporates a catalytic converter within the cryostat for controlled adjustment of the ortho-para spin-isomer ratio. Additionally, a high-pressure Raman spectroscopy cell with a sapphire window enables *in situ*, non-destructive determination of the ortho-para hydrogen ratio under cryogenic conditions.

The cryostat employs a two-stage cryocooler with two OFHC copper radiation shields to reduce radiative heat exchange. Each shield is gold-plated to lower emissivity, while baffled pumping ports eliminate direct line-of-sight radiation while maintaining high vacuum conductance. Analytical heat transfer models were used to estimate temperature distributions, confirming that the thermal shielding design provides excellent temperature uniformity across the pressure vessel [3]. The temperature of the resonator is determined by means of a rhodium-iron resistance thermometer attached to the pressure vessel, while Pt500 platinum resistance thermometers are used in control and monitoring.

The development of this apparatus represents a significant advance in cryogenic acoustic metrology, enabling speed-of-sound measurements with a target relative uncertainty of 0.02%. The resulting data will serve as benchmark-quality references for refining Helmholtz energy-based EoS formulations for hydrogen. The methodologies and design principles are applicable to other light gases of industrial and scientific interest.

This work was supported in part by grants from the UK Engineering and Physical Sciences Research Council, Shell Research Ltd, and the European Partnership on Metrology.

Significant references

1. J. W. Leachman, R. T. Jacobsen, S. G. Penoncello, and E. W. Lemmon, J. Phys. Chem. Ref. Data, vol. 38 (2009), pp. 721–748.
2. L. Ruffine and J. P. M. Trusler, Int. J. Thermophysics, vol. 30 (2009), pp. 1106–1117.
3. J. Ekin, Experimental Techniques for Low-Temperature Measurements, Oxford Univ. Press (2006).

A microwave-resonant cavity for liquid hydrogen boil-off studies

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Hydrogen is a promising clean-energy storage vector that produces no direct CO₂ emissions. However, its low volumetric energy density remains a major barrier to its widespread adoption, particularly as it creates economic challenges for both long-term storage and long-distance transport. Increasing the effective density of hydrogen typically involves compression, liquefaction, or conversion into a chemical “carrier”, each with advantages depending on the application. Liquid hydrogen (LH₂) is particularly attractive for systems requiring a high-purity, easily regasified hydrogen stream [1].

Despite its promise, there are many safety considerations associated with the use of LH₂. The wide flammability range of hydrogen is especially problematic during unplanned releases, including scenarios involving loss of vacuum accidents (LOVA). In a LOVA, failure of the tank’s vacuum insulation leads to rapid heat ingress, which can cause rapid boil-off of the stored H₂ and lead to overpressure scenarios. The complex heat transfer mechanisms which govern these boil-off rates are currently not well understood. The CHALIA project, which is a collaboration between the University of Western Australia and CEA (France) aims to address these knowledge gaps by combining high-resolution measurement and modelling of these heat-transfer mechanisms with measurements of LH₂ boil-off rates under controlled conditions representative of a LOVA.

In this work, we present the design and commissioning of an apparatus to measure the boil-off rates of liquid hydrogen from a litre-scale tank with a cylindrical geometry. The storage tank is suspended from a cryocooler located within a liquid nitrogen-cooled radiation shield housed inside a vacuum chamber. The vertical temperature profile inside the tank is monitored using an array of silicon diode sensors mounted in a central bore. Liquid level sensing is achieved through monitoring of a microwave resonant frequency of the tank, which (when combined with finite element analysis modelling) enables calculation of the liquid height [2]. A LOVA event can be simulated by controlling the heat-ingress rate into the tank using a set of thermofoil heaters mounted on the exterior of the cell. This apparatus enables multiple tank geometries to be investigated and allows LOVA conditions to be reproduced using heat-flux inputs derived from the heat-transfer modelling.

Acknowledgment

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Significant references

1. Al Ghafri, S., et al., *Hydrogen liquefaction: a review of the fundamental physics, engineering practice and future opportunities*. Energy & Environmental Science, 2022. **15**: p. 2690-2731.
2. Tenardi, L.D., et al., *A Composite Microwave Cavity for Liquid Volume Fraction and Simultaneous Phase Permittivity Measurements*. International Journal of Thermophysics, 2024. **45**(12): p. 168.

Freeze-out Measurements of Impurities in Hydrogen with a Microwave Resonant Cavity

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Although the commercial environment for hydrogen production and its viable end-uses remains difficult across much of the world, hydrogen continues to play an important role as a clean energy vector with particular relevance to hard-to-abate sectors. Similar to natural gas, liquefying hydrogen is an attractive means to increase energy density for efficient storage and transport. However, as hydrogen is cooled, impurities can freeze-out and block cryogenic heat exchangers, even at parts-per-million concentration, resulting in reduced hydrogen production and costly plant shutdowns [1]. As hydrogen liquefaction occurs at much lower temperatures than LNG, impurity specification to avoid the risk of freeze-out is even more critical.

Despite the clear operational risks posed by impurity freeze out during hydrogen liquefaction, data on the freeze-out behaviour of trace impurities in hydrogen remains limited. While recent measurement campaigns have focused on the freeze out of nitrogen [2, 3], comprehensive characterisation of other impurities is still lacking. In this project, a re-entrant microwave resonant cavity, developed at the University of Western Australia, has been used to successfully measure the freeze-out conditions of carbon dioxide as an impurity in hydrogen. It measures a resonant frequency dependent on the dielectric permittivity of the fluid contained in the cavity. A change in the measured dielectric permittivity indicates the formation of a new phase. The cavity geometry is designed to have high sensitivity to phase changes in a small region at the base of the cavity where the electric field is strongest [4]. By maintaining a temperature gradient across the cavity with two separately controlled liquid nitrogen heat exchangers, a cold spot is created at the base of the cavity where solids are preferentially formed.

Accurate data could reduce conservative estimates in hydrogen liquefaction process design and improve the efficiency and reliability of process operation. Additionally, data at various pressures and concentrations, and for other impurities including argon, oxygen, and nitrogen, will further advance this effort. This research demonstrates that microwave resonant cavities are a reliable and accurate measurement technology to directly monitor the freeze-out risk of low concentration impurities in high-pressure mixtures at the cryogenic temperatures required for liquid hydrogen.

Significant references

- [1] S. Z. S. Al Ghafri *et al.*, "Hydrogen liquefaction: a review of the fundamental physics, engineering practice and future opportunities," *Energy & Environmental Science*, 10.1039/D2EE00099G vol. 15, no. 7, pp. 2690-2731, 2022, doi: 10.1039/D2EE00099G.
- [2] M. T. J. Barwood, P. J. Metaxas, P. E. Falloon, A. S. D. Milligan, W. Wu, and E. F. May, "Optical measurements of solid nitrogen solubility in hydrogen at cryogenic temperatures," *International journal of hydrogen energy*, vol. 71, pp. 845-856, 2024, doi: 10.1016/j.ijhydene.2024.05.093.
- [3] M. T. J. Barwood, "Solid formation in energy production and cryogenic liquefaction processes," Doctor of Philosophy, Chemical Engineering, University of Western Australia, 2025.
- [4] M. G. Hopkins, A. Siahvashi, X. Yang, M. Richter, P. L. Stanwix, and E. F. May, "A microwave sensor for detecting impurity freeze out in liquefied natural gas production," *Fuel Processing Technology*, vol. 219, p. 106878, 2021/08/01/ 2021, doi: <https://doi.org/10.1016/j.fuproc.2021.106878>.

3.12

Thermophysical Properties

Fluids for CCUS Applications II



Density and Viscosity of MDEA Solutions Promoted by PZ or AMP for CO₂ Capture Applications

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The urgent need to mitigate anthropogenic greenhouse gas emissions has positioned Carbon Capture and Storage (CCS) as a viable technology for industrial sustainability. Aqueous methyldiethanolamine (MDEA), a tertiary amine, is a keystone in chemical absorption processes due to its high CO₂ loading capacity and low enthalpy of absorption, which reduces energy requirements for solvent regeneration. However, the industrial deployment of MDEA is often hampered by its inherently slow reaction kinetics with CO₂ [1-2]. To overcome this limitation, the addition of promoters such as piperazine (PZ) and 2-amino-2-methyl-1-propanol (AMP) is employed to accelerate absorption rates. Precise knowledge of the thermophysical properties of these quaternary systems is fundamental for the rigorous design and optimization of capture units, impacting heat transfer calculations, fluid dynamics, and overall process efficiency.

This study investigates the density and viscosity of aqueous MDEA blends promoted with either PZ or AMP at a constant mass fraction of 0.05. The experimental campaign covered both CO₂-unloaded and CO₂-loaded solutions, with gas loadings reaching up to 0.7 mol-CO₂/mol-amines. Density measurements were performed using a vibrating tube densimeter integrated with an automated kinematic viscometer (Anton Paar SVM 3001), maintaining an expanded uncertainty ($k = 2$) in density of 0.6 kg/m³. Dynamic viscosity was determined using an Ubbelohde capillary viscometer with a relative expanded uncertainty ($k = 2$) of 1 %. Anton Paar viscosity data were discarded due to inferior repeatability. All properties were characterized as a function of temperature across a range from 293.15 K to 353.15 K and at atmospheric pressure, providing a comprehensive dataset for industrial operating conditions [3].

The experimental results highlight the significant influence of CO₂ loading and temperature on the studied properties of the amine blends. To assist in process modeling, the density data were correlated using an empirical model, which yielded an absolute average relative deviation (AAD) of 0.2 %. For dynamic viscosity, a modified Vogel-Fulcher-Tammann (VFT) equation was applied, demonstrating excellent agreement with the experimental values with an AAD of 0.8 %. These results provide reliable thermophysical parameters necessary for the development of more efficient carbon capture technologies.

Acknowledgment

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Significant references

1. N. MacDowell, N. Florin, A. Buchard, J. Hallett, A. Galindo, G. Jackson, C.S. Adjiman, C.K. Williams, N. Shah, and P. Fennell, *Energy Environ. Sci.*, vol. 3 (2010), pp. 1645–1669.
2. Chowdhury, H. Yamada, T. Higashii, K. Goto, and M. Onoda, *Ind. Eng. Chem. Res.*, vol. 52 (2013), pp. 8323–8331.
3. J. Zhang, P.S. Fennell, and J.P.M. Trusler, *J. Chem. Eng. Data* vol. 60 (2015), pp. 2392–2399.

New VLE Data for CO₂-based Binary and Multicomponent Mixtures Relevant to CO₂ Transport for CCUS Applications

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The thermodynamic characterization of CO₂-based mixtures is crucial for the design and safe operation of CO₂ transport and injection systems in CCUS applications. Despite extensive research efforts on experimental investigation, as well as the development and validation of Equations of State (EoS) for CO₂-based mixtures, gaps remain in the available experimental Vapor-Liquid Equilibrium (VLE) data, particularly for multicomponent systems in temperature and pressure conditions relevant to pipeline transport. The main goals of the work are: (i) mapping available datasets and identifying gaps; (ii) validating the experimental setup using binary literature data; (iii) generating new VLE data for CO₂-based mixtures; (iv) evaluating the performance of different groups of EoS.

To address this, four binary mixtures (CO₂/N₂, CO₂/O₂, CO₂/CH₄, CO₂/H₂) were studied to validate literature results and to explore regions where data are missing. In addition, two ternary systems (CO₂/N₂/O₂, CO₂/CH₄/H₂), one quaternary system (CO₂/N₂/H₂/CO) and one five-component blend (CO₂/N₂/O₂/H₂/CO) were selected to represent CO₂-rich streams for which limited or no data exist. Measurements were conducted using an improved static-analytic VLLE test bench [1] with ROLSI capillary vapor/liquid samplers along isotherms between 250 K and 300 K and at pressures up to 200 bar. Two examples of newly acquired data are reported in Figure 1 below.

Measured data has been evaluated using different EoS to calculate the molar percentage of CO₂. EOS-CG-2021 [2] and Peng-Robinson cubic EoS with optimized BIP on binary dataset, showed an Average Absolute Deviation (AAD) of 0.9 mol% for the explored ternary systems. GERG-2008 showed higher deviations, with AAD values reaching 1.8 mol% for CO₂/CH₄/H₂ and 2.6 mol% for CO₂/N₂/O₂ ternary systems. The PC-SAFT EoS evaluated in this work showed highest deviation with AAD values reaching up to 4.3 mol% for these ternary systems. The resulting dataset expands the experimental analysis of CO₂-based systems and supports future improvements and validation of thermodynamic models for CCUS process design.

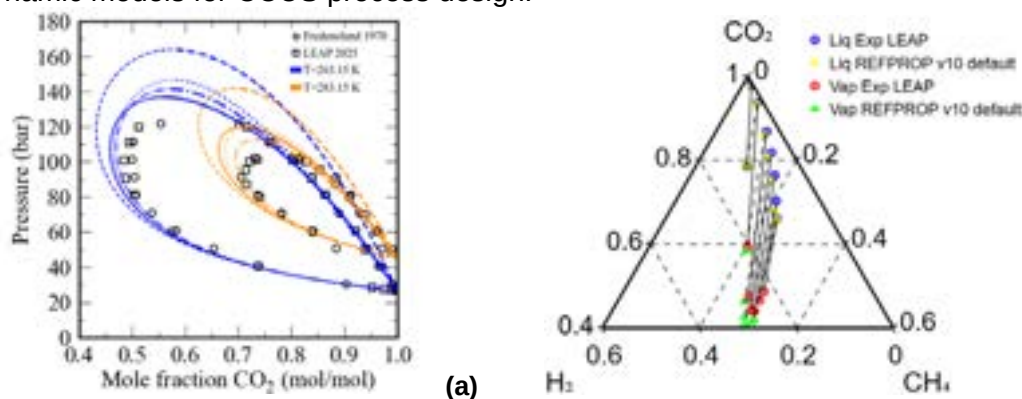


Figure 1. **(a)** VLE measurement and EOS performances for CO₂/O₂ mixtures: (—) EOS-CG-2021, (---) GERG-2008, (---) PR, (····) PC-SAFT; **(b)** VLE measurement for CO₂/CH₄/H₂ mixture at 263.15 K and pressure range between 25 to 150 bar

Acknowledgment

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Significant references

1. S. Lasala, P. Chiesa, D. Di Bona, S. Consonni, *Energy Procedia*, vol. 45 (2014), pp. 1215-1224.
2. T. Neumann, S. Herrig, I. H. Bell, R. Beckmüller, E. W. Lemmon, M. Thol, & R. Span, *International Journal of Thermophysics*, vol. 44 (2023), 178.

Speed of Sound Measurements of Gaseous CO₂ + O₂ Mixtures Using a Spherical Resonator at Temperatures between (280 and 340) K and at Pressures up to 10 MPa

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The speed of sound is a crucial thermodynamic property for the development and validation of high accuracy fundamental equations of state for both pure fluids and mixtures, as it directly relates to caloric properties such as the isobaric heat capacity. A spherical resonator facility developed at Ruhr University Bochum¹ was used to measure the speed of sound in two gaseous (CO₂ + O₂) mixtures with (50 and 75) mol% CO₂. The objective was to provide highly accurate data to support (CO₂ + O₂) fundamental equation of state improvement. Measurements were performed between (280 and 340) K and up to 10 MPa. The temperature-dependent sphere radius was calibrated in the entire investigated temperature range using pure argon as reference fluid, by extrapolating the measurements to zero-pressure limit. Validation measurements with pure nitrogen confirmed agreement within the uncertainty of its fundamental equation of state² after corrections for vibrational relaxation.

As CO₂ (and its mixtures) exhibit long relaxation times relative to the short acoustic period of the sound signal, relaxation times associated with unlike-molecule collisions were estimated from residual half-widths and applied as a correction, adjusting speed of sound values by up to 0.01 %. The maximum expanded combined relative uncertainty ($k = 2$) of the measured points was 0.04 %. Relative deviations between the experimental results and the state-of-the-art EOS-CG³ mixture model predictions are up to 0.8 % at the highest pressure and lowest temperature, still within the reported uncertainty of 1 %. The new dataset provides a benchmark for refining (CO₂ + O₂) fundamental mixture model and reducing uncertainty in speed of sound predictions.

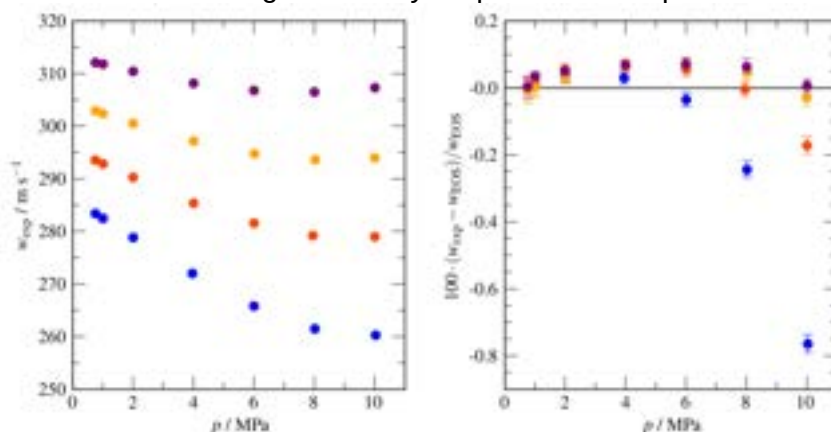


Figure 1. Speed of sound measurements for a 50 mol% CO₂ + 50 mol% O₂ mixture (left) and percentage deviation from EOS-CG (right) as a function of pressure. Colors indicate: ● 280 K, ● 300 K, ● 320 K, ● 340 K

Acknowledgment

To perform this research in the ENCASE project, Politecnico di Milano has received funding by the European Union's Horizon Europe research and innovation programme under grant agreement No. 101094664.

Significant references

1. A. Maurer, *Ruhr-Universität Bochum*, PhD thesis (2022), doi: 10.13154/294-8520
2. R. Span, E. W. Lemmon, R. T. Jacobsen, W. Wagner, A. Yokozeki, *Journal of Physical and Chemical Reference Data* 29.6 (2000): 1361-1433
3. J. Gernert and R. Span, *The Journal of Chemical Thermodynamics* 93 (2016): 274-293

Thermophysical properties of CO₂ and brine: density and viscosity

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Thermophysical properties like density and viscosity are vital for assessing storage capacity, injection pressures, CO₂ plume shape, and buoyant migration for effective geological storage of CO₂ in saline aquifers. When CO₂ dissolves into brine, it raises density at layer interfaces, forming CO₂-rich fingers. This causes convective flow driven by the density difference, with CO₂-enriched brines moving downward.^[2]

To that end, undersaturated densities of CO₂ dissolved in $(1-x)\cdot\text{NaCl} + x\cdot\text{CaCl}_2$ brine where $x = 0.089 \text{ mol}\cdot\text{mol}^{-1}$, were collected using the vibrating tube densimeter. Measurements were taken at temperatures ranging from 278.15 to 463.15 K, at pressures up to 140 MPa, and at salt molalities (b) of 1, 2.5, and 5 mol·kg⁻¹. Additionally, the viscosity of dissolved CO₂ in water was measured at 303.15, 333.15, and 373.15 K and at pressures ranging from 10 to 30 MPa using a capillary viscometer.

For the $(T, P, b, \text{ and } x)$ conditions investigated in this work, the molar volume of the mixture (V_m) was found to have a linear relationship with CO₂ composition, as illustrated in Figure 1, which indicates that the partial molar volume of CO₂ is independent of the CO₂ composition. The apparent molar volume of CO₂ showed a strong dependency on temperature and showed an intricate dependence on pressure, which becomes more pronounced at higher temperatures. The density data were also successfully modelled using the apparent molar volume correlations by García^[2], Hu et al.^[3], and McBride-Wright et al.^[4] and the pure brine density model proposed by Al Ghafri et al.^[5] In addition, under the conditions studied, the viscosity of water increased with increasing CO₂ dissolution.

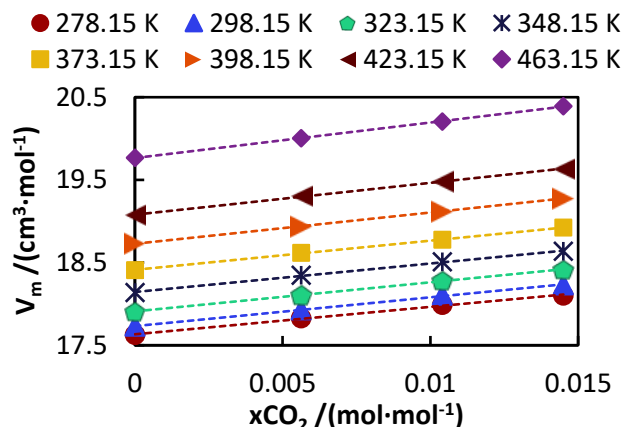


Figure 1. Molar volume of CO₂ + 1m [NaCl + CaCl₂]_(aq) as a function of CO₂ composition at 50 MPa.

Acknowledgment

The authors gratefully acknowledge support from Innovation Fund Denmark, BlueNord, TotalEnergies, Gas Storage Denmark, INEOS, and Harbour Energy.

Significant references

1. Pau, G. S. H.; Bell, J. B.; Pruess, K.; Almgren, A. S.; Lijewski, M. J.; Zhang, K. *Adv Water Resour* 2010, vol. 33 (4), pp. 443–455.
2. García, J. E. Berkeley, CA, 2001.
3. Hu, Q.; Guo, H.; Lü, X.; Lu, W.; Chen, Y.; Zhu, Y.; Geng, L. *Chem Geol* 2016, vol. 424, pp. 60–72.
4. McBride-Wright, M.; Maitland, G. C.; Trusler, J. P. M. *J Chem Eng Data* 2015, vol. 60 (1), pp. 171–180.
5. Al Ghafri, S.; Maitland, G. C.; Trusler, J. P. M. *Chem Eng Data* 2012, vol. 57 (4), pp. 1288–1304.

3.13

Thermophysical Properties

Refrigerants and Lubricant Oils I



Measurement of thermal conductivity of R-454A and R-454B mixtures using transient hot wire method

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R-454A (35% R-32 / 65% R-1234yf) and R-454B (68.9% R-32 / 31.3% R-1234yf) are HFC/HFO blends composed of R-32 and R-1234yf that gained importance as working fluids for refrigeration industry due to their low global warming potential (GWP). Studies [1-2] have shown that R-454A and R-454B are suitable replacements for the high-GWP refrigerants such as R-404A and R-410A respectively. Adaptation of these refrigerants in the industry requires reliable transport property measurement, such as thermal conductivity, where measured data can be used to validate and improve transport property models available in software such as REFPROP 10.0 [3] or TREND [4]. In this research thermal conductivity measurement of these mixtures was conducted with the transient hot-wire (THW) method over the temperature range from 243 to 303 K at pressure 3 to 4 MPa in the liquid phase at measured composition of (38.11% R-32 / 61.89% R-1234yf) and (69.57% R-32 / 30.43% R-1234yf) of R-454A and R-454B respectively. The deviations of the measured thermal conductivity in the liquid phase from those calculated by REFPROP 10.0 using the extended corresponding states (ECS) model were around 2% indicating that these measured data can be used tuning the model.

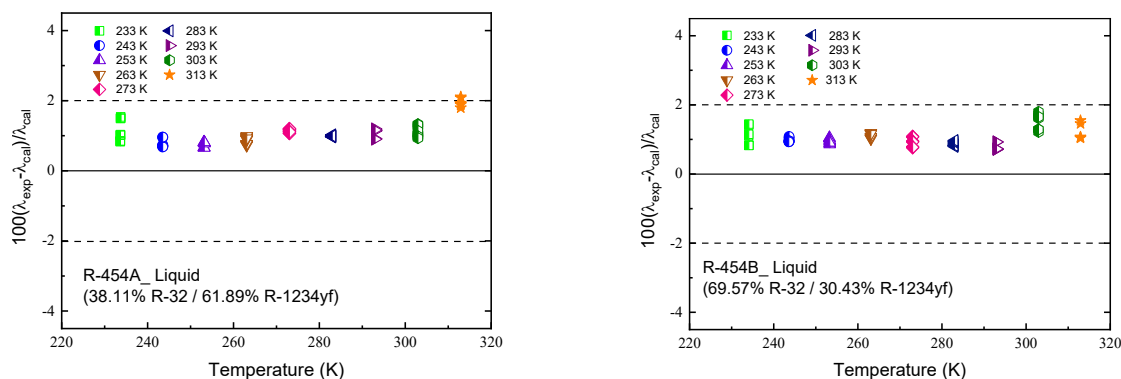


Figure 1. Comparison of the measured thermal conductivity data of R-454A and R-454B with REFPROP 10.0

Significant references

- [1]. Oruç, V., & Devecioğlu, A. G. (2021). Experimental investigation on the low-GWP HFC/HFO blends R454A and R454C in a R404A refrigeration system. *International Journal of Refrigeration*, 128, 242-251.
- [2]. Jajja, S. A., Nawaz, K., & Fricke, B. A. (2022). In tube condensation heat transfer and pressure drop for R454B and R32—Potential replacements for R410A. *International Journal of Refrigeration*, 144, 238-253.
- [3]. Lemmon, E. W., Bell, I. H., Huber, M. L., & McLinden, M. O. (2018). NIST standard reference database 23: reference fluid thermodynamic and transport properties-REFPROP, Version 10.0, National Institute of Standards and Technology. *Standard Reference Data Program*, Gaithersburg, 45-46.
- [4]. Span, R., Eckermann, T., Herrig, S., Hielscher, S., Jäger, A., & Thol, M. (2020). TREND. Thermodynamic reference and engineering data 5.0. *Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum*

Viscosity measurements for various pentaerythritol esters in the range of temperatures between 273.65 K and 373.15 K

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The correct formulation of lubricants is crucial for efficient and environmentally sustainable refrigeration systems. Lubricants must ensure proper compressor lubrication and miscibility with the refrigerant to guarantee stable oil return, particularly with the current transition toward low-GWP refrigerants (ASHRAE Handbook, 2018). Among available candidates, polyol esters (POEs) are attractive due to their thermal stability, compatibility with modern refrigerants, and tuneable viscosity achieved by varying polyol or acid structures. Viscosity strongly influences lubrication performance and overall system efficiency. Nevertheless, data on branched pentaerythritol esters (PEBs)—key precursors for POE blends—remain scarce, while linear pentaerythritol esters (PECs) are better documented (Lin et al., 2020). In this study, the dynamic viscosity of eleven pure pentaerythritol esters—five linear (PEC) and six branched (PEB)—was measured from 273.65 K to 373.15 K using a rotational cone-plate rheometer. The experimental uncertainty was $\pm 5\%$. The new dataset provides reliable reference values for both PEC and PEB esters, supporting future modelling and formulation of POE lubricants for next-generation low-GWP refrigeration applications.

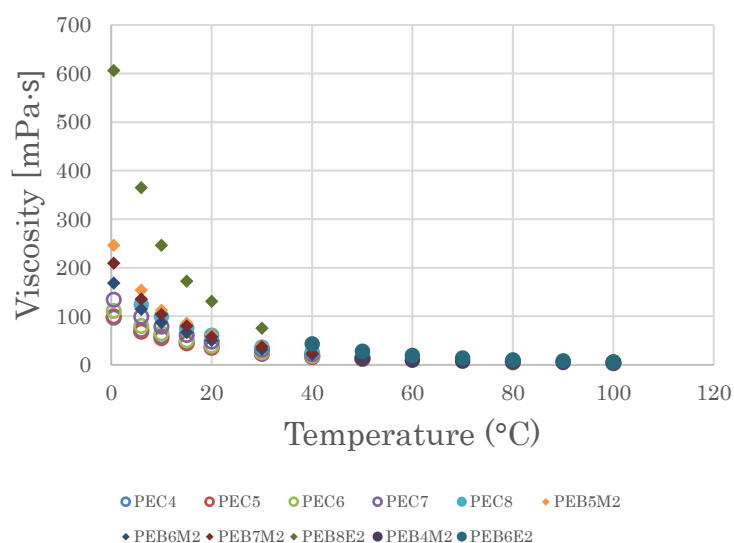


Figure 1. Viscosity of 11 pentaerythritol esters in the range of temperatures between 0.5°C and 100°C

Significant references

1. ASHRAE Handbook — Refrigeration. Chapter 12: Lubricants in Refrigerant Systems. American Society of Heating, Refrigerating and Air-Conditioning Engineers, 2022.
2. Lin, Lingnan, and Mark A. Kedzierski. Density and viscosity of a polyol ester lubricant: Measurement and molecular dynamics simulation. *Int. J. Refrig.*, 118 (2020): 188-201.

Simultaneous Measurement of Speed of Sound and Density for Refrigerant Mixtures Containing Hydrofluoroolefins

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The Kigali Amendment to the Montreal Protocol mandates the replacement of high global warming potential (GWP) refrigerants with alternatives that have a lower environmental impact. Hydrofluoroolefins (HFOs) are promising candidates due to their low GWP; however, their application as pure substances is limited by unfavorable characteristics such as flammability and chemical instability. Consequently, refrigerant mixtures containing HFOs are of significant interest for practical refrigeration cycles, necessitating accurate evaluation of their thermophysical properties.

In this study, we measured the speed of sound and density for selected refrigerant mixtures containing HFO-1123 and HFO-1132(E) in both vapor and liquid phases by using the experimental apparatuses shown in Figure 1. For the vapor-phase measurements, a cylindrical acoustic-microwave resonator was employed to simultaneously determine the speed of sound and density, the latter derived from dielectric permittivity. In the liquid phase, an ultrasonic pulse propagation sensor and an oscillating U-tube densimeter were used for simultaneous measurements. Based on these data, adiabatic compressibility was also evaluated for both phases. The results provide essential property data for the design and optimization of refrigeration systems utilizing low-GWP refrigerant mixtures.

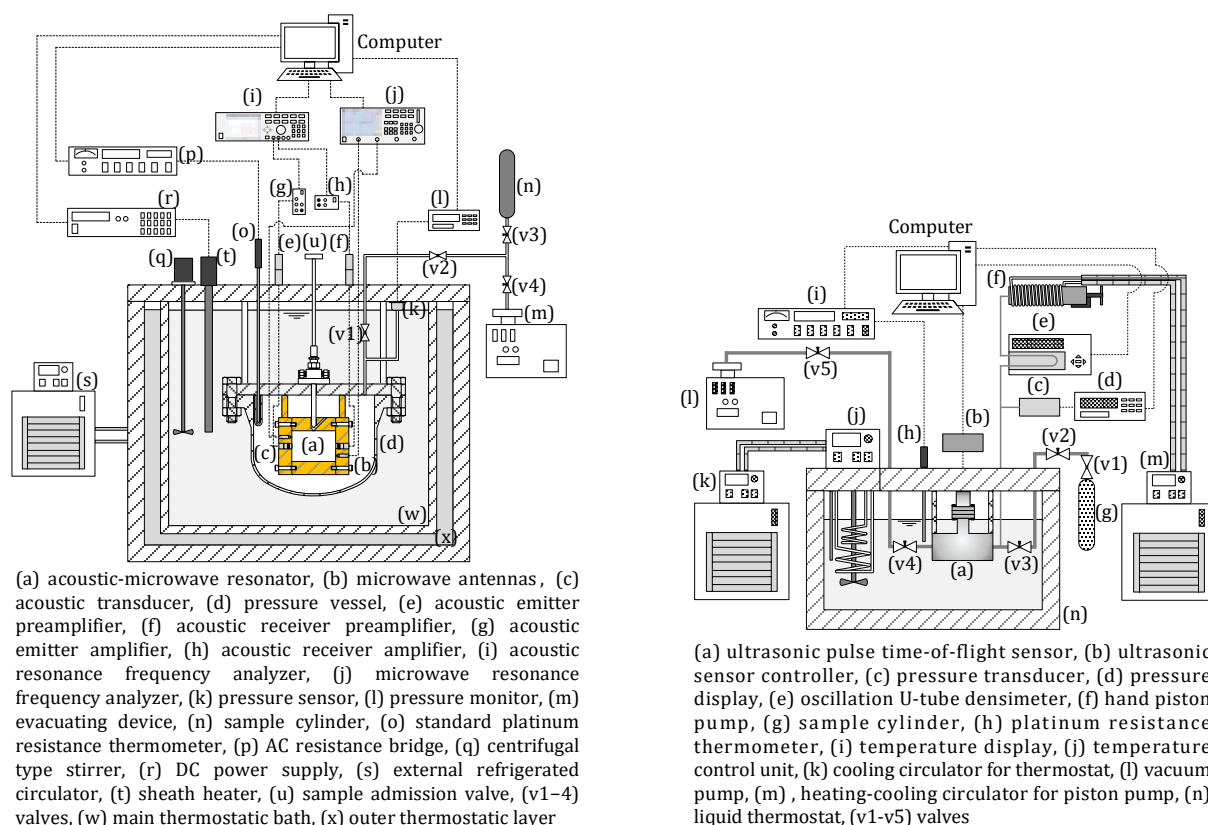


Figure 1. Experimental set-up of simultaneous measurements for speed of sound and density in the vapor (left-hand side) and the liquid (right-hand side) phases.

Acknowledgment

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High-Pressure VTD Employed on Accurate Measurement of Liquid Density of Hydrofluorethers and Other Reference Fluids

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The vibrating tube densimeters (VTDs) belong to the most accurate instruments for the measurement of density of large variety of fluids. The units with glass U-tubes operated usually close to barometric pressure can achieve the resolution of down to 0.001 kg/m³ and the standard uncertainty of around 0.030 kg/m³ [1]. According to firmware procedure, the commercial atmospheric VTDs are typically calibrated with dry air and pure water within a temperature range of several tens of degrees, which is entirely sufficient for most technical applications. For more accurate measurements, some more attention needs to be dedicated to the calibration fluids, liquid viscosity, sample degassing, etc. [1].

In the community of thermophysical properties, the high-pressure VTDs with metal U-tubes start to attract considerable attention during last two decades. When equipped with appropriate filling and pressure setup accompanied with the temperature control system, these instruments can provide accurate density data over wide ranges of conditions reaching, for example, the maximum pressure of 140 MPa in case of current DMA HPM instrument by Anton Paar (Austria). The high-pressure VTDs are typically one to two orders of magnitude less sensitive than the atmospheric units. Considerable attention must be paid to the instrument calibration carried out usually with vacuum, water and some other known fluids such as dry gases. The calibration models by May et al. [2] and Outcalt and McLinden [3] are among the most commonly used. When carefully calibrated the standard uncertainty of obtained density can be around 1.0 kg/m³ [4].

In this work, we introduce density measurements carried out with the DMA HP VTD by Anton Paar equipped with the supporting systems necessary for the instrument operation, adjustment of pressure and temperature recording. The verification measurements were carried out with a series of reference fluids, including nitrogen, water, ethanol, and vacuum. The calibration models by May et al. [2], Outcalt and McLinden [3] are compared among each other and with the temperature-pressure correlation recommended by the manufacturer. The preliminary results for the liquid density at pressures up to 60 MPa are provided for ethylene glycol, a series of hydrofluorethers (Novec fluids by 3M) from HFE-7000 to HFE-7500 and additionally for tetrachlorethylene. Based on large number of experiments the uncertainty of the obtained densities was analyzed.

Acknowledgment

The authors thank Mr. Nicolas Hénin from the Centrale Méditerranée, Marseille (FR) for helping with the development of VTD calibration algorithms in Matlab. This study was supported from the Czech Science Foundation grant no. GF24-10191K and the institutional support RVO:61388998.

Significant references

1. O. Prokopová, A. Blahut, M. Čenský, M. Součková, V. Vinš: Comments on temperature calibration and uncertainty estimate of the vibrating tube densimeter operated at atmospheric pressure *J. Chem. Thermodynamics* 173 (2022) pp. 106855-1 – 106855-11.
2. E.F. May, W.J. Tay, M. Nania, A. Aleji, S. Al-Ghafri, J.P. Martin Trusler, Physical apparatus parameters and model for vibrating tube densimeters at pressures to 140 MPa and temperatures to 473 K. *Rev. Sci. Instrum.* 85 (9), 095111 (2014).
3. S.L. Outcalt, M.O. McLinden, Automated densimeter for the rapid characterization of industrial fluids. *Ind. Eng. Chem. Res.* 46 (24), 8264 (2007).
4. O. Prokopová, M. Čenský, N. Hénin, A. Blahut, M. Součková, V. Vinš: Validated high-pressure vibrating tube densimeter for accurate fluid density data at pressures up to 600 bar, *Acta Polytechnica CTU Proceedings* 2026 (submitted).

3.14

Thermophysical Properties Complex Liquids II



Using sulfate and sulfonate compounds to show hydrotropy as the missing link between salts and surfactants

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The low aqueous solubility of many drugs and drug-like molecules is a significant challenge for pharmaceutical applications, impacting purification, formulation, and bioavailability. Hydrotropes offer an alternative to traditional organic solvents or water/organic solvents mixtures to enhance the aqueous solubility of poorly soluble compounds. This study investigates the hydrotropic behavior of eleven sodium alkyl sulfate salts with different carbon chain lengths, ranging from sodium sulfate to sodium dodecyl sulfate. Carbamazepine was chosen as the model solute due to its non-dissociative behavior in water and pH-independent solubility, allowing a clearer assessment of hydrotropic activity. The sigma profile of each hydrotrope was obtained with the quantum-chemistry-based thermodynamic model Conductor-like Screening Model for Realistic Solvents (COSMO-RS) to calculate the apolar factor of each hydrotrope. The Setschenow constant (K_{Sets}) was determined to characterize hydrotropic mechanisms in the dilute region, where hydrotrope self-association is negligible. Figure 1 presents the change of the K_{Sets} with the apolar factor.¹

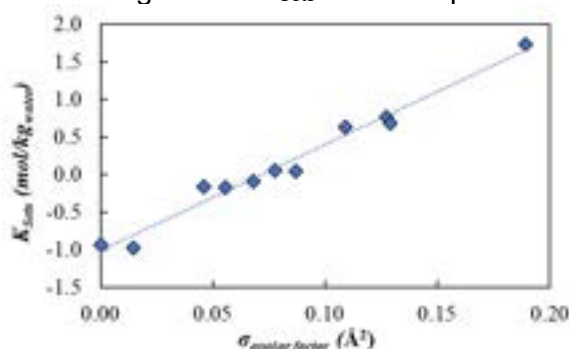


Figure 1. Linear correlation between apolar factor and Setschenow constants for the sodium alkyl sulfate salts.

The solubility curves reveal a salting-out effect for hydrotropes with short carbon chains (less than two carbons), while hydrotropes with longer carbon chains display a clear hydrotropic behavior. A strong linear correlation between the Setschenow constants and the hydrotrope apolar area supports the central role of apolarity-driven interactions in governing hydrotropic enhancement, consistent with the cooperative hydrotropy model and suggesting a common underlying mechanism for salting-in and salting-out effects. NMR analysis shows a systematic shift in the carbamazepine peak with increasing hydrotrope concentration, indicative of a more hydrophobic microenvironment around the solute and increased hydrotrope-solute association.

Acknowledgment

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Significant references

1. B. P. Soares, D. O. Abranches, T. E. Sintra, A. Leal-Duaso, J. I. García, E. Pires, S. Shimizu, S. P. Pinho, and J. A. P. Coutinho, *ACS Sustain. Chem. Eng.*, vol. 8 (2020), pp. 5742–5749.

Predicting the Solubilization of Hydrophobic Solutes in Aqueous Surfactant Systems

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The amphiphilic nature of surfactant molecules drives micellar aggregate formation which enables to significantly increase the aqueous solubility of hydrophobic solutes. In this work, we present a predictive modeling approach that holistically considers both aggregation as well as phase equilibria in complex systems comprising water, surfactants, and hydrophobic solutes. Within this framework, we incorporate PC-SAFT into a novel mixed-aggregate formation model (AFM) which allows for describing solubilization effects on a physically sound basis. Our AFM is based on calculating two-dimensional distribution functions with respect to both mixed-aggregate sizes and compositions while accounting for their corresponding equilibrium geometries. This novel approach accurately captures the sharp increase in the aqueous solubility of hydrophobic components at surfactant concentrations just above the critical micelle concentration (CMC). It enables quasi-quantitative predictions of Winsor Type I liquid-liquid equilibria (LLE) and of solid-liquid equilibria (SLE) in water-surfactant-solute systems.

Our methodology was validated for polyethoxylated alkyl ethers (C_8E_6) as model surfactants. We were able to predict the effects of different C_8E_6 polarities on the maximum solubilization capacity for various solutes in very good agreement with experimental data. On the one hand, the investigated systems comprised a variety of linear hydrocarbons serving as “oil-like” model components for LLE calculations (Figure 1). On the other hand, we were for the first time able to successfully predict the solubility of active pharmaceutical ingredients (APIs) in aqueous C_8E_6 solutions.

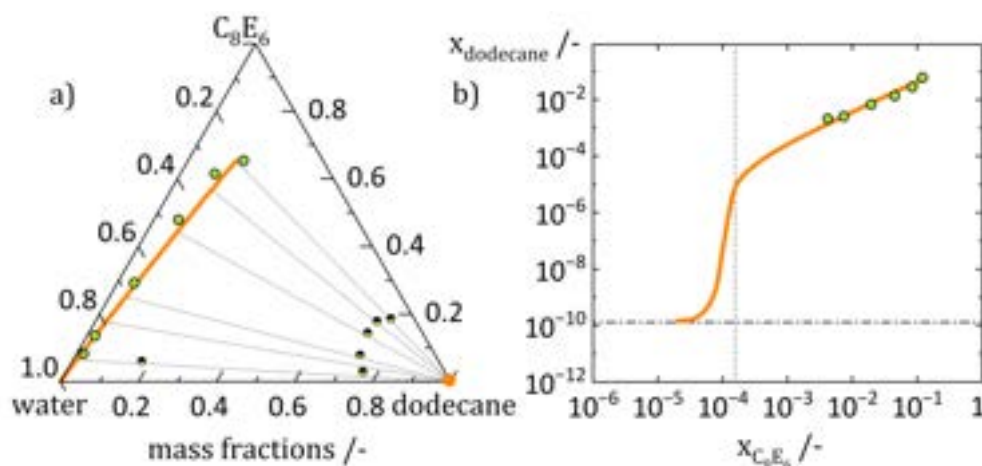


Figure 1. LLE of the system water, C_8E_6 and n-dodecane at 298.15 K. (a) Ternary Diagram. Green circles: experimental equilibrium data, half-black circles: experimental feed points [1]. Orange line: predicted binodal curve, grey lines: predicted tie lines. (b) Concentrations of C_8E_6 and n-dodecane in the aqueous phases along the binodal curve. Green circles: experimental data [1]. Orange line: predictions. Vertical dashed line: CMC of C_8E_6 in water at 298.15 K. Horizontal line: aqueous solubility of n-dodecane in surfactant-free water.

Significant reference

1. J.S. Marland, B.A. Mulley, J. Pharm. Pharmacol. 23 (1971) 561–572.

Physical origin of the non-monotonic behavior of the Soret coefficient in salt solutions

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Temperature gradients can induce partial separation of components in liquid mixtures through thermodiffusion, a process quantified by the Soret coefficient. Recent experiments and simulations have examined the occurrence of minima in the concentration dependence of the Soret coefficient S_T for various aqueous salt solutions [1-4]. We compile and analyze data for twelve electrolytes in water, consisting of various cations (such as lithium, sodium, potassium, cesium, ammonium, and guanidinium) and anions (such as chloride, iodide, acetate, and thiocyanate). One proposed explanation for the non-monotonic behavior of the Soret coefficient relates the concentration at the minimum, $m_{\min}$ to the onset of overlap between ion hydration shells [1]. According to this hypothesis, $m_{\min}$ corresponds to the concentration at which hydrated spheres approach random close packing. Although this picture involves simplified ion-pairing and adjustable parameters, it can account for the fact that some systems exhibit a minimum only at high temperatures. For salts such as cesium iodide and ammonium chloride (Fig.1(a) and Fig-1(b)), the minimum may occur at low temperatures and concentrations that fall outside the experimentally accessible range. This interpretation is supported by observations for aqueous lithium chloride and guanidinium chloride, where $m_{\min}$ shifts to higher concentrations with increasing temperature (Fig. 1(c)). A thinner and more flexible hydration shell at elevated temperatures would naturally shift the minimum in this way. From irreversible thermodynamics, the Soret coefficient can be written as the product of a purely thermodynamic factor and the ratio of two Onsager coefficients. In contrast to trends reported for binary Lennard–Jones mixtures [2], where the minimum of the Soret coefficient coincides with the minimum of the thermodynamic factor, our analysis of 1:1 aqueous electrolytes shows that the dominant contribution to the observed non-monotonic concentration dependence arises from the Onsager-coefficient ratio. For salts sharing the same anion, thermodynamic factors increase with the Pauling radii of the cations, whereas the Onsager-coefficient ratios increase monotonically with the radii of the hydrated cations, highlighting the essential role of hydration structure in thermodiffusion. Overall, our results emphasize that ion hydration is the key determinant of thermodiffusive behavior in aqueous electrolytes.

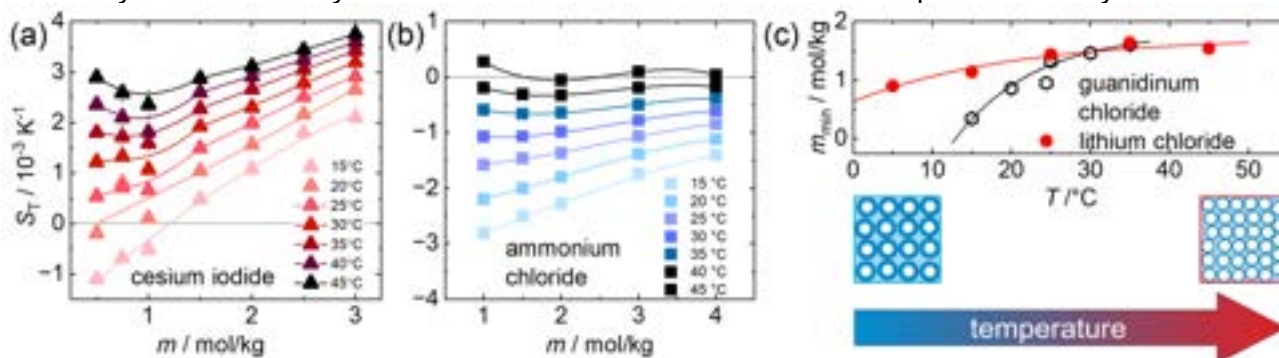


Figure 1. S_T of cesium iodide (a) and ammonium chloride (b) as function of molality for various temperatures. (c) The concentration $m_{\min}$ at which S_T has a minimum increases with temperature in aqueous lithium and guanidinium chloride solutions [3,4].

Significant references

1. Mohanakumar, S., Kriegs, H., Briels, W. J., & Wiegand, S. *PCCP*, 24 (2022), 27380–27387.
2. Gittus, O. and Bresme, F. *PCCP*, 25 (2023), 1606–1611.
3. Lee, N., Mohanakumar, S., Briels, W. J., & Wiegand, S. *PCCP*, 26 (2024), pp. 7830–7836.
4. Rudani, B. A., Briels, W. J., & Wiegand, S. *PCCP*, 27 (2025), pp. 4746–4755.

Experimental determination of enthalpy of mixing, heat capacity and density for CO₂ + γ -valerolactone system

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In recent years, the binary mixture of carbon dioxide (CO₂) and γ -valerolactone (GVL) has attracted growing attention due to its potential in a wide range of sustainable processes. This system has been investigated for applications including CO₂ capture and sequestration [1], biorefining and biomass processing [2], as well as extraction, selective dissolution, and green solvent formulation [3]–[5]. This interest arises from the strong affinity between the two components and their attractive physicochemical properties. CO₂ is a non-toxic, inexpensive, readily available fluid with interesting thermodynamic behavior, while GVL is a stable bio-based solvent with a low volatility and broad applicability in green chemistry.

To design and optimize processes involving (CO₂ + GVL) mixtures, reliable thermodynamic and transport property data are essential. However, available experimental data remain limited in the literature. Beyond high pressure density measurements and vapor-liquid equilibrium data at both high (> 7 MPa [5]) and low (< 0.6 MPa [1]) pressures, no additional thermophysical data have been reported. This lack of data highlights the need for new measurements.

The present work aims to improve the thermodynamic characterization of the (CO₂ + GVL) system by providing new experimental data including enthalpies of mixing, isobaric heat capacities and densities. These properties are crucial for developing accurate equations of state for process design and for gaining insight into molecular interactions. Enthalpies of mixing were determined using a flow calorimetric technique developed in our laboratory [6], covering temperatures from 283 K to 373 K and pressures from 2 MPa to 12 MPa. In addition, we developed a new experimental setup based on a micro-differential scanning calorimeter to measure the isobaric heat capacity of gas-loaded liquids, applied here to the (CO₂ + GVL) mixture. Measurements were performed in static mode at 9 MPa over temperatures ranging from 288 K to 358 K for various CO₂ molar fractions. Mixture densities were obtained over the same composition, pressure, and temperature ranges using a vibrating U-tube densimeter.

Significant references

- [1] D. Deng, G. Han, Y. Jiang, and N. Ai, *J. Chem. Eng. Data*, vol. 60 (2014), pp. 104–111.
- [2] E. D. Nikitin, A. P. Popov, N. S. Bogatishcheva, and M. Z. Faizullin, *J. Chem. Thermodyn.*, vol. 149 (2020), p. 106162.
- [3] L. Manzer and K. Hutchenson, European Patent EP1636203B1 (2004).
- [4] R. A. Bourne, J. G. Stevens, J. Ke, and M. Poliakoff, *Chem. Commun.*, no. 44 (2007), pp. 4632–4634.
- [5] Y. Hou, W. Wu, and M. Poliakoff, *J. Chem. Eng. Data*, vol. 54 (2009), pp. 118–126.
- [6] A. Hajlaoui, L. Rodier, K. Ballerat-Busserolles, J. Y. Coxam, and Y. Coulier, *Ind. Eng. Chem. Res.*, vol. 63 (2024), p 16928-16934.

3.15

Thermophysical Properties

Databases and Reference Data



Thermophysical property data in the AI age

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Thermophysical property data are essential for a wide range of applications, from materials and chemicals design to transportation and safety, as well as scientific research and education. However, property measurements are nontrivial, labor intensive, and expensive. Given recent trends, there is a clear temptation to develop and apply AI-based technologies, like machine learning (ML), as an alternative to labor-intensive property measurements. If AI/ML can give you a reliable estimate for a given property, why bother spending the time and money to measure it? The success of these technologies depends on reliable property data, and publications are a virtual gold mine. However, extracting data from publications is also labor-intensive and nontrivial! The Thermodynamics Research Center (TRC) at the National Institute of Standards and Technologies (NIST) has been developing new technologies for decades to facilitate the critical evaluation of comprehensive and reliable thermophysical property data.

To maximize the value of thermophysical property data, the quality and reliability of the underlying information must be prioritized. In this presentation, the concept of data traceability and its critical role in assessing the reliability of thermophysical property data will be explored. I will discuss the importance of distinguishing between primary data (experimentally determined or calculated from first principles) and secondary data (predicted on the basis of primary ones). Our analysis will reveal that the available primary thermophysical data is insufficient to support reliable modeling of thermophysical properties, highlighting the need for new targeted measurements. To address this need, TRC has developed experiment planning tools that can estimate the expected impact of proposed measurements. As an example, I will introduce a new service for sharing known property data challenges that cannot be resolved with available data validation techniques. Furthermore, the challenges of establishing the accuracy of primary data will be discussed, and the complex, multi-stage process developed at TRC for critical evaluation, as outlined in [1], will be described.

As it will be demonstrated conclusively in this talk, adhering to the Good Reporting Practice principles [2] for primary property data can significantly enhance the impact of publications in this field. Effective implementation of these principles requires a multi-faceted approach, including raising awareness, motivating change, planning, and taking action. TRC is actively working to bring together experimentalists, publishers, and data users to achieve this goal. For instance, we have developed the IUPAC reviewers' support project and service (<https://trc.nist.gov/review-checklist/>) and a public data domain [3]. While modern data technologies, such as large language models, have made significant progress, they cannot replace the need for accurate and complete reporting of professionally conducted measurements. Without drastically improved reporting, collecting and evaluating data remains a labor-intensive and costly process, limiting the ability to meet the needs of AI/ML communities. To address this challenge, TRC is committed to supporting the data needs of the thermophysical AI/ML community.

Significant references

1. V. Diky, A. Bazyleva, E. Paulechka, J.W. Magee, V. Martinez, D. Riccardi, and K. Kroenlein, *J. Chem. Thermodyn.*, vol. 133 (2019), pp. 208-222.
2. A. Bazyleva, J. Abildskov, A. Anderko, O. Baudouin, Y. Chernyak, J.-C. de Hemptinne, V. Diky, R. Dohrn, J.R. Elliott, J. Jacquemin, J.-N. Jaubert, K.G. Joback, U.R. Kattner, G.M. Kontogeorgis, H. Loria, P.M. Mathias, J.P. O'Connell, W. Schröer, G.J. Smith, A. Soto, S. Wang, and R.D. Weir, *Pure Appl. Chem.*, vol. 93 (2021), pp. 253-272.
3. D. Riccardi, C. Muzny, and V. Diky, ThermoData Engine free public version, NIST, USA (2024). <https://doi.org/10.18434/mds2-3179> (accessed 2025-12-08).

A Practical Guide to the Uncertainty Evaluation of Thermophysical Properties

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Ensuring an accurate evaluation of experimental uncertainty is most important when reporting experimental procedures and data. It serves as the cornerstone for the validation and overall reliability of the presented work. Additionally, uncertainty analysis and a detailed investigation of the uncertainty contributions aid with evaluating the experimental system, allowing the identification of possible targeted improvements.

For many years, the main reference for uncertainty evaluation has been the *Guide to the Expression of Uncertainty in Measurement* (GUM)^[1], which offers a rigorous framework but consists of several volumes (and thousands of pages) of highly specialized content. We discuss the challenges associated with applying the traditional GUM framework and alternative methods. Especially in cases involving numerous uncertainty sources or non-linear working equations, deriving partial derivatives and computational demands becomes impractical. As a result, researchers often opt for simplified yet incomplete or inaccurate approaches.

This work presents a practical methodology, which we call the *Sensitivity Analysis Method*^[2], for evaluating the uncertainty of thermophysical property measurements, applicable to systems of varying complexity. This methodology consists of three key steps:

1. estimating the uncertainty of each input parameter according to the GUM guidelines;
2. propagating these uncertainties to the output parameters using the *Sensitivity Analysis Method*; and
3. assessing system performance through the analysis of the resulting sensitivity coefficients.

Using examples of real experimental procedures for thermophysical property measurements, we illustrate each step of the methodology in detail. Particular emphasis is placed on the estimation of individual uncertainty contributions, an essential and unavoidable component of any rigorous uncertainty evaluation. We will cover common input parameters such as temperature and pressure, as well as case-specific parameters relevant to more complex systems. In such situations, the *Sensitivity Analysis Method* offers a robust and accessible alternative to more conventional uncertainty-propagation techniques.

Finally, we assess the presented experimental procedures using the proposed methodology and suggest improvements aimed at reducing the overall uncertainty, informed by the analysis of the sensitivity coefficients.

Significant references

1. BIPM *et al.* Evaluation of measurement data — Guide to the expression of uncertainty in measurement. *Joint Committee for Guides in Metrology*, JCGM 100:(2008).
2. L. Bernardini, M.O. McLinden, X. Yang, and M. Richter, *Int. J. Thermophys.*, vol. 45.164 (2024).

Korea Thermophysical Properties Databank (KDB): Integrated Platform for Critically Evaluated Thermophysical Data and Property Estimation

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Thermophysical properties data are crucial for education, research, process modeling, and operational activities in chemical engineering. Supported by the Korean government, Korea University has been providing this data continuously since 1997 (www.cheric.org). Recently, a new version of the Korean Thermophysical Properties Data Bank (KDB) (www.mdlkdb.com) [1] has been developed and released. This updated version features an expanded database, enhanced calculation capabilities, and support for Python computing packages. It includes critically evaluated data for 1,970 compounds and offers 5,567 binary vapor–liquid equilibrium (VLE) data sets as standard references. These standard references are assessed based on criteria such as uncertainty, reproducibility, predictability, and consistency, ensuring the reliability and quality of the data. Moreover, various Quantitative Structure–Property Relationship (QSPR) methods for thermodynamic properties have been integrated into the web interface and Python packages, which were developed using the NIST/TRC database. Users are enabled to calculate a wide range of thermodynamic properties, from pure-component estimations to phase equilibria at ambient pressure, using both conventional and machine–learning–based approaches. The Python package further supports molecular descriptor generation and provides frameworks for machine-learning–based property estimation. This contribution outlines the functionalities and evaluation procedures of the KDB, which is an ongoing project aimed at enhancing the accessibility and reliability of thermophysical data while also improving precision in chemical process modeling and design.

Acknowledgment

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Significant references

1. Hwang S. Y., Ryu B. C., Kang S. S., Bang H, and Kang J. W., *International Journal of Thermophysics*, vol. 46 (2025), 169.

Collection and Evaluation of Properties for the development of Korean Thermophysical Properties Databank (KDB)

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In the previous study, we presented a collection of pure properties and binary vapor-liquid equilibrium data for organic compounds through our website (mdlkdb.com) [1]. We implemented machine-learning-based prediction methods in the website. In this study, we expanded the database to include experimental properties such as surface tension, flash point, water-octanol partition coefficient, and autoignition temperature, as well as derived properties like the acentric factor and solubility parameter. A total of 2,363 data points were gathered from peer-reviewed journals and evaluated. The evaluation process involved outlier removal, comparisons with predictive models, and assessments against theoretical calculations of reported values. We assessed the uncertainty of the data points using the procedures established in our previous work [1]. Weighted mean estimation and χ^2 validation were used to determine the final reference values with $k = 2$ coverage uncertainties. These frameworks effectively identified inconsistent or erroneous data and validated the reliability of the collected information. The resulting standard reference property database offers high-quality, traceable thermophysical data that supports chemical safety evaluations, process design, and the development of advanced property prediction models.

Acknowledgment

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Significant references

1. Hwang, S.Y., Ryu, B.C., Kang, S.S., Bang, H. and Kang, J.W., *International Journal of Thermophysics*, vol. 46 (2025), 169

3.16

Thermophysical Properties

Hydrocarbon-Based Fluids



Application of CP-PC-SAFT with universal k_{12} value for simultaneous prediction of VLE, LLE and critical loci in systems of gases and aliphatic hydrocarbons with substituted aromatic and heterocyclic compounds.

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One of the major factors determining the extent of phase separations in fluid systems are the interrelations between the pure compound T_c and P_c . The differences between them are expressed in degrees of asymmetry and extends of phase splits. For example, the molar solubilities of gases are clearly dependent on their critical temperatures. As the T_{c1} get lower, the systems become more asymmetric, increasing thus the extends of phase separations and decreasing the solubilities. However, in the cases of more symmetric systems the P_{c1} become particularly important. Typically, higher P_{c1} of solvents results in their higher solubilities. For example, although benzene and *n*-octane have relatively similar T_{c1} values, benzene is much more solvable in various solvents, which could be attributed to its higher P_{c1} . Such considerations may also explain a behaviour characteristic for the homologues series of *n*-alkanes. Unsurprisingly, the largest extends of phase separation occur in the systems of CH₄ and they decrease moving to C₂H₆, C₃H₈, and *n*-C₄H₁₀. Usually, the smallest LLE phase splits and the lowest UCSTs take place in the systems of around *n*-C₄ – *n*-C₆. However, further increasing the chain length of *n*-alkanes results in gradual growth of LLE and rise of UCSTs. On one hand the heavier *n*-alkanes have higher T_{c1} and, therefore, their systems are supposed to be more symmetric, which should reduce the LLE. However, on the other hand, their P_{c1} decrease, which supposed to have quite the opposite effect. Apparently, in the cases of most *n*-alkane's homologues series, influence of the decreasing P_{c1} after *n*-C₆ becomes stronger and the LLE actually increase. The critical constants of solvents also influence the extents of phase splits. In particular, the increase of T_{c2} results in growing immiscibility. Obviously, quantitative portrayal of the systems asymmetry created by interrelations between the pure compound T_c and P_c is a non-trivial task. However, strict adherence to these critical constants is supposed to improve the over-all robustness and reliability of EoS models. The Critical Point-based Revision of PC-SAFT (CP-PC-SAFT)[1] satisfies this criterion. Thus far [2,3], the capabilities of its simplest polarity- and association-neglecting version to simultaneously predict VLE and LLE in systems of Ionic Liquids with universal k_{12} values was considered. The current presentation summarizes its application with the universal $k_{12} = 0.023$ adjusted to the VLE data of the randomly selected system propane – phenol for predicting the VLE, LLE and binary critical data available for a large variety of systems containing non-associative gases and aliphatic hydrocarbons as solutes and various solvents, including substituted aromatic compounds (phenol, *m*-cresol, 2-methoxyphenol, 2-phenylethanol, 2-ethylphenol, pyridine, aniline, benzylamine, *o*-toluidine, acetophenone, and benzaldehyde) along with heterocyclic compounds (*N*-methyl-2-pyrrolidone, pyrrole, furan, tetrahydrofuran, thiophene, 1,4-dioxane, tetrahydrothiophene, γ -valerolactone, 2,3-benzofuran, and sulfolane). It is demonstrated that CP-PC-SAFT reliably predicts both the available high pressure VLE and the UCST data in diverse homologues series. Besides that, this approach accurately estimates the compositions of the solvent-rich LLE phases but overpredicts the content of solvents in the *n*-alkane-rich ones. Predictions of ternary LLE in industrially important systems containing sulfolane are also presented. Impacts of the pure compound T_c and P_c data on the considered phase equilibria are also discussed.

References

1. Polishuk, I. *Ind. Eng. Chem. Res.*, vol. 53 (2014), pp. 14127–14141.
2. Polishuk, I. *J. Mol. Liq.*, vol. 310 (2020) pp. 113266.
3. Polishuk, I., Chiko, A., Cea-Klapp, E., Garrido, J. M. *Ind. Eng. Chem. Res.*, vol. 60 (2021) pp.13084–13093.

Vapor-Liquid-Liquid Equilibria and Their Related Interfacial Properties for Ternary Aqueous Mixtures

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Biofuels are regarded as a short-term solution to reduce reliance on fossil fuels and mitigate emissions of environmentally harmful gases. Exemplary biofuels are low-molecular-weight bioalcohols, which can be used directly as a fuel or as a bio-oxygenate additive for gasoline. Bioalcohols are produced from inexhaustible biomass resources; however, they are usually produced in aqueous media, which is one of the main limitations of their direct use as fuels or oxygenate additives for gasoline engines. Therefore, in order to incorporate them as a renewable fuel, it is necessary to dehydrate them to a technically acceptable water content (i.e. $\leq 1\%$ v/v). In this regard, heterogeneous azeotropic distillation (HAD) is considered to be one of the most advantageous techniques. In the HAD process, a light entrainer is added to the aqueous-alcoholic feed with a view to enhancing the separation by forming a ternary heterogeneous azeotrope. In selecting the most appropriate entrainer, it is necessary to evaluate the thermodynamic properties at the three-phase condition for ternary mixtures comprising water, bio-alcohol, and the entrainer. In this work, a combined approach involving two novel experimental methodologies is presented for measuring vapor-liquid-liquid equilibria (VLLE) and their associated interfacial tensions. Concurrently, a theoretical predictive model is employed, the foundation of which is the SAFT-VR Mie EoS in conjunction with the square gradient theory. This facilitates the modelling of the VLLE and interfacial properties. To illustrate this point, the following figures show the phase equilibria and interfacial properties for the case of water (1) + dimethyl carbonate (2) + 1-butanol (3) ternary mixture.

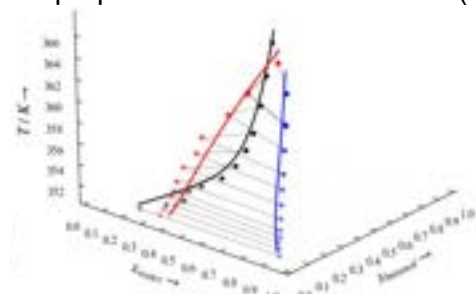


Figure 1. VLLE for water (1) + dimethyl carbonate (2) + 1-butanol (3) ternary mixture at 101.3 kPa. —: SAFT-VR Mie. Experimental data: ●: aqueous phase; ●: organic phase; ●: vapor phase.

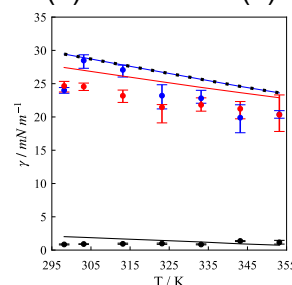


Figure 2. Interfacial tensions for water (1) + dimethyl carbonate (2) + 1-butanol (3) ternary mixture at 101.3 kPa. —: SAFT-VR Mie + SGT. Experimental data: ●: aqueous-vapor; ●: organic-liquid; ●: organic-vapor.

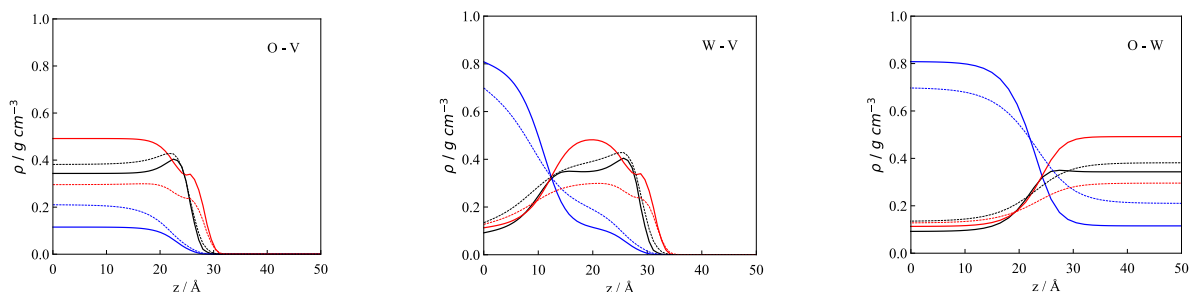


Figure 3. Predicted interfacial profiles ($\rho_i - z$) in Organic-Vapor (OV); Aqueous-Vapor (WV) and Organic-Aqueous (OW) Interfaces. —: water; —: dimethyl carbonate; —: 1-butanol at 303 K and - - -: water; - - -: dimethyl carbonate; - . - : 1-butanol at 353 K.

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Interfacial Tension in Multiphase Systems Consisting of an *n*-Alkane or/and a 1-Alcohol with Carbon Dioxide Using Equilibrium Molecular Dynamics Simulations and Surface Light Scattering

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Mixtures containing organic solvents and carbon dioxide (CO₂) are of importance in various fields of process engineering such as catalysis and separation technology. In the latter field, for example, the use of supercritical CO₂ allows to enhance the mass transport within the bulk phases and across interfaces by reducing viscosity and interfacial tension of hydrocarbons/CO₂ mixtures compared to the values of the CO₂-free systems. It is known that the addition of alcohols can further reduce the interfacial tension and increase the solubilities in mixtures with organic solvents and CO₂, referring to the so-called moderating effects of the alcohols. While studies on the phase behavior of CO₂-based mixtures containing hydrocarbons and/or alcohols are given in the literature, see, e.g., Ref. 1, corresponding information on is scarce, in particular at pressures above about 8 MPa, where liquid-liquid miscibility gaps can be found.² The main objective of the present contribution is to investigate the interfacial tension of binary mixtures of *n*-alkanes or 1-alcohols with CO₂ experimentally and theoretically. These systems represent the underlying binary subsystems of the ternary systems containing *n*-alkanes, 1-alcohols, and CO₂. Surface light scattering (SLS) is applied at macroscopic thermodynamic equilibrium to determine the interfacial tensions simultaneously with viscosities at vapor-liquid, vapor-liquid-liquid, and liquid-liquid equilibrium at temperatures from (298.15 to 338.15) K and pressures up to 20 MPa down to vanishing . These data serve to check the predictive performance of equilibrium molecular dynamics (EMD) simulations based on all-atom or united-atom force fields for the *n*-alkanes and 1-alcohols. To interpret the experimental results, the EMD simulations are used to obtain insight into fluid structure in the bulk of the fluids and at their interfaces. Results will be shown and discussed for CO₂-containing binary mixtures involving the *n*-alkanes *n*-octane and *n*-hexadecane as well as the 1-alcohols ethanol, 1-butanol, and 1-octanol. Based on this, the moderating effects of alcohols on will be analyzed and discussed for a model ternary system consisting of *n*-hexadecane, 1-octanol, and CO₂.

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Significant references

1. A.P.P. Simoncelli, W. Gómez, R.M. Charin, F.P. Fleming, P.M. Ndiaye, F.W. Tavares, *Fluid Phase Equilib.*, vol. 515 (2020) p. 112574.
2. A. Georgiadis, F. Llovel, A. Bismarck, F.J. Blas, A. Galindo, G.C. Maitland, J.P.M. Trusler, G. Jackson, *J. Supercrit. Fluids*, vol. 55 (2010) pp. 743–754.

Thermophysical Properties of Paraffinic, Naphthenic, Polyalphaolefin and Ester Base Lubricants at High Pressures

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The impact of lubricants on energy efficiency, reliability, average life, and noise levels of industrial machinery is significant. A comprehensive understanding of the lubricating properties and the thermophysical characterization of base oils of various natures (mineral, synthetic, and vegetable oils) is imperative. Knowledge of the density at high pressures is essential for hydraulic fluids and to determine the dynamic viscosity as a function of pressure and, subsequently, the pressure–viscosity coefficient and film thickness. The last parameters are crucial for selecting the appropriate lubricant for specific applications. Contact angle measurements are utilized to assess the capacity of lubricants to disperse on a solid surface (i.e., wetting ability). This capacity is a pivotal factor in numerous industrial processes involving two distinct phases and significantly impacts the lubrication performance.

The present work provides high-accurate experimental data on density, isothermal compressibility, thermal expansion coefficient, and viscosity over a temperature range from 278.15 to 373.15 K at a high pressure (up to 100 and 150 MPa for density and for viscosity, respectively) as well as contact angle values at atmospheric pressure of eight base lubricants to analyze the effects of the chemical nature and of the viscosity grade on these properties. Four synthetic oils (polyalphaolefin and ester) and four mineral oils (paraffinic and naphthenic) of two viscosity grades were selected [1]. The oils with the lowest viscosity grades could be used in the formulation for automatic transmission fluids (ATF) in electric vehicle configurations where the ATF and the electric motor are in contact, as the motor is housed within the transmission [2].

Densities were measured with a vibrating tube densimeter (HPM Anton Paar). Dynamic viscosities at high pressures were experimentally determined using a falling body viscometer. Contact angles were measured using the sessile drop method through a Phoenix MT(A) contact angle analyzer.

The ester with the highest viscosity is the most compressible lubricant, while the polyalphaolefin (PAO4) is the least compressible. PAO4 has the lowest contact angle, indicating the best wetting. The most viscous paraffin has the highest contact angle. Mineral naphthenic oils exhibited the greatest increase in viscosity with pressure, resulting in the highest viscosity-pressure parameters, while synthetic polyalphaolefin oils exhibited the least increase. Furthermore, naphthenic base oils show the greatest variation in film thickness with temperature, which could diminish their efficiency compared to other base oils.

Acknowledgment

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Significant references

1. A. Villamayor, M. J. G. Guimarey, F. Mariño, J. M. Liñeira del Río, F. Urquiola, R. Urchegui, M. J. P. Comuñas, and J. Fernández, *Lubricants*, vol. 11 (2023) 55.
2. A.G. Tuero, C. Sanjurjo, N. Rivera, J.L Viesca, R. González, and A.H Battez, *J. Mol. Liq.* vol. 367 (222) 120581.

3.17

Thermophysical Properties Complex Liquids III



Exploring the Solubility Behavior of Kraft Lignin on Alternative Solvents and Their Aqueous Solutions

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The global reliance on fossil resources for energy and chemical supplies is unsustainable due to their finite nature and environmental impacts.¹ Lignocellulosic biomass emerges as a strategic precursor for biorefineries, offering an abundant alternative for producing bio-based fuels and platform chemicals that traditionally derive from fossil sources.¹ However, its effective valorization is hindered by the challenge of fractionating its major components—cellulose, hemicellulose, and lignin—without compromising its chemical structure.² Conventional methods, such as the Kraft process, employ harsh solvents that degrade the lignin structure, limiting its potential applications.³ Therefore, the development of milder, alternative biomass fractionation processes is crucial to unlock the full potential of the lignocellulosic biomass, as well as to develop methods to valorize industrially modified lignin produced in high quantities, such as those obtained from the Kraft process.

This work addresses this challenge by investigating the dissolution behavior of Kraft lignin in neat protic ionic liquids (PILs), aprotic ionic liquids (AILs), eutectic solvents (ESs), and their aqueous solutions. Experimental lignin solubility data were obtained in five pure pyrrolidinium-based PILs, four imidazolium-based AILs, and five betaine-based ESs using the shake-flask method coupled with UV-Vis spectroscopy, at 313.2 K.⁴ Additionally, solubility was measured for aqueous solutions of these solvents across the entire compositional range. To investigate the solvent's influence on the lignin structure, recovered lignin from the solvents without water addition was analyzed by Gel Permeation Chromatography (GPC) and Fourier Transform Infrared (FTIR) spectroscopy.

The results demonstrate that all the pure solvents exhibit good dissolution capacity, with the solubilities consistently exceeding 25 wt%. Generally, the ionic liquids showed higher dissolution capacities than the ESs, with some specific AILs ([BMIM]BF₄) and PILs (pyrrolidinium formate, pyrrolidinium propionate) achieving solubilities over 60 wt%. For the aqueous systems, the solubility curves for the water-ES solutions reveal that maximum peaks occur up to 40 wt% of water. In contrast, ionic liquids typically show a decrease in solubility as water content increases. Regarding the characterization, GPC results indicate that lignin recovered from AILs and ESs is more homogenous, whereas solubilization in PILs leads to increased structural heterogeneity. No substantial chemical modification in any of the recovered lignin samples was identified from the FTIR analysis.

Acknowledgment

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Significant references

1. B. Segers, Pernechele, P. Nimmegeers, M. Spiller, G. Stryjek, E. Jasiukaitytė-Grojzdek, E. Dace, T. Kikas, and J. M. Marchetti, *RSC Sustain.*, vol. 2 (2024), pp. 3730-3749.
2. M. Zhou, O.A. Fakayode, A.G.A. Yagoub, Q. Ji, and C. Zhou, *Renew. Sustain. Energy Rev.*, vol. 156 (2022), pp. 111986.
3. X. Liu, F.P. Bouxin, J. Fan, C. Hu, and J.H. Clark, *ChemSusChem*, vol. 13 (2020), pp. 4296-4317.
4. R.M. Dias, A.M.C. Lopes, A.J.D. Silvestre, J.A.P. Coutinho, M.C. Costa, *Ind. Crop. Prod.*, vol. 143 (2020), pp. 111866.

Integrated COSMO-RS and soft-SAFT Modelling for the Pre-design of Deep Eutectic Solvents in Lignocellulosic Biomass Fractionation

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The selective fractionation of lignocellulosic biomass into lignin and cellulose–hemicellulose streams is a critical step in the development of efficient biorefinery schemes.¹ Deep eutectic solvents (DESs) have emerged as promising, tunable solvents for this purpose. However, their vast chemical design space demands predictive tools capable of screening viable candidates prior to experimental evaluation. In this work, we combine COSMO-RS and molecular-thermodynamic equation-of-state models based on soft-SAFT equation of state to support the pre-design of DESs tailored for biomass separation.² COSMO-RS is employed to estimate activity coefficients for lignin- and carbohydrate-derived species in DES, enabling the calculation of partition coefficients that govern solvent selectivity.

Given the structural complexity of lignin and hemicellulose derivatives, we construct surrogate molecular models that capture the dominant functional groups while reducing computational cost. These surrogates allow systematic exploration of chemical families and facilitate high-throughput screening of DES formulations, that include Choline Chloride with a variety of HBDs, such as Urea, Betaine and Carboxylic Acids. We identify the most promising DES candidates with favorable partition behavior for lignin extraction while maintaining limited solubility of cellulose and hemicellulose. The final selection is modeled with soft-SAFT, providing a physically grounded description of hydrogen-bonding, polarity, and dispersion interactions within DESs, allowing a more accurate description of the main thermophysical properties in a wider range of temperature conditions. The integrated workflow accelerates solvent selection and provides a rational basis for subsequent experimental validation and process design.

Acknowledgment

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Significant references

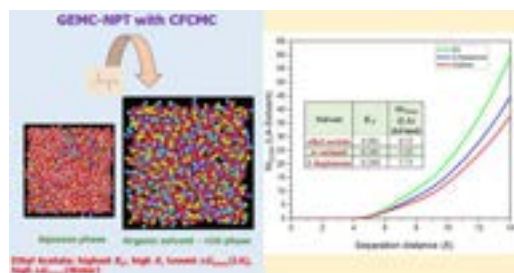
1. M. Wang et al. (2025). *Industrial Crops and Products*, 229, 121028. <https://doi.org/10.1016/j.indcrop.2025.121028>
2. Cheng et al. (2024). *Chemical Engineering Journal*, 499, 1, 155980. <https://doi.org/10.1016/j.cej.2024.155980>.

Solvent Extraction of Levulinic Acid from its Aqueous Solution: A Monte Carlo Simulation Study

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Levulinic acid (LA) is a keto-acid and a versatile building block for producing a wide variety of bulk chemicals. The main objective of this study is to predict the organic solvent which will efficiently and effectively extract LA from its aqueous solution via liquid – liquid extraction using the fundamental molecular simulation approach and also to gain insights into the molecular level structure of the coexisting liquid phases. A GEMC–NPT simulation study [1] of the liquid–liquid extraction of LA from its aqueous solution via six organic solvents has been performed at 313.15 K and 101.325 kPa to identify the optimal solvent. Continuous fractional component Monte Carlo approach [2] (by using Brick–CFCMC) to enable efficient sampling of dense coexisting liquid phases via particle transfer moves for chemical equilibrium has been adopted. The solvent performance indicators (SPIs) are distribution coefficient (K_D), separation factor (S), Gibbs free energies of transfer (ΔG_{trans}) for LA and water from the aqueous to the organic solvent–rich phase. Based on SPIs, ethyl acetate is the optimal solvent; benzene, toluene and xylene are ineffective. The molecular level structure resulting from the complex interplay of interactions present has been investigated by computing the center of mass (COM) – COM radial distribution functions (RDFs) and their corresponding number integrals (NIs) in both the coexisting phases. The NIs from these RDFs for LA – LA, LA – water, solvent – water and water – water molecules in the organic solvent–rich phase exhibit trends which are correlated with those in the SPIs for the solvents. The extent of hydrogen bonding between the hydrogen atom in carboxylic acid group of LA with that of the oxygen atom of the solvent molecule, and with the oxygen atom of water molecule has been investigated by computing site–site intermolecular RDFs. The NIs of LA – LA RDFs including the first two peaks agree with the trends in K_D and ΔG_{trans} of LA for ethyl acetate, *n*-octanol and 2-heptanone. Further, NI values from LA–water site–site RDFs including the first and second coordination shells show trends in agreement with ΔG_{trans} of water.

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(Sanction Order #: CRG/2022/000148 of Anusandhan National Research Foundation (ANRF)).

Significant references

1. Keasler, S.J., Lewin, J.L., Siepmann, J.I., Gryska, N.M., Ross, R.B., Schultz, N.E. and Nakamura, M. Molecular insights for the optimization of solvent-based selective extraction of ethanol from fermentation broths. *AIChE Journal*, 59(8), pp.3065-3070 (2013).
2. Shi, W. & Maginn, E. J. Continuous fractional component Monte Carlo: An adaptive biasing method for open system atomistic simulations. *J. Chem. Theory Comput.* 3 (2007), 1451–1463.



A Comprehensive Analysis of Thermophysical Properties of Nanofluids

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The use of nanofluids in advanced heat transfer applications requires reliable data of their thermophysical properties, which are often subject to significant variability due to inconsistent analysis and research methodologies. This work is presented as a comprehensive analysis of the thermophysical properties of nanofluids that are most complex to evaluate, i.e. thermal conductivity, dynamic viscosity, and surface tension. The authors collected measurements from numerous literature studies and subsequently harmonized them into a unified database. The database contains information on a wide operating range of temperatures, mass and volume concentrations, base fluid types (e.g., simple mixtures) and nanoparticles (e.g., metal oxides, hybrids), dispersion treatments, pH, zeta potential, and stability. The database was used to test correlations available in the literature, and also to develop and validate new semi-empirical models to describe thermal conductivity, dynamic viscosity, and surface tension for a wide range of nanofluids. The findings demonstrate that data standardization and systematic comparison facilitate the identification of robust trends, thereby significantly enhancing the predictive capability of models in comparison to the conventional correlations reported in the extant literature. The analysis therefore provides a unified basis for the thermo-fluid dynamic analysis of nanofluids and supports the design of advanced thermal systems through the use of more reliable properties and more consistent models.

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Thermophysical Properties

Refrigerants and Lubricant Oils II



An Assumption to Simplify the Modeling of Oil-Refrigerant Mixtures in Thermodynamic Cycles

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The presence of oil in thermodynamic cycles alters the properties of the refrigerant when considered in its pure form (enthalpy, density, vapor–liquid equilibrium, etc.), making the evaluation of cycle performance more challenging, particularly at high oil fractions. In particular, oil introduces a temperature glide during phase changes, leading to the appearance of an apparent superheat relative to the saturation temperature of the pure refrigerant.

The assumption introduced here is used to simplify the computational complexity of calculations involving oil–refrigerant mixtures. Let us imagine a two-phase oil–refrigerant mixture embedded in a fixed volume at a given pressure and temperature. The vapor phase is assumed to be composed only of refrigerant, while the liquid phase is an oil–refrigerant solution. A question to be asked is: what could be the states of the refrigerant and the oil to be mixed together in order to obtain this final state? This question introduces the concept of “desolubilization”. In this concept, two states are defined: the “mixed state”, where the solubility equations govern, and the “split state”, where solubility is neglected and the refrigerant behaves like a pure fluid, despite the presence of oil.

Assuming a “split state” consequently allows the simplification of the calculations of heat transfer and compression processes. First, the equations underlying this assumption are presented in this paper. To switch from one state to another, energy and mass conservation can be applied, while a third equation must be added to link pressure and temperature. Finally, the assumption is tested through applications involving heat transfer and compression processes, by comparing the computational time and evaluating the relative error between the case in which the assumption is used and the case in which it is not.

Density and Speed of Sound Measurements of Asymmetric Oil-Refrigerant Mixtures

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Oil-injected rotary-type positive displacement compressors are widely used in refrigeration cycles due to their robustness and high performance. However, their overall efficiency is strongly influenced by complex two-phase surge and gap flows that inevitably arise during operation. These flows involve intricate interactions between refrigerants and lubricating oils within narrow gaps formed by stationary and moving walls, making their characterization particularly challenging. Further technological progress is currently limited by the lack of accurate models describing the thermophysical properties of highly asymmetric oil-refrigerant mixtures. Experimental data for such mixtures remain extremely scarce, hindering the development and validation of theoretical and numerical models essential for reliable compressor design and performance optimization.

To address this gap, we present new experimental data on the density and speed of sound of two surrogate oils, *n*-pentane and squalane, as well as mixtures of *n*-pentane with propane, serving as a first step toward studying more asymmetric oil-refrigerant systems. The measurements were performed using a commercially available vibrating-tube densimeter supported by advanced data analysis and calibration procedures. The temperature range investigated extends from 273 K to 423 K, with pressures up to 90 MPa. The expanded combined uncertainty ($k = 2$) in density is estimated to be $1.93 \text{ kg}\cdot\text{m}^{-3}$. In addition, the speed of sound was measured using the double-path pulse-echo technique, over the exact same temperature and pressure range. The expanded combined uncertainty ($k = 2$) is estimated to be $1.27 \text{ m}\cdot\text{s}^{-1}$.

These accurate combined measurements provide a valuable experimental basis for improving the modeling of thermophysical properties of oil-refrigerant mixtures. The presented dataset will be compared with data available in the literature and with values predicted using mixture models, such as the GERG-2008 equation of state [1]. Furthermore, it supports the development of more reliable equations of state and transport-property models for asymmetric fluid mixtures and contributes to enhancing the predictive capabilities required to optimize next-generation oil-injected compressor technologies in refrigeration and heat-pump applications. The data will be used within the *Archimedes Research Unit*—funded by the German Research Foundation (DFG)—for thermophysical property modeling.

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- [1] O. Kunz and W. Wagner, "The GERG-2008 Wide-Range Equation of State for Natural Gases and Other Mixtures: An Expansion of GERG-2004," *J. Chem. Eng. Data*, vol. 57, no. 11, pp. 3032–3091, Nov. 2012, doi: 10.1021/je300655b.

Gas-Solubility Measurements of Refrigerants in Refrigeration-Oil Surrogates Using Raman Spectroscopy

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Improving compression refrigeration cycles is essential for reducing energy consumption and environmental impact in refrigeration and heat pump systems. Their efficiency can be increased by optimizing compressor performance, which requires a deeper understanding of the complex multiphase flow of the oil-refrigerant mixture within the narrow clearances between the stationary and moving walls of the compressor. To address this challenge, the *Archimedes Research Unit*—funded by the German Research Foundation (DFG)—combines fluid dynamic experiments and simulations with thermophysical property measurements and modeling in a collaborative effort.

This contribution presents an improved optical methodology for gas solubility measurements of natural refrigerants (CO₂, propane) in refrigeration-oil surrogates (*n*-pentane, *n*-hexane, *n*-decane, squalane) using Raman spectroscopy. The method builds on the approach proposed by Lipinski and Richter¹, in which the Raman intensities of the solute are correlated with its partial density. This correlation is established through an initial calibration of the pure solute in the gas phase, enabling the composition of the liquid mixture to be determined from the partial densities of solvent and solute. The approach was previously validated with binary CO₂–water mixtures.¹ However, to apply this methodology to highly soluble, asymmetric oil-refrigerant mixtures with more complex Raman signatures, two major refinements were introduced: (1) an improved correction procedure using simultaneous refractive-index measurements to reconcile and equalize gas- and liquid-phase Raman intensity levels, and (2) a polarization-dependent Raman setup that improves signal quality and reduces background and fluorescence contributions.

The experimental data obtained may help close data gaps and support other subprojects of the *Archimedes Research Unit* in developing improved thermophysical property models, which will ultimately be integrated into fluid-dynamic simulations of complex multiphase surge and gap flows in rotary positive-displacement compressors.

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Significant references

1. G. Lipinski and M. Richter, *Physchem*, 1 (2021), pp. 176–188.

Thermophysical Properties of Binary Mixtures of Refrigerants and Refrigeration-Oil Surrogates by Dynamic Light Scattering

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A detailed understanding of surge and gap flows between the stationary housing and the moving rotor is essential for the efficient design of oil-injected compressors used in refrigeration cycles. Due to the solubility of the gaseous refrigerants in the refrigeration or lubrication oils, the associated working fluid consists of a binary refrigeration oil-refrigerant mixture. The Research Unit “Archimedes” funded by the German Research Foundation combines fluid dynamic experiments and simulations with thermophysical property measurements and modeling for the characterization of the multiphase flow of mixtures consisting of the natural refrigerants carbon dioxide (CO₂) or propane and refrigeration-oil surrogates in the form of linear or branched alkanes.

This contribution presents experimental results for the viscosity, interfacial tension, thermal diffusivity α , and mutual diffusion coefficient D_{11} of binary mixtures of CO₂ or propane dissolved in *n*-pentane, *n*-decane, *n*-hexadecane, or squalane (2,6,10,15,19,23-hexamethyltetracosane). The thermophysical properties were determined at saturation conditions for temperatures ranging from (253.15 to 423.15) K and amount fractions of the refrigerant $x_{\text{refrigerant}}$ up to 0.79. Dynamic light scattering (DLS) experiments were employed to simultaneously access α and D_{11} in the liquid phase by studying the dynamics of microscopic fluctuations in temperature or entropy and concentration in macroscopic thermodynamic equilibrium.¹ By applying DLS to vapor-liquid interfaces, also referred to as surface light scattering (SLS), α of the liquid phase and D_{11} could be determined by studying the dynamics of surface waves, which are caused by the thermal motion of molecules in equilibrium.² The composition of the liquid phase during DLS and SLS investigations was determined using polarization-difference Raman spectroscopy after an initial calibration with solubility data from the literature. On the basis of the investigations, the influence of the molecular characteristics of the refrigerant and the refrigeration-oil surrogate on the thermophysical properties could be derived and used to identify structure-property-relationships. For D_{11} , for example, a decrease with increasing $x_{\text{refrigerant}}$ was found for most binary mixtures with dissolved CO₂. This trend can be explained by the weak interactions between CO₂ and oil-surrogate molecules, which lead to a clustering of CO₂ molecules and, at high x_{CO_2} , even to the transition to a vapor-liquid-liquid equilibrium. In the case of α and D_{11} , a general decrease with increasing $x_{\text{refrigerant}}$ could be found for all mixtures, which might be explained by a weakening of the intermolecular interactions between oil molecules by the refrigerant.

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Significant references

1. C.J. Kankanamge, P. Damp, T.M. Koller, M.H. Rausch, D. Krug, W. Schröder, T. Klein, and A.P. Fröba, *Fluid Phase Equilibria*, vol. 596 (2025), article 114429.
2. F. Lorig, Z. Zhai, C.J. Kankanamge, P. S. Martinez Gonzalez, M. Richter, T.M. Koller, T. Klein, and A.P. Fröba, *Journal of Chemical and Engineering Data*, vol. 70 (2025), pp. 4582–4596.

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Thermophysical Properties Refrigerants II



On the intersection of Thermodynamics and Machine Learning for Designing Sustainable Refrigerant Blends

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The relentless ascent of global temperatures has cemented refrigeration and air conditioning as essential utilities for modern human comfort. Ironically, this very sector, by historically relying on synthetic refrigerants, inadvertently ignited the problem of global warming and facilitates its progression today through the use of high global warming potential (GWP) fluids. Though several global and regional legislations are already in effect to phase out high-GWP refrigerants, the search for pure fluids capable of meeting the stringent balance of environmental, safety, and technical requirements remains challenging. The development of refrigerant blends (binary, ternary, and beyond) emerges as a far more flexible and targeted alternative for designing suitable working fluids. Given the sheer number of available pure refrigerants and the infinite possibilities for their proportions, the experimental development of effective blends is prohibitively taxing. Thermodynamic modelling offers an elegant and rapid alternative for initial screening and design, a process that can be dramatically accelerated by integrating machine learning (ML) tools.

This contribution presents the collective efforts of a long-term project dedicated to the design of sustainable refrigerants and innovative cooling solutions. Through a series of compelling examples, we showcase the powerful intersection of machine learning and molecular thermodynamics in achieving this overarching objective. In one example, machine learning offers a robust methodology to predict flammability, a critical safety property, of pure refrigerants and blends, leveraging complex quantum chemical descriptors [1]. Another example highlights how ML facilitates the rapid parametrization of pure refrigerants' molecular models using the soft-SAFT molecular-based equation of state (EoS), necessary for accurately evaluating technical performance [2]. We further demonstrate the use of ML in predicting the saturation properties of refrigerant blends, assisting in the fine-tuning of molecular-based EoS predictions for phase equilibria, and estimating critical technical parameters like glide temperature [3]. The final example showcases the seamless integration of these tools with soft-SAFT to simplify the entire workflow for designing sustainable refrigerant blends. This integrated approach not only predicts necessary properties, often unavailable experimentally, but also expedites the screening process by dramatically reducing the reliance on high-throughput thermodynamic computations. These collective efforts herald a new era of molecular thermodynamics, where artificial intelligence becomes a cornerstone complementary tool for understanding the profound link between molecular features and macroscopic behavior. It is a shift that moves beyond mere speed, allowing us to truly peer deeper into the fundamental nature of matter and its potential for sustainable transformation.

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Significant references

1. C.G. Alba, I. I.I. Alkhatib, L.F. Vega, F. Llovell, *ACS. Sus. Chem. Eng.*, vol. 12 (2024), pp. 11561-11577.
2. I. I.I. Alkhatib, C. G. Alba, A. Dawrish, F. Llovell, L.F. Vega, *Ind. Eng. Chem. Res.*, vol. 61 (2022), pp. 6214-6234.
3. C.G. Alba, I. I.I. Alkhatib, L.F. Vega, F. Llovell, *App. Therm. Eng.*, vol. 262 (2025), pp. 125316.

Molecular Simulation-Guided Design of Eco-friendly and Safe Refrigerant Blend

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The global countries signed the Montreal Protocol, initiated in 1987, towards the Kigali amendment to phase out the use of CFCs, halon-1211, halon-1304, and halon-2402. HCFC causes notable ozone layer depletion and high global warming potential (GWP), and Hydrofluorocarbons (HFC) cause high global warming potential (GWP), so they must be phased out until new low-GWP refrigerants enter as per the Kyoto protocol signed in 1997 by many countries. Today's world is seeking alternative refrigerants, such as HFO, instead of HFCs due to their low global warming potential (GWP) and zero ozone depletion. However, their low coefficient of performance and mild flammability may cause explosions in the refrigeration system. In this work, the design of the refrigerant blend for eco-friendly and safe use is studied via molecular dynamics simulation. In this, we estimate the thermophysical properties such as density, surface tension, etc., and validate with literature results.

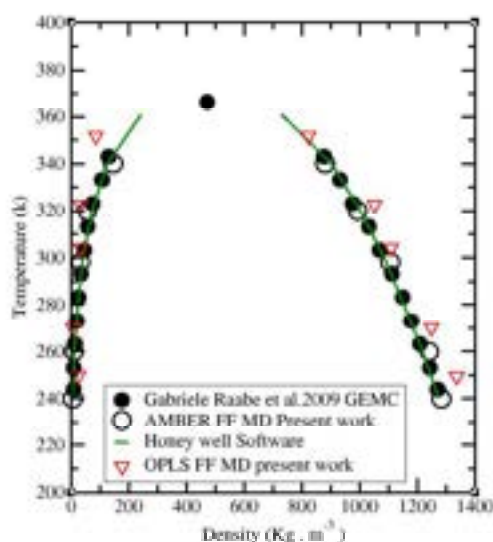


Figure 1 validates the molecular dynamics simulation results with literature results for R1234yf refrigerant

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Significant references

1. Montreal-Protocol-English-2018.pdf
2. Heredia-Aricapa, Y., J. M. Belman-Flores, A. Mota-Babiloni, J. Serrano-Arellano, and Juan J. García-Pabón. 2020. "Overview of Low GWP Mixtures for the Replacement of HFC Refrigerants: R134a, R404A and R410A." *International Journal of Refrigeration* 111:113–23. doi: 10.1016/j.ijrefrig.2019.11.012.
3. Raabe, Gabriele, and Edward J. Maginn. 2010. "Molecular Modeling of the Vapor-Liquid Equilibrium Properties of the Alternative Refrigerant 2,3,3,3-Tetrafluoro-1-Propene (HFO-1234yf)." *Journal of Physical Chemistry Letters* 1(1):93–96. doi: 10.1021/jz900070h.

Thermodynamic Evaluation of Cubic Equations of State for Solid-Fluid Equilibrium Predictions in Deep-Cryogenic Mixtures

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Solid-fluid equilibrium (SFE) at cryogenic temperatures provides essential thermodynamic information for aerospace propellants, mixed-refrigerant refrigeration technologies and high-temperature superconducting systems. However, accurately predicting SFE to prevent freeze-out blockages remains a major thermodynamic challenge. Existing predictive approaches typically rely on ideal-solution assumptions or purely empirical curve-fitting of cubic equations of state (EoS). While adequate for simple hydrocarbons, these conventional models exhibit significant deviations when extrapolated to deep-cryogenic temperatures for highly non-ideal mixtures containing polar fluorinated refrigerants and inorganic gases, as they fail to capture strong asymmetric intermolecular interactions.

To address this critical limitation, we propose an optimized and physically grounded thermodynamic framework. First, to overcome the scarcity of reliable ultra-low-temperature data, solid-liquid equilibrium phase boundaries for selected highly non-ideal mixtures (e.g., systems containing CF₄, R125, and N₂) were experimentally determined using a self-developed cryogenic visual apparatus. Combining this proprietary database with comprehensive literature data, a systematic thermodynamic evaluation based on the Peng-Robinson (PR) EoS was conducted across diverse cryogenic systems, including alkanes, inorganic gases, and hydrofluorocarbons. Crucially, instead of treating the binary interaction parameter k_{ij} as a purely empirical fitting parameter, its underlying physical dependencies were investigated. By systematically correlating regressed k_{ij} values with intrinsic molecular descriptors—namely dipole moment, acentric factor, and melting-point asymmetry—a generalized predictive correlation was developed. This relationship quantitatively reflects disparities in molecular size and polarity between solute and solvent molecules.

Incorporating this physically informed parameter into a rigorous solid-fugacity EoS framework enables accurate reproduction of complex SFE boundaries (p - T phase envelopes) without extensive experimental pre-fitting. The optimized model significantly mitigates the limitations of conventional EoS approaches, reducing temperature deviations to within 2 K. This work not only provides a reliable and generalized thermodynamic tool for anti-freeze design in cryogenic systems but also offers new insights into the microscopic molecular mechanisms governing macroscopic deep-cryogenic phase behavior.

Acknowledgment

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Significant references

1. X. Yang, D. Rowland, C.C. Sampson, P.E. Falloon, E.F. May. Evaluating cubic equations of state for predictions of solid-fluid equilibrium in liquefied natural gas production. *Fuel*. (2022) 314, p.123033.
2. Y. Zhao, X. Wang, W. Yin, Y. Zhao, M. Gong. Investigation on Solid-Liquid Equilibrium for Nitrogen+ Argon and Nitrogen+ Tetrafluoromethane Binary Systems. *Journal of Chemical & Engineering Data*. (2025) 70(10), pp.4204-4213.
3. X. Wang, X. Zhao, W. Yin, J. Zhang, Y. Zhao, X. Dong, M. Gong, A Cryogenic Visual Apparatus for Solid-Liquid Equilibrium and the Measurement of CH₄ + C₂H₆. *International Journal of Refrigeration*. (2023) 153, 110-115.

Density measurements on mixtures relevant for hydrogen liquefaction processes

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Hydrogen plays a key role in concepts for reducing greenhouse gas emissions. For long-distance transport of produced green or blue hydrogen, liquefaction is required. In the precooling stage of advanced hydrogen liquefaction processes, noble gas mixtures are considered as alternative refrigerants in addition to helium and hydrogen to improve the efficiency of the liquefaction process. Accurate thermophysical data and equations of state are essential for the design and optimisation of hydrogen liquefaction systems, enabling improved energy efficiency at cryogenic temperatures. Tkaczuk et al. [1] published new fundamental equations of state (EOS) for binary mixtures of helium, neon, and argon. However, due to the limited availability of experimental data, these EOS still exhibit significant uncertainties in densities calculated at low temperatures. For binary mixtures of neon + argon, no (p, ρ, T) data exist so far for temperatures between (121 and 298) K.

Previously, new (p, ρ, T) state points for helium + neon mixtures were measured [2] and a new EOS was subsequently developed based on these data [3]. In the present study, densities of binary mixtures of helium + argon and neon + argon were measured using a single-sinker magnetic-suspension densimeter. Measurements were carried out in the gas phase over the temperature range from (100 to 298.15) K and at pressures up to 10 MPa. The apparatus relies on Archimedes' buoyancy principle combined with a magnetic suspension coupling. Across the investigated state points, the densities of nearly equimolar helium + argon and neon + argon mixtures were measured with relative expanded combined uncertainties ($k = 2$) between (0.022 and 0.082) % and (0.016 and 0.089) %, respectively. The new measurements fill gaps in the experimental database and provide essential data for developing more accurate EOS for the helium + argon and neon + argon mixtures relevant to cryogenic hydrogen applications.

Acknowledgment

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Significant references

1. J. Tkaczuk, I. H. Bell, E. W. Lemmon, N. Luchier, and F. Millet, *J. Phys. Chem. Ref. Data*, vol. 49 (2020), 023101.
2. N. von Preetzmann and R. Span, *Cryogenics*, vol. 137 (2024), 103765.
3. H. Pamp, *Development of Fundamental Equations of State in Terms of the Helmholtz Energy for Binary Helium Mixtures*, Master's thesis, Ruhr University Bochum (2025).

3.20

Thermophysical Properties Hydrates



Molecular insights into the growth/dissociation of CO₂/CH₄ mixed hydrate: Effects of temperature, addition of NaCl, and CO₂

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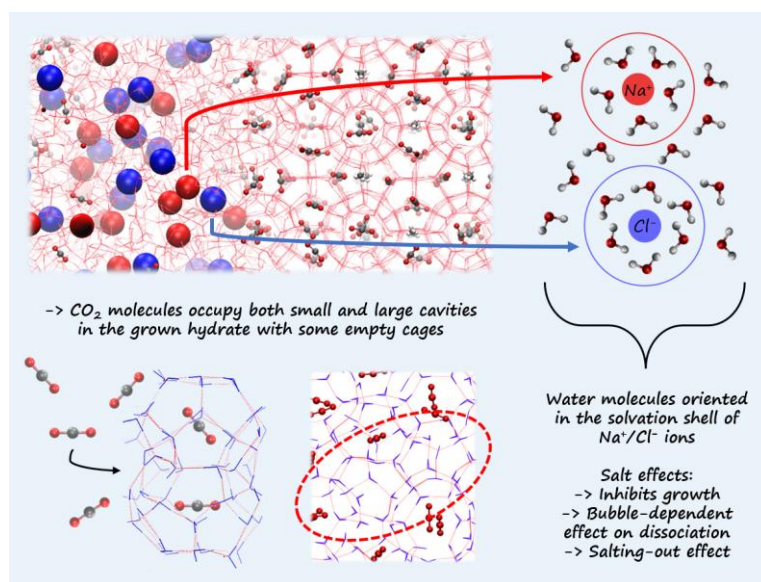
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Recovering CH₄ from hydrate reservoirs by injecting CO₂ has the potential to mitigate climate change by sequestering CO₂ in hydrate form. However, complete CH₄ recovery via this route is impractical, resulting in the formation of mixed CO₂/CH₄ hydrates. Understanding the stability of these mixed hydrates under different environmental conditions is essential for optimizing long-term CO₂ storage. Therefore, we perform molecular dynamics simulations of CO₂/CH₄ mixed hydrates under four conditions: (i) Lw-H phases only, (ii) with additional CO₂ molecules, (iii) with Na⁺/Cl⁻ ions, and (iv) with both CO₂ and salt ions in the aqueous phase. Simulations are performed at 30.5 bar and 250 and 273 K to investigate the tendency of the hydrate to either grow or dissociate. At 250 K, additional CO₂ molecules lead to the growth of CO₂ hydrate, while NaCl inhibits CO₂ hydrate growth by tightly binding water molecules in specific orientations, limiting their availability for hydrate formation. Nanobubble formation and the salting-out effect of NaCl on guest solubility are also observed. We observe that CO₂ molecules occupy both small and large cages in the grown CO₂ hydrate structure, with some unoccupied small and large cavities also present in the structure. At 273 K, hydrate dissociation occurs in all cases, highlighting the dominant influence of temperature. Here, NaCl shows a bubble-dependent influence on dissociation, i.e., enhanced dissociation in the presence of a CO₂ nanobubble and slower dissociation otherwise. The study presented here helps gain insights into efficient CO₂ storage in a hydrate reservoir.



Acknowledgment

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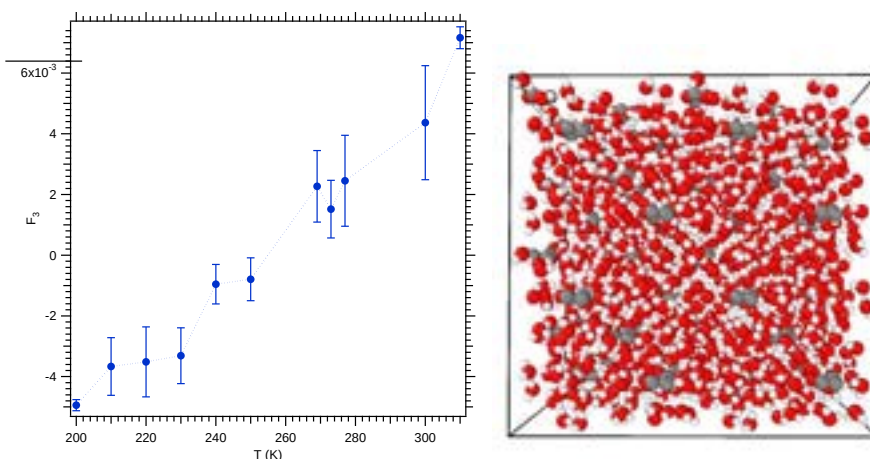
Predicting the Melting Point of THF Hydrate Using Metropolis Monte Carlo Simulations

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THF (tetrahydrofuran) hydrates form at 101.325 kPa and at temperatures at or below 277.15 K. This system is of interest because unlike conventional gas hydrates where the guest is a small hydrophobic molecule, THF is a polar molecule which is capable of forming hydrogen bonds with the water molecules in the cages and is miscible in water. The study of THF hydrates is therefore of interest from a science perspective and also storage of hydrogen is envisioned in THF hydrates at relatively milder conditions. THF hydrates form sII hydrate structure [1] and our initial configuration consists of unit cells with the THF molecules occupying the large cages. The force fields employed in our simulations are TraPPE-UA for THF [2] and TIP4P/Ice for water [3] with the Lorentz-Berthelot combining rules employed for the cross-terms. There are 1088 water molecules and 64 THF molecules. We have performed one-box Metropolis Monte Carlo simulations in the isothermal-isobaric ensemble in the entire temperature range from 200.15 K to 310.15 K at atmospheric pressure using the open source software package, MCCCSTowhee. For the melting point determination, the specific density is one order parameter. For host water molecules, we have also employed other order parameters which measure the deviation from a tetrahedral structure of water such as F_3 , S_g and $\dots$. We have also used two 4-body orientational order parameters, F_4 and F_{4t} which measure the planarity of two oxygen atoms within a spherical cut-off of 3.5 Å. These order parameters have specific values for clathrate-like structures and liquid water enabling the determination of the melting point. We have further explored the structure of the THF hydrates using site-site intermolecular radial distribution functions.



Acknowledgment

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Significant references

1. F. Takeuchi, M. Hiratsuka, R. Ohmura, S. Alavi, A. K. Sum, and K. Yasuoka, Water proton configurations in structures I, II, and H clathrate hydrate unit cells. J. Chem. Phys. 2013, 138, 124504.
2. S.J. Keasler, S.M. Charan, C.D. Wick, I.G. Economou, and J.I. Siepmann, Transferable potentials for phase equilibria-United atom description of five- and six-membered cyclic alkanes and ethers, J. Phys. Chem. B 116, 11234-11246 (2012).
3. J. L. F. Abascal, E. Sanz, R. García Fernández, C. Vega; A potential model for the study of ices and amorphous water: TIP4P/Ice. J. Chem. Phys. 15 June 2005; 122 (23): 234511.

Study of CO₂ solubility in hydrate inhibitor systems: Ethylene Glycol + Methanol

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The phase behavior of methanol + ethylene glycol mixtures with carbon dioxide was investigated experimentally at high pressure using a variable-volume PVT cell and the synthetic visual method. Two mixture compositions (methanol-rich and ethylene glycol-rich) were studied, and 47 transition pressures were determined, including liquid-vapor, liquid-liquid, liquid-liquid-vapor, and near-critical equilibria. Results showed that CO₂ solubility is considerably higher in methanol-rich systems, while ethylene glycol-rich mixtures exhibited limited miscibility. An unusual density inversion phenomenon was observed in methanol-rich systems containing 80 mol % CO₂, attributed to differences in compressibility between the coexisting liquid phases. This behavior was very well studied for CO₂ + hydrocarbon systems [1] and with the addition of an alcohol [2,3]. Thermodynamic modeling was performed using the PC-SAFT equation of state, with new parameters regressed for ethylene glycol and optimized binary interaction parameters for the MEG + CO₂ system. Overall, the model reproduced experimental data satisfactorily, although it could not capture the density inversion behavior. These results provide new insights into hydrate inhibitor-CO₂ phase equilibria and offer relevant data for flow assurance applications in oil and gas systems.

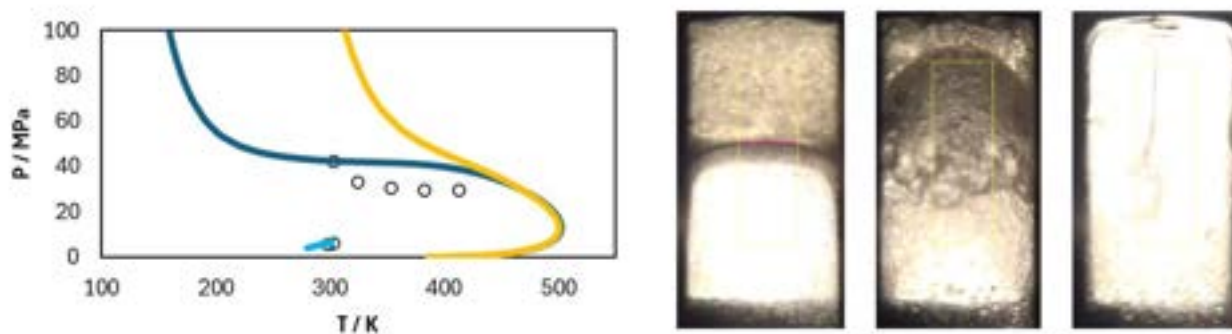


Figure 1. Joule-Thomson coefficient prediction and estimation comparison.

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References

1. S.E. Quiñones-Cisneros, Barotropic phenomena in complex phase behaviour, *Phys. Chem. Chem. Phys.* 6 (2004) 2307–2313. <https://doi.org/10.1039/B316123D>.
2. H. Pöhler, A.L. Scheidgen, G.M. Schneider, Fluid phase equilibria of binary and ternary mixtures of supercritical carbon dioxide with a 1-alkanol and an n-alkane up to 100 MPa and 393 K—cosolvency effect and miscibility windows (Part II), *Fluid Phase Equilib* 115 (1996) 165–177. [https://doi.org/10.1016/0378-3812\(95\)02835-8](https://doi.org/10.1016/0378-3812(95)02835-8).
3. A. Kordikowski, G.M. Schneider, Fluid phase equilibria of binary and ternary mixtures of supercritical carbon dioxide with low-volatility organic substances up to 100 MPa and 393 K: c, *Fluid Phase Equilib* 90 (1993) 149–162. [https://doi.org/10.1016/0378-3812\(93\)85010-J](https://doi.org/10.1016/0378-3812(93)85010-J).

Condensate Effects on Gas Hydrate Equilibrium and Nucleation Behaviour

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Accurate determination of hydrate equilibrium conditions is essential for defining safe operating margins in subsea production systems and for assessing the potential to reduce Mono Ethylene Glycol (MEG) circulation. Existing predictive models—such as Multiflash and ThermoFAST—provide reliable trends but require experimental validation for field-specific gas–condensate compositions. An operating Australian gas system, containing both light hydrocarbons and condensate, presented an opportunity to benchmark model accuracy and quantify the effects of condensate and MEG concentration on hydrate stability over a wide pressure range relevant to field operations.

Hydrate dissociation temperatures were measured using eight high-pressure stirred automated lag-time apparatus (HPS-ALTA) cells, including two ultra-high-pressure variants, operated in parallel under isochoric conditions up to 350 bara. Each stainless-steel cell contained approximately 5 mL of liquid comprising degassed water or MEG solution (0–40 wt %) with or without condensate (up to 50 vol.%). Both field gas and a composition-matched synthetic gas were tested. More than 80 equilibrium points and six hydrate formation-probability curves were obtained over 80–350 bara. Hydrate equilibrium points were determined from the intersection of pre- and post-dissociation pressure–temperature gradients obtained during stepwise heating cycles and refined via segmented linear regression of isochoric (p, T) data. The resulting data were compared with predictions from Multiflash 7.0 and UWA's ThermoFAST 2, including versions that incorporate condensate effects for improved model validation. Formation-probability distributions were constructed from repeated cooling–heating cycles.

Measured methane hydrate equilibria agreed with model predictions within ± 0.1 K, confirming the accuracy of the experimental apparatus. For the field gas, the presence of condensate lowered the measured equilibrium temperatures by more than 2 K at 80 bara and approximately 1 K at higher pressures. Incorporating condensate effects into Multiflash and ThermoFAST reduced these deviations to within ± 1 K. The inhibition effect increased with condensate-to-gas ratio (CGR) but became negligible below about 90 bbl/MMscf. MEG concentration caused a thermodynamic shift in the equilibrium boundary but did not significantly influence formation probability. At high condensate loadings (CGR $\approx$ 190 bbl/MMscf), the mean subcooling increased by roughly 3 K, indicating the inhibitory influence of condensate on hydrate formation. Subcooling distributions obtained from constant-cooling experiments were used to predict induction times, which showed excellent agreement with directly measured induction time distributions under identical conditions. Overall, the results show that existing hydrate models slightly overpredict hydrate stability, supporting the potential for safe MEG-reduction strategies in field systems when condensate effects are properly accounted for.

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3.21

Thermophysical Properties

High-Temperature Materials II



Interfacial reaction and reprecipitation mechanism between CaO-MgO-Al₂O₃-SiO₂ melts and thermal barrier coatings

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Introduction

The surface of Ni-based superalloy turbine blades for jet engines is coated with a thermal barrier coating (TBC) to improve heat resistance. Yttria-stabilized zirconia (YSZ) is often used as TBC. When the YSZ coating is subjected to the volcanic ash, the main constituent of which is CaO-MgO-Al₂O₃-SiO₂ oxides, the CMAS melt spreads wetting and penetrating the YSZ thin film, causing the YSZ to detach from the base material [1]: The YSZ dissolves in the CMAS melt, and monoclinic ZrO₂ with a lower Y content precipitate. [2] Monoclinic ZrO₂ transforms tetragonal and/or cubic crystal structures at higher temperatures, and volume changes due to transformation may cause damage of the film. Thus, it is important to investigate the mechanisms of ZrO₂ reprecipitation. In this study, the microstructure changes induced by the reaction between CMAS melts and single crystal YSZ were observed, and the solubilities of ZrO₂ into CMAS melts were measured using uniaxially pressed ZrO₂ powder tablets to clarify ZrO₂ reprecipitation mechanism.

Experimental

To observe the interfacial reaction, the 23 mol% YO_{1.5}-ZrO₂ single crystal plates (surface orientation {100}) and the 31.0CaO-11.2MgO-5.8Al₂O₃-52.0SiO₂ glass were used as substrates and CMAS melt. 20 mg of the CMAS melt was attached to the substrate and kept at 1300°C for 5 min, 10 min, 1 h and 24 h. The cross-sections of the samples were subjected to SEM and EPMA analyses to observe the microstructures and the line profiles of Ca, Mg, Si, Al, Y and Zr in the vicinity of the substrate-melt interface, respectively. To measure the solubilities of ZrO₂ into CMAS melts, the diffusion couple experiments were carried out: The reagent grade ZrO₂ powders were uniaxially pressed to obtain the tablets, and five different compositions of CMAS glasses were prepared. CMAS glass powders were placed on tablets and heated at 1300°C. The ZrO₂ concentrations in CMAS were measured.

Results

Figure 1 shows the SEM images of the cross-section of the samples heated at 1300°C for 5 min (a) and 1 h (b). The reprecipitation was observed for the sample heated for 5 min. For the sample heated for 1 h, the further reprecipitation (spherical structure) was observed above the firstly reprecipitated and grown phase (cell structure) (b). The line profiles reveal that both cell and spherical structures

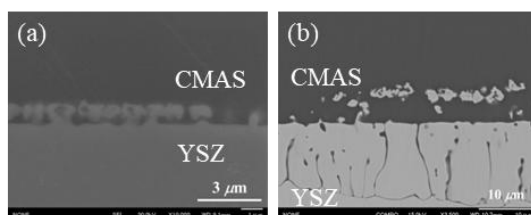


Figure 1 SEM images of the cross-section of the samples heated at 1300°C for 5 min (a) and 1 h (b).

are ZrO₂ containing Y₂O₃, CaO and MgO, and the ZrO₂ concentrations are in the hierarchy of spherical > cell > substrate. The ZrO₂ solubility experiments reveal that the saturated solubilities of ZrO₂ in CMAS is smaller as the CaO and MgO concentrations are smaller and the Y₂O₃ concentrations are larger.

Conclusion

The reprecipitation of ZrO₂ in CMAS at the interface is caused by the change in the saturation solubility of ZrO₂ with the composition change of CMAS due to its reaction with YSZ.

Significant references

1. A. G. Evans, D. R. Mumm, J. W. Hutchinson, G. H. Meier and F. S. Pettit, *Prog. Mater. Sci.*, vol. 46 (2001), pp. 505-553.
2. S. Krämer J. Yang and C. G. Levi, *J. Am. Ceram. Soc.*, vol. 89 (2006), pp. 3167-3175.

Thermophysical Properties of High-Performance Carbon Insulation for Space Applications

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As part of the EU-funded ISBA project, CAE developed nanoporous, fiber-reinforced carbon xerogels as mechanically stable, high-temperature-resistant thermal insulation materials for rocket engines and tiles for reentry vehicles. Consistently meeting the various objectives—mechanical stability, low thermal conductivity, and, due to the application in space, low weight—is a challenging task. Theoretical and experimental investigations were carried out to deepen the understanding of such insulation materials and ultimately obtain an optimized insulation material that can also be manufactured on an industrial scale.

Fibre-reinforced carbon xerogels are monolithic, highly porous carbon materials, which exhibit small pore and particle sizes together with high extinction coefficients for thermal radiation. Hence specifically prepared carbon xerogels with customized properties provide significantly lower thermal conductivities than carbon fibre felts [1], especially at high temperatures up to 2800 °C. Therefore, carbon xerogels are promising for next-generation thermal insulation under extreme conditions.

Generally, the heat transport through porous materials is due to the solid thermal conduction via the skeletal framework, the gaseous conduction within the pores and the radiative heat transfer through the material. These heat transport mechanisms depend on structure and morphology of the porous material, such as porosity, pore and particle sizes as well as on the refractive index of the material. The solid thermal conductivity can be minimized by reducing the density, the gaseous thermal conductivity can be decreased by small pores in the nanometer range and the radiative thermal conductivity can be lowered by increasing the extinction coefficient.

In this work carbon xerogel/fibre-composites have been prepared by pyrolysis of sol-gel synthesized organic xerogel precursors with optimized synthesis and pyrolysis route. For evaluating and improving the performance of the resulting carbon xerogels on the one hand structural characterizations have been performed in order to determine the density, particle and pore sizes as well as specific surface and elastic modulus using for example scanning electron microscope images, nitrogen sorption and ultrasonic measurements. On the other hand, the thermal diffusivity was measured by the laserflash to derive effective thermal conductivity values at high temperatures up to 2100 °C and different atmospheres (vacuum, argon, helium). Analytical models were used to correlate the structural properties and thermophysical properties, especially for the three heat transfer mechanisms mentioned above. By comparing the theoretical models with the experimental results, the properties of carbon xerogels were optimized and their performance validated. At a measurement temperature of 2100 °C, the lowest thermal conductivity value, i.e., $0.346 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ (under helium atmosphere), was determined for a xerogel with an average pore size of about 470 nm and a macroscopic density of 261 kg m^{-3} .

Acknowledgment

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Significant references

1. M. Wiener, G. Reichenauer, S. Braxmeier, F. Hemberger and H.-P. Ebert, *Int. J. Thermophys.*, 30 (2009) 1372-1385.

Optical properties of Cr₂O₃ as a foundation for radiative transfer modeling in chromia-forming alloys

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Chromium is a crucial element in alloys used in aerospace components, which are exposed to high temperatures during service, leading to a Cr₂O₃ oxide layer formation. Consequently, the optical properties of the material, especially the emissivity, change significantly. Therefore, it is essential to know how the formation of a chromia layer affects those optical properties for an appropriate thermal management. Owing to the lack of information about the optical indices of chromia reported in literature [1], an attempt to determine them was done.

The optical indices can be extracted from measurable optical properties, such as the reflectivity. To investigate these relationships, two high-purity chromium targets were analyzed. First, the emissivity of pure chromium was measured at high temperatures and for different emission angles, in vacuum using the HAIRL emissometer of the University of the Basque Country [2]. Based on those measurements, reflectivity spectra were calculated and fitted using a two-carrier Drude model.

In parallel, the second chromium target was oxidized isothermally at 800 °C in pure oxygen, obtaining a micrometric, rough and discontinuous Cr₂O₃ oxide layer, as confirmed by microstructural characterization. In order to extract its optical indices, similar emissivity measurements as those of pure chromium were performed and the calculated reflectivity spectra were fitted using a Drude Lorentz model. An effective medium approximation based on the Bruggeman theory was considered together with the aforementioned model to account for the surface roughness [3]. Finally, optical indices of Cr₂O₃ were determined, with significant differences with respect to single-crystal Cr₂O₃ [1].

The optical indices obtained in this work contribute to filling the gap in the literature regarding chromia and provide a basis for future research on the optical properties of chromia-forming alloys at high temperatures. Future work will be devoted to the study of Inconel 718 and Cr-base medium-entropy alloys.

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Significant references

1. Renneke, D. R., & Lynch, D. W. (1965). *Infrared lattice vibrations and dielectric dispersion in single-crystal Cr₂O₃*. Physical Review, 138(2A), A530–A533.
2. González de Arrieta, I., Echániz, T., Fuente, R., Campillo-Robles, J. M., Igartua, J. M., & López, G. A. (2020). *Updated measurement method and uncertainty budget for direct emissivity measurements at the University of the Basque Country*. Metrologia, 57(4), 045002. <https://doi.org/10.1088/1681-7575/ab84ff>
3. Fodor, B., Kozma, P., Burger, S., Fried, M., & Petrik, P. (2019). *Effective medium approximation of ellipsometric response from random surface roughness simulated by finite-element method*. arXiv. <https://arxiv.org/abs/1902.09903>

Advancing Discharge Crucible Measurements Through Bayesian Experimental Design and Wetting Modeling

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Thermophysical properties such as density, viscosity and surface tension are essential inputs for process modelling in metallurgy and materials processing but remain difficult to measure for reactive and high-temperature liquids. The Discharge Crucible (DC) method offers an attractive option to infer these properties from the transient draining dynamics of a liquid through a nozzle. However, parameter estimation is often poorly conditioned, given that the measured signals can be weakly sensitive to the targeted properties and strongly affected by experimental choices and secondary phenomena. In this contribution, we first introduce a Bayesian, model-based design of experiments (MbDoE) framework to quantify expected posterior uncertainties and identifiability (uniqueness) for target properties as a function of experimental parameters. For example, this enables an objective selection of a nozzle/ crucible geometry before committing to complex high-temperature campaigns. Model adequacy can be assessed using residual diagnostics and posterior predictive checks as well. We then present an updated physics-based DC model that extends the classical cylindrical-jet assumption by explicitly accounting for dynamic wetting and the formation of a meniscus, using a wetting-length derivation calibrated from axisymmetric simulations run in COMSOL Multiphysics. This wetting model quantifies inertia, capillarity and viscous losses to predict meniscus dynamics, the resulting reduction in Laplace-pressure contribution, and overall sensitivity of the draining experiment to surface tension compared to a non-wetting situation. We assess the impact of these effects on the uncertainty and identifiability of the inferred parameters using the Bayesian MbDoE approach. The applicability of this modelling work is illustrated using room-temperature experiments with water and liquid gallium. We apply the framework to analyze archival datasets from previous researchers (e.g., aluminium and steel) and estimate the posterior uncertainty and parameter correlations of the measurements for the inferred properties. Overall, this work proposes a structured methodology combining physics-based modelling and Bayesian MbDoE to optimize future DC measurements.

Acknowledgment

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Significant references

1. T. Gancarz, W. Gąsior, and H. Henein, "The Discharge Crucible Method for Making Measurements of the Physical Properties of Melts: An Overview," *Int J Thermophys*, vol. 35, no. 9–10, pp. 1725–1748, 2014. <https://doi.org/10.1007/s10765-014-1748-2>

4.1

Advanced Experimental Techniques Viscosity



Evaluation of Line-Broadening Effects for an Accurate Determination of Viscosity and Interfacial Tension by Surface Light Scattering

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When applying surface light scattering (SLS) for fluid systems with large surface or interfacial tension, e.g., for metal melts, it is particularly difficult to determine the viscosity and interfacial tension accurately. In these systems, the signal amplitudes obtainable by SLS are relatively small. Therefore, the use of smaller wave vectors is evident to increase signal amplitudes. In this regime, however, line-broadening effects are present and may influence the accuracy of the SLS method, typically resulting in an overestimation of the viscosity and an underestimation of the interfacial tension. Under such conditions, the corresponding SLS signals cannot be described adequately by empirical fitting routines as commonly used in the literature [1].

In the present study, a Monte Carlo-based optimization data evaluation strategy, introduced in an earlier work [2], is further extended and validated. In the earlier study, the method was demonstrated at a single thermodynamic state point 303.15 K and within a limited range of wave vectors. In contrast, in this work, toluene was investigated over a wide range of temperatures (283 to 433) K and capillary wave numbers ($Y \approx 15$ to 1500) of the surface fluctuations in regimes unaffected and affected by line-broadening effects. In the latter case, by the decomposition of the measured SLS signal into a superposition of damped oscillations, the distribution functions for the damping and frequency of the surface fluctuations observed in the SLS experiment are accessible. From these exact distributions and first-order approximations for the dynamics of surface fluctuations, the central wave vector can be accessed. Using the corresponding central values for frequency, damping, and wave vector, even in the presence of line-broadening effects viscosity and interfacial tension can accurately be evaluated through the exact solution of the hydrodynamic dispersion relation. Beside serving as a reliable reference for validation, the additional measurements conducted in a regime not influenced by line-broadening effects could extend the data situation for the viscosity and interfacial tension of toluene up to 433 K.

In summary, this work demonstrates for the first time the application of the Monte Carlo-based data evaluation strategy in the presence of instrumental line-broadening within thermophysical property research. The data from the proposed evaluation strategy applied over an extended temperature range show excellent agreement with the reference data within 5% for both viscosity and interfacial tension, and, thus, confirming the robustness of Monte Carlo-based evaluation method. In future work, the approach will be extended to complex systems, including translucent and opaque fluids.

Acknowledgment

This work was supported financially by the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG) via the project-ID 540431975. The authors gratefully acknowledge funding of the Erlangen Graduate School in Advanced Optical Technologies (SAOT) by the Bavarian State Ministry for Science and Art.

Significant references

1. T. M. Koller, J. Cui, M. Schmidt, J. Knorr, and A. P. Fröba, "Surface light scattering in reflection geometry: capabilities and limitations," *Appl Opt*, vol. 60, no. 29, p. 9042, Oct. 2021, doi: 10.1364/ao.440071.
2. J. Knorr, J. Cui, T. M. Koller, and A. P. Fröba, "Evaluation strategy towards an accurate determination of viscosity and interfacial tension by surface light scattering in presence of line-broadening effects," *J Colloid Interface Sci*, vol. 623, pp. 595–606, Oct. 2022, doi: 10.1016/j.jcis.2022.05.043.

Measurement of gaseous viscosity in thermodynamic equilibrium state: Based on acoustic method

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The gaseous viscosity, owing to its low density and high compressibility, is highly sensitive to temperature and pressure, posing a significant challenge for accurate measurement. In this context, the measurement of gaseous viscosity represents a novel application of acoustic methods in thermophysical property characterization, where viscosity is derived from the energy dissipation of acoustic waves propagating through the gas. During wave propagation, the resulting variation in acoustic pressure is substantially smaller than the total pressure inside the resonator. Even under resonance, the acoustic pressure remains only about $1/10^7$ of the static pressure, indicating that the thermodynamic state of the gas remains effectively undisturbed. This feature makes the acoustic technique especially suitable for high-accuracy viscosity measurements under thermodynamic equilibrium conditions.

In this study, we designed a resonator comprising two chambers connected by a slender duct. Under excitation from an acoustic wave generator, gas oscillates within the narrow duct. This specially designed dual-chamber structure significantly enhances the proportion of viscous dissipation in the total acoustic energy loss, thereby enabling viscosity determination from the resonator's frequency response. For the key parameter ϵ_r characterizing the contraction–divergence flow geometry at the duct ends, we performed calibrations using various gases, including helium, argon, and nitrogen. Treating this parameter as a constant yielded satisfactory results, with most of the measured data deviating from reference values by less than 1%. Additionally, we observed that the signal-to-noise ratio (SNR) considerably influences measurement accuracy. When the SNR exceeds 130, the measurement precision improves markedly, yielding more reliable data.

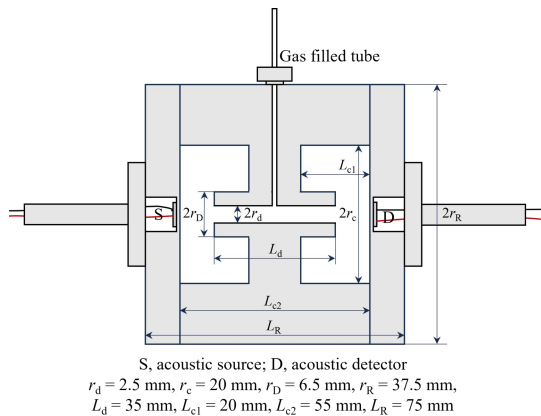


Figure 1. Resonator

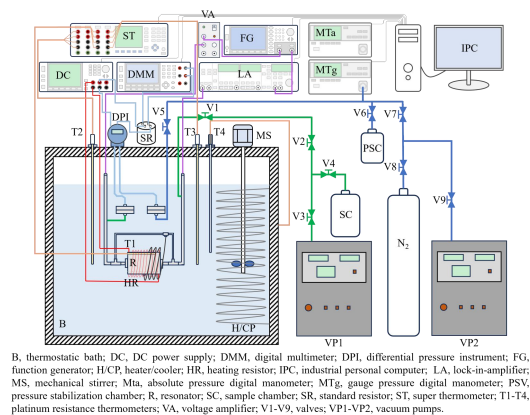


Figure 2. Experimental system

Acknowledgment

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Significant references

1. K. A. Gillis, J. B. Mehl, and M. R. Moldover, *J Acoust Soc Am*, vol. 114(1) (2003), pp. 166-173.
2. J. J. Hurly, K. A. Gillis, J. Mehl, and M. R. Moldover, *Int. J. Thermophysics*, vol. 24 (2003), pp. 1441-1474.

Modernization of an Oscillating Cup Viscometer

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Measuring the viscosity of high-temperature molten salts is highly demanding, especially if this is done at temperatures above 550 °C because of materials compatibility, metal corrosion and chemical reactivity. Our instrument, designed and constructed by the end of last century, was modified to achieve a better uncertainty in the measurements. These modifications included:

- Redesign of suspension/fixing mechanism of the wire, to avoid wire smashing and slipping
- Changing the manual initiation of the oscillation to microprocessor driven automatic initiation
- Improve the optical detection of the oscillation curve, for more accurate determination of the oscillation period and logarithm decrement (laser detectors window, light beam path)
- Improve the inertia disks used to calculate the moment of inertia of the suspension system (same metal, different masses, different radius)
- Data acquisition system redesign, including a new computer, new software (in Linux), and computer/timer and thermocouple interfaces
- Redesign the temperature measuring system, including the temperature controller of the oven, the thermocouple location
- Restructuring the calculation software used to obtain the viscosity.

A brief tour to these modifications and their contribution to decrease the viscosity uncertainty will be reported.

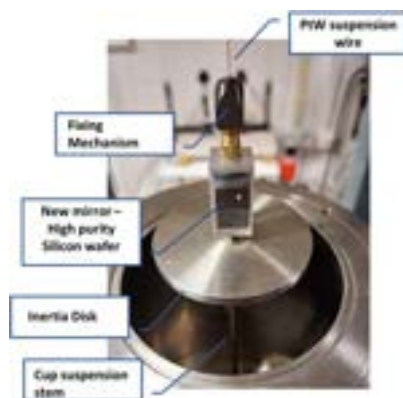


Figure 1. View of some physical modifications done.

Acknowledgment

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Significant references

1. V. B. Nunes, F. J. V. Santos, C.A. Nieto de Castro, *Int. J. Thermophys.*, vol. 19, (1998) pp. 427-435.
2. V.M.B. Nunes, M.J.V. Lourenço, C.A. Nieto de Castro, *Int. J. Thermophys.*, vol. 45 (2024) 64.

4.2

Advanced Experimental Techniques

VLE and Speed of Sound



Automated Vapor-Liquid Equilibrium Measurements with Raman Spectroscopy

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Process design relies on experimental vapor-liquid equilibrium (VLE) data, yet their availability is often limited [1]. Traditional VLE experiments are resource-intensive, with the required effort increasing factorially for multicomponent mixtures due to combinatorial complexity [2]. Some of the authors and co-workers recently introduced a cell for miniaturized VLE measurements using Raman spectroscopy [3]. Still, manual sample preparation and transfer remain as common sources of errors [4]. For liquid-liquid equilibria, some of the authors demonstrated the benefits of combining automation with spectroscopic in-situ measurements [5].

In this work, we present an automated setup for static isothermal VLE experiments. This setup retains key features from earlier designs: miniaturization, in-situ measurements, and a compact Raman sensor [3]. Miniaturization enhances heat and mass transfer, accelerates equilibration and reduces the sample volume to 2 ml. Non-invasive, in-situ Raman spectroscopy in a backscattering configuration enables rapid composition measurements of both phases, even at low pressures (2-300 kPa). The automation includes sample preparation from pure components, sample handling and the execution of experiments. In-situ analytics further allow multiple measurements with a single sample by sequentially altering its composition between measurements through vacuum distillation.

We compare measurements for mixtures of organic molecules to literature data and demonstrate how thermodynamic consistency tests can guide automated VLE measurements using Raman spectroscopy.

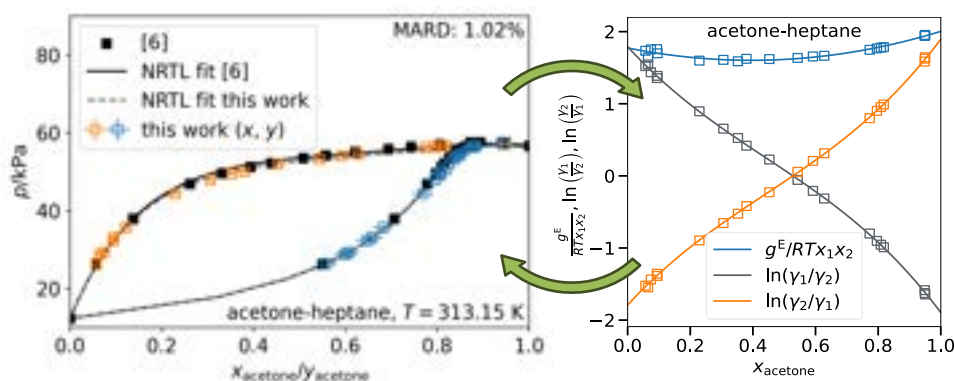


Figure 1. Measurements ($pTxy$) for the system acetone-heptane (left) and corresponding Kojima plot (right).

Acknowledgment

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Significant references

1. S. Gupta, J.R. Elliott, A. Anderko, J. Crosthwaite, W.G. Chapman, and C.T. Lira, *Ind. Eng. Chem. Res.*, vol. 62 (2023), pp. 3394–3427.
2. R. Dohrn, J.M.S. Fonseca, and S. Peper, *Annu. Rev. Chem. Biomol. Eng.*, vol. 3 (2012), pp. 343–367.
3. M. Kasterke, L. Bahr, H.-J. Koß, T. Brands, *Fluid Phase Equilibria*, vol. 594 (2025), pp. 114344.
4. M. Abolhasani and E. Kumacheva, *Nat. Synth.*, vol. 2 (2023), pp. 483–492.
5. M. Kasterke, J. Thien, C. Flake, T. Brands, L. Bahr, A. Bardow, and H.-J. Koß, *Fluid Phase Equilibria*, vol. 567 (2023), p. 113718.
6. G. Kolasińska, M. Góral, Giza, J. Z. phys. Chemie, vol. 2630 (1) 1980, pp. 151–160.

Non-Ideal Polarization Mixing for VLE Measurements with Microwave Resonators

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Microwave resonators have undergone recent development in vapour-liquid equilibrium (VLE) measurement [1, 2]. These devices enable the determination of the dielectric permittivity of a sample fluid contained within the cavity, which is related to fluid density through polarization. Their key advantage for VLE studies is the ability to provide in situ determination of density and composition in two-phase binary mixtures. The current analysis framework relies on polarization mixing rules developed by Harvey and Prausnitz [3], which were validated for non-polar natural gas mixtures and subsequently extended to polar systems using a binary interaction parameter. However, this model is not suitable for non-ideal mixtures of polar and nonpolar components.

In this work, we use a microwave resonator for VLE measurements of the binary system carbon dioxide (CO₂, nonpolar) and difluoromethane (R32, polar). Experiments were conducted for CO₂ mole fractions from 0.2 to 0.8, at temperatures between 203 and 353 K and pressures up to 10 MPa. We explore the challenges of measuring polar fluid mixtures with microwave resonators, propose improvements to the experimental and analytical approach, and introduce a non-ideal contribution to the polarization mixing rule. Our analysis combines a new pure-fluid polarization model for R32 [4] with the established model for CO₂ [5].

We present dielectric permittivity data, liquid volume fractions, and the densities and compositions of the coexisting phases. The results demonstrate that microwave resonators serve as a powerful tool for VLE studies of complex fluid mixtures.

Acknowledgment

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Significant references

1. Y. Leusmann, M.G. Hopkins, E.F. May, P.L. Stanwix, M. Richter, *Int. J. Thermophys.*, vol. 44, 4 (2022)
2. L.D. Tenardi, M.G. Hopkins, M. Richter, E.F. May, P.L. Stanwix, *Int. J. Thermophys.*, vol. 45, 168 (2024)
3. L.D. Tenardi, *PhD Thesis*, The University of Western Australia (2024)
4. A.H. Harvey, J.M. Prausnitz, *J. Solution Chem.*, vol. 16 (1987), pp. 857-869
5. A.H. Harvey, E.W. Lemmon, *Int. J. Thermophys.*, vol. 26 (2005), pp. 31-46

Selection of Scattering Geometry in Brillouin Speed of Sound Measurement

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Spontaneous Brillouin scattering is an important technique for studying fluid properties, originating from the interaction between light and thermally induced phonons. By obtaining the frequency shift or linewidth, the speed of sound and other viscoelastic properties can be determined. Brillouin scattering speed of sound measurement setups are typically based on forward scattering (small-angle approximation, symmetric optical path), backward scattering (180° scattering), or 90° scattering geometry. The characteristics of Brillouin scattering are closely related to the scattering angle. In forward scattering, the small-angle approximation (3°–5°) is often used to eliminate the effect of refractive index, thereby establishing the measurement formula. The additional error introduced by this approximation is about 0.4%, and it increases sharply with increasing scattering angle, which limits the application scope of small-angle measurements (media with low to medium speed of sound, such as most conventional organic liquids and some refrigerants). To overcome these limitations, we propose a symmetric optical path method. By constructing a special symmetric geometric optical path, the dependence on the refractive index can be effectively eliminated without the need for precise determination of the scattering angle. This method has a wide range of applications (suitable for speed of sound measurement in almost all conventional liquids and some gases), but the signal is weak for gases. Backward scattering has a broad measurement range and is widely used, especially for low speed of sound measurements (e.g., gases, liquids with low speed of sound), but it relies heavily on refractive index data. Although various scattering geometries for Brillouin scattering have been extensively studied, the impact of different scattering angles and geometries on actual speed of sound measurements has not yet been systematically investigated. In this paper, an angle-tunable Brillouin speed of sound experimental setup was built. Speed of sound measurements were performed on common alkanes and gases using forward (small-angle, symmetric optical path) and backward scattering (large-angle) configurations. The influence of different scattering geometries (different scattering angles) on speed of sound measurement errors was compared and analyzed. Our results show that when all three methods are applicable, symmetric optical path Brillouin scattering yields better measurement outcomes. However, the measurable speed of sound range of the symmetric optical path is limited by the cell windows size. For low speed of sound measurements, under conditions of limited cell windows and without modifying the setup, the symmetric optical path method still faces certain difficulties, and backward scattering remains the optimal choice. This work provides a reference for the selection of Brillouin scattering geometries for speed of sound measurements.

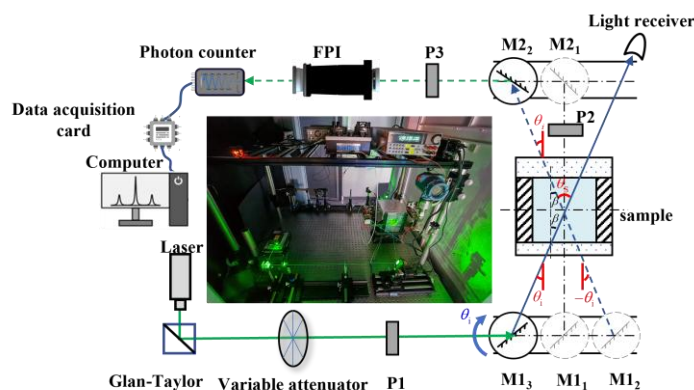


Figure 1. Optical Path Diagram of a Symmetric Optical Path Brillouin Light Scattering Fluid Speed of Sound Experimental System.

Acknowledgment

The supports which are provide by the National Natural Science Foundation of China (No. 52427811).

Significant references

1. Y. Bo, S. Yao, Y. Qi, and F. Yang, *Opt. Lett*, vol. 50 (2025), pp. 2502-2505.
2. A. Fiore, C. Bevilacqua, and G. Scarcelli, *Phys. Rev. Lett*, vol. 122 (2019), pp. 103901.
3. W. Li, K. Ren, H. He, Z. Lei, Y. Chen, M, He and Y. Zhang, *J. Chem. Eng. Data*, vol. 70 (2025), pp. 1583-1589.

4.3

Advanced Experimental Techniques Transport Properties



Development of a Gas Viscosity Measurement System Using Helmholtz Acoustic Resonance

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As one of the thermophysical properties, viscosity affects heat-energy transport systems in a variety of industrial fields, and its precise measurement is widely required. In this work, we have developed a viscosity measurement apparatus for gas samples by using an acoustic resonance mode known as Helmholtz resonance. The Helmholtz resonance is a low-frequency acoustic mode that occurs in a cavity with a duct-shaped opening. This phenomenon occurs when the gas inside the cavity acts as a compressible spring, while the gas inside the duct section oscillates as a mass element. Because the acoustic energy dissipation due to viscous damping in the duct is very large in this mode, the gas viscosity can be determined by precisely measuring the resonance frequency characteristics. The Helmholtz resonator has no moving parts except for microphones used as acoustic transducers and it can be constructed as a robust system capable of operating over wide temperature and pressure ranges [1, 2].

As shown in Figure 1, we have developed a double-Helmholtz resonator which consists of two spherical cavities connected with a narrow duct. To evaluate the reliability of the developed system, we conducted preliminary measurements using argon gas and the results are shown in Figure 2. In this presentation, we will report on the validation of the measurement technique and viscosity measurements for various gases.

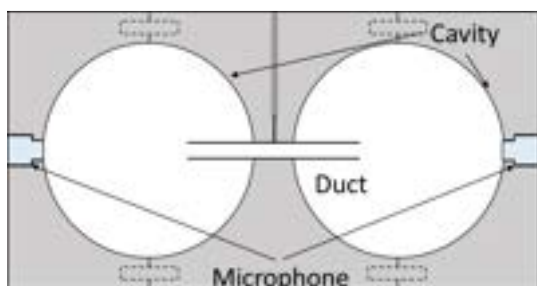


Figure 1. Cross-section view of the double-Helmholtz resonator

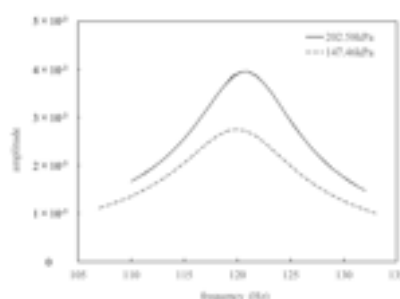


Figure 2. Measurement results for Helmholtz resonant frequency of argon gas

Acknowledgment

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Significant references

1. K.A. Gillis, J.B. Mehl, M.R. Moldover, *J. Acoust. Soc. Am.*, vol. 114 (2003) pp. 166-173.
2. K.A. Gillis, M.R. Moldover, *Experimental Thermodynamics Volume IX: Advances in Transport Properties of Fluids*, Chap.1, The Royal Society of Chemistry, Cambridge (2014) pp.1-18.

Characterization of Semiconductor Process Gases using Acoustic Resonators

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Deposition and etching processes in semiconductor chip manufacturing require accurate metering of process gases into the reaction chambers. To develop accurate physical models for process gas flow metering, high-fidelity thermophysical properties and reliable property models are needed. However, measurements on many of the relevant gases are challenging due to their hazardous and often corrosive nature. Here, we outline the development and application of acoustic techniques for accurate measurements of the thermophysical properties of semiconductor gases.

The speed of sound of non-hazardous gases is measured using a spherical acoustic resonator. For hazardous gases, a cylindrical resonator constructed entirely of corrosion-resistant Monel K-500 is being developed. The cylindrical resonator applies a similar principle as the spherical resonator, relating measured eigenfrequencies and cavity dimensions to speed of sound; although the cylindrical resonator exhibits lower quality factors, it is advantageous for its well-resolved low-order longitudinal peaks and ease of fabrication. A rendering of our cylindrical resonator is shown in Figure 1a.

An acoustic viscometer, referred to as the Greenspan viscometer [1], is being developed for gas phase viscosity measurements. The Greenspan viscometer is a double Helmholtz acoustic resonator that exhibits large viscous dissipation in its central duct. The viscometer follows the design formerly described by colleagues at NIST and is being constructed with Monel K-500 wetted surfaces and no moving parts. A rendering of our viscometer is shown in Figure 1b.

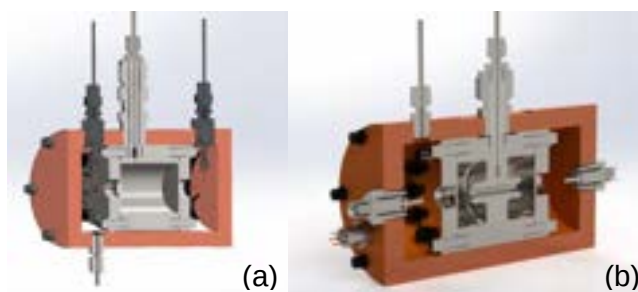


Figure 1. Cross-sectional view of the (a) cylindrical resonator and (b) Greenspan viscometer.

The ratio of the acoustic pressure in the viscometer to the acoustic source strength is proportional to the frequency-dependent complex voltage ratio of the source and detector. Here, we measure and simulate the complex voltage ratios for several frequencies at and near a well-resolved, low-quality-factor Helmholtz resonance peak. The results are fit to a detailed acoustic model previously developed by Gillis et al. to extract viscosity [2]. The design elements, model components, corrections, and FEA simulations used in the development of the viscometer for measurements on corrosive semiconductor process gases are highlighted in this work. First measurements with the viscometer will be presented.

Acknowledgment

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Significant references

1. K.A. Gillis, J.B. Mehl, M.R. Moldover. *Rev. Sci. Instrum.*, vol. 67 (1996), pp. 1850-1857.
2. K.A. Gillis, J.B. Mehl, M.R. Moldover. *J. Acoust. Soc. Am.*, vol. 114 (2003), pp. 166-173.

Efficient Detection of Temperature and Concentration Fluctuations via FFT-Segmented Autocorrelation Photon Correlation Spectroscopy

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Dynamic light scattering (DLS) method with photon correlation spectroscopy (PCS) technique is a successful approach used in chemistry, biology, and physics for studying the relaxation dynamics of fluctuations over a wide range of correlation times [1, 2]. At present, there are two key issues in the correlation analysis. First is the hardware correlators lack flexibility in adjusting channel number and sampling frequency [3], and the other one is the traditional software correlators suffer from low processing efficiency for large-volume data. This work proposes a novel PCS architecture, which is a software correlator that integrates the fast Fourier transform (FFT) and the segmented autocorrelation model, is proposed for DLS. The software correlator integrating FFT and a segmented autocorrelation model enables long-term continuous real-time data acquisition with a minimum temporal resolution of 0.1 μ s, while supporting online calculation and fitting of the correlation function. In the correlation algorithm, the combined use of FFT and the segmented autocorrelation model significantly reduces the calculation time, obtain the correlation data under all lag time, and enable uninterrupted real-time monitoring of the correlation function during data acquisition. The evaluation experiments at several conditions, including the measurement time, the intensity of detected light and the sample time, are tested on the detection of the temperature fluctuations in ethanol, and compared with the hardware correlator. The simultaneous detection of temperature and concentration fluctuations on a large time scale is preliminarily attempted. The results demonstrate that the self-developed software correlator exhibits data processing speed and overall performance comparable to commercial hardware correlators, while offering enhanced flexibility in the statistical analysis of weak microscopic fluctuations, such as temperature and concentration fluctuations. By analyzing the relaxation process of these fluctuations in transparent fluids, this architecture enables accurate determination of thermal diffusivity and mutual diffusivity in DLS experiments, providing a cost-effective and flexible alternative to hardware correlators for photon correlation spectroscopy measurement.

Acknowledgment

The support provided by the National Key R&D Program of China (No. 2023YFC3806401).

Significant references

1. B. J. Berne and R. J. W. Pecora, *Dynamic Light Scattering with Applications to Chemistry, Biology and Physics*, (Robert E. Krieger, Malabar, 1990).
2. B. Chu, *Laser Light Scattering: Basic Principle and Practice*, (Academic, Boston, 1991).
3. J. Dong, R. Bi, J.H. Ho, et al. Diffuse correlation spectroscopy with a fast Fourier transform-based software autocorrelator[J]. *Journal of Biomedical Optics*, 2012, 17(9): 97004-97001.



Thermal Conductivity Measurement: A Comprehensive Review from a Manufacturer's Perspective

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Thermal conductivity plays a pivotal role in optimizing materials for different applications, e.g. thermoelectric materials. This concerns bulk materials as well as thin layers. We want to provide a comprehensive overview of recent advancements and challenges in relation with thermal conductivity measurement techniques, from the perspective of an established commercial manufacturer and partner of the scientific community.

This overview highlights established setups for measuring thermal conductivity of bulk and nano-scaled materials, such as a unique chip-based system, utilizing the three-omega technique, as well as a setup using the frequency domain thermorefectance method (FDTR).

Different measurement solutions will be presented for different types of materials: measurement methods for different thicknesses, directions (in-plane / cross-plane) and thin film production or coating methods.

Significant references

1. Linseis, V., Völklein, F., Reith, H., Nielsch, K., and Woias, P. 2018. Advanced platform for the in-plane ZT measurement of thin films. Review of Scientific Instruments 89, 1, 15110.

4.4

Advanced Experimental Techniques Thermal Properties



Optical Differential Scanning Calorimetry Setup for Modern Material Science at High Temperature

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In modern material science, the development of high-temperature-resistant materials is a cornerstone for advancing the efficiency of thermal energy conversion processes. For instance, ceramic thermal barrier coatings (TBCs) on gas turbine blades are designed to endure operational temperatures, that can greatly exceed the melting point of the metallic substrate they protect. Similarly, in additive manufacturing processes such as laser sintering or melting, materials are melted locally through laser beams. These applications demand increased precision and enhanced process control. Therefore, these aspects are made focal points of current research and development efforts in material science.

Understanding material behavior under extreme conditions is crucial across various applications, necessitating precise knowledge of material properties at high temperatures, specifically above 1000 °C and up to 2000 °C. Thermal conductivity and specific heat capacity are particularly significant. While the laser flash method is a proven technique for measuring thermal diffusivity at temperatures exceeding 2000 °C, the measurement of specific heat capacity has traditionally been limited to temperatures below 1000 °C, due to the reliance on thermocouples that are unsuitable for higher temperature ranges due to stability problems. This creates an urgent need for innovative measurement methods that can address these limitations and provide accurate data at elevated temperatures.

The Project *Optical Differential Scanning Calorimetry for Modern Material Science at High Temperatures (OptiMa)* aims to fulfill this need by developing a new differential scanning calorimetry (DSC) method capable of measuring specific heat capacity within this higher temperature range. The new DSC setup will employ advanced optical detectors, such as radiation thermometers and thermographic cameras, thus eliminating the dependency on error-prone or not sufficiently long-term stable thermocouples. In addition, the project will explore various sample heating methods, including inductive and laser heating techniques. A key innovation is the use of a three-cell sample holder design, which is expected to significantly reduce the number of measurement cycles required, thereby increasing efficiency [1][2].

The contribution will detail the theoretical framework and practical requirements underpinning this new measurement method. It will also showcase numerical simulations that are utilized to optimize the sample holder design with regard to the new measurement method. By addressing these challenges, the project aims to contribute significantly to the field of high-temperature material science, providing crucial insights and methodologies that can be applied across a range of industrial applications.

Acknowledgment

This Project (contract number: 13FH070KX0) has been sponsored as a part of the funding program Forschung an Fachhochschulen by the German Federal Ministry of Education and Research (BMBF).

Significant references

1. B. Wunderlich, J. Therm. Anal., vol. 32 (1987), pp. 1949-1955.
2. Y. Takahashi, Pure Appl. Chem., vol. 69 (1997), pp. 2263-2269.

LNE initiatives in the development of traceable calorimetric measurements for operando battery cells.

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The “Materials Department” of the French National Metrology Institute (LNE) studies caloric quantities [1] in the frame of its leading role in the characterization of the thermophysical properties of materials. It has strong experience in the development of metrological reference facilities for traceable measurements with uncertainties sufficiently low to meet the requirements of the existing and emerging industries [2].

In the framework of the European project 24GRD09 HyMetBat (Hybrid metrology for sustainable and low-carbon footprint battery materials), LNE works on the adaptation of an existing calorimeter for the measurement of total thermal energy dissipated during charges/discharges cycles of different types of electric batteries. The main objective is to perform operando electrical and thermal measurements simultaneously. Modifications have been made to an existing calorimeter to accommodate coin cell geometry batteries and provide integrated cabling for connection to battery cyclers and electrochemical impedance spectroscopy (EIS) equipment. A differential heat-flux calorimeter was developed initially for measurement of specific heat by drop calorimetry up to 3000 °C. It integrates a specific in-situ calibration system for traceability to electrical units [3].

LNE applies this operando calorimetric method during cycling to investigate the thermal behavior of battery cells from room temperature up to 50 °C. The data generated will provide critical insights into heat generation and dissipation mechanisms within the cells, enabling a better understanding of thermal management challenges and material degradation during cycling.

The design of the calorimeter for testing batteries and typical heat dissipation curves obtained during charges and discharges of some type of batteries are presented.

Acknowledgment

The project 24GRD09 HyMetBat has received funding from the European Partnership on Metrology, co-financed by the European Union's Horizon Europe Research and Innovation Programme and from the Participating States.

Significant references

1. R. Razouk, B. Hay and M. Himbert, Uncertainty assessment of enthalpy of fusion measurements performed by using an improved Calvet calorimeter. *Metrologia* 52, 717-729 (2015).
2. R. Razouk, O. Beaumont and B. Hay, A new accurate calorimetric method for the enthalpy of fusion measurements up to 1000 °C, *J Therm Anal Calorim* 136, 1163-1171 (2019).
3. R. Razouk, O. Beaumont, J. Hameury and B. Hay, Towards accurate measurements of specific heat of solids by drop calorimetry up to 3000 °C, *Therm Sci Eng Prog* 26, 101130 (2021).

Measurement of Critical Temperature with Commercial Calorimeters: Resurrection of Unjustly Abandoned Technique

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The PROFHET project (funded jointly by the Czech Science Foundation and the German Research Foundation) aims to investigate the thermodynamic properties of hydrofluoroethers (HFEs) of the Novec fluid family. HFEs are chemically inert, non-flammable, compatible with direct skin contact, and exhibit low viscosity and short atmospheric lifetimes. In addition, they have low water solubility, no known adverse health effects, and high dielectric constants, making them attractive for electronics cooling, including immersion cooling of high-performance computing or military electronic systems. Other applications include their use as cleaning solvents for magnetic and electronic devices, protective atmospheres for thermal treatment of alloys, and as refrigerants or working fluids.

During the course of the PROFHET project, an urgent need arose to determine the critical properties of selected HFEs. Experimental data of this type have been extremely scarce in recent decades, and the development of a new dedicated apparatus would have significantly delayed the project. Therefore, critical temperature and critical density were measured using a commercial differential scanning calorimeter (DSC) equipped with high-temperature, high-pressure stainless-steel pans supplied by TA Instruments (New Castle, DE, USA). The methodology was originally developed at the Bartlesville Thermodynamics Laboratory [1] for compounds with high critical temperatures, where conventional experiments were infeasible due to sample stability limitations or apparatus constraints. Notably, this method enabled the highest experimentally determined critical temperature to date (carbazole, 932 K) [2]. To our knowledge, it has not been adopted by any other laboratory since.

The method relies on detecting the conversion temperature, at which a two-phase system becomes single-phase, by observing a drop in the DSC signal (i.e., a significant change in apparent heat capacity). DSC experiments were performed using a continuous heating method at 10 K·min⁻¹ for several sample loadings corresponding to global densities in the range $0.5\rho_c < \rho < 1.5\rho_c$, where ρ_c was the estimated critical density. To reduce experimental costs, low-cost copper washers were minted and observed to exhibit lower leakage probability than commercial gold-plated washers. The internal volume of the pans was determined both by caliper measurement and by sealing pans underwater, drying them overnight, and weighing; both methods yielded consistent results and agreed with technical drawings. A separate temperature calibration of the DSC with stainless-steel pans was performed using In, Sn, Pb, and Zn.

Evaluation of the experiments consisted of plotting the conversion temperatures T_{step} against global density ρ and fitting them using the critical-exponent relation exponent β . Several values of β were considered, as the original application [1,2] provided no discussion of its selection. Verification of the method using *n*-heptane and HFE-7000, along with an uncertainty analysis, indicates that the method can determine the critical temperature and critical density with expanded uncertainties ($k = 2$) of approximately 1–2 K and $(0.05\text{--}0.10)\rho_c$, respectively. The method has been successfully applied to HFE-7100, HFE-7200, HFE-7300, and HFE-7500, and further experiments are planned.

Acknowledgment

Financial support from the Czech Science Foundation (GACR No. 24-10191K) is acknowledged.

Significant references

1. S. E. Knipmeyer, D. G. Archer, R. D. Chirico, B. E. Gammon, I. A. Hossenlopp, A. Nguyen, N. K. Smith, W. V. Steele, and M. M. Strube, *Fluid Phase Equilib.*, vol. 52 (1989), pp. 185-192.
2. W. V. Steele, *J. Chem. Thermodyn.*, vol. 27 (1995), pp. 135-162.

4.5

Advanced Experimental Techniques Micro- and Nano-Scale



Investigation of measurement conditions for reliable SThM thermal properties measurements on a nanostructured sample

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Thermal management of micro- and nanoscales devices is becoming one of the main challenges facing the semiconductor industry due to the increase in heat flux density inside increasingly smaller chips. Characterizing the thermal properties such as the thermal conductivity of materials used at these sub micrometric scales requires dedicated techniques with suitable spatial resolution. Scanning thermal microscopy (SThM) technique appears to be an appropriate technique to perform local thermal properties measurements [1]. The traceability of thermal conductivity measurement using SThM has been established for materials whose characteristic length is greater than the mean free path of energy carriers [2]. Nevertheless, many precautions must be taken to link observed thermal contrast to studied thermal properties. Some influencing parameters, such as the probed volume, heat transfers through the environment or substrate properties must be taken into account when analyzing results.

This paper presents measurements performed in a correlative metrology way on a nanostructured structure [3] composed of silicon dioxide steps and gold pads deposited on a silicon substrate. The measurements combined dimension and roughness measurements using atomic force microscopy (AFM) technique and thermal contrast measurements using SThM technique. SThM measurements were performed in both vacuum and air using a Pd thermoresistive probe. All measurements were performed on exactly on the same pattern of the device.

Results show that the thermal penetration depth reaches several hundred nanometers for low thermal conductivity materials. This induces an influence of the substrate on the result for a material with thickness lower than this depth. Furthermore, the presence of air as an additional heat transfer channel between the tip and the sample alters the spatial resolution of technique and induces errors on thermal properties estimations especially for high conductivity materials.

This work proposes an assessment of the probed volume in SThM for the Pd probe as a function of measurement conditions and its influence on the interpretation of results.

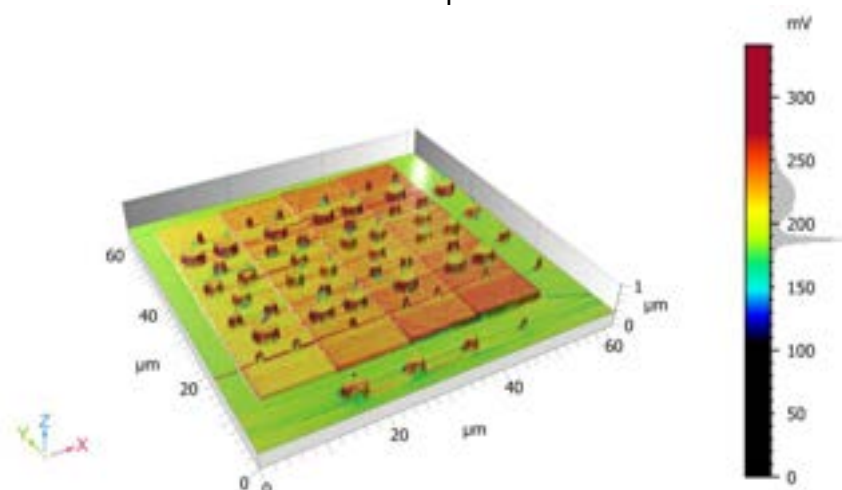


Figure 1. Thermal contrast image on nanostructured sample composed of gold pads deposited on SiO₂ steps on Si substrate.

Significant references

1. Y. Li, J. Wu, J. Luo, J. Wang, W. Yu and B. Cao, *J. Appl. Phys.*, 138, 050701 (2025).
2. N. Fleurence, S. Demeyer, A. Allard, S. Douri. and B. Hay, *Nanomaterials*, 13 (2023), 2424.
3. F. Piquemal, J. Morán-Meza, A. Delvallée, D. Richert and K. Kaja, *Nanomaterials*, 11(3) (2021).

Development of an Optofluidic Diffusion Sensor Using Light-induced Dielectrophoresis for Picoliter-scale Nanofluid Droplet

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Diffusion sensing techniques for small nanofluid droplets are promising for the minute-volume analysis of rare samples, such as pharmaceutical products and industrial nanoparticles, because the diffusion coefficient is sensitive to the sample size, the conformation and the intermolecular interactions. Although several diffusion sensing techniques have been reported, the number of methods to samples dispersed in a small droplet is limited.

In our previous study [1,2], we developed an optofluidic diffusion sensing device using light-induced dielectrophoresis, a manipulation technique for nano- and micro-sized sample. The proposed method enabled label-free measurements within a few seconds by diffractive detection of the diffusion of a microscale lattice-shaped concentration distribution formed by light-induced dielectrophoresis, as shown in Figure 1. Using this method, diffusion measurements of nano-sized sample, such as polystyrene beads [1], and the liposome [2], were performed with a probing volume of several hundred picoliters.

In our recent study [3], we proposed the application of this diffusion sensing method to nano-sized samples dispersed in droplets, as shown in Figure 2. The droplet with several hundred picoliters containing polystyrene beads of ϕ 203 nm and ϕ 100 nm were prepared in the optofluidic device. Differences in the diffusion coefficients arising from particle size were detected from the decay time constant of the diffracted light, demonstrating the applicability of the proposed method. In this presentation, we report on the fabrication and the sensing process using the proposed optofluidic device and the measurement results of nanobeads in droplets.

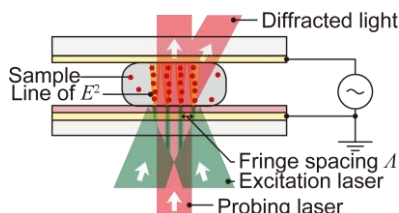


Figure 1. Schematic of diffusion sensing process.

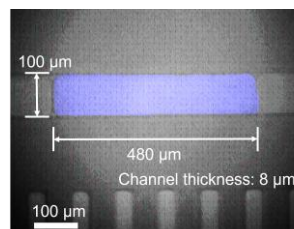


Figure 2. Water in oil droplet generated in microchannel (400 pL approx.).

Acknowledgment

Fabrication was performed in a Clean Room at the Global Nano Micro Technology Business Incubation Center (NANOBI), Kawasaki, Japan, with support from the Academic Consortium for Nano and Micro Fabrication of Four Universities (Keio University, Waseda University, Tokyo Institute of Technology, and The University of Tokyo). This work was partially supported by JSPS KAKENHI Grant Number JP25K01177.

Significant references

1. M. Kamata, Y. Takaba, Y. Taguchi and Y. Nagasaka, *Int. J. Heat Mass Transf.* Vol. 133 (2019), pp. 73-79.
2. M. Kamata, R. Shishido, M. Oura, I. Kojima and Y. Taguchi, *Int. J. Thermophys.*, Vol. 46 (2025), 180.
3. M. Kamata and Y. Taguchi, *Netsu Bussei*, vol. 39 (2025), pp. 135-142 (in Japanese).

Infrared Thermography for Precise Microscale Temperature Measurements on NiTi wires used for actuators and elastocaloric devices

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Nickel–titanium (NiTi) alloys exhibit shape-memory and superelastic effects that make them attractive for actuator technologies and elastocaloric cooling applications. These functional properties arise from a reversible martensitic phase transformation induced by temperature or applied mechanical stress. Owing to their high surface-to-volume ratio and manufacturing flexibility, thin NiTi wires are widely employed in such systems [1, 2]. However, accurate temperature measurement in thin NiTi wires remains challenging, as conventional contact thermometry can perturb the phase transformation and distort the thermal response. Non-contact infrared thermography represents a promising alternative, but its reliable application critically depends on accurate knowledge of the surface emissivity.

This study presents a dedicated apparatus for measuring the emissivity of metallic surfaces at the microscopic scale over a temperature range from 308 K to 423 K, utilizing a self-built reference-quality black body cavity (BBC) [3–5]. NiTi samples with different surface finishes, i.e., unprocessed, polished, electrical discharge machined (EDM), laser-machined, diamond-smoothed, and oxidized, were systematically analyzed. Additionally, the effect of composition was studied by measuring emissivity for two unprocessed NiTi samples with varying compositions.

The results reveal that emissivity strongly depends on surface condition, composition, and temperature. The average emissivity of EDM and oxidized samples was approximately twice that of polished and diamond-smoothed surfaces. Furthermore, temperature-dependent emissivity data for oxidized samples were fitted to a mathematical model and applied to determine the temperature of a 75 μm diameter NiTi wire operating as an electrically powered actuator. A temperature deviation of up to 80 K was observed when comparing corrected and uncorrected emissivity, underscoring the importance of accurate emissivity data for reliable temperature determination.

Acknowledgment

The authors would like to thank the German Federal Ministry of Economic Affairs and Climate Action (reference number HyAct, KK5228102KX1) for funding this project.

Significant references

1. Kirsch, S.-M. et al., 'NiTi-based elastocaloric cooling on the macroscale: From basic concepts to realization', Energy Technology, vol. 6, no. 8, pp. 1567–1587, 2018.
2. Welsch, F. et al., Vacuum Gripper System Based on Bistable SMA Actuation. Smart materials, adaptive structures, and intelligent systems. Vol. 51944. American Society of Mechanical Engineers, 2018.
3. Javed, M. A. et al. "Black Body Cavity Apparatus for Measuring the Emissivity of Nickel-Titanium-Based Shape-Memory Alloys and Other Metals." International Journal of Thermophysics 45, 2024, 157, 2024.
4. Javed, M. A. et al. "Characterization of Thin NiTi-Based Shape Memory Alloy Sheets with Different Surface Properties for Utilization in Elastocaloric Regenerators." Shape Memory and Superelasticity, 1-18, 2025.
5. S. Morozova et al., Vacuum variable-temperature blackbody VTBB100. International Journal of Thermophysics 29, 341–351, 2008.

4.6

Advanced Experimental Techniques

H₂ Mixtures and LNG



Design of a Cryogenic Thermal Conductivity Measurement System Using Transient Hot Wire (THW) Method

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Reliable thermal conductivity measurements of LNG (Liquefied Natural Gas) at cryogenic temperatures are crucial for optimizing LNG storage tank designs, minimizing energy loss, and ensuring safe operation. Currently, LNG storage tank designs rely on theoretical calculations based on LNG component analysis. However, due to the complex mixture properties of LNG, direct measurement technologies are essential for providing more reliable thermal property data. This research aims to develop a reliable measurement system that can directly assess thermal conductivity at cryogenic temperatures, improving the design and safety of LNG storage and transportation systems.

The proposed cryogenic thermal conductivity measurement system utilizes the Transient Hot Wire (THW) method, which is suitable for measuring thermal properties of liquid substances. The system design includes a dual vacuum can assembly, ensuring effective temperature control of the THW sensor. A cryogenic chamber, cooled using liquid nitrogen (LN₂), provides the necessary low-temperature environment for measuring LNG thermal conductivity at temperatures ranging from -170 °C to -150 °C. The system also includes a heat exchanger to facilitate the liquefaction of LNG and a custom-designed cryogenic electrical feedthrough to maintain vacuum conditions at cryogenic temperatures.

The prototype system successfully achieved temperature control of the THW sensor at -163°C with a standard deviation of 50 mK, which is within the required precision for reliable thermal conductivity measurements. The system demonstrated stable operation and the ability to measure thermal conductivity at cryogenic temperatures, providing promising results for future use in LNG-related applications.

This cryogenic thermal conductivity measurement system presents a novel solution to the limitations in current LNG thermal property measurement techniques. The developed system enables precise, real-time acquisition of LNG's thermal conductivity, which can significantly improve the design of LNG storage tanks and transportation facilities. Future work will focus on integrating the measurement system with software for automated analysis, enhancing the practical application and efficiency of the system in industrial settings.

Acknowledgment

This research was supported by Development of Core Technologies for Measurement Standards for Heat and Flow related Properties of Liquefied Natural Gas funded by Korea Research Institute of Standards and Science (KRISS – 2026 – GP2026)

Significant references

1. Hans M. Rober. *Journal of Reserach of the National Bureau of Standards*, vol. 86 (1981), pp. 457-493.
2. S. Y. Kwon and S. H. Lee, *Thermochimica Acta*, vol. 542 (2012), pp. 18-23.

Measurement of thermal conductivity and diffusivity at cryogenic temperatures

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For the storage and transport of liquefied gas, it is useful to know the thermophysical properties of materials. Liquid hydrogen is currently an important area of development. This study focuses on the development of a device for characterising thermal properties at low temperatures.

The device measures the steady-state thermal gradient on a bar of known cross-section. The most commonly used method for measuring the thermal conductivity of metals is the guarded bar method. It consists of heating a metal bar in steady state and measuring the temperature gradient. This method is essential at high temperatures, where radiation represents significant losses.

At cryogenic temperatures, the most significant losses are those due to conduction and convection. To avoid exchanges with the air, the solution is to place the device under high vacuum (1E-5mbar to 1E-6mbar). The sample is heated using an electrical resistance placed on one side of the bar and the other side is cooled using a cold head capable of reaching 10K.

Using a Dirac comb heating regime, it was possible to identify the volumetric heat capacity as a function of temperature.

The device was broken down into quadrupoles representing the different elements through which the heat flow passes. The Dirac comb was chosen to excite the significant frequencies as a function of the assumed thermal diffusivity of the sample and its geometry. The advantage of the Dirac comb is its harmonic richness and the possibility of performing a Fourier series to determine the transfer function between two temperature measurement points. Using an inverse method, the characteristic time of the bar can be found, thereby allowing the thermal diffusivity and volumetric heat capacity to be calculated.

This study is supplemented by a sensitivity study and an uncertainty calculation to evaluate the performance of the device.

Modified vibrating-wire viscometer for measurements of gas mixtures containing hydrogen

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A combined vibrating-wire viscometer and single-sinker densimeter [1] has been modified for measurements of hydrogen-containing gas mixtures. It enables simultaneous viscosity and density measurements at the same state point in the temperature range from 293 K to 493 K at pressures up to 30 MPa. The magnetic field in the vibrating-wire sensors, which is used to excite the vibration of the wire and to measure the free decay of the vibration, is generated by two permanent magnets encapsulated by stainless steel plates. The magnetic field between the magnets was examined by simulations using the commercial software COMSOL. The results of these simulations revealed that the present design leads to a magnetic short-cut in the encapsulation. By exchanging the materials of the stainless steel plates, the short-cut could be eliminated, which yields an improved signal-to-noise ratio of the measurement of the free decay of the vibration.

Because of hydrogen embrittlement, measurements of hydrogen containing mixtures impose strong requirements on the materials of the parts of the instruments, which are in contact with the mixture. To meet these requirements, the material of the vibrating-wire sensors had to be replaced by a hydrogen compatible material. Moreover, since the copper-beryllium alloy of the pressure vessel could not be qualified as a certified material for pressure vessels, the outer stage of the two-stage thermostat, the double-mantle thermostat, which surrounds the pressure vessel, is employed as shatter protection. This required a redesign of the double-mantle thermostat. Furthermore, the automation of the measurements was improved by employing a nitrogen-operated highly accurate pressure controller. The measured gas is separated from the absolute pressure transducers by a differential pressure transducer with a gold-plated membrane. The pressure controller automatically adjusts the pressure in the nitrogen-filled branch of the valve system between the differential pressure and absolute pressure transducers after reducing the pressure of the gas in the pressure vessel.

The apparatus was used to measure the viscosity and density of binary mixtures of hydrogen and nitrogen with molar compositions of $x_{H_2} = 25\%$ ($x_{N_2} = 75\%$) and $x_{H_2} = 50\%$ ($x_{N_2} = 50\%$) in the temperatures range from 293 K to 453 K and pressures up to 30 MPa. Only limited viscosity data for this system is available in the literature with most measurements being primarily taken at ambient pressure. Where a comparison is possible, our results for the viscosity agree with the literature data within 0.3 %, which corresponds to our expanded uncertainty (at the 0.95 confidence level). Our results for the density agree with the most accurate literature data within their relative expanded uncertainty (at the 0.95 confidence level) of 0.1%.

Acknowledgment

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Significant references

1. Seibt, D. Schwingdrahtviskosimeter mit integrierter Ein-Senkkörper-Dichtemessverfahren für Untersuchungen an Gasen in größeren Temperatur- und Druckbereichen. Fortschr.-Ber. VDI, Reihe 6, Nr. 571, 2008.

Advanced Thermal Analysis Under Hydrogen Atmosphere: From Oxide Reduction to Zirconium Hydride Formation

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Hydrogen plays a pivotal role in the transition towards a carbon-neutral energy economy, serving as both a clean fuel and a reductant in industrial metallurgy. However, the interaction between hydrogen and structural or functional materials presents significant challenges, including hydrogen embrittlement and complex phase transitions during storage and processing. Understanding the thermophysical properties - specifically reaction kinetics and thermal expansion behavior - under hydrogen atmosphere is essential for material characterization and development.

This work presents a comprehensive thermal analysis study utilizing a Simultaneous Thermal Analyzer (STA) and Thermomechanical Analyzer (TMA) equipped with a specialized safety system “H₂Secure” enable safe measurements under hydrogen atmospheres, with temperatures reaching up to 1600 °C, and the capability to switch to oxidizing conditions.

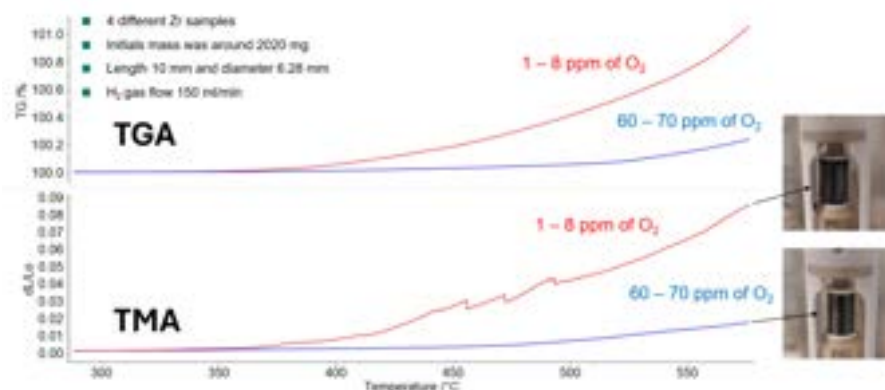


Figure 1. Comparison of TGA and TMA Results for Zr samples under H₂ atmosphere.

Case studies with CuO and Fe₂O₃ illustrate the effectiveness and reliability of the developed system. The reduction of iron(III) oxide (Fe₂O₃) - a key process for green steel production - was investigated thermogravimetrically across various temperatures (390°C, 700°C, 1000°C) and various hydrogen concentrations. The results reveal distinct, temperature-dependent reaction pathways: at lower temperatures, reduction proceeds via magnetite (Fe₃O₄), while temperatures above 570°C trigger the formation of the wüstite (FeO) intermediate phase before complete reduction to metallic iron (Fe). Furthermore, cyclic redox investigations of CuO demonstrated the system's ability to track kinetic changes caused by particle passivation over repeated cycles.

Complementing these thermogravimetric studies, we present novel TMA results on the reaction of zirconium (Zr) with H₂ (Fig. 1). While thermogravimetry detects mass change, it cannot quantify the volume changes associated with hydride formation, as well as formation of mechanical cracks during these processes. Using TMA under a controlled hydrogen atmosphere, the expansion of Zr samples was observed. The results show a pronounced length change corresponding to the phase transformation from metallic Zr to the saturated ZrH_x-hydride phases. Crucially, our experiments highlight that the reaction kinetics are highly sensitive to atmosphere purity. Trace oxygen contents in the ppm level were found to form surface oxide barriers that significantly retard hydrogenation kinetics and alter the saturation profile. This underscores the necessity of rigorous atmosphere control in high-temperature hydrogen experiments.

The combination of TGA/STA and TMA under controlled hydrogen/oxygen atmospheres provides a holistic view of material behavior, linking mass change kinetics with thermal expansion. These findings are directly relevant for the design of hydrogen storage materials, nuclear cladding, and advanced metal processing.

4.7

Advanced Experimental Techniques Thermal Imaging



Coaxial 2D Imaging Method for Thermophysical Properties Using Lock-in Thermography

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With the miniaturization and high integration of semiconductor devices, the heat generation density from electronic equipment is increasing. Since excessive temperature rise causes device performance degradation and failure, effective thermal management is essential. To address this issue, composite materials such as Thermal Interface Materials (TIMs), consisting of high thermal conductivity fillers and resin matrix, are attracting attention. These composites offer a combination of thinness and high thermal conductivity. However, their heterogeneous structure results in a spatially distributed variation of thermophysical properties. Therefore, a method to visualize these distributions is required for the optimization of TIMs.

Our group has developed a periodic heating method using Lock-in Thermography (LIT) to visualize the 2D distribution of through-thickness thermal diffusivity, thermal conductivity, and volumetric heat capacity of composite materials ¹. This method features high spatial resolution, non-contact, non-destructive, and full-field measurement capabilities. However, the conventional method requires placing the heat source and the infrared camera on opposite sides of the sample. This geometric constraint limits its application to manufacturing process monitoring and system miniaturization. Therefore, this study aims to establish a thermophysical property imaging technique based on the Coaxial Front surface heating and Front surface detection (cFF) method, where heating and detection are performed on the same axis.

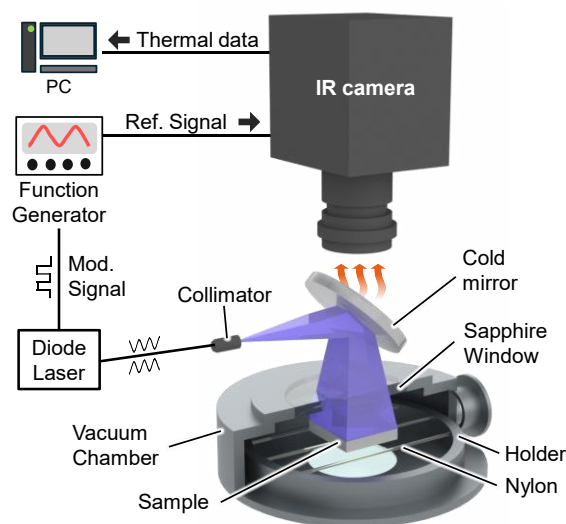


Figure 1. Experimental Setup of the Coaxial 2D Imaging System.

Acknowledgment

This research was partially supported by the JST-Mirai Program (JPMJMI221036344).

Significant references

1. A. Alasli, R. Fujita, H. Nagano, Thermophysical Properties Mapping of Composites by Lock-in Thermography: Applications on Carbon Fiber Reinforced Plastics, Int J Thermophys, Vol.43, p.176, (2022).

In-Situ Detection of Subsurface Defects in PBF-LB/M using High-Speed Infrared Thermography

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Laser Powder Bed Fusion of Metals (PBF-LB/M) produces complex components but faces challenges like internal porosity defects. To address this, the Synchronized Path Infrared Thermography (SPIT) approach is applied for **in-situ monitoring**. This setup uses a dual scan head to independently control the processing laser (1080 nm) and the high-speed infrared camera's (2000–2050 nm) measurement field, enabling precise thermal cooling analysis.

The objective is in-situ detection of subsurface defects by analyzing surface cooling. Defects act as thermal barriers, retarding heat dissipation and causing localized elevated temperature. Synchronizing the sensor's movement with the laser ensures a stable field of view, significantly reducing motion blur for high-resolution thermal data. The methodology was validated using Stainless Steel PH1 with embedded cylindrical defects (300 μm to 1000 μm in diameter) approximately **120 μm below the surface**.

An additional powder layer was fused onto these specimens, varying volumetric energy density and scanning speed to assess reliability. Results show the system reliably detects **subsurface defects down to 356 μm** . A correlation was observed between process parameters and sensitivity; moderate energy densities and scanning speeds offered optimal resolution. The dual scan head successfully decouples the measurement field from the laser, enabling precise monitoring of the heat-affected zone.

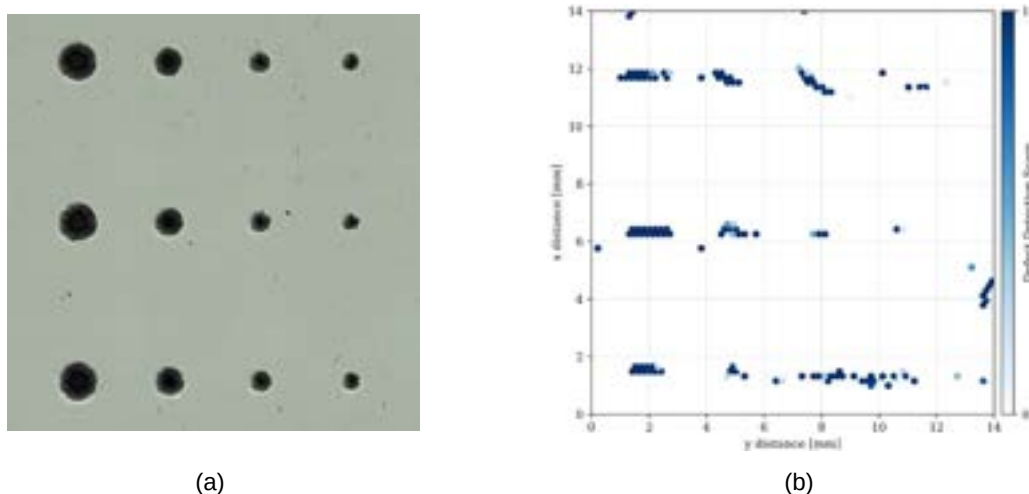


Figure 1. Comparison of the physical specimen and the monitoring results. (a) Micrograph of the specimen containing artificial subsurface defects (diameters 300–1000 μm) approximately 120 μm below the surface. (b) Spatial mapping of the calculated Defect Detection Score.

Acknowledgment

This work was supported by the StMWI Bayern Innovativ Bayerische Gesellschaft für Innovation und Wissenstransfer mbH under Grant 41-6562b/25/2-VAL-2103-0006 and the StMWK for regional transfer of technologies (TTZ-MSP).

Significant references

1. Höfflin D et al., Process Monitoring Using Synchronized Path Infrared Thermography in PBF-LB/M. Sensors 2022 22(16) <https://doi.org/10.3390/s22165943>

Noncontact Measurement of Interfacial Thermal Resistance in Three-Layer Laminates Using Lock-in Thermography

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In recent years, devices such as power semiconductors have been increasingly miniaturized. The resulting increase in heat density is an unavoidable challenge, raising concerns about its impact on device performance and reliability. For the thermal management of these devices, relying solely on bulk material properties or literature values for thermal property evaluation is insufficient; microscopic and highly accurate evaluation is required. The heat dissipation mechanism for power semiconductors consists of three elements: the chip, the insulating heat spreader substrate, and the cooling mechanism such as a heat sink. The insulating heat spreader substrate primarily adopts a three-layer structure: a conductive layer using Cu, an insulating layer made of ceramics, and a Cu layer for thermal diffusion. Interface thermal resistance significantly impacts a device's heat dissipation capability, detailed measurement of the interfacial thermal resistance in three-layer substrates is crucial. The Lock-in Thermography Periodic Heating Method (LIT method) is a technique that combines imaging via thermography with noise reduction through lock-in processing, enabling the detection of smaller temperature changes than simple thermography measurements. In our laboratory, we have previously used the LIT method to measure various thermal properties, including in-plane thermal diffusivity, out-of-plane thermal diffusivity, anisotropy, and interfacial thermal resistance in bilayer materials¹.

In this paper, we report on phase data mapping across the entire sample surface using the LIT method and on interfacial thermal resistance measurements of three-layer samples. First, the validity of the interfacial thermal resistance measurement technique for three-layer samples was confirmed using three layers of isotropic graphite. Subsequently, measurements were performed on three-layer samples with ceramic interlayers, specifically Cu/Si₃N₄/Cu and Cu/AlN/Cu.

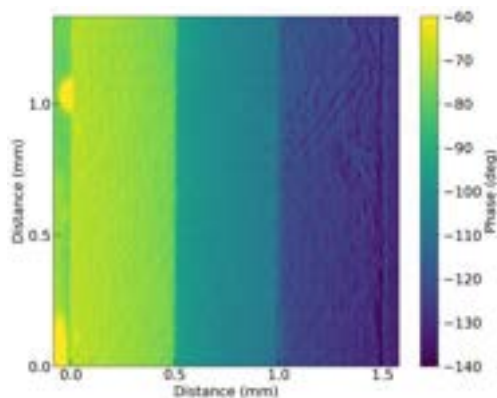


Figure 1. Phase mapping of 3-layer Isotropic Graphite

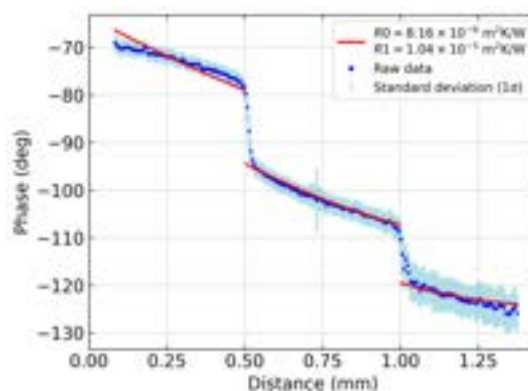


Figure 2. Fitting result of interface thermal resistance

Acknowledgment

The Cu/Si₃N₄/Cu and Cu/AlN/Cu materials used in this research were fabricated by UMAP C o., Ltd.

Significant references

1. Ishizaki, Takuya, et al., Measurement of Local Thermal Contact Resistance with a Periodic Heating Method Using Microscale Lock-in Thermography. *Review of Scientific Instruments* 91, no. 6 (2020)

Anisotropic Approximation to Layered Samples with the Transient Plane Source

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The transient plane source (TPS) method is a measurement technique for thermal conductivity and diffusivity that uses a double-spiral filament lodged between samples as both a heater and a sensor. It can be used for the determination of directional thermophysical properties in samples with organized planar anisotropy, i.e., a radial thermal conductivity in the plane of the sensor and an axial thermal conductivity perpendicular to the sensor [1]. This technique has been applied to layered samples of single material separated at each layer by a thermal contact resistance with the assumption that the measurement would be equivalent to that of an anisotropic sample with radial conductivity equivalent to that of the material and axial conductivity equivalent to an effective thermal conductivity through the samples calculated from the thermal resistance of the sample and the contact resistance between layers [2].

The validity of this assumption is examined by deriving an expression for the temperature rise of an infinite layered system with a disk source and simulating measurements that are then processed through a non-linear fitting procedure using the anisotropic TPS form. Some simple relations are found to describe the bias in measured or derived properties. Under specific conditions, this allows first order corrections to the estimated properties to be made, reducing bias by up to two orders of magnitude. Without correction, it is found that the measurement of directional properties, including the extraction of interface resistance from the directional conductivities, will have less than 2% bias if the sensor radius is greater than ten times the layer thickness and the interface resistance is less than the material resistance through its thickness.

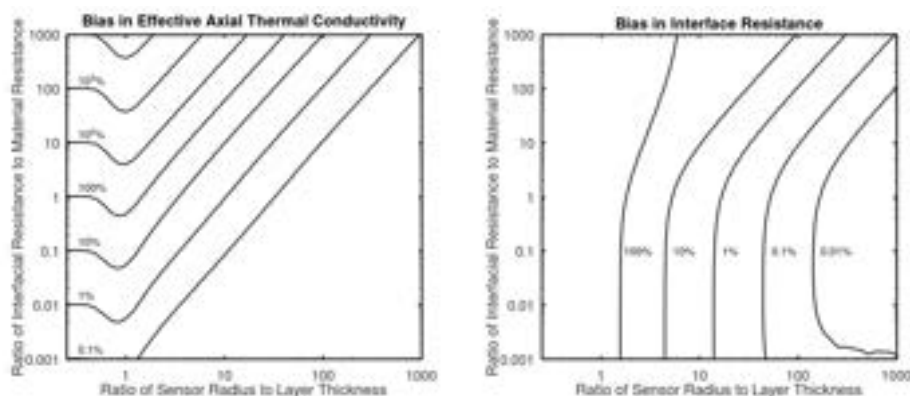


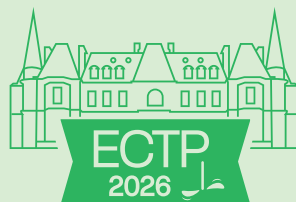
Figure 1. Left: Expected bias in measured effective axial thermal conductivity of layered samples using a TPS configuration and the steady state value. Right: Expected bias in measured interfacial resistance of the same.

Significant references

1. S.E. Gustafsson, B.M. Mihiretie, and M.K. Gustavsson, *International Journal of Thermophysics*, vol. 45 (2024).
2. M. Gustavsson and S.E. Gustafsson, *Thermal Conductivity 26*, Ed. R.B. Dinwiddie. Lancaster, PA, USA (2005), pp. 367-377.

5.1

Advanced Materials Design and Characterisation Radiative Cooling I



EKHI: an open database of thermal radiative data

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Thermal radiative properties of solid materials are difficult to report in a FAIR-compliant manner (<https://www.go-fair.org/fair-principles/>), as they are multidimensional and vary significantly with specimen-specific conditions (such as purity, surface finish, or porosity). Consequently, there is a lack of extensive and freely accessible digital datasets and databases that cover such properties.

In this work, we present a new open database of thermal radiative data, EKHI (<https://thermomat.ehu.eus/ekhi>). EKHI provides open access to a digital dataset that contains more than 1200 curves of emittance, reflectance, transmittance and absorptance values of solid materials, which has been generated from the volumes 7 to 9 of the TPRC Data Series [1]. These curves have been selected only from publications available online, to ensure proper traceability, and their numerical values are displayed in interactive figures, accompanied by experimental and specimen metadata, as shown in Figure 1. All that information is downloadable in structured JSON files, which facilitates the exchange of information and reprocessing of valuable data from older sources with modern programming languages.

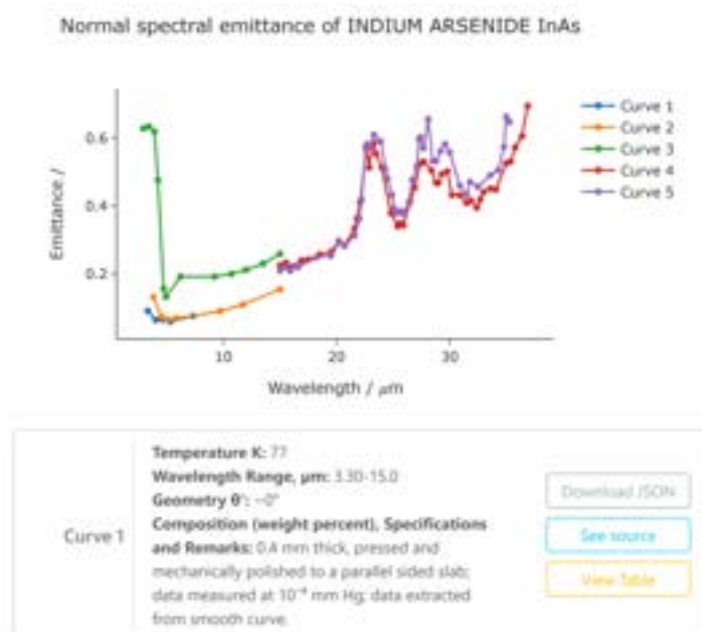


Figure 1. Part of the interface of EKHI that shows an interactive figure and the metadata.

Acknowledgment

This work was supported by the Basque Government (research projects IT-1714-22 and Elkartek KK-2025/00075, and PhD grant PRE-2022-1-0086) and the UPV/EHU (PhD grant PIF 21/06).

Significant references

1. Y. S. Touloukian *et al.*, *Thermal Radiative Properties*, Thermophysical Properties of Matter (TPRC) Data Series, vols. 7–9, IFI/Plenum, New York, 1970–1972.

Predictive numerical modeling of radiative cooling under real atmospheric conditions

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A robust and experimentally validated numerical model has been developed to predict the thermal behaviour of radiative cooling (RC) materials under realistic outdoor environmental conditions. The main objective of this work is to provide a versatile simulation framework capable of accurately predicting the cooling performance of newly synthesised RC materials based on their spectral optical and thermal properties.

The model was implemented using Finite Element Modelling in *COMSOL Multiphysics*®, coupling the Heat Transfer in Solids and Surface-to-Surface Radiation to evaluate the conductive, convective and radiative heat transfer contributions under realistic conditions. The wavelength-dependent optical properties of the RC materials were incorporated from UV-Vis-NIR and FTIR measurements. Real atmospheric conditions, including ambient temperature, solar radiation, relative humidity, atmospheric pressure, and wind speed, were directly obtained from our on-site weather station and also included in the model. Spectrally-resolved atmospheric emissivity data was generated via *libRadtran* based on these real meteorological conditions to consider an accurate estimation of the atmospheric window. This approach overcomes the limitation of constant or simplified emissivity in standard software by dynamically integrating day-specific atmospheric emissivity spectra.

Validation has been performed by replicating an experimental setup developed within the group, comparing simulated and measured temperature profiles for different RC materials (different anodized aluminium oxides and cellulose-based materials) over full 24-hour cycles (Figure 1). Results showed good agreement with experimental data, with deviations remaining within acceptable uncertainty margins defined by ASHRAE Guideline 14-2014. The model accurately captures conductive, convective, and radiative heat transfer between surfaces and the atmosphere, providing a level of robustness, versatility, and spectral fidelity not previously reported according to authors' best knowledge.

In conclusion, this predictive numerical framework offers a reliable tool to assess radiative cooling performance of advanced materials under real environmental conditions. Its integration of spectral atmospheric data with multiphysics finite element modelling provides a foundation for future studies and the design of next-generation RC materials.

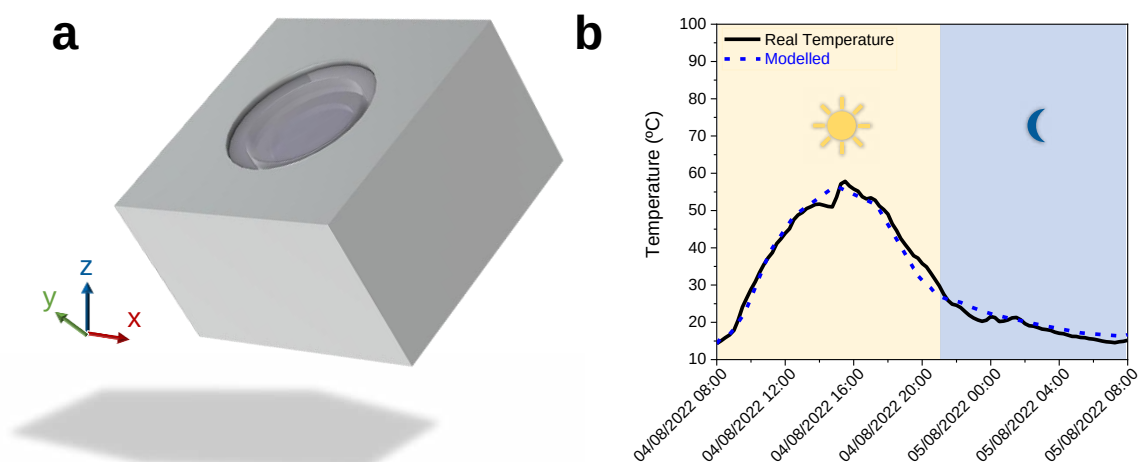


Figure 1. a) Geometry of the model replicating the experimental setup. b) Experimental temperature profile (black) compared with its corresponding simulated temperature curve (blue) during day and nighttime.

Acknowledgment

We acknowledge financial support from “ERC Consolidator Grant No. 101087974 COOLed”.

Development and Thermophysical Characterization of Particle-Based Coatings for Passive Daytime Radiative Cooling

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Cooling demands account for nearly 20% of global electricity consumption and contribute roughly 10% of greenhouse gas emissions. Passive daytime radiative cooling (PDRC) offers a promising low-energy solution for achieving sub-ambient surface temperatures by reflecting incoming solar radiation and emitting thermal radiation through the 8 μm ... 13 μm atmospheric infrared window. This work focuses on PDRC applications in buildings and urban environments, where highly reflective and emissive coatings can be applied to roofs, façades or cooling panels for hydronic cooling in order to reduce heat gains and provide passive cooling without or with very low energy consumption.

Hence coatings with optimized thermophysical (infrared-optical as well as thermal) properties have been developed and characterized in this work. The coatings are based on particles (BaSO_4 , CaCO_3 , etc.) which are highly scattering in the solar spectral region from 0.3 μm to 3 μm . These particles are embedded in a polymeric matrix (polyurethane, acryl, etc.) which is highly emitting in the mid and far infrared, especially in the atmospheric infrared window. In total these coatings provide a significant temperature drop below ambient temperature and thus a passive cooling even under direct sunlight during the day.

For characterization the coatings have been applied on metallic substrates with a high thermal conductivity, such as copper or aluminium, which can be for example used in outdoor cooling panels for hydronic cooling systems. Beside the structural properties, such as particle size distribution, dispersion of the particles, etc. the infrared-optical and thermal properties have been determined and correlated to the structure to optimize the coating.

The spectral directional-hemispherical reflectance and subsequently the spectral directional absorptance (and spectral directional emissivity, which equals the spectral directional absorptance at a given wavelength due to Kirchhoff's law) has been measured using UV-VIS-NIR spectrophotometry with PTFE-coated integrating spheres in the solar spectral region and FTIR-spectroscopy with gold-coated integrating spheres in the MIR- and FIR-range. From these values the solar absorptance and the total normal emissivity as well as the total hemispherical emissivity have been derived. Additionally the thermal diffusivity, the specific heat capacity and the thermal conductivity of the multi-layer system (coating and substrate) have been measured using laser-flash-techniques and differential scanning calorimetry. These values are needed to model the heat exchange between the sample surface and the environment (including the sky) as well as the heat transport through the PDRC-paint and the substrate in order to predict the temperature drop below ambient temperature and the resulting cooling power, respectively.

Furthermore the sub-ambient temperature drop and the passive radiative cooling power have been determined by in-field tests under real conditions using additionally developed on-site setups, in order to validate the predictions from the thermal modelling using the measured thermophysical properties of the coating. Hence these complementary measurements provide a comprehensive and reliable evaluation of the cooling performance.

The results are presented in this work. Firstly, one gets a correlation between the particle sizes and the refractive index of the coating materials and substrate on one side and the scattering of solar radiation and the thermophysical properties on the other side. Secondly, one gets a correlation between the scattering of solar radiation and the thermophysical properties on one side and the temperature drop and the cooling performance under direct sunlight on the other side. The variation of the derived cooling power in dependence on the structural and thermophysical properties of the coating are presented together with the developed outdoor and indoor setups.

5.2

Advanced Materials Design and Characterisation Multi-Scale Modelling



Thermodynamic models across multiple scales to design materials for net zero and the energy transition

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Advanced materials are pivotal in meeting Net Zero targets, enhancing the energy transition, and underpinning the principles of the circular economy. In this presentation, we will delve into the application of polymeric and composite materials in a range of crucial areas. These materials are fundamental in technologies for capturing carbon dioxide, purifying gases, advancing healthcare technologies, creating biodegradable packaging, and ensuring the safe storage and transportation of hydrogen.

We will discuss the innovative development and continuous improvement of sophisticated modeling tools. These tools are essential for the design and enhancement of materials to optimize their performance and minimize the energy consumed during separation processes. This is vital for achieving zero waste in packaging applications and mitigating risks associated with the handling of compressed hydrogen.

This presentation will outline how integrating multi-scale models—from the atomistic level through to finite element methods and continuing up to continuum thermodynamics—can significantly enhance the predictive accuracy and computational efficiency of our simulations. Additionally, we will introduce breakthrough hybrid methods that combine machine learning (ML) with traditional physics-based approaches. These methods are specifically designed for predicting the behavior of high-performance polymer membranes. They facilitate the transfer of knowledge from small molecular systems to more complex macromolecular structures, thus pioneering future developments in this field [1-5].

Acknowledgment

This research forms part of the research program of DPI, projects 844: Modelling and Design of Multiphase Polymeric Materials for High Performance Applications Across Multiple Scales (MuMPol) and 874: “Characterization and Modeling of high-performance polymers for gas barrier applications” (CharMPol). The support of Kidney Research UK through the program Kidney Research UK – Stoneygate Research Project Grant SG_KS_RP_012_20221129 is also gratefully acknowledged.

Significant references

1. O. Atiq., E. Ricci, M.G. Baschetti and M.G. De Angelis, Fluid Phase Eq., 2023, 570, 113798.
2. K. Papchenko, E. Ricci and M.G. De Angelis, Polymers, 2024, 16, 2776.
3. T. Fabiani, E. Ricci, C. Boi, S. Dimartino and M.G. De Angelis, PCCP, 2023, 25, 24069.
4. E. Ricci and M.G. De Angelis, Rev Chem Eng, 2024, 40, 567.
5. H. Ismaeel, D. Gibson, E. Ricci and M.G. De Angelis, J Membr Sci, 2024, 691, 122220.



Accelerating Sustainable Materials Discovery with Artificial Intelligence

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The development of sustainable materials, particularly green solvents, is a critical challenge in the transition towards a circular economy. Many promising solutions, such as deep eutectic solvents (DESs), are complex, multicomponent mixtures whose properties are tunable through careful selection of molecular precursors and compositions. However, discovering optimal formulations through traditional trial-and-error experimentation remains costly, labor-intensive, and time-consuming.

In this work, artificial intelligence (AI), particularly stochastic machine learning models like Gaussian processes (GPs), are leveraged to significantly accelerate the discovery and optimization of sustainable materials. GPs excel in low-data regimes, efficiently interpolating sparse experimental datasets while quantifying uncertainty. This makes them ideal for guiding iterative experimentation via active learning or Bayesian optimization, effectively turning GPs into laboratory companions.

Through several case studies, this work demonstrates how GPs can reduce the experimental burden in solvent design, including the construction of phase diagrams, prediction of solubility curves, and estimation of physicochemical properties from quantum chemistry descriptors (e.g., sigma profiles). Beyond predictive accuracy, the interpretability of GP models provides valuable insights into structure–property relationships, effectively allowing models to "learn chemistry" from limited data. These capabilities position stochastic AI approaches as powerful laboratory companions in the search for sustainable materials, helping accelerate innovation while minimizing environmental and experimental costs.

Acknowledgment

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Assessing the heat transfer performance of an LTES tank with PCM encapsulated in tubes: Scale-up insights

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Climate change and the urgent need for a sustainable energy transition demand to increase the integration of renewable energy sources and to improve techniques for energy management.

Latent thermal energy storage (LTES) is a promising solution to decouple energy supply and demand, offering higher energy density compared to sensible heat storage. In residential applications, LTES can address both heating and cooling requirements depending on the phase change material (PCM) selection and related melting temperature range [1].

This work evaluates the thermal performance of a lab-scale shell-and-tube LTES prototype with an unconventional configuration, where the PCM is encapsulated inside the tubes while the heat transfer fluid (HTF) circulates on the shell side. Two configurations are investigated: a five-tube arrangement and a thirteen-tube arrangement. Moreover, two distinct PCMs are tested for different applications: a Na₂CO₃-water eutectic solution (melting temperature of -2.1 °C) for cold storage utilization, and a commercial paraffin-based PCM (melting temperature of 32 °C) for heating applications.

The experimental setup consists of the LTES tank connected to a thermostatic bath, whose integrated pump circulates an ethylene glycol-water mixture through the shell side. Three complete charging-discharging tests are performed for each configuration, by setting adequate temperature extremes to ensure full phase change transition.

Data analysis allows the quantification of the exchanged latent heat, calculated through the energy balance on the HTF side. The results are compared with differential scanning calorimetry (DSC) measurements, delving into the differences between small-scale laboratory measurements and larger-scale experimental systems. Furthermore, the correlation between the number of tubes and the thermal energy exchanged is investigated and discussed with a view to the design of these systems.

The results directly contribute to the design and scale-up of the LTES demonstration systems for the Horizon EU project ECHO (Efficient Compact Modular Thermal Energy Storage), which aims to develop an innovative TES system integrating both PCMs and thermochemical materials.

Beyond this application, the study offers useful insights into the challenges and opportunities encountered when evaluating the thermophysical properties of PCMs, transitioning from small-scale characterization to real-world prototype testing, an essential step for practical implementation of LTES technologies in residential buildings.

Acknowledgment

This research was funded by the European Union's Horizon Europe research and innovation program within the ECHO project, under grant agreement No. 101096368.

Significant references

1. L. Vallese, H. Javadi, B. Badenes, J. F. Urchueguia, G. Lombardo, D. Menegazzo, Z. Ure, S. Cesari, M. Bottarelli, E. Baccega, M. De Carli, A. Lopez, B. Sánchez, L. Mabe, A. A. Aydin, S. Bobbo, and L. Fedele, *Renewable and Sustainable Energy Reviews* **225**, 116133 (2026).

Comparative Study of CAMD and Graph Diffusion-Based Approaches for Organometallic Molecular Design

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In the field of advanced material development, one of the key challenges is efficiently identifying molecular structures that meet specific performance criteria. To address this issue, computer-aided molecular design (CAMD) has emerged as a leading computational approach. This method has evolved from classical group-contribution and optimization-based techniques [1] to modern deep-learning-based generative models [2]. Recently, graph diffusion models have emerged as powerful tools for inverse molecular design. They offer high flexibility in structural exploration and the ability to incorporate target-aware property guidance during molecule generation [3]. In this work, we present a systematic comparison between conventional CAMD workflows and graph diffusion-based generative models. We focus on their applicability, constraints, and scalability in realistic chemical design tasks. To demonstrate practical implications, both approaches are applied to organometallic compounds, allowing us to assess not only their theoretical performance but also their practical viability in complex chemical systems. Our findings indicate that while CAMD ensures strong interpretability and chemical validity through constraint-driven exploration, diffusion-based inverse design is more efficient in navigating chemical space and converging toward target properties, particularly under multi-objective optimization requirements. This study concludes that combining diffusion-based generative design with CAMD-derived constraint integration presents a promising strategy for molecular design, effectively balancing exploratory capability with chemical feasibility. The results support the development of a hybrid framework that leverages the strengths of both approaches and demonstrates significant potential for application to complex chemical systems, such as organometallic compounds.

Acknowledgment

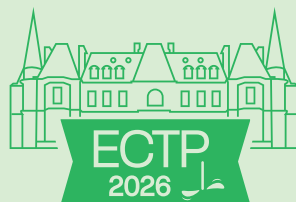
This research was supported by the AI project of Company SK Inc. AX, which builds upon the company's existing AIPS(AI Properties Screening) service. Technical consultation was provided through collaboration with the Molecular Design Laboratory at Korea University. The authors gratefully acknowledge the support and cooperation of both institutions.

Significant references

1. N.D. Austin, N. V. Sahinidis, and D. W. Trahan, *Chemical Engineering Research and Design*, vol. 116 (2016) pp. 2-26.
2. A. S. Alshehri, R. Gani, and F. You, *Computers & Chemical Engineering*, vol 141 (2020): 107005.
3. V. Dorna, D. Subhalingam, K. Kolluru, S. Tuli, M. Singh, S. Singal, N. M. A. Krishnan, and S. Ranu, *arXiv preprint arXiv:2406.01650* (2024).

5.3

Advanced Materials Design and Characterisation Separation Processes



In silico capture of PFAS with cyclodextrin-based adsorbents

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PFAS and other micropollutants in water pose a serious threat to the environment and public health. Current water treatment techniques are often associated with low efficiency/selectivity and unsustainability for these emerging pollutants. Considering the ever-rising intensity of industrial, agricultural, and domestic activities, new sustainable adsorbents for water treatment are urgently needed. Polymers made from cyclodextrins (CD) -cyclic oligosaccharides- and functional cross-linkers can rapidly capture a wide variety of organic micropollutants from water, exhibiting distinct advantages over activated carbon (the conventional material in such processes). CD polymers feature uniform cavities with high adsorption rate and can be easily regenerated many times while the reactivation of activated carbon is energy- and cost-intensive. However, the tailored design and upscaled production of fully sustainable CD polymers that can selectively target emerging micropollutants competing with naturally present organic matter is a major open technological challenge. To this end, we initiated a project called SYROP aiming to design new sustainable and highly efficient CD polymers that can selectively remove PFAS and other high-priority harmful components during water treatment. We use an approach combining molecular modelling and machine learning for in silico designing the new adsorbents, and experiments for fabricating and testing them. In this talk I will present preliminary results from the SYROP project focusing on thermophysical properties, and discuss challenges and plans.

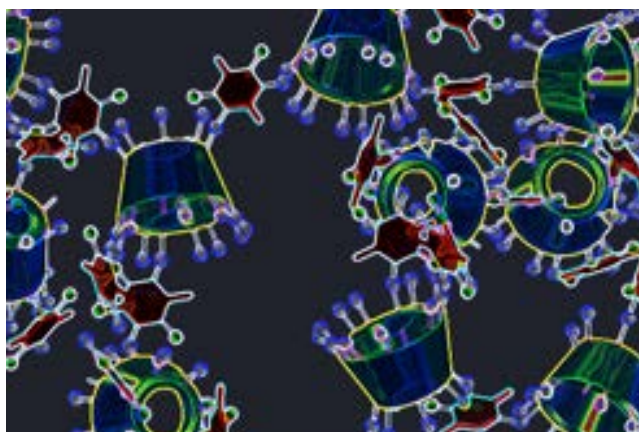


Figure 1. Artistic impression of CD-polymers.

Acknowledgment

The contents of this study are part of the SYROP project, funded by NWO via the OTP scheme. The project is supported by Cyclopure, Waternet, and Witteveen+Bos.

Engineering MOF-on-MOF@Ionic Liquid Composites for Enhanced CO₂ Capture and Selectivity

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In response to the growing global demand for carbon emission reduction, the development of CO₂ capture materials with high adsorption capacity, strong selectivity, and rapid diffusion has become a major research focus^[1]. Although metal-organic frameworks (MOFs) offer highly tunable pore structures, their limitations in molecular recognition and mass transfer efficiency remain significant^[2]. To address these challenges, this work presents an engineered porous liquid (PL) system that integrates a MOF-808@UiO-66-NH₂ core-shell structure with ionic liquids through a structure-interface synergistic strategy. The core-shell MOF is synthesized via PVP-assisted hetero-assembly to couple hierarchical porosity with amino functionalities and is subsequently dispersed into an ionic liquid to form a stable PL with intrinsic microporosity and fluidity. Comprehensive structural characterizations and gas sorption analyses confirm the successful construction of the heterostructure and its effective incorporation into the liquid medium. The resulting PL exhibits enhanced CO₂ adsorption performance, improved CO₂/N₂ selectivity, and accelerated mass transport relative to its individual components. These results demonstrate an effective pathway for advancing next-generation CO₂ capture materials and highlight the promising potential of engineered porous liquids for gas separation.

Acknowledgment

The support which is provided by the National Natural Science Foundation of China (No. 52422607 and 52376165) for the completion of this work is gratefully acknowledged.

Significant references

- [1] F. Kong and W. Chen, "Carbon Dioxide Capture and Conversion Using Metal-Organic Framework (MOF) Materials: A Comprehensive Review," *Nanomaterials (Basel)*, vol. 14, no. 16, Aug 12 2024, doi: 10.3390/nano14161340.
- [2] K. Zhang and R. Wang, "A critical review on new and efficient adsorbents for CO₂ capture," *Chemical Engineering Journal*, vol. 485, 2024, doi: 10.1016/j.cej.2024.149495.
- [3] M. Liu *et al.*, "Metal-organic frameworks for carbon-neutral catalysis: State of the art, challenges, and opportunities," *Coordination Chemistry Reviews*, vol. 506, 2024, doi: 10.1016/j.ccr.2024.215726.
- [4] D. Mei and B. Yan, "Rapid Detection and Selective Extraction of Au(III) from Electronic Waste Using an Oxime Functionalized MOF-on-MOF Heterostructure," *Small*, vol. 19, no. 48, p. e2304811, Nov 2023, doi: 10.1002/smll.202304811.
- [5] H. Sepehrmansourie, H. Alamgholiloo, N. Noroozi Pesyan, and M. A. Zolfigol, "A MOF-on-MOF strategy to construct double Z-scheme heterojunction for high-performance photocatalytic degradation," *Applied Catalysis B: Environmental*, vol. 321, 2023, doi: 10.1016/j.apcatb.2022.122082.
- [6] J. Li *et al.*, "Porous liquids based on ZIF-67@ZIF-8 through the strategy of interface layer reconstruction for CO₂ selective sorption," *Chemical Engineering Journal*, vol. 500, 2024, doi: 10.1016/j.cej.2024.156655.

Uio-66 Based Porous Ionic Liquids: A Synergistic Strategy for Dual Enhancement of CO₂ Solubility and Diffusion Coefficient

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Current research porous ionic liquids (pILs) for CO₂ capture predominantly focuses on ZIF-based MOFs and equilibrium capacities, overlooking the potential of alternative MOF architectures, critical diffusion kinetics, and the effects of low MOF loadings^{1,2}. To address these gaps and thereby enhance the comprehensive CO₂ capture performance, we synthesized pILs using UiO-66 as the porous material and [DMIM][NTf₂] as the sterically hindered solvent with the relatively low UiO-66 proportion from 0.1%-2.0%, achieving dual enhancement of CO₂ solubility and diffusion coefficient. Comprehensive characterization confirmed the structural integrity, well-defined morphology, and correct chemical composition of the synthesized materials. The CO₂ solubility in the low-pressure region was measured by the isochoric saturation method and correlated by the modified Krichevsky-Kasarnovsky equation. Also, the corresponding diffusion coefficients were calculated based on the semi-infinite volume model and correlated by the Arrhenius equation. The results demonstrated that the pILs achieved dual enhancement in both CO₂ solubility and diffusion coefficient. At 303.15 K, the Henry's constant of the 2.0% pILs decreased by 20.80% compared to the pure ionic liquid, while at 343.15 K, the CO₂ diffusion coefficient increased by 22.19%. The variation of UiO-66 proportion in pILs on CO₂ Henry's constant and diffusion coefficient shown in Figure. 1.

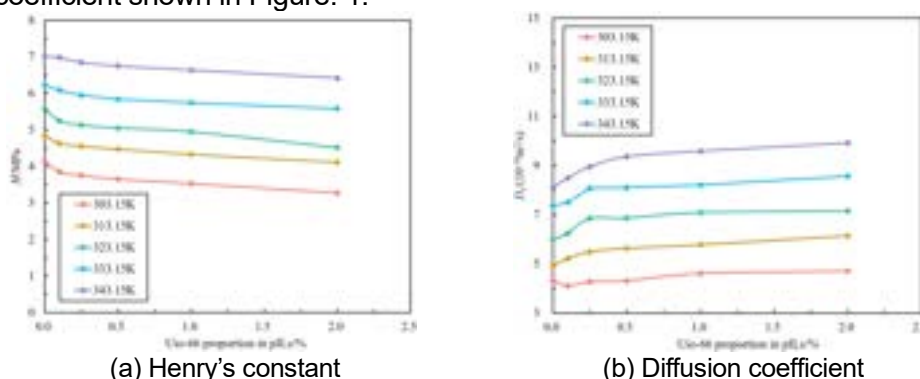


Figure 1. variation of UiO-66 proportion in pILs on CO₂ Henry's constant and diffusion coefficient

Also, high-pressure absorption-desorption isotherms further showed a 20.1% average enhancement in CO₂ solubility at 2000 kPa, with over CO₂ cyclic efficiencies maintained at 94.2%, 97.2%, and 97.3% after five cycles at 500, 1000 and 2000 kPa. These results indicate the significant enhancement and exceptional absorption stability of pILs across a wide pressure range. In summary, the UiO-66 based pILs effectively achieve dual enhancement of CO₂ solubility and diffusion coefficient. Combined with excellent absorption stability and high CO₂ solubility over a wide absorption pressure range, they demonstrate significant improvement of the CO₂ capture performance and potential for the industrial CO₂ capture applications.

Acknowledgment

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Significant references

1. J. Avila, L.F. Lepre, C.C. Santini, M. Tiano, S. Denis-Quanquin, K. Chung Szeto, A.A. Padua and M. Costa Gomes, *Angew. Chem*, vol. 133.23 (2021), pp. 12986–12992.
2. X. Li, D. Wang, Z. He, F. Su, N. Zhang, Y. Xin, H. Wang, X. Tian, Y. Zheng and D. Yao, *Chem. Eng. J*, vol. 417 (2021), pp. 129239.

Impact of Supercritical CO₂ on the Molecular Architecture of Recycled High-Density Polyethylene

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In the context of physical recycling, supercritical fluid extraction (SCFE) using CO₂ is key to remove additives or residues from recycled polyethylene (PE) [1,2]. However, the high pressures and temperatures involved can alter the polymer's molecular weight and molecular architecture. These changes affect the thermal, caloric and rheological properties [3], which are of high importance for the application of recycled PE. It is therefore essential to optimize the recycling process so that the material properties can be adjusted as required [4,5]. This experimental study aims to elucidate the influence of gas solubility under SCFE conditions on the molecular architecture and associated thermal, caloric and rheological properties of high-density polyethylene (HDPE). The structure-property relationships of Ziegler-Natta- and Phillips-catalyzed HDPE samples are investigated. Therefore, the molecular architecture is determined using cross-fractionation chromatography, the degree of crystallinity is measured via high-resolution calorimetry and storage and loss modulus are investigated via rheology. These results show that Phillips-HDPE exhibits drastic property changes under certain process conditions (Figure 1) whereas Ziegler-Natta-HDPE remains the same. Based on the obtained relationships, possible process windows for SCFE are identified and the potential for adjusting the properties through process conditions is analyzed.

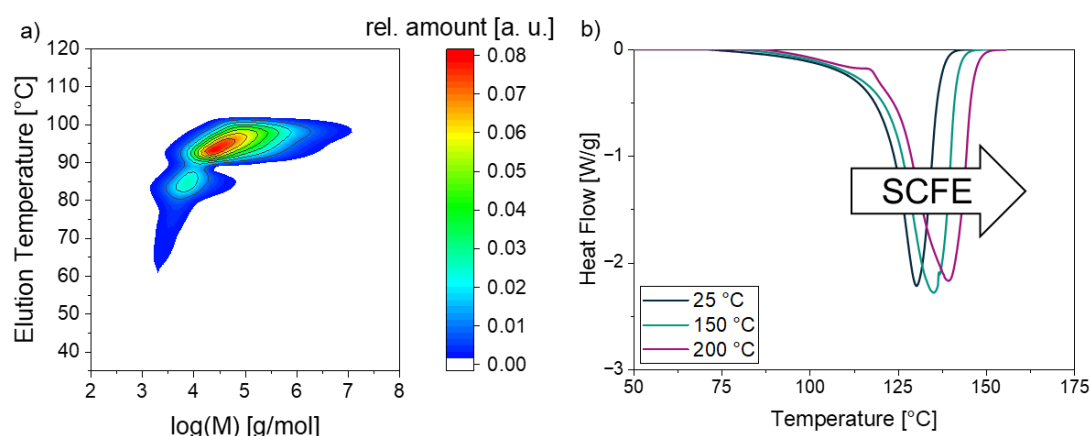


Figure 1. a) Molecular architecture of a HDPE measured by CFC. b) Heat Flow of HDPE before (blue) and after SCFE treatment at 150 °C (green) and 200 °C (pink).

Acknowledgment

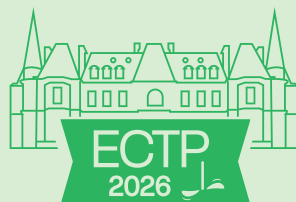
Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – 453715850.

Significant references

1. C.S. Castro Issasi, M. Sasaki, A.T. Quitain, T. Kida, N. Taniyama, J. Supercrit. 146 (2019) 23-29.
2. A. Allassali, N. Aboud, K. Kuchta, P. Jaeger, A. Zeinolebadi, Polymers. 12 (2020) 1347.
3. E. Vicente-Alique, J.F. Vega, N. Robledo, J. Nieto, J. Martínez-Salazar, J. Polym. Res. 22 (2015) 62.
4. Z. Fan, Z. Yu, L. Steuernagel, M. Fischlschweiger, Macromol. Chem. Phys. 223 (2022) 2200206.
5. A. Arumugam, J. Zimmermann, T. Weingartz, M. Fischlschweiger, V. Hirschberg, Polym. Degrad. Stabil. (2025) submitted.

5.4

Advanced Materials Design and Characterisation Energy-Related Materials



Inverse Method for Estimating the Thermal Properties of a Cylindrical Battery Cell

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An inverse thermal model has been developed to estimate both the radial thermal conductivity and heat capacity of a cylindrical Li-ion battery cell. The overall aim of this study is to improve the understanding and modeling of heat transfer within these cells, with the goal of optimizing their thermal management.

The experimental method is based on the hot-wire technique [1], where a heating wire is inserted into the central gap of the jelly-roll structure. One thermocouple is attached directly to the wire, while another is positioned on the outer surface of the cell. These two temperature measurements are used within an inverse method to identify five key thermal parameters of a 1D radial transient model based on thermal quadrupoles [2]: the heat capacity of the heating wire, the thermal contact resistance at the wire-cell interface, the radial thermal conductivity of the cell, the heat capacity of the cell, and the external convection coefficient.

As the experimental requirements involve cutting both end caps of a real battery cell (to minimize side effects and for wire insertion), the validation on actual cells has not yet been performed due to chemical safety considerations. Therefore, this work focuses on a preliminary feasibility study conducted on several reference materials, including PTFE (Teflon), PVC, polyethylene, and extruded polystyrene.

To validate the approach, estimated heat capacities are compared with differential scanning calorimetry (DSC) measurements, while estimated thermal conductivities are compared with results from the hot-plate method [1]. This development aims to determine the most suitable estimation strategy (type of dynamic model: impedance and/or transmittance, measurement duration, etc.) through a sensitivity analysis of the thermal parameters, in order to assess the robustness of the inverse model before applying it to real battery cells.

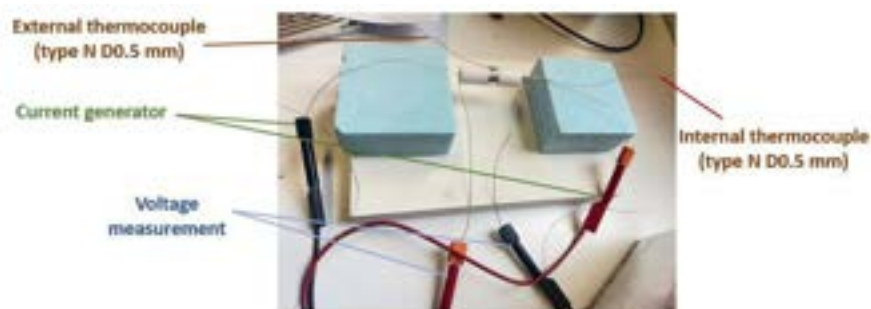


Figure 1. Experimental setup for the hot-wire method using a 18650 Teflon reference sample

Acknowledgment

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Significant references

1. Y. Jannot and A. Degiovanni, *Thermal properties measurement of materials*, ISTE WILEY, 2018.
2. D. Maillet, S. André, J. Batsale, A. Degiovanni and C. Moyne, *Thermal quadrupoles: solving the heat equation through integral transforms*, John Wiley & Sons Ltd, 2000.

Multi-Objective Molecular design of Ionic Liquids on Small Dataset for High-Performance Lithium Metal Battery Electrolytes

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Electrolytes play a critical role in accelerating the commercialization of lithium metal batteries (LMBs). Ionic liquid (IL)-based electrolytes have attracted considerable interest due to their non-flammability, high thermal stability, and wide electrochemical windows^{1,2}. However, the scarcity of experimental data for ILs hinders their targeted design through conventional approaches. In this work, we develop a computational framework integrating variational autoencoder (VAE), multilayer perceptron (MLP), and particle swarm optimization (PSO). Molecular structures are encoded using the Simplified Molecular Input Line Entry System (SMILES), enabling structural featurization for machine learning. The VAE is trained on a limited dataset to construct a continuous latent space, which facilitates property prediction and molecular optimization. Key properties—including the lowest unoccupied molecular orbital (LUMO) of the cation, the highest occupied molecular orbital (HOMO) of the anion, viscosity, and ionic conductivity—are optimized simultaneously to identify ILs that meet the comprehensive requirements of LMB electrolytes. Results show that the IL generated by this model has good comprehensive performance in lithium metal button battery. The proposed strategy offers a robust and efficient platform for the rational design of IL-based electrolytes, with potential extension to other functional material systems.

Acknowledgment

The support which is provided by the National Natural Science Foundation of China (No. 52422607) for the completion of this work is gratefully acknowledged.

Significant references

1. J. Wang and Y. Wang, *J. Chem. Inf. Model.*, vol. 65 (2025), pp. 10961–10976.
2. S. Xue, Y. Liu, K. Hou, M. He, and X. Liu, *J. Power Sources*, vol. 615 (2024), pp. 235097.

The $\text{Li}_2\text{CO}_3\text{--Na}_2\text{CO}_3\text{--K}_2\text{CO}_3$ Molten Eutectic. Challenges and Gaps in Thermophysical Property Data

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This work revisits the $\text{Li}_2\text{CO}_3 - \text{Na}_2\text{CO}_3 - \text{K}_2\text{CO}_3$ eutectic through a critical assessment of the literature from its reported melting point at 397 °C (670 K) up to approximately 1200 K. Using a methodology inspired by IUPAC-supported strategies previously applied to common liquids such as water and hydrocarbons, we examine the quantity, quality, and coherence of existing measurements. Reference correlations are proposed only where the data are sufficiently robust to justify them. The analysis highlights a pressing need for more accurate and comprehensive measurements—particularly for heat capacity, thermal conductivity, and viscosity—to enable the development of reliable standard reference correlations.

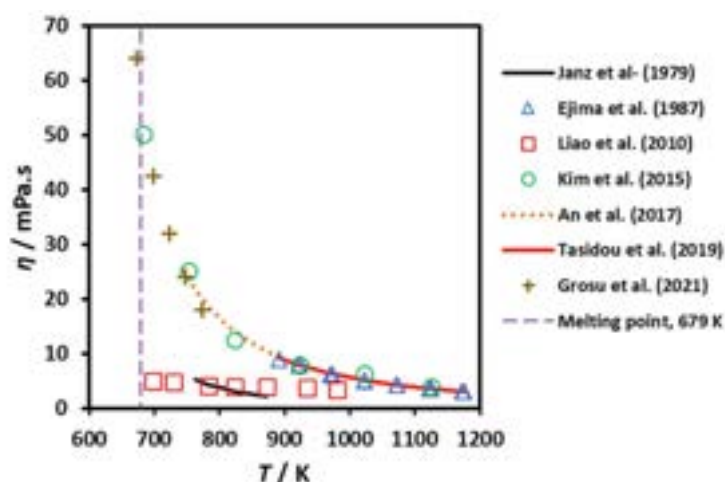


Figure 1. Viscosity of the ternary eutectic $(\text{LiNaK})_2\text{CO}_3$. Lines are equations given by the authors. The points from Liao et al. (2010) and Grosu et al. (2021) were estimated from the available plot.

Acknowledgment

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Significant references

1. V.M.B. Nunes, M.J.V. Lourenço, F.J.V. Santos, C.A. Nieto de Castro, C.A., *Applied Energy*, vol. 242 (2019), pp. 1626-1633.
2. A.R. Starke, J.M. Cardemil, V.R.B. Bonini, R. Escobar, M. Castro-Quijada, A. Videla, *Applied Energy*, vol. 359 (2024), 122689.
3. K.A. Tasidou, J.M. Magnusson, T. Munro, M.J. Assael, *J. Phys. Chem. Ref. Data*, vol. 48 (2019), 043102.

Optical and Thermal Properties of n-Type Porous Silicon Fabricated by Short-Time Electrochemical Etching at Different HF Concentrations.

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N-type porous silicon samples were fabricated from crystalline silicon wafers by electrochemical etching in aqueous HF solutions at concentrations of 20, 30, and 40 wt%, within a time range of 1 to 10 minutes to evaluate the influence of both parameters on pore morphology and, consequently, on the optical and thermal properties of the material. The morphological features were characterized by scanning electron microscopy (SEM) to determine pore surface dimensions and internal structure. Optical characterization included reflectance, absorbance, photoluminescence, and bandgap analyses, performed using reflectance spectroscopy (RS), photoluminescence spectroscopy (PLS), and photoacoustic spectroscopy (PAS). Furthermore, the effective thermal diffusivity was measured using the frequency-resolved photoacoustic technique (PA-f). Increasing HF concentration and processing time produced a 4.2-fold increase in porous layer thickness, a 50.2% reduction in ultraviolet reflectance, and a visible photoluminescence from 776 to 685 nm accompanied by enhanced emission intensity. The effective thermal diffusivity decreased by 52.4%, and the resulting porous-on-crystalline bilayer structure promotes heat dispersion toward the substrate base.

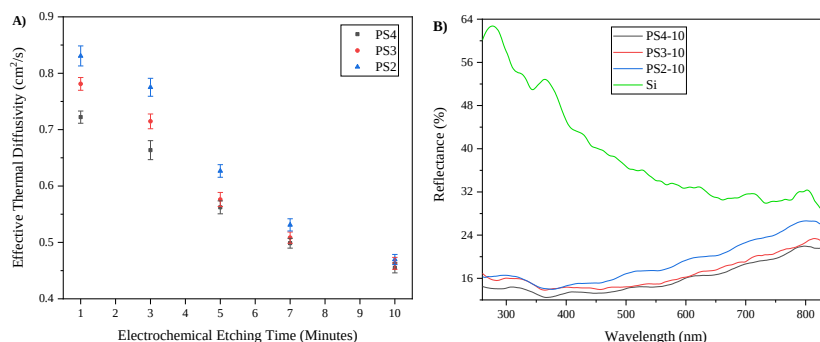


Figure 1. A) Effective thermal diffusivity and B) reflectance spectra of porous silicon as a function of electrochemical etching time and HF concentration.

Table 1. Reduction in the effective thermal diffusivity and reflectance of porous silicon samples as a result of electrochemical etching.

Samples	Effective thermal diffusivity (cm ² /s)	Minimum reflectance (%)
PS-4	0.7222 – 0.4548	17.8158 – 12.4579
PS-3	0.7811 – 0.4629	18.0453 – 13.8139
PS-2	0.8307 – 0.4697	20.8176 – 13.9609

Acknowledgment

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Significant references

1. Benhida, A., Achargui, N., Combette, P., & Foucaran, A. (1998a). The use of experiment charts for the fabrication of porous silicon. *Journal Of Crystal Growth*, 186(4), 565-570.
2. Hasan, P. M. Z., Sajith, V. K., Ansari, M. S., Iqbal, J., & Alshahrie, A. (2017). Influence of HF concentration and current density on characteristic morphological features of mesoporous silicon. *Microporous And Mesoporous Materials*, 249, 176-190.

5.5

Advanced Materials Design and Characterisation

Amorphous and Polymer-Based Materials



How the Thermodynamic Formation History Affects Glass Properties: Defining the Glass Transition Pressure P_g

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Describing the pressure–volume–temperature (PVT) behavior of glass-forming materials, such as amorphous polymers, in the vitreous state and at glass transition has long challenged existing theories and models, because the thermodynamic state of a glass is not uniquely determined by temperature and pressure (Fig. 1). To account for the thermodynamic formation history of glasses, internal state variables are introduced in addition to the natural state variables of the corresponding thermodynamic potential. This approach replaces the conventional equation of state with a dynamic law that governs the temporal evolution of the specific volume. The resulting constitutive models accurately describe the PVT data of amorphous polymers in the equilibrium state, the vitreous state, and at glass transition, under both isobaric and isothermal conditions. This work verifies the Frenkel–Kobeko–Reiner equation,

$$\beta_0 \tilde{\tau}|_{T=T_g} = \text{const.},$$

which relates the cooling rate $\beta_0 < 0$ and relaxation time $\tilde{\tau}$ at the glass transition temperature T_g . Importantly, the findings also imply that the formally identical relation,

$$\gamma_0 \tilde{\tau}|_{P=P_g} = \text{const.},$$

between the compression rate $\gamma_0 > 0$ and relaxation time holds at the glass transition pressure, thus providing a thermodynamically consistent measure for defining the glass transition pressure P_g .

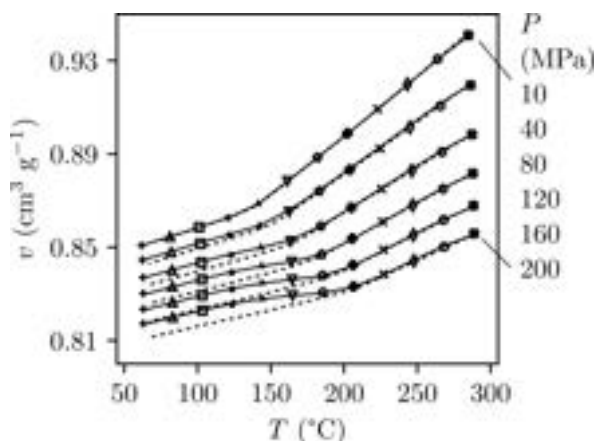


Figure 1. Pressure–volume–temperature (PVT) behavior of the amorphous polymer polycarbonate at glass transition during isobaric cooling (dashed isobars) and isothermal compression (marked quasi-isobars).

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Significant references

1. C. Corbisieri, *Macromol. Theory Simul.*, vol. 34 (2025), e00052.
2. C. Corbisieri, *J. Chem. Phys.*, vol. 162 (2025), 194503.
3. C. Corbisieri, *Macromol. Theory Simul.*, vol. 33 (2024), 2400052.
4. C. Corbisieri, P. Jousset, and M. Roos, *J. Appl. Polym. Sci.*, vol. 138 (2021), e50662.

Upscaling the curing process for the production of large components

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The manufacturing process for parts made of epoxy resin involves a curing reaction. An epoxy monomer is combined with a hardener to create a flowable mixture, which is then poured into a mold. The mold is heated to a temperature determined by the resin-hardener system. This heat triggers a crosslinking reaction, where reactive groups in the resin and hardener bond to form a three-dimensional polymer network. As curing progresses, the material transitions from a liquid state to a rigid, structural solid.

Kinetics analysis is a beneficial tool for optimizing the temperature and time profile of the process, ensuring complete curing of the product, while minimizing cycle time and energy consumption. Such modeling is typically based on laboratory measurements. A preferred method is differential scanning calorimetry (DSC), which works with small samples in the order of a few milligrams.

Upscaling the resin's behavior from laboratory-scale to large-scale parts requires further analysis and simulation procedures. This is because the curing reaction is strongly exothermic, releasing energy in an order of magnitude of 500 J/g [1]. While the heat generated in small parts can easily dissipate, it can generate significant temperature gradients in large molds. Excess heat causes uneven curing and localized degradation, leading to non-uniform shrinkage that impacts dimensional accuracy and mechanical properties.

Therefore, reliable simulation of the curing process within a mold necessitates not only comprehensive understanding of the kinetics of the crosslinking process, but also knowledge of the changes in thermophysical properties during the reaction, including specific heat, thermal conductivity and density.

In this study, the curing behavior of an amine-based epoxy resin is investigated by means of DSC. The measurements are used to perform kinetics analysis taking vitrification into account. The temperature-dependent thermophysical properties — including thermal conductivity, density and specific heat — are determined by a guarded heat-flow meter (GHFM), a thermo-mechanical analyzer (TMA) and temperature-modulated DSC measurements. The respective density is derived from the thermal expansion behavior measured.

All results are transferred to a finite elements simulation software (Termica Neo, NETZSCH-Gerätebau GmbH), allowing deep insight into the temperature profiles and curing processes on a large scale as they occur in an actual mold. The simulation framework is implemented in the manufacturing process of real components.

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Significant references

1. F. Wu, X. Zhou, and X. Yu, RSC Adv. 2018, vol. 8 (2018), pp. 8248–8258.

Impact of Tacticity on the Solid-Liquid Equilibrium of Polypropylene Solutions

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The advantage of polypropylene consists of a high chemical, mechanical, and thermal resistance, low moisture absorption, and low density. The application properties can be tailored by the polymerization reaction leading to different polymer architecture in terms of molecular weight distribution, the degree of branching, and the tacticity. The thermodynamic properties of polypropylene depend also on the polymer architecture. Additionally, the polymer architecture defines the temperature-dependent degree of crystallinity, which estimates the phase behavior, i.e. the gas solubility.

Based on the Lattice Cluster Theory (LCT) [1] and the continuous thermodynamics [2], a theoretical framework [3,4], allowing the calculation of solid-liquid equilibria (SLE) of polymer solutions, was developed. The LCT permits the description of the polymer branching, and the continuous thermodynamics takes the molecular weight distribution function directly into account. Based on the Flory theory of copolymer crystallization [5], the semi-crystallinity can also be considered in this framework [3,4]. Hitherto, the impact of the tacticity was not included, even though, the tacticity plays an important role in polymer crystallization [6].

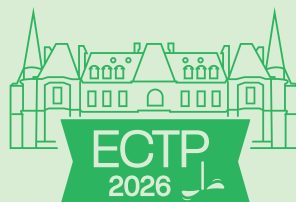
In this contribution, the tacticity is also considered in the expression for the Gibbs energy of the polymer solution. The basic idea is the inclusion of a bending energy in the thermodynamic framework [7]. For example, the steric interactions in olefins typically produce a lowest-energy trans and several higher-energy, possibly degenerate, gauche rotational states. As the difference between trans and gauche conformations grows large, the chain stiffens considerably. Thus, two different energy states are present, where the difference of these energy states is called bending energy. In the case of polypropylene, three different kinds of tacticities occur, namely isotactic, syntactic and atactic, which differ in the number of gauche states and consequently in the bending energy. Finally, the new model can calculate the SLE of polymers in a solvent in dependence of the molecular weight distribution function, degree of branching, tacticity as well as the semi-crystallinity. The model was applied for the calculation of the solubility of different polypropylene samples having different architecture in different solvents (trichlorobenzene, xylol, toluol, decalin). For the investigation of the impact of different architectures model calculations were performed. These model calculations show, that the consideration of the polydispersity leads to a broadening of the melting zone. Polypropylene samples having a different tacticity have also a different degree of crystallinity. Both properties have a large impact on the melting behavior. The molecular weight has an impact only in the oligomer ranch. With increasing the molecular weight, the impact of molecular weight decrease. The model contains only one adjustable parameter, which is the interaction energy between different non-bonded segments. This interaction energy has to be estimated using one data point of the SLE curve. All other parameters include in the model can be estimated using independent experimental data, for instance the molecular weight distribution function from gel permeation chromatography. The calculation results were compared with experimental data taken from the literature.

Significant references

1. K.F. Freed and J. Dudowicz, *Adv. Polym. Sci.* 183 (2005) 63-126.
2. M.T. Rätzsch and H. Kehlen, *Prog. Polym. Sci.* 14 (1989) 1-46.
3. M. Fischlschweiger and S. Enders, *Macromolecules* 47 (2014) 7625–7636.
4. Z. Fan, T. Zeiner, S. Enders and M. Fischlschweiger, *Ind. Eng. Chem. Res.* 61 (2022) 957-967.
5. P.J. Flory, *J. Chem. Phys.* 17 (1949) 223-240.
6. V. Virkkunen, P. Laaria, P. Pitkänen, F. Sundholm, *Polymer* 45 (2004) 3091–3098.
7. K.W. Foreman, K.F. Freed, *Adv. Chem. Physics* 103 (2007) 335-390.

5.6

Advanced Materials Design and Characterisation Thermal Energy Storage



Adapting Smart Materials for Efficient Thermal Energy Storage Systems

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Thermal energy storage (TES) systems are fundamental to achieving net-zero greenhouse gas emissions by 2050, the main objective of the European Green Deal [1]. The increasing penetration of renewable energy sources (RES) and the need for improved energy efficiency require flexible energy systems capable of managing the intermittent nature of renewables. TES supports this transition through electricity load shifting, reducing peak demand and enhancing sector coupling and demand-side flexibility.

Conventional sensible heat storage systems are widely spread but are limited by low energy density and consequent space requirements, motivating the development of innovative storage materials [2]. Thermochemical materials (TCMs) offer the highest values of energy storage density through reversible chemical reactions, enabling long-term storage with minimal losses. Phase change materials (PCMs) provide high volumetric energy density by storing latent heat during phase transitions at constant temperature. A wide variety of PCMs with different thermophysical properties and phase change temperatures are available, making them suitable for different applications. The combination of TCMs and PCMs in hybrid systems creates a beneficial synergy: TCMs enable long-duration energy storage while PCMs can provide thermal buffering and temperature control.

The development of a system of this kind is the objective of the ECHO project, in which the employment of a closed-loop TCM reactor allows to build a compact, modular system for residential applications. In the system, PCMs are used for three purposes: as enhancer for thermal insulation, integrated in a buffer storage, and in a cooling unit to be used in warmer climates. The charging of the system is possible through a heat pump, taking advantage of electricity overproduction, or directly connecting the system to on-site RES. The project demonstrates the potential of integrating TCMs and PCMs to improve the efficiency and flexibility of TES systems.

Acknowledgment

This research was funded by the European Union's Horizon Europe research and innovation program within the ECHO project, under grant agreement No. 101096368.

Significant references

1. In (Communication from the commission to the european parliament, the european council, the council, the european economic and social committee and the committee of the regions, Brussels, 2019).
2. L. Vallese, H. Javadi, B. Badenes, J. F. Urchueguia, G. Lombardo, D. Menegazzo, Z. Ure, S. Cesari, M. Bottarelli, E. Baccaga, M. De Carli, A. Lopez, B. Sánchez, L. Mabe, A. A. Aydin, S. Bobbo, and L. Fedele, *Renewable and Sustainable Energy Reviews* **225**, 116133 (2026).

Thermodynamic, kinetic and structural characterization of Thermochemical Materials for Thermal Storage

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The increasing need for renewable energy sources demands thermal energy storage materials with well-characterized and reliable thermophysical behavior. Thermochemical materials (TCMs) based on solid–gas reactions offer high energy densities, but their practical deployment requires a detailed understanding of the thermodynamic and transport properties governing cycling performance [1]. In this work, we investigate the thermophysical, thermodynamic, and kinetic properties of sodium iodide-based TCMs, a relatively unexplored system capable of incorporating up to two water molecules under conditions relevant for low-temperature heat storage.

Nal was modified via solution doping and subsequently embedded in porous matrices (e.g., vermiculite) at different loadings to enhance heat and mass transfer and to mitigate agglomeration during hydration/dehydration. The structural and microstructural features of the resulting composites were determined by XRD, while SEM–EDX analyses provided morphological and compositional information. Their thermophysical and thermo-chemical behavior was quantified using TGA and DSC under controlled humidity, enabling the determination of hydration/dehydration enthalpies (ΔH), entropies (ΔS), absorption/desorption kinetics, and activation energies. In addition, the impact of porous supporting media on kinetics, heat-transfer properties and cycling stability was assessed.

This study aims to establish correlations between composition, microstructure, and key thermophysical parameters to guide the optimization of Nal-based composites for efficient, reversible, and fast thermochemical heat-storage.

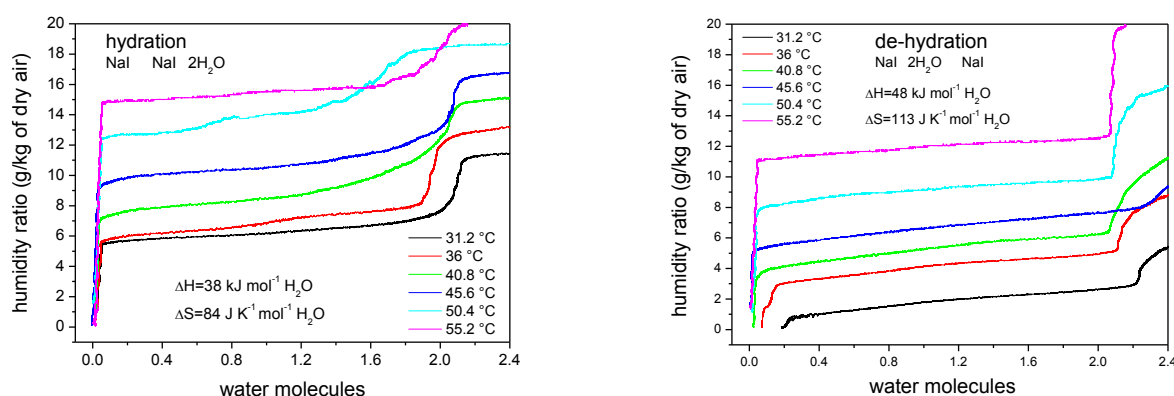


Figure 1. Hydration/de-hydration isotherms of sodium iodide.

Acknowledgment

This research was funded by the Project 1.4 “Frontier materials and devices for energy uses” within the MASE-CNR 2025-2027 Agreement for the research of electrical systems.

Significant references

1. P.A.J. Donkers, L.C. Sögütöglü, H.P. Huinink, H.R. Fischer, O.C.G. Adan, *Appl. Energy*. Vol. 199 (2017) pp. 45–68.

Rational Design of Deep Eutectic Electrolytes for Sustainable Energy Storage

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Deep eutectic solvents (DESs) represent a paradigm in green chemistry, where liquid solvents are prepared by mixing two solid precursors without any chemical reaction.¹ The resulting liquid arises from eutectic-type solid-liquid equilibrium. Recently, this DES framework was extended to the so-called deep eutectic electrolytes (DEEs), which incorporate an electrolyte component as one of the precursors. Instead of dissolving a conventional solid electrolyte in an organic solvent, a solid salt (e.g., LiTFSI) is mixed with a compatible precursor to form a eutectic at room temperature. These DEEs combine the low cost, non-volatility, and environmental benignity of DESs with the high ionic mobility and electrochemical stability required for energy-related applications.

In this work, a combination of computational approaches, namely molecular dynamics and the thermodynamic model COSMO-RS, was employed to investigate the formation of DEEs. The main intermolecular interactions between DEE precursors were studied, enabling the formulation of heuristic rules to readily identify precursor pairs capable of forming liquid DEEs. Moreover, this work demonstrates how negative deviations from ideality can be reliably predicted and achieved, thereby facilitating DEE formation with severe melting point depressions. Finally, based on the developed predictive framework, several new DEEs with high interest for energy-related applications were proposed and experimentally validated.

Acknowledgment

This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UID/50011/2025 (DOI 10.54499/UID/50011/2025) & LA/P/0006/2020 (DOI 10.54499/LA/P/0006/2020), financed by national funds through the FCT/MCTES (PIDDAC). E.E.F thanks Brazilian agencies FAPESP and CNPq for support.

Significant references

1. D. O. Abranches, J. A. P. Coutinho, *Annu. Rev. Chem. Biomol. Eng.*, vol. 14 (2023), pp. 141-163.

Linking Structure and Transport Properties: A CALPHAD Framework for Multicomponent Ionic Melts

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Reliable prediction of transport properties, such as viscosity and electrical conductivity, is essential for understanding and optimizing high-temperature processes involving molten slags and salts. In this work, we present a structurally based CALPHAD framework and databases for modeling transport properties of multicomponent ionic melts across the entire composition and wide temperature ranges. The framework is founded on the ionic two-sublattice liquid model¹, which explicitly represents the structural state of the melt through the site fractions of constituent ionic species.

Within this framework, individual models are developed for viscosity and electrical conductivity, each reflecting the distinct physical mechanisms governing these properties while sharing the same structural foundation. The models take advantage of the site fractions of structural units calculated by minimizing the total Gibbs energy of the system, thereby linking the melt structure directly to the thermodynamic description. This connection enables accurate and physically grounded predictions across broad composition and temperature ranges.

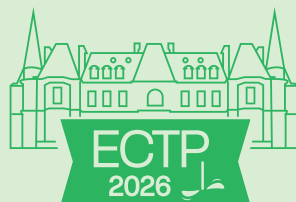
Implemented in the Thermo-Calc software package², the framework enables parameter optimization and predictive property calculations fully consistent with the underlying thermodynamic database. The results demonstrate that incorporating structural information into CALPHAD-based transport property models provides a unified and extensible approach for describing the behavior of complex multicomponent ionic systems.

Significant references

1. M. Hillert, B. O. Jansson, B. O. Sundman, and J. Ågren, *Metallurgical Transactions A*, vol. 16 (1985), pp. 261-266.
2. J.O. Andersson, T. Helander, L. Höglund, P.F. Shi, and B. Sundman, *Calphad*, vol. 26 (2002), pp. 273-312.

5.7

Advanced Materials Design and Characterisation Nuclear Applications



Solidification Reaction Processes in Molten Stainless Steel Containing Boron Carbide

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The Japan Atomic Energy Agency (JAEA) has advanced research on severe accident (SA) phenomena in Generation IV sodium-cooled fast reactors [1]. As established by previous studies, the eutectic reaction and subsequent rearrangement between the control rod material, boron carbide (B_4C), and the core structural material (316 series austenitic stainless steel (SS)), are critical issues in SA assessment. The authors have acquired and reported a variety of thermophysical property data for B_4C -SS melts utilized in simulations of these core melt accidents [2–4]. In the event of core melt accidents, complex core melt behavior emerges as a consequence of the eutectic reaction between B_4C and SS, rendering detailed analysis of the eutectic reaction mechanism imperative. Nevertheless, the solidification process is complicated, and its elucidation has been awaited. Therefore, a combined technique of differential scanning calorimetry (DSC) and electromagnetic levitation (EML) was employed to investigate in detail the solidification behavior of molten SS containing 10 mass% or less B_4C .

First, to comprehend the reaction behavior from a thermal analysis perspective, DSC measurements were conducted on pre-synthesized B_4C -SS samples. Subsequently, based on these results, B_4C -SS samples were levitated using EML to directly observe the solidification process. Furthermore, during the solidification process, the sample was held at a specific temperature for a certain period before being rapidly cooled. The microstructure of the quenched samples was observed using a combination of scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX), while the identification of phases was carried out through X-ray diffraction (XRD). The results of the investigation into the solidification process for various B_4C -SS samples containing up to 10 mass% B_4C are presented herein, based on these experimental findings.

Acknowledgment

This study was supported by the "Technical development program on a common base for fast reactors" entrusted to the Japan Atomic Energy Agency (JAEA) by the Ministry of Economy, Trade and Industry (METI).

Significant references

1. H. Yamano, T. Takai, Y. Emura, H. Fukuyama, H. Higashi, +5 authors, *Proceedings of the 14th International Topical Meeting on Nuclear Reactor Thermal-Hydraulics, Operation, and Safety, NUTHOS 2024*, doi: 10.13182/NUTHOS14-11.
2. H. Fukuyama, H. Higashi, H. Yamano, *J. Nucl. Mater.*, vol. 554 (2021) 153100, doi: 10.1016/j.jnucmat.2021.153100.
3. H. Fukuyama, H. Higashi, H. Yamano, *J. Nucl. Mater.*, vol. 568 (2022) 153865, doi: 10.1016/j.jnucmat.2022.153865.
4. T. Ishikawa, H. Oda, C. Koyama, R. Shimonishi, R. Ikeuchi, P. Paradis, J. Okada, H. Fukuyama, and H. Yamano, *Int. J. Microgravity Sci. Appl.*, vol. 42 (2025) 420202, doi: 10.15011/jasma.42.420202

Thermal Properties Characterization of U_3Si_2 /Al Composite Fuels: Multiscale Experimental and Modeling Approaches

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U_3Si_2 /Al fuel plates are widely used as low-enriched fuels in Materials Testing Reactors (MTRs). This type of fuel consists of three layers: two aluminum alloy (AlFeNi) cladding layers and a central fuel core layer composed of U_3Si_2 particles dispersed in an aluminum matrix. At elevated temperatures or under irradiation, a ternary interaction compound ($U(Al,Si)_{3\pm x}$) forms at the interface between U_3Si_2 and Al as it can be seen in Figure 1. The formation of this compound significantly decreases the thermal conductivity of the fuel core, leading to an increase in operating temperature and potentially causing long-term degradation of the fuel plate [1]. In this study, the thermal properties of U_3Si_2 /Al fuel plates with different U_3Si_2 volume fractions (ranging from 42 to 50 %, which corresponds to uranium loadings ranging from 4.8 to 5.6 gU cm⁻³) in the core were investigated through a series of controlled annealing experiments performed at various temperatures and durations to promote the formation of the interaction compound by thermal activation.

For the first time on this composite fuel, three complementary approaches were implemented to characterize its thermal conductivity at different scales.

The first approach relies on the laser flash analysis technique, a well-established macroscopic method, applied here to tri-layer samples, including tests on specimens without cladding (the latter having been removed by mechanical polishing). The second approach employs infrared microscopy, allowing local-scale measurements of thermal conductivity to investigate the influence of microstructural heterogeneities on thermal property distribution. Finally, numerical simulations using COMSOL Multiphysics® were carried out to estimate the thermal diffusivity and specific heat under various experimental conditions (laser power and pulse duration), providing a complementary modeling perspective to support the experimental results.

The results of these different approaches are compared and discussed. The influence of U_3Si_2 and interaction compound volume fractions on thermal properties is also evaluated.

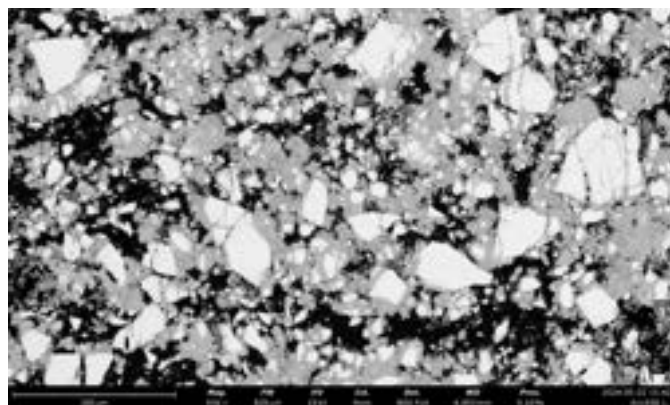


Figure 1. BSE-SEM image of the microstructure of a heat-treated U_3Si_2 /Al sample showing the Al matrix (dark), U_3Si_2 particles (bright), and the $U(Al,Si)_3$ interaction phase (gray).

References

1. Y.S. Kim et G.L. Hofman „Interdiffusion in U_3Si -Al, U_3Si_2 -Al and USi -Al dispersion fuels during irradiation“, J. Nucl. Mater, vol. 140 (2011), pp. 1-9 (doi: 10.1016/j.jnucmat.2010.12.031).

Experimental and numerical study of mesostructural effects on the effective thermal conductivity of granular media

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For Pressurized Water Reactors, understanding the behavior of nuclear fuel under accident conditions is of practical importance. During a hypothetical Loss-of-Coolant Accident (LOCA), the pellet-shaped fuel within the cladding may, under certain conditions, fragment, relocate and form granular media immersed in a gas. Improve our understanding of the mechanisms of heat transfer in such heterogeneous media is important to increase the accuracy of the simulations [1].

This work aims to provide a better understanding of the influence of mesoscale parameters — particle size, shape, and distribution — and of the interstitial gas on the effective thermal conductivity of granular media. A combined experimental and numerical approach has been developed. Transient hot-plane measurements were conducted at ambient temperature under controlled atmospheres and pressures on model oxide powders [2], with granulometries representative of the fragment sizes expected during a hypothetical LOCA fuel fragmentation. The numerical simulations were designed to mirror these experiments : representative microstructures were generated using the DEM method (Discrete Element Method), discretized with the *Merope* software [3], and solved with an FFT-based solver [4] to compute the effective thermal conductivity.

The measurements show that the composition and pressure of the interstitial gas predominantly govern heat transfer, while mesoscale parameters — particle size, shape, polydispersity, and packing fraction — influence the thermal connectivity of the granular bed. The DEM/FFT simulations reproduce the observed behaviors but slightly overestimate the measured conductivity, highlighting the need for a more accurate representation of thermal contacts. This work contributes to the improvement of a homogenized modeling approach for the thermal behavior of fragmented granular media under accident conditions.

Acknowledgment

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Significant references

1. C. Introïni et al. « ALCYONE : the fuel performance code of the PLEIADES platform dedicated to PWR fuel rods behavior ». In : *Annals of Nuclear Energy* 207 (2024)
2. J. Letessier. « Modélisation et caractérisation multi-échelle des propriétés thermiques et microstructurales de milieux granulaires sous différentes atmosphères ». PhD Thesis. Aix-Marseille University (2023)
3. M. Josien « *Méropé: A Microstructure Generator for Simulation of Heterogeneous Materials* » In : *Journal of Computational Science* 81 (2024)
4. F. Bernachy-Barbe, J.M. Vanson et M. Josien. « An application of the DEM-FFT method to predict the thermal conductivity of high burnup fragmented fuel ». In : *Journal of Nuclear Materials* 604 (2025)

DENSITY, SURFACE TENSION AND VISCOSITY OF URANIUM MELTS AT HIGH TEMPERATURES: TOWARDS A NEW DATABASE FOR CORIUM PROPERTIES

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During a severe accident in a nuclear reactor, uranium melts, or corium, can relocate into the reactor vessel lower plenum, and if the vessel fails due to excessive thermal loading, into the reactor pit, in contact with the concrete basement of the power plant.

The relocation of corium either inside or outside the vessel, leading to so-called in-vessel or ex-vessel retention (respectively IVR and EVR) strategies, highly depends on corium behavior at high temperatures, in link with its thermophysical properties. Density and surface tension will influence mass and momentum transfer in the case of IVR, while viscosity will mainly drive the spreading of corium on the basement. In contrast with their significant roles in fundamental mechanisms, these thermophysical properties are mostly unknown, especially because corium is made of multi-elements at high temperature (up to 3000 K), and given the wide range of compositions and temperatures covered by severe accident scenarios.

The present work aims at filling critical gaps in thermophysical properties databases. On the one hand, an experimental approach based on the recent upgrade of the VITI facility of the PLINIUS severe accident platform in CEA Cadarache is proposed. The adaptation of Maximum Bubble Pressure (MBP) and Torsional Pendulum Viscometer (TPV) techniques at high temperatures and compatible with depleted uranium compositions provides original and accurate measurements for a variety of corium compositions and temperatures, contributing to a significant extent of the scarce data available in the literature.

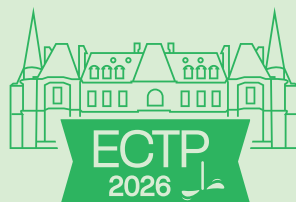
On the other hand, in order to capitalize these data as valuable input for severe accident scenarios codes, CEA undertakes the building of a new database for the thermophysical properties of corium. This database, called CORPRO – for CORium PROperties, is based on the storage, assessment and modelling of experimental data with the aim of extending properties description to parts of the (composition, temperature) domain that will remain inaccessible to experiments. In this work, the first advances of this unified approach are unveiled, focusing on developments linked to surface tension.

Keywords

Nuclear severe accident, corium, thermophysical properties, high temperature, VITI, CORPRO.

5.8

Advanced Materials Design and Characterisation Radiative Cooling II



Cool White: passive radiative cooling technologies for Africa

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Passive radiative cooling (PRC) technologies play an increasingly important role in addressing global climate challenges, as cooling systems in buildings already account for nearly 10 % of global electricity consumption and around 3 % of greenhouse gas emissions. By reflecting solar radiation while efficiently emitting thermal radiation through the 7.1 μm to 13 μm atmospheric transparency window, PRC materials can achieve sub-ambient temperatures even under direct sunlight, without using electricity. To quantify the performance, reliable data of the optical properties are essential for evaluating and further developing these technologies.

The EU project 21GRD03 PaRaMetriC, successfully completed in October 2025, established a metrological framework for traceable and comparable measurements of PRC materials. Building on this foundation, PTB is now strongly engaged in the Cool White initiative, which investigates the real-world cooling effects of white roof coatings applied to schools, hospitals and companies in Rwanda, South Africa, Tanzania and Kenya. Since 2021, the project has been carried out together with national metrology institutes and local partners and aims to objectively quantify the benefits of white roof coatings under diverse climatic conditions. Roofs are coated in collaboration with local painters, while temperature and humidity in the rooms below are continuously monitored using instrumentation provided through the cooperation. In parallel, PTB performs laboratory characterizations of locally produced white paints to determine their reflectance and emittance and to identify coatings that offer optimal passive cooling performance.

Initial results already demonstrate a measurable reduction in indoor temperatures, supporting the potential of white roof coatings as a low-cost, low-tech PRC solution. To further strengthen the metrological foundation of the project, PTB plans to perform on-site measurements of the optical properties of the paints directly on the coated roofs using a portable emissometer, with a particular focus on assessing their long-term stability under natural ageing driven by environmental factors such as solar exposure, rain, dust, humidity, and temperature fluctuations.

In this contribution, we present reflectance and emittance data of selected PRC white paints studied within Cool White, together with the temperature and humidity results collected over several years from measurements in real buildings. We also show the progress achieved within the project to date, the current installation sites across the participating countries, and the next steps planned to further expand and scale up this initiative.

Impact of Low-Emissivity Paints and Films on Radiative Heat Transfer, Thermal Comfort, and Energy Demand: Experimental Characterization and Numerical Simulations

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Low-emissivity (low-e) surface treatments are increasingly adopted as passive strategies to reduce radiative heat exchange and enhance indoor thermal comfort. This study investigates the thermophysical characterization and energy–comfort performance of low-emissivity paints and window films applied to high–radiative-asymmetry environments. First, a low-e paint was experimentally characterized using a spectrophotometer to determine its spectral emissivity and reflectance over relevant wavelength ranges. The resulting optical properties were then implemented in an EnergyPlus model of a representative room to quantify their impact on operative temperature, radiant asymmetry, and energy demand.

The analysis considers different orientations, climatic conditions, and envelope assemblies, as well as scenarios combining low-e paint on opaque walls with low-e films on transparent components for rooms featuring high window-to-wall ratios.

Results show that low-emissivity surface treatments can significantly improve occupants’ thermal comfort at a given air temperature by reducing radiative heat exchange. At the same time, the study highlights the strong sensitivity of both comfort and energy performance to envelope configuration, solar exposure, and climatic context. These findings underline the need for a holistic design approach that accounts for the complex interactions among building components, boundary conditions, and optical–thermal material properties to identify optimal low-emissivity solutions.

All-day Passive Radiative Cooling Performance of Porous Materials: Anodic Aluminium Oxide and Cellulose-derivative Networks

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Nowadays, a third of the total energy demand is destined for cooling due to the consequence of the global warming, which results in higher temperatures and heatwaves. All-day passive daytime radiative coolers (PRC) offer a promising solution for energy-free cooling of buildings and devices. At the same time, it is important to develop low-cost, easy-scalable to industry materials. In this talk, I will present 1D and 3D- anodic aluminium oxide (AAO) nanostructures on Al as a passive daytime radiative cooler. I will analyse how all the morphological properties and chemical structure of porous alumina nanostructures on Al influence on their optical properties and their radiative cooler properties [1, 2]. A maximum cooling temperature of 10.2 °C was reached under direct sunlight in a summer day in Spain for 3D-AAO [3]. This cooling performance results of AAO nanostructures are higher than over previous studies, demonstrating the potential of AAO nanostructures to be used in thermal management applications. Moreover, I will present the use of various cellulose-derivative networks (porous materials) to achieve optimal and stable cooling performance. Our results showed that nitrocellulose network showed the highest cooling temperature, with a significant reduction of 14 °C from the ambient temperature and a power of 124 W/m² during the daytime and at night of 7.7 °C and 72.8 W/m². This study also analysed the dampness's effect on the cooling performance of cellulose-derivative networks. We observed that the cooling performance of nitrocellulose network drops ~3 °C (from 14 to 11.3 °C) when the humidity exceeds ~30%. Our findings indicate that the capacity of a material to absorb water from the surrounding air significantly influences its performance as a passive cooler, primarily due to changes in its optical properties [4]. This is an important insight, as it highlights the need to consider environmental factors like humidity and sample hydrophobicity for PRC systems.

Acknowledgment

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Significant references

1. A. Díaz-Lobo, M. Martin-Gonzalez, A. Morales-Sabio, and Cristina V. Manzano, *ACS Appl. Opt. Mater.*, vol. 2 (2024), pp. 980-990.
2. A. Díaz-Lobo, M. Martin-Gonzalez, Q. Song, A. Morales-Sabio, M. Restch, and Cristina V. Manzano, *ACS Appl. Eng. Mater.*, vol. 2 (2024), pp. 2069-2079.
3. A. Díaz-Lobo, M. Martin-Gonzalez, and Cristina V. Manzano, *Adv. Opt. Mater.*, vol. 13 (2025), 2403158.
4. Cristina V. Manzano, A. Díaz-Lobo, M. Gil-García, O. Rodriguez de la Fuente, A. Morales-Sabio, and M. Martin-Gonzalez, *Adv. Opt. Mater.*, vol. 12 (2024), 2400551.

Radiative Cooling Performance of Nanostructured PMMA inside Anodic Aluminium Oxide

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This work is framed within the current energy and environmental context, in which mitigating climate change and reducing the energy consumption associated with space cooling has become essential. Daytime passive radiative cooling (PDRC) represents a promising approach: it enables heat to be emitted as infrared radiation toward outer space through the atmospheric window, while simultaneously reflecting incoming solar radiation. Therefore, the materials used need to have the following two key optical properties: high infrared emissivity (ϵ_{IR}) and solar reflectance (R_{solar}). Polymers are good IR emitters due to the vibrational modes of their molecular bonds. Additionally, their solar reflectance can be significantly enhanced through their nanostructuration. In this work, nanostructured polymethyl methacrylate (PMMA) inside Anodic Aluminium Oxide (AAO) templates has been investigated for the first time as a potential radiative cooler. The templates used, fabricated through a two-step anodization process, range from structures with only longitudinal channels (1D) [1] to templates containing transversal channels with different spacings (200 nm, 1 μ m, and 10 μ m) [2]. Both PMMA nanostructured with and without AAO were investigated. The average solar reflectance values range from 78 to 82 %, while for the average IR emissivity they vary from 90 to 94%.

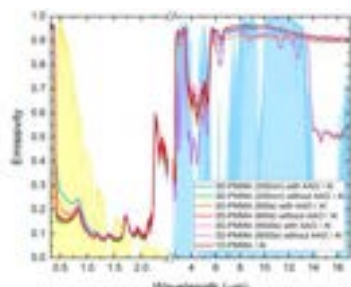


Figure 1. Overall emissivity of PMMA nanostructures along with the solar and the atm. transmission spectra.

Lastly, several outdoor cooling measurements were performed in Madrid during the summer of 2025 using the experimental setup described in ref. [2] to evaluate the samples' behaviour under varying atmospheric conditions. Using the polystyrene empty box as the reference, a temperature reduction of 6 - 11 °C was obtained during daytime, while for night-time case was 2 – 5 °C.

Acknowledgment

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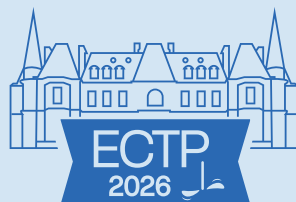
Significant references

1. A. Díaz-Lobo, M. Martin-Gonzalez, A. Morales-Sabio, and Cristina V. Manzano, *ACS Appl. Opt. Mater.*, vol. 2 (2024), pp. 980-990.
2. A. Díaz-Lobo, M. Martin-Gonzalez, and Cristina V. Manzano, *Adv. Opt. Mater.*, vol. 13 (2025), 2403158.

6.1

Thermodynamic Modelling for Sustainable Processes

Thermodynamic Cycles and Working Fluids



The Law of Diminishing Returns: Why Thermodynamics is (and isn't) the Key to Decarbonizing Industrial Heat

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To reach net-zero greenhouse gas emissions, we must solve the “hard-to-abate” problem of industrial process heat. The consensus on the preferred technology is clear: Heat Pumps. Consequently, thermodynamics is at the very core of this transition. For decades, our community has therefore pursued the optimal refrigerant through advancing molecular and process modeling. Yet, industrial heat pumps are rarely deployed in today's factories.

This talk explores why thermodynamic precision is—and sometimes isn't—the key to the energy transition. The is points to the compelling challenge of industrial applications with widely varying temperatures and glides. Here, we demonstrate how allrounder zeotropic mixtures can replace costly, specialized engineering with flexible, high-efficiency heat pumps [1]. In this regime, molecular-scale thermodynamics directly enables commercial viability, allowing a single heat pump platform to address diverse industrial needs.

However, we must also confront the (and isn't) of the title. For process steam, which represents 40% of industrial heat demand, standard refrigerant optimizations have already hit a wall of diminishing returns. A system-level analysis reveals a counterintuitive thermodynamic reality: the optimal high-temperature heat pump is frequently a low-temperature heat pump coupled with mechanical vapor recompression. Furthermore, the ultimate success of these systems depends on their integration with e-boilers and hydrogen systems to navigate volatile energy prices and varying demand.

By expanding our focus to bridge the gap from the molecular all the way to the energy-system scale, thermodynamics can provide a holistic roadmap guiding technology development for the energy transition.

Acknowledgment

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Significant references

1. P. Widmaier, L.P.M. Brendel, S. Bertsch, A. Bardow, D. Roskosch, *ACS Engineering Au*, vol. 5 (4) (2025) pp. 359-369. <https://doi.org/10.1021/acsengineeringau.4c00060>

The Power of Reversible Chemical Reactions in Working Fluids for Thermodynamic Cycles

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The choice of working fluid is a key design variable in thermodynamic cycles for power and heating applications, affecting performance, component size, environmental impact, and safety. Despite ongoing debate on acceptable trade-offs between environmental impact, energy density, and safety, there is a clear need for working fluids with superior thermophysical properties. Although chemical reactions in the working fluid have traditionally been considered undesirable, reversible reactions at equilibrium can enhance thermodynamic performance through coupled thermal and compositional effects along the cycle. Changes in temperature and pressure drive the fluid to new equilibrium compositions, effectively mimicking a variable-composition working fluid tailored to each process.

This work investigates chemically reactive working fluids governed by the dissociation/association reaction $A_2 \rightleftharpoons 2A$ (where A is an arbitrary monomer and A_2 its dimer) as a means of significantly improving thermodynamic cycle performance [1]. The fluid is modeled as a binary mixture of A_2 and A with variable composition, unlike inert binary mixtures [2]. The composition is dictated by the thermodynamic state (T, P) via the chemical-equilibrium constraint. While a binary mixture introduces an additional degree of freedom compared to a pure fluid, the equilibrium reaction constraint removes this extra degree of freedom, so that the reactive mixture $A_2 \rightleftharpoons 2A$ behaves effectively as a pure fluid.

A thermodynamic cycle modeling and optimization framework is applied to power cycles using the reactive working fluids $N_2O_4 \rightleftharpoons 2NO_2$, $Al_2Cl_6 \rightleftharpoons 2AlCl_3$, and $Al_2Br_6 \rightleftharpoons 2AlBr_3$, which were extensively studied by Soviet researchers [3]. The objectives are to re-evaluate their conclusions using more advanced thermodynamic models and optimization algorithms and to benchmark the performance of these reactive fluids against state-of-the-art inert working fluids. The results indicate power output increases of over 30% for cycles employing reactive working fluids compared with their inert counterparts. Although several challenges still hinder the commercialization of reactive working fluids, the demonstrated performance gains justify intensified research efforts to address these obstacles.

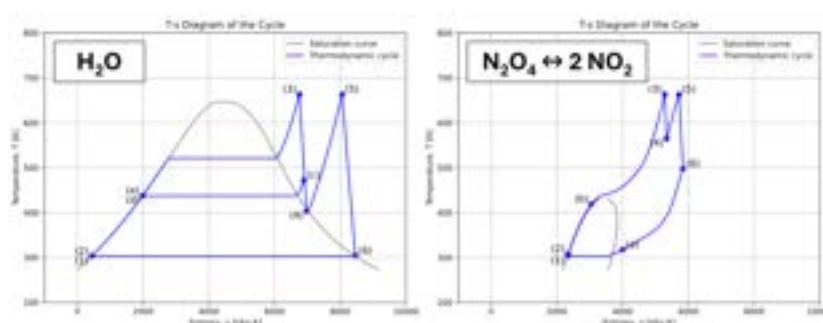


Figure 1. Optimized power cycle operating with water versus reactive $N_2O_4 \rightleftharpoons 2 NO_2$.

Significant references

1. A. Barakat, S. Lasala, P. Arpentinier, and J.-N. Jaubert, "The original and impactful exploitation of chemical energy in heat pumps," *Chem. Eng. J. Adv.*, vol. 12, p. 100400, Nov. 2022, doi: 10.1016/j.ceja.2022.100400.
2. S. Lasala et al., "Application of thermodynamics at different scales to describe the behaviour of fast reacting binary mixtures in vapour-liquid equilibrium," *Chem. Eng. J.*, vol. 483, p. 148961, 2024, doi: 10.1016/j.cej.2024.148961.
3. A. K. Krasin and V. B. Nesterenko, "Dissociating gases: a new class of coolants and working substances for large power plants," *At. Energy Rev.*, vol. 9, no. 1, pp. 177–194, 1971.

Thermodynamic modelling of reactive working fluids for thermodynamic cycles applications

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A predictive framework has been developed to support the thermodynamic characterisation of reactive working fluids for their integration into advanced heat pumps and power cycles. Unlike conventional inert fluids, this work considers media that undergo fast and reversible dimerisation reactions of the form $A_2 \rightleftharpoons 2A$, where the equilibrium shifts across the cycle as the temperature and pressure vary. This chemically induced adaptability can enhance system efficiency, but requires thermodynamic models that can accurately describe reactive fluids, even when there is no experimental data available. To address this, the present methodology relies exclusively on molecular critical properties, acentric factors and ideal-gas properties obtained from ab initio quantum-mechanical calculations. When accurately captured, such reactive behaviour has the potential to significantly improve the performance of thermodynamic cycles by linking chemical transformations to conventional heat-to-work conversion processes [1,2,3].

The framework combines an athermal formulation of the Peng–Robinson equation of state with EoS/a_(res,E,y) mixing rules and molecular Monte Carlo simulations, providing consistent predictions of phase behaviour and reaction equilibria [4]. Single-particle Lennard-Jones force fields that are parametrised directly from critical properties are employed to minimise data requirements and ensure coherence between the two modelling approaches. This methodology has been applied to the $Al_2Br_6 \rightleftharpoons 2AlBr_3$, $Al_2Cl_6 \rightleftharpoons 2AlCl_3$ and $N_2O_4 \rightleftharpoons 2NO_2$ systems and has yielded accurate, fully predictive descriptions of their systems thermodynamic behaviour.

Finally, the predicted properties are used to make preliminary performance calculations for heat pumps and power cycles, focusing specifically on reactive fluids identified as promising candidates.

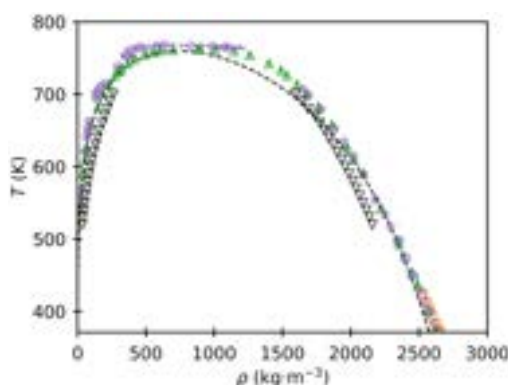


Figure 1. Temperature–density ($T - \rho$) diagram of a reactive fluid. The dashed line indicates the predictions of the equation of state, the coloured symbols represent the experimental data and the black downward triangles correspond to the Monte Carlo results.

Acknowledgment

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Significant references

1. S. Lasala, R. Privat, O. Herbinet, et al., *Energy Convers. Manag.*, vol. 229 (2021), pp. 113685.
2. A. Barakat, J.-N. Jaubert, P. Arpentiner, et al., *Int. J. Refrig.*, vol. 168 (2024), pp. 276-287.
3. S. Lasala, *The Project Repository J.*, vol. 13 (2022), pp. 102-105.
4. S. Lasala, K. Samukov, H. M. Polat, et al., *Chem. Eng. J.*, vol. 483 (2024), pp. 148961.

A Graph-Neural-Network-Enhanced Crossover PR Equation of State for High-Precision Prediction of Working Fluid Thermodynamic Properties

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As the operating conditions of the engineering system increasingly approach the critical zone, and new environmentally friendly working fluids keep emerging, developing a thermodynamic property calculation model with high prediction accuracy and low data dependence across the entire range has become an urgent industrial demand. However, classical equations of state exhibit significant deviations in the near-critical region, while the high-precision multi-parameter model [1] adopted by the REFPROP software heavily relies on a large number of experimental data sets. Neither of these two methods can fully meet the dual requirements of high precision and low data dependence of the model in engineering applications. To address these issues, we combine the Kiselev's crossover method [2] with the Peng-Robinson (PR) equation of state [3] to construct the RG-PR model, which can continuously and smoothly describe the thermophysical properties in the near critical and far critical region. Then, we complete the construction and parameters fitting of the RG-PR model for 44 typical working fluids, and systematically clarify the correlation laws between the system parameters of the model and the critical parameters for the working fluids. On this basis, to further enhance the model's predictive ability for unknown working fluids, we introduce the graph neural network (GNN) technology [4] by constructing a molecular graph dataset containing hundreds of working fluids, which has been trained to directly and accurately predict the critical parameters based on the molecular structure. By substituting the predicted critical parameters into the established correlation formula, the system parameters of the RG-PR model can be obtained, and ultimately a high-precision prediction of the thermodynamic properties of the working fluid can be achieved, thereby constructing a prediction framework for the thermophysical properties of the working fluid. The results show that the proposed GNN-RG-PR model has a prediction deviation of less than 5% for unknown working fluids, effectively filling the gap in the estimation of the thermodynamic properties of new environmentally friendly working fluids during the data absence stage. Additionally, the GNN-RG-PR model can accurately predict a variety of key thermodynamic properties, including saturated vapor pressure, saturated density, p_vT property, and second-order thermodynamic properties. Through detailed evaluation, the average absolute deviations of density and specific heat capacity are less than 2.5% and 5%, respectively. Moreover, the deviations of saturated vapor pressure, saturated liquid density, and saturated vapor density are less than 1.2%, 2%, and 1.5%, respectively, which significantly improve the model's prediction accuracy. This research provides an efficient and reliable computational tool for screening new environmentally friendly working fluids and provides important thermodynamic properties datasets support for engineering applications.

Acknowledgment

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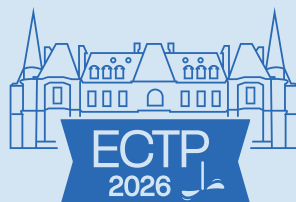
Significant references

1. M. Thol, E.W. Lemmon, Equation of State for the Thermodynamic Properties of trans-1,3,3,3-Tetrafluoropropene [R-1234ze(E)], *Int J Thermophys* 37 (2016) 28.
2. S.B. Kiselev, J.F. Ely, Generalized crossover description of the thermodynamic and transport properties in pure fluids, *Fluid Phase Equilibria* (2004).
3. D.-Y. Peng, D.B. Robinson, A New Two-Constant Equation of State, *Ind. Eng. Chem. Fund.* 15 (1976) 59–64.
4. Z. Xiong, D. Wang, X. Liu, F. Zhong, X. Wan, X. Li, Z. Li, X. Luo, K. Chen, H. Jiang, M. Zheng, Pushing the Boundaries of Molecular Representation for Drug Discovery with the Graph Attention Mechanism, *J. Med. Chem.* 63 (2020) 8749–8760.

6.2

Thermodynamic Modelling for Sustainable Processes

Multi-Scale Modelling



Bridging Modeling Approaches for the predictive description of Thermophysical Properties in Decarbonisation Applications

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Decarbonisation targets and the progressive phase-down of high-GWP refrigerants in Europe demand the development of environmentally sustainable working fluids supported by robust predictive tools. This contribution presents an integrated multiscale modelling framework that bridges molecular-based equations of state, quantum-chemical screening, and artificial-intelligence techniques to enable the accurate prediction of thermophysical properties relevant to next-generation refrigeration and energy-conversion applications.

The methodology combines the polar soft-SAFT equation of state with neural-network models constructed from COSMO-RS molecular descriptors, providing reliable coarse-grained representations without requiring extensive experimental data. These predictive tools feed directly into energy, exergy, economic, and environmental (4E) assessments applied to refrigeration cycles, facilitating the identification of low-GWP candidates compatible with existing systems and minimising retrofitting costs. As illustrative case studies, the framework is applied to the search for replacements for R134a, identifying promising blends with improved sustainability metrics [1,2], and to the evaluation of non-fluorinated alternatives such as CO₂-based cascade cycles. Finally, deep-learning-driven molecular generation and validation through COSMO and molecular dynamics simulations demonstrate the potential of data-driven design of novel refrigerants tailored for decarbonisation-oriented applications.

Acknowledgment

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Significant references

1. C. G Albà, I.I.I. Alkhatib, F. Llorell, L. F Vega. (2023). *Renewable and Sustainable Energy Reviews*, 188, 113806. <https://doi.org/10.1016/j.rser.2023.113806>
2. C. G Albà, I.I.I. Alkhatib, F. Llorell, L. F Vega. (2024). *Applied Thermal Engineering*, 246, 122895. <https://doi.org/10.1016/j.applthermaleng.2024.122895>.

Assessment of the interfacial behavior of ethers-based systems using machine learning for practical industrial applications

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Oxygenated ethers have gained increasing attention as renewable and environmentally compatible fuel additives due to their favorable volatility and ability to reduce particulate emissions within an adequate octane performance. Fluorinated ethers (HFEs) are widely employed as low-GWP working fluids in refrigeration and organic Rankine cycles. In both cases, interfacial phenomena, fluid–fluid and solid–fluid, play a central role. Nevertheless, despite the availability of experimental datasets, traditional modeling frameworks, such as EoSs coupled with Density Functional Theory, are computationally demanding and show limited transferability across the structural diversity of ether-based fluids. Meanwhile, recent developments in machine learning (ML) have demonstrated strong capability for predicting thermophysical and interfacial properties of complex fluids with significantly lower computational cost, motivating the development of generalized ML models capable of capturing the thermophysical behavior of structurally diverse ether molecules [1].

In this work, we develop an integrated ML-based framework to predict the surface tension and contact angles of a broad set of linear, branched, cyclic, and fluorinated ethers over extended temperature ranges, including mixture behavior. The training dataset compiles experimental surface-tension and wettability values from the literature. Technically, some learning algorithms (i.e., Random Forest, CatBoost, and feed-forward neural networks) are trained and compared using molecular and thermodynamic descriptors, such as critical properties, boiling points, and reduced-temperature variables, together with structure-encoded Morgan fingerprints generated with RDKit. The model performance is evaluated via cross-validation and multiple statistical indicators, revealing that ensemble methods deliver the highest predictive accuracy. As an example, Figure 1 shows preliminary results for two machine-learning models used to predict the surface tension of ether molecules.

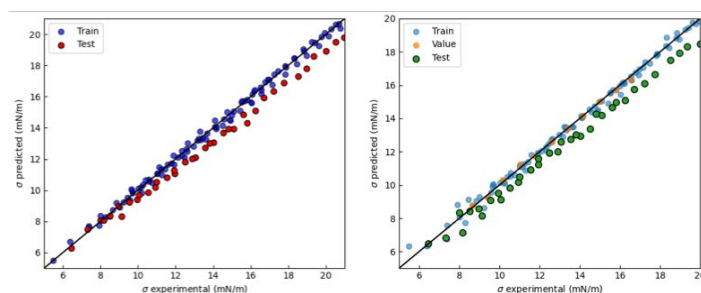


Figure 1. Predicted vs. experimental surface tension for ethers using a) CatBoost and b) Random Forest.

Feature-importance analysis identifies the dominant descriptors, and the validated models serve as rapid screening tools to classify ethers by their interfacial behavior. This approach supports the selection of promising candidates for fuel additives, refrigerants, and working fluids, complementing experimental data and thermodynamic modeling for the accelerated design of sustainable systems.

Acknowledgment

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Significant references

- Schmedding, R., Franssen, M., & Zuend, A. (2025). ACS ES&T Air, 2(5), 808-823.

Compressed liquid density measurements of acetic acid and carbon dioxide mixtures for reactive heat pump applications

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High-Temperature Heat Pumps (HTHPs) are pivotal technologies for industrial decarbonization, enabling the recovery of waste heat at temperatures suitable for process steam generation. To overcome the limitations of conventional inert refrigerants, reactive working fluids are gaining attention as a promising alternative. These fluids exploit reversible chemical reactions—specifically dimerization and association equilibria—to enhance the effective thermal capacity and enthalpy change during compression and expansion cycles [1,2].

In this context, acetic acid represents a benchmark reactive fluid due to its well-known dimerization equilibrium ($2CH_3COOH \rightleftharpoons (CH_3COOH)_2$). The addition of small quantities of carbon dioxide (CO₂) allows to tailor the saturation pressure of the mixture, lifting it to technically viable levels without suppressing the reactive benefits of the solvent.

Accurate thermophysical properties are fundamental for the development of reliable Equations of State (EoS) and the proper design of heat pump devices. However, available experimental data for this reactive system are insufficient for HTHP applications. While recent studies have investigated the phase equilibrium and density of acetic acid + CO₂ mixtures [3], they are largely confined to temperatures below 340 K and CO₂-rich mixtures. Data in the high-temperature compressed liquid region, where the reaction kinetics and thermodynamic benefits are most relevant, remain virtually non-existent.

This work presents new experimental density measurements of pure acetic acid and binary mixtures with carbon dioxide (CO₂ mass fraction < 15%). The data were collected using a vibrating tube densimeter over a temperature range of 300 to 420 K and pressures up to 8 MPa.

The experimental results are used to extend the validation of advanced cubic equations of state [4] into the high-temperature domain. These measurements provide essential insight into the volumetric behavior of reactive mixtures, bridging the gap between low-temperature characterization and real-world industrial process conditions.

Significant references

1. S. Lasala, R. Privat, O. Herbinet, P. Arpentinier, D. Bonalumi, J.N. Jaubert, *Energy Conversion and Management*, vol 229 (2021), 113685.
2. A. Barakat, J.N. Jaubert, P. Arpentinier, P. Tobaly, S. Lasala, *International Journal of Refrigeration*, vol 168 (2024), pp. 276-287.
3. T. Zhu, Y. Li, H. Gong and M. Dong, *ACS Omega*, vol. 6(2021), pp. 6663-6673.
4. D. O. Wasik, S. Lasala, O. Herbinet, K. Samukov, S. Calero, T.J.H. Vlught, *Fluid Phase Equilibria*, vol 594 (2025), 114356.

Turbulent Reactive Phase Change via Reactive Vapor–Liquid Equilibrium Thermodynamics

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Reactive phase change fluids redefine classical vapor–liquid equilibrium (VLE), as chemical reactions coupled to phase transitions fundamentally alter equilibrium characteristics and interfacial transport. This work presents a high-fidelity computational fluid dynamics (CFD) framework specifically designed to capture reactive VLE under turbulent conditions. The model enforces thermodynamic consistency by balancing interphase exchange rates while resolving coupled mass and heat transfer at the interface. As a representative case, the fast reversible reaction $N_2O_4(l, v) \rightleftharpoons 2NO_2(l, v)$ was examined during reactive film evaporation. Rapid kinetics maintains chemical equilibrium at the interface, generating simultaneous endothermic and exothermic responses, shifting critical characteristics, and modifying interfacial balances. Turbulence enhances these dynamics by promoting interfacial mixing, accelerating phase exchange, and driving strong fluctuations in concentration and temperature fields. These results demonstrate that reactive phase change cannot be regarded as a simple extension of classical VLE, but requires a coupled thermodynamic–hydrodynamic description. The new developed CFD framework provides the resolution necessary to capture these mechanisms, offering new insight into reactive mass and heat transfer with applications in thermodynamic efficiency, propulsion systems, and high-performance energy technologies.

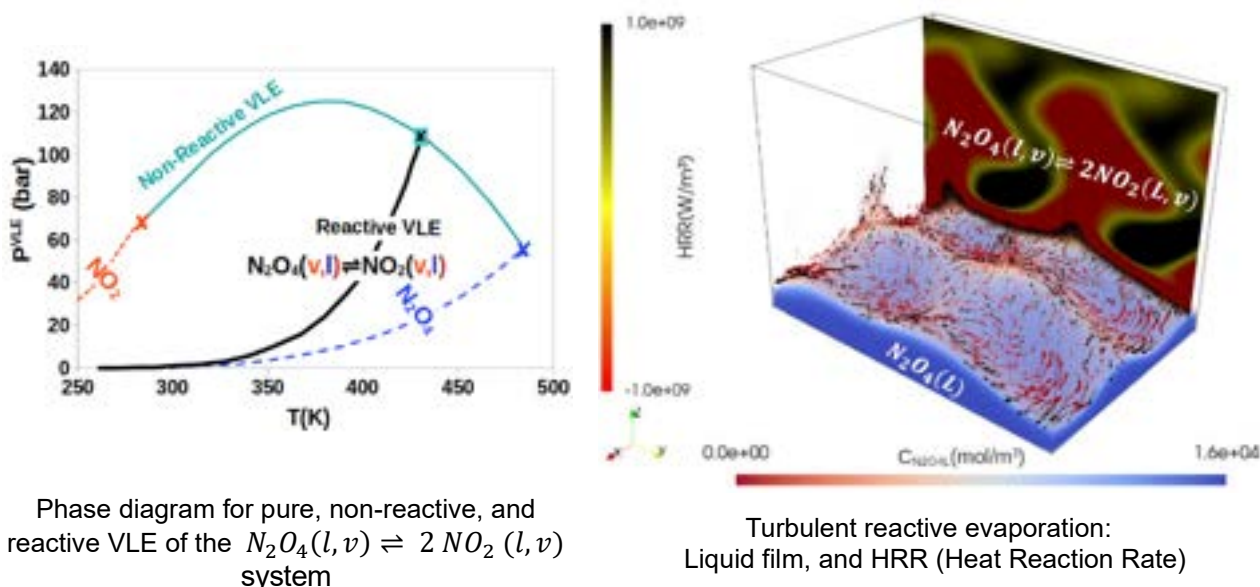
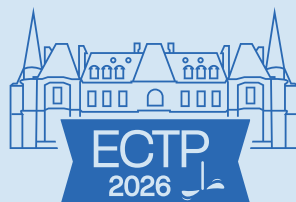


Figure1. Turbulent Reactive Phase Change via Reactive Vapor–Liquid Equilibrium Thermodynamics

6.3

Thermodynamic Modelling for Sustainable Processes

CCUS Applications



Advancing CO₂ Capture Through Molecular Modelling and Transfer-Learning Surrogates

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The development of next-generation CO₂ capture technologies depends on a fundamental understanding of the molecular origins of solvent behaviour and on computational methods capable of navigating the vast design spaces that arise when molecular and process decisions interact. While simple fluids can be described by classical corresponding-states ideas, chemically complex, reactive solvent mixtures, particularly aqueous amines, exhibit rich intermolecular phenomena arising from hydrogen bonding, association, and chemical speciation. In this lecture, I will discuss how statistical-mechanical models, such as the SAFT family of equations of state, allow us to represent these interactions through physically grounded free-energy expressions.

I will present how group-contribution developments within this framework, specifically the SAFT- γ Mie approach, extend our predictive capability to broad families of structurally related molecules. By linking molecular architecture to macroscopic phase and reaction equilibria, these models provide a basis for exploring solvent chemistry in tandem with process performance. Such predictive power is essential for integrated molecular and process design methodologies, where both solvent structure and absorber–stripper conditions must be optimised simultaneously. Yet the computational cost of the underlying thermodynamic calculations places limits on the scale of design spaces we can explore in practice.

To overcome these limitations, machine-learning surrogates trained on SAFT-generated data can be used to accelerate property prediction while preserving the physics encoded in the original model. Transfer learning is especially powerful in this context. By starting from a surrogate trained on a well-characterised solvent, accurate models for related amines can be constructed from small, process-focused datasets. This approach improves predictive fidelity in the operating regions most relevant for process optimisation, while reducing training times. Embedding these surrogates within multi-start optimisation workflows enables extensive and rapid exploration of solvent and process options. When combined with a final multi-fidelity refinement step, the resulting designs recover rigorous optima at minimal additional cost.

The hybrid framework unites molecular insight, thermodynamic rigour, and data-driven acceleration, enabling faster and more reliable identification of promising solvent systems. Together, these developments point to a powerful and scalable strategy for advancing CO₂ capture.

Significant references

1. A. J. Haslam, A. Gonzalez-Perez, S. Di Lecce, S. H. Khalit, F. A. Perdomo, S. Koumopoulos, M. Kohns, T. Lindeboom, M. Wehbe, S. Febra, G. Jackson, C. S. Adjiman, and A. Galindo, *J. Chem. Eng. Data*, vol. 65 (2020) pp. 5862–5890.
2. F. Baakes, G. Chaparro, T. Bernet, G. Jackson, A. Galindo, C. S. Adjiman., *Sys. Control. Trans.*, vol. 4 (2025), pp. 1089-1094.

Evaluation of Equations of State for Predicting Solid CO₂ Formation in CCS and Natural Gas Applications

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Solid-phase CO₂ commonly known as dry ice, can pose a serious risk in numerous chemical processes, including carbon capture, transport and storage (CCS), Liquefied Natural Gas (LNG) applications, and cryogenic biogas upgrading. If temperature or pressure drops sufficiently, solid CO₂ can form and block critical equipment such as vent lines or safety relief systems. A dislodged CO₂ crystal traveling at high velocity can also damage equipment and endanger personnel [1].

Solidification of CO₂ can be predicted by combining equations of state (EoS) for the fluid and solid phases with a phase-equilibrium algorithm. In this work, we assessed a range of model combinations. The most significant difference in the accuracy of the fluid-solid phase equilibrium predictions was due to the choice of fluid EoS. Here, we evaluated three cubic, two multiparameter and three EoS based on statistical associating fluid theory (SAFT).

The evaluation covered a wide range of mixtures and operating conditions. For CCS-relevant mixtures, the simple cubic Peng-Robinson (PR) gave the lowest overall Mean Absolute Percentage Deviation (MAPD) of 1.4% in the solidification temperature. For LNG applications, the multiparameter EoS-CG [2] was the most accurate, yielding a MAPD below 1%. Among the SAFT-type models, PCP-SAFT [3] performed best, underscoring the importance of explicitly accounting for the quadrupole moment of CO₂ in the description.

Because the standard PR gave a better agreement with experimental data than translated-consistent PR (tc-PR) [4], the α -function of tc-PR was refitted by using vapour-pressure data of pure CO₂ below the triple point. This improved the MAPD for solid-liquid equilibria in mixtures from 2.4% (original) to 1.6% (refitted), even though only pure-CO₂ data were used in the regression. If a reliable solid-phase EoS is available, the inclusion of solid-fluid equilibrium data in the EoS regression offers a promising route to improving the pure-fluid formulation and, consequently, the prediction of solidification and solubility limits in mixtures.

Acknowledgment

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Significant references

1. M. Vitali, F. Corvaro, B. Marchetti, and A. Terenzi. International Journal of Greenhouse Gas Control 2022, 114, 103605.
2. T. Neumann, S. Herrig, I.H. Bell, R. Beckmüller, E.W. Lemmon, M. Thol, and R. Span. International Journal of Thermophysics 2023, 44, 178
3. J. Gross, and J. Vrabec. AIChE Journal 2006, 52, 1194–1204.
4. Y. Le Guennec, S. Lasala, R. Privat, and J.-N. Jaubert. Fluid Phase Equilibria, 2016, 427, 513–538.

Experiments and Modeling of Thermophysical and Electrical Properties in CO₂-Rich Mixtures

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In oil fields, the use of Multiphase Flow Meters (MPFMs) is essential for reservoir management and for maximizing oil and gas production¹.

The recent discoveries of pre-salt reservoirs, characterized by high carbon dioxide (CO₂) content², have increased the need to assess the performance of modern flow-metering technologies under such elevated CO₂ conditions. Consequently, significant attention has been directed toward understanding how CO₂ content affects the thermophysical properties of multiphase mixtures and, in turn, influences flow meter performance.

The objective of this study is to carry out an experimental and theoretical investigation into the influence of dissolved CO₂ in the liquid phase of a CO₂-dodecane mixture. The focus is on assessing how the quantity of dissolved CO₂ affects the mixture's thermophysical and electrical properties, with the overarching goal of evaluating how these variations may impact measurements obtained from Multiphase Flow Meters (MPFMs).

Experiments were performed over a wide range of pressures (1 to 170 bar) and temperatures (5 to 80 °C), which directly affected the solubility of CO₂ (from 0 to 100%). This enabled the analysis of how CO₂ solubility influences the viscosity, density, and electrical permittivity of the liquid phase.

A thermodynamic model based on the Cubic Plus Association (CPA) equation of state was implemented to compare the theoretical predictions with the experimental data obtained.

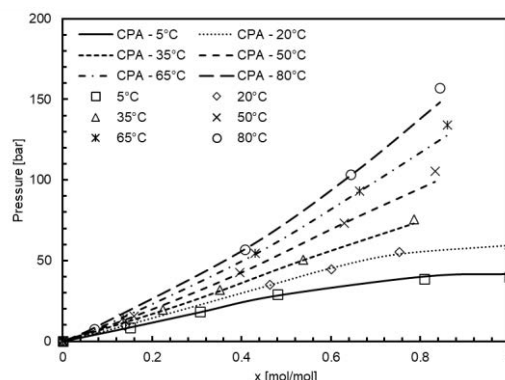


Figure 1. Experimental equilibrium data for the CO₂ + dodecane system alongside model predictions.

Acknowledgment

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Significant references

- 1 M. Meribout, A. Azzi, N. Ghendour, N. Kharoua, L. Khezzar and E. AlHosani, *Measurement*, 2020, **165**, 108111.
- 2 V. A. de Freitas, J. C. dos S. Vital, B. R. Rodrigues and R. Rodrigues, *J South Am Earth Sci*, 2022, **115**, 103760.

Vapor–Liquid Interfacial Properties of CO₂ Mixtures for Sequestration Applications: Molecular Simulations, Classical Density Functional Theory, and Equations of State

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Experimental measurements of thermodynamic and transport properties for the CO₂ mixtures found in transportation systems is costly and time-intensive. To address this challenge, we used Molecular Dynamics (MD) simulations to compute interfacial properties of CO₂ mixtures. Using this approach, we computed phase equilibria, interfacial tension, interfacial thicknesses and enrichment factors at temperatures of 220–273 K. We compared these properties with the phase equilibria and interfacial properties estimated by the Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) Equation of State (EoS) [1], combined with classical Density Functional Theory (cDFT). We show that the phase equilibria computed from the PC-SAFT EoS with binary interaction parameter ($k_{ij} \neq 0$) obtained good agreement with experiments and MD simulations. For the computed phase equilibria, we evaluated the corresponding interfacial tension of binary mixtures and showed that the PC-SAFT EoS had a minor underestimation compared to MD simulations. Using the computed interfacial tension, we investigated the impact of different impurity species on the interfacial tension at different temperatures and pressures. We show that for binary mixtures containing H₂ as an impurity, interfacial tension increases significantly, followed by Ar and N₂, while CH₄ only minimally increases the interfacial tension. Recognizing the high computational cost associated with interfacial tension computation using MD simulations, we evaluated the semi-empirical Parachor and Winterfeld-Scriven-Davis (WSD) models as more efficient alternatives that can be applied readily in computational fluid dynamics simulations. We show that the Parachor model performs best in predicting the interfacial tension of CO₂-CH₄, CO₂-Ar, and CO₂-N₂ mixtures, while the Winterfeld-Scriven-Davis model outperforms the Parachor model for CO₂-H₂ mixtures. Furthermore, we computed and compared the metastable superheating and supercooling limits of impure CO₂ using the computed interfacial tension and classical nucleation theory (CNT) to enable realistic modeling of the rapid phase transitions encountered in CO₂ transportation systems. This work can be further extended toward designing and modeling pipelines for CO₂ transportation systems.

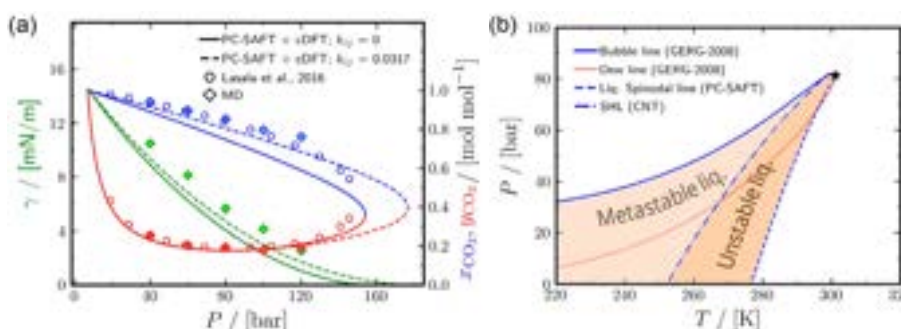


Figure 1. (a) Pxy diagram with interfacial tension (γ) of CO₂-Ar mixtures computed from MD simulations and from the PC-SAFT EoS [1] combined with cDFT for both $k_{ij} = 0$ and $k_{ij} \neq 0$. The computed phase equilibria is compared with the experimental measurements of Lasala et al.,[2]. (b) PT diagram of CO₂-Ar mixtures containing 95 mol% CO₂ and 5 mol% Ar. The bubble and dew lines are calculated using the GERG-2008 EoS and the liquid spinodal line are obtained from the PC-SAFT EoS. The metastable superheat limit estimated using CNT with interfacial tension computed from the Parachor model.

Significant references

1. J. Gross and G. Sadowski, Ind. Eng. Chem. Res., vol. 40 (2001), pp. 1244–1260.
2. S. Lasala, P. Chiesa, R. Privat, and J. N. Jaubert, Fluid Phase Equilib., vol. 428 (2016), pp. 18–31.

Poster Pitches



Thermal Diffusivity Estimation in CFRP and GFRP: A Comprehensive MWIR–LWIR Comparative Study in Reflection and Transmission Pulsed Thermography

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Accurate thermal diffusivity estimation in fiber-reinforced polymer composites is essential for nondestructive characterization, numerical modeling, and structural health assessment. Although pulsed thermography is widely used for rapid inspection, the influence of detector spectral band and acquisition geometry on quantitative diffusivity retrieval remains insufficiently investigated. This work presents a comprehensive experimental study comparing thermal-diffusivity estimation in 2-mm-thick carbon-fiber-reinforced polymer (CFRP) and glass-fiber-reinforced polymer (GFRP) plates using pulsed thermography in transmission and reflection modes, with data acquired simultaneously in the MWIR (3–5 μm) and LWIR (8–12 μm) spectral bands.

Different quantitative approaches were evaluated by the classical Parker (flash) method time-domain processing in transmission mode and by front-surface transient pulsed thermography (PT). The four acquisition geometries (MWIR-transmission, MWIR-reflection, LWIR-transmission, LWIR-reflection) from two composite flat specimens (CFRP and GFRP) were then analyzed and compared.

The study provides quantitative guidelines for selecting optimal imaging band and geometry for diffusivity estimation in polymer composites and demonstrates the potential of multi-band thermography for enhanced material characterization.

Significant references

1. Parker W.J., Jenkins R.J., Butler C.P. and Abbott G.L. "Flash method of determining thermal diffusivity, heat capacity and thermal conductivity," *J. Appl. Phys.*, **32**:1679 (1961). <http://dx.doi.org/10.1063/1.172841>.
2. Bison P.G., Grinzato E. and Marinetti S. "Local thermal diffusivity measurement," *Quantitative InfraRed Thermography Journal*, **1**(2):241–250 (2004). <https://doi.org/10.3166/qirt.1.241-250>.
3. Bison P., Cernuschi F. and Muscio A. "Ermanno Grinzato: a survey on thermophysical properties assessment," *Quantitative InfraRed Thermography Journal*, **21**(6):438–450 (2024) <https://doi.org/10.1080/17686733.2023.2215102>.

Thermal conductivity of an amine-based epoxy resin during curing

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During curing, a thermoset transforms from a low-viscosity liquid with a high degree of flowability into a rigid structure by building a three-dimensional network. This process involves significant changes in the thermal and mechanical properties.

One important aspect to consider is the heat transfer, particularly when manufacturing thick parts. The chemical reaction is strongly exotherm and the heat release may lead to critical temperature gradients within the product. This is related to a risk of thermal degradation, which can lead to the irreversible alteration of the part's properties.

Estimation of the heat transfer requires knowledge of the thermal conductivity. This parameter is affected by the degree of cure because of molecular mobility reduces as the reaction progresses.

In this study, the thermal conductivity of an epoxy resin is determined during isothermal cure at different temperatures by means of different methods. First, the laser-flash method described by Parker et al. [1] is used. In this technique, the thermal diffusivity is measured by determining the temperature change on a material's side over time after a heat pulse is applied on the opposite side. The thermal conductivity is derived from the thermal diffusivity, density and specific heat. As density and specific heat also depend on the degree of cure, these properties were determined by dilatometry and differential scanning calorimetry (DSC), respectively.

Additionally, thermal conductivity during cure is directly measured by means of the hot-wire method. In this technique, a thin platinum wire is immersed into the uncured resin. A voltage is applied to the wire, resulting in a temperature increase of the material surrounding the wire. The thermal conductivity is calculated from the electrical power and temperature increase [2].

Finally, thermal conductivity is also determined on the final, completely cured product. For that, the former method (laser flash) is used. Additionally, measurements are conducted with a guarded heat-flow meter. In this latter technique, the part is placed between two plates controlled at different temperatures. The heat flow resulting from this temperature gradient is measured and used to calculate the thermal conductivity [3].

The results show an increasing thermal diffusivity with a rising degree of cure. A change in the slope of the thermal diffusivity curve highlights the vitrification process as soon as the glass transition temperature of the system (which increases with increasing degree of cure) reaches the material temperature. The slow-down of the reaction kinetics due to vitrification is also detected in the thermal conductivity curves determined by laser flash and hot wire. The measurements performed on the completely cured product indicate an increasing thermal conductivity with increasing temperature.

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Significant references

1. W. J. Parker, R. J. Jenkins, C.P. Butler, and G. L. Abbott, *Journal of Applied Physics*, vol. 32 (9) (1961), pp. 1679–1684.
2. H.-P. Ebert, V. Bock, O. Nilsson, and J. Fricke, *High Temperatures-High Pressures*, vol. 25 (4) (1993), pp. 391-402
3. ASTM E1530-19, *Test Method for Evaluating the Resistance to Thermal Transmission of Materials by the Guarded Heat Flow Meter Technique*, E37 Committee, Beuth Verlag (2019)

Emissivity of porous alumina membranes: phase transitions and spectral selectivity

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Porous ceramics form the backbone of many high-temperature applications, from aeronautics to petrochemical furnaces. Tuning their infrared optical properties is key to optimizing heat flow in these demanding applications, but emittance values typically vary widely in the mid-to-near infrared, where the effects due to radiation scattering at the pores are combined with subtle effects due to composition [1]. In order to decouple the intrinsically optical and the geometric phenomena, we have performed emittance measurements on anodized aluminum oxide (AAO) membranes with controlled pore sizes (40 to 400 nm), using the setup at the CEMHTI laboratory up to 1350 °C [2]. We have observed a rich amount of vibrational overtones in the mid-infrared, which change continuously with the ordering of the aluminum oxide phases ($\gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha\text{-Al}_2\text{O}_3$). A strong emission band at 2300 cm^{-1} is observed and attributed to geometric resonances arising from the relatively monodisperse pore distribution, as this behavior is not observed in conventional or industrial alumina ceramics. The spectral selectivity offered by this approach is suitable for the development of novel materials with tunable optical properties, such as selective emitters for next-generation energy sources.

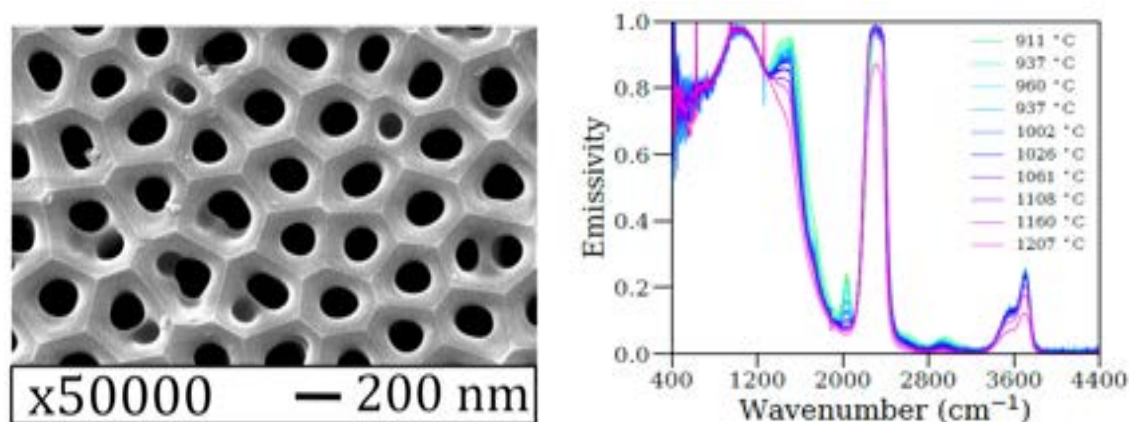


Figure 1. Microstructure and emissivity of a porous AAO membrane (pore size ~ 200 nm) with a rich temperature-dependent overtone structure.

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Significant references

1. L. del Campo, D. De Sousa Meneses, K. Wittmann-Ténèze, A. Bacciochini, A. Denoirjean, and P. Echegut, *J. Phys. Chem. C*, vol. 118 (2014), 13590-13597.
2. D. De Sousa Meneses, P. Melin, L. del Campo, L. Cosson, and P. Echegut, *Infrared Phys. Technol.*, vol. 69 (2015), 96-101.

Platinum-ALD-Modified Graphene Aerogels for Ultralight Thermal Management

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Lightweight thermal management materials are increasingly critical for next-generation electronic, aerospace, and mobile energy systems, where heat must be dissipated effectively despite strict mass and volume constraints. Graphene aerogels (GAs) have emerged as promising candidates due to their ultralow density, high surface area, and tunable porous networks. However, their practical use as thermal interface or heat-spreading components has been limited by intrinsically weak interlayer phonon coupling and structural defects generated during synthesis. Previous studies demonstrated that vapor-phase treatments and ALD-based healing strategies can partially recover phonon transport in graphitic materials [1–3], while high-temperature annealing improves through-plane conductivity in bulk GA networks [4]. Yet, these approaches either require extreme thermal budgets or fail to simultaneously preserve the delicate pore structure that enables convective enhancement.

In this work, we propose platinum atomic layer deposition (Pt-ALD) as an interfacial-bond-engineering route that addresses both limitations concurrently. The Pt-ALD process forms uniform nanoscale Pt nuclei that evolve into Pt–O–C covalent bridges across adjacent graphene sheets, effectively creating additional phonon transmission channels while maintaining the open-cell morphology. Detailed structural and thermal analyses confirm that this dual-mode enhancement—solid-phase conduction reinforced by interfacial bonding and fluid-phase convection supported by preserved porosity—leads to a nearly threefold increase in the effective thermal conductivity of the aerogel. Mechanical testing further reveals substantial improvements in stiffness and long-term cyclic durability, indicating that ALD-derived bonding networks also stabilize the 3D structure against deformation.

Under forced convection, the Pt-ALD-modified GA heat sink exhibits a total thermal resistance approaching that of an identically shaped aluminum reference, yet with only ~12% of the mass. This exceptional mass-specific performance aligns with the airflow-driven enhancement mechanisms reported for porous GA systems [5]. The results demonstrate that ALD-enabled interfacial engineering provides a scalable and thermally efficient strategy that bridges the gap between ultralight carbon aerogels and conventional metallic heat dissipation components. Such capabilities open paths toward practical deployment of GA-based thermal modules in platforms where weight, reliability, and heat management are simultaneously critical.

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Significant references

1. D. Kim, W. Kim, S.M. Lee, T. Luo, C. Moon, J.H. Kim, et al., *Int. J. Therm. Sci.*, vol. 133 (2018), pp. 266–272.
2. S. So, J.Y. Kim, D. Kim, J.H. Lee, *Carbon*, vol. 180 (2021), pp. 77–84.
3. W. Zheng, C.J. McClellan, E. Pop, Y.K. Koh, *ACS Appl. Mater. Interfaces*, vol. 14 (2022), pp. 22372–22380.
4. X. Guo, S. Cheng, B. Yan, Y. Li, R. Huang, J. Li, et al., *J. Colloid Interface Sci.*, vol. 608 (2022), pp. 2407–2413.
5. H. Jo, D. Kim, *Int. Commun. Heat Mass Transfer*, vol. 149 (2023), 107110.

Understanding solubility limits of amino-acid salt solutions for post-combustion carbon capture

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As atmospheric CO₂ concentrations continue to rise, effective climate change mitigation technologies are increasingly needed. One approach is post-combustion carbon capture, where CO₂ is removed from flue gas streams using absorption. Traditional aqueous amine solvents such as monoethanolamine (MEA) offer high absorption capacity but suffer from thermal and oxidative degradation. Amino acid salt solutions (AAS) have emerged as a more stable and environmentally friendly alternative due to their low toxicity and potential resistance to degradation; however, their deployment is hindered by limited solubility and precipitation upon CO₂ addition [1, 2]. These effects arise from the pH-dependent zwitterionic nature of amino acids and the strong influence of temperature and ionic strength on their phase behaviour.

Accurate solubility data for AASs are therefore essential for the development of next-generation post-combustion carbon capture technologies. Despite their importance for process design, solvent selection, and thermodynamic modelling, existing solubility datasets remain sparse and incomplete. This work addresses this gap by generating a comprehensive set of solubility measurements for potassium glycinate and other amino acid salt solutions, with and without CO₂ loading, using a CO₂ screening rig.

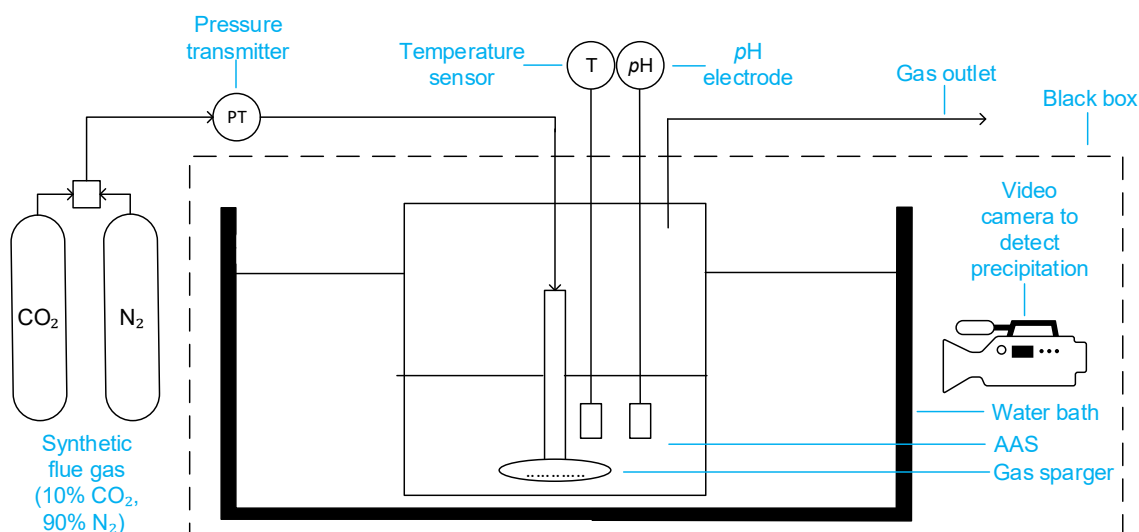


Figure 1. CO₂ screening rig to determine solubility limits of loaded AAS solutions

Acknowledgment

This work was supported by the UKRI EPSRC Centre for Doctoral Training in Green Industrial Futures EP/Y03550X/1.

Significant references

1. Ramezani, R.; Mazinani, S.; Di Felice, R. *Rev. Chem. Eng.* 2022, 38 (3), 273–299. <https://doi.org/10.1515/revce-2020-0012>.
2. Rasmussen, V. E.; Neerup, R.; Stampino, I. G.; Vinjarapu, S. H. B.; Villadsen, S. N. B.; Thomsen, K.; Fosbøl, P. L. *J. Chem. Eng. Data* 2022, 67 (11), 3482–3493. <https://doi.org/10.1021/acs.jced.2c00403>

Fick Diffusion Coefficients and Solubilities in Blowing-Agent-Loaded Polypropylene Melts

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To produce thermoplastic foams by physical foam extrusion, a mixture consisting of a polymer melt with a dissolved blowing agent is extruded through a die, where the pressure drop causes supersaturation of the melt and, thus, induces bubble growth. Here, the bubble growth dynamics depends on the equilibrium and transport properties of the blowing-agent-loaded polymer melt and is decisive for the foam morphology obtained upon solidification of the melt. For the accurate modeling of the bubble growth for the optimized design of foaming processes and the resulting products, accurate data on the blowing agent solubility w_{solute} and the Fick diffusion coefficient D_{11} are required for relevant systems, since they characterize the amount of gas that can be released from the melt as well as the mass transfer of the blowing agent from the bulk to the interface of the formed bubbles.

This contribution reports on the determination of w_{solute} and D_{11} in blowing-agent-loaded polypropylene (PP) melts over a wide range of process-relevant conditions. To develop structure-property relationships, binary mixtures based on linear (linPP) or long-chain-branched (lcbPP) PP as well as ternary mixtures based on their blends reflecting varying degrees of molecular branching were studied with dissolved nitrogen (N_2), carbon dioxide (CO_2), or 1,1,1,2-tetrafluoroethane (R134a) at temperatures T between (433 and 533) K and pressures p corresponding to blowing agent mass fractions w_{solute} of $w_{\text{N}_2} \leq 2\%$ and (w_{CO_2} or w_{R134a}) $\leq 8\%$. For this, conventional and light scattering techniques were applied. To determine w_{solute} , the isochoric-saturation method (ISM) was combined with axisymmetric drop shape analysis (ADSA) used to determine the volume swelling S_w of the blowing-agent-loaded melts required for the evaluation of ISM experiments.¹ To determine D_{11} , dynamic light scattering (DLS)^{2,3} was applied in combination with polarization-difference Raman spectroscopy (PDRS) for the simultaneous determination of w_{solute} associated with T and p studied in DLS experiments. Here, an experimental strategy⁴ based on the calibration of PDRS at a single isotherm using w_{solute} data determined by the ISM was applied. The characterization of the blowing-agent-loaded PP melts indicated a linear relationship of w_{solute} with p within the studied range of thermodynamic states, where $w_{\text{R134a}} > w_{\text{CO}_2} > w_{\text{N}_2}$ at a given T and p . For D_{11} , a w_{solute} -independent behavior is identified, and it is demonstrated that w_{solute} and D_{11} are not significantly influenced by the branching of the studied PP samples. For ternary mixtures based on PP blends, it is demonstrated that the eigenvalue $\hat{D}_1$ of the Fick diffusion matrix accessed by DLS can be interpreted as an effective diffusion coefficient characterizing the quasi-binary mixture consisting of the homogeneous melt and the blowing agent.

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Significant references

1. J.H. Jander, M. Ratka, C. Bonten, T. Klein, and A.P. Fröba, *Measurement*, vol. 256 (2025), article 118016.
2. P.S. Schmidt, J.H. Jander, F. Alhadi, M. Ratka, C. Bonten, T. Klein, and A.P. Fröba, *International Journal of Thermophysics*, vol. 45 (2024), pp. 128:1–13.
3. P.S. Schmidt, C.J. Kankanamge, J. Klose, J.H. Jander, N. Vergadou, I.G. Economou, T. Klein, and A.P. Fröba, *Macromolecules*, vol. 58 (2025), pp. 10238–10252.
4. J.H. Jander, P.S. Schmidt, T. Klein, and A.P. Fröba, *Macromolecules*, vol. 58 (2025), pp. 7795–7801.

Diffusivities in Ternary Electrolyte Mixtures

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Ternary electrolyte mixtures consisting of a salt dissolved in a mixture of two solvents are the working fluids in numerous applications in chemical and energy engineering, including metal-ion batteries. For the efficient design or optimization of such applications, accurate knowledge of the transport properties of the working fluid is essential. In this context, Fick diffusion coefficients are particularly important as they characterize molecular diffusive mass transport driven by concentration gradients, which is often the limiting process during charging and discharging of batteries and, thereby, affects the overall performance. To describe the diffusive mass transport in a ternary electrolyte mixture consisting of four different species, i.e., the cation, the anion, and the two solvents, a second-order Fick diffusion coefficient matrix $\mathbf{D}$ is required.

In the present work, results for the Fick diffusion coefficients D_{ij} for two ternary electrolyte mixtures containing a lithium-based salt and different organic solvent mixtures are presented. The solvent mixtures contain acetonitrile (ACN) and either dimethyl sulfoxide (DMSO) or dimethyl carbonate (DMC). To get a better understanding of the influence of the solvent characteristics and the mixture composition on the diffusive mass transport, a systematic variation of the composition of the solvent mixture and the solute amount fraction was performed in the temperature range between (293.15 and 373.15) K. With the help of dynamic light scattering (DLS), the eigenvalues of $\mathbf{D}$ could be accessed by studying microscopic fluctuations in concentration at macroscopic thermodynamic equilibrium. In addition, molecular dynamics (MD) simulations were employed, which give access to D_{ij} via the separate determination of Maxwell–Stefan diffusion coefficients and thermodynamic factors. Since the eigenvalues of $\mathbf{D}$ are independent of the employed reference frame, the MD simulations could be validated by directly comparing the simulated eigenvalues with those obtained by DLS. Within this work, it could be demonstrated for the first time that a complete characterization of $\mathbf{D}$ is possible by MD simulations for ternary electrolyte mixtures. After validation, MD simulations could be employed to investigate how intermolecular interactions between the solute and solvent molecules and the fluid structure influence the diffusive mass transport. For the mixture based on the solvents ACN and DMC, for example, negative elements of $\mathbf{D}$ were obtained, which indicate a strongly non-ideal behavior of this mixture. With the help of the simulations, this behavior could be related to the formation of stable coordination or solvation shells comprised of ACN molecules around the cations, which hinder the free movement of ACN molecules.

The presented work demonstrates that the combination of DLS and MD simulations is a powerful tool, not only for characterizing diffusion in multicomponent electrolyte mixtures, but also for studying the influence of intermolecular interactions on the diffusive mass transport.

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A Sigma-Profile Prediction Method based on Graph Convolution Network Extended to Silicon-containing Compounds

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Silicon-based components are widely utilized across various industries, including semiconductors, materials, adhesives, and cosmetics. However, limited experimental data are available on their properties, and a growing need exists for predictive methods to address this gap. Hwang [1] proposed a Group Contribution-based Graph Convolution Network (GC-GCN) method to predict the pure properties of organic compounds. To extend this prediction method to mixtures and phase-equilibrium-related properties (such as flammability and flash points), a quantum-mechanics-based approach, such as COSMO-SAC [2], is needed. The COSMO-SAC method requires sigma-profiles, which are derived from time-consuming calculations based on Density Functional Theory (DFT). Ryu [3] proposed a machine-learning-based method to predict sigma profiles for various compounds; however, silicon-based components were not included in their study. In this contribution, we generated sigma-profiles for components that contain silicon and various organic functional groups, thereby extending the applicability of machine-learning algorithms to the prediction of properties of silicon-containing compounds. Our results demonstrate that the proposed method can effectively predict phase-equilibrium properties by combining the GC-GCN method with COSMO-SAC. This framework lays the groundwork for future extensions of the technique to organometallic systems.

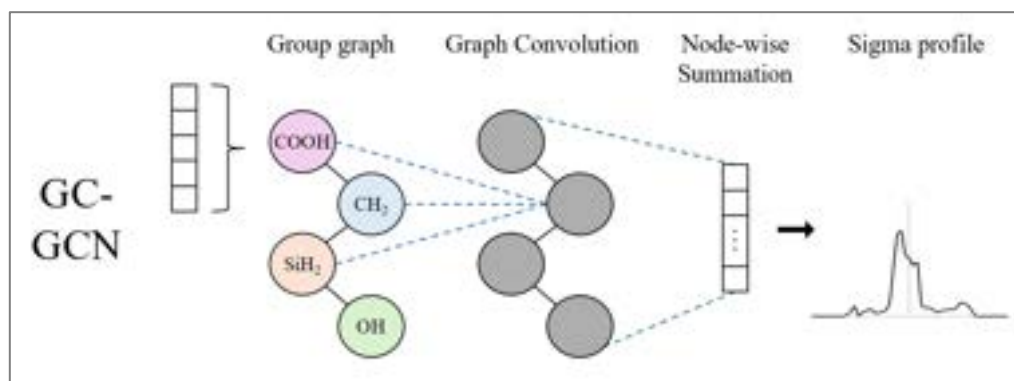


Figure 1. Workflow of the GC-GCN model.

Acknowledgment

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Significant references

1. Hwang S.Y. and Kang J.W., *Int. J. Thermophysics*, vol. 43, 136 (2022).
2. Kang S.S., Lee J.H. and Kang J.W., *Fluid Phase Equilibria*, vol. 521, 112673 (2020).
3. Ryu B.C., Hwang S.Y., Kang S.S., Kang J.W. and Yang D.S., *Int. J. Thermophysics*, vol. 44, 49 (2023).

Investigation of the performance of the LKP-SJT EOS by replacing the base fluids for modeling HFE300, Novec649, CO₂ and their mixture.

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Recently, Sabozin et al. [1,2] developed two improved versions of the Lee-Kesler-Plöcker (LKP) Equation of State (EOS), designated LKP-SJT₁ and LKP-SJT₂, which exhibit higher accuracy in calculating properties of pure fluids (long-chain alkanes and carbon dioxide) and binary mixtures (carbon dioxide or propane with *n*-alkanes) than the original LKP EOS. As mentioned in their work, the best performing combination of the two base fluids found, namely propane and *n*-octane, may not be the most suitable for fluid categories other than alkanes and carbon dioxide. In the research project PROFHET, initial investigations of fluids from the Novec family, such as HFE7300, show a significant improvement in accuracy for various properties when the base fluids are changed, see Figure 1. Therefore, further investigations are carried out in this work to identify suitable base-fluid combinations for a selection of fluids from the Novec fluid family, as well as for carbon dioxide and their mixtures. The accuracy of the further improved EOS is being tested using experimental data. For CO₂ and Novec649, the same data set that was used to fit the multiparameter EOS was also utilized to investigate the LKP. This approach maintains the need of only a few parameters for using the EOS while improving the accuracy and is particularly helpful for fluids and mixtures for which no multiparameter Helmholtz-energy EOS is available.

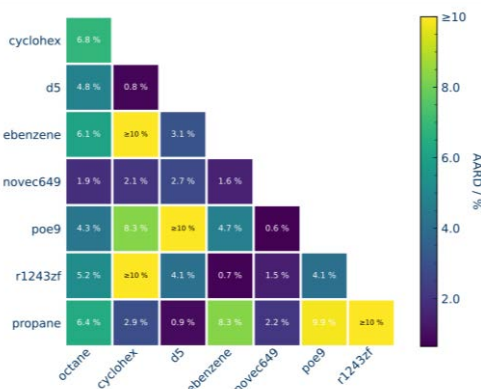


Figure 1. AARD of calculated data from LKP-SJT₂ with various combinations of base-fluid compared to experimental data of HFE7300.

Acknowledgment

Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – 531179941

Significant references

1. Sabozin, F., Jäger, A. & Thol, M. Enhancement of the Lee–Kesler–Plöcker Equation of State for Calculating Thermodynamic Properties of Long-Chain Alkanes. *Int J Thermophys* 45, 69 (2024).
2. Sabozin, F., Schneegans, M. F., Jäger, A., & Thol, M. (2025). Improving the LKP-SJT equation of state: application to alkanes, carbon dioxide, and their mixtures. *International Journal of Thermophysics*, 46(4).

Surface Tension of Binary Aqueous Mixtures with Salts Including the Supercooled Metastable Region

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The surface tension σ of low-temperature water is suspected to exhibit an anomalous behavior in the form of a sudden increase of its trend with decreasing temperature. Our recent experiments with the modified capillary rise technique showed some room for the existence of the so-called Second Inflection Point (SIP) anomaly in the temperature trend of σ , however at considerably lower temperatures below -30 °C than originally expected [1]. The in-house developed experimental apparatus enabling measurements under the supercooled metastable conditions was successfully used for the measurement of low-temperature surface tension of aqueous mixtures such as seawater or binary mixtures with ethylene glycol [2]. Current research focuses on the experiments with electrolytes. The binary aqueous mixtures with salts, such as sodium chloride, potassium chloride, calcium chloride on the one hand or ammonium sulfate and ammonium nitrate on the other, are of importance in many technical applications, environmental, geological and biological processes or by formation of droplets and ice crystals in the upper atmosphere. In this work, we introduce new data for the surface tension of water with sodium chloride and ammonium sulfate collected with the modified capillary rise technique in the low-temperature region and with the Wilhelmy plate method in the medium temperature range.

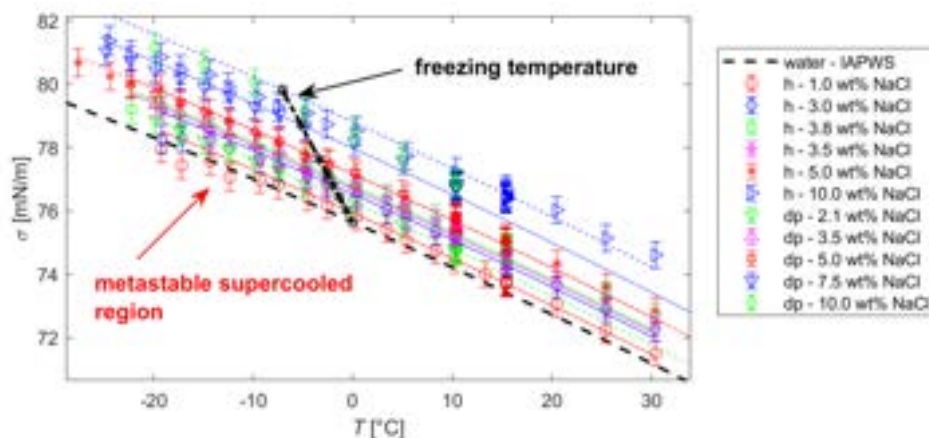


Figure 1. Surface tension of water + sodium chloride at low temperatures; results from the modified capillary rise technique compared to the model by Dutcher et al. [3] (lines) extrapolated into the supercooled region

Acknowledgment

This study was supported from the Technology Agency of the Czech Republic project no. TS01030115 within the Théta 2 Programme, the Czech Science Foundation grant no. GF24-10191K, and the institutional support RVO:61388998.

Significant references

1. V. Vinš, J. Hykl, J. Hrubý, A. Blahut, D. Celný, M. Čenský, O. Prokopová: Possible Anomaly in the Surface Tension of Supercooled Water: New Experiments at Extreme Supercooling down to -31.4 °C , *J. Phys. Chem. Lett.* 11 (2020) pp. 4443-4447.
2. V. Vinš, M. Součková, O. Prokopová, M. Čenský, J. Hrubý, A. Blahut: Density and surface tension of water + ethylene glycol mixtures as key components of heat transfer liquids, *Int. J. Refrig.* 171 (2025) 191-201.
3. C.S. Dutcher, A.S. Wexler, S.L. Clegg.: Surface tensions of inorganic multicomponent aqueous electrolyte solutions and melts, *J. Phys. Chem. A* 114 (2010) pp. 12216–12230.

Convolution and FFT Modeling for new LFA application fields

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Additive manufacturing (AM) enables layer-by-layer fabrication of complex components. Accurate, time-resolved characterization of in situ thermal behavior would contribute significantly to ensure component quality and defect-free production. This work presents a combined analytical and numerical framework to model the front-surface temperature response of layered systems to finite-duration laser pulses, as employed in laser flash analysis (LFA) and in-situ thermography [1]. Using the Green's function approach [2], the analytical solution for the normalized surface temperature is derived for rectangular pulses, capturing the transient rise and decay associated with the pulse onset and termination. Complementarily, a numerical method based on the Fast Fourier Transform (FFT) is implemented, leveraging the convolution theorem to compute the thermal response for arbitrary pulse shapes, including rectangular, triangular, Gaussian, sawtooth, and RC-like profiles. Comparison of the analytical and FFT-based convolutions for the rectangular pulse demonstrates exact agreement in both transient and steady-state behavior, validating the numerical approach. All modeled responses are further compared to experimentally measured LFA and thermography data, confirming the physical accuracy of the models. Application to other pulse shapes reveals distinct transient responses while all curves converge to the same final temperature, demonstrating the potential of the method for time-resolved evaluation of thermal properties, defect detection, and process monitoring in additive manufacturing and layered TBS.

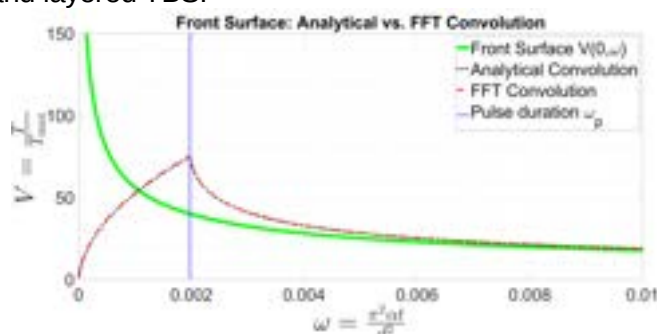


Figure 1. Comparison of the front surface dimensionless temperature responses obtained from the analytical convolution and the Fast Fourier transform (FFT)-based convolution with a rectangular pulse. The red line shows the original adiabatic front surface response to an infinitely short pulse, the blue dotted line shows the analytical convolution, and the black dashed line corresponds to the DFT-based convolution. The cyan vertical line marks the pulse duration in the ω -domain.

Acknowledgment

This work was supported through early-career funding within the framework of the Pro Pere project. This research was funded by EMPIR programme co-financed by the Participating States and from the European Union's Horizon 2020 research and innovation programme, grant number 17IND11 – Hi-TRACE. In addition to that, this work was funded by the German of Research, Technology and Space (grant agreement number 03FH007IN6) as well as the German Federal Ministry of Economic Affairs and Energy (grant agreement number 03ET7082).

Significant references

1. Höfflin, D., et al., Process Monitoring Using Synchronized Path Infrared Thermography in PBF-LB/M. *Sensors*, 2022. 22(16): p. 5943.
2. Jaeger, H.S.C.J.C., *Conduction of Heat in Solids*. 1959, Oxford: Oxford University Press. 92-102.

Emissivity measurements at PTB: development of a new spherical enclosure

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The accurate knowledge of the emissivity of a material is crucial for a variety of technological applications whenever heat transfer by radiation becomes significant. Examples of applications which require very low uncertainties of emissivity knowledge are absorbers for solar thermal electricity generation, coatings of onboard reference blackbodies for missions in space and highly developing passive radiative cooling technologies.

The Physikalisch-Technische Bundesanstalt (PTB) operates two unique facilities [1-3] for angular resolved measurements of the directional spectral, directional total and hemispherical total emissivities under air and in vacuum covering the spectral range from 1.4 μm to 200 μm and the temperature range from -40 °C to 1000 °C. The Emissivity Measurements in Air Facility (EMAF) and the Reduced Background Calibration Facility (RBCF 2) have been operated at PTB for several years and have successfully contributed to several research projects: various European projects funded by EURAMET like VITCEA, EMIRIM, the project series MetEOC 1 to 4, PaRaMetriC and Cool White. Further critical contributions were and are provided to the climate observation missions FORUM of ESA [4] and Libera [5] of NASA. Furthermore, the facilities contributed to several national and international intercomparisons [6]. Additionally, many specific measurements have been performed for various partners or customers based on bilateral research or contract work.

Using the direct radiometric method based on the measurement of the spectral radiance of a sample inside a temperature stabilized spherical enclosure with respect to the spectral radiance of two reference blackbodies at different temperatures, the measurements are traceable to the International Temperature Scale ITS-90. The spherical enclosure acts as a known hemispherical source of irradiance on the sample in our measurement scheme.

Here we present the design of a newly developed spherical enclosure, optimized through FEM simulations to achieve a uniform temperature distribution on its inner surface facing the sample. The updated design accommodates larger samples, incorporates additional calibrated temperature sensors, and features an internal dry-air circulation system. The inner surface is structured and coated with Nextel black to provide a uniform, highly emitting and predictable radiative environment. We also present the metrological characterization of the sphere with respect to its temperature distribution; based on this analysis, we derive measures to further improve temperature uniformity, such as increasing the heat-transfer-fluid flow rate and adding an insulating layer. These improvements refine the existing evaluation method, reducing the overall measurement uncertainty.

Significant references

1. C. Monte, J. Hollandt, High-Temperatures – High-Pressures, 39, 151-164, 2010
2. C. Monte, J. Hollandt, Metrologia, 47, 172-181, 2010, doi: 10.1088/0026-1394/47/2/S14
3. A. Adibekyan, et al., Int J Thermophys. 38, 89, 2017, doi:10.1007/s10765-017-2212-z
4. C. Pachot et al., in International Conference on Space Optics - ICSO 2020, 11852, 904-917, 2021, doi:10.1117/12.2599355
5. Pilewskie, P. and Hakuba, M., 2022, October. Libera Overview and Mission Status Update. In 38th CERES-II Science Team Meeting.
6. L. Hanssen et al., Metrologia, 53, 3001, 2016

Measurements of the Liquid-Phase Speed of Sound for R1132(E) at Temperatures from 10 to 80 °C and Pressures up to 10 MPa

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Accurate equations of state (EOS) are essential for evaluating low global warming potential refrigerants, and their development requires reliable thermophysical property data such as the speed of sound. In this study, the liquid-phase speed of sound for next-generation refrigerants was measured using a commercially available acoustic sensor. Calibration was performed using the established EOS of pure water and R1336mzz(Z), with corrections applied for pressure effects and ultrasonic absorption. These procedures confirmed that sufficiently accurate speed-of-sound measurements can be obtained even with commercial equipment [1,2].

Figure 1 presents the liquid-phase speed of sound data for R1132(E), showing deviations between W_{CORR} (corrected values) and W_{EOS} (values calculated from a developing EOS [3]). Measurements covered a temperature range of 10–80 °C and pressures from near saturation up to 10 MPa. Deviations remained within 3–4% at 10–40 °C, while characteristic changes in deviation trends were observed at 40 °C and above 50 °C. Such behavior reflects the limitations of the current EOS, which was fitted only to vapor-phase speed of sound data. The incorporation of the present liquid-phase speed of sound data is expected to significantly improve the accuracy of the developing EOS and contribute to more reliable property modeling for emerging refrigerants.

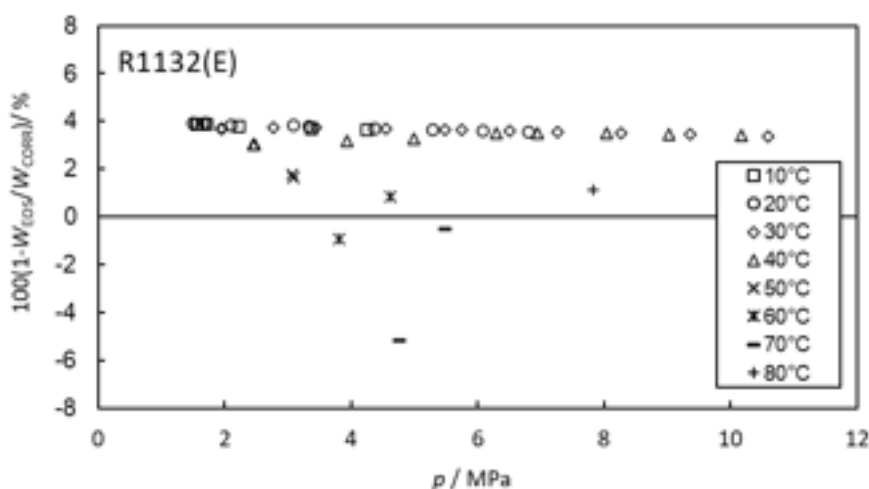


Figure 1. Results of speed of sound measurement in liquid-phase for R1132(E). Relative deviation between the corrected speed of sound W_{CORR} and the calculated speed of sound W_{EOS} .

Acknowledgment

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Significant references

1. T. Nishiyama, R. Uchikoshi T. Kuranari, T. Honda and L. Gao. *Trans. of the JSRAE*, Vol.40, No.1 (2023), pp.27-34 (in Japanese).
2. T. Nishiyama, T. Kuranari, L. Gao, Y. Higashi and R. Akasaka. *Proc. 2nd IIR Int. Conf. on HFO Refrigerants and Blends*, (2021), pp.178-183.
3. R. Akasaka and E. W. Lemmon, *Int. J. Thermophys.*, Vol. 45 (2024), 174.

Influence of Interfacial Enrichment on the Prediction of Surface Tension for Fluid Mixtures: A Molecular Dynamic Simulation Study

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The mixing state at the vapor–liquid interface of various liquid mixtures differs significantly from that in the bulk liquid. Substances with lower surface tension tend to be enriched at the interface, making the prediction of surface tension in mixtures challenging; this phenomenon is known as surface activity. Figure 1 illustrates the surface activity of a water–ethanol system reproduced by molecular dynamics (MD) simulations, where the maximum component density of the solute (ethanol), indicated by the red line in the center and the blue line in the right panel, appears at the interface. In this study, similar behavior was also reproduced for other systems, such as CO₂/PAG mixtures. The degree of interfacial enrichment and relative adsorption was quantitatively evaluated, and differences in the molecular orientation at the interface compared with the bulk liquid were analyzed (Fig. 2).

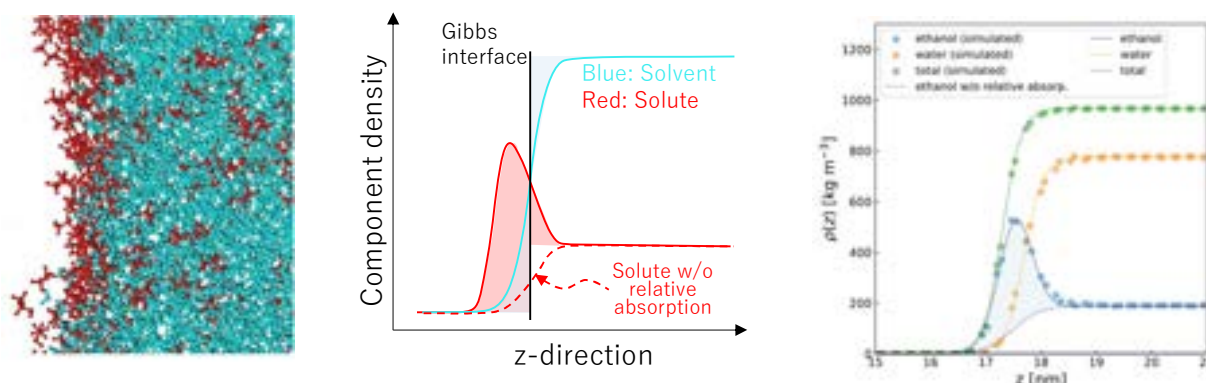


Figure 1. Interfacial enrichment in Ethanol/Water system. (Left) Snapshot of MD. Red and blue molecules represents Ethanol and Water, respectively. (Center) Gibbs model for component density distribution at the interface. (Right) Simulated component density by MD at a liquid ethanol mole fraction of 0.088.

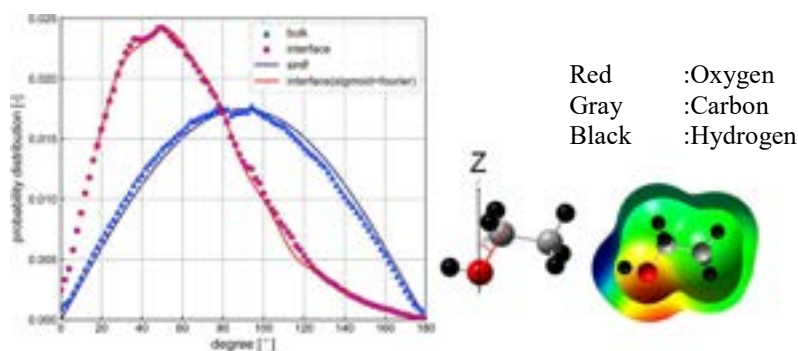


Figure 2. Probability distribution of ethanol molecular orientations near the vapor–liquid interface at 298 K and a mole fraction of 0.088 obtained from MD (left), and the most probable molecular orientation (right). In the bulk liquid (blue line), ethanol molecules exhibit nearly random orientations, whereas at the interface (red line), ethanol molecules preferentially adopt specific orientations with respect to the vapor–liquid interface. The z-axis represents the direction normal to the vapor–liquid interface reproduced by the MD simulations.

Acknowledgment

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Thermophysical Properties of Methyl Butyrate + Diethyl Carbonate Binary mixture

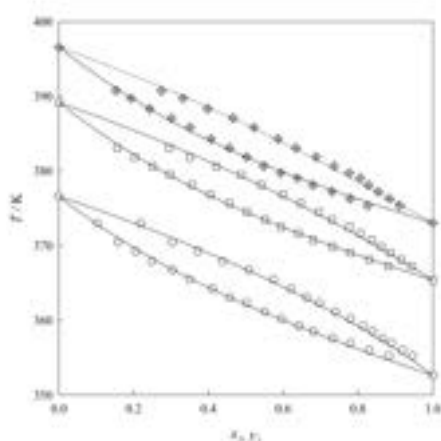
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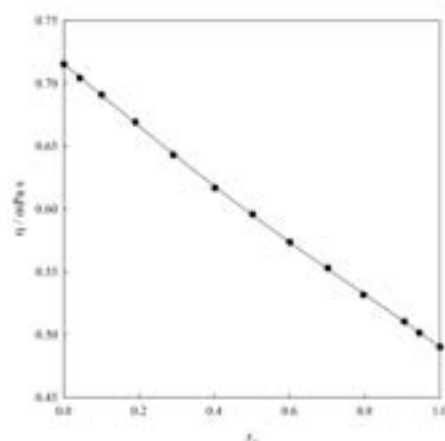
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The anthropogenic use of fossil fuels is causing irreversible environmental damage, increasing water and air pollution, and emitting greenhouse gases that have a global impact on the planet's average temperature. To alleviate this problem, many efforts have been made to shift toward more sustainable energy alternatives. In this area, bioalcohols and bioesters are promising renewable biofuel components that can be used as direct fuels or as oxygenate additives to gasoline. Linear organic carbonates such as diethyl carbonate¹ (DEC) and short-chain methyl esters such as methyl butyrate² (MB) are of particular interest given that both exhibit high oxygen content that can enhance combustion efficiency and reduce harmful emissions to the environment. To evaluate the potential use of a mixture formed by DEC + MB, an accurate determination of its thermophysical properties is required to support process design and molecular-level modeling.

In this ongoing work, the key thermophysical properties of the binary mixture are characterized, including vapor-liquid phase equilibria (VLE), liquid viscosity, and surface tension. Specifically, the VLE measurements were performed at three isobaric conditions (50, 75, and 94 kPa), yielding consistent phase-equilibrium behavior without evidence of azeotropic point. The experimental viscosities display an approximately linear dependence on composition, while surface tensions are expected to behave similarly to the viscosity trend. The measurements will be predicted using the SAFT-VR Mie EoS, coupled with Helmholtz scaling theory (HST) and the square-gradient theory. The following figures show partial results of this work, where the experimental determinations and the theoretical modeling of the selected thermophysical properties show good agreement.



Isobaric VLE for the system MB (1) + DEC (2). Experimental data at: ○: 50 kPa; □: 75 kPa; ◻: 94 kPa. — SAFT-VR Mie EoS.



Liquid dynamic viscosity for the system MB (1) + DEC (2) at 298.15 K and 101.3 kPa. ●: viscosimetry data; — Theory.

Acknowledgment

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Significant references

- [1] K. Shukla and V. C. Srivastava. RSC Advances. 6: 32624–32645, 2016.
- [2] X. He, Q. Xiang, J. Jia, Z. Zhang, J. Yan, Y. Xu, D. Chen, Fuel, 376, 132598, 2024.

A Reference Standard Raman Spectrometer for the Determination of the Hydrogen Isomer Composition

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Growing pressure to curb greenhouse gas emissions is accelerating the global shift toward decarbonization, with hydrogen emerging as a pivotal zero-emission fuel. Liquid hydrogen (LH₂) stands out for its high volumetric energy density, which enables efficient large-scale storage and long-distance transport [1]. A key challenge during liquefaction arises from the highly exothermic conversion between the H₂ spin isomers, which shifts the equilibrium composition from roughly 75% ortho / 25% para at 298 K to about 0.2% / 99.8% at 20 K [2]. Although the conversion is slow, its enthalpy (703 kJ·kg⁻¹) exceeds the vaporization enthalpy of H₂ (446 kJ·kg⁻¹) [3–5]. Accurate determination and monitoring of the spin-isomer composition and conversion kinetics are therefore essential for the safe handling, storage, and transport of LH₂.

Raman spectroscopy is a direct and non-invasive optical technique that is increasingly employed for the in-situ determination of H₂ spin-isomer composition. However, methodological differences—such as selected spectral window and transition type, number of fitted peaks, and the use or omission of instrument calibration—can result in substantial deviations between measured isomer compositions and expected values [6]. Luther *et al.* [7] recently proposed an inherent single-point calibration approach that requires only one hydrogen sample of known composition and temperature, enabling accurate determination of the H₂ spin-isomer ratio independent of temperature and bulk composition, thereby establishing Raman spectroscopy as a rapid and reliable tool for quantitative analysis.

In this work, we present a Raman-based reference system for low-uncertainty determination of the H₂ spin-isomer ratio over a temperature range from 77 K to 298 K. Owing to the slow kinetics of spin conversion, the system can be integrated downstream and operated in line with commercial in-situ Raman probes, while the reference measurement itself is carried out at ambient temperature. Upstream of the view cell, an open-ended catalyst reactor equipped with a calibrated temperature sensor is used to establish a stable spin-isomer composition. After the H₂ is analyzed in situ under cryogenic conditions, it flows into the system's view cell, where its spin-isomer composition is measured with a calibrated spectrometer. The resulting data provide an internal reference to quantify the uncertainty and assess the performance of commercial Raman probes.

Acknowledgment

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Significant references

1. A. Godula-Jopek, W. Jehle, J. Wellnitz, *Hydrogen Storage Technologies*, (n.d.).
2. D. Stolten and B. Emonts, *Hydrogen Science and Engineering, 2 Volume Set: Materials, Processes, Systems, and Technology* (John Wiley & Sons, 2016).
3. A. Godula-Jopek, W. Jehle, and J. Wellnitz, *Hydrogen Storage Technologies: New Materials, Transport, and Infrastructure* (John Wiley & Sons, 2012).
4. J.K. Peng and R.K. Ahluwalia, *Int. J. Hydrogen Energy* 38 (2013), pp. 13664–13672.
5. H. Wang, B. Wang, R. Liu, X. Sun, Y. Wang, Q. Pan, Y. Huang, W. Zhang, and Z. Gao, *Int. J. Hydrogen Energy* 55 (2024), pp. 243–260.
6. A.J. Parrott, P. Dallin, J. Andrews, P.M. Richardson, O. Semenova, M.E. Halse, S.B. Duckett, and A. Nordon, *Appl. Spectrosc.* 72 (2018), p. 000370281879864.
7. F. Luther, G.M. Sellner, M. Richter, and P.L. Stanwix, *Int. J. Hydrogen Energy* 102 (2025), pp. 778–789.

Force Field Development of Organometallic Compounds for Solvation Free Energy prediction

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Due to rapidly increasing resistance to established anti-infectives, there is an urgent need to expand the chemical diversity of the active ingredient pool. Chemical compounds that differ significantly in structure and properties from traditional drug classes, such as N-heterocyclic carbene (NHC)-gold complexes [1], have great potential as anti-infectives. However, a major obstacle for molecular dynamics (MD) studies on gold complexes is the insufficient parameterization of metals in common force fields, which limits the prediction quality. For (NHC)-gold complexes, the accurate mapping of metal-centred intermolecular interactions is also critical, requiring the careful determination of Lennard-Jones (LJ) parameters for the metal atom and bonded key atoms. The aim is to develop transferable models for MD studies on organometallic complexes, which provide reliable solvation free enthalpies ΔG_{Solv} and the derived quantity octanol-water partition coefficients $\log P_{\text{OW}}$.

The molecular model is developed using the sequential Bayesian calibration approach [2] of the Lennard-Jones parameters for new atom types such as Au(I), c1 and c2 (see Fig. 1). The force fields GAFF2/RESP and GAFF/IPolQ-Mod+LJ-fit [3] are extended by these atom types. A support vector machine classifier filters unsuitable ϵ , σ pairings. The admissible pairs train Gaussian process surrogates $\log P_{\text{OW}} = f(\epsilon, \sigma)$, which are subsequently improved by sequential sampling via Bayesian risk minimization in order to reduce posterior uncertainties.

The poster will present the methodology and intermediate results of the calibration of the new LJ parameters, and results of the parameterization of intramolecular interaction terms. Here, the dihedral parameter is determined from the difference between the rotation profiles of *ab initio* and molecular mechanics simulations.

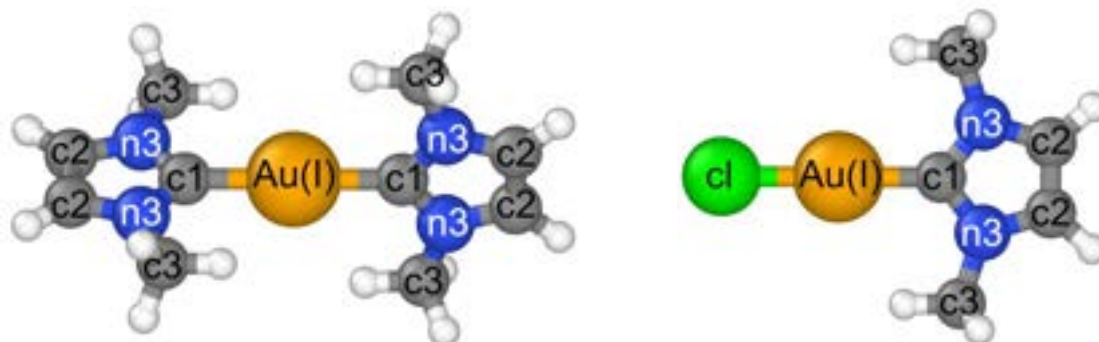


Figure 1. Chemical structures with atom types of the two classes of organometallic drug candidates that are investigated in this work.

Acknowledgment

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Significant references

1. A. Alsalhi, *J. Coord. Chem*, vol. 76, (2023), pp. 847-861
2. G. Raabe, V. P. Chheda and U. Römer, *Ind. Eng. Chem. Res.*, 64.30, (2025), pp. 15109-15119.
3. A. Mecklenfeld, G. Raabe, *ADMET and DMPK*, 8.3, (2020), pp.274-296.

Prediction of liquid-liquid-liquid phase equilibrium

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Bioalcohols are considered a real alternative to renewable fuels. They can be used directly in engines or blended with fossil fuels to increase octane rating, reducing harmful gas emissions from spark-ignited engines and decreasing the fraction of unburned hydrocarbons released into the atmosphere. [1] However, bio-alcohols are usually obtained in aqueous media, where their water content must reach acceptable levels below 1 % v/v to be used as fuels or oxygenate additives. Recently, biobutanol has been promoted as an alternative for bioalcohol due to its reduced water solubility compared to lower alcohols. However, aqueous butanol in hydrocarbon mixtures poses a thermodynamic challenge for modeling their phase equilibria. This difficulty increases with the hydrocarbon chain length.

In this work, we focus on predicting the subcritical liquid–liquid–liquid equilibria (LLLE) of the ternary mixture formed by water, 1-butanol, and hexadecane. Our thermodynamic description relies on the SAFT- γ Mie EoS, which provides a physically grounded framework to model associating and non-associating components in highly asymmetric mixtures. All equilibrium calculations were performed using a modified implementation of SGTpy [2] suite, which includes a robust computational workflow for determining ternary LLLE. This methodology combines tangent-plane distance (TPD) analysis with global minimization of the Gibbs free energy, enabling reliable identification of the LLLE region and the three coexisting liquid phases for any mixture. Pure-component and binary data are used to determine all molecular parameters; therefore, ternary predictions are obtained without additional fitting. Complementary to this, our ongoing project uses molecular dynamics simulations to validate the coexistence behaviour and phase compositions predicted by the equation of state. As illustrated in the following figures, the model predictions exhibit quantitative agreement across the entire triphasic region, and the results agree with the available experimental LLLE data [3].

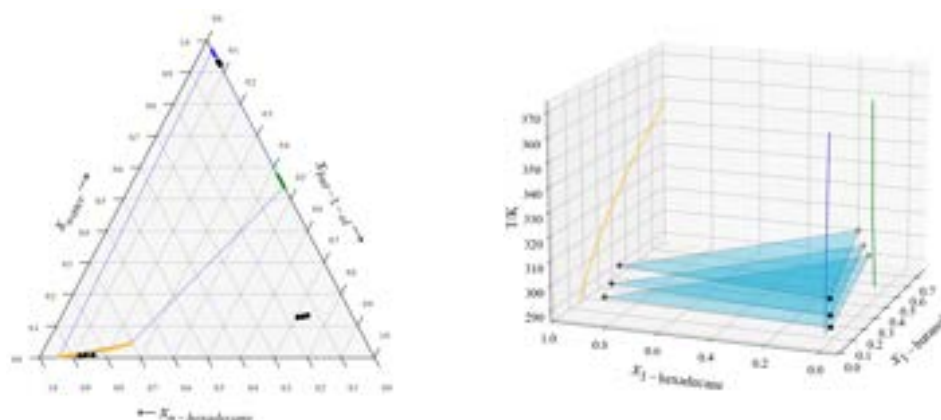


Figure 1. Predicted LLLE for the water + 1-butanol + hexadecane system using saft- γ -Mie, shown together with experimental data [3].

Acknowledgment

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Significant references

1. B. Elvers and A. Schütze. Handbook of fuels. Energy sources for transportation, ed., Wiley-VCH, Weinheim, Germany, 2nd edn, 2022
2. Mejía, A., Müller, E. A., and Chaparro Maldonado, G. J. Chem. Inf. Model, 61:1244 (2022)
3. Seeto, Y., Puig, J., Scriven, L., and Davis, H. J. Colloid Interface Sci., 96:360 (1983)

Carmélide: a new microgravity facility for measuring the viscosity of liquid metals at high temperatures

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It is challenging to determine the thermophysical properties of liquid metals, particularly viscosity, which is influenced by gravity when measured in a ground-based laboratory. First, at high temperatures (between 1500°C and 3000°C in our applications), liquid metals are easily contaminated by support or containers, thus working with levitation techniques is essential [1]. At IRDL lab, aerodynamic levitation is used with argon gas. Once the sample levitates, a high-power laser melts it to get a droplet of liquid metal. Then, the sample is excited at its resonance frequency using acoustic waves. The damping time can be used to estimate the viscosity based on Lamb's theory. However, the viscosity of liquid metal determined on ground-based laboratory is twice or three times higher than expected due to gravity [2]. Thus, the solution is to measure the viscosity in microgravity [3].

This communication presents the Carmélide facility dedicated to parabolic flights to measure viscosity in the Zero-G aircraft. For the first time, aerodynamic stabilization of the droplet is used during the 22 s of microgravity phase. Consequently, this facility will make it possible to study any kind of liquid materials, including metals.

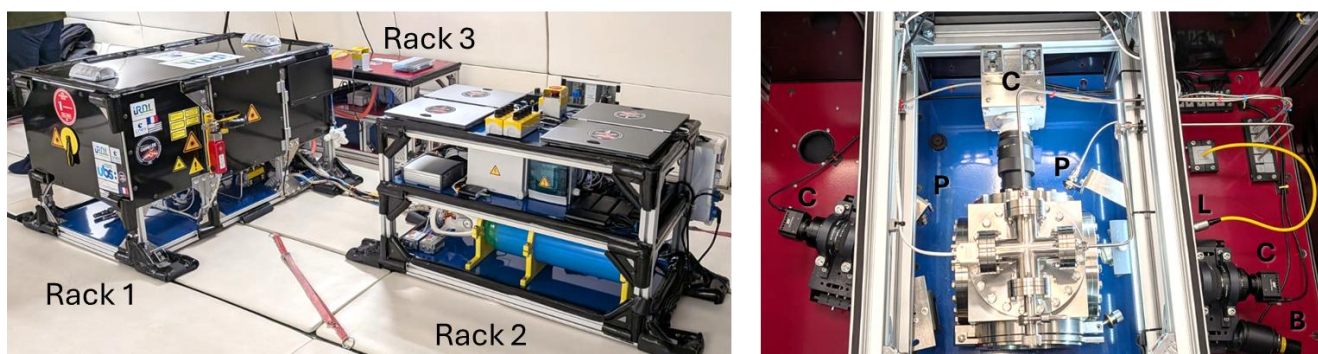


Figure 1. Left: Carmélide facility installed on board the Zero-G aircraft. Right: Core of the experiment with the chamber containing the droplet, and measuring devices (B: backlighting, C: cameras, L: laser, P: pyrometers).

Acknowledgment

This work received the support of the CNES (French Space Agency) for development and parabolic flight campaign, and the IRDL laboratory.

Significant references

1. M. J. Assael, K. Kakosimos, R. M. Banish, J. Brillo, I. Egly, R. Brooks, P. N. Quested, K. C. Mills, A. Nagashima, Y. Sato, and W. A. Wakeham, Reference Data for the Density and Viscosity of Liquid Aluminum and Liquid Iron. *Journal of Physical and Chemical Reference Data*, vol 35 (2006)
2. T. Pierre, M. Courtois, D. Le Maux, M. Carin, and P. Le Masson, Gravity impact on viscosity measurements by aerodynamic levitation. *High Temperatures-High Pressures*, vol. 53 (2024).
3. G. Lohöfer, M. Beckers, T. Blumberg, D. Bräuer, S. Schneider, T. Volkmann, and A. Meyer, TEMPUS A microgravity electromagnetic levitation facility for parabolic flights. *Review of Scientific Instruments*, vol. 95 (2024).

Poster Presentations



Prediction of long-term thermal degradation temperature of ionic liquids using COSMO-based machine learning

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Long-term thermal stability is a critical bottleneck for using ionic liquids (ILs) as high-temperature solvents, absorbents and electrolytes in continuous processes. Conventional ramped thermogravimetric analysis (TGA) data and quoted “decomposition temperatures” often overestimate long-term thermal stability by 100–300 °C[1] relative to isothermal criteria such as $T_{1\%/10h}$, where even small mass losses can accumulate over hours or days of operation. At the same time, reliable long-term stability data exist for fewer than a hundred ILs and are often costly, for each T measurement requires over 4 TGA [1].

Conventional predictive Machine learning models requires large amount of data on the model training and evaluation [2]. This could be a critical point for the training of $T_{1\%/10h}$ considering the limited amount of data (bellow 100 points on the open literature). Here it was proposed a data-efficient framework that combines COSMO-based quantum descriptors with lightweight convolutional neural networks (CNNs) to predict long-term thermal degradation temperatures of ILs. Quantum descriptors (σ -profiles, σ -moments, COSMO volumes and interaction energies) are computed for a curated set of ~70 ILs with literature $T_{0.01/10h}$ values. Cation and anion σ -profiles are concatenated and treated as structured 1D inputs to the CNN, while scalar descriptors encode additional information on polarity, hydrogen-bonding and charge distribution. The architecture is adapted to small-data regimes and evaluated via stratified cross-validation by IL family to test transferability across chemistries.

This work reported that the architecture is adapted to small-data regimes and evaluated via stratified cross-validation by IL family to test transferability across chemistries. The $T_{1\%/10h}$ of few ILs were experimentally measured and compared with the proposed framework predictions. Results indicate promising low deviations for this approach, regardless of the small amount of dataset used on the training. Additionally, long term thermal stability of several ILs were presented providing key information for users interested in applying them on high temperature operational conditions.

Acknowledgment

This work was developed within the scope of the project CICECO Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, financed by national funds through the FCT/MCTES (PIDDAC). This study also received financial support from Ilimited project , financed by Horizon Europe agreement n° 101192964.

Significant references

1. Y. Cao and T. Mu, ‘Comprehensive Investigation on the Thermal Stability of 66 Ionic Liquids by Thermogravimetric Analysis’, Ind Eng Chem Res, vol. 53, no. 20, pp. 8651–8664, May 2014, doi: 10.1021/ie5009597.
2. Y. Qiu et al., ‘Large chemical language models for property prediction and high-throughput screening of ionic liquids’, Digital Discovery, vol. 4, no. 6, pp. 1505–1517, Apr. 2025, doi: 10.1039/D5DD00035A.

Joule-Thomson coefficient from hydrate inhibitor systems: methanol + methane case

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Hydrates are still one of the main issues related to oil and gas production, especially in deep sea environments. As methanol is one of the main chemicals used to avoid hydrate formation, the comprehension of its behavior under high pressure conditions in mixtures with petroleum components are of great need. To estimate such properties, equations of state are used, but for associating systems can lead to mispredictions [1,2], more attenuated for derivative properties [3]. Given the fundamental importance of the Joule-Thomson (JT) effect in flow assurance within the oil and gas industry, the present study reports precise experimental density measurements for methane + methanol mixtures over the temperature range 313.15 - 413.15 K and at pressures up to 100 MPa. From these data, derivative thermodynamic properties, including the isothermal compressibility, isobaric expansivity, and Joule-Thomson coefficient, were determined through correlation using the Tammann-Tait equation and subsequently compared with predictions obtained from the PC-SAFT equation of state. The analysis indicated that the Joule-Thomson coefficient (μ_{JT}) assumes negative values under the investigated conditions, corresponding to a temperature increase upon expansion. The PC-SAFT model demonstrated satisfactory performance in representing the experimental densities and in estimating properties independent of the isobaric heat capacity, despite the inherent complexity of the system. Moreover, a refined binary interaction parameter for the methane/methanol pair was determined and evaluated within the PC-SAFT framework.

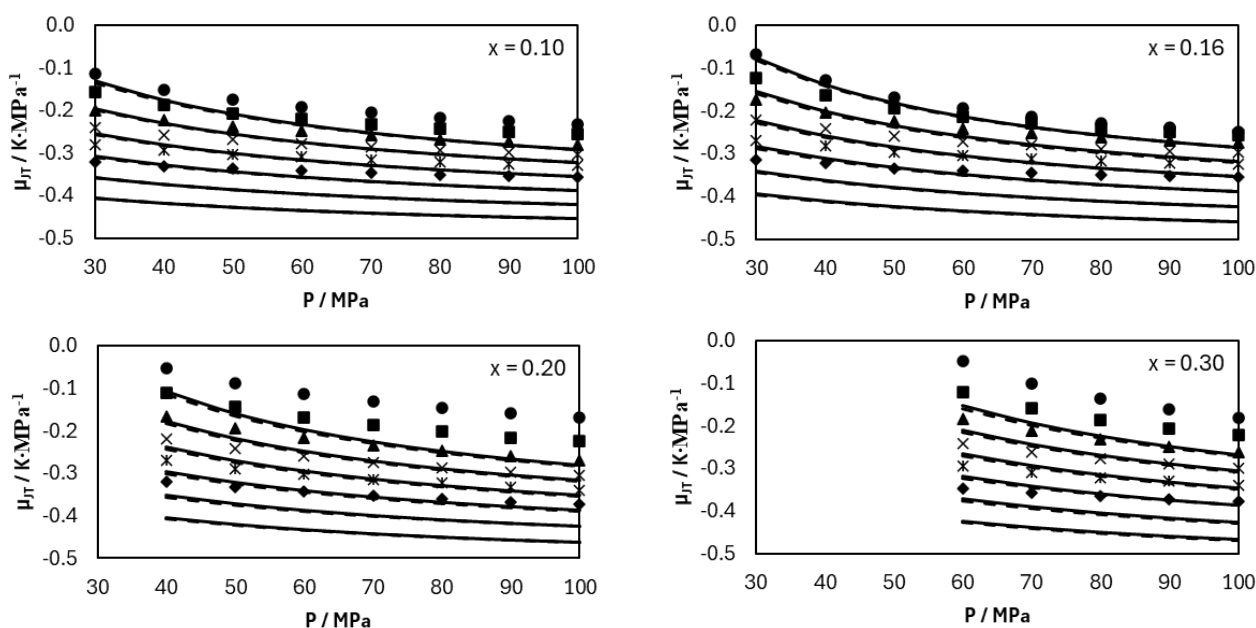


Figure 1. Joule-Thomson coefficient prediction and estimation comparison.

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Significant references

1. M.F.L. da Costa, H.A. de Medeiros, A.A. Araújo Alves, L.H.G. de Medeiros, F.X. Feitosa, H.B. De

- Sant'Ana, Volumetric properties of three nonylphenol ethoxylated nonionic surfactant mixtures with methanol: Experimental study and modeling with Tammann-Tait and PC-SAFT equation of state, *Fluid Phase Equilib* 581 (2024) 114076. <https://doi.org/10.1016/j.fluid.2024.114076>.
2. L.H.G. de Medeiros, M.A.M. de Sousa, E.E.C. da Silva, M.F.L. da Costa, F.X. Feitosa, F. Costa, A.C.M. da Silva, S. Mattedi, H.B. de Sant'Ana, Thermophysical Characterization of Protic Ionic Liquids: Density Measurements, Group Contribution Method, and PC-SAFT Modeling Application, *Ind Eng Chem Res* 63 (2024) 16186–16197. <https://doi.org/10.1021/acs.iecr.4c02480>.
 3. A. Pakraves, F. Zarei, H. Zarei, P. T parameterization of SAFT equation of state: developing a new parameterization method for equations of state, *Fluid Phase Equilib* 538 (2021) 113024. <https://doi.org/10.1016/j.fluid.2021.113024>.

Measurement of Isobaric Heat Capacity of Difluoromethane / Trifluoroiodomethane Binary Mixtures

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The global phase-down of high-GWP hydrofluorocarbons (HFCs), particularly R410A (GWP 2088), has been rapidly accelerated by the Kigali Amendment to the Montreal Protocol and stringent F-gas regulations. Although R32 (GWP 675), the most widely adopted low-GWP alternative, offers excellent thermodynamic performance and high energy efficiency, its mild flammability (ASHRAE Class A2L) continues to raise fire-safety concerns, and its GWP remains too high to meet long-term regulatory targets requiring values below 150.

This study proposes a novel binary refrigerant consisting of R32 and trifluoroiodomethane (CF₃I), an ultra-short-lived substance with negligible global warming potential (GWP < 1), an atmospheric lifetime of approximately 1.2 days, zero ozone depletion potential, and inherently non-flammable and non-toxic properties. The isobaric heat capacity (c_p) of R32/ CF₃I mixtures was precisely measured over a wide range of compositions and temperatures. The addition of CF₃I dramatically suppresses the flammability of R32, enabling blends that approach or achieve full A1 (non-flammable) classification while preserving the high volumetric cooling capacity and superior heat-transfer characteristics of R32. Consequently, the optimized mixtures exhibit overall GWPs of 300–400 (potentially below 150 with higher CF₃I fractions) and deliver cooling capacity and coefficients of performance equal to or better than those of R410A.

Experimental measurements of specific heat capacity were performed using a customized calorimetry system combining a commercial heat-conduction calorimeter (Setaram BT2.15) with dual high-precision syringe pumps (Teledyne ISCO 260x) and an in-line static mixer (Floxlabs BTSP-500-5) for sample preparation and delivery of homogeneous binary mixtures.

The obtained c_p data are essential for establishing an accurate thermodynamic property database for these blends, thereby enhancing the reliability of refrigeration cycle simulations and practical system design. The R32/CF₃I refrigerant system, compatible with existing R410A equipment with minimal modifications, simultaneously satisfies the three critical requirements of flammability mitigation, ultra-low GWP, and high efficiency, positioning it as a highly promising next-generation non-flammable alternative refrigerant.

This work was supported by Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government (MOTIE) (20212020800070, Development of next-generation alternative refrigerant and efficient heat pump system).

Significant references

1. S. Lee, D. Kim, S. Lee, W. Kang, X. Xiao and S. KWon, *High Temperatures–High Pressures*, vol. 54 (2025), pp. 39-50.

Effective Thermal Conductivity of Cyclohexane-Based Nanofluids Containing Cerium Dioxide Nanoparticles

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Nanofluids are defined as dispersions composed of a continuous liquid phase and a dispersed phase consisting of solid particles with diameters of about 100 nm and below. Nanofluids containing highly conductive nanoparticles exhibit enhanced ability to transfer heat compared to the pure base fluid and are considered as promising heat transfer fluids for various applications including, for example, electrical devices, solar collectors, or grinding machines, but also in medicine for thermal therapy. Thus, an important transport property to characterize nanofluids is their effective thermal conductivity (ETC), which quantifies the ability of heterogeneous materials to conduct heat. While it could be shown after a long-lasting debate that the ETC of such nanofluids does not exhibit anomalously large values, contradictory statements on the influence of the particle size on the ETC can still be found in the literature even within the group of nanofluids containing spherical particles. One limitation in corresponding experimental studies is the scarce availability of stable nanofluids with very small particles that can be reliably dispersed at particle volume fractions allowing to resolve their influence on the ETC.

To improve this situation, this contribution presents results from studies regarding the ETC of stable nanofluids containing cerium dioxide (CeO₂) nanoparticles with chemisorbed organic shells dispersed in cyclohexane.¹ With the help of dynamic light scattering (DLS), it could be shown that the hydrodynamic diameter of such particles with varying CeO₂ core diameters and thicknesses of the organic shell in cyclohexane is typically on the order of 10 nm. The influences of the particle characteristics and particle volume fractions of up to 0.05 on the ETC were studied using a guarded parallel-plate instrument at a pressure of 0.1 MPa in the temperature range from (283.15 to 313.15) K with expanded relative uncertainties for the ETC of about 2.5%. The obtained results agree with those calculated by the well-established Hamilton-Crosser model and a recently suggested semiempirical model.² The new model combines two previously developed approaches, where the ETC is calculated via the geometric mean of the thermal conductivity of the base fluid and an effective one related to the particles. The latter contribution considers the thermal conductivity of the particles and a size-dependent Kapitza resistance at the particle/fluid interface. This prediction model has proven to reliably estimate the ETC of various nanofluids consisting of different particle materials and base fluids over broad ranges of particle volume fraction and particle size.

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Significant references

1. F.E. Berger Bioucas, W. Wu, L.M.S. Stiegler, W. Peukert, J. Walter, T. Adschiri, A. Yoko, T.M. Koller, A.P. Fröba, *International Journal of Thermophysics*, vol. 46 (2025), article 12.
2. T.M. Koller, F.E. Berger Bioucas, K. Hahn, M.H. Rausch, A.P. Fröba, *Journal of Physical Chemistry C*, vol. 129 (2025), pp.14265–14281.

Viscosity Measurements of Binary Hydrogen Gas Mixtures Containing Nitrogen and Carbon Dioxide at Temperatures from (243 to 573) K and Pressures up to 20 MPa

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The thermophysical properties of hydrogen and hydrogen-containing gas mixtures are gaining significant importance in the development of hydrogen-based energy systems and the transition to a decarbonized economy. Accurate viscosity data of hydrogen-containing gases are essential for computational fluid dynamics (CFD) simulations and energy balance calculations in applications such as fuel cells, natural gas pipeline transportation with hydrogen blends, and hydrogen-blended combustion in gas turbines. However, experimental viscosity data for hydrogen-containing gases at high pressures and over wide temperature ranges remain limited. In this work, we present a vibrating-wire viscometer designed specifically for hydrogen-containing gases. The core unit of the vibrating-wire viscometer is a tungsten wire with a diameter of 25 μm and a length of 60 mm. The tungsten wire clamped at both ends by stainless steel chucks is placed in a pair of gold-plated samarium cobalt magnets. The wire is electrically isolated from the holder by silicon nitride ceramic substrates. The silicon nitride ceramic substrates are supported by a pair of tungsten rods to reduce the temperature dependence of the vacuum resonance frequency. Temperature control is achieved through two thermostatic units: the outer layer is regulated by a thermostat bath, while the inner layer is controlled by a temperature controller and electric heating wire. The viscometer enables viscosity measurements of hydrogen-containing gases in the temperature range from (243 to 573) K and at pressures up to 20 MPa. The gas viscosities of binary hydrogen gas mixtures containing nitrogen and carbon dioxide were measured using the viscometer.

Revealing phase equilibria and the quadruple point in the CO₂ + *o*-terphenyl system under high-pressure and high-temperature conditions

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The global objective to achieve net-zero carbon emissions by 2050 has accelerated research on technologies capable of capturing and storing CO₂. Processes such as geological storage of CO₂ in depleted oil and gas fields, coal seams, and deep saline aquifers have proven to be effective long-term strategies for mitigating climate change. However, the complex thermodynamics governing the interactions between CO₂ and subsurface fluids is not well understood, particularly in the presence of heavy hydrocarbons representative of residual petroleum fractions [1]. The presence of these heavy hydrocarbons can give rise to complex phase behaviors beyond the simple liquid-vapor equilibria commonly observed [2-3]. In this context, this work focuses on the experimental investigation of the CO₂ + *o*-terphenyl system, where *o*-terphenyl is a heavy aromatic hydrocarbon (C₁₈H₁₄, MM = 230.30 g·mol⁻¹) belonging to the polyphenyl family. To the best of our knowledge, no paper has been published regarding this binary system. The phase behavior of this binary system was investigated using a high-pressure variable-volume visual cell equipped with sapphire windows for full visibility. The experiments were conducted following a visual synthetic method, allowing the direct observation of phase transitions. The mixture was prepared directly inside the equilibrium cell, and the high-pressure phase behavior was investigated along several isopleths. Phase transition measurements were conducted under either isobaric or isothermal conditions, depending on the specific transition point observed along the slope of the critical line. These approaches enable the visual determination of various phase transition types, including liquid-vapor (LV), liquid-liquid (LL), liquid-liquid-vapor (LLV), liquid-solid (LS), and liquid-liquid-solid (LLS). The system was studied for global compositions ranging from 0 (pure *o*-terphenyl) to 97.67 mol% CO₂, at temperatures from 295.53 K to 413.99 K and pressures up to 69.90 MPa. A solid-liquid-liquid-vapor (SLLV) quadruple point (Q-point) given in Figure 1 was experimentally observed. This experimental point was measured and confirmed by the intersection of the LLV and LLS critical lines. The Q-point was consistent with Gibbs' phase rule, confirming its non-variant nature. The results of this work provide new data for validating thermodynamic models and equations of state, offering reference points for model comparison and parameter fitting.



Figure 1. Solid-liquid-liquid-vapor Q-point for carbon dioxide + *o*-terphenyl binary system at 294.57 K and 5.21 MPa with 61,10 mol% CO₂.

References

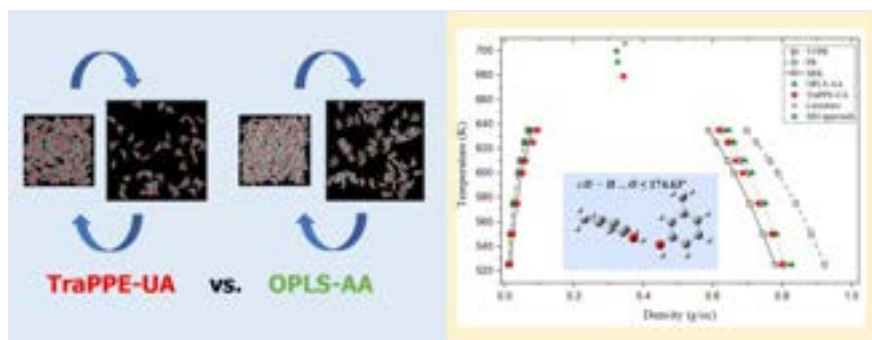
1. J. E. Espinoza Mejia and X. Li, *Industrial & Engineering Chemistry Research*, vol. 62 (2023), pp. 3747–3766.
2. H. A. D. Medeiros, A. A. A. Alves, J. L. Daridon, H. B. de Sant'Ana, and F. X. Feitosa, *The Journal of Supercritical Fluids*, vol. 201 (2023), pp. 106033.
3. W. P. Trujillo Vera, H. A. D. Medeiros, F. E. Benelli, M. Cismondi-Duarte, F. X. Feitosa, and H. B. de Sant'Ana, *The Journal of Supercritical Fluids*, vol. 226 (2025), pp. 106725.

Prediction of thermodynamic properties of m-cresol: Comparison of TraPPE-UA and OPLS-AA force fields

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In this study, we predicted the thermodynamic properties of m-cresol using molecular simulations in conjunction with two force fields, viz., 9-site TraPPE-UA [1] and 16-site OPLS-AA [2] force fields and compared the results. The molecular-level structure of liquid m-cresol at 400.15 K and 101.325 kPa has been investigated via computation of the site-site intermolecular radial distribution functions (RDFs). The coordination number and the average number of hydrogen bonds per molecule have been determined. The geometric criteria for hydrogen-bonds in m-cresol consist of the oxygen-oxygen distance from the RDF and the $\angle \text{O-H}\cdots\text{O} \leq 174.63^\circ$, determined from our density functional theory (DFT) calculations. We have further tested the efficacy of force fields by predicting vapour-liquid equilibrium data via GEMC-NVT [3] simulations and comparing these with experimental results where available. To the best of our knowledge, we have generated the coexistence densities in the temperature range from 525.15 K to 635.15 K for the first time. OPLS-AA force field exhibits a better agreement with available literature data for vapour pressures, normal boiling point, latent heats of vapourization and critical temperature than TraPPE-UA force field. The TraPPE-UA force field is computationally less expensive than the OPLS-AA force field. The molecular insights into the coexisting liquid phases have been obtained via site-site intermolecular RDFs and analyses of orientations of -OH groups and molecules as a whole. The association via hydrogen bonding shows the average number of hydrogen bonds per m-cresol molecule decreases with increase in temperature for both the force fields with OPLS-AA predicting fewer hydrogen bonds than TraPPE-UA. Further, C4-C3 and C4-C6 intermolecular RDFs show differing peak heights which are independent of the non-bonded interaction parameters and can be explained by the proximity of the methyl group to C3.

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Significant references

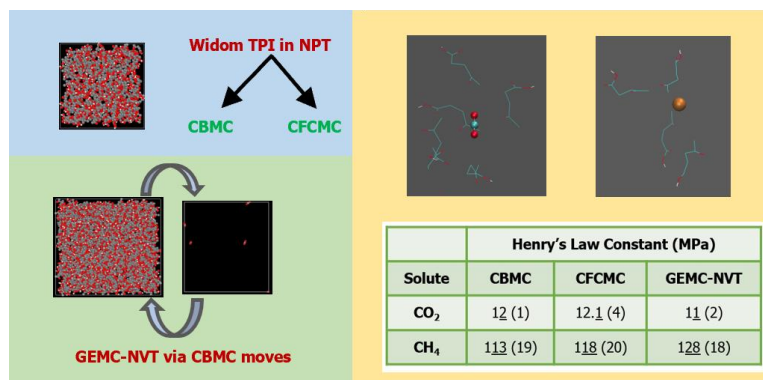
1. A. Z. Panagiotopoulos, "Direct determination of phase coexistence properties of fluids by monte carlo simulation in a new ensemble," *Mol. Phys.*, vol. 61, no. 4 (1987) pp. 813–826.
2. C. D. Wick, M. G. Martin, and J. I. Siepmann, "Transferable Potentials for Phase Equilibria. 4. United-Atom description of linear and branched alkenes and alkylbenzenes," *J. Phys. Chem. B*, vol. 104, no. 33 (2000) pp. 8008–8016.
3. L. S. Dodda, I. C. De Vaca, J. Tirado-Rives, and W. L. Jorgensen, "LigParGen web server: An automatic OPLS-AA parameter generator for organic ligands," *Nucleic Acids Res.*, vol. 45, no. W1 (2017) pp. W331–W336. (accessed in February, 2023)

Prediction of Henry's law constants for CO₂ and CH₄ in Levulinic acid via different Monte Carlo approaches

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Henry's law constants of CO₂ and CH₄ in levulinic acid are predicted at 313.15 K and 101.325 kPa. Widom test particle insertion method (which is based on excess chemical potential computation) in the NPT ensemble via two different Monte Carlo approaches viz., CBMC[1] and CFCMC[2] is implemented. GEMC–NVT[3] simulations are performed to calculate Henry's law constants from the slope of the line fitted to the plot of partial pressure of solute (CO₂ or CH₄) in vapour phase versus the mole fraction of solute in liquid levulinic acid. Henry's law constants estimated via all three Monte Carlo methods and for both the solutes show good agreement within statistical uncertainties. The negative value of Gibbs free energy of transfer (ΔG_{trans}) of CO₂ from vapour to solvent (levulinic acid) phase suggests preference of CO₂ for liquid levulinic acid over vapour phase. The solvation number computed from solute – solvent centre-of-mass radial distribution functions (RDFs) show a higher value for CH₄ than CO₂, contrary to trend in Henry's law constant. Therefore, the local environment around the solute molecule is investigated by computing the solute – solvent site – site intermolecular RDFs. The number integral calculated (up to the first minimum) from site – site intermolecular RDF of C(CO₂) – methyl group of levulinic acid (CH₃(1)) is more than that calculated from CH₄ – CH₃(1) RDF; confirming the higher solubility of CO₂ in levulinic acid than CH₄.

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Significant references

1. Siepmann J. I. and Frenkel D., Configurational bias Monte Carlo: A new sampling scheme for flexible chains, Mol. Phys., 1992, 75(1), 59–70.
2. Shi, W. & Maginn, E. J. Continuous fractional component Monte Carlo: An adaptive biasing method for open system atomistic simulations. J. Chem. Theory Comput. 3 (2007), 1451–1463.
3. Zhang L and Siepmann J. I., Direct calculation of Henry's law constants from Gibbs ensemble Monte Carlo simulations: Nitrogen, oxygen, carbon dioxide and methane in ethanol, Theor. Chem. Acc., 2006, 115(5), 391–7.

Molecular Insights into “Sugaring out” of Acetonitrile from Its Aqueous Solution via addition of n-alkanols

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Aqueous solutions of acetonitrile have been investigated from a fundamental science perspective and because of applications as a solvent in liquid chromatography, hydrometallurgy and electrochemistry. Acetonitrile is volatile and its relatively adverse environmental impact means recovery and reuse of acetonitrile from aqueous waste streams is necessary for sustainable global supply; and environmental, technical and economic feasibility of industrial processes. The ‘sugaring out’ technique is an approach where the additive is a monomeric sugar or disaccharide where the sugars preferentially form hydrogen bonds with water over acetonitrile molecules and the acetonitrile – rich phase segregates out. This same principle forms the basis of our investigation of linear alcohols (viz., methanol, ethanol, propan-1-ol, octan-1-ol) as extractive solvents for recovery of acetonitrile from its aqueous solution at two temperatures (293.15 K and 298.15 K) at 101.325 kPa. In this study, we have employed the fundamental and predictive engineering science approach of using the Gibbs ensemble Monte Carlo (GEMC) simulation technique [1] to predict the effectiveness of the solvents via assessment of the solvent performance indicators (SPIs) which are the partition coefficient of acetonitrile, separation factor, and Gibbs free energy of transfer of acetonitrile from aqueous solution to the organic solvent – rich phase (shown in Table 1 at 293.15 K). We have explored the recovery of acetonitrile from its solution with water where the mole fraction of acetonitrile (x_{ACN}) is 0.23 which is in the intermediate region where microheterogeneity is observed via experiments as well as computer simulations.[2] This intermediate region is also of fundamental interest due to the interesting properties of the interactions of acetonitrile, water and solvent at the molecular level.[3] To understand and elucidate the molecular-level basis for our observations, we study the structural features which characterize the systems containing with optimal solvents at the two temperatures by plotting the site-site intermolecular RDFs and calculating the coordination numbers.

Table 1. Values of SPIs for use of linear alcohols as solvents for the extraction of acetonitrile at 293.15 K

Components	K_{ACN}	$\text{Log}_{10}K_{ACN}$	S	$\Delta_{tr}G(W)$	$\Delta_{tr}G(ACN)$	$\Delta_{tr}G(ROH)$
Methanol	2.789	0.445	5.349	1053.331	-721.306	-284.069
Ethanol	2.366	0.374	4.914	1263.572	-421.526	-794.236
Propan-1-ol	1.066	0.028	1.268	355.657	104.068	-350.094
Octan-1-ol	0.423	-0.374	1.679	2702.127	2702.127	-885.332

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Significant references

1. A.Z. Panagiotopoulos, 1987. Direct determination of phase coexistence properties of fluids by Monte Carlo simulation in a new ensemble. *Molecular Physics*, 61(4), pp.813-826.
2. H. Kovacs and A. Laaksonen, 1991. Molecular dynamics simulation and NMR study of water-acetonitrile mixtures. *Journal of the American Chemical Society*, 113(15), pp.5596-5605.
3. C. D. Wick, J. M. Stubbs, N. Rai, and J. I. Siepmann, 2005. Transferable potentials for phase equilibria. 7. Primary, secondary, and tertiary amines, nitroalkanes and nitrobenzene, nitriles, amides, pyridine, and pyrimidine. *The Journal of Physical Chemistry B*, 109(40), pp.18974-18982.

Thermochemical screening of reactive working fluids for energy conversion cycles

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In order to meet growing energy demands while reducing environmental impact, the development of efficient and sustainable energy conversion technologies such as heat pumps and power plants is essential. One promising way of improving the performance of thermodynamic cycles is to use reactive working fluids instead of conventional inert fluids. Such fluids couple physical and chemical energy to enhance the efficiency.

In the REACHER project, we study reactive fluids that undergo the dissociation/recombination reaction ($A_2 \rightleftharpoons 2A$). We propose an innovative approach to design, rank, and select, dimer molecules following this reversible chemical reaction¹⁻³.

A dedicated Fortran code was first developed to generate all possible monomer/dimer pairs following strict criteria, and using a set of 10 elements (C, N, O, P, S, B, F, Cl, Br, and I).

First, A conformer exploration was carried out to select the most stable conformers. Then, multilevel quantum chemical calculations involving optimizations and dihedral scans have been carried out to assess the stability of the molecules using the Gaussian 09 program package.

The CBS-QB3 method⁴ was used to calculate the thermochemical properties of the molecules not containing iodine, since this method is not adapted for this atom. The iodine-containing molecules have been calculated using the G4MP2-XK protocol. The standard molar entropy corrections were taken into consideration, and the kinetics of the reactions considered as stable were calculated.

Overall, the Fortran code generated 498 reactive fluids, and after performing the quantum chemical characterization, only 153 fluids have been judged to be stable.

Validation of the theoretical results has been done, and the results have been judged to be satisfactory and adequate for screening and discovering new reactive fluids and thermochemical properties prediction.

Acknowledgments

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Significant references

1. S. Lasala, R. Privat, O. Herbinet, P. Arpentiner, D. Bonalumi, and J.-N. Jaubert. (2021), Thermochemical engines: Unexploited high-potential energy converters, *Energy Conversion and Management*, vol 299, 113685 2.
2. A. Barakat, S. Lasala, P. Arpentiner, and J.N. Jaubert (2022), The original and impactful exploitation of chemical energy in heat pumps, *Chemical Engineering Journal Advances*, vol 12. 100400 3.
3. Website of the project REACHER: <https://www.univ-lorraine.fr/erc-reacher/>
4. J. A. Montgomery Jr., M. J. Frisch, J. W. Ochterski, and G. A. Petersson, A complete basis set model chemistry. VII. Use of the minimum population localization method, *J. Chem. Phys.*, 112 (2000) 6532-42. DOI: 10.1063/1.481224
5. B. Chan, A. Karton, and K. Raghavachari, G4(MP2)-XK: A Variant of the G4(MP2)-6X Composite Method with Expanded Applicability for Main-Group Elements up to Radon, *J. Chem. Theory Comput.* 2019, 15, 4478–4484.

Predicting and Understanding Peptide Aggregation using Stochastic Machine Learning

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Peptides can self-assemble into ordered nanostructures such as nanofibers, nanotubes, or sheets. They are promising functional elements for energy harvesting and energy storage systems, and are inherently eco-friendly.¹ Unfortunately, the peptide space is too vast to explore using costly and time-consuming experimental or computational (e.g., molecular dynamics) trial-and-error approaches. As such, a method to convert the discrete set of all synthesizable peptides to a continuous mathematical space, navigable through simple optimization procedures, is proposed in this work based on sigma profiles.²

The aggregation propensity of all possible dipeptides (400) and tripeptides (8000) in water was taken from the literature, estimated using computational simulations. This dataset was split into training and testing sets using stratified sampling. The training data was used to fit a Gaussian process (GP) model, followed by making predictions for peptides never seen before by the model (testing set). The GP model exhibited remarkable performance, attaining testing set coefficients of determination of 0.87 for dipeptides and 0.85 for tripeptides. To minimize model data requirements, GPs were combined with the stochastic frameworks of active learning and Bayesian optimization. This demonstrated that GPs serve as laboratory companions, suggesting amino acid combinations that maximize peptide self-aggregation with only a handful of training examples. All in all, this work establishes a new paradigm on digital molecular spaces for peptides and their efficient navigation by exploiting sigma profiles.

Acknowledgment

This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UID/50011/2025 (DOI 10.54499/UID/50011/2025) & LA/P/0006/2020 (DOI 10.54499/LA/P/0006/2020), financed by national funds through the FCT/MCTES (PIDDAC).

Significant references

1. P. S. Zelenovskii, K. Romanyuk, M. S. Liberato, P. Brandao, et al., *Funct. Mater.*, vol. 31 (2021), 2102524.
2. D. O. Abranches, E. J. Maginn, Y. J. Colón, *Proc. Natl. Acad. Sci. U.S.A.*, vol. 121 (2024), e2404676121.

The Contribution of Vapor Pressure Measurement to Unravelling of Polymorphic Behavior of Organic Compounds

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The number of compounds with reliable vapor-pressure data at multiple temperatures likely exceeds 10,000, whereas reliable sublimation-pressure curves exist for fewer than ~2,000 compounds because common techniques such as ebulliometry or the isotenoscope cannot be applied to solids. Most sublimation-pressure datasets are not assigned to a specific crystalline form but only to “the crystal” or “the solid”. Cases where pressures have been verifiably measured for two or more polymorphs of the same compound probably number only in the tens, limited by thermal stability, the thermodynamic and kinetic stability ranges of the polymorphs, and the pressures themselves.

This situation shows that an important opportunity remains largely unexploited: vapor-pressure measurements can provide both enthalpic and entropic differences between polymorphs. The method avoids solvent effects inherent to solubility measurements and benefits from, rather than suffers from, the kinetic stability of the forms involved. Sublimation pressures can be easily converted to Gibbs-energy differences; their intersection defines the crystal–crystal–vapor triple temperature, and their slope difference gives the transition enthalpy. The main limitation is the need to unambiguously identify the crystalline form, which is not always straightforward.

In our work, measuring sublimation pressures of multiple polymorphs began as a by-product of broader experimental campaigns but has become a deliberate strategy. Compounds are now selected and samples prepared specifically to enable comparison of polymorphs. In parallel, data treatment evolved from simple evaluations of triple temperatures and transition enthalpies to advanced regression procedures that combine calorimetric quantities with vapor-pressure data. This capability was incorporated into the Simultaneous Correlation method (SimCor), a powerful tool for developing a consistent thermodynamic description of experimentally independent datasets.

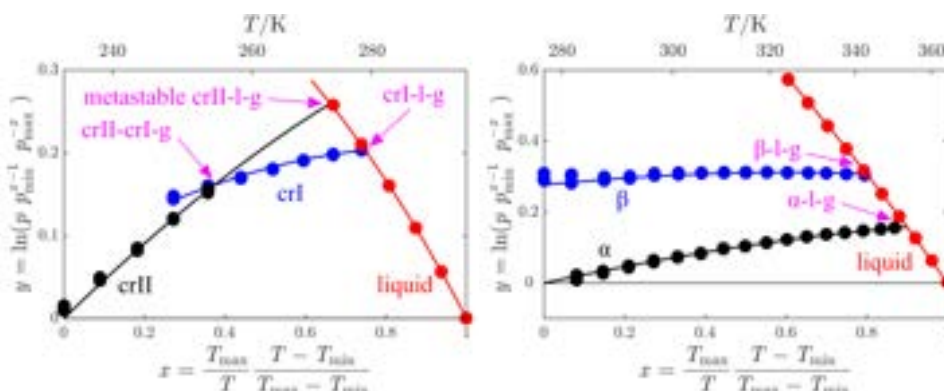


Figure 1. Arc views [1] of vapor pressure data for (±)-3,3-dimethyl-2-butanol [2] (left, enantiotropic system) and acetamide [3] (right, monotropic system) with marked triple points.

Acknowledgment

Support from the COST Action 22107 BEST-CSP: Bringing Experiment and Simulation Together in Crystal Structure Prediction is acknowledged.

Significant references

1. M. Čenský, V. Roháč, K. Růžička, M. Fulem, and K. Aim, *Fluid Phase Equilib.*, vol. 298 (2010), pp. 192-198.
2. V. Štejfal, P. Šimáček, B. Koutek, M. Fulem, and K. Růžička, *Molecules*, vol. 30 (2025), p. 4287.
3. V. Štejfal, S. Chun, V. Pokorný, M. Fulem, and K. Růžička, *J. Mol. Liq.*, vol. 319 (2020), p. 114019.

High-pressure pH measurements for assessing chalk reactivity under CO₂ storage conditions

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Most North Sea reservoirs consist of chalk, a fine-grained form of calcite (CaCO₃) characterized by high porosity and low permeability. These properties make chalk formations attractive candidates for both CO₂-enhanced oil recovery and large-scale CO₂ storage. However, the current understanding of chalk-CO₂ interactions and their implications for reservoir integrity remains limited. High CO₂ partial pressures increase CO₂ solubility and lower the pH of the formation fluid, thereby enhancing calcite dissolution and precipitation processes that can alter permeability and porosity. Quantifying these geochemical reactions is therefore essential to evaluate the suitability of chalk formations for long-term CO₂ storage. Accurate experimental data on chalk dissolution and precipitation kinetics under in-situ reservoir conditions are particularly needed. One approach is to monitor changes in proton activity resulting from mineral-fluid reactions through pH measurements in CO₂-containing brines. However, measuring pH at high pressure, elevated temperature, and high salinity is challenging, especially in systems containing chalk powder, due to both the technical difficulty of handling solids in a closed cell and the rapid reactivity of chalk. In this work, we employed a high-pressure, high-temperature glass pH electrode and a separate Ag/AgCl reference electrode to directly measure the pH of CO₂-saturated brines containing dissolved calcite or chalk. Experiments were conducted at temperatures between 293 and 313 K and pressures from 0.1 to 4 MPa. The results demonstrate rapid dissolution of chalk under CO₂-rich conditions, as well as a clear inhibitory effect on calcite dissolution when chalk grains are coated with oil.

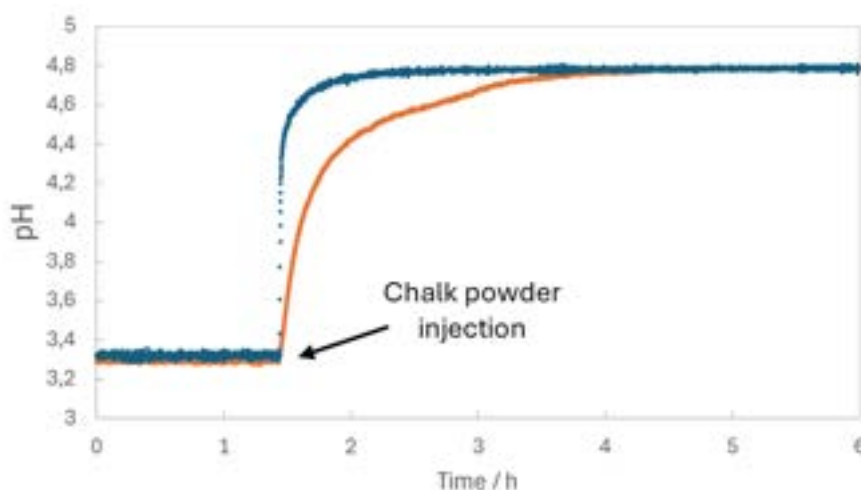


Figure 1. Evolution of pH as a function of time in CO₂-saturated 10 mM NaCl with chalk powder addition at 29 bar and ambient temperature; ●: Stevns Klint, ●: Kraka S13 oil-saturated interval.

Significant references

1. M. Bonto, M.J. Welsh, M. Lüthje, S.I. Andersen, M.J. Veshareh, F. Amour, A. Afrough, R. Mokhtari, M.R. Hajiabadi, M.R. Alizadeh, C.N. Larsen, and H.M. Nick, *Renewable Earth-Science Reviews*, vol. 222 (2021), 103826.
2. M.L. Hjuler, and I.L. Fabricius, *Journal of Petroleum Science and Engineering*, vol. 68 (2009), pp. 151-170.

Degradation of an amine-based epoxy resin

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Due to their excellent mechanical and thermal properties, epoxy resins are used in a variety of applications in the adhesive, coating, automotive and aerospace industries. Particularly for applications involving exposure to high temperatures, resistance to degradation is a key factor in determining the performance, long-term reliability and safety of structural parts made of epoxy resins. Investigating degradation behavior involves characterizing thermal and oxidative stability and understanding of degradation mechanisms.

In this poster, we present a comparison of the modelled kinetics of the degradation reaction for a cured amine-based epoxy resin in inert and oxidative conditions. To this end, thermogravimetric measurements were carried out under dynamic flow of nitrogen and dynamic flow of air at different heating rates. These measurements were then used to create model-based kinetics analysis by means of the Kinetics Neo software (NETZSCH-Gerätebau, GmbH). The study in inert conditions leads to a model with two consecutive stages, compared to five stages for degradation in an oxidative atmosphere. For each step, the activation energy, order of reaction and pre-exponential factor were determined. Figure 1 (left) depicts the curves measured in a nitrogen atmosphere compared to the curves calculated with a two-step model. Figure 1 (right) displays the corresponding curves for an oxidative atmosphere. Additionally, the gases released during the degradation process were analyzed by means of a coupled thermogravimetry gas analysis. This allows for assessing the potential toxicity and environmental impact of the products built during degradation.

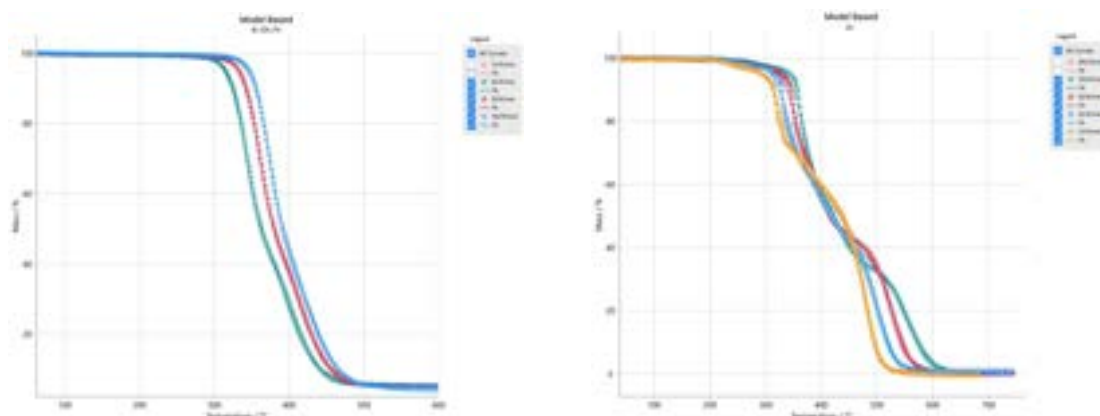


Figure 1. Study in an inert (left) and an oxidative (right) atmosphere. Comparison of the curves measured by thermogravimetric analysis at different heating rates (symbols) and calculated with a model-based kinetics analysis (continuous lines).

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Measurement of the melting-freezing transition temperature of palladium

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The palladium (Pd) freezing point, fixed at 1554.8 °C in the ITS-90, is a key high-temperature reference for calibrating Pt/Rh thermocouples¹⁾. Traditional methods rely on compact alumina-crucible cells or wire-melting techniques. However, repeated calibrations at KRISS using metal and metal-carbon fixed-point cells revealed systematic positive offsets from predicted second- and third-order deviation functions, hinting that the accepted Pd freezing temperature may be too low—possibly by more than the stated 1554.8 °C.

We therefore redetermined the Pd phase-transition temperatures using a primary radiation thermometer traceable to ITS-90. A horizontal blackbody cell was fabricated from an alumina crucible filled with 99.95 % Pd. Emissivity correction was achieved with an identical crucible containing 99.9999 % Cu. The cell was operated under a protective atmosphere of high-purity argon + 0.5 vol% hydrogen inside a horizontal Kanthal-Super furnace.

Three independent runs yielded Pd melting and freezing temperatures of 1557.2 °C and 1556.7 °C, respectively (expanded uncertainty 0.4 °C), as shown in Fig.1. These values, substantially above the ITS-90 assignment, will be analyzed in detail and compared with historical data.

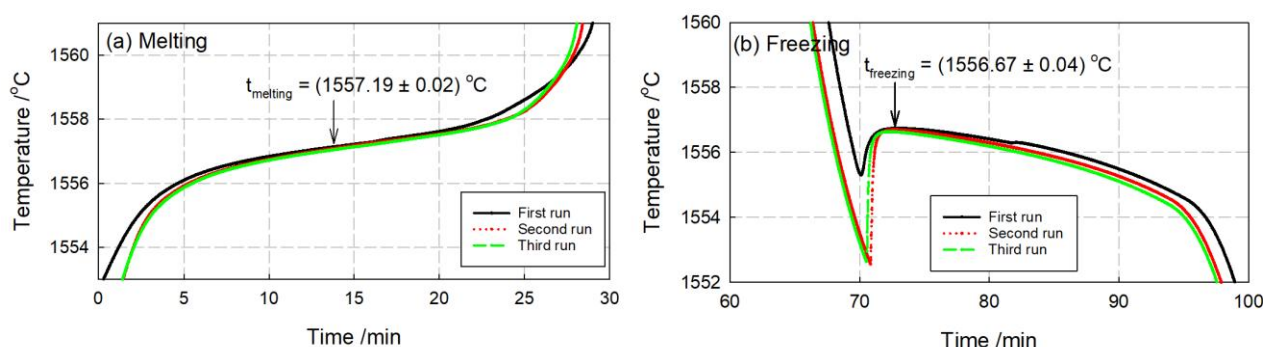


Figure 1. Three melting and freezing curves with its corresponding transition temperature.

Significant references

1. R.E. Bedford, G. Bonnier, H. Maas and F. Pavese, *Metrologia* vol. 33 (1996) 133

Properties of pure and impure carbon dioxide for application in CCS

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As the global community moves to decarbonise, carbon capture and storage (CCS) is set to play a significant role in the decarbonisation of several industries including cement, iron and steel production, pulp and paper, and petroleum refining [1]. The gigaCCS Centre is a Norwegian-led multi-party industry and academic collaboration that aims to build technical knowledge to effectively upscale CCS to the gigaton scale. Achieving efficient and safe deployment at this scale requires a precise knowledge of thermophysical properties across a wide range of conditions in the CCS value chain. Speed of sound is a key thermodynamic property of great use in the development and validation of equations of state. Other thermodynamic properties can also be derived from the speed of sound through thermodynamic integration. By delivering high-accuracy speed of sound and density data for pure CO₂, this research enables the development of more accurate ultrasonic flow metering technologies. Accurate fiscal meters in custody transfers support transparent CO₂ accounting and build confidence in large-scale CCS deployment. These measurements also provide critical input for refining equations of state, which underpin process design and operational safety in CCS systems.

Two new measurement apparatus are designed and constructed to undertake high-accuracy measurements of the speed of sound in both pure and impure CO₂. The dual-path pulse echo device, typically used for liquid measurements, features a piezoelectric disc transducer positioned asymmetrically relative to plane parallel reflectors, where it functions both as an ultrasonic source and detector. In this method, the sensor is operated in a transient mode at a relatively high frequency, and the speed of sound is obtained from the difference between the two path lengths and the time differences between returning echoes. On the other hand, cylindrical acoustic resonators operate in steady-state mode at low frequencies with a standing wave in the cavity, the resonance frequency of which gives the speed of sound divided by a characteristic length. In the present work, we use the second longitudinal mode of the cylindrical cavity for which the characteristic length is the full length of the cylinder.

CO₂ has high sound absorption due to molecular relaxation effects, making measurements of speed of sound particularly challenging [2]. This necessitates an innovative design and data analysis procedure for both the pulse echo device and the acoustic resonator. Density measurements in the compressed supercritical and liquid phase complement speed of sound measurements, where data is currently lacking for both properties.

Acknowledgment

These results have been produced with support from gigaCCS – Norwegian Research Centre of Excellence for Carbon Capture and Storage, performed under the Norwegian research programme “Centre for Environmentally-friendly Energy Research” (FME), administrated by the Research Council of Norway ([350370](https://www.researchcouncil.no)).

Significant references

- [1] M. Bui *et al.*, “Carbon capture and storage (CCS): the way forward,” *Energy Environ. Sci.*, vol. 11, no. 5, pp. 1062–1176, 2018, doi: 10.1039/C7EE02342A.
- [2] C.-W. Lin and J. P. M. Trusler, “Speed of Sound in (Carbon Dioxide + Propane) and Derived Sound Speed of Pure Carbon Dioxide at Temperatures between (248 and 373) K and at Pressures up to 200 MPa,” *J. Chem. Eng. Data*, vol. 59, no. 12, pp. 4099–4109, Dec. 2014, doi: 10.1021/je5007407.

Viscosity of Selected Reference Liquids and New Data for Hydrofluoroethers Measured with Rotational Viscometers

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Accurate viscosity measurements are essential in chemistry, materials research, and industrial quality control. We present calibration measurements and a comparison of two commercial instruments by Anton Paar (Austria): the rotational viscometer ViscoQC 100, which determines the liquid viscosity from spindle torque in the temperature range 15–80 °C, and the Stabinger SVM 3001, which derives the dynamic viscosity from the equilibrium speed of a free-floating rotor and operates from –60 to 135 °C. While the ViscoQC 100 offers simple handling and easy maintenance, its open measuring system and lower accuracy represent certain limiting factors. The SVM 3001, by contrast, provides a closed cell, higher precision, and simultaneous density measurement using the serially installed vibrating tube densimeter. In our laboratory, both instruments were tested to verify measurement repeatability and to estimate the uncertainty of the obtained data. The tests included certified viscosity standards as well as measurements of well-characterized liquids such as squalane (–20 to 95 °C) and ethylene glycol (–10 to 130 °C). The results agreed with the established temperature correlations reported by Mylona et al. [1] for squalane and those given in the VDI Wärmeatlas [2] for ethylene glycol. In addition to these reference liquids, we also measured a series of alternative engineering hydrofluoroether-based liquids marketed as Novec (3M): HFE-7000, HFE-7100, HFE-7200, HFE-7300 and HFE-7500. As only limited viscosity data are currently available for these substances, our measurements provide new experimental values that help expand the existing dataset. The hydrofluoroethers were measured in the temperature range from –20 to 95 °C, or to lower temperatures where required by their respective boiling points.

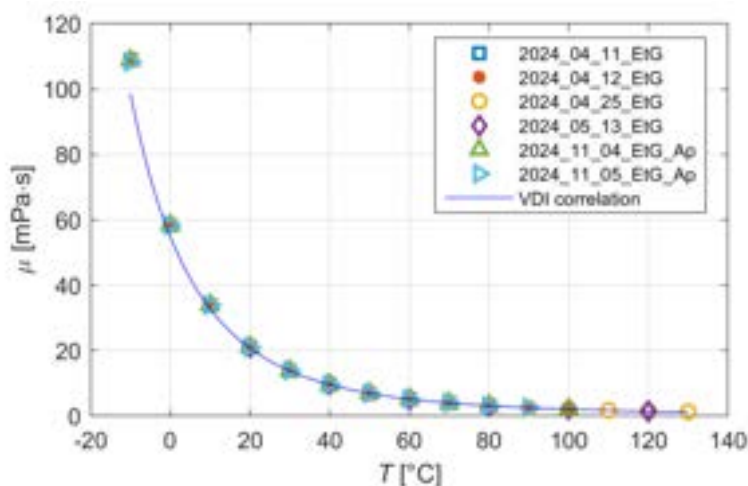


Figure 1. Dynamic viscosity of ethylene glycol; data from Stabinger SVM 3001 compared to VDI correlation [1].

Acknowledgment

This study was supported from the Czech Science Foundation grant no. GF24-10191K and the institutional support RVO:61388998.

Significant references

1. S. K. Mylona et al., Reference Correlations for the Density and Viscosity of Squalane from 273 to 473 K at Pressures to 200 MPa, J. Phys. Chem. Ref. Data 43, 013104 (2014)
2. M. Kleiber, R. Joh, VDI-Wärmeatlas, 11., bearbeitete und erweiterte Auflage (Springer-Verlag Berlin Heidelberg, 2013), chap. Stoffwerte von sonstigen reinen Fluiden, pp. 357–488

Water-glycerol – density measurements entering supercooled region

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Glycerol is well known cryoprotectant, disrupting hydrogen-bonding network present in pure water and thus lowering the temperature of ice formation. Pure glycerol, even though its melting temperature is around 18 °C, is naturally found in the liquid state at much lower temperatures thanks to its high supercooling tendencies.

In this work, we present results of accurate density measurements from ambient pressure up to 70 MPa and entering the supercooled region for two water-glycerol mixtures with very different glycerol mass fractions, namely 0.01 and 0.36. A dual-capillary dilatometer, which has been successfully employed within studies of supercooled ordinary water, heavy water and seawater^{1,2}, was used for the measurements. A sensitive vibrating tube densimeter (VTD) was used for complementary measurements at ambient pressure up to 85 °C. Since preparation of dual-capillary experiments involves degassing of samples, which leads to slight change of glycerol concentration in a mixture, the VTD was also used as an analytical tool to determine glycerol content in the mixture after degassing. We compare our results with older measurements of Huck et al.³ Simultaneously, we discuss the effect of glycerol addition using our data for supercooled ordinary water and equation of state for supercooled water of Holten et al.⁴.

Significant references

1. A. Blahut, J. Hykl, P. Peukert, V. Vinš, and J. Hrubý, *Relative density and isobaric expansivity of cold and supercooled heavy water from 254 to 298 K and up to 100 MPa*, J. Chem. Phys. 151, 034505 (2019)
2. A. Blahut, J. Hykl, P. Peukert, and J. Hrubý, *Dual-capillary dilatometer for density measurements of supercooled water*, EPJ Web Conf. 264, 01004 (2022)
3. J. Huck, J. Dufour and A. Bondeau, *Density of supercooled glycerol-water solutions*, Ninth International Conference on Conduction and Breakdown in Dielectric Liquids, Salford, UK, 1987
4. V. Holten, J. V. Sengers, M. A. Anisimov, *Equation of State for Supercooled Water at Pressures up to 400 MPa*, J. Phys. Chem. Ref. Data 43, 043101 (2014)

Generative and Predictive Approach for the Design of Energy Fluids Using Deep Learning

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The design of high-performance energy fluids for thermodynamic cycles requires accurate prediction of their thermodynamic properties. Traditional computational methods remain time-consuming and resource intensive. This work, developed within the SPARTA project and connected to the ongoing REACHER research project [1], presents a methodology combining a variational autoencoder (VAE) and artificial neural networks (ANNs) for predicting formation enthalpy and entropy, enabling both the property prediction of existing molecules and the generation of new candidate reactive fluids.

Thermodynamic data are sourced from the DIPPR database [2] and scientific literature [3]. After preprocessing, 18830 molecules were retained, represented by their canonical SMILES notations. A VAE based on recurrent neural networks [4] learns compact latent representations of molecules. The bidirectional encoder transforms SMILES into latent vectors, while the decoder enables reconstruction and generation of new molecules, ensuring structurally similar molecules are close in the latent space. Molecular descriptors capturing physicochemical characteristics are calculated using RDKit, preprocessed to eliminate low-variance and highly correlated descriptors, then normalized and concatenated with VAE latent vectors. A multilayer neural network is trained independently to predict formation enthalpy and entropy.

For enthalpy prediction, the optimal model achieves $R^2 = 0.99$ on the test set with an RMSE of 34.7 kJ·mol⁻¹ and an MAE of 18.1 kJ·mol⁻¹ at 298 K. For entropy, performance reaches $R^2 = 0.98$, with an RMSE of 21.9 J·mol⁻¹·K⁻¹ and an MAE of 12.3 J·mol⁻¹·K⁻¹. Results demonstrate good correlation between predicted and actual values. The synergy between representations learned by the VAE and explicit physicochemical descriptors enables accurate predictions. The approach also enables generation of new candidate molecules via the VAE decoder with immediate prediction of their properties, accelerating the design of new fluids.

This study presents an effective approach for predicting thermochemical properties of reactive fluids, combining deep learning and molecular descriptors. Results demonstrate the model's ability to accurately predict formation enthalpy and entropy. The methodology particularly targets reactive fluids that undergo reversible chemical transformations ($A_2 \rightleftharpoons 2A$) driven by temperature and pressure variations in thermodynamic cycles, alongside traditional inert fluids. It enables both accurate property prediction and generation of new molecules.

Acknowledgment

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Significant references

1. REACHER project, <https://www.univ-lorraine.fr/erc-reacher/>
2. Rowley R.L., Wilding W.V., Oscarson J.L., Yang Y., Zundel N.A., Daubert T.E. and Danner R.P., DIPPR® Data Compilation of Pure Chemical Properties, Design Institute for Physical Properties, AIChE, New York, NY, 2010.
3. Dobbelaere M.R., Lengyel I., Stevens C.V. and Van Geem K.M., "Geometric deep learning for molecular property predictions with chemical accuracy across chemical space", Journal of Chemical Information and Modeling, 2021.
4. Cho K., van Merriënboer B., Gulcehre C., Bahdanau D., Bougares F., Schwenk H. and Bengio Y., "Learning Phrase Representations using RNN Encoder-Decoder for Statistical Machine Translation", Proceedings of the 2014 Conference on Empirical Methods in Natural Language Processing (EMNLP), 2014, pp. 1724-1734.

Experimental long term thermal stability of ionic liquids with minimum TGA experiments

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Ionic liquids (ILs) are known for presenting negligible vapor pressure, high thermal stability, and having tunable molecular structures, making them attractive candidates for high-temperature processes. However, most reported stability data rely on short-term thermogravimetric measurements, such as onset decomposition temperatures (T_{onset}), which can significantly overestimate true operational stability [1]. Long-term studies have shown deviations of 100–300 °C between short and long-term degradation behavior, highlighting the need for reliable long-term stability metrics for designing IL-based high-temperature applications [2].

A common approach to assess the long-term stability of an ionic liquid is to determine the temperature at which it loses 1% of its mass over 10 hours ($T_{0.01/10h}$). This requires multiple isothermal TGA experiments (typically 5–6), making the procedure time-consuming and costly. Consequently, only a limited number of experimentally determined $T_{0.01/10h}$ values are available in the literature [2].

To address this limitation, this work evaluates an alternative experimental strategy to estimate $T_{0.01/10h}$ using only 3–4 TGA measurements. The method consists of fitting kinetic model parameters from two non-isothermal TGA ramps, predicting $T_{0.01/10h}$ from the resulting kinetics, and validating it through a single isothermal TGA at the estimated temperature. If deviations are observed, the isothermal curve is incorporated to refine the kinetic model and update the prediction. The ionic liquid 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM][NTF₂]) was used for validation and to compare the performance of this reduced-experiment methodology against the conventional multi-isothermal approach.

This simplified protocol offers a promising approach to estimate $T_{0.01/10h}$, potentially reducing the number of experiments required. It may provide a faster and less resource-intensive way to obtain long-term thermal stability data, supporting more efficient screening of ILs for high-temperature applications.

Acknowledgment

This work was developed within the scope of the project CICECO Aveiro Institute of Materials, UID/50011/2025 (DOI 10.54499/UID/50011/2025) & LA/P/0006/2020 (DOI 10.54499/LA/P/0006/2020), financed by national funds through the FCT/MCTES (PIDDAC). This study also received financial support from Illimited project, financed by Horizon Europe agreement n° 101192964.

References

1. C. Maton, N. De Vos, and C. V. Stevens, "Ionic liquid thermal stabilities: Decomposition mechanisms and analysis tools," *Chem Soc Rev*, vol. 42, no. 13, pp. 5963–5977, Jun. 2013, doi: 10.1039/c3cs60071h.
2. Y. Cao and T. Mu, "Comprehensive investigation on the thermal stability of 66 ionic liquids by thermogravimetric analysis," *Ind Eng Chem Res*, vol. 53, no. 20, pp. 8651–8664, May 2014, doi: 10.1021/ie5009597.

Application of PC-SAFT EoS to DES systems with a Group Contribution Method

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The thermophysical properties of deep eutectic solvents (DESs) are essential for their industrial applications, yet an optimal modeling approach remains unclear due to their complex intermolecular interactions. In this work, the thermodynamic behavior of DESs is systematically investigated using the PC-SAFT equation of state (EoS). DESs are modeled either as pseudo-pure fluids or as mixtures of hydrogen-bond donors (HBDs) and hydrogen-bond acceptors (HBAs). The EoS parameters are developed using a predictive approach that incorporates first-order and second-order group contributions. Rather than focusing on a single property, we aim to improve the overall performance of the EoS. Accordingly, density, heat capacity, vapor pressure, gas solubility, and liquid-liquid equilibrium (LLE) are calculated to evaluate model accuracy. Special attention is paid to assessing the influence of different modeling strategies. To this end, three association schemes with 2, 4, and 10 binding sites, as well as a polar non-associating model, are examined. Finally, the contributions of association and dipolar interactions to the thermophysical properties of DESs are analyzed to assess the reliability of each modeling approach from a microscopic perspective.

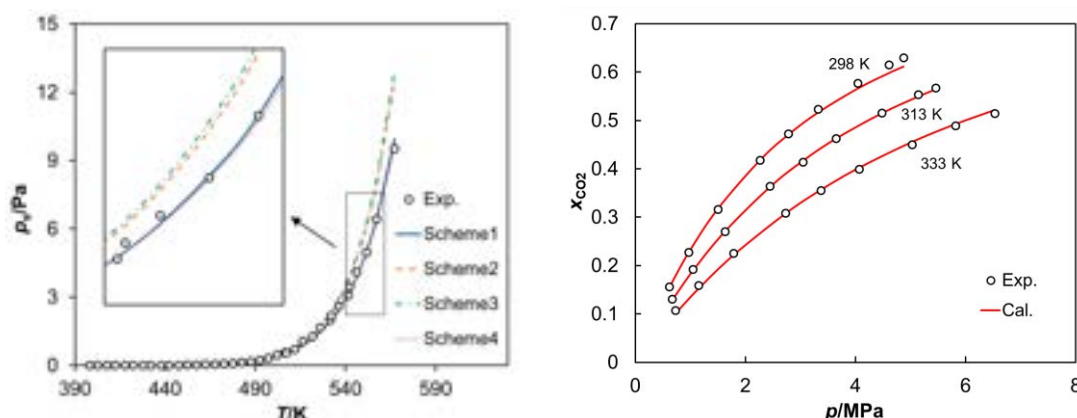


Figure 1. Comparison of calculated results with experimental data

Acknowledgment

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Significant references

1. C. Zhu, M. He, X. Liu, et al. J. Chem. Eng. Data 2020, 65 (12), 5654-5676.
2. C. Zhu, M. He, X. Liu, et al. ACS Sustainable Chem. Eng. 2021, 9 (22), 7602-7619.

Calibration and performance assessment of equations of state for supercritical CO₂ mixtures applied to the NET Power cycle

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The development of a reliable thermodynamic model for the supercritical CO₂-based oxy-combustion NET Power cycle demands highly accurate predictions of the phase equilibrium and volumetric behavior of the working fluids using thermal equations of state (EoS) [1]. In this work, the interaction parameters of six EoSs were calibrated using experimental density and phase equilibrium data for supercritical mixtures containing CO₂ with H₂O, CO, H₂, O₂, N₂, Ar, and CH₄ collected from the literature under cycle-relevant conditions: 1 – 49 MPa, 293.15 – 423.15 K and 72.6 – 99.8 % mol CO₂ [1]. The Peng-Robinson (PR), Soave-Redlich-Kwong (SRK), Lee-Kesler-Plöcker (LKP), Benedict-Webb-Rubin-Starling (BWRS), perturbed chain-SAFT (PC-SAFT), Cubic-Plus-Association (CPA) EoSs were considered. Their performance was also compared with the multiparametric GERG-2008 EoS based on the average absolute relative deviation (AARD), and their influence on an isentropic compression process from 7.4 MPa and 303.15 K to 30 MPa was assessed. The calibrated LKP EoS exhibits the lowest AARD (2.03%) in predicting the dew and bubble points of supercritical CO₂-H₂O mixtures. Regarding volumetric modeling, GERG-2008 demonstrates the highest accuracy (AARD of 1.34%), whereas SRK reaches a maximum AARD of 5.30%. It was found that the cubic EoSs tend to underestimate the fluid density in the pseudo-critical phase-transition region, particularly within the dense supercritical regime. Analysis of the compression process of the cycle's recirculating fluid mixture reveals that only CPA and GERG-2008 EoSs properly capture the thermodynamic property transition from the supercritical liquid-like to gas-like state, with the former predicting a specific work of 33.02 kJ·kg⁻¹. In contrast, the PR, SRK, LKP, and PC-SAFT EoSs yield values between 1.53 and 1.70 times higher. These findings suggest that an inappropriate choice of EoS can lead to deviations in cycle efficiency of up to 1.7% and to the oversizing of compression and heat transfer units, resulting in additional costs and operational challenges [2,3].

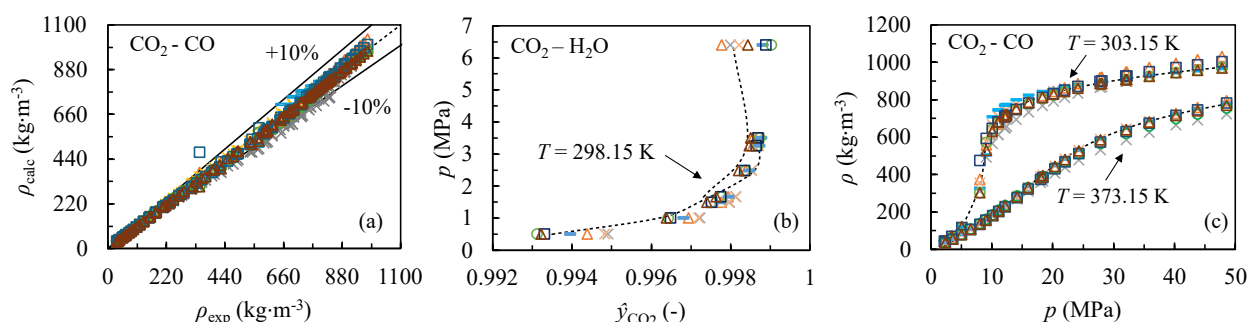


Figure 1. (a) calibration parity plot for CO₂-CO, (b) p-xy diagram for CO₂-H₂O, and (c) density evolution for CO₂-CO. (-----) Exp. data, (Δ) PR, (×) SRK, (✕) LKP, (—) BWRS, (○) PC-SAFT, (□) CPA, (◻) GERG-2008

Acknowledgment

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Significant references

1. I. Velázquez, F. Demeyer and M. Reyes, J. Supercrit. Fluids, vol 225 (2025), 106693.
2. I. Velázquez, F. Demeyer and M. Reyes, Appl. Therm. Eng., vol. 273 (2025), 126491.
3. I. Velázquez, D. Cantero, F. Demeyer and M. Reyes, Appl. Therm. Eng., vol. 285 (2026), 129206.

Modeling Reactive Mixtures as Working Fluids for Power Cycles

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To deal with the environmental challenges of the 21st century our energy production systems are required to be more efficient and sustainable. The implementation of power cycles operating with reactive working fluids is being studied and proposed as a possible way to achieve the needed performances [1]. These working fluids consist of chemically reactive mixtures whose composition is affected by changes in temperature and pressure, as a result of a reversible dimerization reaction that achieves chemical equilibrium quasi-instantaneously. In general terms, these reactions can be represented in the form $A_2 \rightleftharpoons 2A$, where A is a monomer and A_2 is the corresponding dimer. Thus, the occurrence of these reactions in a thermodynamic cycle has a relevant impact on the thermophysical properties of the fluid itself.

Recently, in the context of the project REACHER, Lasala et al. [2] have developed a multi-scale methodology using a cubic equation-of-state to accurately describe the thermodynamic properties of reactive fluids. Our team has applied this methodology to predict the performance of power plants operating with a series of reactive working fluids designed internally, and it has been found that the utilization of these fluids can substantially affect the performance of the power cycle. The present work studies how the particular behavior of the thermophysical properties of the fluid, such as the effective heat capacity (figure 1), affects the performance of the cycle in each of its transformations. As such, preliminary calculations using the N_2O_4 reactive system show an improvement in efficiency and net specific work of up to 5% and 25% respectively, compared to common fluids like water.

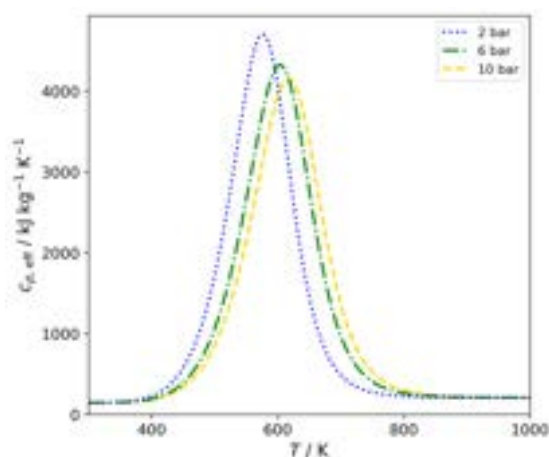


Figure 1. The effective heat capacity at constant pressure of a selected reactive mixture.

Acknowledgement

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Significant references

1. Lasala, S.; Privat, R.; Herbinet, O.; Arpentiner, P.; Bonalumi, D.; Jaubert, J.-N. Thermo-Chemical Engines: Unexploited High-Potential Energy Converters. *Energy Conversion and Management* 2021, 229, 113685.
2. Lasala, S.; Samukov, K.; Mert Polat, H.; Lachet, V.; Herbinet, O.; Privat, R.; Jaubert, J.-N.; Moulτος, O. A.; De Ras, K.; J. H. Vlught, T. Application of Thermodynamics at Different Scales to Describe the Behaviour of Fast Reacting Binary Mixtures in Vapour-Liquid Equilibrium. *Chemical Engineering Journal* 2024, 483, 148961.



Predictive approach to the thermodynamic properties of working fluids using machine learning models

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In this paper, we developed a ML-QSPR method to predict three important thermodynamic and environmental properties: the enthalpy of formation and entropy of formation in their ideal gas states for a set of working fluids and the global warming potential. Datasets used for enthalpy and entropy of formation were obtained by merging two databases, DIPPR [2] and [3], resulting in a total of 7230 molecules for enthalpy and 11872 molecules for entropy. For GWP, data were extracted from the Scientific Assessment of Ozone depletion 2022 report [4], yielding a dataset of 735 molecules. All molecules were characterized using Mordred, an open-source tool that generates 1826 molecular descriptors per compound [5]. In addition, infrared (IR) spectra were incorporated to improve the prediction of GWP. A preprocessing step was performed to retain only the most relevant descriptors. Traditional methods based on classical calculations often reach their limits when estimating such complex physicochemical properties with high accuracy. To address these challenges, we investigated several machine learning algorithms such as SVR, LGBM, GBR and MLP. We used an ensemble learning approach to predict enthalpy and entropy properties. The best base learner for the ensemble learning was the multilayer perceptron (MLP) achieving the best performance for both. This approach achieved coefficients of determination (R^2) of 0.98 for enthalpy and 0.94 for entropy on the test sets. The physical relevance of the models was also investigated, an aspect that is rarely addressed in the literature. Our models successfully captured the physical meaning of alkanes whose behaviour is already known, demonstrating consistency with established thermodynamic trends. For GWP prediction, the inclusion of IR spectra led to a R^2 value of 0.98. This approach was primarily developed to predict the properties of reactive fluids satisfying the criteria for reversible chemical transformation ($A_2 \rightleftharpoons 2A$) under temperature and pressure variations in the thermodynamic cycles investigated within the ERC-REACHER project. Finally, a comparison with existing approaches from the literature showed that our models achieve competitive performance while providing physically meaningful predictions

Acknowledgment

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Significant references

1. ERC-REACHER Project, <https://www.univ-lorraine.fr/erc-reacher/>
2. THOMSON, G. H. The DIPPR® databases. International journal of thermophysics, 1996, vol. 17, no 1, p. 223-232.
3. DOBBELAERE, Maarten R., LENGYEL, István, STEVENS, Christian V., et al. Geometric deep learning for molecular property predictions with chemical accuracy across chemical space. Journal of Cheminformatics, 2024, vol. 16, no 1, p. 99.
4. Scientific Assessment of Ozone Depletion, <https://www.csl.noaa.gov/assessments/ozone/2022/>
5. MORIWAKI, Hiroto, TIAN, Yu-Shi, KAWASHITA, Norihito, et al. Mordred: a molecular descriptor calculator. Journal of cheminformatics, 2018, vol. 10, no 1, p. 4.

Influence of γ -Valerolactone on the Flash Point of Fatty Acid Ethyl Ester Mixtures

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Since the Industrial Revolution, global energy demand has increased substantially, underscoring the need to diversify the energy matrix away from fossil fuels. In this context, biodiesel stands out as a promising renewable alternative produced from the transesterification of triglycerides obtained mainly from animal fats and vegetable oils. Beyond its renewable nature, biodiesel emits less net CO₂ and fewer greenhouse gases than petroleum diesel. However, additives are often required to enhance properties such as viscosity and cold-flow behavior.¹

Process safety is a key concern, particularly regarding fire and explosion risks (FER). The main indicator for FER assessment is the flash point (FP);² however, reliable FP data for biodiesel blends, particularly with additives, remain scarce. Accordingly, this work investigated the influence of γ -valerolactone (GVL) on the FP of mixtures containing fatty acid ethyl esters (FAEEs). First, the FP behavior of five binary mixtures containing GVL and a FAEE (ethyl laurate, ethyl myristate, ethyl palmitate, ethyl stearate, and ethyl linoleate) and three ternary mixtures containing GVL and two FAEEs (laurate + myristate, myristate + stearate, palmitate + stearate) was measured using the closed-cup ASTM D6450 protocol.² Notably, the FAEE pairs composing the ternary mixtures were specifically selected based on the compositional profiles of natural biodiesel matrices.³ Subsequently, the Liaw approach⁵ combined with the ideal, NRTL, and UNIFAC models was applied to describe the FP behavior using the FLAMMA algorithm.⁴

Results revealed that the FP of the binary and ternary mixtures decreased with increasing GVL content, with a pronounced drop in the 0–20 mol% GVL range. Regarding modeling, the NRTL and UNIFAC satisfactorily predicted the experimental data (AAD < 4% for binary, < 2% for ternary), whereas the ideal model showed substantially higher deviations (up to 17.18%). Overall, these findings indicate that while GVL is a viable additive, it is important to employ robust thermodynamic models, such as the activity-coefficient-based NRTL and UNIFAC, to accurately represent the FP behavior of GVL + FAEE mixtures.

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Significant references

1. R.M. Dias, R.T. Aquino, M. A. Krähenbühl, M.C. Costa. *Flash Point of Fatty Acid Methyl Ester Binary Mixtures*. J. Chem. Eng. Data, vol. 64 (2019), pp. 3465–3472.
2. ASTM INTERNATIONAL. *Test Method for Flash Point by Continuously Closed Cup (CCCFP) Tester* (2021).
3. A.M.B. Neto, D.C. Nascimento. M.C. Costa. *FLAMMA: Flash Point Multicomponent - Methods and Algorithm*. INPI - Instituto Nacional da Propriedade (2019).
4. D. Singh, D. Sharma, S.L. Soni, S. Sharma, D. Kumari. *Chemical Compositions, Properties, and Standards for Different Generation Biodiesels: A Review*. Fuel 253 (2019), pp. 60-71.
5. H.J. Liaw, Y.Y. Chiu. *A General Model for Predicting the Flash Point of Miscible Mixtures*. J. Hazard. Mater. vol.137 (2006), pp.38-49.

Theoretical investigation of thermo-mechanical properties of epoxidized natural rubber composites

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Effective thermal transport in polymeric materials is essential for the advancement of wearable electronics, soft robotics, and sustainable composite systems. However, most polymers exhibit inherently low thermal conductivities κ . This intrinsic limitation is further intensified in heterogeneous or multiphase systems, where the interfaces between dissimilar components create supplementary resistance to thermal conduction. Known as interfacial thermal resistance (ITR), for composites this phenomenon predominates the overall thermal properties. Finding new composite compositions, however, do also face the problem of reasonable mechanical stability. Theoretical investigations addressing those two problems are discussed here.

Molecular dynamics (MD) [1], [2] simulations provide a reliable atomistic approach for directly measuring heat transport and interfacial phenomena. EMD and NEMD will be applied to investigate soft-soft interfaces between polymers like epoxidized natural rubbers (ENR) and poly (butylene succinate) (PBS). ENR, a modified version of natural rubber, delivers polar epoxy groups capable of engaging in hydrogen bonding and covalent reactions. PBS, a biodegradable aliphatic polyester, offers partial crystallinity and polar ester linkages, facilitating strong dipolar interactions with ENR. The interface between these two phases thus provides a controllable balance of flexibility and polarity, permitting phonon transport to be tuned via interfacial chemistry rather than filler loading. Despite extensive NEMD work on polymer–filler systems comparable studies on purely polymer–polymer interfaces remain limited. This research intends to fill this gap by employing EMD and NEMD simulations to investigate interfacial thermal resistances as well as thermo-mechanical properties for PBS-ENR-PBS layered systems. The focus is set on different epoxidation level and transesterification crosslinking and their effect on interfacial heat transport and mechanical stability. The outcomes here may not only be applicable to soft composites but rather give an opportunity to a broader understanding of complex interactive fiber-rubber composites (I-FRCs) with an enhanced thermo-mechanical behavior.

In detail, layer specific conductivities were calculated and interpreted. The temperature and normalized density profiles will be presented as well as the relevant cumulative energy exchange thermostat regions from NEMD. The effect of the variation of crosslinking will be shown and can be justified by formation of transesterification bridges stiffening the interface and thus facilitates phonon transmission. A maximum of 30 % of crosslink bridges for this effect was found and will also be shown as well as the accompanying thermo-mechanical properties.

Acknowledgment

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Significant references

1. Alamfard, T.; Breitkopf, C. Thermo-Mechanical Properties of Cis-1,4-Polyisoprene: Influence of Temperature and Strain Rate on Mechanical Properties by Molecular Dynamic Simulations. *Polymers* 2025, 17(9), 1179.
2. Vasilev, A.; Lorenz, T.; Breitkopf, C.: Prediction of thermal conductivities of rubbers by MD simulations - new insights. *Polymer Physics and Theory. Special Issue: Molecular Simulation and Modeling of Polymers* 2022, 14, 2046.

Accurate Predictions of the Fugacity of Pure Molecular Solids

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Molecular solids are found in a diverse range of natural and engineered environments. In industrial settings such as cryogenic liquefaction processes and refrigeration their formation threatens safe and reliable operation. In the pharmaceutical industry, by contrast, they are valuable products whose crystallisation must be controlled and optimised. Beyond terrestrial processes, many “ices” including solid H₂O, N₂, CO₂, and CH₄ as well as more complex molecules such as benzene (and its derivatives) form solid phases elsewhere in the Solar System. Understanding the stability of these ices is essential for the modelling of planetary and atmospheric cycles. Despite this diversity of applications, no rigorous assessment has yet been undertaken of the extent to which the thermodynamic stability of these phases can be predicted quantitatively.

The fugacity, f , is a fundamental and important quantity in phase equilibrium analysis. As a convenient and mathematically robust measure of the chemical potential, fugacity governs phase stability at thermodynamic equilibrium and so its precise determination is essential across a wide range of scientific and engineering problems. In a multicomponent system, chemical equilibrium occurs when the partial fugacity of each component in each phase is equal; the thermodynamically stable state is therefore the one where this requirement is satisfied. For molecular compounds, assessing the conditions under which a solid phase is stable requires reliable methods for calculating fugacities in both the fluid and solid states. The fugacity of fluid phases can be calculated from equations of state or activity coefficient models, and a wide variety of such approaches (with differing levels of complexity and accuracy) have been developed.

In contrast, the fugacity of solid phases has received relatively little attention, and the accuracy with which it can be calculated remains unquantified. A variety of methods exist for this purpose, ranging from equations of state [1] to constructions based on simplified thermodynamic paths [2]. The reliability of these approaches depends not only upon the validity of their thermodynamic assumptions, but also on the experimental data used to constrain their parameters. Here, we present an evaluation of the common methods for the calculation of the fugacity of pure molecular solids, including equations of state and thermodynamic pathways. We assess which types of experimental data are most essential for each method, enabling researchers to map the fugacity of molecular solids in the most data-efficient, accurate manner.

Significant references

1. Trusler, J. P. M., *Equation of state for solid phase I of carbon dioxide valid for temperatures up to 800 K and pressures up to 12 GPa*. Journal of Physical and Chemical Reference Data, 2011. **40**(4): p. 043105.
2. Prausnitz, J.M., R.N. Lichtenthaler, and E.G. De Azevedo, *Molecular thermodynamics of fluid-phase equilibria*. 1998: Pearson Education.

Overview of the ThermoFAST Software Package

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ThermoFAST is a specialized thermodynamic property package engineered for solid-liquid-vapour equilibrium calculations in mixtures relevant to hydrocarbon, CO₂ and hydrogen value chains. It contains implementations of many different thermodynamic and transport property models for fluid, solid and clathrate hydrate phases, including several state-of-the-art descriptions anchored to experimental data. In particular, it features the physically-based Cage-Specific Hydrate electrolyte (CaSH-e) model of Zhu et al.¹ which has a demonstrated accuracy matching or exceeding that of equivalent models, but with 40% fewer parameters. Physically-based Helmholtz energy equations of state are also available for a number of industrially-relevant substances, including carbon dioxide, benzene and argon². Thermodynamic and transport properties are computed from Helmholtz-energy equations of state combined with advanced models (such as the Thorne-Enskog model for diffusivity and ortho-para ratios for equilibrium hydrogen). Solid-fluid equilibrium data from the Cryosolids database³ can be accessed through an interface that enables tuning of fluid binary interaction parameters to experimental measurements.

The recently released version 2 of ThermoFAST is freely available for download as a desktop application for Windows and can also be accessed online as the web application ThermoFAST Web⁴. Plug-ins and packages for a range of other environments, including Excel, Python, Mathematica and CAPE-OPEN, are available or under active development. This poster presents an overview of ThermoFAST's capabilities and planned improvements.

Significant references

1. D. J. Zhu, P. M. May, B. W. E. Norris, Z. M. Aman, and E. F. May, *Energy Fuels*, vol. 38 (2024), 5714-5728.
2. X. Xiao, S. Sriskandaruban, H. E. Maynard-Casely, M. Thol, P. Falloon, R. Span, E. F. May, *Int. J. Thermophys.*, vol. 46 (2025), 14.
3. D. Rowland, C. Baker, and E. F. May, *JESS: Cryogenic Solid Solubility Database* (<http://jess.murdoch.edu.au/cryobase.html>).
4. P. E. Falloon, C. J. Baker, and E. F. May, *ThermoFAST Web 2.2.1: Thermodynamic Calculator for Fluid Mixture Properties*, Fluid Science and Resources Research Group, The University of Western Australia (<https://thermofastweb.net>).

Mechanism of Edge Hot-Spot Formation in GaN HEMTs: Multiphysics and Trap-State Modeling

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This study introduces a self-consistent 3D multi-physics simulation framework for GaN high-electron-mobility transistors (HEMTs) that integrates a 2.5D Technology Computer-Aided Design (TCAD) electrical model with a 3D Finite Element Method (FEM) thermal-mechanical solver. Validated through spatially resolved Raman spectroscopy, transient current, and DC characterization, the model accurately captures the bidirectional coupling between carrier transport, stress-dependent polarization, and thermal-dependent trap dynamics. Systematic analysis reveals that detrimental edge hot spots are driven by a coupled feedback loop: thermal expansion mismatches between the AlGaN barrier and SiNx passivation at device boundaries induce localized compressive stress and a significant charge thinning effect. This non-uniformity triggers conduction band distortion and spatially varying trap ionization, resulting in intense width-direction electric-field crowding and an additional lateral current component that drives excessive Joule heating. These high-temperature regions were experimentally confirmed via FIB-SEM characterization to be primary sites for physical breakdown under high-stress conditions. To mitigate these reliability issues, a dual-layer passivation strategy is proposed, utilizing a tensile-stressed second layer outside the active region. Simulations demonstrate that this approach effectively smooths the piezoelectric charge gradient, successfully reducing the peak temperature and temperature gradient by 35.1%. This work provides a predictive foundation for region-specific stress engineering to optimize the thermal management and long-term operational stability of high-power GaN electronics.

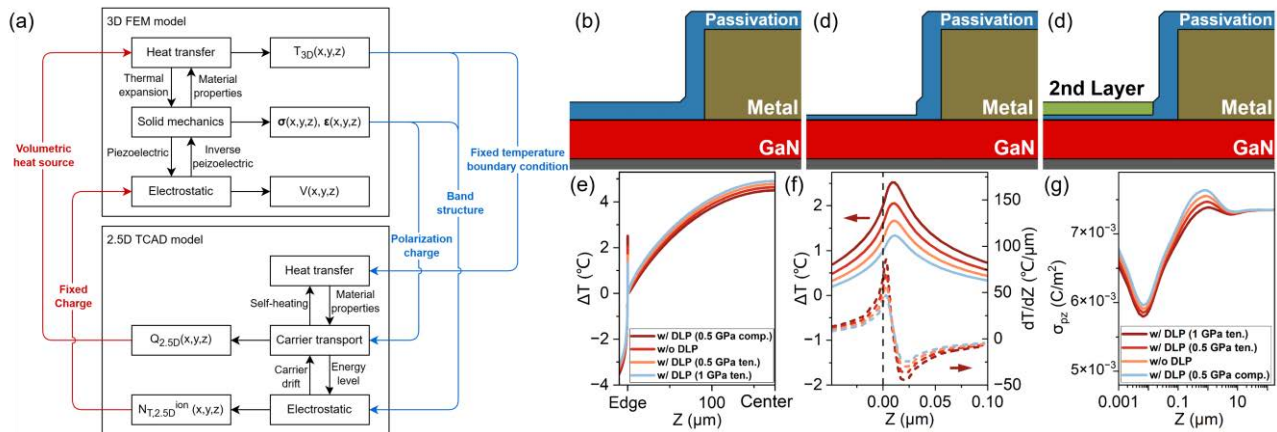


Figure 1. (a) Multiphysics simulation framework. (b–d) Dual-layer passivation structure. (e) Temperature profile. (f) Edge temperature and gradient. (g) Polarization charge density.

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Significant references

1. Li F., Xue J., Fan A., Li Y., Ma W., Xie H., & Zhang X., Appl. Phys. Lett., vol. 125, no. 19 (2024), pp. 193502.

Thermophysical Properties of Normal Hydrogen Probed by Monte Carlo Simulation

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High-precision prediction of the thermophysical properties of normal hydrogen across a wide temperature range is an essential requirement for advancing hydrogen production, storage, transportation, and utilization in the hydrogen energy supply chain. Molecular simulation serves as a valuable complement to experimental measurements, with potential energy function models enabling accurate characterization of the thermodynamic behavior of normal hydrogen systems. In this work, we employed an iterative grid search strategy combined with continuous local refinement to optimize the Lennard-Jones parameters and ϵ , and propose a new single-point force field specifically for pure hydrogen to describe intermolecular interactions. The proposed model exhibits enhanced accuracy in simultaneously predicting essential thermodynamic properties, including saturated vapor-liquid densities, saturation pressures, critical parameters, and supercritical densities, when compared to various widely utilized hydrogen force fields, including 1-LJ, 2-LJ, 1-LJq, 2-LJ3q, and 1-Mie. This work provides a comprehensive computational framework for further investigations into low-temperature, high-pressure hydrogen storage and hydrogen adsorption in porous materials.

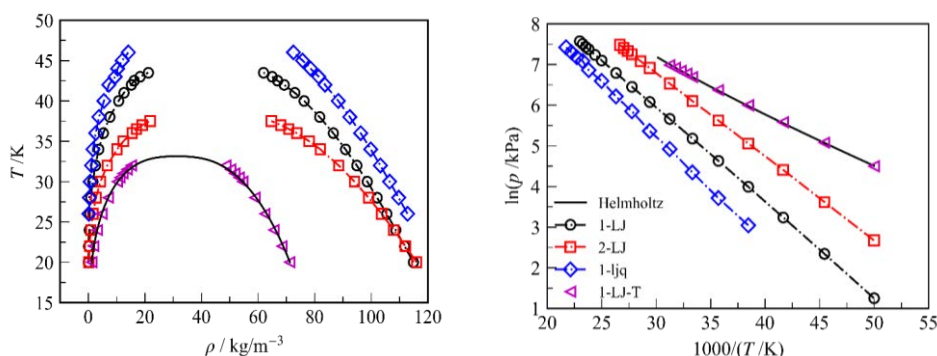


Figure 1. The vapor-liquid coexistence curve and Clausius-Clapeyron plot

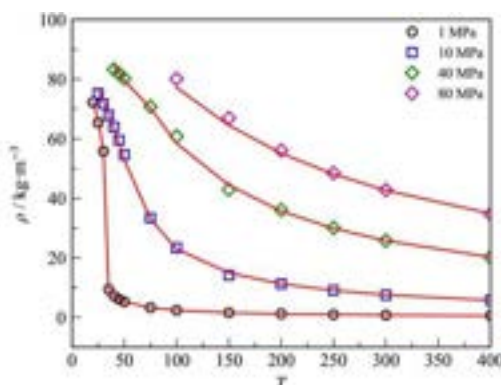


Figure 2. The vapor-liquid coexistence curve and saturated vapor pressure curve

Acknowledgment

The authors acknowledge the financial support of the National Natural Science Foundation of China (No. 52206217 and U22B20112).

Significant references

1. T Yang, JI Siepmann, and JT Wu, Ind. Eng. Chem. Res., 2022, 60, 739-752.

Machine learning-driven discovery of environmentally friendly solvents for polylactic acid recycling

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3D printing is a technique that is advancing constantly, and as a consequence there is an increase in polylactic acid (PLA) waste, a material widely used in this type of printing. Global PLA production is expected to exceed 2.4 million metric tonnes annually by 2027, which makes waste management a significant challenge, as failed prints, support structures, and end-of-life products contribute substantially to the volume of discarded plastics. Even though PLA is a biodegradable polymer, current recycling methods for printed PLA are often limited by thermal degradation, additive contamination, and loss of mechanical properties after repeated melting.

This study aims to integrate alternative solvents and computational modelling for the recycling of PLA waste from 3D printing, identifying solvents capable of selectively dissolving PLA, allowing the separation of additives commonly used in the context of additive manufacturing, such as plasticizers, chain extenders, fillers, and dyes.

Experimental dissolution studies were conducted in combination with theoretical approaches, including Hansen Solubility Parameters and predictions from the Conductor-like Screening Model for Realistic Solvents (COSMO-RS), to understand the interactions between different solvents and PLA. COSMO-RS predictions were based on activity coefficients at infinite dilution to select conventional and emerging solvents, including ionic liquids and those derived from biological sources. Experimental evaluation confirmed that several candidates completely dissolved the polymer under moderate thermal conditions. Dissolution behavior was also explored above and below the polymer's glass transition. The resulting dataset was used to train machine learning models, which demonstrated predictive accuracy in distinguishing between good and bad solvents and identifying promising new candidates.

Overall, the integration of computational chemistry, experimental validation, and ML-driven optimization highlights a promising path towards more sustainable solvent systems for polymer recycling, contributing to the circular economy of bio-based materials.

Acknowledgment

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Thermally Reversible Networked Polydithiourethanes: Self-Healing and Recyclability via Dynamic Covalent and Hydrogen Bonding

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In recent years, as society increasingly recognizes the importance of cleaner production methods and sustainable products, there is a growing demand for polymeric materials that support carbon neutrality within a circular economy framework. One effective strategy to meet this challenge involves designing polymers that can be efficiently broken down into their constituent components and recycled without relying on complex or resource-intensive processes.

Many studies have explored recyclable polymers through equilibrium polymerization of cyclic monomers and dynamic covalent chemistry. However, when high-performance properties—such as thermal stability, mechanical strength, electrical conductivity, or optical performance—are prioritized, the resulting polymers often become too durable, compromising their degradability and recyclability. Therefore, achieving a balance between durability and recyclability while maintaining superior functionality remains a key objective in advancing sustainable materials for modern society.

Prior research demonstrated that adding a base catalyst to diisothiocyanates and dithiols enables the synthesis of high-molecular-weight poly(dithiourethane)s (PDTUs) at room temperature. Additionally, thermal treatment of these PDTUs can degrade them into oligomers with reactive end groups. Upon reintroducing a base catalyst, these oligomers can repolymerize, restoring the original molecular weight. Consequently, networked PDTU films can be disassembled via thermal de-crosslinking and regenerated through room-temperature re-crosslinking. Beyond their recyclability, these films exhibit exceptional properties, including high transmittance, refractive index, dielectric constant, and metal absorption capacity, as well as self-healing capabilities. In this study, various PDTUs—differing in composition and structure—are extensively analyzed experimentally for their self-healing behavior, wettability, and biocompatibility.

Acknowledgment

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Significant references

1. Schirmeister, C. G., & Mülhaupt, R. (2022). Closing the carbon loop in the circular plastics economy. *Macromolecular rapid communications*, 43(13), 2200247.
2. Vidal, F., van der Marel, E. R., Kerr, R. W., McElroy, C., Schroeder, N., Mitchell, C., ... & Williams, C. K. (2024). Designing a circular carbon and plastics economy for a sustainable future. *Nature*, 626(7997), 45-57.
3. von Vacano, B., Mangold, H., Vandermeulen, G. W., Battagliarin, G., Hofmann, M., Bean, J., & Künkel, A. (2023). Sustainable design of structural and functional polymers for a circular economy. *Angewandte Chemie International Edition*, 62(12), e202210823.

Thermodynamic Model assessment of LTHP working with Reactive Carboxylic Acids and development of Compression Units suitable to these specific fluids

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Heat pump technologies (HPs), both low- and high-temperature (LTHP-HTHP), represent a key component in the energy transition process. This already existing technology may be brought to a higher level of efficiency by switching from the use of inert working fluids to reacting working fluids as thermodynamic mean. The use of these fluids is thought to be of interest because of the endothermic dissociative reaction and the respective compositional change of the mixture, allowing for a reduction of the outlet temperature of the compressor [1], and therefore increasing the overall COP of the cycle. A first approach in modelling these fluids was done by accounting for fictitious reactive systems undergoing the reaction $A_2 \leftrightarrow 2A$ [2] along a reverse ideal Brayton cycle. The results have shown – in a first stage – an increase on the COP up to two times with respect to the inert reference, under isentropic and ideal conditions. However, by extending the study and integrating real machines efficiencies, it can be observed how, at the same operating conditions, a substantial decrease in COP with respect to the fully isentropic case arises. Reverse Rankine instead of Brayton cycle is required when switching to real fluids, namely carboxylic acid (especially formic and acetic acids), since they undergo VLE transformations (two-phase) [3]. With that configuration, even if a lower impact on the compression section is expected, it is clear how the design and integration of this component play a crucial role. In this case, the implementation of a multistage compression cycle allows to work at formic acid pressure operating conditions (which are lower than inert fluids conditions) while obtaining the desired pressure ratio. The aim of this project is then performing in depth cycle calculation and compression train integration for LTHPs running on carboxylic acids, as a first step towards the realisation of a residential HP prototype operating with formic acid. At first, the calculations are going to be performed with fixed operative conditions and, eventually, the cycle will get optimized in its operative conditions on the basis of external goals to reach the optimum performance.

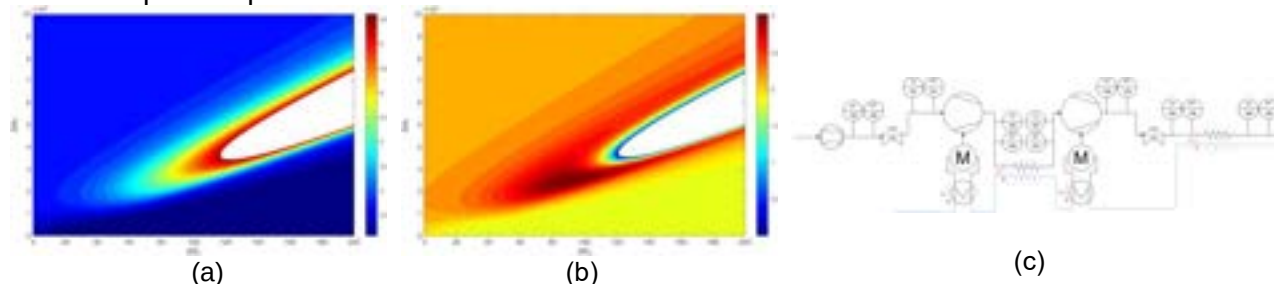


Figure 1. (a) Isentropic and (b) real compression resulting maps for the COPs of reverse Brayton based HP. (c) Layout of the compression train.

Acknowledgment

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Significant references

1. Arpagaus et al., *Energy*, 152, 985-1010 (2018). DOI: 10.1016/j.energy.2018.03.166
2. A. Barakat et al., *Chemical Engineering Journal Advances*, 12, (2022), DOI: 10.1016/j.cej.2022.100400.
3. D. O. Wasik et al., *Fluid Phase Equilibria*, 594, (2025), DOI: 10.1016/j.fluid.2025.114356

Cross-Property and Cross-Method Consistency Validation of High-Temperature Thermophysical Properties of Refractory Metals by Multi-Stepwise Pulse Heating

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Thermophysical properties of refractory metals (e.g., W, Mo, Nb, and Ta) at high temperatures are essential for the design and performance prediction of advanced heat-resistant alloys. Among the available techniques, pulse-heating methods, a class of transient techniques, have been widely used to measure enthalpy, heat capacity, hemispherical total emissivity, and electrical resistivity above 1500 K. However, significant discrepancies have been reported in heat capacity and emissivity data obtained by different researchers and under different experimental conditions, as well as systematic deviations from steady-state measurements, raising significant concerns about the reliability of the data.

Figure 1 shows the present results together with representative literature data for the hemispherical total emissivity (a) and isobaric heat capacity (b) of niobium at high temperatures. While a general level of agreement is observed at lower temperatures, the literature heat-capacity data exhibit a pronounced upward deviation above 2600 K near the melting point, exceeding the present results. In this temperature range, both transient and steady-state methods have inherent advantages and limitations, making it difficult to identify a priori which method provides more reliable results.

In this study, the reliability of thermophysical property data obtained by a multi-stepwise pulse heating method¹⁻³, in which the specimen is rapidly heated in a stepwise manner, is assessed through (i) cross-property consistency between calorimetrically measured hemispherical total emissivity and values derived from simultaneously measured electrical resistivity, and (ii) cross-method consistency of enthalpy and electrical resistivity obtained quasi-simultaneously from transient and steady-state analyses within a single experiment. This dual-consistency approach provides a physically grounded framework for evaluating the reliability of high-temperature thermophysical data.

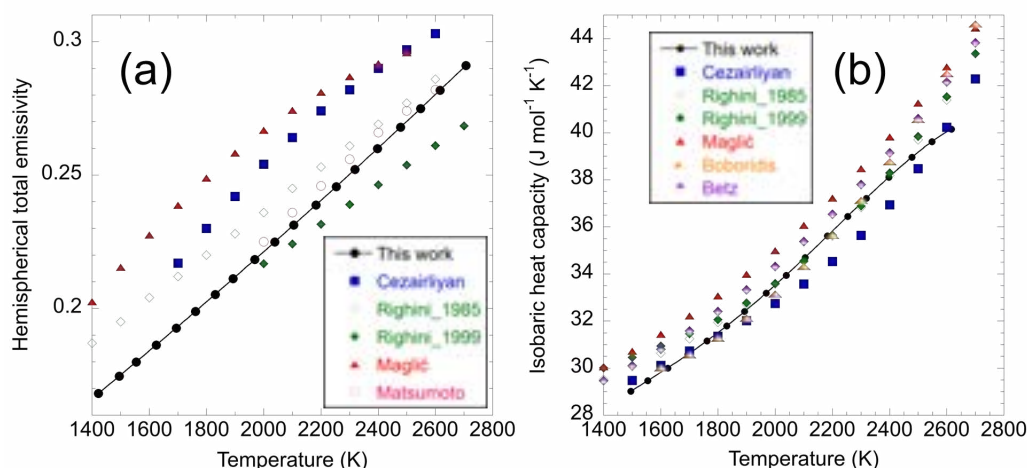


Figure 1. Comparison of the present results with representative literature data for niobium at high temperatures: (a) hemispherical total emissivity and (b) isobaric heat capacity. The literature heat-capacity data exhibit a pronounced upward deviation above 2600 K.

Significant references

1. H. Watanabe, K. Morimoto, M. Watanabe, M. Kato, Y. Arita, and K. Konashi, *Thermochim. Acta*, vol. 693 (2020), 178763.
2. H. Watanabe, *Thermochim. Acta*, vol. 728 (2023), 179594.
3. H. Watanabe, *Int. J. Thermophysics*, in press. <https://doi.org/10.1007/s10765-026-03765-z>

- Sant'Ana, Volumetric properties of three nonylphenol ethoxylated nonionic surfactant mixtures with methanol: Experimental study and modeling with Tammann-Tait and PC-SAFT equation of state, *Fluid Phase Equilib* 581 (2024) 114076. <https://doi.org/10.1016/j.fluid.2024.114076>.
2. L.H.G. de Medeiros, M.A.M. de Sousa, E.E.C. da Silva, M.F.L. da Costa, F.X. Feitosa, F. Costa, A.C.M. da Silva, S. Mattedi, H.B. de Sant'Ana, Thermophysical Characterization of Protic Ionic Liquids: Density Measurements, Group Contribution Method, and PC-SAFT Modeling Application, *Ind Eng Chem Res* 63 (2024) 16186–16197. <https://doi.org/10.1021/acs.iecr.4c02480>.
 3. A. Pakraves, F. Zarei, H. Zarei, P. T parameterization of SAFT equation of state: developing a new parameterization method for equations of state, *Fluid Phase Equilib* 538 (2021) 113024. <https://doi.org/10.1016/j.fluid.2021.113024>.

Comparative analysis of polyurethane aerogel specific heat study tests results obtained using two DSC techniques

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The study focuses on the experimental determination of the specific heat of polyurethane aerogel using DSC techniques. The investigated material is characterized by extremely low density and thermal conductivity, as well as a highly porous microstructure [1]. In such an instance, there are difficulties not only with the preparation of a sample of sufficient mass and compactness, but also with the interpretation of the test results as in the case described in [2]. The aim of the present work was to provide data characterizing the tested material or more precisely material structure as well as to determine the effectiveness and accuracy of the applied measurement methods and procedures.

The comparative analysis was based on experimental results obtained using a PerkinElmer Pyris 1 scanning calorimeter [2, 3] and a Mettler-Toledo DSC 3 scanning calorimeter [4]. Measurements were carried out up to 130°C under a controlled inert gas atmosphere. The tests used repeated heating and cooling cycles to check the expected moisture release effects for the sample in its initial - as-delivered state. Two procedures for determining specific heat were applied: a standard method based on direct conversion of the DSC signal in the case of the Mettler-Toledo DSC 3 instrument and a modified three-curve method relative method referencing a tested sample signals to a sapphire reference data [5]. A modification of the latter method involved segmenting the heating and cooling cycles [2, 3]. The use of isothermal stops allows for obtaining reliable data for calculating the specific heat for both the heating and cooling stages. Data from such a measurement, especially when the thermal properties of the tested sample have stabilized, provide a good basis for comparing the results of different testing procedures.

The analysis of the results allowed the assessment of the metrological limitations of both methods, taking into account baseline stability, detector sensitivity, and the influence of crucible geometry on the recorded signal. Typical results of the DSC data processing is shown in Fig. 1. Comparison of the data obtained from both instruments showed consistent temperature trends in the obtained specific heat data, although differences were observed in heating and cooling stage results. The analysis revealed differences in noise levels and in the sensitivity of each system to the highly porous structure of the aerogel. In both cases, a clear discrepancy was observed between the first and subsequent heating cycles. They can be considered as typical for highly hygroscopic and porous material. It is obvious that the first heating cycle revealed processes related to the removal of residual moisture and structural stabilization, while the second cycle allowed obtaining stable and repeatable values of specific heat, which are not influenced by irreversible phenomena. However, the research carried out allows us to determine the scale of these effects and their parameterization. This, in turn, results in the possibility of a reliable comprehensive assessment of thermophysical properties and provides the opportunity to analyze heat transfer phenomena in the tested material structures.

To sum up, it can be stated that in addition to the data characterizing the heat capacity of the tested material the findings expand the current knowledge on the methodology of thermal analysis of highly porous materials and provide a basis for optimizing DSC procedures in studies of aerogels and other ultralight functional materials.

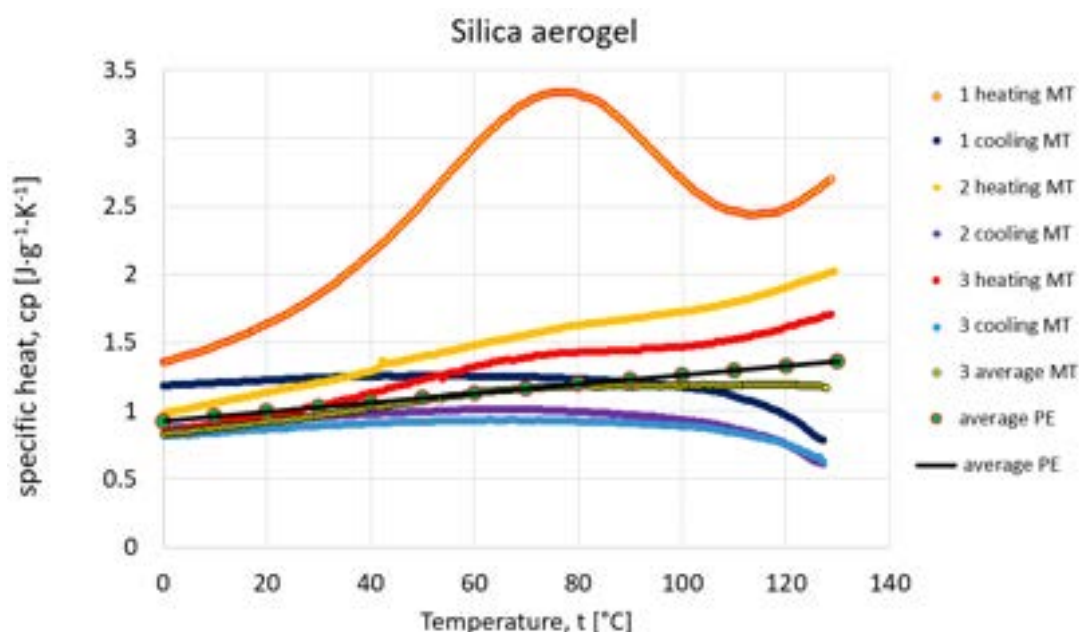


Figure 1. Comparison of the obtained specific heat data of the tested polyurethane aerogel specimens (PE – PerkinElmer Pyris 1 data, MT – Mettler-Toledo DSC 3 data)

Significant references

1. J. Lledó, J. Martín-de León, T.E. Gómez Álvarez-Arenas, M.A. Rodríguez-Pérez, B. Merillas, *Journal of Materials Research and Technology*, vol. 36, (2025), pp. 641-652, <https://doi.org/10.1016/j.jmrt.2025.03.135>.
2. S. Żmuda, P. Zaborowski, A. J. Panas, Microcalorimetric investigations of human hard tissues in thermocycling in *Thermal Conductivity 26 / Thermal Expansion 14*, Dinwiddie R. B., Mannello R. Eds., DEStech Publications, Inc., Lancaster PA, 2005, pp. 291-298
3. A. J. Panas, Comparative dilatometric and calorimetric studies of phase transitions in Co in *Thermal Conductivity 26 / Thermal Expansion 14*, Dinwiddie R. B., Mannello R. Eds., DEStech Publications, Inc., Lancaster PA (2005), pp. 530-539
4. R. Szczepaniak, A. J. Panas, Ł. Omen, M. Starczewski, M. Kowalski, Comparative experimental studies of the specific heat of Fe and Ni using scanning calorimetry methods, *Monograph NR M170: Solutions in Heat and Mass Transfer*, Wydawnictwo Politechniki Świętokrzyskiej, (2025), pp. 771-784. (in polish)
5. J. L. McNaughton, C. T. Mortimer, *Differential Scanning Calorimetry*. IRS; Physical Chemistry Series 2, Volume 10 (1975), Butterworths, London

Enhancing the electrical conductivity of electric vehicle transmission fluids with nanomaterials and ionic liquids

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Many automotive manufacturers have adopted the integrated powertrain configuration of electric vehicles (EVs), in which the electric motor, power electronics, gears, and bearings are all housed in a single unit called an electrified powertrain or integrated drive unit. EV transmission fluid (e-fluid or ETF) is responsible for two fundamental functions: the lubrication of gears and bearings, and the cooling of electronic components and the motor. The electrical conductivity of the ETF, κ , should fall within the static dissipative range (10^{-11} to 10^{-4} S m⁻¹) [1,2]. An oil with high electrical conductivity ($>10^{-4}$ S m⁻¹) is in the conductive range and does not offer protection against stray currents. However, if the electrical conductivity of the oil is insufficient (insulating range, $<10^{-11}$ S m⁻¹), the accumulation of static charges can build up and discharge in the form of arcs, which can damage or even destroy sensitive components (Fig. 1). In general, base oils exhibit insulating properties. To increase their electrical conductivity to the dissipative range, the utilization of additives is necessary. In this work, the effect of several nanoadditives and one ionic liquid (IL) on κ of three base oils is analyzed.

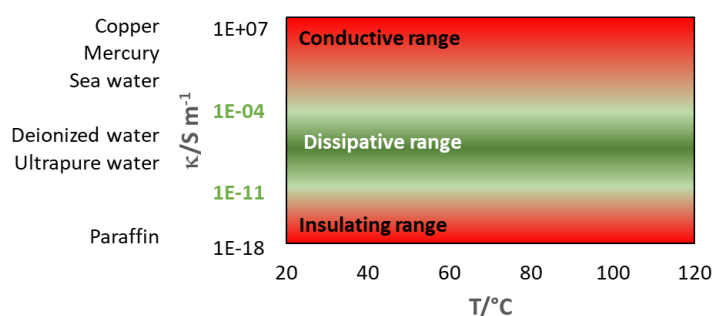


Figure 1. Electrical Conductivity ranges: insulating, dissipative, conductive [2].

The low viscosity base oils are two polyalphaolefins PAO4 and PAO6 and a mineral base oil, GIII. The nanoadditives are nanoparticles of silanized Fe₃O₄, ionic liquid-polyoxometalate hybrid nanoadditives, IL-POMs, Carbon Nanofibers, CNFs, and Carbon Dots, CDs. The ionic liquid was trihexyltetradecylphosphonium bis(2-ethylhexyl)phosphate. Two electrical conductivity meters Emcee 1153 were used, ranging from (2 to 2000)10⁻¹² S m⁻¹ and from (20 to 20000) 10⁻¹² S m⁻¹, both with an accuracy of 10%. These devices work according to ASTM Standard Test Method D2624. At least five replicates were measured for each fluid and condition. The highest values of κ were found for PAO6 + 1 wt% IL, followed by PAO4 + 1.5 wt% CD.

Acknowledgment

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Significant references

1. F. Mariño, Ó Giner-Rajala, E.R. López, A. Amigo, and J. Fernández, *Applied Surface Science*, vol. 706 (2025) 163528.
2. Perspective on Electric Vehicles. 2019 Annual Report, *Lubes'n'Greases*, (2019) pp. 22–36.

Thermodynamic, spectroscopic, and computational studies of binary mixtures containing water + ionic liquid (IL) *n*-butylammonium propanoate (N4Prop)

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Ionic liquids (ILs) are salts whose ions are not well organized and have one or more delocalized charges. Besides, at least one ion derives from an organic compound. These characteristics explain why ionic liquids are not solids but rather solvents, most of which are green solvents, even at temperatures below 100 °C and at room temperature (RTIL). These solvents are divided into two groups: aprotic and protic ILs, whose origin comes from a proton transfer from a Brønsted acid to a Brønsted base. Particularly, ionic liquids based on the butylammonium anion have been studied in separation processes and in the treatment of coir fiber for bioethanol generation [1]. In this work, new data for density and viscosity of binary mixtures containing water + ionic liquid (IL) *n*-butylammonium propanoate (N4Prop) were determined over the whole composition range, in the temperature range of $T = 288.15 - 303.15$ K and at atmospheric pressure ($p = 92.3$ KPa). These results were used to calculate the excess molar volume, viscosity deviation, and Gibbs excess activation energy, which were correlated by a Redlich-Kister polynomial. The ionic liquid N4Prop was synthesized in our laboratory by neutralization, dripping propanoic acid on *n*-butylamine under stirring and controllable conditions, i.e. temperature range between 293.15 – 303.15 K, according to the methodology previously described in the literature [1]. Its characterization by ¹H-NMR, ¹³C-NMR, and FTIR spectroscopy techniques presented a purity of more than 99.7 %. A Karl Fischer titration was used to determine the water content in the IL. The amount was less than 0.3198 % w/w. The N4Met was not dried in a high vacuum, because it generates amide, and then its purity decreases. A rotational viscometer/densimeter manufactured by Anton Paar (Model Stabinger SVM 3000) was used to measure the viscosities of pure components and their solutions. In addition to the thermodynamic approach, Nuclear Magnetic Resonance (NMR), ¹H NMR, and ¹³C NMR, were investigated to elucidate intermolecular interactions among the species in solutions. An Advance III 600 HD Bruker spectrometer has been used to analyze ¹H-NMR (operating at 600 MHz) and ¹³C-NMR (operating at 150 MHz). Deuterated chloroform (CDCl₃) has been used as a solvent with tetramethylsilane (TMS) as standard. Furthermore, theoretical calculations using Density Functional Theory (DFT) at B3LYP-GD3(BJ)/6–311++G(3df,2p) level of theory were performed to understand the inter-interactions between the compounds present in the mixtures. The results were discussed in terms of specific interactions between chemical species present in the solution. The spectroscopic and computational results were in good agreement with the thermodynamic data.

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References

1. J.C.A. Neto, A.S. Cabral, L.R.D. Oliveira, R.B. Torres, A.A. Morandim-Gianneti, *Carbohydrate Polym.*, vol. 143 (2016), pp. 279-287.

Thermodynamic, spectroscopic, and computational approach of binary mixtures containing gamma-valerolactone (GVL) and alcohols

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Substances derived from biomass have drawn attention from scientific and industrial fields, as these compounds represent a group of renewable solvents, whose physicochemical properties present great potential for applications in several areas of science and industry, namely in biorefineries, which have been seen as sustainable and promising since they produce chemicals from biomass, substituting partially products derived from crude oil [1]. In this work, new data for density, speed of sound and viscosity of binary mixtures containing gamma-valerolactone (GVL) + ethanol, or + 1-propanol, or + 1-butanol, or 1-pentanol were determined over the entire composition range, in the temperature range of 293.15-313.15 K and at atmospheric pressure ($p = 92.3$ kPa). These results were correlated with the Jouyban-Acree equation and used to calculate the excess molar volume, partial molar volume, apparent molar volume, excess partial molar volume, isentropic compressibility deviation, viscosity deviation, and excess Gibbs energy of activation of viscous flow, which were correlated by a Redlich-Kister polynomial. A commercial density and speed of sound analyzer manufactured by Anton Paar (Model DSA 5000) and operating at a frequency of 3 MHz has been used to measure the density and speed of sound of the pure components and their solutions. The Peltier device of the equipment made it possible to automatically keep the temperature constant at ± 0.01 K. A rotational viscometer/densimeter manufactured by Anton Paar (Model Stabinger SVM 3000) was used to measure the viscosities of pure components and their solutions. All of the excess and deviation properties revealed negative values, except excess molar volumes, which resulted in both negative and positive values. In addition to the thermodynamic approach, Nuclear Magnetic Resonance (NMR), ¹H NMR, and ¹³C NMR, were investigated to elucidate intermolecular interactions among the species in solutions. Spectroscopic analyses of nuclear magnetic resonances (NMR) of hydrogen (¹H) and carbon (¹³C) were carried out by using an Avance III 600 HD Bruker spectrometer at 600 MHz for proton and 150 MHz for carbon, and a Fourier transform infrared spectrometer Nicolet, with attenuated total reflectance (FTIR-ATR), model 6700, generated the IR spectra. Spectroscopic results agreed with thermodynamic discussion and also proved that chemical effects indeed occur, namely, weak hydrogen bonds. Furthermore, theoretical calculations using Density Functional Theory (DFT) were performed to understand the inter interactions between the compounds present in the mixtures. All DFT computations were executed using Gaussian 16 [2] and Grimme's D3 dispersion correction with Becke-Johnson damping. The spectroscopic and computational results were in good agreement with the thermodynamic data.

Acknowledgment

This study was financed in part by the Fundação Educacional Inaciana Padre Sabóia de Medeiros (FEI), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) (Process 406586/2023-3), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Finance Code 001, and Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) (Process Nº 2009/14556-5).

References

1. G. Strappaveccia, L. Luciani, E. Bartollini, A. Marrocchi, F. Pizzo, L. Vaccaro, *Green Chem.*, vol. 17 (2015), pp 1071-1076.
2. Gaussian 16 Revision C.01, Frisch et al., Gaussian Inc., Wallingford, CT, 2016. gaussian.com/gaussian16.

Process Simulation of a Thermodynamic Cycle Operating with Reversible Chemical Reactions

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Inserted in the context of energy efficiency, the study of thermodynamic cycles shows great importance in terms of proposing alternatives for improving the cycle efficiency. Previous articles related to the REACHER project (Reactive Fluids for Energy – Université de Lorraine) have explored the advantages of employing reactive fluids compared with inert fluids in thermodynamic cycles [1,2]. Considering a Stirling engine cycle, the present study proposes to analyze how the chemical reaction of $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ can affect the efficiency of the system, aiming to scale it up with a process simulation approach so it can be applied to industrial plants, for example. The software ASPEN PLUS was employed to run simulations and data collection, considering sensitivity analysis and constraints to ensure the expected isochoric or isothermal steps (Figure 1). After the simulations were completed, the data were exported to MS Excel, and, supported with MATLAB and Python, the determination of efficiencies [3] and filtering the possible results were performed, considering the scenarios with physical meaning. With the data collected, it was possible to check the pressure, temperature, density, and molar fraction variations during the process, and how they affect efficiency. A regenerative system was considered to partially integrate the energy collected from the cooling operation with the energy required in the heating operation, from which some results showed how the regenerative system is more effective with the chemical reaction than with air (inert fluid) as the working fluid. In some cases, the chemical reactive fluid achieved a cycle 33% more effective than air, enabling the possibility to substitute the air as the working fluid in this scenario.

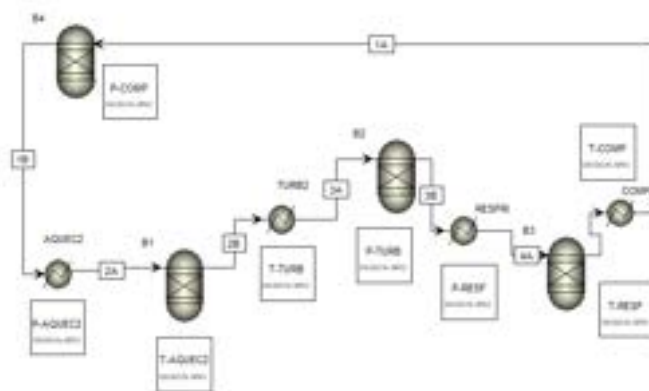


Figure 1. Aspen flowsheet of the process.

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Significant references

1. A. Barakat, S. Lasala, P. Arpentiner, P. Tobaly, and J.-N. Jaubert, *Energy Conversion and Management: X*, vol. 22 (2024), pp. 100573.
2. S. Lasala, R. Privat, O. Herbinet, P. Arpentiner, D. Bonalumi, and J.-N. Jaubert, *Energy Conversion and Management*, vol. 229 (2021), pp. 113685.
3. J.M. Smith, H.C. Van Ness, and M.M. Abbott, *Introduction to Chemical Engineering Thermodynamics*, 8th ed. (2007).

Investigation of the apparent thermal diffusivity of polyurethane aerogel using a modified method of temperature oscillation

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The study focuses on the experimental determination of the apparent thermal diffusivity of polyurethane aerogel, a material characterized by extremely low density and thermal conductivity, as well as a highly porous microstructure [1]. The studies were carried out using a modified temperature oscillation method [2, 3]. The main tests were carried out in an air atmosphere in the scanning mode over a temperature range from approximately 5°C to approximately 80°C. In addition to examining the effect of temperature changes on the determined values of apparent thermal diffusivity, it is also planned to determine the effect of variable pressure and type of gas on this parameter [4, 5]. An example of the obtained results is depicted in Figure 1.

The main objective of the research was to document the properties of the tested structure and to provide calculation data enabling the determination of the apparent thermal conductivity coefficient of the tested structure. Since the results of preliminary measurements have already shown a large influence of complex and coupled heat transfer phenomena, there is a need to precisely identify these effects. The effect of the discussed phenomena is a discrepancy between the amplitude and phase values of the thermal diffusivity, as seen in Figure 1.

In this context, the work also takes on metrological significance. From a methodological perspective, it is important to consider the potential conversion of thermal diffusivity values determined in measurements into apparent thermal conductivity characteristics. This applies to transient methods. The temperature oscillation method, due to the possibility of using the amplitude change and phase delay simultaneously, provides unique opportunities for early detection of the effects of deviations from the model measurement conditions. The supplementary objectives of the work were to verify the influence of selected parameters of the oscillatory excitation of the applied research method and the ambient gas type and pressure value on the value of the identified parameter.

In addition to expanding knowledge about the structure being studied, the research results provided data for planned numerical studies of the metrological conditions of porous structures.

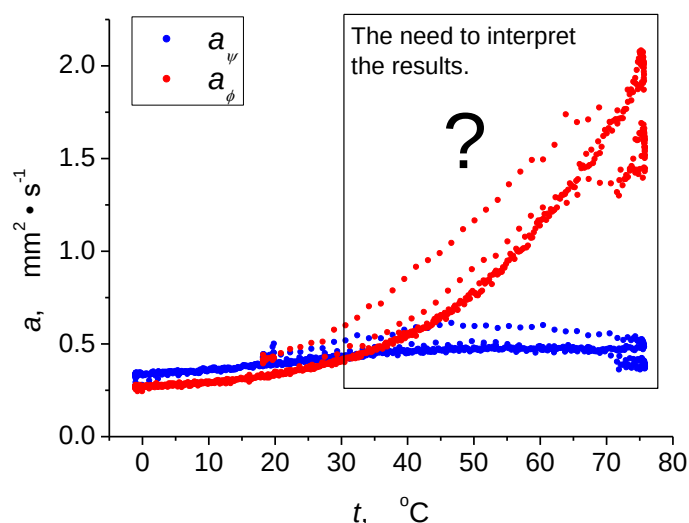


Figure 1. Temperature dependence of the amplitude a_ψ and phase a_ϕ values (comp. [3]) of the obtained thermal diffusivity values of polyurethane aerogel from repeated heating–cooling measurement sequences

Significant references

1. J. Lledó, J. Martín-de León, T.E. Gómez Álvarez-Arenas, M.A. Rodríguez-Pérez, B. Merillas, *Journal of Materials Research and Technology*, vol. 36 (2025), pp. 641-652
2. J.M. Belling, J. Unsworth, *Rev. Sci. Instrum.*, vol. 58 (6), (1987), pp. 997 -1002
3. A. J. Panas, IR Support of Thermophysical Property Investigation in Medical and Advanced Technology Materials Study, chapter in: Prakash, R.V. (Ed.), *Infrared Thermography*, InTech, Rijeka (2012); pp. 65-90
4. A. J. Panas, B. Fikus, P. Płatek, I. Kunce, S. Dyjak, M. Michalska-Domanska, K. Witek, P. Kuziora, A. Olejarczyk, L. Jaroszewicz, M. Polański, *Int. J. Hydrogen Energy*, vol. 41 (2016), pp. 16974-16983
5. Ł. Omen, M. Kowalski, R. Szczepaniak, A. J. Panas, Experimental studies of heat diffusion in a bulk deposit under conditions of coupled energy transport and phase transition mechanisms, *Monograph NR M170: Solutions in Heat and Mass Transfer*, Wydawnictwo Politechniki Kieleckiej, Kielce (2025), pp. 536-562