Thermodynamics'2019

The 26th Conference. 26-28 June 2019

A B S T R A C T B O O K

Conference Partners









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Welcome to Thermodynamics 2019

Dear Thermodynamics 2019 conference participants,

On behalf of the International Scientific Committee, I would like to welcome all of you to *Thermodynamics 2019* conference. It is a great pleasure and honor to organize this event in Punta Umbría, Huelva (Spain). Thermodynamics is undoubtedly a cornerstone for many scientific and engineering disciplines including physics, chemistry, chemical engineering, petroleum engineering and materials science. It provides the basis for the design and optimization of new sustainable industrial processes and the development of advanced materials and products. The combination of experiments, theory and simulation allows scientists and engineers to study complex systems from the molecular scale all the way to macroscopic level.

Thermodynamics has been evolving rapidly in recent years, partially due to the advances in experimental techniques and in computer simulations, which help to complement experiments and theory. Thanks to these new developments and synergies, thermodynamics now spans over a large range of domains: life sciences, with their complex supramolecular arrangements; nanomaterials, where short-range interactions are dominant; complex fluids, such as liquid crystals, polymers and ionic fluids; critical behavior and extraction processes; behavior of materials in extreme conditions, and many more.

The *Thermodynamics 2019* conference is the 26th meeting in a series of thermodynamics conferences initiated in 1964 by Harold Springall, championed throughout the 1960s and 1970s by Max Glasham and Sir John Rowlinson. It is the fifth time that the conference is held outside the UK. The conference consists of invited lectures, oral presentations, short oral talks and poster presentations. The highlights of the conference include the 2019 Lennard-Jones Lecture and Prize, awarded by the Statistical Mechanics and Thermodynamics Group of the Royal Society of Chemistry to Professor Denis J. Evans and the Taylor and Francis Molecular Physics Lecture that will be delivered by Professor Peter T. Cummings. In addition to that, we will present the Christopher Wormald Prize awarded to a young scientist, Dr. Jorge R. Espinosa, for his innovative research in Thermodynamics. We also present two additional prizes, the Guggenheim Medal for Excellence in Thermodynamics, awarded by the Institution of Chemical Engineers (IChemE) to Professor Doros Theodorou, and the EFCE Excellence Award in Thermodynamics and Transport Properties, awarded by the European Federation of Chemical Engineering to Dr. Mónia Martins.

With a total number of more than 170 participants from different countries from academia and industry, *Thermodynamics 2019* will be a forum to develop new ideas and research collaborations for the future. First at all, we would like to acknowledge the Royal Society

of Chemistry, and particularly the Statistical Mechanics and Thermodynamics Group, for the opportunity to organize this conference for the first time in Spain. I would also like to thank the International Scientific Committee for the thoughtful selection of invited lectures and the evaluation of all abstracts submitted, their support and recommendations over the last two years. We are indebted to the sponsors for the support provided. I am mostly grateful to my colleagues and friends of the Local Organizing Committee from the Spanish Molecular Simulation Network for their endless efforts and commitment over the last year to make this conference a success. Finally, I would like to thank all of you for your participation to this conference.

I wish you an enjoyable stay in Punta Umbría.

Punta Umbría, 26 June 2019

Felipe J. Blas
Conference Chairman
Center for Sustainable Chemistry (CIQSO)
University of Huelva
Huelva, Spain

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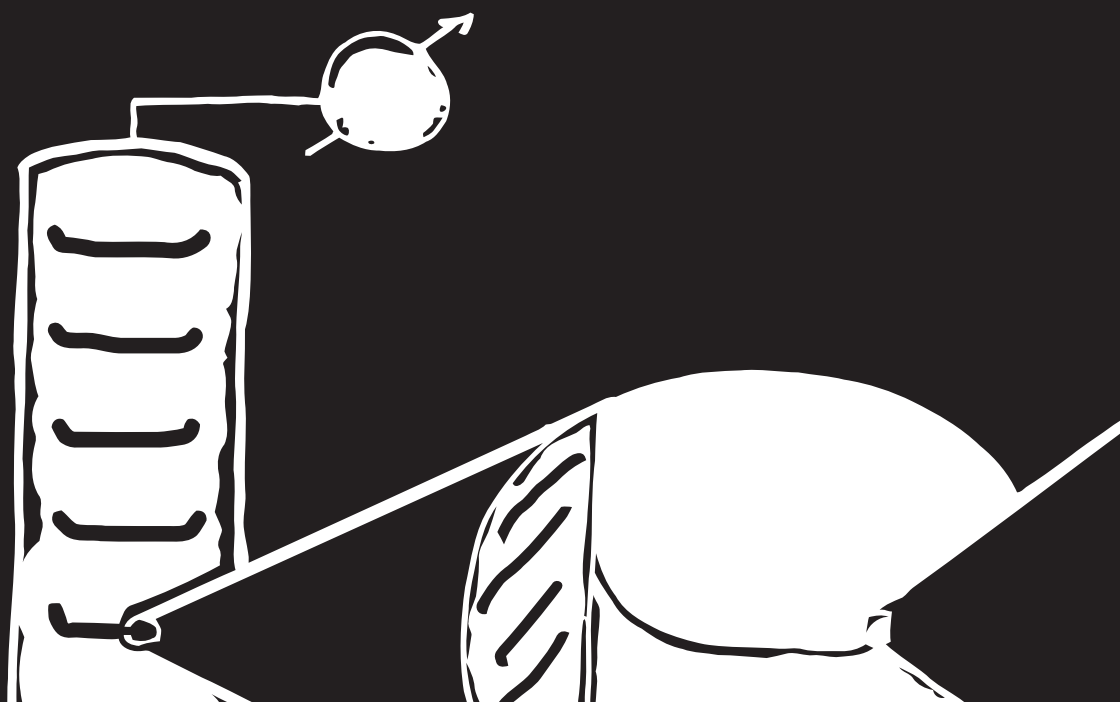
Plenary talks



Lennard-Jones Lectureship and Prize

Dissipation and the Foundations of Statistical Thermodynamics

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Introduction

In this talk I discuss a number of logical inconsistencies in the application of Clausius' Inequality to irreversible processes. We then go on to discuss the derivation of the postulates of classical statistical mechanics, from the laws of mechanics and the axiom of causality. In order to do this we discuss three main theorems: the Fluctuation Theorem[1] that gives the relative probability that path integrals of the dissipation take on equal but opposite values; the Dissipation Theorem[2] that relates the linear and nonlinear response of nonequilibrium averages to time integrals of correlation functions concerning that same phase variable and the time zero value of the instantaneous dissipation and the Equilibrium Relaxation Theorem[3] that shows how under easily satisfied conditions, nonequilibrium systems will relax towards equilibrium. The mathematically well defined dissipation function is central to each of these theorems[4]. It enables us for the first time, to give a mathematical definition of an equilibrium system. Finally we show how the Gibbs Equation of classical thermodynamics can be derived using our Equilibrium Relaxation Theorem.

All of this material and much more is the subject of our recent book, Fundamentals of Classical Statistical Thermodynamics[5].

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The Molecular Simulation Design Framework (MoSDeF): Capabilities and Applications

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Molecular simulation plays an important role in many sub-fields of chemical engineering, just as it does in science and engineering in general. Soft matter systems (those easily deformed at room temperature - e.g., liquids, polymers, foams, gels, colloids, and most biological materials) are ubiquitous in chemical engineering, 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 computational screening capability, we have been developing the Molecular Simulation and Design Framework (MoSDeF) software suite, including the open-source mBuild [1] and Foyer [2] packages. We will introduce MoSDeF and its capabilities in this presentation. We will also illustrate how, by combining with the Glotzer group's Signac-flow workflow manager [3], we have facilitated screening of soft matter systems over chemical/structural parameter spaces.

We will report results for two timely applications: lubrication of nanoscale devices featuring surfaces functionalized by monolayers in sliding contact, and understanding diffusion of ionic liquids in organic solvents (related to energy storage devices). In both cases, automation of the simulation through use of the MoSDeF tools enables screening and reproducibility.

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Christopher Wormald Prize

Physical Determinants of Liquid-Liquid Phase Separation of Protein Mixtures

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The cell interior contains heterogenous mixtures of thousands of different components that need to be organised in space to facilitate control of function. Such organisation is achieved through the formation of compartments and organelles that are sustained by either physical membranes or the physical chemistry of liquid-liquid phase separation (LLPS)[1,2] of protein and protein-nucleic-acids mixtures. Systems containing highly flexible intrinsically disordered protein (IDP) regions favour LLPS[3]. Here we show that while multivalency and promiscuous protein binding favour LLPS, the flexibility of the binding sites has a marginal effect on LLPS as long as not increases the effective valency of proteins. By combining the well-established physics of self- assembly of colloidal patchy particles with a novel continuous potential[4] optimised for fast and scalable molecular dynamics simulations, we demonstrate that fine-tuning of the characteristics of the protein-protein attractive interactions transforms the full phase diagrams of mixtures of thousands of proteins and the stability of the liquid-liquid coexistence region. Reducing the valency, gradually shifts the L-L critical point towards lower temperatures and packing fractions until its disappearance at a valency of 2. The topological distribution of binding sites on the protein surface also emerges as an important player in transforming the protein phase diagrams, with topologies that spread out the binding sites far from each other favouring LLPS. Our results[4] suggest that of intrinsically disordered protein regions favours protein liquid-liquid phase separation because it facilitates exposure of protein interaction sites and, hence, increased valences, but not because flexibility per se favours phase separation. Also, our results show a general mechanism by which cells can easily control the stability of their liquid-liquid coexisting phases without changing the total protein concentration: protein-rich drops can be dissolved through chemical modifications that decrease the number of active binding sites on proteins, similarly condensation of protein-rich liquids can be triggered through chemical changes that increase the valency of proteins to values of three or higher.

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EFCE Excellent Award in Thermodynamics and Transport Properties 2019

Studies for the development of new separation processes with terpenes and their environmental distribution

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Terpenes belong to what is probably the largest and most diverse class of natural products with applications in several industries due to their flavour and fragrance. Due to terpenes large structural variety and chemical complexity, there are still many questions to be answered concerning their thermophysical properties, phase equilibria and environmental impact.

In this work, it is shown that terpenes can be used to prepare sustainable and cheap hydrophobic solvents within the eutectic solvents framework. Moreover, based on the activity coefficients at infinite dilution measurements and COSMO-RS predictions, a selection of ILs with potential for terpenes fractionation is made. Aiming at the development of new separation processes of terpenes, eutectic solvents composed of ammonium salts and monocarboxylic acids are formulated and characterized. Finally, targeting the development of accurate models for the fate of terpenes in the environment, a range of essential physicochemical properties of terpenes is measured and modelled.

Guggenheim Medal for Excellence in Thermodynamics

Atomistic and mesoscopic simulations of polymer melts

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In this talk we will discuss multiscale molecular modelling and simulation efforts aimed at understanding and predicting the physical properties of polymers in the melt state. The characteristic lengths and times governing structure and molecular motion in polymer melts span many orders of magnitude; as a consequence, predicting their properties defies conventional atomistic simulation techniques. Fortunately, one can develop systematic statistical mechanics-based approaches that meet the challenge of long time and length scales.

Monte Carlo simulations that rearrange the connectivity of repeat units along chain backbones, while respecting a prescribed molar mass distribution, achieve vigorous sampling of the complex configuration space of dense long-chain polymer systems and yield accurate predictions for their structure and volumetric properties [1]. Through topological analysis of the resulting well-equilibrated melt configurations one can estimate the molar mass between entanglements [2]. For melts of complex chemical constitution, a useful strategy is to coarse-grain, e.g., by Iterative Boltzmann Inversion, the atomistic representation into one involving fewer degrees of freedom, equilibrate at the coarse-grained level, and reverse-map back to the atomistic level. This strategy has allowed predicting changes in the glass transition temperature accompanying the dispersion of nanoparticles in polymer melts [3].

To predict the rheological properties of long-chain polymers one can invoke "mesoscopic" models in which chain segments containing ca. 50 skeletal atoms are mapped into single interaction sites or "beads" (Figure 1). Entanglements are represented through slip-springs connecting different chains and capable of sliding along their contours, while the excess Helmholtz energy of nonbonded interactions is calculated from the local density via an equation of state. Effective bonded interactions are obtained directly from distribution functions accumulated in the course of atomistic simulations. Through such hybrid particle-field mesoscopic Brownian Dynamics/kinetic Monte Carlo (BD/kMC) simulations it has been possible to predict the shear viscosity, the chain self-diffusion coefficient, and the storage and loss moduli of the melt [4]. Applying the melt simulations under nonequilibrium (flow) conditions, nonlinear viscoelastic properties (shear thinning, first and second normal stress differences) have been predicted and explained in terms of changes in the orientation, conformation, and state of entanglement of the chains [5].

The properties of polymer melts at interfaces are very important in plastics processing and adhesion applications. Well-equilibrated atomistic simulations of molten polymer films, in which long-range nonbonded interactions are carefully accounted for, have yielded accurate estimates of the surface tension, of the work of adhesion to solid substrates, and of the dependence of these properties on molar mass and temperature [6]. Mesoscopic simulation strategies have been extended to deal with free surfaces of polymer melts by incorporating a square density gradient contribution to the Helmholtz energy. These mesoscopic simulations save 2 to 3 orders of magnitude in computation time relative to atomistic ones and reproduce very successfully the conformational distribution, the interfacial free energy, and the dynamics of chains in the surface region [7].

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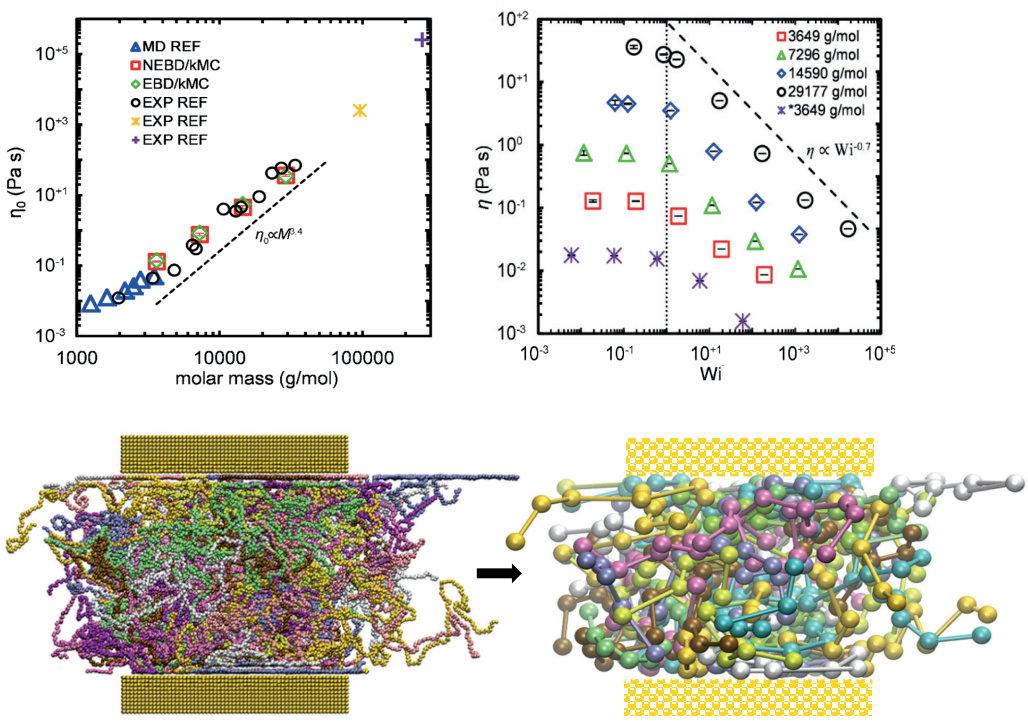

Figure 1: *Top Left*: Predictions for the zero shear viscosity of monodisperse polyethylene melts at 450 K as a function of their molar mass, as obtained from equilibrium (EBD/kMC) and nonequilibrium (NEBD/kMC) mesoscopic simulations, being compared to atomistic molecular dynamics (MD) and experimental results. *Top Right*: Shear viscosity as a function of Weissenberg number as obtained from NEBD/kMC simulations of polyethylene for various molar masses. The Weissenberg number $Wi = \dot{\gamma}\tau_d$ equals the product of the shear rate $\dot{\gamma}$ times the disengagement time τ_d of the melt. Thanks to the computer time savings afforded by BD/kMC, the linear regime of small *Wi* can be accessed, which is impossible by atomistic MD. The shear-thinning exponent from the simulations is consistent with experiments [5]. *Bottom*: Pictorial representation of atomistic (left) and mesoscopic (right) model of a polyethylene film capped by gold on both sides.

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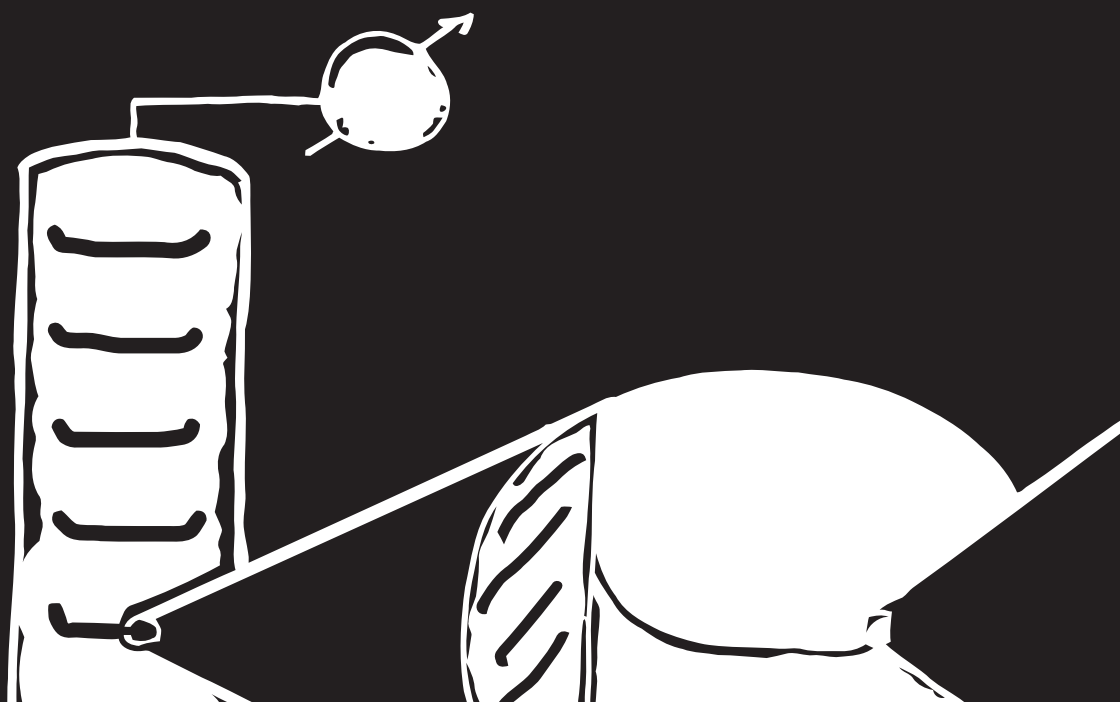
Invited talks



Peptide Co-assembly into Amyloid Structures: Molecular Simulation and Sequence Design

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Peptide self-assembly has long been recognized as a key technology for preparing nanomaterials with desired structures and functions for medical and biotechnology applications. Recently, co-assembly of peptides with complementary partial charges has emerged as a new platform for preparing peptide-based nanomaterials. Two different peptides co-assemble into fibrils rich in β-sheet when mixed together but remain random coils when by themselves. It has been hypothesized that peptides with opposite partial charges adopt an alternating arrangement in the fibril, but there is no direct evidence at the molecular level to support this hypothesis. We investigate the co-assembly of two charge-complementary peptide systems, CATCH4+ (QQKFKFKFKQQ and CATCH 6- (EQEFEFEFQE), using discontinuous molecular dynamics simulations and check our predictions using solid state NMR and standard biophysical measurements. Both simulation and solid-state NMR support the alternating peptide hypothesis but show exceptions in which peptides with the same charge are adjacent to each other. Molecular modeling further shows that the peptides can co-assemble into a β-barrel structure; the role of this oligomer in the co-assembly processes is discussed. Finally we use an in-house peptide search algorithm that screens >10,000 peptide sequences for their potential to co-assemble into fibrillar structures and test the co-assembling ability of the top peptide candidates using DMD simulations and biophysical characterization experiments .

$A = -kT \ln Q$

Molecular ballet of water near interfaces: Elucidating the mechanisms of heterogeneous ice nucleation

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Nucleation – that is the onset of a new phase from a metastable phase – is a difficult phenomenon to study both experimentally and computationally. Nucleation relevant spatial and temporal resolution is difficult to access in experiments. In contrast, while computer simulations are perfectly suited to probe these length and timescales, sampling statistically relevant number of nucleation events is computationally expensive. In our research, we use advanced sampling techniques in conjunction with molecular dynamics simulations to sample hundreds and thousands of nucleation events.[3,5] We apply these methods to study heterogeneous ice nucleation and gas hydrate nucleation.

Heterogeneous ice nucleation relates to freezing of water driven by the presence of an impurity such as a mineral surface. Interestingly, it is not yet understood what about a surface promotes or inhibits the formation of ice. We use simulations of salt (silver iodide) and mineral (kaolinite) surfaces to provide insights into the properties of a surface that facilitate ice formation.[1,2] These findings can help design surfaces that either inhibit ice nucleation (for example in cases such as wind mills, power lines, and transportation) or that promote ice nucleation (for example in cases such as food preservation and cryopreservation). Further we have developed methods to study heterogeneous nucleation in a computationally efficient manner. We will discuss these results and illustrate their benefit especially when studying poor ice nucleators.

Gas hydrates are crystalline (ice-like) solids formed by water forming cages around guest molecules such as methane, carbon dioxide and tetrahydrofuran. These form at low temperatures and high-pressure conditions and are a flow assurance problem in the oil and gas industry. In addition, hydrates can be potential energy source, and be used for gas separation and water desalination. The fundamental question that remains unanswered is -- how does the solution of guest and water transform into this crystalline solid. Our simulations provide insights into the mechanisms of hydrate nucleation and highlight its dependence on the water solubility of the guest molecules.[3] We will also discuss the role of surfaces on hydrate nucleation.[4]

Collectively, my talk provides an overview of the intricate behavior of water molecules in transforming from liquid to the solid phase.

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Self-assembling outside equilibrium: emergence of structures mediated by dissipation

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A set of disordered interacting building blocks may form ordered structures by means of a self-assembling process. An external intervention to the system by adding a chemical species or by applying forces or gradients leads to different self-assembly scenarios with the appearance of new structures. For instance, the formation of microtubules, gels, virus capsides, cells and living beings among others takes place by self-assembly under non-equilibrium conditions. A general evolution criterion able to account for why nature selects some structures outside equilibrium and not others is lacking. Nevertheless, progress in the understanding of non-equilibrium self-assembly mechanisms has been made thanks to the formulation of models that take particular situations into consideration. We review recent efforts devoted to describing self-assembling outside equilibrium [1], focusing in particular on gelation processes [2] and formation of Liesegang rings [3].

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$A = -kT \ln Q$

Simulations of water: challenges after fifty years

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In 1969, the first paper dealing with computer simulations of water was published by Barker and Watts [1] followed by the pioneering papers of Rahman and Stillinger [2]. Typically, water is described since the classical paper of Bernal and Fowler [3] by using simple models that use partial charges and Lennard Jones centers. In the early days, computer simulations focused mostly in obtaining the properties of water in the liquid phase. The parameters of the potential were obtained to reproduce the radial distribution function, densities and vaporization enthalpies. Studies about phase equilibria started in the late 80's. Firstly the vapor-liquid equilibria was determined using new developed methodologies. Freezing properties and phase diagrams were calculated in the last fifteen years. That allowed to develop a model TIP4P/2005 that probably represents the limit of what can be done with a simple non-polarizable potential. The failure of the model teaches a lot about the physics of water: the importance of nuclear quantum effects, the special role of the dielectric constant in the modeling of water, and also the importance of polarizability. Important progress has been done in the recent years with polarizable models and more recently on neural networks to describe water interactions. The increase in computer power allowed to study problems such as nucleation of ice, quasi-liquid layer, or even speculating on the behavior of supercooled water and its possible liquid-liquid transition. Finally I shall discuss the kind of problems we face in computer simulation of mixtures by presenting some results for two simple systems: salt solutions and hydrates. Both of them illustrate that there is nothing wrong in leaving standard combination rules or even with more provocative ideas to describe ions in water.

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Nematics in and out of equilibrium on curved toroidal surfaces

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We will discuss our recent results with active nematic liquid crystals on toroidal surfaces and show how, despite the intrinsic activity and out-of-equilibrium character of our system, we still observe remnants of the expected curvature-induced defect unbinding predicted for nematics in their ground state. In our experiments, however, the number of defects is far larger than what one would expect for conventional nematics. In addition, these defects move throughout the toroidal surface and arrange in unexpected ways when compared to conventional nematics. Comparing our results to numerical simulations, we unravel the key role of activity in these findings via defect creation and annihilation events.

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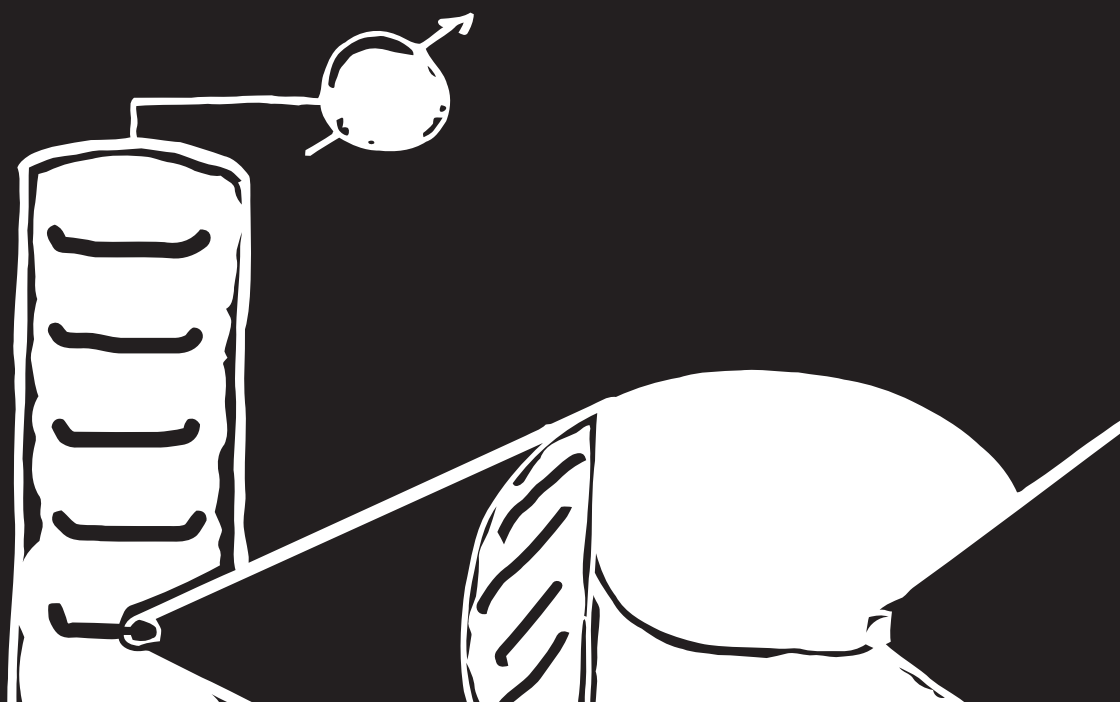
Oral Presentations:
Advances in Molecular Simulation



Determination of Thermal, Caloric and Transport Properties Under Extreme Conditions Using NEMD Simulations

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Molecular dynamics simulations are widely used for determining material properties, but they are still computationally expensive. We have recently introduced an efficient non-equilibrium molecular dynamics (NEMD) simulation method for studying different thermal, caloric, and transport properties of fluids [1,2]. The method is characterized by a superposition of a temperature gradient and a velocity gradient. It is therefore called 'two-gradient method'. This approach allows to determine data on the pressure, internal energy, enthalpy, isobaric heat capacity, thermal expansion coefficient, thermal conductivity, shear viscosity, and self-diffusion coefficient simultaneously in a single simulation run. Yet, the computational cost is similar to that of common NEMD methods from which typically only a single property is determined.

Different application cases of the two-gradient method are presented. (1) By applying a large temperature gradient, we show that the hypothesis of local equilibrium is valid. Thus, all aforementioned properties can be determined even more efficiently for a series of state points at different temperatures and constant pressure from a single simulation run. (2) Applying a large velocity gradient instead allows to study also rheological effects. For instance, the structure of the fluid can be affected by shear stresses, which results in changes of the fluid properties.

All application cases were studied extensively over wide ranges of thermodynamic states using the Lennard-Jones fluid truncated and shifted at 2.5 σ as an example. The different data sets are comprehensively compared to literature data and highly accurate equations of state. Thereby, the two-gradient method is shown to be accurate and extremely efficient.

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$A = -kT \ln Q$

Simulating transport in particle-polymer solutions with multiparticle collision dynamics

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The dynamics of nanoparticles in complex fluids are of great interest for applications in drug delivery, oil recovery, and materials processing. Particle mobility is well described by the generalized Stokes-Einstein (GSE) relation when the nanoparticles are much larger than the polymers. Violations of GSE predictions are observed, however, when the size of nanoparticles is comparable to or smaller than length scales in polymer solutions [1]. We investigate the microscopic origin of this anomalous behaviour using multi-particle collision dynamics (MPCD) [3], an advanced algorithm for rigorously modelling solvent-mediated hydrodynamic interactions in coarse-grained, mesoscale simulations. We apply MPCD to study transport in nanoparticle-polymer systems and the effects of many-body hydrodynamic interactions on this behaviour. We demonstrate that the translational centre-of-mass motions of both nanoparticles and polymers are sub-diffusive on short times before transitioning into a diffusive regime on longer time scales [2]. The long-time diffusivities of nanoparticles collapse according to scaling predictions [4], in accord with recent experiments [1]. The sub-diffusive behaviour predicted by MPCD simulations, by contrast, agrees with experiments [1], but significantly deviates from theoretical predictions. We show that this disagreement is due to a hitherto unreported transport mechanism characterized by the tight coupling of the translational motions of the nanoparticle and polymer centres-of-masses, which is not accounted for in current theories. Finally, we investigate the influence of polymer flexibility on particle transport. As the persistence length of the polymers increases, the nanoparticle dynamics become more subdiffusive and decouple from the dynamics of the polymer chain centre-of-mass [5].

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Dielectric Constant: Reconciling Simulation and Experiment

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The dielectric constant of liquids assumes great importance in a variety of applications, from electrochemical devices to protein-ligand binding. However, it is notoriously difficult to accurately predict using classical non-polarizable models. Even very recent benchmark studies, using large systems and long simulation runs to ensure convergence, found very strong systematic deviations between experimental dielectric constants and predictions from classical models [1-3]. We argue that these deviations arise from the inherent neglect of polarization effects in those models. Indeed, most classical non-polarizable models account for polarization implicitly, in a mean-field sense, by fitting the parameters to pure liquid properties (e.g. density). However, the parameters (most importantly, the point charges) obtained by fitting to the potential energy surface (PES) are not adequate for describing the dipole moment surface (DMS), upon which the dielectric constant directly depends [4]. Moreover, non-polarizable models are intrinsically unable to describe the purely electronic response of the fluid, quantified in the high-frequency dielectric constant [5]. These limitations cannot be resolved by simply reparameterizing the models, as this would sacrifice agreement with properties that depend mostly on the PES.

In this presentation, we propose an alternative approach, based on applying a *post facto* correction to the dielectric constant predictions from classical non-polarizable models. This correction takes into account the missing electronic response, by estimating it from the experimental index of refraction of the pure liquids, and the mismatch between the PES and the DMS, through a multiplicative factor based on the ratio of dipole moments of the model and of the real liquid [6]. We apply this correction to the results of recent benchmark studies, carried out for a large variety of compounds and with different molecular models [1-3]. Our approach is able to eliminate systematic deviations between simulations and experiments, leading to a computationally expedient way of improving the accuracy of model predictions. Moreover, we have observed that the PES/DMS scaling factor depends on the type of functional group present in each molecule, with highly polar moieties (like hydroxyl, ketone, ester and nitrile) requiring much larger corrections than moieties of lower polarity (like hydrocarbons, ethers and halogenated substituents). This work is part of a concerted effort to develop a new modelling paradigm based on a rigorous consideration of polarization effects in non-polarizable models [7].

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$A = -kT \ln Q$

Molecular Modeling of Solute Precipitate Nucleation

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Modeling the nucleation of molecular crystals, and particularly nucleation from solution, is critical to many applications in the food, chemical, construction, and pharmaceutical industries, among others. Despite its apparent simplicity, however, understanding this process poses major challenges both to experimental and theoretical studies. Critical nuclei often comprise only a handful of molecules, and the stochastic nature of nucleation makes it extremely hard to design experiments to observe such small aggregates. On the other hand, simulation approaches are limited due to the slow nature of nucleation compared to molecular relaxation times.

In this work, we present recent results for the nucleation of drug molecules from solution, and show the effect of different solvents on the nucleation rates. We use a unique approach where order parameters for the crystal are constructed directly from the crystal structure [1], and construct a minimum free energy path for nucleation on this order parameter space using the String Method in Collective Variables [2, 3]. Our approach allows for simulating nucleation at constant supersaturation, by maintaining constant chemical potential of the solute, solvent, or both. This eliminates solution depletion artifacts in the simulations [4].

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The role of molecular structure and solvent in the lubricating properties of ionic liquids

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The ability to control and manipulate friction force is extremely important in many research fields such as biomedicine, engineering, chemistry, physics, and nanotechnology [1]. Friction plays a central role in nanoscale devices where the presence of a thin nano metric liquid film between solid surfaces modify shear and adhesion between surfaces. Ionic liquid are being actively investigated as lubricants given their unique thermophysical properties: chemical and thermal stability, low vapour pressure and low melting temperature [2].

Previous investigations showed that the friction force can be tuned by changing the properties of solid surface, such as surface charges or potential [3, 4, 5], as well as the composition of the ionic liquid [6, 7]. The importance of solvent effects has also been highlighted experimentally and in computer simulations [7, 8].

We investigate here the impact of molecular structure and solvent on friction, by studying both coarse grained and atomistic models of 1-*n*,2-methyl-imidazolium tetrafluoroborate [$C_{n=2..6}$MIM][BF_4], ionic liquids under nanoconfinement conditions. We use a non-equilibrium molecular dynamics method discussed recently to investigate the friction between charged surfaces [3]. Both, coarse grained and atomistic models predict similar dependence of the friction with surface charge and pressure. The comparison of these two models highlights the relevance of the molecular specificity of the ionic liquid and solvent properties on the lubrication process.

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Mechanisms of aggregation of graphene dispersion in electrolytes

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As ways to efficiently produce quantities of graphene are explored, the use of liquid-phase exfoliation has shown to be promising. One of the questions that have not yet been answered in this context is what is needed to keep the monolayer flakes from reaggregating once they have been exfoliated, as well as how long the dispersion will maintain its stability. In addition, studies of graphene interactions with polar liquids[1] and electrolytes[2] show a degree of adsorption of the charged and polar particles on the surface of the flakes. However, an analysis of the attraction between the liquid and the graphene flakes is not sufficient to fully describe the behaviour of dispersions.

In this study using Molecular Dynamics simulations and a new polarizable force field [2], we systematically explore the mechanisms of aggregation of graphene flakes dispersed in electrolyte solutions. The electrolytes studied are aqueous solutions of common salts as $CaCl_2$, LiCl, KCl, $MgCl_2$ and NaCl. All these salts show attraction to the graphene surface and the formation of an electric double-layer on its surface[2], for this reason it would be expected that they would hinder aggregation. Experiments however show that single flakes dispersions in such electrolytes are not stable. [1] We rationalise the simulation results in terms of flake rigidity, ions type and identify three main aggregation pathways as a function of the flake elastic properties and ions dehydration free energies.

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Are the Bjerrum defects in ice topological or Coulomb charges?

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The structure of the H-bond network in ices and clathrates is determined by the Bernal–Fowler "ice rules": (i) each oxygen is covalently bonded to two hydrogens, (ii) each oxygen forms two hydrogen bonds to two other oxygens, and (iii) there exists exactly one hydrogen between a pair of neighboring oxygens. The rules are violated by the Bjerrum defects [1, 2]: An oxygen–oxygen bond without a proton is called an L-defect, whereas two protons present at the bond constitute a D-defect. In real ices, the Bjerrum defects affect kinetics of proton disorder.

We study the mutual interaction of the defects in ices Ih and Ic at two levels of abstraction.

In the lattice ice models, all configurations satisfying the ice rules are assumed to have the same energy, whereas each Bjerrum defect contributes by a unit positive energy [3]. Due to the Gauss theorem for the "H-bond flux" (see the Figure), the defects act as topological charges [4, 5]. In other words, their apparent interaction mediated by the entropy of proton disorder [6] is Coulomb-like. We calculate the charge magnitude by fitting the potential of mean force of a pair of defects (minus log of the simulated 3D distribution function) in the periodic boundary conditions to the Ewald summation energy.

For atomistic models (TIP4P/2005, TIP4P/ICE, BK3, POL4D), the effective Coulomb charge of a defect is calculated as a sum of Gaussian-smoothed charges of interaction sites. The limits for infinite system and infinite Gaussian width are made. Since such a charge is screened by the surrounding dielectric, it must be multiplied by the ice non-configurational dielectric constant. We evaluate it by applying an electric field to a model ice crystal with a fixed proton disorder. The procedure is tested on vacancies in the structure of NaCl.

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Modelling cosolvent effects on aqueous polymer solubility

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I will discuss recent advances in molecular simulation of cosolvent effects on the water solubility of polymers [1-6]. The thermodynamic approaches discussed include the application [1,3,7,8] of Kirkwood-Buff theory of solutions [9] to predictively model solubility changes, and the Widom potential distribution theorem [10] to uncover the molecular driving forces that lead to polymer collapse and swelling transitions. Several intriguing polymer solubility problems will be discussed: polymer coil-globule collapse and swelling transitions in mixed good solvents ("cononsolvency") [2-4], polymer coil-globule collapse and swelling transitions in mixed salt solutions [6], and opposite cosolute effects on the solubility of thermo-responsive polymers with chemically modified side chains [1].

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Thermodynamic properties and interatomic interactions from *ab initio* data

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For some time the challenge in molecular thermodynamics has been to study systems of increasing molecular complexity. The motivation for this can be attributed to the important role that large molecules such as polymers and proteins have for critical processes in biology, medicine and manufacturing. The challenge has been partly addressed by increasingly sophisticated equations of state [1] that incorporate molecular-level detail [2] and the development of advanced force fields [3] for the exact evaluation of thermodynamic properties via molecular simulation [4].

The widely used approach for the development of either force fields or molecular-based equations of state is to separately account for the different contributions to intermolecular interactions, i.e., non-bonded, bonded, dipole interactions etc. These contributions are either represented by semi-empirical potentials or approximate terms. For example, the Lennard-Jones potential [4] forms the basis of non-bonded interactions in the overwhelming majority of molecular force fields and many equations of state. In contrast to this semi-empirical approach, progress is being increasingly made in obtaining intermolecular forces from first principles [5]. However, the *ab initio* potentials [6] resulting from first principles are almost exclusively confined to relatively simple systems and are both computationally costly and difficult to implement.

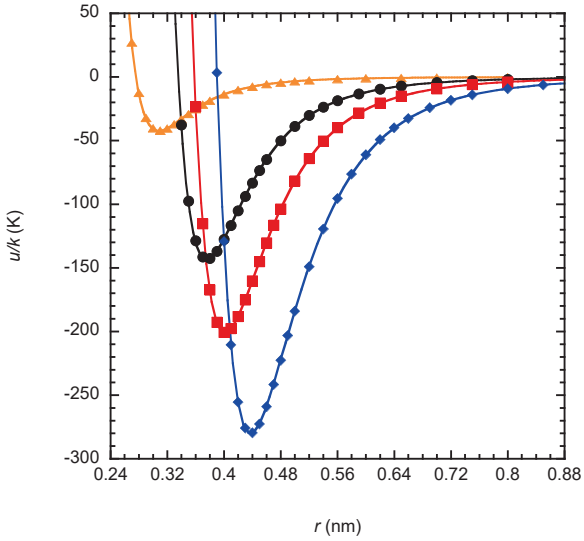

FIG. 1. Comparison of two-body potential energies obtained from first principles for Ne (▲), Ar (●), Kr (■) and Xe (◆) with *ab intio* potential calculations [7].

$A = -kT \ln Q$

It is evident from the comparison given in Fig. 1 that *ab initio* potentials accurately reflect the interaction energies obtained from first principles. Therefore, it is highly desirable to use *ab initio* potentials for the calculation of thermodynamic properties because the accuracy of the underlying intermolecular interactions should yield improved predictions.

This work demonstrates how *ab initio* potentials can be made useful for the prediction of thermodynamic properties by overcoming the related impediments of complexity and computational cost. Two alternative strategies are employed. One strategy involves the use of Mie potentials [8] to accurately represent *ab initio* data. The other strategy involves a simplified approach for representing *ab initio* energies that avoids the complexity of current *ab initio* potentials. Molecular simulations using the new *ab initio*-based potentials are reported for thermodynamic properties such as heat capacities and vapor-liquid equilibria.

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Statistics of small length scale density fluctuations in supercooled viscous liquids

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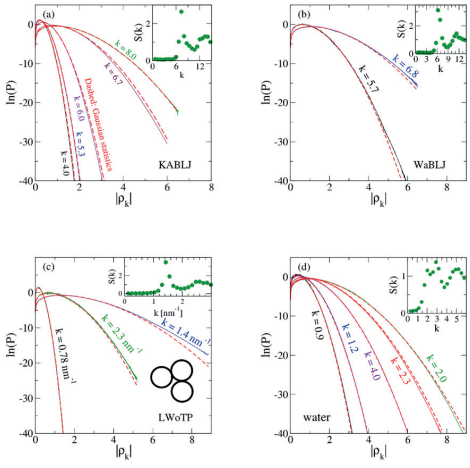
Many successful theories of liquids near the melting temperature assume that small length scale density fluctuations follow Gaussian statistics. Reference [1] presents a numerical investigation of density fluctuations in the supercooled viscous regime using an enhanced sampling method. Five model systems are investigated: the single component Lennard-Jones liquid, the Kob-Andersen binary mixture, the Wahnström binary mixture, the Lewis-Wahnström model of ortho-terphenyl and the TIP4P/Ice model of water. Results show that the Gaussian approximation persists to a good degree into the supercooled viscous regime, however, it is less accurate at low temperatures (see figure below). The analysis suggests that non-Gaussian fluctuations are related to crystalline configurations. Implications for theories of the glass transition are discussed.



Natural logarithm of probability distribution of ρ_k (the collective density field) for (a) the KABLJ mixture (b) the WaBLJ mixture (c) LWoTP trimer molecules, and (d) tip4p/ice water model in the supercooled viscous regime. Dashed lines are Gaussian predictions. The insets shows scattering functions. The agreement with the Gaussian prediction is good, however, deviations are apparent in the tails of the distributions. These are likely attributed to crystalline structures.

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$A = -kT \ln Q$

Fissioning of giant SALR clusters

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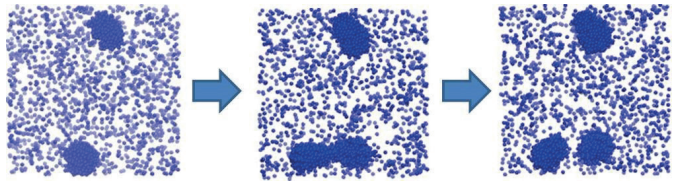
Particles with short-range attractions and long-range repulsions can form giant clusters under suitable conditions. I show, using theory and simulation, that these clusters can spontaneously fission, or 'reproduce' [1]. I highlight the implications this discovery has for soft matter in general, with a focus on complex coacervates, membraneless organelles within biological cells, and the origin of life and artificial life.



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Why do liquids form?

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The liquid state of matter, though ubiquitous in nature, occupies only a small area of the phase diagram of a substance. The standard textbook definition of a liquid includes statements such as: an ability to flow under vanishing shear stress, will form a free surface, can be obtained by isothermal compression of a gas, lacks long range molecular order *etc*. While there is no route to the solid phase without passing through a phase transition, it is possible to pass continuously between the liquid and the vapour states. This latter fact means that it is difficult to distinguish liquids from vapours except when they coexist, and thus possess an interface.

Statistical mechanics provides a link between the nature of intermolecular forces and equilibrium properties. Despite the success of statistical mechanics, it is perhaps surprising that the question of what is the sufficient and necessary condition for a liquid phase to form has not been completely answered. One component fluids of hard spheres or hard disks possess a melting transition, but no liquid phase, suggesting that attractive forces must be present for a stable liquid phase to be observed. On the other hand, the liquid phase appears to be absent in some molecular systems governed by pair potentials containing an attractive tail. In these cases, the liquid-vapour coexistence curve lies below the sublimation line so that the liquid-vapour transition is metastable with respect to the fluid-solid transition.

Hagen and co-workers failed to observe a stable liquid phase in their Monte Carlo simulations of C_{60} [1] though later simulations by another group contradicted this by observing a narrow liquid range [2]. The *range* of the potential seems to be the governing factor. Hagan and Frenkel, for instance, found that a stable liquid phase for the hard-sphere attractive Yukawa system vanishes when the range of the attractive part is approximately one sixth of the hard-core diameter [3]. Tejero and co-workers studied a family of continuous pair potentials based on a double Yukawa term. Their theoretical work found that the liquid phase can be expected to vanish when the range of the attraction relative to that of repulsion falls below 1.6 in reduced units.

Despite a flurry research on this topic in the 1990s, the subject largely fell out of favour. In this work we revive interest in the question of what makes a liquid. Two families of continuous short ranged pair potentials are studied in an attempt to isolate the key feature which guarantees the observation of a stable liquid phase. We use a combination of perturbation theory and truncated virial expansions to generate coexistence curves and Joule-Thomson inversion curves for sets of pair potentials with differing range and shape of their attractive interactions. We also

$A = -kT \ln Q$

discuss the simulation of coexistence with an explicit interface and the use of isobaric-isenthalpic molecular dynamics simulations and draw some conclusions about the liquid state.

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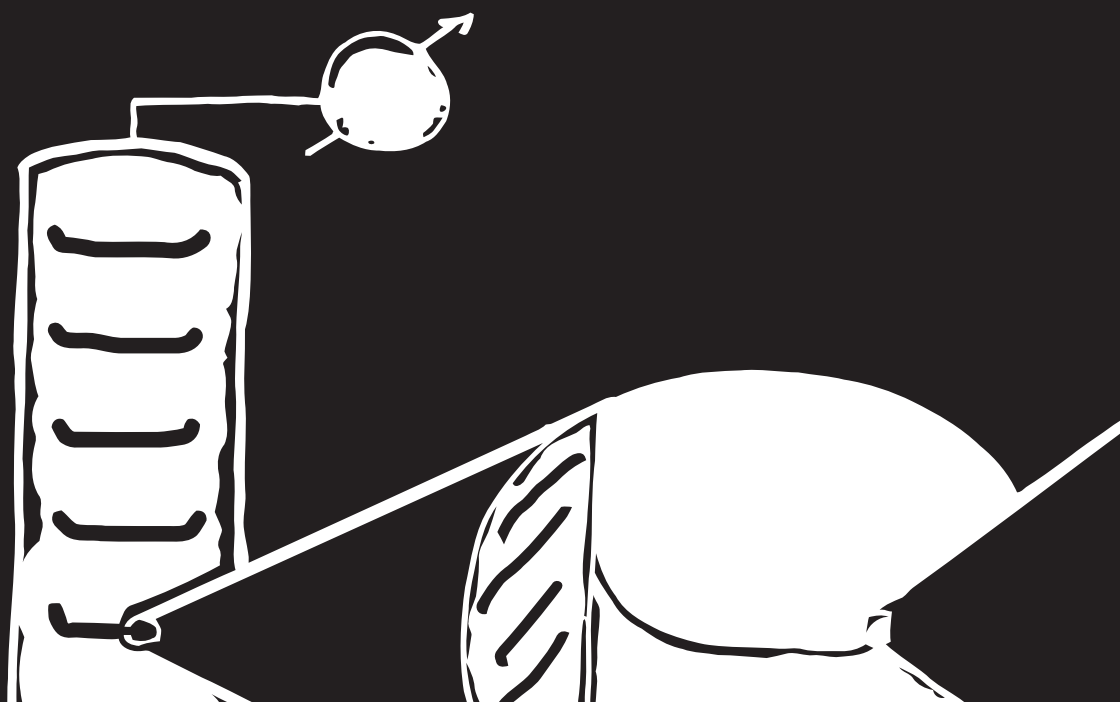
Oral Presentations: Challenges and advances in fluid phase equilibria



Water's two-critical-point scenario in the Ising paradigm

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Water exhibits an unusual pattern of thermodynamic behaviour both at ambient conditions and in the low-temperature region where it exists as a supercooled liquid. Underlying this phenomenology are the specific features of hydrogen bonding, which are known to lead to transient "ice-like" molecular arrangements in the liquid state. Such ice-like structural order propagates to longer distances as temperature is lowered. In fact, recent work on deeply supercooled water reports [1] a growing correlation length consistent with the sharp increase in thermodynamic response functions observed long ago at *ca.* 240 K [2-4].

It has been conjectured [5] that this behaviour reflects that supercooled water should undergo a liquid-liquid phase transition terminating at a critical point at which, as usual, the correlation length and the response functions diverge. This physical picture, often referred to as the "two-critical-point scenario", has gained significant support over the last years from experimental, computational, and theoretical studies [6,7]. A strong implication is that a (one-component) substance can exist as a liquid in two distinct forms. This has been proved by careful computational analyses for the ST2 force field of water [8-10] as well as for tetrahedral patchy colloids [11] and model fluids of particles interacting via a variety of core-softened pair potentials [12].

Incorporating water's unusual thermodynamics into a tractable equation of state is a challenging task. Early approaches to this problem successfully reproduced the two-critical-point scenario from a model free energy composed of a van der Waals component and an additional contribution accounting for the effect of hydrogen bonding [13,14]. On the other hand, regarding liquid water a regular mixture of two species of distinct local structure yields an expression for the Gibbs free energy that describes satisfactorily experimental data as well as results from simulations of water force fields [15,16].

All this theoretical work exploits the fact that water's ice-like order is characterized by local structures of low energy, entropy, and density. Recently, using the concept of "fluctuating cell volumes" in lattice models [17], such features have been implemented in a spin-1/2 Ising-like model in which, instead of employing occupied and vacant cells for describing the dense states of liquid water, singly-occupied cells with two accessible volumes and an appropriate energy-entropy-volume coupling are used [18]. It was concluded that such a *compressible cell model* may serve as an Ising prototype for the hypothesized liquid-liquid phase transition, while its mean-field solutions were shown to provide hints on the analytical form of the equation of state of water.

Here we further elaborate upon this by analysing a spin-1, three-state Ising model in which, in addition to occupied cells with two distinct volumes, vacant cells are considered. The model has two order parameters that drive two phase transitions akin to the standard gas-liquid transition and water's hypothesized liquid-liquid transition (see Fig. 1). Its mean-field equation of state enables a satisfactory description of results from experiments and simulations for the ST2 and TIP4P/2005 water force fields, from the phase diagram, the density maximum, or the deeply "stretched" states to the behaviour of thermodynamic response functions at low temperatures at

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which water exists as a supercooled liquid. It is concluded that the model may be regarded as a most basic prototype of water's two-critical-point scenario.

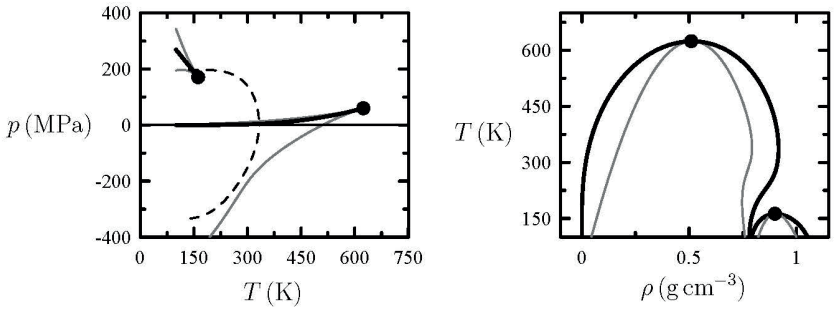

Figure 1. Binodals (solid, black) and spinodals (solid, grey) of our water-like spin-1 Ising model in the pressure-temperature and temperature-density planes. Curves end at two critical points which are identified as the gas-liquid critical point (high *T*) and the hypothesized liquid-liquid critical point (low *T*). Also shown is the locus of density maxima along isobars (dashed).

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Simulation of the structured phases of aqueous monoglycerides using SAFT-γ coarse-grained force fields

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Liquid-liquid equilibrium is ubiquitous in nature from the formation of the cell membrane to the folding of proteins. The often amphiphilic nature of these molecules results in the formation of interesting phases distinguishable not (necessarily) in concentration, but rather in structure. The group contribution formulation of the statistical associating fluid theory (SAFT-γ) based on the Mie potential [1] has been shown to be a reliable top-down coarse-graining methodology and has been applied to a range of systems [2]. In our current work, we develop new force fields for monoglycerides and assess the prediction of the different liquid phases in aqueous solution.

Monoglycerides are known to assemble into a variety of mesophases in water [3]. This behaviour makes the molecules viable for, amongst other things, drug delivery and protein crystallization applications [4]. Experiments suggest that the phase behaviour of these molecules is strongly influenced by the length and level of saturation of the hydrocarbon tail [4]. The SAFT-γ Mie EoS is used to develop the inter-molecular (non-bonded) force-field parameters from thermodynamic data, where possible, and pseudo-experimental data generated from more detailed SAFT models, where there is a lack of experimental data. These potentials are supplemented by bonded (intra-molecular) potentials obtained from direct Boltzmann Inversion of atomistic simulations using a modified TraPPE-UA force field [5], which has been shown to improve structural and transport property prediction [6].

Although one is not able to directly predict structured phases with the SAFT platform, molecular dynamics (MD) simulations using the same force-fields can be used to this end. We attempt to self-assemble the experimentally observed structured phases [3] using MD simulations and thus map the phase behaviour. We study the effects of the nature of the monoglyceride tail and the tail length on the phase diagram. Besides micellar, lamellar and isotropic phases, more complicated bicontinuous phases are observed in our simulations.

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$A = -kT \ln Q$

Probing the uncertainty of first-principles modeling of molecular crystals: calculation of sublimation thermodynamic properties

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The knowledge of thermodynamic properties, phase behavior, and phase stability of molecular crystals is indispensable in variety of applications, such as crystal engineering, polymorph screening in pharmaceutical research, and environmental modeling. An experimental determination of sublimation thermodynamic properties remains a challenging task, as evidenced by a poor interlaboratory agreement among experimental data [1, 2]. Although several experimental methods were established for the measurement of sublimation thermodynamic properties, they become less reliable as the crystal volatility decreases or are even not applicable for extremely low volatility crystals. Experimental studies of sublimation thermodynamic properties also require a development of special non-commercial equipment when low uncertainty data are targeted. As a result, it is estimated that experimental data on sublimation pressure are available for less than 1700 compounds. Nevertheless, given the immense number of newly synthesized compounds, experimental determinations can never, in general, keep pace with data demand, and predictive models must be sought. The empirical estimation methods for sublimation thermodynamic properties may unpredictably fail when applied to systems significantly differing from those based on which they were developed and require several input information, such as the normal boiling temperature, melting temperature or enthalpy of fusion, which may be not be readily available. Computational methodologies based on first-principles approaches ensuring a broad transferability can thus play a significant role in predicting sublimation thermodynamic properties, especially for extremely low volatile crystals.

In this contribution, current possibilities of first-principles approaches to predict thermodynamic data as a function of temperature and phase diagrams for molecular crystals with a special focus on the sublimation equilibrium are discussed. The performance of computational methodologies is demonstrated based on benchmark studies performed for crystal heat capacities, enthalpies of sublimation, and sublimation pressures, which due to their exponential dependence on both enthalpic and entropic contributions present a very stringent test of computational methodologies.

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Development and Application of Robust Phase Equilibrium Algorithms for Binary and Multicomponent Mixtures

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Accurate knowledge of the bubble and dew point boundaries of binary and multicomponent mixtures is of great importance for many applications and processes in chemical industry. An immediate example refers to avoiding condensation of a single phase petroleum fluid during pipeline transportation, which is crucial for safe and continuous operation. Calculation of phase diagrams with equations of state (EoS) poses different computational challenges depending on the type and the overall complexity of the physical behavior of the mixture under study, but also on the type of the diagram itself. Some significant computational challenges that are related to the calculation of saturation points are mentioned below.

Firstly, the formulation as an optimization problem of a thermodynamic potential cannot be performed in a straightforward and robust manner, because of the fixation of temperature or pressure and phase fraction. Secondly, the calculation of saturation points entails the implication that the number of solutions is not known a priori at specified conditions of pressure (or temperature) for mixtures. Furthermore, the rate of convergence becomes slow at elevated pressures and can be intolerably low in the vicinity of critical points. Finally, the most common methods employ initial estimates calculated from ideal solution approximations, such as Wilson's approximation, which deteriorate significantly at high pressures. This results frequently in divergence of the iterative procedure.

In this work, new algorithms for calculating saturation points of mixtures are presented. The proposed numerical methods are based on the derivation of the equifugacity relations, using the stability criterion of Gibbs and applying a modification, thus resulting in new sets of independent variables and iterative procedures. An additional change of variables is performed to obtain optimal scaling in the minimization problem which is nested in the proposed iterative schemes. The algorithms can be applied to calculate at will the lower / upper pressure or low / high temperature bubble or dew point parts of phase diagrams, thus being robust tools at retrograde regions. A simple initialization method is utilized and implementation guidelines are given to ensure robust iterative procedures. The new algorithms are tested by calculating saturation points of binary and multicomponent mixtures and prove to be efficient and robust, even in the proximity of critical points in some cases [1].

The new sets of variables proposed are also used in Euler-Newton Predictor-Corrector numerical methods that sequentially trace the entire family of solutions (phase diagrams), corresponding to given specifications. The target is to find a suitable choice of equations with specific sets of independent variables, so that robust methods with a sufficient convergence radius and good conditioning are obtained [2].

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The proposed methods are applied in combination with regression routines to fit binary interaction parameters (BIPs) using VLE data for binary mixtures of methane (CH_4) with long-chain normal alkanes (*n*-alkanes). Two sets of binary VLE data are used. One from available experimental VLE data and one produced from Gibbs Ensemble Monte Carlo (GEMC) simulations. The SRK, PR and PC-SAFT EoS are considered. The ability of each EoS to correlate the VLE data is assessed and the selected ones are used to predict the constant composition VLE phase envelopes of multicomponent gas condensate mixtures [3].

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Co-Oriented Fluid Functional Equation for Electrostatic interactions – Phase Equilibria, Orientation Distribution and Electric Permittivity

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The description and prediction of thermo-physical properties has undergone substantial progress in the past decades especially using equations of state (EOS). Still, there are many substances, which cannot be described with this kind of theory. This is especially true, if not only pure compounds, but also mixtures are considered. Substances that have a polar character and tend to form local structures have turned out to be especially challenging to model. Probably the best-known substance from this class is water.

In this contribution, focus lies on much simpler molecules, namely two model fluids:

a) The Stockmayer fluid with a Lennard-Jones (LJ) sphere and a central dipole.
b) A model with a LJ sphere and a dipole shifted from the center along its axis.

Despite their simplicity, no EOS is currently available that can model all these fluids. The models are graphically depicted in Figure 1.

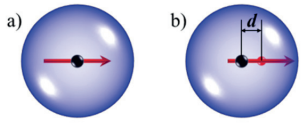

Figure 1: Depiction of two different model fluids included within the new theory. The blue large spheres depict the reference potential centered at the black small spheres. Red arrows show dipole moments with center in the small red spheres. From left to right the depictions are reference potentials with a) central dipole, b) dipole shifted by d*.

A new perturbation approach is presented that allows incorporating the unknown structure of the dipolar models in the form of their orientation distribution function (ODF) without the need for iterations. The resulting EOS – Co-Oriented Fluid Functional Equation for Electrostatic interactions (COFFEE) [1] – has a functional part describing the impact of ODF on the free energy and a non-functional part consisting of the usual ideal part, the reference part and a far field contribution where it is assumed that outside the first coordination shell no ordering occurs. The missing parameters of the functional part are fit to molecular simulation data of model a)'s ODF. For verification purposes, the ODFs of fluid b) are predicted. The remaining parameters of the far field are fitted to the vapor liquid equilibrium (VLE) data for fluid a) and again the VLE data for fluid b). Results are very good for both ODF and VLE for low to intermediate dipole moments.

In addition to these properties, the dielectric constant is predicted from the orientation data for the Stockmayer fluid with $\mu^* = 1.0$ and compared to molecular simulation data of Kohns [2]. The results are in good mutual agreement. Furthermore, the theory is applied to hydrogen chloride for which it shows better performance than literature models using PC-SAFT or PCP-SAFT.

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$A = -kT \ln Q$

SAFT models versus cubic models: evaluation and comparison of their actual performances

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In spite of repetitive criticisms mainly issued from the academic community, Cubic Equations of state (CEoS) that were derived from the seminal work of Van der Waals, appear nonetheless as reference models for people from industry working on the simulation and design of processes involving non-associating compounds. As a noticeable feature, CEoS models are nearly all parameterized in a similar way based on the application of critical constraints. As a result, pure-component CEoS have the capacity to provide accurate description of phase-equilibrium (vapor pressure, enthalpy of vaporization ...) and energetic properties as well (heat capacity, enthalpy ...) but, as main limitations, they fail in correlating liquid-density and isothermal-compressibility data.

On the other hand, SAFT-type EoS (that are issued from the Statistical Associating Fluid Theory) are receiving a considerable interest from the academic community for more than 20 years as they offer as main advantages:

- The capacity to account explicitly for association phenomenon,

- the possibility to get a coherent description of matter from the knowledge of molecular interactions and their – more or less empirical – quantification.

Beyond fashionable effects, this statistical theory is primarily popular because it makes it possible to build a bridge between atomic and macroscopic scales. It is well acknowledged that such models show accurate description of volumetric properties but overestimate pure-component critical pressures for the reason that they are not constrained to reproduce the experimental critical temperature and pressure (contrary to CEoS). Generally, SAFT parameters are indeed fit on vapor-pressure and liquid-density data.

It is often said that SAFT EoS over perform CEoS because of their stronger theoretical bases. In this study, it is shown that both types of models are mainly influenced by the parameterization method and in a less extent, by model foundations. An optimal and universal way to parameterize pure-component SAFT-type and cubic EoS is then proposed. It makes it possible to conclude that SAFT and CEoS exhibit the same performance for non-associating compounds.

Excess molar enthalpies of binary systems carbon dioxide + renewable solvent

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Renewable solvents have been attracted attentions as promising candidates of alternative solvents for green chemistry to replace toxic organic solvents and volatile organic compounds (VOCs). They can be easily produced from biomass feedstocks. Ones such renewable solvents, butyl levulinate and ethyl lactate, have excellent properties such as low toxicity, relatively low volatility, low viscosity, recyclability, high lubricity, flashpoint stability, and better flow properties under cold condition. They are used as additives for gasoline and diesel [1], flavorings in fragrance industries [1], pharmaceutical and food additive [2], and reaction solvents in the organic synthesis. Recently, mixtures of carbon dioxide (CO_2) and renewable ester have been paid much interests for applications to supercritical fluid extraction [3], gas anti-solvent (GAS) process [4], and preparation of mesoporous gelatin particles [5].

In the design and development of these processes, thermophysical properties of the mixtures CO_2 and these renewable ester are crucial. To our knowledge, vapor-liquid equilibrium (VLE) data of the system CO_2 + ethyl lactate have been reported by several authors [6, 7]. However, excess molar enthalpy (H^E) data are not available. In our previous works, the mixtures CO_2 + ester compound show a large heat effect in comparison to its behavior at low pressure near the critical point of CO_2 [8-10]. Therefore, H^E data is also important for the processes using CO_2 and renewable esters.

We studied the behavior of H^E for binary systems CO_2 + butyl levulinate or ethyl lactate near the critical point of CO_2. We determined the H^E of two systems at temperatures 298.15 and 303.15 K and pressures 5.0 -7.0 MPa using a flow-type isothermal microcalorimeter. Maximum about 8.0 kJ mol^{-1} of the large heat effect could be obtained as in the case of our previous works. The experimental H^E data were correlated using a composition-dependent equation and the Peng–Robinson equation of state with the conventional mixing rule. The prediction of H^E using two mixing rules, i.e., MHV1 and Wong-Sandler models, was also tested on the basis of the VLE data.

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$A = -kT \ln Q$

Can Cholinium Chloride form Eutectic Solvents with Organic Chloride-based Salts?

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The high melting point of a large number of organic salts with potential ionic liquid-like properties, hinders their applicability as solvents. Considering the success of cholinium chloride on lowering the melting temperature of several substances and its success on forming deep eutectic solvents, this work studies its mixing with organic chlorides to lower their melting points producing eutectic ionic liquids.

The solid-liquid phase diagrams for binary mixtures composed of cholinium chloride and ten organic halides were experimentally measured. Surprisingly, cholinium chloride presented, for all these systems, significant positive deviations from ideal liquid behaviour that restricted its ability to lower the melting points of these mixtures. Only for mixtures with ammonium chloride, tetramethylammonium chloride, bis(2-hydroxyethyl)dimethylammonium chloride or cholinium bromide was cholinium chloride able to significantly lower the melting point of the mixture, but without reaching values close to room temperature. For a better understanding of the results obtained, the solid-liquid phase diagrams of four alkylammonium chloride-based mixtures were experimentally assessed and used to show that these compounds are better than cholinium chloride at inducing negative deviations to ideality, thus forming deep eutectic solvents.

Acknowledgments

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Thermodynamics of Natural Gas Containing Organic Sulfur Species (OSS): Phase Equilibrium Measurements and Modeling Using the Cubic-Plus-Association Equation of State

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Natural gas and petroleum industries are dealing with raw materials containing variable concentrations of acid gases (CO_2, H_2S) and traces of OSS like mercaptans and dimethyl disulfide, dimethyl sulfide and many others. Treatment processes have to remove not only H_2S and CO_2 but also OSS and prohibited compounds because worldwide regulations for environmental protection are forcing the petroleum industry to decrease the sulfur content in petroleum fluids. The phase behavior of the organic sulfur species like mercaptans, dimethyl sulfide (DMS), dimethyl disulfide (DMDS) and COS is of interest in various applications in the chemical, oil, and gas industries. They can occur naturally in the environment and can also be present in numerous industrial gaseous streams dealing with petroleum, natural gas, some chemical industries like the pulp and paper industries. Herein we will present vapor-liquid equilibrium (VLE) data for methyl mercaptan (MM) + methane (CH_4), methyl mercaptan (MM) + nitrogen (N_2) and methyl mercaptan (MM) + carbon dioxide (CO_2), Dimethyl sulfide (DMS) + water (H_2O) and Dimethyl sulfide (DMS) + methane (CH_4) + water (H_2O), performed at three temperatures (303, 330, and 362 K) in the 1 to 8 MPa pressure range. A "static-analytic" method was used for performing all the measurements. The objective is to provide experimental VLE data for which no data are available in the open literature. These data will allow industry to model sulfur emissions. The new VLE data as well as VLE data of some binary systems from literature containing organic sulfur species + Hydrocarbon, organic sulfur species + Water and some ternary systems containing organic sulfur species in hydrocarbon and water have been modeled successfully with Cubic-Plus-Association (CPA) equation of state. Useful remarks are presented about the application of Henry's constant values to estimate binary interaction parameters of the CPA EoS for the description of whole vapor-liquid equilibria. The results using CPA EoS shows that, the cross association interactions in methyl mercaptan + water system and ethyl mercaptan + water system should be considered. In aqueous mixtures of higher mercaptans the consideration of such interaction does not improve the calculations, indicating that are rather weak.

$A = -kT \ln Q$

Modeling organic salts using the SAFT-γ Mie equation of state: Thermodynamic models and simulation benchmarks

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Thermodynamic modelling of electrolyte solutions proves particularly challenging for complex systems characterized by the presence of organic electrolytes, which are generally non-spherical molecules. SAFT-γ Mie [1,2] is a successful statistical thermodynamic framework to model bulk thermodynamic properties. SAFT-γ Mie is essentially the SAFT-VR Mie equation of state casted in a group contribution formulation, where each component can be constructed using functional groups that represent various molecular moieties. SAFT-VR Mie has been recently used to study ionic solutions [3] by incorporating the Mean Spherical Approximation (MSA) approach to account for the Coulombic interactions between ions in the presence of solvent molecules; the polar-polar and ion-polar interactions are implicitly treated with a separate Born solvation energy term. However, both of these electrostatic terms are limited to spherical molecules and further approximations are required to treat non-spherical species.

Molecular simulations have been widely used to assess the necessary approximations to develop statistical mechanical theories of fluids. In this work we compare the Coulombic contribution to the chemical potential predicted using the MSA approach against simulation data for model systems that incorporate the solvent explicitly. Estimating the chemical potential of charged molecules using traditional molecular simulation techniques is challenging. Thus, we have used the expanded ensemble transition matrix method [4] to run these calculations robustly and efficiently. The theoretical predictions were compared with simulation data to provide a better understanding of the implications of the assumptions employed within the SAFT-γ Mie electrolyte framework.

Finally, the methodology is applied to real systems like brine-CO_2 mixtures and short chain carboxylate salt solutions. The fitted models for these mixtures are characterized by good accuracy and can be used to model properties like salt and CO_2 solubility, vapor pressures and densities.

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From nano-emulsions to phase separation: Evidence of nano-segregation in (Alkane + Perfluoroalkane) mixtures using ^{129}Xe NMR Spectroscopy

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Abstract

In this work we demonstrate that mixtures of (hexane + perfluorohexane) above the upper critical solution temperature, segregate by forming domains at the nanometric scale.

^{129}Xe NMR spectra obtained for solutions of xenon in liquid mixtures of (hexane + perfluorohexane) as a function of temperature, suggest the existence of domains richer in the hydrogenated component, in which xenon "prefers" to be solvated. The average local concentration within the xenon coordination sphere is at least 0.05 mole fraction higher in hexane than the nominal concentration of the mixture. Atomistic molecular dynamics simulations support this analysis in excellent agreement with the experimental data. Additionally, ^{129}Xe NMR spectra in pure perfluoroalkanes allow a detailed analysis of the liquid structure, in sequence to that previously reported for the liquid alkanes.

It should be emphasised that nano-segregation is here observed in fluids governed exclusively by dispersion interactions, contrarily to other examples in which hydrogen bonding and polarity play important roles. Given its simplicity, this case study is thus prone to have a general impact in understanding the early mechanisms of segregation, phase separation and self-assembly.

$A = -kT \ln Q$

Statistical associating fluid theory for quantum fluids: He, Ne, H_2 and their mixtures

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Hydrogen, helium and neon are examples of quantum fluids, so named because they exist in the fluid state at sufficiently low temperatures for quantum effects to be significant. An accurate equation of state for mixtures of quantum fluids is crucial to model and optimize cryogenic processes such as in hydrogen liquefaction [1]. Quantum fluids can be described by classical statistical mechanics, provided that the classical interaction potential is modified with so-called Feynman—Hibbs corrections to model the particle-wave duality that becomes relevant at sufficiently low temperatures [2]. The resulting pair potential is temperature- and mass-dependent but, except for a few subtleties, one can still apply the Barker—Henderson perturbation theory used successfully in equations of state such as SAFT-VR Mie [3] and SAFT-γ Mie [4]. We present a new equation of state [5,6], which accurately reproduces the thermodynamic properties of particles interacting via Feynman—Hibbs-corrected Mie potentials. We fit and compare the new equation of state to experimental data, including the fascinating phase behavior of binary mixtures of quantum fluids. We also compare to results from Gibbs Ensemble Monte Carlo simulations to demonstrate the consistency of the perturbation theory in terms of representing the underlying potential.

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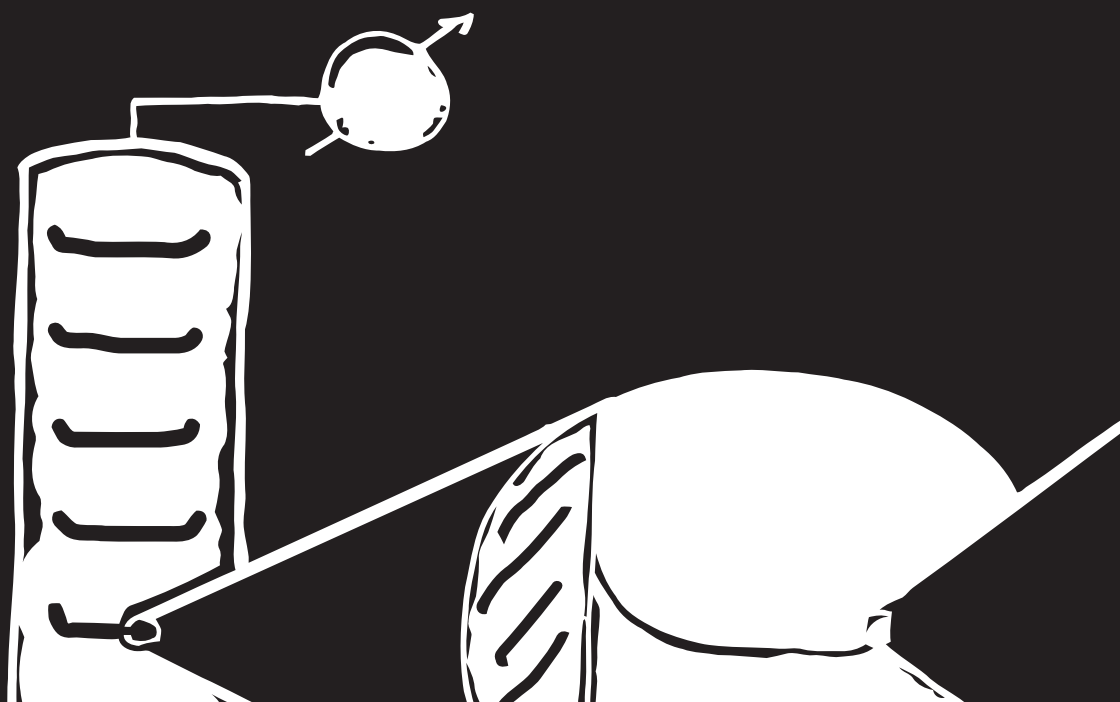
$$A = -kT \ln Q$$

Oral Presentations:
Interfacial and confined phenomena



High-Pressure Phenomena in Adsorbed Films: A New Route to an Experimental Determination of Effective Tangential Pressure

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High-pressure phenomena have been observed in many studies of adsorbed films on strongly wetting solid substrates. These include chemical reactions that normally require a high pressure (e.g. 10,000 bar or more), the formation of high-pressure solid phases and spectra indicating strong compression of the film. While it is possible to measure the pressure acting normal to the substrate surface, P_N, no method has been developed so far to measure the tangential pressure, P_T, parallel to the surface. However, this tangential pressure is of particular interest, since it is usually much larger than the normal pressure, and is the main driving force for high-pressure phenomena in these films.

While the normal pressure is uniquely defined for a planar surface, the tangential pressure at a point **r** is not uniquely defined at the nanoscale. In the commonly used 'virial-route' the average of the intermolecular forces acting in the direction parallel to the surface is obtained. The resulting tangential pressure then depends on the fraction of these forces that are assigned to a particular point in space, **r**. We show that by integrating $P_T(\mathbf{r})$ over a small region of space, roughly the range of the intermolecular forces, we obtain an effective tangential pressure that is unique and well-defined. The grand canonical Monte Carlo simulation results show that this characteristic integration range has negligible correlation with the wetting parameter, which denotes the strength of the solid-fluid interaction, and the characteristic length remains as a constant for large pores. Further investigation reveals that the characteristic length of convergence is related to the density distribution of adsorbed layers, which explains its weak dependence on the wetting parameter. Based on this characteristic length, we propose a new route, the '2D-route', to the effective tangential pressure free from the ambiguities in the definition of the 'virial-route' local tangential pressure. The only input parameter for this '2D-route' is the molecular cross-sectional area. In practice, we can obtain the input parameter by combining standard experimental adsorption data with a 2D equation of state derived from statistical mechanics. We expect this '2D-route' to be the first experimental route to the pressure enhancement in the adsorbed layers.

$A = -kT \ln Q$

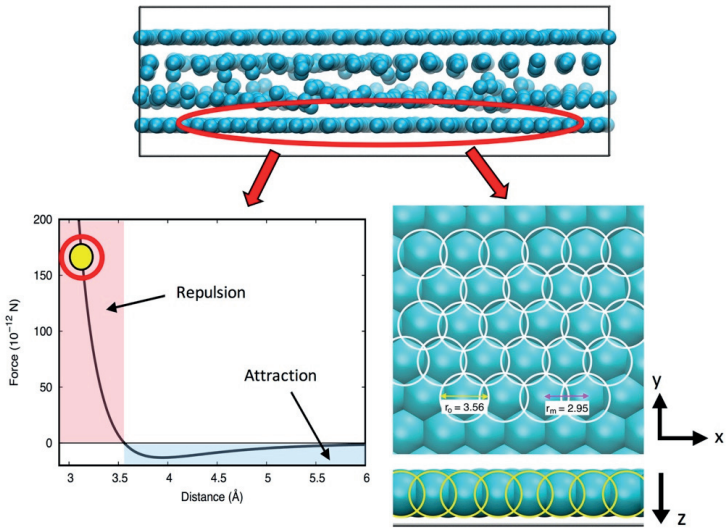

Figure 1. Simulation snapshots showing the quasi-2D layer near the slit-pore surface and the strong repulsion between argon molecules inside the layer [1].

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Enrichment at Vapour-Liquid Interfaces: Origin and Influence on Mass Transfer

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Interfacial properties play an important role, for example in separation processes in chemical engineering. In classical theory, a vapour-liquid interface is a two-dimensional object. In reality it is a region in which the density changes smoothly from its liquid bulk to its gas bulk value. While the total density changes monotonously from the bulk vapour to the bulk liquid, this does not hold for the number density of the components. The number density of the light boiling component can have a distinct maximum at the interface, which is considered here as enrichment. That enrichment would be an insurmountable obstacle to mass transfer according to the Fickian theory. In fact, it is shown in this work, that the enrichment has an influence on the mass transfer. The origin of the enrichment and the influence on the mass transfer is investigated by molecular theory (here: density gradient theory + EoS) and computer experiments for Lennard-Jones model mixtures.

Large enrichment is usually found in mixtures with a wide boiling behaviour which is in general favoured by large boiling point differences of the components and a low miscibility, e.g. mixtures where the light boiling component is supercritical or mixtures that exhibit a light boiling azeotrope. There is a relation of the enrichment with a wetting transition that is observed at VLLE phase boundaries. Upon approaching the three phase line, a precursor of the second liquid phase is observed in VLE in such systems. This precursor layer has similar thermodynamic properties (composition and density) as the second liquid phase that appears at the three-phase line. This is predicted consistently by computer experiment and molecular theory.

In a second part of the present work, the interfacial properties (surface tension, surface excess, enrichment, interfacial thickness) of 90 binary Lennard-Jones mixtures of different ratio of dispersion energies of two components $\varepsilon_2 / \varepsilon_1$ and the binary interaction parameter ξ in the modified Lorentz-Berthelot combination rule were investigated. A symmetry was observed regarding the interfacial properties of different mixtures in the $\varepsilon_2 / \varepsilon_1$, ξ space. This symmetry is put into a relationship with the symmetry of a conformal solution theory of the liquid phase.

In a third part, the mass transfer through the interface and the influence of the enrichment on the mass transfer is discussed by presenting results of non-equilibrium molecular dynamics simulations. The Lennard-Jones mixtures that were discussed above are therefore applied in two new simulation scenarios, a stationary and an instationary one. A mass flux through the vapour-liquid interface is imposed in both scenarios which enables an estimation of the mass transfer resistance of the interfacial region. The study reveals that the enrichment has an important influence on the mass transfer rates, which were found to be lowered by about an order of magnitude for scenarios with high enrichment.

$A = -kT \ln Q$

Active lubrication with ionic liquids

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Ionic liquids have been the subject of intense investigation in the last years. They feature high thermal stability and ionic conductivity, as well as good properties as lubricants. External electrostatic fields modify the structural and dynamical properties of the liquids, and potentially their performance as lubricants. The use of electrostatic fields might provide an approach to achieve tuneable lubricity. We have investigated the impact of confinement and electric fields on the lubrication performance of ionic liquids. This problem can be addressed using non-equilibrium molecular dynamics simulations and coarse-grained force-fields. The computational studies provide insight into the dependence of the friction force with the magnitude of the external fields, and clues in the quest of super-lubrication.

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Assessing Salt-Surfactant Synergistic effects on Interfacial Tension from Molecular Dynamics Simulations

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One of the common practices to reduce interfacial tension (IFT) between crude oil and formation water in Enhanced Oil Recovery (EOR) is the application of surfactants [1-3]. When the IFT is reduced, the capillarity forces within the reservoir are weakened and the mobility of the crude oil is increased, thus improving production. For this reason, many efforts have been carried out in the last years trying to reduce water/oil IFT to ultralow values. Generally, an effective way to achieve an ultralow IFT is by using a combination of surface-active compounds [4-5] (e.g., a surfactant with a co-surfactant), who act cooperatively to enhance their individual effects. However, salinity is also present in crude oil reservoirs, which is capable of interacting with polar molecules or functional groups. These interactions can change the thermophysical properties of solutions significantly, and their comprehension is of vital importance to propose and/or develop new surface-active compounds that optimize the oil recovery under different brine conditions. In fact, there are several experimental works where a cooperative effect between different salts and surfactants was observed, even achieving ultralow IFT under some conditions [6-8]. From these experimental works, different mechanisms were proposed to explain the synergy between salts and surfactants. Unfortunately, the information provided by molecular simulation in this area is scarce.

In this contribution we apply Molecular Dynamics simulations to evaluate the effect of three different salts (i.e., NaCl, $CaCl_2$ and $MgCl_2$) on the IFT of a water/dodecane model system with the presence of non-ionic surfactants at a concentration under the Critical Micelle Concentration. We intend to reproduce the salt-surfactant synergistic effect observed through experimental observations and shed some light from a molecular point of view on the different mechanisms and phenomena produced in the salt-surfactant synergistic effect.

From our simulation results (Figure 1), we observed that the IFT of a water/dodecane system is increased by the addition of all the studied salts. However, the IFT of the water/surfactant/dodecane system can be reduced for certain salt/surfactant combinations. According to our calculations we observed that cations feel a relatively strong attraction towards the polar head groups of surfactants affecting their coordination shell. This modification also changes the packing pattern of surfactant headgroups potentially affecting the value of IFT. Additionally, surfactants can change their orientation at the interface, driven by cation – head group interactions allowing surfactants to occupy the interface more effectively. Moreover, the difference in cation – head group and anion – head group interactions produce a small electric double layer close to the surfactants that polarizes the interface probably affecting IFT.

$A = -kT \ln Q$

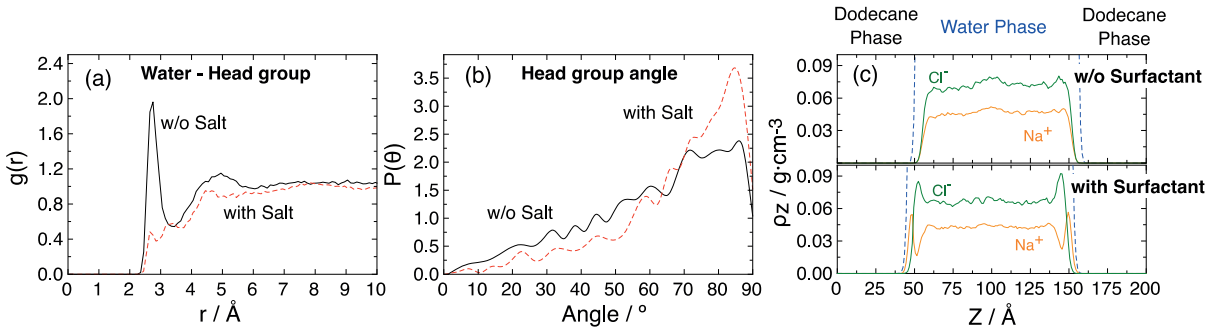

Figure 1. Example of different magnitudes that changed due to the salt-surfactant synergistic effect: (a) shows the Radial Distribution Function between water and surfactant head groups in absence and presence of salt; (b) represents the angle of the surfactant head group with respect to the interface perpendicular axis with and without salt; and (c) shows the molecular distributions along the z-direction of the simulation cell, where one can see the formation of an electric double layer of NaCl at the interface in the presence of surfactants. In (a) and (b) the dashed and the solid lines refer to the system with and without salt respectively, whereas in (c) the dashed line correspond to the density of water and the solid lines correspond to the Na^+ and Cl^- densities according to the inserted labels.

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Microscopic structure and interfacial properties of confined fluids in porous materials of various geometries

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The study of adsorption, for systems presenting an interface between a fluid and a solid, can be undertaken theoretically with the statistical physics formalism, at the microscopic scale. The objective of my PhD thesis is to propose a molecular modelling of fluids like methane, confined into porous materials of various geometry. This way, the theoretical framework is directly developed at the microscopic scale and its results are compared with molecular simulations. At the macroscopic scale, the theoretical formalism leads us to obtain the same results than experimental measurements of isotherm and heat of adsorption.

First of all, we consider the main results of the classical density functional theory (cDFT), which describes the fluid density as a local function, to deal with inhomogeneous fluids. A molecular equation-of-state has also to be considered as a reference. The statistical associating fluid theory (SAFT) [1], formulated with the free energy of the system has been chosen. Then, the interaction potential of a molecule such as methane is described by a hard-sphere surrounded with an attractive range. The hard-sphere is described with the fundamental-measure theory (FMT) [2], using weighted densities, corresponding to functions defined in a point of the space, but depending on the immediate neighbourhood of this point. Weighted functions are necessary for inhomogeneous fluids modelling confined at the microscopic scale. The study undertaken from the FMT led us to define new weighted functions, allowing us to describe fluids of attractive spheres [3]. With this new theoretical framework, it is necessary to use approximations of the free energy functional. Four different approaches are proposed allowing to predict the spatial distribution of the fluid density (see Figure 1). The first approximation considered is a mean-field applied on the pair correlation function of the attractive contribution to the free energy. This approximation is very common in cDFT applications, but the density profiles and the excess adsorbed quantities we obtain are not good quantitatively. Three other approximations are tested, considering correlations beyond the mean-field, in order to improve the microstructure description. Thermodynamic sum rules are also considered to test the consistency of the formalism. Because the profiles are described at the microscopic scale, Monte Carlo molecular simulations have been performed in order to evaluate their quality by comparison, for systems defined with an equivalent potential. Thereby, one of the new formulations of the inhomogeneous fluid has been selected for its superiority among the others. Finally, this study shows the importance to take into account weighted densities in the pair correlation function, to catch the correct behaviour of the attractive contribution to the free-energy of the fluid [4].

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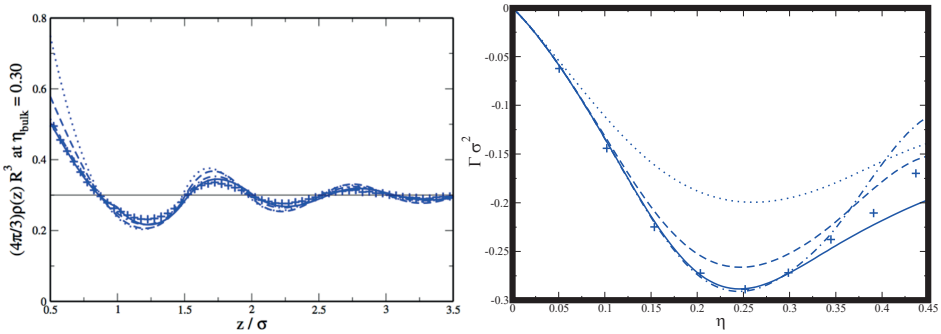

Figure 1. *Left*: density profiles of a square-well fluid with four approximations on the pair correlation function: mean-field (dotted), bulk (dashed), weighted according to the diameter of fluid molecules (dotted-dashed), weighted according to the radius (solid line), and Monte Carlo simulation data (points). *Right*: excess adsorbed quantity Γ computed from density profiles.

Then, special attention has been given to the modelling of the solid. Indeed, most of the existing approaches use analytical expressions of weighted densities to that extent, which limits studies to porous media with simple and ideal geometries. In particular, an important number of cDFT models are limited to planar pores, where the density varies along one dimension of the space only. In our work, we propose to compute weighted densities with fast Fourier transforms in a three-dimensional space, for any pore geometry. The consequence of this approach is that a numerical discrete space is considered. As usual in cDFT, the fluid-solid resulting interaction is described by an external potential, but here, we have to take into account the curvature of the solid in the three-dimensional discrete space. This implies the use of mathematical results from discrete geometry, in order to correctly compute interactions between the fluid and any discrete solid surface. In particular, a special attention has been given to the attractive part of the fluid-solid interaction. This new combination of density functional theory and discrete geometry has allowed us to study methane adsorption in cylindrical pores of silica. To do so, experimental measurements have been performed on new silica substrates specially synthetized and characterised for this thesis. Theoretical predictions were compared with experimental isotherms and heat of adsorption. It allowed to validate the whole formalism presented in the thesis and developed both for the fluid and the solid modelling from the microscopic to the macroscopic scale.

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Augmented scaled particle theory

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The original motivation for scaled particle theory (SPT) is to derive a simple equation of state for a bulk hard sphere (HS) fluid [1]. It was recognized later that SPT provides also the surface tension of a HS fluid near a spherical hard wall. This surface tension contains three terms, i.e., the surface tension at a flat hard wall and two contributions due to surface curvatures (mean and Gauss curvatures). Investigations of more complex inhomogeneous systems, e.g., fluids adsorbed in various porous materials, arouse increasing interests in interfacial properties. Although early investigations go back to Tolman [2], it might appear surprising that our knowledge about curved interfaces is still quite limited. Mecke and co-workers have proposed a general framework, named as morphological thermodynamics, to account for more complex surface morphology (see e.g., [3]). According to Hadwiger theorem in integral geometry, the morphological thermodynamics postulates that the thermodynamic potential of an inhomogeneous system is determined only by four terms, i.e., one bulk contribution proportional to system's volume and three surface contributions proportional respectively to surface area, mean and Gauss curvatures of the interface. Within the framework of SPT, the chemical potential for creating a spherical cavity inside a fluid is assumed to have this form. The foundation of morphological thermodynamics has been questioned recently. From molecular dynamics simulations, B.B. Laird et al found that contributions from the terms beyond the four Hadwiger's terms are not negligible [4]. By examining the diagrammatic expansion of surface tension, I. Urrutia [5] and H. Hansen-Goos [6] revealed also non vanishing contribution from a non Hadwiger term. From these recent advances, it is clear now that the thermodynamic expression for chemical potential in the original SPT does not account for the contribution from non Hadwiger terms. One can raise naturally the following questions. Is it possible to include some non Hadwiger terms in SPT? How this can be carried out in a simple way, e.g., obtaining still analytic results? These issues are addressed in this work and we obtained an augmented version of scaled particle theory (ASPT). ASPT allowed us to obtain analytical results for all the bulk and surface thermodynamic properties for a one- or a multi-component HS fluid but significantly improves the accuracy with respect to the original SPT. We will also show how to use the ASPT results for surface tension in morphological thermodynamics to study complex confined fluids.

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$A = -kT \ln Q$

Interfacial tension of water/crude oil. Direct comparison of experiments and dissipative particle dynamics

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Chemical Enhanced Oil Recovery (cEOR) techniques consist in injecting into a petroleum reservoir an ASP (Alkaline/Surfactant/Polymer) formulation. This formulation aims at mobilizing the oil trapped in the reservoir by reducing the water/crude oil interfacial tension (IT). Molecular simulations are capable of providing information about such process and phenomena occurring at the molecular and mesoscopic level. It is then necessary to have a consistent workflow to provide realistic models of crude oils able to reproduce the macroscopic thermodynamic properties of such complex fluids.

In this work we have used mesoscopic simulation methods, Dissipative Particle Dynamics (DPD) and coarse grained Monte Carlo, to quantitatively predict the water/crude oil IT. These two methods are based on a coarse-grained model in which different molecular entities are represented by a particle (bead). An approach to parametrize the interactions between beads has been developed and validated using liquid-liquid ternary systems [1] in addition to a thermodynamic model (SRK-MHV2-UNIFAC). We propose a workflow able to reproduce compositions of bulk phases and to quantitatively predict the IT. In addition, we are able to identify the main type of functional groups required to model complex hydrocarbon mixtures as can be seen in Figure 1.a.

A representation methodology of crude oil has been developed based on different experimental data (distillation curve, elemental analysis, mean average molecular weight and Saturate/Aromatic/Resin/Asphaltene –SARA– analysis) measured for a 32 API crude oil. The crude oil was separated according to the number of carbon atoms into two fractions: $C20^-$ and $C20^+$. A lumping approach was applied to the $C20^-$ fraction [2] and a stochastic reconstruction approach was employed for the $C20^+$ fraction [3]. A crude representation was obtained with only 13 representative constituents including some large resin molecules as can be seen on Figure 1.b. DPD simulations of the proposed crude oil model provides after a production run (average of four independent simulations of about 70ns each with L_x=L_y=19.3nm x L_z=38.8 nm and 162 000 beads) an IT value of 30.05±0.61 mN/m which is in good agreement with the experimental value of 29.3±0.2 mN/m @ 25°C. This allows us to enhance our study from a molecular point of view. We have analyzed the local density profile of the representative crude oil as illustrated in Figure 1.c. Our results show that two species (pyridine and thiol) belonging to the $C20^+$ fraction tends to accumulate at the interface and acts as natural "surfactant" for the crude oil. We have validated this observation by computing independently the IT of the $C20^-$ and $C20^+$ fractions with water. In this case we observe a lower value for the heavy fraction (26.70±0.54 mN/m) compared to the value obtained for the light fraction (38.05±0.24 mN/m). We have tested the robustness of our approach by performing several tests including: 1) changing all the species of the $C20^+$ in agreement with the stochastic reconstruction approach where asphaltene molecules are included, 2) modifying the strength of the intramolecular interactions of the large molecules (bending and some improper angle for poly-aromatic structures). Test #1 reveals a slight increase of the IT (32.22±0.62 mN/m) with respect to the first representation, but still in good agreement with the

experimental result. Test #2 has no influence in the final value of the IT from a statistical point of view. Work is in progress to extend our methodology to model the IT of other crude oil with different API grades and asphaltene contents.

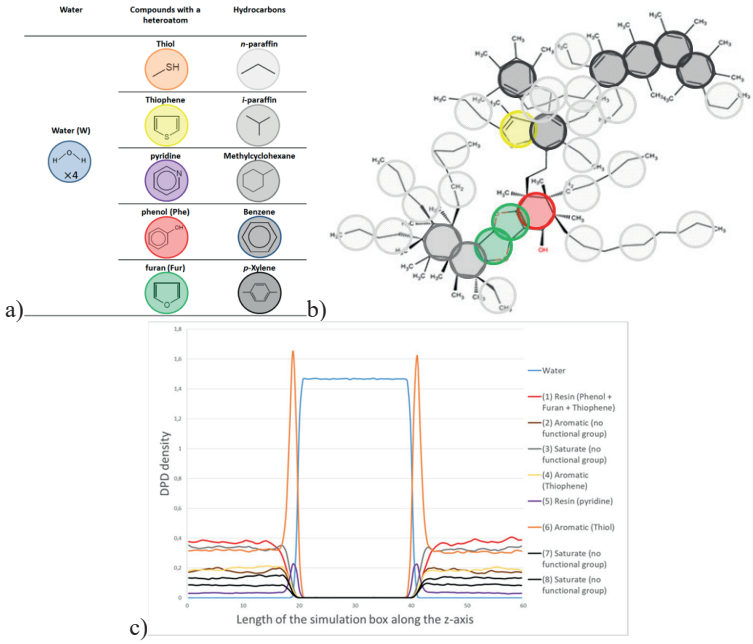

Figure 1. a) Different DPD beads used in our work to model the crude oil components, the coarse grain level given by the size of the bead corresponding to 4 water molecules. b) Mesoscopic representation of a resin structure present in the realistic model of a crude oil with a concentration of 5.43% w/w. c) Density profile (in DPD units) of the water-crude oil interface containing only the main constituent of the mixture. Two species show an enhancement of their concentration at the interface (thiol and pyridine).

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$A = -kT \ln Q$

Novel Design of Zeolitic-Imidazolate Frameworks for Membrane-Based Gas Separations

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Zeolitic-imidazolate frameworks, is a subfamily of metal-organic frameworks (MOFs), and are considered as highly promising membrane materials for gas separation. Their separation efficiency can be tailored through structural manipulation at the molecular level: the parts comprising the basic tetrahedral unit (Figure 1), can undergo complete or partial replacement. These replacements offer the means to control the size of the aperture connecting the framework cages, and subsequently, to control the separation performance for targeted mixtures.

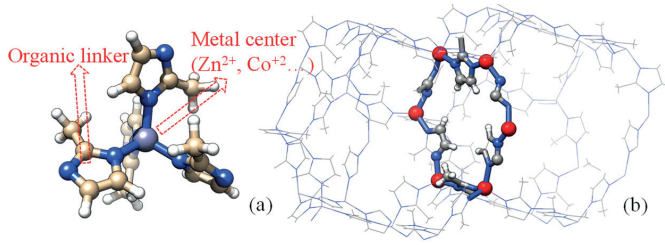

Figure 1. (a) The basic tetrahedral unit of the ZIF-8 topology, where a metal center bridges organic linkers and (b) the aperture bridging the cages of ZIF-8.

We used ZIF-8, the most studied ZIF topology for gas separations, and we adopted metal and linker replacement, which resulted to the following ZIF analogues:

1. Cd^{2+} - based (namely CdIF-1), Co^{2+} - based (namely ZIF-67) and Be^{2+} - based (namely BeIF-1) [1],
2. a mixed-linker ZIF-8 with methylimidazolate (mIm) and benzinimidazolate (bim) linkers [2] (namely ZIF-7-8).

We developed force fields for all the cases studied, with the help of density functional theory (DFT), which we employed in molecular level simulations. The five frameworks (considering the original ZIF-8) exhibit a sequence of descending aperture size (Figure 2). The diffusivities and solubilities of He, H_2, O_2, CO_2, N_2 and CH_4 were calculated, in order to evaluate the permeabilities. The ideal selectivity is the ratio of the single gas permeabilities of two species. The example of Figure 3 highlights the exceptional performance of our modifications against competing materials.

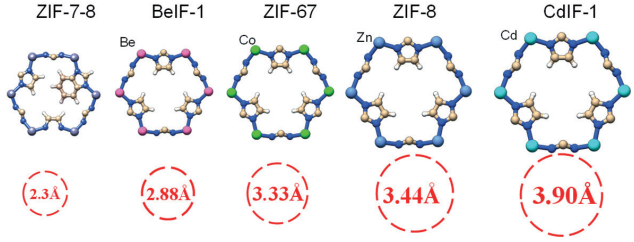

Figure 2. Aperture size control with linker and metal replacement

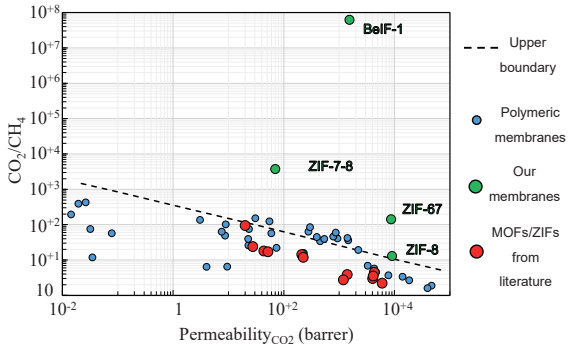

Figure 3. Robeson plot for CO_2/CH_4 selectivity of the proposed ZIF-8 modifications against membrane data from literature.

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$A = -kT \ln Q$

Nanodrops of a discotic liquid crystal in contact with an attractive wall: A Monte Carlo study

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We present results obtained by Monte Carlo computer simulations of a nematic drop of a liquid crystal formed by oblate molecules in presence of an unstructured attractive wall. As in previous studies [1,2], the fluid interaction is modeled by a Gay-Berne potential with molecular elongation $\kappa=0.5$. The other parameters of the potential are such that the drop presents homeotropic anchoring [3]. By fixing the reduced temperature $T^*=0.5$ and the number of molecules N=32000, we study the contact angle of the drop with the surface by varying the intensity of the wall-fluid interaction, paying special attention to the orientational order inside the drop. A disclination ring, as well as biaxiality, is observed for contact angles larger than $\pi/2$, similar to the reported results for free drops [2].

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Interfacial properties of the water + hexane mixture along three-phase line

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Introduction. The physical description of the interfacial properties of aqueous n-alkane mixtures constitutes a challenging task for applied thermodynamics due to the interplay between the sharp asymmetry in the intermolecular forces of the pure fluids and the need to continuously progress between two essentially pure phases at their interface. Water + n-alkane [$n \geq 2$] mixtures are classified as Type III [1], characterized by the fact that a branch of the critical line ends in an upper critical end point (UCEP) of a three-phase line, while the other one diverges to the high-pressure range. This implies that at subcritical conditions, mixtures of this type can display, in addition to vapor-liquid and liquid-liquid equilibria, vapor-liquid-liquid equilibria (VL_1L_2E). In the latter case, interfacial behavior is governed by the interplay of three interfacial tensions (IFT) at each of the possible interfaces, namely γ^{VL1}, γ^{VL2}, γ^{L1L2}. Assuming that $\gamma^{VL1} > \gamma^{L1L2} > \gamma^{VL2}$ these IFTs are interrelated by the expression: $\gamma^{VL1} \leq \gamma^{VL2} + \gamma^{L1L2}$. The equality denotes the situation of total (or perfect) wetting of the L_2 bulk phase in L_1V interface, whereas the inequality describes the situation of partial wetting of the L_2 bulk phase in L_1V interface. The transition from total to partial wetting (or vice versa) is denoted the wetting transition. [2]
In this work, we present an approach that combines experimental determinations and molecular dynamics simulations to describe interfacial properties (*i.e.*, interfacial concentrations, interfacial tension and wetting transition) for the case of water + hexane mixture along the VLLE line.

Experimental determinations and molecular dynamics simulations. The IFT between a drop of an α phase surrounded by a β phase ($\gamma^{\alpha\beta}$), where α, and β denote L_1, L_2 or V, is measured by a pendant drop tensiometer (IFT-10, Temco Inc., USA). This device uses the geometry information of the drop (*i.e.,* the equatorial and sessile diameters of the drop) and the corresponding bulk densities (ρ^{α}, ρ^{β}) to calculate $\gamma^{\alpha\beta}$. In this work, ρ^{α}, and ρ^{β} are measured using a DMA 5000 densimeter (Anton Paar, Austria). Molecular Dynamics (MD) simulations of the mixture at VLLE are performed in the canonical ensemble using a coarse-grained (CG) model. In the CG model, the molecules are represented by a set of "super"-united-atoms interacting through a Mie potential. Water is modeled as a single isotropic sphere [3], whereas hexane is described as two tangent Mie spheres [4]. In order to guarantee the simultaneous formation of the three interfaces of interest (*i.e.,* $L_1 - L_2$, $L_2 - V$ and $L_1 - V$), the rectangular cuboid simulation cell MD was elongated in one Cartesian direction; i.e., $L_x = L_y > 10\,\sigma$ and $L_z = 8\,L_x$. The concentration profiles were evaluated along the z-direction, and the IFTs were calculated from the Hulshof integral [5] which uses the diagonal elements of the Irving-Kirkwood pressure tensor. [6]

Results. Figure 1 shows a snapshot of a MD configuration at 350 K. From this snapshot it is possible to observe the VLLE and its three interfacial regions. The corresponding concentration profiles (ρ_i) along the z - coordinate are displayed in Figure 2.

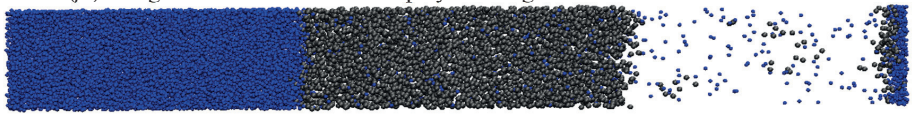

Figure 1. Snapshot of the VLLE of water + hexane at 350 K. (●) water; (●●) hexane

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Figure 2 displays the high surface activity (accumulation) of hexane at the L_1V interface, whereas water shows a low surface activity in the L_2V interface. Figure 3 shows the results of the IFTs as a function of the temperature. From these results, it is possible to observe the fair agreement between experimental data and MD simulations. In this figure, an extra curve corresponding to $\gamma^{L2V} + \gamma^{L1L2}$ was also included to predict the wetting behavior: the crossing point of this curve with the extrapolation of the γ^{L1V} data provides an estimate of the wetting transition (T_w) of 347.2 K, whereas MD predicts T_w = 350.83 K, in close agreement with the value of 345.4 K reported by Bertrand et al. [7]. From Fig. 3, it is also possible to observe that as the temperature increases, $\gamma^{L1V} \rightarrow \gamma^{L1L2}$ and $\gamma^{L2V} \rightarrow 0$. Further extrapolating of IFT experimental values, it is possible to estimate the temperature where $\gamma^{L1V} \simeq \gamma^{L1L2}$ and $\gamma^{L2V} \simeq 0$, which corresponds to the UCEP temperature, 540 K commensurate with the value of 517 K calculated from theoretical predictions of IFT [8] and the experimental value 495.82 K [9].

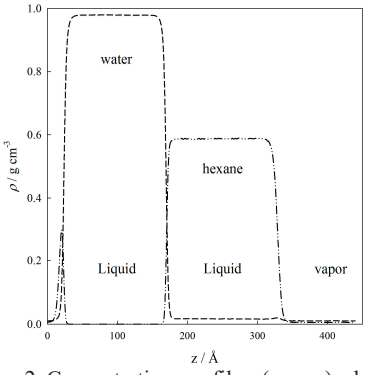

Fig. 2 Concentration profiles ($\rho_i - z$) along interfacial region at VLLE of water + hexane at 350 K.

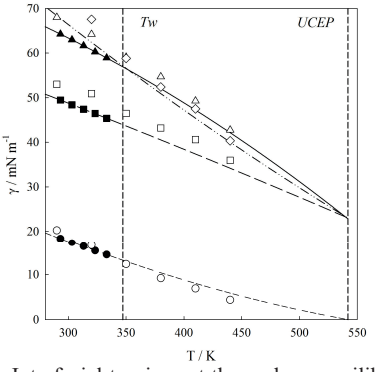

Fig. 3. Interfacial tensions at three-phase equilibrium for water + hexane. Experimental data: ●, γ^{L2V}; ■, γ^{L1L2}; ▲,γ^{L1V}. Quadratic extrapolation: - - -, γ^{L2V} ; – –, γ^{L1L2}; —, γ^{L1V}; -·-·-, $\gamma^{L2V} + \gamma^{L1L2}$. MD results: ○, γ^{L2V}; □, γ^{L1L2}; △,γ^{L1V}; ◇, $\gamma^{L2V} + \gamma^{L1L2}$.

Conclusion. Interfacial tensions along three-phase equilibrium for water + hexane binary mixture have been experimentally measured and determined from molecular dynamics simulations. Both approaches show a fair agreement with each other. On the basis of the experimental results it is possible to estimate both the wetting transition (347.2 K) and UCEP temperature (540 K), which are close to literature values. MD simulations additionally provide the concentration profiles along the interfacial region, and the surface activity of water and hexane.

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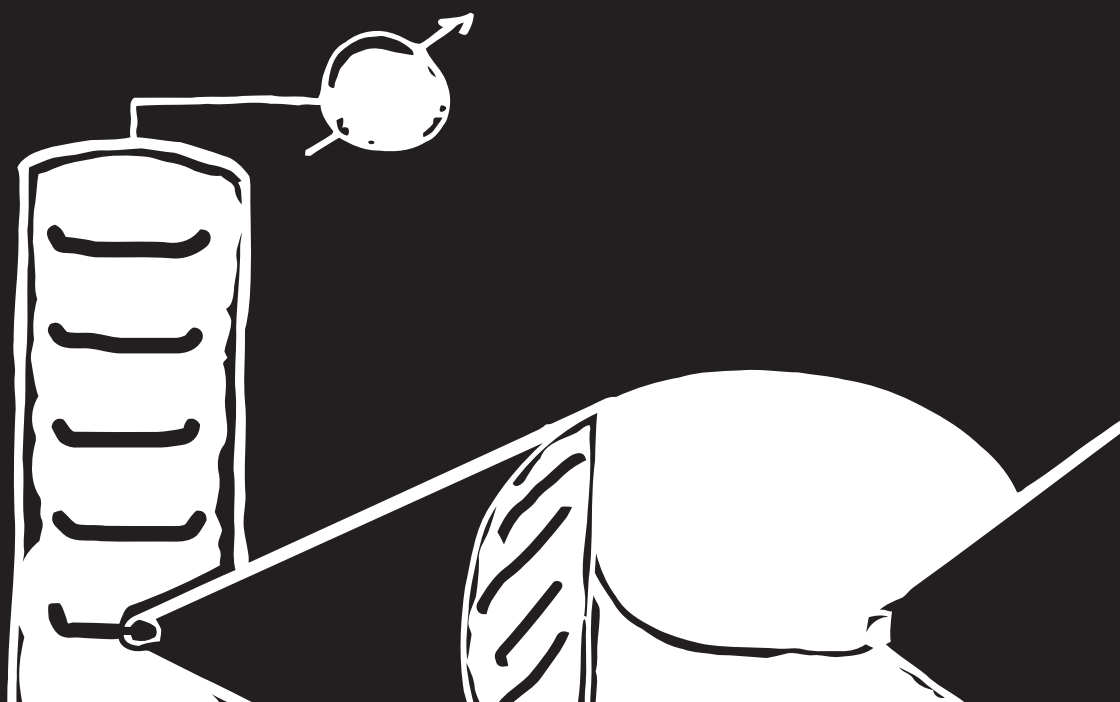
Oral Presentations: Carbon capture and other industrial applications



Computationally Efficient Molecular Simulation of Chemical Reaction Equilibrium and its Application to CO_2 Reactive Absorption

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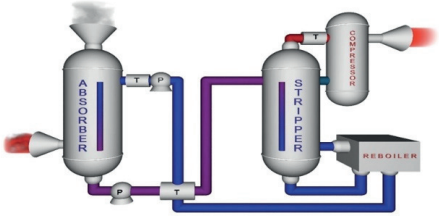

Post-combustion carbon capture from CO_2 point sources by reactive absorption in a suitable solvent is a relatively mature technology, and is being used in existing installations [1]. Most solvents have been based on aqueous monoethanolamine or similar solvents. The main drawbacks have been identified as the energy cost of solvent regeneration and high fluid viscosities. The search for improved solvents has involved many reactive absorption studies involving experiments and their modelling by means of macroscopic thermodynamic models whose parameters are fitted to experimental data [2]. It is important to note that these models should be primarily regarded as correlations rather than predictions. We also note that different sets of models are required to predict thermodynamic and transport properties.

The discovery of potentially improved solvents can be facilitated by a more predictive approach that minimizes the need for experiments. An alternative is the use of molecular simulation methodology. One version of this approach entails the use of a classical force-field model for the species involved, from which both thermodynamic and transport properties may be obtained by suitable simulation algorithms. The primary difficulty in implementing the predictions arises from simulating the chemical reactions modelling the complex CO_2 – solvent interactions. Thus, although many molecular dynamics simulation studies have been performed to study the structural [3] and mixing [4] properties of the solutions, the continuing challenge is to model the chemical reactions in a computationally efficient manner. The goal is to predict the equilibrium CO_2 solubility, the solution species concentrations resulting from chemical reaction, and the CO_2 partial pressure in contact with the solution. Once the equilibrium composition is known, the enthalpy of solution is readily calculated; in addition, the transport properties may be separately simulated using the same force field.

The Reaction Ensemble Monte Carlo (REMC) algorithm [5,6] has been the principal methodology for the molecular simulation of chemical reaction equilibria. Although it has been successfully applied to many systems of relatively simple molecules [7], its routine implementation for systems involving complex molecules, strong intermolecular interactions, high densities, and low temperatures is not easily formulated, since its computational efficiency depends on the specific nature of the molecules involved. For all but the simplest of systems, it requires the incorporation of special MC techniques, such as replica exchange, configurational bias, continuous fractional component, and related approaches [8,9].

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The recently developed Reaction ensemble Molecular Dynamics (ReMD) algorithm [10] overcomes the requirement for a system-specific approach by combining macroscopic free energy minimization principles with any widely available Molecular Dynamics molecular simulation software package, which results in a rapidly convergent and generally applicable algorithm for modeling the reaction equilibrium composition of even highly nonideal systems. The algorithm is based on a fixed-point minimization algorithm that entails the iterative calculation of reference states for ideal solution approximations to the system chemical potentials.

In this talk, we describe the algorithm and demonstrate its use for CO_2 reactive absorption simulations involving both aqueous alkanolamine and ionic liquid solvents.

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Design of Phase Change Solvents for Post-Combustion CO_2 Capture based on Molecular Thermodynamics

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One of the most affordable technologies for post-combustion CO2 capture in absorption/ desorption processes is the use of aqueous amine solutions that usually achieve high degree of CO2 removal. The main drawback of this sort of processes has been the high consumption of energy-oriented to solvent recovery [1]. One alternative for overcoming this drawback is the use of lipophilic solvents (LS) [2] which consist of miscible solute-solvent mixtures (aqueous solutions of amines) which undergo liquid-liquid phase separation over certain temperature range. The CO2 captured is concentrated in one of the phases which can sent to the stripper while the aqueous lean amine phase can be sent back directly to the absorber , with the result that the overall energy requirement is reduced. Multiple combinations of potential phase-change solvent candidates can be proposed and there is a need for combined consideration of numerous thermodynamic criteria prior to selecting the solvent with optimum capture features. Moreover, during the absorption process complex chemical reactions, which need to be taken into account, take place. The accurate prediction of these phenomena is a demanding test for any thermodynamic model. To address these challenges, we use the SAFT-γ Mie group contribution approach[3],[4] which enables the prediction not only solvent-CO2-water vapor-liquid-liquid equilibria for selected solvents but also the compositions of the ionic species present in the system as a consequence of the speciation reactions that take place during the CO2 absorption[5].In this work, we present the results obtained for the chemisorption of CO2 by means aqueous solutions of a specific type of cyclohexyl amines, which exhibit interesting features as phase-change solvents. The developed model allows us to predict important properties linked to the nature of the solvent such as low critical solubility temperatures (LCST), as well as to describe the phase behavior of the reactive LS + CO2 + H2O ternary and quaternary mixtures and to study the evolution of the phase equilibrium behavior varying the Pressure and Temperature conditions.

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High Pressure Thermodynamic Properties Data of Complex Mixtures and Their Application to Liquified Natural Gas (LNG) Industry

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Thermodynamic properties data presently available are insufficient to confidently design gas gathering and processing equipment at pressures near system critical points and cricondenbars. Poor understanding of supercritical fluid properties at these pressures lead to over-design and higher operating and capital costs, where current uncertainties in fluid property predictions typically lead to equipment over designs of 15% or more. In this work, we present a wide range of experimental density, heat capacity and surface tension data made for different binary and ternary mixtures relevant to LNG processing. For this purpose, specialized state of art apparatuses were designed and validated over the temperature range (200 to 423) K at pressures above the mixture critical points, up to 35 MPa. Single and bubble-point measurements were then made over the temperature range (203 to 423) K, pressures up to 35 MPa and different compositions, with a combined overall standard uncertainty of 0.3% for density, 5% for heat capacity and 5% for surface tension. Mixtures studied include ($CH_4 + C_3H_8$), ($CH_4 + C_3H_8 + CO_2$) and ($CH_4 + C_3H_8 + C_7H_{16}$); in the last of these the heptane contents was up to 15 mol %.

Different procedures for preparing and loading the mixtures were used depending on the experimental apparatus [1]. The standard uncertainty in the mole fraction of the prepared mixtures were taken to be $u(x) = 0.02$. A vibrating wire apparatus (Figure 1) was constructed to measure the viscosity of homogenous pure fluids or mixtures [2]. The wire was operated in steady-state mode and the amplitude of the wire's vibration was monitored by observing the electromagnetically induced voltage. Isobaric heat capacities of liquid and gas mixtures were measured using a specialized differential scanning calorimeter (DSC) apparatus [1]. This instrument has previously been used for measurements of heat capacities, enthalpies of phase transitions and phase transition temperatures. The densities of the binary and ternary mixtures were measured with a commercial, high-pressure vibrating tube densimeter (VTD), (Anton Paar, DMA HPM) [1]. The VTD is designed to measure the density of liquids and gases at pressures up to 140 MPa and temperatures up to 473 K using a U-shaped vibrating tube of 2 mL total volume. The surface tension was measured using a capillary rise method, allowing for the calculation of surface tension based on equations developed from a force balance across the liquid meniscus [3].

Experimental data were compared with the prediction made by existing reference models for these mixtures. The relative deviations of the measured densities from those calculated using the GERG 2008 reference model [4] implemented in REFPROP v10.0 span between (-2.5 to 4) %, while the relative deviations of the measured heat capacities from those calculated using the GERG 2008 model in REFPROP v10.0 span between (-5 to 20) % for all mixtures. The relative deviations are systematically dependent on mixture density and heptane content, which may indicate that there could be a systematic error in the model and that further tuning is required. The Parachor model implemented in REFPROP 9.2β and the Macleod-Sugden Advanced implemented in Infochem Multiflash with the GERG-2008 equation of state (EOS) represented most of the surface tension experimental data within the measurement uncertainty. In many cases the discrepancies between the predictions of different engineering models for these mixtures was large, and the high quality data allowed erroneous but often widely-used models to be identified. The data enabled the

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development of new and improved models, to be implemented in process simulation software, so that the fluid properties needed for equipment and process design can be predicted reliably which is essential for LNG industry. This in turn minimized environmental impacts and enabled reduced capital and operational expenditure by the LNG industry.

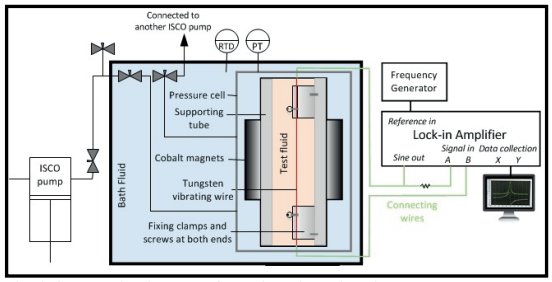

Fig. 1. Schematic diagram of the vibrating wire viscometer assembly.

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Physicochemical characterization of Deep Eutectic Solvents as alternative solvents for gas recovery

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Nowadays, the reduction of greenhouse gas (GHG) emissions into the atmosphere has become a priority for most governments and international agencies, due to the devastating consequences caused by their impact on climate change. Research on new sustainable technologies are mainly focused on carbon dioxide (CO_2) capture, although there is an increasing effort in replacing some compounds with high global warming potential (GWP), such as hydrofluorinated gases (HFCs), commonly used in refrigeration. For CO_2 capture, the most common process is the absorption in aqueous amines, although their corrosiveness and volatility are drawbacks that generate an important energy penalty for their application at large scale. As far as the recovery of HFCs is concerned, there is not a developed technology to efficiently recover them, being incineration the current methodology employed in waste agencies.

In the seek for sustainable alternatives, Deep Eutectic Solvents (DESs) have received recent attention. DESs are systems formed between a Hydrogen Bonding Acceptor (HBA), which is normally a halide salt, and a Hydrogen Bonding Donor (HBD), which is a neutral complexing agent. The hydrogen-bonding effect causes a decrease of the melting point than that of the individual components. DESs are non-volatile, biodegradable and do not react with water, becoming good candidates for gas absorption [1]. However, the mechanisms behind their physicochemical properties are not well understood yet, becoming a constraint for the design of separation processes involving DESs. Advanced equations of state or models considering hydrogen bonds are very suitable for an accurate thermodynamic characterization. In particular, SAFT-type equations have proven to provide reliable results for complex mixtures where hydrogen bonds are present.

In this work, the soft-SAFT EoS [2], an accurate variant of the original SAFT is used to calculate the thermodynamic properties of several [Tetraalkylammonium][Chloride] and [Bromide]-based DESs, including the solubility of several gases in them, so as to assess the potential of DESs for gas separation applications. A consistent and transferable molecular model approach is used, explicitly considering the molecular parameters of each individual compound forming the DES [3,4], overcoming the limitations of the one-compound approach. The choice of the number of association sites is assessed combining previous experience with the analysis of the molecules charge density distribution using the COSMO-RS software. The molecular parameters are fitted to the density of the DESs at different ratios. As a result, a unique set of parameters for each compound allows the description of a eutectic mixture, independently of its composition. This methodological approach, (summarized in Figure 1) based on transferable parameters, enables a qualitative prediction of gas phase equilibria in these solvents.

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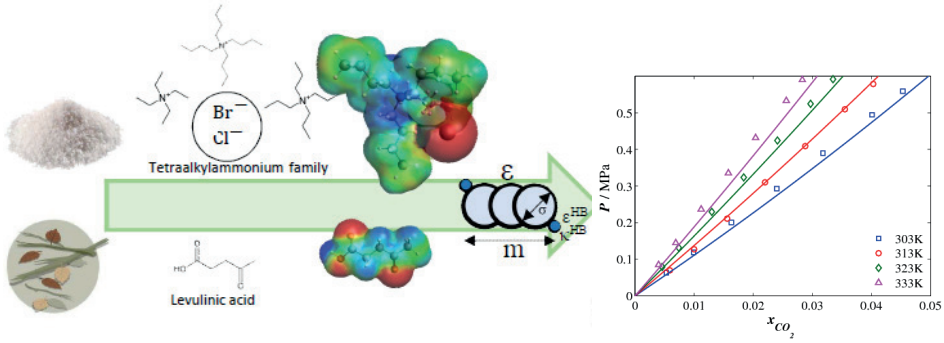

Figure 1. Graphical abstract of the contribution presented. Charge distribution of the [Tetraalkylammonium][Bromide] and [Chloride] with Levulinic Acid, estimated with COSMO-RS + molecular model built with soft-SAFT to describe CO_2 solubility in these DESs.

Acknowledgements

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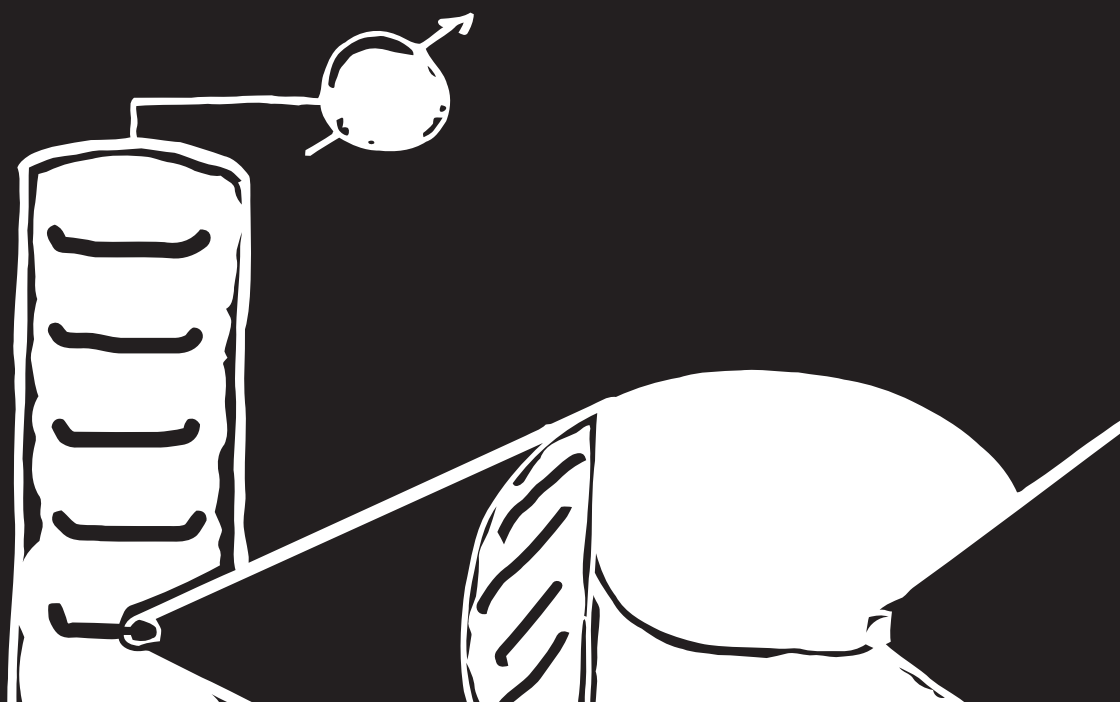
Oral Presentations:
Engineered self-assembly



Modelling the Formation of Complex Morphologies via Block-Copolymer Self-Assembly

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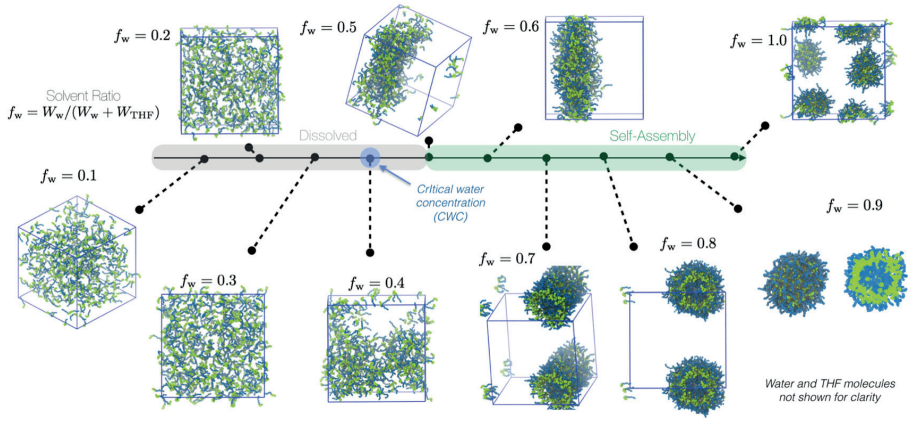
Novel routes for the synthesis of hierarchical porous materials have recently highlighted the relevance of methacrylate-based copolymers, which in mixtures of selective and common solvents are able to spontaneously self-assemble into colloidal size aggregates such as vesicles or more complex mesophases including polymeric nanospheres with bicontinuous internal structure (BPNs) [1]. Nevertheless, the phase behaviour of this family of structure directing agents is only partially understood [2]. In this regard, computer simulations can be effective to provide a clear insight into the physical laws governing the associated kinetics and equilibrium. Motivated by their essential role in the preparation of complex self-assembled morphologies, we have developed transferable and computationally efficient coarse-grained (CG) models that reproduce the behaviour of a family of methacrylate-based copolymers in aqueous and organic solutions, melts and interfaces [3]. The CG potential derivation is based on a hybrid thermodynamic-structural approach which incorporates macroscopic and atomistic-level information. The target properties in the parameterisation are those that govern the self-association mechanism (i.e. interfacial tension, chain conformational entropy and excluded volume repulsive interactions [4]).

By direct molecular simulation, using our CG models, we obtain phase diagrams of methacrylate-based copolymers in mixtures of THF and water (Figure 1), which act as common and selective solvents, respectively. In particular, we focus on the morphological transformations of self-assembled aggregates as a function of the selective/common solvent ratio, polymer concentration and chain architecture. Our results demonstrate that in addition to chain related properties, solvent correlations play a fundamental role on determining and stabilising the



polymer structures.

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Figure 1. Morphological phase diagram of PEO_6-b-$PBMA_4$ at 10wt% in mixtures of water and THF for different solvent ratio (*fw*). In the simulation snapshots the PBMA and PEO blocks correspond to green and blue beads, respectively.

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Development of a Coarse-Grained Model of Graphene Oxide for use in Aqueous Solution and Hydrated Membranes

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Graphene oxide (GO) is an appealing material for water purification applications such as desalination or nuclear effluent treatment. This is due to its favourable 2D geometry (maximising the surface area to volume ratio) and an abundance of oxygen-containing functionalities that provide active sites for adsorption and stabilise GO in aqueous solution. GO can be used to treat water in two separate ways; either as an adsorbent where contaminants bind directly to the oxygen-containing functionalities [1], or by using the precursor GO flakes as building blocks for multi-layered materials that can be used in membrane filtration [2].

Recently the development of GO materials for water purification has accelerated, in part driven by the availability of realistic atomistic models [3]. However, atomistic simulations of GO are severely limited with respect to both the time and length scales that can be accessed; the size of flakes that can be considered in atomistic simulations (~10 nm) is much smaller than that of the real material (100 – 500 nm). A coarse-grained (CG) representation is required to move beyond existing spatiotemporal limitations to establish structural, thermodynamic and mechanical properties and guide the design of GO materials for water purification. For instance, in the case of adsorption, it is not yet fully understood how to maximise adsorption capacities and stabilise GO dispersions, and in the case of membrane filtration, knowledge of how to simultaneously maximise water permeation and solute rejection rates is urgently required.

In this work, a coarse-grained model of GO was developed, using a 4:1 mapping scheme, for use in simulating aqueous GO dispersions and hydrated GO membranes. The CG potential was initially parameterised using a small reference GO flake and an iterative Boltzmann inversion approach. Reference distribution functions were first obtained from atomistic simulations in which water molecules were clustered, using the k-means algorithm, to ensure compatibility of the developed potential with the four-bead polarisable Martini water model. Separate particle types were defined for pristine graphene, plane-oxidised graphene and edge-terminating carboxylic acid (protonated and deprotonated) particles.

Using the developed model and a potential of mean force approach the aggregation and self-assembly of GO flakes was simulated and flake size effects investigated. The transferability of the potential (flake oxygen content and distribution) was investigated and it was demonstrated that the oxygen content, pH and ionic strength significantly affect the aggregation-dispersion behaviour of GO flakes in aqueous solution, as well as the interlayer structure of GO membranes. The developed potential could be combined with other available CG potentials (e.g. Martini model) in order to investigate other materials such as graphene-polymer composites. In addition, the general approach outlined in this work could be extended to other systems involving novel 2D materials.

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Multi-scale Modelling of Bio-inspired Silica Materials

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Porous silica materials play a crucial role in a myriad of applications, but despite their success, relatively little is known about how they self-assemble from aqueous solution [1]. Understanding the synthesis mechanisms of porous materials is crucial to enhance our ability to control and design their properties, but it is also highly challenging as it relies on a delicate interplay of chemical reactions, self-assembly and phase equilibrium, taking place over a wide range of time and length scales. This talk will report recent advances by our group in the development of a new multi-scale modelling approach to describe the synthesis of nanoporous silica materials, that bridges time and length scales from the quantum to the mesoscale levels. We have applied this model to describe the synthesis of bio-inspired silica. Inspired by the natural process of biosilicification, this strategy makes use of pH-responsive polyamine templates to produce porous silica materials under much more environmentally friendly conditions (ambient temperature and pressure, near-neutral pH) than currently employed in industry [2].

Our simulations of the synthesis of mesoporous silica have revealed unprecedented details of the molecular-level interactions that control the process. The addition of silica to an aqueous surfactant solution initially gives rise to micelle size increase and micelle fusion, promoting a shape transition from spherical to rod-like aggregates. The strong adsorption of silicates at the micelle surface facilitates silica polymerisation. Once silica oligomers are present in the system, they act as multi-dentate binders inducing the formation of a hexagonally-ordered mesophase [3]. It is this mesophase that ultimately determines the pore network structure of the solid, upon further condensation and template removal. Our results conclusively demonstrate that the "neutral templating route", which has been tacitly accepted by the scientific community, is not viable under the experimental synthesis conditions. Instead, the mechanism hinges on charge-matching interactions between precursor molecules [4]. These predictions have been confirmed by recent experimental data for this system [5], paving the way for computational design of this exciting new class of materials. Our multi-scale model not only correctly describes experimental observations, but also makes useful predictions for future design of these materials.

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Depth and Interfacial Fluctuations in Multi-Component Gel-Phase Lipid Bilayers

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The barrier function of human skin is known to be localized to its outermost layer, the stratum corneum (SC), which is composed of a dense lipid matrix surrounding dead skin cells (corneocytes). Since the lipid matrix presents the only continuous path through the SC, determining the link between composition and structure is essential for understanding barrier function. While the chemical makeup of the SC lipids is known, the molecular level details of the structure is not, in part due to the fact that over 14 unique ceramides of varying chain length, along with cholesterol, and free fatty acids, have thus far been identified. As such, experiments often consider simplified mixtures of synthetic lipids, whose composition can be precisely controlled, in order to gain insight into this complex system. However, even simple systems can lead to different hypotheses (e.g., whether two-tailed ceramide lipids adopt a hairpin or extended conformation in lamellar structures) due to the inability to precisely locate different lipid species and their confirmations. Molecular simulation is an important complement to these experimental studies, as simulation provides a direct 3D molecular-level resolution and precise control over composition.

We present both atomistic and coarse-grained (CG) molecular dynamics simulations of simplified mixtures of SC lipids, namely cholesterol, free fatty acid, and ceramides. Atomistic simulations of pre-assembled bilayer structures are used to probe the impact of the individual lipid components on structure and examine the role of ceramide tail length [1]. CG MD simulations are used to examine self-assembled structures that complement the atomistic studies. The CG force fields were parameterized using the multi-state and multi-ensemble iterative Boltzmann inversion method (MS-IBI) [1] based on simulation data from fully atomistic models [3]. The CG results examine structural differences between bilayer and multilayer structures, and due to their computational efficiency, allow a larger range of parameters to be explored, including the role of free fatty acid chain length. The CG results also demonstrate that the intramolecular conformations of the ceramides are dependent on the lipid composition of the system, where increasing the number of lipid components gives rise to a greater fraction of extended ceramide conformations, helping to elucidate the 3D structure of these mixtures.

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$A = -kT \ln Q$

Self Assembly of SW Trimer Particles by Discrete Molecular Dynamics Simulation

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Studies about self-assembling spheres and dimers are now abundant in the literature,[1] less so of more complicated elements such as trimers.[2] Here we analyse the rich phase behaviour and structure formation of a class of trimers made up by hard-spheres, HS, and square wells, SW. The types considered are made of i) three square wells, SW-SW-SW, ii) two square wells and one hard sphere, with two subtypes: SW-HS-SW and SW-SW-HS, and iii) one square well and two hard spheres, also with two subtypes: SW-HS-HS and HS-SW-HS. The spheres have all the same diameter σ.

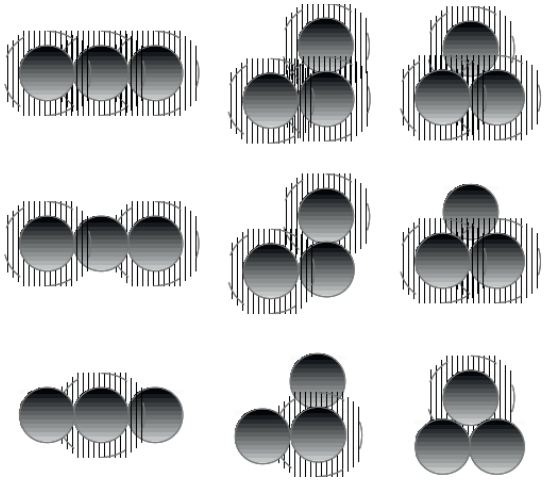

Figure 1. Main trimer types considered in this work. The inner spheres are hard and the shaded spheres portray SW attractions-

Of particular interest is the systematic study of these systems as two main features are varied: the first is the range λ of the SW interactions, which is varied between λ = 2 and λ = 1.125, and the second is the 'bond angle', i.e. the angle made by the two bonds with the central sphere, which is taken as 180º (linear configuration), 120º (open angle), 90º (rectangular) and 60º (equilateral). The systems were studied by the Discrete Molecular Dynamics method in the NVT ensemble.[3] The phase separation was obtained by the 'slab' or 'drop' procedure and the various structures determined by direct inspection and cluster analysis.

Variation of the bond angle induces a radical change in the possible vapour-liquid, V-L, phase separation, whose extension in the temperature axis is enhanced for some configurations while it is inhibited for others. The V-L separation is destroyed by the appearance of different types of structures by the trimers. Variation of the SW range also produces strong effects. The longer ranges λ = 2 are necessary for the, SW-HS-HS and HS-SW-HS trimers to exhibit V-L coexistence, whereas for the shorter λ = 1.125 even the SW-SW-SW trimer exhibits phase separation.

The appearance of structures (small clusters, micelle-like and tubular arrays) is promoted in those trimers that show a more marked anisotropy in their attraction, in itself produced by the presence of repulsive HS elements that tend to restrict the attraction for certain angles only.

Acknowledgement. This work was supported by project Fronteras de la Ciencia FDC 2015-2 1450 of CONACYT, México.

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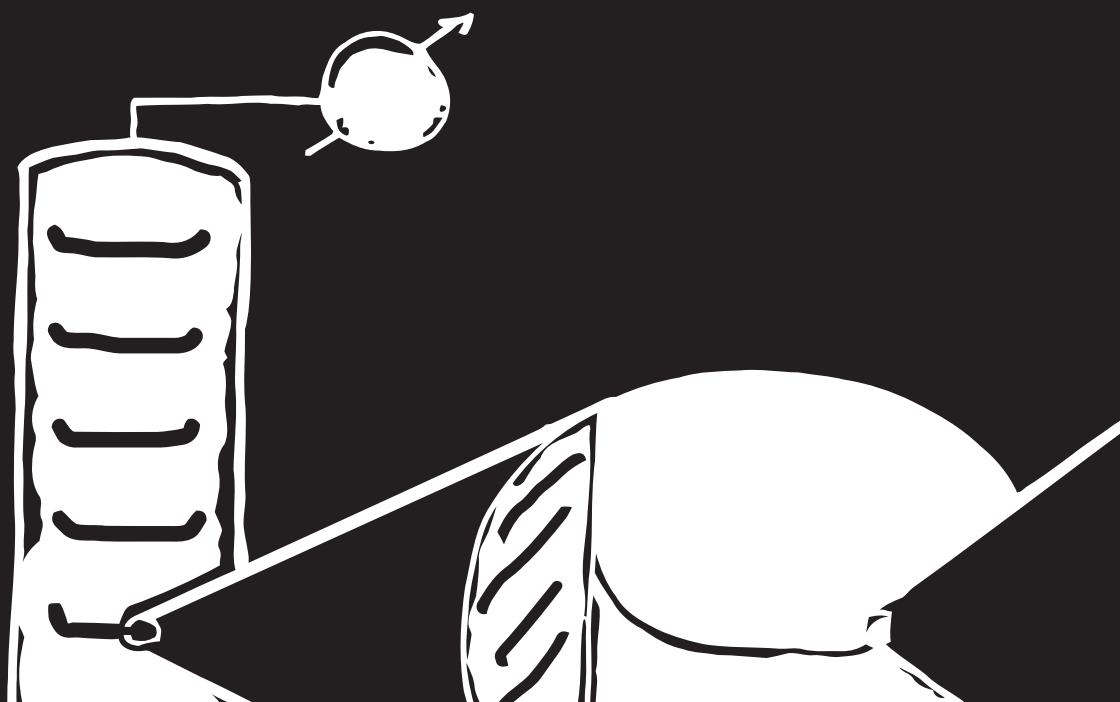
Oral Presentations:
Non-equilibrium thermodynamics



Heat Flux Beyond Fourier's Law

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It has been known for some time, though not widely so, that the heat flux for a liquid under shear involves additional couplings apart from the well-known Fourier law which is proportional to the temperature gradient. This is true in the linear regime, arbitrarily close to equilibrium [1-3]. In this work, we use nonequilibrium molecular dynamics (NEMD) to explore the effect of shear flow on heat flux [4]. By simulating a simple fluid in a channel bounded by tethered atoms, the heat flux is computed for two systems: a temperature driven one with no flow and a wall driven, Couette flow system. The results for the temperature driven system give the Fourier's law thermal conductivity, which is shown to agree well with experiments.

Through comparison of the two systems, we quantify the additional components of the heat flux parallel and normal to the walls due to shear flow. To compute the heat flux in the flow direction, the Irving-Kirkwood equations [5] are integrated over a volume, giving the so-called volume average form, and they are also manipulated to get expressions for the surface averaged and method of planes forms [6-12]. The method of planes and volume average forms are shown to give equivalent results for the heat flux when using small volumes.

The heat flux in the flow direction is obtained consistently over a range of simulations, and it is shown to vary linearly with strain rate, as predicted by theory. The additional strain rate dependent component of the heat flux normal to the wall is obtained by fitting the strain rate dependence of the heat flux to the expected form [12].

As a result, the additional terms in the thermal conductivity tensor quantified in this work should be experimentally testable.

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$A = -kT \ln Q$

Tracer transport in slowly-relaxing supercooled liquids and glasses

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Dynamic coupling of small penetrants to slow, cooperative relaxations within crowded cells, supercooled liquids, and glassy polymer matrices has broad consequences for applications ranging from drug delivery to nanocomposite processing. Interactions between the constituents of these and other disordered media alter the cooperative relaxations, but their effect on penetrant dynamics remains incompletely understood. We use molecular dynamics simulations, supplemented by dynamic x-ray scattering experiments, to probe the effects of matrix structure and dynamics on the transport and localization of penetrants. Using molecular dynamics simulations, we show that the motions of hard-sphere tracer particles probe differences in local structure and cooperative relaxation processes in attractive and repulsive glassy liquid matrices with equal bulk packing fractions and long-time diffusivities [1]. Coupling of the tracer dynamics to collective relaxations in each matrix affects the shape of tracer trajectories, which are fractal within the repulsive matrix and more compact in the attractive. These results reveal that the structure of relaxations controls penetrant transport and dispersion in cooperatively relaxing systems and provide insight into dynamical heterogeneity within glassy liquids. Matrices at higher volume fractions, by contrast, do not structurally relax on long time scales, but remain out of equilibrium and evolve via a slow aging process. In these systems, tracers can instead become localized within the disordered structure of the matrix. We investigate the transport and localization of tracer probes in a glassy matrix as a function of relative size using dynamic x-ray scattering experiments and molecular dynamics simulations [2]. The quiescent alpha-relaxations of tracer particles evolve with increasing waiting time t_w. The corresponding relaxation times increase exponentially at small t_w and then transition to a power-law behavior at longer t_w. As tracer size decreases, the aging behavior weakens and the particles become less localized within the matrix. These localized dynamics are coupled to the matrix elasticity until the tracers delocalize at a critical size ratio $\delta_0 = 0.38$. Localization does not vary with sample age even as the relaxations slow by approximately an order of magnitude, suggesting that matrix structure controls tracer localization when the penetrant dynamics are well separated in time from those of the matrix.

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Negative thermophoretic force in the strong coupling regime

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Negative thermophoresis (a particle moving up the temperature gradient) [1, 2, 3] is a somewhat counter-intuitive phenomenon which has thus far eluded a simple thermostatistical description. In this letter, we propose a mechanism that describes the advent of a thermophoretic force acting from cold to hot on systems that are strongly coupled to a non-isothermal heat bath (see ref. [4] for a recent survey). When a system is strongly coupled to the heat bath, the macrostate energies ε_j become temperature-dependent. This adjustment of the energy levels allows the system to take heat from the environment $+d(\varepsilon_j)$ and return it as work $-d(T\cdot d\varepsilon_j/dT)$. This effect can make the temperature-dependence of the effective energy profile non-monotonous. As a result, particles may experience a force in either direction depending on the temperature.

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$A = -kT \ln Q$

Continuum models and nonequilibrium molecular dynamics simulations of melting at the nanoscale

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The development of nanodevices is driving ongoing efforts to describe heat transfer at the nanoscale. Understanding the ultrafast heating and phase change of nano-thin films is of great importance for a new generation of microelectronic devices such as phase change memories, optical circuits and flexible displays [1, 2]. The ability to manipulate thermal energy can be crucial to nanodevice performance [3] and a lack of temperature regulation can lead to melting and device failure [4]. Understanding nanoscale heat transfer and phase change is therefore crucial for current and future applications of nanotechnology.

Classical heat transfer theory, based in the continuum approach (or continuum theory), offers a well known straightforward description of phase change processes without the need of computer simulations. Presumably, classical heat transfer theory breaks down at length scales of the order of the phonon mean free path and time scales smaller than the heat flux relaxation time [5,6]. However, in the case of phase change processes, these length and time scales are yet to be determined accurately and will vary depending on the material. An atomistic approach such as molecular dynamics (MD) can provide a very accurate description of the thermal state of a physical system containing tens of thousands of atoms. Therefore, nonequilibrium MD simulations provide a route to assess the accuracy of the classical continuum models to describe phase change at the nanoscale.

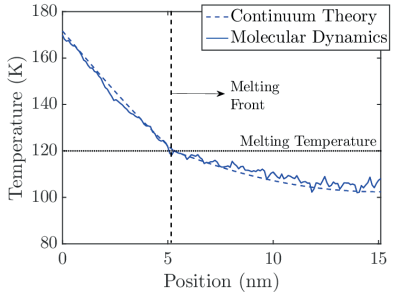

Figure 1: Temperature profiles for a melting nano-slab from nonequilibrium MD simulations and continuum heat transfer theory [7].

In this talk, we will present our recent results on the study of transient melting at the nanoscale using both continuum theory based on the heat diffusion equation and nonequilibrium MD simulations [7]. We will show how for simple atomic solids and sufficiently large times and length scales, the temperature profiles predicted from continuum theory show excellent agreement with MD simulations (see Fig. 1). Unexpectedly, we identify an intermediate time scale (larger than the heat flux relaxation time where continuum theory presumably breaks down) where continuum

theory deviates from the MD simulations. We will rationalize this results in terms of the activated nature of the melting process. We will close the talk by introducing new MD simulation results for the water-ice system and the corresponding comparison with continuum theory.

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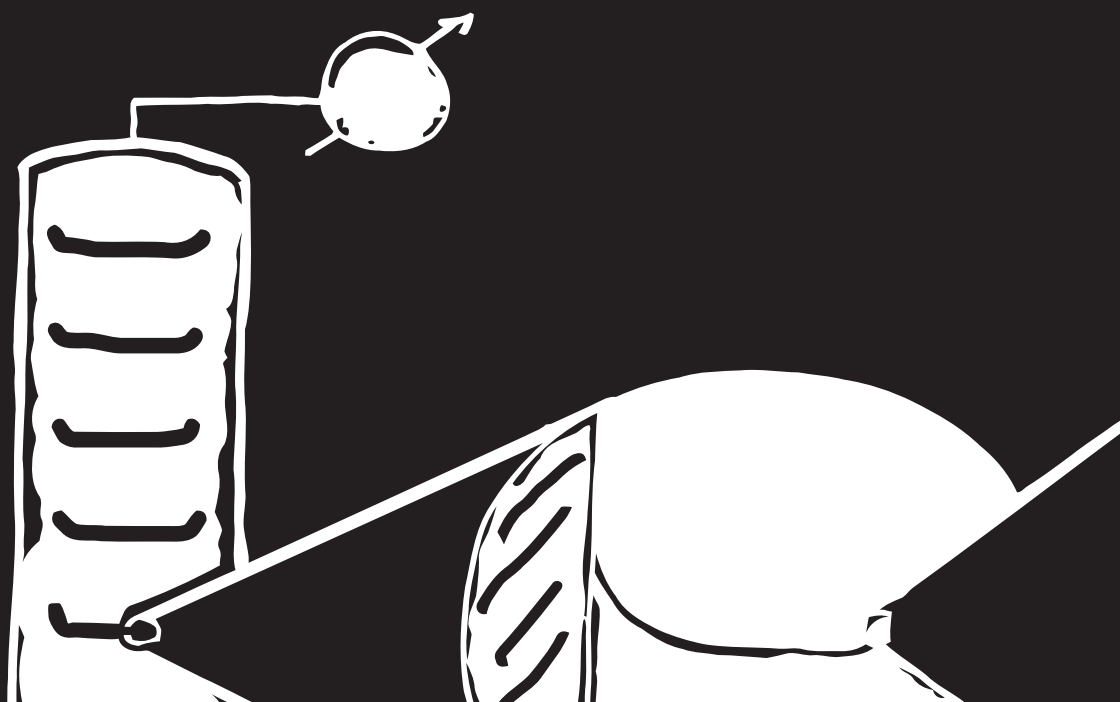
Short Oral Presentations: Advances in Molecular Simulation



Designing thermal responsive systems; unraveling the interactions between triblock-copolymers and surface-active ionic liquids by computer simulations

Germán Pérez-Sánchez[1], Filipa A. Vicente[1], Nicolas Schaeffer[1], Inês S. Cardoso[1], Sónia P. M. Ventura[1], Olivia N. Sobek[2], Miguel Jorge[2] and João A. P. Coutinho[1,]*

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Palabras clave: Pluronic, coarse-grain model, surfactants, cloud point, molecular dynamics simulations.

The outstanding characteristics of ionic liquids (ILs) and liquid triblock copolymers (TCs) known as Pluronics enhance the design of liquid thermo-responsive systems. Promising applications of such systems include the extraction of valuable biomolecules, drug delivery nanocarriers, recovery of pharmaceuticals from waste water among others. However, the nano-scaled interactions directing aggregation in such systems are complex and experimentally difficult to determine.

Coarse-Grained Molecular Dynamics (CG-MD) simulations, with the transferable MARTINI force field, can address such complex systems.[2] However, only a few MD studies were developed to date. Furthermore, such studies focused on specific TCs, with the consequent loss of transferability to other TCs.

In this work, a CG model for TCs in aqueous solutions was developed.[3] TCs are constituted by sequences of polyoxyethylene-polyoxypropylene-polyoxyethylene - (PEO)n(PPO)m(PEO)n and polyoxypropylene-polyoxyethylene-polyoxypropylene - (PPO)m(PEO)n(PPO)m, where the polar character increases with the amount of PEO and the apolar with the PPO units. In this regard, four archetypical TCs: two normal, L-31 and L-35 and two reverse, 10R5 and 17R4, were chosen owing to their diverse PEO/PPO content and distribution. The model was validated against experiments developed in our laboratory bearing in mind their applications as a thermo-responsive system. Our CG-MD approach captures the essential characteristics, especially at the cloud point (CP) temperature in which the system separates into two phases and provides a molecular-level

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interpretation of the intricate behavior observed in experiments. The CG-MD simulations presented in this work rationalise the impact of PEO and PPO content (mainly the amphiphilic character) and distribution (micelle surface shape) in the vicinity of the CP. In particular, our CG-MD simulations demonstrate, for the first time, the pronounced impact of the formation of physically cross-linked micelles in reverse TCs at the CP.

The impact of adding surface active ILs (SAIL) such as 1-methyl-3-tetradecylimidazolium chloride - [C_{14}mim]Cl and tributyltetradecylphosphonium chloride - [$P_{4,4,4,14}$]Cl, was also evaluated in this study.[4] A set of different Pluronic/SAIL mixtures in aqueous solution were analyzed over a wide range of temperatures and concentrations. The MD simulations show the essential role of the SAILs in the Pluronic micelle self-assembly, the formation of mixed micelles and the intricate interactions between them around the CP temperature. Imidazolium- and phosphonium-based SAILs depict a quite different behavior at the CP temperature. The phosphonium system presents a lower CP as a result of how the SAIL is arranged in the micelle surface to form mixed Pluronic/SAIL micelles. The screened charge of the SAIL head group seems to be essential in the very distinct thermo-response of both types of Pluronic/SAIL mixtures found in our laboratory. This suggests that mixtures of Pluronics and SAILs are preferable for designing thermo-controlled solvents. The properties of the selected pluronics and SAIL in the mixture, as well as the temperature or the concentration of each component can be used to control the thermal-response of the system.

***Acknowledgements*:** This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, FCT Ref. UID/CTM/50011/2019, financed by national funds through the FCT/MCTES", and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement. The authors are also grateful for the national fund through the Portuguese Foundation for Science and Technology (FCT) for the doctoral grant SFRH/BD/101683/2014 of F.A. Vicente. S.P.M. Ventura acknowledges FCT for the contract IF/00402/2015 under the Investigador FCT 2015. GPS knowledges the research contract under the project CENTRO-01-0145-FEDER-000005: SusPhotoSolutions: Soluções Fotovoltaicas Sustentáveis. NS acknowledges financial support by BATRE-ARES project (ERA-MIN/0001/2015) funded by ADEME and FCT.

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Thermodynamics of supersaturated steam:

TIP4P/Steam interaction model and equation of state

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According to AIPWS (Int. Assoc. for Properties of Water & Steam) documents, there is a continuous demand for research of thermodynamic properties of supersaturated steam – the working agent in steam turbines. The problem is that no experimental data from this region are available and extensions of empirical equations for stable water are unreliable. Further progress can thus go only via molecular simulations and molecular based theory.

It is well known that the common/popular non-polarizable models of water fail to describe the low density phase for a simple reason: they all use the dipole moment of water molecules adjusted to liquid properties and are not thus able, in principle, to reasonably estimate even the second virial coefficient. Polarizable models must therefore be used. There are three main problems associated with this approach: (i) because of cluster formation, the generation of simulation data for supersaturated steam is not straightforward and requires certain simulation tricks, (ii) necessity to devise a scheme to reconcile the simulation data for a model system with real steam, and (iii) to develop a molecular-based theory which can use only data from the stable phase but can reproduce also the data in the metastable phase.

We will briefly review the results of the first two problems and then focus on the development of a new non-polarizable TIP4P-type model and a theoretical equation of state.

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$A = -kT \ln Q$

The thermodynamic factor: The key to understand complex diffusion behavior in fluid mixtures

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Most separation processes in chemical engineering, such as distillation, absorption or extraction, are affected by diffusion. In recent years, molecular modelling and simulation has become an alternative tool not only to accurately predict dynamic properties of fluids, but also to interpret experimental data because it offers access to microscopic details which are often inaccessible with experimental techniques. In preceding work of our group [1,2,3], it was shown that transport properties of pure fluids, binary and ternary mixtures of non-polar to hydrogen-bonding species can be accurately predicted with simple, non-polarizable molecular models.

We present the results of a molecular simulation study of fluid mixtures, where complex diffusion behavior has been experimentally found and offer an explanation based on the hydrodynamic and thermodynamic components of the Fick diffusion coefficient. Special attention is given to mixtures near critical and demixing regions, where in many cases strong discrepancies between different measurements of the Fick diffusion coefficients are found. Molecular simulations in these regions are challenging and require extensive sampling due the presence of pronounced density fluctuations.

In molecular dynamics simulations, the Fick diffusion coefficient is typically calculated from the Maxwell-Stefan diffusion coefficient and the derivative of the chemical potential in form of the thermodynamic factor. Because the chemical potential cannot be measured by experiment, this factor is usually estimated from vapor-liquid equilibrium or excess enthalpy data, employing an equation of state or an excess Gibbs energy model [4]. Nevertheless, it can also be estimated from molecular simulations, as it was done in this work.

Near the infinite dilution limit, the thermodynamic factor is usually assumed to be unity and to have an insignificant influence on the value of the Fick diffusion coefficient. However, under certain conditions, even for solvent concentrations of a few mole percent, the thermodynamic factor may approach values of zero, having a major impact on the Fick diffusion coefficient. As an example, Figure 1 shows how the thermodynamic factor of a 1 mole% mixture of benzene in carbon dioxide changes with temperature, reaching values of around 0.5 in the near-critical region. Thus, the anomalous behavior of diffusion found experimentally in this region for this mixture and the strong composition dependence of the Fick diffusion coefficient can be rationalized, if the thermodynamic factor is taken into account.

Furthermore, for highly non-ideal mixtures and those approaching a demixing region, the contribution of the thermodynamic factor to the observed Fick diffusion coefficient may become much more important than the hydrodynamic contribution given by the Maxwell-Stefan diffusion coefficient.

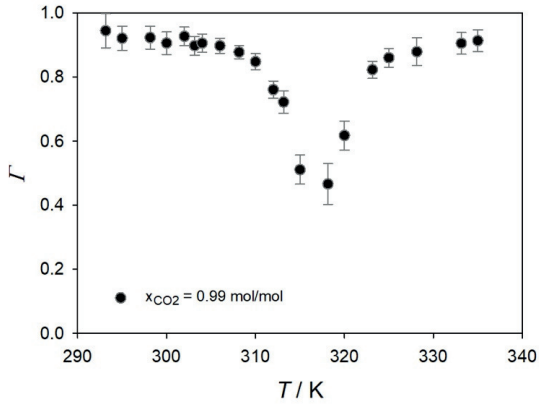

Fig. 1 Temperature dependence of the calculated thermodynamic factor of the benzene + carbon dioxide mixture at 9 MPa.

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$A = -kT \ln Q$

Atomistic Scale Simulations of the Enthalpies of Dissociation and Enclathration of Gas Hydrates

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1. Introduction

Methane hydrate formation is a major issue in flow assurance-related problems, associated with gas/oil transportation in pipe lines at cold climates or off-shore production [1]. Furthermore, oceanic hydrate deposits are currently under consideration to be used as a potential future source of methane for energy applications [2].

In addition to the pressure and temperature conditions along the three-phase (Hydrate – Liquid water – Vapor; H–L_w–V) coexistence (i.e., equilibrium) line, other thermodynamic properties are important to studies related to such industrial applications. One such property is the enthalpy of methane hydrate formation/dissociation. The enthalpy of dissociation is a key thermal property that is involved in the heat balances that are used by reservoir simulators [3].

2. Results and Discussion

We present a detailed overview of the calculation of the enthalpy of dissociation of methane hydrates, focusing primarily on methods that are based on either the Clapeyron equation or the direct calculation of the enthalpies of all the components that are involved in the hydrate dissociation reaction. Molecular dynamics simulations are used extensively in order to calculate the enthalpies and molar volumes of water, methane, and sI methane hydrate (with variant degree of occupancy) at pressure and temperature conditions along the three-phase (Hydrate – Liquid water – Vapor) equilibrium line [4].

While for temperatures lower than 304 K there is a consensus that the enthalpy of dissociation is independent of temperature, the case for temperatures higher than 304 K is not that clear, particularly for the case when the Clapeyron equation is used. Therefore, new experimental measurements are required for the higher temperatures to shed light to the problem.

A similar study, currently in progress, extends also the results to the case of carbon dioxide hydrates. The current study uses the TIP4P/Ice [5] water model, the OPLS-UA model for methane [6] and the TraPPE [7] model for carbon dioxide.

The approach of the direct calculation of the enthalpies of all the components that are involved in the hydrate formation reaction is also used for the calculation of the enclathration enthalpies of methane hydrates. Results from molecular dynamics simulations are compared with results from Monte Carlo simulations.

Acknowledgement

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$A = -kT \ln Q$

Structure and dynamics of water inmolecular models of hydratedpolyvinylamine membranes

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Membrane separations is a promising technology for CO_2 capture. Facilitated Transport Membranes is an emerging class of polymer materials, developed for this application. A membrane based on polyvinylamine (PVAm) is one of the most extensively studied examples of an FTM. The key feature of these membranes is the presence of mobile or fixed amine groups that, in the presence of water, engage in a reaction with dissolving carbon dioxide. Currently, little is known about the organization of these membranes on a molecular level, reaction mechanisms, detailed chemical balance, and transport of water or other species dissolved (ions and/or gas). The objective of this study is to understand how the mobility of water, ions and gas molecules in the membrane is affected by the structural properties of the membrane, such as the free volume, pore limiting diameter, pore size distribution as well as temperature and protonation. For this, we employ all atom molecular dynamics and molecular models of PVAm membranes as a case study.

We observe that even at the highest experimentally explored hydration levels, the mobility of water in PVAm matrices is significantly lower than that in bulk water; the ions also exhibit much slower diffusion in confined water, compared to the diffusion in bulk mixtures; this in turn affects the diffusion of water, which also diminishes in the presence of ions.

Furthermore, from the fundamental perspective we observe a number of water diffusion regimes that do not follow the well-known Einstein relation between the mean squared displacement and time, on the timescale of simulations here. There regimes are often called sub-diffusive regimes. Under low water content some fraction of water molecules are either confined indefinitely in a cage, or diffuse via a single file diffusion mechanism. In this presentation, we discuss the nature of these regimes, the characteristic time scales involved and how these properties depend on hydration levels of the membrane, temperature and presence of ions.

Adsorption of water and induced pore pressures in nanopores

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Many nanoporous solids (*e.g.* activated carbons, zeolites, MOFs) can exhibit non-monotonic deformation upon adsorption, alternating between contraction and expansion stages according to the thermodynamic conditions and pore sizes. The case of water is particularly interesting, not only for its importance in many industrial applications and natural processes, but also because the adsorptive behaviour of this latter is complex and presents varied mechanisms. This study aims at characterising the adsorption-induced pore pressure of water in nanoscopic slit pores by molecular non-local density functional theory (DFT). The DFT is coupled [1] with the statistical associative fluid theory for potential of variable range (SAFT-VR) which is highly accurate for the modelling of the bulk phase and equilibrium thermodynamic properties of water [2]. This SAFT-DFT coupling has already been applied to methane confined in graphitic slit-like nanopores. While retaining the accuracy of molecular simulations at pore scale, the model has a very low computational cost that allowed obtaining highly resolved pore pressure maps as a function of both pore width and thermodynamic conditions [3].

In this work, several configurations are explored for confined water by changing both the thermodynamic conditions and the pore sizes. For instance, the capillary condensation and evaporation are investigated with the theoretical model in micro- and mesopores. The adsorption hysteresis gives rise to a pressure hysteresis for which consequences on the mechanical behaviour are investigated. The influence of the surface activation on water adsorption and pore pressure is also explored.

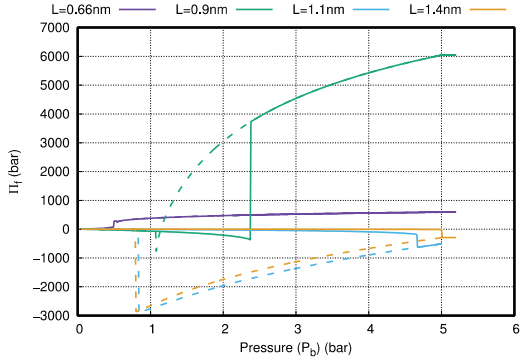

Fig. 1. Adsorption induced pore pressures of water at 425 K for different pore sizes as a function of bulk pressure. *Full lines* : adsorption. *Dash lines* : desorption.

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Molecular insight into thermodynamics of the liquid isopropanol+water mixture

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There is significant interest in aqueous alcoholic mixtures e.g. due their importance for numerous technical applications, like electron transfer reactions, heterogeneous catalysts or fuel cell technology [1]. Their high complexity in terms of physico-chemical properties also makes their study attractive for the development of theoretical approaches. Molecular modeling and simulation has become a powerful route for interpreting experimental data on thermodynamic properties, but it critically depends on the force field that describes the molecular interactions. There has thus been a continuous effort with respect to the development of force fields that are able to cover a wide variety of physical properties, employing, among others, quantum chemical calculations [2-5]. In this work, a new force field for isopropanol is presented which is based on quantum mechanical data and it allows to accurately predict the experimental time-dependent and time-independent physico-chemical properties of this secondary alcohol. Additionally, simulation results of the vapor-liquid equilibria by using the present force field are consistent with a recently proposed criterion [6].

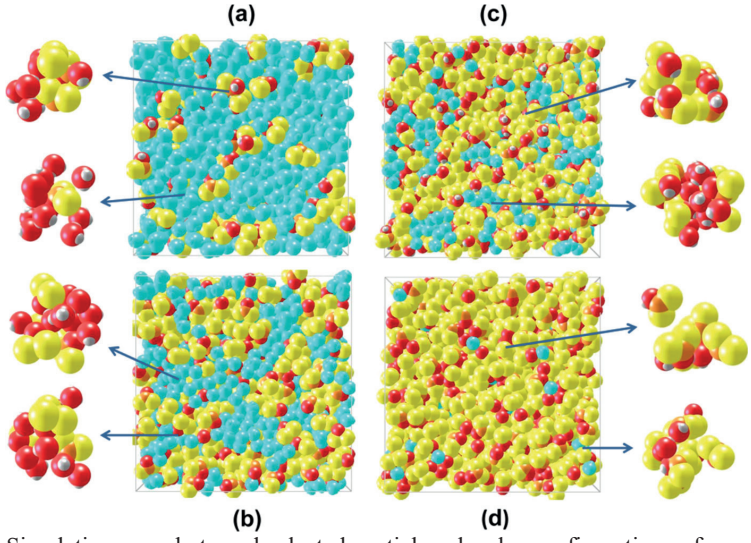

Figure 1. Simulation snapshots and selected spatial molecular configurations of propan-2-ol + water at 298.15 K and 0.1 MPa with x_{IPA} = 0.1 (a), 0.3 (b), 0.5 (c), and 0.9 mol mol−1 (d). Water molecules are colored in blue [7].

Having validated the performance of the force field for the pure alcohol, a wide range of properties of the binary mixture 2-propan-ol + water are predicted with different molecular simulation techniques in the entire composition range. The predictions reproduce experimental transport

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coefficient data of the binary liquid mixture at 298.15 K and 0.1 MPa and are in good agreement with the excess volume and enthalpy. These results are interpreted from a molecular point of view and the association pattern, which can convincingly be sampled by molecular simulation, offers an explanation to the physico-chemical behavior of this aqueous alcoholic mixture. Molecular simulations results show inhomogeneous mixing on the microscopic level, given by the presence of segregation pockets as can be observed in Figure (1).

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Finite-size Effects of Binary Mutual Diffusion Coefficients in Molecular Dynamics Simulations

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The accurate self- and mutual diffusion coefficients computation is crucial, e.g., for the design of separation processes in chemical engineering industries. Dünweg and Kremer [1] and Yeh and Hummer [2] observed that computed self-diffusion coefficients in molecular dynamics (MD) simulations change depending on the size of the system. To account for this, an analytic correction for self-diffusion coefficients was developed, which is a function of temperature, viscosity, and the size of the simulation box. While the self-diffusivity is an important property, mass transport in chemical engineering is actually determined by mutual diffusion coefficients. Thus, accurate mutual diffusion coefficients are required for both ideal and non-ideal mixtures. To study the system size dependency of mutual diffusion coefficients, we performed MD simulations for a large number of binary Lennard-Jones systems and several binary molecular mixtures of methanol, water, ethanol, acetone, methylamine, and carbon tetrachloride. A strong dependency of the computed mutual diffusion coefficients on the system size is also observed. The analysis of the system size dependency of these systems suggests that the correction term proposed by Dünweg and Kremer [1] and Yeh and Hummer [2] for self-diffusivities requires a correction factor when applied to mutual diffusion coefficients. This modification factor is shown to be the inverse of the thermodynamic factor for the Maxwell-Stefan (MS) diffusion coefficient [3]. Moreover, the finite-size effects of self-diffusivities can be "exploited" in order to obtain the shear viscosity of the system [4]. For all the above computations we have created and used a new plugin for LAMMPS, the OCTP (On-the-fly Computation of Transport Properties). OCTP uses the Einstein relations combined with the order-n algorithm to improve the sampling of the dynamic variables (Fig. 1) [5]. The new plugin can be downloaded as open-source code from the GitHub repository of our group.

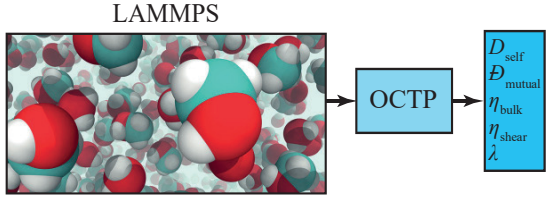

Figure 1. We present a new plugin for LAMMPS for On-the-fly Computation of Transport Properties (OCTP) in a single MD simulation. The tool can be used to calculate the self- and Maxwell-Stefan diffusivities, the bulk and shear viscosities, and the thermal conductivity of pure liquids and mixtures.

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Bulk and interfacial properties of ionic liquids and their mixtures: insights from computer simulations

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Molecular dynamics (MD), density functional (DFT) and ab initio MD simulations have revealed as fundamental tools to elucidate the structure and complex dynamics of room temperature ionic liquids (RTILs), a novel class of liquids formed completely by ions that have revolutionized the field of solvents in the last two decades, and of their mixtures with electrochemically and optically relevant solutes. In the present communication we review some novel and previously reported results regarding features of the solvation of molecular cosolvents, inorganic salts (lithium, magnesium, aluminium), ILs and nanostructures in these amphiphilically nanostructured, designer solvents [1-7]. Moreover, several own contributions on the structure and single-particle dynamics of the IL ionic species and those of solute particles, both in the bulk and at the electrochemical interface, are discussed, as well as under nanoconfined conditions. Specifically, MD calculations of the structure of the innermost layers of the electric double layer of mixtures of ILs are detailedly discussed, including striped to hexagonal pattern transitions at neat and defective interfaces, which crucially determine the 3D structure of the electric double layer and the transmission of metal cations at the electrochemical interface [8-13]. DFT calculations of the structure, stability and electronic properties of metal-anion complexes in bulk mixtures and at interfaces are briefly reviewed [14], and peculiarities of charge transfer reactions in these densely ionic environments are also glanced at [15].

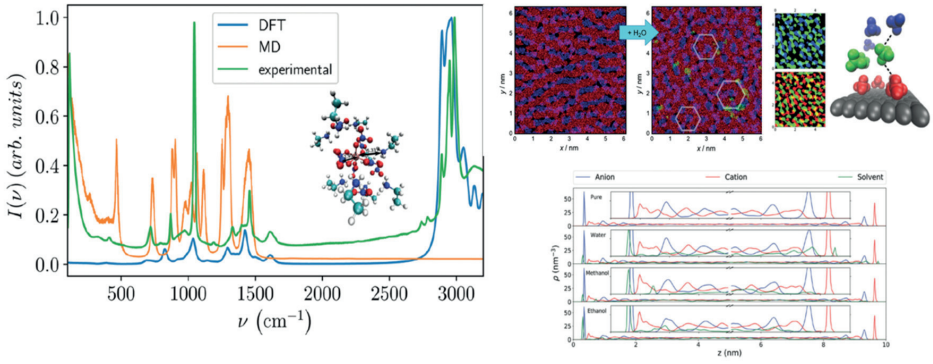

Fig.1 DFT calculated structure of aluminium-anion complexes and MD, DFT and experimental Raman spectra of mixtures of $AlNO_3$ with ethylammonium nitrate (left) [14]. Perpendicular and lateral structure of imidazolium-based ILs and their mixtures with water at graphene interfaces (right) [5,11].

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The temperature-pressure phase diagram of $CaCO_3$ via *ab initio* approaches: the quasi-harmonic approximation formalism

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The possibility to compute the temperature-pressure phase diagram of a solid is a fundamental result of enormous importance and numerous applications. The quasi-harmonic approximation is a first-principles approach ideal for this purpose in the solid-state, in which harmonic phonons are calculated at several volume constraints. In particular, this approach excels due to its capability to reproduce the phase boundary of soft phonon mode mechanisms, i.e, phase transitions driven by an imaginary phonon mode, which involves symmetry breaking and distortion of the unit cell. In this work, the quasi-harmonic approximation has been followed to study three known $CaCO_3$ polymorphs (calcite I, II and aragonite), using GGA and hybrid exchange density functional theory in the all-electron linear combination of atomic orbitals approximation. The theoretical temperature – pressure phase diagram of the calcite I – calcite II soft-phonon mode phase transition is compared to the available measurements. In addition, the mechanism of several phase transitions between polymorphs are examined. For example, imaginary phonon frequencies in the aragonite phase suggest pathways to three distinct alternative phases that involve symmetry breaking and distortion of the unit cell. Predictions of the structure for these phases will be reported along with their computed Gibbs free energies.

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Molecular Simulation of Thermodynamic Properties with the Osmotic Equilibrium Approach: Accessing Activities in Complex Concentrated Liquid Phases

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Thermodynamic properties such as activities of complex concentrated liquid phases are a key parameter for describing chemical equilibria by means of mass action law. The mass action law and the corresponding equilibrium constant provide a measure for the direction of any chemical equilibrium. Equilibrium constants calculated from the activities of all compounds involved in a given equilibrium process are for example crucial for understanding and improving solvent extraction systems used in separative approaches for waste management of rare earth elements and spent nuclear fuels [1].

The osmotic equilibrium approach has been developed for accessing activities for a huge bandwidth of complex liquid systems up to high solute concentrations [2,3,4]. Starting from Molecular Dynamics (MD) simulations of vapour-liquid interfaces using explicit polarization for all compounds simulated provides a direct access to the activity by comparing the mean amount of evaporated molecules of a given species in the vapour phase for a mixture and for the pure species, respectively. The evaporating molecules are usually sufficiently volatile solvents such as water or smaller organic molecules such as ethanol or *n*-heptane. Activities and activity coefficients of the non-evaporating solutes species are calculated by using extended Debye-Hückel theory in the case of ionic solutes and *via* excess Gibbs energy models in the case of non-ionic systems. Obtained structures and thermodynamic properties showed a very good agreement with previous experimental and theoretical studies on various aqueous electrolyte solutions and organic solvent phases up to high solute concentrations [2,3,4,5,6]. The osmotic equilibrium approach allows validating force fields for MD by the means of their thermodynamic performance [7]. The observed statistics of the evaporation process are used for calculating the error resulting from this methodology and they allow calculating the time scale required for a given precision and selectivity.

Ongoing work on this method covers the investigation of the influence of aggregate structures such as micelles and their structure and shape on the resulting thermodynamic properties, but also studying possibilities in improving the computational efficiency of the method itself. Increased simulation times reduce the error of the method and increase the selectivity for very similar compounds such as the series of the lanthanide nitrate salts.

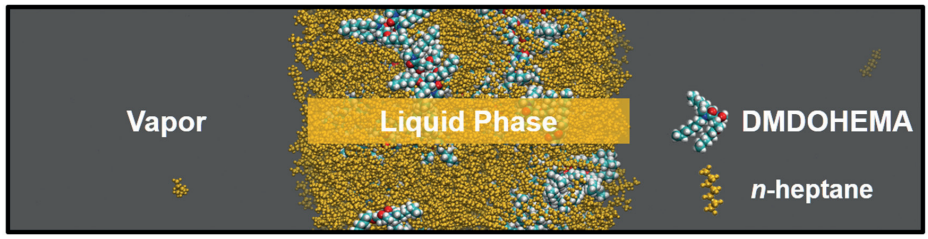

Fig. 1.: Snapshot of a simulation box of a binary mixture containing an extractant (DMDOHEMA) and an organic diluent species (*n*-heptane). The liquid phase (orange) is in equilibrium with the adjacent vapour phase (gray). Two evaporated *n*-heptane molecules are found in the vapour phase.

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A Polarization-Consistent United-Atom Model for Alcohols

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Classical non-polarizable models, normally based on a combination of Lennard-Jones (LJ) sites and point charges, are extensively used to model thermodynamic properties of fluids. An important shortcoming of this class of models is that they do not explicitly account for 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 parameters of the model, usually by fitting to pure liquid properties (e.g. density). A problem arises 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). Fully polarisable models present a natural route for addressing these limitations, but at the price of a much higher computational cost. In this work, we combine the best of those two approaches, by running fast simulations using non-polarizable models and applying *post facto* corrections to the computed properties in order to account for the effects of polarization. This idea, which makes use of recent developments in the field [1-4], allows us to improve the accuracy of classical non-polarizable models while maintaining their computational efficiency. Our main aim is to obtain a model that is able to predict both pure liquid properties and solvation free energies with a high degree of accuracy.

We apply this modelling paradigm to develop a new united-atom force field for alcohols. Apart from their practical importance as solvents, alcohols are also interesting from a fundamental point of view, as they are the simplest molecules that combine a hydrophobic moiety with a hydrogen-bonding functional group. Our starting point is the TraPPE force field [5] with modified parameters for hydrocarbons that eliminate systematic deviations from experimental solvation free energies [6]. We optimized the LJ parameters of the oxygen atom and the partial charges of the hydroxyl group by fitting to the experimental density, enthalpy of vaporization and diffusion constant of methanol, propanol, pentanol and heptanol. The optimization was carried out using metamodels [7] to approximate the results of simulations in a computationally expedient way, thus avoiding the need to run molecular simulations on the fly during optimization and allowing us to more extensively explore the space of forcefield parameters. Our new model is able to accurately describe the density, enthalpy of vaporization and diffusion of a large range of alcohol molecules. Furthermore, the model accurately predicts the free energy of self-solvation and the dielectric constant of those alcohols. Crucially, the success of the predictions relies on a rigorous application of polarization corrections to the simulation results for the enthalpy of vaporization, solvation free energy and dielectric constant.

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Study of aggregation and deposition of asphaltenes via coarse-grained molecular dynamics simulatons

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Asphaltenes are the most polar and heavy fractions of crude oils, exhibiting a strong propensity to aggregate and deposit out of solution causing a multitude of problems in the production, transport and processing of petroleum. Experimental efforts to understand the behaviour of these systems are affected by the difficulties in characterizing these complex fluids from a molecular standpoint. In this work, we present results from molecular dynamics (MD) simulations of an archipelago-like asphaltene model depicted following a coarse-grained (CG) representation, where the interactions are modelled as Mie potentials with parameters obtained via corresponding-states correlations based on the Statistical Associating Fluid Theory [1,2] and validated against fully atomistic simulations [3]. The model is used to perform large-scale simulations of bulk systems consisting of up to 2000 asphaltenes in mixtures of toluene and heptane. We report from these studies aggregation trends at different asphaltene concentrations and solvent compositions. In a second set of simulations, we place these solutions in intimate contact with model gold, graphite, and α-alumina surfaces. Simulation boxes with each type of solid are studied for some selected cases of asphaltene concentration and solvent composition to examine the corresponding adsorption characteristics. We observe trends in the adsorption resulting from the compromise between asphaltene–solvent and asphaltene–solid interactions (see Figure 1). Finally, we discuss possible relations between adsorption and the behaviour of the system at bulk conditions.

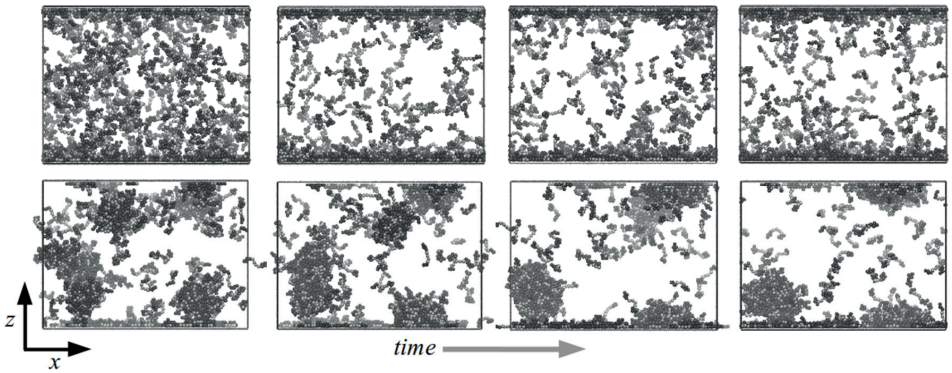

Figure 1. Side views of simulation boxes with 500 asphaltenes in toluene (top) and heptane (bottom) in the presence of graphite walls (at $z = 0$ and $z = L_z$) at 50, 100, 150, and 200 ns of simulation.

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$A = -kT \ln Q$

Surface Permeation of Benzene in Silicalite Zeolite

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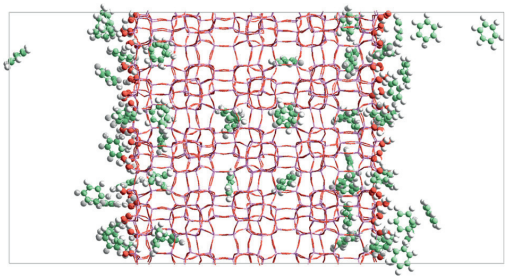
Molecular dynamics simulations have been carried out to determine the uptake and release rates for benzene in an idealized (without defects) crystal of silicalite (the pure silica form of ZSM-5 zeolite) with two external surfaces perpendicular to the straight channel [010] and terminated as silanol gropus (≡SiOH). With a 2×2×2 cell (40×40×26 Å) of silicalite containing 768 atoms and the unit cell of the system including a reservoir for sorbate molecules along [010], making the y-length 80 Å, this realistic model has been employed to simulate a system in which the **uptake kinetics** are controlled by the combined effects of surface resistance (pore blocking at the external surface) and intracrystalline diffusional resistance. A full-atom forcefield for both zeolite and adsorbate has been employed that provides adsorption enthalpies close to the experimentally obtained for benzene, so that the thermodynamics of the system mimics the real conditions of sorbate adsorption (benzene) in a microporous solid material (zeolite). The system has been treated using periodic boundary conditions and, to simulate uptake, the benzene molecules are initially located in the reservoir (outside the silicalite crystal). For the calculation of the release, the benzene molecules are all located initially within the crystal, and the periodicity along the length of the reservoir is removed so that the molecules are released at zero pressure.

The effect of a surface barrier has been investigated by considering three systems with different degrees of channel entrance blocking (0, 50, and 87.5%). This mimics the real crystals where faults, defects, and dislocations, pose a considerable restraint to the uptake of molecules. The resulting calculations of uptake and release make it possible to estimate the relative importance of surface resistance (pore blocking) and intracrystalline diffusion in determining the sorption rate. It is shown that the classical model based on the formal solution of the one- dimensional diffusion equation, taking account of the finite rate of permeation through the crystal surface (i.e., surface resistance) via the boundary condition, provides a good representation of the kinetic behavior. For comparison, self-diffusion and tracer exchange are also simulated for the same system under comparable conditions.



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Magnetic performance of Fe-doped porous carbons materials from hydrothermal treatment of biomass

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Growing awareness for clean water consumption coupled with the rising number of water treatment plants owing to government subsidies have made the overall market of activated carbons (AC) growth during last decades, especially in industrialized countries. As the AC market increases, researchers all over the world work hard in order to get the range of precursors widened, the production processes optimized and the suitability of adsorbents for specific applications improved.

In general, ACs for a given application must satisfy several requirements; among them, one can cite a suitable adsorption capacity, durability, cyclic use and low cost. Recently, the potential magnetic behaviour has been seen as remarkable an advantage, since it can allow a fast and simple AC recovery after use, just by approaching a magnet to the adsorption system. Magnetic properties can be provided to ACs by doping them with specific metals following different methods. However, the process is complex since the simple deposition of these compounds alone will not be effective if the metal element is not in the appropriate.

This work aimed to study the production of magnetic carbons by Fe-assisted hydrothermal carbonization (HTC), a novel and cost effective method based on the heating of biomass under moderate temperature and pressure conditions. Almond shell, an abundant biomass waste in Spain was used as starting materials and HTC was conducted on a 0.15 L autoclave (Berghoff) followed by pyrolysis in specific cases. The carbon material was then subjected to a thoughtful textural and surface chemistry characterization and afterwards the magnetic measurements were made in a self-made installation consisting of a cylindrical tube containing the sample, located in an external alternating magnetic field. A pickup coil over the sample measures the electromotive force, which is integrated to find the apparent magnetic flux and susceptibility. A comparative study with a ferromagnetic and diamagnetic media gives an idea of the efficiency of the processes.

Acknowledgements

The authors are grateful to MINECO and the Junta de Extremadura, for finantial help by projects CTM2016-75937-R and IB16108, respectively, and also to the programme "Ayudas a grupos de la Junta de Extremadura-Fondos FEDER".

$A = -kT \ln Q$

Towards a better understanding of interfacial properties: a machine learning potential for boron nitride

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The rise of nanomaterials, such as graphene and hexagonal boron nitride (h-BN), has raised hopes to revolutionise the world of membranes. Their small dimensions enable these materials to act as a molecular sieve, comprising high mechanical robustness and chemical stability while overcoming the existing trade-off between selectivity and permeability [1, 2]. Recent experiments [3, 4] and simulation studies [5, 6] sparked a high interest in the inorganic equivalent to graphene, h-BN, which shows superior properties with respect to ease of manufacture, oxidation resistance [7] and sorption performance [8].

In order to achieve a deeper understanding of the mechanisms and physics behind flow and adsorption processes at the interface, classical molecular dynamics (MD) is seemingly the ideal tool of choice. However, considerable doubts are cast about whether existing potentials accurately mimic the solid-fluid interactions [9-12] which strongly influence the behaviour at the nanoscale [13]. To overcome this issue, new potentials are required to be built on a higher level of theory to account for local phenomena such as polarisation. The emergence of machine learning (ML) has led to a paradigm shift in the development of force fields, where a massive amount of ab-initio data is processed providing a highly transferable and robust potential to faithfully represent the potential energy surface (PES) [14]. This offers the opportunity to expand the simulation time and systems size way beyond the density functional theory (DFT) scale while retaining the accuracy of ab-initio data for a fraction of the usual costs [15].

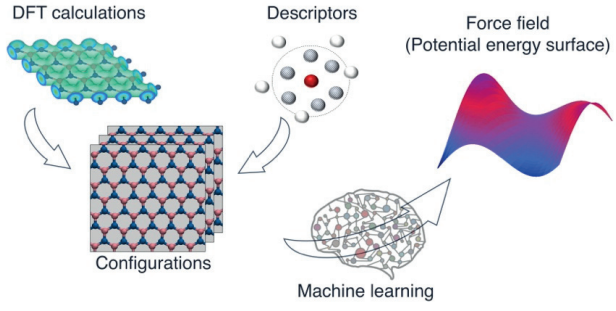

Figure 1: The GAP framework: A databank of high quality DFT calculations on relevant configurations is created where a set of appropriate descriptors serves as a fingerprint of the atomic structure. The PES and, thus, the force field is then obtained by using a machine learning algorithm to interpolate the atomic energies in the descriptor space and mapping them to forces.

As a first step towards a sensible model for the solid-fluid interactions, we introduce an interatomic potential for h-BN constructed using the Gaussian approximation potential [16] (GAP) machine learning methodology. The general procedure of the GAP framework is

visualised in figure 1. The training set consists of configurations generated with ab-initio MD sampled over a broad range of temperatures. Benchmarking the ML-based potential against other popular empirical force fields with respect to both ab-initio and experimental data reveals an excellent performance of the GAP which is on the same level as DFT.

This accurate potential for the solid phase represents the starting point for achieving a faithful description of the solid-fluid interaction. Thus, future work will involve an expansion of the training set with configurations comprising water. Later, the updated GAP model should be used to perform adsorption and steady-state flow non-equilibrium MD to make a contribution to the field of membrane development and desalination. Eventually, we hope to have linked macroscopic properties, such as permeabilities or diffusivities, obtained by these simulations to the electronic structure level.

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$A = -kT \ln Q$

Thermodynamic properties study of $U_{1-y}Pu_yO_2$ MOX fuel using classical molecular Monte Carlo simulation method

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Abstract

UO_2 has been widely studied as the conventional fuel for Light Water Reactors (LWR). It can also be blended with other actinide powders, in particular PuO_2 to form Mixed Oxide (MOX) fuel. Up to date, MOX fuel is used in Light Water Reactors with a low Pu content (~9 at %). In order to encourage fuel recycling, to save resources, to reduce waste and amount of spent nuclear fuel from LWR, and also to burn minor actinides, MOX fuel is envisaged as the reference fuel for generation IV Sodium Fast neutron Reactors (SFR) with a higher Pu content (between 25-30 at %). To ensure safety and fuel performance in the fuel qualification process, a complete investigation of MOX properties is required. To have an extensive knowledge of structural, mechanical and thermodynamics properties among others, is essential for fuel performance codes. However, experimental studies of Pu and its compounds are difficult to handle due to the high toxicity of the plutonium. Moreover, experiments dedicated to the measurements of MOX thermodynamic properties are quite expensive. Therefore, atomistic simulation could be an alternative way of obtaining these properties.

Molecular Monte Carlo method [1] in combination with the interatomic Cooper's potential [2] is used for the first time to investigate stoichiometric mixed oxydes $U_{1-y}Pu_yO_2$. The implementation of this Monte Carlo method for mixed oxydes simulation was carried out involving two algorithms, one without cations exchange and another with cations exchange. The use of these two Monte Carlo algorithms allowed us to test the effect of the substitutional disorder implied by the coexistence of two types of cations. Structural, thermodynamic and mechanical properties of stoichiometric mixed oxydes fuel $U_{1-y}Pu_yO_2$ over a wide temperature range (from 300 to 3300 K) and plutonium content (from 0 to 100 at %) have been investigated. Our study shows that the exploration of cationic configurations through the cations exchange algorithm is required for a complete description of mixed oxydes fuel $U_{1-y}Pu_yO_2$ properties especially atomic structural properties. The curves of our computed specific heat show peaks for all plutonium content around 2300 K *i.e* at ~0.8 * T_m (T_m = melting temperature). The same behaviour is observed for the linear thermal expansion coefficient. These peaks also observed in previous studies are related to the Bredig transition known to occur around 0.8 * T_m [3, 4]. The good agreement between our results, experience and previous calculations is found up to around 2100 K. Above this temperature our calculations show different behaviour compared to experimental recommendations. The efficiency of the Monte Carlo method with its cations exchange algorithm has been proved for mixed oxydes simulation.

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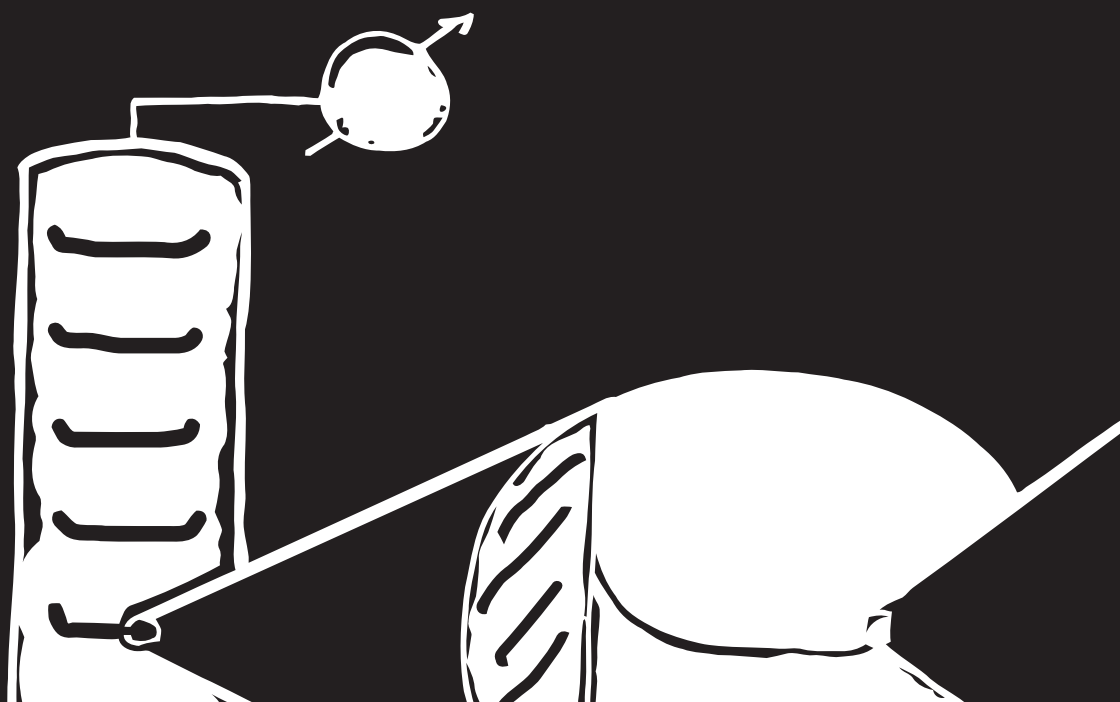
Short Oral Presentations: Challenges and advances in fluid phase equilibria



Biaxial nematics in binary mixtures of thermotropic liquid crystals

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By means of Monte Carlo simulations in the isothermal-isobaric ensemble we investigate the formation of an ordered, biaxial nematic phase in a binary mixture of thermotropic liquid crystals. The orientation dependence of the interaction between molecules of each pure component is the same as in the well-known Maier-Saupe model. Thus, each pure component of the mixture is capable of forming a uniaxial nematic phase.

For the interaction between molecules of different components we use the same Maier-Saupe model but change the sign of the coupling constant. As a consequence, a T-shaped arrangement of these molecules is energetically favoured.

The formation of the biaxial phase occurs in two steps. At higher temperatures T, one of the two mixture components turns out to form a uniaxial nematic phase whereas the other one is in a quasi two-dimensional, restricted isotropic liquid state. We develop a simple theoretical model to understand the surprisingly high degree of (ostensible) nematic order in the latter.

At lower T, the second component of the mixture becomes nematic and then the entire mixture of the two ordered compounds has biaxial symmetry. The biaxial nematic phase does not decompose into domains rich in molecules of one or the other species under conditions chosen here. We analyse the changes in orientational structure in terms of a two-dimensional orientation distribution function which exhibits a substantial system size effect.

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Dynamic and Transport Property Predictions using continuous Wertheim-like Models

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In SAFT-γ Mie [1, 2] molecules are modelled as Mie (generalised Lenard-Jones) reference fluid decorated with square-well (SW) association sites in a Wertheim-like manner [3]. Having such a close correlation between the equation of state (EoS) and the underlying molecular potential creates a direct pathway for the parametrisation of coarse grained (CG) molecular simulation models, to be used in the simulation of complex fluids [4]. There has been considerable success in employing CG models parametrised in this way [5-8]. These parametrisations, however, have mainly been confined to the non-associating representation of molecules. Discontinuities in the SW association potentials are mainly the reason for this, as they prove problematic when employed in conventional molecular dynamics (MD); the same models are still suitable for implementation in Monte Carlo (MC).

With no precluding factor towards the geometric form of the association potential existing, it is possible to map the more commonly used SW into continuously differentiable alternatives through the association free energy contribution. Use of these new continuous potentials has been successfully explored and, providing care is given with regards to the 'steric incompatibilities' [4] in the underlying Wertheim theory, can faithfully represent the original SW model in MD applications. The new continuous association models thus present a bridge between the EoS and the dynamic and transport properties of a system.

In this study, the new continuous association models are exemplified through the development of intermolecular potentials for molecules of interest such as: H_2S, NH_3 and H_2O. An advantage that these models have over other available options is that their parametrisation through the EoS involves averaging over the whole free energy landscape of the fluid, thus providing accurate predictions not only for the volumetric properties, but for other properties not included in the fitting procedure such as interfacial tension, viscosities and diffusion coefficients.

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Thermodynamic properties of the Lennard-Jones/spline system

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The Lennard-Jones/spline (LJ/s) potential is a good alternative to the Lennard-Jones (LJ) potential as a model for many real systems, in particular the noble gases. The LJ/s model was introduced by Holian and Evans in 1983 [1]. Although reports on the properties of the LJ/s model have been published, a systematic study appears to be lacking. The LJ/s potential is uniquely defined (no arbitrary truncation) and has a shorter range than the LJ potential truncated at common separation distances, which gives shorter simulation times. From a qualitative perspective, the LJ/s model gives essentially the same thermophysical properties as the LJ model.

The model is defined by the following pair potential

$$u_{ij}(r) = \begin{cases} 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right] & \text{for } r < r_s \\ a_{ij}(r - r_c)^2 + b_{ij}(r - r_c)^3 & \text{for } r_s < r < r_c \\ 0 & \text{for } r > r_c \end{cases} \quad (1)$$

with the parameters a, b, and r_c determined such that the potential and its derivative are continuous at the LJ potential's inflection point r_s and the cut-off distance r_c.

In this work, we present results for thermodynamic data generated by molecular dynamics (MD) and Monte Carlo simulations and the virial expansion. Some of these results are compared

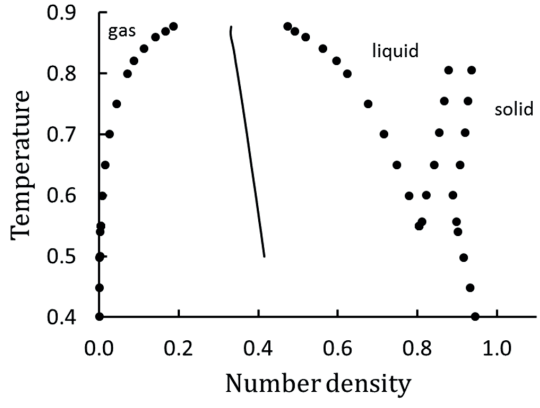

Figure 2. Phase diagram for the Lennard-Jones/spline model. The points show the gas-liquid, liqiud-solid, and the gas-solid coexistence curves. The critical temperature is estimated to $\boldsymbol{T^*_{cp} = 0.880 \pm 0.005}$ and the triple-point temperature to $\boldsymbol{T^*_{tp} = 0.55 \pm 0.01}$. The line is the rectilinear diameter. All numbers are in Lennard-Jones units.

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to an equation of state for the vapor and liquid phases of the LJ/s fluid that makes rigorous use of the Barker-Henderson high-temperature perturbation theory [2].

A key result is the phase diagram found by direct MD simulation of gas-liquid, gas-solid, and liquid-solid two-phase equilibria as shown in Figure 1.

The simulations were made with LAMMPS and in-house MD- and Gibbs ensemble MC codes. The thermodynamic data include *PV*-isotherms over a wide range of temperatures and densities, the five first virial coefficients, the Joule-Thomson inversion curve and other lines of constant values of the Joule-Thomson coefficient, the binodal line shown in Figure 1, the spinodal line, and data for the speed of sound.

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Modeling of solid-liquid phase equilibria of hydrated salts for the screening of new phase change materials

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Phase change materials (PCMs) are frequently employed to construct latent heat storage systems through heat accumulators in power plants, industrial processes or buildings [1]-[2]. The adoption of such systems can improve the efficiency and reduce the load fluctuations thanks to the precise tailoring of the working temperature range and their high heat storage density. The ability to predict phase equilibria diagrams of different binary or ternary mixtures is essential to understand their thermal melting behavior at different composition levels and to design new PCMs for different applications and temperature ranges. The knowledge of the phase diagrams is a considerable advantage to have an estimation of the temperature design conditions of potential PCM candidates as well as the expected melting transition, i.e., congruent or incongruent melting.

In this work, as part of the PCM Screening project, the analysis is focused on salt hydrates as suitable cost-effective solutions, particularly, on hydrates of sulfate and nitrate salts. The utilized methodology relies on the calculation of the corresponding Gibbs' free energies for the aqueous solution and solid phase of every reported hydration level.

Regarding the solid phases, the Gibbs' free energy model is built by gathering thermodynamic data of the heat capacity, standard enthalpy of formation, and standard entropy of formation for all hydration levels from the literature and own experimental investigations. These data is then fitted to a suitable thermodynamic model such as the NASA 9 polynomial equation [3]. Concerning the liquid phases, an excess Gibbs' free energy model is assembled to account for the non-ideal behavior of aqueous solutions by the use of a Pitzer temperature dependent model [4]. Its corresponding ion interaction parameters depend on the composition of such aqueous solution. Both models are then incorporated into a Villars–Cruise–Smith (VCS) non-ideal equilibrium solver [5] to obtain the solid-liquid equilibria in the form of phase diagrams.

First calculations showing phase diagrams of some salt hydrate compounds will be presented and compared to experimental data to verify the aptness of the described model and its prospects.

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$A = -kT \ln Q$

A comparative study of the thermophysical behaviour of binary mixtures of Eugenol with short chain alcohols (C_2-C_3). Modeling $C_{p,m}^E$ with COSMO-RS

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In this communication we analyze the thermophysical behavior of binary mixtures between eugenol and a short chained alcohol (ethanol or propan-1-ol). These binary mixtures has been chosen as they are in the scope of our research activity focused at present on supercritical processes as, supercritical fluid extraction (SFE) or supercritical antisolvent fractionation (SAF). This researching activity are developed near the nowadays considered as sustainable chemistry handling natural products (extracts from natural plants) and green solvents such as short chain alcohols (ethanol or propan-1-ol).

Thermophysical data for natural products necessary in supercritical processes design [1] are scarce in literature, so that it result interesting to know the behavior of some thermophysical properties for pure natural compounds or its binary mixtures with one short chained alcohol.

Eugenol or 2-Methoxy-4-(prop-2-en-1-yl) phenol, figure-1, is a natural monoterpenoid present in some spices as nutmeg, cinnamon, clove oil, basil and bay leaf. Also eugenol is a major component found in some plants as Lemon balm (*Melisa officinalis)*.

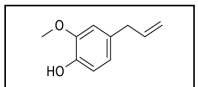

Figure-1. Eugenol

For all the binary mixtures between eugenol and ethanol or propan-1-ol, a number of thermophysical properties have been experimentally determined following the methodology and using the equipment described elsewhere [2-3]. All experimental measurements have been carried out at atmospheric pressure and in the temperature interval ranging from 298.15 to 328.15 K at every 10 K degrees.

The molar excess volumes, V_m^E, for the binary mixtures of eugenol + (ethanol or propan-1-ol) are negatives in the entire composition range at the four temperatures, showing quite high absolute values (figure 2, on the left).

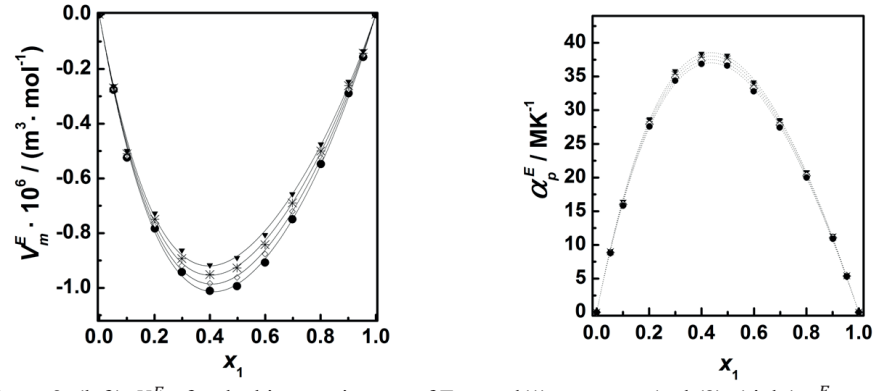

Figure 2. (left) V_m^E , for the binary mixtures of Eugenol(1) + propan-1-ol (2). (right) a_P^E , at the temperatures: (●) 298.15; (M) 308.15; (□) 318.15 y (▼) 328.15 K.

Also the behavior of V_m^E, with temperature, $(\frac{\partial V_m^E}{\partial T})$, agree with the positive values found for excess isobaric expansivity, a_p^E (figure 1, on the right) as they are related by the expression [4]:

$$a_p^E = \frac{1}{V_m^{id}}\left[\left(\frac{\partial V_m^E}{\partial T}\right) - a\, V_m^E\right]$$

The possibility of formation of hydrogen bonds between the alcohol group of both alkanols with either the alcohol group or the ether group or even the double bond or the π cloud of eugenol would lead to the low values observed for the excess molar volumes.

The experimentally derived excess isobaric molar heat capacities (atmospheric pressure) $C_{P,m}^E$ are positive in the entire composition range at the four temperatures and for both ethanol and propan-1-ol, as it is shown in figure 3, and agree with the values predicted by COSMO-RS

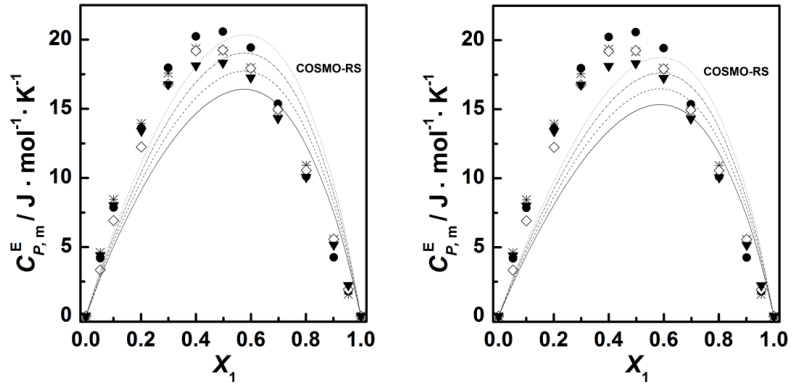

Figure 3. Isobaric excess molar heat capacities, $C_{P,m}^E$, for the binary mixtures of eugenol (1) + ethanol (2) (left) and eugenol (1) + propan-1-ol (2) (right). In both cases $C_{P,m}^E$, values at the temperatures: (●) 298.15; (M) 308.15; (□) 318.15 y (▼) 328.15 K values and (—) 298.15 ; (- - -) 308.15 ; (— • —) 318.15 y (□) 328.15 K for Cosmo RS modeling results.

1-ol are very sımılar.

Acknowledgements

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$A = -kT \ln Q$

Multi-Phase Coexistence in Rod-Polymer Mixtures

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We present theory that predicts the liquid crystalline phase behaviour of dispersions containing hard rods mixed with non-adsorbing polymers, modelled as penetrable hard spheres. By only taking into account excluded volume interactions a rich number of different phases and phase coexistences are found, shown in Figure 1. This is a result of the depletion effects mediated by the polymers in a colloidal dispersion as is well described by Free Volume Theory [1]. Among the results we find four-phase coexistences as is much in line with recent results for mixtures of plates with penetrable hard spheres [2]. It will be discussed whether this finding contradicts the Gibbs' phase rule in our athermal two-component system, from which a maximum of three coexisting phases is initially expected. In this talk our theoretical approach and the possible phase equilibria will be discussed.

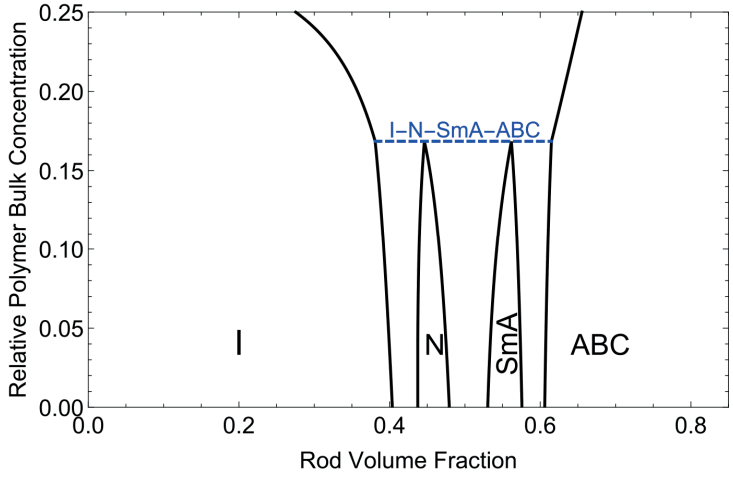

Figure 1 Example of a phase diagram of hard spherocylinders mixed with penetrable hard spheres showcasing a four-phase coexistence between the isotropic, nematic, smectic A, and ABC crystal phase. Here the aspect ratio of the spherocylinders is 4 and the diameter of the penetrable hard spheres is roughly half the diameter of the spherocylinders.

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Predictions of gas phase thermochemical properties and solvation free energies from ab initio calculation. Applications the thermal decomposition of biomass

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The kinetics of biomass thermal decomposition is still not well understood, as it involves many chemical species. During the decomposition process, chemical reactions may occur in both gas and liquid phases. Green and co-workers proposed an approach to predict kinetic constants in liquid phases, which is based on a correction of the kinetic constants in the gas phase. The correction term in Green's approach involves solvation Gibbs free energies of the chemical species. Therefore, a reliable kinetic study in liquid phase require accurate values for both gas phase properties and solvation free energies.

The prediction of gas thermochemical properties such as enthalpies of formation and ideal gas heat capacities is of crucial importance. However, these properties may not be known for chemical species encountered in the decomposition of biomass. Predictive methods based on ab initio calculations [1-3] can be very accurate for predicting gas phase thermochemical properties and are usually more versatile than group contribution methods. In this work, we extend the work of Paulechka and Kazakov [3] and propose a general predictive approach based on the very accurate and efficient DLPNO-CCSD(T) ab initio calculation, to determine the enthalpies of formation of broad variety of molecules. New sets of regressed atomic contributions are proposed for a larger number of elements: H, C, N, O, F, Si, P, S, Cl and Br, and different ab initio methods for the calculation of the electronic energies and the determination of the optimal molecular geometry [4]. Excellent predictions are obtained for most studied compounds (bio-oil compounds, refrigerants, …), apart from certain types of compounds for which the experimental measurements can be discussed. The combination of DFT and DLPNO-CCSD(T) with the def2/J and def2-QZVPP/C auxiliary basis sets and the RIJCOSX approximation provide a computationally very efficient low cost path for the calculation of formation enthalpies.

Concerning solvation Gibbs free energies, several predictive models of solvation energies have been compared to the large set of experimental data taken reported by Moine and coworkers. A reoptimized version COSMO-SAC model is proposed in this work, and is found to be much more accurate and versatile than the Abraham solvation model that is commonly used in liquid phase kinetic studies.

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$A = -kT \ln Q$

The role of pressure and the crystalline structure on the spontaneous doping of ice Ih, Ic, III, V and VI from aqueous salty solutions

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Ice-doping processes are of great interest in fields such as atmospheric chemistry, astrophysics and geophysics. In recent years, various studies revealed the existence of subsurface salty oceans and the presence of high-pressure ice polymorphs in the interior of some planetary bodies such as Jupiter's satellites or exoplanets such as Proxima b [1,2]. These ices, stable over several gigapascals and hundreds of Kelvin, can contain a significant number of small ions in their structure. The presence of doped ice suggests a plausible explanation for the behaviour and different physical properties observed in the interior of these icy bodies.

When it is added to ice, the salt first dissolves in the liquid water layer that is always present on the surface, thereby lowering its freezing point below the ice coexistence temperature. Moreover, when water freezes from aqueous salty solutions, the salt ions are rejected from the solid phase and saturate the liquid phase giving rise to the appearance of the phenomenon known as brine rejection. Pockets of brine form inside the polycrystalline blocks of ice.

In addition to the brine phase, during the ice growth a small amount of ions can be accommodated in the solid lattice causing ice doping [3,4]. The ice-doping process raises fundamental questions concerning the mechanisms by which ions are incorporated into the ice structure, and what their positions and effects are once they get there. Experiments evidenced that the presence ion dopants in the lattice modifies the properties of ice, as the incorporation of ions causes the appearance of extrinsic defects in the lattice that increase the static conductivity of the system and affect the dielectric properties of doped ice. A small amount of doping impurities is sufficient to induce considerable changes in these properties [5].

In this work molecular dynamics simulations on microsecond time scale have been performed on an aqueous solution of TIP4P/2005 water and NaCl by using the direct coexistence technique to study the ice growth and the interface ice/liquid water. At different pressures, for temperatures above the eutectic point of the salt and at several concentrations the brine rejection phenomenon and the spontaneous growth of an ice slab doped by the salt are obtained, as found in natural terrestrial and planetary environments. Experiments indicate that Cl^- goes substitutional to ice sites. In line with these evidences we find a new result for ice Ih: the Cl^- ion included in the lattice always substitutes not one but two water molecules leaving the ice structure around not distorted. The Na^+ ion shows lower probability to be included in the ice and it occupies an interstitial site, causing a local distortion of the lattice [6]. We compare the results obtained for the ice Ih and ice Ic to the same conditions of pressure and temperature analyzing the influence of the crystalline structure. Further, we extend the study for stable ices at high pressures such as ice III, V and VI and we study the role of pressure and the different type of crystalline structure on the spontaneous doping process [7].

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$A = -kT \ln Q$

Liquid-vapor equilibrium and critical properties of fatty acids by means of molecular dynamics simulation

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In recent years, the biodiesel production has emerged as an option for renewable and green fuel generation due to the constant reduction of fossil fuel reservoirs. However, costs are not allowable for a large-scale production; thereby, several novel processes have been proposed (*e.g.* reactive distillation) to overcome this situation. An inconvenient for the development of these processes is the few information in literature about critical properties of the fatty acids present in biodiesel. Calculation of critical properties for fatty acids through experimentation is difficult because of their high values, due to their associative nature. One alternative is the group contribution method, which is based on the structure of the molecule; however, results can greatly vary between different approaches of this method. Another alternative (and the focus of this work) for determination of these properties is through molecular simulation.

In this work, liquid-vapor equilibrium and critical properties of three fatty acids (linoleic, oleic and palmitic acid) were calculated with the method of direct determination of phase coexistence using molecular dynamics. Simulations were performed with the software GROMACS, in which the TraPPE-UA forcefield (Transferable Potentials for Phase Equilibria United Atom) was implemented.

Molecular dynamic simulations were done following the direct phase coexistence methodology [1], using the software tool package GROMACS v5.1.4 [2]. Considering that the aim of this work is to analyse the liquid vapor equilibria (LVE), we choose the TraPPE-UA forcefield [3]. The algorithm leap-frog was used to solve Newton motion law equations, with a timestep of 2 fs. Periodic boundary conditions were applied in the three dimensions. Long range corrections were not present, as the system is in an inhomogeneous state [4]. So, the cut-off radius was setup to 3.0 nm to consider the long-range effects in the Lennard-Jones potential. Dimensions of the system box were 13.5 nm x 13.5 nm x 27 nm to avoid finite size effects [5], with 3000 molecules in each system. Simulations were run in the NVT ensemble in a range of temperatures from 600 K until the critical temperature had been reached using the Berendsen thermostat for equilibration for 2 ns. Then, production run simulations were done with the Nose-Hoover thermostat for 10 ns.

Liquid vapor phase diagram, critical properties (temperature, pressure, density) and surface tension are reported. Liquid and vapor densities were obtained by computing the density profile in the x direction and fitting to a hyperbolic tangent function [6]. Critical properties of palmitic, oleic and linoleic are presented in Table 1.

Component	T_b (K)	T_b exp (K)	T_c (K)	T_c exp (K)	ρ_c (Kg m^{-3})	P_c (bar)
Palmitic acid	600.36	612.15[7]	785.62	785.22[8]	243.17	15.78
Oleic acid	657.82	NA	847.94	NA	251.62	15.42
Linoleic acid	686.16	NA	895.60	NA	258.79	15.34

Table 1. Critical properties and boiling temperature obtained by molecular dynamics.

Critical properties were obtained by extrapolation of the LVE curve. The critical temperature was estimated with a Wegner expansion [9]. The critical pressure was obtained using the

Clausius-Clapeyron equation. Surface tension was calculated using the mechanical definition of the pressure tensor [10].

In this work we have calculated critical properties and liquid-vapor equilibria of fatty acids with atomistic simulations done by molecular dynamics through the direct phase coexistence method (slab geometry). In the case of palmitic acid, the critical temperature is in a very good agreement (< 1%) with respect to the experimental value. The boiling point estimated by simulation is also good (<2%) in comparison to the literature value.

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$A = -kT \ln Q$

Comparison of the associative and polar SAFT-VR Mie molecular models to acetone and their mixtures

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1. Introduction

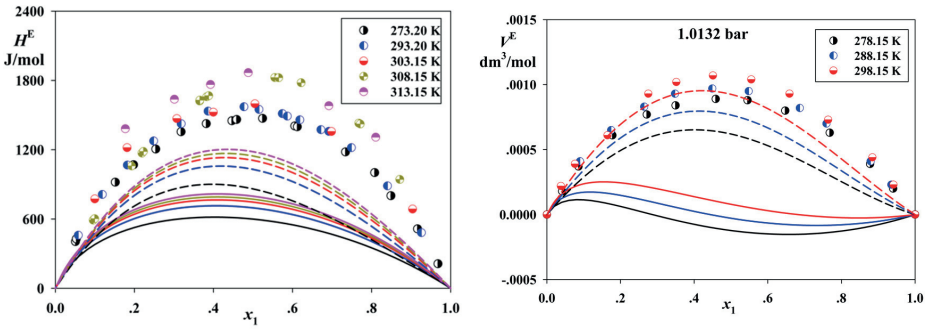
Accurate thermodynamic properties of pure compounds as well as mixtures in particular phase equilibrium properties over a wide range of temperature and pressure are important for process design or optimization in chemical industry. Being known as common industrial solvents, ketones are good representative of polar compounds whose phase equilibria is not trivial to predict; some of them, like acetone play an important role as basic feedstocks or intermediates in the chemical and process industries. The oxidative desulfurization process is a typical example in which acetone among other polar solvents (e.g. DMSO, acetonitrile, DMF, etc) can be used as extraction solvent to remove sulfur-containing compounds from gasoline and diesel fuels [1-3]. Acetone is chosen as the extraction solvent, since it has a relatively low boiling point (56.29 °C) and is separated easily from the sulfones by distillation. From the point of view of process design, knowledge of the liquid–liquid immiscibility of acetone+n-alkane biphasic systems is also needed. From a theoretical perspective the development of universal molecular models suitable for reliable predicting the entire set of properties in mixtures containing acetone and hydrocarbons is required. Recently, two molecular models have been developed for acetone on the bases of the SAFT-VR Mie framework [4]. On the one hand, taking the molecular association effects into account Sadeqzadeh et al. [5] model the acetone as a fussed dimer with two association sites, one labeled as type “H” and one as type “e” used to mediate the strong dipolar interaction present in pure acetone. On the other hand, Cripwell [6] consider only dispersion forces with an explicit dipolar contribution coupled to SAFT-VR Mie. To our best knowledge, there is no direct comparison between the associative and polar model. With the aim to gain a deeper insight into the interactions as well as the phase behaviour these solutions without any binary/unlike interaction parameter, the SAFT-VR Mie with the associative and polar contributions is applied to the characterization of acetone + n-alkanes mixtures.

2. Molecular Models

In this contribution the SAFT-VR Mie was used to model the available experimental data of Acetone(1) + n-alkanes(2) considering the entire thermodynamic phase space and various thermodynamic properties. The kernel model was developed by Lafitte el al. [4] where molecules are represented as homo or heteronuclear chains formed from Mie spherical segments. The development of the model also considers an improved perturbation theory for the monomer reference and a refined radial distribution function for representing the chain formation. Lately, outstanding advances on the original framework have been generated in order to model highly associative [5] and polar fluids [6]. Particularly both versions of SAFT-VR-Mie were used in this contribution.

3. Results and Discussion

In Figure 1, qualitative agreement for the associative model and quantitative agreement for polar model for excess volumes and enthalpies are observed in. Predictions in Figure 1 for Acetone(1) - n-Hexane(2) serve to confirm that probably the associative model is not able to reproduce the experimental Liquid- Liquid equilibrium (LLE) at low temperature range. Although not shown, we can confirm a similar behavior found in comparison with the Acetone(1) - n-Heptane(2), n-Octane(2).



(a) (b)

Figure 1. Excess enthalpies and volumes in Acetone(1) – *n*-Hexane(2) system without interaction parameter (k_{12} = 0). Experimental data– points. Solid lines –predictions of Associative SAFT-VR-Mie. Dashed lines –predictions of Dipolar SAFT-VR-Mie.

4. Conclusions

Although the associative A-SAFT-VR-Mie is the more sophisticated model having a stronger molecular background, it does not exhibit an over-all advantage over P-SAFT-VR Mie. Specifically, the latter approach is more accurate in predicting phase equilibrium, excess properties (volume and enthalpy) and critical azeotropy

5. References

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Some Observations Regarding the Association Kernel of SAFT-VR-Mie. Is the molecularly-inspired contribution always necessary?

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1. Introduction

The actual thermodynamic data of fluid systems are defined by various molecular phenomena which currently cannot be precisely described even by the most advanced theories. Hence, a principle question that deserves in-depth consideration is following: is the price payed for the ongoing sophistication of molecular models [1,2] always justified? In this respect it should be emphasized that the adjustment of models to the data might hinder their evaluation and comparison. Indeed, it is not always clear if the accuracy has been achieved due to the appropriate theoretical backgrounds of the models themselves, or just thanks to the successful fitting strategies. In a view of the above, it seems essential to evaluate the performance of thermodynamic approaches in the entirely predictive manner without previous contemplation of experimental data. Consequently, the current study compares the performances of the sophisticated molecular-inspired and the simpler analytical associative contributions to the Helmholtz free energy of SAFT-VR-Mie equation of state in estimating the global phase behavior of water – hydrocarbon systems in the entirely predictive manner, i.e. while keeping zero values of the binary adjustable parameters in all the considered cases. Special attention is paid to the effect of the induced association treatment on the critical and sub-critical (VLE, LLE and VLLE) data of water + aromatics, indicating the strengths and the limitations for both association contribution.

2. Molecular Models

In this contribution the sophisticated molecular-inspired [3] and the much simpler analytical [4] associative contributions to the Helmholtz free energy of SAFT-VR-Mie equation of state in predicting the thermodynamic properties of pure water and the global phase behavior of water (1) – hydrocarbon (2) (alkanes, alkenes and aromatics) systems was implemented in the entire thermodynamic phase-space. These approaches are attaches by the classical van der Waals one-fluid mixing rules with zero values of the binary adjustable parameters. For clarity, the three models are denoted by SAFT-VR-Mie-HS, SAFT-VR Mie-Mie and SAFT-VR-Mie-LJ, where the initials after the last dash (HS, Mie and LJ) indicate the type of intermolecular potentials utilized in deriving the association Kernel.

3. Results and Discussion

The accuracy of the considered approaches in predicting the elevated pressure data outside the parameter fitting ranges is an important test for their over-all robustness and reliability. In addition, these results are informative in a context of their potential implementation in astronomy and geo-planetary sciences [5,6]. Figure 1 compares the predictions of sound velocities and densities of pure water up to the extreme pressure of 100,000 bar. As seen, SAFT-VR-Mie-HS yields the nearly precise predictions of the densities in the entire pressure range, which is not a case of the two more theoretically-advanced approaches. Eventually, their superior compliance with the reference monomer fluid doesn't contribute to the accuracy in predicting the densities of water outside the fitting range. These results indicate that the Wertheim TPT1 treatment is particularly sensitive to the approximations employed for estimating the pair correlation function of the reference fluid.

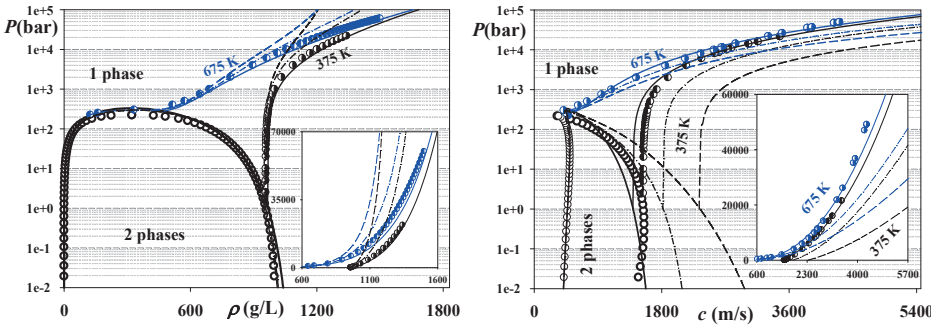

Figure 1. Densities and sound velocities of water. Literature data[5,6] —points. Solid lines — SAFT-VR-Mie-HS, Dashed lines —SAFT-VR-Mie-Mie and dot-dashed lines —SAFT-VR-Mie-LJ.

4. Conclusions

The current study has aimed at contributing to a general awareness concerning the actual practical value of the ongoing complexity of SAFT models in attempt to achieve their better agreement with the results of molecular simulations. Obviously, there is a price to pay for such complexity: it hinders wide implementation of the advanced molecular approaches, increases the computation times and might introduce unexpected numerical problems. Therefore, a fundamental question that should be asked is does this complexity necessarily guarantee an over-all improvement of accuracy in predicting experimental data? Recent developments of SAFT approaches typically evolve introduction of additional intermolecular contributions and further sophistication of the existing ones. The in-depth analysis of the supplementary intermolecular contributions is not trivial since it is not easy to evaluate the actual reasons for the reported improvements. Indeed, it is not always clear if these improvements are achieved due to the more advanced molecular background or just thanks to introduction of new substance-specific adjustable parameters. Such an analysis has been performed in the current study.

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$A = -kT \ln Q$



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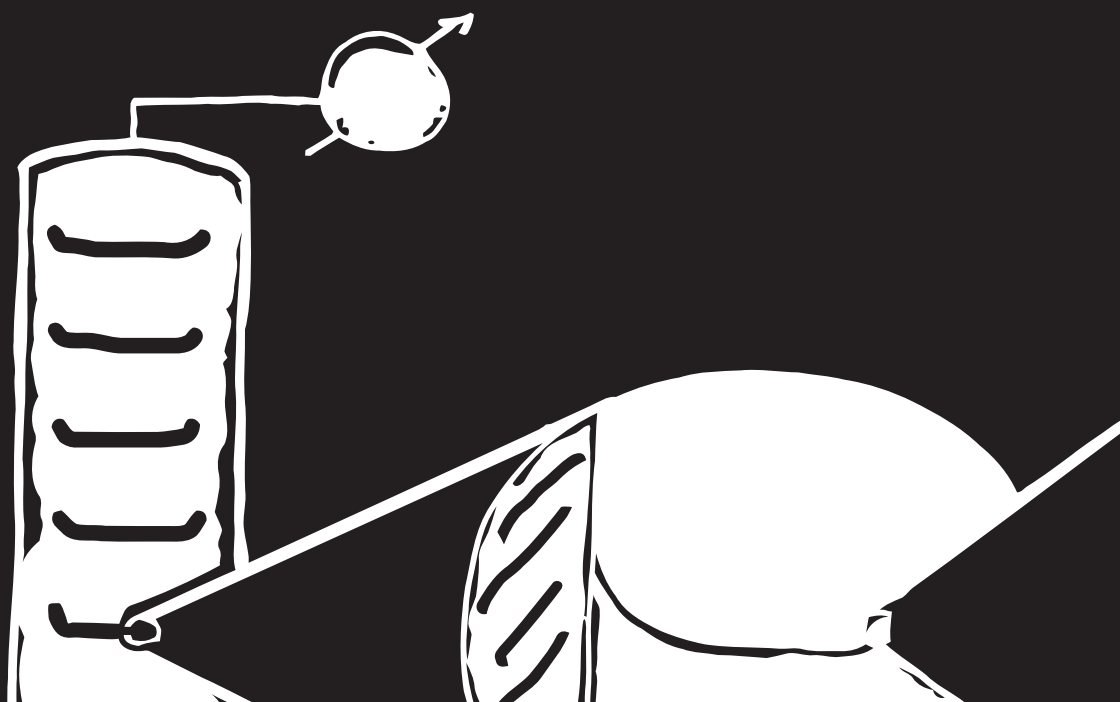
Short Oral Presentations:
Interfacial and confined phenomena



Intrinsic structure and adsorption properties of the interfaces between gas and ionic liquid phases

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Supported liquid phases (SLPs) are considered as promising materials for gas adsorption and separation, catalysis and other applications. One of the challenges in application of SLPs in gas adsorption and separation is the loss of the solvent due to evaporation and the need to recover it downstream. To alleviate this problem ionic liquids have been proposed as attractive solvents since they have essentially zero vapour pressure. Large chemical space of ionic liquids opens further avenues for their engineering towards high gas capture capacity and selectivity.

The key functional element of an SLP or supported ionic liquid phase (SILP) is a thin film of liquid spread over the surface of solid support. The gas adsorption process by this liquid film is governed by the properties of the interfacial region between gas and liquid, and is fundamentally different from the gas absorption into the liquid phase. Understanding the intrinsic structure of the gas-liquid interfaces and altering their interactions with gases is of principal importance for the advancement of gas adsorption and separation processes beyond the current state-of-the-art.

The objective of this study is to explore properties and structure of thin films of ionic liquids on a molecular level. Specifically, we focus on a thin film of a well-known ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate, $[BMIM]^+[PF_6]^-$, interacting with a gas phase consisting either of a single component such as carbon dioxide or nitrogen, or a mixture of components. We employ molecular dynamics and advanced computational techniques to elucidate the intrinsic structure of the gas-liquid interface [1, 2]. Using the detailed information on the structure of the interfacial regions, we explore several approaches to accurately delineate the bulk gas region of the system, the bulk ionic liquid region and the interfacial region of the system.

Having determined clear boundaries between three phases, we further explore the gas uptake capacity and selectivity of the thin film of the ionic liquid. Ionic liquids exhibit the non-uniform density at the gas-liquid interface associated with the ordered structure of the liquid film extended up to two molecular layers. Both carbon dioxide and nitrogen gases accumulate in the vicinity of and form a layer on the surface of the film, however, only carbon dioxide penetrates into the bulk liquid phase region of the film. This observation indicates a favourable interaction between gas molecules and the surface of the ionic liquid in comparison to the bulk volume of the film. Moreover, interfacial molecules of the ionic liquid are capable of adsorbing 3-5 times more CO_2 per molecule compared to the bulk phase. Calculations of gas selectivity as a function of film thickness demonstrate low CO_2/N_2 selectivity of < 10 for the interfacial region and high CO_2/N_2 selectivity of ~ 80 for the bulk liquid phase. Therefore, in comparison to bulk ionic liquid thin films of $[BMIM]^+[PF_6]^-$ exhibit high capacity and low selectivity towards CO_2.

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$A = -kT \ln Q$

Study of grain boundaries in UO_2 using atomic scale simulations: formation energy of defects and temperature effects

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It is well known that grain boundaries play a major role in the macroscopic properties of polycrystalline materials. That is particularly true for uranium dioxide ceramic that is currently the most widely used nuclear fuel worldwide, and which has to withstand severe conditions. Under irradiation, grain boundaries are strongly affected both by the thermomechanical stress induced by the temperature gradient and by the accumulation of fission gas bubbles. Depending on the operating conditions of the reactor, these two phenomena eventually induce the decohesion of grain boundaries. Consequently, a better knowledge of grain boundaries properties in UO_2 including formation energies, cleavage energies and mechanical properties such as toughness is needed. That is why we propose to study UO_2 bicrystals using atomic simulations.

Atomic configurations of grain boundaries (GBs) were built using GBStudio [1], and molecular dynamic (MD) simulations with LAMMPS [2] were performed to relax them properly. Then, formation and cleavage energies as well as atomic structures of the GBs were determined, and the impact of the presence of the GB on formation energy of defects and incorporation of fission gas products were analysed. The effect of the temperature was also investigated from 300 to 2000 K. In this presentation, calculation results will be presented, and compared to experimental measurements performed in our group, especially linear fraction of GBs from EBSD experiments, and energy data on GBs from thermal grooving [3].

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Explicit calculation of the pair distribution function: application to the liquid-vapour interface

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In this work we aim at calculating interfacial properties using the pair distribution function. Starting from the general pair distribution function $g^{(2)}(\mathbf{r_1},\mathbf{r_2})$, we use a dedicated set of coordinates to describe the cylindrical geometry of a planar interface. Considering the heterogeneity of the system along z-axis, $g^{(2)}$ only consists of a 3-dimensional array which is easily manageable with modern computers.

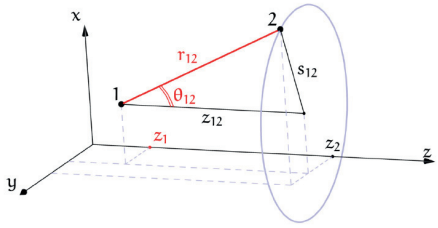

Fig.1: set of coordinates for pair 1-2.

We have calculated the pair distribution function for a model system which consists of an explicit liquid-vapour interface, generated by Monte Carlo molecular simulations using the Lennard-Jones interaction potential. The practical issues and parameters are discussed, such as the choice for the set of coordinates and the size of the calculated data. The conversion between $g^{(2)}$ and the radial distribution function is checked in both bulk phases and interfacial region.

The surface tension can be derived directly from $g^{(2)}$, starting with the general Kirkwood-Buff (KB) definition:

$$\gamma = \frac{1}{4}\int_{-\infty}^{+\infty} \mathrm{d}z_1 \int \mathrm{d}\mathbf{r}_{12}\left[\frac{r_{12}^2 - 3z_{12}^2}{r_{ij}}\right] v'(r_{12})\,\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$$

We have calculated both short-range and long-range contributions of the surface tension for the Lennard-Jones fluid and compared with other methods.

We extend the KB formalism to a three-body potential and deduce a way of calculating the long-range correction of the surface tension by approximating the three-body distribution function. Using argon as a reference system, we investigate the effect of the 3-body cutoff on the different contributions of the surface tension.

$A = -kT \ln Q$

Microphase separation of confined binary liquids

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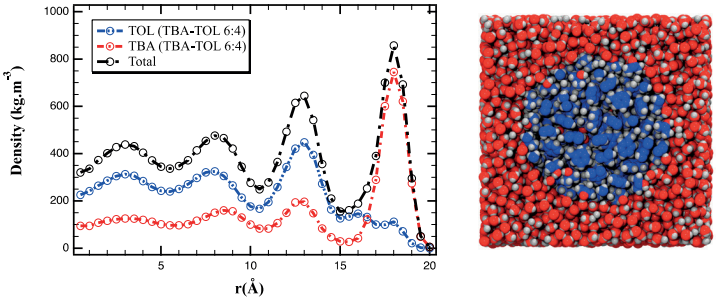
Self-association and formation of supermolecular assemblies are important phenomena in diverse processes, from the creation of micro-emulsions, to the drug delivery and to the assembly of proteins into the functional complexes. Among the self-organizing liquids, we consider alcohols as good models given their ability to form complex structures from hydrogen bonds. It is now well established that the physical properties of these liquids are firmly connected to their structure.

Recently, Hamid et al. have shown that a mixture of toluene (TOL) and *tert*-butanol (TBA) can demix and form a core-shell organization in a confined medium [1], where this mixture is absolutely homogeneous in the bulk phase. Obviously, we have shown that this binary mixture of TBA and TOL can induce a strong spatial heterogeneity in confined media [2].

In order to better understand this behavior at the nanoscale, it is essential to get a good description of the hydrogen bond network. In this work, we aimed characterizing the connection between the hydrogen bonding (HB) network and the different physical properties such as transport, structure and interfacial properties. For that, molecular dynamics simulations of alcohols and their mixture were carried out, with TOL and Cyclohexane (CX) in bulk and confined phases. These mixtures have been structurally and dynamically characterized and anomalous behaviors such as unusual dynamics and microphase separation were captured.



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Gas adsorption at the nanoscale:

Effect of molecular morphology and pore geometry

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Nanoporous materials have become a common staple in modern membrane separation, catalysis, and adsorption engineering. At this level of confinement, it is the energetical and morphological molecular-level interactions that dominate the observed macroscopic behaviour, as opposed to the more classical macroscopic fluid descriptors, such as viscosity and pressure, whose sheer definition breaks down in this highly anisotropic nanodomain.

It is well known that the structure and energy of the pore walls control the shape of adsorption isotherms. An important feature of the pore structure is the geometry as it directly influences the interactions between the particles and the walls. The pore geometry has a significant influence on the ultimate shape of the adsorption isotherm [1], and it can affect other aspects of interfacial phenomena such as nucleation kinetics due to orientational order effects [2]. Moreover, angles and wedges within pores influence the hysteresis behaviour in the adsorption isotherms when comparing adsorption and desorption [1].

When considering adsorption, besides the structure of the pore, the morphology of the fluid molecules (i.e., their overall shape) is equally relevant as the unique peculiarities of the molecular configuration may lead to different adsorption behaviour. Depending on the pore structure, there are some molecular morphologies that are preferred over others leading to unexpected selectivities [3] and/or enhanced permeability [4].

The main objective of this work is to perform molecular simulations to study both the effect of molecular shape and pore geometry on the adsorption isotherms. For the former, Molecular Dynamics (MD) simulations are used to analyse how the molecular morphology affects the adsorption of model trimers into cylindrical nanopores. The model fluids are composed of three tangentially bonded Lennard-Jones interactions sites with three distinct morphologies; a flexible chain, a rigid "stiff" linear configuration, and a rigid triangular ring. The adsorption and diffusion of these three different morphologies in cylindrical nanopores are studied here for different pore sizes and different values of fluid-solid energy interaction.

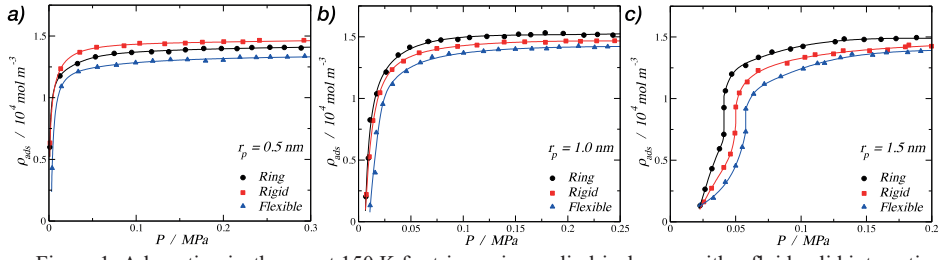

Figure 1: Adsorption isotherms at 150 K for trimers in a cylindrical pore, with a fluid-solid interaction of ε_p/k_b = 19.3 K per particle. (a) r_p = 0.5 nm, (b) r_p = 1.0 nm, and (c) r_p = 1.5 nm. The symbols in the isotherms correspond to rings (filled black circles), rigid linear chains (filled red squares), and fully flexible chains (filled blue triangles). Solid lines are empirical nonlinear fits. Error bars are of the size of the symbols.

$A = -kT \ln Q$

The effect of pore geometry is studied by conducting Grand Canonical Monte Carlo (GCMC) simulations of model fluids in well-defined pores with different cross section shapes but identical pore cross-sectional area. The proposed pores have triangle, square, pentagon, hexagon, octagon, decagon and circular cross-sections. The study quantifies the effect that the energetical and morphological heterogeneities have on adsorbed fluid behaviour. In order to do this, three different cross-sectional areas and three different fluid-solid interaction values are used. It is observed that the key property in the porous structure is the presence of the energetic heterogeneities at the corners of the pores, and that otherwise the influence of the pore shape is rather unnoticeable. The results have relevance as guidelines to the design of nanoporous adsorbents and membranes.

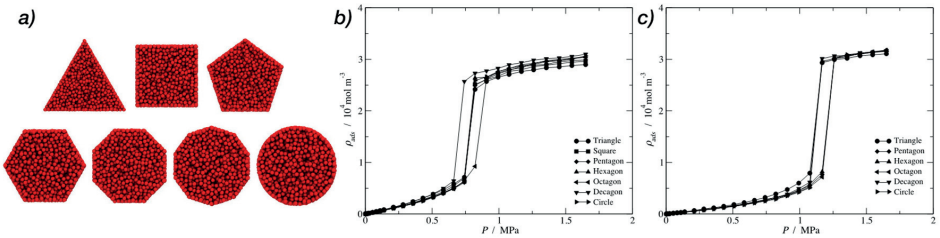

Figure 2: Adsorption isotherms at 100 K for monomers in different pore geometries, with a fluid-solid interaction of ε_p/k_b = 5.0 K per particle. (a) Different pore geometries used in this study, (b) Bigger pores, cross-sectional area, A_c = 12.5 nm^2, and (c) Smaller pores, cross sectional area, A_c = 3.14 nm^2.

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Role of solid-liquid interfacial fluctuations in the spontaneous translation of droplet over heterogeneous surfaces due to thermal cycles

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We discuss our efforts to design systems that show spontaneous motion of nanodroplet over a heterogeneous surface due to thermal cycles. We propose a thermodynamic model (Droplet Engine abbreviated as DropEng) that helps us to identify the constraints on the interfacial properties of such a system. The above model identifies a pair of surfaces (surface-couples) that when combined, results in the spontaneous translation of liquid droplet between them when the temperature is changed between two values. Using molecular simulations we show that the difference in solid-liquid interfacial fluctuations near the two surfaces govern the existence of such pairs. We use model fluid interacting with different crystalline faces to study the indirect effect [1] of interfacial fluctuations due to attractive and repulsive parts of the solid-fluid interaction. Particularly, we realize that variation of interfacial fluctuations due to the repulsive part of solid-fluid interaction favours the existence of surface-couples. However, the dampening of fluctuations due to soli-liquid attractive interaction disfavours the existence of surface-couples.

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$A = -kT \ln Q$

On the Structure and Dynamics of Confined Glycerol

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Equilibrium and transport properties of fluids are deeply affected under 2D or 3D confinement [1]. Knowledge of molecular level properties of confined systems is especially relevant in a wide spectrum of technological applications, including catalysis, oil recovery and membrane separations [2]. Of special interest is the case of viscous glass-forming liquids in mesoporous materials, where a deeper understanding of the physics of the fluid under confinement, based on relationships between structure and mobility, is required in order to fully understand thermodynamic and kinetic properties [3]. Particle-based simulations can provide a detailed insight into this multifaceted problem [4], which is dramatically determined by the complex nature of inter-molecular interactions. In this work, we present results from classical Molecular Dynamics (MD) simulations of condensed interfacial-Glycerol on Gamma-Alumina. Model systems of slit-shaped pores at different degree of saturation and thin films are studied. The heterogeneity imposed by the presence of the solid surface is analysed in terms of the dynamic and structural properties of the liquid in the proximity of the interface and sufficiently far from it. In particular, spatial ordering of Glycerol into quasi-discrete molecular layers is observed and the confinement is also seen to influence the relaxation dynamics as a result of the slowing down of the average molecular motion (translational and rotational) at the solid-liquid interface. In the case of slit-shaped pore geometries, this results in an overall decrease of the molecular self-diffusion when compared to the unperturbed bulk fluid at the same density. Interestingly, an accelerated dynamics is detected for the outermost layers of glycerol molecules in the thin film geometry and not fully saturated pores. Such a behaviour could explain the enhanced self-diffusion of Glycerol on Gamma-Alumina that has been reported in recent experimental observations [5].

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van der Waals Forces at the ice surface

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The Lifshitz theory has been used for the determination of Van der Waals forces at the ice/water/air interface using optical properties of bulk water and ice.

The ice surface plays a crucial role in the growth and evaporation of snowflakes, the reactivity of adsorbed species in the atmosphere and the frost heaving of soils. Particularly, close to the melting point the most significant feature of the ice surface is the growth of a liquid film of premelted ice. In this conditions, the premelted layer can adopt from nanometer to micron thickness, and the equilibrium value is mainly determined by long range van der Waals forces [1].

In the modern view of surface interactions, the role of van der Waals surfaces can be calculated using Lifshitz theory (also known as DLP theory). The crucial quantity here becomes the Hamaker function, rather than the more well known Hamaker constant which provides only the limiting behavior at short distances. The full Hamaker function accounts for retardation effects, and can be calculated from knowledge of frequency dependent optical constants of the materials [2].

Several optical properties from liquid water and ice spectra were reviewed and compared from the biography available. For the determination of the Van der Waals forces, a critical study of these references is made, with an appropriate discussion of the temperature effect. The bibliographic data were obtained from several different optical properties like the complex dielectric function or the complex refraction index. They were converted to a single magnitude, the imaginary part of the complex refraction index: the extinction index, and fit to a Lorentz-type curve, following the Parsegian-Ninham model [2].

With the appropriate adjustment parameters for each curve, a real dielectric function referred to an imaginary frequency was determinated and employed to estimate the interactions. A comparison with the results of similar works is made [3].

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$A = -kT \ln Q$

Understanding the mechanism in gold nanorod formation

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During the last years a great variety of nanoparticles synthesis methods have been developed aim to generate monodisperse nanoparticles that have a great potential for applications ranging from optics to biomedicine.[1] In this context, it is more frequent to use colloidal preparations to generate nanoparticles whose size and shape are perfectly controlled, thus maximizing all nanometric properties and increasing the applications of these materials.

During the development of nanoparticles synthesis it is very common to use surfactants that can adsorb and aggregate readily on their surface.[2] Yet, our understanding on the structure and function of these aggregates remains very limited. In the preparation of gold nanoparticles, for example, coating of the surface by the cationic surfactant cetyltrimethylammonium bromide (CTAB) not only serves as a stabilising agent against aggregation, but also is believed to have an important role in determining growth rates and particle shape.[3] In this paper, we study the structure of CTAB coatings adsorbed onto a gold surface using Molecular Dynamics simulations. We developed a new forcefield model that was employed in simulations with the Gromacs package, using SPC water as a solvent. In our study, we focus on the structural changes that occur on the surface of gold as a function of surfactant concentration, and also consider the role played by ionic force and the presence of co-surfactants and additives. Our results reveal a very rich behaviour of the adsorbed surfactants, which ranges from the formation of stable dimers, to small aggregates or micelles, as well as fully developed bilayers or wormlike micelles depending on the conditions.[4] We will try to discuss how depending the type of aggregates can facilitate the growth of the nanoparticle.

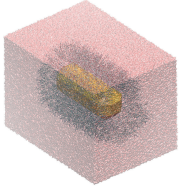

Fig 1. Nanorod gold type single crystal coated by CTAB molecules and SPC.

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A novel coarse-grained model for high molecular weight polymers on solid surfaces

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The adsorption and dynamics of polymer chains on solid surfaces play an important role in many applications, especially in polymer nanocomposites, where inorganic fillers such as carbon black are dispersed in the polymer matrix to improve composite mechanical and rheological properties [1].

In order to predict the impact of the filler on the final structural and thermodynamic properties of the nanocomposites a detailed structural understanding of the polymer-filler interface is needed. It is indeed at the nanoscale that the adhesion between the polymer and the solid substrate is defined.

One of the major challenges in simulations of polymer nanocomposites is to model realistic molecular weight and surface roughness [2].

In this contribution we developed a new coarse-grained (CG) model employed to simulate a realistic carbon black surface in contact with an entangled melt of polyisoprene.

By performing molecular dynamics simulations we characterized the structure of the polymer adsorbed on graphite (Figure 1) which is the main component of carbon black [3]. The roughness of the surface was imparted by the presence of different energy sites, where the energy values were experimentally calculated from the gas adsorption isotherms of ethene in contact with carbon black [3]. A bead-spring model for representing polymer chains in the melt state [4] was used since we demonstrated that this simple CG model is able to reproduce the structural features of polyisoprene.

Using this model we also investigated the behaviour of the adsorbed chains in the presence of plasticizers, low molecular weight diluents, which are added to modify the glass transition temperature of the polymer.

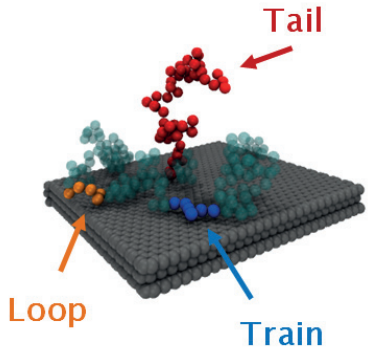

Figure 3 A pictorial representation of a polyisoprene chain adsorbed on the solid surface.

$A = -kT \ln Q$

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Analysis of the diffusion of hydrogen in hydroquinone clathrates using quantum and classical molecular simulations

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Hydroquinone (HQ) is a well-known clathrate former molecule. The detailed study of its different crystalline clathrate phases is promoted by different potential applications that have been recently proposed. One of them is the preferential affinity for carbon dioxide molecules as structure guests, which might represent an alternative for the separation and capture of this gas. Another one is the possibility of using this structure for storage of gases like hydrogen, because the high mobility inside the structure has been pointed out [1].

With the aim to study the interactions and the structure of the HQ clathrate we have used quantum mechanics calculations with periodic conditions to simulate the crystal phase. The PBE functional has been employed in Gaussian to calculate the potential energy landscapes and intercage energetic barriers of the hydrogen diffusion in the crystal phase. In addition, the diffusion process at small times has been studied using quantum molecular dynamics with the same calculation level.

Classical molecular simulations have been also performed for the same system. In a previous work, an initial characterization of hydrogen diffusion within HQ clathrate was presented [2], using a molecular model for HQ based in the original OPLS [3] forcefield, recently proposed by Comesaña *et. al* [4]. Now this study has been performed for wide temperature and occupation conditions, considering effects as structure vacants or multiple occupancy. All the calculations show the high mobility of this guest molecule inside the structure, supporting its possible use for the application of hydrogen storage and transport.

Acknowledgements

The authors acknowledge the financial support from Spanish Ministerio de Economía y Competitividad (project FIS2015-68910-P, cofinanced by the European Regional Development Fund, ERDF) and the computational resources provided by Centro de Supercomputación de Galicia (CESGA, www.cesga.es)

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$A = -kT \ln Q$

Thermodynamics in 1- and 2-Dimensions

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Major qualitative differences in thermodynamic behavior are found between 3-, 2- and 1-dimensional systems, and are a result of the much smaller phase space available in systems of reduced dimensionality. Some examples of such differences are listed in Table 1. Notable are the much smaller entropy and coordination numbers, and much larger fluctuations in thermodynamic variables (volume, density, pressure, internal energy, etc.) that are expected as dimensionality is decreased. For the canonical variables, (N,V,T), the smaller entropy in 2-D and 1-D will result in a less negative thermodynamic potential, $A=E-TS$, so that for a truly equilibrium 2-D or 1-D system to form spontaneously the internal energy must be correspondingly more negative, as may occur due to the strongly directional sp^2 molecular orbitals for carbon atoms.

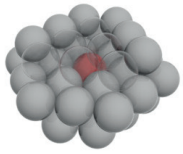
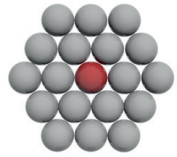
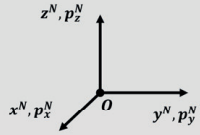
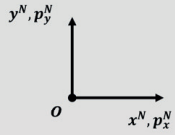
	3D	2D	1D
Image			
Phase Space			
Coordination Number	12	6	2
Number of States, Ω	n^3	n^2	n
Entropy, $S/(k_B \ln n)$	3	2	1
Configurational Energy, $U_c/(N\varepsilon_{sw})$	-6	-3	-1

Table 1. A thermodynamicist's view of reduced dimensionality. For illustrative purposes we employ a 3D face-centered cubic lattice.

Following the preparation of single-layer graphene by Andre Geim and coworkers [1] in 2004, there has been much interest in such '2-D materials', followed by interest in so-called '1-D materials'. Much of the recent work in this area has focused on their electronic properties and the promise of high electronic flux. Little attention has been given to their thermodynamic behavior.

While strictly 1-D and 2-D systems may be rare in nature (or even non-existent, in the sense of thermodynamic equilibrium states), there are a number of applications where the system is 'quasi-2D' or 'quasi-1D'. Examples include the 2-D and 1-D van der Waals materials [2], monolayers adsorbed on planar liquid or solid substrates [3], 2-D solid crystals formed by some proteins on lipid bilayers, and conducting sulfur 'wires' formed inside narrow carbon nanotubes [4]. Strictly 1-D or 2-D systems can serve as reference states in such cases, connected to the real 3-D system via application of an external field or through perturbation expansions.

We first illustrate the qualitatively different thermodynamic behavior for various dimensionalities for materials composed of Lennard-Jones particles, for which accurate equations of state have been developed for both fluid and solid phases [5]. Notable are the impact of dimensionality on those thermodynamic properties that are measures of fluctuations. We also report molecular simulation results for a simple molecular model for materials such as graphene, that can form atomically thin 2-D films.

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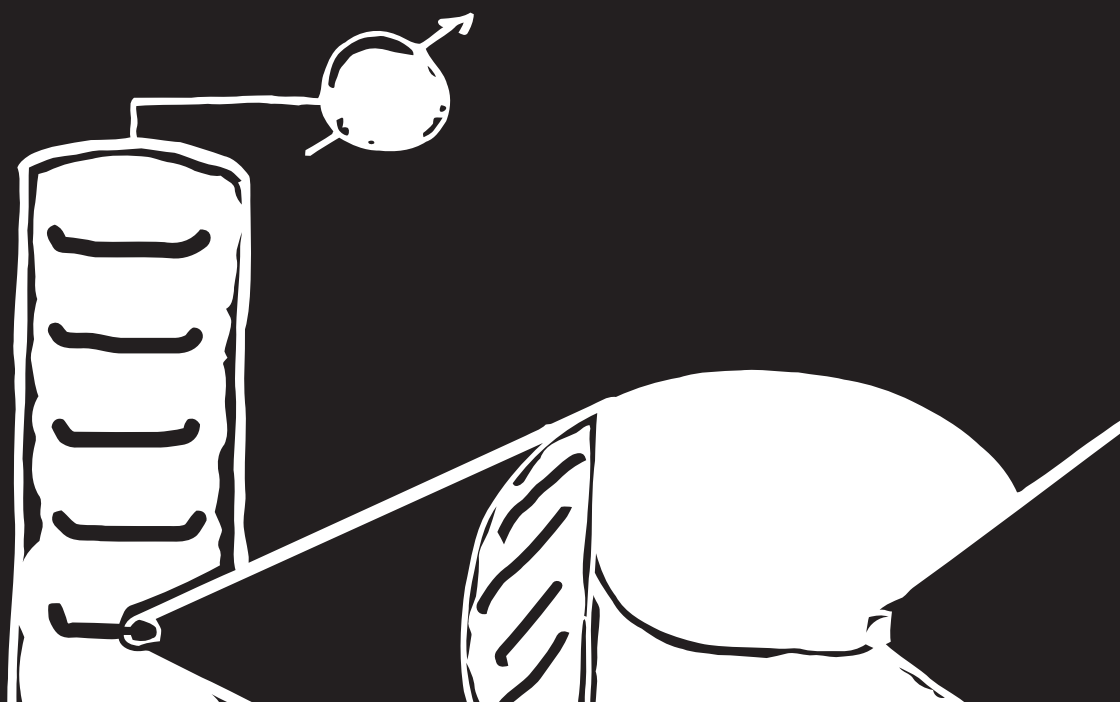
$A = -kT \ln Q$



$$A = -kT \ln Q$$

Oral Presentations: Carbon capture and other industrial applications



Molecular simulation of volumetric and acoustic properties of carbon dioxide + n-heptane binary mixture under pressure up to 70 MPa

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Injecting light gases such as carbon dioxide into oil fields may improve oil displacement and therefore can enhance oil recovery for a wide range of oil types. To simulate such enhance oil recovery processes, as well as for seismic monitoring, volumetric and acoustic properties are key quantities. In particular, the knowledge of volumetric properties as a function of CO_2 content in reservoir conditions is required to predict oil swelling and change in oil compressibility. With this aim in mind, an experimental and molecular simulation investigation of thermophysical properties of binary liquid systems containing supercritical CO_2 and n-heptane has been initiated in our laboratory. To complement recent experimental work on that subject [1], we have used molecular simulation to predict the volumetric and acoustic properties of CO_2 and n-C_7H_{16} mixtures in various proportions at two temperatures (303 and 313 K) in the vicinity of the critical temperature of pure carbon dioxide (304.13 K) and at pressures from 10 to 70 MPa, i.e. above the critical pressure of the pure components. The molecular simulations have been performed by using classical Monte Carlo (MC) techniques and the aforementioned properties have been determined from Kirkwood-Buff (KB) and Statistical Fluctuation (SF) theories [2,3]. By doing so, simulations allowed to better understand and explain some experimental results by providing microscopic physico-chemical insights, in particular regarding the "clustering" effect [1]. Thus, it will be shown that molecular simulation techniques are mature enough to accurately predict the thermophysical properties of such complex systems.

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$A = -kT \ln Q$

Monte Carlo molecular-simulation study of CO_2 in calcite pores

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We perform Monte Carlo simulations of carbon dioxide in a calcite pore. Three different scenarios are considered: (i) a calcite pore containing only carbon dioxide; (ii) a calcite pore containing methane and carbon dioxide; and (iii) a calcite pore containing methane, water and carbon dioxide. The system comprises the calcite pore itself in which the contained fluid is in equilibrium with a bulk-fluid reservoir. Simulations are performed in the grand canonical ensemble; increasing the carbon dioxide content in the bulk (via an increase in its the chemical potential) thereby increases the amount of carbon dioxide in the pore. We examine variations in confined-fluid density as a function of the carbon dioxide content. The behaviour of confined fluids is further analyzed with the help of individual fluid-density profiles in the direction normal to the fluid–solid interface, and coarse-grained fluid-molecule–solid potentials obtained using the free-energy-averaging method of Forte *et al.* [1]. The relative adsorption affinity to the calcite surface is found to be water > carbon dioxide > methane. In line with the trend of adsorption affinities, fluid–solid interfacial phenomena are observed and changes in these interfaces due to variation in carbon dioxide content are discussed. Ultimately, it is hoped that the insights from this study will aid the development of multiscale modelling of reservoir fluids.

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Experimental Measurement and Assessment of Equilibrium Behaviour for Phase Change Solvents used in CO_2 Capture

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Keywords: CO_2 capture, Phase change solvents, DMCA, MCA, AMP, MAPA

Aqueous amine solutions that phase separate at elevated temperatures were suggested as solvents for CO_2 capture applications, in order to minimize the heat duty in the desorber. Consequently, the phase behavior of such mixtures attracted particular scientific interest. In this study, the phase behavior of various aqueous amine solutions, was experimentally investigated. A new experimental apparatus was developed and evaluated by determining the CO_2 solubility in aqueous monoethanolamine (MEA) solutions at 40, 60 and 80 ºC. Upon validation of the experimental setup, new experimental data were obtained for aqueous solutions containing *N,N*-dimethylcyclohexylamine (DMCA), methylcyclohexylamine (MCA) and 2-amino-2-methyl-1-propanol (AMP) at 40, 60 and 90 ºC, which exhibit phase change behavior. It was observed that the investigated solutions present vapor – liquid equilibrium (VLE) at 40 ºC and vapor-liquid-liquid equilibrium (VLLE) at 60 and 90 ºC for CO_2 partial pressures up to app. 70 kPa. In addition, screening experiments were performed using sulfolane, which has been previously used for gas sweeting applications, instead of AMP in the DMCA-MCA mixture. However, such system presents relatively low CO_2 solubility, compared to the aforementioned (DMCA-MCA-AMP) system and aqueous MEA solutions. Finally, additional screening experiments were performed for two aqueous DMCA – 3-methylaminopropylamine (MAPA) amine solutions at different concentrations.

In addition, a Computer Aided Molecular Design and Pareto optimization procedure resulted in the suggestion of a novel solvent (S1) for CO_2 capture. Subsequently, experimental VLE data were obtained for CO_2 systems with aqueous solutions of S1 and mixtures of S1 and DMCA, at 40-90 ºC and CO_2 partial pressures ranging from 10 to 100 kPa. S1 solutions exhibited high CO_2 loading values and VLE behavior at all investigated conditions. The addition of DMCA in such S1 aqueous mixtures (DMCA:S1 3:1 mole ratio) resulted in the liquid-liquid phase separation and, thus, the observation of a VLLE behavior, rendering such solvent system as a potential phase change solvent.

$A = -kT \ln Q$

Influence of amorphous $CaCO_3$ in scallop shell powder on Sr^{2+} removability

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Abstract

Polluted water containing radioactive elements leaked during the Fukushima nuclear accident in 2011. As a result of this accident, significant costs will be incurred for the maintenance and decommissioning of nuclear reactors, and it will be difficult to spend further resources on nuclear facilities. Therefore, in this study, we aimed at developing inexpensive materials that can remove radioactive elements from aqueous solution. We found that powders obtained by milling scallop shells, which were discarded in large quantities, removed Sr^{2+} from aqueous solution. Since the Sr^{2+} removability of scallop shell powder improved as the milling time increased, it was considered that the increase in the specific surface area influenced Sr^{2+} removability. Thus, we evaluated the Sr^{2+} removability of unmilled $CaCO_3$ and milled scallop shells, which have the same specific surface area. It was found that the scallop shell powder had a higher Sr^{2+} removability than the unmilled $CaCO_3$. Thus, we found that in addition to the surface area, the partially amorphous structure of $CaCO_3$ produced by milling influences Sr^{2+} removability.

Introduction

Water contaminated with radioactive elements such as Sr-90 and Cs-137 leaked during the accident caused by the Great East Japan Earthquake at the Fukushima Daiichi Nuclear Plant in 2011. Consequently, approximately 800 thousand tons of contaminated water remains around nuclear power plant facilities in 2018[1]. This continues to seriously damage the Fukushima prefecture. Japan paid about 70 trillion yen for the Fukushima nuclear power plant, and it became clear that significant expenditure is necessary for maintaining and decommissioning nuclear plants[2]. Moreover, it is very difficult to pay additional costs for measures to prevent accidents like the one that occurred at the Fukushima nuclear power plant.

We have developed an inexpensive material that can remove radioactive elements and will use it at nuclear power plants as a precautionary measure. We focused on $CaCO_3$ because it is harmless to the human body and is abundantly available on Earth. It can also be applied to the 60 nuclear reactors in Japan[3]. In this research, further cost reduction was achieved by using scallop shells, which are composed of 95 % $CaCO_3$. Approximately 200 thousand tons of these shells are generated annually in the form of generated as waste from the industry in northern Japan[4]. The use of these scallop shells to remove radioactive elements simultaneously reduces costs and helps recycle shell waste.

Experiments were conducted with this objective, and it was found that the scallop shell powder can remove Sr^{2+} from aqueous solution[5]. Thus, we aimed to obtaining basic knowledge about the mechanism of Sr^{2+} removal by the scallop shell powder.

Method

Scallop shell powder was suspended in an aqueous solution of Sr^{2+} 10 mg/L, after filtration, the Sr^{2+} concentration was evaluated by an atomic adsorption spectrophotometer (Thermo, iCE3300). Differential scanning calorimetry (DSC) (Rigaku, Thermo plus EV02 DSC8231) was used to measure the presence or absence of amorphous structure contained in the sample.

Results and discussion

We hypothesized that the specific surface area of scallop shell powder increases on milling, which influences its Sr^{2+} removability. Figure 1 shows the Sr^{2+} removability of unmilled $CaCO_3$-A (specific surface area: 0.40 m^2/g), unmilled $CaCO_3$-B (6.6 m^2/g), and 3-h milled scallop shell powder (6.3 m^2/g). The Sr^{2+} removability was observed to improve by increasing the specific surface area. However, the Sr^{2+} removability of scallop shell powder was found to be higher than that of $CaCO_3$-B although they have the same specific surface area. Thus, amorphization via milling likely affects the Sr^{2+} removability of scallop shell powder. Figure 2 shows the DSC measurement results of the amorphous $CaCO_3$-B and scallop shell powder. Neither the endothermic nor exothermic peak confirmed the presence of $CaCO_3$-B; however, an endothermic peak arising due to water evaporation at 100 ℃ could be attributed to scallop shell powder. In addition, an exothermic peak due to crystallization at approximately 300 ℃ could be attributed to the amorphous $CaCO_3$. Therefore, to investigate the effect of amorphization on the Sr^{2+} removability of scallop shell powder, we evaluated the Sr^{2+} removability of $CaCO_3$-B and scallop shell powder that were heated at 400 ℃ (Fig. 3). Although a change in the Sr^{2+} removability of $CaCO_3$-B was not observed regardless of the heat treatment, the Sr^{2+} removability of scallop shell powder decreased on heating. Finally, on heating, the amorphization of $CaCO_3$ by milling resulted in its recrystallization; therefore, the Sr^{2+} removability of $CaCO_3$ decreased because of the amorphous crystallization.

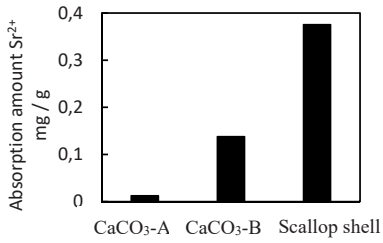

Fig.2 The Sr^{2+} removability of $CaCO_3$ with different specific

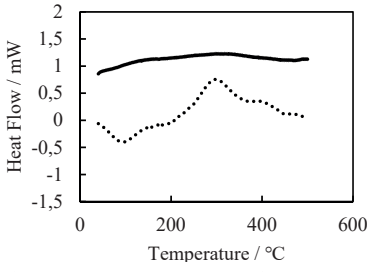

Fig.2 DSC measurement of $CaCO_3$ and Scallop shell powder
－：$CaCO_3$-B, ⋯Scallop shell powder

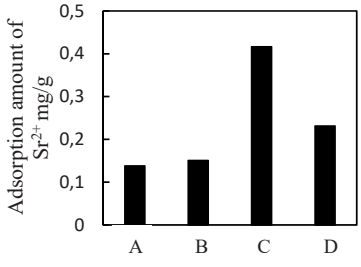

Fig.3 Influence of heat treatment on the Sr^{2+} removability
A：$CaCO_3$-B, B：$CaCO_3$-B-heat,
C：Scallop shell , D：Scallop shell-heat

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$A = -kT \ln Q$

Modeling of Gas Solubility in Aqueous Electrolyte Solutions using the Electrolyte Cubic-Plus-Association Equation of State

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In addition to being able to clog natural gas pipelines, gas hydrates also have some interesting application possibilities such as gas separation and storage, different electrolytes can work as thermodynamic inhibitors or promoters for hydrate formation.

Study of gas solubility in aqueous electrolyte solution of hydrate systems is important for hydrate application. This work presents a modeling study the solubilities of some gases in several aqueous electrolyte solution systems with the electrolyte Cubic-Plus-Association Equation of State.

The ion-water interaction parameters (for some quaternary ammonium salt solutions) are obtained by fitting the experimental data of mean ionic activity coefficients and osmotic coefficients, and the ion-gas interaction parameters are obtained by fitting the experimental data of gas solubility in aqueous electrolyte solutions.

The results show that e-CPA can satisfactorily correlate single gas solubilities at hydrate formation temperature and pressure ranges, the salting-in/salting-out regions and the influencing factors of salt effect are also studied.

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A molecular simulation approach for the removal of pharmaceuticals from wastewater

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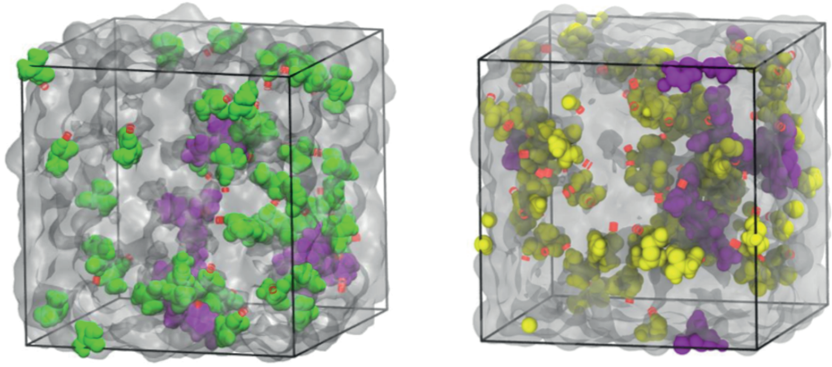
Nowadays, several pharmaceuticals that are difficult to handle by conventional treatments are both ubiquitous and on the rise in sewerage [1]. These unprocessed drugs are having a worldwide negative impact, due to their persisting accumulation in aquatic environments.

Pharmacological drugs that have been incompletely metabolised and secreted by our bodies present the main point of entrance to the wastewater network. For instances, recent reports on environmental analysis suggest substantial contamination of water with Prozac (Fluoxetine) a common antidepressant, which has a negative impact on aquatic life [2].

Therefore, it is of significant interest to reduce these drugs concentration - before they reach the wastewater treatment plants - by developing and deploying specific adsorbents at key nodes, like hospitals.

Here, different molecular simulation methodologies are used to study various drugs aqueous systems at the molecular level to produce polymeric matrixes following the molecularly imprinted polymers (MIP) principles [3,4]. The design of high-affinity porous materials towards selected drugs will be guided by in-silico studies of their solubility, self-diffusion, octanol-water partition coefficient, and the complexation step of drug-MIP functional monomers in different solvents.



Equilibrated pre-polymerization mixtures containing stoichiometric functional-monomer:Prozac:Acetonitrile ratio of 8:1:150, for methacrylic acid (left) and itaconic acid (right).

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$A = -kT \ln Q$

A combined approach to monitor gas mixtures, containing CO_2, in geological system :aquifers

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One major concern of the geological storage of CO_2 is the leakage and diffusion of CO_2 into the adjacent aquifers. This requires regular monitoring of the aquifers and field sampling tests from these geological systems. One known inconvenience of the conventional industrial sampling equipment is the degassing of the sample during the transfer and analysis from aquifer.

In this work a state-of-the-art apparatus capable of taking samples at reservoir conditions *i.e.* the depth of 3500 meters and temperatures up to 400 K is presented. The monitoring apparatus offers a combined chain of 1) in depth measurements and sampling, 2) single phase sample transfer to the surface 3) dissolved gas composition measurements and 4) thermodynamic prediction of the composition of the dissolved gas in the aqueous phase. One of the major advantages of the presented measuring tool in comparison to the existing industrial tools is the capability of keeping, transferring and analysing the sample in reservoir conditions.

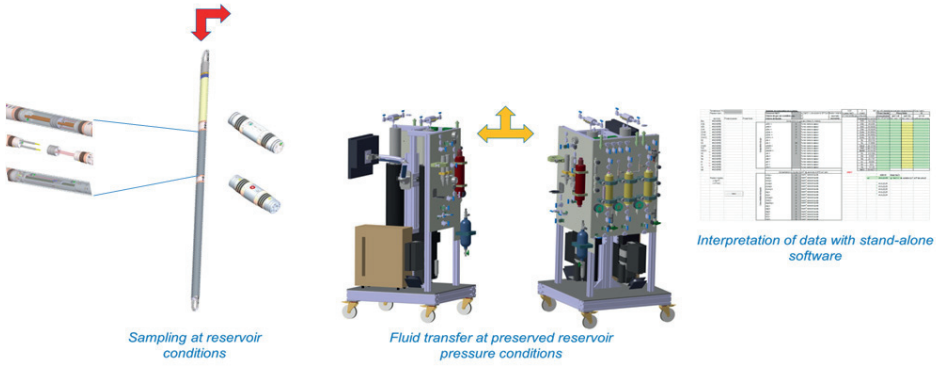

Figure 4 - Schematic of the combined measurement tool for monitoring dissolved gas in aquifers

Solubility of CO_2 in Green Solvents: Experiments and Modelling Using Peng-Robinson Equation of State

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The potential rising solvent-based separation process has been focused on applicable of carbon dioxide capture and sequestration research. Understanding the phase behavior of CO_2 + absorption solvent mixtures is fundamentally important to evaluate its performance of CO_2 capture. In this work, two philic-protic ammonium-based ionic liquids (PILs), diisopropylethyl-ammonium propanoate [DIPEA][C_2COO] and diisopropylethyl-ammonium butanoate [DIPEA][C_3COO], were synthesized and the method for the PILs preparation is completely the same as that reported in our previous work [1]. The purity levels of the synthesized ammonium-based PILs were confirmed by ^1H NMR spectra and their water-contents were analyzed with Karl-Fischer titration. Two aqueous buffer solutions of 3-[4-(2-hydroxyethyl)piperazin-1-yl]propanesulfonic acid (EPPS) and *N*,*N*-Bis(2-hydroxyethyl)glycine (Bicine) were also selected to be investigated in this study. The vapor-liquid phase boundaries (bubble points) were measured at temperatures from 303.2 K to 348.2 K and pressures up to 10 MPa, by using a visual and volume-variable phase equilibrium analyzer (PEA). The operation procedure of the PEA to determine the bubble point has been described elsewhere [2]. In brief, the jacketed high-pressure visual cell comprises a manual hand pump with a maximum internal volume of 38 cm^3, a sapphire window, and a pressure transducer (PDCR 407-01, Druck, accuracy ± 0.04%). The temperature inside the a visual cell was controlled by using circulated thermostatic oil (B-402L, Firstek, accuracy ± 0.1 K) and was measured by an inserted calibrated thermocouple (TM-917, Lutron, accuracy ± 0.1 K). The empty visual cell was purged several times with carbon dioxide to remove the entrapped impurities under room temperature. After evacuating the visual cell, a fixed amount (~36 g) of selected absorption solvent was initially loaded into the visual cell by a syringe pump (Teledyne Isco Inc., model 260D). A known amount of CO_2 was then loaded into the visual cell by using another syringe pump (Teledyne Isco Inc., model 260D). These two precision syringe pumps were operated under constant temperature and pressure. The mass of each loaded compound into the visual cell was calculated from the difference of charged volume (accuracy ± 0.01 cm^3) before and after loaded compound as well as its density at the feeding condition. The densities of carbon dioxide were obtained from the NIST Chemistry WebBook, while the densities of the absorption solvents were determined experimentally by a high pressure densitometer (DMA 512P, Anton Paar, accuracy ± 0.0001 g/cm^3) with an oscillation period indicator (DMA 48, Anton Paar, accuracy ± 0.0001 g/cm^3) [3]. At a fixed temperature and composition, the bubble pressure was visually observed as the pressure at which the first bubble appeared at the top of the visual cell. The bubble pressure was determined experimentally at least five times for every measurement. Vapor-liquid phase transition was isothermally observed for CO_2 + selected absorption mixtures under a certain amount of CO_2 loadings in mole fraction. The solubility of carbon dioxide in [DIPEA][C_2COO] is illustrated in Fig.1. For an example, the binary system of CO_2 + [DIPEA][C_2COO] at 303.2 K with the mole fraction of CO_2 to be 0.1022. A homogeneous liquid phase was observed as pressures higher than 0.42 MPa. First small bubble appeared in the visual cell as pressure decreased down to 0.29 MPa. Similar phase transition behaviour were also observed from CO_2 + [DIPEA][C_3COO] and two systems containing aqueous buffer solutions. Fig. 2 shows that the bubble pressure increases with increasing the mole fraction

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of CO_2 in [DIPEA][C_2COO] system. Fig. 3 compares the solubilities of carbon dioxide in [DIPEA][C_2COO] and [DIPEA][C_3COO], indicating that the CO_2 solubility in [DIPEA][C_2COO] is much higher than that in [DIPEA][C_3COO] under the same condition. Additionally, Fig. 4 also shows that ionic liquid [DIPEA][C_2COO] is better than 10 mass% Bicine aqueous buffer solution for CO_2 capture. In this work, a thermodynamic model based on the Peng-Robinson equation of state [4] with the two-parameter *vdW* one-fluid mixing rules (*PR-vdW*) was used for representing the phase behavior of CO_2 + the absorption solvent systems. The smoothed lines in Fig. 2 are the calculated results from the *PR-vdW*. The agreement between calculated and experimental values is excellent.

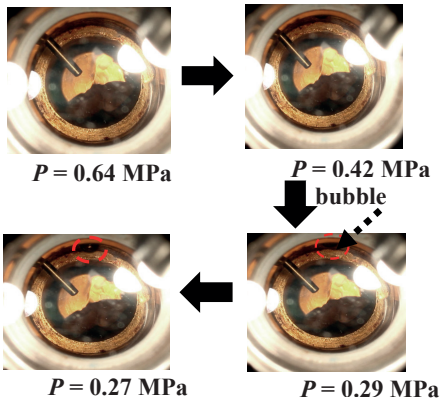

Fig. 1 Photographs of VLE phase transition for CO_2 (1) + [DIPEA][C_2COO] (2) at 303.2 K and x_{CO2} = 0.1022.

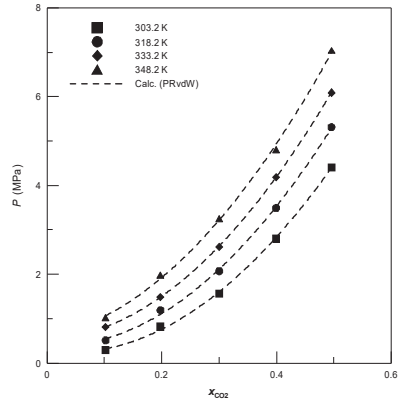

Fig. 2 Comparison of the calculated results from the *PR-vdW* with experimental results of CO_2 + [DIPEA][C_2COO].

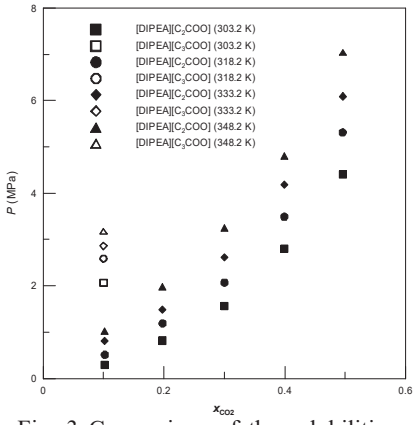

Fig. 3 Comparison of the solubilities of CO_2 in [DIPEA][C_2COO] and in

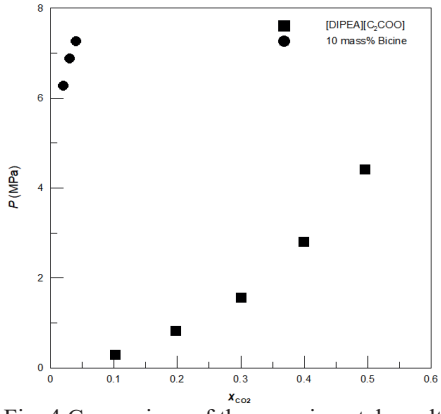

Fig. 4 Comparison of the experimental results of CO_2 + [DIPEA][C_2COO] and CO_2 + 10 mass% Bicine aqueous solution at 303.2 K.

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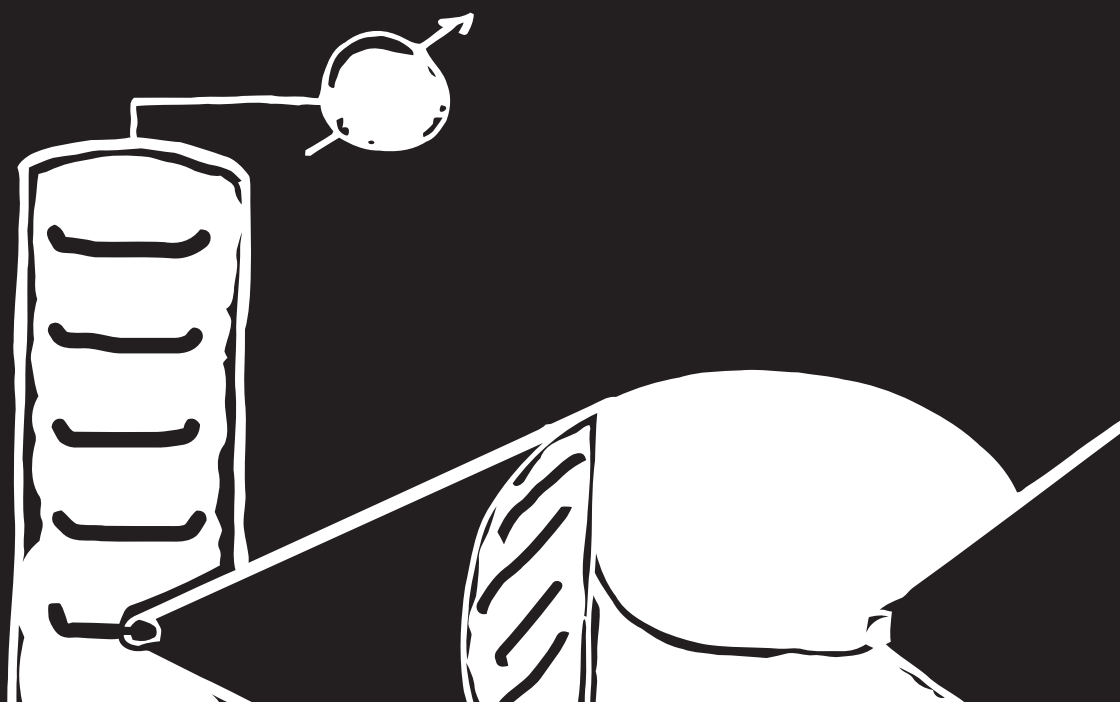
Short Oral Presentations: Engineered self-assembly



Phase behavior of hard board-like particles in an external field

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In the light of our recent work on the self-assembly of colloidal suspensions of hard board-like particles (HBPs) [1], we now report our simulation results on their phase behavior under the effect of an external field and assess the still disputed occurrence of the biaxial nematic (N_B) liquid crystal phase [2]. The external field promotes the rearrangement of the initial isotropic (I) or uniaxial nematic (N_U) phase and the formation of the N_B phase. In particular, very weak field strengths are sufficient to spark a direct I-N_B or N_U-N_B phase transition at the self-dual shape, where prolate and oblate particle geometries fuse into one. By contrast, forming the N_B phase at any other geometry requires stronger fields and thus reduces the energy efficiency of the phase transformation. Our simulation results show that self-dual shaped board-like particles with moderate anisotropy are able to form N_B liquid crystals under the effect of a surprisingly weak external stimulus and suggest a path to exploit low-energy uniaxial-to-biaxial order switching.

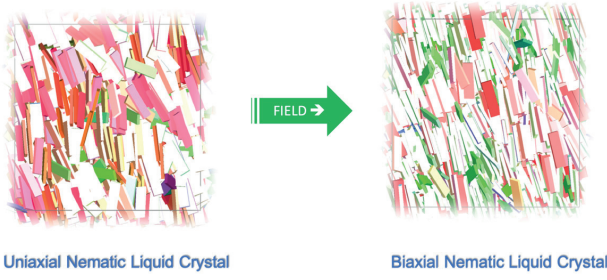

Fig. 1. Uniaxial-to-biaxial switching resulting from the application of an external field.

Our results suggest that it is indeed possible to observe biaxial nematics in colloidal suspensions of monodisperse HBPs. To this end, one needs to apply an external field whose strength is comparable to the particle thermal energy. In particular, the self-dual shape is the most appropriate particle geometry for energy-efficient I-N_B and N_U-N_B phase transitions. Although these conclusions agree well with past theoretical works [3], *de facto* they indicate that this agreement is the consequence of restricting particle orientations and/or neglecting the occurrence of positionally ordered phases, which artificially enhance the stability of the N_B phase.

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Manipulation of Cholesteric Liquid Crystal Phases Behaviour and Molecular Assembly by Molecular Chirality

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Cholesteric liquid crystals (LCs), transferring molecular chirality to macroscopic scale, are fascinating materials which exhibit chiral-ordered structures. Using of a flexible chain model with helical interaction sites (FCh) [1] and molecular dynamics simulations, we study the LC phase behaviour with varying molecular chiralities in order to deepen the understanding of the connection between molecular chirality and phase helicity. Three types of LC phases, isotropic, cholesteric and nematic, are identified. The FCh model with no molecular chirality exhibits isotropic-nematic transition, and the FCh model with weak to moderate molecular chiralities, shows isotropic-cholesteric phase transition. The FCh model with a large internal chirality shows isotropic-cholesteric-nematic phase transitions. The analysis of simulation data further reveal the fluid structures and molecular assemblies in different phases. As the temperature decreases, the FCh model with moderate internal chirality exhibits two phase transitions, first from isotropic to cholesteric, and then to a new phase with twisted alignment of molecules.

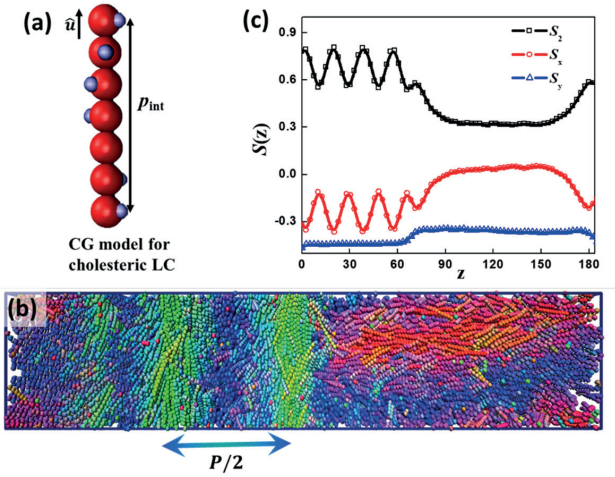

Fig. 1 (a) Coarse-grained molecular model for cholesteric LCs: flexible chain particle with helical interactions (FCh) model; (b) isotropic-cholesteric coexistence of FCh systems; (c) Orientational order parameter distribution S(z).

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Thermodynamics of clusters of colloidal magnetic particles

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In this work we present a simple model of colloidal magnetic particles with short-ranged depletion interactions to study their self-assembly at finite temperature and under a possible external magnetic field. Using basin-hopping global optimization [1], we obtain the putative global energy minima up to N=50. The structures we find include linear chains, circular rings, stacks of two and three circular rings, as well as compact configurations [2]. The combined effects of temperature and external magnetic field on those relevant structures, probed using parallel tempering Monte Carlo simulations, are found to be both significant, and tentative phase diagrams of selected sizes in the (temperature, magnetic strength) plane are presented [3].

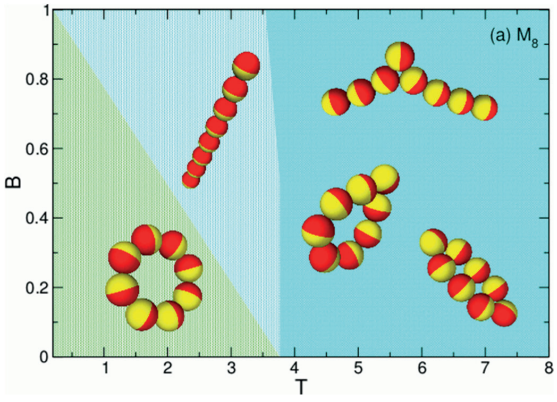

Fig1. Structural phase diagram for eight colloidal magnetic particles.

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Unipletion in colloid-polymer mixtures

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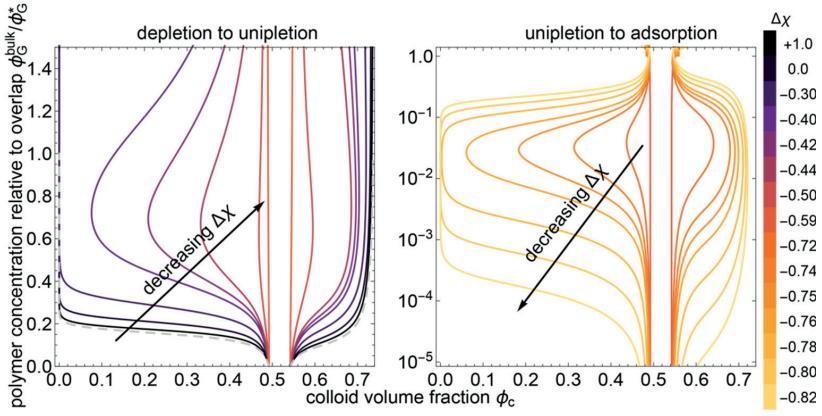
Addition of polymers to a colloidal dispersion modulates the interactions between the colloids [1]. The precise effect on the colloidal phase behaviour sensitively depends on the effective colloid-polymer interactions [2]. We present a theoretical framework to predict the phase behaviour of colloid-polymer mixtures for varying affinities between colloid and polymer, ranging from polymer depletion to adsorption (see Fig. 1). For certain conditions, polymers are neither depleted nor adsorbed: the polymer concentration is essentially constant up to the colloidal surface, which we term 'unipletion'. Near this condition, the calculated phase diagrams reveal a stable-unstable-restabilization transition with increasing polymer concentration. Similar effects have been reported experimentally, for instance as a function of temperature [3], which may modulate the effective polymer-colloid affinity. Understanding unipletion opens up the possibility of preparing highly dense, yet stable colloid-polymer mixtures.



Phase diagrams generated. Dashed grey curve corresponds to the phase diagram obtained using generalized free volume for polymers under Theta-solvent conditions. The effective colloid-polymer affinity is denoted via $\Delta\chi$. For $\Delta\chi \approx -0.59$, unipletion takes place, and thus the colloidal fluid-solid coexistence for all depletant concentrations remains at the same colloid volume fraction as in the depletant-free case.

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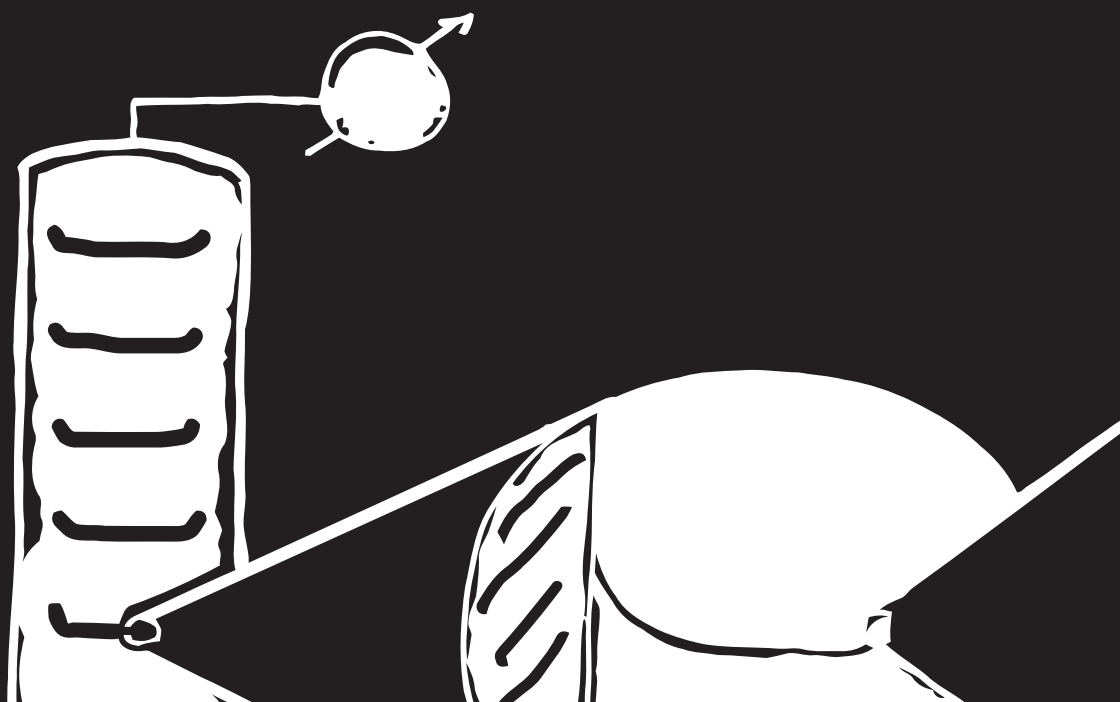
Short Oral Presentations: Non-equilibrium thermodynamics



Thermal conductivity of Fullerene C60 Nano-Fluid using the Transient Hot-Wire Method

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Presented in this paper is an investigation on the thermal conductivity of a nano-fluid obtained by dispersing in 1,2,3,4-Tetrahydronaphthalene varying concentrations of Fullerene C60. A custom-made transient hot-wire apparatus was employed. The transient hot-wire method is the calorimetry technique generally used to measure the thermal conductivity of liquids. The technique was implemented by adopting a measurement protocol that involved the use of a calibration fluid of known thermal conductivity; so as to reliably utilize the transient hot-wire method to the mixtures as a function of temperature. The study was conducted within the temperature range of 263 K to 324 K.

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Definition of frame-invariant Soret coefficients for ternary mixtures

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The definition of the Soret coefficient of a binary mixture includes a concentration prefactor, $x(1\text{-}x)$ when mol fraction x is used, or $w(1\text{-}w)$ when mass fraction w is used. In this presentation the physical reasons behind this choice are reviewed, emphasizing that the use of these prefactors makes the Soret coefficient invariant upon change in the reference frame, either mass or molar. Then, it will be shown how this invariance property can be extended to ternary mixtures by using an appropriate concentration prefactor in matrix form. The presentation will be completed with some considerations of general non-isothermal diffusion fluxes, binary limits of the concentration triangle, selection of the dependent concentration in a ternary mixture, and, finally, extension to multi-component mixtures.

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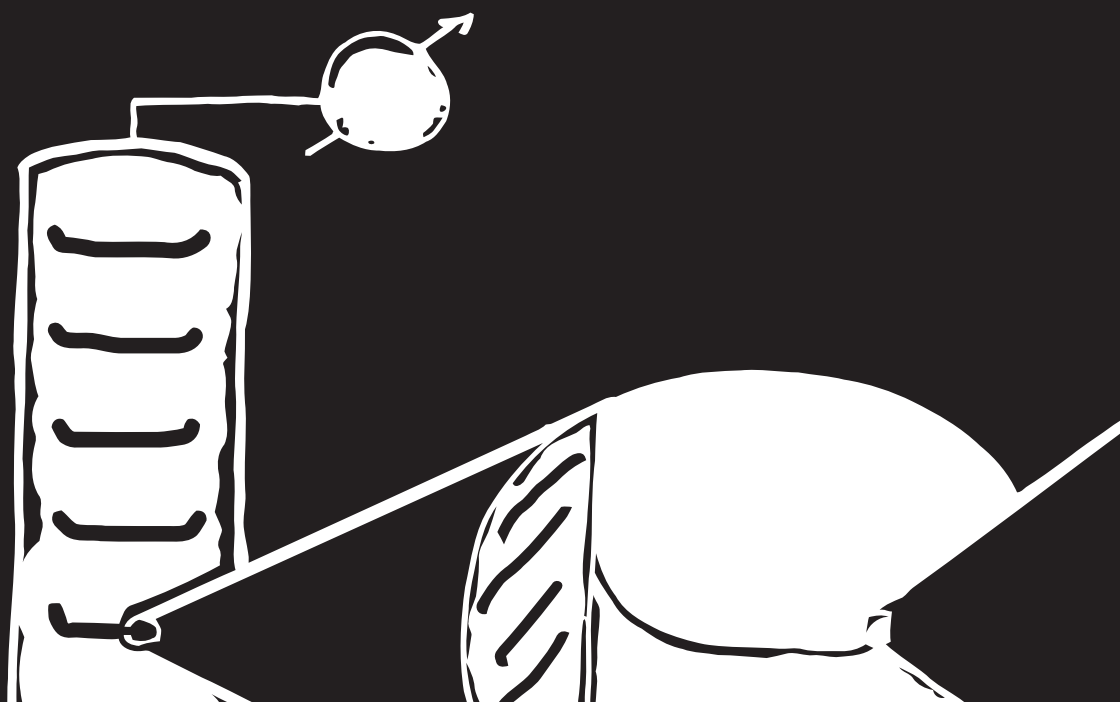
Poster Presentations: Advances in Molecular Simulation



Compartmentalisation of tiny depletants in crowded discotics

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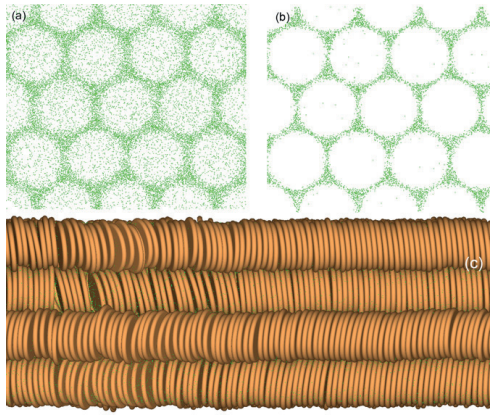
Whenever dispersed colloidal particles are mixed with non-adsorbing species, an indirect, entropy-driven attraction between the colloids emerges [1]. The range of the resulting depletion interaction is set via the size of the so-called depletant. Here, we study the effects of adding *tiny* depletants to a discotic system. This gives rise to a low-density columnar phase (C_1) coexisting with a denser one (C_2) [2]. Theoretically, we account for the volume available for depletants in the columnar state on geometrical grounds [3]. The performed direct coexistence Monte Carlo simulations enable to determine the C_1-C_2 equilibria and its stability. Tie-lines from theory and simulations are in remarkably close. Deviations can be explained from different mesogenic colloids considered in theory and simulations [4].



Simulation snapshots of colloids (brown) and depletants (green). **(a, b)** Snapshots from the {0001} plane of the depletants present in the equilibrium lower-density [C_1, **(a)**] and higher-density [C_2, **(b)**] columnar phases (colloids not shown). **(c)** Snapshot from the {1100} plane of a final direct-coexistence simulation, where the C_1 phase occurs on the left and the C_2 on the right of the simulation box.

It becomes clear that an accurate account of the compartmentalization of these tiny depletant over the different high-density phases is key to understanding the coexistence at hand. In the lower-density columnar phase (C_1) depletants are present between the flat faces of the discotics [snapshot **(a)**], as opposed to the denser phase (C_2) [snapshot **(b)**]. Consequently, the C_1-C_2 coexistence is driven by the depletant partitioning *along* the columns. Only hard (repulsive) colloid–colloid and depletant–colloid interactions are considered: entropy suffices to explain crystalline-like coexistences at high colloidal densities, where depletants compartmentalise among the pockets of the colloidal phases. Our results provide a fundamental understanding on partitioning effects in highly concentrated and size-asymmetric environments, relevant in biological systems [5, 6].

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Vapor pressure depression in protic and non-protic electrolyte solutions from direct Gibbs ensemble simulation

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Thermodynamic properties of electrolyte solutions are a central feature in applications spanning from batteries and supercapacitors to reactive gas processing and facilitated transport membranes. However, thermodynamically accurate molecular models for electrolyte solutions remains an elusive challenge, evidenced by several new electrolyte models proposed in recent years based largely on the properties of aqueous solutions [1]. In practice, more complex mixtures are often encountered in electrolyte systems, such as organic solvents or polymers. Given the sensitivity of electrolyte molecular models to the water model with which they were developed, it is unlikely for thermodynamic properties to be well described in systems comprising non-aqueous solvents or other organic species.

In this study, we address the issue of electrolytes in non-aqueous systems by characterizing solvent activity in protic and non-protic electrolyte solutions as a function of molality. For each of the solvents methanol, acetone, and acetonitrile we characterize vapor pressure depression in response to selected alkali halide electrolytes, using models by Joung and Cheatham [2], Horinek et al., [3], and Reiser et al. [4]. Solvents are in each case represented by the TraPPE [5-7] force field. Osmotic coefficients are estimated together with liquid densities at the saturation pressure. Direct Gibbs ensemble simulation is employed for simulation of liquid and vapor properties, an attractive alternative to existing free energy and membrane-based methods due to its direct physical correspondence with experimental methods and elimination of possible surface effects.

For each solvent-electrolyte combination we assess model accuracy by comparison with experimental values of the osmotic coefficient and liquid density as function of concentration. We argue that improved transferability can be achieved through the inclusion of non-aqueous systems in the model development, paving the way for the next generation of electrolyte molecular models to go beyond water as the singular solvent.

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Unraveling the mechanism behind the cloud point temperature anomaly of ionic liquid mixtures in aqueous solutions by computer simulations

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Stimuli-responsive systems, capable of changing their state or properties in response to external stimuli such as temperature, magnetism, light or pH are of crucial relevance to the design of innovative materials and more efficient catalytic and separation processes. In this context, the use of temperature-responsive systems has provided a fresh boost to solid-liquid and liquid-liquid extraction processes in which extraction can occur under homogeneous conditions prior to the preferential partition of products and impurities in separate phases after temperature adjustment.[1,2] The temperature-responsive solubility of systems, which manifests itself by the presence of an upper or lower critical solution temperature (UCST/LCST), is attributed to dominant entropic (LCST) or enthalpic (UCST) effects from the interactions between the solute and water, most prominent of these being hydrogen bonding and strong polar interactions.[3]

Despite these promising aspects, temperature-responsive systems are traditionally restricted to non-ionic polymeric and surfactant systems with few ionic systems presenting temperature dependent phase separation.[4] Ionic liquids (ILs) are low-temperature melting salts that have emerged as a viable alternative to volatile organic solvents due to their negligible vapor pressure and extended solvation ability which can be further tailored by varying the cation and anion structure. In this work, aqueous ionic mixtures of tetraalklylammonium chloride ([N_{4444}]Cl) and the anionic surfactant sodium dodecylsulfate (SDS) are taken as a basis to explore ILs mixtures as temperature-responsive systems. The ([N_{4444}]Cl – -SDS mixtures present an anomalous temperature dependent behaviour as a function of the [N_{4444}]Cl to SDS ratio, *c.f.* Figure 1.

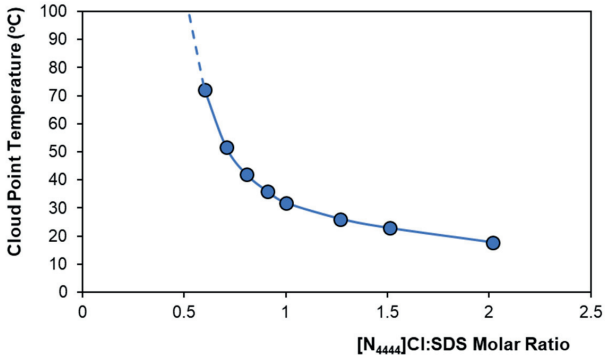

Figure 1. Cloud point temperature of the aqueous [N_{4444}]Cl – SDS system as function of the [N_{4444}]Cl to SDS molar ratio ([SDS] = 0.2M).

A complimentary experimental and simulation approach is developed to better understand the underlying molecular mechanisms contributing towards the thermo-responsiveness of this system. To this end, a new MARTINI coarse grain model is developed to probe the relationship

between the extent of $[N_{4444}]Cl$ adsorption onto the SDS micelle surface and the presence of an accessible cloud point temperature. Results indicate the charge diffuse nature of the $[N_{4444}]^+$ cation allow it to strongly adsorb onto the SDS micellar surface, shielding the electrostatic repulsion between neighbouring micelles. The ability of $[N_{4444}]^+$ to shield the micelle charge confers the $[N_{4444}]Cl$ – SDS system a non-ionic character as well as properties traditionally associated such systems, foremost being a temperature-responsive behaviour.

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$A = -kT \ln Q$

Dynamic Monte Carlo algorithm for out-of-equilibrium processes in colloidal dispersions

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Colloids have a striking relevance in a wide spectrum of industrial formulations, spanning from personal care products to protective paints. Their behaviour can be easily influenced by extremely weak forces, which disturb their thermodynamic equilibrium and dramatically determine their performance. Motivated by the impact of colloidal dispersions in fundamental science and formulation engineering, we have designed an efficient Dynamic Monte Carlo (DMC) approach to mimic their out-of-equilibrium dynamics. Our recent theory, which provided a rigorous method to reproduce the Brownian motion of colloids by MC simulations, is here generalised to reproduce the Brownian motion of colloidal particles during transitory unsteady states, when their thermodynamic equilibrium is significantly modified. To this end, we investigate monodisperse and bidisperse rod-like particles in the isotropic phase and apply an external field that forces their reorientation along a common direction and induces an isotropic-to-nematic phase transition. We also study the behaviour of the system once the external field is removed. Our simulations are in excellent quantitative agreement with Brownian Dynamics simulations when the DMC results are rescaled with a time-dependent acceptance ratio, which depends on the strength of the applied field.

Novel Gear-like predictor-corrector integration methods for molecular dynamics

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The choice of an integration method can significantly affect the result of any simulation by molecular dynamics (MD) and the amount of computer time needed [1]. The most frequently used Verlet algorithm is time-reversible (even symplectic), but it is only of the second order. It can lead, for example, to a systematic error in frequencies. Moreover, certain problems and procedures, such as rotations of rigid bodies and Nosé-Hoover thermostat make its application cumbersome [1, 2].

Higher order symplectic (and thus time-reversible) methods have been discovered, but their usage is limited by the amount of computation involved, since they require multiple calculation of intermolecular forces [3].

The application of Gear's predictor-corrector (PC) methods is restricted by the demand for energy conservation during the integration. On the other hand, PC methods can be of any order requiring still only one calculation of forces. Furthermore, they can be easily applied in all problematic cases mentioned above.

Our aim is to modify the original Gear's PC methods [4] in order to ameliorate the time-reversibility and thus also the energy conservation. The original methods are constructed to be of the highest order and of the best stability possible [4]. Either of these restrictions can be relaxed to obtain a degree of freedom needed to improve the time-reversibility [5].

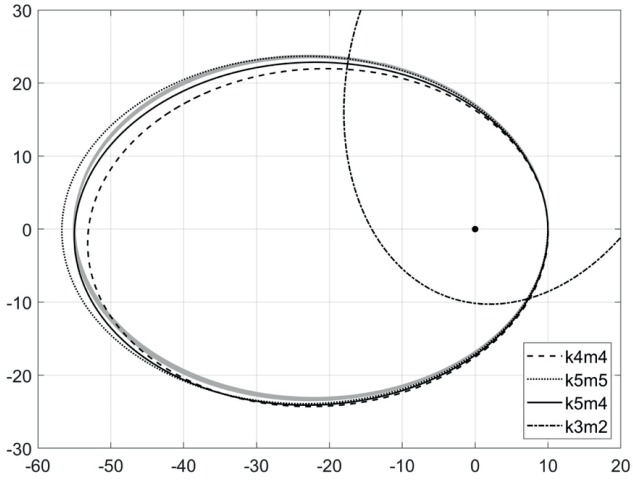

Figure 5. Integration of a planet revolving around a star (reduced units, step = 0.1). The first 5 revolutions are displayed in grey and the 500th revolutions are shown for different methods: original Gear's method of 4th (dashed line) and 5th order (dotted line), improved PC method of 4th order (solid line) and Verlet method (dash-dotted line).

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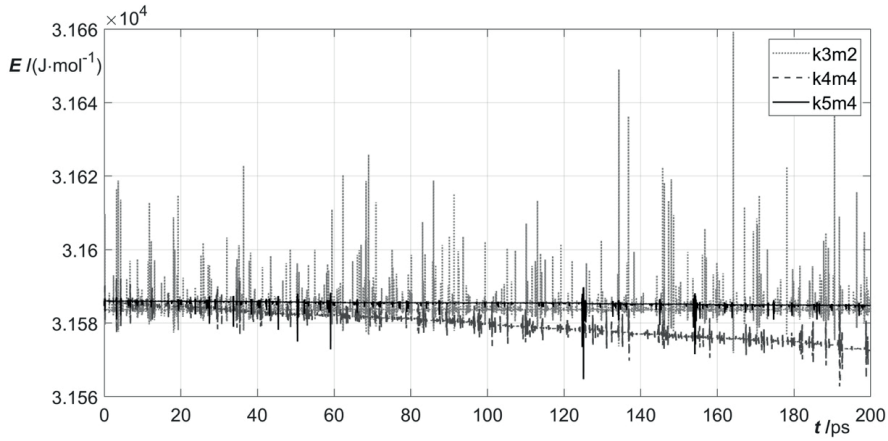

Figure 6. Energy (E) as a function of time (t) during the integration of liquid argon modelled by the Lennard-Jones fluid by different integration methods: Verlet method (dotted line), original Gear's method of 4th order (dashed grey line) and improved PC method of 4th order (solid black line).

In this work several integration algorithms for MD are compared focusing mainly on time-reversibility, energy conservation, the order of the method and the amount of computation involved. The pros and cons of each method are considered, helping choose appropriate algorithm for any specific MD simulation. Tests were done using harmonic oscillator, planet revolving around a star and two simple MD systems – Lennard-Jones fluid of 16 argon atoms and a diamond-like crystal of 51 carbon atoms.

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New interests in the Tolman length for homogeneous crystal nucleation

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We explored the connections between two simulation techniques used to study homogeneous crystal nucleation. One is the seeding technique [1], and the second, which we also apply theoretically, is the finite size technique [2,3]. In both cases, spherical seeds of hard sphere crystals are immersed in a fluid of the same interactions. In the first one (performed in the NPT ensemble), the cluster will either disolve whether its size is below the critical size for the given pressure or continuously grow otherwise. However, in the second (performed in the NVT ensemble), the seed will remain surrounded by the fluid as long as the sphere is the most stable geometry for the global density of the system. We found that the only variable determining the dimensions for both critical clusters in seeding, and stable clusters in finite size, is the density of the fluid. Although, for the latter, the global density of the system must be constrained to certain regions depending on the cluster size we want to apply. Moreover, in both cases for a given fluid density, the magnitude of the critical cluster in seeding agrees with the magnitude of stable (and metaestable) clusters of the finite size method. This ensures that the tolman length is general and apply both for non equilibrium (seeding) and equilibrium techniques (finite size). This presents the advantage that, once the tolman length is known, it is possible to approximate homogeneous nucleation rates with quite basic simulations. We present the tolman length obtained for different models: PHS, LJ (truncated and shifted), and the mW and TIP4P-Ice waters.

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$A = -kT \ln Q$

Fused-sphere SAFT-γ Mie for copolymers: Assessing the transferability of shape factors

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Copolymers, macromolecules comprising multiple types of monomer units, are widely used in many commercial products due to advantageous physical, chemical, or thermal properties. A complex materials design space encompassing chemical composition, comonomer sequence, stereochemistry, and chain architecture may be explored efficiently using coarse-grained molecular dynamics (CGMD) simulations. Most existing polymer CG force fields have been developed using a combination of structural data from all-atom simulations, and refinement of nonbonded parameters through iterative MD or Monte Carlo (MC) simulations to match experimental thermodynamic data. SAFT-γ Mie,[1] a molecular group-contribution equation of state rooted in statistical associating fluid theory, is a highly efficient alternative in that monomer vapor-liquid equilibria (VLE) data is used to directly parameterize a Mie potential.

We recently developed a coarse-graining framework[2] which incorporates bonded potentials derived from all-atom MD simulations into fused-sphere SAFT-γ Mie homopolymer chains. Instead of rigidly bonded tangent Mie spheres, a shape factor parameter is used to allow for bead overlap and structural consistency with the all-atom model. We found that the optimal Mie parameters for a range of fixed shape factor values provide nearly equal representations of the target VLE data. Empirical correlations between shape factor and optimal Mie parameters thus represent a locus of solutions for monomer chemical fragments. Applying bond and angle potentials derived from the all-atom reference system, we determined the shape factor which best reproduces all-atom polymer density through a series of NPT MD simulations.

In this work, we explore the extension of the fused-sphere SAFT-γ Mie approach to copolymers. The transferability of shape factors for copolymers is evaluated for chains of various sequence distributions ranging from diblock to random. We test the capabilities of the fused-sphere SAFT-γ Mie force field on several non-associating model copolymers, as well as a complex poly[(vinyl alcohol)-co-(vinyl butyral)] (PVB) system. We found that a set of shape factors determined from separate homopolymer models does not in general accurately reproduce random copolymer density, when standard SAFT-γ Mie mixing rules are used. This limitation was most evident in the PVB model, in which the lack of association sites leads to overestimation of the strength of nonbonded interactions between vinyl alcohol and vinyl butyral beads. However, performing density matching for a 50:50 copolymer, with only one of the homopolymer shape factors fixed, resulted in a model which correctly predicted copolymer density over a wide range of chemical compositions and sequences. Our model was able to accurately reproduce experimental glass transition temperature and solubility parameter as a function of chemical composition for random PVB copolymers. Additionally, we demonstrate successful reverse-mapping from fused-sphere SAFT-γ Mie copolymer melts to the all-atom model from which bonded potentials were derived.

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Speed-of-Sound Measurements and Virial Equation of State for Krypton

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At the Helmut-Schmidt-University, comprehensive and accurate speed-of-sound measurements in compressed krypton were performed with a pulse-echo instrument. The measurements cover the temperature range between 200 K and 420 K at pressures from 6 MPa to 100 MPa. The expanded uncertainties of the data (95% confidence interval) amount to 2.1 mK for temperature, 0.005% for pressure and 0.01% for speed-of-sound with the exception of a few state points in the vicinity of the critical point, where the uncertainty increases to 0.02%. Between 260 K and 420 K the speed-of-sound in compressed krypton has not yet been measured. The present measurements fill this void.

At the University of Rostock, second to eighth virial coefficients were calculated by the Mayer-sampling Monte Carlo technique using a potential energy curve for the krypton dimer developed in Rostock from first principles [1]. The contributions of the non-additive three-body interactions were approximated by an extended Axilrod–Teller–Muto potential.

The experimental speeds of sound agree with the virial equation of state at low and moderate pressures within 0.1% or less. Comparisons with literature data and the fundamental equation of state of Lemmon and Span [2] demonstrate the high quality of the speed-of sound data and virial coefficients and reveal a considerable potential for improvement of the fundamental equation of state.

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$A = -kT \ln Q$

pK_a Shifts of Carboxylic Acids at the Water-Air Interface from *Ab Initio* Molecular Dynamics

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Understanding the behavior of ions at the water-air interface is of fundamental and practical importance. This is illustrated by the fact that around two thirds of the Earth's surface is the ion rich water-air interface, not to mention sources of atmospheric water and technologically important processes that occur at this interface. Thus, the surface pK_a values of molecules are crucial: along with the composition and structure of the bulk phases, these interfacial pK_a values control the protonation state of the system, interfacial speciation, the sorption of ions, and the energetics of these processes.

It is now well established that the surface pK_a values of organic molecules can differ significantly from their bulk values. However, predicting (or even reliable measuring) this shift remains an open challenge [1-5]. We determine, using *ab initio* molecular dynamics simulations the pK_a shift of carboxylic acids at the water-air interface, in addition to (less directly) the associated absolute surface pK_a values. We adapt the thermodynamic integration scheme developed by Sprik and co-workers where both solute and solvent are treated at the DFT level [6-8].

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Energetic and entropic contributions to the hydrophobic solvation free energy

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The thermodynamics of aqueous solutions of sparingly soluble, hydrophobic solutes such as methane or argon has been the subject of a large amount of work. The primary focus is placed on the solvation free energy or excess chemical potential μ, which can be expressed in terms of the constant-volume solvation energy u_V and solvation entropy s_V [1]:

$$\mu = u_V - Ts_V , \qquad (1)$$

with T the temperature. Thus, the dependence of μ on solute size has received a great deal of attention. Specifically, it has been shown [2] that for small solutes μ increases linearly with solute volume, whereas for large solutes it does so with solute area. It is then natural to ask how this size scaling of μ stems, in the light of Eq. (1), from that of u_V and s_V. Here we answer this question with the aid of molecular simulation.

We have determined μ, u_V, and s_V for pseudo hard spheres (PHS) [3] of various molecular sizes in TIP4P/2005 water [4]. The TIP4P/2005 oxygen site was used to define the cross parameters of the intermolecular potential, their values being $\varepsilon = 0.8802$ kJ·mol^{-1} and σ from 0 to 20 Å. No cross interactions with the remaining TIP4P/2005 sites were considered.

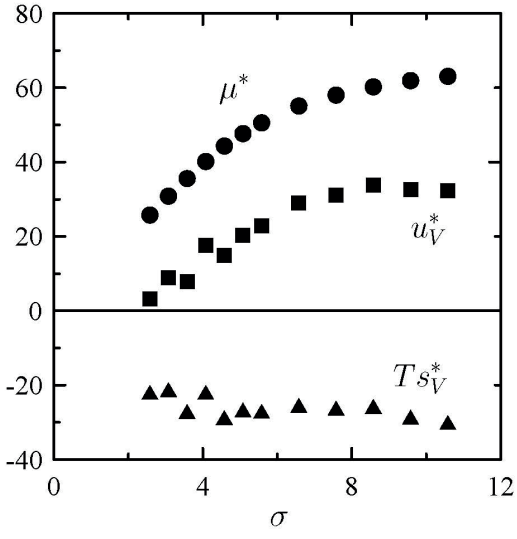

Figure 1. Solvation free energy, μ, and its energetic and entropic contributions, u_V and Ts_V, for pseudo hard spheres with cavity radius σ in TIP4P/2005 water; σ is in Å and μ, u_V, and Ts_V in mJ m^{-2}.

$A = -kT \ln Q$

With these settings, *NpT* molecular dynamics simulations were performed at p = 1 bar and T= 298.15 K using GROMACS software (version 2018.3) with a step time of 2 fs [5]. Solvation of a single solute molecule in a cubic box containing 4465 water molecules was studied under periodic boundary conditions. Following Espinosa *et al.* [6], PHS interactions were implemented in the form of a tabulated intermolecular potential. Electrostatic interactions were treated using the Particle Mesh Ewald technique [7] with a 1 Å mesh and a fourth-order interpolation for the Fourier part of Ewald sums. The Lennard-Jones interactions and the real part of the Ewald sums were evaluated using a cutoff radius of 20 Å with the Lennard-Jones long-range corrections switched off. Temperature and pressure were settled using a Nose-Hoover thermostat [8,9] and a Parrinello-Rahman barostat [10,11] with a relaxation time of 2 ps. Equilibration was reached after 4 ns, while the subsequent 20 ns were used for production. Standard results of these simulations were combined with thermodynamic integration [12] and exact thermodynamic relations [13] to obtain μ , u_V , and s_V . Figure 1 shows preliminary results.

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Implicit solvent simulations: The virial theorem and the calculation of the osmotic coefficient

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In the so-called "implicit solvent simulations", a given system such as a NaCl aqueous solution, is studied without considering the solvent molecules in an explicit way [1]. This approach corresponds to treating the solution at the so-called McMillan-Mayer level (MM), as proposed by Friedman [2]. Effective forces are employed in a stochastic simulation for the calculation of the osmotic coefficient ϕ, defined "… as the pressure divided by the ideal gas pressure" [1]. In reality they are obtaining the osmotic pressure of the solution π, and after that computing the ratio with the van`t Hoff's ideal osmotic pressure. In doing so, they are assuming that the virial theorem of Clausius [3,4] is valid for $\pi$ (van`t Hoff's analogy [5]). As a final result, they present the variation of ϕ with concentration in the range 0-2 mol/kg. The comparison with the experimental values allows the analysis of the different force fields used in the simulations.

In this work it is shown first that within the framework of the McMillan-Mayer (MM) theory of solutions [2, 6-7], in the semigrand isochoric canonical ensemble, that exist an osmotic version of the virial theorem which allow us to understand properly the meaning of the effective forces. The second problem which is addressed has a more thermodynamic nature. It is related with the comparison of the computed values of the osmotic coefficient with the experimental ones. In the simulations the pressure of the solution in osmotic equilibrium changes with the concentration. However, the obtained osmotic coefficients are different from those measured experimentally because in this case the pressure on the solution is held constant [8]. The thermodynamic corrections which are necessary to take into account for this difference will be presented and discussed.

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$A = -kT \ln Q$

A new coarse-grained model for silicic acid

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There is a developing interest in the use of Periodic Porous Materials (PPMs) synthesized from silicic acid and amphiphilic block co-polymers in drug delivery and catalysis. Existing studies of the formation of PPMs have not drawn a clear conclusion as to the formation mechanism. In the prior studies two formation mechanisms were suggested; the first is Liquid Crystal Template (LCT), where the formation is driven by the self-assembly of the amphiphilic block copolymers and silicic acid plays no active role in the formation. The second one is the Co-operative Mechanism (CM), where the silicic acid and the amphiphilic block copolymer are equally important in driving the reaction. We are interested in investigating how the presence of silicic acid affects the self-assembly of these block copolymers with the help of molecular dynamics simulations of coarse-grained (CG) models of these molecules. In this work, we have specifically focused on the development of coarse-grained models of silicic acid. Earlier studies with an existing CG silicic acid model [1] reproduce the silicic acid solubility in water at higher pH ranges, as observed experimentally [2]. The solubility of silicic acid in water is highly dependent on pH. In this work, we are interested at lower pH (range from 1-5). Hence, we have developed a new silicic acid CG model, to reproduce the silicic acid – water behaviour at the pH range of interest. This model has been developed by comparing the solvation free energy of silicic acid in solvent with the values obtained from DFT calculations.

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A hydrogen bonding definition based on spatial distribution functions and its extension to quantitative structural analysis of general intermolecular bonds in solutions and other fluids

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We propose a general approach to define and quantify intermolecular bonds in molecular simulations of liquids and solutions, including hydrogen bonds [1]. The approach is base on finding a continuous *bond region* in the surroundings of a local maximum of a spatial distribution function, enclosed by an isosurface going through the *nearest significant saddle point*. The definition does not require any choice of cut-off values nor any symmetry of the bond region; it can be straightforwardly used at different thermodynamic conditions and in different systems including polarizable models and complex molecules; and the obtained bond regions agree well with the actual kinetics of the bonded particles.

To provide deep insight into the intermolecular bonding, the bond region can be characterised by a number of relevant properties such as the number of bonds per molecule, volume of a bond region per molecule, bond stability/strength, and hydration number.

The approach is first demonstrated for pure water and aqueous NaCl solutions under different thermodynamic conditions and compared with results obtained using commonly-used bond definitions. Second, the approach is used to characterise different selected solutions of electrolytes and associating fluids both in the liquid phase and in supercritical states.

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$A = -kT \ln Q$

Towards accurate force fields for electrolytes: crystalline NaCl, aqueous NaCl, and hydrohalite

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Currently available force fields for electrolytes and their aqueous solutions do not predict well thermodynamic properties including phase equilibria. For example, none of different 13 NaCl force fields studied in our previous work simultaneously yields reasonable values of density and chemical potential, and the incorrect chemical potential values of crystals result in wrong predictions of electrolyte solubility [1]. Wrong solubility predictions may cause spurious precipitation, strong ion pairing, and low mobility of ions [2], and thus limit usability of the models.

First, we explain the origin of this problem, and we propose a computationally inexpensive procedure for refining current ion-ion force fields in order to improve their predictions of density and chemical potential in the crystalline phase. We employ the procedure both for simple pairwise additive and complex polarizable models of solid NaCl. The resulting models of crystals predict the density and the chemical potential of solid NaCl very well, and their predictions for the lattice energy, bulk modulus, shear modulus, and isochoric thermal pressure coefficient are also in good agreement with experiments.

Second, we combine our accurate ion-ion models with models of ion-water interactions from literature to study electrolyte aqueous solutions at ambient conditions. We show that this combined force field performs reasonably well, predicting the experimental solubility within the statistical uncertainty of the simulation.

Finally, we study if the force field is capable to accurately describe also properties of crystalline $NaCl.2H_2O$ (hydrohalite) at low temperatures.

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Properties of TIP4P/Ice water model in the supercooled region

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The existence of the liquid-liquid critical point (LLCP) of water has been a long-discussed problem and the arguments that speak in favor of its existence are usually based on simulation data. However, these data depend on the used molecular model, which was in most cases fitted at standard thermodynamic conditions. The results in the supercooled region thus, potentially, may represent only artifacts of the chosen model. In a recent paper [1] we pointed to differences in the structural properties of different water models in supercooled region. Specifically, significant differences from other models were shown in the case of the ST2 model underlying most arguments of the LLCP existence [2--5]. As a suitable candidate for study of water properties in the supercooled region, therefore, appears to be the TIP4P/Ice model [6] which was specifically designed to reproduce solid-phase properties. Moreover, at atmospheric pressure, this model relatively well corresponds to experimental data for isothermal compressibility, despite the fact that the temperature of maximum density is considerably shifted (295 K) [7].

A series of simulations were performed for TIP4P/Ice model at different pressures and temperatures and a structural analysis, based on measured data of isothermal compressibility, has been performed in regions that might indicate a liquid-liquid phase transition. In addition to commonly used various ad hoc introduced order parameters to characterize the structure [8], we focus on parameters based on the Deluanay triangulation and Spatial Distribution Function (SDF). The obtained results may serve as a spring board for further studies of qualitative structural changes that may take place in water with changes of thermodynamic conditions, and for introduction of other more apposite parameters characterizing restructuring of supercooled water.

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$A = -kT \ln Q$

Molecular dynamics study of racemic mixtures: Temperature dependence of separation of ibuprofen racemic mixture with β-cyclodextrin in methanol solvent

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Active pharmaceutical ingredients are very often chiral molecules, with one enantiomer having the desired biological effect while the other being often even harmful. Methods for separation racemic mixtures or enantioselective synthesis used nowadays are costly or time consuming [1,2,3]. In the search for more efficient and cost-effective ways of obtaining optically pure, and thus less harmful, drugs, membrane separations seem to be very promising [4]. In a recent paper [5] we presented a computational model of chiral recognition using a membrane with β-cyclodextrin active site as a chiral selector for separation of (R)- and (S)- ibuprofen. At temperature 278.15 K differences in enantiomers affinity to β-cyclodextrin were found. However, from results of liquid chromatography it is known that the temperature dependence may be more pronounced and may thus affect the separation considerably [6].

In this work we present therefore a molecular simulation study of temperature dependence of separation of racemic mixture of ibuprofen with β-cyclodextrin in methanol solvent. Cyclodextrine molecules are either freely placed in the system or they are tethered on the solid surface and formed enantionselective wall. The interaction of different enantiomers of quest molecule with the chiral selector moiety is investigated by inspecting the average interaction energy, hydrogen bonding, and differences in structural orientation between ibuprofen enantiomers and β-cyclodextrin.

The obtained results may serve both experimentalists and theorists as a benchmark for the development of a coarse-grained model to study the role of the structure of molecules and their intermolecular interactions for separation of racemic mixtures.

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Computational study of the inter-cage transitions of small hydrofluorocarbon gases inside type I hydrate

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Clathrate hydrates are water ice-like crystalline solids containing polyhedral cavities, with hydrogen-bonded water molecules forming each vertex of the polyhedra. These cavities can enclathrate substances of low molecular weight as N_2, H_2 or H_2S as a guest. Short chain hydrocarbons as methane, ethane or propane can be stored inside the cage hydrate as well. Clathrate hydrates are known to form mainly in three crystalline structures [1]: type I structure (sI), type II (sII) and type H structure (sH). Both sI and sII hydrates have a cubic lattice. The hexagonal sH, with bigger cavities, is formed when larger guest molecules are present during crystallization. The unit cell of type I consists of 46 water molecules, forming two types of cavities: a small dodecahedral cage (D) and a larger one (T) with the shape of a tetrakaidecahedron. The unit cell is made of two D cages and six T cages.

Hydrofluorocarbons (HFCs) are organic compounds containing fluorine and hydrogen, which are widely employed in the preparation of refrigerant gases for home and industrial uses. HFCs are also of great interest nowadays due its very high global warming potential, GWP, as high as 12400 (time horizon of 100 years) for HFC-23 (CHF_3). In this work, we studied the sI hydrates of single carbon HFCs: CH_4, CHF_3 and CF_4.

The transport phenomena of the guest molecules inside the hydrate structure depend on several factors, being the most important one, at the microscopic scale, the transition through the hexagonal and pentagonal faces shared by two adjacent cages. Therefore, energy profiles for the movement of the CH_4, CHF_3 and CF_4 molecules through those faces were calculated quantum-mechanically, using a strategy previously tested for other guests [2]. Firstly, the most probable paths the guest will follow during the transition from one cage to another were obtained using QTAIM [3]. Then, the energy barriers along the transition paths were calculated with Gaussian 09 software package [4]. All calculations were performed using Density Functional Theory (DFT) approximation [5] with the X3LYP functional [6], being X3LYP/6-31+G(d,p) the chosen level of theory.

Transition barriers were found, as expected, to be higher for the guest molecules with greater volume, and transitions trough hexagonal faces were found significantly more probable than through pentagonal ones. Interestingly enough, the fluorine atoms tend to install between the oxygen atoms of the transition face while the carbon remains at the centre of the window during the guest transition. Some of the hydrogen bonds between water molecules are broken during the process, and recovered when the guest arrives the other cage. Therefore, overall lattice structure of the crystal is preserved in spite of the temporal breaking and reordering of the hydrogen bonds.

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Phase classification in molecular dynamics direct coexistence simulation method using linear discriminant analysis

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Molecular dynamics direct coexistence method is employed in the simulation of properties and, particularly, phase equilibrium curves, of thermodynamic systems. Unfortunately, the existence of an objective and reproducible strategy to place the result of a single simulation of this kind in the correct location of the phase diagram is unclear. When a result is ambiguous, the corresponding simulation is often extended over time, making difficult the justification of using different times of simulation for different points in the same essay. Which is worse, the final decision of assigning one particular simulation point to a particular phase in the diagram is often heuristic, and somewhat arbitrary, because most of the simulations near the coexistence curve cannot be clearly assigned to one particular phase, mostly because of the high impact of the fluctuations due to size scaling effects.

In this communication, we propose the use of a well-tested statistical technique, linear discriminant analysis, to classify the set of points of a direct coexistence simulation into their corresponding phase. Using this approach, the line that optimally divides the phases can be considered as an estimation of the calculated coexistence curve. In addition, we obtain several advantages over the traditional procedure: the method can be reproduced and traced, the analysis provides an estimation of the uncertainty, and, perhaps the most important one, opens the door to the automation of the whole calculation, from the simulation box to the coexistence curve.

We have used data from type I methane clathrate hydrates in thermodynamic conditions which are compatible with the natural environment in the ocean floor [1], obtaining promising results, in good agreement with the experimental measurements of the coexistence curve [2], and with similar calculations in the literature [3]. Simulations were carried out with Gromacs [4] molecular dynamics software, and linear discriminant analysis was done using R statistical package [5].

Acknowledgments

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$A = -kT \ln Q$

A force field for Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, and SO_4^{2-} in aqueous solution based on the TIP4P/2005 water model

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Recently it has been shown [1] for NaCl that the combination of the TIP4P/2005 [2] model of water with a non-polarizable force field for the ions where the charges are scaled by 0.85 [3] is able to provide a quite good description of a number of properties of the sodium chloride solution. Here we shall show that the same idea can be applied not only to Na^+ but also to other cations as Li^+, K^+, Mg^{2+}, Ca^{2+} and also to other anions beyond Cl^- as for instance SO_4^{2-}.

In this way a new force field for these ions in water (described by the TIP4P/2005 model) has been proposed. We have performed Molecular Dynamics of a number of salts (involving these ions) at 0.1 MPa, 298.15 K for different concentrations. To validate the reliability of the proposed force field we compared predictions from this work with available experimental data [4-8] for densities, self-diffusion coefficients and shear viscosities. Other structural properties (as ion-water distances and solvation numbers were also considered). Densities were predicted extraordinary well and the same is true for the hydration number of each ion. The predictions for the viscosities were reasonable at moderate concentrations although they deviated from experiment at high concentrations. Estimates of the diffusion coefficient at infinite dilution were also predicted reasonably well. Notice that for many other force fields of salts solutions proposed previously, spontaneous precipitation was found at concentrations below the experimental value. For the new force field proposed here, we never observed spontaneous precipitation of the salts at the experimental values of the solubility.

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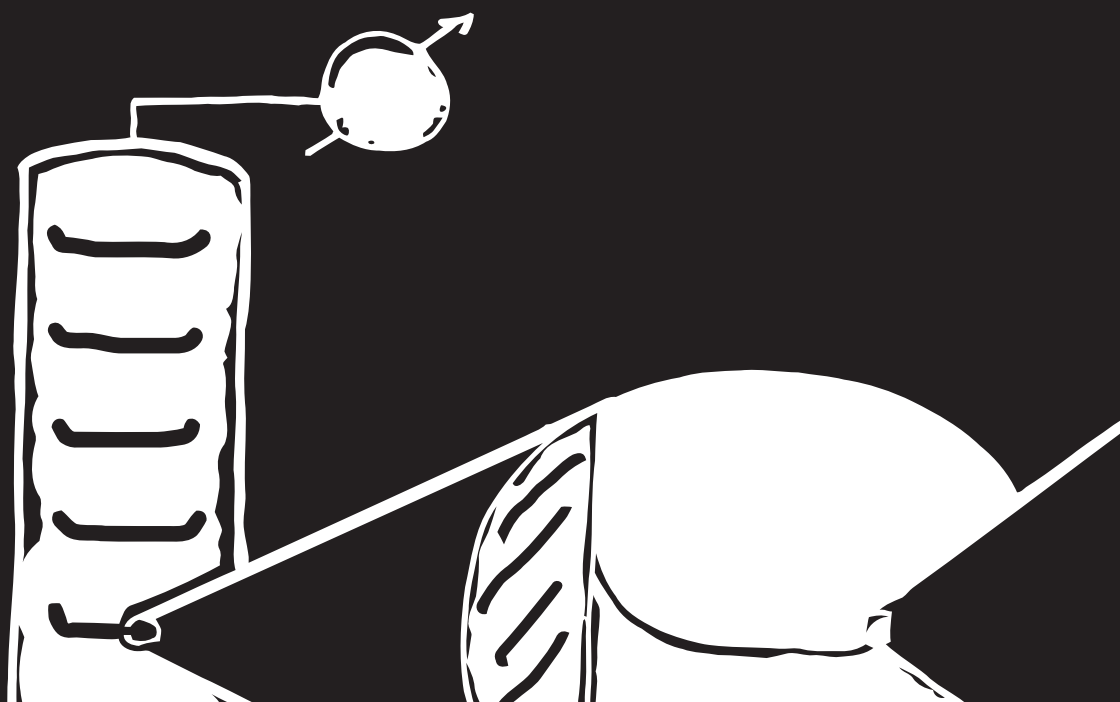
$$A = -kT \ln Q$$

Poster Presentations: Challenges and advances in fluid phase equilibria



Consideration of associating phenomena for the development of a reference database aimed at benchmarking equations of state

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While people are continuously developing equations of state sharing more or less the same objectives, that are, be able to reproduce phase-equilibrium and energetic property data of a large (if not, the largest) possible set of pure compounds and related mixtures, there is currently no mean to evaluate all these models on a same and fair basis. Any thermodynamic model developer might expect the existence of a reference database for benchmarking his model, including consistent experimental data for a wide number of properties and systems deemed as well representative of the variety of molecular interactions occurring in nature.

Indeed, as stated by Hendriks et al (Ind. Eng. Chem. Res. 2010, 49, 11131–11141) "there are databases (NIST-TRC, Dechema-Detherm) that are used by individuals [but] their use is still not widespread enough." Therefore, new published models are not evaluated on the same experimental datasets, making any kind of comparison almost impossible.

Our work in intended to fill this gap by proposing both a reference database of binary systems data and a procedure for evaluating deviations between model correlations and data.

For selecting data present in our database, we developed first a methodology to predict associative behaviors in solution for both pure compounds and binary systems from their chemical structure (associating phenomena being considered as important indicator of molecular interactions in binary systems). This led us to define 9 families of binary systems ranging from non-associating to highly-associating systems and containing both ideal and non-ideal systems (well illustrative of enthalpic and entropic effects). For each system, accurate, reliable and thermodynamically-consistent data associated with various kinds of thermodynamic properties (vapour-liquid, liquid-liquid, vapour-liquid-liquid equilibrium data, critical points, azeotropic points, enthalpy and heat-capacity of mixing data …) were included. In the end, we used our database, made up of 200 binary systems, to benchmark the Peng-Robinson equation of state.

$A = -kT \ln Q$

Aromatic Deep Eutectic Solvents from Phenolic Compounds

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In the recent past, eutectic solvents (ES) have been investigated as a green extraction media for natural phenolic compounds. It is interesting to note that, however, few aromatic-based ES have been studied. Since most natural phenolic compounds are poorly water soluble the use of aromatic solvents could boost their extraction due to the formation of pi-pi-interactions between solvent and solute. Thus, it is expected that the best eutectic solvents to extract phenolic compounds, or other aromatic compounds for that matter, could be aromatic themselves.

The objective of the present work is to use simple aromatic molecules (mostly phenolic compounds and pyridine derivatives) as building blocks to find mixtures of these compounds that i) are liquid at room temperature, ii) form very strong hydrogen bonds when mixed, leading to strong deviations from ideality, iii) do not form cocrystals and iv) are non-toxic and cheap; ultimately, the objective of this work is to find green aromatic-based deep eutectic solvents. Model COSMO-RS is used as a predictive tool.

Acknowledgments

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Using COSMO-RS to Design Choline Chloride Pharmaceutical Eutectic Solvents

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Eutectic solvents present interesting properties, mostly connected to their solvation ability, have been subject to much research in the recent past. Currently, the discovery of new eutectic solvents is accomplished by experimentally measuring the eutectic point of random systems, often using choline chloride as a hydrogen bond acceptor.

In this work, the eutectic temperatures of new choline chloride-based eutectic systems were experimentally assessed. These data, along with other previously reported in the literature, were used to evaluate a method based on COSMO-RS to predict the eutectic temperature of choline chloride binary mixtures. The predictive methodology herein developed allows for the quick scanning of a large matrix of systems in order to identify those more promising to be in the liquid state at a given temperature. To validate the method, the eutectic temperature of binary mixtures containing pharmaceutical drugs was predicted, and then assessed experimentally, showing that COSMO-RS is useful for the design of liquid drug-based formulations.

Acknowledgments

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Multivalency and promiscuity but not flexibility favour liquid-liquid phase separation of proteins

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The cell interior contains heterogenous mixtures of thousands of different components that need to be organised in space to facilitate control of function. Such organisation is achieved through the formation of compartments and organelles that are sustained by either physical membranes or the physical chemistry of liquid-liquid phase separation (LLPS) of protein and protein-nucleic-acids mixtures. Systems containing highly flexible intrinsically disordered protein (IDP) regions favour LLPS. Here we show that while multivalency and promiscuous protein binding favour LLPS, of binding sites has a marginal e effect. By combining the well-established physics of self-assembly of colloidal patchy particles with a novel continuous potential optimised for fast and scalable molecular dynamics simulations, we demonstrate that fine-tuning the characteristics of the protein-protein attractive interactions transforms the full phase diagrams of mixtures of thousands of proteins and the stability of the liquid-liquid coexistence region. Reducing the valency, gradually shifts the L-L critical point towards lower temperatures and packing fractions until its disappearance at valencies of 2. The topological distribution of binding sites on the protein surface also emerges as an important player in transforming the protein phase diagrams, with topologies that spread out the binding sites far from each other favouring LLPS. Our results suggest that of intrinsically disordered protein regions favours protein liquid-liquid phase separation because it facilitates exposure of protein interaction sites and, hence, increased valencies, but not because flexibility per se favours phase separation. Our results show a general mechanism by which cells can easily control the stability of their liquid-liquid coexisting phases without changing the total protein concentration: protein-rich drops can be disolved through chemical modifications that decrease the number of active binding sites on proteins, similarly condensation of protein-rich liquids can be triggered through chemical changes that increase the valency of proteins to values of three or higher.

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Liquid vapour equilibrium (VLE) of ternary system (Water + Ethanol +Trifluoroethanol) experimental and correlations data

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Several works concerning the thermodynamic properties of liquid mixtures containing fluorinated derivatives have been carried out in our laboratory.
In this sense, we present the experimental data of liquid - vapor equilibria at T = 323,15K of the ternary system Water (1) + Ethanol (2) + Trifluoroethanol (3). The experimental data of the three corresponding binaries are also presented.
The apparatus used is a phase-circulating ebulliometer similar to that described in the literature.
The experimental results of the liquid - vapor phase diagrams of the three binaries as well as those of the ternary mixture were correlated by the two - parameter models of Margules, Wilson, Uniquac and NRTL.

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$A = -kT \ln Q$

A critical assessment of molecular simulation data and equations of state of the Lennard-Jones fluid

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The Lennard-Jones (LJ) fluid is of significant importance for the development of theories and methods in soft-matter physics. Equations of state (EOS) for the LJ fluid are useful for such studies and have therefore been developed by many groups. The present work makes two contributions to this field: First, the available data from computer experiments (CE) of the LJ fluid are systematically and critically assessed and compared to the available EOS for that fluid. About 15 000 data points and 20 different EoS are considered. Second, a general parameterisation procedure is proposed that considers the fact that the need for describing different thermodynamic properties in different fluid regions will result in conflicting objectives. That procedure is then applied to optimise a new LJ-EOS. The resulting EOS is found to be as good as the best empirical EOS from the literature [1] for most properties, but it is simpler.

The thermophysical properties considered here are bulk (gas, liquid, supercritical, metastable, and VLE) and interfacial properties. For the bulk properties *pvT*, internal energy, chemical potential, speed of sound, heat capacity, compressibility, virial coefficient, Joule-Thomson coefficient etc. data is considered; for the interfacial properties the surface tension and the nanoscale interfacial thickness. The systematic comparison of CE data and EOS from the literature enables an evaluation of strengths and weaknesses of different EOS and also enables the identification of outliers in the CE data. Empirical EOS have the advantage, that they are more accurate for example regarding *pvT*, internal energy, and speed of sound data, but have the disadvantage of showing unphysical behaviour in the metastable region [1]. Vice versa, EOS based on theory mostly show a reasonable behaviour in the metastable region but are usually less accurate elsewhere. A detailed and systematic discussion of these results will be presented.

The parameterisation procedure proposed in this work consists of a combination of global and multi-criteria optimisation. The simulation data from Thol et al. [1] was employed as underlying dataset, as it contains CE results of 200 state points of the LJ fluid for the residual Helmholtz energy and its temperature and density derivatives up to second order. A hierarchy of three weight-function levels is introduced for the optimisation. The first level assesses the weight of different fluid regions, the second level of different thermophysical properties and the third level the statistical uncertainty of each numerical value in the dataset. While the third level is uniquely defined by the reported statistical uncertainties [1], the weights on the first and second level are assessed by multi-criteria optimisation. To test this procedure, we have chosen the mathematical framework of the PC-SAFT EOS and have optimised its universal constants. This new LJ-EOS is compared to LJ-equations of state from the literature and found to be among the best available EOS.

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Prerequisites for rigorous calculation of zero-point and room-temperature sublimation enthalpy for proteinogenic amino acids

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Extensive and thorough collecting and classification of reliable primary thermodynamic data, however disregarded and disrespected, is indispensable for filling in the grey zones of scientific knowledge. A recent paper [1] pointed out noticeable deficiencies in thermodynamic data for proteinogenic amino acids and contemplated possibility of their completion by involvement of large number of undergraduate laboratory programs. Such intention could be however contra-productive due to highly probable ambiguity and large uncertainty of such data, especially for the tough-to-obtain properties.

This contribution discloses the process behind the task to rigorously determine and describe sublimation behaviour of proteinogenic amino acids. An ultimate result of the project are low-uncertainty sublimation enthalpies at room temperature and 0 K. Even the room temperature values were seldom reported and show large discrepancies since the experimental difficulties and disregard of the authors for accurate evaluation of difference in heat capacities for recalculation to 298.15 K. For example, for the most studied amino acid, glycine, four values can be obtained from the literature: 130.5 ± 2.1 [2], 138.1 ± 4.6 [3], 140.0 ± 5.0 [4], and 143.7 ± 4.4 [5] (calculated using the suggested temperature correction), where the difference in heat capacity was always roughly estimated or neglected.

Rigorous determination of room-temperature sublimation enthalpy presented in this work requires larger amount of input data and more advanced tools:

i) Determination of sublimation enthalpy. The sublimation enthalpy of extremely low-volatile compounds has to be determined at elevated temperatures (for amino acids typically at 400 to 450 K) using vaporization calorimeter or temperature dependence of vapour pressures. Data are currently available only for simple amino acids and possess large uncertainties.

ii) Heat capacities of crystalline phase. Several calorimeters of different types (adiabatic, relaxation, Tian-Calvet, DSC) have to be utilized to stretch the heat capacity data over the desired temperature range 0 to 450 K. While several amino acids were studied with adiabatic calorimetry at low temperatures, data above 350 K were not presented for any of them yet.

iii) Phase behaviour. Temperatures and enthalpies of phase transitions have to be determined over the same temperature range, however different experimental setup and methodology is typically required for the phase behaviour studies than for heat capacity measurements.

iv) Heat capacities in the ideal gaseous phase. Being unmeasurable, ideal-gas heat capacities of amino acids have to be calculated by an adequate statistical thermodynamics model. A suitable model for amino acids was presumably not available until we recently presented R1SM approach [6].

v) Simultaneous correlation of vapour pressures and thermal properties. Since the vapour pressures and sublimation enthalpies are typically determined over a longer temperature range, it is convenient to treat them simultaneously with difference in the heat capacities and obtain superior description compared to commonly used regression techniques.

$A = -kT \ln Q$

Gaps in the knowledge of thermodynamic properties of several proteinogenic amino acids were filled in within this project by measurement of vapour pressures using a newly constructed Knudsen effusion apparatus with QCM sensor, four calorimeters (relaxation calorimeter PPMS, power-compensation DSC, heat-flux DSC, and Tian-Calvet calorimeter capable of measurement of superior-accuracy heat capacities) and the developed R1SM model. Finally, the available data were described using the method of simultaneous correlation and sublimation enthalpies were calculated at 298.15 and 0 K.

Relative stabilities and sublimation behaviour of molecular crystals is a frequent goal of *ab initio* theoretical calculations, where lattice energies are the primary step. Since the lattice energies lack appropriate experimental counterpart, they are commonly compared to experimental sublimation enthalpies with the zero-point vibrational energies and thermal corrections being neglected or roughly estimated [7]. The presented zero-point sublimation enthalpies are thus, beside other applications, highly desired for benchmarking of theoretical calculations representing closest experimentally achievable property to lattice energies with significantly lower uncertainties than available until now.

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Modeling the Phase Equilibria of Asymmetric Hydrocarbon Mixtures Using Molecular Simulation and Equations of State

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The significant progress and development in the drilling technology has made possible the exploitation of deep, high pressure - high temperature (HPHT) oil reservoirs for hydrocarbon production. These wells differ significantly from the conventional ones with respect to temperature (T), pressure (P) and composition [1]. The temperature in such reservoirs can vary from 150 to 260 ºC and the pressure from 70 to 200 MPa [2]. The fluid composition can be very asymmetric, with methane (CH_4) being the dominant component, mixed with long-chain normal alkanes (*n*-alkanes) [1, 3]. The asymmetric nature of these reservoir fluids results in a more complex phase behavior, compared to those extracted from conventional wells [3]. A class of hydrocarbon mixtures that are present in HPHT reservoirs are the so-called gas condensate mixtures. The detailed design and optimization of processes associated with these mixtures require accurate knowledge of the physical properties and the phase equilibria conditions as functions of temperature, pressure and composition.

These properties can be predicted by thermodynamic models in the form of Equations of State (EoS), which provide a good balance between accuracy and computational efficiency. Prediction of the vapor-liquid equilibrium (VLE) of multicomponent mixtures with improved accuracy requires the use of binary interaction parameters (BIPs), which are regressed from experimental VLE data of binary mixtures. However, experimental data for mixtures of CH_4 with long chain *n*-alkanes, especially at high pressures, are relatively limited.

Monte Carlo simulation in the Gibbs Ensemble (GEMC) has proven to be a powerful tool for the accurate prediction of binary mixture phase equilibrium. However, simulation data for asymmetric mixtures of hydrocarbons are scarce. This should be attributed, among others, to the low acceptance probability for the exchange of the long-chain hydrocarbons. At these conditions, advanced simulation techniques such as configurational-bias Monte Carlo (CBMC) [4, 5] and continuous fractional component Monte Carlo (CFCMC) [6] can be used to increase the acceptance probability of the molecule exchange trial move.

The aim of this work is to develop a methodology for the prediction of the VLE of multicomponent gas condensate mixtures by combining molecular simulation with EoS. GEMC simulations with the TraPPE-UA force field [7] are used for the calculation of VLE data for various binary CH_4 - *n*-alkane mixtures. In total, 5 binary mixtures are investigated: the mixtures of CH_4 with *n*-$C_{10}H_{22}$, *n*-$C_{12}H_{26}$, *n*-$C_{16}H_{34}$, *n*-$C_{20}H_{42}$ and *n*-$C_{24}H_{50}$. Initially, the GEMC simulation results are validated against the available experimental data and subsequently new calculations are performed at conditions in which no experimental measurements exist. Two sets of k_{ij}

$A = -kT \ln Q$

parameters for two cubic (SRK, PR) and one higher order (PC-SAFT) EoS are then regressed; one from the available experimental VLE data for the 5 binary mixtures and a second one using the GEMC simulation results. The ability of each EoS to correlate the VLE data depending on the available range of conditions is assessed. Finally, the EoS considered in this work are used to predict the VLE of multicomponent gas condensate mixtures with both sets of k_{ij} parameters and a comparison between the models is performed [8].

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Temperature of maximum density for aqueous solutions of α-CT and BSA

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Maybe the most important anomaly of liquid water is the appearance of a maximum at 3.98 ºC in the density-temperature curve at isobaric conditions [1]. The microscopic origin of this behaviour is related with the balance of the equilibrium between a ordered ice-type structure of low density and disordered closed packed configuration of higher density; since the former dominates at temperatures close to melting and the latter at higher temperatures, the density maximum appears in a natural way. Addition of a small quantity of solute to water modifies this equilibrium and changes the temperature of maximum density (TMD). Wada and Umeda [2] found that some alcohols were able to increases the TMD, promoting the formation of low density ordered structures in water. This behaviour is, however, an exception, since most solutes induce partial destruction of the ice-type structure making the TMD lower [3-9].

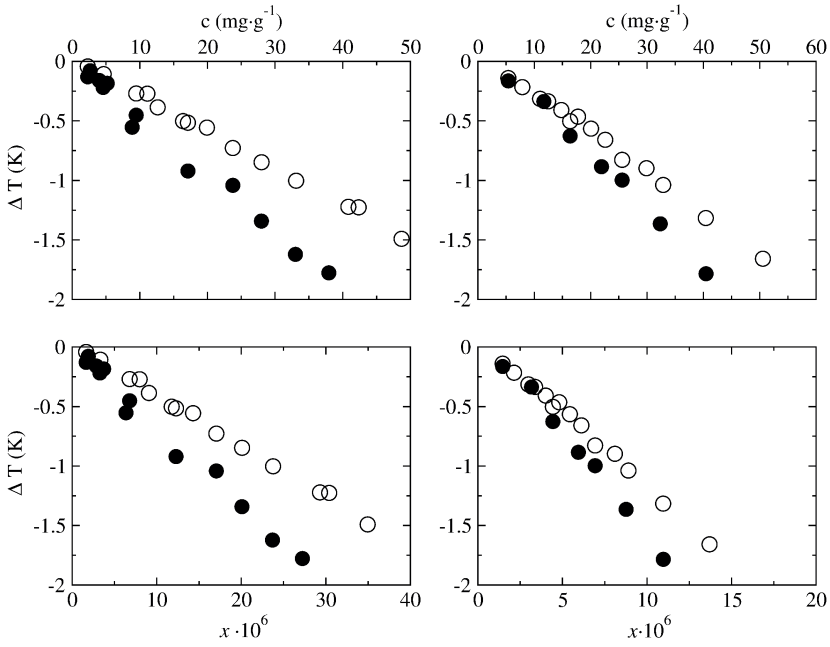

Figure 1. Difference ΔT between the TMD of aqueous solutions of a protein and that of pure water plotted as a function of protein concentration *c* (upper graphics) and protein mole fraction *x* (lower graphics). Empty and filled circles corresponds to the folded and unfolded states, respectively. Left graphics refers to α-CT and right ones to BSA.

$A = -kT \ln Q$

In this work, we study the effect in the TMD of the addition of small quantities of α-Chymotrypsin (α-CT) and Bovine Serum Albumin (BSA) in both the folded and the unfolded states. To this end, aqueous solutions of these proteins in the folded state were prepared with concentrations varying from 0 to 50 mg/g. The samples with the unfolded protein were obtained from the formers after heating them at high temperature during several hours. Their densities were determined at atmospheric pressure from 0.5 ºC to 10 ºC by using the Anton Paar 5000 vibrating tube densimeter. Calibration was performed with Milli-Q water and vacuum, according to the technical specifications of the equipment. Densities were fitted to a second order polynomial in order to have an estimation of the TMD. Preliminary results are given in Figure 1.

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Simple Second-Virial SW Model for Protein Aggregation

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We present a very simple model for protein aggregation based on a second virial coefficient. The model proposes a mixture of two components, each represented by a square-well, SW, interaction of suitable hard-core diameter σ, energy depth ε and attractive range λ. Both components have $\sigma_{AA} = \sigma_{AB} = 2.0$ nm. Components have energies $\varepsilon_{AA}/k = 1$ K and $\varepsilon_{BB}/k = 310$ K, and SW ranges $\lambda_{AA} = 1.25$ K and $\lambda_{BB} = 1.25$. Lorentz-Berthelot rules are assumed for the cross interaction parameters. The system is taken as a SW mixture whose second virial coefficient $B_{mix}(T)$ has a simple analytic form and depends on the system parameters and the mole fraction x_B of the second component. Properties are calculated at a temperature $T_{body} = 309$ K characteristic of mammal body temperature. The tendency of B component to aggregate is manifested on a Boyle temperature $T_{Boyle} = 432.1$ K, higher than T_{body}. In fact, T_{Boyle} for the mixture equals T_{body} for $x_B = 0.771$. Further, T_{Boyle} is linear in the energy depth ε_{BB}, as shown in figure 1.

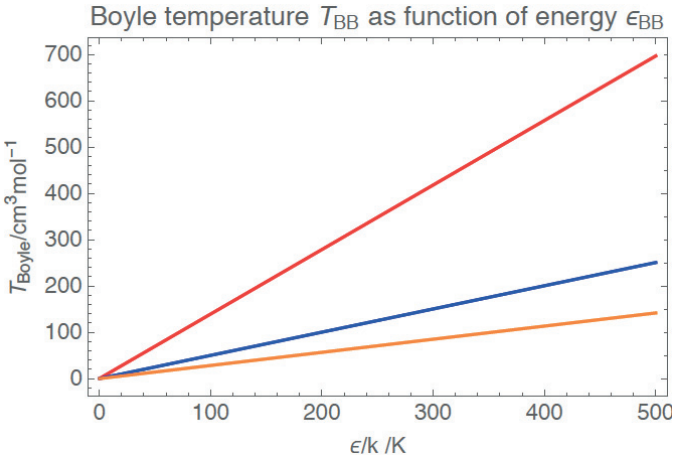

Figure 1. T_{Boyle} of the BB interaction as function of ε_{BB}. $\lambda_{BB} = 1.25$ (top), $\lambda_{BB} = 1.05$ (middle), $\lambda_{BB} = 1.01$ (bottom).

$A = -kT \ln Q$

Thermodynamic Modelling of Gas Mixtures in Amine Solvents: Lessons from ePC-SAFT

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In processes such as natural gas dehydration, CO_2 capture from flue gas streams, natural gas and biogas upgrading, and in the development of renewable energies, acid-gas capture and sequestration is of integral importance [1]. Gas separations based on the chemical absorption / desorption process with aqueous alkanolamine solvents is currently considered as the state-of-the-art technology and is similar to other end-of-pipe environmental control measures [2]. Particularly, methyldiethanolamine (MDEA) has been utilised extensively for acid-gas processing in an industrial context since the 1930's [3]. As the absorption and desorption of low molecular weight species in or from optimal solvent blends is a subject of considerable interest to-date, the need to accurately model the behaviour of these electrolyte systems in lieu of experimental observation is evident [4].

The literature proposes several thermodynamic frameworks to model the behaviour of aqueous electrolyte systems, including activity coefficient models, classical cubic Equations of State, and statistical-mechanics based approaches. The most suitable model for practical purposes would be to use a theoretically-grounded functional form of an Equation of State with parameters adjustable to experimental data; treatment in this way guarantees modelling accuracy, transferability to mixtures, and generality [5]. Accordingly, an Equation of State based on Statistical Associating Fluid Theory (SAFT), namely the Electrolyte Perturbed Chain SAFT Equation of State [6,7], is used to explore the solubility of gas mixtures containing CO_2, H_2S, and CH_4 in aqueous MDEA solvent. In each system of consideration, the vapour-liquid equilibria are characterised as a function of the gas loading in solution and the model performance is assessed by direct comparison with available experimental data. In select ternary systems, the enthalpy of absorption is also calculated and compared to experimental data.

The primary objective of the work is to explore the capability of ePC-SAFT to predict phase behaviours of ternary and higher order systems in a broad range of process conditions using only pure or binary component data for model training, with the aim of providing valuable insight into where the model gives quantitative agreement, qualitative agreement, or otherwise fails to predict experimental observation.

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$A = -kT \ln Q$

Study of thermal properties of peloids used in Spas of Galicia

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The peloids are heterogeneous systems consisting of mixtures of a solid substrate with mineral water or seawater used for therapeutic purposes in thermal centres [1]. Thermotherapy is one of the therapeutic applications of peloids, that is, the use of heat for therapeutic purposes [2]. In this work the density, the thermal conductivity, the specific heat and the thermal diffusivity of mixtures of clays with medicinal mineral waters of Galicia are presented.

The materials used were: clays (bentonite, kaolin and montmorillonite); the waters come from the Spas of Laias and Lobios in the province of Ourense and the Spa of Mondariz in the province of Pontevedra. Density of peloids was determined by the pycnometer method described in Caridad et al 2014 [3]. Thermal conductivity data were measured using a Decagon KD2 Pro thermal properties analyser [4]. Specific heat was determined by a CALVET microcalorimeter using the method described in Glavas et al. (2017) [5]. Thermal diffusivity is calculated from density, specific heat and thermal conductivity data [6]. The mixtures were prepared by weight, using an Acculab ALC-210.4 analytical balance. The ratio of clay / mineral water for each mixture was chosen to have a texture similar to that of sludge prepared with the same clay used in the thermal centres. Nine mixtures were prepared by mixing the clays with the mineral waters in different percentages, as shown in table 1. All measurements were made at 309.15 K (application temperature of the mixtures in the thermal centres) and atmospheric pressure.

Table 1. Percentages of mineral water used in mixtures

% Mineral water	Bentonite	Kaolin	Montmorillonite
Lobios	85	55	48
Laias	80	50	42
Mondariz	70	35	40

Figure 1a shows the density of the mixtures studied, observing that the density decreases with increasing water concentration. Figure 1b shows the specific heat, which increases with increasing water concentration. Figure 1c shows the thermal conductivity, observing that it decreases when the water concentration increases. Figure 1d shows the thermal diffusivity, observing that it decreases when the water concentration increases. The mixtures with Mondariz mineral water present the highest values of density, thermal conductivity, and thermal diffusivity. While for the mixture with Lobios mineral water the highest value is for specific heat.

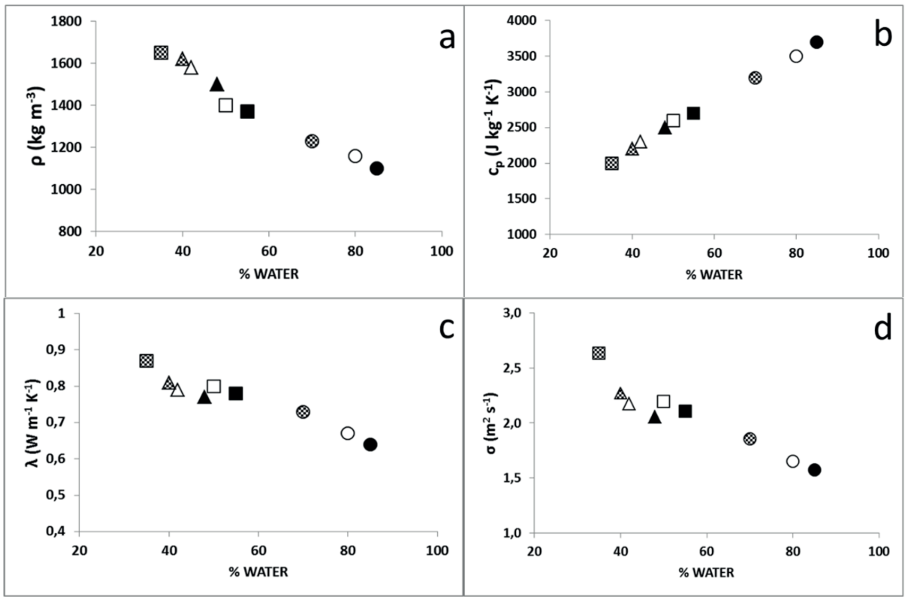

Figure 1. a) Density; b) Specific heat; c) Thermal conductivity; d) Thermal diffusivity of peloids. Circle) Bentonite; Triangle) Kaolin; Square) Montmorillonite; Black) water from Lobios; White) water from Laias; Black and White) water from Mondariz.

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$A = -kT \ln Q$

Density Measurements under Pressure for the Binary System Di-isopropyl ether + 1-Heptanol at Temperatures up to 373.15 K and at Pressures up to 100 MPa

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In order to improve the properties of new bio-fuels, oxygenated compounds such as alcohols and ethers are being included in the formulation of gasoline and diesel blends. Ethers have been widely used due to its stability, high volatility and solubility similar to that of the alcohols, whereas alkanols were introduced as an alternative to bioethanol as a transportation fuel.

Di-isopropyl ether (DIPE) is considered as a good octane enhancer when used as a gasoline blend stock. It was introduced as an oxygenate additive to biofuels due to its non-toxic and non-polluting profiles [1, 2]. This dialkyl ether has some desirable thermophysical properties such as a relatively high boiling point, and low solubility in water [3]. It can be used either as pure compound or in mixture with other fluids, as is the case of alkanols. This mixture can be employed for several purposes including the abovementioned as well as in cleaning processes, solvent extraction, and in the manufacture of paints.

This contribution gathers a number of high pressure density data for the binary system Di-isopropyl ether + 1-Heptanol over the complete composition range, at temperatures from 298.15 to 393.15 K, and at pressures up to 100 MPa.

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Density Measurements under Pressure for the Binary System Diethylene glycol mono methyl ether + 1-Propanol at Temperatures up to 373.15 K and at Pressures up to 100 MPa

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Many efforts have been carried out during the last decades in order to reduce greenhouse gas emissions. Concerning industry fluids, the search of new environmentally friendly products with desirable properties such as high boiling points and solubility in water, together with low global warming potentials (GWP), amongst others, has led to consider Glycol ethers as one of the most promising alternatives to be used in different applications.

Glycol ethers are a class of fluids based on Ethylene glycol alkyl ethers (ethers type E; RO-(CH_2-CH_2) nO-R ') or Propilene glycol (ethers type P: RO-(CH_2-CH (CH_2)) nO-R '). Most of them are used in the manufacture of varnishes, paints and inks, in the cosmetics industry, and as oxygenate additives to biofuels. Moreover, glycol ethers are biodegradable and only some of them are considered as toxic [1].

Diethylene glycol mono methyl ether, also known under its trade name, Methyl Carbitol, is an industrial solvent that can be used for anti-icing control, as brake fluid component and as solvent used in printing inks, resins and waxes [2]. Property data of its mixtures with alkanols are very scarce in the literature.

In this work, experimental high pressure density measurements have been carried out for the binary system Diethylene glycol monomethyl ether + 1-Propanol over a wide range of temperatures (from 298.15 to 373.15) K, and in the pressure range (0.1 – 100) MPa, by using a vibrating tube densitometer. High pressure density data have been fitted to a Tait-type equation, giving a good agreement between the experimental values and those given by the correlation equation.

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$A = -kT \ln Q$

Understanding the reaction chemistry and thermodynamics of HTC

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As the scenario of world primary energy consumption shifts towards a greater contribution of alternative renewable sources of energy, the use of biomass wastes by green sustainable methods, such as hydrothermal carbonization (HTC) becomes a major challenge for scientists all over the world. Last years have witnessed the popularity of this novel method by which biomass is converted to a carbon material with tuneable surface functionalities, involving great energy and economic savings in relation to traditional pyrolysis. Despite the increasing number of papers published about HTC, there is little work available about the reaction chemistry of the process applied to heterogeneous biomass; only a few pieces of research have addressed the reactions involved during the HTC of model components, and suggests that whole biomass processes should be a combination of them [1]. The complex interplay of reactions (dehydration, decarboxylation, decarbonylation, aromatization, condensation, re-polymerization…) occurring according to a parallel network rather than as consecutive reaction steps makes the study of the process a big challenge.

The main objective of this work is to study the reaction chemistry of HTC when applied to the walnut shell; characteristic HTC reactions are considered, and the results obtained in the characterization of solid and liquid phases are discussed and related to each other. Special attention was paid to the formation of high-interest compounds such as hydroxymethylfurfural (HMF) and Levulinic acid.

The reactions were accomplished in continuous mode, in a Parr 4848 reactor, under experimental conditions fixed based on previous experimentation (T:250 ºC; heating rate:5 ºC; biomass/water load: 1/3; initial volume: 0.8 L). Liquid samples were taken at fixed times from 200 ºC at time intervals before, during and after the process and analysed in terms of pH, TOCs, furfural, hydroxymethylfurfural, formic acid, acetic acid, levulinic acid and phenolic compounds. The hydrochar was analysed by thermogravimetry, proximate and ultimate analysis, infrared spectroscopy, N_2 adsorption and FT-IR spectroscopy

Acknowledgements

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Spontaneous doping of ice Ih, Ic, III, V and VI from aqueous salty solutions

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Ice-doping processes are of great interest in fields such as atmospheric chemistry, astrophysics and geophysics. In recent years, various studies revealed the existence of subsurface salty oceans and the presence of high-pressure ice polymorphs in the interior of some planetary bodies such as Jupiter's satellites or exoplanets such as Proxima b [1,2]. These ices, stable over several gigapascals and hundreds of Kelvin, can contain a significant number of small ions in their structure. The presence of doped ice suggests a plausible explanation for the behaviour and different physical properties observed in the interior of these icy bodies.

When it is added to ice, the salt first dissolves in the liquid water layer that is always present on the surface, thereby lowering its freezing point below the ice coexistence temperature. Moreover, when water freezes from aqueous salty solutions, the salt ions are rejected from the solid phase and saturate the liquid phase giving rise to the appearance of the phenomenon known as brine rejection. Pockets of brine form inside the polycrystalline blocks of ice.

In addition to the brine phase, during the ice growth a small amount of ions can be accommodated in the solid lattice causing ice doping [3,4]. The ice-doping process raises fundamental questions concerning the mechanisms by which ions are incorporated into the ice structure, and what their positions and effects are once they get there. Experiments evidenced that the presence ion dopants in the lattice modifies the properties of ice, as the incorporation of ions causes the appearance of extrinsic defects in the lattice that increase the static conductivity of the system and affect the dielectric properties of doped ice. A small amount of doping impurities is sufficient to induce considerable changes in these properties [5].

In this work molecular dynamics simulations on microsecond time scale have been performed on an aqueous solution of TIP4P/2005 water and NaCl by using the direct coexistence technique to study the ice growth and the interface ice/liquid water. At different pressures, for temperatures above the eutectic point of the salt and at several concentrations the brine rejection phenomenon and the spontaneous growth of an ice slab doped by the salt are obtained, as found in natural terrestrial and planetary environments. Experiments indicate that Cl^- goes substitutional to ice sites. In line with these evidences we find a new result for ice Ih: the Cl^- ion included in the lattice always substitutes not one but two water molecules leaving the ice structure around not distorted. The Na^+ ion shows lower probability to be included in the ice and it occupies an interstitial site, causing a local distortion of the lattice [6]. We compare the results obtained for the ice Ih and ice Ic to the same conditions of pressure and temperature analyzing the influence of the crystalline structure. Further, we extend the study for stable ices at high pressures such as ice III, V and VI and we study the role of pressure and the different type of crystalline structure on the spontaneous doping process [7].

$A = -kT \ln Q$



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Excess calorimetric properties of the binary mixtures Methyl Carbitol + n-heptane as fuel representative

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Glycol ethers are a group of solvents based on alkyl ethers of ethylene glycol or propylene glycol commonly used as solvents and additives. These solvents typically have a higher boiling point, together with the favourable solvent properties of lower-molecular weight ethers and alcohols. Most glycol ethers are water-soluble, biodegradable and only a few are considered toxic.

Diethylene Glycol Monomethyl Ether, also known under trade name Methyl Carbitol, is an industrial solvent and is also commonly used as a fuel system icing inhibitor (FSII) in jet fuels [1]. It is a clear, colourless, hygroscopic liquid. Structurally it is an alcohol and an ether, with a formula $C_5H_{11}O_3$. Property data of its mixtures with hydrocarbons are very scarce in the literature.

This work presents a study on excess enthalpies of mixtures Methyl Carbitol + n-heptane at 298.15 K and 328.15 K. Excess enthalpies have been measured with a quasi-isothermal flow calorimeter.

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$A = -kT \ln Q$

High pressure and high temperature volumetric properties of the binary system HFE-7100 + Methanol

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Hydrofluoroether fluids (HFEs) are a class of environmentally friendly fluids that can be considered as substitutes of hydrofluorocarbons (HFCs), perfluorocarbons (PFCs) and perfluoropolyethers (PFPEs) in many applications such as solvents, refrigerants, high precision cleaning fluids, and as heat transfer media. These fluids exhibit near-zero ozone depletion potential (ODP), low global warming potential (GWP), as well as short atmospheric lifetimes (ALT) [1]. Moreover, HFEs are non-flammable, and they have low toxicity profiles [2].

Methyl nonafluorobutyl ether, also known as HFE-7100, can be used as cleaning and rinsing agent, lubricant carrier, and as low temperature heat transfer fluid. Its mixture with methanol forms an azeotrope at a mole fraction of approximately $x = 0.6300$ of HFE-7100. This mixture is suitable to replace HCFC-225ca/cb for solvent cleaning operations, amongst others.

The knowledge on thermophysical properties is of great importance for scientists and also for the industry. Since density is one of the most interesting ones, due to other properties can be derived from it, the determination of high pressure densities both for the pure components and for the mixture provides valuable information.

This work reports experimental high pressure density data for six different mole compositions of the binary mixture HFE-7100 + methanol. Measurements were taken in the pressure range (0.1 – 140) MPa, and in the temperature interval (298.15 – 393.15) K. A Tait-type equation, which is considered to be a good equation to correlate density values over wide temperature and pressure ranges, was used to fit the experimental values, giving a good agreement between both series of data. No data were found in the literature for this binary system.

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A comparative study of predictive tools for the free energy of solvation

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The Gibbs free energy of solvation for a given solute in a solvent, usually considered at infinite dilution, provides a simple thermodynamic description of the solution and is related to numerous solution properties. From the perspective of the pharmaceutical industry, the free energy of solvation has been used in quantitative drug design as the effectiveness of a drug depends in part on solubility and permeability. [1] In the context of solution chemistry, the effects of solvents on equilibrium constants and reaction rates can also be quantified using the free energy of solvation. [2] Given the importance of the Gibbs free energy of solvation, many predictive tools have been developed to predict this property, spanning quantum-mechanical (QM) methods, empirical methods, and classical methods. The methods proposed vary in terms of the mixtures to which they are applicable and in terms of computational cost, but there is a lack of systematic studies covering a range of techniques. In this work, we carry out a comparative study of predictive methods with relatively low computational cost using a large set of solutes and solvents.

The methods studied include a group-contribution equation of state, the statistical associating fluid theory (SAFT-γ Mie), [3, 4] a universal quasi-chemical functional-group activity coefficients model (UNIF_DMD), [5] the hybrid QM/activity coefficient model (COSMO-SAC), [6] and a partial-least squares (PLS) model. [7] In this study, we evaluate these models based on a set of free energies of solvation for 400 solute / solvent systems. We then assess the strengths and weaknesses of each method based on the overall data set and for specific subsets of solute / solvent systems (e.g. aqueous / non-aqueous systems). Furthermore, the solute / solvent systems are then classified according to molecular type (e.g. self-associating / non-associating) and further analysis is carried out.

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$A = -kT \ln Q$

Hard-sphere glass transition in strong confinement

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A supercooled liquid of hard spheres can form an amorphous solid known as a glass. Confining hard spheres between two hard walls induces a similar solidification transition at a lower density when the pore width is less than ten particle diameters. Confinement below three particle diameters generates reentrant dynamics as a function of pore width, in which diffusion parallel to the walls increases as confinement approaches two particle diameters [1]. The appearance of reentrant dynamics suggests that distinct physical mechanisms control arrest near two and three particle diameters, but these mechanisms remain poorly understood. Competing theories propose that arrest is driven by changes in structure, quantifiable via medium-range crystalline order [2], or by cooperative dynamics [3]. Testing these different mechanisms requires systematic investigations of the glass transition of hard spheres as a function of confinement. We perform molecular dynamics simulations of hard spheres of various polydispersities and volume fractions that are confined between two hard walls to explore the role of particle density and disorder in arrest. We also vary the confinement length scale to determine if reentrance signals a changing arrest mechanism. We derive the length scales quantifying the extent of medium-range crystalline order [4] and dynamic heterogeneity [5] to determine their respective contributions to arrest. We correlate the degree of decoupling between particle diffusion parallel and normal to the wall plane with the extent of either the dynamic or ordered length scales in the plane to directly connect the mechanism of arrest with the microscopic dynamics. Our work provides insight into the effects of entropic ordering and dynamical heterogeneity on the mechanism of glass formation and elucidate the differences between two and three-dimensional glasses.

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A closer look at the classical Soave α-function

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The developed equations of state based on the intermolecular interactions have been classified into two categories [1], where van der Waals family cubic equations of state (CEoS) are one of the main bodies. The CEoS was presented by van der Waals [2] based on attractive and repulsive terms. It faced some amendments [3] and modifications [4] to improve performance in predictions of volumetric properties of real gases. As a measure of the molar Gibbs energy of a real gas, fugacity may be beheld upon as a saturation pressure modified to denote properly the fugitive propensity of the molecules from one phase into the other. The fugacity coefficient for a single component may be expressed in terms of the compressibility factor using the thermodynamic relationship [5]:

$$Ln(\varphi) \equiv Ln\left(\frac{f}{P}\right) = \int_0^P \frac{Z-1}{P} dp \tag{1}$$

The very first key reference for reconstruction of a CEoS for a proper Vapor-Liquid-Equilibrium (VLE) predictive tool was made by Wilson [6] in looking for a better tool for prediction VLE of cryogenic systems. He suggested that a CEoSs should be adjusted with a function of temperature to improve the prediction of the pure-compound vapor pressure. Wilson [7] recommended that the temperature dependence of the parameters can be relatively simple and only two vapor pressure points (the critical pressure and the vapor pressure near the boiling point) are necessary to determine the temperature dependence.

Soave [8] considered CEoS of Redlich and Kwong [4] and by considering Wilson recommendation [7] proposed α and modify the parameter a to ($a\alpha$) and declared α is the real root of the Equation 3 for a given set of saturation temperature and pressure.

$$Z^l - Z^v - Ln\left(\frac{Z^l - B}{Z^v - B}\right) - \frac{A}{B} Ln\left(\frac{Z^v}{Z^l} \times \frac{Z^l + B}{Z^v + B}\right) = 0 \tag{3}$$

In the checking the hypothesis for ethylene, propane, cyclopentane, toluene, n-octane, and n-decane he came up that there is a linear relation between the square root of α and the square root of T_r with an intercept of one at a critical point. So α represented by a function as

$$\sqrt{\alpha} = 1 + m\left(1 - \sqrt{T_r}\right) \tag{4}$$

To generalize the slope (m) of Equation 4, Soave [8] applied the acentric factor (ω) proposed by Pitzer [9]. Assumed ω values are ranging from zero to 0.5 with a step of 0.05, for each of the eleven values of ω, corresponding values of m could be determined by rearranging acentric factor equation as $P_{r\ @T_r=0.7} = 10^{-\omega-1}$. The values of m fit over a quadratic equation as

$$m = 0.480 + 1.574\omega - 0.176\omega^2 \tag{5}$$

Le Guennec et al. [10] declared a decreasing function of temperature; its first derivative has not only to be negative but has also to cancel out at the infinite temperature limit to ensure a finite α-value. Yang and colleges [11] concluded at any temperature above the triple point first derivative of α-function must be less than zero.

However, while these approaches seem to be good for simple molecules but they need a correction (which is in term of De Broglie wavelength) to be able for working for fundamental materials of Hydrogen and Helium that have behaviors with quantum effects [12]. This theory can be proved when the true value of α be calculated based on the saturation pressure of Hydrogen and Helium (saturation pressure data from DIPPR [13]). Figure 1 shows the true value of α for Helium and Hydrogen, for RK-CEoSs while the same figure shows the result of Equation 4.

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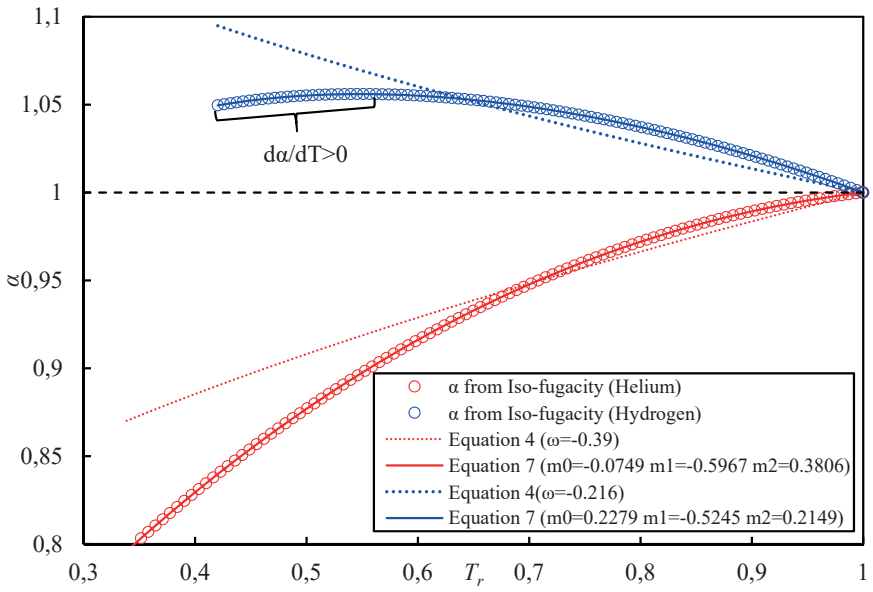

Figure 1. *Comparison of the value of α from iso-fugacity concept against empirical correlation of Equation 4.*

Based on this justification it is better to revise the working conditions regarding first and second derivative of α-function when there is an obvious dominant quantum effect. While the acentric factor proposed by Pitzer provide a promising result in the determination of the α for different chemicals through liner correlations; for better results of saturation properties, higher order of equations [14] are needed.

$$\sqrt{\alpha} = 1 + m_0\left(1-\sqrt{T_r}\right) + m_1\left(1-\sqrt{T_r}\right)^2 + m_2\left(1-\sqrt{T_r}\right)^3 \tag{7}$$

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Ultrasonic and volumetric properties of the binary mixtures of Eugenol (1) + Ethanol (2)

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The use of techniques involving supercritical CO_2 for extraction or fractionation of natural compounds from plants is a well grown field of investigation and has been the focus of the activity of our research group for years. In these techniques ethanol plays an important role as co-solvent in extraction processes [1] or solvent in fractionation ones. Then, the knowledge of the thermophysical behavior of mixtures of ethanol with a compound representative of the extract can be an important help in the design of those processes. In this study, densities, ultrasonic speed and isobaric molar heat capacities have been experimentally determined for the binary mixtures of eugenol and ethanol. All measurements have been carried out at atmospheric pressure and at temperatures ranging between 298.15 K y 328.15 K. Eugenol, a compound with pharmacological properties [2] is the main component in the extracts of clove and several species of cinnamon and basil [3,4].

For the mixture (eugenol + ethanol) excess molar volumes, shown in figure 1-a, and excess compressibilities both isentropic and isothermal are negative in the entire composition range at the four temperatures whereas deviations of speed of sound are positive. All these results point to a better packing of the molecules in the mixture than in the pure compounds. This better packing can be attributed to the prevalence of the interactions formed between eugenol and ethanol molecules over the breaking of interactions in the pure compounds, being, presumably, the main interactions hydrogen bonds in all cases. It must be taken into account that the alcohol group of ethanol could form hydrogen bonds with the alcohol group, the ether group, the double bond and the π cloud of eugenol, a fact that would explain the high absolute values obtained for all these properties.

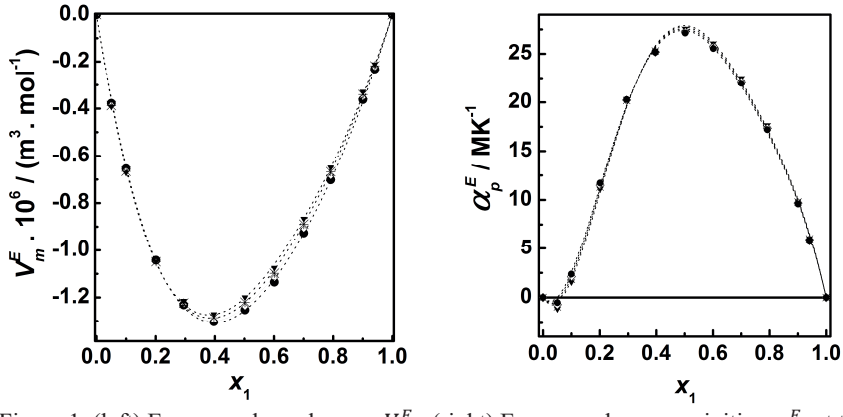

Figure 1. (left) Excess molar volumes, V_m^E , (right) Excess molar expansivities, a_p^E ,at the temperatures: (●) 298.15; (M) 308.15; (□) 318.15 y (▼) 328.15 K.

$A = -kT \ln Q$

This is supported by the fact that the mixtures (carvacrol + ethanol), where hydrogen bonds can be established only between the alcohol group of ethanol and the alcohol group and the π cloud of carvacrol, show a similar behavior but the absolute values of the properties, especially of excess molar volumes, are significantly lower [5].

The absolute values of excess molar volumes slightly increase as the temperature increases, a fact which is in agreement with the positive values found for excess isobaric expansivity [6] whose values are shown in figure 1-b. On the other hand, the absolute values of deviations of speed of sound and both compressibilities decrease as the temperature rises.

Excess molar heat capacities at atmospheric pressure as well as calculated excess isochoric molar heat capacities are positive in the entire composition range at the four temperatures. Consequently, the excess molar enthalpies increase as the temperature increases and, according to interpretation of the volumetric excess properties, the prevalence of hydrogen bonds formed in the mixture would be weakened as the temperature increases. The variation of these properties with temperature is somewhat complex because they increase from 298.15 K to 308.15 K, are very similar at 308.15 k and 318.15 K and finally decrease at 328.15 K. In any case the effect of temperature is almost negligible for the excess isobaric molar heat capacity.

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Thermophysical characterization of the Eugenol (1) + propan-1-ol (2) binary mixtures: Isobaric and isochoric molar excess heat capacities

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Our research team has been working on supercritical techniques applied to natural products present in natural plants in the frame of sustainable chemistry. In this field the use of short chain alcohols as ethanol and propan-1-ol is preferable to other solvents. As thermophysical data about natural products and its mixtures are scarce in literature its knowledge results of interest from the point of view of the design of those supercritical processes [1]. So in this study the densities, speed of sound and isobaric molar heat capacities for the binary mixtures of eugenol and propan-1-ol have been experimentally determined. The measurements of all these thermophysical properties have been carried at isothermal conditions between 298.15 and 328.15 K, every 10 K, and at atmospheric pressure. Besides, from the isobaric molar heat capacity and the properties derived from ultrasonic data the isochoric molar heat capacity, $C_{v,m}$, has been calculated, being this a property difficult to obtain experimentally. Finally, several excess molar properties have been calculated so that some insights about molecular interactions are obtained. The chemicals used have the following characteristics: Eugenol (99.1% purity) and propan-1-ol (99.99 % purity) both of them supplied by Sigma Aldrich. The equipment used for carrying out the experiments (Calorimeter Calvet C80 and Densimeter and Sound Analyzer from Anton-Paar) has been previously described [2].

The molar excess volume for the mixtures (eugenol + propan-1-ol) is negative in the entire composition range at the four temperatures, showing quite high absolute values. Then, the molecules are better packed in the mixtures than in the corresponding pure components. This would point out to a prevalence of interactions between dissimilar molecules over the rupture of interactions in the pure components, being the interactions mainly hydrogen bonds. The possibility of formation of hydrogen bonds between the alcohol group of propan-1-ol with either the alcohol group or the ether group or the double bond or the π cloud of eugenol would lead to the low values observed for the excess molar volumes. The deviations of speed of sound for the mixture (eugenol + propan-1-ol) are positive whereas the excess compressibilities both isentropic and isothermal are negative in the entire composition range at the four temperatures. The signs of these properties are in agreement with the better packing indicated by the excess molar volumes. A very similar behavior of these same properties has been obtained for mixtures (eugenol + ethanol) [3] and can be explained in the same way. But the absolute values are lower for the mixture with propan-1-ol whose greater size would presumably increase the breaking of hydrogen bonds as well as hinder the formation of new ones between it and eugenol.

The experimentally determined excess isobaric molar heat capacities (atmospheric pressure) $C_{P,m}^{E}$ and the obtained isochoric molar heat capacities $C_{v,m}^{E}$ are positive in the entire composition range at the four temperatures as it is shown in figure 1.

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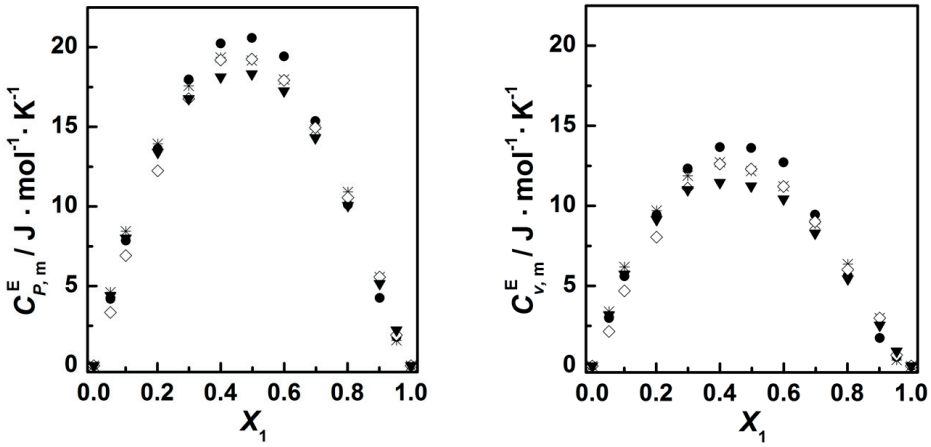

Figure 1. (left) Isobaric excess molar heat capacities, $C^E_{P,m}$, (right) isochoric excess molar heat capacities, $C^E_{v,m}$, at the temperatures: (●) 298.15; (M) 308.15; (□) 318.15 y (▼) 328.15 K.

Consequently, the excess molar enthalpies increase as the temperature increases, then less hydrogen bonds and/or weaker ones are formed in the mixture as the temperature rises, a behavior that, once again, coincides to that observed for the mixtures (eugenol + ethanol) [3]. In the case of excess molar heat capacities the values for the mixtures with ethanol and propan-1-ol are very similar.

Acknowledgements

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Improving Salting Out of Methane from Aqueous Electrolyte solutions using the Madrid Model

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The solubility of methane in water decreases when a small amount of salt (NaCl) is present in water. This is usually denoted as the salting out effect (i.e the methane is expelled from the solution when it contains small amounts of salt). The effect is important and in fact in a 4m solution of NaCl, the solubility is reduced by a factor of three. In previous work [1] we have studied the salting out effect using the TIP4P/2005 model of water, and a simple Lennard-Jones model for methane. The NaCl was described using the popular Smith Dang model of NaCl. These previous simulations predict correctly the salting out effect although it was overestimated. In fact, it was found that the solubility of methane was reduced by a factor of ten. Of course, this points out to limitations of the force field used in the simulations.

In the recent years, the idea of using scaled charges to describe electrolytes in water is becoming more popular. In these models, the charge assigned to the Na cation or Cl anion is not one (in electron units) but is reduced to a certain fraction. The justification behind this approach is to assume that there is a certain transfer of charge from the hydration water molecules to the ions. Recently we have developed a model of NaCl which use the concept of scaling of charges. The model has been denoted as the Madrid model [2] and the charge assigned to the ions is of 0.85 (in electron units). In this work, we shall use direct coexistence simulations for a pressure of 200 bar to determine the solubility of methane in pure water and in a 4m solution of NaCl in water described by the Madrid model.

Again, the salting out effect will be predicted qualitatively, but now the reduction of the solubility is estimated to be of a factor of five in better agreement with the experimental value of three. Thus, the reduction of charge of the ions seems to be also improving the description of the salting out effect of methane in water. We shall also show that the model predicts an increase of the surface tension of the solution as compared to that of pure water. It is well known that electrolytes tend to increase the interfacial free energy of liquid water, and this seems also to be the case for the interface with methane.

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$A = -kT \ln Q$

Thermodynamic modelling of weak electrolytes using the SAFT-VRE Mie equation of state

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Electrolyte solutions are important in many natural and industrial processes. A sound modelling of the thermodynamic properties of electrolyte solutions is needed in both fields. Equations of state (EOS) are a versatile tool to describe the thermodynamic properties fluids. To describe electrolyte solutions, EOS for mixtures of molecular species are usually augmented with additional terms accounting for the long-ranged coulombic interactions present in these solutions. There has been significant progress in EOS modelling of solutions of strong electrolytes recently, e.g. with the eCPA [1], the ePC-SAFT [2] and the SAFT-VRE Mie [3] EOS. In contrast, solutions of weak electrolytes have so far only been studied with ePC-SAFT [4].

In this work, the SAFT-VRE Mie EOS is extended to model weak electrolytes. To incorporate the dissociation reactions, thermodynamic equilibrium constants from experiments are taken from the literature and are coupled with the SAFT-VRE Mie modelling. Exemplary, models for three important inorganic acids are developed: nitric acid, sulphuric acid and carbonic acid. The models for the solvent water and the hydronium ion (H_3O^+) are taken from previous work [3]. New models for the molecular acids and their anions are developed based on a fit to experimental data only of the respective acids in water. It is found that this parameter estimation is best carried out using data on the degree of dissociation and either phase equilibrium or activity data. The obtained SAFT-VRE Mie models describe different thermodynamic properties of the aqueous acids, such as densities, osmotic coefficients, activity coefficients, and vapour pressures of the solutions reliably over a wide temperature range.

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Thermodynamics of Saline Produced Water Utilization

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Approximately four barrels of water are extracted for every barrel of oil originating from the Permian Basin [1]. The management of this saline/hypersaline hydrocarbon-produced water is therefore an essential practical consideration in Enhanced Oil Recovery (EOR) solutions. Engineering companies specialized in the processing of large volumes of produced water require reliable, predictive modelling tools – ultimately grounded in sound electrolyte solution theory. This is especially so when produced water streams are utilized in membrane-based processes for osmotic energy recovery – e.g. pressure-retarded osmosis (PRO) – where an accurate representation of thermodynamic driving force associated with salinity gradients is essential.

This work presents the results of equation of state (EoS) development for electrolyte solutions. This has included the derivation of generalized expressions explicit in chemical potential for the slope of a solubility curve at any point along the curve – applicable to ternary electrolyte solutions. Slope expressions have been incorporated into objective functions for parameter optimization of the eSAFT-VR Mie EoS [2]. The parameter optimization methodology utilizes data only in the limit of the solubility of the single-salt solution; resulting EoS parameters enable adequate prediction of the entire solubility curve, as well as single-salt mean ionic activity coefficient isotherms.

A robust simulation tool [3] to model PRO processes has also been developed – based on the Q-Electrolattice EoS [4] for electrolyte solutions and a detailed mass transfer model. The salinities of draw and feed inlet streams are specified such that they are representative of produced water and seawater, respectively. By integrating fluxes over discrete elements, the simulator is able to capture the effects of continuous dilution on thermodynamic property profiles across the membrane area. This has implications for the scalability of coupon-scale power density measurements. The quantitative impact of electrolyte solution non-ideality on calculated energy recovery is evaluated based on a representative PRO process configuration.

This study was made possible by grants from the Qatar National Research Fund under its National Priorities Research Program award numbers NPRP10-1231-160069 and NPRP8-1648-2-688. The statements made herein are solely the responsibility of the authors.

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$A = -kT \ln Q$

Transport properties of fluorinated alcohols and their mixtures with hydrogenated alcohols: viscosity and diffusion coefficients

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Perfluorinated liquids have become key fluids in a wide range of fields due to their chemical inertness, biocompatibility and peculiar physical properties. These range from medical applications, as oxygen carriers in blood substitute formulations, fluids in eye surgery and emulsions for liquid ventilation, to technological applications such as solvents for biphasic synthesis or lubricants.

In spite of their structural similarity, hydrogenated and fluorinated chains display quite different thermophysical and mechanical properties. Perfluorinated chains are not only highly hydrophobic, but also lyophobic, i.e. they segregate hydrogenated chains. The explanation of the effect at the molecular level is far from being fully understood. Albeit its technological importance, namely in material sciences, data on the transport properties of mixtures of fluorinated and hydrogenated substances are very scarce. We have recently shown that liquid mixtures of hexane and perfluorohexane display an enhanced lowering of the viscosity [1], an effect that can be advantageously used in many technological applications. At the origin of this anomaly is the mutual phobicity between hydrogenated and fluorinated chains.

In this work, the viscosity of liquid fluorinated alcohols and their mixtures with the corresponding hydrogenated alcohols were measured as a function of composition and temperature. Molecular Dynamics (MD) simulations were performed to model and interpret the experimental data. Additionally, diffusion coefficients of the fluorinated and hydrogenated components were simulated in both fluorinated and hydrogenated media. The influence of the weak interaction between hydrogenated and fluorinated chains in the transport properties of their mixtures is assessed.

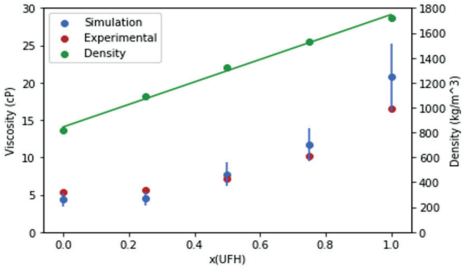

Figure 1. Viscosity and density of (hexanol + perfluorohexanol) mixtures at 293 K.

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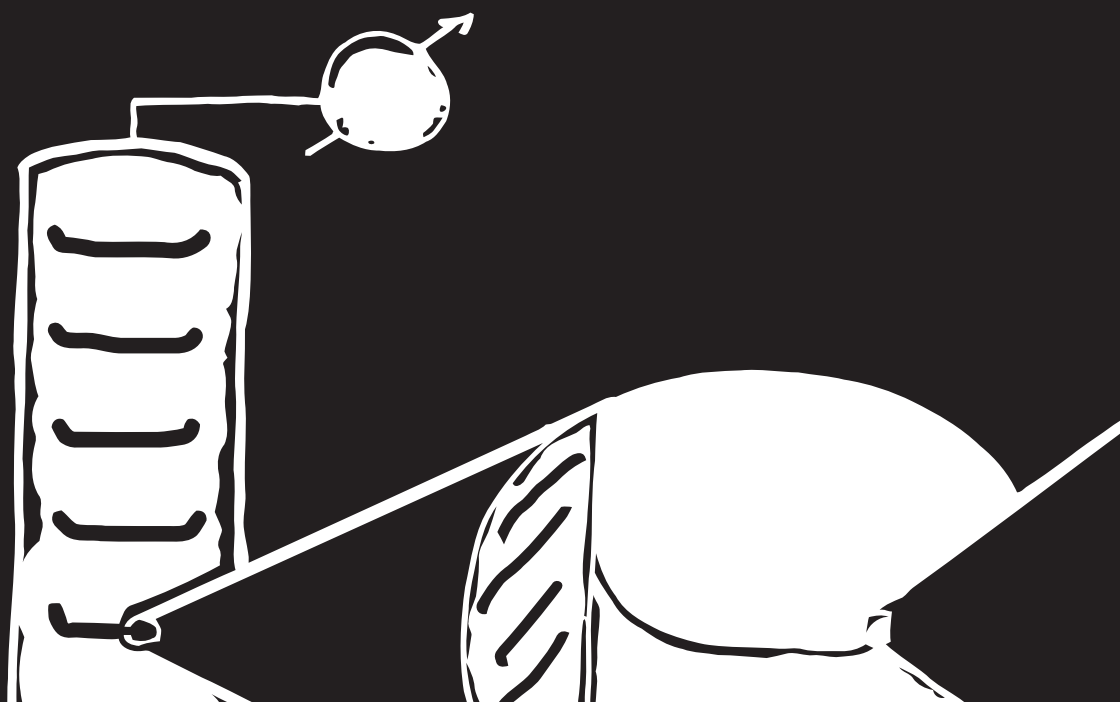
Poster Presentations:
Interfacial and confined phenomena



Prediction of vapor – liquid – liquid equilibrium and its interfacial properties for aqueous ternary mixtures using IPython

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Introduction. One of the most appropriate and effective technique to dehydrate (bio)alcohols is the heterogeneous azeotropic distillation. In this unit operation, a third component (entrainer) is added to the water + (bio)alcohol mixture to form a heteroazeotropic mixture, from which the water content can be eliminated. During the process design, it is mandatory to count with experimental data and predictions for the of vapor – liquid – liquid equilibrium (VLLE) and its interfacial properties (*i.e.*, interfacial concentration, ρ_i, along the interfacial region, z; adsorption; interfacial tension, γ; etc) as a function of thermodynamics variables (*i.e.*, temperature, T; pressure, P; mole fraction, $\underline{x},\underline{y}$; bulk densities, ρ). Unfortunately, the experimental data are scarce [1], and their predictions are very limited and sometimes unreliable. Focused on the thermodynamics predictions, VLLE calculations need to carry out with care to avoid unstable solutions from the traditional isofugacity method [2]. On the other hand, interfacial properties are difficult to obtain due to the multi bulk phases, which causes high non-monotonic behaviour of the interfacial concentration [3]. In this contribution, an algorithm that combines phase equilibria calculations couple to phase stability has been implemented in IPython for the consistent predictions of VLLE. The phase equilibrium predictions (*i.e.*, T, P, $\underline{x}^{L1}$, $\underline{x}^{L2}$, $\underline{y}$, ρ^{L1}, ρ^{L2}, ρ^{V}) are used as a boundary conditions to solve the interfacial concentrations ($\rho_i - z$) and interfacial tensions (γ^{L1V}; γ^{L2V}; γ^{L1L2}) by applying the Square Gradient Theory (SGT). In this contribution, SGT is solved by using orthogonal collocation [4] which notoriously reduce the numerical effort.

Theoretical Modelling and Results. Phase equilibria calculations for aqueous ternary mixtures in VLLE have been carried out by using an approach that combines the traditional phase equilibria conditions with the stability criteria proposed by Gupta et al. [5] and Michelsen and Mollerup [2]. The former established an algebraic system of equations for simultaneous equilibrium and stability computations, which can be solved by a combination of Newton's method and successive substitution. The latter relies on a minimization of the Gibbs free energy using second-order methods. These methods for solving multiphase equilibrium have their advantages and disadvantages. Specifically, the Gupta's method [5] is capable of convergence even when a poor initial guess is supplied, although successive substitution implies a low convergence rate. On the other hand, Michelsen's second order method [2] is known to be fast, but it requires a good initial estimated. In this work, the best of both approaches has been implemented. First finding a solution by Gupta's method and limiting the number of iterations, then if not solved the algorithm proceeds to perform the minimization. The proposed methodology has been implemented with the Peng-Robinson equation of state [6] extended to mixtures by using the MHV mixing rule [7], which uses the Non-Random Two Liquids (NRTL) [8] as activity coefficient model. Figure 1 illustrates the prediction of the VLLE for the water + n-Butanol + MTBE ternary mixture at 101.3 kPa. For this prediction, all interactions parameters were fitted from binary data. This figure also includes the experimental data obtained in our lab [9]. As can be observed, the predictions of the proposed approach are in good agreement to the experimental equilibrium composition.

For the case of interfacial properties of the mixture, the SGT was applying as a predictive theory for mixtures. In other words, SGT uses some interfacial parameters, which are traditionally

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called the influence parameters (c_{ii}, c_{ij}). For the pure fluids, c_{ii} are obtained from experimental interfacial tension (IFT) data of pure fluids. For the case of mixtures, the cross interfacial parameters, c_{ij}, are calculated by using the geometry mixing rule: $c_{ij} = (1-\beta_{ij})(c_{ii}\, c_{jj})^{1/2}$, where β_{ij} is fixed from experimental IFT data of binary mixture. Therefore, for the case of ternary mixtures, the SGT proceeds as a predictive theory. In this work, orthogonal collocation is used to solve the SGT. As an illustration, Figure 2 shows the interfacial concentration profiles (ρ_i – z) for the case of the aqueous ternary mixture explored in this work at a single condition (373.15 K and 101.3 kPa). The reported profiles have been calculated by using $\beta_{ij} = 0$. From this figure, it is possible to observe that MTBE and n-butanol slightly adsorb on the interface of the vapor and liquid phase of lower density. For the condition illustrated in Figure 2, the corresponding interfacial tension are: $\gamma^{L1L2} = 1.12$ mN/m; $\gamma^{L2V} = 20.11$ mN/m, and $\gamma^{L1V} = 21.23$ mN/m. Comparing the values of the interfacial tension, $\gamma^{L1V} = \gamma^{L2V} + \gamma^{L1L2}$, it is possible to state that at this condition, a perfect wetting is observed.

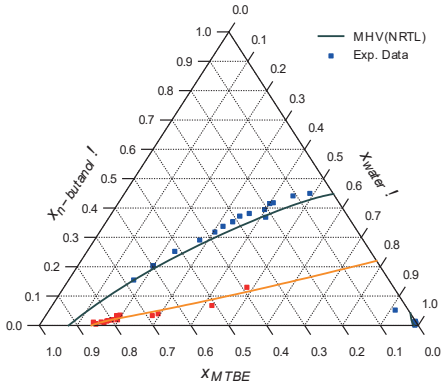

Fig. 1 VLLE for water + n-butanol + MTBE at 101.3 kPa.

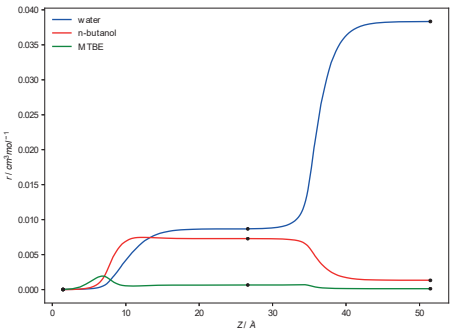

Fig. 2 Interfacial profiles at VLLE for water + n-butanol+ MTBE at 357.84 K and 101.3 kPa.

Conclusions. In this work, two numerical algorithms have been implemented to describe the three-phase equilibrium and their interfacial properties for aqueous ternary mixtures using IPython. The phase equilibrium algorithm uses both equilibrium condition and stability restriction, which allow us to predict stable and consistency results. The interfacial properties algorithm is based on the square gradient theory and uses orthogonal collocation, which notoriously reduces numerical effort. As an example, VLLE and selected interfacial tension properties have been reported by water + n-Butanol + MTBE ternary mixture at 101.3 kPa, but the results cover other mixtures as well as other interfacial conditions.

Acknowledgments. This work was financed by FONDECYT (Chile), Project 1150656.

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Cross-over in the dynamics of polymers confined between two liquids of different viscosity

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The study of structural and dynamical properties of polymers at liquid/liquid interfaces is crucial to understand technological and biological systems. Polymers are indeed confined at liquid interfaces in many industrial processes, such as liquid/liquid extractions, solvent displacement methods, or emulsifications, and also in biological applications, such as drug nanocarriers. Depending on the relative solubility of the polymer chains, they can dissolve in one of the two solvents or reside at the interface. In the latter case the polymers adsorbed at the interface minimize the interfacial free energy of the system, behaving as active molecules [1].

By performing molecular dynamics simulations, we characterized the dynamics of polymer chains with different molecular weights, entrapped at the interface between two immiscible liquids of different viscosity. We showed that increasing the viscosity of one of the two liquids the dynamic behaviour of the chain changes from a Zimm-like dynamics typical of dilute polymer solutions, to a Rouse-like dynamics where hydrodynamic interactions are screened [2].

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$A = -kT \ln Q$

Connect the Thermodynamics of Bulk and Confined Fluids: Confinement Adsorption Scaling

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A fluid (a gas or a liquid) adsorbed in a porous material can behave very differently from its bulk counterpart [1-5]. The advent of various synthesized materials with nanopores and their wide applications have provided strong impetus for studying fluids in confinement because our current understanding is still incomplete. From a large number of Monte Carlo simulations and scaled particle theory (SPT) [6-10], we found a scaling relation that allows for connecting some thermodynamic properties (chemical potential, free energy per particle, and grand potential per particle) of a confined fluid to the bulk ones. The scaling factor takes into account of porosity, adsorption amount and the pressure of the bulk fluid in equilibrium with the adsorbed one in a porous solid. Upon rescaling the adsorbed fluid density, the adsorption isotherms for many different confining environments collapse to the corresponding bulk curve, as illustrated in Figure 1. This scaling relation implies the invariance with respect to confining environments of Helmholtz free-energy per particle and grand-potential per particle of confined fluids when they are expressed as function of chemical potential. We also reveal the intimate connection of the reported scaling relation to Gibbs theory of inhomogeneous fluids and morphological thermodynamics. The advance in our understanding of confined fluids, gained from this study, also opens attractive perspectives for circumventing experimental difficulty for directly measuring some fluid thermodynamic properties in nanoporous materials.

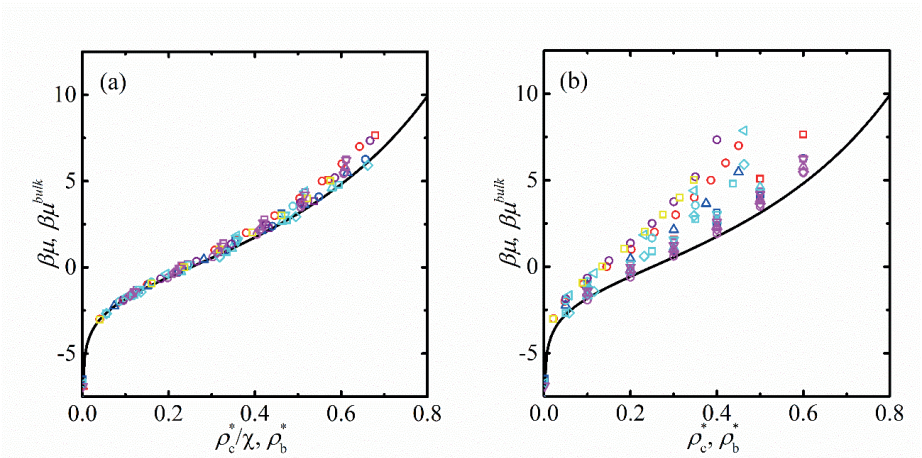

Figure 1. Monte-Carlo simulation results for a hard sphere fluid confined in 23 different confining environments: a) Chemical potential, $\beta\mu$, as function of scaled density ρ_c^* / χ; b) Chemical potential, $\beta\mu$, as a function of non scaaled density ρ_c^*. Full line is the bulk $\beta\mu^{bulk}$ □ ρ_b^* isotherm.

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$A = -kT \ln Q$

Phase behaviour of hydrocarbons in nano-pores

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Unlike conventional reservoirs where pore size distribution has a micrometer scale, tight oil and shale gas reservoirs are made up of a very heterogeneous pore size distribution ranging from several nano-meters to micro-meters. The part of micro (below 2 nm) and mesopores (between 2 and 50 nm) are generally much smaller than that of the macropores (more than 50 nm) but can reach more than 20% of the volume distribution [1]. They are mainly associated with clay minerals and kerogen [2]. As hydrocarbon molecules range between 0.5 and 10 nm, interaction forces between confined fluid and pore wall molecules become as significant as inter-molecular interactions within the confined fluid, which can change dramatically the fluid phase behaviour. Understand and study the thermodynamic behaviour of such fluids is of great interest for chemical, food and pharmaceutical industries. However getting all fluid properties in confined media through experiments is still very challenging because of many technical limitations. In this context, molecular simulation is a good alternative to study the phase behaviour of fluids in confinement. Recent works have been devoted to model the fluid phase equilibria of confined fluids through Grand Canonical Monte Carlo (GCMC) simulations of pure components [3] and mixtures [4]. In this case the precise determination of the equilibrium chemical potential is still cumbersome [5]. Other authors use grand canonical transition matrix Monte Carlo (GCTMMC) and configurational-bias grand-canonical transition matrix Monte Carlo simulations but only for confined pure components properties calculations [6]. However, to the best of our knowledge, analyses related to confined mixture properties and liquid and vapour pressures using Gibbs ensemble Monte Carlo (GEMC) are not available in the literature.

In this work, we propose a new and robust method in the GEMC ensemble aiming to get thermodynamic properties of mixtures and confined liquid and vapour pressures at equilibrium. Thermodynamic properties of pure and mixture hydrocarbons have been determined in confined spaces, emulating those in kerogen pores in shale reservoirs using GEMC ensemble as suggested by Panagiotopolous [7]. The pores are modelled by a Steel 9-3 slit pores with graphite walls with different sizes whereas hydrocarbons are modelled with the anisotropic united atom intermolecular (AUA4) potential. Pure components and mixtures are modelled with a modified version of the NVT GEMC including confinement. In the case of mixtures, initial configurations required for NVT GEMC are generated through NPT bubble point Gibbs ensemble Monte Carlo (GEMC-NPT-BPMC) simulations. All algorithms are implemented in the Gibbs MC code. The workflow used to compute the phase behaviour of confined fluids can be observed in Figure 1.a.

We have computed the LVE of pure (CH_4, C_2H_6, C_5H_{12}, $C_{10}H_{22}$) and mixtures (CH_4+C_2H_6, C_2H_5+C_5H_{12}) hydrocarbons in confinement [8]. The case of $C_{10}H_{22}$ can be observed in Figure 1.b where we observe the expected reduction of the critical temperature (and pressure) with the reduction of the pore size. This behaviour is also observed for mixtures (figure not shown). Using the pressure-molar fraction diagrams for different isotherms (not shown), a pressure-temperature diagram can be constructed for a specific concentration of C_2H_6/C_5H_{12}. Indeed, one value of molar fraction corresponds to one value of dew-point pressure and bubble point pressure for each isotherm. An example of this diagram for a mixture of 59.7% of C_2H_6 and 40.3% of C_5H_{12} is shown in Figure 1.c. It is observed that the phase envelope of the confined fluid is shifted and closes itself from its bulk value. The critical temperature and pressure are shifted from the bulk value to a lower value and the bubble point pressure is decreased as the dew point pressure is

increased. This observation is valid regardless of the proportion of C_2H_6 and C_5H_{12} in the mixture. This information can be used to improve the description of confined fluids by EOS calibration.

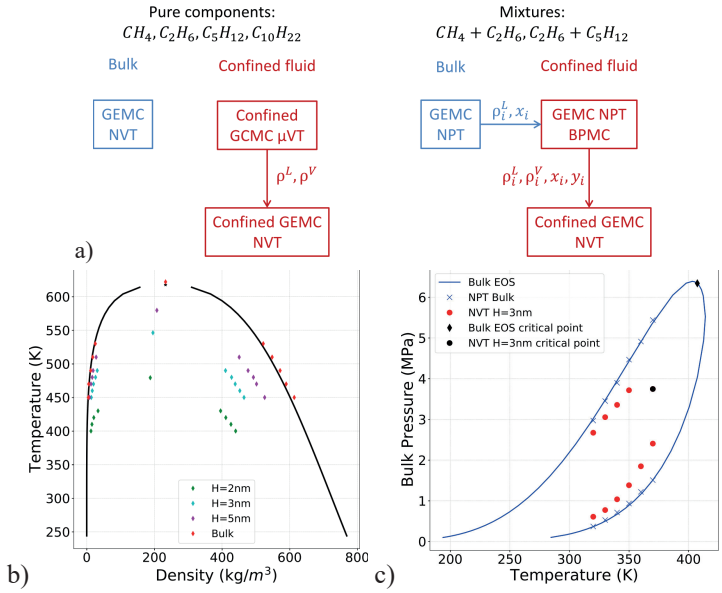

Figure 1. a) Schematic of the simulation workflow used in this work. b) Results of the liquid-vapour NVT GEMC for $C_{10}H_{22}$ for different pore sizes. Black line is the experimental bulk LVE from NIST database. c) Pressure-Temperature diagram for a mixture of 59.7% of C_2H_6 and 40.3% of C_5H_{12}. Blue line is the PR EOS with critical point (diamond), x-symbols correspond to bulk NPT GEMC and red circles correspond to confined NVT GEMC (following the procedure indicated in Figure 1.a) for a pore of 3nm width (the critical point of the confined system corresponds to the black circle).

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$A = -kT \ln Q$

Critical micelle concentration of anionic surfactants: experiments and Dissipative Particle Dynamics simulations with electrostatic interactions

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Surfactants are commonly used in the industry as detergents, dispersants and emulsifiers, and are part of the composition of many different industrial products. Amphiphilic molecules contain both hydrophilic head groups and hydrophobic tails. Due to their limiting solubility in water, they tend to aggregate into micelles. The formation of such structures occurs only when the concentration is higher than the critical micelle concentration (CMC). The CMC value is related to the molecular composition of the surfactant and solvent, and conditions such as the temperature. The aggregation process and the variation of the CMC with composition have been extensively studied using experiments and molecular simulations. The advantage of molecular simulations techniques is to get access to the micellar structure as a function of the nature of the surfactant and composition, which is quite complicated from an experimental point of view. The key point to rely on simulation results is the availability of a realistic molecular model for involved species (water, surfactants and salts) as well as accurate intermolecular potentials to describe their interactions. If an atomic description is used, sampling can become quite complicated when dealing with liquid-liquid interfacial properties.[1,2] Alternatively, coarse grained or mesoscopic models can be used to reduce the degrees of freedom of the system to enhance the capability of the simulations to longer time and length scales.[3,4] There are several types of coarse grained approaches available in the literature, among them we can mention the MARTINI model and force fields, and the dissipative particle dynamics (DPD).

In this work, we have used combined experimental and simulation approaches. DPD simulations including electrostatic interactions are employed to model the aggregation process and the CMC of aqueous solutions of anionic surfactants (sulfonate, $Cn\text{-}SO_4^-Na^+$ with n from 6 to 12). In addition, we have used the Wilhelmy plate and the spinning drop experimental techniques to determine the CMC of these surfactants in function of the concentration of additional NaCl in the solution.

Standard methods used in the literature to parameterize DPD parameters are no longer valid due to the combination of repulsive and electrostatic interactions.[5,6] We have used a recent thermodynamically consistent approach based on the calculation of the osmotic pressure of the ionic species in solution to optimize the magnitude of repulsive interactions for ions.[7] In this context, the different repulsion parameters can be estimated by means of the Free energy of hydration of ions in solution as can be seen in Figure 1.a.

Our preliminary results show that our DPD model including electrostatic interactions is able to reproduce the variation of the osmotic coefficient (ϕ) of sodium dodecylsulfate (SDS) when compared to available experimental data, cf. Figure 1.b. The dashed vertical line shows the experimental CMC of SDS (0.008 mol/l). Simulation results show the abrupt change in the slope of ϕ when the concentration of SDS is greater than the CMC. Independent calculation of the CMC using a cluster approach confirms that our ionic DPD model returns CMC values in agreement with the experimental CMC value. We have also measured the variation of the CMC with the concentration of NaCl added to the solution as can be seen in Figure 1.c.

The parameterization strategy proposed in this work allows us to establish a robust and thermodynamically consistent DPD model for surfactants belonging to the sulfate family, that can be easily extended to other families of ionic surfactants. Work is in progress to compute CMC as a function of the concentration of NaCl as well as the variation of the CMC of a mixture of surfactants of different types from the sulfonate family. Finally, the presented model helps to understand the relation between the local structure of micelles formed and the concentration of the different species in solution.

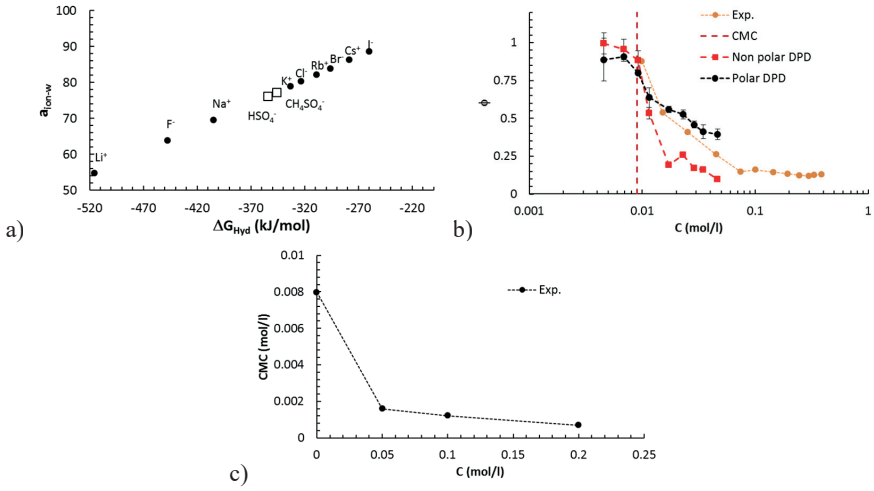

Figure 1. a) Variation of the ion-water DPD repulsion parameter (a_{ion-w}) as a function of the ionic free energy of hydration (ΔG_{hyd}). b) Variation of the osmotic coefficient (Φ) as a function of the sodium dodecylsulfate (SDS) concentration, comparison of the experimental data[8] with results obtained with the ionic model proposed in this work and the results obtained with the non-polar model of Mai et al.[9] c) Experimental results of the variation of the CMC of SDS as a function of the concentration of NaCl in the solution.

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$A = -kT \ln Q$

A '2D Route' to the Effective Tangential Pressure in Adsorbed Films: High-Density Equation of State for a Two-Dimensional Lennard-Jones Solid

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The estimation of the tangential pressure in adsorbed films on planar surfaces and in slit-shaped pores remains a challenge in both experiment and theory. While the normal pressure is uniquely defined for a planar surface, the tangential pressure, P_T, at a point **r** is not uniquely defined at the nanoscale. In the commonly used 'virial-route' the statistical mechanical equation for $P_T(\mathbf{r})$ requires an integration of the intermolecular forces over a contour connecting the interacting particles, so that the numerical value of the tangential pressure depends on the choice of this integration path. Therefore, it is useful to have an alternative route to estimate the effective tangential pressure.

In this work we propose a new route, the '2D-route', to P_T based on the observation that adsorbed films on a planar solid surface consist of quasi-two-dimensional (2D) layers near the surface. We present a new equation of state for a 2D Lennard-Jones solid (2D LJ-EOS) that is valid at high densities. The new 2D LJ-EOS is of analytic form, consisting of a zero-temperature contribution and vibrational contributions up to and including the second anharmonic term. Comparisons between the 2D LJ-EOS and Monte Carlo simulation results show that the 2D LJ-EOS is very accurate over a wide range of temperature in the high-density region. A criterion to find the temperature range over which the 2D LJ-EOS is applicable is derived. We calculate an effective tangential pressure for the adsorbed contact layer near the wall in a slit-pore system, and show that the tangential pressures predicted by this '2D-route' are in qualitative agreement with those found by the more traditional virial route of Irving and Kirkwood [1].

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Microphase separation of confined binary liquids

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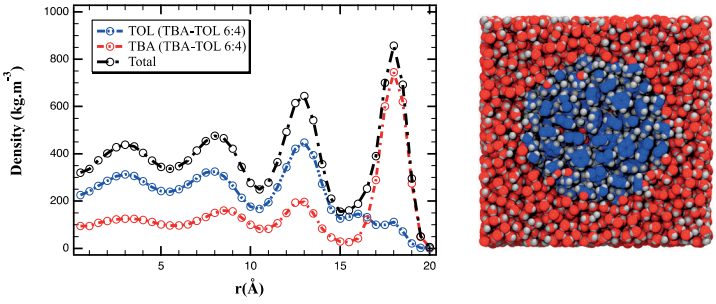
Self-association and formation of supermolecular assemblies are important phenomena in diverse processes, from the creation of micro-emulsions, to the drug delivery and to the assembly of proteins into the functional complexes. Among the self-organizing liquids, we consider alcohols as good models given their ability to form complex structures from hydrogen bonds. It is now well established that the physical properties of these liquids are firmly connected to their structure.

Recently, Hamid et al. have shown that a mixture of toluene (TOL) and *tert*-butanol (TBA) can demix and form a core-shell organization in a confined medium [1], where this mixture is absolutely homogeneous in the bulk phase. Obviously, we have shown that this binary mixture of TBA and TOL can induce a strong spatial heterogeneity in confined media [2].

In order to better understand this behavior at the nanoscale, it is essential to get a good description of the hydrogen bond network. In this work, we aimed characterizing the connection between the hydrogen bonding (HB) network and the different physical properties such as transport, structure and interfacial properties. For that, molecular dynamics simulations of alcohols and their mixture were carried out, with TOL and Cyclohexane (CX) in bulk and confined phases. These mixtures have been structurally and dynamically characterized and anomalous behaviors such as unusual dynamics and microphase separation were captured.



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$A = -kT \ln Q$

Water droplets on ice

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Does water wet ice? As the triple point is approached, the surface disorder grows steadily at the ice-air interface, and a liquid film of premelted water is formed. Whether this film attains a finite thickness or diverges at the triple point has remained a controversial issue for a long time. However, recent confocal microscopy experiments confirm early observations of water droplets standing on the surface of ice very close to the triple point, while ice crystal terraces grow and spread below the droplet [1,2].

Whereas the appearence of an incomplete wetting state of very low energy has been predicted theoretically on the basis of the Lifshitz theory of van der Waals interactions [3], still a great number of open questions remain to be solved. Indeed, in the experiments by Murata et al., the droplets are formed only significantly above saturation, and likewise, disappear reversibly above saturation as the vapor pressure is decreased. Furthermore, a second wetting state seems to appear in this systems at higher saturation, since a thick film appears to emerge below the droplets. More strikingly, the authors observe the formation of distinct droplets well below the vapor-liquid coexistence line.

In this paper we will pursue previous computer simulations studies [4] and new mesoscopic models to describe and rationalize the puzzling physics of water droplets on ice. The modeling requires to address simultaneously the properties of vapor-liquid and ice-liquid interfaces, as well as the terraced structure of the disordered solid interface. Furthermore, because of the occurrence of premelting on this surface, one needs to take into consideration the interaction of such surfaces via the interface potential, which is dominated in the nanometer scale by retarded interactions. A successful explanation of these experiments thus requires understanding the physics of the problem from the tenth of a nanometer to the micrometer scale. From atomistic simulations of the premelting film and its surface fluctuations to the
mesoscopic modeling of spreading droplets.

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Surface van der Waals forces in a nutshell

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The famous power law decay of r^{-6} that is known since the times of London for atoms at a distance r, adds up to yield the well known Hamaker power law L^{-2} decay for the surface energy between two plates a distance L apart [1]. However, it has been known for a long time that both the r^{-6} and L^{-2} power laws are merely the exact small distance limit of van der Waals forces. At larger distances, these simple laws become much more complicated due to retardation effects. As a result, the London-Hamaker regime of interactions is transformed into the Casimir regime, where interactions fall off as r^{-7} and L^{-3}, respectively. This behavior can only be explained under the framework of quantum electrodynamics. It is related to the time photons of all the electromagnetic spectrum take to communicate intermolecular forces between distant molecules. Eventually, at finite temperature, all of the high frequency contributions to the intermolecular forces are suppressed, only the static part remains, and the power law behavior recovers the Hamaker regime albeit with different coefficients [2].

Unfortunately, the quantitative account of these effects is extremely complicated and requires a specialized numerical calculations [3]. As a result i) essentially all of the relevant retardation effects of intermolecular forces are neglected in most applications and ii) not only are they neglected, but also have remained widely unknown to some of us until recently.

In this paper, we derive from first principles a simple closed expressions that allows one to determine quantitatively the distance dependence of surface van der Waals forces at all ranges from the tenths of nanometer to the micrometer and beyond [4].

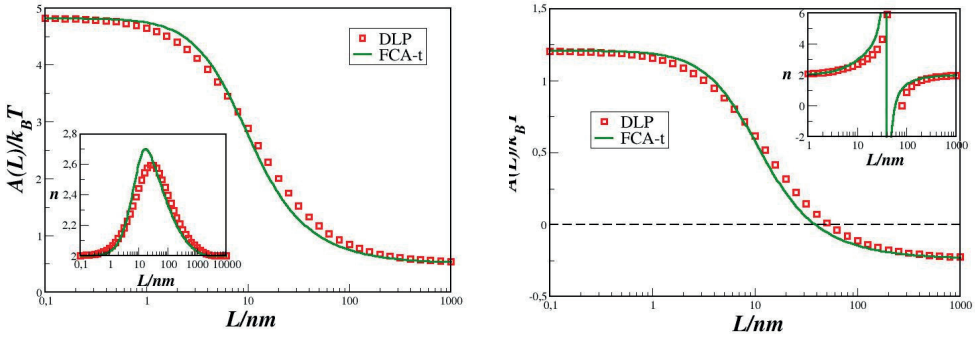

Figure 1: Hamaker function A(L) for the surface energy g(L) = - A(L)/12π L^2 between two plates at a distance L. Symbols are results for the exact numerical quantum electrodynamic calculation from DLP theory. Lines are resuls for a simple working equation which uses refraction indexes and high energy absorption frequency as only imput. Left: Interactions between two mica plates in water. Right: Interactions between water and air across octane. Insets show the effective power law exponent for g(L).

The formula accounts for a smooth variation of the effective power law exponent from the Hamaker result at short distances, to the Casimir regime at tenths of nanometer to the exact

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asymptotic limit at infinite distances. This is achieved without introducing any more significant algebraic complexity than is required to determine Hamaker constants in conventional applications [1]. Importantly, it is found that the Casimir regime of intermoelcular forces that has been consistently neglected in computer modeling becomes relevant at distances of just a few nanometers. We hope this result will help to achieve a better quantitative description of surface forces but also to appreciate the full complexity of intermolecular forces at all ranges.

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Surface tensions of phenolic mixture separated from kukersite oil shale oil

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Property data of various oils, resource for chemicals, are essential for design and sustainable use. In this regard, properties of phenolic compounds and their naturally occurring mixtures are of wide interest. The aim of present work is to evaluate surface tensions of phenolic part of the kukersite shale oil (complex mixture of phenolic compounds), of the oil obtained from Galoter type commercial ex-situ retorting process. One unique characteristic of the Kukersite oil shale (Estonia) retort-oil is the high content of phenolic compounds (over 30%). In this study, the phenolic part was isolated by extraction with 10% sodium hydroxide. From this oil fraction with phenolic composition, narrow boiling range cuts were prepared by simple distillation at reduced pressure (at about 0.5 kPa). The narrow boiling range fractions had average atmospheric boiling points from 250 to 450 ºC.

The surface tensions of selected narrow boiling range phenolic oil cuts were determined by a pendant drop method as a function of temperature under atmospheric pressure. The temperature range covered was from 40 to 150 ºC. The surface tension was measured by Rame-Hart Instruments Co. tensiometer (model 260), accompanied with a high temperature chamber and a syringe.

As simple correlative models based on easily measurable bulk properties are of practical interest, then the narrow boiling point cuts were characterized by phenolic OH content, average boiling point, molecular weight and density (specific gravity). From the experimental data empirical models were developed for practical industrial applications.

$A = -kT \ln Q$

Alcohol-water adsorption in hydrophobic porous media

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We present a comparative study of different alcohol/water mixtures adsorption into structured hydrophobic adsorbents, two small channel zeolites (MEL and MFI) and graphite slit pores in order to analyse their respective performance as potential materials to facilitate the process of alcohol purification. One observes that in mixtures, both components present similar diffusivities at all pore sizes, which is explained in terms of the coupling of molecular movements due to strong hydrogen bonding between methanol and water molecules. In the case of slit pores, one observes that water diffusivities present a non monotonous dependence with pore size, due to the effects of confinement and the dynamic anomalies of water [1]. For the adsorption in zeolites, it is observed that the more energetic adsorption into the zig-zag channels of MFI, leads to a higher selectivity for alcohol adsorption[2]. In both hydrophobic adsorbates, water co-adsorption due to the affinity of the alkyl chains for the adsorbate walls and hydrogen bonding, makes possible the diffusion of water molecules into the pores.

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Direct MD simulation of water nucleation in molecular beams

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Molecular beams can be created by expansion of saturated water vapor through a small orifice into vacuum. As the vapor accelerates to supersonic speeds, it cools below the freezing point and nucleates. The resulting ice clusters of various sizes may serve as models of atmospheric ice particles. Experiments indicate that larger clusters are of irregular shape, probably as a result of secondary aggregation.

We simulate this process by a method binding the equations of fluid dynamics with classical MD simulation. Initially, a periodic simulation box (carved out from the flowing gas) is simulated with the time development of density, $\rho(t)$, calculated from ideal gas in steady flow. However, this evolving box does not know anything about pressure and velocity in the other parts of the nozzle; in other words, the fluid dynamics equations are not coupled with the MD part. From the obtained time evolution of pressure via integration of the Bernoulli equation we get the flux along the path; this flux should be constant. If it is not, the expansion protocol $\rho(t)$ must be modified to satisfy the steady flow condition.

In this work, we propose and test a piece-wise algorithm to correct $\rho(t)$ during simulation. After a short time interval, the flux is determined. If it is not constant enough, a correction to $\rho(t)$ in this interval is calculated and the simulation is rerun.

$A = -kT \ln Q$

Methane Dissolution Inside Bulk or Porous-Medium-Confined Water Near Hydrate Equilibrium Conditions

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1. Introduction

Upward gas migration due to buoyancy forces and immiscible fluid displacement inside a porous medium are two important processes occurring naturally in the subsurface (Chanton et al., [1]), as well as during anthropogenic applications (e.g., during enhanced oil recovery or soil remediation; Blunt and Christie [2]).

Under appropriate conditions of pressure, temperature and salinity the migrating gas phase can form solid hydrates inside the water-saturated porous medium. Conditions that favour hydrate formation include high pressures and low temperatures and salinities. Hydrates are crystalline, ice-like, non-stoichiometric compounds formed by the self-assembly of hydrogen-bonded, water molecules into cages that are stabilized (through van der Waals forces) by the presence of guest molecules (e.g., CH_4, CO_2, N_2, etc.) with appropriate size to fit within the cages [3].

Of significant interest is the case of methane migration in the subsurface, and the possible formation of methane hydrate. Oceanic or permafrost, naturally-occurring, methane hydrates are important because they are considered a possible future source of methane for energy uses (Collett, [4]), and a possible environmental threat (due to sudden release in the atmosphere of methane which is a strong "green-house" gas; Giavarini and Hester, [5]).

2. Results and Discussion

In this study we perform a series of mass-balance-type calculations, in order to estimate the minimum volume of liquid water required to dissolve completely a single methane-gas bubble, located inside different types of domains that are near hydrate equilibrium pressure/temperature conditions. We examine the case of methane bubble dissolution in the bulk, along with the cases of methane bubble dissolution within simple networks of pores, where all pores have the same size. In our calculations we consider experimental values for the equilibrium solubilities of methane in water, near hydrate forming conditions, as well as, values obtained from predictive tools that are based on different thermodynamic models. The effect of aqueous NaCl solutions on the results is also investigated. As a result of the relatively low solubility of methane in water, large volumes of water are required for complete dissolution of a methane bubble.

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Wettability study of natural roughness using molecular dynamics

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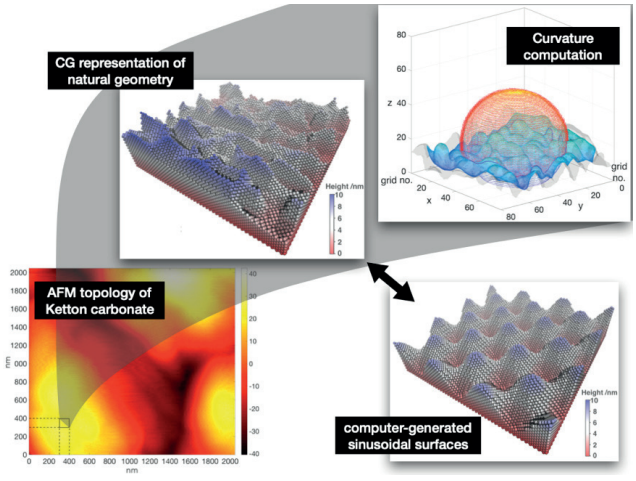
A new approach is presented to study the wetting of a model surface rendered with natural roughness at the nanoscale. Using atomic force microscopy (AFM) with a resolution of 0.943 nm, the surface topology of a Ketton carbonate was measured, and based on which a model surface is computationally constructed with the aid of coarse-grained (CG) beads. This surface, along with a model flat surface and seven other sinusoidal surfaces of various wavelengths are put in contact respectively with a model fluid, n-decane, which is also represented by CG beads. The CG fluid parameters that can be used directly in molecular modelling are obtained by employing a top-down approach, where an accurate equation of state - SAFT-VR Mie is fitted over a wide range of macroscopic thermodynamic properties [1] [2]. We perform canonical (NVT) molecular dynamics (MD) simulations of drops of fluid on top of these model surfaces. A least-squares sphere fitting method is implemented to identify the fluid/solid contact lines and compute the fluid curvatures on the different surfaces [3].



We carried out a sensitivity analysis to understand how the computed curvature changes with respect to the droplet size. While the nano-scale contact angle differs from the macroscopically-observed one, we see that it is possible to reach the ultimate size limit with current computational resources when using roughly over 5000 fluid molecules. The local molecular rugosity the surface has only a small effect on the average measurable contact angle, hence surrogate models may be useful in describing microscopical effects.

$A = -kT \ln Q$

This work provides a strategy for converting the topography of a natural surface measured from AFM experiments into a synthetic surface, thereby allowing the effective wettability to be assessed at the nanoscale. Results shown that the fluid droplet curvature over a structured sinusoidal surface of 4 nm amplitude and nm wavelength resembles that of a surface with natural geometry. Future work involves placing this synthetic surface in contact with various model synthetic crude oil and comparing with experimental data.

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Surface free energy analysis of biomass activated carbons determined by immersion calorimetry

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Carbons materials have many technical and industrial applications in different fields such as adsorption (at the gas-solid and liquid-solid interphases), wettability, catalysis and adhesion, due not only to their high surface area, thermal stability and hydrophobicity, but also to their surface free energy (SFE), because all these applications are related, in one way or another, to different kinds of interactions with the carbon surface. Therefore, the SFE, which describes the interaction potential of a solid, has a crucial effect on the behavior and final performance of the carbon materials and its knowledge has allowed significant progress in all their applications [1]. Then, a complete characterization of carbon materials should include the determination of the SFE and its components [2].

The SFE is the result of unbalanced molecular forces at the surface of the solid, and it can be considered to be formed by the contribution of two different components, a dispersive component, corresponding to results from Lifshitz-van der Waals forces, and a non-dispersive (or polar) component describing all the other types of interactions (such as acid-base, electrostatic ones, etc.) [3].

The dispersive or Lifshitz-van der Waals component depends on the heterogeneity and defects present at the surface of the solid, and it is the component responsibles of the behavior of nonpolar adsorbent, such as carbon materials. Meanwhile, the non-dispersive component has its origin on surface interactions of polar nature and, hence, it is related to the presence the heteroatoms (oxygen, nitrogen, sulfur...) on the surface.

Immersion calorimetry technique provides a relatively simple method for the determination of the components of the surface free energy of a solid and, therefore, it is employed quite often for this purpose. Immersion measurements in liquids with different polarity (water, benzene, formamide, n-dodecane, etc.) allow one to evaluate the surface free energy of a given solid and its components.

So, the purpose of this work has been to evaluate the SFE and its components of different activated carbons (obtained from almond shell biomass using different design conditions), from the results obtained calorimetrically from the immersion in liquids of different polarity.

Acknowledgments

The authors are grateful to MINECO and the Junta de Extremadura, for financial help by projects CTM2016-75937-R and IB16108, respectively, and also to the programme "Ayudas a Grupos de la Junta de Extremadura-Fondos FEDER.

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Nucleation of pseudo-hard spheres and dumbbells at moderate metastabilities: appearance of A15 Frank-Kasper phase at intermediate elongations

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In this contribution we present results of crystal nucleation of repulsive hard-dumbbells from the sphere to the two tangent spheres limit at moderately high metastabilities obtained by brute-force molecular dynamics simulations. Nucleation rates are in good agreement with previous simulations of hard-spheres [1] and dumbbells [2]. Icosahedral structures formed by twinned face-centred-cubic tetrahedral sharing five-fold symmetry axes and icosahedral centers are often found in spheres and dumbbells with either small (L/σ =0.1 and 0.2) and large (L/σ=1) elongations. These structures are incompatible with long range crystalline order but are able to survive up to quite large sizes. On the contrary, at intermediate elongations (L/σ =0.3), corresponding roughly to the bond length of molecular nitrogen, the fluid crystallizes into three distinct solid structures, namely, a low density plastic crystal, a hexagonal close-packed plastic crystal (with the same structure as β-N_2), and an A15 Frank-Kasper phase (cP8 structure corresponding to δ-N_2). At the lower pressures studied the hexagonal close packed plastic crystal is the most stable phase, but at the higher pressures the stable phase is an orientationally ordered solid designated as CP1 that is never spontaneously formed in our crystallization simulations [3].

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$A = -kT \ln Q$

Modelling aqueous dissolution of sodium chloride in clays at thermodynamic conditions of hydraulic fracturing by molecular dynamics simulations

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To address a high salinity of flow-back water during hydraulic fracturing we use molecular dynamics simulations and study the dissolution of a cubic NaCl nanocrystal immersed in aqueous NaCl solutions of varying concentration, confined in clay pores of the width comparable to the crystal size. We consider a typical shale gas reservoir condition of 365 K and 275 bar, and we represent the clay pores as pyrophyllite and Na-montmorillonite (MMT) slits. We employ the Joung-Cheatham model for ions and SPC/E model for water [1], and CLAYFF [2] for the MMTs. The pressure is applied along the normal direction and slit width varies from about 23 to 28 Å when the salt concentration increased from zero to a high concentration. By varying salt concentrations, we observe two scenarios. First, the crystal dissolves and its dissolution time increases with increasing the salt concentration. We describe the dissolution process in terms of number of ions in the crystal and the crystal shape. After the crystal dissolution, we characterise an equilibrium confined system of water molecules and dissolved ions by evaluating the structure, orientation and in-plane diffusion of water and ions, along with ion conductivities. Second, when the salt concentrations reach a saturation threshold the crystal growths and attains a new equilibrium size. The crystal becomes in equilibrium with the surrounding saturated solution [3].

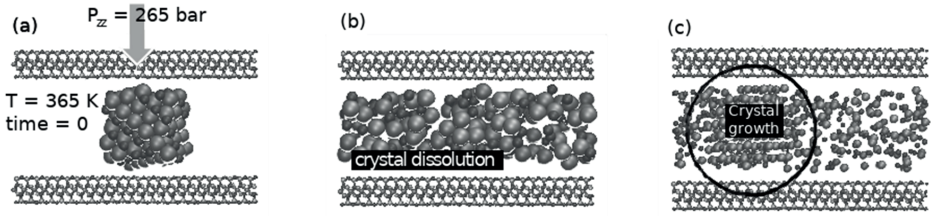

Fig. 1: *(a) NaCl nanocrystal immersed in aqueous NaCl solution (only nanocrystal shown), (b) crystal dissolution, (c) crystal growth.*

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Phase equilibria and interfacial properties of tetrahydrofuran + methane vapor-liquid binary mixture from experiments, simulation and theory

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Tetrahydrofuran, or simply THF, is one of the most known and used thermodynamic hydrate promoters (THP) since many years. In particular, THF is able to reduce the equilibrium pressure dramatically and it makes it possible to treat gas hydrates under mild pressure conditions [1-4].

This study is a continuation of a set of previous works about the study of molecular models of THF and his binary mixture and should be consider as a preliminary study to predict the phase equilibria of THF hydrates and hydrates of mixtures of THF with methane using molecular dynamics simulation [5] and the SAFT-VR formalism [6]. In addition to that, experimental measurements are also made in order to validate our simulation results and theoretical predictions. In this work, we have used an approximate rigid and planar THF model [7]. This model has been studied in previous works with excellent results [8]. CH_4 has been modeled as a spherical single interaction site [9].

We have determined the phase equilibria and interfacial properties of the THF + CH_4 binary mixture from direct coexistence simulations of the vapour-liquid interface at 300 and 370 K and several pressures. The simulations have been performed in the Molecular Dynamics (MD) *NVT* canonical ensemble. We have obtained the density profiles, pressure-density and pressure-composition phase equilibria diagram and interfacial tensions. The interfacial properties, and particularly, the interfacial tension are extremely sensitive to molecular models details of the system, so the interfacial tension can be used to check the accuracy of the molecular models to predict the interfacial properties.

The vapour-liquid interfacial tension is evaluated from the normal and tangential components of the pressure tensor according to the mechanical virial route. In addition, we have also obtained the experimental pressure-density diagram and the experimental interfacial tension. We have also used the equation of state SAFT-VR to obtained the pressure-density and pressure-composition diagram. The simulation results have predicted accurately the vapour-liquid phase equilibria of the system, in good agreement with theoretical predictions and experimental results. Predictions for interfacial tension obtained from simulation also have been compared with experimental results, being this agreement excellent in all cases (Fig. 1).

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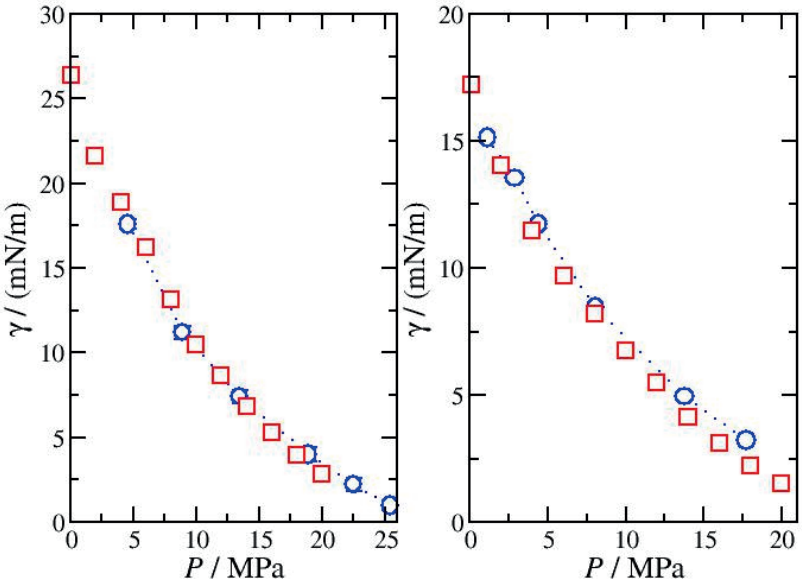

Figure 1: Interfacial tension of the THF + CH_4 binary mixture at 300 (right) and 370 K (left) as a function of pressure. Red empty squares correspond with experimental measures and blue empty circles with MD-NVT simulation results. The doted curves are included as a guide to the eye.

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Determination of the free energy adsorption in solid-liquid systems

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The understanding of adsorption phenomena at the solid-liquid interphase requires the evaluation of the free energy of adsorption due to the different kinds of forces acting across the interface. The adsorption of an adsorbate on a solid adsorbent is established by the interactions between both phases through the solvent, which is the third phase involved in the process. The intensity of such interaction, and, as a consequence, the adsorption behavior of the systems is reflected by the experimental adsorption isotherms, and if some the theoretical model is assumed, the free energy of adsorption can be predicted. On the other hand, it is also possible to evaluate this magnitude from the knowledge of the surface tensions and its components of each the phases interacting in the process.

The model of Van Oss permits evaluates the interfacial free energy of two phases immersed in a third one, from the components of the surface tension of the interacting phases [1]. The model assumes that the interfacial free energy of adsorption depends only on two contributions: Lifshitz-van der Walls and acid-base interactions.

There is an important number of papers dealing with the adsorption of non-ionic surfactants on activated carbons (ACs). However, there is a lack of studies relating the adsorption process on a solid surface from aqueous solutions and the molecular interactions between the adsorbent, adsorbate, and the solvent.

In this paper, we have analyzed, in light of the molecular interactions, the predictions obtained from the equilibrium adsorption isotherms from aqueous solutions of a well-known non-ionic surfactant on different biomass activated carbons obtained from almond shell.

Acknowledgments

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$A = -kT \ln Q$

Thermodynamic properties of collections of identical, classical particles confined to a single dimension with zero curvature: Lennard-Jones and harmonic interactions

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We consider the thermodynamic properties of finite-sized systems of identical, classical particles existing and interacting in a single spatial dimension having zero curvature, and in the absence of any external potential. In the first system, the particles interact according to the Lennard-Jones 12-6 potential, with no cut-off length for the interaction. In the second system, the particles interact according to the harmonic oscillator potential, and interactions occur only between nearest neighbours. Such models may serve as reference states for more detailed analysis of quasi-one-dimensional materials in higher-dimensional spaces.

The statistical and thermodynamic properties of general one-dimensional and nearly one-dimensional systems were considered in detail by numerous authors in the mid-20th century[1-9]. We begin from one such set of general solutions, published by John A. Barker[7], and proceed to derive specific solutions, in the form of integral equations, for the Gibbs energy, density, entropy, heat capacity, and compressibility of our two model systems. We also present estimates of these properties obtained from Monte Carlo simulation. We compare the results obtained via the two methods, which are in good agreement except at low temperature.

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Fluid-solid direct coexistence simulations to determine a binary phase diagram

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In this study, we use fluid-solid direct coexistence simulations to determine the phase diagram of a binary pseudo-hard sphere (PHS) mixture with a diameter ratio of 0.85 between the smaller and larger PHS. We are using PHS [1] instead of the hard sphere model in order to be able to carry out the simulations using molecular dynamics with GROMACS simulation package.

The growth of the crystal is monitored by determining the number of particles belonging to the solid at the simulation. For this we used the averaged local bond order parameters presented by Lechner *et al.* [2].

A similar phase diagram has been calculated by Frenkel *et al.* [3] and Ganagalla *et al.* [4], although they used Monte Carlo simulations and a hard sphere model. At low pressures the system is fluid, and at high pressures it is a fcc solid. Moreover this system exhibits a eutectic point and a miscibility gap, a region where two solids coexist.

Finally, our aim is to compare our results with the ones of the literature. This way we are learning how to obtain a phase diagram of binary mixtures by fluid-solid direct coexistence simulations, and checking the agreement with free energy calculations.

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$A = -kT \ln Q$

The role of inert gases on the surface properties of ice

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Inert gases such as nitrogen and oxygen are major components of the atmosphere, but their role in the study of water surface properties is assumed to be negligible. Indeed, from Henry's constant data, it is expected that the concentration of nitrogen in water at 0~C and one bar is not more than 10^{-3} mol/L, and likely far smaller in ice. Furthermore, adsorption studies of nitrogen on ice consistently yield small BET adsorption energies which are only 2.5 kJ/mol at 77 K. [1]
Intringuinly, laboratory studies of surface structure and crystal growth rates have recurrently reported significant differences between experiments performed on either a controlled nitrogen or pure water vapour atmosphere.[2-5] Particularly, crystal growth experiments report that the surface saturation corrected growth rates are strongly influenced by nitrogen,[2,3,5] decreasing the surface kinetics selectively on the prismatic facet by factors as large as 1/100 at T= -11 C, and 1/20 at T= -15 C, compared to experiments in pure water vapor.[2,3] In this study, we perform computer simulations in order to investigate the role of inert gases on the properties of the ice surface. Our results provide layer thickness and adsorption isotherms as a function of ambient pressure, and allow us to calculate the contribution of inert atmospheric gases on the surface tension of ice.

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Structure of the ice surface close to the triple point.

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At low saturation, ice mono-crystals in the atmosphere adopt simple prismatic shape. Intriguinly, the aspect ratio of these prisms changes with temperature. Close to 0~C, they appear as plates, then change into columns at -10~C, and back to plates at about -20 C. [1] These habit transitions reveal a crossover in the growth rate of basal and prismatic facets. However, the origin of the crossover is as yet completely unknown. Likely candidates for an abrupt change in the relative growth rates are surface phase transitions, but the characterization of the ice surface has not attained a degree of detail sufficient to identify or locate clearly any sharp phase transition. [2] In this paper we pursue our studies of a novel methodology employed for the study the structure of the ice/vapor interface in the neighborhood of the triple point,[3-4] where a premelting quasi-liquid layer of ice is found. Particularly, we probe the fluctuations of the ice/film and film/vapor surfaces that separate the liquid film from the coexisting bulk phases at basal and primary prismatic planes. This provides a wealth of information, such as step free energies, and allows us to determine whether these facets are smooth or rough, as well as to investigate the likelihood of a roughening transition. We discuss the results in the context of the Nakaya diagram of ice crystal habits in the atmosphere.

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$A = -kT \ln Q$

Water - perfluoroalkyl alkanes interactions: solubility and liquid-liquid interfaces

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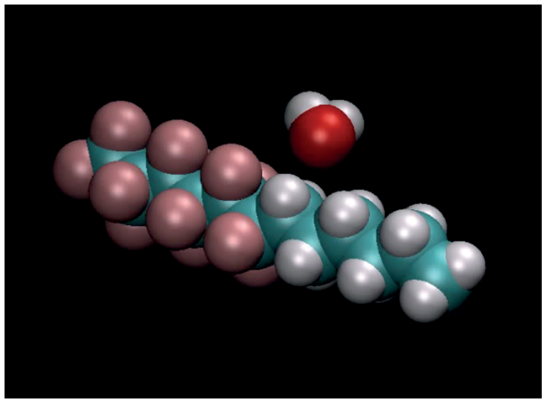
Perfluorinated chains are known to display an enhanced hydrophobicity, relatively to their hydrogenated analogues. In spite of its technological importance, namely in material sciences, the explanation of the effect at the molecular level is far from being fully understood. Semifluorinated alkanes, which are molecules that possess the two types of segments, have been recently found to display anomalous water solubility and liquid-liquid interfacial tensions.

In this work, atomistic Molecular Dynamics simulations was used to study the interaction between water, perfluoroalkanes and perfluoroalkyalkanes. The thermophysical properties of a number of mixtures of water, perfluoroalkanes and perfluoroalkyalkanes, in particular water solubility, was investigated. Simultaneously, the SAFT-gamma-mie Equation of State was used to model the same systems. The specific interaction between water and perfluoroalkyalkanes surfactants was addressed.

Finally, the water - semifluorinated alkanes liquid-liquid interface was simulated. The interfacial tensions of a number of mixtures of water and semifluorinated alkanes were computed and compared with original experimental data.



Figure– Specific interaction between water and the dipole of perfluorohexylhexane (F6H6).

Surface tension of fluorinated alcohols and their mixtures with hydrogenated alcohols: experimental, soft-SAFT-DGT modeling and MD simulations

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The ability of fluorinated liquids to dissolve large quantities of respiratory gases, allied to their biocompatibility and chemical inertness and has triggered their potential use in biomedical and therapeutic applications such as perfluorocarbons-in-water emulsions for in vivo oxygen delivery (blood substitutes) and reverse water-in-PFC emulsions for pulmonary drug delivery in liquid ventilation.

The use of these micro-heterogeneous systems in biomedical applications implies being able to control, thus understand, the stability of the emulsions. The knowledge of the surface and interfacial tension in presence of effective co-surfactants is obviously of utmost importance to control the stability and performance of both water-in-FC and in FC-in-water emulsions.

This work focuses on the study of interfacial properties of co-surfactants used to stabilize PFC/water emulsions. The interfacial properties of fluorinated alcohols and their mixtures with the corresponding hydrogenated alcohols have been investigated.

The surface tension of the pure fluorinated alcohols was measured as a function of temperature and the soft-SAFT equation of state, coupled with a density gradient approach was used to model the corresponding interfaces.

The surface tension of the mixtures was also measured as a function of composition at 293.15K. Interestingly, all mixtures display aneotropes, i.e., minima in the surface tension vs composition curve, which is a very unusual behaviour. Within a range of compositions, the surface tension of the mixture is lower than that corresponding to the surface being completely covered by the component with the lower surface tension. soft-SAFT-DGT calculations were also performed to model and interpret the complex interfacial behaviour of such mixtures.

Finally, molecular dynamics simulations of the interface were carried to investigate the detailed orientation and distribution of molecules at the interface.

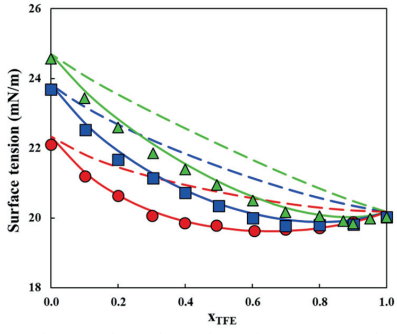

Figure. Surface tension of Trifluoroethanol + ethanol, 1-propanol and 1-butanol, experimental and soft-SAFT-DGT predictions.

$A = -kT \ln Q$

Prediction of densities and interfacial tensions for acid methyl esters (from methyl formate to methyl heptanoate)+water binary mixtures by molecular simulations

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FAMEs (Fatty Acids Methyl Esters) are very interesting for being used as biodiesel, an alternative to fossil fuels [1]. Besides, these compounds can be used for removing contaminants from water. For these reasons, knowledge about the behavior of binary mixtures of FAMEs and water is important.

In this work, we have studied the liquid-liquid phase equilibria and interfacial properties of a family of methyl esters (from methyl acetate to methyl heptanoate) and water, using molecular dynamic simulations (MD) [2] in the isobaric-isothermic ensemble (NPzT) with the direct coexistence technique. Methyl esters are composed by a methyl ester group and an alkyl-chain, whose length varies in the family of molecules. The methyl esters have been modeled using TraPPE-UA (Transferable Potentials for Phase Equilibria-United Atoms). The parameterization for the chemical groups and torsional and bending potential have been taken from the works of Kamath *et al.* [3,4] for the methyl ester group and from the work of Chen *et al.* [5] for the alkyl-chain.

The work is focused in the study of liquid-liquid phase equilibria for the mixtures of different methyl esters with water at 1.013MPa of pressure and several temperatures (from 278.15 to 358.15K). We have obtained the density profiles, temperature-density phase diagram, molar fractions and interfacial tensions. Our simulation results have been compared with experimental data taken from literature [6].

The agreement between simulation results and experimental data is good for density in the whole range of conditions studied. The simulation results give a good prediction for molar fractions in aqueous phase for all methyl esters, except for methyl acetate, whose molar fraction is underestimated. Results for molar fractions in organic phase are underestimated. Interfacial tensions obtained are overestimated in the whole range of conditions studied. It is important to notice that interfacial properties are very sensitive to molecular model details, so these models give good predictions for densities but not for other interfacial properties.

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Interfacial properties of acid methyl esters (from methyl acetate to methyl heptanoate) by molecular simulations

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Fatty Acids Methyl Esters (FAMEs) have become very important in last years due to their use as biodiesel, this is third or fourth generation of biofuels [1]. FAMEs are produced by transesterification process between mono-alkyl esters and methanol [2]. FAMEs are good substitutes for petroleum-based fuels.

In this work, we have studied the vapor-liquid phase equilibria and interfacial properties of a family of methyl esters (from methyl acetate to methyl heptanoate) using molecular dynamic simulations (MD) [3] in the canonical ensemble (NVT) with the direct coexistence technique. Methyl esters are formed by a methyl ester group and a variable length alkyl-chain. The methyl esters have been modeled using TraPPE-UA (Transferable Potentials for Phase Equilibria-United Atoms). The parameterization of the different chemical group and torsional and bending potential have been taken from the works of Kamath *et al.* [4,5] for the methyl ester group and from the work of Chen *et al.* [6] for the alkyl-chain.

We have focused on the study of the vapor-liquid phase equilibria of the different methyl esters systems at several temperatures (from 300 to 550 K). We have obtained the density profiles, temperature-density and pressure-temperature phase diagrams and interfacial tensions. We have also obtained the critical pressure, temperature and density from the vapour-liquid equilibrium results using the scaling laws [7,8] and the corresponding law of rectilinear diameters. We also compare our MD simulation results with experimental data base taken from literature.

The agreement between simulation results and experimental data are excellent for all the systems and in the whole range of conditions studied. It is important to remark, that the interfacial properties, and especially, interfacial tension are extremely sensitive to molecular models details and this models are able to predict the interfacial behavior of the system. This work can be consider as a previous study to determinate the interfacial properties and phase equilibria of the methyl esters + water binary mixtures.

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$A = -kT \ln Q$



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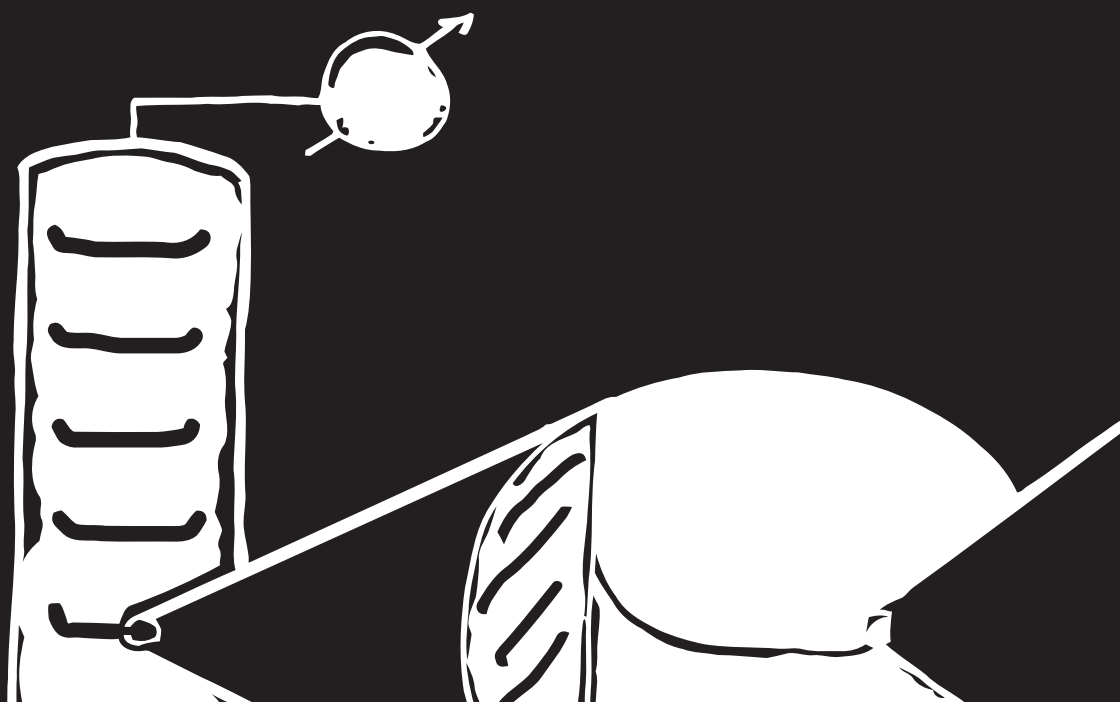
Poster Presentations: Carbon capture and other industrial applications



Tuning the surface properties of biomass adsorbents to optimize their performance towards gaseous radioactive effluents

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Tuning the porosity of activated carbons (ACs) in order to configure specific surface and pore size distribution to satisfy a particular demands is essential to optimize the performance of filtering AC systems. By physical activation, this can be done by selecting appropriate gasifying agents (water steam, carbon dioxide, air…) and experimental conditions (temperature, time, presence of catalysts…). Besides, the adsorbent surface chemistry is also a determining factor since it will enhance the affinity and/or selectivity of the AC towards the adsorbate.

One application in which the surface functionalities of the adsorbent play a very important role is the use of AC as radioactive methyl iodide adsorbent under high humidity conditions. In this case, the use of impregnants as triethylenediamine (TEDA) can provide a better and more stable retention efficiency owing to the reaction TEDA-CH_3I^{131}, to for quaternary ammonium salts. However, the way in which the impregnant is diffused on the carbon matrix (by sublimation subsequent to the activation process) can yield to different adsorption results because steric hindrance effects.

Previous pieces of research have suggested that the study of the surface free energy of a carbon can give important information regarding the dispersive and non-dispersive forces of the material which, at the same time, will influence the way in which the adsorbate is placed on the carbon. In this work a surface free energy analysis was made on ACs and the results obtained were correlated to the impregnant deposition at the carbon interface. This was also related to the adsorption performance of the materials and it was found that the way in which the impregnant is placed on the surface affects the AC adsorption capacity.

Acknowledgements

The authors are grateful to MINECO and the Junta de Extremadura, for finantial help by projects CTM2016-75937-R and IB16108, respectively, and also to the programme "Ayudas a grupos de la Junta de Extremadura-Fondos FEDER".

$A = -kT \ln Q$

Thermodynamic Study on Ionic Liquid-Water as Alternative Working Pairs for Absorption Refrigeration Cycle

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Absorption refrigeration can utilize low-grade thermal energy such as waste heat and solar energy, and the equipment is simple and easy to operate. But the traditional working pair water-LiBr presents crystallization and corrosion.

For some ionic liquids, the hydrophilic, small heat capacity, ignorable vapor pressure, high chemical and thermal stability make their aqueous solutions have potentials to work as new working pairs for absorption refrigeration cycles.

In this work, thermodynamic modeling with the electrolyte Cubic Plus Association Equation of State have been done for saturated pressure, activity coefficient coefficients, and excess enthalpy of ionic liquid-water binary systems. Single stage absorption refrigeration cycle is also calculated with these binary systems. The thermodynamic performance of these potential working pairs has also been evaluated.

The results show that e-CPA can predict vapor liquid equilibrium of these ionic liquid-water binary systems well, and the cycle calculations show that some binary systems have potentials to work as alternative working pairs.

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Effect of water on the CO_2 adsorption capacity of polyamine/graphene oxide adsorbents

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Solid adsorbents have the potential to mitigate the excessive amounts of thermal energy which are consumed in the conventional CO_2 capture processes with solvents, in order to heat and evaporate huge amounts of water. Herein, graphene oxide (GO) based adsorbents were functionalised with Poly(propyleneimine) Dendrimers (DAB) and hyperbranched poly(ethyleneimines) (PEI) with the targets to enhance the CO_2 capture capacity and limit the amounts of co-adsorbed water. This work makes an attempt to investigate key performance indicators (KPIs) of the adsorbents and propose the next steps for their improvement. These investigations pertain to the effect of water vapour on the CO_2 adsorption capacity and kinetics, as well as to the effective control of adsorbent's hydrophilicity to avoid excess energy consumption for evaporating large amounts of adsorbed water during regeneration. One of the conclusions of the current work is the absence of any correlation between the CO_2 adsorption capacity and the MW of the polyamines (Figure 7). This can be attributed to the interplay between three competing and complementary elements namely; i) low-MW polyamines lead to the formation of 3D structured, PEI and DAB intercalated adsorbents, hosting interlayer channels that contribute significantly to the CO_2 adsorption capacity, ii) the high MW of the polymers means high number of amine groups available for CO_2 capture and iii) the use of high-MW polyamines does not necessarily results to high population of amine functional groups on the GO's surface since the surface electrophilic groups on GO (-epoxy groups) might be shielded by the neighboring bulky polymer chains leading to moderate polymer loading and stabilization on the GO's surface.

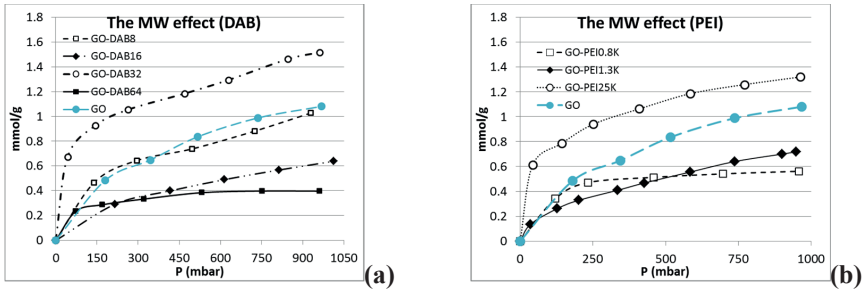

Figure 7: CO_2 adsorption isotherms at 36°C on (a) DAB functionalised adsorbents. (b) PEI functionalised adsorbents.

These competing attributes concluded to an optimum MW for enhanced CO_2 adsorption. This was the DAB32 for the Poly(propyleneimine) Dendrimers and the PEI25K for the hyperbranched poly(ethyleneimines). It is characteristic that the grafting of these specific polyamines on the surface of GO has led to enhanced rather than suppressed CO_2 adsorptivity as compared to that

$A = -kT \ln Q$

of pristine GO (Figure 7). In all other cases the CO_2 adsorption capacity was lower compared to that of GO. Applied in a CO_2 capture process, amine functionalized adsorbents gain substantial benefits when the gaseous stream is wet. This is attributed to the capacity of water, as free-base, to facilitate the formation of bicarbonates in addition to carbamates. Moreover, the co-adsorbed water, even at relative humidity (RH) as low as 0.4%, prohibits the undesired formation of urea type linkage with CO_2 during thermal regeneration, thus enhancing the adsorbents' stability [1]. A distinguishing feature between the various adsorbents developed in this work is that low relative humidity (<10% RH) affects negatively the CO_2 adsorption capacity of the low-MW polyamine modified adsorbents, while the CO_2 adsorption capacity of adsorbents modified with the high-MW polyamines remains unaffected. A second differentiation is that the presence of 36% RH concludes to a two-fold increase in the CO_2 adsorptivity of the GO-PEI25K and a one-fold increase in the case of GO-DAB32, (see Figure 8). This difference is attributed to the different types and number of amine groups included in the molecular structure of each polymer. PEI25K hosts primary, secondary and tertiary amine groups at a higher number per mass as compared to DAB32. Moreover due to the linear shape of the polymer, most of the amine groups are accessible by water and CO_2 and therefore water has a more intense contribution in the CO_2 adsorption capacity.

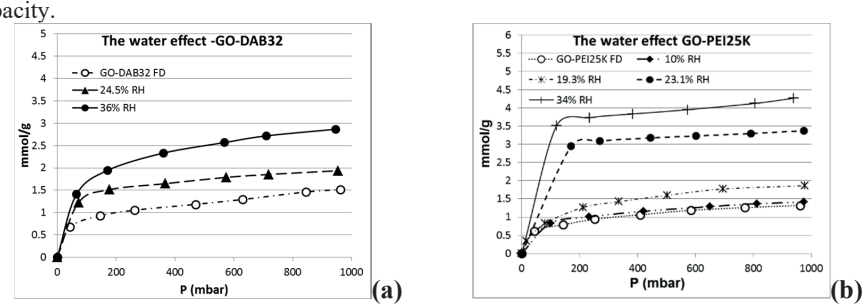

Figure 8: Effect of water on the CO_2 adsorption capacity of: (a) DAB32, (b) PEI25K.

Wet gaseous streams are also beneficial for the kinetics of adsorption which became 2-3 orders of magnitude faster in the presence of water as compared to a dry stream. Though, the water content of the industrial stream is highly beneficial for the CO_2 adsorption capacity and kinetics, the high amount of co-adsorbed water may have adverse effects on the energy efficiency for regeneration (large amount of water to evaporate). The DAB32 functionalised material adsorbed 6.35 mmol/g of H_2O at 36% RH while the respective amount of CO_2 at 200 mbar of partial CO_2 pressure was 2 mmol/g. The GO-PEI25K adsorbent was closer to the target of a lower adsorptivity for water as compared to CO_2, adsorbing 4.2 mmol/g of H_2O at 36% RH while the respective amount of CO_2 at 200 mbar of partial CO_2 pressure was 3.7mmol/g. In this context, we have proceeded with the application of a simple post-reduction procedure on both PEI25K and DAB-32 functionalised GO, using sodium borohydride and the results showed significant attenuation of the H_2O/CO_2 molar ratio, from 3.1 to 0.78 for DAB 32 and from 1.14 to 0.88 for PEI25K without any significant effect on the CO_2 adsorption capacity.

Acknowledgement
"We acknowledge support of this work by the project MIS 5002567, implemented under the "Action for the Strategic Development on the Research and Technological Sector", funded by the Operational Programme "Competitiveness, Entrepreneurship and Innovation" (NSRF 2014-2020) and co-financed by Greece and the European Union (European Regional Development Fund)."

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Experimental Measurements and Molecular Simulations of Density, Derivative Properties, and Viscosity of n-Hexane + n-Dodecane Binary Mixtures

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Asymmetric mixtures of hydrocarbons are widely present in many oil and gas processes. Consequently, the thermophysical characterization of those asymmetric mixtures is of primary importance in order to optimize oil production and processing. Thus, we designed a set of experimental measurements and molecular simulations of thermophysical properties such as the density, the isothermal compressibility, the thermal expansion, the heat capacity, the sound speed, and the viscosity on model asymmetric mixtures to test existing and new models on well controlled systems. In a first step, we have investigated quasi-ideal binary mixtures of n-hexane + n-dodecane. Experimental measurements were performed on six sample mixtures ranging from 0 to 100 % of n-hexane, at temperatures from 293.15 to 333.15 K and pressure up to 100 MPa. In parallel, we have evaluated the performance of molecular simulation techniques including Monte Carlo (MC) and Molecular Dynamics (MD) to predict the aforementioned thermophysical properties of the studied mixtures. Two different force fields were evaluated. An in-house coarse grained model based on the Mie chain fluid [1] and a widely employed fine grained model, the Transferable Potential for Phase Equilibria united atom force field [2]. The main outcome is that the two force fields are robust enough to enable a reasonable prediction of volumetric derivative properties for pure components and their mixtures with a good accuracy, although they were calibrated only on first order thermodynamic properties of pure fluids. In addition, we found that, the use of a viscosity data in the parametrization of the Mie chain coarse grained force field model makes it more reliable for transport property prediction than the TraPPE-ua force field.

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$A = -kT \ln Q$

Improving Olefin Purification Using Metal Organic Frameworks with Open Metal Sites

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The separation and purification of light hydrocarbons is challenging in the industry. Recently, a ZJNU-30 metal−organic framework (MOF) has been found to have the potential for adsorption-based separation of olefins and diolefins with four carbon atoms [1]. Our computational study corroborates this finding rationalizing the adsorption behavior in terms of the atomic connectivity (Figure 1), but Fe-MOF-74 is found a more efficient candidate for the separation (Figure 2). As shown in Figure 3, molecular simulations and DFT calculations evidence this high interaction for the diolefin with the open metal site atom of Fe-MOF-74. Using this MOF, we propose in Figure 4 a separation scheme to obtain a high-purity product.

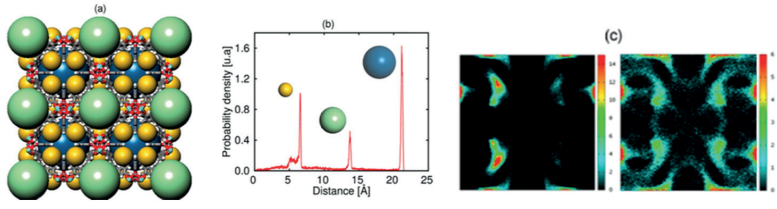

Figure 1. (a) Schematic representation of the atomic connectivity of ZJNU-30. Carbon atoms in gray, oxygen atoms in red, hydrogen atoms in white, and zirconium atoms in turquoise. The spheres represent the pore cages. (b) PSD of ZJNU-30. (c) Average occupation profiles for ZJNU-30 from MD simulations using one molecule of 1,3-butadiene (left: initial position in small cages, right: initial position in large or medium cages).

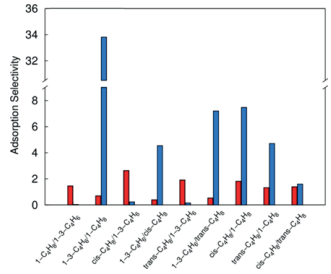

Figure 2. Adsorption selectivity for 2-cis-butene/1,3-butadiene, 1,3- butadiene/2-cis-butene, 2-trans-butene/1,3-butadiene, 1,3-butadiene/ 2-trans-butene, 2-cis-butene/1-butene, 2-trans-butene/1-butene, and 2- cis-butene/2-

trans-butene calculated from the a adsorption isotherms of equimolar quaternary mixtures in ZJNU-30 and Fe-MOF-74 at 298 K and 10 kPa via Grand-Canonical Monte Carlo simulations.

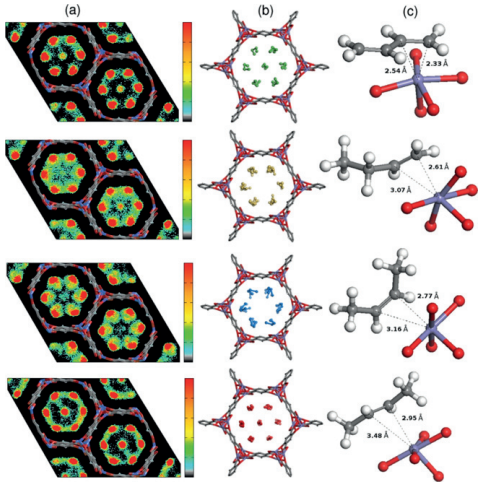

Figure 3. (a) Average occupation profiles (b) and equilibrium positions from classical minimizations at saturation conditions and (c) equilibrium distances between C_{sp}^2 and the metal center of the structure from DFT calculations. From top to bottom: 1,3-butadiene, 1-butene, 2-cis-butene, and 2-trans-butene in Fe-MOF-74.

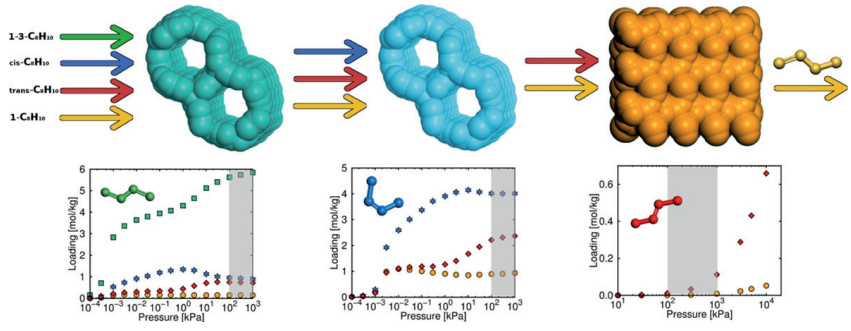

Figure 4. Proposed adsorptive-based separation process of 1-butene from the C4 alkene mixture. Multicomponent adsorption isotherms in Fe-MOF- 74 (a,b) and RRO zeolite (c) at 298 K. 2-cis-Butene (blue), 2-trans-butene (red), 1-butene (yellow), and 1-3-butadie (green).

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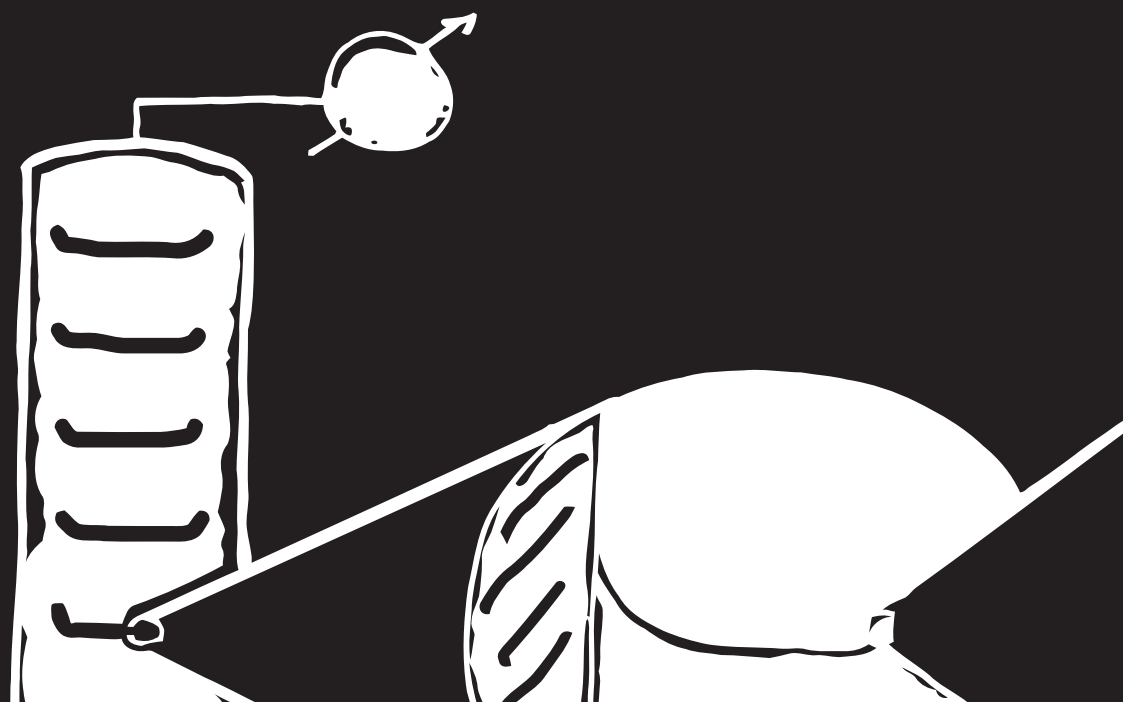
Poster Presentations:
Engineered self-assembly



Coarse-Grained Molecular Dynamics Study of the Self-Assembly of Triblock Bolaamphiphiles with SAFT-γ Mie CG Forcefield

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T-shaped triblock bolaamphiphiles (TBAs) constitute a family of thermotropic liquid crystals that exhibit a plethora of columnar and network phases. Complex two-dimensional tiling patterns have been observed both in experiments [1] and simulations [2-6]. Given the length-scales of these complex patterns and long equilibration times required to observe self-assembly, previous simulation studies have relied on model systems to phenomenologically investigate the mesophase behaviour of this family of liquid crystals.

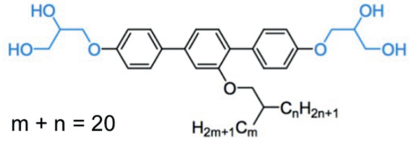


Figure 1: Swallow-tail triblock bolaamphiphiles studied in this work

The main objective of this work is to develop thermodynamically accurate coarse-grained models of TBAs using the SAFT-γ Mie CG forcefield [7] in order to have an accurate *in silico* representation of the aforementioned molecules. For each functional group, namely the phenyl backbone, glycerol end groups and the flexible alkyl side chains, a top down approach is used to fit Mie potential parameters to experimental data using SAFT-γ Mie equation of state (EoS). Subsequently, molecular dynamics simulations using the model developed are carried out to predict the mesophase behaviour of recently investigated swallow-tail TBAs.

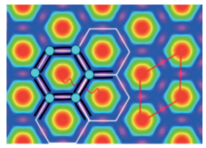
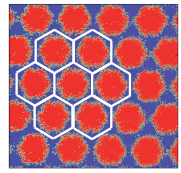
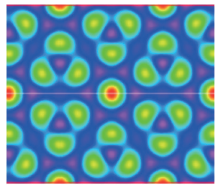
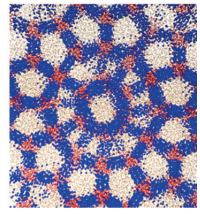
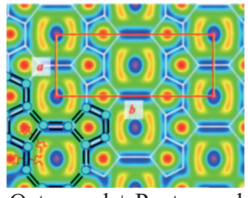
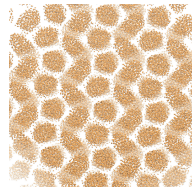
Poppe et al. [8] have observed some of the most complex tiling patterns of TBAs (Table 1), by changing the structure of the lateral side chains from a single chain of 20 carbons to a swallow-tail (Figure 1) whilst conserving the total number of carbons. Given the susceptibility of these molecules to changes in phase behaviour with the slightest changes in the morphology of the lateral side-chains, swallow-tail TBAs are used as ideal candidates to assess the predictability of the proposed potential parameters in accurate modelling of these liquid crystals.

A comparison between the experimental results and simulations is presented in Table 1, with our proposed model correctly predicting the morphology of the honeycomb and the pentagonal-hexagonal columnar phases. Moreover, inter-column distances and columnar-isotropic transition temperatures are calculated for every system. For the hexagonal columnar phase, an inter-column distance of 4.2 nm is correctly predicted with a slight under-prediction in the columnar-isotropic transition temperature. This is also observed in the other columnar phases studied in this work.

It is therefore shown that the SAFT-γ Mie CG methodology proposed in this work can be a viable and more realistic alternative to other CG methodologies used to study mesophase behaviour of TBAs. Given the reliability of our model in predicting the correct phase behaviour experimentally, a systematic phase map exploration is carried out, with observation of new columnar phases and three-dimensional networks.

$A = -kT \ln Q$

Table 1: Comparison of the mesophase behaviour of the molecules presented in Figure 1 as seen in experiments [8] and predicted by molecular dynamics simulations in this work

Number of Carbons in each of the tails: m,n	Experiments [8] (Electron Density Map)	SAFT-γ Simulations
20, 0 (single chain)	 Hexagonal Columnar (Honey Comb)	
16, 4 14, 6	 Hexagonal + Pentagonal Columnar	
10, 10	 Octagonal + Pentagonal Columnar	

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Engineered Self-assembly of metastable phases with orientational potentials applied to oblate spherocylinders

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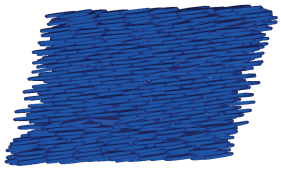
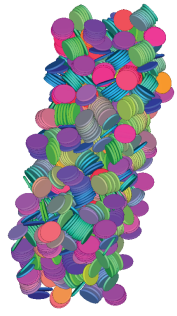
More than ten years ago the GBK (Gay-Berne-Kihara) [1] was proposed to study prolate spherocylinders and later on for oblate ones [2]. But the GBK model has an unlimited combination of parameters, what results in different orientation-dependent attractive interactions. Knowing this, a thermodynamic study of a particular set of parameters would appear pointless in a first approach.

In this study we classify sets of parameters according to the possible outcomes when applied to oblate shapes. Keeping this view point, we simulated isotherms for cases of special interest as examples of their type. Here we report the formation of structures beyond the foreseeable nematic, columnar or tilted phases, showing the smectic, uniaxial and cubatic as metastable phases. Aside of thermodynamical variables the formation of this novel phases are dependent of the tunable parameters of the model which can be adjusted to favor a desired orientational interaction.

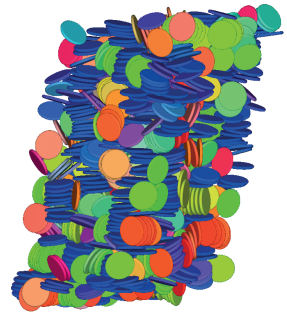
Hence, with only a numerical change in parameters, the OGBK potentials allow us to model very different types of system, like cationized horphyrines, discotic mesogens or laponites. This can have many technological applications in different fields.



1.Smectic



2.Cubatic



3. Uniaxial

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$A = -kT \ln Q$

Allosteric effects in phase behaviour of SW trimer particles, Thermodynamic Perturbation Theory

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Trimers formed by hard spheres, HS, and square well, SW, particles, show a rich structural and phase behaviour. In this work we extend the first-order perturbation theory in order to allow for allosteric effects. The types considered are made of equal-diameter spheres with i) three square wells, ii) two square wells and one hard sphere, and iii) one square well and two hard spheres.

The phase behaviour of some of these systems presents a challenge to standard high-temperature perturbation theory, HTPT; because the phase split occurs at particularly low temperatures. This fact requires a reconsideration of truncated HTPT to incorporate a resummation scheme, which is done here by two alternative approaches. One is the resummation procedure introduced by Ghobadi and Elliot,[1] and the second was proposed by some of the authors of this work [2] based on the work of Sastre et al.[3]

A second difficulty presented by these systems is the need to take into account the allosteric effects due to the screening of one of the spherical sites in one molecule by the presence of the other centres. This effect has been proven to be almost negligible in hard-sphere dimers,[4] but is clearly enhanced when various SW interactions are present. In this case, the allosteric effect depends on the angle distended by the two bonds to the central sphere. The contribution to the free energy due to the formation of chains of three spheres is calculated in the spirit of Wertheim's PT as is developed in Statistical Associating Fluid Theory, SAFT.[5]

The results of the extended PT are compared with the outcome of Discrete Molecular Dynamics calculations.

Acknowledgement. This work was supported by project Fronteras de la Ciencia FDC 2015-2 1450 of CONACYT, México.

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Modelling silica in aggregates of block copolymers

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There is a developing interest in the use of Periodic Porous Materials (PPMs) synthesized from silicic acid and amphiphilic block co-polymers in drug delivery and catalysis. Existing studies of the formation of PPMs have not drawn a clear conclusion as to the formation mechanism. In the prior studies two formation mechanisms were suggested; Liquid Crystal Template (LCT), where the formation is driven by the self-assembly of the amphiphilic block copolymers and silicic acid plays no active role in the formation. The second one is the Co-operative Mechanism (CM), where the silicic acid and the amphiphilic block copolymer are equally important in driving the reaction. In this study, we aim to investigate how the presence of silicic acid affects the self-assembly of these block copolymers by performing molecular dynamics simulations of coarse-grained models of these species. Earlier studies with an existing CG silicic acid model [1] reproduce the silicic acid solubility in water at higher pH ranges, as observed experimentally [2]. The solubility of silicic acid in water is highly dependent on pH. In this work, we are interested at lower pH (range from 1-5). Hence, we have developed a new silicic acid CG model, to reproduce the silicic acid – water behaviour at the pH range of interest. This model has been developed by comparing the solvation free energy of silicic acid in solvent with the values obtained from DFT calculations.

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$A = -kT \ln Q$

Rational and accidental design of patchy colloid models assembling into complex ordered structures

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Advances in the synthesis of nanoparticles with ever increasing control over the particles interactions have led material scientists to envision a new class of smart, responsive materials which assemble spontaneously from appropriately designed nanoparticles [1]. Thus understanding the effect of the particles shape and interactions on their assembly behaviour is not only an interesting fundamental question, but also one that can have important practical implications. In spite of much effort, designing models that assemble into a desired ordered structure is still challenging, both due to the appearance of competing structures and the tendency of these systems to get stack in kinetic bottlenecks [2]. In this contribution, we will analyse a few relatively simple cases to exemplify these difficulties.

Firstly, we will present results on the phase behaviour of a simple model of three-patch particles under planar confinement. One would expect that this system forms a honey-comb lattice at low temperature and pressure, but, instead, if the patches are narrow enough, the system organizes into an exotic solid phase consisting of a honey-comb lattice whose voids can be continuously filled without crossing a phase transition [3].

Secondly, we will introduce a simple scheme to design model systems that assemble into complex ordered structures, such as, e.g, clathrate crystals. Our results show that incorporation of specificity and/or torsional contributions to the interactions can be exploited both to design models for which the target crystal is the global free energy minimum and to favour the kinetics of crystallization [4]. What is the minimal amount of information required to assemble complex ordered structures will also be discussed.

We will end up by showing that clathrate crystals can also be assembled from tetrahedral patchy particles with narrow patches, an example that again challenges our intuition on what structure will emerge from particles with a given geometry [5].

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Supramolecular organization of Perfluoroalkylalkanes - *primitive surfactants* - using the SAFT-γ force field

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Perfluoroalkylalkanes, often named primitive surfactants, are linear di-block copolymers formed from an alkyl and a perfluoroalkyl segments bonded together, with general formula F(CF2)n(CH2)mH (FnHm). The distinct amphiphilic character imparted by these two mutually phobic chains is known to promote the formation of a variety of supramolecular structures, micelles and reverse micelles, gels, liquid crystals, etc.

In this work, Molecular Dynamics (MD) simulations were used to study the self-assembly and interfacial behaviour of PFAAs and their mixtures with hydro- and fluorocarbon solvents. A recently developed heteronuclear coarse-grained (CG) force field of the SAFT-γ-Mie family was used. [1]

This work is expected to contribute to refine the industrial use of fluorinated compounds as well as the understanding of supramolecular organization within this important family of surfactants.

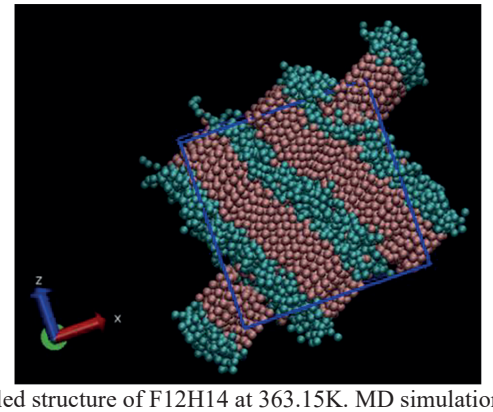

Figure 9: Self-assembled structure of F12H14 at 363.15K. MD simulation snapshot using the SAFT-γ-Mie CG forcefield.

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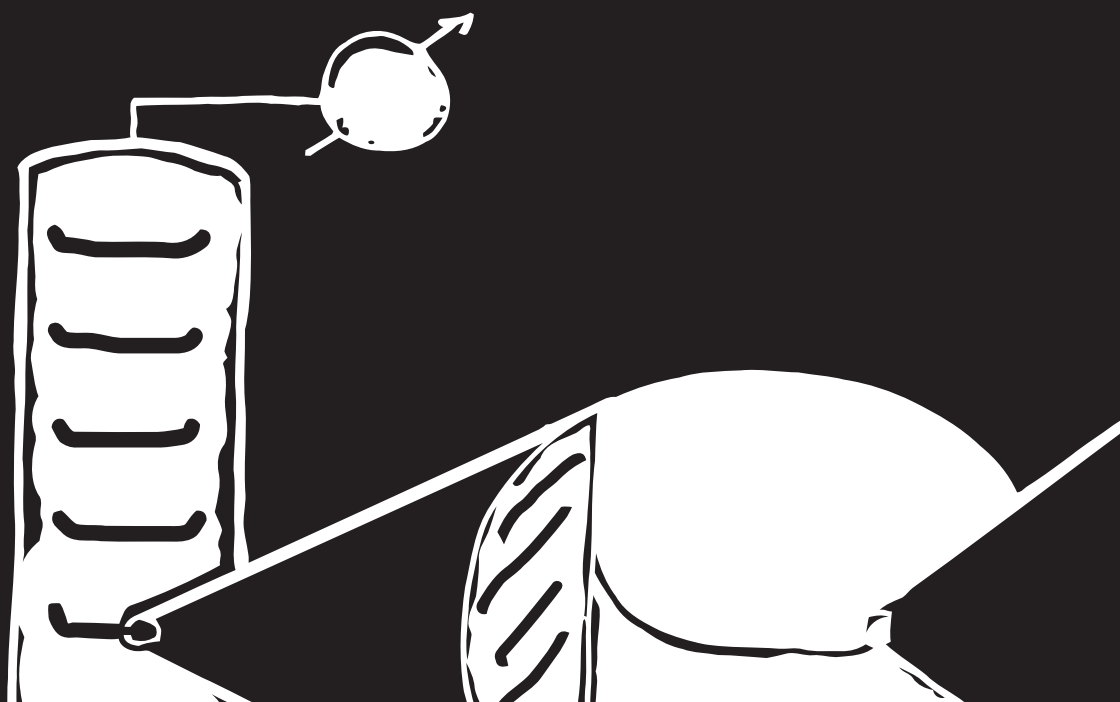
$A = -kT \ln Q$



$$A = -kT \ln Q$$

Poster Presentations:
Non-equilibrium thermodynamics



Modelling thermophoretic transport across nanopores

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Thermal gradients applied to aqueous solutions give rise to fascinating coupling phenomena, such as the Ludwig-Soret (thermodiffusion or thermophoresis) and the Seebeck (thermoelectricity) effects, with the temperature gradients inducing concentration gradients or electric fields, respectively. Innovative applications of thermal coupling phenomena involve nanofluidics devices. These devices provide new opportunities for probing or manipulating single molecules, pumping or mixing, and separation of fluids.
Thermal gradients can drive the motion of molecular motors [1], the selective transport of macromolecules (proteins or DNA), [2] and potentially translocation of molecules across nanopores [3]. Thermophoretic nanopores may provide a route to design single molecule sensors to detect biomolecules. An advantage of thermal coupling phenomena lies on the high sensitivity of the thermophoretic response to the solute-solvent interactions and the solution properties. These characteristics might be exploited to realise thermophoretic nanopores with higher selectivity.
We have performed non-equilibrium molecular dynamics simulations of LiCl aqueous solutions to quantify the thermophoretic transport in bulk and salt solutions under confinement. Thermal gradients were applied across amorphous silica nanochannels and the effect that the confinement has on the thermophoretic response of the solution was investigated as a function of the nanopore diameter.
We found that the Soret coefficient increases with temperature for both bulk and confined solutions, being of the order of $\sim 10^{-3}$ K^{-1}, in good agreement with available experiments in bulk solutions [4]. Confinement effects influence the structure of the solvent and the ion solvation. These changes translate in an enhancement of the thermophilic response of the electrolyte solution.

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$A = -kT \ln Q$

Thermophoretic Response of Rod-Like Colloids with Mass Asymmetry: The Effect of Internal Composition

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The application of a thermal gradient to a colloidal suspension induces a concentration gradient. This physical phenomenon is known as thermophoresis. Recent studies showed that the thermal gradient impart a specific orientation to molecular fluids [1]. Homogeneous elongated particles suspended in a fluid feature an anisotropic thermophoretic response. It has been concluded that the thermophoretic drift takes place with a specific orientation of the particle with respect to the imposed thermal gradient [2]. Recently, it was shown that internal degrees of freedom of colloid, e.g., an internal mass distribution, couple with the thermal gradient, with the gradient imparting a net orientation in a homogenous thermal field [3,4].

In this work we investigate the effect of an inhomogeneous mass distribution on the thermophoretic response of rod-like colloids in the dilute regime [5]. We propose a theoretical approach to model the dependence of the Soret coefficient with the orientation of particle, imparted by the thermal gradient. Our theoretical predictions show excellent agreement with non-equilibrium molecular dynamics simulations. Using both theory and simulation, we show that the average orientation and Soret coefficient: (i) can be predicted for an arbitrary mass distribution; (ii) can be directly linked, eliminating the dependence on fitted phenomenological coefficients; and (iii) can depend very sensitively on the internal mass distribution of the colloid. In particular, this last point suggests that colloids with the same total mass but different mass compositions feature significantly different thermophoretic responses, opening a route to exploit the thermal orientation effect in thermal fractionation applications.

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New Data and thermodynamics modeling of Physiochemical properties of (Ionic Liquids) protic ionic liquids (PIL) mixed with adenosine triphosphate (ATP) + water mixtures at different temperatures from 298.15 K to 348.15 K

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Extended Abstract: The 1-H-3-methyl imidazolium acetate and 1-H-3-methyl imidazolium hydrogen sulphate are excellent ionic liquids used for the removal of CO2 form multipale source stream in oil and gas as well as waste CO2 management design systems. In this work we have calculated the densities of adenosine triphosphate + water + 1-H-3-methyl imidazolium acetate mixture and adenosine triphosphate + water + 1-H-3-methyl imidazolium hydrogen sulphate mixtures at five different concentrations of adenosine triphosphate namely from 25mg/ml to 45mg/ml. The densities of pure 1-H-3-methyl imidazolium acetate and 1-H-3-methyl imidazolium hydrogen sulphate and their solutions in water has also been calculated at different temperatures from 298.15 K to 348.15 K using Rudolph Research Analytical Density Meter. The thermal expansion coefficients, molar volumes, standard entropy and crystal lattice potential energies has also been calculated and their relation with temperature and density change has also been investigated at a temperature range from 298.15 K to 348.15 K. The excess volume property for the mixture of adenosine triphosphate + water + protic ionic liquids was also estimated. The excess volume properties for these ternary mixtures were estimated from Redlich Kister equation. It was found that the calculated excess molar volumes were positive for a specific ATP concentration. The thermal expansion coefficients, molar volumes, molecular volumes and standard entropy of ternary mixtures increases with increase in temperature and lattice potential energy of above mentioned ternay mixtures decreases the increasing temperature.

$A = -kT \ln Q$

Effect of a constant drift in the reptation dynamics of entangled polymers

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The most successful theory to describe the dynamical response of entangled polymer melts is the reptation/tube theory of de Gennes and Edwards [1-2]. In the basic version of the theory, a single tracer polymer chain moves through the matrix created by surrounding polymers, which create topological restrictions (entanglements) due to the uncrossability of the chains. The explicit matrix is replaced by a mean field representation (a tube of diameter a), and the chain is free to diffuse along the axis of the tube (the primitive path). This diffusion motion (called reptation by de Gennes) constitutes the main relaxation mechanism of well entangled linear polymer chains. The original model has been modified and updated thoroughly in the past decades with many additional relaxation modes (contour length fluctuations [3], constraint release [4-5], tube dilution [6-7], convective constraint release [8]) that allow the model to explain experimental data of binary blends and branched polymers in linear and non-linear flow conditions.

In addition, the tube theory has been useful to describe the diffusion of charged biomolecules in electrophoresis experiments, in the form of the biased-reptation theory [9]. In the experiments, a long, charged polymer diffuses through a gel under the effect of an external electric field, which enforces the chain to reptate preferentially in the direction of the electric field and tends to align the end-to-end vector in the same direction. Here, we consider a similar but different setup: we envision a linear, flexible polymer chain which, due to some internal activity or to the effect of a conformational asymmetry along its contour, reptates with a constant drift velocity that always points from tail to head and is not fast enough to perturb the random walk statistics of the chain. When this kind of drift is introduced in the classic reptation model of de Gennes, the dynamical behaviour of the system (e.g. the tube segment survival function, the segmental motion, the dynamic structure factor, etc) changes dramatically. In this work, we explore these changes by means of analytical theory and simulations.

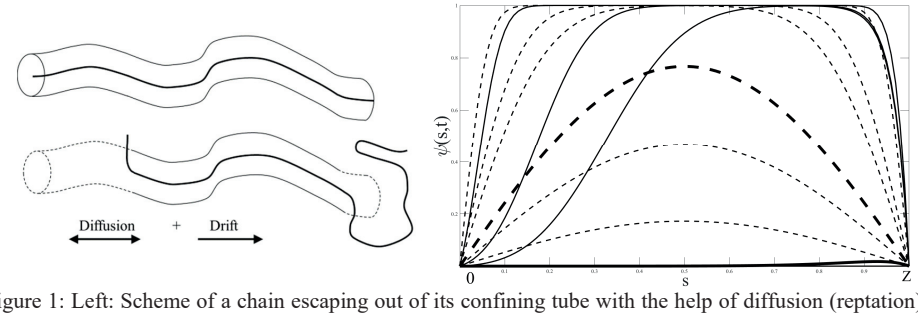

Figure 1: Left: Scheme of a chain escaping out of its confining tube with the help of diffusion (reptation) and drift. Right: tube segment survival function for pure reptation (dashed lines) and reptation with drift $c = 1/Z^2$ (solid lines), computed at times $t =$ (0.01, 0.05, 0.1, 0.5, 1, 2)$\times \tau_d$ (the highlighted curve corresponding to $\tau_d/2$).

The most important hypothesis in our theory is that there is a constant drift that always points in the same direction along the tube and that is fast enough to affect diffusion at long times, but slow enough so that the tube ends are free to explore all possible orientations when they exit the

tube (See Figure 1). Within this well-defined framework, we have solved analytically the partial differential equations of reptation with drift for the tube survival function, the segmental motion and the dynamic structure factor, and compared them to the solutions found in the seminal work of Doi and Edwards in the case of pure reptation [2]. As an example, in Figure 1, the tube segment survival function is compared in two extreme cases (very low and very high drift velocity).

From our analytical results, we have inferred the range of velocities for which the drift mechanism governs over reptation. Non-surprisingly, diffusion governs the molecular motion at very small times (displacement scales with $t^{1/2}$) whereas drift may govern at long times (motion scales with t), if the drift velocity is larger than a critical value that scales with Z^{-2}. Therefore, no matter how small the drift is, there is always a sufficiently large number of entanglements that make the drift win over reptation in the terminal region.

All our theoretical results have been verified by Brownian dynamics simulation of a discrete version of the tube model (a 1D Rouse model diffusing inside a 3D random walk). If the kind of drift motion that we hypothesize in our work can be found, it will allow to create very high molecular weight polymeric materials with very low viscosity.

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$A = -kT \ln Q$

The Influence of Radiation Emission on the Thermodynamics Properties of Liquid Systems

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In the biological systems alongside with the change of kinetic coefficients, which are defined by molecular distribution functions of the third order, the influence of radiation emission on phase transitions of various types is a matter of special importance. With the sufficient precision the shift of phase transition parameters, as well as of macroscopic characteristics of the system, can be evaluated, using only the correlation functions of the second order. The state of a liquid system under irradiation is not that of equilibrium, because radiation induces a permanent deviation from the equilibrium. In the framework of the approach let us consider the case where a biphasic system, which is in the state of thermodynamic equilibrium characterized by the given temperature, pressure, and particle number, undergoes irradiation by a source with a constant power. The further evolution of the system is exclusively governed by the time dependences of the temperature, pressure, and radiation source power, irrespective of the initial distribution of molecules in the phase space. In this case, according to the Prigogine theorem about the stationary state, the system transits into a state with the entropy production minimum. In the range of thermo-dynamic branch stability, using the hypothesis about the existence of local equilibrium, one may unambiguously introduce local thermo-dynamic functions and consider phase transitions in the framework of equilibrium thermo-dynamics. In the framework of this approach, we consider the influence of irradiation on the evolution of possible phase transitions of the first kind in liquids. In order to evaluate the contribution of energy factors to a shift of the phase transition temperature and in addition to the thermal equation of state for the basic system, its radial distribution function, $g_{20}^{i}\left(\mathbf{r}, T, p\right)$, as well as the potentials of pair interactions "excited particle–excited particle" and "excited particle–unexcited particle". The radial distribution function of argon atoms was found, by using the numerical simulation in the framework of a canonical ensemble and applying the molecular dynamics methods. The influence of radiation on the thermodynamic properties of liquid systems that are governed by the radiation induced change in the chemical potentials of the liquid and its components has been studied. The irradiation of coexisting phases in the stationary state is shown to result in a shift of the phase transition point parameters. The temperature shift of the first order phase transition under the influence of radiation is evaluated with regard for both the entropy and interaction factors in the chemical potential of the system. The work obtained results of the MD simulation of the radiation influence on 10% saline quantitatively confirm the predictions of the introduced theoretical model of the irradiation process. To verify our theoretical assumptions concerning modifications in the local structure of the examined saline (NaCl aqueous solution at 10%), experiments under the influence of irradiation were done.

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