ESAT 2024

33rd European Symposium on Applied Thermodynamics

1974-2024: the 50th anniversary

Edinburgh, 9-12 June 2024

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Introduction

It is with great pleasure that the International Steering Comittee, the local Organising committee and the University of Edinburgh welcome you to **ESAT 2024**, marking the **50th anniversary** of the European Symposium on Applied Thermodynamics series. When it started, in 1974, Europe was still divided in blocks and the conference took place in west Berlin. Since then, ESAT has been hosted by Northern, Southern, Eastern and Western European Countries to represent the diversity and richness of our culture. We will celebrate this with a special anniversary ceremony during our social dinner. We will also present the EFCE Michael L. Michelsen Award 2024 to Prof. Jean Noel Jaubert, who will give a speech entitled „*Some insights on the development of equations of state over the past 30 years*“ and award three Helmut Knapp prizes to the best poster presenters.

ESAT is a truly European conference with a global flavour that proudly hosts contributions from all continents. As British scientists, we are particularly excited to celebrate our Association to European scientific schemes such as Horizon and continue a tradition of succesful collaborations. As a Scottish Institution, we are proud to celebrate the numerous Scottish scientists who have contributed to the field of Applied Thermodynamics, who built their strenght through mutual **collaborations**, such as those between Joseph Black and James Watt, Peter Tait and Lord Kelvin, James C. Maxwell and James Dewar. As the challenges we are facing, such as sustainability, energy transition and climate change, become ever more pressing, we need to collaborate and interact and we hope that ESAT 2024 will strengthen existing connections and foster new ones.

On behalf of the organizing and IS committee, welcome to Edinburgh!

The ESAT conference series

EDITION	Year	ORGANISER	LOCATION	COUNTRY
33rd	**2024**	**University of Edinburgh**	**Edinburgh**	**Scotland (UK)**
32nd	2022	TU Graz	Graz	Austria
31st	2021	IFP Energies nouvelles	Paris / online	France
30th	2018	The Czech Academy of Sciences	Prague	Czech Republic
29th	2017	Polytechnic Univ. Bocarest	Bucarest	Romania
28th	2015	Nat. Tech. Univ. Athens	Athens	Greece
27th	2014	Eindhoven University of Technology	Eindhoven	The Netherlands
26th	2012	TU Berlin and DECHEMA	Potsdam	Germany
25th	2011	St. Petersburg State Univ, Russian Acad.Sci, The Mendeleev Russian chem. Soc.	St. Petersburg	Russia
24th	2009	ETSE.Univ, Santiagp de Compostela	Santiago de Compostela	Spain
23rd	2008	ENSIC-INPL, Nancy	Cannes	France
22nd	2006	Tech. Univ. Denmark	Elsinore	Denmark
21st	2005	Warsaw Univ. of Tech.	Jurata	Poland
20th	2003	VDI-GVC, Dusseldorf + Bayer AG, Leverkusen + Univ. Kaiserslautem	Lahnstein	Germany
19th	2002	Nat. Tech. Univ. Athens	Santorini	Greece
18th	2000	ICT, Prague + ICPF, Prague	Kutna Hora	Czech Republic
17th	1999	Univ. Porto + Univ. Aveiro	Vilamoura	Portugal
16th	1997	Univ. Metz + ENSIC-INPL, Nancy	Pont-a-Mousson	France
15th	1996	ICI, Runcom	Runcom	United Kingdom
14th	1994	Nat. Tech. Univ. Athens	Marathon	Greece
13th	1993	Univ. Marseille	Marseille	France
12th	1991	Tech. Univ. Berlin	Berlin	Germany
11th	1990	Tech. Univ. Denmark	Rungsted	Denmark
10th	1988	Univ. Porto	Ofir	Portugal
9th	1987	Norsk Hydro, Posgrunn	Bergen	Norway
8th	1985	Univ. Trieste	Trieste	Italy
7th	1983	Univ. Dortmund	Dortmund	Germany
6th	1982	Institut Français du pétrol	Rueil Malmaison	France
5th	1980	Linde AG, Munchen	Sachrang	Germany
4th	1979	Shell, Amsterdam	Amsterdam	The Netherlands
3nd	1978	Tech. Univ. Denmark	Lyngby	Denmark
2nd	1976	Tech. Univ. Berlin	Berlin (West)	Germany
1st	1974	Tech. Univ. Berlin	Berlin (West)	Germany

Committees

International Steering committee

Honorary members:

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Ivo Nezbeda, Prague, Czech Republic

Cor Peters, Abu Dhabi, United Arab Emirates / Eindhoven, The Netherlands

Catinca Secuianu, Bucharest, Romania

Alexey Victorov, Saint Petersburg, Russia

Nontas Voutsas, Athens, Greece

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Ana Soto, Santiago de Compostela, Spain

Maria Grazia de Angelis, Edinburgh, Scotland

Tim Zeiner, Graz, Austria

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Giulio Santori, University of Edinburgh

Martin Sweatman, University of Edinburgh

Felipe Perdomo, University of Edinburgh

Peter Cummings, Heriot-Watt University, Edinburgh, UK

Amparo Galindo, Imperial College London, UK

Claire Adjiman, Imperial College London, UK

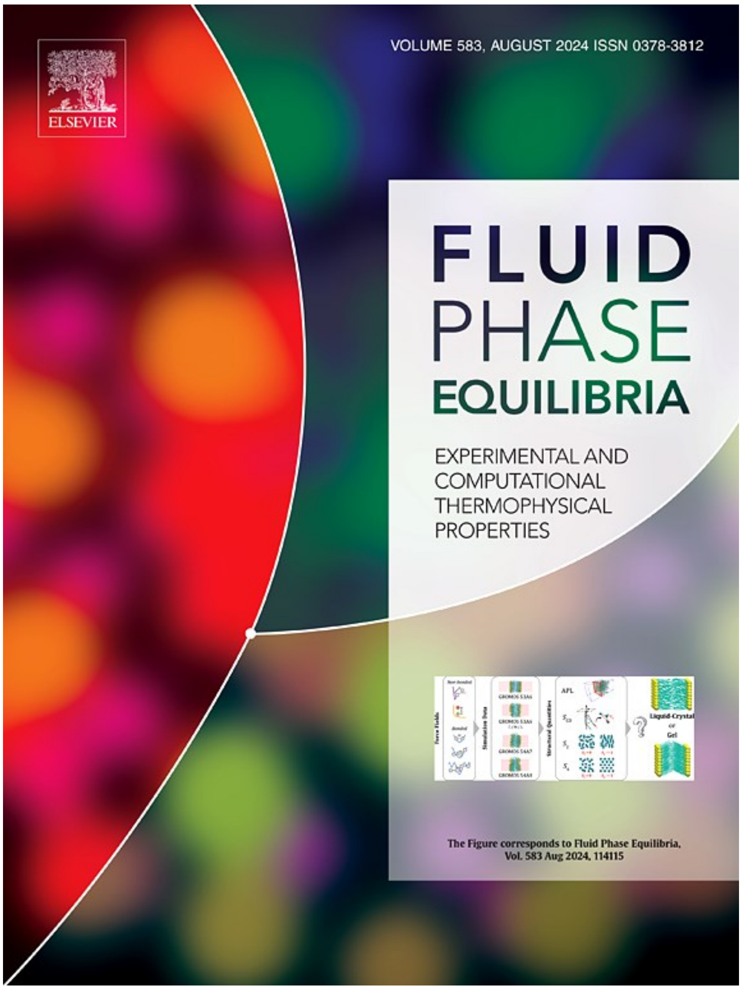
Matteo Minelli, University of Bologna, Italy

Cara E. Schwarz, Stellenbosch University, South Africa

Local Support team

Kseniya Papchenko, Hasan Ismaeel, Thomas Fabiani, Maryam Zarghamidehagahani, Diane Reid, Megan Hammell, University of Edinburgh, UK

Sponsors



Fluid Phase Equilibria publishes high-quality papers dealing with experimental, theoretical, and applied research related to equilibrium and transport properties of fluids, solids, and interfaces. Subjects of interest include physical/phase and chemical equilibria; equilibrium and nonequilibrium thermophysical properties; fundamental thermodynamic relations; and stability. The systems central to the journal include pure substances and mixtures of organic and inorganic materials, including polymers, biochemicals, and surfactants, with sufficient characterization of composition and purity for the results to be reproduced. Naturally occurring systems that cannot be completely characterized will be considered only if they are of high practical interest and the work leads to significant new findings. In all cases, enough detail must be given to permit independent verification, and authors are also expected to provide physical or chemical interpretations of the results.

See more at: https://www.sciencedirect.com/journal/fluid-phase-equilibria

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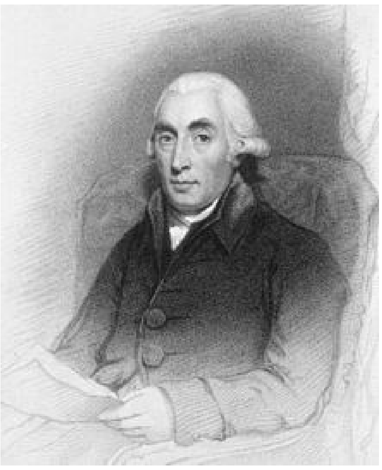
Applied Thermodynamics in Scotland

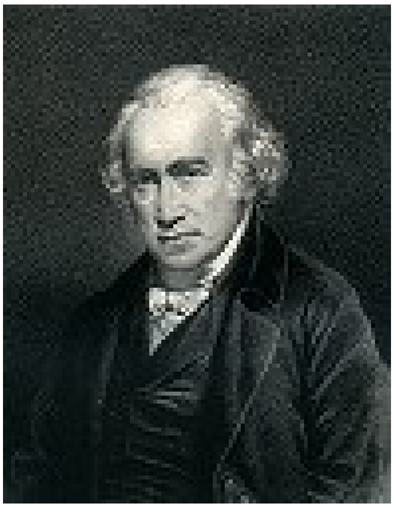
Scotland was the birthplace or workplace of many scientists who have contributed enormously to the field of applied thermodynamics. The section below, taken from open access sources such as Wikipedia and the Scottish Engineering hall of fame website, aims to pay a small tribute to their contribution to the advancement of this discipline and emphasise their mutual collaborations.

Joseph Black (1728-1799)



Joseph Black was a physicist and chemist, known for his discoveries of magnesium, latent heat, specific heat, and carbon dioxide. He was Professor of Anatomy and Chemistry at the University of Glasgow for 10 years from 1756, and Professor of Medicine and Chemistry at the University of Edinburgh from 1766. The chemistry buildings at the University of Edinburgh are named after him. Around 1750, while still a student, Black developed the *analytical balance*, which far exceeded the accuracy of any other balance of the time and became an important scientific instrument. In 1761, he deduced that the application of heat to boiling water does not result in a rise in temperature of a water/steam mixture, but rather in an increase in the amount of steam. From these observations, he concluded that the heat applied must have combined with boiling water and become latent. *The theory of latent heat marks the beginning of thermodynamics*. Black also found that calcium carbonate could be heated or treated with acids to yield a gas (CO_2) he called "fixed air". In the last part of his career, he devoted himself exclusively to teaching. His lectures had a powerful effect in popularising chemistry and attendance at them even became a fashionable amusement. Black's grave is in Greyfriars Kirkyard in Edinburgh. In 2011, scientific equipment believed to belong to him was discovered during an archaeological dig at the University of Edinburgh. The session on ***Carbon Capture and Storage*** in **ESAT 2024** is dedicated to him.

James Watt (1736-1819)



James Watt was born in Greenock, near Glasgow. He was an inventor, mechanical engineer, and chemist who developed the *Watt steam engine* in 1776, which was fundamental to the Industrial Revolution.

After leaving school, he started working as a mathematical instrument maker and set up a workshop within the University of Glasgow in 1757. There, he became friends with chemist Joseph Black and economist Adam Smith.

There is a popular story that Watt was inspired to invent the *steam engine* by seeing a kettle boiling, the steam forcing the lid to rise and thus showing the power of steam. In reality, Watt did not invent the steam engine, but significantly improved the efficiency of the existing one by adding a separate condenser, consistent with the new principles of *thermal efficiency*. He came to realise the importance of *latent heat*, which his friend Joseph Black had previously discovered. The science of thermodynamics would not be formalised for nearly another 100 years.

Watt was a proficuous inventor, and, together with Matthew Boulton, who owned the Soho Manufactory works with some of the best iron workers in the world, formed a hugely successful partnership. Watt combined theoretical knowledge of science with the ability to apply it practically. The *watt*, the unit of power incorporated in the International System of Units is named after him. In 2009, the Bank of England released a £50 note depicting Boulton and Watt. Watt is commemorated by statuary in Princes Street, Edinburgh, while a painting „*James Watt contemplating the steam engine*“ is visible at the National Gallery of Scotland. **ESAT 2024** has dedicated the ***Electrochemical Process*** session to him, hoping that his work can inspire a new Industrial Revolution, based on a new energy transition.

John Leslie (1766-1832)

Leslie was born in Largo (Fife). At 13 years of age he entered the University of St Andrews. On completion of his course in 1784, he studied divinity at the University of Edinburgh but gained no further degrees. He then worked as a private tutor, employing his spare time in experimental research and continued his physical studies, which resulted in numerous papers and in the publication (1804) of the *Experimental Inquiry into the Nature and Properties of Heat*, a work which gained him the Rumford Medal of the Royal Society of London.

In 1805, after having been rejected in several attempts to obtain a Chair at a Scottish university, Leslie was elected to succeed John Playfair in the chair of mathematics at Edinburgh, despite violent opposition from a party who accused him of heresy (he was an atheist). With reference to his invention (in 1810) of a process of *artificial ice-making*, he published in 1813 *A Short Account of Experiments and Instruments depending on the relations of Air to Heat and Moisture.* When John Playfair died in 1819, Leslie was promoted to the more congenial chair of natural philosophy, which he held until his death. Leslie's main contributions to physics were made by the help of the differential thermometer, which he was able to employ to study photometry, hygroscopy and the temperature of space. The **ESAT 2024** will honour him through the ***Water and Aqueous*** solutions session.

Robert Stirling (1790-1878)

Robert Stirling was born in Perthshire. Though he had a natural inclination for engineering, he began attending Edinburgh University in 1805 at the age of 15 to study divinity in hopes of becoming a minister. He finished his studies there and continued at Glasgow University where he studied the classics, philosophy, theology and mathematics. Robert was licensed to preach in the Church of Scotland in 1816. Stirling is considered as one of the fathers of *hot air engines*. None of Stirling's experimental work or papers survived except for two model engines built by him when he was a Minister at Kilmarnock. At Edinburgh university Stirling's engine was used in student classes and it is now on display in the Royal Scottish Museum. At Glasgow university the engine lay forgotten until discovered in 1847 by William Thomson, who later became Lord Kelvin. Thomson used the model in lectures to show that Stirling's machine worked on *a reversible cycle*. In 1816, at the age of 26 Stirling patented an engine which produced motive power from heated air. He continued to refine his ideas and, with his brother James, registered patents for improvements in 1827 and 1840. The principles of his revolutionary engine are increasingly being adopted and adapted as conventional fuels for internal combustion engines become scarcer. Today's applications include heat pumps; the NASA MOD I and II automotive engines; various hybrid electric vehicles; Stirling powered submarines - and many more. As conventional fuels become ever scarcer, the Scottish clergyman's ideas from almost 200 years ago are of more relevance today than ever. For his contributions, **ESAT 2024** has dedicated the ***New models*** session to him.

Thomas Graham (1805-1869)

Thomas Graham was born in Glasgow, the son of a textile manufacturer, who wanted him to join the Church of Scotland. Instead, he became a student at the University of Glasgow and developed a strong interest in chemistry. He later studied medicine at the University of Edinburgh. After taking a professorship at the University of London, he founded the Chemical Society of London in 1841.

Thomas Graham is known for his studies on the behavior of gases, which resulted in the formulation of two relationships, now known as "*Graham's Laws*," regarding gas *diffusion* and effusion. In applied areas, Graham also made fundamental discoveries related to *dialysis*, a process used in research and industrial settings, as well as in modern health care. Graham's study of colloids resulted in his ability to separate colloids and crystalloids using a so-called "dialyzer", using technology that is a rudimentary forerunner of technology in modern kidney dialysis machines. These studies were foundational in the field known as *colloid chemistry*, and Graham is credited as one of its founders. He also proposed the association theory which claimed that the substances such as cellulose that we now know are *polymers* are composed from smaller molecules hold together by unknown forces. A statue of Graham in Glasgow was erected by the city in 1872. The **ESAT 2024** has decided to dedicate its session on ***Transport Properties*** to him.

William Rankine (1820-1872)

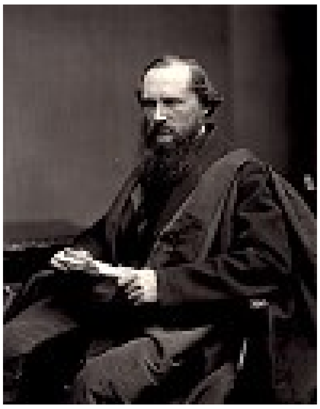
William John Macquorn Rankine, born in Edinburgh, was a mathematician and physicist. In 1836, he began to study a number of scientific topics at the University of Edinburgh, leaving it in 1838 without a degree and starting to work, as his father, in the Railways. There he developed a technique, the *Rankine's method*, for laying out railway curves. For Queen Victoria's visit to Scotland, he organised a large bonfire on Arthur's Seat, which served to initiate a chain of other bonfires across Scotland. From 1855 he was Professor of Civil Engineering and Mechanics at Glasgow University.

By 1849, he had discovered the relationship between saturated vapour pressure and temperature and between the temperature, pressure and density of gases, as well as for the latent heat of evaporation of a liquid. In 1851 he set out to calculate the *efficiency* of heat engines and used his theory to deduce the principle that the maximum efficiency possible is a function only of the two temperatures between which it operates. In 1853, he coined the term *potential energy*. From 1854, he made wide use of his thermodynamic function which he later realised was identical to the *entropy* of Clausius. He published a definition of energy in terms of capacity of performing work, which quickly became the standard general definition. In 1859 he proposed the *Rankine scale of temperature*, an absolute scale whose degree is equal to a Fahrenheit degree.

The *Rankine cycle* is an analysis of an ideal heat-engine with a condensor. One of King’s Buidings campus buildings at the University of Edinburgh is named after him. The ESAT 2024 has decided to dedicate ***Fluid Phase Equilibria* IV** session to William Rankine for his studies on the relationship between thermodynamic quantities.

Lord Kelvin (1824-1907)

William Thomson, 1st Baron Kelvin, was a mathematician, mathematical physicist and engineer born in Belfast. He was the professor of Natural Philosophy at the University of Glasgow for 53 years, where he undertook significant research and mathematical analysis of electricity, the formulation of the *first and second laws of thermodynamics*, and contributed significantly to unifying physics, which was then in its infancy of development as an emerging academic discipline.



Absolute temperatures are stated in units of kelvin in his honour. While the existence of a coldest possible temperature, absolute zero, was known before his work, Kelvin determined its correct value as approximately −273.15 degrees Celsius. In 1892, he became the first British scientist to be elevated to the House of Lords. Thomson had a fruitful, though largely epistolary, collaboration with James P. Joule: Joule conducting experiments, Thomson analysing the results and suggesting further experiments. The collaboration produced discoveries including the Joule–Thomson effect.

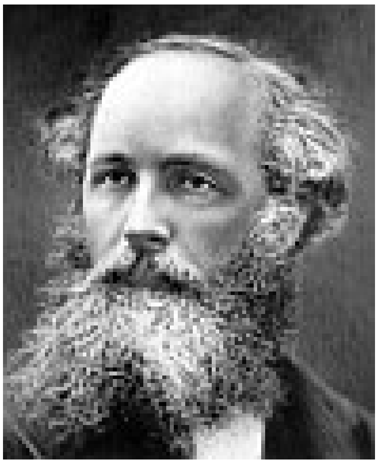
He also had a career as an electrical telegraph engineer and inventor which earned him wealth, fame, and honours. For his work on the transatlantic telegraph project, he was knighted in 1866 by Queen Victoria, becoming Sir William Thomson. He had extensive maritime interests and worked on the mariner's compass.

He was ennobled in 1892 in recognition of his achievements in thermodynamics. Despite offers of elevated posts from several world-renowned universities, Kelvin refused to leave Glasgow, remaining until his retirement in 1899. Active in industrial research and development, he was recruited around 1899 by George Eastman to serve as vice-chairman of the board of the British company Kodak Limited.

The Hunterian Museum at the University of Glasgow has a permanent exhibition on the work of Kelvin, which includes many of his original papers, instruments, and other artefacts, including his smoking pipe.

ESAT 2024 honours his contributions to applied thermodynamics, and the bicentennial of his birth, through the session ***Phase Equilibria* III**.

James Clerk Maxwell (1831-1879)



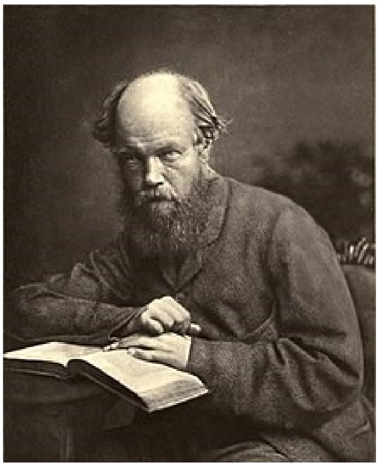
James Clerk Maxwell was born in 1831 at 14 India Street, Edinburgh, now hosting a museum operated by the omonomious Foundation. Maxwell was sent to the Edinburgh Academy where he became friend with Peter Tait. In 1850, he left Scotland for Cambridge, where in 1854, graduated from Trinity in mathematics. Maxwell was Chair of Natural Philosophy at Marischal College, Aberdeen and at King's College, London; and in 1871 became the first Cavendish Professor of Physics in Cambridge.

He was responsible for the classical theory of electromagnetic radiation, which was the first theory to describe electricity, magnetism and light as different manifestations of the same phenomenon and it is considered the "*second great unification in physics*" after the one of Newton. The unification of light and electrical phenomena led to his prediction of the existence of *radio waves*. Maxwell was the first to derive the *Maxwell–Boltzmann distribution*, a statistical mean of describing aspects of the kinetic theory of gases given the fraction of gas molecules moving at a specified velocity at any given temperature. His work on thermodynamics led him to devise the thought experiment that came to be known as *Maxwell's demon*, where the 2nd law of thermodynamics is violated by an imaginary being capable of sorting particles by energy. In 1871, he established *Maxwell's thermodynamic relations*, between the second derivatives of the thermodynamic potentials with respect to different thermodynamic variables. Maxwell proved that the rings of Saturn were made of small particles, winning the 1857 Adams prize, and providing an explanation that was confirmed by direct observations by the Voyager probe in the 1980s.

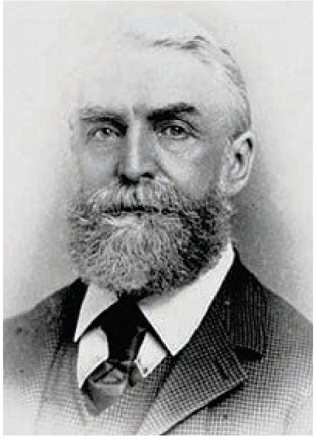
He is also known for presenting the first durable *colour photograph* in 1861 and he is responsible for modern *dimensional analysis*. Maxwell is also recognized for laying the groundwork for *chaos theory*. His discoveries helped usher in the era of modern physics, laying the foundation for such fields as *special relativity* and *quantum mechanics*. Many physicists regard Maxwell as the 19th-century scientist having the greatest influence on 20th-century physics.

ESAT 2024 decided to dedicate the session of ***Machine Learning*** to Maxwell, for his ability to utilise mathematical methods to describe physics laws.

Peter Guthrie Tait (1831-1901)



Tait was born in Dalkeith (Scotland) on 28 April 1831. He was educated at the Edinburgh Academy. He studied Mathematics and Physics at the University of Edinburgh, and then went to Peterhouse, Cambridge. Two years later he took up the professorship of mathematics at Queen's College, Belfast. His work on knot theory contributed to the eventual formation of *topology* as a mathematical discipline. His name is known in graph theory mainly for *Tait's conjecture* on cubic graphs. In 1860, Tait became professor of natural philosophy at the University of Edinburgh. In 1871, he emphasised the significance and future importance of the principle of the dissipation of energy (2nd law of thermodynamics). Researches on "Charcoal Vacua" with James Dewar led him to see the true dynamical explanation of the Crookes radiometer in the large mean free path of the molecules of highly rarefied air. From 1879 to 1888, he engaged in difficult experimental investigations on the corrections required for thermometers operating at high pressure, for the benefit of the Challenger expedition for observing deep-sea temperatures, which led to the *Tait equation* (of state). Between 1886 and 1892 he published a series of papers on the foundations of the kinetic theory of gases. With Lord Kelvin, he collaborated in writing the well-known *Treatise on Natural Philosophy* an all-comprehensive treatise on physical science. He is buried in the second terrace down from Princes Street in the burial ground of St John's Episcopal Church, Edinburgh. Tait's house was at 17 Drummond Place, Edinburgh. He was a lifelong friend of James Clerk Maxwell. One of the chairs in the Department of Physics at the University of Edinburgh is the Tait professorship. Tait Road at the University of Edinburgh King's Buildings complex is named in his honour. The **ESAT 2024** session ***Equations of state*** is dedicated to him.



David Boyle (1837-1891)

Born in Johnstone (Scotland), he emigrated to the USA at 21 and studied refrigeration texts at the San Francisco Mechanics' Institute. Boyle developed an improved form of ice making machine in a time when most ice was harvested in winter from lakes and rivers, transported long distances and stored for months. He is credited with being the first person to make use of *ammonia* as the working fluid in *a vapour-compression refrigeration system* reliable and commercially successful and he established an *ice machine manufacturing* company in the very early days of mechanical refrigeration. He developed an improved form of compressor valve which became the standard way of achieving inlet and outlet control in many makes of compressors. Boyle’s success with his ammonia compression system led to the rapid adoption of ammonia as the preferred refrigerant for industrial systems. This created a huge industry in America and Europe. Boyle's machines continued to be sold by his or successor companies after his death until about 1905. The **ESAT 2024** has named the session on ***New Refrigerants*** after him.

James Dewar (1842-1923)

James Dewar was born in Kincardine, Fife, in 1842. He studied Chemistry at the University of Edinburgh under Lyon Playfair, becoming his personal assistant. His investigations regarded the physiological action of light, the spectroscopic analysis of gases separated from atmospheric air at low temperatures, the electrical behaviour of substances at very low temperatures. His name is most widely associated to the liquefaction of the permanent gases at temperatures close to absolute zero. In 1874 he discussed the "*Latent Heat of Liquid Gases*" before the British Association. He built a machine from which the liquefied gas could be used as a cooling agent, and obtained solid oxygen.

Around 1892, he had the idea of using vacuum-jacketed vessels for the storage of liquid gases – the *Dewar flask* – the invention for which he became famous, although he did not patent it, and lost a court case against Thermos who exploited the design commercially.

In 1898, using a high-pressure machine based on the Joule–Thomson effect, he was able to collect liquid hydrogen for the first time, solid hydrogen following in 1899. He tried to liquefy the last remaining gas, helium, but owing to a number of factors, including a short supply of helium, Dewar was preceded by Onnes as the first person to produce liquid helium, who would later be awarded the Nobel Prize in Physics – Dewar was nominated several times, but never succeeded in winning. In 1905, he began to investigate the gas-absorbing powers of charcoal when cooled to low temperatures and applied his research to the creation of high vacuum, which was used for further experiments in atomic physics. Dewar continued his research work into the properties of elements at low temperatures, specifically low-temperature calorimetry, until the outbreak of World War I. The Royal Institution laboratories lost a number of staff to the war, and his research during and after the war mainly involved investigating surface tension in soap bubbles, reason for which the **ESAT 2024** has dedicated the ***Surfactants*** session to him.

Kenneth Denbigh (1911-2004)

Kenneth George Denbigh was a chemical engineer and scientific philosopher. He wrote much on the issue of time in relation to thermodynamics.

He was born in Luton and attended the University of Leeds graduating with a BSc in 1932. He then undertook his doctorate under Robert Whytlaw-Gray gaining a PhD in 1934. He worked for Imperial Chemical Industries (ICI) until 1938 when obtained a post of Lecturer in Chemistry at the University of Southampton. In the Second World War he was taken back into industry, as head of the laboratories for the Royal Ordnance Factory at Bridgwater. This led him into his first hands-on experience with practical issues concerning thermodynamics.

In 1948 he received a post lecturing at the Chemical Engineering Department at the University of Cambridge and this provided a stepping-stone to be Professor of Chemical Technology at the University of Edinburgh in 1955. This in turn took him to Imperial College, London in 1960. In 1966 his final move was to be principal of Queen Elizabeth College in London. The University of Edinburgh named the Kenneth Denbigh Building at King's Buildings in his honour. The School of Engineering of The University of Edinburgh awards the Kenneth Denbigh Medal in support of his scientific legacy. The Medal has been first established in 2023. Among his publications *The Thermodynamics of the Steady State* (1951), *Thermodynamics and the Sense of Time* (1953), *The Principles of Chemical Equilibrium* (1955), *Entropy in Relation to Incomplete Knowledge* (1985).

For his contributions to Chemical Engineering the **ESAT 2024** honors his memory with the Session on ***Adsorption***.

Venue

Located at the foot of Edinburgh's iconic extinct volcano, Arthur's Seat, the **John McIntyre Conference Centre** (JMCC) offers flexible state-of-the-art facilities.

Address: Pollock Halls, **18 Holyrood Park Rd**, Edinburgh EH16 5AY.

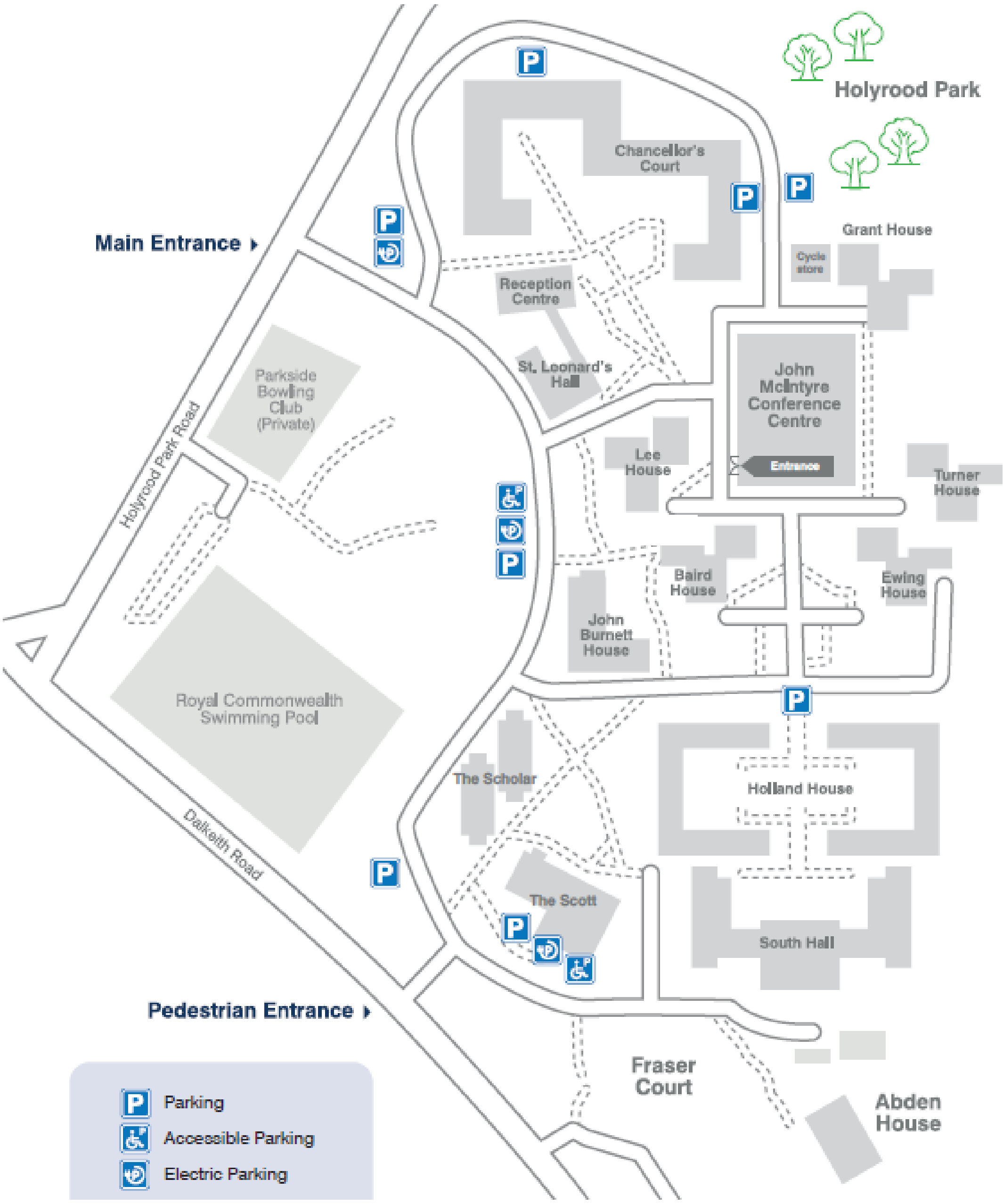
Conference contact: esat2024@ed.ac.uk

Registration: ESATregistration@ed.ac.uk

Pollock Halls E-mail: estates.helpdesk@ed.ac.uk

Pollock Halls Phone: 0044 0131 651 2189

Accessibility: https://www.accessable.co.uk/the-university-of-edinburgh/accommodation-residences/access-guides/pentland-west



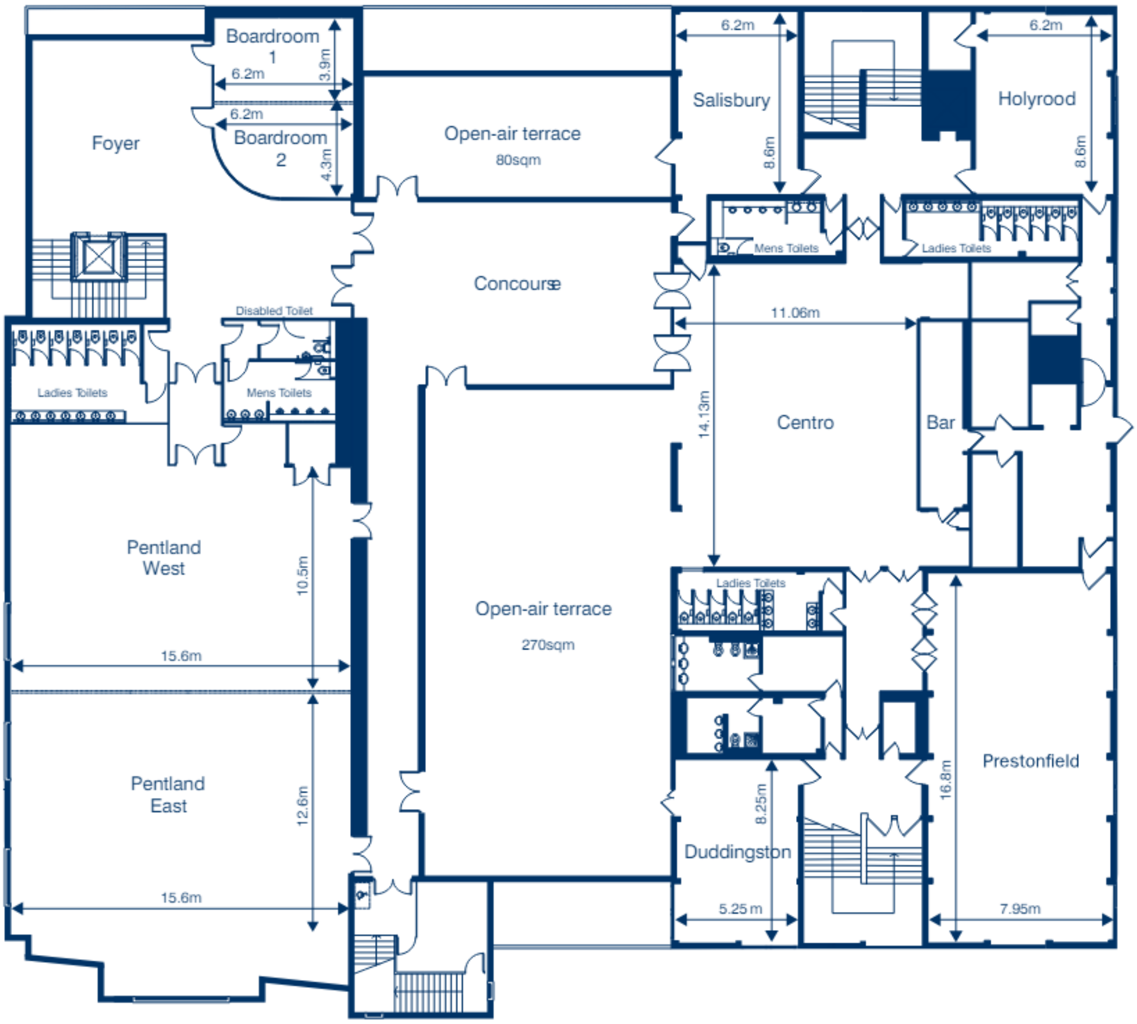
Hotels:

- Scholar Hotel https://www.uoecollection.com/hotels/the-scholar/
- Scott Hotel https://www.uoecollection.com/hotels/the-scott/
- Chancellors Court https://www.uoecollection.com/summer-stays-at-the-university-of-edinburgh/chancellors-court/

Catering options (meals during the Conference will be provided)

- Scholar Restaurant: Offers an informal evening à la carte service. https://www.uoecollection.com/hotels/the-scholar/the-brasserie-lounge-bar/
- JMCC Restaurant**:** Buffet. Breakfast: 07:30 - 10:00. Dinner: 18:00 – 20:00
- Arthur's Food & Drink: barista coffee, cookies, classic pub food and Crafty pizza alongside craft tap beers and a range of spirits, wines and seltzers. Monday – Sunday: 12:00-23:00. Serving food: 12:00-21:30

JMCC Floorplan



Programme

SCAN ME

Sunday Afternoon

Sunday 9 June		
15:00	18:00	**Registration**
18:00	18:15	Pentland Theatre **Conference Opening** Prof. Maria Eugénia **MACEDO**, ESAT International Steering Committee Chair, Prof. Maria Grazia **DE ANGELIS**, ESAT 2024 Chair
18:15	19:15	Pentland Theatre **Michael M. Michelsen Award Lecture** Sponsored by **Fluid Phase Equilibria** - an Elsevier Journal - Introduced by Prof. Ioannis **ECONOMOU** *Some insights on the development of equations of state over the past 30 years* Prof. Jean- Noel **JAUBERT** - Université de Lorraine - Michelsen Awardee 2024
19:15	21:00	**Centro-JM Conference Centre** **Welcome Reception**

Monday Morning

Monday 10 June Morning				
Plenary talks - Pentland Theatre				
Chairs: Ralf Dohrn, Sabine Enders				
08:30	09:15	*Atomistic and Mesoscopic Modeling of Structure-Property Relations in Polymers* Prof. Doros N. **THEODOROU**, National Technical Univ. of Athens, Greece		
09:15	10:00	*Exploiting active learning for porous material screening* Prof. Tina **DÜREN**, University of Bath, UK		
10:00	**10:30**	**Coffee Break**		
SESSIONS		**Carbon capture & Storage (CCS) I** **Chair: Sandra Kentish** *Pentland East*	**Adsorption (the Kenneth Denbigh's session)** **Chair: Tina Düren** *Prestonfield*	**Molecular design: membranes & interfaces** **Chair: Doros Theodorou** *Pentland West*
10:30	10:50	*Modelling the phase behaviour of fluid systems relevant for carbon-capture processes: the importance of SOx and NOx* Dr. Andrew **HASLAM**, Imperial College London, UK	**Keynote** - *On Adsorption Azeotropy and a Classification Based on the Dual Site Langmuir Isotherm* Prof. Stefano **BRANDANI**, Univ. of Edinburgh, UK	*Dynamically Switchable Monolayer Coatings: Improved Understanding of Group Contribution to Surface Tension* Nicholas **CRAVEN**, Vanderbilt Univ. USA
10:50	11:10	*A robust and efficient augmented free-water flash method for CO$_2$-water-hydrocarbon mixtures* Dr. Dan **NICHITA**, Univ. de Pau et des Pays de l'Adour, France		*Computational Design and Assessment of Mixed Matrix Membranes using Coarse-Grained Molecular Modeling* Dr. Amro **MOHAMED**, Texas A&M University at Qatar, Qatar
11:10	11:30	*Understanding the CO$_2$ Capture Performance of amine-functionalized Silica and Carbon-based materials Using Molecular Simulations* Prof. Lourdes **VEGA**, Khalifa Univ., UAE	*Predicting Adsorption with 3D classical Density Functional Theory based on PC-SAFT* Nadine **THIELE**, Univ. of Stuttgart, Germany	*Wetting, adsorption, and desorption behaviour of polymers on surfaces* Prof. Vasileios **KOUTSOS**, Univ. of Edinburgh, UK
11:30	11:50	*Integrating Theoretical Approaches for Profiling the Thermophysical Behavior of DESs in Greenhouse Gas Treatments* Dr. Fèlix **LLOVELL**, Univ. Rovira i Virgili, Spain	*Impact of Force Field Choice on Adsorption Predictions in MOF* Connaire **McCREADY**, University of Strathclyde, UK	*Decoding the Interplay Between Topology and Surface Charge in Graphene Oxide Membranes During Humidity Induced Swelling* Prof. Paola **CARBONE**, Univ. of Manchester, UK
11:50	12:00	Break		
SESSIONS		**Machine Learning I** **Chair: Erich Müller** *Pentland*	**Polymers I** **Chair: Michael Fischlschweiger** *Prestonfield*	**Equations of State (the Peter G. Tait Session)** **Chair: Ioannis Economou** *Pentland West*
12:00	12:20	*Improvement of diffusion coefficient prediction by active learning* Zeno **ROMERO,** RPTU Kaiserslautern, Germany	*Predicting Gas Solubilities in Semi-crystalline Branched Polyolefin Systems with the Lattice-Cluster-Theory-EoS* Simon **LEUBE**, KIT, Germany	*Can we hope for a revival of the equations of state by coupling the Peng-Robinson model and an uncharted activity-coefficient model?* Prof. Romain **PRIVAT**, Univ. de Lorraine, France
12:20	12:40	*Predicting solvation free energy in binary solvents using graph neural networks* Roel **LEENHOUTS**, KU Leuven, Belgium	*High throughput screening of polymers: properties prediction and structures discovery* Dr. Vittoria **FANTAUZZO**, Univ. of Liverpool, UK	*Decorrelating equation of state parameters with mixture data* Dr. Philipp **REHNER**, ETH Zurich, Switzerland
12:40	13:00	*Thermodynamic Modeling of Poorly Specified Mixtures using NMR Spectroscopy and Machine Learning* Dr. Thomas **SPECHT** , RPTU Kaiserslautern, Germany	*Thermodynamics characterization of CO$_2$ sorption in polymers for CO$_2$ transport applications* Virginia **SIGNORINI**, Univ. of Bologna, Italy	*Comparison of CP-PC-SAFT and CS-SAFT-VR-Mie in predicting fluid phase behavior in systems of phenolic compounds, aromatic amines, acetophenone and benzaldehyde* Prof. Ilya **POLISHUK**, Ariel Univ., Israel
13:00	**14:00**	**Lunch**		

Monday Afternoon

Monday 10 June Afternoon				
SESSIONS		**Carbon capture & Storage (CCS) II - (The Joseph Black's session)** **Chair: Lourdes Vega** *Pentland East*	**Molecular Design: Materials** - sponsored by the Henry Royce Institute **Chair: Eleonora Ricci** *Prestonfield*	**Phase equilibria I** **Chair: Catinca Secuianu** *Pentland West*
14:00	14:20	*Exploring Thermophysical Properties of Phosphonium-Based Ionic Liquids in CO_2 Capture Applications through a Multiscale Approach* Dr. Sabrina **RODRIGUEZ REARTES**, Univ. Rovira i Virgili, Spain	*From Chemical Drawing to Electronic Properties of Semiconducting Polymers in Bulk: A Tool for Chemical Discovery* Dr. Hesam **MAKKI**, University of Liverpool, UK	*Liquid-Liquid Equilibria of the Binary Systems Biodiesel/Glycerol and Biodiesel/Water* Dr. Giulio **SANTORI**, Univ. of Edinburgh, UK
14:20	14:40	*Enhanced Acid Gas Removal from Natural Gas Using Phase Change Amine Solvents* Soultana **TZIMA**, National Technical Univ. of Athens, Greece	*Thermodynamic of Phase Change Material Based on Stearic Acid with Graphene Nanoplatelets* Dr. Yolanda **SANCHEZ VICENTE**, Northumbria University, UK	*A Robust Setup for Efficient Characterization of Multicomponent Vapor-Liquid Equilibria Using Raman Spectroscopy -* Marvin **KASTERKE**, RWTH Aachen Univ., Germany
14:40	15:00	*Predictive Post-Combustion CO_2 Reactive Absorption Framework Combining Electrolyte Thermodynamics with Electronic Structure and Atomistic Simulation Methodologies* Prof. William **SMITH**, Univ. of Guelph, Canada	*Rational Design of Nanoparticle Surface Patterning for Directed Self-Assembly* Dr. Thi **VO**, Johns Hopkins University, USA	*Investigating the solute + solute interactions observed in ternary mixtures of CO_2 + (n-alkanes and/or methyl esters and/or 1-alcohols and/or carboxylic acids)* Prof. Cara **SCHWARZ**, Stellenbosch Univ., South Africa
15:00	15:20	*Enrichment at fluid interfaces and its impact on mass transfer at elevated pressures* Prof. Tim **ZEINER**, Graz Univ. of Technology, Austria	*Sticky-MARTINI – A Reactive Coarse-Grained Model for Self-Assembly in Materials Synthesis* Dr. Miguel **JORGE**, Univ. of Strathclyde, UK	*Analysis of the quality of published experimental and correlated binary and ternary VLE data. Proposal for an adequate planning of their experimental determination and correlation* Prof. Antonio **MARCILLA**, Univ. of Alicante, Spain
15:20	**15:50**	**Coffee Break**		
SESSIONS		**Transport properties (the Thomas Graham's Session)** **Chair: Amparo Galindo** *Pentland East*	**Polymers II** **Chair: Tim Zeiner** *Prestonfield*	**New refrigerants (the David Boyle's session)** **Chair: Romain Privat** *Pentland West*
15:50	16:10	*Generalised dissipative particle dynamics with coupled energy and mass transfers: A coarse-grain framework for simulations of thermodiffusion* Prof. Martin **LISAL**, Czech Academy of Sciences, Czech Republic	*A multi-scale modeling approach for the prediction of hydrogen transport properties in semi-crystalline polymers* Dr. Omar **ATIQ**, Univ. of Bologna, Italy	*The Role of 4E Analysis and Thermodynamic Modeling in the Rational Design of Low-GWP Refrigerants as Drop-in Replacements* Carlos **ALBÁ**, Univ. Rovira i Virgili, Spain
16:10	16:30	*Entropy Scaling for Thermal conductivity with critical Enhancement -* Julia **BURKHARDT**, Univ. of Stuttgart, Germany	*Thermomechanical Modeling of Microstructural Influences on Gas Solubility in Semi-crystalline Polyethylenes* Jana **ZIMMERMANN**, TU Clausthal, Germany	*A comprehensive approach to incorporating intermolecular dispersion into COSMO-RS model* Daria **GRIGORASH**, TU Denmark
16:30	16:50	*Application of the Significant Structure Theory for the Viscosity Modeling of Ionic Fluids* Dr. Ricardo **MACIAS-SALINAS**, ESIQIE - Instituto Politecnico Nacional, Mexico	*Molecular insight on Energetic Interactions and their Contribution to Diffusion of Small Molecules in Polyesters* Dr. Kseniya **PAPCHENKO**, Univ. of Edinburgh, UK	*Biomass-derived working fluids as sustainable alternatives to classical absorption refrigeration systems* Dr. Gabriel **ZARCA**, Univ. de Cantabria, Spain
16:50	17:00	Break		
17:00	18:30	**Poster session I** - Afternoon Tea		
18:30	20:00	Break		
20:00	23:30	**Scottish Ceilidh dances and musical entertainment, South Hall (onsite), with food platters and drinks. Music by the Reel Time Band, Drinks and Food Platters**		

Tuesday Morning

Tuesday 11 June Morning				
Plenary talks - Pentland Theatre				
Chairs: Maria Eugenia Macedo, Alex Victorov				
08:30	09:15	*Towards linking engineering workflows: Phase behavior, self-assembly, and fluctuations from thermodynamic perturbation theory and molecular simulation* Prof. Walter **CHAPMAN**, Rice University, USA		
09:15	10:00	*Applied Thermodynamics – Examples from Industrial Applications* Dr. Stephanie **PEPER**, Bayer AG, Germany		
10:00	10:30	**Coffee Break**		
SESSIONS		**Phase equilibria II** **Chair: Felix Llovell** *Pentland East*	**Electrochemical processes (the James Watt's session)** **Chair: Georgios Kontogeorgis** *Prestonfield*	**Surfactants (the James Dewar's session)** **Chair: Helena Passos** *Pentland West*
10:30	10:50	*A Comparison of the UNIFAC Model vs. Graph Neural Network-based Models for the Prediction of Binary Vapor-Liquid Equilibria* Egdar **SANCHEZ MEDINA**, Otto-von-Guericke Univ., Germany	**Keynote**-*Molecular Simulation of Supercapacitors* Prof. Peter **CUMMINGS**, Heriot-Watt Univ, UK	*Investigation of coalescence and Ostwald ripening of bubbles of varying sizes and distance using the Navier-Stokes-Korteweg approach* Christian **WACHSMANN**, Univ. of Innsbruck, Austria
10:50	11:10	*Thermodynamic modelling of the systems involved in TEG dehydration of Natural Gas* George **TASIOS**, National Technical Univ. of Athens, Greece		*Polarizable water models for dissipative particle dynamics simulations of micellar solutions* Dr. Rachel **HENDRIKSE**, Durham Univ. UK
11:10	11:30	*Vapor-Liquid Equilibria for Tri-ethylene glycol in high pressure methane: Experiments and Modelling* Prof. Sandra **KENTISH**, Univ. of Melbourne, Australia	*Alkali metal ion intercalation of molybdenite for enhanced* CO_2 *reduction* Eszter **MADAI**, Delft Univ. of Technology, NL	*Computer-Aided Molecular Design of Surfactants Using Classical Density Functional Theory* Pierre **WALKER**, California Institute of Technolgy, USA
11:30	11:50	*Phase Equilibria and Fluid Properties Modelling for a Hydrogen-based Economy* Dr. Antonio **QUEIMADA**, KBC, UK	*Exergy Based Conceptual Design of Hybrid Electrolyser Systems for PtX* Faisal **SEDEQI**, German Aerospace Centre (DLR), Germany	*Describing Hydrophobic Interactions Using Heterosegmented PC-SAFT – Application to Surfactants* Marius **ROTHER**, TU Dortmund, Germany
11:50	12:00	Break		
SESSIONS		**Polymers III** **Chair: Walter Chapman** *Pentland East*	**Machine Learning II (the James Clark Maxwell's session)** **Chair: Gabriele Sadowski** *Prestonfield*	**Electrolytes I - sponsored by IFPEN** **Chair: Christoph Held** *Pentland West*
12:00	12:20	*Direct shock simulations of several polymer melts* Claire **LEMARCHAND**, Université Paris-Saclay, France	*Coarse Grained Molecular Simulations of Polymers using Machine Learned Potentials* Dr. Eleonora **RICCI**, Univ. of Edinburgh, UK	*EleTher JIP: A quaternary system for investigating the effect of acid-base equilibria on volatilities* Dr.Jean-Charles **DE HEMPTINNE,** IFPEN, France
12:20	12:40	*Modeling Swelling and Drying in Electronic Encapsulation* Stefan **WAGNER**, Graz Univ. of Technology, Austria	*Differentiable Equations of State for Machine Learning Thermodynamic-Property Prediction* Michael **GADALOFF**, Imperial College London, UK	*Thermodynamics-assisted kinetic model for esterification reactions based on ePC-SAFT: Application to levulinic acid* Marcel **KLINKSIEK,** TU Dortmund, Germany
12:40	13:00	*Solubility of Organic Fluid Mixtures in Glassy Polymers* Lorenzo **MERLONGHI**, Univ. of Bologna, Italy	*Modeling Transport Properties of Aqueous Potassium Hydroxide with Machine Learning Molecular Force Fields* Dr. Jelle **LAGERWEIJ**, Delft Univ. of Technology, NL	*Ion-pairing in BiMSA ePPC-SAFT for aqueous and mixed-solvent alkali halide solution* Abtin **RAEISPOUR SHIRAZI**, IFPEN, France
13:00	**14:00**	**Lunch**		

Tuesday Afternoon

Tuesday 11 June Afternoon				
SESSIONS		**Phase equilibria III (the Lord Kelvin's session)** **Chair: Cara Schwarz** *Pentland East*	**New trends in Ionic liquids** **Chair: Sabine Enders** *Prestonfield*	**New models (the Robert Stirling's session)** **Chair: Eirini Karakatsani** *Pentland West*
14:00	14:20	*Phase equilibria of clathrate hydrates of carbon dioxide and different substrates-* Prof. Catinca **SECUIANU,** National Univ. of Science and Technology Politehnica Bucharest, Romania	*Acidic aqueous biphasic systems: a novel approach for recovering critical metals from e-waste* Prof. Helena **PASSOS**, Univ. of Porto, Portugal	*Multilayer Quasichemical Model of a Nonuniform Fluid Mixture that Contains Chainlike and Associating Species* Prof. Alexey **VICTOROV**, St. Petersburg State Univ., Russian Federation
14:20	14:40	*A general Gibbs free energy minimization algorithm for modelling solid-fluid equilibria involving miscible solids, pure solids, hydrates, and cocrystals* Wen Hwa **SIAH**, ARMINES Mines Paris - PSL,France	*Choline-Amino Acid Ionic Liquids: from synthesis to application in ATPS* Pedro **VELHO**, University of Porto, Portugal	*First-order perturbation theory using a short-range Lennard-Jones fluid reference* Dr.Andrij **TROKHYMCHUK,** Univ. of Ljubljana, Slovenia
14:40	15:00	*Solid-Liquid Equilibria of Selected Ternary Systems Containing Diphenyl Carbonate, Alcohol, Dialkyl Carbonate, and Phenol* Prof. Hiroyuki **MATSUDA**, Nihon University, Japan	*Eutectic solvents for fish skin valorization. From fundamentals to application* Cristina **GALLEGO,** Univ. de Santiago de Compostela, Spain	*A general method for calculating metastable fluid properties* Dr. Ailo **AASEN**, SINTEF Energy Research, Norway
15:00	15:20	*Tunable alkali-aluminosilicates geopolymers and composites as solid adsorbents for* CO_2 *capture applications* Prof. Matteo **MINELLI**, Univ. of Bologna, Italy	*Development of a hybrid platform for molecular design and selection of Ionic Liquids for* CO_2 *capture and conversion* Dr. Felipe **PERDOMO**, Univ. of Edinburgh, UK	*Cluster-Based Discrete Modeling Approach for Activity Coefficients of Molecular Liquids* Prof. Thomas **WALLEK**, Graz Univ. of Technology, Austria
15:20	**15:50**	**Coffee Break**		
SESSIONS		**Machine Learning II** **Chair: Joao Coutinho** *Pentland East*	**Molecular Design: porous & crystalline materials** **Chair: Matteo Minelli** *Prestonfield*	**Electrolytes II** **Chair: Jean-Charles de Hemptinne** Pentland West
15:50	16:10	*Estimating Gas Sorption in Polymeric Membranes from The Molecular Structure: A Machine Learning Based Group Contribution Method For The Non-Equilibrium Lattice Fluid Model (ML-GC-NELF)* Hasan **ISMAEEL** , Univ. of Edinburgh, UK	*In-silico approach to screen new nanoporous materials for urea capture from spent dialysate* Thomas **FABIANI**, Univ. of Edinburgh, UK	*Overview of the ERC project: "New Paradigm in Electrolyte Thermodynamics"* Prof. Georgios **KONTOGEORGIS**, TU Denmark
16:10	16:30	*Machine learning paradigm for parametrizing soft-SAFT molecular models for pure refrigerants* Dr. Ismail **ALKHATIB,** Khalifa Univ. of Science and Technology**,** UAE	*Designing selective nanoporous materials for VOC capture applied to breath diagnostics: insights from simulation and experiments* Dr.Scott **BOBBITT** , Sandia National Lab., USA	*Analysing Helmholtz energy contributions of model electrolyte systems using molecular simulations* Anja **REIMER**, Univ. of Stuttgart, Germany
16:30	16:50	*Neural Network-Based Tensor Completion: Advancing Predictions of Activity Coefficients and Beyond* Tobias **AVERBECK**, TU Dortmund, Germany	*On the formation of colloidal clathrates and diamond crystals-* Dr.Łukasz **BARAN**, Univ. Lublin, Poland	*Applying open COSMO-RS to Electrolyte Systems from Infinite Dilution to the Ionic Liquid State* Dr. Simon **MÜLLER**, TU Hamburg, Germany
16:50	17:00	Break		
17:00	18:30	**Poster session II**		
18:30	19:20	Break		
19:20	23:00	**Social Dinner, Playfair Library** **Knapp Poster Awards, sponsored by CCP5++**		

Wednesday Morning

Plenary Talks - Pentland Theatre			
Chairs: Ana Soto, Jean-Noel Jaubert			
08:30	09:15	*Measurement of Vapour Liquid Equilibrium Thermodynamic Properties Until the Critical Point and modelling* - Prof. Cristophe **COQUELET**, IMT Mines Albi, France	
09:15	10:00	*Utilizing the Molecular Simulation Design Framework (MoSDeF) to Screen Soft Matter Systems* Prof. Clare **McCABE**, Heriot-Watt University, UK	
10:00	10:30	**Coffee Break**	
SESSIONS		**Pharmaceutical applications** **Chair: Ilya Polishuk** *Prestonfield*	**Statistical Mechanics - Sponsored by the RSC** **Chair: Peter Cummings** *Pentland*
10:30	10:50	*Water in glassy carbohydrates: thermodynamic analysis and molecular dynamics simulations* Prof. Vitaly **KOCHERBITOV**, Malmö University, Sweden	***Keynote*** *- Computational Design of Peptides as Sensors and Drugs* Prof. Carol **HALL**, North Carolina State Univ., USA
10:50	11:10	*Influence of pH and Salts on the Solubilities of Active Pharmaceutical Ingredients* Espen **FRITSCHKA**, TU Dortmund, Germany	
11:10	11:30	*Prediction of API solubility: an overview of the recent developments of the SAFT-g Mie approach* Dr. Thomas **BERNET**, Imperial College London, UK	*Runaway Transition in Irreversible Polymer Condensation with Cyclisation* Dr. Maria **PANOUKIDOU**, Univ. of Edinburgh, UK
11:30	11:40	**Break**	
SESSIONS		**Water & aqueous solutions (the John Leslie's session)** **Chair: Giulio Santori** *Prestonfield*	**Phase Equilibria IV (the William Rankine's session)** **Chair: Clare McCabe** *Pentland*
11:40	12:00	*Prediction of water anomalous properties by introducing the two-state theory in SAFT* Dr. Nefeli **NOVAK**, TU Denmark	*Application of DFT calculations in the correlation of phase equilibria: estimating non-randomness factors* Prof. Eugénia A. **MACEDO,** Univ. de Porto, Portugal
12:00	12:20	*Maximizing solubilities in aqueous solutions* Prof. Joao **COUTINHO**, Univ. of Aveiro, Portugal	*MCA+PZ and MCA+AMP aqueous solutions:* CO_2 *solubility experiments and modelling* Dr. Fragkiskos **TZIRAKIS**, CeRTH, Greece
12:20	12:40	*The shape of water – how cluster formation explains the hydrophobic effect* Dr. Martin **ANDERSSON**, King Fahd Univ., Saudi Arabia	*Crystallization risk of aromatic compounds in LNG production: Part III: the solubility of o-xylene in methane-rich mixtures down to cryogenic temperatures* Dr. Salem **HOCEINI**, ARMINES MinesParis PSL, France
12:40	**13:00**	**Conclusive remarks, PPEPPD 2025 and ESAT 2026**	
13:00	**14:00**	**Lunch**	

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Oral Presentations

Some insights on the development of equations of state over the past 30 years

Jean-Noël Jaubert, Université de Lorraine, Nancy, France

Equations of state (EoS) are one of the most commonly used tools in chemical and process engineering due to their capacity of predicting thermodynamic properties of pure compounds and mixtures at any given state.

To be used by industry, an EoS must however satisfy various criteria:

- the method used to derive the compound-specific parameters needs to follow an entirely transparent and universal protocol
- the numerical inputs for each pure component have to be readily available
- Parameter databases must exist.
- Their performance must have been evaluated on multiple data sets.
- Complex mixtures must be accurately correlated.

However, in order to properly correlate binary systems, an EoS must be able to accurately represent the pure-compound properties first. This is the reason why it was decided to build a database containing over 300,000 pseudo-experimental data points for pure components. In the first part of this presentation, devoted to pure-components, it was decided to focus on 3 EoS that include a cubic and two molecular-based equations that are: the PC-SAFT, the *Industrialized*-PC-SAFT (I-PC-SAFT) and the *translated-consistent*-Peng-Robinson (*tc*-PR) EoS. It was decided to evaluate the capabilities, strengths and weaknesses of these models in their most basic form, i.e., without adding an associating term. The influence of the parameterization on the accuracy of the different EoS will be discussed in details.

A second part of the presentation is devoted to the correlation of binary systems with a cubic EoS, and more particularly, it is proposed to revisit the ways used to derive the advanced EoS/g^E mixing rules at infinite and zero reference pressure. In particular, we conclude that: Equating the complete expression of g^E stemming from the cubic EoS to the same quantity from an external activity coefficient model is always inconsistent. Only the residual parts of the excess Gibbs energies can be consistently compared. Using the previous result, it becomes possible to revisit the derivations of the HV and MHV mixing rules; this led us to claim that these 2 mixing rules lead actually to a unique mixing rule. Results obtained with the *tc*-PR EoS coupled with the Wilson g^E model for complex systems are shown.

Atomistic and Mesoscopic Modeling of Structure-Property Relations in Polymers

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Molecular-based approaches for understanding and tailoring structure-property- processing relations in materials, based on the fundamental principles of quantum and statistical mechanics, have gained ground in academic research and industrial practice. The broad spectra of length and time scales governing structure and dynamics in real-life materials have demanded the advancement of multiscale modeling strategies, involving several levels of representation, to bridge atomistic constitution and interactions with macroscopic properties.

We will discuss three examples of molecular modeling of structure-property relations in polymeric materials: (a) prediction of linear and nonlinear rheological properties of high-molecular weight polymer melts, such as polyethylene and cis-1,4 polyisoprene, through hybrid particle-field mesoscopic simulations employing slip-springs to represent entanglements and parameterized on the basis of atomistic calculations1),2); (b) tracking structural relaxation in polymer glasses, such as polystyrene, as a sequence of elementary transitions between basins on their energy hypersurface, with transition rate constants computed from atomistic infrequent-event analysis3); (c) quantifying the morphology developing upon crystallization of polyethylene films formed from the melt through the Machine Direction Orientation process. In each example we will outline how scale-hopping algorithms can be devised, based on rigorous statistical mechanical principles, to meet the challenges of long time and length scales in polymers in a computationally tractable way. The computational results lead to property predictions that are validated by available experimental measurements and elucidate molecular-level processes that are critical to materials design.

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Exploiting active learning for porous material screening

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With a sheer infinite number of hypothetical and already synthesised MOFs and COFs to choose from, molecular simulations combined with machine learning are invaluable for identifying promising candidates for applications such as gas storage or advanced separations. They are significantly cheaper than experimental synthetic approaches, allowing many materials to be assessed in quick succession. Numerous large-scale screenings of porous materials have been conducted, assessing the performance of hundreds of thousands of structures. However, they can lack accuracy, often relying on finding a compromise between computational costs and calculating the property of interest for all structures precisely as traditional machine learning approaches rely on large training sets.

Combining Bayesian optimisation and molecular simulation we have developed a new approach, which we call the Autonomous Materials Investigator (AMI), which allows us to identify the top performing materials of a database without having to calculate the property of interest for 10,000s of individual structures. One of the core attractions of this new methodology is that our model can make recommendations based on limited information, updating itself in-situ from molecular simulation of performance for a given application. For example, the AMI identifies 90 of the top 100 performing structures from 69,480 hCOF structures with less than 500 calculations for methane storage. This performance allows us to perform screening for more computationally expensive applications involving more complex guest molecules. Moreover, our method can also integrate experimental inputs in addition to simulations to allow for further aspects of the materials to be considered during screening or be adapted to assess materials for materials performance targets beyond adsorption.

Modelling the phase behaviour of fluid systems relevant for carbon-capture processes: the importance of SO_x and NO_x

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The fluid phase equilibria of carbon dioxide in aqueous carbon-capture solvents, such as monoethanolamine and other more-sophisticated solvents, have been studied in depth over recent years. However, real flue-gas streams contain impurities, such as SO_x and NO_x; these can adversely affect carbon-capture plant as well as influencing the phase equilibria. The development of a modelling capability to assess the impact of these impurities on the thermodynamics of these fluid systems is a necessary precursor to the design and operation of successful carbon-capture infrastructure. Here, using the state-of-the-art group-contribution SAFT-γ Mie equation of state, working within the framework of HiRECORD, a “world’s-first” project to demonstrate a 10t/d CO_2 capture plant using Rotating-Packed-Bed absorber and desorber with a bespoke designer solvent, we embark on the first step of this task via the development of models for sulphur dioxide (SO_2), nitrogen (II) oxide and nitrogen (IV) oxide, three of the more-important SO_x and NO_x in this context. The nature of each of these fluids presents challenges to modelling. For example, the behaviour of SO_2 is strongly influenced by the large dipole and quadrupole moments. Moreover, each of NO and NO_2 are free radicals; the octet rule is not fulfilled for the nitrogen in either of these molecules, providing a driving force for dimerization and resulting in both nitrogen (II) oxide and nitrogen (IV) oxide comprising mixtures of two NO_x: NO + N_2O_2, and NO_2 + N_2O_4 (respectively); this chemistry introduces interesting subtleties in the model development. We examine the impact of these SO_x and NO_x impurities on the phase equilibria of mixtures relevant for carbon capture. The facility of SAFT-γ Mie to incorporate intermolecular association renders it an ideal tool to address these challenges.

A robust and efficient augmented free-water flash method for CO2-water-hydrocarbon mixtures

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There is a significant demand for CO2 storage in depleted hydrocarbon reservoirs, as an effort to reduce the amount of CO2 in the atmosphere. Three-phase equilibrium calculations for water-CO2-hydrocarbon mixtures are required in the compositional simulation of such applications. The very low solubility of hydrocarbon components in water leads to a special mathematical structure of the problem. Several techniques were suggested, such as the free-water flash (FWF) and the augmented the free-water flash (AFWF); in the former, the aqueous phase is pure water, while in the latter only certain components, CO2 and methane for example, are dissolved in the aqueous phase. In this work, a robust and efficient AFWF method is proposed, using hybrid successive substitutions-modified Newton iterations and a new sequential phase stability-flash strategy. A detailed description of second-order methods in a Gibbs energy minimization framework for AFWF is presented here for the first time, for several choices of the independent variables, including the negative flash option. In the AFWF, the dimension of the problem and the number of function evaluations (thus the computation time) are significantly reduced. Moreover, it is mathematically proven that the augmented method always has better convergence properties than its conventional multiphase flash counterpart, in both first- and second-order methods. The new AFWF method is tested for various hydrocarbon-water-CO2 mixtures and proved to be highly robust and efficient, systematically outperforming the conventional approach. Unlike in previous AFWF formulations, the number of components soluble in water is not limited, leading to an accuracy extremely close to that of a full three-phase equilibrium, even at high pressures or large amounts of CO2. The proposed method is not model-dependent (any EoS can be used to describe the equilibrium phases). Finally, application of the new AFWF method to a variety of phase equilibrium problems, such as solid phase precipitation, presence of mercury, asphaltenes, gas hydrates, etc. is discussed.

Understanding the CO_2 Capture Performance of amine-functionalized Silica and Carbon-based materials Using Molecular Simulations

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Amine-based absorption process, the most used technology nowadays to capture CO_2 and the only one applied at a large scale, has disadvantages such as high regeneration energy, corrosion, and degradation risks [1]. Adsorbents (*i.e.*, solid materials) have been explored as alternative, as they avoid the above-mentioned drawbacks by eliminating the liquid phase. Nevertheless, the adsorption process is often limited by poor performance at low CO_2 partial pressures. In this regard, silica and carbon-based adsorbents have been studied due to their thermally and mechanically robust, as well as providing a wide variety of pore sizes and geometries. Such structures also possess the advantage of being functionalized by relatively simple processes with molecules that can tightly bind with carbon dioxide (*i.e.*, chemisorption). Hence, in this contribution, we apply Molecular Dynamics and Monte Carlo simulation techniques to study the CO_2 physisorption and predict the chemisorption performance by analyzing the accessibility and orientation of amine chains inside different hierarchical structures (including both micro and mesopores) such as MCM-41 and zeolite templated carbons. Functionalization includes primary monoamines and diamines, with simulation results in good agreement with experimental CO_2/N ratios [2],[3].

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Integrating Theoretical Approaches for Profiling the Thermophysical Behavior of DESs in Greenhouse Gas Treatments

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The study of Deep Eutectic Solvents (DES) has become a fascinating field of study, given the numerous applications that these mixtures may pontentially have. The key of the tunability of DESs is based on the possibility to modify the hydrogen bond donor and hydrogen bond acceptor compounds, providing a versatility similar to that of Ionic Liquids. However, the hydrogen bonding network may be affected by the presence of water and other cosolvents, strongly affecting their thermophysical properties and future performance in a particular process.

This contribution presents a practical approach to characterize the thermophysical properties of DESs within the context of greenhouse gas capture applications. The core of the process is the use of the soft-SAFT equation of state, in combination of other theoretical approaches of different nature. Turbomole-COSMO is utilized to perform a charge distribution analysis to identify the predominant number of hydrogen bonds. An artificial neural network uses this information to predict the viscosity of DESs. In parallel, soft-SAFT is employed to provide a simple yet robust coarse grained model, where DES is treated as a mixture, to describe the density, derivative properties and activity coefficients of aqueous DESs [1], as well as the solubility of CO_2 and fluorinated refrigerants. The impact of variables such as pressure, temperature, and structural characteristics of the DES (e.g., type of HBA, HBD, number of fluorine atoms) is briefly discussed [2]. This approach enables a swift screening process to pinpoint optimal conditions for specific gas capture applications.

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On Adsorption Azeotropy and a Classification Based on the Dual Site Langmuir Isotherm

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Adsorption azeotropy is a phenomenon that has been known for nearly a century, often associated with the crossing of the pure component isotherms, yet few properties have been formally proven. Four general properties of adsorption azeotropy in porous materials are shown to apply irrespective of the isotherm, including the fact that there is always a lower bound on the pressure at which an azeotrope may be present. It is possible to demonstrate that molecules of different size will most likely lead to adsorption azeotropy, albeit possibly at very high pressures.

This study will consider in detail the thermodynamically consistent dual site Langmuir model which requires equal saturation capacities of all absorbates and therefore azeotropy is solely the result of the heterogeneity of the adsorbent without entropic effects. Six categories of adsorption azeotropes, which can be grouped into three pairs of mirror cases, are formally identified for this model. Dimensionless ratios allow to determine formally each category and the analysis also includes a discussion of the crossing of the pure component isotherms. The heterogeneity of the adsorbent is shown to allow all known types of adsorption azeotropes without local nonideality. This includes azeotropes that can have an upper bound on pressure; that can occur even if the pure component isotherms do not cross; and can be present below the pressure at which the pure component isotherms cross.

Finally, the analysis allows to identify also the ranges of parameters for which the pure component isotherms cross but an azeotrope is not present.

Predicting Adsorption with 3D classical Density Functional Theory based on PC-SAFT

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Classical density functional theory (DFT) is a powerful tool for investigating interfacial properties on molecular length scales, such as the adsorption of fluid molecules in porous media. Intermolecular force fields can model the intermolecular interactions between the fluid molecules and the solid porous media structure. This allows the systematic optimization of porous media for specific applications.

In this work, we employ 3D-DFT in combination with Helmholtz energy functionals based on the Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) equation of state [1] implemented in the FeOs framework [2] to predict adsorption isotherms for pure substances and binary mixtures and compare them with molecular simulation data. We use the computed adsorption isotherms to assess and optimize adsorption processes. Our focus is on the numerical aspects and computational performance of classical DFT computations in three dimensions.

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Impact of Force Field Choice on Adsorption Predictions in MOFs

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Grand-Canonical Monte Carlo (GCMC) simulations are playing an increasingly important role in screening and designing Metal-Organic Frameworks (MOFs) for gas separation. However, GCMC predictions rely heavily on the accuracy of the underlying force field. Often, force field parameters are taken "off the shelf" from the literature, with little or no validation and testing, and there has been no systematic assessment of the effect of force field choice on the accuracy of the results. In this work, we fill this gap by systematically investigating the effect of varying different force field parameters on adsorption isotherm predictions in a series of prototypical materials that represent the most widely studied MOF "families". Using this information, we compute an adsorption "master curve" from simulations and compare it against a manually curated set of experimental data from the NIST Adsorption Database[1] and from a comprehensive literature survey on the target MOFs. By considering a large number of experimental isotherms measured by different groups and eliminating outliers in the data using statistical analysis, we can reliably quantify the associated uncertainty. Our results show that: 1) the uncertainty in both experimental and simulated isotherms can be quite large (~20%) and depends on the particular system under study; 2) the standard approach of comparing simulation predictions to a single experimental data set is flawed, as it does not account for the above uncertainty; 3) standard force fields can provide reliable predictions for some systems but can fail dramatically for others; 4) the choice of point charges can cause quite significant variations in predicted isotherms and this is more pronounced as the polarity of the adsorbate increases[2]. Our results question the widely held assumption that good performance for a particular gas/MOF pair implies accurate predictions over a wide range of systems.

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Dynamically Switchable Monolayer Coatings: Improved Understanding of Group Contribution to Surface Tension

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Monolayer films are well recognized as a tool to control surface tension through modification of the film chemistry.[1] Efforts have been made to design films that are responsive to external media, such as different solvents or pH.[2,3] However, these films are typically prohibitively slow in their response. Monolayer coatings capable of molecular level structural changes, or surface switchability, are a way to offer immediate levels of responsiveness. Using molecular dynamics simulations, we study the effects that surface switching has on interfacial tension for such coatings under a variety of different environments. Using the MoSDeF[4] toolkit realistic configurations for a wide range of molecular monolayers (~7-13 carbons) have been studied. An array of chemical terminal groups that exhibit complex structural changes in response to changing solvent are examined and the relationship between the interface switching, chemistry, and environment detailed. Silane monolayers with a similar chemically heterogeneous surface composition were also synthesized to evaluate experimentally these structural changes under exposure to different solvents. The nature of the relationship between chemistry and interface structure provides a better understanding of the interdependence that these components have on resultant surface properties and demonstrates exciting ways this understanding can be used to identify other surfaces with dynamic properties.

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Computational Design and Assessment of Mixed Matrix Membranes using Coarse-Grained Molecular Modeling

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Mixed Matrix Membranes (MMMs) consist of a paradigm shift in the realm of gas separation, representing a synergistic combination of the advantageous attributes of both polymeric and inorganic membranes. These innovative membranes not only offer superior separation efficiency but also retain the processability characteristic of polymeric counterparts. The integration of two distinct entities – the filler and the polymer – within MMMs gives rise to specific interactions, a subject that has garnered considerable attention in both experimental and computational studies.

In this project, we delve into the intricate surface interactions between ZIF-8 and 6FDA-DAM polyimide within an MMM framework, employing molecular simulations for an in-depth analysis. Our approach utilizes two coarse-grained (CG) models developed by our team, facilitating the preparation of the MMM system at a CG scale. These CG models were evaluated initially to determine physicochemical properties and to assess gas separation capabilities. Through this methodology, one can examine large-scale systems and introduce ZIF-8 nanoparticles within the polymeric matrix, a task not easily achievable with atomistic-scale models.

Our investigation encompasses a comprehensive assessment of various properties, including interaction energy, structural characteristics of the filler and polymer in the MMM, and other relevant parameters. Among the key findings are the impact of nanoparticle size and weight composition of the filler, as well as the identification of an optimal size of the filler nanoparticle for maximizing the mechanical properties of the MMM system. In all cases, comparison with available experimental data reveals excellent accuracy of the model. This study serves as a crucial milestone in advancing our understanding of composite materials, particularly in the context of gas separation using MMMs. The employment of large-scale systems through CG models has enabled us to model substantial defects and spatial disorder within ZIF nanoparticles, aspects previously beyond the reach of detailed atomistic simulations. This development paves the way for a deeper comprehension of the mechanics in MMM systems, thereby contributing to the field of material science and engineering.

Wetting, adsorption, and desorption behaviour of polymers on surfaces

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Polymer interactions with surfaces play a significant role in many applications ranging from polymer composites and nanocomposites where macromolecules are in contact with fibres, fillers, and additives to tribology and adhesion where the polymeric products need to perform well in close proximity with a solid surface.

Atomic force microscopy (AFM) and Monte Carlo simulations were used to study the behaviour of polymers on surfaces [1, 2, 3]. The phenomena studied include the differences in the nanoscale wetting behaviour when different substrates were used and the increased elastic modulus of polymer nanodroplets due to surface 'pinning' [4]. Single polymer chain droplets were observed to lie flatter and wet the substrate more than chemically identical multi-chain droplets of the same size (same total number of monomers), which attain a more globular shape and wet the substrate less. Monte Carlo simulations revealed the conformational behaviour of the polymer chains within the droplets. The adsorption statistics showed that isolated chains exhibit a monotonic adsorption fraction trend with chain length, while chains in multi-chain droplets modify (decrease or increase) their adsorbed fraction with chain length depending on their population. This mode of internal chain adsorption allows the droplet as a whole to arrange the chains at the droplet–substrate interface in the most thermodynamically preferable way. Furthermore, it leads to significant differences in the wetting behaviour: In agreement with the AFM observations, single polymer chain droplets were found to lie flatter and wet the substrate more than chemically identical multi-chain droplets of the same size (same total number of monomers), which attain a more globular shape and wet the substrate less.

Furthermore, the desorption force of poly(styrene-co-butadiene) random copolymer thin films on mica, silicon, and graphite substrates is quantified at the single polymer chain level by performing a systematic study with atomic force microscopy (AFM) force-distance curves [5]. The results reveal the single-chain polymer-polymer and polymer-substrate interaction contributions allowing a detailed discussion of single-chain pull-out and desorption phenomena from their films on different substrates. Chain pull-out events were found to be dominated by surface energy contributions. The polymer desorption force was strongest on the graphite substrate and weakest on the mica. The single-chain adhesion and friction effects are discussed in terms of scaling theory. It is shown that AFM force-distance curves can provide information regarding the structure of the thin film and in addition, also elucidate the interactions of natural rubber with carbon black in aqueous media [6]. The implications of these studies on rubber processing and manufacturing will be discussed

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Decoding the Interplay Between Topology and Surface Charge in Graphene Oxide Membranes During Humidity Induced Swelling

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Graphene oxide (GO) membranes are known to have a complex morphology that depends on the graphene flake degree of oxidation and the membrane preparation technique. In this study, using Grand Canonical Monte Carlo simulations we investigate the mechanism of swelling of GO membranes exposed to different relative humidity (RH) values and show how this is intimately related to the graphene surface chemistry. We show that the structure of the GO membrane changes while the membrane adsorbs water from the environment and that graphene oxide flakes become charged as the membrane is loaded with water and swells. A detailed comparison between simulation and experimental adsorption data, reveals that the flake surface charge drives the water adsorption mechanism at low RH when the membrane topology is still disordered, and the internal pores are small and asymmetric. As the membrane is exposed to higher RH (80%) the flake acquires more surface charge as more oxide groups deprotonate, and the pores grow in size yet maintaining their disordered geometry. Only for very high relative humidity (98%) the membrane undergoes structural changes. At this level of humidity, the pores in the membrane become slit-like but the flake surface charge remains constant. Our results unveil a very complex mechanism of swelling and show that a single molecular model cannot fully capture the ever-changing chemistry and morphology of the membrane as it swells. Our computational procedure provides the first atomic resolved insight into the GO membrane structure of experimental samples.

Improvement of diffusion coefficient prediction by active learning

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Information on the diffusion coefficients in mixtures is essential in chemical engineering, e.g., for modelling transport phenomena and simulating thermal separation processes. Unfortunately, experimental data are extremely scarce; thus, models for the prediction of diffusion coefficients in mixtures are paramount in practice. However, their training also requires a sufficiently large database. Pulsed-field gradient (PFG) nuclear magnetic resonance (NMR) spectroscopy is a highly interesting technique for measuring diffusion coefficients, which is only rarely used in engineering. We have recently applied this technique for measuring diffusion coefficients at infinite dilution and have shown that it efficiently yields data with high accuracy [1,2]. Furthermore, in a recent work [3], we have demonstrated that matrix completion methods (MCM) from machine learning are well suited for the prediction of diffusion coefficients at infinite dilution in binary mixtures and provide more accurate results than established semi-empirical models. However, these data-driven MCM suffer from the small data sets that are available for their training.

In the present work, we substantially extended the experimental data base of self-diffusion coefficients in binary liquid mixtures by PFG NMR measurements at temperatures between 298 K and 333 K. These measurements were planned by applying established strategies from active learning (AL), namely by performing those experiments, for which the new data are expected to provide the largest increase of the prediction accuracy; as selection strategy, uncertainty sampling was used in this work. In a stepwise procedure, the new data were used for retraining a hybrid MCM for the prediction of diffusion coefficients [3]. The model performance was evaluated at each step and the results demonstrate that the prediction accuracy can be improved substantially with comparatively small experimental effort using active learning strategies.

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Predicting solvation free energy in binary solvents using graph neural networks

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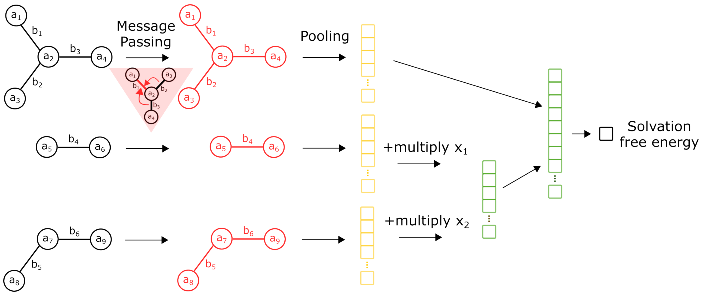
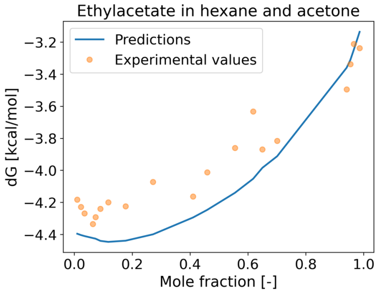
Solvation free energy of active pharmaceutical ingredients (API) is an important property for organic synthesis and industrial chemistry. Machine learning has been used to predict solvation free energies in organic solvents with great success, however only monosolvents have been considered so far [1]. During process development, mixtures of solvents can offer a greater chemical diversity than monosolvents. In this work, a message passing neural network architecture for the prediction of solvation free energies in solvent mixtures is proposed. This invariant architecture enables prediction of trends in solvation free energies for binary solvents, whilst learning from monosolvent data.





As part of this work a QM dataset is constructed containing one million solvation free energies from COSMO-RS in binary solvents. The machine learning model is trained on QM data for binary- and monosolvents and fine-tuned on monosolvent experimental data to achieve experimental accuracy. Finally, the model is validated on a dataset of experimental solvation free energies in binary solvents. A RMSE of 0.42 (kcal/mol) and MAE of 0.34 (kcal/mol) is achieved, comparable to monosolvent predictions. Additionally, the ability to predict trends for varying mole fractions at different temperatures is validated. Enabling the application of transfer learning to mixtures of a varying number of molecules can be an important help for problems where data availability is an issue. During the design of a solvent extraction unit, the constructed models can be beneficial.

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Thermodynamic Modeling of Poorly Specified Mixtures using NMR Spectroscopy and Machine Learning

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Mixtures of unknown or incompletely known composition, i.e., poorly specified mixtures, are a common challenge in chemical engineering since their properties cannot be described with classical thermodynamic models, which require a complete specification. In this work, we present a framework for dealing with such mixtures in process design and optimization, which does not require elaborate component elucidation. In the first step, fingerprints consisting of qualitative and quantitative information on the structural groups of the mixtures are recorded. NMR spectroscopy is used for this purpose, and a support vector classification from machine learning (ML) is employed for an automated analysis [1, 2]. In the second step, the obtained group-specific information is combined with results from pulsed-field gradient (PFG) NMR experiments, which enables the determination of self-diffusion coefficients and, thereby, the automated meaningful definition of pseudo-components with ML clustering algorithms [3]. Finally, the resulting characterization of the poorly specified mixture is combined with thermodynamic group-contribution G^{E} models and equations of state to predict fluid properties [3]. The approach's applicability is demonstrated by studying a variety of poorly specified mixtures: on the one hand, by considering them as unknown solvents and predicting gas solubilities, and, on the other hand, by considering them as unknown feed mixtures and simulating different thermal separation processes, including liquid-liquid extraction and distillation [4]. Excellent agreement of the predictions with results for the fully specified cases is obtained, even if mobile low-field benchtop NMR devices are used.

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Predicting Gas Solubilities in Semi-crystalline Branched Polyolefin Systems with the Lattice-Cluster-Theory-EoS

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The solubility of gases in polymers plays an important role in production and processing, e.g. for unreacted monomers and comonomers after polymerization, which are sorbed in the polymer particles just produced, changing the product properties.

The gas solubility depends on the semicrystallinity as well as on the degree of branching, where the gas solubility decreases with an increasing degree of crystallinity for linear polymers. The impact of the degree of branching is more complex because the degree of branching has also an influence on the degree of crystallinity.

Whereas the impact of the degree of crystallinity can be modeled with an equation of state, for instance, the Sanchez-Lacombe-Equation of State (SL-EoS) [1], using the so-called eigen-pressure [2], the impact of the degree of branching could not be modeled. The eigen-pressure represents the intrinsic stress acting from the crystalline to the amorphous phase, which was used by Minelli and de Angelis [2] as an adjustable parameter. Fischlschweiger et al. [3] derived an analytical expression for the eigen-pressure based on continuum mechanics allowing the prediction of this eigen-pressure.

A new method will be introduced to predict the degree of crystallinity as a function of the degree of branching. The basic idea is the extension of the so-called car parking problem [4] by the theory by Flory [5] describing the crystallization of copolymers. For the development of a theory for the description of the gas solubility of semicrystalline and branched polymers, the SL-EoS is replaced by the Lattice Cluster Theory in his compressible version, originally developed by Dudowicz et al. [6] and reformulated by Langenbach et al. [7]. The Lattice Cluster Theory allows the incorporation of the branching a priori without additional adjustable parameters.

The new theoretical framework for the calculation of the gas solubility in semicrystalline and branched polyolefins is validated by comparison to experimental data taken from the literature [e.g. 8] and used for model calculations to analyze in detail the gas solubility in polyethylene as a function of the degree of branching and the degree of crystallinity.

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High throughput screening of polymers: properties prediction and structures discovery

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High-throughput screening of polymers is proposed to address the imbalance between that vast number of polymers that are synthesised for a variety of applications and the much smaller numbers of polymers that can be subject of atomistic computational studies.

While experimental high throughput studies seem to have advanced rapidly, the computational counterpart is still not as efficient. The aim of this work is to create an automatic workflow that allows to study extensive libraries of polymers as quickly and efficiently as possible.

This workflow uses a readily available python toolkit (Polymer Structure Predictor, PSP[1]) to generate the structures of the oligomer starting from their SMILEs.

The force-fields are then produced using a local version of LigParGen[2], which converts the structures of said oligomers into GROMACS[3] input files.

Our python toolkit executes a double annealing of the polymers and automatically produces sanity checks for the calculations.

We have started testing the workflow with a library of polyolefins. The advantage of performing calculations on extensive libraries of polymers is being able, as a following step, to discover new compounds and predict their properties.

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Thermodynamics characterization of CO_2 sorption in polymers for CO_2 transport applications

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Carbon Capture and Storage (CCS) is one of the most viable solutions to limit the CO_2 release in the atmosphere aiming to reach net-zero CO_2 emissions, and thus, to prevent global warming. In the CCS value chain, pipelines and ships represent the unique solution to transfer the liquefied carbon dioxide from the captured emission point to the storage site. To increase transport efficiency, CO_2 must be compressed and transported as a liquid or supercritical fluid, conditions that might affect the performance of the materials employed. Polymers may be used as gaskets and sealants, or as liners for the protection of metal gas transport equipment due to their excellent thermal, chemical, and mechanical resistance to harsh environments.

To this purpose, an extensive experimental characterization is performed on different commercial polymers (either thermoplastic and elastomers) at different temperatures, to better understand the effects of pressurized-CO_2 on polymers, coupled with the modeling description of the results by thermodynamic equation of state approach (Lattice Fluid/NELF EoS).

Moreover, the CO_2 transport in supercritical phase must account for the solubility behavior of the penetrant and the changes in the diffusion coefficient with concentration, function of the kinetic mobility coefficient and the thermodynamic factor. In this concern, the Standard Transport Model (STM) has proved to be very reliable in the description of gas permeability behavior as a function of pressure and solubility. That allows to comprehend the penetrant-polymer interaction, together with the effect of dense phase CO_2 on polymer-based materials, as well as to predict the molecular behavior of these commercial polymers in the desired operating conditions: low temperature, high pressure, and presence of contaminants even in cryogenic environments.

Synergy in this approach is a unique perspective for understanding the compatibility between supercritical CO_2 and polymers in view of their future use in CCS industrial applications.

Can we hope for a revival of the equations of state by coupling the Peng-Robinson model and an uncharted activity-coefficient model?

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The Wilson equation

60 years ago, Grant Wilson proposed the first successful activity coefficient model based on the local composition concept he introduced. It has not dominated the chemical engineering practice compared to models proposed a few years after (NRTL and UNIQUAC) possibly because of an important shortcoming. The Wilson equation could never represent liquid-liquid equilibria whatever the values of the model's parameters. While this is well-known, the "physical" reasons for this deficiency have not been fully explored. In this study, we present and explore the mystery of the Wilson equation related in terms of its ability to predict partial miscibility. We show how it can be modified to produce liquid-liquid phase separation.

Coupling the Wilson model and a cubic equation of state: which mixing rule should we use?

To build a cubic model for mixtures, we started with a cubic model for pure species, namely, the tc-PR (translated and consistent Peng-Robinson) cubic EoS which is the most accurate cubic EoS ever developed in terms of vapor pressure, liquid density and liquid heat capacity estimation.

In a second step, based on the works of Huron-Vidal and Michelsen on mixing rules, we derived *theoretically sound* mixing rules, paying particular attention to the description of the combinatorial and residual contributions separately. The tc-PR EoS and the Wilson activity coefficient model were then coupled using the proposed mixing rules. While the Wilson model was (almost) never been considered before for such a coupling, because it was suspected that it would prevent the global model from predicting unstable liquid phases, we show here that this suspicion is incorrect: the tc-PR Wilson model can correlate liquid-liquid equilibria in general with a high degree of accuracy.

Finally, the parametrization of the tc-PR Wilson is discussed and its potential and performance are illustrated over 200 binary systems containing from non-associating / non-polar to associating / polar compounds.

Decorrelating equation of state parameters with mixture data

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Molecular equations of state provide properties and phase equilibria for a broad range of fluids relevant to the chemical industry. Popular examples are the statistical associating fluid theory (SAFT) and its derivatives [1]. Molecular equations of state distinguish themselves from simpler cubic equations by state explicitly incorporating intermolecular interactions. Dispersive attraction, multipolar interactions, and hydrogen bonding each contribute to the overall Helmholtz energy and, thus, to the properties of the fluid. However, more contributions to the Helmholtz energy, in general, add new model parameters. Usually, the model parameters are adjusted to pure-component properties like vapor pressures and liquid densities. The additional parameters can render the optimization underdetermined with different combinations of parameters delivering similar accuracies in the description of pure components [2].

At the same time, the pure-component parameters often need to be amended with adjusted binary interaction parameters [3] to quantitatively describe mixtures. However, even for common components, experimental data is publicly available only for a fraction of all possible binary mixtures.

In this work, we explore the capability of using mixture data to improve the parametrization of equations of state. The mixture data adds information on the relative contribution of different intermolecular interactions and hence on the magnitude of pure-component parameters. Moving from parametrizing individual components to a large set of molecules simultaneously requires handling large data sets and efficient phase equilibrium calculations. To overcome this impediment, we build on the increasing capabilities of machine-learning methods designed to work with large data sets and our previous work on efficient calculations of phase equilibria and their derivatives with automatic differentiation [3]. Based on this framework, we explore the decorrelation of pure component parameters using mixture data.

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Comparison of CP-PC-SAFT and CS-SAFT-VR-Mie in predicting fluid phase behavior in systems of phenolic compounds, aromatic amines, acetophenone and benzaldehyde.

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This presentation compares the capabilities of the Critical Point-based Revision of PC-SAFT (CP-PC-SAFT) and the Corresponding States-based SAFT of Variable Range and Mie Potential (CS-SAFT-VR-Mie) to simultaneously predict VLE, LLE and critical data available for 74 binary systems of phenol, m-cresol, 2-methoxyphenol, 2-phenylethanol, 2-ethylphenol, pyridine, aniline, benzylamine, *o*-toluidine, acetophenone, and benzaldehyde with nitrogen, carbon monoxide, methane, ethane, propane, *n*-alkanes, *iso*-alkanes, and other hydrocarbons. For both models the universal k_{12} values adjusted to the VLE data of the system propane(1) – phenol(2) were applied. It was found that these models yield comparable and, in most cases, accurate estimations of vapor pressures and the pure compound saturated liquid densities. However, CP-PC-SAFT is superior in predicting the high-pressure density and sound velocity data. CS-SAFT-VR-Mie is able to predict the VLE data fairly accurately in most of the considered cases. However, it establishes an unrealistic transitional behavior from Type I to Type II via Type VI, which seriously affects its predictions of LLE. CP-PC-SAFT exhibited better overall reliability. In particular, in most cases it is superior in estimating VLE and yields reasonably accurate predictions of the upper critical solution temperatures. According to the global analysis performed in this study, these results could probably be attributed to the obeying of the pure compound T_c and P_c. At the same time, it systematically underestimates the widths of the LLE phase splits and, as a result, yields inaccurate predictions of the alkane-rich phases.

Exploring Thermophysical Properties of Phosphonium-Based Ionic Liquids in CO_2 Capture Applications through a Multiscale Approach

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The quest for efficient separation systems in CO_2 capture is pivotal in the pursuit of controlling greenhouse gas emissions. Among the solvents employed in absorption circuits, amines are the most widely utilized, but face environmental and economic challenges due to evaporation and degradation during operation. Beyond these concerns, there is a current imperative to identify alternative solvents capable of functioning across a spectrum of CO_2 concentrations, ranging from 15% in flue gases to *ppm* in the air. Ionic Liquids (ILs) emerged as a compelling option for CO_2 sorbents owing to their low vapor pressure and the capacity to tailor their solvent power by combining different ions. Notably, certain phosphonium cation/anion pairings have shown promising results in literature, although a comprehensive characterization is still necessary to identify the optimal CO_2 absorber.

This study adopts a multiscale approach to investigate CO_2 gas absorption in phosphonium-based ILs featuring various anions. New molecular models are developed using the soft-SAFT [1] methodology, leveraging existing soft-SAFT coarse-grain models for this ILs family [2], analyzing molecule charge distribution through Turbomole-COSMO software for new ILs, and approximating association parameters via DFT calculations. Subsequently, soft-SAFT is employed to accurately simulate and predict the thermodynamic and absorption properties [2] of these ILs across a wide range of conditions. The molecular models account for specific CO_2-IL cross-association interactions to accommodate chemisorption phenomena, if present. Additionally, the presence of hydration is discussed. The analysis encompasses diverse CO_2 compositions and is completed by estimations of Henry's law constants, solvation enthalpies, and entropies, ultimately proposing the most promising solvents.

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Enhanced Acid Gas Removal from Natural Gas Using Phase Change Amine Solvents

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Natural gas, as extracted, contains impurities that decrease its heating value and can become damaging to the equipment. Specifically, acid gas which is a mixture of CO_2 and H_2S, it's highly toxic and corrosive in the presence of water [1]. Currently, the predominant method for removing acid gases involves absorption processes that use water-based alkanolamines [2]. Even though chemical absorption is a process resulting in high purity natural gas, it presents some disadvantages such as high regeneration heat requirement, corrosion and foaming in the pipelines [3,4]. Multiple alternatives have been proposed in order to optimize the process, with physical and hybrid absorption being among them [5]. Lately, phase change solvents (PCS) are also of interest because they exhibit the unique ability to form liquid-liquid equilibrium in the presence of acid gases, resulting in separate lean and acid gas-rich liquid phase [6]. Thus, after the separation of the two, only the rich liquid phase proceeds to the stripper and the lean one returns to the absorption column [6]. This property leads to a significant reduction in energy consumption during solvent regeneration [7]. The present study explores a novel approach for acid gas removal by using PCSs in the amine process. The proposed process is simulated using UniSim, employing the CPA EoS. The findings are quite promising regarding the optimization of chemisorption process, offering a more energy-efficient and environmentally sustainable solution.

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Predictive Post-Combustion CO_2 Reactive Absorption Framework Combining Electrolyte Thermodynamics with Electronic Structure and Atomistic Simulation Methodologies

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Although post-combustion reactive absorption from point sources is a leading technology for CO_2 capture, currently used solvents are based on first-mile improvements to almost century-old solvent methodology. The conventional discovery of new solvents involves identifying a prospective solvent by chemical intuition, followed by fitting the parameters of a macroscopic reaction-based thermodynamic model to experimental data, using commercial or in-house-developed software to calculate the chemical speciation. We recently developed a novel combined molecular-based and thermodynamic framework ([1,2]) that permits the large-scale screening of potential solvents at a fraction of the enormous time and cost of this approach.

The framework involves an electrolyte solution thermodynamic model for the CO_2-loaded solvent based on reaction equilibrium constants pKa and pKc, which can be calculated using electronic structure and molecular dynamics software. Current enhancements include improved methodology for force-fields and the use of open-source Gibbs Energy Minimization software to calculate the speciation.

We show results for a range of pure and mixed alkanolamine-based solvents, including validation for currently used solvents and predictions for unstudied systems, and uncertainty predictions for the calculations. We also describe extensions of the framework to predict the effects of flue-gas impurities. We emphasize the importance of under-appreciated aspects that must be implemented carefully and correctly.

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Enrichment at fluid interfaces and its impact on mass transfer at elevated pressures

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A fundamental understanding of interfacial properties of systems at elevated pressure is essential for key industrial processes in the context of energy transition, such as the storage of CO_2, hydrogen, or methane. Employing rigorous thermodynamic models allows for predictive determination of interfacial properties as well as mass transfer in these systems and are required for the simulation of the respective scenarios.

This study therefore investigates interfacial properties and mass transfer in ternary mixtures of CO_2 with solvents of different polarity at sub- and supercritical conditions with respect to this gas. CO_2 is known to exhibit significant enrichment at interfaces, which can significantly influence the interfacial mass transfer [1,2]. Based on prior investigations of binary CO_2-systems with n-dodecane, n-butanol and water [2], the role of simultaneous enrichment of two components at the interface is elucidated in this study. Corresponding phase equilibria are described using the PCP-SAFT equation of state [3,4]. Interfacial properties, particularly the interfacial tension and density profiles, are modeled by combining PCP-SAFT with the density gradient theory (DGT) [5]. Interfacial mass transfer calculations are conducted applying the dynamic DGT [6] considering the gradient of chemical potentials as driving force for diffusion.

In this contribution, we present the modeling results for interfacial properties at equilibrium as well as the interfacial mass transfer. Furthermore, we discuss the influence of simultaneous interfacial enrichment on the mass transfer, based on the dynamic DGT modeling results.

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From Chemical Drawing to Electronic Properties of Semiconducting Polymers in Bulk: A Tool for Chemical Discovery

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Semiconducting polymers (SCPs) are the core material for flexible electronics with many applications including organic photovoltaics and field effect transistors. The modular approach to their synthesis lends itself to a natural approach to molecular design, namely the selection of a sequence of conjugated monomers and sidechains in the repeat unit structure for a targeted application. The design rules (i.e., the prerequisite for molecular design) naturally emerge from structure-property datasets obtained from a homogenous study of many compounds. Recent advances in the automation of quantum chemistry (QC) calculations show that great insight into the design rules can be obtained by considering large datasets of SCPs. However, so far, the high-throughput methods have been only reserved for ideal polymer chains in vacuum, which ignores the (undeniable) role of intermolecular interactions and the electrostatic effect of the SCP chains in bulk. Molecular dynamics (MD) is an ideal method to construct high-quality SCP bulk models1-2, from which one can include the intermolecular and electrostatic effects through a hybrid QC/MD method. Such an approach consists of three main steps: (i) atomistic model construction, (ii) equilibration of the models, and (iii) QC calculations on the equilibrated models, neither of which are currently optimised to give consistent and comparable results for many SCPs due to various reasons, e.g., different and tedious ways of force field parametrisation, a wide range of SCP relaxation times, and the lack of a standard QC method.

In this research, we put forward a **unified workflow to develop chemical-drawing-to-atomistic models** for SCPs and **an accelerated and accurate QC/MD approach to obtain electronic structure properties**, which takes into account the inter-molecular interactions and electrostatic environment of the surrounding chains. The accuracy of our algorithmic QC/MD method is evaluated for five different benchmark SCPs having various microstructures and a wide range of electronic structures.

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Thermodynamic of Phase Change Material Based on Stearic Acid with Graphene Nanoplatelets

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Abstract

Renewable energy sources must supply between 30 and 45 % of the global energy consumption to achieve "net zero" emissions. However, renewable sources, such as solar, are intermittent, so they must be combined with thermal energy storage (TES) to continue supplying energy. Organic phase change materials (PCMs) that include fatty acids, sugar alcohols, and polymers have recently been explored as materials for TES because they store significant amounts of latent heat, are thermo-chemically stable, and are non-toxic. In recent years, bio-organic PCMs such as stearic acid have attracted too much attention since they come from renewable sources and retain the same properties. However, organic PCMs have poor thermal conductivity, limiting heat transfer into the storage. One of the methods to enhance thermal conductivity is the incorporation of highly conductive nanoparticles such as metal, metal oxide, and carbon-based nanoparticles. Graphene is one of the carbon-based particles that is used because of its high thermal conductivity, relatively low densities, and large aspect ratio. [1] The fundamental thermophysical properties to design a TES application are heat capacity, thermal conductivity, latent heat, viscosity, and density. These data significantly influence the simulation results and, as a consequence, the design and operation of the TES.[2] In this context, we present experimental thermal conductivity, viscosity, and density data of stearic acid with 2 wt%, 4 wt%, and 6 wt% graphene nanoplate. This work provided new knowledge on the impact of graphene nanoplate on the thermal conductivity, density, and viscosity of the stearic acid matrix of PCMs. Molecular dynamics simulations carried out to compute the thermodynamics properties listed below. They were compared to experimental results providing a novel molecular behaviour about the interaction between graphene and stearic acids.

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Rational Design of Nanoparticle Surface Patterning for Directed Self-Assembly

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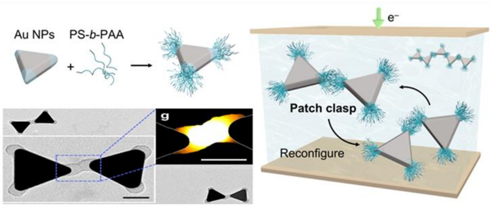
Synthesizing reconfigurable nanoscale synthons with predictive control over shape, size, and interparticle interactions is a holy grail for bottom-up self-assembly. However, grand challenges in their rational design lie in the large space of potential experimental parameters and complex synthetic protocols. Here, we present a strategy for designing complex, reconfigurable building blocks that addresses the above limitations. Our work encompasses three major components. The first involves a joint theory, simulation and experimental work aimed at designing symmetry breaking polymeric grafting on anisotropic nanoparticles (NPs). The second presents a strategy to design complex polymer patterning on anisotropic NPs that expand synthetic capabilities beyond the patchy limit to give rise to striped and periodically ordered NP surface patterning. The third leverages thermodynamic perturbation theory to predict the self-assembled structures of the various polymer-grafted NPs, which are then validated by via both experiments and simulations. Our work show that the designed polymer-grafted NPs can be utilized to synthesize both colloidal polymers as well as provide robust control over NP orientational ordering in self-assembled morphologies, allowing for *a priori* design of complex building blocks for novel materials fabrication.

Symmetry Breaking Polymeric Grafting



Complex Nanoparticle Surface Patterning

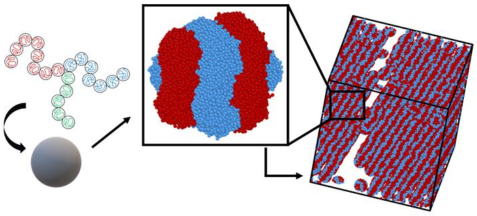


Figure 1. (Top) Patchy particle design and synthesis.
(Bottom) Design of complex patterning on NP surfaces

Sticky-MARTINI – A Reactive Coarse-Grained Model for Self-Assembly in Materials Synthesis

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Computer simulations have been increasingly employed, with remarkable success, to study the phase behaviour and synthesis mechanisms of porous materials. The main challenge, however, is that such processes involve multiple physical phenomena – self-assembly, chemical reactions, phase separation, electrostatic interactions – taking place over a wide range of time and length scales. In particular, the ability to simultaneously describe mesoscale self-assembly processes and chemical reactions has remained an elusive goal. Typically, highly coarse-grained (CG) classical models are required to describe mesophase self-assembly [1], while describing chemical reactions usually relies on computationally expensive and/or parameter-rich approaches such as Quantum Mechanical calculations, kinetic Monte Carlo or reactive force fields that are restricted to small system sizes and short times [2]. In this work, we bridge this gap and propose a new molecular modelling paradigm to describe silica polymerization reactions in aqueous solutions at conditions that are representative of realistic experimental processes like biosilicification or porous silica synthesis – i.e. at close to ambient temperatures and over a wide range of pH. The key innovation is to describe the Si-O-Si chemical bond formation and breakage process through a continuous potential with a balance between attractive and repulsive interactions between suitably placed virtual sites and "sticky" particles – hence the name "Sticky-MARTINI" [3]. The simplicity of the model, its applicability in standard parallelized molecular dynamics codes, and its compatibility with the widely used MARTINI coarse-grained force field [4] allows for the study of systems containing millions of atoms over microsecond time scales using an explicit solvent formalism.

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Liquid-Liquid Equilibria of the Binary Systems Biodiesel/Glycerol and Biodiesel/Water

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Transesterification of vegetable oils is the chemical reaction used in industry to produce biodiesel. This reaction involves an alcohol reacting, in presence of a catalyst, with the triacylglycerols contained in vegetable oils or animal fats to produce a liquid heterogeneous mixture of methyl-esters and glycerol.

In this work, liquid-liquid equilibria (LLE) for the biodiesel/glycerol and biodiesel/water binary systems are experimentally measured because they play a key role in the purification steps downstream to the reaction. The measurements are performed through the high-performance liquid chromatography procedure at atmospheric pressure and in the temperature range from 310.35 K to 338.15 K.

The experimental data are then used to determine the binary interactions parameters (BIPs) of the UNIQUAC model for the LLE of the two binary systems. To ensure a thermodynamically consistent representation of the phase behaviour, the BIPs are regressed by means of a bilevel algorithm proposed by some authors of this study [1,2]. The algorithm is able to both minimize the composition deviations and match the common tangent plane condition by varying the experimental temperatures, compositions, and UNIQUAC structural parameters.

Finally, the behaviours of the presented measurements and calculations were compared with LLE data for biodiesel/glycerol and biodiesel/water binary systems collected from the literature.

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A Robust Setup for Efficient Characterization of Multicomponent Vapor-Liquid Equilibria Using Raman Spectroscopy

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Vapor-liquid equilibrium (VLE), a crucial thermodynamic property in diverse industrial processes, assumes paramount significance in the development, optimization, and operation of separation processes and various applications [1]. Despite their central role, large sample volumes, long measurement times and the handling of the apparatus are a challenge for the precise determination of VLE data [1,2].

In response to these challenges, we present an innovative Raman spectroscopy-based measurement setup that enables fast, accurate and user-friendly characterization of VLE. The application of Raman spectroscopy enables non-invasive analysis of vapor and liquid phases in small sample volumes (<2 ml) for multiple VLE data points. The usage of a compact isothermal VLE measurement cell ensures rapid and reliable VLE control. The combination of the equilibrium cell with a highly confocal fiber-coupled Raman probe and a high-throughput spectrometer establishes an efficient setup for quantifying VLE data.

Our commitment to user-friendliness during the setup's development, simplifying both measurement and evaluation processes. Despite existing skepticism in industrial practice regarding the application of Raman spectroscopy for substance data determination, our setup, employing Indirect Hard Modeling, streamlines the process to be accessible even to non-specialized users.

The use of small sample volumes, rapid Raman spectroscopy measurements, and user-friendly operation fulfill crucial requirements to pave the way for this efficient technology to enter the industry.

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Investigating the solute + solute interactions observed in ternary mixtures of CO_2 + (*n*-alkanes and/or methyl esters and/or 1-alcohols and/or carboxylic acids)

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Supercritical fluids (SCFs) such as CO_2 have recently gained traction as attractive alternatives to traditional organic solvents, due to them being cost-effective, non-toxic and “generally regarded as safe” (“GRAS”). CO_2 is thus a viable option for processing in the foodstuff, pharmaceutical and cosmetic industries, where the remaining solvent residue and final product quality are very strictly regulated. It has previously been shown that ternary systems containing CO_2 + 1-alcohol + *n*-alkane exhibit complex phase behaviour phenomena due to significant solute + solute interactions. These complex phase behaviour phenomena directly affects the feasibility of SCF processes and complicates thermodynamic modelling of these systems. To date, a large portion of the SCF research has focused on investigating binary solvent + solute systems. This, however, does not provide insight into to solute + solute interactions and the effect these interactions have on the phase behaviour in ternary systems.

The present study investigated the phase behaviour and solute + solute interactions observed in ternary systems containing CO_2 and binary mixtures of *n*-alkanes, methyl esters, 1-alcohols and carboxylic acids. Twenty-four new ternary high-pressure bubble- and dew-point data sets for 50-50 wt% solute + solute mixtures were investigated. Measurements were conducted on a variable volume view cell between 308 – 358 K at total solute mass fractions of 0.015 to 0.65, ensuring that the bubble, dew and mixture critical regions were characterised. The measured data was evaluated to deduce the possible solute + solute interactions that are present in these systems. Solute + solute interactions that significantly affected the mixture phase behaviour (enhanced mixture solubility or in co-solvency) were identified in the (1-alcohol or *n*-alkane) + (methyl ester or *n*-carboxylic acid) systems. In contrast, the *n*-carboxylic acid + methyl ester group behaved essentially as an average of the two comprising binaries. The enhanced solubility was found to be least prominent in the 1-alcohol + *n*-carboxylic acid as not one of the considered systems were co-solvent.

Analysis of the quality of published experimental and correlated binary and ternary VLE data. Proposal for an adequate planning of their experimental determination and correlation

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A revision of the way VLE data for binary and ternary systems are reported and correlated by activity coefficient models has revealed severe problems and inconsistencies, that are not widely known and could lead to serious errors. To illustrate these issues, we have randomly selected a small sample of experimental data of ten ternary VLE systems at constant pressure from DECHEMA database. The corresponding NRTL parameters have been located from three different sources: i.e.: DECHEMA database, Aspen Plus and CHEMCAD. We have also located the experimental data for the binaries involved, and also the corresponding NRTL parameters reported. 3D graphs have been represented including: the calculated (NRTL) T/x,y surfaces for the liquid and vapor phases, the experimental VLE data for the ternary region and also for the three binary subsystems. Half of the systems analysed present questionable results of different nature, which seem to have passed unnoticed, and it may lead to dramatic errors when attempting design calculations.

Obviously, this situation requires specific actions to be corrected. A high discrepancy exists in many cases between the experimental VLE binaries and those calculated using the published parameters from ternary VLE data correlation, leading to the spurious and unreal predictions. Conversely, when using parameters from simulation software, an acceptable representation of the binaries is frequently obtained, but the ternary VLE region for many systems may be very different from the experimental one. The independent correlation of the binary and the ternary data, in addition to a non-systematic experimental study in the equilibrium regions, may be the reasons of such results. A deeper analysis of the experimental data and the correlation results seems to be required in order to validate the parameters obtained and reported. Some recommendations are presented in this work to overcome such problems.

Generalised dissipative particle dynamics with coupled energy and mass transfers: A coarse-grain framework for simulations of thermodiffusion

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We present the complete description of energy and material transport within the generalized energy-conserving dissipative particle dynamics with mass transfer (GenDPDE-M) methodology. In particular, the dynamic coupling between mass and energy is incorporated into the GenDPDE-M, which was previously introduced with dynamically decoupled fluxes [1, 2]. From a theoretical perspective, we have derived the appropriate fluctuation-dissipation theorems along with Onsager's reciprocal relations, suitable for mesoscale models featuring this coupling. Equilibrium and non-equilibrium simulations were performed to demonstrate the internal thermodynamic consistency of the method, as well as the ability to capture the Ludwig-Soret effect, and tune its strength through the mesoscopic parameters. In view of the completeness of the presented approach, GenDPDE-M is the most general Lagrangian method to deal with complex fluids and systems at the mesoscale, where thermal agitation is relevant.

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Entropy Scaling for Thermal conductivity with critical Enhancement

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The prediction of transport properties is essential for process and apparatus design. Entropy scaling has shown to provide a powerful framework for developing predictive models for transport coefficients, such as thermal conductivity. Entropy scaling was introduced by Rosenfeld[1], who showed that dimensionless transport coefficients show a univariate behavior with residual entropy, to surprisingly good approximation. For thermal conductivity, however, a significant deviation from univariate behavior is observed in the vicinity of the critical point. This so-called critical enhancement can be explained by long-ranged fluctuations and can be described through mode coupling theory. Perkins et al.[2] proposed an analytic model for the critical enhancement.

Our work shows that an entropy scaling approach leads to a very good description of thermal conductivities in the entire fluid region, if the critical enhancement is accounted for. Specifically, we apply the model of Perkins et al. in combination with an analytic equation of state.

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Application of the Significant Structure Theory for the Viscosity Modeling of Ionic Fluids

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Abstract

The present work introduces the application of a modified significant structure theory (SST) in order to obtain improved representations of the dynamic viscosity of several representative last-generation ionic fluids: pure ionic liquids (ILs) and deep eutectic solvents (DESs). The thermodynamic potentials (residual internal energy, liquid and solid molar volumes) present in the resulting modified SST model were estimated from two simple cubic equations of state of the van der Waals type: Soave or Peng-Robinson. The modifications introduced to the SST approach were successfully verified during the correlation and prediction of experimental dynamic viscosities of 3 families of imidazolium-based ILs ($[C_x mim][BF_4]$, $[C_x mim][PF_6]$ and $[C_x mim][Tf_2N]$), one pyridinium-based IL ($[b3mpy][BF_4]$), one pyrrolidinium-based IL ($[P14][Tf_2N]$) and one ammonium-based IL ($[N1114][Tf_2N]$) over a temperature range varying from 273.15 to 353.15 K and at pressures from 1 to 3,000 bar. We also considered three archetypal choline chloride-based DESs for model validation: Reline, Ethaline and Glyceline within a temperature range varying from 293.15 to 373.15 K and at pressures from 1 to 1,000 bar.

A multi-scale modeling approach for the prediction of hydrogen transport properties in semi-crystalline polymers

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A multiscale modelling platform was developed for the prediction of both hydrogen sorption and diffusion coefficients in HDPE; the permeability across the material was ultimately estimated according to the solution-diffusion model. Molecular Dynamics (MD) simulations of semi-crystalline HDPE structures having tailored fractions of inter-crystalline connections (tie-chains), representative of different thermal histories, were carried out. The sorption coefficient was estimated by means of the Lattice Fluid Equation of State which was fully parametrized on the MD simulation results [1]. The diffusion coefficient was evaluated from the Mean Square Displacement (MSD) of hydrogen molecules within the structures during MD simulations and scaling the latter with the impermeable crystalline domains induced tortuosity which was reproduced using a Finite Volume model of the 3D spherulitic morphology. At experimental level, a time-lag equipment was used to determine diffusivity and permeability on the different polyethylene samples whose degree of crystallinity was determined through X-Ray analysis. The modelling strategy allowed to establish useful correlations between the polymer molecular structure and the barrier performance paving the way for an enhanced screening and optimization of hydrogen polymeric liners.

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Thermomechanical Modeling of Microstructural Influences on Gas Solubility in Semi-crystalline Polyethylenes

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The ability of semi-crystalline polymers to dissolve gas is crucial for a number of industrial processes, such as polymer recycling techniques [1] or gas-phase synthesis of novel polymers [2]. Gas solubility mainly occurs in the amorphous regions of the polymer, resulting in heterogeneous solubility distributions depending on the respective morphologies [3]–[5], i. e. the microstructure of the polymer composed of the crystalline and amorphous phases. Due to the microstructure, there are complex interactions between the morphological constitution and the macroscopic property gas solubility. Recently, a new multiscale thermo-mechanics approach [6] has been developed which has successfully predicted the gas solubility of ethylene in semi-crystalline polyethylene grades. Important for this approach is the access to the mechanical properties, i.e. the shear modulus and the Poisson's ratio of the amorphous phase, and the geometric behaviour of the microstructure. This access can be provided by micromechanical models using the macroscopic bulk properties as input. In this contribution, the Mori-Tanaka model [7] is used as a micromechanical-model in order to consistently describe the influence of the inclusion geometry on the strain field and to consider the stress-strain interactions between the inclusions via the matrix. This model allows a more precise inverse determination of the mechanical properties of the respective phases, so that the macroscopic property gas solubility can be predicted more accurately. This is demonstrated for the CO_2-solubility in different molecularly architected polyethylene grades.

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Molecular insight on Energetic Interactions and their Contribution to Diffusion of Small Molecules in Polyesters

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The diffusion coefficients of gas molecules characterize their mobility in the polymeric matrix. In particular, diffusion of small molecules in polymers is generally inversely correlated with penetrant molecular size. Such correlation arises from models linking diffusion to the effective cross-sectional area of gas molecules [1]. However, molecular size descriptors used to scale diffusion coefficient, like kinetic diameter, d_k, or critical volume, V_C, generally do not account for molecular shape anisotropy or for favorable interactions between gas and polymer. Indeed, the diffusion coefficient of polar gases, such as CO_2, can deviate from the general trendline, when favorable interactions with functional groups in the polymer are present [2,3]. Molecular dynamics (MD) simulations allow to investigate gas transport in polymeric materials while offering a molecular insight on transport mechanism.

In the present work MD description was used to study diffusion of small molecules, namely H_2, He, O_2, N_2, CO_2, and CH_4, in six polymers containing ether or ester functional groups. Gas diffusion coefficients were calculated from Mean Square Displacement (MSD) and correlated to the Gas-Polymer interaction energy. Additionally, radial distribution functions, $g(r)$, were used to evidence the preferential interaction sites between gas molecules and polymeric atoms, while free volume distribution in polymers was used to understand and compare structural and energetic influence on the mechanism of small molecules diffusion in polymeric materials.

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The Role of 4E Analysis and Thermodynamic Modeling in the Rational Design of Low-GWP Refrigerants as Drop-in Replacements

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Abstract

Considering the future prospects of F-gases emissions, the Kigali Amendment has committed to reducing the use of high global warming potential (GWP) third-generation refrigerants in current refrigeration and air conditioning systems (RAC). Notably, about 20% of existing RAC units using hydrofluorocarbons (HFCs) are anticipated to be replaced within this decade, in line with European environmental directives [1]. In response, the polar soft-SAFT molecular-based equation of state (EoS) has been used to identify and develop low-GWP fluorinated refrigerant alternatives, specifically targeting top-produced HFCs like R134a (GWP=1300) and R410A (GWP=1924) [2]. A detailed thermodynamic model has been established for this aim, effectively simulating refrigerants' properties, including vapor-liquid equilibrium and thermophysical characteristics, as well as binary mixtures on a coarse-grain scale [3]. The model is systematically applied to evaluate the suitability of alternative refrigerants, considering retrofitting needs through a comprehensive 4E analysis (energy, exergy, environmental, and economic factors) in addition to evaluating safety and technical aspects. Additional analysis of environmental impact and projected cost is included to quantify the impact associated with their use and emissions, aiding in the identification of appropriate substitutes from a techno-environmental-economic perspective.

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A comprehensive approach to incorporating intermolecular dispersion into COSMO-RS model

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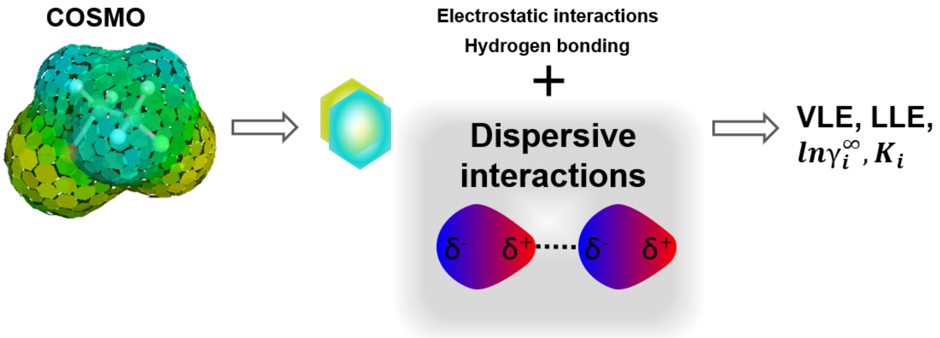
In recent decades, computational chemistry shaped predictive thermodynamic models based on COSMO [1]. The pioneering work by Klamt [2] gave rise to COSMO-RS. In COSMO-RS, molecules are fragmented into interacting segments. Initially, only electrostatic interactions and hydrogen bonding were considered, while dispersion was disregarded in fluid mixtures. Later, dispersive interactions appeared in the COSMO-SAC-dsp model [3] and recent versions of COSMO*therm* [4]. In this work, dispersive interactions between the contacting segments were incorporated into openCOSMO-RS [5]. We evaluated several parametrizations, obtained by regressing the extensive dataset, consisting of VLE, LLE, infinite dilution activity coefficients and partition coefficients. Furthermore, we explored the impact of different combinatorial terms on the performance of the model. Finally, the possibility to use the local polarizabilities predicted with quantum chemical calculations for segment-segment interactions was tested. The implementation of the proposed modification improved modeling of VLE and LLE for haloalkanes and refrigerant mixtures compared to prior models.



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Biomass-derived working fluids as sustainable alternatives to classical absorption refrigeration systems

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With an increasing demand for refrigeration and air conditioning, research on more efficient refrigeration systems is required. In this context, absorption refrigeration systems (ARS) can be a competitive alternative to compression-assisted refrigeration, particularly if low-grade thermal energy from renewable resources is available. Conventional ARS use ammonia/water or water/LiBr for low- and moderate-temperature applications, respectively, which presents several disadvantages, e.g., toxicity, flammability, corrosion, and crystallization problems. To overcome these issues, new working pairs are being assessed based on CO_2, hydrofluorocarbons (HFCs) and low global warming potential hydrofluoroolefins (HFOs) coupled with high-boiling point solvents (e.g., triethylene glycol dimethyl ether), and low-viscosity ionic liquids (ILs), which was the scope of our previous work [1]. Now, we propose the use of biomass-derived absorbents as a greener alternative to ILs to improve the environmental performance of ARS. To that end, a set of organic solvents of high-boiling point, low viscosity and wide liquid range have been selected based on environmental, health and safety considerations to characterize the solubility of five common refrigerants (HFC-32, HFC-134a, HFC-125, HFO-1234yf and HFO-1234ze(E)) and the natural refrigerant CO_2. The isochoric saturation method was applied to report vapor-liquid equilibrium data over 283.15-323.15 K and up to 0.9 MPa, and the data were fitted accurately to the NRTL activity coefficient model. The results showed high solubility of the HFCs and HFOs, particularly in oxygenated solvents, and low solvation enthalpies. These properties, along with their more sustainable nature and low cost, make these bio-based solvents potential candidates to replace the classic systems used in absorption refrigeration.

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Towards linking engineering workflows: Phase behavior, self-assembly, and fluctuations from thermodynamic perturbation theory and molecular simulation

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A goal of our research program has been to link engineering workflows with molecular theory across scales for bulk fluid properties and phase behavior, interfacial properties, and prediction of self-assembly. The vision is to have models and transferable model parameters that scale across these systems, allowing the user to move seamlessly from engineering models for bulk fluid phase behavior to mesoscale models of self-assembly and finally to molecular simulation, matching the level of model complexity to the system and properties of interest. We base the approach on rigorous statistical mechanics based theory for these systems that has been validated versus molecular simulation. An advantage of this approach is that the theories are predictive with known approximations and limitations.

In this talk, we will provide an overview of recent advances and applications from our research group. Our recent research has moved in two directions: firstly, simplifying our molecular theories to provide accurate statistical mechanics based engineering models with known approximations. At the same time, we have discovered unrecognized approximations in current engineering models. In a second direction, we have extended molecular theory by incorporating new degrees of realism, such as diblock and triblock surfactants / copolymers and patchy colloids, enabling calculations of self-assembly in ever more complex systems. Other directions and advances in our research program will be highlighted.

Applied Thermodynamics – Examples from Industrial Applications

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The knowledge of thermophysical property data and of phase equilibria are essential for almost all process steps in the production of pharmaceutical and crop protection products. In this presentation examples from industrial practice are given for cases in which Applied Thermodynamics played an important role to optimize a process or a product.

Sustainability: Solvents are key auxiliaries in the fine chemicals and pharmaceutical industries. Several solvent selection guides were developed and published in the past which take health, safety, and environmental aspects into account. To improve the pre-selection of solvents, new supplemental process-related indicators were introduced.

Formulation development: Self-Micro-Emulsifying Drug Delivery System (SMEDDS) formulations are typically mixtures of 3-5 components. There are countless possible variations regarding the composition of the mixtures. Prediction methods are almost indispensable for pre-selecting suitable compositions. COSMO-RS methods were applied to evaluate whether and how they can support the formulation development.

Process design: Many biological pharma products undergo freeze/thaw steps during production. It is known that biomolecules loose some of their bioactivity in these freeze/thaw steps. To generate insights of freezing and thawing processes of cryopreservation solutions, solid-liquid equilibria of complex solutions were investigated.

Process design: Coatings are an essential part in the formulation of active pharmaceutical ingredients. If organic solvents are used for film coatings, it must be ensured that the residual solvent content in the tablet is below the approved specification. Based on the investigation of the release behavior during the drying step, suitable measures for reliably reducing the solvent content could be derived.

Safety: According to the worldwide safety standards, a classification for transport and handling is required for every single mixture. To reduce the experimental effort needed for the classification of multicomponent mixtures of polyurethane raw materials, existing predictive methods for the initial normal boiling point and for the flash point have been extended and a predictive method for the auto ignition temperature has been developed.

A Comparison of the UNIFAC Model vs. Graph Neural Network-based Models for the Prediction of Binary Vapor-Liquid Equilibria

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Recent advancements in machine learning, specifically Graph Neural Networks (GNNs), have opened new frontiers in the prediction of thermophysical properties [1,2]. The prediction of binary vapor-liquid equilibria (VLE) is crucial in early stages of separation process design and can serve as a suitable framework for studying the performance of GNN-based methods compared to more established solutions in the form of excess Gibbs energy models. This work presents a rigorous comparison between both approaches for predicting binary VLE, highlighting the benefits and current limitations of both methods. By leveraging the inherent graph structure of molecules and molecular interactions, GNN-based models appear to be a promising alternative for a fast and accurate estimation of VLE for a wide range of binary mixtures under various conditions. A GNN-based model that predicts infinite dilution activity coefficients coupled with the Extended Margules equation for predicting activity coefficients at finite concentrations is compared to the UNIFAC-Dortmund model. The insights and limitations of data-driven models trained on infinite conditions and extrapolating to finite concentrations are discussed. Moreover, a second GNN-based model trained on extensive experimental VLE data is compared to the two previously mentioned models. The specific benefits of incorporating experimental finite concentration information as part of the learning framework are reviewed.

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Thermodynamic modelling of the systems involved in TEG dehydration of Natural Gas

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Abstract

Among the era of an ever-increasing global energy demand, Natural Gas (NG) has been established as the current most valuable resource for meeting these escalating needs. Until converting the energy mixture to sustainable zero carbon footprint technologies, NG poses a reliable source, with a lower carbon footprint compared to conventional fossil fuels.

NG as produced from the reservoir is saturated with water, potentially forming a free-water phase where impurities can be diluted, inducing corrosive and hydrate formation conditions, hence, threating the equipment, product quality and the operation in total. For this purpose, NG enters a Triethylene Glycol (TEG) dehydration unit to ensure that no free water will ever drop.

Such an application poses the need of a highly accurate thermodynamic model, which will optimize the design of the dehydration process. In this work, the UMR-CPA EoS [1], which couples the UMR-PRU [2] model with CPA [3] for associating fluids, is employed and extended to water, TEG and the key binaries of them. At first, new sets of parameters of pure water and TEG are calculated by fitting to vapor pressures, densities and heat capacities. Then, the quite challenging Liquid-Liquid-Equilibrium (LLE) in water-HC, TEG-HC systems and the Vapor-Liquid-Equilibrium (VLE) in water-gas and TEG-gas systems are described. Finally, the model is validated for the prediction of the phase equilibrium in multicomponent systems including water and TEG.

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Vapor-Liquid Equilibria for Tri-ethylene glycol in high pressure methane: Experiments and Modelling

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Large deposits of sludge have recently been observed in natural gas pipelines within Australia. The nature of this sludge has been identified as a mixture of corrosion by-products and tri-ethylene glycol(TEG). It is possible that the TEG accumulation occurs both because of liquid carryover from upstream dehydration units and from vapor carryover due to excessive temperatures within the dehydration absorber (40-60ºC). There is, however, a lack of vapor-liquid equilibria for the TEG-methane system within this temperature range to quantify the vapor losses. We have recently conducted a sequence of experiments between 40-60ºC at up to 134 bar, to provide this data. These experiments were extremely challenging due to the high pressures and the very low concentrations of TEG (less than 1ppm) in the vapor phase. The resulting data has been successfully modelled using the Cubic-Plus-Association (CPA) model using existing model parameters.

Phase Equilibria and Fluid Properties Modelling for a Hydrogen-based Economy

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Hydrogen is the most abundant chemical element in the universe. Pure hydrogen has been widely used in the chemical industry as a reactant and energy carrier, but it's use as a direct source of power and heat has been limited. The production of hydrogen from water electrolysis and renewable energy (green hydrogen) is a highly energy intensive process and hydrogen transport and storage requires much higher pressures, lower temperatures and specialized equipment, which are clear disadvantages over the current petroleum-based fuels. Nevertheless, hydrogen is the cleanest of all chemical energy sources, as it's use only generates water. For this reason, a hydrogen-based economy, where hydrogen will hypothetically replace most petroleum products as energy sources, approaching net zero (or very low) carbon has been in the political agenda of the European Union and the UK government, among others.

In this work we will look at the current performance of equation of state and transport property models to represent the physical properties of hydrogen-rich mixtures [1], including mixtures of hydrogen with natural gas which can potentially be introduced in the current energy infrastructure. We will consider properties of relevance for transport, storage and use of hydrogen mixtures, such as density, viscosity, heat capacity, compressibility, expansivity and Joule-Thomson coefficient. We will also consider the phase behaviour of hydrogen-rich mixtures, including the solubility of hydrogen in aqueous salt solutions and the potential formation of solids from impurities such as the formation of mixed gas hydrates or pure solid phases.

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Molecular Simulation of Supercapacitors

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Molecular dynamics (MD) simulations using the constant potential method (CPM) have been proven to be an essential technique for studying the charge storage and charging dynamics of *homogeneous* electrodes. We will provide an overview of recent work [1] on CPM MD *operando* simulations for charging of nanoporous carbide-derived carbon supercapacitors with four distinct electrolytes, including ionic liquid (IL), mixed IL-solvent, and solvent-in-salt electrolytes. However, the CPM cannot capture the distinct atomic nature of *heteroatomic* electrodes, such as MXenes, a class of two-dimensional inorganic compounds that consist of atomically thin layers of transition metal carbides. To overcome this limitation, we developed the heteroatomic constant potential method (HCPM) for MXene supercapacitors. The proposed HCPM model takes into account the electronegativities of different atoms in heteroatomic electrodes. A brief overview of results obtained with Li-TFSI/AN (lithium bis(trifluoromethane sulfonyl)imide / acetonitrile)-based solvent-in-salt electrolytes will be provided [2].

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Alkali metal ion intercalation of molybdenite for enhanced CO_2 reduction

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Reduction of greenhouse gas emissions that cause climate change, requires unlocking the full potential of modern-day and novel energy production and conversion systems. Important pillars towards a sustainable energy transition include CO_2 conversion strategies to mitigate and compensate hard-to-abate residual emissions. New synthetic carbon cycle pathways in the production of CO_2-based synthetic fuels and chemicals are gaining momentum. However, to create this cycle, an optimal catalyst in terms of cost efficiency, durability, process efficiency and raw materials availability has to be found.

Molybdenite (MoS_2), an affordable layered semiconductor, has demonstrated selectivity for CO_2 reduction in non-aqueous environments. The 2D structure not only provides a substantial specific surface area but also facilitates the intercalation of various ions which enhances the material conductivity through electron donation from the intercalated species.

Our research focuses on potassium and sodium ion intercalation into MoS_2 layers and examines the impact of the intercalated ions on CO_2 reduction efficiency. The intercalation mechanism is studied on both the micro- and macroscale. On the microscale, molecular dynamics (MD) simulations employing umbrella sampling are used to obtain Gibbs free energy profiles of intercalating ions after the optimization of cross-interaction parameters between the MoS_2 cluster and water molecules. On the macroscale, electrochemical impedance spectroscopy and X-ray photoelectron spectroscopy are used to experimentally study the intercalation, whereas the gaseous products of CO_2 reduction are measured with gas chromatography. Our results indicate that the intercalation efficiency of different ions is dependent on the strength of their hydration shell. Once the intercalation barrier is overcome, the intercalation improves the conductivity and enhances the CO_2 reduction efficiency in organic media.

Exergy Based Conceptual Design of Hybrid Electrolyser Systems for PtX

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Electrochemical reactors provide a valuable means to electrifying industries relying on fossil derived feedstocks. By converting electricity to chemical energy vectors such as hydrogen and syngas, the coupling of the electrical and chemicals sectors becomes realisable. Several technologies capable of this exist, with their own advantages and limitations spanning a wide range of technical (and economic) criteria. High temperature Solid oxide electrochemical reactors (SOE) provide very high efficiencies, can perform co-electrolysis for direct syngas generation and can operate reversibly, while alkaline water electrolysers (AEL) are capable of operating at higher pressures and may be more economical. Hybridising these technologies may provide a path for realizing large scale power-to-X (PtX) systems by combining the benefits of both technologies. Moreover, the different operating conditions may help promote synergies for example by utilizing excess heat from one process for another. However, the optimal level of hybridization is still undefined as well as the main influences to optimality. Furthermore, the key performance indicators (KPIs) utilised vary, making it difficult to compare between studies, necessitating a more consistent basis.

Here, a PtX plant for ammonia synthesis using SOE and AEL reactors is considered. Both electrochemical reactors generate hydrogen with different operating demands such as temperatures, pressures and feeds – which all impact the system performance. Using our in-house Python based conceptual modelling tool, CELESTE, we develop a model for the hybrid electrolyser system for ammonia synthesis to answer this question. We then use thermodynamic based KPIs such as energy and exergy efficiencies to characterize the performances of the systems and find the optimal level of hybridization and thermodynamic limits of such hybrid systems. Exergy methods are helpful here to bring all valuable flows in the PtX system to a comparable value. From the basis of specific work and exergy efficiency it was found that high contributions of SOE improved system performance. It was also found that enough heat was available for steam generation for SOE from a thermal exergy balance.

Investigation of coalescence and Ostwald ripening of bubbles of varying sizes and distance using the Navier-Stokes-Korteweg approach

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In a variety of technical processes, such as those used in fermentation or rectification, the presence of dispersed phases is of utmost importance for the design and execution of these operations. Utilizing modeling to gain understanding has a significant advantage for example including information about the velocity field. However, many modeling methods face challenges in fully resolving the interfacial regions and often rely on auxiliary models for various thermophysical properties, such as interfacial tension. This situation makes it difficult to predict the behavior of disperse systems, especially when they are kinetically stabilized.

An alternative approach is the Navier-Stokes-Korteweg method, which is based on the density gradient theory and an equation of state (EoS), here, for a simplified model fluid (Perturbed, Truncated, and Shifted). This approach incorporates a square gradient energy term to represent interfacial free energy [1]. The key advantage of this approach is that it inherently encompasses properties like phase equilibria and interfacial tensions due to the utilization of an EoS and density gradient theory. Nevertheless, it currently faces limitations in terms of spatial and temporal scales, as a sub-nanometer resolution is needed to resolve interfacial regions.

In this work, the NSK approach is scaled with a simple local grid refinement approach to overcome current limitations. A fully implicit model is used to solve the resulting finite element discretization. After a brief validation of this method, simple coalescence phenomena of bubbles of the same size at various distances are demonstrated. This includes discussion of the initial thermal coalescence range. Furthermore, simulations of the coalescence of dissimilar bubbles are examined, including interplay of Ostwald ripening with coalescence, thereby taking the method a step further towards the description of many-bubble systems.

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Polarizable water models for dissipative particle dynamics simulations of micellar solutions

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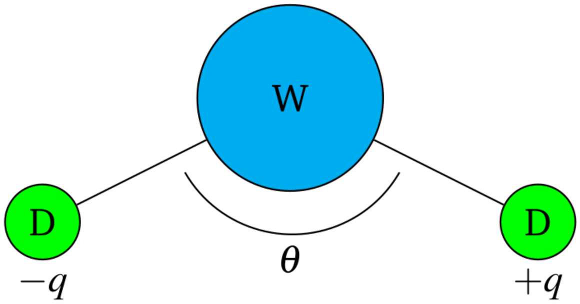

Figure 1 Each particle is made up of a central water bead (W) attached to two charged Drude beads (D) possessing charges ±q

Dissipative particle dynamics (DPD) has become a popular simulation technique for studying surfactant solutions, in particular micelle formation. The enhanced computational speed DPD offers over traditional molecular dynamics techniques allows quantities such as the mean aggregation number N_W to be determined. However, recently developed DPD models for anionic surfactants significantly underestimate N_W. This is in contrast with calculated non-ionic surfactant aggregation numbers, which are typically well predicted using DPD.

One proposed reason for this underprediction is due to the treatment of water ‘beads’ in DPD models (where coarse-graining means that a single bead represents a number of atoms). Typically, water beads are modelled as neutral, and dielectric permittivity is represented by applying a uniform dielectric constant over the simulation domain. This approach fails to reflect changes in the water molecules close to the micellar surface, and in particular the expected decrease in dielectric constant close to the surface. The shielding of electrostatic interactions between head groups is greatly thought to influence the aggregation, however, there is little work in literature investigating this.

In this work we present a coarse-grained water model which aims to address this problem. A polarizable water model more accurately reflects the behavior of charges and water molecules in ionic micellar solutions. We show that the behavior of ions in the simulations is markedly improved over standard approaches, where quantities such as the degree of dissociation of counter-ions more closely matches experimental data. However, we also show that improved dielectric screening of the head groups does not completely solve the problem of under-predicted of aggregation numbers, leading us to conclude that this is an area of research requiring further investigation.

Computer-Aided Molecular Design of Surfactants Using Classical Density Functional Theory

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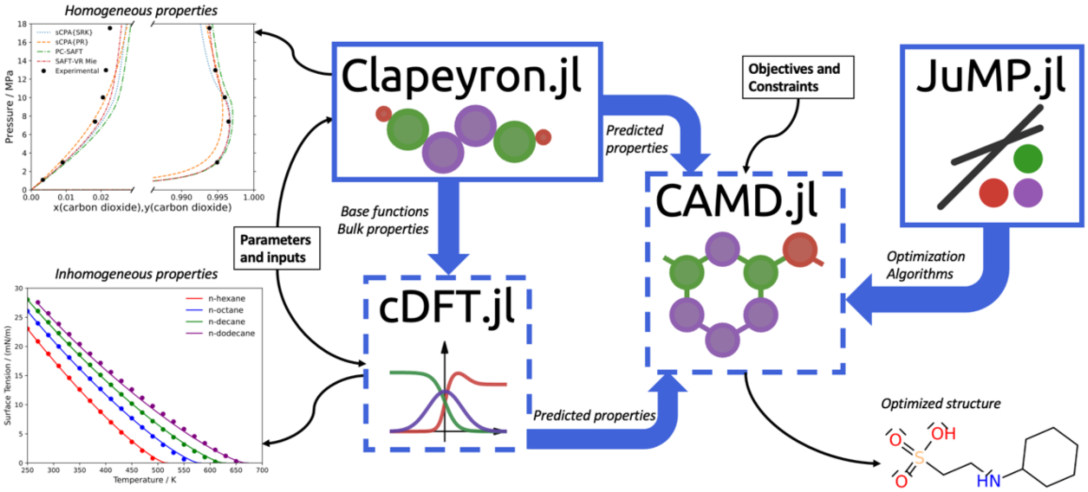
The investigation of innovative surfactants is a highly active research area, particularly regarding the identification of surfactants suitable for specific applications such as enhanced oil recovery. However, due to the scarcity of large-scale experimental databases, the implementation of machine-learning tools for the design of such molecules is a challenging task. Nonetheless, predictive models, such as classical density functional theory (cDFT), can be used in combination with a group-contribution methodology to overcome this problem, enabling the use of computer-aided molecular design (CAMD) frameworks. Therefore, in this study, we have developed open-source, generalized frameworks for both cDFT and CAMD. By implementing these tools, we utilized the well-established PC-SAFT functional coupled with mixed-integer non-linear optimization algorithms to design surfactants. The proposed molecules aligned with our anticipated structures for such surfactants, some of which have yet to be examined experimentally or through molecular dynamics simulations. Our intention is to expand our current framework to design anionic, cationic, and zwitterionic surfactants. Furthermore, these frameworks can also be extended to explore other design problems such as electrolytes for battery applications and solvents for carbon capture absorption.



Describing Hydrophobic Interactions Using Heterosegmented PC-SAFT – Application to Surfactants

Marius Rother, Gabriele Sadowski, TU Dortmund, Dortmund, Germany

Despite their importance for industry and pharmaceuticals applications, description of aqueous systems that contain non-polar components is still a challenging task in thermodynamic modelling. This is caused by the complex interactions between water and non-polar molecules, which result in the so-called hydrophobic effect. Over the last decades, there have been several attempts to model these kinds of interactions. The main challenge is to represent the asymmetry of the mutual solubilities of water and a hydrophobic component as well as the solubility minimum of the hydrophobic component in the aqueous phase.

This work employed the heterosegmented Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) to model these systems, which is used as a group-contribution (GC) method [1]. We propose a method to explicitly account for the hydrophobic effect, which improves the description of aqueous systems that contain non-polar moieties. The model accurately describes aqueous mixtures of n-alkanes and n-alcohols with a unique set of parameters over a wide range of conditions, providing a rigorous test of any GC method. Furthermore, the framework was applied to describe the behavior of surfactants molecules, which are known for their special behavior in aqueous systems. The model demonstrated its transferability between surfactants of different tail lengths by accurately correlating thermodynamic properties of an entire surfactant class, such as pure-component data, thermodynamic activities in binary mixtures with hydrocarbons, and surfactant partition coefficients between water and n-alkanes or water and n-alcohols. Partition coefficients have revealed special relevance as a key property to many quantitative structure–activity relationships [2].

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Direct shock simulations of several polymer melts

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Understanding the behavior of polymers under shock loading is essential for their applications in car equipment, aircraft, space structure and plastic bonded explosives. Despite much effort, both experimentally and numerically over the last twenty years [1,2], there are specificities of the shock behavior of polymers that are still unclear. These include the relation of the shocked state to the dynamic glass transition and the deviation of the Hugoniot locus from the usual linear relation $u_s = c + S\,u_p$, with u_s the shock velocity, c the bulk sound velocity, u_p the particle velocity and S an empirical fitting parameter. In this presentation, I will address these questions using molecular dynamics. Direct shock simulations of three different polymers, cis-1,4-polybutadiene, polystyrene and phenoxy resin, with different glass transition temperatures, were performed [3]. First, I will show that the polymer melts created in this work have a structure factor and a Hugoniot locus very close to their experimental counterparts. Second, I will focus on two aspects of the behavior of polymers under shock loading. (i) The deviation of the Hugoniot locus from the linear relation $u_s = c + S\,u_p$ is related to a change in the relative contribution to the shock energy of the bonding and non-bonding potential energies as the shock strength increases. (ii) The shear stress relaxations behind the shock front are compared for the three polymers. It is found that the polymers with the highest glass transition temperature have the most slowly relaxing shear stress behind the shock front.

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Modeling Swelling and Drying in Electronic Encapsulations

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For the protection of sensitive electronics against harsh environmental conditions, highly crosslinked polymers play a crucial role as they act as a barrier against the surrounding solvent phase. However, these polymers are also capable of taking up solvent by themselves, which can cause electric malfunctioning.

In previous works, the absorption behavior of epoxy and polyphenolic resins, as well as silicon, was investigated [1,2]. In this context, the thermodynamic properties were calculated using the PC-SAFT equation of state in combination with a network term [3], and the solvent uptake was measured gravimetrically. However, alongside the solvent uptake, the drying of polymeric networks is also of high interest for many applications. Especially for electronics, the drying behavior connected to the heat flux generated by active electronic components is of special interest. Therefore, the developed model will be extended with an energy balance, and the influence of heat transfer on mass transfer will be considered.

In this contribution, a three-dimensional model approach will be presented, and the applicability of the model to consider both the swelling and the drying process will be discussed.

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Solubility of Organic Fluid Mixtures in Glassy Polymers

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Solubility of organic fluids in glassy polymers is important in separation processes such as organic solvent nanofiltrations [1], [2]. In this work, the solubility of the acetone-methanol liquid mixture in a glassy Matrimid was predicted using the non-equilibrium (NE) version of the PC-SAFT and compared to experimental data obtained through FTIR-ATR spectroscopy at 35°C and 1 atm. Pure solvents parameters were selected from the literature [3], [4] by fitting available data on vapor pressure and saturated liquid and vapor densities. Parameters obtained by fitting densities of rubbery DMSO solutions and glassy liquid-liquid equilibrium data [1] were used for Matrimid. Liquid vapor equilibrium experimental data of acetone-methanol mixture at 35°C [5] were then fitted using the PC-SAFT, to retrieve the binary interaction parameters of the two fluids. In addition, experimental solubility data of pure vapor solvents in Matrimid [2] were used to retrieve binary interaction parameters and swelling coefficients of the NE PC-SAFT model. Binary coefficients were finally used to predict ternary data obtaining a satisfactory agreement between the model and the experimental data by using a new mixing rule to account for the polymer dilation due to each penetrant inside the polymer matrix.

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Coarse Grained Molecular Simulations of Polymers using Machine Learned Potentials

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Molecular simulations offer deep insight into the molecular mechanisms underlying the macroscopic behavior of materials, supporting theoretical developments and the discovery of structure-property relationships for a rational materials design. Recently, Neural Networks have shown great promise in the development of improved atomistic force fields, trained on quantum mechanical calculations. The implementation of Machine Learning (ML) for the generation of coarse grained (CG) force fields on the basis of atomistic simulations is a much less explored topic. However, great untapped potential lies in the integration of ML techniques into multiscale molecular simulation methods of macromolecular systems, such as polymers, in particular in the context of CG simulations, significantly contributing towards the development of general hierarchical modelling schemes [1].

In this work, we adopted Graph Convolutional Neural Networks (CGNN) architectures [2] to develop CG Machine Learned potentials, implementing a scheme [3] that includes a force-matching procedure [4]. The obtained models were used to perform CG Molecular Dynamics simulations of polyethylene and a polymer of intrinsic microporosity (PIM-1). The structural and thermodynamic properties of the CG systems were compared with the underlying atomistic reference, examining the effect of the CGNN model size and hyperparameters tuning on the simulation results. This methodology has the potential to streamline the generation of CG force fields, enabling systematic multiscale studies of complex macromolecular systems.

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Differentiable Equations of State for Machine Learning Thermodynamic-Property Prediction

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In recent work, representations of molecules have been used to generate the parameters for SAFT equations of state (EoS) using a machine-learning (ML) model [1,2,3]. We use the Julia SciML ecosystem to elaborate on these studies, presenting an ML model developed using a differentiable SAFT EoS. We train the model on saturation data to generate SAFT-VR Mie parameters from a molecular fingerprint. In differentiating both the EoS and the nonlinear solvers that are used to obtain the saturation properties, we incorporate the exact physics into our ML model. This allows us to account for the degeneracy of the SAFT parameters [4], and our model can be trained on any type of experimental data.

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Modeling Transport Properties of Aqueous Potassium Hydroxide with Machine Learning Molecular Force Fields

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Abstract

The added value of Machine Learning (ML) molecular Force Fields (FF) is showcased by successfully calculating transport properties of KOH (aq). The vast majority of Molecular Dynamics (MD) simulations use FFs which comprise simple 2-body potentials. Such MD simulations can predict macroscopic properties of fluids, e.g., density, heat of evaporation, and self-diffusivity relatively accurately and with reasonable computational costs. However, simulations with such FFs fail to capture more complicated phenomena, e.g., 3-body interactions and chemical reactions. Ab Initio Molecular Dynamics (AIMD) is able to overcome these challenges, but it is computationally more expensive than MD and is limited to small systems (hundreds of atoms) and short simulation times (tens of picoseconds). To accurately determine transport properties, such as viscosity, self-diffusivity, and electric conductivity, long simulation times (in the order of tens and hundreds of nanoseconds) and relatively large system sizes (thousands of atoms) are required. ML is used as a tool to bridge the gap between the quantum and nanoscale by training coefficients of general interatomic potentials. We showcase this by modeling the proton (Grotthuss) transfer enhanced diffusion of OH^- in water using MLFFs, which has not been accurately predicted with simple FFs. MLMD simulations of 100 ps are performed, at standard conditions with 1 mol KOH per kg of water. Implemented post-processing methods recognize the OH^- and are used to calculate the MSD of this ion. The computed self-diffusion coefficient is $(6 \pm 2) \times 10^{-9}$ m^2/s, a value being very close to experimentally measured diffusivity, i.e., 5.27×10^{-9} m^2/s and the simulated electric conductivity is (29 ± 6) S/m, within error estimate of the 26 S/m experimental value.

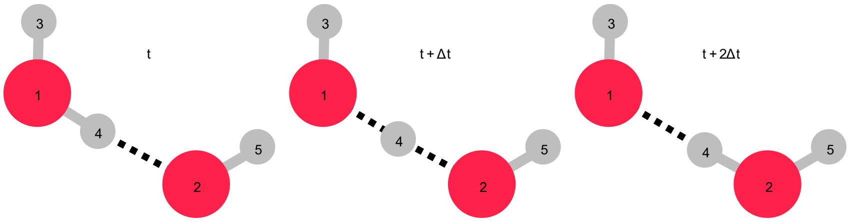

Figure 1: A schematic description of the Grotthuss transfer, where the OH^- takes a hydrogen of the H_2O molecule. The time propagation of the reaction is shown from the left to right (time t till $t + 2\Delta t$). This reaction is an identity switch, causing no change in the concentration of the mixture. It does effect the mobility of OH^- and thus the self-diffusion coefficient and the electric conductivity of the electrolyte.

EleTher JIP: A quaternary system for investigating the effect of acid-base equilibria on volatilities

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The importance of the study of electrolyte containing systems from a thermodynamic point of view has been stressed several times recently [1–3]. The aim of the EleTher Joint Industry Project (www.elether.fr) is to benchmark fluid phase equilibrium modelling approaches on some well-designed electrolyte systems.

Ionic mixtures are far from ideal, thus requiring an activity coefficient model that may need adjustable parameters. In addition, the reactivity results in the fact that additional species may form, which significantly impacts the thermodynamics of the system. The number of parameters may thus increase dramatically. It was decided within the JIP to work with quaternary fluid phase systems, containing, in addition to water, an acid, a base and a cosolvent. This way, both the effect of pH and the effect of dielectric constant could be investigated. The quaternary becomes in practice a 9-component system when the reactivity is taken into account.

In this work, the vapour-liquid equilibrium of the system of water with acetic acid, potassium hydroxide and methanol is investigated in depth, and best practices for parameterization in the presence of only few data are proposed.

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Thermodynamics-assisted kinetic model for esterification reactions based on ePC-SAFT: Application to levulinic acid

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Proton activity is a key thermodynamic property that determines the charge state of species within a mixture. Thus proton activity exerts a direct influence on the equilibria and kinetics of acid-catalyzed reactions. Such reactions, particularly esterification reactions, commonly take place in non-aqueous media. Despite the well-established principles of acid−base chemistry, the knowledge on proton activity in non-aqueous solvents is still limited [1].

In this study, we predicted proton activities along the reaction coordinate of the esterification of levulinic acid. This required free energies of proton solvation and concentration-dependent proton activity coefficients along the reaction coordinate, and both were predicted with ePC-SAFT [2]. The protons stem from the acid catalyst (sulfuric acid), for which the dissociation equilibria of sulfuric acid were also solved along the esterification coordinate. The finally obtained proton activities were used to build a kinetic model for the esterification of levulinic acid with various alcohols. Utilizing this thermodynamics-assisted kinetic model, the influence of various reaction parameters (co-solvent composition, reactant ratios, catalyst concentrations) on kinetics and equilibria was systematically investigated. This analysis includes all esterification reactions involving methanol, ethanol, and 1-propanol. It has been demonstrated that the model allows predicting the kinetics of the various reaction conditions [3]. A key finding was the notable reduction in kinetic activity caused by the presence of water, which was predicted by the model and validated by experimental observations.

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Ion-pairing in BiMSA ePPC-SAFT for aqueous and mixed-solvent alkali halide solutions

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Abstract

Thermodynamic modeling of electrolyte solutions is relevant to design and optimize industrial processes. Recent developments use equations of state (EoS) adapted to electrolyte solutions. Their approach is often based on the use of a dispersive contribution to describe ion-ion or ion-solvent interactions. When weak salts are considered, ion pairing needs to be taken into account through the introduction of a chemical reaction. This implies that a new species must be defined, with all its parameters. The approach proposed by our team uses the Wertheim association term to describe the short range interactions between two ions or between ion and solvents. Recent papers showed the quality of this approach for aqueous alkali halide systems. In the case of mixed solvent (water + alcohol), the strong salts become weak because of the low dielectric constant of the medium. The use of an association term to describe this phenomenon is then particularly well adapted.

In this work the electrolyte polar perturbed chain statistical associating fluid theory (ePPC-SAFT) is used to model strong electrolyte solutions in water (alkali halide salt-water) and mixed solvents (alkali halide Salt-water-alcohol) according to the Binding MSA theory. In fact, the presence of alcohol as a co-solvent lowers the dielectric constant which as a result increases the concentration of ion-pairs .

Different versions of the mean spherical approximation theory (MSA) were implemented such as the Simplified-MSA (SMSA) and the Simplified Binding-MSA (SBIMSA). Moreover, the Bjerrum and Wertheim approaches were added to account for the association of ions(electrostatic ion-pairing or chemical association).

Phase equilibria of clathrate hydrates of carbon dioxide and different substrates

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Inspired by the growing interest in lowering the amount of CO_2 in the Earth's atmosphere, we have examined in the past few years the phase behaviour of CO_2 and organic materials from various classes that may be used as substrates for clathrate hydrates or as physical solvents for carbon capture. Furthermore, many other sectors depend on the study of the phase behaviour, thermodynamic, or transport aspects of mixtures containing carbon dioxide.

A very recent literature study [1] revealed that in the last years, carbon dioxide captured by using clathrates is increasingly researched. A new installation for investigating the phase behaviour of clathrate hydrates was built, tested, and validated. The main component is a 250 cm^3 autoclave, connected with a high-pressure Teledyne Isco syringe pump and a recirculator bath (Julabo) which operates between -50 and 200°C. Phase equilibria of clathrate hydrates of carbon dioxide + methyl cyclopentane, + cyclopentane or cyclohexane were investigated. The new data were compared with literature ones and modelled.

Acknowledgement

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A general Gibbs free energy minimization algorithm for modelling solid-fluid equilibria involving miscible solids, pure solids, hydrates, and cocrystals

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At a fixed temperature and pressure, a mixture is said to be at equilibrium if and only if the total Gibbs free energy is at its global minimum. In other words, phase equilibria calculations can be viewed as optimization problems as the minimization of the Gibbs free energy represents the sufficient condition for phase equilibria. Nevertheless, the necessary condition of equilibrium resulting from the iso-fugacity condition of individual component in each guess equilibrium phase is easier to compute and thus more used. This being said, metastable solutions can occur if phase equilibria were solved using the latter. On the whole, minimization of Gibbs free energy should be prioritized as it is the only approach that provides the real thermodynamic state of a given mixture since it considers the overall Gibbs free energy of the system.

A general algorithm based on the Gibbs free energy minimization approach is presented in this work. Provided that suitable fluid-phase and solid-phase models are selected, this algorithm allows the calculation of fluid-fluid phase equilibria and solid-fluid equilibria; given the system features (number of components, global composition, temperature, and pressure), the algorithm is able to evaluate the main features of the most stable thermodynamic state (number, nature, composition of the equilibrium phases) without guessing in advance their values.

To the authors knowledge, the proposed Gibbs free energy minimization approach is the first allowing the calculation of solid-fluid equilibria involving different kinds of solids: from totally miscible solids (like in the N_2+Ar and CH_4+Kr systems), partially miscible solids (like in the N_2+O_2 and CH_4+Ar systems), pure solids (like in the N_2+CO_2 and CH_4+C_2H_6 systems), and hydrates (like in the CH_4+H_2O system), to cocrystals having both congruent (like in the CH_3OH+H_2O) and incongruent melting (like in the C_6H_6+C_2H_3N system).

Solid-Liquid Equilibria of Selected Ternary Systems Containing Diphenyl Carbonate, Alcohol, Dialkyl Carbonate, and Phenol

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A non-phosgene process, i.e., a process for polycarbonate (PC) production from carbon dioxide, ethylene oxide, and bisphenol A, has been developed. This process provides an effective use for carbon dioxide, which is a greenhouse gas and an abundant carbon resource, and has attracted much attention in terms of greener and more sustainable chemistry. Recently, a new process that uses only carbon dioxide and bisphenol A has also been developed. This new process uses less energy and is cheaper than the existing non-phosgene process. Diphenyl carbonate (DPC) is an important intermediate material in these processes. The DPC purity directly affects the downstream PC quality. High-purity DPC is important in the production of PC for optical media applications. One of the options for DPC purification is crystallization. Knowledge of solid-liquid equilibrium (SLE) data is crucial in the design and development of crystallization processes.

We previously reported the experimental SLE data of selected binary systems containing DPC [1, 2]. In this work, we investigated the SLE of five ternary systems containing DPC, alcohol, dimethyl carbonate (DMC), diethyl carbonate (DEC), and phenol, i.e., methanol + DMC + DPC, ethanol + DEC + DPC, phenol + DMC + DPC, DEC + phenol + DPC, and ethanol + phenol + DPC in the reaction involved in the non-phosgene PC processes. The SLE data of these ternary systems were experimentally determined by a synthetic, visual technique designed in our previous work [2]. These SLE measurements were done as pseudo-binary systems, setting α of the DPC free basis mole fraction of binary system. The experimental SLE data were compared with the predicted ones by the NRTL model using the binary interaction parameters determined from the binary constituent systems. The prediction was also tested by the NIST-modified UNIFAC group contribution method.

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Tunable alkali-aluminosilicates geopolymers and composites as solid adsorbents for CO_2 capture applications

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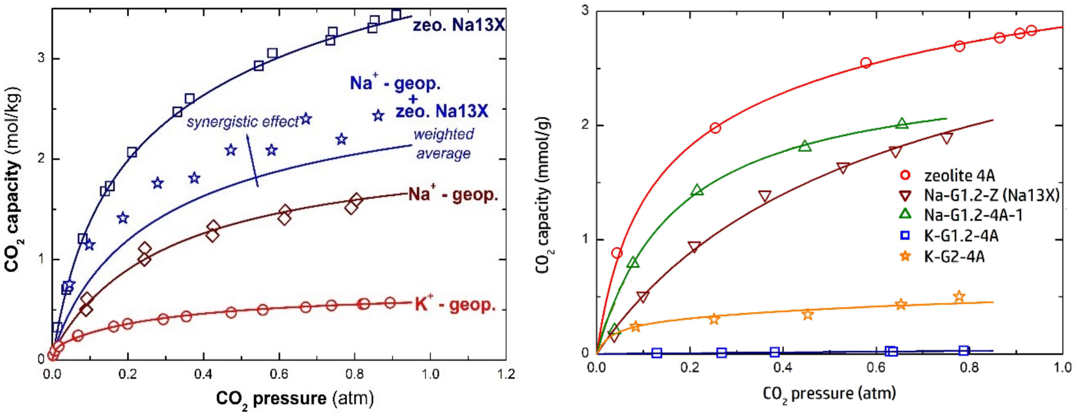
Novel geopolymeric formulations have been developed to fabricate materials and composites to be used as solid adsorbents for the removal of CO_2 from gaseous streams, e.g. for carbon capture. The geopolymer stoichiometry, phase composition and combination with other aluminosilicates such as zeolites have been considered in order to tune the resulting adsorptive performances, for targeted application. In particular, the Si/Al ratio has been varied from 1 to 2, using either K^+ or Na^+ silicates, and combined to different zeolites (including Na13X and NaA type).

The results obtained indicated that Na^+-based geopolymers present a superior CO_2 capacity than those based on K^+, as illustrated in the Figure, while a CO_2/N_2 selectivity results larger for the latter system. Interestingly, the addition of a zeolite fillers further enhances the CO_2 capacity, often revealing a synergistic interplay among the phases; the effect is due to positive interactions obtained by efficient chemical mixing and the geopolymerization reaction, with the formation of a crystalline phase (NaA-type). When combined to zeolite Na4A, the obtained CO_2 capacity reaches values comparable to those of benchmark adsorbents, identifying an optimal Si/Al ratio equal to 1.2.



CO_2 adsorption capacity in geopolymers and geopolymer/zeolite composites

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Acidic aqueous biphasic systems: a novel approach for recovering critical metals from e-waste

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Metals are indispensable commodities crucial for the advancement of modern society and play a pivotal role in transitioning toward a greener economy. However, metals are finite resources, and despite the current record-high mining rates, the recovery of concentrated metals from urban waste remains suboptimal. To confront this challenge, ionic-liquid-based acidic aqueous biphasic systems (IL-based AcABS) have emerged as a pivotal tool in establishing sustainable and efficient procedures for recycling valuable and critical metals from secondary sources like e-waste.

The formation mechanism of IL-based AcABS has undergone extensive investigation, revealing the adaptability of these systems in separating diverse metal types by the careful selection of suitable acids and/or IL anions. The separation of metals between phases is primarily driven by ion exchange mechanisms, enabling the achievement of complete selective separation of analogous metals, such as cobalt and nickel, in a single step. Additionally, the evaluation of temperature-induced behavior in AcABS underscores their thermoreversible nature, a pivotal characteristic for their application in integrated hydrometallurgical processes. In conclusion, IL-based AcABS present a promising solution for the efficient and sustainable recovery of critical metals from e-waste, offering a pathway toward enhancing resource utilization and minimizing environmental impact.

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, and UIDB/50020/2020 and UIDP/50020/2020 (LSRE-LCM), and LA/P/0045/2020 (ALiCE), funded by national funds through FCT/MCTES (PIDDAC). This work was also financially supported by national funds through FCT – Fundação para a Ciência e a Tecnologia, I.P., within the scope of the project PlatILPlus (2022.04478.PTDC, DOI: 10.54499/2022.04478.PTDC). N. Schaeffer acknowledges the national funds (OE), through FCT, in the scope of the framework contract foreseen in the numbers 4, 5, and 6 of the article 23, of the Decree-Law 57/2016, of August 29th, changed by Law57/2017, of July 19th.

Choline-Amino Acid Ionic Liquids: from synthesis to application in ATPS

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Active Pharmaceutical Ingredients (APIs) are a class of emerging pollutants, mainly originated from hospital and household effluents, which are known to pose profound consequences to aquatic environments, such as the feminization of fish, for which finding sustainable extractive methodologies for these contaminants is a must.

Choline-Amino Acid Ionic Liquids (CAAILs) constitute a greener alternative to classical ionic liquids, such as the ones based on imidazolium cations, given their ease of synthesis from natural sources and their significant biodegradability [1]. Moreover, their substantial insolubility in aqueous solutions of inorganic salts provide favourable extraction conditions in Aqueous Two-Phase Systems (ATPS) [2], and their relatively mild conditions allow the extraction of valuable biomolecules and of APIs [3].

This work includes the synthesis of green novel ionic liquids based on choline, the thermophysical characterisation (density, viscosity and refractive index) of their binary mixtures with water, ternary liquid-liquid equilibria determinations and partition studies of pharmaceutical pollutants. More specifically, CAAILs based on L-alanine, glycine, leucine, and L-serinate were synthesized, and their chemical structures were validated by comparing the experimental Fourier-Transform Infrared Spectra (FTIR) with predictions from computational chemistry. Then, ATPS based on these CAAILs and with good scale-up potential were used in the liquid-liquid extraction of pharmaceutical pollutants (such as amoxicillin and acetaminophen) at 298.15 K and 0.1 MPa.

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Eutectic solvents for fish skin valorization. From fundamentals to application

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Global fish processing industry needs to face a pressing challenge: the growing problem of waste, which contributes to significant environmental burdens and economic losses. Recovering and revaluing fishery by-products offer a contemporary solution to reduce disposal costs, minimize environmental impact, and create new commercial opportunities.

Fish protein hydrolysates are rich in essential amino acids, peptides, and bioactive molecules, rendering them valuable products for various applications in nutraceutical and pharmaceutical industries. Some traditional techniques for obtaining protein hydrolysates from fish discards involve the use of harsh chemicals and high temperatures, leading to potential degradation of amino acids and environmental concerns. Other methods are based on the use of enzymes but require longer processing times and higher costs.

This study explores the application of the eutectic solvent constituted of urea and sodium acetate trihydrate, as an innovative and eco-friendly approach to extract protein hydrolysates from fish discards. In a first stage of the study, the solid-liquid equilibrium of the binary system was determined to ascertain the eutectic composition. In a second stage, the solubility of different amino acids in the eutectic was measured. The results showed good solubility values for some of the major amino acids found in fish collagen, so the solvent was tested with yellowfin tuna skins, a commonly discarded by-product. A soaking process was carried out with the eutectic at 35 °C, a temperature at which the formation of the eutectic allows working in a liquid phase, followed by extraction with water at 45 °C. The yield of the extraction reached values close to 0.30 g of protein hydrolysates per gram of wet skin. The product was characterized by determining the amino acid composition, molecular weight distribution, FT-IR, degree of hydrolysis, and rheological properties.

The use of this eutectic solvent offers notable advantages over traditional methods, such as enhanced yields, lower energy consumption, and a more sustainable footprint.

Development of a hybrid platform for molecular design and selection of Ionic Liquids for CO_2 capture and conversion

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Ionic liquids (ILs) have been of great interest in recent years due to by tuning the structure of their ions their physicochemical properties can be adjusted to meet specific requirements. Their remarkable selectivity for removing CO_2 makes ILs highly appealing for applications such as gas sweetening and precombustion gas separation. In contrast, a notable drawback is their limited capacity to capture CO_2 at low partial pressures posing a significant challenge for their integration into post-combustion capture processes. A potential solution to this issue involves incorporating functional groups into their ions capable of reacting with CO_2 [1]. However, the introduction of these modified ILs may result in a more viscous solvent medium, presenting another critical consideration. Therefore, it is required a more innovative and ingenious design of their chemical structures. By designing the optimal molecular structure of potential ILs, it becomes possible to overcome the challenges associated with both selectivity and capacity in CCS technologies. To effectively assess a considerable portion of the available chemical space of ILs suitable for CO_2 capture is necessary to critically evaluate their thermodynamic, kinetic, and intrinsic properties. This work aims to develop a novel platform that combines thermodynamics and data-driven techniques for designing innovative classes of ILs specifically tailored for CO_2 capture processes. We employ perturbation theory for discrete potentials of monomeric fluids (DPT) [2] to develop primitive models for ILs structures. This theory only necessitates the implementation of an accurate equation of state (EoS) for square-well (SW) fluids. To describe the thermodynamics of the systems involved, we utilize the GC SAFT – γ SW EoS [3]. Additionally, we incorporate screening strategies based on machine learning to rapidly evaluate a vast library of chemical structures.

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Multilayer Quasichemical Model of a Nonuniform Fluid Mixture that Contains Chainlike and Associating Species

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A recently developed Multilayer Quasichemical Model (MQM) [1] extends Smirnova's theory of a nonuniform solution near a flat solid wall [2] to fluid interfaces of varying geometry. Pair correlations between interacting functional groups of the molecules are described within the Guggenheim quasichemical approximation; the propagation of molecular chains in the fluid is described as a random walk, renormalized locally in every direction by the system geometry (planar, spherical or cylindrical) and by the competition for accommodation between the chain's segment and other species. MQM gives very detailed structural description, including spatial distributions of monomeric molecules and chain's segments, the profiles of orientations of the chemical bonds along the chainlike molecules, the local orientations of different functional groups and orientations of hydrogen bonds in a multicomponent nonuniform fluid.

In this work, we apply MQM for the interfaces between bulk liquid phases, micelles, reverse micelles, lamellae, and droplets in mixtures that contain water, nonionic amphiphiles, and nonpolar chains in different combinations. We predict relative stability of different structures and calculate the interfacial tension, the adsorption, and the profiles of local pressures. For water-containing mixtures, we calculate the polarization of the interfaces. Fine details of different local structures obtained from the model are discussed. Our theoretical results are compared with predictions from iSAFT [3], as well as with experiment and MD simulation data from the literature. We discuss the transferability of MQM parameters estimated from fluid phase equilibria data for predicting the interfacial properties and the structural characteristics of aggregates.

Acknowledgments

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First-order perturbation theory using a short-range Lennard-Jones fluid reference

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Abstract

To develop an equation of state for fluids is one of the ultimate goals of applied molecular physics. To reach this goal, a perturbation approach is the only theoretical tool available. It comprises three steps: (1) choice of a reference system (fluid), (2) description of the reference, and (3) evaluation of the correction terms. We argue, that recently proposed [1, 2] criterion to split the pair interaction energy of the system into two parts, one of which – the reference system – is forced to be responsible the most accurately as possible for excluded volume free energy of the entire the system, results in the first-order perturbation theory that performs extremely accurately over a wide range of thermodynamic conditions. To illustrate, the proposed theory first is applied to Lennard-Jones-like Yukawa fluid – the case, when all calculations within steps (2) and (3) can be reduced to the closed analytical expressions using the solution of MSA theory [3]. Generalization to the Lennard-Jones fluid equation of state then is presented using the short-range Lennard-Jones fluid reference [4].

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A general method for calculating metastable fluid properties

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Metastable fluids are at the heart of diverse phenomena, ranging from cloud formation, geological fluid inclusions, and choked flow through nozzles. In contrast to stable fluids, a universally accepted method for computing their thermodynamic properties remains elusive. Contemporary multiparameter equations of state, such as the IAPWS formulation for water [1], have unparalleled accuracy for stable states but cannot reliably calculate metastable properties. This work introduces a method for calculating metastable fluid properties applicable to real fluids, by using only properties of stable states as input. We validate our approach against high-accuracy monte carlo simulations of a Lennard-Jones system.

Additionally, modern theories for interfacial properties, such as classical density functional theory, and the simpler density gradient theory, require estimates of thermodynamic properties for *unstable* states. Our method also addresses this need, as evidenced by its successful application in calculating the surface tension of water by use of the IAPWS equation of state with density gradient theory.

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Cluster-Based Discrete Modeling Approach for Activity Coefficients of Molecular Liquids

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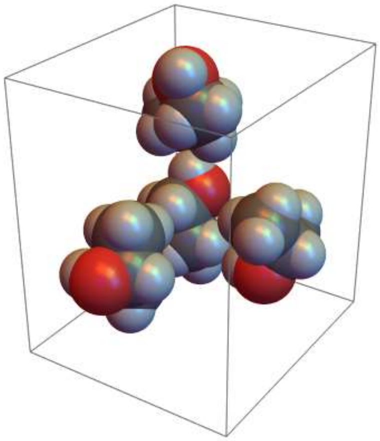
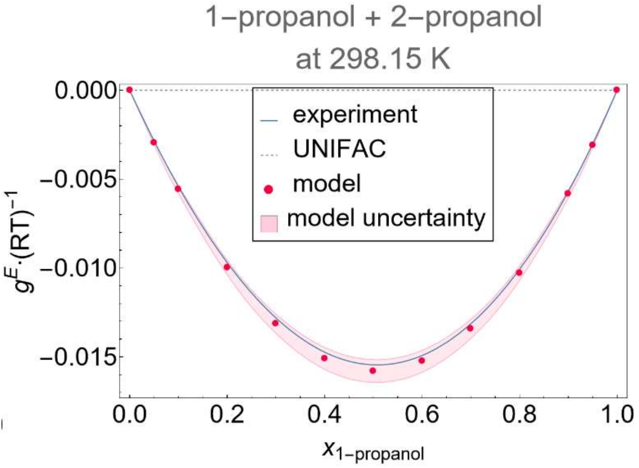
A recently published g^E-model for two-component liquid molecular mixtures is based on discrete clusters of molecules. [1] These clusters contain the three-dimensional geometric information about local molecular neighborhoods that determine the interaction energies of the clusters. In the sense of a discrete Markov chain, the clusters are used for the hypothetical construction of the mixture by means of sequential insertion steps. In the course of this, each cluster is assigned a probability of occurring in an equilibrated system which is determined by constrained minimization of the Helmholtz free energy. For this, informational Shannon entropy based upon these probabilities is used synonymously with thermodynamic entropy, which represents the core of the discrete modeling approach. [2]

For coupling the model to real molecules, a first approach for a molecular sampling algorithm is used which determines the cluster energies using the OPLS-AA force-field. Exemplary applications illustrate the model's ability to describe a variety of g^E-curves including the ability to distinguish between structural isomers.





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Estimating Gas Sorption in Polymeric Membranes from The Molecular Structure: A Machine Learning Based Group Contribution Method For The Non-Equilibrium Lattice Fluid Model (ML-GC-NELF)

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According to the solution-diffusion model, the solubility of gases plays a critical role in determining the overall performance of a polymeric membrane for gas saperation processes. Since it's inception, the Non-Equilibrium Lattice Fluid (NELF)[1] model has become a vital tool in correlating and predicting the gas solubility behavior in glassy polymeric membranes. However, just like it's equilibrium counter-part (i.e. the Sanchez and Lacombe (SL) equation of state [2]), the applicability of the NELF model is often limited to the availability of the pure component parameters of the polymers. In our recent publication[3], we have addressed this issue by building a machine learning group contribution (ML-GC) model, based on a modified version of the Marrero and Gani's method [4], that predicts these parameters from the chemical structure. The model was successful in reproducing the pure polymer parameters of our database and the results were also validated against experimental data. Furthermore, we have estimated the parameters of high performing polyimides that did not participate in the ML training procedure, and modelled the gas solubility isotherms in them accurately.

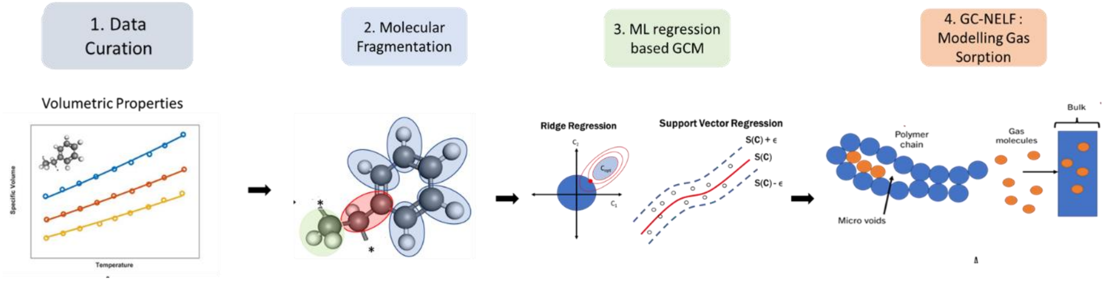

Figure 1. The workflow adopted to build the ML-GC-NELF

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Machine learning paradigm for parametrizing soft-SAFT molecular models for pure refrigerants

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The primary culprit for global warming is the use of refrigerants with high ozone depleting and global warming potentials, directing the search for replacement green refrigerants [1]. Molecular-based equations of state (EoSs), such as polar soft-SAFT [2], have the ability to appropriately quantify dipolar interactions governing the thermodynamic behavior of sustainable refrigerants [3]. However, they require experimental data for parametrizing system-specific molecular parameters.

In this work, we present a novel integrated approach employing machine learning algorithms for predicting thermophysical properties of low GWP refrigerants. The approach allows obtaining molecular parameters to be used in the polar soft-SAFT EoS using molecular descriptors obtained from COSMO-RS. The predicted parameters were used in polar soft-SAFT towards the holistic evaluation of pure refrigerant thermophysical properties providing comparable level of accuracy to molecular parameters obtained from standard fitting to experimental data. This included density, vapor pressure, heat capacity, heat of vaporization and speed of sound, predicted at an accuracy of 1.3 – 10.5%. These parameters provided comparable level of predictive accuracy when extended to modeling phase equilibria of binary mixtures. The results of this work enable bridging the gap in properties data of alternative refrigerants, hindering their technical evaluation.

We acknowledge the financial support of Khalifa University through the Research and Innovation Center on CO_2 and Hydrogen (RICH Center, RC2-2019-007).

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Neural Network-Based Tensor Completion: Advancing Predictions of Activity Coefficients and Beyond

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Equations of state like PC-SAFT require binary interaction parameters, which are typically adjusted or determined using group contribution methods. Moreover, it is feasible to adjust these parameters based on properties predicted through machine learning techniques, leading to the advancement of Jirasek's et al. methodology for the estimation of γ^∞ [10.1021/acs.jpclett.9b03657]. Although existing tensor completion methods have made progress in predicting two- and three-dimensional data, they still struggle to effectively capture nonlinearities and temporal dependencies in relational data. We introduce the novel 3D-DMF-H method for tensor completion, a neural network-based approach extending Deep Matrix Factorization (DMF) to handle nonlinear data structures and incorporate additional data points. This method is versatile for various three-dimensional tensor completion problems, achieving exceptional accuracy in predicting activity coefficients for phase equilibria modeling. Remarkably, 3D-DMF-H surpasses the UNIFAC thermodynamic model (figure 1, left) and improves azeotrope predictions with PC-SAFT (figure 1, right). These results underscore the potential of machine learning in the chemical industry and the need for ongoing algorithmic refinement and exploration.

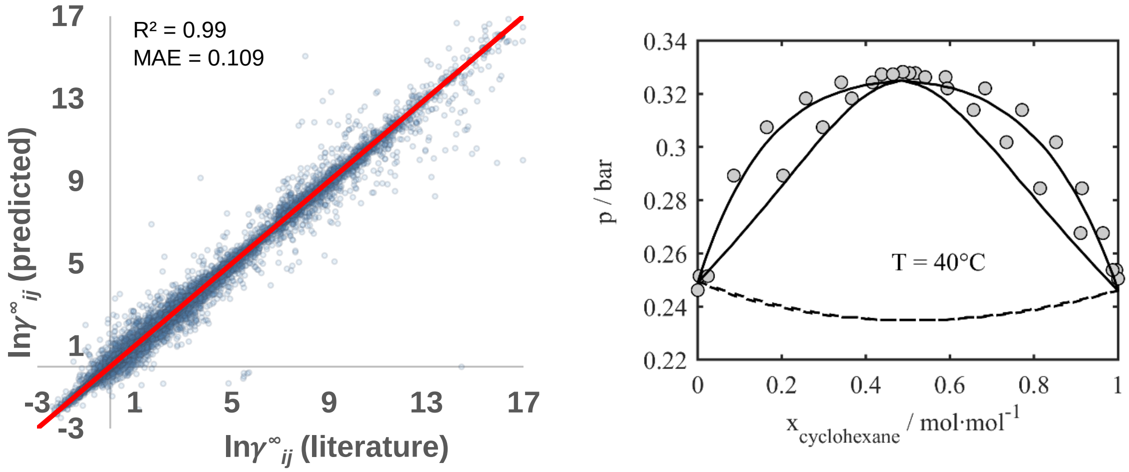

Figure 1: Left: parity plot of the activity coefficient predictions using experimental values as input for the 3D-DMF-H algorithm. Right: Vapor–liquid equilibrium for the cyclohexane/ethyl acetate system. The VLE was calculated with PC-SAFT using either the adjusted binary interaction parameter k_{ij} (solid line) from the 3D-DMF-H predicted activity coefficients or $k_{ij} = 0$ (dashed line). For comparison, the according literature data (circles) is shown for the system. (Patent pending under future reference 102023211154.3 at the DMPA)

In-silico approach to screen new nanoporous materials for urea capture from spent dialysate

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Hemodialysis (HD) is a life-saving treatment for 2.6 million end-stage kidney failure patients globally. HD uses a semipermeable membrane to clear uremic toxins (UTs) from the blood, diffusing into the dialysate. In 2017, lack of affordable treatment caused 1.2 million deaths. HD is delivered 2-3 times weekly in hospitals and severely impacts patient lifestyle, causing vascular stress and post-treatment issues. Each session requires 120 L of dialysate reducing portability and making this treatment water-intensive. A wearable artificial kidney (WAK) technology targets the removal of UTs and usually involves enzymatic or electrochemical urea conversion, but concerns about safety of these strategies exist. A safe alternative, not involving any reaction, is the capture UTs through adsorption. Mixed matrix membrane adsorbers are based on a porous polymeric support with filler particles, adsorbing UTs offer optimal conditions with low energy consumption [1]. Organic Frameworks (MOFs and COFs) are potential candidates, but their effectiveness in capturing UTs needs exploration. This project aims to create a computational protocol for screening crystal structures to capture urea and other UTs from dilute solutions. Experimental structures from crystallographic databases were assessed for safety and stability and 500 structures were chosen. Zeo++ was used to calculate pore size and surface area, while Widom's insertion method and MD simulations determined chemical potential, selectivity, and binding sites. Organic framework pore functionalization played a crucial role, but heteroatom composition, surface area, and pore size were insufficient parameters. MD simulations emphasized Coulomb's intermolecular interactions and validated binding sites [2]. The approach identifies experimental candidates and establishes a structure-property relationship for UTs adsorption. Hypothetical databases offer a vast resource for computational investigation, guiding future material design for hemodialysis.

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Designing selective nanoporous materials for VOC capture applied to breath diagnostics: insights from simulation and experiments

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There are numerous volatile organic compounds (VOCs) present in exhaled human breath. Different diseases or metabolic states produce unique profiles of some of these VOCs, providing a chemical fingerprint that has potential to be used as a diagnostic tool or provide insight to the health of the body. However, detecting these specific molecules in a complex mixture of air, water, CO_2, and other non-marker VOCs is a significant challenge. Fundamentally, it is a separations problem. Metal-organic frameworks (MOFs) are porous crystalline materials consisting of inorganic nodes connected via organic linkers. MOFs offer a variety of pore sizes, pore shapes, and chemical properties, implying that they can be tailored to specific adsorption applications.

We use high-throughput molecular simulation to design or choose sorbents tailored to adsorb specific target VOCs with high selectivity over competing molecules (e.g. water, CO_2). We will discuss thermodynamic properties of VOC adsorption and VOC diffusion in several MOFs of interest, including challenging isomer separations such as 1-propanol/2-propanol and cis/trans isomers.

We have identified and synthesized several promising MOFs with high selectivity for VOCs of interest—including some known to be indicators for COVID-19 -- and validated their adsorption capacity and selectivity in realistic synthetic breath streams. These MOFs have also been tested for thermal and chemical stability.

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On the formation of colloidal clathrates and diamond crystals

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Department of Theoretical Chemistry, Maria Curie-Sklodowska University in Lublin, Poland

The endeavor to selectively fabricate a cubic diamond is challenging due to the formation of competing phases possessing similar free energy. Examples of such are: stacking hybrids of interwoven hexagonal and cubic diamonds with (i) its liquid phase, (ii) arrested glasses, or (iii) clathrates, all depending on the relative patch size, despite being within the single association regime [1, 2]. The necessity to selectively achieve cubic diamond is of paramount importance since the cubic diamond is the only polymorph exhibiting a complete photonic bandgap, making it a promising candidate in view of photonic applications.

Herein, we demonstrate that due to the presence of an external field and delicate manipulation of its strength we can attain selectivity in the formation of a cubic diamond in a one-component system comprised of designer tetrahedral patchy particles, despite the formation of stacking hybrids in bulk [3]. Moreover, we also show that although tetrahedral patchy particles with narrower patches assemble into clathrates in bulk, this can be suppressed by the application of an external surface potential [4]. Depending on its strength we can attain the aforementioned stacking hybrids or the selective formation of cubic diamond. The driving force of such a phenomenon is the structure of the first adlayer which is commensurate with the (110) face of the cubic diamond.

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Overview of the ERC project: “New Paradigm in Electrolyte Thermodynamics”

Georgios M. Kontogeorgis and Xiaodong Liang, Department of Chemical and Biochemical Engineering, Technical University of Denmark, Denmark

This presentation will summarize some of the major results of this ERC project that has as overall target to arrive at a fundamental understanding of electrolyte thermodynamics and thus enable the engineering of a new generation of useful, physically sound models for electrolyte solutions. These models should be general and applicable to a wide range of conditions so that they can be potentially used for many applications. The aim is both to achieve a fundamental understanding of electrolyte thermodynamics but also ensure contact with stakeholders (industry, etc) where electrolyte thermodynamics is expected to be relevant and useful. The ambition is to make advances, which can clarify major questions and misunderstandings in electrolyte thermodynamics, and create a new paradigm that will ultimately pave the way for the development of new engineering models for electrolyte solutions. The behavior of electrolyte solutions is expected to be affected by the major solvent present, water, and thus the accurate description of water properties is also of paramount importance in electrolyte thermodynamics.

Acknowledgement

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Analysing Helmholtz energy contributions of model electrolyte systems using molecular simulations

Anja Reimer, Isabell Reisch, Joachim Gross, University of Stuttgart, Stuttgart, Germany;

One can distinguish two different concepts for describing electrolyte systems: The primitive model and the non-primitive approach. In the non-primitive approach, the (dipolar) solvent is considered explicitly and ion-ion, ion-solvent and solvent-solvent interactions are taken into account. In the primitive model, the solvent is implicitly considered as a dielectric continuum with relative permittivity ε_r. Commonly used expressions for the Helmholtz energy contributions in electrolyte systems based on the primitive model are variations of the Debye-Hückel (DH) equation [1], the mean spherical approximation (MSA) [2] and the Born term (discussed in ref. [3]). Various electrolyte equations of state, such as ePC-SAFT advanced [4], combine the primitive and the non-primitive approach by explicitly modelling the short-range interactions of the solvent molecules and then adding the DH equation or the MSA expression to account for the ion-ion interactions and the Born term to account for the ion-solvent interactions.

In this work, we analyse whether this combination of the two concepts and the assignment of the theoretical expressions to the specific electrostatic Helmholtz energy contributions is appropriate. For this purpose, we perform molecular simulations in the non-primitive model and determine the permittivity and the Helmholtz energy contributions resulting from ion-ion, ion-solvent and solvent-solvent interactions for different electrolyte systems. We compare our simulation results with the DH equation, the MSA and the Born term.

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Applying openCOSMO-RS to Electrolyte Systems from Infinite Dilution to the Ionic Liquid State

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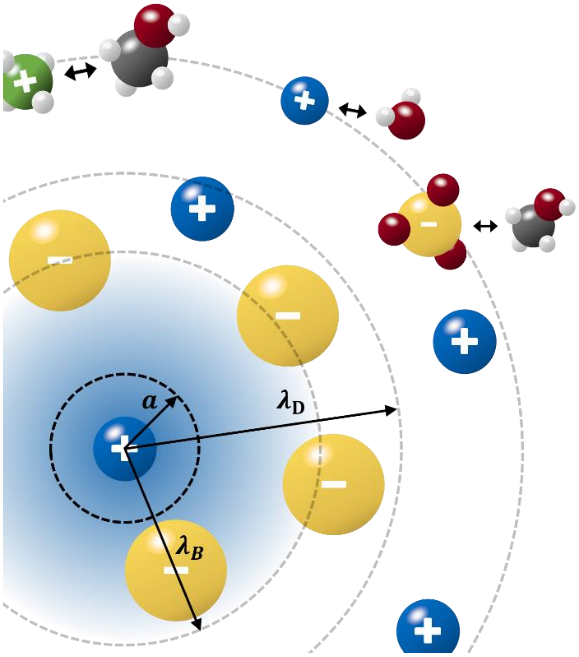
According to the Working Party on Thermodynamic and Transport Properties of the European Federation of Chemical Engineering (EFCE), electrolyte thermodynamics stands out as a topic of high complexity with a strong need for predictive models. [1] In the past years, we have developed a predictive model for electrolyte systems based on the COSMO-RS theory. [2] This was done based on our own open source implementation of the model **openCOSMO-RS** [3]. By integrating additional a priori information into the model efficiently, it allows refining the descriptions of the interaction energies, making the prediction of complex systems feasible in the first place.



We have shown that by using only first principles information, the model has been able to predict mean ionic activity coefficients, liquid-liquid equilibria and solid-liquid equilibria for strong electrolytes in water, mixed solvents and completely non-aqueous systems.[3]

In this work, we show the latest improvements of the model, which allow **predicting mixed solvent phase equilibria** for **strong electrolytes** and for **ionic liquids** at the same time. Widening the range of application of the model from infinite dilution to the ionic liquid state.

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Measurement of Vapour Liquid Equilibrium Thermodynamic Properties Until the Critical Point and modelling

Christophe Coquelet, IMT Mines Albi, CNRS UMR 5302 and Mines Paris, PSL University

In chemical engineering, the difference in composition between two phases, such as between liquid and vapor or between two liquid phases at equilibrium, forms the basis of most separation processes. For instance, notable methods include distillation, liquid-liquid extraction, and supercritical fluid extraction, where the second phase is obtained through the addition of a separating agent (solvent). In mechanical engineering, the design of heat exchangers, compressors, and fluid selection requires information regarding the thermodynamic properties of fluids at equilibrium. In oil and gas engineering, as well as the transportation of natural gas/CO2, thermodynamic properties are also crucial for process design. Experimental data are also essential for developing thermodynamic models and adjusting their parameters, including interaction parameters. These models aid engineers in determining phase diagrams and finding optimal thermodynamic conditions for phase separation, compression, cooling, heating, storage, or chemical reactions.

In general, experimental methods for studying low and high-pressure phase equilibrium are classified into closed or open circuit categories. These methods can be divided into two primary classes based on how composition is determined: analytical methods and synthetic methods. In analytical methods, the composition of each phase is obtained through analysis after sampling (direct sampling method). In synthetic methods, the global composition of the mixture is known in advance, and no sampling is required. Thermodynamic properties are determined by measuring temperature, pressure, and volume of the equilibrium cell. The composition of each phase can be determined by solving mass balance equations (indirect methods) or by using an appropriate thermodynamic model.

In this communication, following a recap of the various experimental techniques that can be employed for data acquisition, a selection of experimental techniques will be presented for determining phase diagrams at both low and high pressures, including volumetric properties near and around the critical point. Several examples related to acid gas removal or working fluids will be showcased.

Utilizing the Molecular Simulation Design Framework (MoSDeF) to Screen Soft Matter Systems

Clare M^{c}Cabe, Heriot-Watt University, Edinburgh, Scotland, UK

Soft matter systems (those easily deformed at room temperature - e.g., liquids, polymers, foams, gels, colloids, and most biological materials) are ubiquitous in chemistry, but they pose particular computational challenges since the differences in potential energy between distant configurations are on the same order as the thermal motion, requiring time and/or ensemble-averaged data to be collected over long simulation trajectories for property evaluation. Furthermore, performing a molecular simulation of a soft matter system involves multiple steps, which have traditionally been performed by researchers in a “bespoke” fashion. The result is that many soft matter simulations published in the literature are not reproducible based on the information provided in the publication, and large-scale screening (as envisaged in the Materials Genome Initiative) of soft materials systems is a formidable challenge.

To address the issues of reproducibility and automation needed to enable computational screening, we have been developing the Molecular Simulation and Design Framework (MoSDeF, http://mosdef.org) software suite. We will also show how MoSDeF facilitates the screening of soft matter systems over chemical/structural parameter spaces. Furthermore, while MoSDeF enables us to determine systems with favorable properties more rapidly than could be accomplished through experiment, the screening process still requires a significant amount of time and computing resources. We will illustrate the value of coupling MD simulations with machine learning (ML) in order to guide the screening process and reduce the simulations needed in order to optimize system designs.

Results will be presented for a number of screening projects, including the design of lubricants for nanoscale devices, surfaces that switch in response to changes in solvent, and membranes for the dehydration of polar solvents.

Computational Design of Peptides as Sensors and Drugs

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We describe our efforts to develop an efficient computational algorithm that searches for peptides that bind strongly and selectively to specific biomolecular targets, and to use that algorithm in the design of peptide-based sensors, drugs and affinity chromatography ligands. The algorithm is a Monte Carlo-based iterative procedure that involves as many as 50,000 sequence mutation moves and/or peptide backbone conformation moves to arrive at the peptide sequence and conformation that has the lowest binding energy to the target. The top scoring peptides are then further evaluated by performing explicit-solvent atomistic simulations of the peptide–target complex to determine their binding free energies. The best-performing peptides are sent to the laboratories of our collaborators for experimental verification. Two projects that illustrate the use of this technique will be described: (1) design of peptide affinity ligands for detection of the heart attack biomarker, Cardiac Troponin, and (2) design of peptides to block the action of the toxins secreted by C- difficile bacteria in the large intestine.

Runaway Transition in Irreversible Polymer Condensation with Cyclisation

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The polymer condensation process, involving the formation of bonds between reactive end-groups, is not only a crucial aspect of various natural phenomena, such as DNA ligation, but it also plays a pivotal role in numerous industrial applications. For instance, the formation of linear-shaped micelles can be examined through the lens of a condensation process. This intricate interplay of molecular connections not only mirrors the elegance of nature but also finds practical significance in shaping industrial processes. Here, we focus on the DNA ligation which is a vital biological process that consumes energy to repair double-strand DNA breaks by ATP-driven DNA end-joining reactions. While engineered ligase enzymes are now routinely used in cloning, their role as material actuators is elusive. We study generic systems undergoing polymer condensation in competition with cyclisation. Using a generalised Smoluchowski theory, molecular dynamics simulations and experiments using DNA and T4 ligase, we find that this system displays a transition, from a regime with finite-length ring-shape chains at infinite time to one dominated by linear polymers that grow in time. Finally, we show that fluids prepared close to the transition may have profoundly different compositions and rheology at large condensation times. Our work, inspired by the biology of DNA repair, offers a way to realise non-equilibrium “topologically active” complex fluids that can pave the way for responsive and adaptive materials.

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Water in glassy carbohydrates: thermodynamic analysis and molecular dynamics simulations

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Hydration of polysaccharides and small sugars has been one of the main topics in academia - industry collaborations at Malmö University during past two decades [1- 3]. The primary reason for industrial interest in this topic is the application of carbohydrates as excipients in solid-state pharmaceutical formulations, including formulations of biologics [4]. In glassy carbohydrates, the water activity values deviate from the expected equilibrium values, often leading to a sorption-desorption hysteresis [5]. The partial molar enthalpy of mixing of water (often referred to as hydration enthalpy) is negative in the glassy state [1,2,6] and in many cases shows relatively complex profiles. This behavior was recently explained based on the glass transition properties of the components [7]. To further develop this approach, we derived an expression for water activity in glassy materials, where the deviation from the equilibrium activity values is related to heat capacity changes of the components of the system [8].

To gain further insights into the properties of water in glassy carbohydrates, we conducted molecular dynamics (MD) simulations of water in glassy trehalose. The glassy carbohydrate matrix was obtained by gradual cooling of the system from liquid to glassy state. Then the glassy system was gradually dehydrated to fully dry state to mimic the process of water desorption. In these simulations, the hydration enthalpies observed in experiments are accurately recovered. The analysis of hydrogen bonding obtained in simulations provided detailed explanation of the origin of the exothermic hydration of glassy carbohydrates.

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Influence of pH and Salts on the Solubilities of Active Pharmaceutical Ingredients

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The efficiency of active pharmaceutical ingredients (APIs) is often limited by their very low aqueous solubility. pH and salts may have a significant influence on the API solubility in the intestinal fluid. Both pH and salt concentration in the human body strongly depend on the location (gastric or intestinal system) and the time of intake (saturated or fasted state). Thus, predicting the influences of pH and salts on API solubility are of great interest.

The aim of this work was to predict the influence of pH and salts on the aqueous API solubilities and to investigate the pH range, where the salts formed between ionized APIs and pH-changing agents precipitate. To achieve this, ePC-SAFT was used to convert concentration-based acid constants of the APIs from literature into acid constants based on thermodynamic activities to model the dissociation of acidic and basic APIs.

Unavailable model parameters of the ionized APIs were derived from those of the non-ionized APIs. The ionized APIs have a significant impact on the overall aqueous solubility, which increases by many orders of magnitude when ionized API forms. Moreover, we identified, that using the BORN term was crucial for modeling the ionized APIs. It accounts for the ionic interactions between the pH-changing agents and the ionized APIs. No binary interaction parameter between the non-ionized and the ionized API was used. The binary interaction parameter between the non-ionized API and water was adopted from previous works. However, in contrast to these works, we did not use a binary interaction parameter between the ionized API and water for predicting pH-dependent aqueous solubilites of APIs.

Experimental solubility data of four APIs, namely Naproxen (acidic), Lidocaine (basic), Fenofibrate (neutral) and Griseofulvin (neutral) were obtained via UV/Vis spectroscopy. The precipitated solid was analyzed via Powder X-Ray Diffraction to distinguish between API and API-salt. Moreover, the influence of the biorelevant salts sodium chloride and magnesium chloride on the pH-dependent solubilities of the APIs was measured. The developed modeling approach predicts the influence of both pH and salts on the aqueous API solubilites in very good agreement with the experimental data.

Prediction of API solubility: an overview of the recent developments of the SAFT-γ Mie approach

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Abstract:

The prediction of the solid–liquid equilibrium solubility of active pharmaceutical ingredients (APIs) is a significant challenge which is of importance in pharmaceutical applications and solvent selection. The SAFT-γ Mie group-contribution equation of state [1] has been recently extended to model the phase behavior and solubility of mefenamic acid, a nonsteroidal anti-inflammatory drug, in a range of solvents [2]. The SAFT-γ Mie approach has also been applied to the prediction of aspirin solubility, octanol–water partition coefficients for a range of APIs, and pH–solubility profiles of aqueous buffered solutions of ibuprofen and ketoprofen [3].

Literature data for the vapor pressure, single-phase density, saturation density, vaporization enthalpy, bubble temperature, dew temperature, and bubble pressure are used to characterize the new group interactions. Solubility data are used to characterize the new group-group interactions only if there are no other experimental data available. The transferability and predictive accuracy of the new models are assessed by comparing the theoretical predictions with the experimental solubility data. 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. Very good agreement with the experimental data is obtained for the considered systems.

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Application of DFT calculations in the correlation of phase equilibria: estimating non-randomness factors

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The application of thermodynamic models such as Non-Random Two-Liquid (NRTL) [1] and UNIversal QUAsi Chemical (UNIQUAC) [2] in the description of phase equilibria is often hindered by the inclusion of fixed values for parameters with well-defined physical meaning, making the prediction of equilibrium composition in the absence of copious experimental data very problematic.

The non-randomness factor (α), which appears in both the NRTL and UNIQUAC models, is a parameter related to the randomness of spatial orientation of the chemical species and, consequently, to the randomness of the surrounding local composition. Theoretically, it goes from 0 (completely random spatial orientation of the particles) to 1 (completely defined spatial orientation), but most applications fix this parameter between 0.20 and 0.47 [3].

In this work, an innovative methodology used Density Functional Theory (DFT), an *ab initio* simulation method, to estimate the non-randomness factors of pure components at 298.15 K, 0.1 MPa and liquid state. As expected, larger values were obtained for more polar molecules (*e.g.*, for water: $\alpha = 0.33$), while very non-polar ones presented practically null values (*e.g.*, for toluene: $\alpha = 0.01$). After validating the determined parameters by correlating ternary liquid-liquid equilibria (LLE) data, it was concluded that the proposed methodology could ease the interpretation of phase equilibria by better describing azeotropes and hinting non-ideality.

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MCA+PZ and MCA+AMP aqueous solutions: CO_2 solubility experiments and modelling

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Towards the reduction of CO_2 emissions, post-combustion CO_2 capture attracted significant research interest. To that aim, promising blends using *N*-methylcyclohexylamine (MCA) were examined. In particular, The CO_2 loading of aqueous *N*-methylcyclohexylamine and 2-amino-2-methyl-1-propanol (MCA+AMP) and *N*-methylcyclohexylamine and piperazine (MCA+PZ) solutions were experimentally measured at various temperatures and for CO_2 partial pressures between 10 and 700 kPa. It was observed that MCA+AMP (containing app. 30 % wt. MCA and 8.3% wt. AMP) and MCA + PZ (containing 31.6 % wt. MCA and up to 8% wt. PZ) aqueous mixtures, exhibit high CO_2 solubility and one liquid phase upon the addition of CO_2 at all investigated CO_2 partial pressures and temperatures. Furthermore, the addition of AMP or PZ increases CO_2 loading, expressed as moles of CO_2 per kg of solvent, at 313 and 333 K. In addition, the modified Kent-Eisenberg model was used to predict equilibrium lines for both systems. MCA+PZ solution contains a carbamate and a non-carbamate forming amine, while MCA+AMP solution consists of two non-carbamate forming amines. The model predicts satisfactorily the experimental results of this work and from literature with average AAD% of 6%.

Acknowledgements

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Crystallization risk of aromatic compounds in LNG production: Part III: the solubility of o-xylene in methane-rich mixtures down to cryogenic temperatures

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Following a series of works dealing with the experimental determination of the solubility limits of the BTEX components in methane rich-mixtures down to cryogenic temperatures, this work presents new measurements for the solubility of solid o-xylene in solvents methane, (90%mol/mol) methane + (10%mol/mol) ethane, and (90%mol/mol) methane + (10%mol/mol) nitrogen. The measurements have been obtained using a static-analytic method that allows sampling the fluid phase in equilibrium with the solid one at temperatures from 273 K down to 122 K at nominal pressures of 3 and 6 MPa.

Despite the importance of BTEX in assessing the risk of crystallization during the liquefaction of natural gas, the solubility of o-xylene in methane rich mixtures was not known in the literatures. As a consequence, these original data will give new insight into the thermodynamic behaviour of the BTEX in LNG production and then provide crucial information for the proper tailoring of the purification units upstream the liquefaction unit.

Measured solid-liquid and solid-vapor equilibria have been compared to the modelling results obtained by coupling a cubic equation of state and a model for the solid phase. The results confirm the conclusions reported in our previous studies: *i)* the non-monotonic variation of the solubility with temperature when crossing the critical region of the solvent, *ii)* binary interaction parameters regressed on vapor-liquid equilibrium could be used for accurately predicting the solubility limit down to cryogenic temperatures.

Keywords: LNG, o-xylene, Crystallization, Solubility, Solid-liquid equilibrium, LNG

Prediction of water anomalous properties by introducing the two-state theory in SAFT

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Water is one of the most abundant substances on earth, but it is still not entirely understood. It shows unusual behaviour, and its properties present characteristic extrema unlike any other fluid. This unusual behavior has been linked to the two-state theory of water, that proposes that water fluctuates between different structures, one with high density and one with low density which may even form two distinct liquid phases at low temperatures [1]. Models incorporating the two-state theory manage to capture the unusual extrema of water, unlike traditional equations of state who fail.

In this work we incorporated the two-state theory of water in the Statistical-Associating-Fluid-Theory (SAFT) [2]. More specifically, we have assumed that water is an ideal solution of high density water molecules (HDW) and low density water molecules (LDW) which are in chemical equilibrium. Using this assumption, we have generalized the association term of SAFT to allow for the simultaneous existence of the two water types, which have the same physical parameters, but different association properties. We have incorporated the newly derived association term in the context of the Perturbed Chain – SAFT (PC-SAFT) [3] and we have succeeded in predicting the characteristic extrema of water properties, such its density and speed of sound maximum etc., without loss of accuracy compared to the original PC-SAFT. This new framework is readily extended to mixtures and PC-SAFT-TS manages to capture the solubility minimum of hydrocarbons in water in a straightforward manner.

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Maximizing solubilities in aqueous solutions

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Water is known as the “universal solvent” and it usually dissolves anything except what one is trying to dissolve. To enhance the dissolution of hydrophobic compounds in water co-solvents, salts, surfactants or hydrotropes can be used. The mechanisms of solvation on these mixed solvents vary but their understanding is what allows the design of new aqueous mixed solvents with improved capability to dissolve target compounds.

Some compounds present solubility maxima in mixed solvents and aqueous mixed solvents are not an exception. These maxima are quite useful from a practical point of view and very curious from the conceptual side. Although an easy qualitative explanation for them is provided in textbooks the solvation mechanisms behind the maxima can be related not only to changes in the solvent but also on the solute conformations making the modelling of these maxima quite challenging. The presence of maxima in various systems will be reported and with the help of COSMO-RS the solubility maxima in aqueous solutions of cyrene or of alcohols will be discussed as two extreme examples where the changes in the solvent (cyrene) or the solute (vanillin) with concentration significantly impact the solubility and thus must be taken into account.

The shape of water – how cluster formation explains the hydrophobic effect

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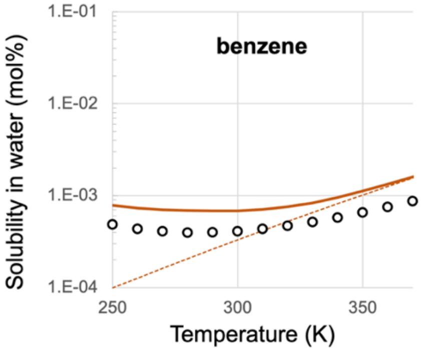
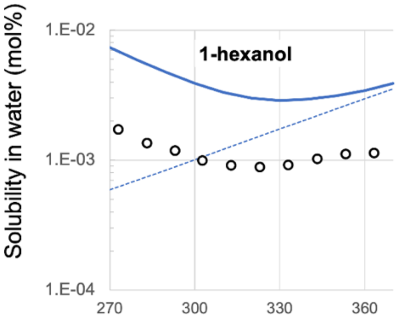
The hydrophobic effect refers to the observation that hydrophobic molecules or hydrophobic parts of molecules avoid contact with water. It is a particular characteristic of water, which in its pure form exhibits more anomalous properties than any other known liquid. However, a molecular scale mechanism providing a unified explanation of how water's anomalies are connected to the hydrophobic effect is lacking. We have used quantum chemistry, the COSMO-RS implicit solvent model and statistical thermodynamics to predict the equilibrium formation of water clusters in water from monomeric water molecules. We have found that our unifying first-principles based model for water cluster formation explains water's anomalous properties such as deviations in density, heat capacity and compressibility with temperature and pressure. Without modification, our model also naturally explains the thermodynamics of organic molecule solubility as well as surfactant self-assembly. COSMO-RS predictions for hydrophobic and amphiphilic compounds are equally accurate (solid lines include clusters, dashed lines are for monomeric water):





Our model provides an intuitive explanation that water becomes more hydrophobic as temperature decreases, because higher concentration of clusters favour internal hydrogen bonds, which leads to fewer opportunities for interactions with solutes. The fact that such a fundamental concept as chemical equilibrium between water and water clusters of certain shape is able to simultaneously explain the thermodynamics of pure water's anomalous properties as well as the hydrophobic effect could lead to improved rational design of aqueous system-based processes.

Posters

Development of Lorentz cycle power generation for low grade heat source utilization

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Applying unutilized renewable heat energies such as geothermal and waste heat are an important issue due to low energy self-sufficiency rate in Japan. Japan is a volcanic country with abundant geothermal resources, and low-grade heat such as hot springs exists even in remote areas. The Organic Rankine Cycle or ORC is one of the thermoelectric conversion technologies that can generate electricity using these heat energies. However, the ORC has some problems such as low thermoelectric conversion efficiency and expensive power generation cost. Therefore, it is necessary to develop the high efficiency ORC.

The Lorenz cycle uses a zeotropic mixture as the working fluid. In this study, we focused on the Lorenz cycle power generation system that has typical characteristic, which called temperature glide. The temperature glide is the phenomenon that the phase changes along with the temperature change of the heat source, and there is a possibility of generating electricity using low-grade heat that is not normally available ORC for power generation. We proposed a design method in which a small ORC was considered using temperature glide and could generate power using low flow rate of heat sources. The heat source has a temperature of 373 K such as hot springs, flow rate of 4,000 kg/h. Three zeotropic mixtures were selected and used as working fluid for Lorenz cycle under the same design conditions, and their power generation performance was evaluated using their composition as a parameter. The power generation of the Lorenz cycle was 0.4 to 10.5 kW. The Lorenz cycle was shown to be effective for lower grade heat by showing the relationship between temperature and heat transfer in the heat exchange process.

Design of a Tesla Turbine: Transcritical CO_2 Two-Phase Flow Analysis

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The efficiency of CO_2 heat pumps is optimal only under transcritical conditions, which poses challenges in isenthalpic expansion and subsequent energy waste. This study explores the potential of recovering energy through isenthalpic expansion, which transitions the fluid from supercritical to subcritical state.

The Tesla turbine emerges as a solution for energy recovery, but its application introduces complexities, especially in handling two-phase flow. Attention is directed towards designing critical parameters, crucial from a fluid mechanics perspective. Constraints, such as limited fluid availability and considerations for pipeline design pressure, further shape the experimental setup.

This research focusses on estimating the critical speed and pressure in two-phase CO_2 flow for Tesla turbine design. It proposes a method that combines elements from Andrianova et al. (1981) while extending the range of critical pressure analysis, bypassing the need for an ideal-gas approach. The method relies on an energy conservation analysis of local flow speed through enthalpy variation $w_{cr} = \sqrt{2(h_0 - h_{cr})}$, contrasted with the definition of speed of sound $a_* = \sqrt{-\left(\frac{\partial P}{\partial V}\right)_S (v)^2}$. A comparative analysis with the ideal gas approach enhances understanding. The stagnation properties, derived from CoolProp, including temperature, pressure, enthalpy, and other thermodynamic properties, form the basis for the design points. The methodology employs a comprehensive representation of the results, incorporating isobars, isotherms, and intersection points between the local flow speed and the sound speed. Computational efficiency is ensured through interval divisions and careful consideration of invalid intersections, while three-dimensional plots depict critical speeds and speed times density. In conclusion, this research contributes valuable information on the critical dynamics of two-phase CO2 flow in Tesla turbine applications, providing a foundation for optimising energy recovery processes and designing more efficient CO2 heat pump systems.

The performance of Ionic Liquid / water mixtures as working fluids in absorption refrigeration systems

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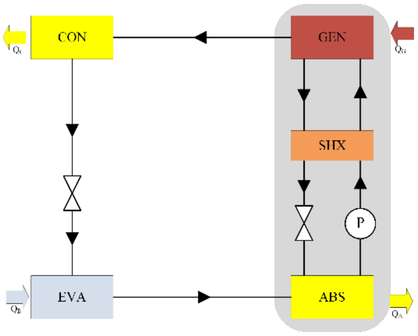
Abstract

Absorption chillers represent a technology that facilitates the recuperation of low-grade thermal energy. Commonly used working fluids, such as water/lithium bromide (LiBr) and ammonia/water, exhibit several drawbacks, including issues related to corrosion, crystallization, toxicity, and explosiveness in the case of ammonia. Water/ionic liquids (ILs) are considered as promising alternative working fluids due to their high efficiency, and they have recently sparked significant scientific interest [1]. This study aims at investigating the thermodynamic properties and phase behaviour of different IL + water mixtures. Vapor-liquid equilibrium (VLE) data of binary systems ([C_2mim]Br-H_2O, [C_3mim]Br-H_2O, [C_4mim]Br-H_2O, [Bmim][SCN]-H_2O, and [Hmim][Cl] -H_2O) have been measured using a static isothermal method [2]. The NRTL and e-NRTL models were then used to correlate the data, revealing a substantial decrease in saturated vapor pressure as the IL concentrations is increased, and a strong deviation from the ideal solution. The COSMO-SAC model has been used to screen potential IL-water working pairs by comparing the water activity coefficients in IL solutions. Finally, the coefficient of performance (COP) of single-effect absorption chillers with IL+water as working fluids have been predicted. It is found that the COP of IL-H_2O working pairs is about 0.8, which is slightly lower than that obtained with LiBr-H_2O (0.83) [3], but much higher than that of H_2O-NH_3 (0.65) [3]. The COP obtained for Hmim][Cl] -H_2O can even be higher than that of LiBr-H_2O under certain working conditions



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Exploring zwitterionic ionic-liquid-like compounds (ZILs) for thermoreversible separation and biocatalysis

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The remarkable attributes of ionic liquids (ILs) and the growing interest in utilizing them as alternative solvents have spurred the exploration and development of novel compound families derived from their properties. One such innovative class, termed zwitterionic ionic-liquid-like compounds (ZILs), shares high structural resemblance with ILs and has recently been proposed. Unlike ILs, which consist of discrete ions, ZILs are characterized by a covalently bonded ion pair linked via an alkyl spacer, resulting in a neutral overall charge. Similar to ILs, these compounds offer customizable structures and properties through variations in headgroups, spacers, and functional groups. However, despite their structural similarity, ZILs demonstrate increased complexity and diversity, suggesting that their properties and behaviors differ from those of ILs. To explore the potential advantages of employing ZILs, we have pioneered the design and development of new ZILs, investigating their properties and potential applications across diverse fields. This work presents an overview of our recent endeavors focused on making use of various ZILs for creating thermoreversible separation systems and integrating biocatalytic processes. Our research also addresses the aquatic toxicity of ZILs and examines the correlation between their structure and ecotoxicity. Our findings indicate that the studied ZILs exhibit a more benign environmental impact compared to their IL counterparts, shedding light on their potential as environmentally friendly alternatives.

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, and UIDB/50020/2020 and UIDP/50020/2020 (LSRE-LCM), and LA/P/0045/2020 (ALiCE), funded by national funds through FCT/MCTES (PIDDAC).

Tris(2-hydroxyethyl)ammonium based protic “ionic liquids”

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Four tris(2-hydroxyethyl)ammonium based protic ionic liquids incorporating lactate, hydrogen succinate, hydrogen malate, and dihydrogen citrate as anions, were synthesized by applying the usual methodologies described in literature. That is, an equimolecular amount of tris(2-hydroxyethyl)amine (TEA) is treated with the corresponding acid at room temperature for 24h or by reflux in MeOH or another solvent for 1h [1,2]; finally, the reaction product is heated in vacuum in order to eliminate the solvent and water. However, our results have shown that these procedures lead to the formation of impurities due to the decomposition of the salt, by likely forming the corresponding amide by condensation [3]. The problem increases with the time of heating.

With the purpose of avoiding decomposition, in this work, optimization of the reaction conditions was carried out. Results have shown that TEA-based ionic liquids derived from: lactate ([TEA][LAC]), hydrogen succinate ([TEA][HSUC]), hydrogen malate ([TEA][HMAL]), and dihydrogen citrate ([TEA][DHCIT]), can be obtained with high purity by treating the acid with the base without any solvent, heating at 50 ºC during short reaction times (from 15 min to 1 hour depending on the acid). Later lyophilization obtains completely dried and pure reaction products.

An ^{1}H NMR study of the obtained product spectra compared with that of [TEA][Cl] has shown that the percentage of ionized species is high in [TEA][DHCIT] and [TEA][HMAL] (86 and 70 % respectively), but low in [TEA][LAC] and [TEA][HSUC] (23 and 20 % respectively). So, it can be said that while [TEA][DHCIT] and [TEA][HMAL] are mainly composed of ions, [TEA][LAC] and [TEA][HSUC] are mostly H-bonded molecular complexes. When considering these compounds, the term “ionic liquid” must be used with caution.

Finally, Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were used to investigate the thermal behavior of the synthesized compounds. Isothermal TGAs confirmed the relatively low decomposition temperature of these “ionic liquids”.

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Solubility of collagen-forming amino acids in 1-ethyl-3-methylimidazolium propionate

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Fish waste is being increasingly recognized as a profitable resource for obtaining high-value products [1]. Discards from ships or canning industries, must be considered raw materials, thereby promoting economic growth and sustainable development. Collagen is a structural protein that is typically found in the skin, scales, bones, and other connective tissues of fish. This protein and its hydrolysates are of great interest to pharmacological and material industries.

1-Ethyl-3-methylimidazolium propionate $[C_2C_1im][CH_3CH_2COO]$ is a room-temperature Ionic Liquid (IL) with an anion characterized by its high hydrogen bond basicity. Thus, it has been successfully used in the treatment of lignocellulosic biomass via hydrogen bonding disruption [2]. So, it could be an interesting alternative to break the complex matrix of a fish residue. With this hypothesis, and as a fundamental study prior to the investigation of collagen extraction from fish residues with this IL, solubilities of the main collagen-forming amino acids were determined in $[C_2C_1im][CH_3CH_2COO]$ at several temperatures and atmospheric pressure.

Namely, the studied amino acids were: glycine, β-alanine, L-proline, trans-4-hydroxy-L-proline, L-arginine, L-glutamic acid and L-aspartic acid. The range of temperatures covered from 298.15 to 328.15 K. As mixtures with water drastically decrease the viscosity of pure ILs and facilitate their application, solubilities in mixtures of $[C_2C_1im][CH_3CH_2COO]$ and water (50% in weight) were also determined. Amino acid in excess was added to the IL or its mixtures with water at the target temperature. The concentration of the solute in the saturated solution was determined by densitometry. To that aim, calibration curves were previously prepared.

Solubilities in the IL and its mixtures with water increased with increasing temperature. The van't Hoff model was effectively employed to correlate the experimental data and determine the apparent properties of dissolution. Moreover, the influence of the anion on the solubilities was analyzed by comparing the results with those previously determined for $[C_2C_1im][CH_3COO]$.

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soft-SAFT Molecular Model for DBU based CO_2 Binding organic liquids Solvents for CO_2 Capture using New experimental data.

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Climate change, primarily driven by CO_2 emissions, continues to pose a significant threat to our planet. Despite the effectiveness of aqueous amine solutions in capturing CO_2 from post-combustion streams, the notable limitations such as high energy consumption, corrosion, and thermal degradation necessitate the exploration of alternative solvents. In this regard, Carbon Dioxide Binding Organic Liquids (CO_2BOLs)[1,2] have been developed as a viable substitute for traditional solvents employed in the physiochemical absorption of CO_2. In this study, DBU-based CO_2BOLs are formulated from 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) superbase with several alcohols/ethers including Butanol, Hexanol, EGME (Ethylene Glycol methyl ether) and EGEE (Ethylene Glycol ethyl ether) and measure their physicochemical properties such as density, viscosity and vapor pressure, CO_2 solubility and heat of absorption of the CO_2BOLs were also measured. Furthermore, a molecular based equation of state, soft-SAFT [3] is utilized to accurately model the thermophysical properties (*i.e.,* density, vapor pressure and viscosity), CO_2 solubility and heat of absorption for DBU-based CO_2BOLs. The results of the proposed models were in excellent agreement with the experimental data at a specific molar ratio. The CO_2 chemisorption process was mimicked through the addition of two specific reactive sites on the CO_2 molecule with specific associating parameters were fitted to available CO_2 solubility isotherms in these solvents, showing excellent agreement with experimental data.

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Identifying novel aqueous amines for CO_2 capture using molecular modeling

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A significant barrier for commercializing amine-based absorption for CO_2 capture is the high solvent regeneration energy demand [1], increasing the need for novel alternative amine molecules. However, evaluating their performance is challenging due to limited experimental data for detailed techno-economic evaluation. Given the recent advancement in molecular modeling tools, molecular-based equations of state provide a suitable platform for the design of modelling screening frameworks. The main objective of this work is to develop a robust solvent screening tool using the polar soft-SAFT molecular-based equation of state (EoS) [2] to obtain relevant thermodynamic properties for assessing novel solvents for CO2 capture. A collection of 36 alternative novel amines were included in this work, belonging to six families: (1) aminoalcohols, (2) alkylethanolamines, (3) dialkylaminoalcohols, (4) cyclic amines, (5) diamines, and (6) multiamines, modelled as associating chainlike molecules, with transferable associating parameters, effectively fitting only the three non-associating parameters.

For CO_2 solubility, formation of reaction products was mediated through the formation of physical aggregates by adding associating sites on CO_2 molecule forming highly localized interactions with the nitrogen on the amine molecules, with associating parameters fitted to available CO_2 solubility isotherms, and used in a transferable manner either to predict CO_2 solubility across a single molecular family, or transferred to multiamine molecules [3]. This work highlights the predictive power of soft-SAFT EoS in cases where no experimental data was available.

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Developing the s-SAFT-γ Mie Equation of State Toward Nonaqueous Alkanolamine-Based Carbon Capture

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A barrier to the wide-scale adoption of alkanolamine-based chemical absorption carbon capture processes are their high energy requirements. A potential solution to this issue may lie in replacing water, the traditional cosolvent for these processes, with an organic alternative. However, there is a very wide range of organic species to choose from, and little available thermodynamic data for these systems. Accordingly, an apt starting point for assessing nonaqueous alkanolamine-based carbon capture systems is the development of a predictive thermodynamic modeling tool.

Firmly grounded in fundamental physics, the Statistical Associating Fluid Theory (SAFT) equations of state (EoSs) present a rigorous approach to thermodynamic modeling. Pertinently, SAFT EoSs have been developed that model thermodynamic systems as interactions between functional groups, as opposed to molecules. These group-contribution (GC) approaches can provide predictions where data are unavailable. This renders GC-approach SAFT EoSs particularly useful in the data-scarce context of nonaqueous alkanolamine-based carbon capture.

Accordingly, the aim of this work was to develop a state-of-the-art GC-approach SAFT EoS, s-SAFT-γ Mie, toward a description of alkanolamine solvent/CO_2/organic cosolvent systems. s-SAFT-γ Mie was capable of qualitatively reproducing the effects of temperature, liquid-phase composition and organic cosolvent structure on CO_2 solubility. This holds for lower pressures, where CO_2 solubility is driven by chemical absorption, as well as higher pressures, where CO_2 is dissolved by physical absorption.

These robust predictive capabilities render s-SAFT-γ Mie well-suited to comparing CO_2 solubility in several alkanolamine solvent/organic cosolvent formulations, highlighting its potential future use within the context of a solvent/cosolvent screening tool.

Prediction of the excess enthalpy in binary mixtures through the use of probabilistic matrix factorisation

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In our study, we propose a machine learning approach tailored specifically for the prediction of excess enthalpy within binary mixtures. We employ matrix completion (MC), a family of methods used to infer missing entries in an incomplete matrix $\boldsymbol{A} \in \mathbb{R}^{N\times M}$, by means of matrix decomposition and subsequent low-rank approximation.. MC has been successfully applied in predicting several infinite dilution properties, including activity coefficients (Jirasek et al., 2020) and Henry's constants (Hayer et al., 2022). More recently the UNIFAC parameters were predicted for the prediction of VLE (Jirasek et al., 2023).

Our methodology centers on probabilistic matrix factorization (PMF), which avoids assumptions about underlying data. PMF decomposes $\boldsymbol{A}$ into $\boldsymbol{U} \in \mathbb{R}^{r\times N}$ and $\boldsymbol{V} \in \mathbb{R}^{r\times M}$ latent variables such that $\boldsymbol{A} \approx \boldsymbol{U}^T\boldsymbol{V}$ is a low rank approximation. We take a Bayesian approach, using Markov Chain Monte Carlo sampling methods, to estimate the distribution of the lower rank matrices.

We present two distinct approaches: pure MC and hybrid MC. In the pure MC strategy, we discretize the excess enthalpy data such that we populate matrices at fixed composition intervals. MC is then independently conducted on each of the fixed composition matrices before being recombined for the full data set. The hybrid MC approach involves fitting the NRTL model to the excess enthalpy data before estimating the parameters τ_{ij} and α for the missing systems according to the MC approach and assessing the model predictions.

The shortcoming of pure MC is that we are not guaranteed a smooth function, as the compositions are regressed independently from one another. Hybrid MC overcomes this issue by explicitly incorporating compositional dependence using the NRTL model.

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Utilizing AI and molecular dynamics for property estimation of CO_2-loaded solvents

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Carbon Capture and Storage (CCS) is one of the viable solutions that can effectively reduce CO_2 emissions from hard-to-decarbonize industries, but there are key barriers for large-scale CCS implementation. One of the common strategies for carbon capture is to absorb CO2 chemically or physically using liquid solvents, e.g., aqueous amine solutions. The energy cost of regenerating amine solvents can be equivalent to 20-30% of a typical power plant output. Other drawbacks of various CO_2 solvents include high viscosity, high toxicity, and high manufacturing costs. To identify possible solvents for use in CCS applications a wide-reaching screening of potential carbon capture (CC) solvents is required. For an effective solvent screening, accurate models for the prediction of transport and thermodynamic properties are needed, which ultimately need to be coupled with flowsheet calculations/optimization. While there are many available computationally efficient models in literature for the prediction of thermodynamic properties [1], for transport properties that is not the case. In this work, we develop predictive machine learning (ML) models that take as input chemical groups and output transport properties (mainly viscosity), similar to Ref. [2].

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Evaluation of Phase Equilibria for Mixtures Containing Environmentally Benign Solvents Using ASOG Method

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1. Introduction

As alternative solvent for green chemistry [1], the phase equilibria are useful for systems containing esters carbonate, esters lactate, 2-methyl tetrahydrofuran and cyclodextrins. This paper deals with prediction of those using ASOG method [2] and comparison with predicted values using modified UNIFAC (Do).

2. Evaluation of Phase Equilibria using ASOG Method

In order to evaluate the phase equilibria, ASOG group contribution method has been used.

a) Systems containing esters carbonate [3]: Dimethyl carbonate is a non-toxic substance that is widely used as a replacement of dimethyl sulfate, methyl halides, and phosgene in methylation and carbonylation reactions..

b) Systems containing esters lactate [4]: Ethyl lactate has excellent properties as a solvent, such as low toxicity, relative low volatility, low viscosity, and good biodegradability, and recyclability. Consequently, it has attracted much attention in recent years as a promising candidate to replace toxic organic solvents and volatile organic compounds.

c) Systems containing 2-methyl tetrahydrofuran: 2-Me THF is one of the second generation of biofuels and is acid stable, low toxicity. It can be synthesized from biomass feedstock [1].

d) Systems containing cyclodextrins [5, 6]: Cyclodextrins are co-solvent to increase the solubility in water of drug.

The evaluation of VLE, LLE and SLE using ASOG has been carried out and the comparison with those using modified UNIFAC (Do) are carried out.

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Proposing predictive hybrid group contribution + artificial intelligence models for the heat capacity of Deep Eutectic Solvents

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Deep Eutectic Solvents (DESs) have come to the forefront in recent years as appealing substitutes for conventional solvents. It is imperative to have a thorough grasp of the essential properties of DESs to expand the employment of these compounds in brand-new procedures. Numerous scientific articles contain experimental data on the physical properties of DESs, but collecting physical properties and describing them in an understandable machine-learning format is preferred. Most frequently, one of the crucial physical properties of a DES that must be precisely determined is its heat capacity. In this study, nonlinear models were developed to predict the heat capacity of DESs by combining the group contribution (GC) method with the multilayer perceptron (MLP), a well-known feedforward artificial neural network, and the Least Square Support Vector Machine (LSSVM) algorithm. The models go by the names MLPANN-GC and LSSVM-GC. A dataset of 505 heat capacity data points for various DESs at various temperatures (from 278.15 to 363.15 K) was gathered to build MLPANN-GC and LSSVM-GC models. By using temperature, molar ratios, and functional groups as inputs, the results indicate that the suggested models can predict the heat capacity of DESs with extremely high accuracy. The MLPANN-GC and LSSVM-GC models yield average absolute relative deviations (AARDs%) of 1.45% and 4.12% and squared correlation coefficients (R2) of 0.99 and 0.98, respectively.

High pressure carbon dioxide and methane solubility in the DES (2 menthol + 1 lauric acid)

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Deep Eutectic Solvent (DES) is one of the introduced green solvents to the scientific community. From 2003 up to now, researchers could find various applications for DESs according to their special characteristics and sustainability aspects. One of the most important applications for DES is their high gas solubility. By considering their sustainability, and also cheap prices, they are high-potential candidates to be used in various industries. Following the mentioned importance, in this study, CO_2 and CH_4 solubilities in the DES (2) menthol + (1) lauric acid were measured at the four temperatures of 308.15, 318.15, 328.15, and 338.15 K and pressures up to 95 bar. The solubility measurements were performed by the designed and built high-pressure solubility apparatus by our group. The measured CO_2 and CH_4 solubilities were compared to each other at constant temperature to find the ideal selectivity of DES for separating CO_2 from CH_4. According to the measured data, with the DES of (2) menthol + (1) lauric acid the ideal selectivity of 4 was obtained, which shows acceptable solvent power for the separation of CO_2 from CH_4 especially at high pressures. For both CO_2 and CH_4, the decreasing gas solubility by increasing temperature behavior was observed by different decreasing slopes. The measured solubility data were modeled by the cubic plus association (CPA) and the Soave-Redlich-Kwong (SRK) equations of state (EoS) and both EoSs showed acceptable correlative abilities for both gas mixtures.

Pressure-volume-temperature-composition relations for CO_2 and carboxylic acid based deep eutectic solvents

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Abstract

Recently, we reported the CO_2 solubility of a deep eutectic solvent (DES) comprising chlorine chloride (ChCl) and ethylene glycol (EG) in a 1:2 molar ratio (ChCl2EG)1). In this study, DES comprising tetrabutylammonium bromide (TBAB) and hexanoic acid (HA) or octanoic acid (OA) in a 1:3 molar ratio (TBAB3HA and TBAB3OA) were selected to increase the CO_2 solubility. The CO_2 solubility and saturated density of the CO_2 + TBAB3HA and CO_2 + TBAB3OA systems were measured using a static-circulation-type apparatus equipped with two vibrating-tube densimeters (DMA 512P) at 298.15, 313.15, 333.15 K, and up to 10 MPa (mass balance method2)). In addition, the high-pressure density of TBAB3HA and TBAB3OA were measured using a vibrating tube densimeter (DMA HP), under the same temperature and pressure conditions. The CO_2 solubilities of TBAB3HA and TBAB3OA were almost the same and approximately three times higher than that of ChCl2EG. The high-pressure densities of TBAB3HA and TBAB3OA were correlated using the Tait equation3). The pressure-volume-temperature-composition relationships for the CO_2 + TBAB3HA and CO_2 + TBAB3OA systems were correlated using our proposed density correlation equation. The partial molar volume of CO_2 was determined using the density correlation equation. The method of Lyckman *et al.*4) was applicable to partial molar volumes of CO_2 at infinite dilution in TBAB3HA, TBAB3OA, and ChCl2EG.

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Assessing the Influence of Parametrization Strategies on the Evaluation of Extraction-based Processes

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The design and simulation of chemical processes relies strongly on physical properties and accurate phase equilibrium data. However, there are numerous methods for generating and integrating these data into process simulations: A common industrial approach is to regress and correlate experimental data using classical models, e.g., excess Gibbs energy models (G^E) such as UNIQUAC or NRTL[1]. There are also newer, more physically based models, e.g., PC-SAFT type models or CPA as equation of states, which have a better predictive character when fully parameterized with experimental data. In addition, purely predictive methods based on quantum mechanics (e.g., COSMO-RS) or model parameters based on machine learning approaches[2,3] expand the possibilities for model users to calculate equilibrium data.

However, an area that is much less researched is how thermodynamic models of interest can reliably be parameterized and a comparison between different parameterization strategies is seldom done[4]. The parameterization strategy should be evaluated considering process criteria, since the main application of thermodynamic models is to design, evaluate or optimize processes. Furthermore, it is desirable to determine model parameters with easy-to-use experiments and as little experimental data as possible to minimize experimental effort.

This contribution focuses on evaluating two NRTL type G^E models: (1) the original NRTL formulation[5] and (2) a more recent “predictive” extension of NRTL incorporating associative interactions based on Wertheim’s theory[6]. We assess the influence parametrization strategies on the evaluation of extraction-based processes for associating multicomponent systems. In light of “novel” molecules in chemical processes, we restrict on obtaining model parameters using small-scale experiments. For this purpose, differential scanning calorimetry experiments on a microliter scale are performed to collect binary phase equilibrium data.

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Preventing Contamination Related to Global and Climate Change

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The presence of contaminants of emerging concern (CECs) in soil, water, air and food is of concern and worry throughout society. Among the CECs, per- and poly-fluoroalkyl substances (PFAS, considered “forever chemicals”), and pharmaceuticals are referred to as the families of compounds that cause the most hazardous effects in the environment. These CECs are used intensively, and their disposal is not normally done correctly. Then, the detection of these different CECs has been consistently detected in alarming concentrations. High exposure levels to these compounds increase the risk of dangerous health issues for humans. Remediation techniques have been demonstrated not to be useful in reducing the presence of these compounds in the environment because they are limited or inefficient or are based on incineration emitting harmful air pollutants, such as fluorinated greenhouse gases (F-gases). These emissions contribute to those coming from refrigerants based on F-gases, by far the most relevant greenhouse gases from a climate perspective. Although F-gas emissions have been falling since 2015 and most of these refrigerants are currently being phased out, recycled pure F-gases are valuable because they can be reused in new-generation gas blends with much lower global warming potential. Since the recycling rates of F-gases in the EU are extremely low, the development of green technologies for the selective separation of these gases is vital to apply a circular economy and achieve the EU's goals for the climate.

This work is focused on the design (bio)materials to develop climate-friendly processes to separate PFAS and pharmaceuticals. The most appropriate (bio)materials will be custom-designed and evaluated for each specific application. The results are promising, opening a very interesting path to the optimization of a more sustainable process, which helps to solve one of the current environmental and health issues of great concern in Europe achieving a cleaner environment for the species and ensuring the well-being of species.

Extraction of per-fluorinated alkyl substances using ionic liquids and porous solid matrices

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Per- and polyfluoroalkyl substances (PFAS) are a subgroup of aliphatic fluorinated substances composed of one or more carbon atoms in their structure, where the hydrogen substituents are replaced by fluorine. These substances are highly harmful to humans, animals, and the environment because they accumulate and are persistent and toxic in different media such as water, soil, and air. High exposure levels to these compounds increase the risk of dangerous health issues for humans, such as kidney and testicular cancer, thyroid problems, and reduction of the effectiveness of vaccines in infants, among others. The objective of this work is to evaluate the capacity of fluorinated ionic liquids (FILs) and porous solid matrices, such as activated carbons, to extract per-fluorinated alkyl substances in aqueous solution. For this purpose, FILs were synthesized, and the extraction capabilities were analysed. The results are promising, opening a very interesting path to the optimization of a more sustainable process of PFAS water treatment, which helps to solve one of the current environmental and health issues of great concern in Europe achieving a cleaner environment for the species and ensuring the well-being of species.

Ionic-liquid-based aqueous biphasic systems for platinum group metals recovery

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Platinum Group Metals (PGM), namely platinum, palladium, rhodium, osmium, iridium, and ruthenium are underscored by the European Union (EU) for their high supply risk. Automotive catalytic converters are the most relevant application of PGM but reaches only 50% of recyclying within the EU. The recovery of PGM from secondary sources is of extreme importance and can be achieved through a hydrometallurgical process of three main stages: leaching, purification, and refining. Within this study is implemented an alternative leaching approach, employing aluminum salts for the dissolution of metals, as opposed to the conventional use of environmentally hazardous highly acidic solutions.The proposed purification method involves a multistep solvent extraction, initially focusing on the separation of PGM from other metals and subsequent isolation of each individual metal. This approach involves using ionic-liquid-based aqueous biphasic systems by combining the salts present in the leachate with hydrophilic ILs for the formation of two immiscible aqueous phases with metal complexes that are not typically stable in water. Systems of ILs containing phosphonium cations, including tetrabutylphosphonium chloride ($[P_{4444}]Cl$), demonstrate remarkable results with extraction reaching the efficiency of 100% for platinum.

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, and UIDB/50020/2020 and UIDP/50020/2020 (LSRE-LCM), and LA/P/0045/2020 (ALiCE), funded by national funds through FCT/MCTES (PIDDAC).This work was also financially supported by national funds through FCT – Fundação para a Ciência e a Tecnologia, I.P., within the scope of the project PlatILPlus (2022.04478.PTDC, DOI: 10.54499/2022.04478.PTDC). Nicolas Schaeffer acknowledges the national funds (OE), through FCT, in the scope of the framework contract foreseen in the numbers 4, 5, and 6 of the article 23, of the Decree-Law 57/2016, of August 29th, changed by Law57/2017, of July 19th. F.H.B. Sosa and F. Braga acknowledge FCT for the researcher contract CEECIND/07209/2022 and the Ph.D. grant 2023.01749.BD, respectively.

Model-based solvent screening: Modeling of multicomponent mass transfer in liquid-liquid extraction columns

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Liquid-liquid extraction processes represent widely employed separation technology, with their performance significantly contingent upon the solvent selection. Model-based solvent screening emerges as a promising avenue for identifying economically advantageous solvents.

Kampwerth et al. (2020) introduced a framework for model-based solvent screening, incorporating investment and operational costs into evaluating extraction processes involving extraction and distillation columns. To balance precision against computational complexity, the model adopts a rate-based approach incorporating fluid dynamics for the extraction column, employing shortcut models for the distillation column. The model achieves complete predictability by leveraging tabulated pure component properties and various physical-empirical correlations from literature, facilitating comprehensive solvent comparisons. However, it is limited by considering only one transfer component and disregarding mutual solubility between carrier and solvent phases, precluding the description of coupling products or the impact of auxiliary substances such as catalysts.

In addressing these limitations, our work introduces a multicomponent mass transfer model, utilizing the Maxwell-Stefan equations to accommodate an arbitrary number of components. This mass transfer model intricately captures the interplay among all components in multicomponent liquid mixtures. Notably, the enhanced mass transfer model retains predictivity without relying on additional experimental data. Experimental validation focuses on the quaternary system levulinic acid - formic acid - MIBK - water. Liquid-liquid equilibrium studies precede the regression of NRTL parameters from equilibrium data. Pilot plant pulsed sieve tray extraction column experiments are then conducted to measure concentration profiles, evaluating the proposed model with the embedded regressed NRTL parameters.

This contribution delineates the overarching design framework, specifically emphasizing the extension of the extraction column model. Our findings demonstrate that the extended model achieves a remarkable average deviation of less than 1% between measured and predicted concentration profiles for all pilot plant experiments.

Bioprivileged Ionic Liquids for Biologics Purification and Drug Formulation

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Sustainability challenges have advanced the research in unconventional solvents, separation techniques and drug development. A thriving research field is the use of ionic liquids (ILs) in biologics purification and pharmaceutical applications.

ILs have emerged as one of the most attractive solutes for aqueous biphasic systems (ABS), with outstanding performance in the extraction of targeted biologics. Recently, we proposed a benign cholimium-based ILs route for ABS, disclosed novel ABS composed of fluorinated ILs (FILs) and demonstrated that FILs reduce the impact of the addition of water upon the IL's H-bond acceptance ability. Herein, bioprivileged ILs were implemented to develop more versatile and amenable to be tuned ABS. To understand their potential as extractive platforms of biologics, the ternary phase diagrams, the polarity parameters of the coexisting phases, and the partition coefficients, stability and activity of the targeted biologics were determined. Finally, to highlight the interactions between model biologics and the ABS-phase components and better understand the interactions ruling the partition, intrinsic fluorescence, nano-differential scanning calorimetry, circular dichroism and microscale thermophoresis measurements were attained. One of the promissing results was the simultaneous purification of IFN-α2b and albumin in a single-step with a high purification factor and yield. Additionally, the standard batch (macroscale ABS) was compared with flow-through processes (microfluidic setups).

Either, the development of ILs that are themselves active pharmaceutical ingredients (API-Ils) and IL-based pharmaceutical eutectics are advantageous building-up platforms, granting the potential to modulate the water solubility and the membrane permeation properties of an API. The attained results unequivocally demonstrate that, within the green chemistry framework, an IL-based platform constitutes a feasible alternative to augment the bioavailability and diverse pharmacological properties of commonly available over-the-counter APIs.

Adsorption Processes for the Reclamation of Single-Component Refrigerants from Refrigerant Blends using BPL Activated Carbon

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Fluorinated gases (F-gases) are a family of synthetic gases used in refrigerant systems and air conditioning equipment. F-gases are powerful greenhouse gases (GHG) with global warming potential (GWP) up to 20 000 times greater than CO_2.[1] Many refrigerants with market value are being destroyed because they cannot be feasibly reclaimed for reuse, due to numerous reasons, which includes lack of appropriate technology or multi-component complex mixtures (all the collected refrigerants in the waste managers facilities are mixed in cylinders for incineration). The development of technologies for efficient reclamation of F-gases is relevant, not only to reduce GHG emissions to the atmosphere, but also to reuse the single-component refrigerants contained in the blends. A good example is the EU phase-down of R-410A (one of the most used refrigerants in air conditioning equipment; R-32 and R-125, 50/50 wt.%), which is driving the switch from R-410A to R-32 (neat or in blends with lower GWP).

The adsorption of F-gases in porous solid matrices have been used by us to develop new processes for the reclamation of F-gases.[2-4] In this work, adsorption processes are optimized to reclaim single-component refrigerants (R-32, R-125, and R-134a) from commercial refrigerant blends (R-410A, R-407C, and R-404A), using a BPL activated carbon as adsorbent. We studied the equilibrium and kinetics of adsorption of pure F-gases. Additionally, several breakthrough experiments were performed to study the dynamic behavior, validate a mathematical model for process design by simulation, and develop novel adsorption processes to reclaim high purity single-component refrigerant (99.5 wt% - AHRI standard)[4] with increased recovery.

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A Computational Approach to Assess the Flammability of Refrigerant Mixtures using Artificial Neural Networks Strategies

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Abstract

With the European Union's initiative to phase out high Global Warming Potential (GWP) refrigerants gaining momentum [1], the air-conditioning industry faces the challenge to find new low-GWP alternatives. One of the critical aspects is related to the flammability of these new mixtures. This paradigm shift underscores the urgency for a rapid, reliable screening method to assess the flammability of emerging 4th generation refrigerant blends. In this study, we develop, evaluate, and further validate an Artificial Neural Network (ANN) to meet this need, enabling the prediction of the Normalized Flammability Index (NFI) for a wide range of pure, binary, and ternary mixtures. The chosen ANN architecture (61x14x24x1) demonstrates an exceptional fit to the data, evidenced by excellent performance metrics. Exhaustive assessments are conducted to ensure the most efficient architecture without compromising accuracy. Furthermore, the detailed analysis of Standardized Residuals (SDR) and Applicability Domain (AD) confirms fine control and consistency over the data points. External validation with quaternary mixtures further proves the model's adaptability and predictive strength. The exploration into the relative contribution of descriptors leads to the identification of 23 key sigma descriptors derived from COSMO that account for 90.98% of the total contribution, revealing potential avenues for model simplification with minimal loss in predictive accuracy. Moreover, the model reliably forecasts the behavior of mixtures relevant to the industry [2], reinforcing its reliability and paving the way for the exploration of new, untested mixtures in the current landscape.

Acknowledgments: *This research is supported by the Spanish Ministry of Science and Innovation MCIN/AEI/10.13039/501100011033 and by the European Union Next Generation EU/PRTR, under R + D + I project NEW-F-TECH (TED2021-130959B-I00), as well as by Khalifa University of Science and Technology (project RC2-2019-007).*

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An artificial neural network approach to predict the solubility of hydrofluorocarbon refrigerants in ionic liquids

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Ionic liquids (ILs) have been proposed as entrainers to separate close-boiling hydrofluorocarbon (HFC) and hydrofluoroolefin (HFO) refrigerant mixtures by means of extractive distillation processes. However, the huge number of existing ILs and the remarkable solubility differences among HFCs and HFOs hinders the selection of the optimal IL entrainer, so developing a tool that allows to predict their solubility behavior has a great interest. Here, we propose the use of an artificial neural network (ANN) for the prediction of vapor-liquid equilibrium (VLE) of fluorinated refrigerants with ILs. The ANN was trained to learn and predict the refrigerant solubility in ILs from easily accessible properties and features of the pure compounds. A total of 4396 VLE data of 52 ILs with 24 fluorinated refrigerants (included in the UC-Refrigerant Absorption in Ionic Liquids Database [1]) were used for optimizing the ANN structure. The dataset was divided in training, validation, and test sets (70/15/15% of data, respectively) to ensure the predictive power of the resulting network and avoid overfitting. The best ANN had three hidden layers with 13 inputs to predict the equilibrium molar fraction of refrigerant absorbed in the IL [2]. The average absolute relative deviation (AARD) of the ANN was very similar for each set (10.16%, 10.98%, and 13.25%) showing that there was not overfitting during the training process. The analysis of the ANN with a partial derivative method (PaD) showed that the refrigerant critical temperature had the greatest influence on the solubility. Additionally, data published after optimizing the ANN for absorption pairs not contained in the original database were predicted with an AARD lower that 11%. Thus, the ANN exhibited enhanced predictive prowess and can be used for prescreening ILs for the absorption separation of fluorinated refrigerants.

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A compilation of hydrofluorocarbons and hydrofluoroolefins solubility data in polymer membranes

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Reclaiming fluorinated refrigerants (F-gases) to formulate novel refrigerant blends with low global warming potential (GWP) is currently a huge separation challenge due to the near-azeotropic behavior of typical F-gas mixtures. Thus, innovative membrane processes are being developed to assess the separation performance of hydrofluorocarbons (HFCs) and hydrofluoroolefins (HFOs). In this work, HFC-32, HFC-125 and HFO-1234yf sorption experiments were performed in film membranes made of three different polymers, Pebax®1657, PIM-1 and 6FDA-TMPD, to determine the solubility contribution to gas permeability. The F-gas sorption isotherms were significantly different for each polymer, highlighting the importance of the molecular structure in the polymer-F-gas interactions. On the one hand, the elastomeric nature of the polyether-block-amide Pebax®1657 results in lower gas sorption in the polymer matrix (HFC-32: 10, HFC-125: 4, HFO-1234yf: 4 cm^3_{STP} cm^{-3}_{pol} at 2 bar [1]). Conversely, the glassy nature of PIM-1 and 6FDA-TMPD exhibited the highest F-gas sorption (HFC-32: 66 and 48, HFC-125: 55 and 34, HFO-1234yf: 68 and 32 cm^3_{STP} cm^{-3}_{pol} at 2 bar for PIM-1 [2] and 6FDA-TMPD) due to the presence of microcavities and the higher free fractional volume within the polymer matrix. In terms of model fitting of the experimental data, the sorption isotherms in Pebax®1657 followed the Flory-Huggins model, while the PIM-1 and 6FDA-TMPD isotherms fit perfectly the Dual Mode Sorption (DMS) and Guggenheim, Anderson, and de Boer (GAB) solubility models, respectively. In addition to the DMS, the GAB model reflects the bulk condensation of F-gas in multiple layers, emphasizing the effect of the polymer molecular structure on the gas solubility. Therefore, work in progress is aimed at using the molecular-based NELF model to describe the adsorption of target HFCs and HFOs in glassy polymers.

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Acknowledgements

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Modelling thermodynamics for solvent-based plastic recycling

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Solvent-based processes of plastic recycling can be employed in additives removal, polymer separation from waste/composites and polymer fractionation. They could offer economically feasible alternative for closed-loop recycling. However, the development of the processes is limited by the insufficient fundamental scientific description caused by the chemical complexity of the relevant systems. We aim to aid in the design and optimization of solvent-based recycling unit operations by applying the state-of-the-art thermodynamic models capable of modelling complex mixtures of non-polar, polar and hydrogen-bonding species. We employed our implementation of the PC-SAFT equation of state, incorporating associating and polar terms, for phase equilibria calculations. Model parameters for various additives within the PC-SAFT framework were estimated using validated group contribution methods, including both homo- and hetero-segmented variants. Key advantage of our thermodynamic model is its capability to calculate phase equilibria in multi-component mixtures with multiple condensed phases, such as semi-crystalline polymers with liquid diluents and gases. We place significant emphasis on the thermodynamic description of the partial transformation of the crystalline phase into the amorphous polymer phase when solvents are introduced. Our work contributes to a comprehensive understanding of the process.

Modelling Gas and Vapor Sorption in Copolymer Membranes: A Predictive Approach Using PC-SAFT & the Dry Glass Reference Perturbation Theory

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The solubility of gases and vapors is one of the most important metrics that are used to evaluate the performance of polymeric membranes for gas separation processes. As such, relying on accurate mathematical models to describe the penetrants sorption is vital for the discovery of novel, high performing polymeric materials for such applications. A large part of the vast chemical space of promising polymer materials may exist in the copolymer domain. As a result, In this work, we utilize the copolymer PC-SAFT [1] equation of state to correlate the sorption behavior across the monomer composition range, thereby reducing the reliance on experimental data to determine the solubility. Moreover, we use the Dry Glass Reference Perturbation Theory (DGRPT) [2] framework to account for the departure from non-equilibrium exhibited by glassy polymers and the swelling of the polymer matrix. Figure 1. showcases some of our successful predictions made by the resultant non-equilibrium version of PC-SAFT (i.e NE-PC-SAFT).

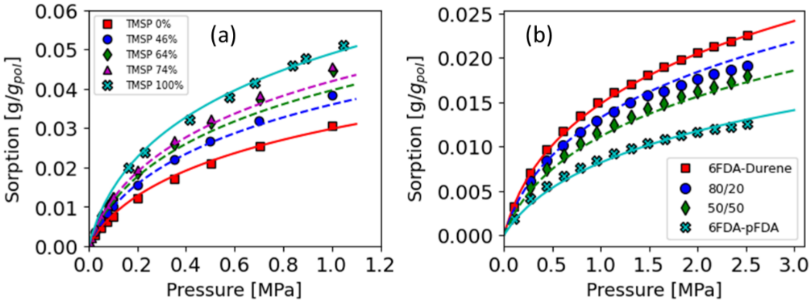

Figure 1. (a) CO_2 sorption in PSSU/TMSP and (b) CH_4 sorption in 6FDA-durene/pFDA. The homopolymer NE-PC-SAFT calculations (solid curves) have been fitted to experimental data and the copolymer calculations are predicted (dashed curves). Compositions of the monomers are given in molar percentage. Experimental data (shown as discrete points) are taken from ref. [3] and [4].

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Modelling solubility of CO_2 in rubbery and glassy polymers with the SAFT-γ Mie group-contribution approach

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Understanding the sorption of CO_2 in polymers is important in the process industry as excessive sorption can reduce separation efficiency and cause failure of sealing components from polymer swelling. The sorption behaviours of polymers vary depending on the polymer nature and thermodynamic conditions. Rubbery polymers are used above their glass transition temperature (T_g) and their flexibility is desirable for sealing applications. Glassy polymers operate below T_g and they offer advantages in many separation applications due to their mechanical strength and enhanced selectivity.

Rubbery polymers are at thermodynamic equilibrium (EQ) and can be modelled with equations of state (EoS). The SAFT-γ Mie approach is a recent group contribution (GC) development of the statistical associating fluid theory (SAFT) EoS family that stem from the thermodynamic perturbation theory of Wertheim to account explicitly for chain connectivity (and directional hydrogen bonding interaction, when relevant) (1). In SAFT-γ Mie, the Helmholtz energy contributions of the constituent functional groups are combined to deliver accurate predictions of the properties and mixture phase behaviours comprising functional groups whose contributions have been previously studied.

Glassy polymers are “frozen” in nonequilibrium (NE) states and demand special treatment. The Non-Equilibrium Thermodynamics for Glassy Polymer (NETGP) framework allows any EoS to use measured polymer density in the NE CO_2-polymer mixture together with the EQ state variables (temperature, pressure, composition) to completely describe the system (2).

In this contribution, the NETGP framework is applied to the SAFT-γ Mie EoS in order to model the solubility of CO_2 in rubbery and glassy polymers. Polystyrene (PS) and polymethylmethacrylate (PMMA) of 1000 repeating units are presented. The resulting model delivers good agreement with experimental data up to a moderate pressure range (below 10 MPa) in rubbery and glassy states for CO_2-PS but not CO_2-PMMA, and the reason is elucidated and discussed. Coupled with a method to approximate actual polymer density in the NE mixture from pure polymer PVT data, the NE model is used to predict solubility of CO_2 in glassy polymers. Comparison against experimental data shows the model is useful in describing the swelling effect of CO_2 and plasticization-induced glass-to-rubber transition points at low to moderate pressure.

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Process synthesis of membrane-adsorption multi-stage CO_2 Separation by using Statistical Model

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Carbon dioxide capture and storage (CCS) technology has become important to reduce carbon dioxide emissions. Adsorption and membrane separation processes for CO_2 capture have gained attention as they are considered more energy efficient than gas absorption using amine. However, the capture efficiency of these processes is low and their application to CCS has not yet progressed. While combining these two processes is one way to improve separation performance, research on the configuration of these combinations or multi-stage processes is still insufficient. Membrane separation is operated in a steady state and adsorption separation is in an unsteady state, which makes the design a hybrid process complex. Recently, the use of machine learning for process design has been proposed. We have applied machine learning to the design of multi-stage CO_2 separation processes. Models were developed for each adsorption and membrane process with variables such as operating pressures of compressors and vacuum pumps, CO_2 composition in the feed gas, and flow rates. This data was used to build statistical models with neural networks to perform multi-objective optimization. Adsorption and membrane separation processes were optimized and found that neither process could achieve the CCS requirements. Adsorption has a higher separation performance than membrane, but it also consumes more energy. Next, a two-step process was developed by combining statistical models of the adsorption and membrane processes. In the multi-objective optimization performed for this process, it was shown that the combined membrane and adsorption process meets the CCS requirements and reduces the energy consumption of the compressor and vacuum pumps compared to the single-stage process. This research indicated the potential of using statistical models to synthesize multi-stage processes.

Multiscale High-Throughput Screening of Polymer Membranes for Ethanol-Water Dehydration

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Membrane-based processes have the potential to reduce both the energy consumption and capital cost of performing liquid-liquid separations. The performance of the membranes is strongly linked to the physical properties of the membrane materials; however, the development of new materials is a largely empirical process. To address this challenge, a high-throughput screening workflow has been developed to optimize the properties of polymeric membranes for achieving efficient liquid-liquid separations, focusing in particular on ethanol-water dehydration. Our approach aims to guide the experimental synthesis of new membrane materials based on dicyclopentadiene norbornene diacyl chloride (NBDAC) monomers. NBDAC monomers polymerize to create a polymer featuring two reactive acyl chloride groups. The resulting reactive NBDAC scaffolding imparts diverse functionalities to membranes by incorporating side chains through the acyl group, these side chains can be compounds previously demonstrated as effective in ethanol dehydration studies, thereby enhancing membrane properties. Leveraging the multi-engine capabilities of the MoSDeF toolkit, we have developed a generalizable two-step screening process for membranes based on monomers with different functional groups (Figure 1). In the first step the adsorption of water from an ethanol-water mixture on a single NBDAC monomer with different functional groups is examined. The candidates demonstrating the highest affinity towards the solute (water) will undergo a second stage, which involves examining the absorption of water within a polymeric membrane constructed from the NBDAC functionalized monomer.

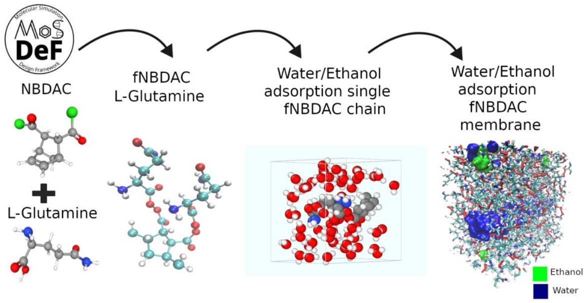

Figure 1. Schematic of simulation workflow.

Comprehensive Modelling Strategy for Gas Transport in Polymers: Analysis of Swelling and Non-Swelling Agents at High Pressures

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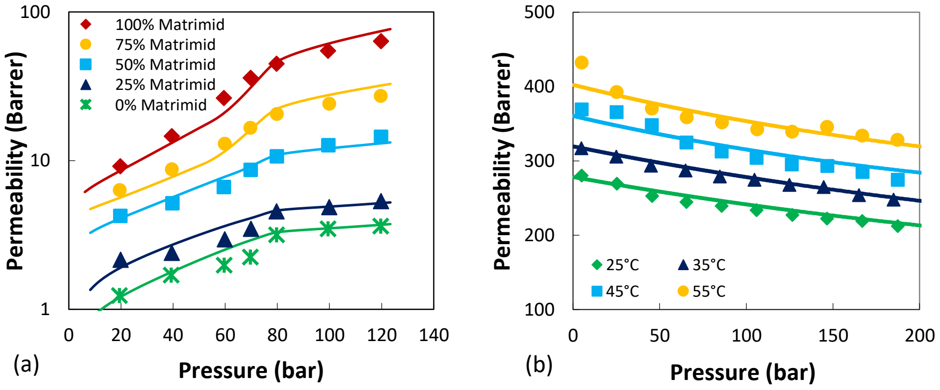
The solubility and permeability of a swelling agent, CO_2, and two non-swelling agents, N_2 and Ar, were modelled in a broad range of pressures, from sub- to supercritical conditions, in various polymeric systems: blends of two glassy polyimides, Matrimid and P84, co-polymer Nafion, and two rubbery polymers, namely natural rubber and PDMS. Solubility was modelled using the Sanchez-Lacombe Lattice Fluid (LF) equation of state (EoS) and its nonequilibrium version, the Non-Equilibrium Lattice Fluid (NELF) model [1]. EoS parameters for Nafion and P84 were obtained in this work. The Standard Transport (ST) model [2] was used for permeability.

Notably, the modelling framework adopted showed high versatility in describing the very different trends displayed by all these diverse systems, with only few adjustable parameters, in particular accounting for: i) the state of equilibrium (rubber) or non-equilibrium (glass) of the polymer, ii) phase changes of the penetrants with pressure, iii) the sorption-induced rubbery transition, if the polymer was initially glassy, iv) the dependence of the penetrant diffusivity on concentration. Furthermore, the model allowed to gain insight on the interplay between penetrant swelling and mechanical compression at high pressure conditions.



(a) CO_2 permeability in Matrimid/P84 blends Lines: model calculations. Symbols: Exp. data from [3] (b) N_2 permeability in PDMS. Lines: model calculations. Symbols: Exp. data from [4]

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Thermodynamics Aspect of CO_2 Transport: Phase Equilibrium and Transport Properties

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For any CCUS project, to precisely design equipment such as pumps and compressors as well as pipeline sizing, a clear understanding of the thermophysical properties of the fluid, is crucial.

In this study, molecular dynamic simulation was used and the vapour-liquid phase equilibrium densities for pure CO2 and N2 systems were calculated and compared with the predictions of reference EoS models. Different forcefield models for CO2 such as the EPM2, TraPPE, and the Zhang have been tested and compared with predictions of the EoS model. The results of our study show that the TraPPE model can estimate the phase equilibrium coexistence densities for pure CO2 and N2 very well with an AARD of less than 1.5 %. Excellent agreement was achieved for equilibrium density data at low temperatures. However, near the critical region deviation between molecular simulations results and the EoS models increases. Furthermore, density and viscosity of pure liquid CO2 and binary mixtures of CO2 + N2 were calculated at CCUS operating conditions. Our results show good agreement with the model predictions as well as the literature data with deviations less than 1 % for density and 5% for viscosity.

The effect of other impurities such as the CH4 and SO2 and the Monte Carlo simulation method are aimed to be investigated in the next phase of the project.

Keywords: CCUS, Molecular dynamics simulation, thermophysical properties,

Solubility and swelling calculations in semi-crystalline polymers using the PC-SAFT equation of state

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Abstract

The solubility of a gas in a polymer is affected by the mechanical constraints that may result, either from external sources (i.e. hydrostatic pressure) or from internal stresses (as in semi-crystalline polymers). The objective of this work is to analyze the solubility and swelling behaviour of gases to eventually improve the description of the gas permeability. In a first stage, the existing published data are presented and discussed. We focus the analysis on systems composed of PE or PP with CO_2 or CH_4. It appears that a large scatter may exist among the different publications. They may be attributed to an insufficient characterization of the polymer, especially when it is semi-crystalline. In a second stage, the PC-SAFT equation of state (Gross et Sadowski, Industrial & Engineering Chemistry Research, 138, 19. 2001)is employed with several parameterization schemes to describe, first the behaviour of molten polymers, and then that of semi-crystalline polymers (solid state). The model is able to describe with good agreement molten polymers data. For semi-crystalline polymers the “constraint pressure” theory proposed by (Minelli et Angelis, Fluid Phase Equilibria, 367, 173-181. 2014) and (Fischlschweiger, Danzer et Enders, Fluid Phase Equilibria, 506, 112379. 2020) has been included in the PC-SAFT equation to evaluate the capacity of the model to reproduce the data. This internal pressure stands for the stress applied by the rigid network formed by the crystallites on the amorphous phase. The conclusion shows that the required constraint pressure strongly depends on the sample that is analyzed, and the missing details on the material description (such as the crystallinity for instance) make it difficult to reach a reasonable level of predictivity. Our work therefore points to the need for a more detailed description of the polymer samples.

Utilization of experimental methods: mass transfer and sorption equilibria of small gaseous penetrants in polyolefins

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The monomer mass transfer behavior during the polymerization reaction is one of the essential information for polymer engineers to control reaction conditions and properties of final polymer. Nevertheless, quantitative description of diffusion of small molecules in semi-crystalline polymers is still a challenging problem, relevant also to membrane performance and polymer recycling. In this contribution we employ several experimental methods to investigate mass transfer and sorption equilibria in semicrystalline polymers, namely we utilize differential pressure decay, Raman spectroscopy, gas chromatography and magnetic suspension balance.

The objective of our research was to systematically develop a large set of data for diffusion and sorption of low-hydrocarbon gases in semicrystalline polyolefins. Polyolefins consist of two phases: crystalline (rigid) and amorphous phase. The research [1] showed that amorphous phase can be further divided into free amorphous phase (mobile) and constrained amorphous phase (semi-rigid). Penetrant molecules have to pass through regions with different permeability and thus there is a significant effect of the polymer sample composition. Recent work [2] showed that penetrant molecules (ethylene and propylene) reduce crystalline phase content, thus further complicating the theoretical description of diffusion. To employ a theoretical model for diffusion, e.g., Free Volume Theory [3] with all effects changing paths for penetrants, we need comprehensive experimental data first. In this contribution we are comparing diffusion coefficients for different hydrocarbon penetrants (C2-C6) or aromatic hydrocarbons (toluene or xylene). Each penetrant is used for various semicrystalline polymer samples (with different density and thus different content of crystalline and amorphous phase), temperature conditions and penetrant concentration in the polymer sample or surroundings. Results of alternative or complementary experimental methods are compared.

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Modelling of shear-induced mixing behaviour of polymer blends

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Polymer blends tend to separate often showing a large miscibility gap. In the absence of shear, the miscibility gap can be modelled using lattice theories, such as the Flory-Huggins approach [1, 2], or the Lattice Fluid Theory proposed by Sanchez and Lacombe [3]. If a special shear rate is applied to polymer blends, the miscibility gap will be extended or reduced, depending on the rheological properties of the considered polymer blends. The rheological behaviour is mostly shear thinning, which is the non-Newtonian behaviour of fluids whose viscosity decreases under shear strain. The impact of shear on the phase behaviour can be modelled according to the theoretical framework of Wolf [4] and Horst and Wolf [5]. The principal idea of this theoretical framework is the addition of the Gibbs energy of mixing and the stored energy during flow, which reflects the rheological properties of the blend. Unfortunately, no analytical expression for the stored energy during flow with respect to the blend composition is provided [4, 5]. The aim of this contribution is to present an analytical expression for the chemical potential that incorporates the rheological properties of the polymer blend, enabling the utilization of experimental rheological data in the calculation. The new approach is inspired by Soontaranun et al. [6], which consider only Newtonian fluids. With the new approach, rheological data and the phase behaviour of quiescent polymer blends can be utilized to predict the behaviour of these polymer blends under the influence of shear. The model is applied to experimental data from the literature [7, 8] for both the polystyrene/poly(vinyl methyl ether) system and the styrene-acrylonitrile copolymer/poly(methyl methacrylate) system. Own rheological measurements are shown for the first system. In addition, both the use of a G^E- model and an equation of state for the description of the Gibbs energy of polymer blends are discussed.

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Molecular insight into the photonastic phenomenon: study of the coupling between the photochemical reaction and the intramolecular relaxation of the polymer

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Photonastic materials perform light-induced movements, transforming light energy into mechanical energy, akin to the motions observed in plants and flowers. This project focuses on bio-inspired polymeric photoactuators. A polymer thin film containing photochromes, can exhibit significant shape changes upon light excitation. By employing molecular dynamics (MD) simulations, we investigate the molecular processes governing the macroscopic behavior of these systems, which in our case consists of a derivative of azobenzene (AZ) embebbed in a polybutadiene (PB) matrix. Our aim is to propose a strategy to investigate the coupling between the photochemical reaction and the intramolecular relaxation of the polymer. In a previous study, we assumed that these processes occurred at different time scales (J. Chem. Theory Comput. 2020, 16, 7017). However, subsequent results indicate that their characteristic times are roughly the same (~ 100 fs to 1 ps). To improve the description of the system, we consider both phenomena simultaneously in the following way. A purely classical molecular mechanics model of AZ photoswitches in both their ground and first excited states (S_0 and S_1) is calculated. The photoreaction is modelled by switching between these two potential energy surfaces (PES) along the photoreaction coordinate, while allowing the polymer chains to rearrange concomitantly. The local pressure tensor maps of the whole system are analyzed as a function of time after the switch to the S_1 PES. Moreover, we extend our research to study the same phenomena with another photochrome, diethienylethene (DTE), and its derivative DTE-Upy within a PB matrix. This molecular-scale exploration contributes to a comprehensive understanding of photonastic phenomena and the mechanical response of polymer-photochrome systems.

Ecosystems as open thermodynamic systems: Entropy production as a measure of carbon capture and utilisation

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The work presents a cybernetic insight in ecosystem functioning as open thermodynamic systems, realized through modelling of energy flow conversions according to the first two principles of steady-state thermodynamics applied after the ”surface-boundary approach SBA” in biothermodynamics’. Considering that the carbon cycle is fundamental to life on Earth, quantification of water-energy-carbon coupling is the key for determining the carbon utilisation at specific climate.

Methodologically, applying equations of state according SBA, the free energetic losses accompanying ecosystem functioning are quantified to serve as a measure of specific ecosystem-site efficiency to utilize the solar energy into biochemical energy and related carbon storage (yield). The entropy production (characterised by function of dissipation,Φ) in the main photosynthetic apparatus (canopy leaves) is used as such a complex thermodynamic quantity. This is calculated for agricultural field (winter wheat) at a variety of microclimates across Bulgaria (Eastern Mediterranean climate influence) and compared with crop yield production. Long-term meteorological data records (2007-2023), regional SVAT_bg model output, global ECMWF model forecasts, land surface temperature (LST) from Meteosat information, are used for thermodynamic modelling of Φ and its approximation using satellite information.

Results indicate that the entropy production in vegetation canopy is sensitive to climate variability and microclimate differences and can captured the energetic loses. The relation between Φ and carbon utilisation (yield) is analytically described and allows the ranking of the relation in three categories: high-intermediate-low carbon storage. The temperature difference between surface temperature and air at 2m, (LST-T2m), as a first-order sensible heat approximation, appears to be sensitive to reflect variability of Φ and climate.

This approach is applicable at any other region accounting for specific crop, climate, soil environment, and reveals the importance of entropy production in biota to reflect natural carbon storage capacity.

Evaluating the EoS-based modelling of the CO_2-water equilibrium for CO_2 storage

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Accurate thermodynamic modelling of CO_2-brine equilibrium is crucial for the effective design and implementation of geological CO_2 storage in saline aquifers and depleted petroleum reservoirs. While numerous models have been proposed, those employed in CO_2 storage simulation are primarily various γ-φ models and those based on cubic equations of state (EoS). It is intriguing to investigate whether other EoSs, especially more sophisticated and advanced models, can enhance the equilibrium modelling.

CO_2-brine mixtures are complex due to the presence of many intermolecular interactions. In this work we focus on the CO_2-water system, as correct description of this system is required before adding an additional layer of complexity introduced by salts. We evaluate how well a wide range of EoSs describe the CO_2-water equilibrium using a large CO_2-water database. The evaluated models cover cubic EoSs, PC-SAFT, and GERG-type models. Different parameterisations are investigated, as well as the possibility of using phase-specific interaction parameters. While the latter approach is thermodynamically inconsistent, it has been used successfully in the form of the Søreide-Whitson EoS in reservoir simulations. A comparison is also made with the γ-φ model used in PHREEQC, whereby strengths and weaknesses are thoroughly analysed. For the EoS-based modelling, particular emphasis is placed on modelling CO_2 solubility accurately at both low and high pressures. Special attention is given to the significance of accurate CO_2 fugacity modelling to the calculated CO_2 solubility in water.

Atomistic Simulations of Active Brazing

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Active brazing is a high temperature joining method that is often used to make hermetic joints between dissimilar materials, like metals and ceramics. A common issue in active brazing is run-out that occurs when a wetting instability causes the braze alloy to flow out of the joint. The spreading is controlled by the wetting of the two substrates by the braze alloy, and this is directly related to the thermodynamic properties of the materials and interfaces, namely (a) surface energies of the solids, (b) surface tension of the liquid braze alloy and (c) the interfacial energies between them. If these quantities are known, then the wetting angles can be predicted using Young's equation. Understanding how these energies vary as a function of composition and temperature is crucial for designing a high quality braze process, but these quantities are hard to measure experimentally. Atomistic simulations provide a route for determining these energies, but methods for treating the metals and the ceramics in the same model are difficult to parameterize and computationally expensive. We present results of a newly developed reactive force field able to accurately model brazing of a model steel to alumina with a AgZr alloy. The brazing is essentially a three step process in which (1) Zr migrates to the alumina surface, and scavenges oxygen to form a ZrO_2 surface layer, (2) liberated Al diffuses through the braze alloy to the steel surface where extensive mixing of the liquid and solid metals form a multicomponent alloy and (3) the (predominantly) Ag braze alloy wets the two surfaces to form the final joint. We present the results of atomistic simulations aimed at accurately representing the full braze process, including reactions and wetting at both the ceramic and metal surfaces. Surface and interfacial energies are computed using thermodynamic integration to avoid the excessive run times (> 150 ns) necessary for direct wetting simulations. We demonstrate that after calculating these energies Young's equation accurately predicts the wetting angle for a variety of materials. Finally, we use the atomistic simulations to develop a data-driven constitutive model that is implemented in a finite element code to simulate the full brazing process at the manufacturing scale. Results from the simulations are compared to experiments, and the conditions that lead to run-out will be discussed.

Molecular Modeling and Prediction of the Physicochemical Properties of Carbohydrates and Polyols

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ROQUETTE is a producer of plant-based ingredients. Modeling, simulation, and predictive thermodynamic models are the tools to characterize the physicochemical properties of the matter flows in order to optimize and control their industrial processes. This relates to aqueous mixtures of carbohydrates and polyols with a high dry matter content. The polyols mannitol and sorbitol are diastereoisomers that have a nearly identical chemical structure, but very different physicochemical properties: for example, the solubility of sorbitol in water is 2.5 kg/kg of water, while mannitol has a solubility of 0.25 kg/kg of water at 25°C. Therefore, predicting liquid-solid equilibrium properties in this case requires sophisticated solution models that cannot be based solely on chemical group contributions, knowing that for mannitol and sorbitol the chemical constitutive groups are the same. In this context, previous works carried out by Institut Pascal's - GePEB team have shown that robust consideration of the solvation phenomena of polyols is essential for accurately predicting water activity in such systems. Focusing its efforts on modeling the residual terms of activity coefficients using COSMO-type models, the team has developed the COSMO-UCA model, which has the structural advantage of using quantum mechanics tools to predict formation and phase equilibrium properties. In this work, we present a methodology to predict physicochemical properties of complex solutions, taking as sole input the three-dimensional structure of the molecules in the medium. Computational chemistry tools and molecular dynamics simulations are used to generate the input data for the model. Finally, by developing knowledge models, we represent some physicochemical properties (activities and solubilities) of aqueous solutions of sorbitol and mannitol.

Structure and Dynamics of Fluids Confined in Nanometer-sized Porous Silica

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Mesoporous materials play an important role as catalyst support. Due to the confinement effect, they can for example influence the selectivity of a chemical reaction. A fundamental understanding of mesoporous materials allows design adjustments to improve the performance of the catalytic reaction. Molecular simulation techniques can be used in conjunction with experimental data to study physical processes inside mesopores in more detail. We are developing an open-source software tool referred to as PoreMS to create silica pores for moleculear dynamics (MD) simulations [1]. The generated structures can then be used to examine a wide variety of systems. For this purpose, we developed another Python package called PoreSim, which provides a complete setup for the MD simulation program GROMACS to run the system. The third package PoreAna enables the analysis of the simulated trajectory and provides density and diffusion profiles. The static and dynamic quantities enable a better understanding of the systems. As an example, a modeling approach for atomic-resolution studies of supported ionic liquid phase (SILP) systems in silica mesoporous confinement [2] is used to investigate the structure and dynamics of a two-phase system composed of heptane and an ionic liquid (IL) confined in a single-digit nanopore. The purpose of the IL is to immobilize a catalytic complex at or close to the heptane-IL interphase. By varying the layer thickness of the IL-phase the degree of confinement can be tailored. Here, molecular dynamics simulations are employed to gain insight into the heptane-IL interphase and the accessibility of the catalytic complex by reactants at various degrees of confinement compared to the unconfined scenario. Another investigated system is the ring expansion metathesis polymerization. This project deals with the influence of the pore diameter on the molecular weight distribution of cyclic polymers. Here the molecular simulations will help to rationalize the experimental work.

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Relation between double layer structure, capacitance and surface tension in electrowetting of graphene and aqueous electrolytes

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Deciphering the mechanisms of charge storage on carbon-based materials is pivotal for the development of next generation electrochemical energy storage systems. Graphene, the building block for graphitic electrodes, is an ideal model for probing such processes on a fundamental level. Herein, we investigate the thermodynamics of the graphene/aqueous electrolyte interface by utilizing a multiscale quantum mechanics – classical molecular dynamics (QM/MD) approach to provide insights into the effect of alkali metal ion (Li^+) concentration on the interfacial tension (γ_{SL}) of the charged graphene sheet/electrolyte interface. We demonstrate that the dependence of γ_{SL} on the applied surface charge exhibits an asymmetric behaviour relative to the neutral surface. At the positively charged graphene sheet, the electrowetting response is amplified by electrolyte concentration, resulting in a strongly hydrophilic surface. On the contrary, at negative potential bias, γ_{SL} shows a weaker response to the charging of the electrode. Changes in γ_{SL} greatly affect the total areal capacitance predicted by the Young-Lippmann equation but have negligible impact on the simulated total areal capacitance indicating that the EDL structure is not directly correlated with the wettability of the surface and different interfacial mechanisms drive the two phenomena. The proposed model is validated experimentally by studying the electrowetting response of highly oriented pyrolytic graphite over a wide range of electrolyte concentrations. Our work presents the first combined theoretical and experimental study on electrowetting using carbon surfaces, probing the charge storage mechanism at the electrochemical interface and its structural characteristics.

Effects of mobile framework cations on the adsorption isotherm of light gases in zeolites using classical Density Functional Theory

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The design of adsorption-based processes, such as carbon capture and energy storage, requires efficient computation of adsorption isotherms. This work employs Grand Canonical Monte Carlo (GCMC) simulations to predict the adsorption properties of a working fluid with zeolites. As a surrogate model that tremendously reduces the computational time, we use classical density functional theory (DFT) based on the perturbed-chain statistical associating fluid theory (PC-SAFT). Building upon Kessler et al.'s findings, which demonstrated good correspondence between adsorption isotherms of light gases in covalent organic frameworks (COFs) from GCMC and from DFT[1], we extend our predictions to aluminosilicates containing mobile cations. Mobile framework cations have been identified in GCMC simulations to alter the adsorption isotherm. In this work, we take a significant step forward by accounting for these mobile cations in DFT through delocalizing framework cations based on their density profiles in aluminosilicates. This methodology opens avenues for applying DFT calculations to flexible frameworks, addressing the computational challenges associated with such systems.

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Electrical Double Layer and the Zeta Potential at the Quartz Interface Via Molecular Dynamics Simulations

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In contact with an electrolytic solution, the solid-liquid interface develops an anisotropic region in the fluid phase known as Electrical Double Layer (EDL). We investigate the EDL at the interface between quartz and aqueous solution of sodium chloride by molecular dynamics (MD) simulations. We compare classical integer charge (SD) with scaled charge (Madrid) electrolytes force fields (FF). At homogeneous conditions, classical FF describes better equilibrium properties, although providing a higher degree of ionic association, which decreases the ionic conductivity. We simulate the confined fluid in a range of NaCl concentrations. A compact counter-ion layer screens the surface, which leads to charge inversion at higher salt concentrations. We compute transport properties, such as diffusion coefficient, viscosity, and electroosmotic mobility. From the Helmholtz-Smoluchowski equation, we compute the zeta potential, accounting for the salinity effect on the water dielectric constant and viscosity. Our MD simulations suggest that the magnitude of the negative zeta potential increases with decreasing salt concentration. Compared against the experimental data, a better agreement is achieved with classical (SD) and scaled charge (Madrid) FF at lower and higher salinity, respectively (Figure 1). The scaled charge FF describes better the ion-ion interactions and predicts the EDL saturation (i.e., constant zeta potential at higher salinity). We also compute the streaming potential coupling coefficient, and the result of both FF models agree with the experimental data in terms of both, the overall trend and values. MD simulations provide insights into underlying mechanisms of formation of the EDL and the zeta potential at a molecular level.

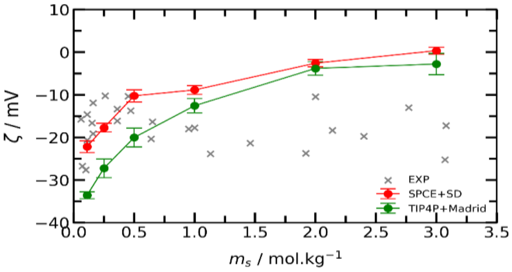

Figure 1: Zeta Potential from MD simulations using classical and scaled charge FF.

Ruling molecular mechanisms over the anisotropy of confined fluids transport coefficients

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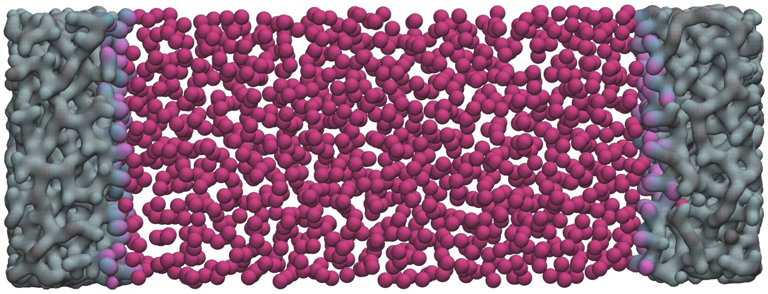
Porous materials are employed in a wide variety of areas such as biomedicine, catalysis, separation, and purification of gases and liquids. Their unique features such as high surface area, specific affinity for chemical groups or selection of pore size inside them offer resources for industrial projects and technological applications. Given the scale at which confinement effects occur on the fluids inside them, it seems careless to rely on common engineering approaches to compute transport properties of these systems, which are key elements for the projects that include them. The complex geometry and the presence of mechanisms at the molecular level require a tool capable of evaluating the behavior of the system at this scale. Using equilibrium molecular dynamics simulations, we evaluate the thermal effects of a fluid confined under different thermodynamic conditions. The system under study is built as a slit pore, and contemplates the interaction between amorphous silica and methane; a combination that is widely present in natural gas reservoirs. Moreover, we evaluate the thermal conductivity of the solid, considering its finite effects, and the anisotropy of energy transport in the fluid, highlighting the behavior of both the region under confinement/adsorption effect and inside the pore. The results are also compared with the residual entropy scaling approach, to assess a possible extension of the methodology.



Confined methane (United-Atom model) within a silica slit pore.

Exploring the Potential of Hierarchical Zeolite-Templated Carbons for High-Performance Li-O_2 Batteries: Multiscale Modeling Approach

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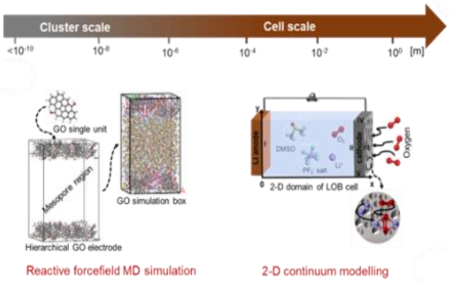
The Li-O_2 battery is considered an emerging class of power storage device because of its high energy specific energy [1]. However, the lower discharge capacity is one of the main challenges, induced by the sluggish kinetics and formation of insoluble lithium peroxide (Li_2O_2) inside the cathode. As is imperative to prevent pore choking due to Li_2O_2, while improving gas species mobilization through the pores, hierarchical zeolite templated carbons (H-ZTCs) [2] are a good option as cathodes owing to their ultrahigh surface area, pore volume and ordered micro/meso-porous framework. Understanding the mechanisms occurring at the electrochemical interface is key to explaining the improvement in performance provided by the hierarchical cathode.

Therefore, in this contribution, we present results from an implemented multiscale computational scheme [3], spanned over the continuum models at macroscopic level to classical and reactive-forcefield-based molecular dynamics (ReaxFF-MD) methods. This allowed us to critically evaluate the system performance of four distinct H-ZTCs, namely RHO, FAU, MFI, and BEA. Particularly, diffusion coefficients of the gas species (*i.e.*, Li and O_2), were found to show an increase of 3 to 5 orders of magnitude upon the addition of mesopores. Notably, the hierarchical RHO-ZTC based Li-O_2 battery delivered maximum discharge performance with high capacity (2523 mAh/g), energy density (7006 Wh/kg) and power density (1300 W/kg) at a discharge current density of 0.1 mA/cm^2. The study presented here comprises an innovative approach to enhance the performance of lithium-oxygen batteries, offering a promising solution for clean and sustainable energy storage. The support by Khalifa University under the Research and Innovation Center on CO_2 and Hydrogen (RICH) RCII-2019-007 is greatly acknowledged.



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Implications of the Interfacial Tension on Brine/H_2/CO_2 Systems for Underground Hydrogen Storage: A Molecular Dynamics Study

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With the increasing need to curb greenhouse gases emissions, hydrogen's capacity to decarbonize essential sectors (such as the transportation and industrial) makes it interestingly appealing. Nonetheless, one of the most challenging aspects for hydrogen utilization as an energy carrier is its low density. Geological reservoirs are currently being studied for practical and cost-effective underground hydrogen storage (UHS), allowing storing excessive hydrogen volume for longer durations. Besides, to better facilitate the withdrawal of the injected hydrogen, CO_2 is a viable option as cushion gas for pressure support and permanent CO_2 sequestration.

One of the critical parameters that govern the flow behavior of the injected fluids is the interfacial tension (IFT), which is an essential to determine the fluids displacement and the storage stability inside the storage medium. Hence, this study employs Molecular Dynamics (MD) simulations- in the isobaric-isothermal (NPT) ensemble- to examine hydrogen solubility in multi-component mixtures consisting of brine, hydrogen and carbon dioxide. The investigation is conducted across a broad range of reservoir conditions (P=10-60 MPa, T=323-388 K). Results show that the insertion of CO_2 molecules into the hydrogen phase resulted in a substantial drop in the interfacial tension of the system (*e.g.*, drop from 59.3 to 30.6 mN/m as the CO_2 concentration increased from 0 to 100%, P=60 Mpa). Notably, the impact of pressure on the different mixtures was found to be dependent upon the CO_2 mole fraction. Moreover, the rise in temperature notably decreased the IFT, showing less impact for systems with higher CO_2 concentration. This reduction in the interfacial and fluid-fluid boundary activity, as the concentration of the cushion gas (CO_2) increases, is reflected in a lower storage medium capillary entry pressure, thereby facilitating enhanced hydrogen size of the hydrogen plume in the storage media. Additional examination of the radial distribution functions of the various mixtures revealed that when CO_2 concentrations are low, CO_2 tends to accumulate at the interface of the brine due to the formation of weak hydrogen bonds, while higher molar fractions result in CO_2 aggregation. Financial support for this work has been provided by Khalifa University (project RC2-2019-007).

Applying Data Version Control to Molecular Simulations

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Data Version Control (DVC)

DVC is a tool that brings version control benefits to data science and was originally developed to be used in the context of machine learning. It helps manage and track changes to datasets, models, and experiments, ensuring transparency, reproducibility, and collaboration. It integrates with Git and simplifies data management in data science projects. DVC can be used in the context of molecular dynamics simulations to manage and track changes to simulation data, allowing for versioning of input data such as molecular structures, force field parameters, and initial configurations. By versioning these inputs, we can easily compare and reproduce simulations using different datasets, ensuring transparency and reproducibility in our research. DVC helps in tracking different molecular dynamics experiments and their associated parameters, settings, and results by treating each experiment as a versioned entity. This is particularly useful when conducting parameter sweeps, optimization studies, or exploring different simulation conditions.

Case study: Non-equilibrium Molecular Dynamics Simulations for Viscosity of Deep Eutectic Solvents

Aqueous eutectic mixtures are challenging systems to model due to highly non-ideal behavior and electrostatic interactions [1]. The possible combinations of molecular ratios, components, and temperature rapidly increase the phase space available to choose the best option for the desired application. Taking advantage of the molecular simulation potential, we perform a parameter study to monitor the best approach to predict properties of a choline chloride/glycerol aqueous mixture in a reliable and reproducible manner, applying a range of external forces to the system (periodic perturbation method [2]) and using DVC to track the experiments and monitor the results.

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An Intelligent Decision System for the Efficient Prediction of Thermodynamic Properties with a Successive Improvement Framework

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The project's objective is to develop an intelligent decision system for enhancing thermodynamic models in chemical product development, with a primary focus on the pharmaceutical industry. Traditional methods of collecting thermodynamic property data are often resource-intensive and time-consuming. Thermodynamic models can offer estimates; however, their accuracy and reliability, especially for novel compounds and unexplored process conditions, are limited. To address this challenge, our proposed approach leverages machine learning techniques, specifically gradient-enhanced radial basis functions (GRBFs)[1], to construct mathematical models. These models can estimate uncertainties and help guide the selection of the most effective experimental measurements or simulation data. By doing so, they improve the accuracy of thermodynamic predictions. It's essential to note that not all experimental measurements are of equal value; some contribute more information than others, and determining the optimal choice can be ambiguous. [2] This system empowers users to iteratively refine their models by incorporating new data until their predefined criteria are met. Beyond the pharmaceutical industry, this methodology has broader applications, supporting the efficient and reliable construction of accurate thermodynamic models, a vital element in chemical manufacturing process design.

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Extending the Domain of Applicability of Group-Contribution Models for Pure Component Properties

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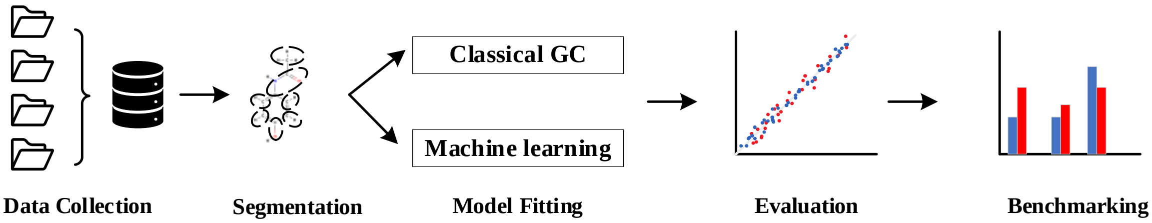
Abstract

Pure component properties provide the basis for many chemical engineering applications: P-V-T calculations, risk assessment, and chemical product design. While many data-driven approaches have emerged and been successfully applied for the prediction of these properties, linear additive group-contribution models remain a widely used and accepted method due to their simplicity, transparency, and "acceptable" accuracy. The models developed by Hukkerikar et al. (2012) and Constantinou-Gani (1994) are among the most widely used models. However, their range of applicability is very limited due to the amount of data used for parameter fitting. Despite efforts to develop ways for predicting the contribution of missing groups (e.g. atom connectivity indices), they have not been well-established and widely used.

In this work, we extend the domain of applicability of currently available GC models by expanding on the data used during regression (through digitization of a wide range of data sources) as well as employing machine-learning to account for non-linearity in the properties.



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Predicting Solvation and Dielectric Properties of Mixtures Using Polarization-Consistent Force Fields

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An important shortcoming of widely used classical non-polarizable models based on simple Lennard-Jones (LJ) sites and point charges is the lack of explicit polarization effects - i.e. a description of how the electron density responds to changes in the molecular environment. Instead, polarization is implicitly included, in a mean-field sense, into the parametization, usually by fitting to pure liquid properties (e.g. density). Problems arise when trying to describe thermodynamic properties that involve a change of phase (e.g. enthalpy of vaporization), solutions/mixtures (e.g. solvation free energies), or that directly depend on the electronic response of the medium (e.g. dielectric constant). In this work, we demonstrate a new approach based on finding the optimal point charge values to approximate polarization effects, followed by the application of *post facto* corrections to properties computed by non-polarizable models.

We have applied our new Polarization-Consistent Approach (PolCA) [1] to develop new atomistic models for alkanes, alcohols and ketones, leading to better predictions of pure liquid properties (e.g. density, self-diffusion, enthalpy of vaporization), but also to much more accurate predictions of solvation free energies in heterogeneous systems (e.g. polar/non-polar mixtures) and dramatically improved predictions of the dielectric constant for pure fluids and mixtures [2,3]. Finally, we also describe the recently developed Self-Consistent Electrostatic Embedding method that is able to predict realistic liquid phase dipole moments with a reasonable computational cost [4,5]. Overall, the PolCA framework and associated toolkit signifies a paradigm change in force field development.

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Transport Properties of Binary Mixtures from Equilibrium MD Simulations using TAMie force field

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Force fields such as TAMie (Transferable Anisotropic Mie) are used in molecular simulations to describe molecular interactions. The TAMie-parameters are adapted to experimentally determined vapor-liquid equilibria and liquid densities. Transport coefficients such as shear viscosity, thermal conductivity or diffusion coefficient are predictive quantities. This means that transport properties are not included in the objective function of the force filed optimization [1]. For an accurate description of transport properties, TAMie parameters must be further optimized [2]. For the optimization and validation of the TAMie force field parameters to transport properties, results from MD simulations of pure substances and mixtures are required.

In this work, we use equilibrium MD simulations and the Green-Kubo formalism [3, 4, 5] to determine dynamic transport properties such as viscosity, thermal conductivity and self-diffusion coefficients for binary mixtures. The simulation results are used to develop the TAMie force field.

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A Multiscale Molecular Dynamics Study of Skin Lipids Forming the Short-Periodicity Phase

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Molecular dynamics (MD) simulations enable the investigation of the molecular-level effects of composition on the structure and arrangement of lipid lamellae in the outermost skin layer called the stratum corneum (SC). MD simulations of coarse-grained (CG) models can be performed on larger spatial and temporal scales than is possible through atomistic simulations alone, allowing the self-assembly of multi-lamellar structures. Previously, we developed CG models for lipids commonly found in the SC: ceramides (CERs), cholesterol (CHOL), and free-fatty acids (FFA). Using these models to self-assemble multi-lamellar systems by reverse mapping the CG configurations back to the atomistic scale, we can then make direct comparison with experimental scattering patterns. Using this approach, here we apply our CG models to simulate compositions that are prevalent in the short periodicity phase (SPP) of the SC. Simulations of CER, CHOL and FFA mixtures have been performed to examine the effect of the chemistry of the CER head group on the lipid organization and structure. Through a combination of CG and atomistic MD simulations in conjunction with experiments, we provide a detailed molecular view of the organization of the lipids in the SPP and the role of CER chemistry.

Encapsulation of anticancer drug Chlormethine inside carbon nanotube from a thermodynamic point of view

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Abstract

Carbon nanotube (CNT) is a promising candidate to function as a drug nanovehicle due to its sufficient interior volume and capability of penetration to cells, bacteria, and tissues. However, from a thermodynamic point of view, it is of high vital to comprehend the interactions between the drug and nanotube to assess the performance of CNT as a drug carrier. In this study, the encapsulation processes of the anticancer drug Chlormethine inside the CNT (8,8) in aqueous solution are explored using molecular dynamics (MD) simulation. The interaction parameters between the constructing atoms of Chlormethine were obtained from the DREIDING force. Regarding the penetration process of the drug within CNT, the drug Chlormethine was very quickly adsorbed into the cavity of CNT and remained stably encapsulated, revealed as a very decreasing van der Waals (vdW) interaction energy between the drug and CNT to the value of -55 kcal.mol^{-1} at the end of the simulation. Furthermore, the free energy of the insertion process was calculated to be -22.5 kcal.mol^{-1}, suggesting a spontaneous encapsulation phenomenon. The larger contribution of the enthalpy alteration compared to the entropy changes in decreasing the free energy confirmed that this simulation was enthalpy-driven. This study offers encouraging proof that CNT should be further investigated for a variety of advanced anti-cancer drug carrying uses.

Keywords: Carbon nanotubes; molecular dynamics simulation; DREIDING force filed; anticancer drug Chlormethine; drug delivery

Thermodynamic Modeling for Nucleic Acid Therapeutic Manufacturing

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Nucleic acid therapeutics (NATs) have recently emerged as an exciting therapeutic modality for a range of indications, most notably as vaccines for SARS-CoV-2. The manufacturing of both the drug substance (nucleic acid construct) and drug product (e.g., as lipid nanoparticles (LNPs)) are complex multi-step processes that involve physical and chemical transformations of various species. Thermodynamic modeling to obtain properties of interest such as solubility and excess Gibbs free energy is essential for driving advances in understanding and improvements in product and process quality. We present three case studies of how thermodynamic modeling is facilitating the mechanistic investigation and intensification of NAT manufacturing.

In-Vitro Transcription (IVT) for RNA Synthesis

Modeling of the IVT reaction requires a description of solution thermodynamics of the system as the onset of crystallization of magnesium pyrophosphate, a byproduct of IVT, impacts RNA yield. Solubility of magnesium pyrophosphate in the IVT reaction is determined by a complex ionic speciation network. Past work has shown that simple speciation-based models are insufficient to describe the process dynamics.

Precipitation of mRNA for Separation and Purification

Precipitation as a downstream purification step can be used to isolate mRNA from solution. This step involves the addition of species such as polyethylene glycol (PEG), organic solvent such as ethanol, and different salts, which decrease the solubility of mRNA. A predictive model for mRNA solubility in these systems can accelerate process development.

Modeling of the Formation of LNPs Encapsulating Nucleic Acids

Continuum-scale simulation techniques such as population balance models (PBMs) and phase-field models (PFMs) can model important properties of LNPs such as the particle size distribution and LNP structure. The use of PBMs and PFMs require a description of the excess Gibbs energy of mixing to formulate a well-posed and physically accurate model.

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[1] N.M. Stover, V. Tenberg, and P.J. Walker contributed equally to this work.

Preparation and Characterization of Biomaterials for Pollutant Removal.

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The proliferation and widespread application of emerging pollutants are a growing concern globally. These contaminants pose harm to human health and the environment. Consequently, research into cost-effective techniques for eliminating such pollutants is underway, utilizing materials such as activated carbons that are well-known for their ability to capture contaminants through adsorption. However, the production cost of these materials hinders their widespread usage. Therefore, there has been a search for biomasses with a high lignocellulosic content, which can serve as the raw material for the production of activated carbons. Activated carbons are created by undergoing both chemical and physical treatments in order to enhance their structural features. Different treatments of biomaterials promote the development of structural features including surface area, total pore volume, and functional groups on the surface of activated carbons. The utilization of biomass offers the benefit of increasing the value of these wastes as they can be utilized to produce activated carbons with superior adsorption capacity. In this work, different activated carbons have been produced from different biomasses through the use of chemical and physical treatments to generate distinct structural characteristics in the materials. The materials were characterized using elemental analysis, thermogravimetric analysis (TGA), and textual analysis for surface area and pore size determination. Finally, the performance of the biomaterials for pollutant removal was evaluated and compared with commercial activated carbons.

Extraction and quantification of emerging pollutants in environmental water

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Emerging pollutants (EPS) are substances generated mainly by human activities, which are released into the environment and for which no environmental regulations have been defined [1]. Two of the major groups of EPSs are pharmaceutical residues and per- and poly-fluoroalkyl substances (PFAS). These EPS play a vital role and are widely used in industry, but once excreted they can become highly toxic in ecosystems, and even bioaccumulative. PFAS are highly persistent and bioaccumulated in air, water and soil, and together with pharmaceutical residues, generate serious contamination of land, effluents, surface water, groundwater and oceans, being detectable in drinking water and even rainwater. Bioaccumulation in humans increases the risk of developing cancer, hepatic and immune disorders, as well as birth defects. Reliable analytical methods and toxicity assessment methods are the basis for the management or elimination of EPS. This work describes the development of a method for the extraction, purification and quantification of pharmaceutical and PFAS contained in aqueous matrices, evaluating the limits of detection and quantification using the versatility of the UHPLC MSMS system. For the method development, each analyte was tested separately (3 pharmaceutical compounds and 3 PFAS compounds and their respective internal standards) and then the method was optimized for a mixture of the analytes in a synthetic aqueous matrix. The SPE (Solid Phase Extraction) method was optimized and validated for the extraction and purification step, at different volumes and concentrations of the analytes. Finally, the extraction and quantification methods are validated on real samples in different environment aqueous matrices and will also be used as a method for quantification and verification of the effectiveness of different EPS adsorption and removal treatments.

A COSMO-RS based approach for predicting the solubility of vanillin in aqueous mixtures

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Vanillin is a widely recognized flavour that presents antioxidant activity, preventing oxidative damage to human cells. Given that the solubility of vanillin in water is much lower when compared with several organic solvents, increasing its solubility could benefit the incorporation of vanillin into water-based products from pharmaceutical and food industries. In this work, the Conductor-like Screening Model for Real Solvents (COSMO-RS) was used to predict the solubility of vanillin in mixtures of water and organic solvents with two optimized conformers, the first aiming to increase the intermolecular interactions and the second aiming to decrease intermolecular interactions by rotating the hydroxyl group inwards. The conformer weight was adjusted to fit experimental solubility data of vanillin binary mixture in water or organic solvents. For the mixed solvents, the conformer weights were calculated using a linear regression considering the weights fitted for the pure solvents.

By adjusting the conformer weight to fit experimental solubility of the pure solvents, the model provided better predictions than the default conformation for solubility calculations, improving the description of the solubility maxima. This work proposes a semi-predictive approach to COSMO-RS that requires experimental solubility values of the target solute in pure solvents. This methodology improves the predictions of solubility in mixed solvents and emphasizes the importance of the distribution of conformers throughout the solvent mixtures and its impact on predictions.

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Exploring Green Solvent for Lupin Debittering via *In Silico* COSMO-RS Predictive Screening

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Andean lupins have been widely cultivated in the Andean highlands for the enrichment of the soil, animal feeding and as a food crop. Their seeds are nutrient-rich in terms of their high content of protein (about 50%) and oil (about 20%). However, the presence of toxic quinolizidine alkaloids, including sparteine, lupanine, and 13-OH-lupanine, in the seeds limits their industrial applications.

Several ionic liquids (ILs) and eutectic systems (ESs) have been reported in the literature to extract alkaloids from plant materials with the advantages of sustainability, biodegradability as well as adjustable polarity to dissolve polar and non-polar compounds. However, identifying an optimal IL or ES from the large number of possible combinations is quite challenging. To address this issue, the COSMO-RS (COnductor-like Screening MOdel for Real Solvents) model has emerged as a reliable computational tool that can screen numerous compounds or mixtures based on different thermodynamic properties.

The current study demonstrates the dissolution behavior of quinolizidine alkaloids in ILs and ES using the COSMO-RS model. Several combinations were attempted and evaluated by predicting the logarithmic activity coefficient ($\ln(\gamma)$) of typical quinolizidine alkaloids (sparteine, lupanine, and 13-OH-lupanine) in conventional solvents, ionic liquids and natural-based eutectic solvents.

Through this research, we aim to develop a novel separation method based on the use of green solvents, to debitter the Andean lupin beans, i.e., to remove the toxic alkaloids, and to unveil efficient and environmentally conscious strategies for maximizing their use in the food industry.

Exploring the synergism of hydrotrope-based DESs for improved kraft lignin aqueous dissolution

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Lignin holds significant potential for generating valuable aromatic compounds. However, achieving this potential requires the development of effective lignin dissolution methods. Previous investigations have demonstrated the remarkable capability of hydrotropes to enhance the aqueous solubility of lignin. Notably, deep eutectic solvents (DESs) have exhibited hydrotropic functionality, significantly increasing non-polar solute solubility in water, making them an attractive option for lignin dissolution. Inspired by the recently proposed cooperative mechanism of hydrotropy, this study explores the influence of hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD) on the performance of DESs as hydrotropes for lignin dissolution in aqueous solutions and proposes possible lignin solubility mechanisms in different water/DES compositions. The capacity of six polyols (glycerol, ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol) and cholinium chloride to enhance the aqueous solubility of Kraft Lignin was primarily investigated. A correlation between the capacity of polyols to enhance the solubility of Kraft Lignin and the size of their alkyl chains was observed. This was rationalized in terms of the competition between hydrotrope-hydrotrope and solute-hydrotrope aggregates, with the latter being maximized for 1,4-butanediol. Interestingly, in the diluted region, it is observed that the hydrotropic effect of the DESs is well represented as the independent sum of the contributions from the corresponding HBAs and HBDs. Conversely, n the concentrated region, lignin solubility is higher with pure hydrotropes than with their combined form as a DES.

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Modelling the solid–liquid solubility of amino acids and oligopeptides and their speciation under pH changes using the SAFT-γ Mie group-contribution framework

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Abstract

As peptides gain increasing ground as active pharmaceutical ingredients (APIs)[1], robust modelling of their properties in solution is central in the screening, development, and design of the drug product and its manufacturing process. We use the SAFT-γ Mie GC approach to model the solubility of peptides and their constituent amino acids in various pure and mixed solvent media, at a wide range of temperatures and solvent compositions. Additionally, the speciation of amino acids under changing pH is modelled by solving the phase- and chemical-equilibrium equations, simultaneously. This is made possible by the ability of the model to account explicitly for the zwitterionic nature of amino acids and peptides. With minimal use of experimental data, especially that of solubility, the model produces accurate solubility predictions for many binary, ternary, and multicomponent systems containing a variety of amino acids and oligopeptides.

The SAFT-γ Mie group-contribution (GC) approach is a model based on the statistical associating fluid theory (SAFT) in which molecules are treated as heteronuclear chains of interacting spherical segments. Thermodynamic properties of the system of interest are derived from the Helmholtz free-energy expression [2]. The advantage of using such a model for peptides and amino acids lies in the transferability of its parameters, since peptides and amino acids are made up of a small set of functional groups.

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A group-contribution framework to account for the intra-molecular hydrogen bonding in aqueous solutions of glycine homopeptides

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The phase transitions and closely related non-equilibrium formation of gels of therapeutic peptides in solution are of direct relevance to peptide-drug development. From a modelling stand-point, theoretical progress can deliver accurate predictions of complex phase behaviour, including solid–liquid solubility and liquid–liquid de-mixing, and can account for detailed molecular features. We implement SAFT-γ Mie [1] which is a group-contribution approach based on a heteronuclear model of fused segments interacting via Mie potential. These segments also feature association sites when necessary to interpose directional interactions that mimic hydrogen bonds. This approach account for chemical functionality, ring size, molecular size, connectivity, and strong polar interactions. This theory is used to predict the solid–liquid solubility of glycine homopeptides (up to hexaglycine) in water. In peptides intramolecular bonding and the zwitterionic nature of the molecules critically affect the observed solubility, and lead to complex phase transitions, which pose a stringent test to modelling approaches. The deviations in the SAFT-γ Mie solubility prediction from the experimental data motivate an assessment of the impact of intramolecular hydrogen bonding in the theoretical approach. Eight conformers of neutral diglycine are considered, based on number and type of hydrogen bond: each with a different intramolecular bond between –NH or =O groups of the peptide-bond group (C=ONH) and the end groups (NH2 and COOH) in the glycine peptides. The models which deliver the best prediction of diglycine solubility those accounting for intramolecular hydrogen bonds as the following cases: (i) [–NH and –NH2], [=O and –COOH] and (ii) [–NH2 and =O], [–NH and COOH]. As a next step, zwitterionic form of glycine homopeptides will be modelled to assess the impact of presence of charged species in aqueous solution on the solubility predictions.

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Prediction of the glass temperature of amorphous solid dispersions with an equation of state

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The bioavailability of active pharmaceutical ingredients (APIs) can be enhanced using an amorphous solid dispersion (ASD). These formulations enable the API to be dissolved in amorphous form by hindering the molecular mobility of the particles dispersed inside a glassy polymer matrix. However, ASDs might exhibit undesired miscibility gaps [1, 2]. Therefore, the correct prediction of the phase equilibria and glass temperature of the mixture polymer + API is of utmost importance for the development of new formulations.

Equations of states have already been applied to describe the phase behavior of ASDs [1, 3, 4]. Nevertheless, the glass temperature is often calculated using empirical models which need to be fitted to binary experimental data. In this work, a new framework using a combination between the generalized entropy theory (GET) [5, 6] and the Sanchez-Lacombe (SL) equation of state [7] was developed to calculate the phase equilibria (SLE and LLE) and to predict the glass temperature of ASDs.

This framework was applied to describe the phase behavior of the ASDs formed by poly vinyl pyrrolidone (PVP) and indomethacin, ibuprofen and griseofulvin, respectively. The influence of water sorption on the glass temperature of the pure components and the ASDs was also investigated.

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Properties of the RPM-like electrolyte reference

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Abstract

As an attempt to develop a ‘realistic’, and yet theoretically tractable reference system for the development of a perturbed molecular-based equation of state for ionic fluids, the RPM-like model system with a short-range attractive part has been constructed and studied. The approach we applied follows one that was used in the case of simple liquids [1,2]. The phase diagram of the RPM-like model system has been determined along with its structure and some other thermodynamic properties using the FMSA theory [3] and Monte Carlo computer simulations. The model reproduces the structure of the parent RPM electrolyte and its critical point falls below the critical point of the RPM electrolyte. Since under FMSA theory RPM-like model is also amenable to a closed analytical treatment, it may be considered as a suitable realistic reference model for the entire class of ionic fluids and in a wide range of thermodynamic conditions.

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PREDICTION OF MULTI FLUID HELMHOLTZ ENERGY APPROXIMATION (MFHEA) EOS BINARY INTERACTION PARAMETERS USING GROUP CONTRIBUTION METHOD

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The accurate prediction of fluid properties by Equations of State (EoS) relies on representative experimental data, which, in many cases, may not be readily available for a wide range of systems or may not cover the required temperature and pressure ranges. To deal with this challenge, it was conceived as part of the objectives of this research, a predictive tool (model) which yields values for the binary interaction parameters for MFHEA equation of state for natural gases and similar fluids be developed in a way like the work of (Jaubert & Mutelet, 2004). To achieve this, a group contribution method (GCM) will be employed, where components constituting the binary mixtures under investigation will be systematically decomposed into simpler groups. These components include normal alkanes, cycloalkanes, branched alkanes, carbon dioxide, nitrogen, hydrogen Sulfide, inert gases (e.g., helium, argon, xenon), and aromatics (Faramawy et al., 2016). However, inert gases will not be considered in this study due to their reported trace amounts in natural gas and gas condensates. The simplified groups selected for this research encompass C2H6, CH4, CH3, CH2, CH, C, CO2, N2, H2S, Caro, CHaro, Ccycl, and CHcycl. Interaction parameters for each of these individual groups will be determined through the utilization of a model equation, developed in this work, and fine-tuned using the simplex optimization algorithm. Subsequently, the accuracy of the model will be assessed by comparing results for Vapour-Liquid Equilibrium (VLE) calculations utilizing BIPs from this research against those obtained from the original BIPs (like GERG-2008 EoS). Any deviations observed will be thoroughly examined and reported to validate the efficacy of the developed predictive tool.

Clapeyron.jl: An Extensible, Open-Source Thermodynamics Toolkit

Pierre J. Walker, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, United States of America

Thermodynamic models are essential for characterising complex systems, including natural gas, electrolyte, polymer, pharmaceutical, and biological systems. However, the historically challenging and cumbersome implementations of these models have restricted access to black-box commercial tools. Clapeyron.jl represents a groundbreaking open-source fluid-thermodynamics toolkit for developing and utilising thermodynamic models. Built-in Julia, a modern language for scientific computing known for its ease of use, extensibility, and first-class support for differentiable programming, Clapeyron.jl has simplified access to thermodynamic modelling. Our toolkit supports more equations than any other package available, including most commonly used standard cubic (SRK, PR, PSRK, etc.), activity-coefficient (NRTL, UNIFAC, etc.), COSMO-based, and SAFT equations. We also provide a range of property estimation methods for single- and multi-component systems, including bulk, equilibrium, and critical properties. With Clapeyron.jl, researchers and enthusiasts alike can concentrate on the applications while minimising concerns about the implementation. Furthermore, Clapeyron.jl provides a mechanism for researchers in the field to implement their equations or algorithms, benchmark them, and make them available to the broader research community. This will greatly accelerate the development and acquisition of new thermodynamic tools. The future looks promising, with an ever-growing collection of models, including electrolyte approaches, chemical-reaction models, and new group-contribution approaches, planned for future Clapeyron.jl releases. Our toolkit provides a valuable and powerful resource for researchers and industry professionals alike, offering new opportunities for innovation and discovery in thermodynamics.

Toward Advanced, Predictive Mixing Rules in SAFT Equations of State

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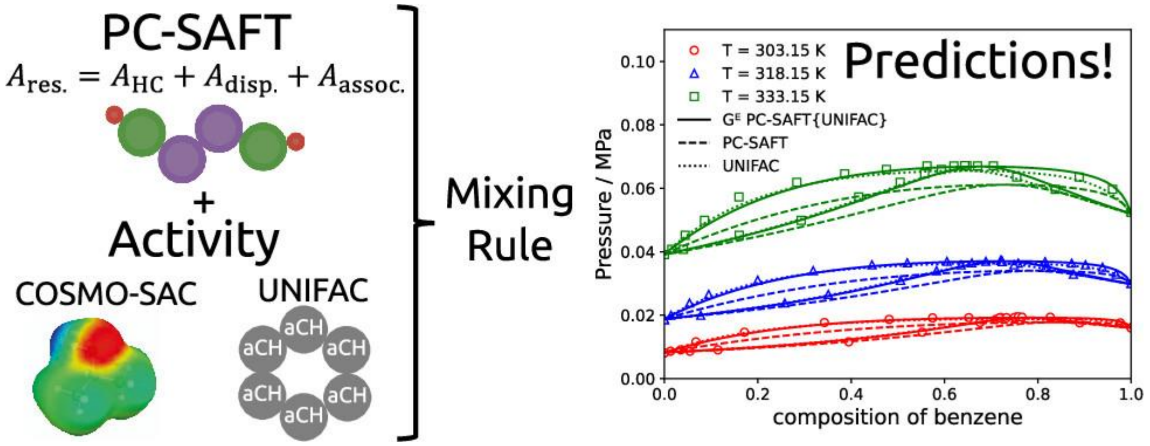
A novel mixing rule that bridges the Statistical Associating Fluid Theory (SAFT)-type equations of state and activity coefficient models is proposed. Applying this mixing rule to the PC-SAFT equation of state is the focus of this article. In comparison to the original PC-SAFT equation, and even the underlying activity coefficient model, this mixing rule provides high-accuracy predictions of equilibrium properties for a range of mixtures, being able to predict phenomena that neither PC-SAFT or the underlying activity coefficient model would be able to predict on their own. A few limitations are identified including the case of cross-associating mixtures, due to the difficulty of separating associative interactions from dispersive interactions in activity coefficient models. Nevertheless, it is also shown that the new mixing rule is able to predict bulk properties very accurately, including volumetric properties which activity coefficient models alone are not able to predict. Given that one is able to use predictive activity coefficient models within this mixing rule, such as UNIFAC and COSMO-SAC, this new mixing rule opens the doors for the development of fully predictive SAFT equations of state for mixture systems.



Confidence-Interval and Uncertainty-Propagation Analysis of SAFT-type Equations of State

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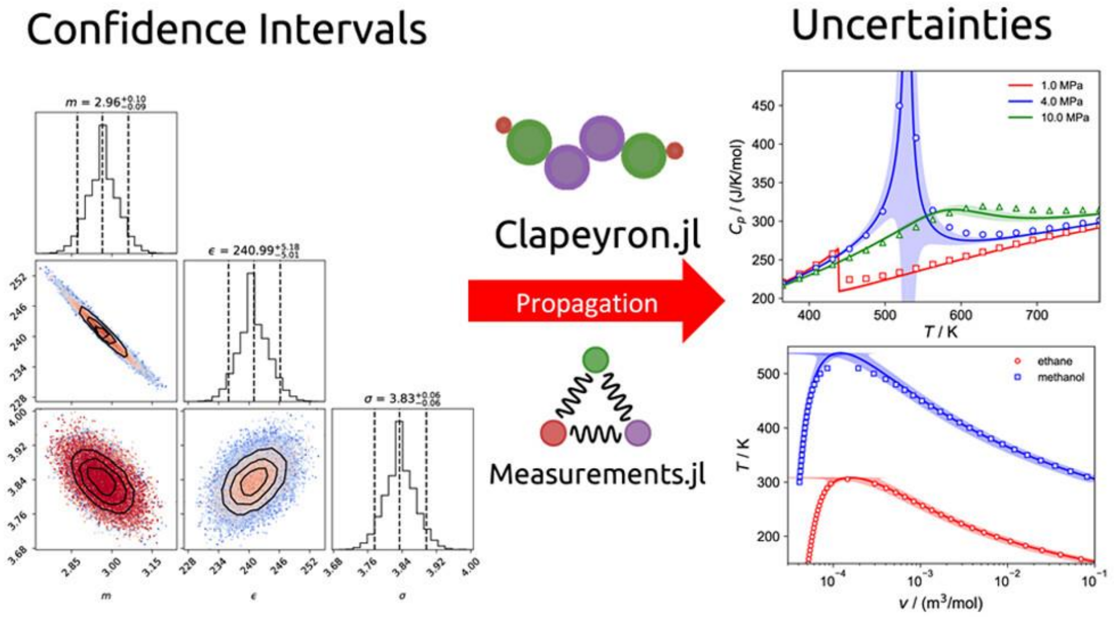
Thermodynamic models and, in particular, Statistical Associating Fluid Theory (SAFT)-type equations, are vital in characterizing complex systems. This paper presents a framework for sampling parameter distributions in PC-SAFT and SAFT-VR Mie equations of state to examine parameter confidence intervals and correlations. Comparing the equations of state, we find that additional parameters introduced in the SAFT-VR Mie equation increase relative uncertainties (1%–2% to 3%–4%) and introduce more correlations. These correlations can be attributed to conserved quantities such as particle volume and interaction energy. When incorporating association through additional parameters, relative uncertainties increase further while slightly reducing correlations between parameters. We also investigate how uncertainties in parameters propagate to the predicted properties from these equations of state. While the uncertainties for the regressed properties remain small, when extrapolating to new properties, uncertainties can become significant. This is particularly true near the critical point where we observe that properties dependent on the isothermal compressibility observe massive divergences in the uncertainty. We find that these divergences are intrinsic to these equations of state and, as a result, will always be present regardless of how small the parameter uncertainties are.



A mixed-EoS strategy for multiphase equilibrium problems on energy transition applications

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The transition to a carbon neutral energy supply relies heavily on the development of subsurface technologies. Typically, these technologies encounter a wide variety of fluid and solid phases and conditions span across large ranges of pressure and temperature. Modelling and simulation of the physical processes involved requires advanced compositional reservoir simulation techniques with accurate description of fluid phase thermodynamics. Many full-EoS simulation models are concerned with a single EoS that describes all fluid phases, which is the most elegant and thermodynamically consistent approach. However, considering the nonideality of a common and typically highly saline aqueous phase, a simple cubic EoS is not sufficiently accurate. Although improvements are at hand, modified mixing rules have a limited range of applicability and more advanced association models demand more computational effort. The use of an activity model instead simplifies the computational complexity while maintaining improved accuracy of thermal-compositional flow and transport in comparison with a uniform cubic EoS. This is at the expense of thermodynamic consistency across phase boundaries and critical point, but as we will demonstrate, it provides a useful modelling practice provided that one is located within the appropriate range of applicability. Besides, the possible occurrence of solid phases, such as clathrate hydrates, salts or ice, inherently requires the use of multiple EoS which essentially loses full consistency. In this study, we perform a thorough Gibbs energy analysis to investigate the applicability of a mixed EoS strategy. We demonstrate the practical aspects and its limitations for use in stability test and multiphase flash algorithms. Finally, we study the prediction of thermodynamic properties to assess the applicability of the approach to phase equilibrium problems at other state specifications.

Development and management of advanced thermodynamic models with *Simulis Thermodynamics*

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As a chemical engineering simulation software provider, Fives ProSim provides a large thermodynamic library with the required models parameters, thus allowing to cover a wide range of industrial applications (chemicals and petrochemicals, gas and oil production, refining, energy and many other areas: alcohols, air separation, carbon capture and storage, bio-fuels, pharmaceuticals, ingredients, flavors and fragrance, pulp and paper, food industry, metallurgy…).

Moreover, *Simulis Thermodynamics* (the Fives ProSim calculation server for thermophysical properties and phase equilibria calculations) can also be used by the scientific community to regress parameters or to develop, test and compare the capabilities of models (all calculations - flash, critical point, thermodynamic properties... - can be performed directly in Microsoft Excel®).

At the frontier between research and industry, Fives ProSim is constantly trying to build bridges: by gathering new requests from industry on thermodynamic models for new applications, but also by participating in the development of these new models or by enriching parameter databases. Through collaborative projects between Fives ProSim, industry and the research community, this presentation will show the capabilities acquired by Fives ProSim, particularly regarding:

- The parameterization of electrolyte models for different applications, such as the representation of complex electrolyte mixtures (co-solvents, mixtures of weak and strong electrolytes) through the EleTher collaboration project, or the representation of hydrogen solubility in Water/NaCl brine. These projects raise questions about the current limitations of these models and the developments still required.
- The simple and flexible use of predictive models, which are constantly evolving and being updated, *e.g.* by the UNIFAC consortium. These models are highly appreciated and very used in the industry for their predictive capabilities.
- The addition of new models for future applications such as the representation of mixtures containing hydrogen spin isomers.

These examples also highlight the current requirements linked to the industrial challenges and the new avenues to explore for the implementation of thermodynamic models in the future.

Describing compressible mixtures of cross-associating structural isomers

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Current trends in the chemical industry towards the increased use of more renewable resources lead to an increased occurrence of structural isomers in the product streams. To design processes with such product streams, one needs to account for the properties of the isomers. Most thermodynamic models can not consider the structure of a molecules. They treat each isomer as a separate kind of molecule and adjust their parameters to pure substance data of each isomer. But many pure isomers are hardly commercially available. An experimental investigation of these for pure substance data or the designing of the process is, therefore, not possible. In recent years the lattice cluster theory (LCT) by Freed et al [1] was able to predict the phase properties of branched molecules based on their linear analogues. The LCT is able to achieve this by considering the structure of the isomer, but only if the functional groups occupy the same positions on molecule.

A new model was developed through the combination of the LCT with a chemical association approach similar to Chemical Association Lattice Model (CALM) by Browarzik [2]. This approach creates many association clusters, which enables it to account for the position of functional groups. Continuous thermodynamics by Rätzsch and Kehlen [3] is applied to deal with the large number of clusters. The model predicts the phase properties of isomers with a single set of parameters.

In this contribution, the application on the description of liquid-liquid as well as vapor-liquid equilibria is shown.

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Ion pairing is hidden inside Poisson-Boltzmann, and lost when deriving the Debye-Hückel equation

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The Debye-Hückel equation[1] is among the most famous and successful theories to model electrolyte solutions. In this work, we demonstrate how the vital linearization step in its derivation removes the ion pairing phenomenon naturally enclosed within the Poisson-Boltzmann equation. Following a pragmatic approach, we derive the Ebeling's association constant [2], which describes the reaction of formation of ion pairs following Bjerrum's approach [3], from an analytical approximated solution to the Poisson-Boltzmann equation, demonstrating how the activity coefficient of free ions and the mass action law are contained within the difference between the Poisson-Boltzmann and the Debye-Hückel equations. We conclude that the Poisson-Boltzmann equation naturally considers the ion pairing phenomenon within its higher-order electrostatic contributions, which are left out when it is linearized to derive the Debye-Hückel equation. We also provide an explanation on the "negative deviations" of the Poisson-Boltzmann equation when compared to the Debye-Hückel limiting law, which can now be physically attributed to the ion pairing phenomenon.

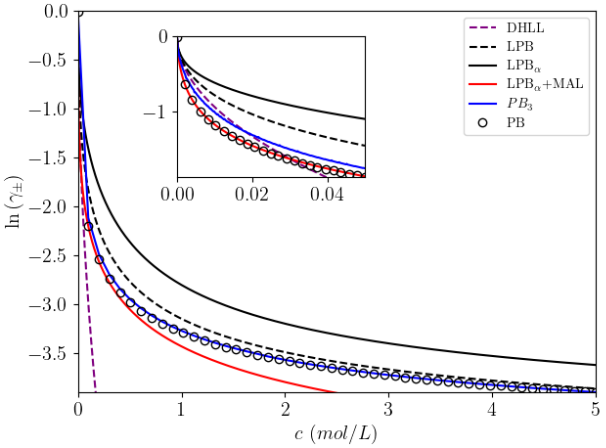

Figure 1. Mean Ionic Activity Coefficient of the mixture $MgSO_4$+water at 25°C for different models.

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Measurement and modelling of monomer fraction in solvating systems

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Mixtures containing oxygenated species are ubiquitous in applications ranging from traditional chemical process to more targeted pharmaceutical applications. In the presence of associating species like alcohols, these species disrupt association multimers and form solvating complexes which pose a thermodynamic modelling and subsequently process design challenge.

The monomer fraction, directly quantifiable within the association contribution in any SAFT framework, is considered as a direct measure of the extent of hydrogen bonding in associating and solvating systems. Indeed, the potential of the property garnered interest in the late 2000s as a potential simplifying solution to parameter multiplicity in SAFT type models [1]. However, due to inconsistent literature data and the spectroscopic expertise required to generate new data, the academic interest waned until recently [2,3].

This work aims at using alternative chemometric processing techniques to decompose newly measured spectra of ethanol-ester mixtures. In particular, we aim to quantify the monomer fraction in the dilute-solute range on each end of the compositional spectrum (i.e. ester in alcohol *and* alcohol in ester). In particular, we are interested in the experimental trends in the data, and how different approaches to accounting for solvation in the SAFT literature (pseudo-association [4], induced association [5] and the “N” scheme [6]) compare to the experimental data. Finally, we reassess the role of these data in parameterizing the SAFT models and raise questions about the suitability of the underlying TPT1 theory applied to these systems – in support of similar questions being asked in the contemporary applied thermodynamics literature.

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Ammonia based fuel properties calculations in the thermodynamically metastable state

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To counter the global warming due to the use of fossil fuels, it is urgent to develop low-carbon solutions in the transportation and distributed power generation. Ammonia based fuels are currently evaluated as promising solutions (Valera-Median *et al.*, 2021, *Energy & Fuels*, *35*, 6964-7029), thanks to the following properties:

- As a hydrogen-carrying molecule for high density storage and long-distance transportation;
- It can be converted back to hydrogen;
- It can be used pure or in blends for combustion in a gas turbine.

Some experimental studies (Lamanna *et al.*, 2014, *International Journal of Multiphase Flow*, *58*, 168-184; Pelé *et al.*, 2021, *Fuels*, *2*, 253-271) have shown that the flash boiling of superheated ammonia is very sensitive to the ambient pressure and liquid temperature; and the liquid spray droplets observed in the chamber could be in a thermodynamically metastable state.

Very few computational fluid dynamics (CFD) solvers can correctly simulate the flash-boiling phenomena. In this work, we developed an extended version of the real-fluid model (RFM) (Jafari *et al.*, 2022, *The Journal of Supercritical Fluids*, *182*, 105557; Gaballa *et al.*, 2023, *International Journal of Multiphase Flow*, *160*, 104372), considering the liquid spinodal curve in the calculations of thermodynamic and transport properties in the metastable region. In this new model, the metastability index is defined as a measure of the energy barrier required to create nuclei. Then, the required properties are calculated with our in-house thermodynamic library Carnot (de Hemptinne *et al.*, 2023, *Science and Technology for Energy Transition*, 78, 30), in either the single-phase, metastable, or two-phase region, depending on the input data range in temperature, pressure, and composition. Then the generated table is used by the RFM model already implemented in the CFD Converge™ solver.

Predicting transport properties of simple fluids using an extended FMSA model

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Tang and Lu's First Mean Spherical Approximation (FMSA) equation of state [1], extended by Dridi et al [2], has recently been successfully used to predict rare gas phase equilibria from ab initio interaction potentials. The corresponding radial distribution functions are used here to model systematically the transport properties (shear viscosity, self-diffusion coefficient and thermal conductivity) of simple Mie n-6 fluids and noble gases within the framework of a simplified coupling mode theory approach based on the work of Egorov [3]. The approach is tested throughout the whole phase diagram (from dilute to dense fluid) for theoretical (by comparison with simulation data [4-6]) and real fluids (by comparison with experimental data).

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Thermodynamic properties (bubble points and density) of H_2 in CO_2-rich binary systems: experimental measurements and model correlations

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ABSTRACT

This study conducted experimental measurements on the bubble points of binary mixtures containing varying concentrations of CO_2 (99.5%, 99%, 98.5%, and 98%) with hydrogen (H_2) (with composition uncertainty of ±0.134%). These measurements were carried out at low temperatures (247.69-273.31 K – with uncertainties of ±0.14 K) using constant composition expansion methods. Densities of 0.995 CO_2 + 0.005 H_2, and 0.95 CO_2 + 0.05 H_2 binary mixtures were measured using a vibrating tube densitometer (with uncertainty of ±0.77 $kg.m^{-3}$) at four isotherms (278.15, 298.34, 323.55, and 348.41 K - with uncertainty of ±0.02 K) and pressures up to 34.63 MPa (with uncertainty of ±0.01 MPa). The experimental bubble point and density data were used to validate two thermodynamic models - the Peng-Robinson and Multi-Fluid Helmholtz Energy Approximation Equation of state. (PR-EoS and MFHEA-EoS). From the results, the presence of H_2 caused a significant (16-68%) increase in the bubble points of CO_2.This effect intensified with higher concentrations of H_2 and decreased with rising temperatures. Both models demonstrated good agreement with the experimental bubble point data, exhibiting less than 5% deviation for all data points. Notably, the PR-EoS model outperformed the MFHEA-EoS, showing less than 2% average deviation. Furthermore, even at low concentrations (0.5%), the presence of H_2 led to a substantial reduction (>59%) in the density of CO_2, with this effect becoming more pronounced at higher temperatures and concentrations of H_2. Both models predicted the densities of the system well (with less than 2% deviation), though MFHEA-Eos was more accurate with less than 0.5% deviations for all the data points.

Keywords: CO_2; H_2; CCUS; EoS; Bubble point; Density.

Dynamic evaluation of zeta potential measured for interfaces oil-brine and rock-brine at 25 and 60 ºC

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Zeta is an electrical potential exhibited by any suspended particle, macromolecule, or material surface. The zeta potential (ZP) is widely used to explain phenomena such as the miscibility of fluids and the stability of mixtures. It is useful as an initial screening tool for selecting brines to enhance oil recovery. However, there is a gap in studies of brine-oil and brine-rock interfaces. There is no consensus in the literature on the sample stabilization time before ZP measurements. This work contributes to filling this gap and improving the reproducibility of ZP data. A Brazilian pre-salt oil, Indiana Limestone powder, and 11 types of synthetic brine were used. The brine concentrations were 170 kppm (formation water), 5 kppm (desalinated water), and 5, 15, and 30 kppm for desulfated, semi-desulfated, and sulfated water. The samples were prepared by mixing 0.1 mL of oil or 0.1 g of rock powder in 10 mL of brine and homogenized in the sonicator for 4 min. Samples were kept at rest for stabilization for 5 h, 24 h, and 7 days. ZP data were measured in triplicate at 25 and 60 ºC by the Malvern Zetasizer analyzer. The largest deviation on oil-brine ZP, up to 24 hours, occurred for the system with the 30 kppm desulfated brine (+/- 3 mV) at 25 ºC and with 30 kppm sulfated brine (+/- 4 mV) at 60 °C. For the other brines, deviations were below 2 mV. For 7 days of stabilization, the oil-formation water ZP reached a maximum variation of 32.96 mV due to the instability of the sample. The rock-brine ZP experimental data provided low deviations for 5 hours, with a maximum variation of 4.8 mV at 25 ºC for the 30 kppm desulfated brine and 5.11 mV at 60 ºC for 15 kppm desulfated brine. High deviations were observed from 24 hours onwards due to the instability of most brines, with a difference of up to 34.84 mV between measurements for the formation water. The rock-desulfated brine ZP data (5, 15, and 30 kppm) were measured at 1, 3, 5, 6, and 7 hours as further study to find the stabilization time with lower errors resulted in the smallest deviations between 3 and 5 hours. Depending on the stabilization time, the load variation at the interface can be large enough that the charge is positive or negative in the same system. Based on the experimental runs, the recommended stabilization time for ZP measurements should be between 3 and 5 hours due to the highest stability of the samples disclosed in this interval.

Effect of Brine Composition in the Interfacial Tension of a Brazilian Pre-salt Oil Sample

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Verônica J. Pereira, Gloria M.N. Costa, Silvio A.B. Vieira de Melo

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Studies have tried obtaining low-salinity water that reduces interfacial tension (IFT) to improve oil recovery. This work evaluates the role of brine composition in the dynamic IFT between low-salinity water and oil's surface-active components. IFT between recombined oil and five synthetic brines was measured using the pendant drop method in a drop shape analyzer (Krüss/Eurotechnica DSA100). The brines selected for evaluation were formation water (FW, 170 kppm), desulphated seawater (DW, 30 kppm), diluted desulphated seawater (DDW, 5 kppm), semi-desulphated seawater (SDW, 5 kppm) and desalinized seawater (NaCl, 5 kppm). All measurements were carried out at 250 bar and 60 °C to mimic oil reservoir conditions. The dynamic behavior of recombined oil/brine IFT under the evaluated conditions does not reach equilibrium, indicating that a diffusion-type process controls the IFT. Therefore, the time required for the solute to transfer from the bulk to the subsurface is much longer than the time needed to move between the subsurface and surface (adsorption). After 30 hours, the highest IFT value was obtained for the FW (19.45 mN/m) and the lowest one for the SDW (15.52 mN/m), followed by DW (15.75 mN/m), desalinized seawater (16.31 mN/m) and DDW (17.39 mN/m). For the high salinity FW, the high ionic concentration leads to the stronger repulsion of ions that migrate from the interface to the bulk phase, increasing the IFT (salting-out effect). The concentration reduction of low salinity waters leads to IFT reduction compared to the reservoir original's recombined oil/FW IFT. However, as each type of ion interacts differently in the interface, there is an optimum composition (concentration and type of ion) to achieve the minimum IFT. For desalinized seawater, composed only of NaCl, the solvation shell of water molecules around the Na^+ cation makes their interaction with the surfactant components of the oil difficult. Similarly, the dilution of DW brine (DDW 5kppm) results in a concentration reduction of potential ions that interact with the surface-active components of the oil, leading to a low decrease of the original recombined oil/FW IFT. In turn, for SDW and DW, the potential ions concentration promotes the salting-in effect, leading to greater IFT reduction when compared to the FW.

Comparison of High temperature simulations of molten salts and other strongly bonded fluids with predicted quantum minimum viscosity values.

Margaret-Ann Withington, Prof. Kostya Trachenko, Queen Mary University of London, London, United Kingdom;

The fundamental constants of physics can be used to define a hard limit on the minimum value of many physical properties such as thermal conductivity and kinematic viscosity. Previous research has shown that the predicted minimum value falls close to the simulated or experimental values for fluids, such as CO2, H20, N2 and many more. Here we seek to expand the selection of fluids to include fluids which are strongly bonded to confirm that the behavior of viscosity and the predictability of the viscosity minimum remains accurate. We compare our simulated values of the minimum kinematic viscosity with values predicted using an equation derived only from the fundamental constants of physics. We take a particular focus on modelling the molten salt Lithium Fluoride which forms a part of the eutectic mixture FLiNaK. This mixture is currently being considered for use in developing molten salt reactors. As the viscosity minimum occurs between the states of liquid and gas, approximately at the boiling point, we hope to be able to use this property to separate liquid-like and gas-like behaviour in supercritical fluids. Our simulations are done using the parallel molecular dynamics package DL_POLY4.

Liquid—liquid equilibria of ternary systems containing ε-caprolactam + water + n-hexadecane/o-xylene

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Understanding the phase equilibrium behaviour plays an important role in the design and optimization of industrial chemical processes. Furthermore, experimental data concerning the phase equilibrium is essential for the accurate development of thermodynamic models. However, these experimental data are not always available for numerous combinations of different compounds that may co-exist in a chemical process. Therefore, this research aims to investigate the phase equilibrium behaviour of ternary systems not reported before that contain ε-caprolactam + water + n-hexadecane/o-xylene.

This study reports the liquid–liquid equilibria (LLE) for the ternary system of ε-caprolactam + water + hexadecane or o-xylene. The LLE was measured at 298 – 323 K. The experimental phase equilibria were predicted by applying the UNIFAC-Dortmund model presented in Figure 1 and Figure 2. The results are further analysed based on the standard phase equilibrium models.

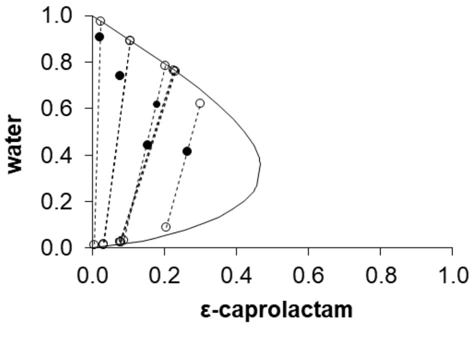

Figure 1 LLE phase compositions in mole fractions for the ternary system ε-caprolactam + water + o-xylene at T = 298 K: (○) experimental tie-line points, (●) feed points, (—) UNIFAC-Dortmund prediction

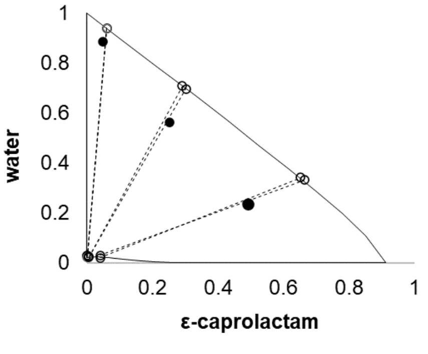

Figure 2 LLE phase compositions in mole fractions for the ternary system ε-caprolactam + water + n-hexadecane, at T= 323 K: (○) experimental tie-line points, (●) feed points, (—) UNIFAC-Dortmund prediction

Describing Protonation of Trioctylamine at the Liquid-liquid Interface of Biphasic Systems

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Background

Driven by the vision of a circular bioeconomy, biobased platform chemicals for the chemical industry become increasingly relevant. One dominant purification technology for these molecules is reactive extraction with tertiary amines dissolved in a diluent[1,2]. Tertiary amines can be protonated at the liquid-liquid depending on amine concentration, diluent choice, and pH value[2]. Governed by the degree of protonation, extraction occurs by a combination of hydrogen and ion pair bonds[2,3]. These overlapping mechanisms enable extraction of multiple components over a broad pH range, but also pose challenges regarding selectivity[4]. To predict the pH range for selective extraction, the protonation of tertiary amines in a biphasic system needs to be determined.

Results

We present a method to describe amine protonation at a liquid-liquid interface using trioctylamine (TOA) as an exemplary amine. Based on titration experiments with hydrochloric acid and sodium hydroxide we validate liquid-liquid equilibrium experiments for the determination of TOA protonation. Contrasting to literature[2], we consider hydrochloric acid extraction separately, thereby enabling a more accurate prediction of pH dependent extraction. Subsequently, we apply our method to compare TOA protonation in different diluents. Finally, competitive extraction of itaconic acid and chloride is chosen as exemplary artificial fermentation broth to describe the influence of TOA protonation on selectivity within a bioprocess.

Conclusion and Outlook

In future work, our method can be combined with an experimental and model-based approach to describe extraction of carboxylic acids and complex formation in the organic phase. This model can play a vital role tailoring reactive extraction systems to biotechnological applications.

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Phase Behaviour and Uncertainty Analysis for the Liquid-Liquid Equilibria Present in the Water + Ethanol + n-Hexane System

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Hexane is a possible alternative entrainer for the separation of water and ethanol via heterogeneous azeotropic distillation (HAD). One of the key separation points in HAD is the decanter. In order to design the decanter, the liquid-liquid equilibrium (LLE) within the decanter needs to be well described. The aim of this work is to consider the phase behaviour and the effect of experimental uncertainty on the LLE of the (water + ethanol + hexane) system.

The effect of temperature on the (water + ethanol + n-hexane) system's liquid-liquid equilibria (LLE) was investigated via experimental measurements at ambient pressure and temperatures of 293.15, 298.15, 303.15 and 308.15 K. The phase behaviour showed that with an increase in temperature, the ethanol concentration in the organic phase became enriched while the ethanol concentration in the aqueous phase became depleted. At the same time, the heterogeneous region size decreased. Moreover, the decanter water recoveries for this system decreased with an increase in temperature. Higher decanter operating temperatures, however, are preferred in practise to avoid additional reflux heating requirements. This can be explained by considering the effect of temperature on the polarities of the system compounds.

The NRTL model as implemented in Aspen Plus® V11 was used to model the system. The effect of experimental uncertainties on the (water + n-hexane) binary interaction parameters (BIPs) were determined from two thousand Monte Carlo Simulations. Binary VLE data for the (water + ethanol) and (ethanol + n-hexane) was used to correlate the binary parameters for these binary pairs, while the measured (water + ethanol + n-hexane) LLE data was used to obtain the binary (water + n-hexane) parameters. The correlations obtained predicted heterogeneous regions where miscible points were measured, calling for improved calculation method of ternary LLE. The Monte Carlo simulations showed that the compositional uncertainties affected the confidence in the (water + n-hexane) BIPs significantly, while the effect of equilibrium temperature uncertainty is not as significant.

Measurement, modelling and uncertainty propagation of low-pressure phase equilibrium data for 1-alcohols and n-alkanes

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Phase equilibrium data are important to the design of chemical separation processes. These data are associated with uncertainties. An increasing amount of research is being performed on the propagation of these uncertainties to thermodynamic model and process design outputs. From the various uncertainty propagation (UP) techniques employed, Monte Carlo Simulation (MCS) is the most popular. However, in addition to experimental uncertainties, there are uncertainties inherent in the regression of model parameters. A few uncertain regression elements have been investigated in literature, but to the best of the author's knowledge none of the UP studies have performed a thorough investigation on the comparison of these two types of uncertainties. The aim of this work is to investigate the effect of model parameterization and experimental uncertainties in the thermodynamic modelling of low-pressure phase equilibrium data for 1-alcohol + n-alkane systems using the NRTL model. For the model parameterization, the choice of model parameter initial guesses and objective function are investigated. Furthermore, three different combinations of temperature (in)dependent parameters (TDPs) are employed.

This work uses the isobaric PTxy data as the uncertain input variables in a MC approach and shows that neglecting correlation between the input variables can lead to the overestimation of the model output uncertainties. While the magnitude of the input uncertainties is important, the inclusion of vapour pressure data uncertainties is less important. For the model parameterization, the effect of model parameter initial guesses is important. While the choice of objective function is less important in the modelling of the reported VLE data, it is important in the experimental UP. The experimental UP results are specific to the TDP modelling approach and are system specific. Engineers are thus encouraged to investigate the model parameterization before performing the experimental UP. The current investigation can be extended to other thermodynamic models and systems.

The Influence of a Second Alcohol on LLE, VLLE, and VLE Phase Behaviour of (Water + Ethanol + 1-Propanol + Entrainer) System

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Short chain alcohols are a suitable alternative fuel source. Many processes produce these short-chain alcohols in dilute aqueous streams such as the Fischer-Tropsch process' aqueous product and fermentation broths. However, the alcohols are required to be anhydrous for optimal performance. Due to the presence of water + alcohol azeotropes advanced separation techniques are required to produce anhydrous alcohols. Heterogeneous azeotropic distillation (HAD) with cyclohexane as entrainer is a viable industrial separation process to produce anhydrous alcohols from aqueous streams. To design such a process phase behaviour data are required.

While numerous sets of phase behaviour data are available for the ternary (water + alcohol + entrainer) systems, little research has been done on systems where multiple short-chain alcohols are present. **The aim of this work is to improve the understanding of the phase behaviour of (water + alcohol + entrainer) systems in the presence of a second alcohol**. To achieve this, liquid-liquid equilibria (LLE), vapour-liquid equilibria (VLE), and vapour-liquid-liquid equilibria (VLLE) data of the quaternary (water + ethanol + 1-propanol + cyclohexane) system were experimentally determined and evaluated at 1 atm. The quaternary data were determined at four ethanol to 1-propanol ratios and compared to the ternary data.

The LLE data (measured at 298.2 – 328.2 K) show that the presence of a second alcohol has a significant influence on (i) both the total and individual alcohol recovery to the organic phase, (ii) the alcohol distribution ratios as well as (iii) the size and shape of the heterogenous region of the quaternary system. The influence of the second alcohol can be attributed in part to the alcohol-alcohol interactions as well as the complex water-alcohol and cyclohexane-alcohol interactions. Similar trends are seen in the experimental VLE and VLLE data. The temperature and compositional profiles of the VLLE indicate the absence of a quaternary azeotrope and that the vapour distillate product tends towards the ethanol ternary azeotrope.

High-pressure fluid-phase equilibria: New trends, experimental methods, and systems investigated (2017–2020)

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Recently, the review series [1-5] on high-pressure was extended with the 2013 – 2016 period. The paper "High-pressure fluid-phase equilibria: Experimental methods, developments and systems investigated (2013–2016)" contains relevant data for more than 4000 systems [6].

The review series on high-pressure (above 1 MPa) phase equilibrium data presenting new trends, the compilation of systems investigated, and the experimental methods is continued with the articles published between 2017 and 2020. We considered phase equilibria of vapour, liquid, and solid phases, hydrates, critical points, solubility of high-boiling substances in supercritical fluids, solubility of gases in liquids, and solubility (sorption) of volatile components in ionic liquids and in polymers.

Acknowledgement

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Phase equilibrium behavior of the acetonitrile + methane system, application to planetary science and methane transportation

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The purpose of this work is to give insights into the global phase equilibrium behavior of the acetonitrile (ACN) + methane (CH_4) system, including fluid and solid phases, in order to support the comprehension of phenomena occurring on the surface of Titan, the largest moon of Saturn.

In addition, studies on the Titan's surface (90 K and 1.5 bar) have shown that (i) ACN forms co-crystals with other molecules [1], and (ii) methane liquefaction is a naturally occurring process [2]. As a consequence, the determination of the phase equilibrium behavior of the CAN + CH_4 mixture (totally unknown nowadays) will also address the possible formation of a co-crystal between these two molecules, which in turn could be a potential alternative for the transport and storage of methane on Earth.

The ACN + CH_4 system has been experimentally investigated from ambient temperature (298K) down to cryogenic temperature (100K), and for pressures varying from 10 bar to 90 bar. Two apparatuses using a "static-analytic" method were used to determine vapor-liquid, solid-vapor and solid-liquid equilibria of the system. Experimental results have been compared with modeling results, and the global phase equilibrium behavior of the system has been determined. Solid CAN appears to be poorly soluble in methane, and further measurements are currently carried out by a NETZSCH Siruis calorimeter to confirm obtained results. This calorimeter is capable of working down to liquid nitrogen temperature and with a new crucible under development loaded with both liquid acetonitrile and gaseous methane under pressure at ambient conditions.

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Vapor-Liquid Equilibrium of heptan-2-one + α,ω dichloroalkanes mixtures at differente temperatures

INTRODUCTION

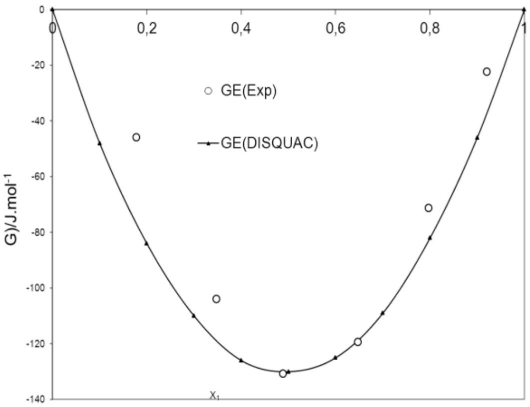
The present work is focused on the study of binary mixtures of heptan-2-one +1,4-dichlorobutane or 1,6-dichlorohexane with view to study the effect of specific interaction (Hbond) on the excess Gibbs energies over the entire composition range and at different temperature .

The excess Molar properties, of a liquid mixture depend on the size, on shape of the molecule and the specific interaction like hydrogen bonding or dipole-dipole and dipole-inducted dipole interaction.

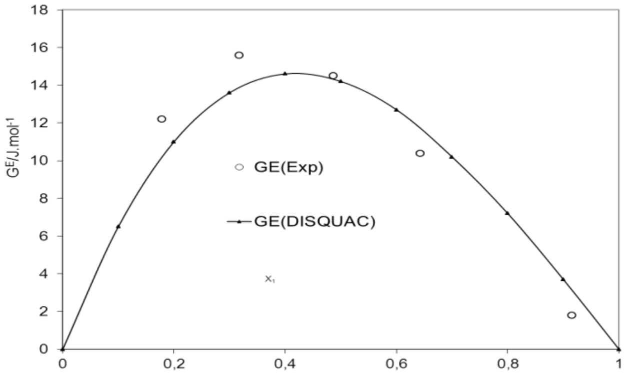
Carbon atoms of chloroalkane compounds are know to act as proton donors in hydrogen bonds in mixtures with oxygenated solvents.

DESCRIPTION OF THE WORK

The vapor pressure of the pure compounds and the two binary mixtures were measured by means of the static apparatus[1] and [2] at temperatures between 263,15 K and 343,15 K. The experimental data of excess molar Gibbs energies, G^E, have been compared with values using the DISQUAC [3,4,5,] group contribution Model



Comparison of theory and experimental for the molar excess Gibbs energy G^E at 303.15 K for heptan-2-one(1) + 1,4-dichlorobutane(2)



Comparison of theory and experimental for the molar excess Gibbs energy G^E at 303.15 K for heptan-2-one(1) + 1,6-dichlorohexane(2)

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Isobaric Vapor-liquid Equilibrium of Water + Polyethylene glycols Measurement and Modeling

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INTRODUCTION

The present works focussed on the study of isobaric vapor−liquid equilibria (VLE) of binary mixtures containing water with polyethylene glycol.

The glycols hydroxyl end groups make the polyethylene glycols popular intermediates in a large number of reactions, such as esterification, while low molecular weight glycols are commonly used in fibers treatment, paper,adhesives, printing inks, leather processes and natural gas processing, as dehydration agents, or precursors for polyester fibers and resins, polyurethanes, polyethylene terephthalate plastics, plasticizers, and coolants.

The physical properties and equilibrium data of glycols are extremely important in industry for the development of new technologies and the enhancement/optimization of existent processes.

DESCRIPTION OF THE WORK

We present new experimental data on the isobaric vapor−liquid equilibria (VLE) of four binary mixtures of water with ethyleneglycol, diethylene glycol, triethylene glycol, or tetraethylene glycol , measured at three pressures (0.05, 0.07, and 0.1 MPa).

The soft statistical associating fluid theory equation of state was used to describe the experimental VLE data of these highly non ideal systems, providing insights into the molecular interactions leading the macroscopic behavior of the mixtures.

Soft-SAFT accurately reproduces the experimental data using one single, state independent, binary interaction parameter to correct the mixtures dispersive energy. It is further shown that the parametrization obtained from the pure glycols can be used to provide accurate predictions of the water activities in aqueous solutions of PEGs of higher molecular weight

Differential Scanning Calorimetry for Collection of Thermodynamic Phase Equilibria in Small-Scale

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The transformation from established petrochemical-based processes to greener bio-based processes is giving rise to many novel separation processes, leading to a multitude of yet unknown thermodynamic phase equilibria of novel products with high relevance for the chemical industry [1]. Although qualitatively good results in predicting thermodynamic phase equilibria can be achieved with methods like COSMO-RS and modern machine learning tools [2,3], experiments are still necessary to obtain reliable thermodynamic data. To derive thermodynamic, data differential scanning calorimetry (DSC) is a fast, small-scale measurement method which matches the low availability and urgency of novel products.

Currently, DSC is used almost exclusively for the characterization of solid samples, while its use for measuring vapour-liquid equilibria is scarce in literature. Only a few examples of successful determination of bubble point lines in binary mixtures were recently published. These studies mainly adress process parameters influencing the accuracy of the measurement procedure, such as heating ramp, sample volume, and pin-hole size [4]. However, these process parameters were only varied in a narrow range and only binary mixtures with low boiling point differences (below 50 K) were investigated due to inapplicability of the measuring procedure caused by pre-evaporation of the low-boiling compound. Hence, the need for improved DSC procedures in the quantification of binary mixtures with large boiling point differences is raised [5].

To this end, we present and discuss limitations in DSC measurements of thermodynamic phase equilibria in the present state and propose a strategy to extend its field of application. The method benefits from adjustment of the main process parameters (heating ramp and volume size), broadening the window of applicability for DSC in measuring bubble point lines of binary mixtures.

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Vapor-Liquid Equilibrium Measurements and Cubic-Plus-Association (CPA) Modeling of Triethylene Glycol Systems

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As a part of a series of studies that aim to expand the experimental database used to assist the design of gas processing facilities 25 new vapor-liquid equilibria data points were measured for the systems: triethylene glycol (1) + methane (2), triethylene glycol (1) + ethane (2), triethylene glycol (1) + ethane (2) + water (3), and triethylene glycol (1) + gas mixture (2), at high-pressures. The new data include both gas liquid composition, with relative experimental uncertainties below 18%. Furthermore, the Cubic-Plus-Association (CPA) Equation of State (EoS) modeling has provided a good description of the newly measured data, with average absolute relative deviation (AARD) ranging between 9−43%. Binary interaction parameters regressed solely from the corresponding binary data were used for all multicomponent predictions with CPA.

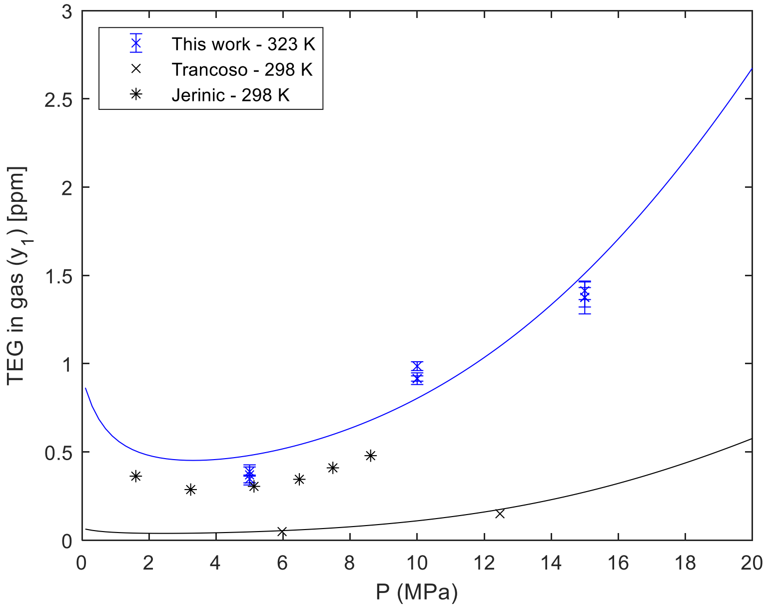

Figure 1 - Experimental data for TEG in the gas phase (y_1) of Jerinic et al. (*) and Trancoso et al. (x) at 298 K and this work (x) at 323 K. Lines represent CPA modeling.

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Bubble Point Pressure Measurement and Prediction of VLE and VLLE for Dimethyl ether - 2-Butoxyethanol and Dimethyl ether - Water - 2-Butoxyethanol at 293.15 K

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Abstract

Propane and dimethyl ether (DME) have been widely used as splay propellants as R290 and RE170, respectively. However, the propellants show poor miscibility with water, and VLLE were reported at x_1=0.1795 for DME – water at 295.37 K [1]. Then, authors proposed a usage of 2-butoxyethnaol to enhance the miscibility window for DME – water, and the bubble point pressure was measured for DME - 2-butoxy-ethanol and DME - water - 2-butoxyethnaol by use of a static apparatus at 293.15 K. A pressure resistance glass cell, with the volume of 40 cm^3 was employed. After loading DME by applying a distillation technique directly from the DME cylinder, the sample liquid was successively loaded into the cell by using a HPLC pump. The overall composition was determined by weighing the mass of the sample at the preparation. For the ternaries, the ratios of water: 2-butoxyethnaol were set to 95:5 and 50:50 on the mole basis at loading. The cell was soaked in a water bath (Thomas TRL 101FEZ, Tokyo). The equilibrium temperature and pressure were measured by a thermistor thermometer (Technoseven SXA-33, Yokohana,Japan) and an absolute pressure sensor (Kyowa PHS-B-500KP, Tokyo), with the capacity of 500 kPa, respectively. The mole fraction of liquid phase was assumed to be the same as that at preparation because of the low pressures. DME - 2-butoxyethnaol and DME - water - 2-butoxyethnaol (water: 2-butoxyethnaol = 50:50) showed VLE at any mole fractions of liquid phase. On the other hand, DME - water - 2-butoxyethnaol (water: 2-butoxyethnaol = 95:5) showed VLLE in the DME mole fraction range from x_1=0.5164 to 0.7682. The data were compared with the calculations using NRTL model whose parameters were determined from the experimental and literature data of constituent binary VLE and VLLE [1,2]. The detail calculation procedure and the results will be described at the symposium.

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LLE determination and correlation for green ATPS based on polyethylene glycol (PEG) and polyvinylpyrrolidone (PVP)

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Aqueous Two-Phase Systems (ATPS) constitute a liquid-liquid extraction technique with significant application in the textile and cosmetic industries. Amongst the most used phase formers in ATPS, green polymers such as polyethylene glycol (PEG) and polyvinylpyrrolidone (PVP) are known for their hydrophilic properties and high biocompatibility, which make them safe media for the partition of biomolecules such as amino acids, vitamins and antioxidants [1-3]. Salt-polymer ATPS often apply organic salts as salting-out agents given their lower environmental impact and generally provide useful immiscible areas and high water-content in both phases.

In this work, the liquid-liquid equilibria (LLE) of Aqueous Two-Phase Systems (ATPS) containing organic salts and polyethylene glycol (PEG) or polyvinylpyrrolidone (PVP) were determined at 298.15 K and 0.1 MPa. Moreover, the Othmer-Tobias and Bancroft-Hubbard correlations were applied to the obtained data and the recently developed Porto's approach on the UNIversal QUAsi Chemical (UNIQUAC) model was used to describe tie-line composition.

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Hydrogen and air storage in salt caverns: a thermodynamic model for phase equilibrium calculations

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When storing a gas in a salt cavern, it occupies most of the excavated volume, but the lower part of the cavern inevitably contains residual brine, in contact with the gas. The design of hydrogen and compressed air storage in salt caverns requires to have a thermodynamic model able to accurately predict both phase properties such as densities, and phase equilibrium (gas solubility and water content of the vapor phase). This work proposes a parameterization of the e-PPC-SAFT equation of state in this context. Experimental data of pure components and mixtures of light gas + pure water and light gas + salted water are reviewed and used to fit pure component parameters for hydrogen, nitrogen, oxygen and the brine, and binary interaction parameters between H_2, O_2, N_2 + water and H_2, O_2, N_2 + ions (Na^+ and Cl^-), for temperature ranging from 273 to 473 K and salinities up to NaCl saturation (6 mol/kg). The model developed delivers a good accuracy in reproducing data: the average deviation between experiments and calculated data is between 3 and 9% for gas solubility in saturated brine. More interestingly, the model has been validated on its capability to predict data not included in parameterization database, including composition of the vapor phase, and on its extension to mixture, such as air. Finally, it has been used in a case-study of compressed air storage (CAES) to evaluate the water content of the gas produced during injection-withdrawing cycles.

Measurement and modelling of VPO and density data for binary aqueous solutions of choline salts at 313.15 K

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Experimental phase equilibria determinations, particularly concerning vapour-liquid equilibria (VLE) data, are essential for a better description of electrolyte-containing systems [1-3]. Together with the assessment of liquid density, a rigorous knowledge on VLE eases the parameterization of equations of state (EoS) and the development of new thermodynamic models.

Recently, there has been a growing interest on novel extractive processes containing either salts (*e.g.*, cholinium bitartrate) or solvents (*e.g.*, ionic liquids) based on choline, which is an essential nutrient commonly found in meat and egg yolks. Nevertheless, these systems have seldomly been characterized, which hampers their modelling.

In this work, the vapour pressure osmometry (VPO) technique was used to determine the osmotic and activity coefficients of several aqueous binary solutions containing salts based on the cholinium cation, at T = 313.15 K. These results were then modelled with a Modified Pitzer Model [4] for mixed electrolytes, achieving a very satisfactory description of the systems. Additionally, the density of these binaries was measured at (298.15 or 313.15) K and 0.1 MPa and fitted to second-degree polynomials.

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Modeling liquid-liquid equilibria of aqueous surfactant solutions

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Surfactants are amphiphilic molecules, which cover a broad range of application including e.g. oil recovery and membrane science. The low toxicity of nonionic surfactants allows for further applications in pharmaceutical formulations. Existing modeling approaches, which often solely cover the description of the surfactants' critical micellar concentration (cmc), are usually limited to the highly dilute regime. We expand the applicability by using a novel approach of combining a non-idealized micellization model with PC-SAFT. It was successfully applied to the surfactant series of polyethoxylated alkyl ethers (commonly denoted as C_iE_j). The approach includes calculating the activity coefficients of water, of the surfactant monomer and of the micellar aggregates and not only applies at infinite dilution but also in concentrated surfactant solutions. This enables simultaneously solving the required equilibrium conditions for aggregate formation as well as for two coexisting aqueous micellar phases (LLE). As a result, the cmc, binodal curves as well as aggregate-size distributions can now be described in even quantitative agreement with experimental data.

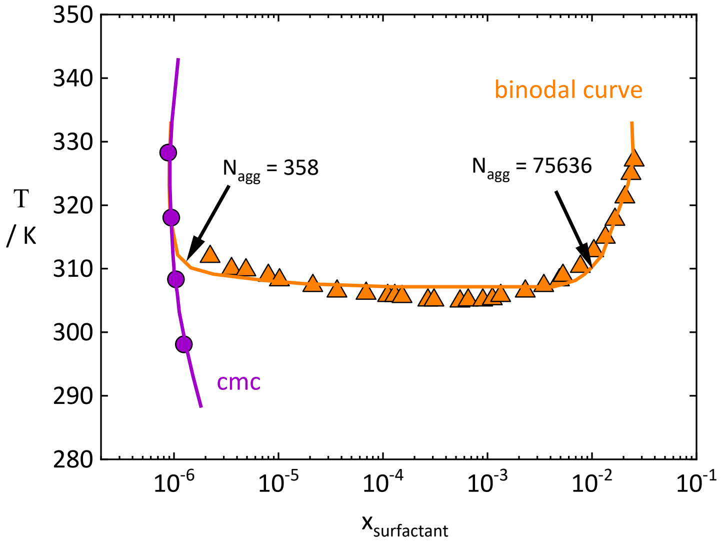

Figure 1: Binodal curve and cmc in the system $C_{12}E_5$ and water. Symbols are experimental literature data [1, 2] and lines are modelling results. The arrows indicate the calculated mean aggregation number N_{agg} in two coexisting phases.

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Thermal and transport properties of aqueous organic systems

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The thermal and transport properties of aqueous organic systems are needed in several of our processes but sometimes we have noticed a lack of experimental data and/or modeling efforts to estimate them (density, viscosity, thermal conductivity, surface tension, heat capacity and enthalpy are among the most important ones). Especially the properties of binary aqueous systems with organic solvents that present both hydrophilic and hydrophobic parts, may be difficult to predict based on solely theoretical considerations (f.ex. alkanediols) [1], while by adding one more organic solvent, the excess properties of all three sub-binary systems need to be known when developing appropriate estimation methods, and this may not always be the case (f.ex. when dealing with the enthalpy of aqueous systems of methyldiethanolamine and piperazine).

We would like to share some examples of industrially relevant aqueous systems where we believe there is room for improvement, keeping in mind the expected errors when using estimation methods per property as described in the recent edition of “The Properties of Gases and Liquids” [2] and the accuracy requirements of common engineering-design calculations [3].

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Vapor-liquid-liquid equilibria of binary and ternary aqueous systems containing C_6-hydrocarbons

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To develop process for separating water and C6-hydrocarbons, the vapor-liquid-liquid equilibrium (VLLE) data of the related mixtures are fundamentally important. The mutual solubilities at vapor-liquid-liquid equilibrium (VLLE) of binary and ternary mixture of water-C_6 hydrocarbons (benzene, *n*-hexane, and cyclohexane) were measured at temperature ranges from 343 K to 383 K in a modified static-type apparatus equipped with a visual cell as shown in Figure 1. Thermodynamic models of these new measurements have been carried out by NRTL-HOC and UNIQUAC-HOC models. The experimental results of the binary systems reveal the temperature and molecular structure effects on the saturated compositions in three coexistent phases. The experimental ternary VLLE properties form a basis to verify the prediction by using the determined parameters of constituent binaries and also to modify the values of the binary parameters for improving the ternary VLLE calculations. The results of this study provide new phase equilibria data and are useful for exploring better operating conditions for the related separation processes.

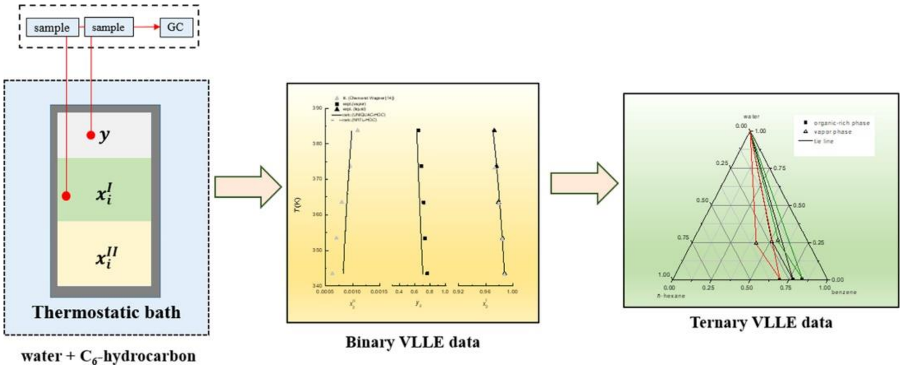

Figure 1. The schematic diagram of VLLE measurements

Keywords: VLLE; water; benzene; *n*-hexane; cyclohexane

Excess infrared spectra modelling of water/alcohol and water/alcohol/electrolyte systems

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Excess spectroscopy is a spectra processing technique that utilizes the notion of excess thermodynamic properties for the analysis of the interspecies interactions in liquid solutions. Room temperature attenuated total reflectance (ATR) spectra of the fundamental hydroxyl stretching bands of water-alcohol and alcohol-alcohol solutions are measured, and the excess spectra are calculated. Chemometrics methods are then utilized for identifying patterns that arise from mixing the hydroxyl group-containing solvents, with the measurements on the methanol-ethanol system providing a proof-of-concept for the correlation of excess spectra and non-ideality.

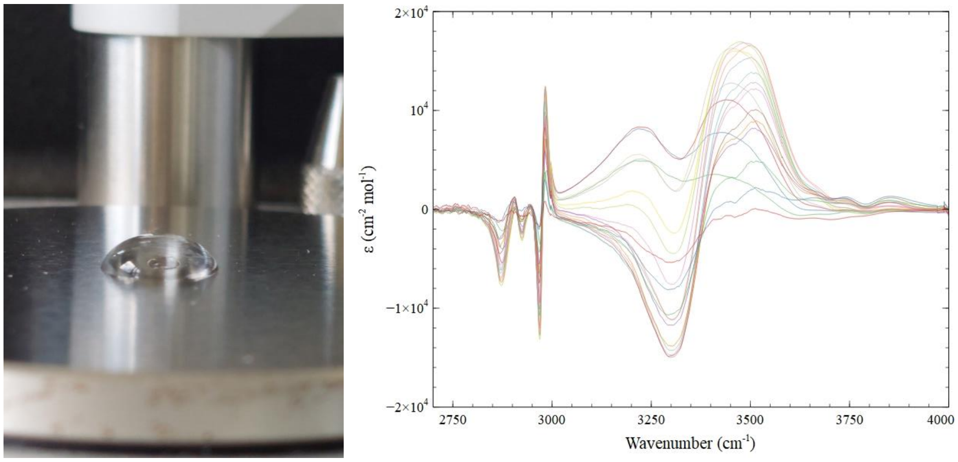

Figure: (left) water droplet on an ATR crystal, (right) concentration-varied excess spectra of water-ethanol at room temperature expressed in extinction coefficients.

The excess spectroscopy framework will be used to describe the effects of alkali salts on interspecies hydrogen bonding in the binary mixtures, in order to provide a clear picture of solvation processes and Hofmeister-type effects. The present study aspires to provide reliable and novel experimental conclusions to the modelling community for the augmentation of electrolyte theories/thermodynamic models.

The authors would like to thank the European Research Council (ERC) for funding this project under the European Union’s Horizon 2020 research and innovation program (Grant Agreement No. 832460), ERC Advanced Grant project “New Paradigm in Electrolyte Thermodynamics”.

Free Energy of Solutions with Effective Potentials (McMillan-Mayer Level): Einstein's Proof of Van 't Hoff's Law for Osmotic Pressure

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In his celebrated paper about the Brownian motion published in 1905 [1], Einstein presented a derivation of the Van't Hoff's law for the osmotic pressure of the suspended (solute) particles. The derivation was based in his own version of the statistical mechanics in the canonical ensemble. This proof has been scarcely cited and discussed but constitutes the first use (at least in an implicit way) of the so-called effective interactions approach in liquid (soft matter) physics [2] and in the classical theory of solutions [3]. In this work, the method used by Einstein is analyzed, the implicit assumptions discussed, and the adequate formulation of the thermodynamics presented. Posterior extensions and/or versions of this approach by R. H. Fowler (1929), E. A. Guggenheim (1932), L. Onsager (1933), G. S. Rushbrooke (1940), I. M. Lifshitz & I. Stepanova (1957), L. D. Landau & E. M. Lifshitz (1958) and others will be briefly mentioned leading a formulation of the effective interactions approach in the canonical ensemble. Finally, the free energy of the (reduced) system and the thermodynamics that can be derived from the corresponding effective canonical partition function is presented jointly with the comparison with the experiment.

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Phase equilibrium predictions at low and high pressures with a COSMO-SAC based model

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Abstract

Separation and recovery methods require knowledge of the phase equilibrium of the mixtures involved. The lack of experimental data as well as the difficulty and cost of performing experiments for measuring the phase equilibrium and other thermodynamic properties, especially in complex mixtures, demand the existence and application of high accurate thermodynamic models. Over the past two decades COSMO-based models such as COSMO-RS and its variant COSMO-SAC [1] combine molecular simulation quantum-chemical calculations and statistical thermodynamics for the prediction of thermodynamic properties of pure compounds and mixtures. With the advantage of using only a few global general input parameters, COSMO-based models have been proved to be reliable tools to directly predict thermodynamic properties even in particularly complex mixtures, without the requirement of experimental data.

In this work, a new variant of the COSMO-SAC model has been developed using an improved combinatorial term and an advanced description of the hydrogen bonding interactions. The new model's performance is studied for vapor-liquid equilibrium at low pressures and infinite dilution activity coefficient predictions and it is benchmarked with respect to COSMO-SAC and COSMO-SAC 2010 [2] models. Furthermore, the new model is combined with the Peng Robinson equation of state via the Universal Mixing Rules (UMR) [3], and it is applied for high pressure vapor-liquid equilibrium predictions. Finally, preliminary results on model's performance in predicting phase equilibrium of mixtures containing novel solvents, such as ionic liquids and DESs, is presented.

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Estimating the melting temperatures of salts mixtures for recovery precious metal from spent catalytic converters

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Spent catalytic converters (SCCs) represent valuable secondary reservoirs of precious metals, particularly platinum group metals (PGMs). The conventional recovery methods for these metals often involves the use of highly corrosive aqua regia, posing significant safety hazards and causing environmental pollution. In this work, an alternative approach to recover precious metals from spent catalysts is proposed based on a “salt aqua regia” in which concentrated chloride and nitrate salt mixtures substituted inorganic acids. However, the application of these salts is constrained by their solubility in water, potentially limiting their effectiveness. Conversely, combining two or more salts in specific proportions can yield a eutectic mixture with a lower melting point than individual pure salts. This often results in the formation of liquid eutectic mixtures at room temperature, enabling direct application for metal leaching. This study focuses on investigating the solid-liquid phase diagram of various combinations of inorganic salts, previously identified in the literature for their potential to dissolve PGMs. Using COSMO-RS (COnductor-like Screening MOdel for Real Solvents), we evaluated its ability to predict the solid-liquid equilibrium of these salt mixtures. The results, obtained with COSMO-RS (TZVPFINE), demonstrated satisfactory accuracy in predicting the tendency of eutectic points, accompanied by a notable reduction in the melting point of the salt mixtures. The findings highlight the safety and non-volatility of the salt mixture, positioning it as a promising candidate for solubilizing PGMs.

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, and UIDB/50020/2020 and UIDP/50020/2020 (LSRE-LCM), and LA/P/0045/2020 (ALiCE) financed by national funds through the FCT/MEC (PIDDAC) and national funds through FCT – Fundação para a Ciência e a Tecnologia, I.P., within the scope of the project PlatILPlus (2022.04478.PTDC). F.H.B. Sosa and F.N. Braga acknowledge FCT I.P. for the researcher contract CEECIND/07209/2022 and the Ph.D. gran t2023.01749.BD., respectively.

Efficient solution of the COSMO-based models

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COSMO-RS [1], based on the COSMO method [2], provides a powerful solution that bridges quantum chemistry computations and macroscopic phase equilibrium calculations. Another influential counterpart, COSMO-SAC [3], shares a similar methodology. Both models utilize the σ-profiles from COSMO calculations to determine the residual contribution to the activity coefficients and employ the Staverman-Guggenheim formula for the combinatorial contribution. The computation of the residual contribution involves solving the consistency equation, accounting for pairwise interactions among all surface segments in the mixture. Several commercial software products and open-source codes are available nowadays for COSMO-based models. Nevertheless, computation speed remains a significant challenge compared to classical macroscopic thermodynamic models. The primary bottleneck lies in solving the consistency equation. This study investigates how to enhance the computation efficiency of COSMO-based models, facilitating their more effective application in the phase equilibrium calculations of diverse mixtures.

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In-silico prediction of toluene/water partition coefficients of APIs using COSMO-RS and Neural Networks

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Precise computation of log P partition coefficients holds significance in cost reduction and driving drug design processes. It provides important insights into the bioavailability, pharmacokinetics, and toxicity of diverse drug candidates. However, the efficacy of existing methodologies remains ambiguous, raising uncertainties about their practical applicability in drug discovery. To determine the effectiveness of these methodologies, a sequence of SAMPL challenges has been undertaken in recent years, focused on facilitating the creation and validation of predictive models. Within the context of the SAMPL9 challenge, wherein the objective was to predict toluene/water partition coefficients for 16 molecules, our project introduces two distinct contributions. Both submissions, labelled A and B, employ the COSMO-RS approach. Notably, they follow slightly disparate procedures to calculate transfer free energies from water to toluene for the challenge molecules, consequently determining their respective log P values.

In the outcome analysis, COSMO-RS submission A emerges as the frontrunner, boasting an R^2 value of 0.93. However, it secures the second position in the SAMPL9 challenge in root-mean-square error (RMSE) with a value of 1.23 log P units. Meanwhile, COSMO-RS submission B achieves an R^2 value of 0.83 and an RMSE value of 1.48 log P units. Additionally, log P values were also predicted using a neural network model, pre-trained on COSMO-RS data, yielding an R^2 of 0.92 and an RMSE of 1.04 log P units.

Comparatively, against preceding SAMPL challenges, all contributions display substantial deviations in predicting the toluene/water partition coefficient. These pronounced deviations underscore the imperative need for further research aimed at developing precise and dependable methodologies for modelling solvent effects on transfer-free energies of small molecules.

Numerical Investigation of Interfacial Phenomena in Incompressible Multi-Phase Systems

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Interfacial phenomena in the context of multi-phase flows are in the focus of scientific discussion since decades as they determine the mass transfer between two phases and the formation of droplets, but there is still a lack of understanding [1]. This lack of understanding mainly originates in the complexity of the interface due to the interaction between the fluid flow field, capillary forces and the superimposed mass transfer. Furthermore, a detailed investigation of the interface is experimental laborious because of its small scale and its fluid character. Based on the experimental evaluations the resulting mathematical models for multi-phase flows often need expensive parametrization.

In this contribution, we suggest a thermodynamic consistent modeling approach to resolve the interface and investigate interfacial phenomena in more detail. The model is based on the incompressible density gradient theory developed by Cahn and Hilliard (CH) [2] in combination with the Navier-Stokes (NS) equations in a novel introduced CHNS model. Furthermore, the NRTL [3] model is incorporated into the CHNS framework. Since the CHNS framework consists of a system of highly non-linear partial differential equations it is implemented into OpenFoam® and solved via the Finite Volume Method.

The CHNS model approach enables detailed 3D simulations of interfacial behavior in liquid-liquid systems such as droplet coalescence and its effect on convective and diffusive mass transport. Furthermore, complex interfacial effects like Marangoni convection and droplet sedimentation are investigated in more detail. By doing so, the different gradients in velocity and chemical potential are evaluated to deepen the understanding of interfacial behavior.

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Novel Cleaning Procedure for Contact Angle Measurements

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Contact angles are a decisive parameter, e.g. for the printability of polymers, but also provide information about the surface quality, as they depend on the material pairing, but also on other surface properties. However, the contact angle depends not only on the surface itself and the fluids, but also significantly on the history of the surface, as there is a strong correlation between contact angle and substances adsorbed on the surface.

Experiments often show large scattering of several degrees between the individual measurements on well-defined surfaces, which are hardly reproducible and demonstrably depend on the adsorbate layer on the surface [1]. The chemical composition of this adsorbate layer is in turn largely dependent on the previous cleaning procedure, which is usually carried out with solvents. Depending on the surface energy, liquid solvents can form thick adsorbate layers even after drying, whereas gases often only form monolayers if the pressure is correspondingly low [2]. This paper therefore proposes to carry out the final cleaning of the surface with gases directly in the measuring cell to avoid unknown adsorbates at the surface.

In the proposed experimental procedure, both the history of the surface itself and the measuring environment are well defined and therefore, the adsorbate layer on the sample is a controlled variable. It is shown that by controlling this key variable, the contact angle can be measured with high repeatability.

For this purpose, different samples are exposed in several steps to a gas under pressure and then flushed with it in order to experimentally influence the possible prior history. The measurement itself takes place in a closed and thermostated measuring chamber to precisely define the measuring conditions. Furthermore, by using different contaminants and pre-cleaning methods, the viability for highly contaminated surfaces is investigated. The proposed method, its parameters, as well as first results are presented. The results are presented.

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Dynamic Contact Angles from Hydrodynamic Density Functional Theory

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Our goal is to describe dynamic processes in porous media at the molecular level, especially the processes at solid-fluid interfaces. To achieve this, we apply hydrodynamic density functional theory [1] in combination with Helmholtz energy functionals based on the PC-SAFT equation of state [2]. This approach extends classical density functional theory (DFT) to non-equilibrium systems and has been shown to be capable of describing the dynamics of one-dimensional droplet and bubble coalescence. The model requires transport coefficients for the constitutive transport equations and a molecular model for the Helmholtz energy. We present recent developments in two areas:

1) We predict viscosities for inhomogeneous systems by generalizing residual entropy scaling [3]. In particular, we extend and evaluate the ability of the entropy scaling approach to predict the viscosity in the vicinity of solid-fluid interfaces. We compare the results of our model with non-equilibrium molecular dynamics simulations of a Couette flow.

2) We apply two-dimensional hydrodynamic DFT to predict the dynamic contact angles of droplets on solid surfaces (on the nanometer scale). We compare different inhomogeneities of the solid surface that can cause the appearance of advancing and receding contact angles.

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Ab-Initio Study of Reaction Mechanism of Catalysed Phosgenation

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Polycarbonates (PCs) are versatile industrial products e.g., in electronics and construction materials due to their compelling properties such as transparency and mechanical stability. However, achieving high industrial standards necessitates high quality production of the PCs. The “Carbon2Polymers” project investigates a novel approach for PC production by utilising blast furnace gases generated in the steel industry. This approach utilises the carbon-rich waste replacing the conventional sources of carbon to produce phosgene. By using this waste to produce phosgene, which is a key reactant in the PC production process, production of PCs becomes more environmentally sound. This approach poses challenges as the blast furnace gases include impurities when not elaborately purified. This causes highly undesirable properties, like colouration, in the PCs. Hence, the project focuses on optimising the process minimising the yield of the colour-forming species.

To get a comprehensive understanding of the phosgenation process, a reaction network is proposed and all the elementary reactions in the network are studied using ab-initio methods. Initially, Ti-catalysed phosgenation is studied in the absence of any impurities. All the molecules in the reaction network and all the transition states are geometrically optimised in Gaussian at DFT level. Solvation free energies are also computed using COSMO-RS to account for the solvation effects of the solvent. To validate the proposed mechanism a ‘’2-phase’’ reactor model is constructed. Results of the reactor model are compared with empirical data and they show good correspondence. A qualitative analysis corroborates the proposed reaction mechanism and demonstrates the integration of several elementary reactions within it. Nonetheless, the phosgenation process is undergoing further investigation, entailing the incorporation of the impurities (for example NH_3) into the network. To identify the constituents generating colouring within the system, UV/vis spectroscopy will be conducted in Gaussian prior to optimising the reactor model to reduce the yield of these colour-forming products.

Combination of PC-SAFT and Taft equation to predict the effect of solvent and reactant on esterification reactions

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The relationship between the chemical structure of the reactants and the reactivity of the system plays a key role in chemical synthesis. Linear free energy relationships, e.g. Taft equation, are structure-reactivity methods that link reaction kinetics with the structure of the reactants considering different effects (e.g., steric or polar effects). Once these effects (expressed as Taft substituent parameters) are known, the Taft equation allows predicting the effect of the –R group of an alcohol on reaction kinetics.

Although being powerful, such structure-reactivity methods do not take into account the reaction conditions. Since literature Taft parameters have been estimated from experimental reaction kinetics at different conditions (solvent, concentrations, catalyst), they might be inconsistent. However, there are methods to predict the influence of these conditions on reaction kinetics via thermodynamic activities[1-2], e.g. using PC-SAFT. In turn, PC-SAFT does not allow predicting the –R substituent effect on reaction kinetics and equilibria.

Thus, in this work we combined PC-SAFT with the Taft equation to re-estimate the Taft substituent parameters using a thermodynamic activity-based approach. The new Taft parameters can be considered universally valid (independent of solvent or concentration), and the combination of this with PC-SAFT allows then predicting the effect of changing the –R substituent on kinetics and equilibria of esterification reactions. This talk will show the results for esterification of some carboxylic acids with several alcohols. The results demonstrate the power of the new combined method by comparing the predictions with new experimental data as well.

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Raman-Spectroscopy-based Determination of Reaction Rates in Continuous Plug Flow Capillary Reactors with In-situ Extraction

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Reaction rates are a fundamental aspect of process engineering, representing the relationship between the amount of substance per volume and time. However, the presence of mass transfer limitations significantly influences the reaction rate [DOI: 10.5772/22962]. Unfortunately, distinguishing between the contributions of the reaction rate and mass transfer in two-phase liquid-liquid reaction systems poses a challenge, because homogeneous reactions in one phase and extraction via mass transfer into the second phase occur simultaneously and are intimately linked. Accurate determination of the individual effects becomes crucial for predicting the overall performance of the two-phase liquid-liquid reaction system under various conditions [DOI: 10.1016/S0920-5861(03)00056-7].

The (double) stirred cell is a common method for investigating reaction rates in liquid-liquid reaction systems. Despite its versatility and ease of use, determining the reaction rate independently proves challenging. Even with robust mixing, convective mass transfer in the phases cannot be neglected. To overcome and neglect this limitation, rotor-stator spinning disk reactors utilize droplets with extreme small dimensions and high surface-to-volume ratio [DOI: 10.1016/j.ces.2021.116706]. However, this setup is unsuitable for all liquid-liquid reaction systems due to high shear forces and challenging isothermal temperature management.

In our work, we introduce a novel method by combining a capillary microreactor with Raman spectroscopy. The liquid-liquid reaction system inside a capillary forms a plug flow with alternating phases. The vortices within the plug lead to strong mixing. Due to the high surface-to-volume ratio of the plugs, the influence of mass transfer can be neglected and it enables isothermal reactions, even for highly endo- or exothermal reactions. Raman spectroscopy allows fast in-situ analysis in single plugs across a broad temperature and pressure range without disrupting the flow regime. Moreover, the combination of a capillary microreactor and Raman spectroscopy minimizes sample consumption. As a proof of concept, we present measured reaction rates of a liquid-liquid reaction system in comparison to literature and modeled data.

Nucleation and growth of mixed carbon dioxide and propane hydrates through molecular dynamics simulations

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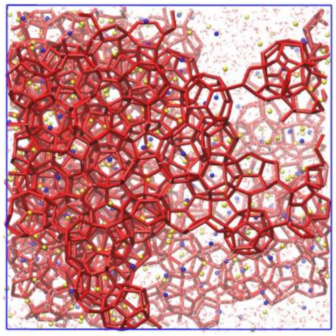

Gas hydrates are crystalline structures composed of water and light gases, in which cavities formed by hydrogen bonds of water molecules are occupied by guest gas molecules. The most common structures, Types I and II, are formed respectively by the presence of small and large guest molecules. Molecular dynamics simulations can be a powerful tool when studying the nucleation mechanisms of these systems, as it is unfeasible to experimentally observe this process, which occurs on scales of nanometers and nanoseconds. Hydrate nucleation simulations were performed in this work for the water/CO_2/C_3H_8 system with GROMACS. Three gas composition conditions were analyzed, with proportions of 1:1, 1:2 and 2:1 (CO_2:C_3H_8). The TIP4P/Ice, OPLS/UA, and EPM2 models were used to describe the behaviors of water, propane, and carbon dioxide, respectively. To ensure a statistical analysis of the results, 10 production simulations (from 3 to 8 µs) were performed for each proportion. Pressures between 1000 and 1500 bar were applied to the systems so that the driving force was sufficient to nucleate the hydrate on the microsecond scale. Hydrate nucleation was observed in 100%, 70% and 40% of the 1:1, 2:1 and 1:2 simulations, respectively. An extensive analysis of the simulations was carried out through the evolution of the number, type, and occupancy of the cavities. The first cavities that form in each system were determined, along with the first stable clusters and its compositions. The presence of domains of Types I and II structures and how they coexist in the simulations was also verified. These analyzes provided important information on how propane and CO_2 interact in the formation of gas hydrates.

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