2022

EMLG

Theory • Simulation • Experiment

UNIVERSITAT DE BARCELONA

INDEX

FOREWORD

EMLG
Theory • Simulation • Experiment
September 12-16, 2022 • Barcelona (Spain)

On behalf of the Organising and the International Scientific Committees, we take great pleasure in welcoming you to Barcelona (Spain) for this new edition of the EMLG/JMLG International Conference (EMLG2022)

The EMLG/JMLG (European/Japanese Molecular Liquids Group) is an interdisciplinary group covering the molecular aspects of liquids in Physics, Chemistry, and Biology. The European group was founded in 1981 and was joined by the Japanese group in 1996 as a sister organization to cooperate and coordinate activities in the field. JMLG became the international division of the Japan Association of Solution Chemistry (JASC) in 2005.

The EMLG/JMLG has organised annual conferences since 1981 in different European countries and with different focuses. The first joint EMLG/JMLG conference was held in Fukuoka in 1999 as a post-symposium of the International Conference on Solution Chemistry. The last joint conference in 2019 was in the Czech Republic, a few months before the pandemic started. This is the first post-pandemic edition, initially planned for 2020.

We are indebted to the following Scientific Institutions for their help and financial support: Universitat de Barcelona (UB) and Institut de Nanociència i Nanotecnología / UB (IN2UB).

We also would like to thank all the speakers and participants that joined us in person this year.

Hope to see you again in the next edition of EMLG.

EMLG2022 Organising Committee

MAIN ORGANISER

The University of Barcelona is one of the public institutions of higher education in Catalonia, catering to the needs of the greatest number of students and delivering the broadest–and most comprehensive–offering in higher educational courses. The UB is also the principal center of university research in Spain. It has become a European benchmark for research activity in terms of the number of projects it conducts and its excellence. Its history is closely tied to the history of Barcelona and Catalonia. It combines the values of tradition with its position as an institution dedicated to innovation and teaching excellence: a university that is as outward-looking and cosmopolitan as the city from which it takes its name.

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The Faculty of Physics of the University of Barcelona was created in 1974 to manage the courses in physics that the Faculty of Sciences had previously taught. It shares a building on Avinguda Diagonal with the Faculty of Chemistry, in the core university area of the city, which focuses much of Barcelona's scientific teaching and dissemination infrastructure. Every year the Faculty is home to some 1,700 students across its range of courses. Its four departments cover each main area of study: Electronic Engineering and Biomedics, Quantum Physics and Astrophysics, Condensed Matter Physics, and Applied Physics. It also operates the interdisciplinary research institutes ICCUB and IN2UB.

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IN2
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The main goal of the Institute of Nanoscience and Nanotechnology of the University of Barcelona (IN2UB) is to coordinate and enhance multidisciplinary research among groups from the Faculties of Chemistry, Physics, Pharmacy and Food Sciences, Biology, Earth Sciences, and Medicine and Health Sciences that work on the different phenomena occurring at the nanoscale. This collaborative spirit aims to integrate both internally and internationally interdisciplinary activities that combine, in equal parts, basic and applied research. IN2UB gathers around 200 researchers, organized into research groups distributed among seven major research areas.

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2D-confined water. Phases and dielectric response

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Two-dimensionally confined water to 0.8 nm of width was studied by means of molecular dynamics simulations using both empirical force fields (TIP4P 2005), and first-principles forces, following intriguing findings on melting lines of different character (see e.g. Ref [1]). The Structural and dynamical properties will be reviewed for the various phases as well as the response to perpendicular electric fields, for varying lateral pressure and temperature. The anomalously low perpendicular dielectric response observed in Ref. [2] is addressed. It had already been predicted from simulations (see e.g. Refs [3,4]), but not as extremely low as measured. The response is here found to vary relatively little with lateral pressure, with a very slight increase of the effective dielectric constant towards the transition between the liquid and the hexatic phase. The ionic vs electronic response will be discussed.

REFERENCES

[1] S. Han, M. Choi, P. Kumar, and H. E. Stanley, Nat. Phys**.** **6**, 685 (2010).
[2] L. Fumagalli, A. Esfandiar, R. Fabregas, S. Hu, P. Ares,A. Janardanan, Q. Yang, B. Radha, T. Taniguchi,K. Watanabe, G. Gomila, K. S. Novoselov, and A. K.Geim, Science **360**, 1339 (2018).
[3] C. Zhang, F. Gygi, and G, Galli, J. Phys. Chem. Lett. **4**, 15, 2477–2481, (2013).
[4] J. Zubeltzu, F. Corsetti, M. V. Fernandez-Serra, and E. Artacho, Phys. Rev. E **93**, 062137 (2016).

FIGURES

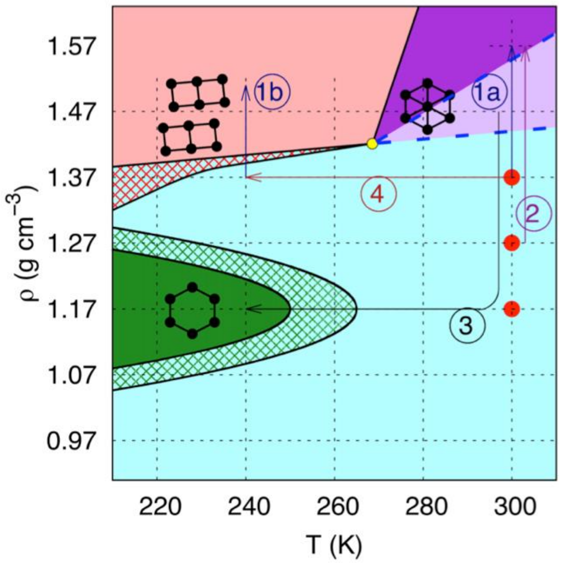

Figure 1: Density-temperature phase diagram for water confined to two dimensions to a thickness of 0.8 nm (bilayer water). Blue indicates the liquid, green and orange indicate solid phases, and light/dark purple indicate a plastic phase in which oxygens order (orientationally or translationally) but hydrogen atoms do not.

Taming Complex Fluids with external field: a computational journey

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Abstract

Thermal and electromagnetic fields induce a range of non-equilibrium effects in complex fluids consisting of nanoparticle suspensions (e.g., Soret, Seebeck, Peltier effects), which can be exploited in energy conversion (thermoelectrics), analytical devices for detection of biomolecules, or nanoparticle transport and assembly. The combination of non-Equilibrium multiscale simulations and non-equilibrium theory has paved the way to elucidate the physical behaviour of complex fluids under external fields, showing that their response is much richer than previously anticipated. I will discuss the use of these techniques to predict and observe novel non-equilibrium effects in complex fluids and to quantify the impact of confinement on heat and mass transport, hence opening new avenues for energy conversion and tuneable nano-tribology.

REFERENCES

[1] Jiang, M. et al., J. Chem. Phys., 156 (2022) 0074912
[2] Olarte-Plata et al., ACS Nano, 30 (2022)
[3] Di Lecce et al., Nanoscale, 12 (2020) 23626
[4] Olarte-Plata et al., J. Chem. Phys., 152 (2020) 204902.
[5] Gittus et al., J. Chem. Phys., 153 (2020) 204053
[6] Di Lecce et al., ACS Nano, 14 (2020) 13256
[7] Muscatello et al., Phys. Rev. Lett., 119 (2017) 045901
[8] Tascini et al., Phys. Chem. Chem. Phys., 19 (2017), 3244

A critical role for glassy states Biomolecular Condensates in Nanoscale Regulation of Biology

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Nanoscale objects are processed by living organisms using highly evolved and sophisticated endogenous cellular networks, specifically designed to manage objects of this size. While these processes potentially allow nanostructures unique access to and control over key biological machineries, they are also highly protected by cell or host defence mechanisms at all levels. A thorough understanding of bionanoscale recognition events, including the molecules involved in the cell recognition machinery, the nature of information transferred during recognition processes and the coupled downstream cellular processing, would allow us to achieve a qualitatively novel form of biological control and advanced therapeutics. Here we discuss evolving fundamental microscopic and mechanistic understanding of biological nanoscale recognition. We consider the interface between a nanostructure and a target cell membrane, outlining the categories of nanostructure properties that are recognized, and the associated nanoscale signal transduction and cellular programming mechanisms that constitute biological recognition.

REFERENCE

Dawson KA, Yan Y, *Nature Nanotechnology* volume 16, pages 229–242 (2021)

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Computational Studies of Supercooled Water with an *Ab-Initio* Deep Neural Network Model

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Abstract

Using a combination of computational chemistry, machine learning and advanced sampling, it is possible to study, with *ab-initio* accuracy, problems involving time and length scales that until recently were only accessible using classical, empirical models [1]. This approach will be illustrated through three examples. First, the phase behavior of supercooled water is investigated via equation of state [1] and free energy calculations [2]. Both approaches yield evidence consistent with the existence of a metastable first-order phase transition between two different liquids, terminating at a liquid-liquid critical point. The second example involves calculations of ice homogeneous nucleation rates in supercooled water at ambient pressure, which yields predictions that are in good agreement with experiments [3]. Finally, melting curve calculations for several ice polymorphs allow the computational re-creation of the Mishima-Stanley experiment [4], which for many years provided the strongest evidence in support of the existence of a metastable critical point in supercooled water. The computational results suggest a different interpretation of experimental observations than that proposed by Mishima and Stanley [5].

REFERENCES

[1] Gartner III, T.E., Zhang, L., Piaggi, P.M., Car, R., Panagiotopoulos, A.Z., and Debenedetti, P.G., PNAS, 117 (2020) 26040.
[2] Gartner III, T.E., Panagiotopoulos, A.Z., Car, R., and Debenedetti, P.G., in preparation (2022).
[3] Piaggi, P.M., Weis, J., Panagiotopoulos, A.Z., Debenedetti, P.G., and Car, R., submitted to PNAS (2022).
[4] Mishima, O. and Stanley, H.E., Nature, 392 (1998) 164.
[5] Piaggi, P.M., Gartner III, T.E., Car, R., and Debenedetti, P.G., in preparation (2022).

The stressed solvent: Terahertz calorimetry probing the solvent in action

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Key concepts of characterizing solvent thermodynamics are firmly established in the sense of global properties of homogeneous bulk systems under thermodynamic equilibrium conditions. However, it is intriguing to see how local solvation phenomena in nano-heterogeneous environments determine the reactivity and selectivity in solution, receptors, and enzymes, and even the function of electrocatalysts. While macroscopic solvation can be tracked by traditional calorimetry approaches, local solvation and processes in non-equilibrium cannot. Terahertz (THz) spectroscopy probes the intermolecular interaction between water molecules provides an opportunity to determine the contribution of the solvent to the total free energy of a reaction. Systematic spectroscopic studies revealed that the THz spectrum fingerprints any changes with respect to hydrogen bond strength, tetrahedrality, dynamics, which are all of major importance to rationalize and predict the outcome of a reaction. While the individual changes might be small, the large amount of solvent involved makes this contribution a major driving force for fundamental reactions. We present here a spectroscopic approach, which gives direct access to the two main contributions at : Using THz spectroscopy to probe the frequency range of the intermolecular stretch (150-200 cm^{-1}) and the hindered rotations (450-600 cm^{-1}), the local contributions due to cavity formation and hydrophilic interactions can be traced back [1]. This allows to deduce separately the hydrophobic (i.e. cavity formation) and hydrophilic (enthalpic) contributions to thermodynamics, as shown for hydrated alcohols as a case study. THz calorimetry have also uncovered when local mutation serves as a game changer for protein dynamics [2]. These measurements allow conductivity measurements in micelles, and probe hydration within supramolecular nanocages, or even in the vicinity of an electrified interface. Local “solvation hotspots”, such as the so-called liquid liquid phase separation membraneless compartments in a cell are suspected to trigger neurotoxic protein aggregation. There are indications that the phase separation is entropy driven, with the solvent playing a decisive role. In the future, time resolved THz probe experiments will allow to dissect hydration contributions in inhomogeneous mixtures and under non-equilibrium conditions. Typically, especially for biological reactions, there is a subtle balance between a favourable enthalpy and an unfavourable entropic term, which almost cancel, thus allowing to fine tune reactions based on THz screening.

REFERENCES

[1] S. Pezzotti, F. Sebastiani, E.P. van Dam, S. Ramos, V. Conti Nibali, G. Schwaab, M. Havenith, Angew. Chem. Int. Ed., e202203893 (2022)
[2] E. Adams, S. Pezzotti, J. Ahlers, M. Rüttermann, M. Levin, A. Goldenzweig, Y. Peleg, S. Fleischmann, I. Sagi, M. Havenith, JACS Au 1, 1076–1085 (2021)

Two Aspects of the Osmotic Second Virial Coefficient

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Hydrophobic interactions are the effective interaction between hydrophobic molecules or moieties in aqueous solutions. One way to quantify those interactions is to measure the osmotic second virial coefficient B, which is related with the effective solute-solute pair potential $w(r)$ in solution via

$$B = -\frac{1}{2}\int [e^{-\frac{w(r)}{kT}} - 1]\, d\tau$$

where $d\tau$ is the infinitesimal volume element and the integral is over the whole space. Here we report two aspects of the osmotic second virial coefficient for hydrophobic solutes, one concerning salt effects and the other pertaining to length scales of hydrophobic interactions.

The ion-specific effect on the solubility of gases in aqueous solutions is measured by the Setschenow coefficient K_s. Recently the reverse order of lithium and sodium ions in the cation size dependence of K_s has been examined based on molecular simulation [1]. We now introduce an analogous quantity, the salt-enhanced association (SEA) coefficient C_I, which is a measure of the ion-specific effect on the osmotic second virial coefficient [2]. It is shown that the SEA coefficient is explicitly related to the Setschenow coefficient: For ions and solutes that are not very large, the quadratic relation, $C_I \approx \frac{1}{4} K_s$, is derived.

The other aspect of the osmotic second virial coefficient to be discussed is its solute-size dependence. It is known that the second virial coefficient for gases is proportional to the cubic power of the molecular diameter for typical model pair potentials with the well-depth fixed. We evaluated *osmotic B* for hydrophobic molecules of different sizes in water based on molecular simulation [3]. It is found that osmotic B is much more strongly dependent on the molecular size than in vacuum: Specifically, it is proportional to the sixth or higher power of the solute diameter when the solutes are taken to be Lennard-Jones particles with the energy parameter chosen to be that of methane. It is also shown that a similar power law is observed for solutes in a non-polar solvent. Robustness of the power-law dependence of B is discussed from theoretical points of view.

REFERENCES

[1] H. Katsuto, R. Okamoto, T. Sumi, and K. Koga, J. Phys. Chem. B, **125** (2021) 6296.
[2] R. Okamoto and K. Koga, J. Phys. Chem. B, **125** (2021) 12820.
[3] H. Naito, R. Okamoto, T. Sumi, and K. Koga, J. Chem. Phys., **156** (2022) 221104.

2D materials-based intelligent membranes

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Permeation through nanometre-pore materials has been attracting unwavering interest due to fundamental differences in governing mechanisms at macroscopic and molecular scales, the importance of water permeation in living systems, and relevance for filtration and separation techniques. Latest advances in the fabrication of artificial channels and membranes using two-dimensional (2D) materials have enabled the prospect of understanding the nanoscale and sub-nm scale permeation behavior of water and ions extensively. In particular, several laminate membranes made up of 2D materials show unique permeation properties such as ultrafast permeation of water and molecular sieving. In my talk, I will discuss our recent results on controlling molecular transport through various 2D materials-based membranes by an external parameter and will discuss the prospect of developing next-generation intelligent membranes based on 2D materials.

REFERENCES

1. Nair *et al.* ***Science*** **335**, 442 (2012).
2. Joshi *et al.* ***Science,*** **343,** 752 (2014).
3. Su *et al.* ***Nature Communications*** **5**, 4843 (2014).
4. J. Abraham *et al.* ***Nature Nanotechnology*** **12**, 546-550 (2017).
5. Q. Yang *et al.* ***Nature Materials*** **16**, 1198 (2017)
6. A Esfandiar *et al.* ***Science*** **358**, 511-513 (2017)
7. K. G. Zhou et al. ***Nature*** **559**, 236-240 (2018)
8. Huang *et al.* ***Nature Communications*** **11**, 1097 (2020)
9. Zou et al. ***Nature Materials*** **20**, 1677-1682 (2021)

Water in a living cell probed by a Raman microscopy

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We have used Raman microscopy to investigate the structures and functions of biomolecules and cells, especially in relation to water [1–4]. In this presentation, we propose that "intracellular water" can be a new parameter for understanding the intracellular environment.

[Water distribution in a cell] Plotting the Raman intensity of a single HeLa cell in the C-H and O-H stretching Raman band regions (Figure 1) showed that the O-H Raman intensity of water was higher in the nucleus than in the cytoplasm [1]. Calculation of the difference spectrum subtracting the cytoplasm from the nucleus confirmed a positive peak in the O-H stretching region and a negative peak in the C-H stretching region. These results indicate that the water density in the nucleus is higher than in the cytoplasm. The water density in the cytoplasm was estimated to be about 3% smaller than that in the nucleus. The intracellular environment is highly crowded with biomolecules such as proteins and lipids, called macromolecular crowding. In this study, the magnitude of molecular crowding in the nucleus is found to be smaller than that in the cytoplasm. We proposed to evaluate macromolecular crowding from the Raman image of water in each organelle.

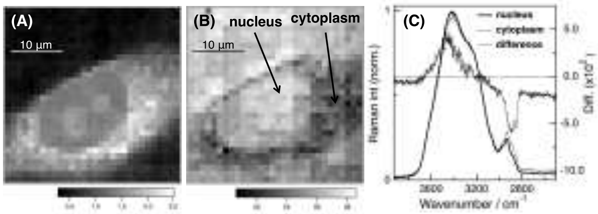

Figure 1: Raman images of a HeLa cell in the C–H (A) and O–H (B) stretching bands. (C) Difference Raman spectrum (solid) of a HeLa cell obtained by subtracting the spectrum of cytoplasm ((b) dotted) from the spectrum of nucleus ((a) thin-solid) [1].

[Label-free evaluation of intracellular temperature] We have applied Raman imaging of intracellular water to evaluate the temperature in a single living cell in a label-free manner [1]. This method utilizes the change in the shape of the O-H stretching Raman band of water with temperature. First, the temperature dependence of the O-H stretching band of the medium, nucleus, and cytoplasm was measured to obtain a calibration curve between temperature and the Raman band in each region. Next, using this calibration curve, we evaluated the temperature at each region and its change after adding FCCP (uncoupling reagent) into the cell. We succeeded in measuring the temperature increase in the cytoplasm after adding FCCP using the O-H stretching band (Figure 2). We were also able to obtain the temperature gradient between the cell and the medium. This label-free imaging using water is a promising new method for intracellular temperature studies.

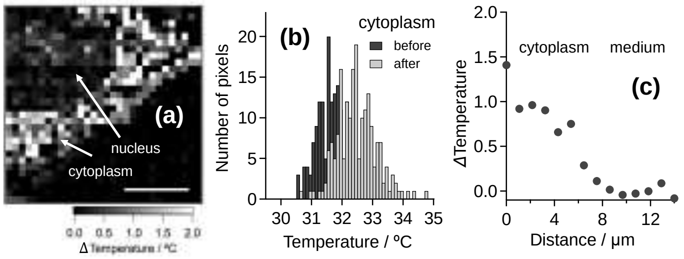

Figure 2: (a) The image of temperature change in a HeLa cell by subtracting the temperature image before the FCCP treatment from that after the FCCP treatment. (b) Histograms of cytoplasm temperature before and after the FCCP treatment. (c) Cross section of the temperature change from cytoplasm to medium [2].

REFERENCES

[1] M. Takeuchi, S. Kajimoto, T. Nakabayashi, J. Phys. Chem. Lett. 8 (2017) 5241.
[2] T. Sugimura, S. Kajimoto, T. Nakabayashi Angew. Chem. Int. Ed. 59 (2020) 7755.
[3] D. Shibata, S. Kajimoto, T. Nakabayashi, Chem. Phys. Lett. 779 (2021) 138843.
[4] K. Murakami, S. Kajimoto, D. Shibata, K. Kuroi, F. Fujii, T. Nakabayashi, Chem. Sci. 12 (2021) 7411.

Recent Advances in Bottom-up Coarse-Graining of Liquids

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Abstract

Recent advances in theoretical and computational methodology will be presented for studying complex liquid systems and other soft condensed matter across multiple length and time scales. The approach provides a systematic connection between all-atom molecular dynamics, coarse-grained (CG) modeling, and mesoscopic phenomena. At the heart of the approach is the multiscale coarse-graining method for rigorously deriving coarse-grained models from the underlying molecular-scale information. In the design of high-fidelity CG models, the structure and dynamics at the molecular level should be accurately reproduced at the CG level. This talk will cover statistical mechanical theories that have been developed in my group over the last few years allowing for such treatment. Structural correlations are captured by designing the many-body CG potentials of mean force for the CG variables. Nevertheless, many-body correlations present at the finer molecular level are often lost at the simplified CG resolution. I will present two theoretical approaches that can resolve this limitation. One approach is to explicitly include the many-body interactions at the CG level while maintaining efficiency by projecting these many-body interactions onto a lower order interaction. This idea is further utilized to develop a new CG model for water at low computational cost and with great accuracy. Alternatively, many-body correlations can be imposed by introducing internal states to the coarse-grained sites or “beads” similar to quantum mechanical states. By designing these internal states to modulate many-body correlations, these ultra-coarse-grained (UCG) models greatly expand the possible range of systems amenable to accurate modeling, such as hydrophobic aggregation and heterogeneous interfaces. While structural correlations can be preserved by precisely designing conservative interactions in CG models, missing fluctuation and frictional forces often result in accelerated dynamics at a renormalized level and with incorrect kinetics. To develop dynamically-consistent CG models, an alternative strategy based on the excess entropy scaling relationship will be introduced for liquids. Based on our findings on the universality of scaling between the atomistic and CG liquid systems, I will show the scaling relationship for simple liquids in order to systematically bridge the CG and reference molecular-level dynamics. Lastly, a combined theoretical and computational effort in these two directions will be applied to develop a bottom-up reactive CG model of the hydrated excess proton (aka “hydronium cation”) in water, which is critical to many areas of chemistry, biology, and materials science.

REFERENCES

[1] James F. Dama*, Jaehyeok Jin*, Gregory A. Voth, J. Chem. Theory Comput. 13 (2017) 1010–1022 (*: Equally contributed)
[2] Jaehyeok Jin, Gregory A. Voth, J. Chem. Theory Comput. 14 (2018) 2180–2197
[3] Jaehyeok Jin, Yining Han, Gregory A. Voth, J. Chem. Theory Comput. 14 (2018) 6159-6174
[4] Jaehyeok Jin, Alexander J. Pak, Gregory A. Voth, J. Phys. Chem. Lett. 10 (2019) 4549-4557
[5] Jaehyeok Jin, Alvin Yu, Gregory A. Voth, J. Chem. Theory Comput. 16 (2020) 6823-6842
[6] Jaehyeok Jin, Yining Han, Alexander J. Pak, Gregory A. Voth, J. Chem. Phys. 154 (2021) 044104
[7] Jaehyeok Jin, Yining Han, Alexander J. Pak, Gregory A. Voth, J. Chem. Phys. 154 (2021) 044105
[8] Jaehyeok Jin, Kenneth S. Schweizer, Gregory A. Voth, In preparation (2022)
[9] Jaehyeok Jin, Zhefu Li, Gregory A. Voth, In preparation (2022)

Angstrom-scale capillaries: Ionic selectivity and dehydration

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Abstract

Understanding ion transport in nano/angstrom scale channels has practical relevance in applications such as membrane desalination, blue energy, supercapacitors and batteries, as well as in understanding ionic flow through biological channels. Synthetic Å-channels are now a reality with the emergence of several cutting-edge bottom-up and top-down fabrication methods. In particular, the use of atomically thin 2D-materials and nanotubes as components to build fluidic conduits has pushed the limits of fabrication to the Å-scale. In this talk, I will discuss about angstrom (Å)-scale capillaries, which can be dubbed as "2D-nothing". The Å-capillary is an antipode of graphene, created by what is left behind after extracting one-atomic layer out of a crystal [1]. What is intriguing here is, the dimensions of these channels being comparable to the size of a water molecule.

The Å-capillaries have helped probe several intriguing molecular-scale phenomena experimentally, including: water flow under extreme atomic-scale confinement [1] complete steric exclusion of ions [3,5], specular reflection and quantum effects in gas reflections off a surface [2,7], voltage gating of ion flows [4] translocation of DNA [6]. I will present ionic flows induced by stimuli (electric, pressure, concentration gradient) and discuss the importance of ionic parameters that are often overlooked in the selectivity between ions, along with ionic memory effects [8]. The mass production and the robustness of the nano/angstrofluidic devices for large-scale applications are still the main challenges. Toward the end of the talk, I will discuss strategies to scale the production of Å-capillaries.

REFERENCES

[1] B. Radha et al., Molecular transport through capillaries made with atomic-scale precision. ***Nature*** 538, 222 (2016).
[2] A. Keerthi et al., Ballistic molecular transport through two-dimensional channels, ***Nature*** (2018), 558, 420.
[3] A. Esfandiar et al., Size effect in ion transport through angstrom-scale slits. ***Science*** 358, 511 (2017).
[4] T. Mouterde et al., Molecular streaming and voltage gated response in Angstrom scale channels. ***Nature*** 567, 87 (2019).
[5] K. Gopinadhan et al., Complete ion exclusion and proton transport through monolayer water. ***Science*** 363, 145 (2019).
[6] W. Yang et al., Translocation of DNA through ultrathin nanoslits. ***Advanced Materials*** 2007682, (2021).
[7] J. Thiruraman et al., Gas flows through atomic-scale apertures, ***Science Advances*** 6, eabc7927, (2020).
[8] P. Robin et al., Long-term memory and synapse-like dynamics of ionic carriers in two-dimensional nanofluidic channels, ***arXiv:2205.07653***, (2022).

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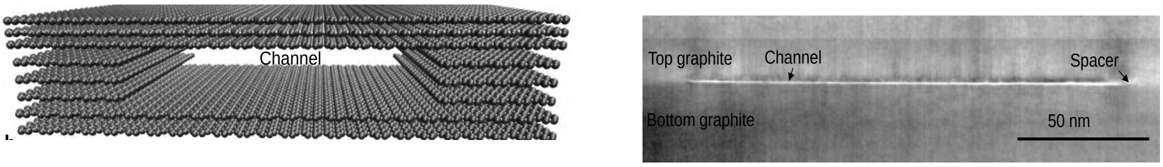

Figure 1: *Left, General schematic of Graphene capillary device. Right, Cross-sectional bright field image of a bilayer capillary (h □ 7 Å) in a scanning transmission electron microscope.*

On the design of optimal porous crystals for adsorption and purification processes

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In September 2000, we launched the Materials Modelling and Simulation (MSM) Group at the Department of Applied Physics, Eindhoven University of Technology, the Netherlands. This group uses high-performance computers to simulate materials that can revolutionise renewable energy and green technology. The MSM group is integrated with the Eindhoven Institute for Renewable Energy (EIRES) and the Eindhoven Artificial Intelligence Systems Institute (EAISI). In this unique environment, and in close collaboration with industry, we develop and apply both quantum and classical methods, jointly encompassing a comprehensive multiscale approach to study complex materials and molecules from the atomistic to the nanoscale. The systems we are currently focusing on include, among others, porous crystalline materials, novel semiconductors and hybrid nanomaterials [1,3]. This invited lecture will focus on the former, discussing the state of the art, current work and what we foresee in the short and long term.

Crystalline porous materials have much to offer. However, establishing unique relationships between chemical composition, physical properties and their functionalities in the final application is still a chimera. Our motivation is to use theoretical analysis and computational modelling to "invent" materials and redesign processes that respond to the current energy and environmental challenges of our society . To this aim we use our own methodology, force fields and software [4-7]. The RASPA software is a classical general-purpose simulation package especially suited to study adsorption and diffusion in nanoporous systems. In addition, we have recently implemented iRASPA which is an advanced visualisation package. These software package are optimised to be fast and accurate, allowing a quick evaluation of the structures of storage and/or separation devices (ref RASPA and iRASPA).

For effective adsorption and separation, it is necessary to find materials with high adsorption selectivity and suitable capacity for use in the traditionally used fixed-bed devices . Therefore, crystalline structures need to be examined for their ability to perform gas separation based on adsorption equilibrium, selectivity, diffusion, permselectivity, structural characteristics and kinetics. In most cases, the efficiency depends mainly on the optimal combination of selectivity and effective pore volume, and this can be obtained from our simulations and experiments[8-10]. I will discuss all these issues, as well as the development of high-throughput methods to automatically calculate properties and provide adsorption processes. I will conclude by showing some innovative approaches to assess material stability and to identify and design high-performance, stable crystalline porous materials.

REFERENCES

[1] Gutierrez-Sevillano, J. J., Podsiadły-Paszkowska, A., Szyja, B. M. & Calero, S., 2021, In: Applied Surface Science. 560, 7 p., 149884.

[2] Balestra, S. R. G., Vicent-Luna, J. M., Calero, S., Tao, S. & Anta, J. A., 2020, In: Journal of Materials Chemistry A. 8, 23, p. 11824-11836.

[3] Gutiérrez-Sevillano, J. J. & Calero, S., 2020, New Developments in Adsorption/Separation of Small Molecules by Zeolites. Valencia, S. & Rey, F. (eds.). Springer, p. 57-83 27 p. (Structure and Bonding; vol. 184).

[4] Dubbeldam, D., Calero, S., Ellis, D. E. & Snurr, R. Q., 2016, In: Molecular Simulation. 42, 2, p. 81-101.

[5] Dubbeldam, D., Calero, S. & Vlugt, T. J. H., 2018, In: Molecular Simulation. 44, 8, p. 653-676.

[6] Dubbeldam, D., Vreede, J., Vlugt, T. JH. & Calero, S., Mar 2019, In: Current Opinion in Chemical Engineering. 23, p.,1-13

[7] Dubbeldam, D., Calero, S., Vlugt, T. J. H. & Snurr, R. Q., 1 Nov 2020, Handbook Of Porous Materials: Synthesis, Properties, Modeling and Key Applications : Characterisation and Simulation of Porous Materials. Rothenberg, G. (ed.). World Scientific, Vol. 2. p. 199-319 121 p. (Mat and Energy; vol. 16).

[8] Luna-Triguero, A., Vicent-Luna, J. M., Jansman, M. J., Zafeiropoulos, G., Tsampas, M. N., van de Sanden, M. C. M., Akse, H. N. & Calero, S., 15 Feb 2021, In: Catalysis Today. 362, p. 113-121.

[9] JaraÍz-Arroyo, I., Martin-Calvo, A., Gutiérrez-Sevillano, J. J., Barranco, C., Diaz-Diaz, N. & Calero, S., 15 Apr 2020, In: Industrial and Engineering Chemistry Research. 59, 15, p. 7212-7223.

[10]Gutiérrez-Sevillano, J. J., Martin-Calvo, A., Dubbeldam, D. & Calero, S., 15 Dec 2021, In: Separation and Purification Technology. 277, 10 p., 119422.

Fast rearrangement dynamics of water in biomolecules hydration shell: results from extended depolarized light scattering experiments

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The Extended frequency range Depolarized Light Scattering (EDLS), has been demonstrated to be a powerful tool to access the fast dynamics of water in a variety of binary systems, including sugars and proteins' aqueous solutions. EDLS enables one to disentangle solute from solvent dynamics and, into the latter, bulk from hydration water contributions [1-6]. The use of EDLS has been then extended to ternary systems by studying a lysozyme-trehalose aqueous solution over a broad time scale, from hundreds to fractions of ps. Experimental evidence has been given that the sugar, present in the ternary solution in sufficient quantity for biopreservation, strongly modifies the solvation properties of the protein. By comparing aqueous solutions of lysozyme with and without trehalose, it has also been shown that the combined action of sugar and protein produces a significant slowdown in the restructuring of a fraction of water molecules around the protein, namely more than twice the corresponding value in the absence of trehalose [7-8]. This hyperslow water close to lysozyme is believed to be preserved from crystallization by the presence of trehalose in the mixture, thus playing a key role in bioprotection.
Finally, it will be shown how significant improvements in instrumentation toward the use of microscopies can make it possible to study submicrometric regions in systems relevant to many fields [9].

REFERENCES

[1] Perticaroli, S.; Comez, L.; Paolantoni, M.; Sassi, P.; Lupi. L.; Fioretto, D.; Paciaroni, A.; Morresi, A. J. Phys. Chem. B, 24 (2010) 8262.
[2] Lupi L., Comez L., Paolantoni M., Perticaroli S., Sassi P., Morresi A., Ladanyi B.M., Fioretto D., J. Phys. Chem. B, 116 (2012) 14760.
[3] Perticaroli, S.; Comez, L.; Paolantoni, M.; Sassi, P.; Morresi, A.; Fioretto, D. J. Am. Chem. Soc., 133 (2011) 12063.
[4] Comez, L.; Lupi, L.; Morresi, A.; Paolantoni, M.; Sassi, P.; Fioretto D. J. Phys. Chem. Lett., 4 (2013) 1188.
[5] Comez, L.; Paolantoni, M.; Sassi, P.; Corezzi, S.; Morresi, A.; Fioretto D. Soft Matter, 12 (2016) 5501.
[6] Corezzi, S.; Bracco, B.; Sassi, P.; Paolantoni, M., Comez, L., Life, 11 (2021) 995.
[7] Corezzi, S.; Paolantoni, M.; Sassi, P.; Morresi, A.; Fioretto, D.; Comez, L., J. Chem. Phys. 151 (2019) 015101.
[8] Lupi, L.; Bracco, B.; Sassi, P.; Corezzi, S.; Morresi, A.; Fioretto, D.; Comez, L., Paolantoni, M., Life 12 (2022) 572.
[9] Scarponi, F. et al., Physical Review X 7 (2017), 031015.

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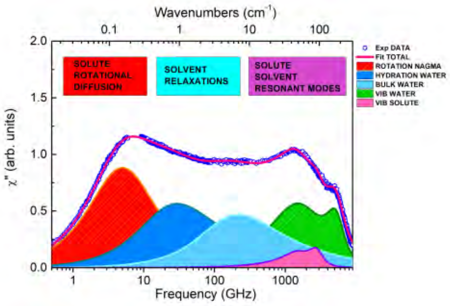

Figure 1: EDLS spectra of a peptide-water solution.

Exploiting the interfacial properties of ion-exchange polymers: from fundamental aspects to the development of self-propelled micro/nanosystems

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Ion-exchange polymers such as Nafion exhibit surprising interfacial phenomena. One of the most striking one is the formation of a long-range solute exclusion zone (EZ) in contact with water. The mechanism of such EZ formation has been the subject of a controversial and long-standing debate with explanations rooted either on the interfacial water structuration that excludes solutes[1] or on the ion-exchange process itself which generates ion diffusion/ion gradients, driving solute repulsion by diffusiophoresis[2].

Combining different experimental techniques, theory, and simulation, we show that multi-ionic diffusiophoresis is indeed the mechanism explaining the formation of the EZ. We have also found that an electric field built-up during the ion-exchange process is a key player in the EZ formation[3]. Such electric field, pointing towards Nafion, arises due to the different ion mobilities during the ion-exchange process and can be tailored to develop self-propelled pumps and swimmers of high interest in biomedical and nanotechnological applications. These ion-exchange machines have many advantages: they can use salts as fuel, are reusable and can work at high salt concentrations. In addition, we will show how a proper micro/nanostructuration of Nafion can be used to guide flows in arbitrary directions[4]. Finally, we will demonstrate the potentialities of taming these systems to applications in water remediation.

REFERENCES

[1] B. Chai, H. Yoo and G. H. Pollack, J. Phys. Chem. B, 2009, 113, 13953–13958.
[2] D. Florea, S. Musa, J. M. R. Huyghe and H. M. Wyss, Proc. Natl. Acad. Sci. U. S. A., 2014, 111, 6554–6559.
[3] M. J. Esplandiu, D. Reguera, J. Fraxedas, Soft matter 16, 3717-3726, 2020.
[4] M. J. Esplandiu, D. Reguera, Romero-Guzmán, A. Gallardo-Moreno, J. Fraxedas. Nature Comm., 13, 2812, 2022.

Slow dynamics and local structure of water at interfaces

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Recent Molecular dynamics simulation results of the behavior of water at interfaces are discussed for three systems: water in the proximity of a protein, water and trehalose in proximity of a protein, the Lysozyme, and water and premelting-layer/ice in the proximity of an ice nucleating particle (INP), the K-Feldspar, present in the atmosphere. Translational dynamics of the hydration water of a Lysozyme protein upon cooling is studied through the self van Hove function and the mean square displacement [1]. In the deep supercooled region it shows two different temperature activated relaxation mechanisms. The low-temperature hopping regime has a time scale of tenths of nanoseconds and a length scale on the order of 2–3 water shells and it is also present in bulk water. The second hopping regime is active at high temperatures, on the nanoseconds time scale and over distances of nanometers. This regime is connected to water displacements driven by the protein motion and it is observed very clearly at high temperatures and for temperatures higher than the protein dynamical transition. Modification of dynamics in presence of trehalose is discussed [3]. A detailed local structural analysis assessing the difference between the hydration water influenced by the protein and bulk water in terms of high density and low density distribution in local structures is also shown and discussed [2]. Finally results on the local structure of supercooled water and of the premelting layer and ice in vicinity of K-Feldspar with the aim to study the affinity of this INP with ice are shown [4]. This latter system is studied at two different pressures.

REFERENCES

[1] L. Tenuzzo, G. Camisasca and P. Gallo Molecules, 25 (2020) 4570
[2] G. Camisasca, L. Tenuzzo and P. Gallo, in preparation (2022)
[3] G. Camisasca, M. De Marzio and P. Gallo, J. Chem. Phys. 153 (2020) 224503
[4] B.V. Ramirez, L. Lupi and P. Gallo, submitted (2022)

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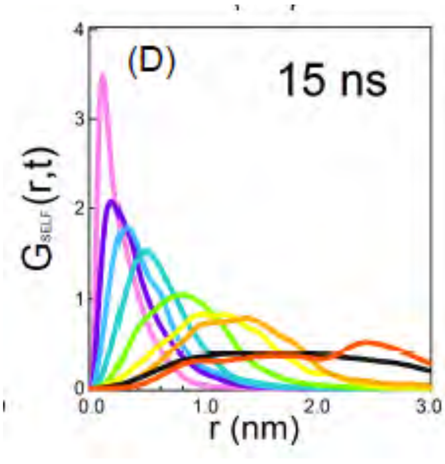

Figure 1: Long time hopping phenomena in the Van Hove Self Correlation Function of Hydration Water in the proximity of lysozyme. The different curves, calculated for time t=15ns, span from T=200 K (Pink curve) to T=300 K.

Role of water mediation on biological and non-biological interfaces

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Abstract

The interactions that water forms with molecules which make up the interfaces of biological and non-biological soft materials play a significant role in the structural and dynamical properties of these interfaces, as well as their interactions with other molecules in their aqueous environment. Recently, my group has combined all-atom molecular dynamics simulations, graph theoretic approaches and machine learning to provide a detailed description of these interactions and how they affect the structure of peptides and various soft interfaces. In this talk, I will discuss how we have used this combination of tools to provide a detailed understanding of how water mediation plays a significant role in the interfacial properties of lipid membranes and polymeric nanoparticles.

REFERENCES

[1] Dabkowska, A. P. et al., Langmuir, 30 (2014) 8803-8811.
[2] Gillams, R. J. et al., J. Chem. Phys. 144 (2016) 225101.
[3] Smith, P. et al., Phys. Chem. Chem. Phys. 21 (2019) 9845-9857.
[4] Ziolek, R. M. et al., Macromolecules 54 (2021) 3755-3768.

Electrochemically Generated Nanobubbles

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Gas evolving reactions are ubiquitous in the operation of electrochemical devices, and can result in the formation of bubbles that block the electrode and decrease reaction rates. The deleterious effect of bubbles is amplified by the current trend of miniaturization of electrodes to nanoscopic sizes, as a single nanobubble can grow to cover the whole reactive area. This presentation will discuss our work using molecular simulations and theory to understand the electrochemical formation an stationary states of bubbles on nanoelectrodes, how the size and shape of the electrodes impact the currents that can be obtained when a bubble forms, and how we can use that knowledge to maximize conversion rates on gas producing electrochemical reactions.[1-4]

REFERENCES

[1] Y. A. Perez Sirkin, E. Gadea, Damian Scherlis, Valeria Molinero, ""Molecular Modeling of the Nucleation of Electrochemically Generated Nanobubbles", *J. Am. Chem. Soc. 141* (2019) 10801-10811

[2] E. D. Gadea, Y. A. Perez Sirkin, V. Molinero, and D. A. Scherlis, "Electrochemically Generated Nanobubbles: Invariance of the Current with Respect to Electrode Size and Potential", J. Phys. Chem. Lett.11 (2020) 6573–6579.

[3] E. D. Gadea, Y. A. Perez Sirkin, V. Molinero, and D. A. Scherlis, in preparation

[4] K. Wang, E. D. Gadea, D. A. Scherlis, and V. Molinero, in preparation

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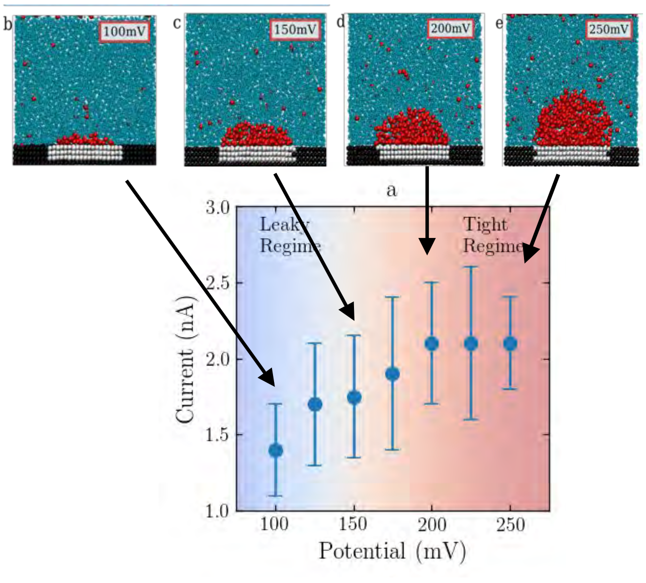

Figure 1: The stationary current of the electrode with a pinned nanobubble has two regimes. The current increases with applied potential at low overpotentials ("leaky" regime) and is constant at large overpotentials ("tight" regime). The size of the stationary bubbles increases monotonously with potential along these two regimes.

Ionic liquids confined in nanopores

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Ionic liquids are mixtures of cations and anions which stay in the liquid state at room conditions, a feature making them potentially ideal electrolytes for energy storage and conversion technologies. In these applications (*e.g.*, supercapacitors) ionic liquids are often found in contact with solid interfaces, or even constrained in pores whose size can be less than a nanometer. In such extreme environments the properties of matter are drastically modified compared to the bulk counterparts.

In this context one can address a primary issue: Does the phase nature of an ionic liquid change when it is confined in pores of nanometric size? The simplicity of this question is misleading. Experiments which probe ionic liquids at the nanoscale, in fact, are extremely difficult[1][2] and sometimes in mutual contradiction, failing so far to provide a generally accepted answer.

I have tackled this issue systematically by massive Molecular Dynamics simulation of a simple model ionic liquid confined in slit nanopores[3]. In this talk I will discuss how, by appropriately tuning size and temperature of the latter, I have revealed unexplored phase modifications. For instance, following an increase of the confinement, I have observed the formation of ionic liquid-crystal structures, which unexpectedly transform into plain stable liquid states and subsequently freeze in new crystal phases, with a remarkable reentrant behavior.

I will also show how these changes reflect on the relative organization of the ions (charges) and on their dynamical state. Building on the simulation results, I will try to provide a consistent general picture of these systems, by involving in the discussion disparate theoretical and experimental inspiring work.

REFERENCES

[1] J. Comtet et al., Nature Materials, 16 (2017) 634
[2] R. Futamura et al., Nature Materials, 16 (2017) 1225
[3] S. Mossa, Physical Review X, 8 (2018) 031062

Thermodynamic properties of water from SAFT and CPA equations of state: Critical assessment

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The performance of eight versions of the representative and most commonly used Statistical-Association-Fluid-Theory (SAFT) equations of state for water along with the Cubic-Plus-Association (CPA) equation are examined in detail both throughout the entire liquid phase region and at supercritical conditions. In addition to the temperature--pressure dependence of density, these response functions, the isothermal compressibility, isobaric heat capacity, and coefficient of isobaric expansivity, have been evaluated and compared with experimental data along five isobars ranging from P=0.1 MPa up to 1000 MPa, and along four isotherms from the melting point up to T=750 K. It turns out that to draw a general conclusion on the quality/accuracy of these equations is practically impossible with different equations predicting reasonably well different properties and at different thermodynamic conditions but failing in other instances. In general, the equations seem to be able to capture simple pressure dependence at isothermal conditions but fail primarily in estimating isobaric properties. All the equations (i) tend to perform reasonably well at pressures above the critical one where the excluded volume begins to predominate and the effect of hydrogen bonding becomes insignificant, (ii) but fail again at very high pressures, and (iii) have the most serious problems with predicting isobaric heat capacity.The most successful results are obtained from the recently developed Association Dependent PC-SAFT equation, which can be mainly attributed to its fitting using a broader set of experimental data compared to other equations; nonetheless, its performance still cannot be considered as overall reliable.

Hidden Mesoscopic Liquids properties: from “static” elasticity to thermo-elasticity

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Thermo-elasticity couples the deformation of an elastic (solid) body to its temperature and vice-versa. It is a solid property. Highlighting such property in liquids is a paradigm shift: it requires long-range collective interactions that are not considered in current liquid or viscoelastic descriptions. We present pioneering studies providing evidence for such solid-like correlations in ordinary fluids. We show that ordinary liquids (glycerol, Polypropylene glycol, liquid water...) emit a modulated thermal hot and cold signal when applying a low frequency (Hz) mechanical shear stress (figure 1) [1]. The thermal wave reaches a sizable amplitude. As consequence, the liquid converts the energy of shear waves in a non-uniform thermodynamic state. These dynamic thermal changes support the hypothesis of the excitation of macroscopic shear elasticity which range is limited to small scale, in accordance with recent non-extensive theoretical models [2,3] and the identification of the generic sub-millimeter shear elasticity revealed in polymer melts, glass formers, ionic liquids and molecular liquids a couple of years ago [4]. It should thus no longer be assumed that liquids exhibit (shear) elasticity at high solicitation frequencies (MHz or GHz) only.

REFERENCES

[1] E. Kume, P. Baroni & L. Noirez, Strain-induced violation of temperature uniformity in mesoscale liquids. Scientific Reports (2020) 10, 13340 doi: 10.1038/s41598-020-69404-1.
[2] Zaccone, A.; Trachenko, K. Explaining the low-frequency shear elasticity of confined liquids. PNAS (2020), 117, 19653–19655.
[3] Alessio Zaccone and Laurence Noirez, Universal G’ ∼ L–3 Law for the Low-Frequency Shear Modulus of Confined Liquids, J. Phys. Chem. Lett. (2021), 12, 1, 650–657.
[4] B.V. Derjaguin, U .Bazaron, K. Zandanova, O. Budaev, O. The complex shear modulus of polymeric and small-molecule liquids. Polymer (1989), 30, 97 – 103.
[5] L. Noirez, H. Mendil-Jakani, P. Baroni, P. Identification of finite shear-elasticity in the liquid state of molecular and polymeric glass-formers. Philosophical Magazine (2011), 91, 1977–1986.
[6] H. Mendil, P. Baroni, L. Noirez, Solid-like rheological response of non-entangled polymers in the molten state. Eur. Phys. J. E 19, 7785 (2006), L. Noirez, P., Baroni, Revealing the solid-like nature of glycerol at ambient temperature. J. Mol. Struct. 972, 16-21 (2010).

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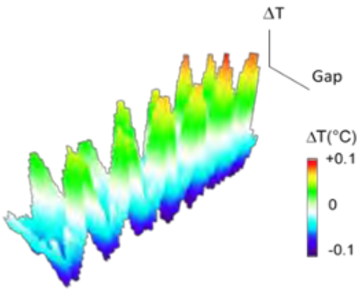

Figure 1: By applying a low frequency mechanical stimulus (⍰ ~ Hz), the liquid emits a modulated thermal signal synchronous with the stimulus (real-time mapping of the temperature of the PPG-4000 confined in a 240µm gap). E. Kume et al, Scie. Reports (2020) 10, 13340.

Information theory tools to study liquid structure

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The study of the structure of disordered phases is inherently complicated. Short range order of liquids is encoded in a six-fold Probability Distribution Function (PDF) which describes the most probable relative position and orientation of two molecules at a given distance. For plastic phases, the degree of complexity is slightly lower since, at least, the molecular position is fixed by a long range ordered crystalline lattice. But still, the relative position of molecules with respect to this lattice, and the relative position of two molecules, i.e. the short range order, must be again encoded in a multi-dimensional PDF.

The aforementioned PDFs, or at least their 2D and 3D projections, can be investigated to provide an exact description of molecular ordering at a given distance. But many of the times we are not interested to investigate the structure at such a level of specificity. That's why we have applied the tools based on Information Theory, such as Shannon entropy, mutual information, or the Kullback-Leibler divergence to the description of disordered phases. These tools allow us to obtain a global description of the structure of disordered phases. Moreover, these calculations guide us to focus on the research of some features of the structure that might be worth to investigate with more detail.

REFERENCES

[1] L. C. Pardo, A. Henao, A. Vispa, J. non-crystalline solids, 407 (2015) 220-2027
[2] A. Henao S. Busch, E. Guàrdia, J. Ll. Tamarit, L. C. Pardo, PCCP, 18 (2016) 19420-19425
[3] A. Henao, D. Angulo-García, G. J. Cuello, P. Negrier, L. C. Pardo, J Mol. Liq., just accepted.

FIGURES

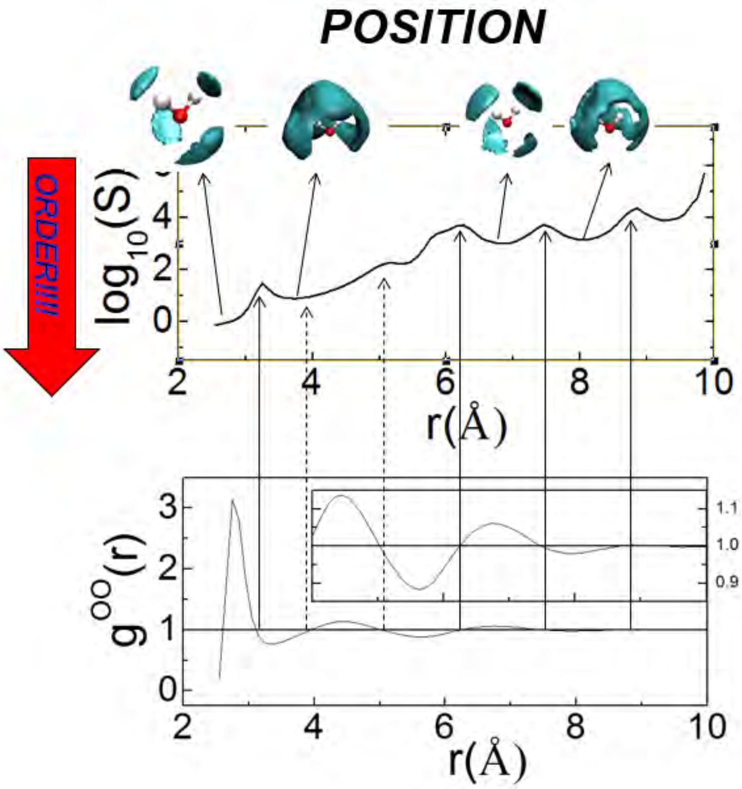

Figure 1: Oxygen - oxygen radial distribution function of water in the lower panel. In the upper panel Shannon entropy related to the positional molecular ordering, together with the 3D-density maps associated to molecular positions.

Solvation and self-assembly of nucleic acids in non-conventional solvents/water mixtures: from the improved structural stability to the formation of ionogels

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Although nucleic acids are considered to be reasonably stable in aqueous solutions, there are several bottlenecks of DNA technology in water as a conventional bulk solvent. Since DNA in aqueous solutions is susceptible to oxidative and hydrolytic denaturation for long-term storage and its helix structure can be damaged by extreme conditions of temperature, pH and ionic strength, finding appropriate media that ensure the long-lasting stability of DNA and help to overcome the limitations of aqueous buffers remains a challenging task. This is a critical point especially for the molecular analysis of DNA in forensic science and biology where it is essential to optimize the storage of the sample to avoid loss of DNA quality. Moreover, this vulnerability limits the use of nucleic acids as building blocks for realizing innovative devices based on 3D ordered structures of DNA and hybrid materials in nanotechnology and biomedical technology. Using nucleic acids in non-conventional solvents such as Ionic liquids (ILs) and deep eutectic solvents (DESs) offers a promising alternative to organic solvents both for stabilizing and preserving the native structure of DNA in solution over the long term and for designing innovative DNA nano-systems such as thermo-reversible ionogels with an unprecedented degree of freedom. This is thanks to the unique capacity of both these molecular liquids in acting as electrolytes and solvents. Additionally, when ILs and DESs are mixed with water, the resulting mixtures exhibit some interesting and unique properties that make them capable of behaving as functional fluids in DNA science [1-4]. In this contribution, we will address the question of the effectiveness of ILs versus DESs, in mixture with water, for the solvation and self-assembly of oligonucleotides and large nucleic acids. Even these molecular liquids are claimed to have similar physicochemical properties, recent studies evidenced that ILs and DESs exhibit substantial differences in the solvation behavior of bio-macromolecules such as DNA. The joint combination of advanced spectroscopic techniques such as synchrotron radiation-UV Resonance Raman spectroscopy (SR-UVRR) and molecular dynamics (MD) simulations enables the measurement of experimental quantities directly related to pair hydrogen bond strength and base stacking forces in nucleic acid strands and the probing of structure specific interactions between the solvent and different sites of DNA. This approach allows to detect defined structural transitions of DNA that involve specific base-tracts during thermal unfolding pathway and to give a comprehensive description of the self-assembly mechanism leading to the formation of nucleic acid hydrogels. Overall these experimental-computational studies reveal a more effective thermal-protective effect operated by hydrated choline-based DESs on the double-helix structure of DNA respect to imidazolium-based ILs. This finding has been related to the establishment of preferential H-bonds interactions between specific DES moieties and the guanine and adenine bases in the DNA groove that lead to a more effective stacking between of these bases even at high temperature values. These results could facilitate the designing of effective stabilizing eco-friendly organic co-solvents for their exploitation in biomedical and life science field.

REFERENCES

[1] C. Bottari, S. Catalini, P. Foggi, I. Mancini, A. Mele, D. R. Perinelli, A. Paciaroni, A, Gessini, C. Masciovecchio, B. Rossi, J. Mol. Liq. 330 (2021) 115433

[2] B. Rossi, M. Tortora, S. Catalini, J. Vigna, I. Mancini, A. Gessini, C. Masciovecchio, A. Mele, Phys. Chem. Chem. Phys. 23 (2021) 15980

[3] M. Tortora, J. Vigna, I. Mancini, A. Mele, A. Gessini, C. Masciovecchio, B. Rossi, Crystals 11 (2021), 1057

[4] F. Fadaei, M. Tortora, A. Gessini, C. Masciovecchio, S. Catalini, J. Vigna, I. Mancini, A. Mele, J. Vacek, D. Reha, B. Minofar, B. Rossi, J. Mol. Liq. 347 (2022), 118350

Design of novel hybrid graphene oxide membranes for water treatment

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Membrane filtration is an attractive technique to secure clean water in an energy efficient manner. In recent years, graphene-derivatives membranes are emerging as attractive candidates for efficient water treatment, attributed to their unique nanochannel networks and robust chemical and mechanical stability [1]. In particular, graphene oxide (GO) is regarded as a versatile platform for separating ions or contaminants, with the possibility of regulating the nanochannels through approaches such as cross-linking, pressure compression and molecular intercalation [2,3], establishing an energy barrier originated from steric hindrance and electrostatic repulsion during permeation. Optimal interlayer spacing combined with appropriate charges could make possible attaining outstanding performance in terms of both parameters.

As part of the collaborative project between KAIST and KU, we have developed novel hybrid GO membranes for water desalination [3,4], following two different strategies: (1) Complexion of crown ethers and cation-intercalated GO composite membranes to tune the GO nanochannel for an effective desalination, and (2) Forming amide-bonded polymer-crosslinked structures with controllable compressed and charged nanochannels. A combined experimental – molecular modeling approach was followed in both cases. Following the first strategy, stable structures were found in which salt rejection rate could be increased up to 60% compared to the neat GO membrane, simultaneously achieving the adequate water permeance. In the second strategy, a simple pressurization process was used to adjust the interlayer distance of the polymer-intercalated GO structure, which varied the relative interaction distance of inserted molecules in nanochannels and the H-bond network inside them. The compressed channels cause a change in the polymer morphology during the insertion, forming different numbers of amide bonds; thus, obtaining narrower interlayer distances and simultaneously obtaining zwitterionic properties in the nanocapillaries. In this case, the salt diffusion rate was slower down up to 5 times compared to the neat GO membrane due to the modified channel, while maintaining a similar water flux.

Overall, it is inferred from these studies that interlayer spacing and appropriate membrane electrostatic properties can be controlled based on molecules intercalation, while making possible attaining outstanding performance of hybrid GO membranes in terms of water permeability and ions rejection. This methodology can also be implemented for the removal of recalcitrant contaminants, including dyes and pharmaceuticals.

This work has been developed as collaborative project between KAIST (project 2018R1D1A1B07048233) and Khalifa University, (RC2-2019-007).

REFERENCES

[1] Geim AK, Novoselov KS. Nat Mater 6 (2007) 183-191.
[2] Bang KR, Bahamon D, Vega LF, Cho ES. Adv Mater Interfaces 7 (2020) 1901876.
[3] Li W, Wu W, Li Z. ACS Nano 12 (2018) 9309-9317.
[4] Bang KR, Bahamon D, Vega LF, Cho ES. Environm. Sci.: Nano 8 (2021) 3312–3321.

FIGURES

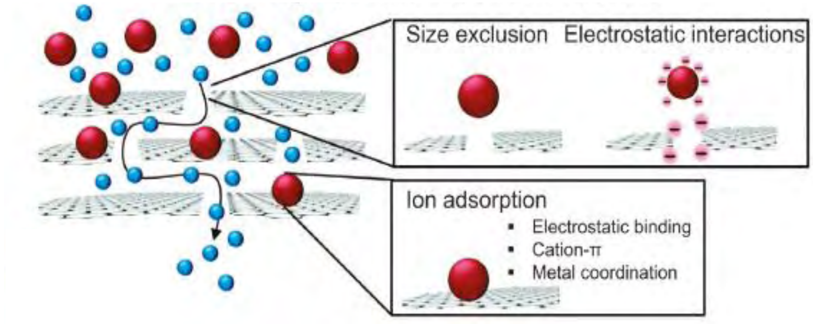

Figure 1: Schematic of the strategies followed for designing effective hybrid GO membranes for water desalination

The Madrid force field for electrolytes in water and some thoughts on our understanding of the dielectric constant in computer simulations

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In this work, we present the Madrid force field [1,2,3] for electrolytes in water . The force-field, denoted as Madrid-2019, does not include polarizability and uses the TIP4P/2005 [4] model of water and scaled charges for the ions. A charge of ±0.85e is assigned to monovalent ions. This new force field developed provides an accurate description of aqueous solution densities over a wide range of concentrations up to the solubility limit of each salt studied. The model is able to describe 35 different electrolytes. Good predictions of viscosity and diffusion coefficients are obtained for concentrations below 2 m. Structural properties obtained with this force field are also in reasonable agreement with the experiment. The number of contact ion pairs has been controlled to be low so as to avoid precipitation of the system at concentrations close to the experimental solubility limit. With this force field we estimate the freezing point depression [5] and the shift in the maximum in density provoked by the presence of the electrolytes [6] (including new experimental results in this case). The impact of the presence of salts on ice nucleation will be discussed [7]. Finally we shall discuss the role of the dielectric constant in computer simulations, and why it is a property absolutely different from the rest of properties determined in computer simulations. In our opinion, we have not properly understood its singular character in the past, and it is time to reformulate the problem properly [8].

REFERENCES

[1] A.L.Benavides et al., J.Chem.Phys.,147,104501,(2017)
[2] I. M. Zeron, J. L. F. Abascal, and C. Vega, J. Chem. Phys. 151, 134504 (2019).
[3] S. Blazquez, M. M. Conde, J. L. F. Abascal and C. Vega, J. Chem. Phys., 156, 044505,(2022).
[4] J. L. F. Abascal and C. Vega, J. Chem. Phys. 123, 234505 (2005).
[5] C.P.Lamas,C.Vega and E.G.Noya, J.Chem.Phys.,156,134503,(2022)
[6] L.F.Sedano,S.Blazquez,E.G.Noya,C.Vega and J.Troncoso,J.Chem.Phys.,156,154502,(2022)
[7] G.D.Soria, J.R.Espinosa,J.Ramirez,C.Valeriani,C.Vega and E.Sanz, J.Chem.Phys.,148,222811,(2018)
[8] C.Vega, Mol.Phys., 113,1145,(2015)

A Nanoscale Shape-Discovery Framework Supporting Systematic Investigations of Shape-Dependent Biological Effects and Immunomodulation

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Since it is now possible to make, in a controlled fashion, an almost unlimited variety of nanostructure shapes, it is of increasing interest to understand the forms of biological control that nanoscale shape allows. However, a priori rational investigation of such a vast universe of shapes appears to present intractable fundamental and practical challenges. This has limited the useful systematic investigation of their biological interactions and the development of innovative nanoscale shape-dependent therapies. Here, we introduce a concept of biologically relevant inductive nanoscale shape discovery and evaluation that is ideally suited to, and will ultimately become, a vehicle for machine learning discovery. Combining the reproducibility and tunability of microfluidic flow nanochemistry syntheses, quantitative computational shape analysis, and iterative feedback from biological responses in vitro and in vivo, we show that these challenges can be mastered, allowing shape biology to be explored within accepted scientific and biomedical research paradigms. Early applications identify significant forms of shape-induced biological and adjuvant-like immunological control.

REFERENCES

Zhang W, Lopez H, Boselli L, Bigini P, Perez-Potti A...16 more, *ACS Nano* 2022, 16, 1, 1547–1559

FIGURES

Typical at glance but interesting when analyzed in detail: The story of Tris hydration

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Tris (2-amino-2-hydroxymethylpropane-1,3-diol), a well-known buffer component, has been recently considered as a promising absorbent in wet-CO_2 absorption technology [1]. A 30% Tris solution in water exhibits a CO_2 absorbing capacity comparable to aqueous monoethanolamine of the same concentration [2]. In addition, Tris is a cheap, non-toxic, non-volatile and non-flammable substance, which allows overcoming significant disadvantages of liquid amines commonly used in the industrial CO_2 sequestration cycles.

In the present work we show the results of dielectric relaxation spectroscopy of aqueous Tris solutions covering concentrations up to its solubility limit ($c \approx 3.3$ mol dm^{-3}) and frequencies from 50 MHz to 89 GHz. We show that the dielectric spectra can be best fit by a sum of 1 Cole-Cole and two Debye modes arising from the solute- and solvent-associated relaxations, respectively. The analysis of the amplitudes reveals that a Tris molecule is hydrated by ~7 H_2O molecules over the entire concentration range. Indeed, hydrodynamics friction coefficients extracted from Tris reorientation times indicate rather strong interactions between the solute and its near solvent surrounding. However, according to the size and structure of a Tris molecule and taking into account hydration patterns of previously studied solutes [3-5] it is very unlikely that all 7 H_2O molecules interact with Tris stronger than with each other. To get more information on the type of solute-solvent and solvent-solvent interactions in the Tris/water system, the dielectric spectra were described by a superposition of 4 Debye relaxations with the slowest mode arising from reorientation of the solute, the second slowest from dynamically retarded hydration water and the two fastest modes assigned to bulk (rather unperturbed) water. Analysis of the data within the framework of this model indicates that although Tris indeed slows down ~7-8 H_2O molecules their interaction strength with the solute is rather weak compared to their inherent H-bonds. Additionally, the results of quantum chemical calculations performed in the spirit of the step-by-step thermodynamics of hydration strongly support the findings of dielectric spectroscopy.

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REFERENCES

[1] F. Bougie, M.C. Iliuta, Chem. Eng. Sci., 1 (2009) 153.
[2] J.-Y. Park, J. Yoon, H. Lee, J.-H. Yoon, J.-G. Shim, J.K. Lee, B.-Y. Min, H.-M. Eum, J. Chem. Eng. Data, 4 (2002) 970.
[3] J. Hunger, K.-J. Tielrooij, R. Buchner, M. Bonn, H.J. Bakker, J. Phys. Chem. B, 16 (2012) 4783.
[4] V. Agieienko, R. Buchner, Phys. Chem. Chem. Phys, 4 (2016) 2597.
[5] V. Agieienko, C. Hölzl, D. Horinek, R. Buchner, J. Phys. Chem. B., 22 (2018) 5972.

Statistical Mechanics Study of Strong Attraction between Like-Charged Particles in an Electrolyte Solution

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Negatively charged particles repel each other in a vacuum. However, they are not necessarily repulsive under any conditions. The effective attraction between like-charged particles has been observed in an electrolyte solution. Zhang et al. showed the effective attraction experimentally and indicated important progress regarding the ion-specific effects on proteins [1-3]. The results go beyond generic Hofmeister interactions. In their experiments, the like-charged particles were acidic proteins which were negatively charged particles, and the electrolyte solution had multivalent cations, such as Y3+. The effective attraction appeared only under certain electrolyte concentrations. So, the electrolyte concentration dependence of the interaction showed a reentrant behavior. In a dilute electrolyte concentration, the effective interaction was repulsive. And the strong attraction appeared when the concentration became higher. However, the strong attraction disappeared if they added more electrolytes to the solution. The effective attraction and the reentrant behaviors are not only interesting in the phase behaviors of the protein solution but also important properties in the crystallization of protein.

We calculated the effective interaction between like-charged particles using the integral equation theory, such as the HNC-OZ equations[4]. The numerical solutions showed the reentrant behavior when the Coulomb interaction was dominant. The correlation functions suggested that the cations mediated the effective attraction between negatively charged particles. When the cations localize at mediation site A (See Fig. 1), the cations attract negatively charged particles. The small anions are excluded from site A due to the direct Coulomb repulsion. Thus, the effective interaction depends on the local density of the cation at site A. The effective interaction becomes attractive when the total attractive interaction becomes larger than the repulsive interaction between the negatively charged particles. We confirmed this story of the reentrant behavior based on the correlation functions obtained by the integral equation theory.

The strong attraction and the reentrant behavior have been explained based on the Coulomb interaction. On the other hand, solvent granularity strongly assists the behaviors[5]. We examined explicit and implicit solvent models. The calculated results indicated that the solvent granularity enhanced the effective attraction, and the reentrant behavior became clearer. This assistance is not a simple depletion force between macroanions. We analyzed this enhancement mechanism based on the calculated correlation functions. The results showed that the depletion force induced by the solvent granularity enhanced the effective attraction between a macroanion and a cation. However, the enhancement is not significant. Indeed, the increased amount is almost similar to that of the uncharged system, and we can estimate the increase using the Asakura-Oosawa theory. However, this minor enhancement leads to the significant enhancement of the effective attraction between macroanions because of the minor increase of local density as site A, namely the mediation site of the effective attraction.

We also studied the effects of cation exchange[6] and ionic sizes[7] using the HNC-OZ theory. And we discussed the phase diagrams [8]. We are also calculating the effective interaction using molecular simulations. In this presentation, we will review these results. And we will discuss the effect of solvent granularity and some new results.

REFERENCES

[1] F. Zhang, M. W. A. Skoda, R. M. J. Jacobs, S. Zorn, R. A. Martin, G. F. Clark, S. Weggler, A. Hildebrandt, O. Kohlbacher, and F. Schreiber, Phys. Rev. Lett. 101 (2008) 148101.

[2] F. Zhang, S. Weggler, M. J. Ziller, L. Ianeselli, B. S. Heck, A. Hildebrandt, O. Kohlbacher, M. W. A. Skoda, R. M. J. Jacobs, and F. Schreiber, Proteins 78 (2010) 3450.

[3] M. K. Braun, M. Wolf, O. Matsarskaia, S. Da Vela, F. Roosen-Runge, M. Sztucki, R. Roth, F. Zhang, and F. Schreiber, J. Phys. Chem. B 121 (2017) 1731.

[4] R. Akiyama, R. Sakata, J. Phys. Soc. Jpn., 80 (2011) 123602.

[5] A. Suematsu, and R. Akiyama, J. Chem. Phys., 154 (2021) 034902.

[6] S. Fujihara, and R. Akiyama, J. Mol. Liq., 200 (2014) 89-94.

[7] A. Suematsu, T. Sawayama, and R. Akiyama, J. Chem. Phys. 149 (2018) 074105

[8] Y. Tamura, A. Yoshimori, A. Suematsu, and R. Akiyama, EPL(Europhysics Letters), 129 (2020) 66001.

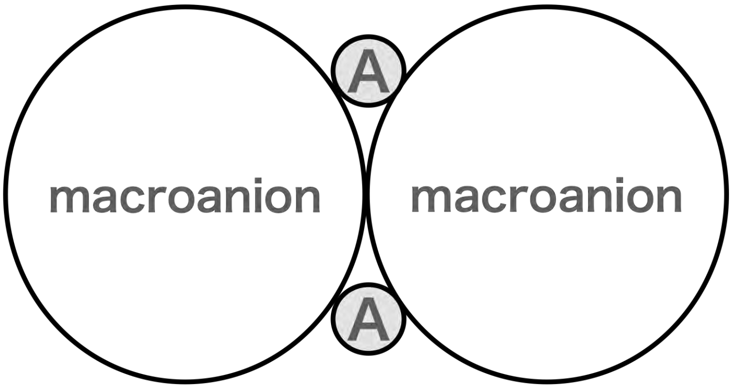

Figure 1: Schematic diagram illustrating the association of two macroanions. The cations are localized at site A due to the Coulomb interaction. The macroanions effectively attract each other when the attraction mediated by the cations is stronger than the direct Coulomb repulsion between the macroanions. This is similar to a classical picture of the covalent bond.

Nuclear quantum effects: their relevance in topology of hydrogen bonded network and diffraction studies of hydrogen bonded liquids

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0It is well established for molecular liquids that can form hydrogen bonds (HB, H-bond) that their structutural and dynamical properties depend on nuclear quantum effects (NQE), too Differences in terms of density, dynamic and thermodynamic properties between deuterated and hydrogenated forms of many liquids are well known, while the nature of deviations in terms of the atomic structure can be quite complex. The main goal of the present work is to shed some light on the structural aspects at leas three different aspect.

1. The proper description of NQE effect on intra and intermolecular radial distribution function
2. Proper validation of isotopic substitution method in neutron diffraction.
3. NQE effect on different topological properties of Hydrogen bonded liquids. These properties can represented the local topological arrangements (Local structure index, tetrahedrality …) or the cooperative behaviour of hydrogen bonded network. It would be also shown a significantly different behaviour exist in the simulations, which are incorporated the effect of polarizability (AIMD, AMOEBA)

Additionally based on extensive benchmark studies between our newly developed method (’Generalized Smoothed Trajectory Analysis’ (GSTA)1,2) GSTA filtered and PIMD simulation results, reasonably good agreement between the two methods is presented.

1. Berta, D., Ferenc, D., Bakó, I., Madarász, Á., Nuclear Quantum Effects from the Analysis of Smoothed Trajectories: Pilot Study for Water J. Chem. Theory Comput. 2020, 16, 3316
2. Imre Bakó, Ádám Madarász, László Pusztai Nuclear quantum effects: their relevance in neutron diffraction studies of liquid water J. Mol. Liq.2021, 325 115192

Computer simulation of the carbon dioxide hydrate – water interfacial free energy

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Carbon dioxide hydrates are ice-like nonstoichiometric inclusion solid compounds with importance to global climate change, and gas transportation and storage [1]. The thermodynamic and kinetic mechanisms that control carbon dioxide nucleation critically depend on hydrate-water interfacial free energy. Only two independent indirect experiments are available in the literature [2,3]. Interfacial energies show large uncertainties and overestimated values due to the conditions at which experiments are performed. Under these circumstances, computer simulation tools over a way to estimate interfacial energies at coexistence conditions from a molecular perspective. We propose a novel implementation of a computational methodology based on the definition of interfacial energy [4] and the use of realistic and reliable models of water (TIP4P/Ice) [5] and carbon dioxide (TraPPE) [6] that have proven to predict accurately the ice-water interfacial energy and the dissociation line of carbon dioxide hydrates [7]. We found that simulations provide an interfacial energy value, at coexistence conditions, consistent with the experiments [2,3] from its thermodynamic definition [8]. This is the first calculation of the CO_2 hydrate interfacial energy using molecular dynamics simulations at coexistence conditions from fundamental principles, including the definition of interfacial free energy, Thermodynamics, and Statistical Mechanics. This pioneering work opens a door to estimate accurate interfacial energies of hydrates from a molecular perspective [8].

REFERENCES

[1] E. D. Sloan and C. Koh, Clathrate Hydrates of Natural Gases, 3rd Edition, CRC Press, New York (2008).
[2] T. Uchida, T. Ebinuma, S. Takeya, J. Nagao and H. Narita, *J. Phys. Chem. B* 106 (2002) 802.
[3] R. Anderson, M. Llamedo, B. Tohihi and R. W. Burgass, *J. Phys. Chem. B* 107 (2003) 3507.
[4] J. R. Espinosa, C. Vega, and E. Sanz, *J. Phys. Chem. C* 120 (2016), 8068.
[5] J. L. F. Abascal, E. Sanz, R. G. Fernández, and C. Vega, *J. Chem. Phys.* 122, (2005) 234511.
[6] J. J. Potoff and J. I. Siepmann, *AIChE Journal* 47 (2001) 1676.
[7] J. M. Míguez, M. M. Conde, J.-P. Torré, F. J. Blas, M. M. Piñeiro and C. Vega, *J. Chem. Phys.* 142 (2005) 124505.
[8] J. Algaba, E. Acuña, J. M. Míguez, B. Mendiboure, I. M. Zerón, and F. J. Blas, *J. Colloid and Interface Sci.* (in press).

Hydration of the Neurotransmitter γ-Aminobutyric Acid and its Isomer α-Aminobutyric Acid

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Upon release by the pre-synaptic cell, neurotransmitters (NTs) ensure unidirectional signal transport in living organisms by diffusion across the synaptic cleft connecting two neurons or joining a muscle cell and a neuron, followed by subsequent binding to an appropriate post-synaptic receptor. NT diffusion, interaction with the phospholipid cell membrane, and binding to the receptor strongly depend on NT hydration [1]. Whilst numerous investigations on NT-receptor interactions can be found, surprisingly little is known on NT-H_2O interactions. With this communication we extend our previous studies devoted to acetylcholine (a cation) [2] and glutamate (an anion with additional zwitterionic moiety) [3] to the zwitterionic NT γ-aminobutyric acid (GABA).

The extremely water-soluble (~12.6 mol/kg) GABA is the predominant inhibitory NT regulating neural activities in the mammalian central nervous system and crucial for the mental and physical health of humans [4]. This contrasts with the behaviour of its structural isomer α-aminobutyric acid (AABA), which is only moderately soluble (~2.2 mol/kg), does not act as a neurotransmitter and is thought to be of only minor pharmacological importance.

We used dielectric relaxation spectroscopy (DRS) in the microwave region to characterize the cooperative dynamics of aqueous GABA and AABA solutions up to the saturation limit. The thus obtained total effective hydration numbers, Z_t, could be split into contributions of Z_{ib} strongly and Z_s moderately bound H_2O molecules. 1D- and 3D-RISM calculations were used to locate these hydrating water molecules in the primary hydration shells of GABA and AABA, revealing fairly different hydration patterns for both solutes.

REFERENCES

[1] P. A. Postila and T. Róg, Mol. Neurobiol., 57 (2020) 910.
[2] S. Friesen, M.V. Fedotova, S.E. Kruchinin, M. Bešter-Rogač, Č. Podlipnik, and R. Buchner, Phys. Chem. Chem. Phys., 23 (2021) 25086.
[3] S. Friesen, M.V. Fedotova, S.E. Kruchinin, and R. Buchner, Phys. Chem. Chem. Phys., 23 (2021) 1590.
[4] P.V. Ramachandran and A. Shekar, Future Med. Chem., 3 (2011) 139.

When Like-charged Ions Attract: Controlling the Size and Distribution of Cation Clusters in Ionic Liquids by Adding Molecular OH-catchers

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Attraction between opposite-charged and repulsion between like-charged particles is a commonly accepted concept in science. In contrast, like-charged attraction seems to be counterintuitive at first glance. Unexpectedly, the formation of cation clusters in ionic liquids with specifically designed OH-functionalized cations was observed at room temperature. [1-4] These clusters are formed via hydrogen bonding between the hydroxyl groups terminating the alkyl chains of the cation and strongly affect the structural and dynamical properties of those materials.

By utilising neutron diffraction experiments as well as molecular dynamics simulations, we probe the liquid nanostructures of the IL [HOC_4Py][NTf_2] in mixtures with the molecular liquid DMSO. The latter acts as an OH-catcher through its strong proton acceptor S=O group, controlling the delicate balance of cation-anion and cation-cation cluster distributions. We observe three types of hydrogen bonding situations in one solution, indicated by their characteristic bond lengths (H···O) and (O···O. Moreover, we address the important question, whether DMSO prefers to catch the hydroxyl groups of the cation-anion or the cation-cation clusters. The study is aimed at a better understanding of the relationship between clusters and larger scale nanostructures.

REFERENCES

[1] A. Knorr et al., Phys. Chem. Chem. Phys. 17 (2015) 30978.
[2] A. Knorr, R. Ludwig, Sci. Rep. 5 (2015) 17505.
[3] A. Knorr et al., ChemPhysChem 17 (2016) 458.
[4] A. Strate, T. Niemann, R. Ludwig, Phys. Chem. Chem. Phys. 19 (2017) 18854.

FIGURES

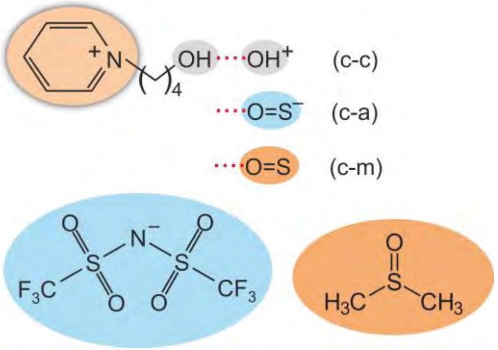

Figure 1: Three possible types of hydrogen bonding by diluting the IL [HOC_4Py][NTf_2] with DMSO

Metastable Confinement of Molecular Hydrogen in Double Wall Carbon Nanotubes bundles

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Carbon nanostructured materials are regarded to have high potential for the storage and management of H_2 at cryogenic temperatures, and so they are of an outstanding practical importance. H_2 has many advantages as energy vector but an efficient storage is technologically challenging since the needed physical conditions are demanding even at a theoretical level. For instance, the strong quantum character of the H_2 molecule and its condensates leads to theoretically unexpected behaviours under confinement [1]. During our search for materials and processes of interest in energy applications, we have observed isothermal large hysteretic hydrogen adsorption in samples made out of Double Wall Carbon Nanotubes bundles at 50 K, 77 K and 150 K and up to 15 bar of pressure (see Figure 1). Adsorption metastability opens remarkable possibilities: it can be used to lower the working pressure for a given uptake; to increase the usable capacity; or to facilitate thermal management – see Ref. [2] for the analogous situation with methane. The case of metastable H_2 adsorption has been barely explored, mostly in the context of Metal-Organic Frameworks (MOFs) as adsorbents [3] and linked to structural deformations of the frameworks. For nanostructured carbons, hysteresis has been associated with chemisorption in metallic particles [4], characterized by undesirably high desorption energy barriers. In order to gain information about the microscopic spatial structure and dynamics of the observed phenomenon we made a series of inelastic neutron scattering measurements at various temperatures and H_2 loads. The elastic signals (diffraction) at different H_2 loads are consistent with the uptake of the H_2 within the interstitials of the bundles. The quasielastic signal (centred around the null energy transfer) display an anomalous dependence on momentum transfer (i.e., in spatial correlations) which is nicely reproduced by an accurate 1D dimensional diffusion model (as expected from interstitial confinement of the H_2 fluid) while the complete inelastic signal precludes the possibility of chemisorption onto the sample metallic impurities. Once discarded a chemisorption mechanism, we developed a 2D dimensional model that allowed us to restrict the parameters space and the computational times to a feasible size (Figure 2). The 2D model reveals a narrow range of microscopic parameters where the hysteresis shows up as the same time nicely reproducing the qualitative behaviour of the real system. The metastability emerges as consequence of the hierarchical structure of energy barriers, a structure that is sensitive to the H_2 uptake through the expansion/contraction of the bundle configuration. Preliminary neutron diffraction results confirm the appearance of this structural hysteresis validating the proposed microscopic mechanisms responsible for the metastability.

REFERENCES

1. C. Cabrillo *et al*, Carbon, 175 (2021) 141.
2. A. Mason *et al*, Nature, 527 (2015) 357.

3. A. D. P. Broom *et al,* Applied Physics A, 122 (2016) 151.
4. S. H. Barghi, T. Tsotsis & M. Sahimi, International Journal of Hydrogen Energy, 39 (2014) 1390 .

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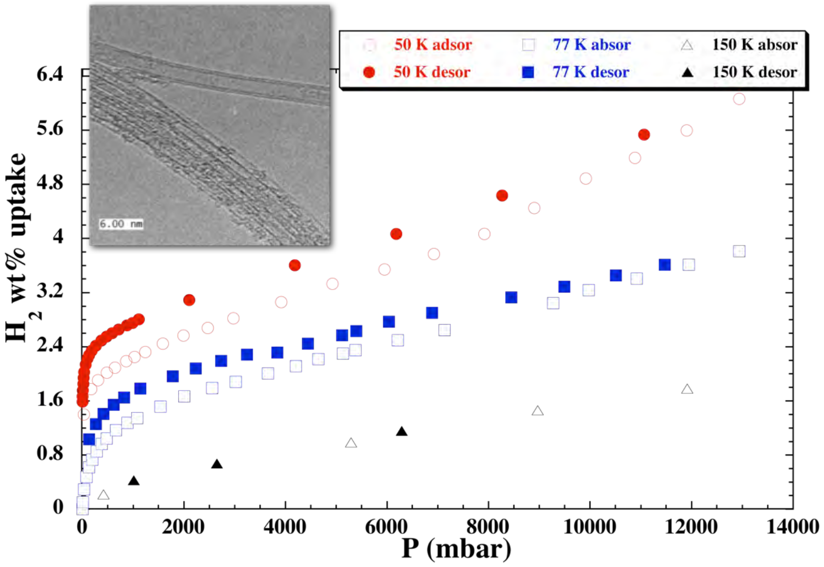

Figure 1: Isothermal H_2 adsorption/desorption cycles in DWCTNs bundles at 50 K, 77 K and 150 K. In the superimposed picture at the left-up corner a transmission electron microscopy image of one of the bundles is shown.

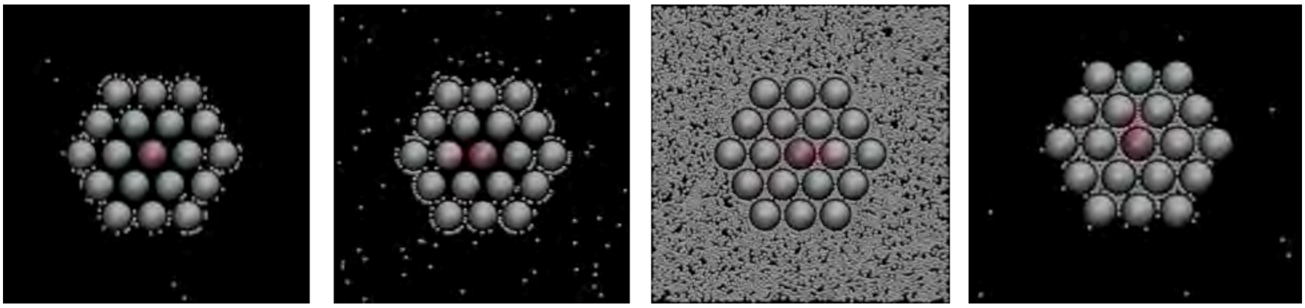

Figure 2: Snapshots of the two-dimensional uptake of H_2 molecular discs (represented by small white spheres) within a bundle of disks (represented by large spheres) along an isothermal adsorption/desorption cycle displaying adsorption hysteresis.

Shear and bulk viscosity of water up to 1.5 GPa

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Liquid water flows under high pressure in the Earth's crust, and is involved in subduction and ore formation. Despite this major role of water in natural processes, viscosity measurements under high pressure are scarce and report conflicting values [1-3]. Here we present shear viscosity data deduced from the Brownian motion of 350 nm polystyrene spheres [4]. Our measurements using a diamond anvil cell extend up to 1.5 GPa, i.e. in the metastable liquid above its freezing pressure. Our results agree with values from [1,2]. By simultaneously recording Brillouin spectra from water, we also obtain the bulk viscosity of the liquid. The ratio of bulk to shear viscosity, nearly constant around 2.75 at low pressure, shows a marked decrease at elevated pressure, exceeding -50%. We compare our results to molecular dynamics simulations with the TIP4P/2005 model.

REFERENCES

[1] E.H. Abramson, Phys. Rev. E, 76 (2007) 051203
[2] R.W. Bowman et al., Phys. Rev. Lett., 110 (2013) 095902
[3] M. Frost and S.H. Glenzer, Appl. Phys. Lett., 116 (2020) 233701
[4] A. Dehaoui, B. Issenmann, and F. Caupin, Proc. Nat. Acad. Sci. USA, 112 (2015)

Role of Surface Chemistry on Protein Conformation at Solid-Liquid Interfaces

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The formation of dense, linear arrays (fibrils) by biomolecules is the hallmark of many degenerative diseases, such as Alzheimer's and type-2 diabetes. Protein fibrils have also attracted interest as building blocks for new materials. It has long been recognised that surfaces can affect the fibrillation process, with the effect of surfaces dependent on both surface chemistry and protein structure[1]. As the behaviour of proteins on surfaces depends on the complex interplay of many different effects (e.g. protein sequence, surface physiochemical properties, protein mobility) and understanding this requires detailed microscopic information. In this presentation work using molecular dynamics simulations the conformation of intrinsically disordered proteins on surfaces will be discussed. This will focus on typical fibril forming proteins, human Islet Amyloid Polypeptide (hIAPP)[2] and amyloid beta fragments[3], on a range of material surfaces. Notably hIAPP adopts largely alpha-helical conformations on hydrophobic surfaces (Figure 1), which are unfavourable for fibril formation. This is consistent with experimental observation that hydrophobic surfaces inhibit hIAPP fibrillation[4]. Understanding the relationship between surface properties and protein conformation can help us decipher the mechanism of protein fibrillation on both naturally-occurring (e.g. cell membrane) and synthetic surfaces.

REFERENCES

[1] A. Keller, G. Grundmeier, *Appl. Surf. Sci.*, **2020**, *506*, 144991
[2] D. L. Cheung, *Biointerphases*, **2020**, *15*, 051001
[3] K. P. Somers, D. L. Cheung, *Biophysica, in press*
[4] R. Hajiraissi, M. Hanke, Y. Yang, B. Duderija, A. Gonzalez Orive, G. Grundmeier, A. Keller, *Langmuir*, **2018**, *34*, 3517

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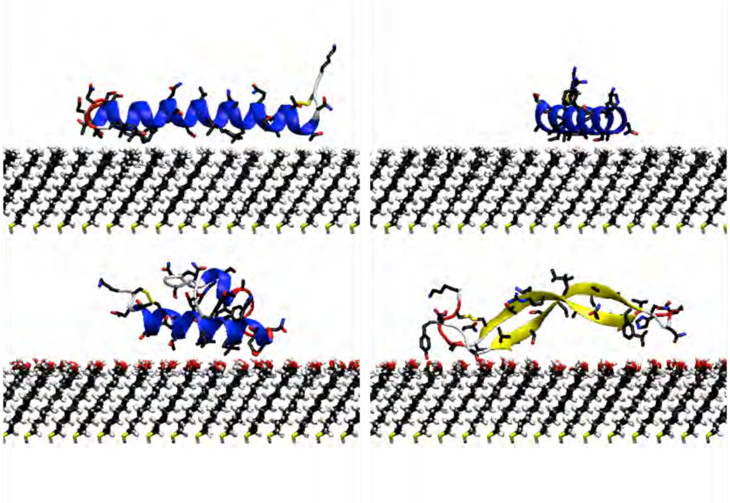

Figure 1: Typical conformation of human Islet Amyloid Polypeptide on hydrophobic (top) and hydrophilic (bottom) surfaces.

Computer simulations of the effect of surfactants to the SARS-CoV-2 virion

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The novel coronavirus SARS-CoV-2 emerged in December 2019 as a human pathogen that causes the COVID-19 pandemic. From the point of view of Soft Matter, this virus is made by a vesicle-like envelope of proteins and lipids of 90 nm of diameter which tightly encapsulate the viral genetic material. The virion particle has a large protruding spike S glycoprotein (24 nm long) that covers the viral particle and give its crown-like characteristic appearance (hence the latin name "corona"). During these two years of pandemic, a wealth of structural information about the viral nanoparticle has been accumulating, including detailed 3D images of the envelope, protein structures with atomistic-resolution and many other molecular and supramolecular details.

In our group, we have been employing this information in two main research line. The first line was to develop atomistic molecular dynamics simulations of the interaction of the virus with materials such as cellulose, graphite, polystyrene or the human skin [1-3] in order to provide physico-chemical basis for questions such as the design of better protective equipment or the possible role of indirect virus transmission. After our success in the study of virus-materials interaction, we have considered the question of the interaction of the virus with common disinfection chemical agents such as surfactants. In spite of the importance of the use of soap as a virucidal agent not only in the particular case of SARS-CoV-2, but for enveloped viruses, little is known about the molecular details of the action of surfactants over an enveloped virus. Questions such as the possible inactivation of the virus (by a coverage or denaturation of the spike protein by surfactants) or the damage of the virus integrity (by opening of a pore or hole at the lipid-protein envelop structure) or even the possibility of virus envelope dissolution are discussed here by Molecular Dynamics simulations. For a general exploration of the relative importance of surfactant characteristics and the relative importance of different interactions (surfactant-lipid envelope or surfactant-protein envelope) we have considered coarse-grain (CG) model of a full virus a CG models of surfactants. For a more detailed exploration in the case of common surfactants, we have considered all-atomic MD simulations of representative patches of the virus envelope (containing a mixture of lipids and membrane M proteins at realistic compositions with and without inserted S protein) in contact with common anionic and cationic surfactants such as SDS and CTAB.

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REFERENCES

[1] D.C. Malaspina and J. Faraudo, Biointerphases 15 (2020), 051008. [Featured article]
[2] M. Domingo and J. Faraudo, Soft Matter 17 (2021) 9457-9468.
[3] M. Sahihi and J. Faraudo (submitted)
[4] A. Yu, A.J. Pak, P. He, V. Monje-Galvan, L. Casalino, Z. Gaieb, A.C. Dommer, R.E. Amaro, G.A. Voth, Biophysical Journal, 120 (2020) 1097-1104.

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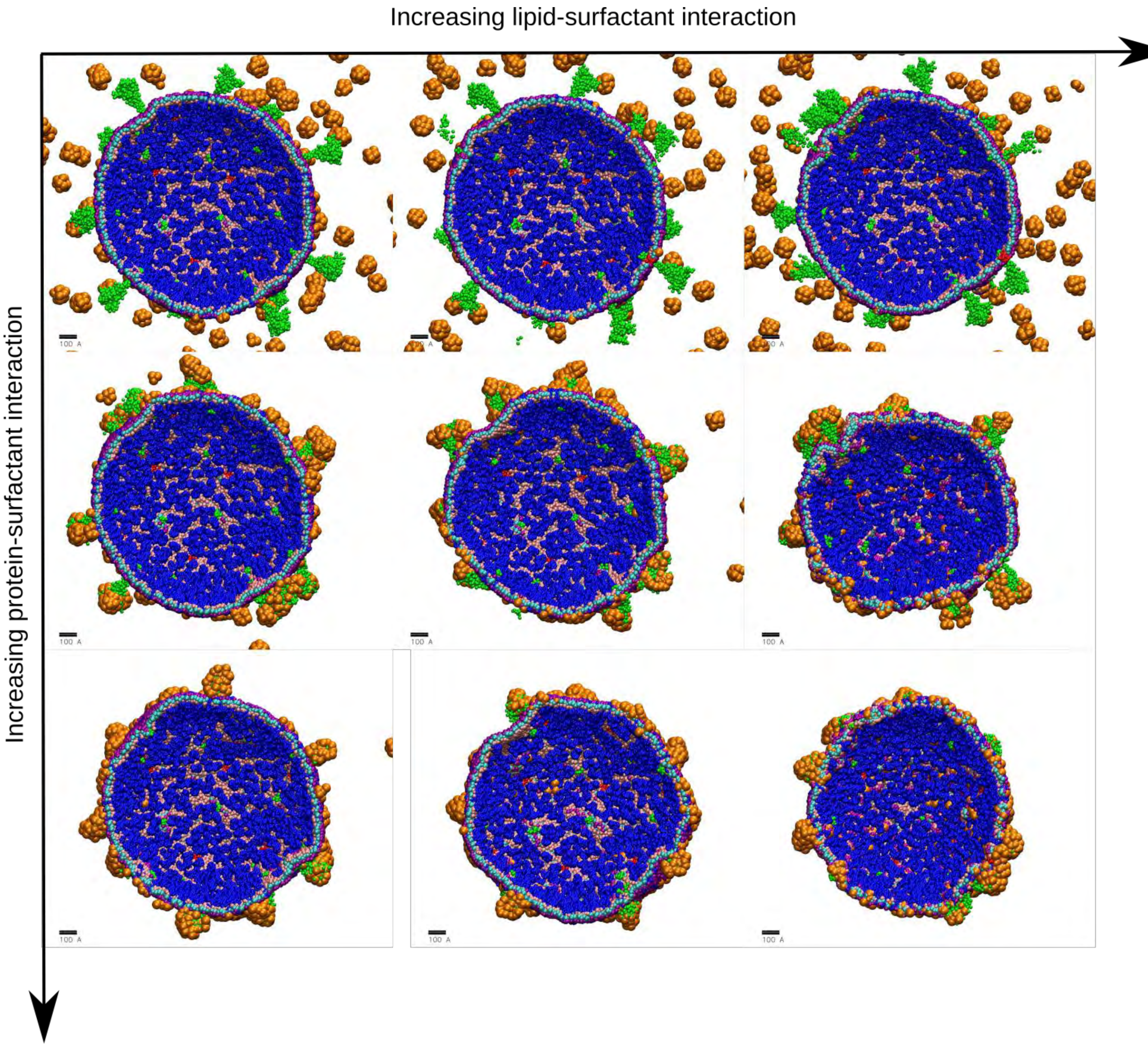

Figure 1: Simulation snapshots showing the effect of surfactant on the structure of a virion particle from CG molecular dynamics simulations for different strengths of the relevant interactions between the surfactants and the virion components. The surfactants are shown in orange, the Spike, M and E virus structural proteins are shown in yellow, blue and red respectively and the different beads of the phospholipids of the envelope are shown in cyan and pink. The scale bar corresponds to 10 nm.

Insight into Molecular Dynamics and Thermodynamics in a Simple Ellipsoidal Model near the Glass Transition via Invariants of Density Scaling

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Since the beginning of this century, the density scaling idea has attracted a lot of interest as bearing hallmarks of universality in the study of the glass transition and related phenomena [1]. The primary advantage of this idea relies on a simple link between macroscopic phenomena near the glass transition and a simple effective short-range intermolecular potential mainly dependent on the inverse power law (IPL) of intermolecular distances. What is important, the IPL exponent is related to the scaling exponent γ, which enables to scale onto one master curve different dynamic quantities X, for instance structural relaxation time and viscosity, as a function of the single variable ρ^{γ}/T (where ρ-density, T-temperature), and can be found from the density scaling criterion,

$$\log_{10}\rho = \gamma\log_{10}T + const(X) \text{ at } X=const \qquad (1)$$

Despite many achievements of this approach, there are some unsolved fundamental problems with its theoretical grounds. The crucial flaw of the most popular theoretical explanation of the density scaling behavior, called the isomorph theory, is its phenomenological character based on many simulation experiments carried out in simple isotropic models based on the Lennard-Jones potential. However, the real molecular shapes are anisotropic in the vast majority, and the anisotropic force fields seem to be much more adequate to model physicochemical properties of such materials. Guided by this premise, very recently we have successfully employed a well-known Gay-Berne (GB) model earlier parametrized to achieve a supercooling and glass transition at zero pressure [2] in order to find the glass transition points and investigate volumetric and dynamic properties in the supercooled liquid state at elevated pressure [3]. In this way, we have been able to explore the density scaling fundamentals in the GB model characterized by the well-defined anisotropy in both the molecular shape and the intermolecular potential. Among other things, we have confirmed that Eq. (1) provides the best method for evaluating the scaling exponent γ, which enables to scale both translational and rotational relaxation times of the supercooled GB liquid (Fig. 1), while the isochoric virial - potential energy correlation promoted by the isomorph theory is not useful in the anisotropic case. Moreover, we have argued that the reduced units of the isomorph theory should not be used to analyze the vast majority experimental data measured in isobaric or isothermal conditions, because these units are not applicable in the isobaric-isothermal statistical ensemble.

In the next step, we have focused on the thermodynamic aspect of the density scaling and its relation to the dynamic one [4]. First, in the supercooled liquid GB model, we have successfully verified the novel invariant earlier reported for molecular glass formers [5], which is the ratio of thermodynamic and dynamic moduli B_T/M_{V-T}, where B_T is the inverse of isothermal compressibility and M_{V-T} is the ratio of isochoric activation energy and activation volume. Consequently, we have discussed the recent suggestions about a state-point dependence of the density scaling exponent γ. Second, we have investigated the molecular anisotropy effect on the role of entropy in the thermodynamic evolution of the time scale of molecular dynamics near the glass transition by comparing our new results obtained from the molecular dynamics simulations in the GB model with our previous investigations of supercooled van der Waals and ionic liquids, and polymer melts [6,7]. Considering the total system entropy S, the configurational system entropy S_{conf}, and the excess system entropy S_{ex}, which is an excess of the ideal gas entropy in the same thermodynamic conditions as the GB liquid is examined, we gain a new insight into the linkage between molecular dynamics and thermodynamics near the glass transition.

REFERENCES

[1] A. Grzybowski, M. Paluch, Universality of Density Scaling. In The Scaling of Relaxation Processes; Eds. F. Kremer, A. Loidl,; Springer International Publishing AG: Berlin/Heidelberg, Germany, (2018) 77–120.

[2] V. Kapko, Z. Zhao, D.V. Matyushov, C.A. Angell, “Ideal glassformers” vs “ideal glasses”: Studies of crystal-free routes to the glassy state by “potential tuning” molecular dynamics, and laboratory calorimetry. J. Chem. Phys. 138 (2013) 12A549.

[3] K. Liszka, A. Grzybowski, K. Koperwas, M. Paluch, Density Scaling of Translational and Rotational Molecular Dynamics in a Simple Ellipsoidal Model near the Glass Transition, Int. J. Mol. Sci. 23 (2022) 4546. https://doi.org/10.3390/ijms23094546

[4] K. Liszka, A. Grzybowski, K. Grzybowska, K. Koperwas, M. Paluch, Invariants of Density Scaling in a Simple Ellipsoidal Model near the Glass Transition (in preparation).

[5] A. Jedrzejowska, A. Grzybowski, M. Paluch, In search of invariants for viscous liquids in the density scaling regime: investigations of dynamic and thermodynamic moduli, Phys. Chem. Chem. Phys. 19 (2017) 18348.

[6] K. Grzybowska, A. Grzybowski, S. Pawlus, J. Pionteck, M. Paluch, Role of entropy in the thermodynamic evolution of the time scale of molecular dynamics near the glass transition, Phys. Rev. E 91 (2015) 062305.

[7] E. Masiewicz, A. Grzybowski, K. Grzybowska, S. Pawlus, J. Pionteck, M. Paluch, Adam-Gibbs model in the density scaling regime and its implications for the configurational entropy scaling, Sci. Rep. 5 (2015) 13998.

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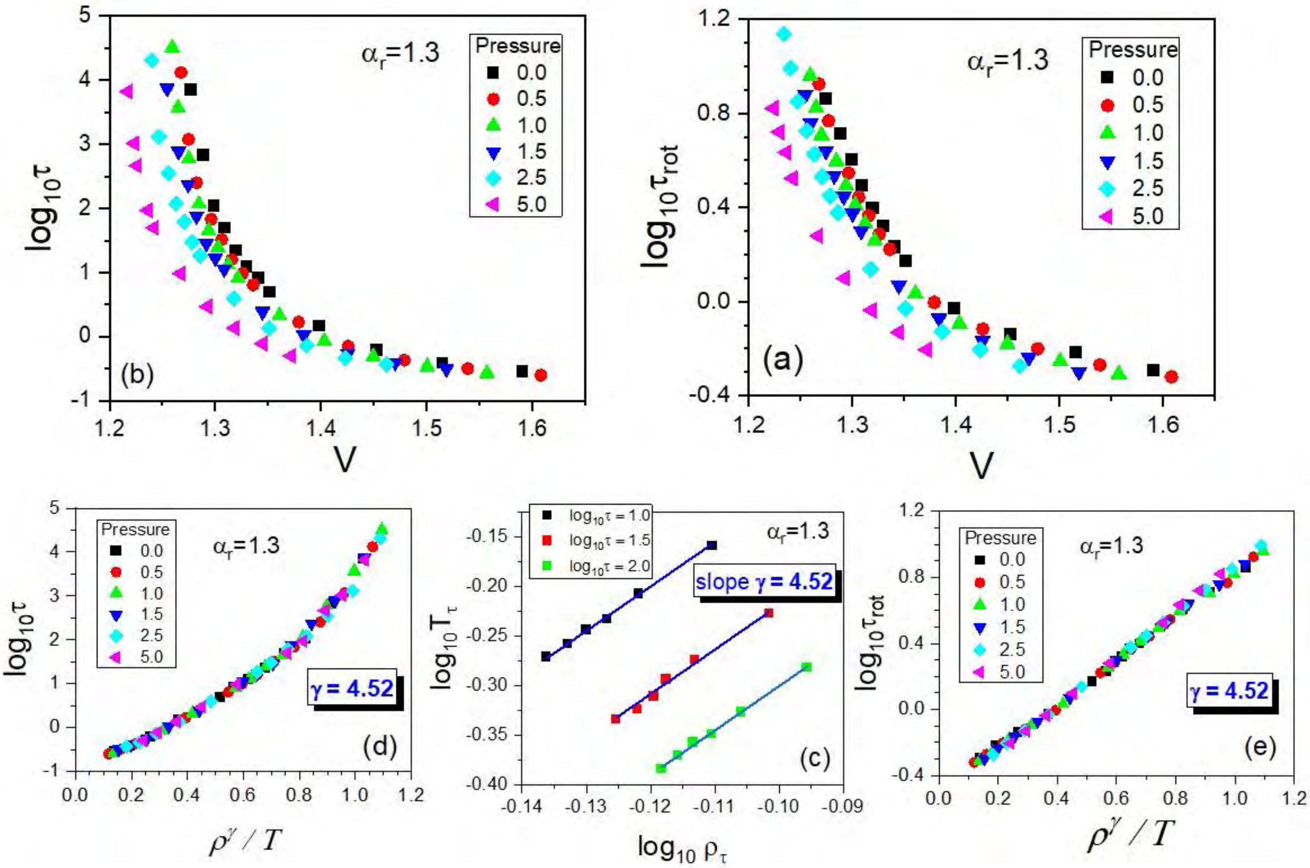

Figure 1: Illustration of the density scaling of translational and rotational relaxation times in the supercooled GB liquid of the anisotropy aspect ratio $\alpha_r = 1.3$. All quantities are in the LJ units. (a) Dependences of translational relaxation times τ on volume V. (b) Dependences of rotational relaxation times τ_{rot} on volume V. (c) Density scaling criterion (Eq. 1) implemented for τ. (d) Density scaling of τ . (e) Density scaling of τ_{rot}.

Associating fluid theory for an explicit hard spherocylinder solvent ionic model in a disordered porous matrix

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We have developed a theoretical approach to describe the thermodynamic properties of the ionic solution modelled by the primitive model with an explicit consideration of the neutral hard spherocylinder solvent. The solution is studied in a disordered porous confinement presented as a uniform dispersion of immobile spherical particles (Figure 1). The proposed theory is based on a combination of two approaches: the scale particle theory for the description of the reference system represented by a mixture of hard spheres and prolate hard spherocylinders immersed in a matrix [1] and the associative mean-spherical approximation for taking into account Coulomb interactions between ions [2]. For the considered solvent explicit model in a matrix, analytical expressions for pressure, free energy and partial chemical potentials are derived for the first time [3]. Using these expressions, the liquid-liquid phase transition is studied, where one phase is enriched with ions and another one – with solvent particles. In the solvent-rich phase, the isotropic-nematic phase transition is observed due to the orientational ordering of the spherocylinder solvent particles at different porosities of a matrix. The effects of the matrix confinement and of the solvent particle elongation on the liquid-liquid and isotropic-nematic phase transitions are studied at different pressures. The role of association phenomena appearing between positively and negatively charged ions in phase behavior of the considered ionic solutions under confinement is discussed.

REFERENCES

[1] M. Hvozd, T. Patsahan, M. Holovko, J. Phys. Chem. B., 122 (2018) 5534.
[2] M. Hvozd, T. Patsahan, O. Patsahan, M. Holovko, J. Mol. Liq., 285 (2019) 244.
[3] M. Hvozd, O. Patsahan, T. Patsahan, M. Holovko, J. Mol. Liq., 346, (2022) 11788.

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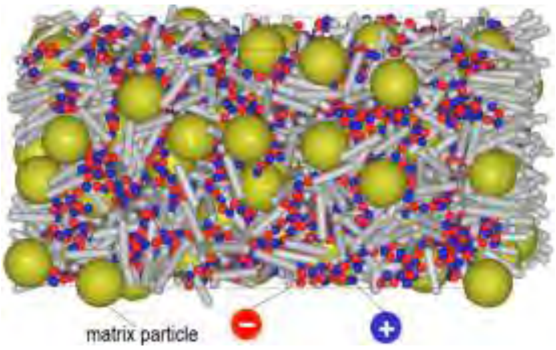

Figure 1: Hard spherocylinder solvent ionic model in a disordered porous medium

Analysis of the effect of the translational-rotational coupling on the pseudo-diffusion along the molecular axes of glass forming liquid meta-cresol: A molecular dynamics analysis

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We investigated by molecular dynamics simulations the dynamical properties (translation and rotation) of the glass-forming liquid meta-cresol. This system was investigated at 19 temperatures from T=600K down to 220K. This temperature range encompasses the liquid and glassy state of meta-cresol. In order to get insight into the coupling between the translation and rotation motions, the center of velocity autocorrelation function was calculated along the meta-cresol principal axes. We showed then that the time behavior of the velocity and angular velocity is connected to the change in the locale structure. Indeed, the long time negative region in the velocity autocorrelations was associated with a caging effect while the occurrence of a short time negative region in these functions was considered as a signature of specific interaction. The time evolution of the rotation translation coupling was evaluated from the difference $\Delta_i^{RTC}(t)$ between the velocity autocorrelation function calculated with respect to the molecular frame *(i=x,y,z)* of the meta-cresol molecule and that of the same function calculated in the frame of the hypothesis that there is no statistical correlation between the translation and rotation motions. The positive regions of $\Delta_i^{RTC}(t)$ *(i=x,y,z)* indicate an occurrence of a cooperative effect which means that the each of the two motions is realized in the favor of the other. Conversely, negative regions indicate that the rotation and translation motions are anti cooperative. The change in the local structure was investigated by using the nearest neighbor approach. The change in the radial and the mutual orientation nearest neighbor distributions is shown to be consistent with the fact that the translation rotation coupling is more effective along the x and z axes.

Ionic memory in two-dimensional nanochannels

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Abstract

Memristor, or memory resistor, is a device whose resistance depends on its previous history of applied voltage. In 2008, Hewlett-Packard (HP®) group announced the discovery of the memristor and they experimentally demonstrated its properties which opened the way to the emergence of several memristive systems [1]. The vast majority of these memristors are solid state with quite a few ionic-liquid based memristors which require high voltage application and complex experimental conditions. It was demonstrated that the loop style (crossing or touching at the origin of current-voltage curve) depends on the mechanism behind the memristive effect [2]. Herein, we use 2D slit shaped angstrom-scale channels with pristine MoS_2 walls or activated carbon walls to study the memristor effects in two-dimensional channels [3, 4]. The confinement in the 2D (height of the channel <10 nm) was necessary to observe the memristive effects. The surface charge and the composition of the electrolyte played an important role in the determination of the style of the memristive IV loop. The main advantage of this new memristor is the use of simple electrolyte salts (HCl, KCl, NaCl, $CaCl_2$, $AlCl_3$, etc.) rather than complex ionic liquids and the application of up to hundred times smaller voltages (within the water oxidation window) which can potentially reduce the energy consumption [5]. Indeed, the MoS_2 2D channel devices showed interesting versatility, with different memristor loop styles and even we can observe them reversibly in the same device, by simple modification of the salt type, concentration, pH, frequency, the channel height etc. The existence of memristor effects was confirmed by the dependence of the IV loop area on the alternative voltage frequency. Finally the memristor showed interesting synapse-like dynamics and long/short memory effects. This discovery can pave the path toward the real life application in digital logic circuits, random access memory, signal processing, random number generator, artificial intelligence and neuromorphic computing.

REFERENCES

1. Strukov, D.B., et al., The missing memristor found. Nature, 2008. 453(7191): p. 80-83.
2. Sun, B., et al., A Unified Capacitive-Coupled Memristive Model for the Nonpinched Current–Voltage Hysteresis Loop. Nano Letters, 2019. 19(9): p. 6461-6465.
3. Radha, B., et al., Molecular transport through capillaries made with atomic-scale precision. Nature, 2016. 538(7624): p. 222-225.
4. Emmerich, T., et al., Enhanced nanofluidic transport in activated carbon nanoconduits. Nature Materials, 2022. 21(6): p. 696-702.
5. Robin, P., et al., Long-term memory and synapse-like dynamics of ionic carriers in two-dimensional nanofluidic channels. arXiv preprint arXiv:2205.07653, 2022.

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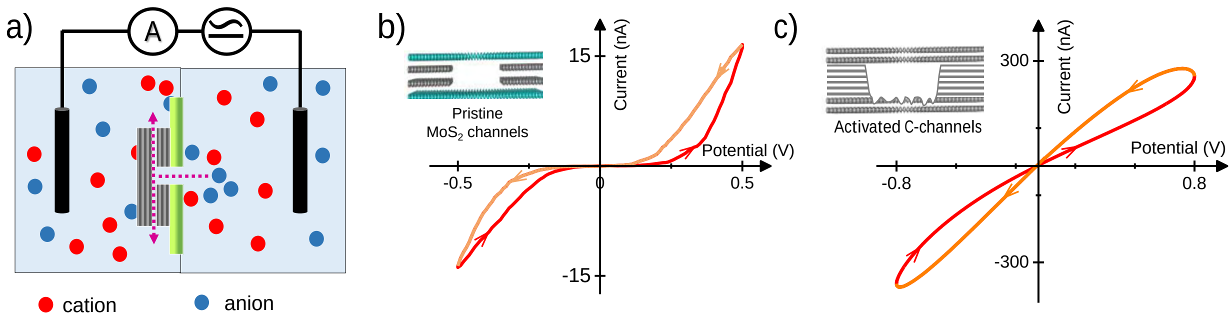

Figure 1: a) Schematic view of the set-up used for memristor device based on the application of alternating voltage using two Ag/AgCl electrodes dipped in electrolyte solution. Typical memristor current-voltage graph observed in b) pristine MoS$_2$ channels (height = 1 nm, salt concentration = 3 M) showing touching style loop c) activated carbon channels (height = 5 nm, salt concentration =1 M) showing crossing style loop.

Viscosity of supercooled water under pressure and a lower bound on its putative liquid-liquid critical point

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Many of water's physical properties are anomalous compared to other liquids. Several thermodynamic scenarii have been put forward to explain those anomalies [1]. One of them is a putative liquid-liquid transition (LLT) between a low-density and a high-density phase. ST2 and TIP4P/2005 simulations predict that the Stokes-Einstein ratio, that relates dynamical characteristics of water (viscosity and self diffusion coefficient) is related to the temperature difference with the Widom line, that is the line of correlation length maxima associated with the LLT [2,3].

I will present the Stokes-Einstein ratio that we deduced from our measurements of the viscosity of deeply supercooled water under pressure [4,5] using existing self-diffusion data [6]. I will compare to the Stokes-Einstein ratio that we could deduce from our measurements on deeply supercooled heavy water [7,8,9]. Comparison with molecular dynamics simulations shows that, if a liquid-liquid critical point exists in water, its pressure is above 150 MPa.

REFERENCES

[1] P. Gallo *et al.*, Chem. Rev. (2016), 116, 7463-7500.
[2] P. Kumar, S. V. Buldyrev, S. R. Becker, P. H. Poole, F. W. Starr, H. E. Stanley, PNAS (2007), 104, 9575-9579.
[3] P. Montero de Hijes, E. Sanz, L. Joly, C. Valeriani, F. Caupin, J. Chem. Phys. (2018), 149, 094503.
[4] R. Berthelard, PhD Thesis, (2019), https://hal.archives-ouvertes.fr/tel-02485182
[5] L. P. Singh, B. Issenmann, F. Caupin, PNAS (2017), 114, 4312-4317
[6] F. X. Prielmeier, E. W. Lang, R. J. Speedy, H.-D. Lüdemann, Ber. Bunsenges. Phys. Chem. (1988), 92, 1111-1117.
[7] F. Caupin, P. Ragueneau, B. Issenmann, arXiv:2112.09010v3 [physics.chem-ph]
[8] P. Ragueneau, F. Caupin, B. Issenmann, arXiv:2112.09024v3 [physics.chem-ph]
[9] W. S. Price, H. Ide, Y. Arata, O. Söderman, J. Phys. Chem. B (2000), 104, 5874

Prediction of High Pressure Thermodynamic Properties of Ionic Liquids

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Thermophysical properties of compressed liquids are quantities of great interest in several physics and physical chemistry fields. Thus, many studies have been devoted to experimental measurements of the thermophysical properties of liquids and their mixtures. Significantly, temperature and pressure dependences of thermophysical properties have been investigated by experiments for hundreds of molecular systems and mixtures. The state of any fluid is something that engineering chemists often find it necessary to specify clearly. Such a specification must include the density (or specific volume) of a substance, the pressure, and the temperature. The mathematical relationship that links them is the Equation of State (EoS), which remains the basis of thermodynamics. Although many EoSs were introduced either to understand the physical background of liquids or use practical calculations instead of extensive direct measurements, there is no "universal predictive recipe,", especially for liquids with complex inter-particle interactions. One of the most important examples of such media are ionic liquids, which are of great modern interest from the fundamental view of physical chemistry as well as prospective practical applications.

In this work, we demonstrate the possibility of calculating the high-pressure properties of ionic liquids using their thermodynamic parameters determined at ambient pressure addressing the scaling properties revealed for thermodynamic fluctuations, especially the inverse reduced density fluctuations and reduced pressure fluctuations. Our method, which led to the so-called Fluctuation Theory-based Equation of State (FT-EoS), already demonstrated its predictive capacity for density of the dataset of 80 different ILs with an overall relative absolute average deviation close to 0.14% [1] and got strict mathematical support from the theory of thermodynamic linear analysis. Its further development resulted in the predictive approach to the speed of sound's predictions based on the pressure fluctuations [2]. By applying our method, the agreement, well-coordinated with the possibilities of the actual experimental method, is observed between experimental and predicted high-pressure speed of sound data for all collected ILs from the ILTermo database; see, for example, Fig. 1. An overall relative average absolute deviation is close to 0.85%.

REFERENCES

[1] M. Chorążewski, E.B. Postnikov, B. Jasiok et al. *Scientific Reports*, 7 (2017) 5563.
[2] E.B. Postnikov, B. Jasiok, V.V. Melent'ev et al. *Journal of Molecular Liquids*, 310 (2020) 113016.

FIGURES

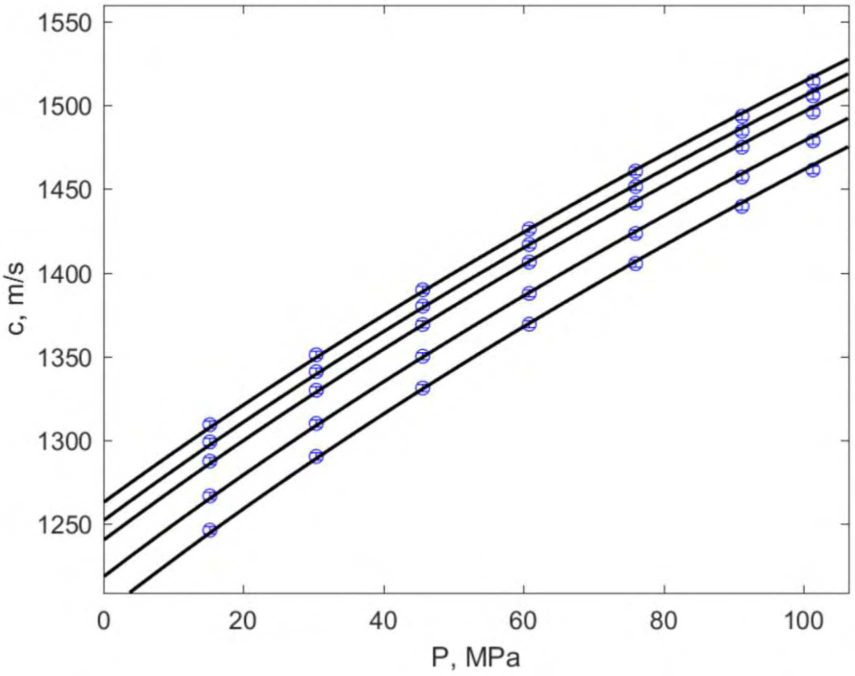

Figure 1: A comparison of the pressure dependence of the speed of sound between FT-EoS and collected experimental results for 1-ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide for (288, 292, 298, 308 and 318) K from up to down.

Contribution of different molecules and moieties to the surface tension in aqueous surfactant solutions

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The calculation of the lateral pressure profile in computer simulations of anisotropic systems is an important problem in various respects; however, it is not a straightforward task at all. The difficulty stems from the fact that pressure is an inherently non-local quantity, which has to be localized in the profile calculation. Further, if an Ewald summation-based method is used to account for the long range part of the intermolecular interactions, the reciprocal space term of this correction is not pairwise additive. We have proposed an accurate and computationally very efficient way of calculating the profile of the lateral pressure, which can also take into account the reciprocal space term when using the sPME method. Further, this way the lateral pressure can be distributed among the interacting atoms in the system as if it were a pairwise additive quantity. Since the surface tension is the integral over the imbalance of the lateral and normal pressure components, and the latter of them is constant, this method allows us to calculate the contribution of the individual particles, molecules and moieties to the surface tension. Recently, we have used this method to determine the surface tension contribution of the different molecules and moieties (i.e., water, headgroup, tail, and, if present, also counterions) in aqueous surfactant solutions. We have considered five different amphiphilic molecules, representative of anionic, cationic and non-ionic (alcoholic) surfactants in this respect. We have found that the headgroups of alcoholic surfactants give a negligible contribution to the surface tension, while the opposite is true for ionic surfactants and counterions, which give much larger (positive and negative) contributions than the total surface tension itself. [1] We investigate the effect of the counterion type and charge sign in this respect. [2,3] Concerning the type of the counterions, the observed trends are qualitatively compatible with the Hofmeister series, with the notable exception of sodium. [3] In the artificial system where the counterion and surfactant charges are inverted in sign, the surface tension contributions of the counterions, surfactant headgroups and water molecules even change their sign. [3] Since the charge inversion makes the counterions considerably harder, the results stress the key role of the hardness of the counterions in this respect. However, the hydration free energy gain of the counterions, occurring upon charge inversion, is compensated by the concomitant free energy loss of the headgroups and water molecules, leading to negligible change in the surface tension of the entire system.

REFERENCES

[1] Gy. Hantal, M. Sega, G, Horvai, P. Jedlovszky, J. Phys. Chem. C 123 (2019) 16660-16670.
[2] Gy. Hantal, M. Sega, G, Horvai, P. Jedlovszky, Coll. Interfaces 4 (2020) 15-1-15.
[3] Gy. Hantal, M. Sega, G, Horvai, P. Jedlovszky, J. Phys. Chem. B 125 (2021) 9005-9018.

Amphiphilic Poly(ethylene oxide)-Poly(propylene oxide) Alternating Multiblock Copolymers in Aqueous Solution

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ABSTRACT

Poly(ethylene oxide) (PEO)–poly(propylene oxide) (PPO) alternating multiblock (AMB) copolymer is an amphiphilic macromolecules. Since its characteristic primary structure, the morphology of the polymer assemblies has attracted keen interests. In this study, we have prepared two types of PEO–PPO AMB copolymers, $(EO_{220}PO_{33})_n$ and $(EO_{68}PO_{33})_m$, where EO is the ethylene oxide unit, PO is the propylene oxide unit, and the subscripts indicate the number of repeat units. It is found that the aqueous solution of $(EO_{220}PO_{33})_n$ and $(EO_{68}PO_{33})_n$ undergoes phase separation with a lower critical solution temperature (LCST). The precipitation fractionation enables us to prepare various samples having different molecular weight. The phase boundary of the aqueous solution for $(EO_{220}PO_{33})_n$ shifts to higher temperature region without changing its shape. On the other hand, the shape of those for $(EO_{68}PO_{33})_n$ significantly changes depending upon the molecular-weight. LCST of the aqueous solution of $(EO_{220}PO_{33})_n$ is much higher than that of $(EO_{68}PO_{33})_n$, because the latter has a shorter PEO block. The morphology of the unimer and associate of these copolymers are investigated by dynamic light scattering and small angle X-ray scattering techniques.

EXPERIMENTAL

The PEO-PPO AMB copolymer (Fig. 1) was prepared by a dehydrated condensation reaction according to the literature [1]. Briefly, α,ω-diamino PPO (JEFFAMINE D-2000; weight-average molecular weight, M_w, $=2.0\times10^3$) was kindly supplied by Huntsman Corporation. α,ω-Disuccinimidyl PEO (SUNBRIGHT DE-100 HS; $M_w=1.0\times10^4$)was purchased from NOF Corporation. The reaction was carried out in $CHCl_3$ at 0 °C. The crude sample was recovered by dialysis against water, followed by freeze-drying. Precipitation fractionation of the copolymer was performed by phase separation in an acetone/*n*-hexane mixture at 25-50°C. The characterization details can be found in previous reports [1,2].

RESULTS & DISCUSSION

Fig.2 shows the phase boundary curve for the aqueous solution of $(EO_{220}PO_{33})_n$ and $(EO_{68}PO_{33})_n$, which are estimated by the measurement of the cloud point. The phase boundary of $(EO_{68}PO_{33})_n$ locates a lower temperature region, indicating that the copolymer is more hydrophobic. The phase boundary for $(EO_{220}PO_{33})_n$ shifts to a higher temperature region with decreasing M_w, which has often been reported for amphiphilic polymers. On the other hand, the M_w dependence on the phase boundary for $(EO_{68}PO_{33})_n$ is relatively complicated. The lower critical solution temperature (LCST) for the system can be obtained as the minimum of the phase boundary curve. The M_w dependence of LCST for $(EO_{220}PO_{33})_n$ series can be analyzed by means of Shultz-Flory plots [3], which gives rise to the theta temperature (T_θ) of 44 °C. The $(EO_{220}PO_{33})_n$ may form a micelle above the temperature. Fig. 3 represents the M_w dependence of the hydrodynamic radius for $(EO_{220}PO_{33})_n$ and $(EO_{68}PO_{33})_n$ in water at 0.1 wt % and 25 °C. The results indicate that the single chain of $(EO_{220}PO_{33})_n$ forms a shrunk coil in water under T_θ, whereas that of $(EO_{68}PO_{33})_n$ exists as an anisotropic coil.

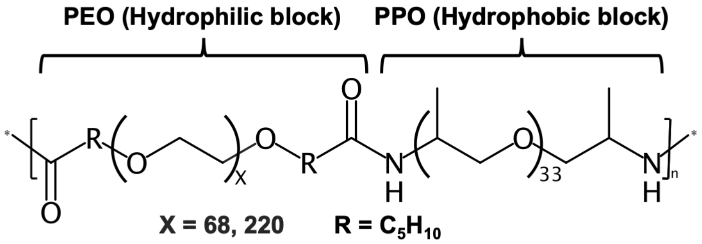

Figure 1: Chemical structure of PEO-PPO AMB copolymer.

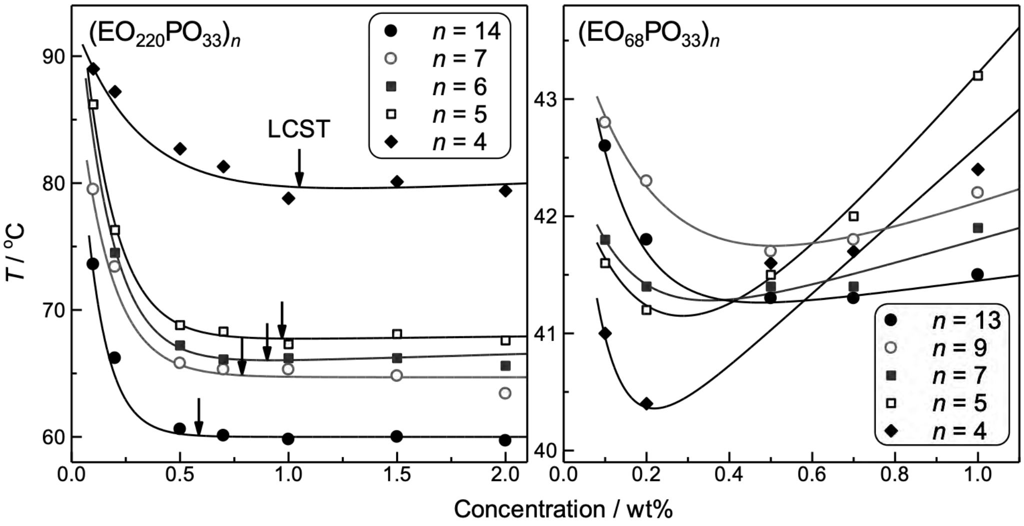

Figure 2: (Left)Phase diagram for the aqueous solution of $(EO_{220}PO_{33})_n$. (Right) that of $(EO_{68}PO_{33})_n$.

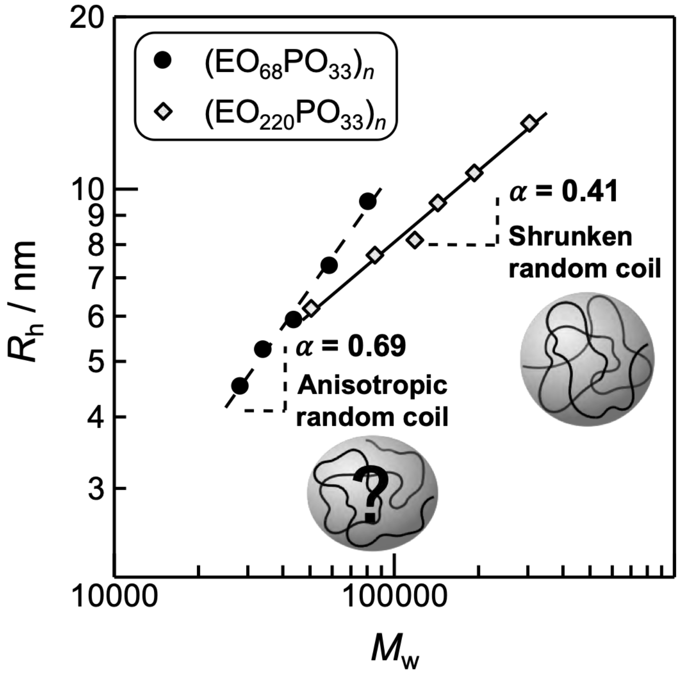

Figure 3: M_w dependence of the hydrodynamic radius for $(EO_{220}PO_{33})_n$ and $(EO_{68}PO_{33})_n$ in water at 0.1 wt % and 25 °C.

REFERENCES

[1] T. Horiuchi, et al. Langmuir 33 (2017) 14649-14656.
[2] K. Rikiyama, et al. Polymer(Guildf) 156 (2018) 102-110.
[3] A. R. Shultz and P. J. Flory, J. Am, Chem. Soc. 74 (1952) 4760-4767.

Dissecting the mobility of ion pair from cationic clusters in hydroxylated ionic liquids by ^{2}H NMR

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Ionic liquids (IL) attract major attention as advanced electrolytes, solvents and reaction control agents. However, up to date, their structure-property relationship remains mostly empirical. Despite being essentially a Coulomb-type system, in many aspects their properties are governed by weaker interactions – hydrogen bonding and even dispersion interactions. Although the Coulomb interaction is more than an order of magnitude stronger than the hydrogen bond, the local and directional nature of the hydrogen bond matters and influences characteristically the properties of these fluid salts. Normally, the formation of hydrogen bonds between cation and anion increases the attractive Coulomb interaction and tightens the interaction between the oppositely charged ions, resulting in preformation of ion-pairs, i.e. the (c-a) pairs. Recently, using a combination of IR and solid state ^{2}H NMR, we have shown [1-3], that rational desing of hydroxyl functional groups into the alkyl side chains in the pyridinium or piperidinium-based cations creates the possibility of formation of stable positively charged hydrogen bonded cationic (c-c) clusters both in liquid an solid states of the IL.

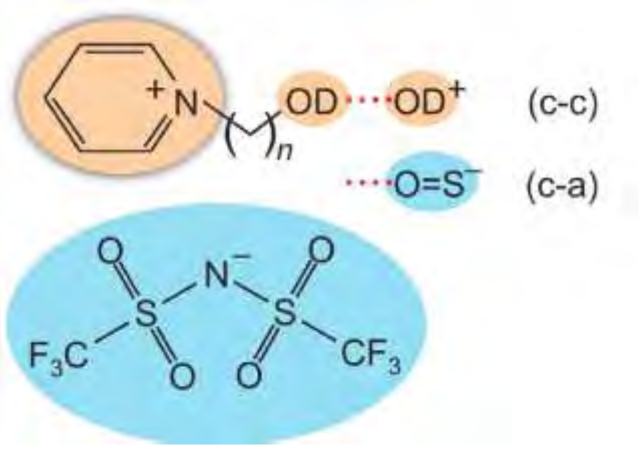

Figure 1: OD Groups of the Hydroxy-Functionalized 1-(n-Hydroxyalkyl)pyridinium Cations with n = 2−4. These OD groups form hydrogen bonds either with the oxygen of the OD groups of another cation or with the oxygen of the O=S group of the anion bis(trifluoromethylsulfonyl)imide, resulting in (c-c) clusters or (c-a) ion pairs.

In this contribution we discuss, that the presence of these somewhat counteintuitive (c-c) clusters greatly affect the physical properties of the ionic liquids, their molecular scale structure and dynamics. In particular, we show that the presence of (c-c) clusters alters the nature of the phase transition from liquids-solid to liquid-glass type, preventing thus the crystallization process. By means of the ^{2}H NMR T_1 and T_2 relaxation analysis we show, that the mechanism of the isotropic diffusion, and consequently of the microscopic viscosity, is greatly affected by the availability of the the (c-c) clusters: for such liquids the isotropic rotational diffusion is driven by two distinct rate constants, one operating in the range of low temperatures and supercooled region and the second one govering the dynamics at high temperatures. Notably, when only the (c-a) pairs are present, the isotropic diffusion is characterized the a single rate constant in the whole range of temperatures. . We finally discuss the role of the dispersion interactions for the observed phenomena, by inspecting cations with variable alkyl-chain lenght.

This work has been supported by the Russian Science Foundation (grant № 21-13-00047) and the Alexander von Humboldt Foundation.

REFERENCES

[1] A. E. Khudozhitkov, J. Neumann, T. Niemann, D. Zaitsau, P. Stange, D. Paschek, A. G. Stepanov, D. I. Kolokolov, R. Ludwig, *Angew. Chem., Int. Ed.* (**2019**), *58*, 17863-17871.

[2] A. Strate, J. Neumann, T. Niemann, P. Stange, A. E. Khudozhitkov, A. G. Stepanov, D. Paschek, D. I. Kolokolov, R. Ludwig, *Phys. Chem. Chem. Phys.* (**2020**), *22*, 6861-6867.

[3] A. E. Khudozhitkov, T. Niemann, P. Stange, M. Donoshita, A. G. Stepanov, H. Kitagawa, D. I. Kolokolov, R. Ludwig, *J. Phys. Chem. Lett.* (**2020**), *11*, 6000-6006.

About the interaction of (bio)molecules and materials surfaces in aqueous ionic solutions – an atomistic study

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It is well known that interactions of molecules depend not only on their own architecture. Rather, water which is always present in a biological environment significantly determines the nature of molecular contacts. Especially for molecules or particles with titratable surface groups, additional environmental influences, such as ionic strength or pH thus contribute to the electrostatic distribution of the molecular surfaces and determine the nature of the contacts. These effects on the molecular level are able to trigger macroscopic morphological changes of the adsorbed material.
Using atomistic simulations in the area of force field and density functional applications, I will highlight the role of specifically water and ions as well as the local surface charge distribution on adsorption processes using selected examples of protein - protein and protein - bioceramics interfaces. Namely, I will talk about the comparative adsorption of lysozyme, chemotrypsin and fibronectine [Figure1] on three different oxides (SiO_2, TiO_2 and Al_2O_3) which span a wide range of PZCs [1-4].

REFERENCES

[1] N. Hildebrand, S. Köppen, L. Derr, K. Li, M. Koleini, K. Rezwan and L. Colombi Ciacchi, JOURNAL OF PHYSICAL CHEMISTRY C, 119 (2015) 7295-7307
[2] L. Derr, N. Hildebrand, S. Köppen, S. Kunze, L. Treccani, R. Dringen, K. Rezwan and L. Colombi Ciacchi, BIOINTERPHASES, 11 (2016) 011007
[3] N.Hildebrand, M. Michaelis, N. Wurzler, Z. Li, J. D. Hirst, A. Micsonai, J. Kardos, A. Gil-Ley, G. Bussi**,** S. Köppen, M. Delle Piane, and L. Colombi Ciacchi, *ACS Biomater. Sci. Eng.,* 4, 12 (2018) 4036–4050
[4] M. Kulke, M. Uhrhan, N. Geist, D. Brüggemann, B. Ohler, W. Langel, and S. Köppen, *J. Chem. Inf. Model.*, 59 (2019) 4383–4392

FIGURES

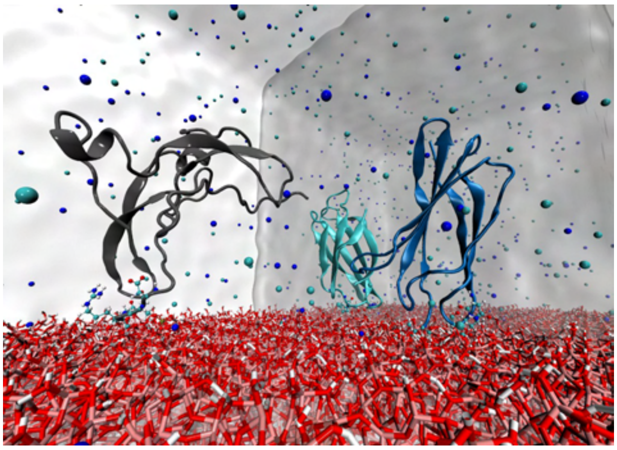

Figure 1: The C-terminal interchain domain of fibronectine (gray), as well as the modules 10FnIII (cyan) and 7FnIII (blue) in an aqueous ionic solution adsorbed on an amorphous alumina surface. The visible liquid wall in the background indicates the size of the simulation cells

Density Scaling of Translational and Rotational Molecular Dynamics in a Simple Ellipsoidal Model near the Glass Transition

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For the first time, the single-component ellipsoidal Gay-Berne model has been successfully used to the simulation study of the supercooled liquid state and the glass transition at elevated pressure [1]. Contrary to the single-component Lennard-Jones liquid model, the GB supercooled liquid has turned out to be characterized by the sufficient glass formation ability (Fig. 1) in the thermodynamic range giving the possibility of quite convenient investigations of the translational and rotational molecular dynamics near the glass transition. It seems that this advantage of the GB model over the LJ one originates from the molecular anisotropy inherent in both the ellipsoidal shapes of interacting species and the anisotropic intermolecular potential of the GB model compared to the point interacting species and the isotropic intermolecular potential of the LJ model. One could suspect that the thermodynamic range of supercooling in the GB model might be extended by studying binary mixtures of ellipsoidal species of different α_r, which is worth testing in the future. We have thoroughly explored the density scaling properties in the supercooled liquid state in the anisotropic GB model. We have confirmed the validity of the density scaling of translational (Fig. 2) and rotational relaxation times expressed by some functions and in case of the GB supercooled liquids of four different anisotropy aspect ratios αr, finding that the density scaling exponent γ is the same for τ and τ_{rot} at a given αr and increases with increasing α_r. We have shown that the best way to evaluate the proper value of γ consists in the use of the density scaling criterion, and hence it should be treated as a macroscopic parameter related to the effective short-range intermolecular potential U_{eff} commonly suggested to be composed of a dominant repulsive inverse power law term and a weak attractive background. Our investigations of the supercooled liquid state and the glass transition in the anisotropic GB model clearly show that the anisotropic models constitute a promising alternative to the isotropic ones towards a better understanding and proper reflecting physicochemical properties of the glass forming materials.

REFERENCES

[1] K. Liszka, A. Grzybowski, K. Koperwas, M. Paluch, Density Scaling of Translational and Rotational Molecular Dynamics in a Simple Ellipsoidal Model near the Glass Transition, Int. J. Mol. Sci. 23 (2022) 4546. https://doi.org/10.3390/ijms23094546

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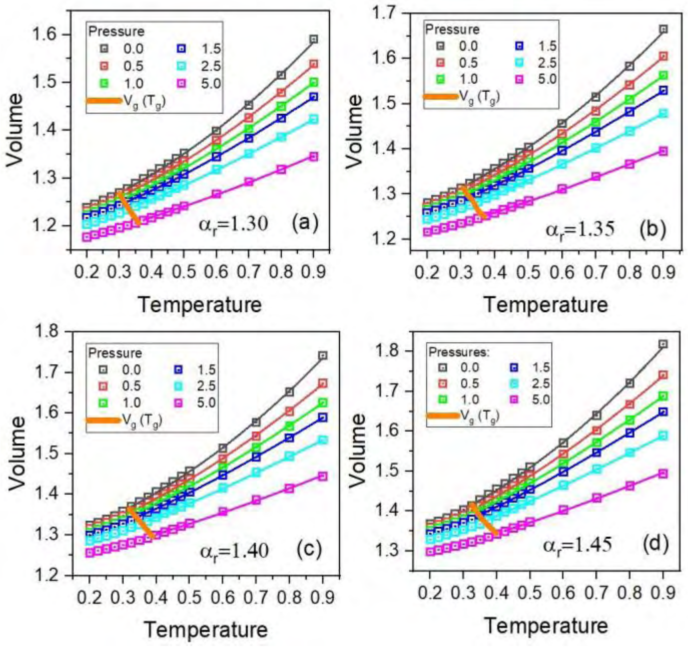

Figure 1: The plots of the isobaric dependences of the particle number volume *V* on temperature *T* in the glassy and supercooled liquids states in the GB model for different anisotropy aspect ratios α_r. The solid curves crossing the isobaric dependences *V* on *T* denote the glass transition curves.

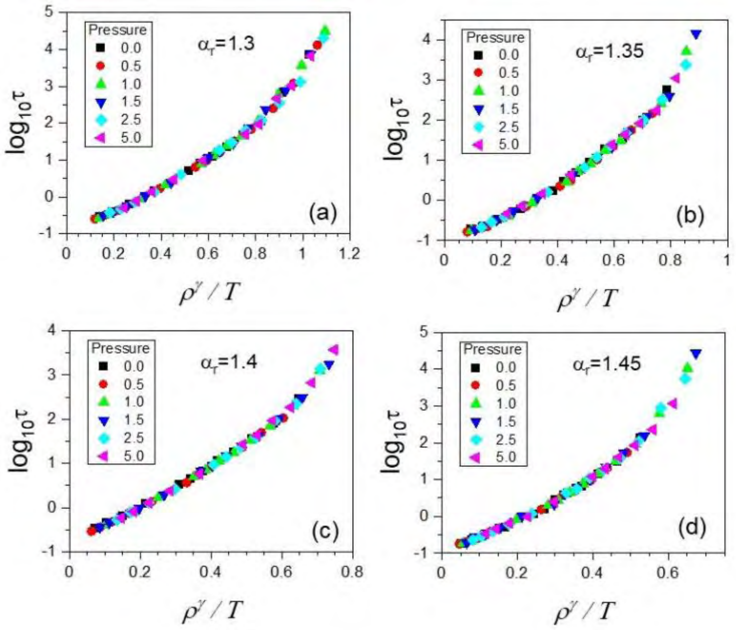

Figure 2: Plots of the high quality density scaling of the translational relaxation times τ collected in the supercooled liquid state in the GB model for different anisotropy aspect ratios α_r, which have been obtained by using the values of the density scaling exponent γ evaluated based on the density scaling criterion.

Dynamical correlations in simple disorder and complex disorder liquids

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Liquids are disordered and they come in two variants [1]: simple disorder, such as Lennard-Jones liquids, CCL4, or weakly polar liquids such as acetone, and complex disorder, such as water, alcohols, hydrogen bonding liquids, or soft-matter and biological liquids. The second variant differs from the first in the intriguing duality between concentration fluctuations and clustering [2]. In Ref.[1] we described this difference using statistical quantities such as atom-atom pair correlation functions, in particular the pre-peak feature [3]. In this presentation, we extend this study to dynamical atom-atom van Hove correlation functions and the associated memory functions, as obtained from molecular dynamics simulations. Interestingly, dynamical complexity is characterized by the difference between real time and kinetic time, the latter which is an emerged quantity, just as clusters are, due to the fact that associated entities appear as supra-particles, distinct from the real molecules in the system. The analysis highlights many new properties of dynamical correlations in molecular liquids.

REFERENCES

[1] M. Požar *et al.*, Simple and complex disorder in binary mixtures with benzene as a common solvent, *Phys. Chem. Chem. Phys.*, 17 (2015) 9885-9898
[2] A. Perera, M. Požar and B. Lovrinčević, Camel back shaped Kirkwood–Buff integrals, J. Chem. Phys. 156 (2022) 124503
[3] A. Perera, From solutions to molecular emulsions, Pure Appl. Chem. 88 (3) (2016) 189–206

On Slippery Ice

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Abstract

Sliding on ice is a familiar experience, but the reason why ice has such a low friction has a long and controversial history. For many years, it has been assumed that the main reason for the low friction of ice is due to the formation of a thick lubrication layer of melt water. However, there is no consensus on the origin of the melt water film. Among the different hypothesis enumerated are pressure melting, ice premelting and frictional heating of the surface [1]. Very recently, however, it has been suggested that lubrication plays no role whatsoever, and that ice friction is mainly given by adhesive and mechanical properties of ice [2].

Unfortunately, these hypothesis cannot be easily confirmed by macroscopic experiments. What is the actual thickness of the watery lubrication film under static conditions? Does it change significantly with the nature of the substrate? Does it become thicker upon increasing the pressure or shearing? Is the resulting thickness sufficient for the establishment of a lubricating Couette flow?

In this work we borrow tools from our recent investigations on the structure of ice premelting in order to understand better the microscopic origin of the low friction coefficient of ice [3-5].

REFERENCES

[1] Rosenberg, Phys. Today, 58 (2005) 50.
[2] Liefferink, Hsia, Weber and Bonn, Phys.Rev. X, 11 (2021) 011025 .
[3] Llombart, Noya, Sibley, Archer and MacDowell, Phys. Rev. Lett. 124 (2020) 065702.
[4] Llombart, Noya and MacDowell, Sci. Adv. 6 (2020) eaay9322.
[5] Sibley, Llombart, Noya, Archer and MacDowell, Nature Comm. 12 (2021) 239.

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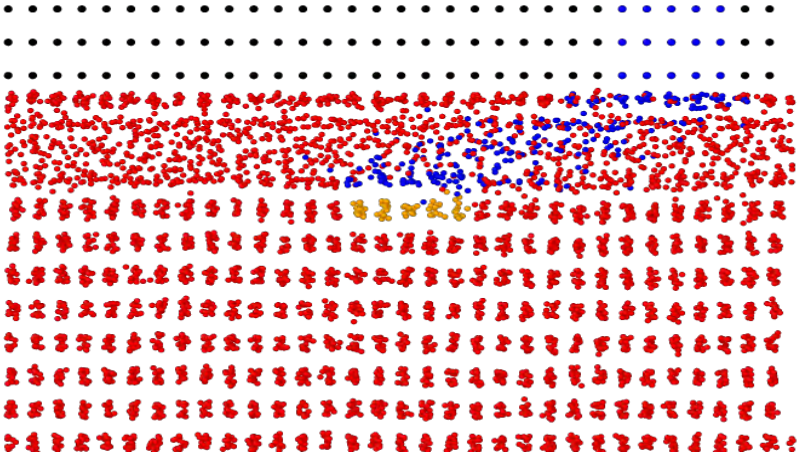

Figure 1: Flow pattern of an interfacially premelted ice film upon shearing by a slider. How close is this to macroscopic Couette flow ?

Thermophysical properties of molecular liquids from simulation, experiment, and equation of state

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Molecular Dynamics (MD) simulations are used to investigate thermophysical properties of molecular liquids such as 1-chloropropane, 2-chloropropane and water as a function of temperature and pressure. Investigated properties include the density, the constant pressure and constant volume heat capacities, the isobaric thermal expansion coefficient, the isothermal compressibility and the speed of sound. For chloropropanes, experimental data for density have been reexamined [1-3] and used together with other experimental data [4] to fit the Span-Wagner equation of state (EoS). For water, an extensive MD study is performed with the SPC/E model and compared to prediction of a Span-Wagner-type EoS and to experimental results [5].

REFERENCES

[1] B. Jasiok, M. Chorążewski,A. A. Pribylov, E. B. Postnikov, P.Friant-Michel, C. Millot, J. Mol. Liq., 358 (2022) 119137
[2] V. V. Melent'ev, E. B. Postnikov, J. Chem. Eng. Data, 62 (2017) 3409-3413
[3] A. R. Lowe, B. Jasiok, V. V. Melent'ev, O. S. Ryshkova, A. K. Radchenko, E. B. Postnikov, M. Spinnler, U. Ashurova, J. Safarov, E. Hassel, M. Chorążewski, Fuel Process. Technol., 199 (2020) 106220
[4] ThermoData Engine (TDE) Version 10: NIST standard reference database 103b (2015)
[5] F. Mallamace, C. Corsaro, H. E. Stanley, Sci. Rep., 2 (2012) 993

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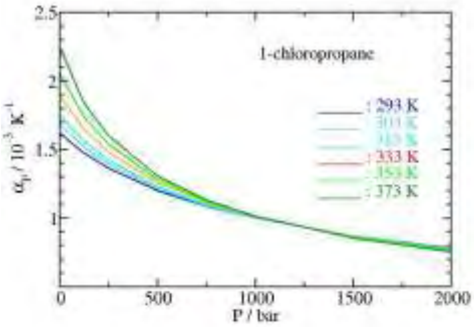

Figure 1: Isobaric thermal expansion coefficient of 1-chloropropane from MD simulation results

Gel—Sol transition points of Binary Organogels Comprising *p*-Chlorophenol and AOT: Analyzed by Hansen Solubility Parameters

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Abstract

Organogels comprise gelator(s) and solvents where both components have organic nature. *p*-Chlorophenol and a surfactant AOT, bis(2-ethylhexyl)sulfosuccinate serve as organogelators in nonpolar solvents [1, 2], if they are combined in solvent. We have studied such binary organogel structures, optical properties, and mechanical properties or Young's modulus, in our earlier publication [2]. Thermal properties have not been analyzed adequately yet with conventional procedures. In this contribution we show Hansen solubility parameters can be applied to go over gel–sol points of the binary oraganogel systems. To our knowledge, this study firstly applies Hansen solubility parameters to binary organogels.

Materials and data analysis

The reader finds details of organogel synthesis in our previous study [2]. Briefly, equivolume solutions of gelators with a 0.1 mol dm^{-3} concentration are mixed to obtain organogels by self-organization. We use a dropping point system DP70, from Mettler Toledo, to get drop points, T_{drop}, as a measure of the gel–sol transition point. The Hansen solubility parameters package (version 5.0.03) determines the solvent parameters. We use the Hansen distance between materials 1 and 2, R_{a}, which is calculated as

$$R_{\mathrm{a}}^2 = 4(\delta D_1 - \delta D_2)^2 + (\delta P_1 - \delta P_2)^2 + (\delta H_1 - \delta H_2)^2 \qquad (1)$$

where *D*, *P*, and *H* stand for dispersion, polarizability, and hydrogen bond terms of solvent interaction, respectively. We take the Hansen distance between the solvent and 3-methylpentance, where the latter corresponds to the effective interaction-site of the gelator AOT.

We study 28 organic solvents in the organogel synthesis. 23 of them are nonpolar solvents and they gel the geletors to form organogel. The remaining systems are with polar solvents, and they stay in sol. Polar solvents are intentionally chosen for comparison.

Results and discussion

We firstly try to make a clear explanation of T_{drop} with a help of the boiling points of solvent, $T_{\mathrm{b,\,solv}}$. Figure 1 plots T_{drop} in correlation with $T_{\mathrm{b,\,solv}}$. Obviously, T_{drop} values are scattering around the plot. We see $T_{\mathrm{b,\,solv}}$ cannot be a suitable measure for T_{drop} in a global solvent species. With a closer look, meanwhile, we see somewhat positive correlations within four solvent groups (aromatics, acyclic alkanes, cyclic alkanes, cyclic alkenes). We need to have another manner to obtain understandable correlations with T_{drop}.

In the abscissa of Figure 2, we use R_{a} instead. When R_{a} goes up, T_{drop} comes down. Mutual correlation is clearer than plots in Figure 1. The behavior in Figure 2 is reasonable. This is because as the chemical properties are somewhat similar in between the gelator and solvent, the R_{a} value becomes small. With more solid interactions between them, we may obtain higher T_{drop}. At the conference site we talk about more molecular views regarding gelator—solvent interactions.

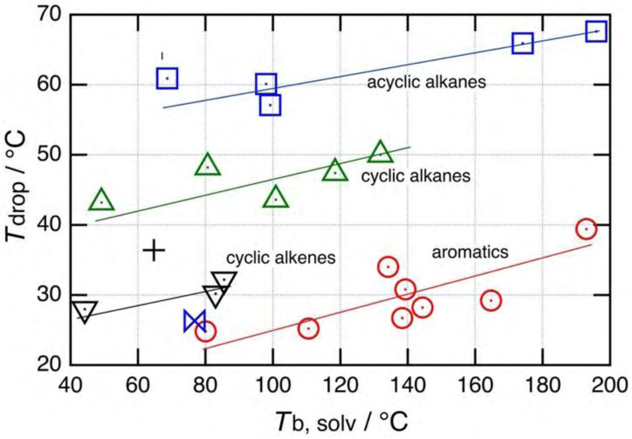

Figure 1. Plots of T_{drop} versus $T_{b,\ solv}$. Solvent groups are found inside the graph. Two solvents that are independent of the solvent groups are perhaloalkane, or carbon tetrachloride (|><|), and acyclic alkene, or 2-butyl-1-butene (+). The solid lines are guide to eye.

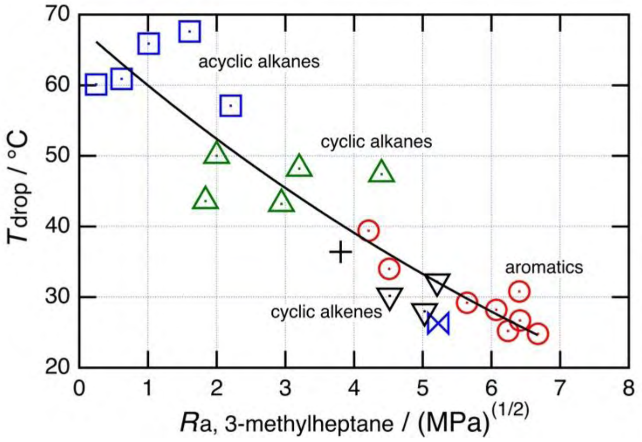

Figure 2. Plots of T_{drop} versus R_a. Solvent groups are found inside the graph. Two solvents that are independent of the solvent groups are perhaloalkane, or carbon tetrachloride (|><|), and acyclic alkene, or 2-butyl-1-butene (+). The solid line is guide to eye.

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REFERENCES

[1] B.A. Simmons, C.E. Taylor, F.A. Landis, V.T. John, G.L. McPherson, D.K. Schwartz, R. Moore, J. Am. Chem. Soc. 123 (2001) 2414–2421.

[2] S. Katsube, M. Kinoshita, K. Amano, T. Sato, Y. Katsumoto, T. Umecky, T. Takamuku, T. Kaji, M. Hiramoto, Y. Tsurunaga, K. Nishiyama, Langmuir 32 (2016) 4352–4360.

Rheology and topology of a magnetic nanogel

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Magnetic nanogels (MNG) -- soft colloids made of polymer matrix with embedded in them magnetic nanoparticles (MNPs) -- are promising magneto-controllable drug carriers. In order to develop this potential, one needs to study MNG's behavior in various microfluidic systems, one of which can be modelled as a channel with a shear flow. At the same time, MNG motion can be governed by an external magnetic field, alongside with other factors, such as temperature, quality of the solvent or gels topology. The latter is usually controlled by spatial distribution of crosslinkers in the gels polymer matrix. Thus, a clear understanding of the interplay between magnetic, topologic and hydrodynamic influence on MNGs dynamics will be an essential step to facilitate their usage in targeted drug delivery [1].

Considering the size of the MNG and typical time and velocity scales involved in their nanofluidics, experimental characterisation of the system is challenging. In this work, we perform molecular dynamics (MD) simulations combined with the Lattice-Boltzmann (LB) scheme [2] aiming at describing the impact of the shear rate and applied magnetic field on the shape, magnetic structure and motion of an MNG with a given topology: uniform, with shifted centre of mass, with Gaussian distribution from the centre to periphery and reverse. An example of a simulated system shown in Fig. 1.

We find that in a shear flow, the centre of mass of an MNG tends to be in the centre of a channel and to move, preserving the distance to both walls. The MNG monomers along with translation are involved in two more types of motion, they rotate around the centre of mass and oscillate with respect to the latter. It results in synchronised tumbling and wobbling of the whole MNG accompanied by its volume oscillates. The fact, the MNG is a highly compressible and permeable for the carrier liquid. It makes its behaviour different from a simple droplet in an emulsion. We show that the volume oscillations and rotations are two faces of the same periodic process whose frequency is a growing function of the shear rate [3]. We find that the stronger magnetic interactions between MNPs are, the higher is the frequency of this complex oscillatory motion, and the lower is its amplitude. Finally, we show how this frequency depends on gels topology, external magnetic field and density of MNPs filling.

REFERENCES

[1] C Biglione, J Bergueiro, S Wedepohl, B Klemke, M C Strumia and M Calderón, Nanoscale, 2020, 12, 21635-21646

[2] A Arnold, O Lenz, S Kesselheim, R Weeber, F Fahrenberger, D Röhm, P Košovan, and C Holm, Lecture Notes in Computational Science and Engineering, Volume 89, Pages 1–23. Springer Berlin Heidelberg, 2013

[3] IS Novikau, EV Novak, ES Pyanzina, SS Kantorovich, Journal of Molecular Liquids 346, 2022, 118056

FIGURES

Figure 1: Simulation snapshot of an MNGs with shifted center of crosslinking in shear flow under and external magnetic field; arrows are MNPs and crosslinking bonds are represented by sticks.

Amyloid aggregation in self-crowded conditions

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Fundamental studies on protein aggregation are of great interest in several areas. A huge number of investigations have concerned amyloid fibrils, due to their role in relevant diseases [1]. More recently, amyloid aggregates were also exploited to develop functional hydrogels, as novel biomaterials for biomedical and biotechnological applications [2]. The role of amyloid aggregation as a way to improve food products was also considered [3]. Interestingly, the capability of forming amyloid aggregates upon denaturation, seems a rather general property of globular proteins, independently on their secondary structure [4,5]. In this context, lysozyme was deeply studied as a model protein, owing to its tendency to form amyloid fibrils in acidic conditions [4]. Very often, protein samples at relatively low concentrations were considered, while less efforts were devoted to study highly concentrated systems (protein concentrations greater than ~100 mg/ml), when excluded volume and viscosity effects could be relevant in determining unfolding and aggregation features. Nevertheless, protein assembly in self-crowded samples might represent a convenient route to form specific amyloid aggregates and hydrogel with tailored features, of possible relevance in different fields including biology, pharmaceutics, food technology and material science. In this contribution, a procedure will be presented to rapidly form lysozyme hydrogels in highly concentrated samples (~240 mg/ml). Molecular insights on the gelation process were obtained by *in situ* FTIR spectroscopy. These were then connected with the results of related approaches, which probe structural properties at mesoscopic and macroscopic length scales [4]. Our results demonstrate that transparent and thermoreversible protein hydrogel can be easily produced in self-crowded conditions. Their properties were explained considering the formation of amyloid oligomers that further interconnect through weak (reversible) interactions. This type of hydrogels, constituted by amyloid oligomers, might represent an interesting class of functional biomaterials, in analogy with the more conventional fibrillar hydrogels.

REFERENCES

[1] F. Chiti, C. M. Dobson, Annu. Rev. Biochem., 86 (2017) 27.
[2] G. Wei, Z. Su, N. P. Reynolds, P. Arosio, I. W. Hamley, E. Gazit, R. Mezzenga, Chem. Soc. Rev., 46 (2017) 4661.
[3] Y. Cao, R. Mezzenga, Adv. Colloid Interface Sci., 269 (2019) 334.
[4] S. Catalini, D. R. Perinelli, P. Sassi, L. Comez, G. F. Palmieri, A. Morresi, G. Bonacucina, P. Foggi, S. Pucciarelli, M. Paolantoni, Biomacromolecules, 22 (2021) 1147.
[5] L. Comez, P. L. Gentili, M. Paolantoni, A. Paciaroni, P. Sassi, Int. J. Biol. Macromol., 177 (2021) 40.

Why Do Liquids Mix? The Effect of Hydrogen Bond Redistribution on the Mixing Behavior of Protic Ionic Liquids

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We study hydrogen bond (HB) redistribution in mixtures of two protic ionic liquids (PILs) sharing the same cation: triethylammonium-methanesulfonate ([TEA][OMs]) and triethylammonium-triflate ([TEA][OTf]). The mixture is exhibiting large negative excess energies of mixing. Based on results obtained from atomic detail molecular dynamics (MD) simulations, we derive a lattice model, discriminating between HB and nonspecific intermolecular interactions. We demonstrate that due to the ordered structure of the PILs, mostly the HB interactions contribute to the mixing energy. This allows to us to connect the equilibrium of HBs to each of the two anion species with the excess energies and entropies of mixing. The entropy associated with HB redistribution is shown to be negative, and even overcompensating the positive entropy associated with a statistical distribution of the ions in the mixture (see Figure 1). This is suggesting that the mixing process is driven by enthalpy, not entropy. In addition, we use a combination of calorimetry, and 1H-NMR chemical shift measurements to determine the difference in HB strength favouring the [TEA]-[OMs] interaction. Both, the results from MD-simulation and from experimental calorimetry and 1H-NMR chemical shift data show a qualitatively similar behaviour and can be explained within the same theoretical framework.

FIGURES

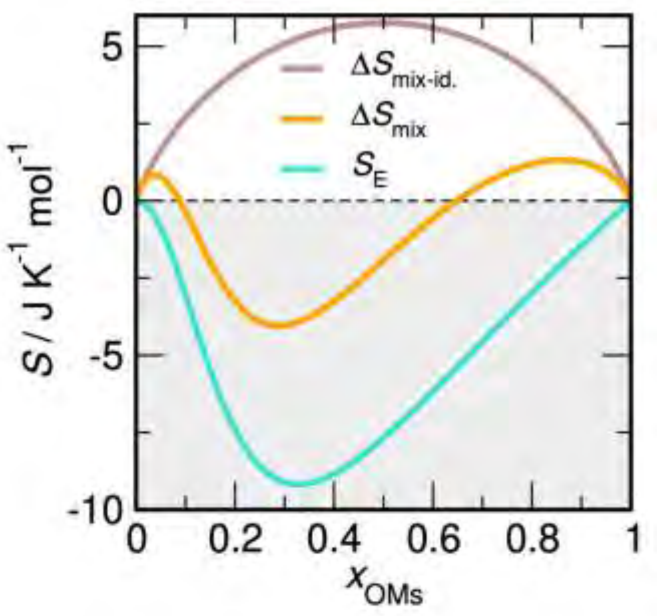

Figure 1: The excess entropy S_E due to HB redistribution is negative, even overcompensating the positive ideal contribution $\Delta S_{\text{mix-id.}}$ due to the statistical distribution of the anions in the mixture in the range $0.1<x_{\mathrm{OMs}}<0.65$.

Hydration of carbohydrate molecules

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Carbohydrates are among the most essential biomolecules that play principal roles in several biological processes such as molecular recognition, and structural stabilization and modification of proteins and nucleic acids that can act as cryoprotective molecules for living cells. Additionally, they play a significant role in many industrial applications related to, e.g., food, biotech, and cosmetics industries. [1] Although carbohydrates are generally considered hydrophilic compounds, they have substantial hydrophobicity that varies with their structure. In the gas phase, the energetically most stable conformations are the ones where hydroxyl groups form a well-defined intramolecular H-bonded pattern. [2] The competition of these intramolecular H-bonds with the intermolecular ones, which are formed between the carbohydrate ring oxygen and the water molecules, along with the hydrophobic interactions, determine the solvation shell of these molecules.

In this presentation, we consider four simple sugars, α-D-glucose, α-D-glucose, α-D-galactose, and α-D-mannose, whose molecular structures are very similar, yet their solubilities in water are rather different. We calculated different properties that characterize the hydration of carbohydrate molecules and reveal the differences between them. These include, among others the average number of acceptor and donor H-bonds, the average length of acceptor and donor H-bonds, and the properties of three and four-coordinated water molecules around carbohydrate molecules.

Using classical and ab initio molecular dynamics simulations provides a very strong base for our results. Thus, in the next step applying these tools, we investigated the hydration shell (hydrophobic and hydrophilic) of more systems, namely the cyclodextrin family. These molecules are cyclic oligosaccharides composed of D-glucose units which are linked through α−1,4 glycosidic bonds. Cyclodextrins have a hollow truncated cone shape with a hydrophobic inner and hydrophilic outer surface. It is a widely spread, although not properly proven, statement that water molecules in the cavity of CD molecules interact mainly with the central molecule by hydrophobic interaction. For a proper description of this interaction, we applied state-of-the-art correlation methods and energy decomposition analyses. Additionally, the strengths of intramolecular hydrogen bonds on the upper and lower rims of CDs have been analyzed using several quantum chemical descriptors.

REFERENCES

[1] Raymond A. Dwek Glycobiology: Toward Understanding the Function of Sugars Chem. Rev. 1996, 96, 683−720

[2] Tvaroška, I.; Carver, J. P. Ab Initio Molecular Orbital Calculation of Carbohydrate Model Compounds 6. The Gauche Effect and Conformations of the Hydroxymethyl and Methoxymethyl Groups. J. Phys. Chem. B 1997, 101, 2992−2999

The influence of charge ordering in the microscopic structure of monohydroxy alcohols

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Monohydroxy alcohols are well known to form hydrogen bonded clusters of various linear shapes [1, 2, 3]. The signature of this clustering is faithfully reproduced through the pre-peak feature of the calculated Xray scattering intensities, as obtained from computer simulations with various force fields, and more importantly in excellent agreement with experiments [4, 5]. Since classical force fields simulate the Hbonding through the Coulomb association, it is naturally tempting to interpret the related clustering from a pure electrostatic point of view. Since charge order, *i.e.* the alternated positioning of positively and negatively charged atoms, dominates the microscopic distribution of molecular entities, it is interesting to examine how the constraints of oppositely charged oxygen and hydrogen atoms of the hydroxyl groups, as well as the constraints posed by the neutral atomic groups of the hydrophobic tails, act on the charge ordering and the molecular clustering. The influence of the branching of the tails is equally examined. The atom-atom pair correlation functions, which appear in calculation of the Xray scattered intensities (through the atom-atom structure factors) are the focus of this study. The role of the cancellation of the positive like-charge correlations and negative cross correlations contributions to the pre-peak feature are analyzed. The analysis reveals several non-intuitive details about how charge ordering and neutral tail correlations adjust to each other to produce the actual structure of these monohydroxy alcohols.

REFERENCES

[1] Narten, A. H.; Habenschuss, A. J. Chem. Phys. 80, 3387−3391 (1984)
[2] Vahvaselkä , K. S.; Serimaa, R.; Torkkeli, M. J. Appl. Crystallogr. 28, 189−195 (1995)
[3] Tomšič , M.; Jamnik, A.; Fritz-Popovski, G.; Glatter, O.; Vlček, L. J. Phys. Chem. B 111, 1738−1751 (2007)
[4] Požar, M.; Bolle, J.; Sternemann, C.; Perera, A. J. Phys. Chem. B 124, 8358-8371 (2020)
[5] Bolle, J.; Bierwirth, P.; Požar, M.; Perera, A.; Paulus, M.; Münzner, P.; Albers, C.; Dogan, S.; Elbers, M.; Sakrowski, R.; Surmeier, G.; Böhmer, R.; Tolan, M.; Sternemann, C. Phys. Chem. Chem. Phys. 23, 24211-24221 (2021)

Computing the coexistence lines of the sodium chloride–water mixture

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NaCl aqueous solutions are ubiquitous. They can crystallize into ice, NaCl or $NaCl{\cdot}H_2O$. These crystallization transitions have important implications in geology, cryopreservation, or atmospheric science.

Computer simulations can help understand the crystallization of these solids, which requires a detailed knowledge of the equilibrium phase diagram. We use molecular simulations in which we put at contact the solution with the solid of interest to determine points of the solid-solution coexistence lines. We follow two different approaches, one in which we narrow down the melting temperature for a given concentration [1], and another one in which we equilibrate the concentration for a given temperature [2], obtaining consistent results. The phase diagram thus calculated for the selected model (TIP4P/2005 for water molecules and Joung-Cheatham for the ions) correctly predicts coexistence between the solution and ice.

We were only able to determine $NaCl{\cdot}H_2O$-solution coexistence points at higher temperatures and concentrations than in the experiment [3], so we could not establish a direct comparison in this case. On the other hand, the model underestimates the concentration of the solution in equilibrium with the NaCl solid. Our results, alongside other literature evidence, seem to indicate that ion-ion interactions are too strong in the model. Our work is a good starting point for the improvement of the potential model and for the study of the nucleation kinetics of the solid phases involved in the phase diagram [4].

REFERENCES

[1] Ladd, A. J. C., and L. V. Woodcock. Chemical Physics Letters 51.1 (1977): 155-159.

[2] Espinosa, J. R., et al. The Journal of Chemical Physics 145.15 (2016): 154111.

[3] Li, Dongdong, et al. Calphad 53 (2016): 78-89.

[4] V. Bianco, et al. The Journal of Chemical Physics 156 (2022): 064505.

The unique structural features of water, ranging from ambient liquid up to supercritical, extreme-pressure conditions: Insights from classical and *ab initio* molecular dynamics simulations.

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Abstract

The complex behavior of water has motivated the scientific community to develop novel theories and methodologies to provide deeper insight into the molecular causes of its anomalies compared to most liquids. A molecular understanding of the water properties is crucial in numerous processes in chemistry, physics, geosciences, biology, and life evolution. Despite long-lasting research efforts, new intriguing properties are still being described and even the phase diagram of water, although systematically explored in the past, is far from being complete. From a theoretical point of view, the investigation of these characteristic structural features of water and the temperature and pressure effects upon them could be achieved by employing multi-scale modeling techniques, ranging from classical or *ab initio* molecular simulation techniques to coarse-graining methods. Our recent multi-scale simulation studies of water [1-7] at a very wide range of temperatures and pressures will be systematically presented, aiming to shed some light on the unique structural features of water at ambient liquid up to supercritical, extreme-pressure conditions.

REFERENCES

[1] Ioannis Skarmoutsos, Andres Henao, Elvira Guardia, Jannis Samios, J. Phys. Chem. B 125 (2021), 10260.
[2] Ioannis Skarmoutsos, Stefano Mossa, Elvira Guardia, J. Chem. Phys. 150 (2019), 124506.
[3] Ioannis Skarmoutsos, Elvira Guardia, Jannis Samios, J. Supercrit. Fluids 130 (2017), 156.
[4] Ioannis Skarmoutsos, Elvira Guardia, Marco Masia, Chem. Phys. Lett. (2016), 648, 102.
[5] Elvira Guardia, Ioannis Skarmoutsos, Marco Masia J. Phys. Chem. B, 119 (2015), 8926.
[6] Ioannis Skarmoutsos, Giancarlo Franzese, Elvira Guardia, *submitted* (2022).
[7] Ioannis Skarmoutsos, Jannis Samios, Elvira Guardia, *submitted* (2022).

Tetrabutylammonium salt/phenol-based deep eutectic solvents: Structure elucidation from combined Infrared and DFT calculations.

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Abstract

Deep Eutectic Solvents (DESs) are a new class of solvents with promising properties for a large number of applications such as gas separation and sequestration, electrochemistry, catalysis and the extraction of natural compounds for cosmetic or pharmaceutical applications.[1-4] These solvents are usually prepared by mixing two components, one hydrogen bond donor (HBD) and an hydrogen bond acceptor (HBA) and are characterized by a significant depression in their melting point compared to those of the neat constituents. As reported in many recent publications on DESs, hydrogen bonding is believed to be the key intermolecular force leading to the melting point depression observed during the DESs formation.[5] Nevertheless, anion-cation interactions as well as steric effects could also play a significant role. Therefore, efforts are still needed to identify the solvation mechanisms at work at a molecular level that govern the structure–property relationships in this class of solvents.

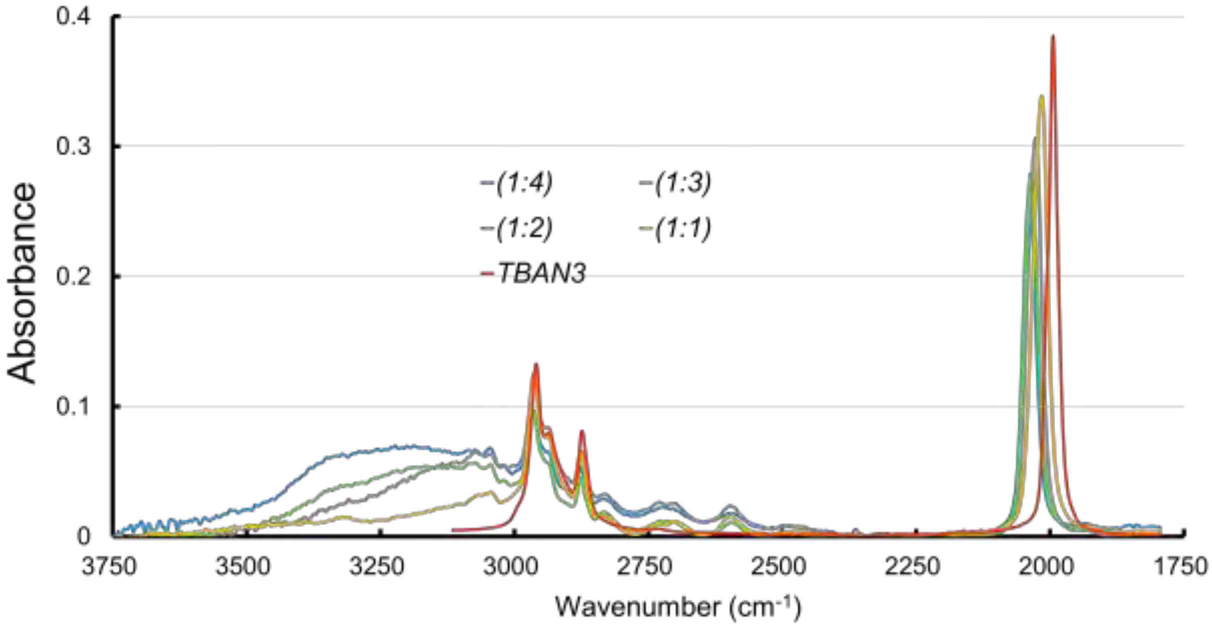

Figure 1: ATR-IR spectra of the $TBAN_3$-Phenol DES with various HBA-HBD ratios 1:1, 1:2, 1:3 and 1:4. The spectrum of the neat $TBAN_3$ salt is reported for comparison.

In this study, a series of new DESs composed of phenol as the HBD and tetrabutyl ammonium (TBA) salts with different anions as HBA were prepared and investigated by ATR-IR spectroscopy and DFT calculations in order to get insights into the local order existing in these DESs. In particular, a characteristic vibrational mode of the azide anion (N_3^-) in the $TBAN_3$-Phenol DES with various HBA-

HBD ratios displays significant shifts in frequency in comparison with that measure for the neat $TBAN_3$ salt (see figure 1). Similarly, the OH stretching mode of phenol is significantly shifted in the DESs in comparison with that reported for neat phenol. These frequency shifts were interpreted by DFT calculations as related to specific hydrogen bonding interactions between the azide anion and phenol molecules. Thus, such solvation effects are believed to be responsible for the formation of a liquid phase at room temperature in these ammonium salt/phenol-based DESs.

REFERENCES

[1] Deep Eutectic Solvents for Medicine, Gas Solubilization and Extraction of Natural Substances, in: S. Fourmentin, M.C. Gomes, E. Lichtfouse (Eds.), Springer, Cham, 2021, pp. 312.

[2] B.B. Hansen, S. Spittle, B. Chen, D. Poe, Y. Zhang, J.M. Klein, A. Horton, L. Adhikari, T. Zelovich, B.W. Doherty, B. Gurkan, E.J. Maginn, A. Ragauskas, M. Dadmun, T.A. Zawodzinski, G.A. Baker, M.E. Tuckerman, R.F. Savinell, J.R. Sangoro, Chem Rev, 121 (2021) 1232-1285.

[3] Q. Zhang, K. De Oliveira Vigier, S. Royer, F. Jerome, Chem Soc Rev, 41 (2012) 7108-7146.

[4] M. Francisco, A. van den Bruinhorst, M.C. Kroon, Angew Chem Int Ed Engl, 52 (2013) 3074-3085.

[5] C.R. Ashworth, R.P. Matthews, T. Welton, P.A. Hunt, Phys. Chem. Chem. Phys., 18 (2016) 18145-18160.

Salt effect on diffusion signal reveals selective photoinduced dimerization site of a BLUF domain of EB1

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Conformation changes of proteins and biomolecular interactions are important for biological functions. For the detection of these processes, a variety of techniques have been developed. UV/vis absorption spectroscopy or emission spectroscopy are very powerful to trace the time development of reactions. However, these techniques have a limitation to detect the conformation changes of proteins and biomolecular interactions. Our group found that the translational diffusion coefficient (D) can be a useful and sensitive probe to detect the conformation change as well as the intermolecular interaction changes. Although many techniques, e.g., dynamic light scattering, Taylor dispersion, capillary method, NMR spectroscopy, have been developed to monitor molecular diffusion, D has never been considered as a time dependent property during reactions. We have been developing a method based on the pulsed-laser induced transient grating (TG) technique to detect the time-dependent diffusion. Here, we studied the dimerization reaction of eBLUF, which is a photosensor BLUF domain from EB1, using the time-resolved diffusion method. EB1 is a C-terminal construct of Bldp1 from the magnetotactic bacterium *Magnetococcus marinus*. We found a significant salt effect on the dimer stability using transient grating (TG) and dark recovery measurements, indicating that electrostatic interactions play a critical role in mediating the stability of protein complexes. These results will be very useful to produce a new protein tool for optogenetics.

The TG method can sensitively detect the diffusion coefficients in the time-domain. The principle of the TG method and experimental methods to measure time-dependence of D have been reported previously [1].

To detect the dimerization dynamics, the TG signal of eBLUF was measured at a sufficiently weak light pulse (~a few μJ/pulse). Figure 1 shows typical TG signals. The signal intensity immediately rose after excitation (<ns) representing light (L)-state formation. After the thermal grating signal, a decay-rise component in the milliseconds time range (Fig. 1) is observed, which is attributed to a protein diffusion process (diffusion signal). Comparing the changes in the refractive index of the thermal grating ($\delta n_{th}<0$) and of the diffusion signal enabled us to determine the signs of the refractive index changes of the rise and decay components as negative and positive, respectively. From these signs, the rise and decay components of the diffusion signal are assigned to the diffusions of the reactant and product, respectively. Because the rate of the rise component is faster than that of the decay component, the diffusion coefficient of the product (D_P) is apparently smaller than that of the reactant (D_R). This change is reasonable for the assignment of the reaction, that is, dimerization. On the basis of these observations including the cncentration dependence measuermens, we found that eBLUF mostly exists as a monomer in the dark state (D-state). Upon photoexcitation, two types of dimers are formed: one that consists of two L-protomers (LL-dimer), and another that consists of L- and D-protomers (LD-dimer). The laser power dependence of the TG signal indicated that the stability of the LD-dimer is much higher (selective dimerization). Moreover, the dark recovery of the LD-dimer is approximately 20 times slower than that of the LL-dimer and L-monomer. These characteristic features are particularly interesting as potential optogenetic tools, because the LD-dimer is a heterodimer.

Using this heterodimer, we could selectively induce the interaction of different proteins. The dissociation constant Kd of the LD-dimer (Kd(LD)) of eBLUF was ~25 μM in a buffer solution containing 300 mM NaCl. However, for applications involving light control in cells, a smaller Kd may be desired. Moreover, identifying the dimerization site is important for future improvement of the protein using site-directed mutation techniques. For improving these aspects, we studied the salt-effect on the dimer formation of eBLUF in detail using the TG method and multi-angle light scattering (MALS) method. It was found that the presence of salt decreased Kd by more than 100 times compared with that in a buffer without salt, and this salt effect mostly originated from the cation but not from the anion. These results indicate that the monomer–dimer equilibrium is determined by a balance between the hydrophobic interactions at the dimer interface, which favor the dimer formation, and electrostatic repulsion between the negatively charged sites, which favors the monomer formation. This implies that the addition of salt decreases the electrostatic repulsion by cation binding and results in stabilization of the dimer. On the basis of this finding, we succeeded in identifying a possible dimerization site close to the end of the C-terminal helix. Using this information, we prepared a mutant of D137N, and found that it exhibited much higher stability of the LD-dimer and higher selectivity for dimer formation than the wild-type (WT)-eBLUF.

The results and discussions in more detail will be presented.

REFERENCES

[1] M.Terazima,Time-Dependent Intermolecular Interaction during Protein Reactions, Phys.Chem.Chem.Phys., 13, 16928-16940 (2011).

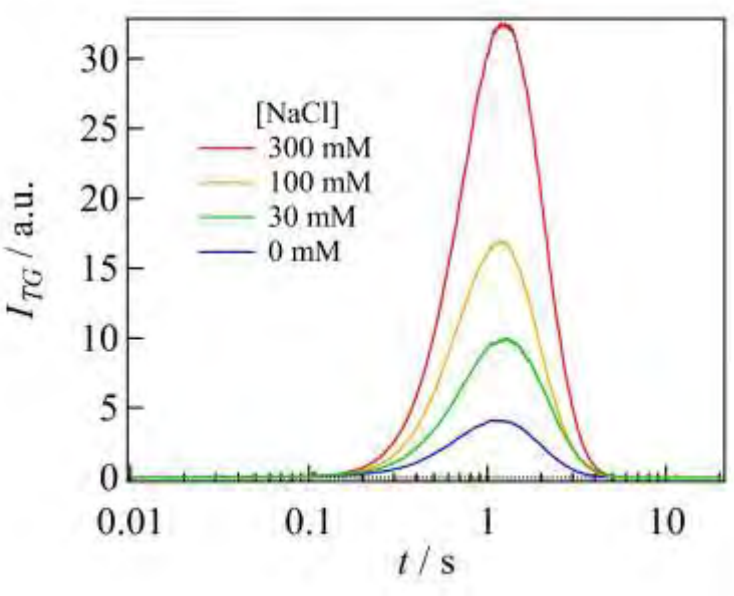

Figure 1: Diffusion signals from the TG measurement at $q^2 = 1.1\times10^{10}$ m^{-2} after the photoexcitation of eBLUF (50 µM) at various NaCl concentrations. The concentrations are indicated in the legend.

Molecular Interactions Derived from Water Activity and Specific Salting-in and Salting-out Effects in Solutions of Two- and Three-Basic Amino Acids and their Salts at 298.15 and 310.15 K

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For the elaboration of interpretations, models, and theories of functioning and activating of protein channels in nerve and muscle cells, the data on Na^+, K^+, Mg^{2+}, Ca^{2+} salts of excitatory amino acids are needed [1,2]. Sodium salts of (S)-aminopenthanedioic acid and (S)-aminobutanedioic acids (glutamate and aspartate) are especially important in the system of nerve impulse transmission. To investigate such complexes of proteins containing hydrophilic anions as aspartate or glutamate is of paramount interest, because colloidal self-assembly is a mean to create a new generation of materials with complex shape and surface chemistry [3,4]. Liquid patches can create robust bonds in super-colloidal architectures.

In this work the study of ion-specific interactions of cations and anions with proteinogene amino acids is undertaken: non-polar amino acid with small aliphatic radical – glycine (ambiphilic), and with the polar hydrophilic amino acids – glutamic acid, aspartic acid, histidine and their salts with charged carboxylic and amino groups playing important role in affinity on protein. With the help of a colligative property – vapour pressure measuring – the cation and anion affinity to the amino acids and their salts has been studied at T=298.15 K and 310.15 K. The cations are alkali (Na^+, K^+) and alkali-earth (Mg^{2+}, Ca^{2+}) metal ions as well as aminomethanamidine (guanidinium, $Gndm^+$) as an ion with irregular charge distribution and complex geometry that stimulates "salting-in" of proteins and shows specific cation binding to acidic amino acid residues, used for denaturation and recurrent protein folding [5]. The anions are OAc^-, Cl^-, NO_3^-, SCN^- varying from salting-out to salting-in.

Activities of water, activity coefficients of water and the corresponding osmotic coefficients of the mixtures have been calculated, both being directly related to the chemical potentials of the different species and therefore to their Gibbs energy.

Ion-specific effects are analyzed based on the concentration dependence of the experimental osmotic coefficients of the solutions of glycine, glutamic acid, aspartic acid, histidine and their salts.

Models of electrostatic and structural contribution are used to fit the experimental data to obtain the corresponding dual and triple interaction parameters. Hard-sphere and electrostatic parts of the osmotic coefficients of aqueous solutions of symmetrical (2-2, 1-1) and non-symmetrical (2-1) amino acid salts are calculated at 298.15 K and 310.15 K in the framework of the equations of g^E (excess Gibbs free energy) model. Mean Spherical Approximation yields reasonable fitting parameters and a picture that is consistent with the experimental data for glutamate and aspartate aqueous solutions.

The modeling of chemical potential in ternary systems is done by an EoS (equation of state). Electrolyte Perturbed-Chain Statistical Associating Fluid Theory has been used to model ternary amino acid + salt + water systems and amino acid salt + salt + water systems. It include the TPT1 of Wertheim, takes into account along with dispersion interactions also association and dipolar interactions in explicit form.

Assuming the hard chain, dispersive and association energy [6,7] as ionic parameters permits the correct description of the maximums and minimums of the osmotic coefficients at both temperatures. Beside of electrostatic interactions, also specific interactions like van der Waals, dispersion, and ion-dipole effects has been shown to occur in these systems. Thermodynamic properties of these solutions such as fugacity coefficients and activity coefficients of the mixture components are also calculated with ePC-SAFT.

Also, two-parameter fitting (third order terms in the power series) was applied to calculate solute activity coefficients in the ternary solutions.

The decrease in the chemical potential of amino acid salts corresponds to the Hofmeister series. A strong interaction between amino acid and salt due to specific dispersion interactions in amino acid salt systems containing guanidinium-based salt has been revealed to be in agreement with MD and half-empirical quantum-chemical calculations.

REFERENCES

[1] Marcus, Y., Ions in Water and Biophysical Implications: From Chaos to Cosmos, Dordrecht: Springer (2012) 215 p.

[2] Kunz, W. (Ed.): Specific Ion Effects, London: World Scientific (2010)

[3] Duclohier, H. (Ed.): Biophysics of Ion Channels and Deceases, Kerala: Research Signpost (2010)

[4] Harding, S.E., Biophys. Chem., 93 (2001) page 87- 246

[5] Makhatadze, G. I., Fernandez, J., Freire, E., Lilley, T.H., Privalov P.L., J. Chem. Eng. Data, 38 (1993) page 83-87

[6] Gross, J., Sadowski, G., Fluid Phase Equilibr., 168, (2000) page 183-199

[7] Barker, J.A., Henderson, D., J.Chem.Phys., 47, (1967) page 2856

Molecular Versus *Ionic* liquids: Development of a Thermodynamic Framework for Predicting Vaporization Thermodynamics

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Ionic liquids based on the pyridinium cations show good result in desulfurization of fuels. The knowledge of their vaporisation thermodynamics is of practical importance. The standard molar enthalpies of vaporization of pyridinium based ionic liquids were derived from the vapor pressure temperature dependences measured by the quartz-crystal microbalance method. We have collected available primary experimental results on vapour pressures, and enthalpies of phase transitions (solid-solid, crystal-gas, and liquid-gas) of analogous molecular species – substituted pyridines. These data were evaluated using the structure-property correlations. The consistent sets of evaluated thermodynamic data on the *molecular* and *ionic* liquids were used to develop the "centerpiece" based group-additivity method for predicting enthalpies of vaporization of *molecular* and *ionic* compounds.

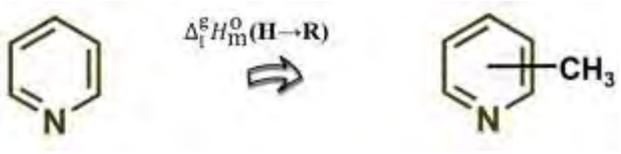
The main idea of this work is demonstrated in Fig. 1. The general transferability of the contributions to the enthalpy of vaporization from the *molecular* liquids to the *ionic* liquid has been established [1]. Indeed, the vaporization enthalpies of *e.g.* of pyridine derivatives can be reliably predicted with the help of a simple contribution, $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(H→**R**), representing the replacement of a H-atom in pyridine with any substituents (see Eq. 1). It has been found, that for pyridinium based ionic liquids the same numerical values for the contributions $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$**(H→R)** can be used to estimate their vaporization enthalpies $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) as given by Eq. (2).

The "centerpiece" approach is closely related to the broadly used group-additivity (GA) methods. In conventional GA methods, the energetics of a molecule of interest is gathered from a possibly small groups (based on the idea of a "LEGO® bricks") with well-defined contributions. In contrast, the idea of the "centerpiece" approach is to select a potentially large "core" molecule that can mimic the structure of the molecule of interest, but the selected "core" molecule is supposed to possess well-established thermodynamic properties. For example, the [C_4-Py][NTf_2] can be considered as one of the potential "centerpiece" molecules (see Fig. 1, Eq.2), which is related to prediction of ILs vaporization enthalpies using the $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$**(H→R)** contributions evaluated in this work. Different substituents can be attached to this "centerpiece" in various positions. The visualization of the "centerpiece" approach for R-substituted [C_4-Py][NTf_2] ionic liquid is given in Fig. 1. A small, but not negligible correction term was supposed to reconcile estimated results with experiment. The corrected "centerpiece" approach was recommended to predict vaporization enthalpies of ILs [2].

REFERENCES

[1] Verevkin, S.P.; Zherikova, K.V.; Martynenko, E.A., J. Mol. Liq. 350 (2022) 118576.
[2] Verevkin, S.P., Zaitsau, D.H., Ludwig R., Molecules 27 (2022) 2321.

FIGURES



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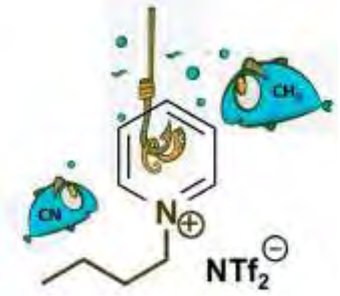

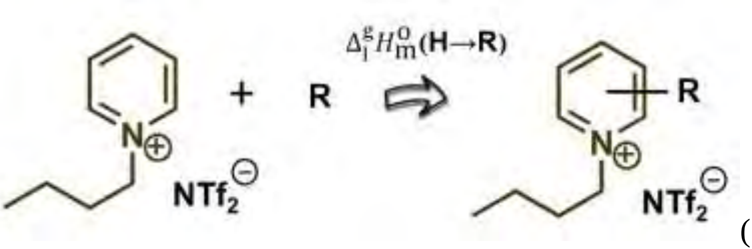

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Figure 1: Assessment the enthalpy of vaporization, $\Delta_l^g H_m^o$(298.15 K) in *molecula*r (Eq. 1) and in *ionic* liquids (Eq. 2), and visualization of the "centerpiece" approach for the substituted the [C4-Py][NTf2] (left). Estimation of $\Delta_l^g H_m^o$(298.15 K)-values for [R-1-C$_4$-Py][NTf$_2$] ionic liquids (right).

pyRISM – Python Implementation of the Reference Interaction Site Model

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The Reference Interaction Site Model (RISM) equation is a molecular integral equation theory (IET) method for molecular liquids formulated by Chandler et al.[1] and further developed over the years to apply to polar and ionic molecular liquids. It is a rigorous statistical mechanical approach to predicting liquid structure and solvation thermodynamics[2]. There are very few widely available open-source and modern implementations of the RISM equation. pyRISM is an open-source python implementation of the RISM equation. It calculates radial distribution functions and various correlation functions for neat liquids as well as solute interactions under the assumption of infinite dilution. Using the correlation functions, solvation free energy can be computed from RISM theory. It can also calculate the solvation free energy density profile of a liquid[3]. The RISM equation is a nonlinear integral equation and is treated as a fixed-point problem. This problem is solved iteratively and quickly using the Modified Direct Inversion in the Iterative Subspace (MDIIS) method for accelerating convergence. The convolutional integrals are solved with Fast Fourier Transform (FFT). NumPy[4] and SciPy[5] are utilised to make use of their built-in functions implemented in C, and Numba[6] is used to speed up any parts of the code that cannot be vectorised by NumPy. An extension of the code enables chemically accurate predictions of solvation free energies in both aqueous and organic solvents at a wide-range of temperatures using a novel deep learning derived solvation free energy functional.

REFERENCES

[1] Andersen, H. C.; Chandler, D. Optimized Cluster Expansions for Classical Fluids. I. General Theory and Variational Formulation of the Mean Spherical Model and Hard Sphere Percus-Yevick Equations. *J. Chem. Phys.* **1972**, *57* (5), 1918–1929. https://doi.org/10.1063/1.1678512.

[2] Ratkova, E. L.; Palmer, D. S.; Fedorov, M. V. Solvation Thermodynamics of Organic Molecules by the Molecular Integral Equation Theory: Approaching Chemical Accuracy. *Chem. Rev.* **2015**, *115* (13), 6312–6356. https://doi.org/10.1021/cr5000283.

[3] Palmer, D. S.; Mišin, M.; Fedorov, M. V.; Llinas, A. Fast and General Method To Predict the Physicochemical Properties of Druglike Molecules Using the Integral Equation Theory of Molecular Liquids. *Mol. Pharmaceutics* **2015**, *12* (9), 3420–3432. https://doi.org/10.1021/acs.molpharmaceut.5b00441.

[4] Harris, C. R.; Millman, K. J.; van der Walt, S. J.; Gommers, R.; Virtanen, P.; Cournapeau, D.; Wieser, E.; Taylor, J.; Berg, S.; Smith, N. J.; Kern, R.; Picus, M.; Hoyer, S.; van Kerkwijk, M. H.; Brett, M.; Haldane, A.; del Río, J. F.; Wiebe, M.; Peterson, P.; Gérard-Marchant, P.; Sheppard, K.; Reddy, T.; Weckesser, W.; Abbasi, H.; Gohlke, C.; Oliphant, T. E. Array Programming with NumPy. *Nature* **2020**, *585* (7825), 357–362. https://doi.org/10.1038/s41586-020-2649-2.

[5] Virtanen, P.; Gommers, R.; Oliphant, T. E.; Haberland, M.; Reddy, T.; Cournapeau, D.; Burovski, E.; Peterson, P.; Weckesser, W.; Bright, J.; van der Walt, S. J.; Brett, M.; Wilson, J.; Millman, K. J.; Mayorov, N.; Nelson, A. R. J.; Jones, E.; Kern, R.; Larson, E.; Carey, C. J.; Polat, İ.; Feng, Y.; Moore, E. W.; VanderPlas, J.; Laxalde, D.; Perktold, J.; Cimrman, R.; Henriksen, I.; Quintero, E. A.; Harris, C. R.; Archibald, A. M.; Ribeiro, A. H.; Pedregosa, F.; van Mulbregt, P.; SciPy 1.0 Contributors. SciPy 1.0: Fundamental Algorithms for Scientific Computing in Python. *Nature Methods* **2020**, *17*, 261–272. https://doi.org/10.1038/s41592-019-0686-2.

[6] Lam, S. K.; Pitrou, A.; Seibert, S. Numba: A LLVM-Based Python JIT Compiler. In *Proceedings of the Second Workshop on the LLVM Compiler Infrastructure in HPC*; LLVM '15; Association for Computing Machinery: New York, NY, USA, 2015. https://doi.org/10.1145/2833157.2833162.

Ionic transport in soft subnanometric films

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In February 2022, the Intergovernmental Panel on Climate Change (IPCC) report [1] has been published by the UNO, which stated the critical situation and the environmental emergency to reduce greenhouse gases emission to keep the global warmth below 1.5°C. Thus, an effort has to be made to be able to harvest energy with a minimal CO_2 emission; nanofluidics appears to be one of the promising field to address this challenge.

Nanofluidics is a booming research field considering fluidic transport – such as hydrodynamic, electrical or thermal transport – in nanoconfined liquids. At such scales, the surface to volume ratio is extremely large and transport properties are mainly governed by interactions at interfaces.

Whereas macroscopic continuous models for electrostatics and hydrodynamics predict well ionic transport for 1-10 nm thick nanochannels, some anomalous properties have been reported in the regime of ultraconfinement, below 1 nm, where a continuous description fails, such as dielectric anomalies in confined water [2], anomalous ionic mobilities in angstrom-scale confined water [3] and other unexpected behaviors [4]. An effort has to be made to precisely understand such behaviors in ultraconfined system, with the ultimate goal to enhance the harvesting of energy in nanofluidic systems.

In the present work, this regime of ultraconfinement is investigated. For that, the conductance of water soft films that condense spontaneously from undersaturated vapor on hydrophilic silica surfaces (see figure below) is measured as a function of their thickness. This thickness is modulated by the relative humidity above the substrate. To our knowledge, this experiment is one of a kind to control continuously the confinement down subnanometric scales. Despite some aging effects, the measurements are very stable and reproducible. A regime of surface conductivity is recovered for large humidity, i.e. for thickness above 1 nm but fails below. A model based on a hindered diffusion layer close to the interface is developed to explain the measurements below the hydrodynamic limit (1 nm). These experimental results open the way to new transport descriptions in ultraconfinement.

REFERENCES

[1] Shukla, P.R., *et al.*, Cambridge University Press, IPCC, 2022: Climate Change 2022: Mitigation of Climate Change. Contribution of Working Group III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change (April 2022)

[2] Fumagalli, L., Esfandiar, A., Fabregas, R., Hu, S., Ares, P., Janardanan, A., Yang, Q., Radha, B., Taniguchi, T., Watanabe, K., Gomila, G., Novoselov, K. S., & Geim, A. K., Science, Anomalously low dielectric constant of confined water (2018), 360(6395), 1339–1342.

[3] Esfandiar, A., Radha, B., Wang, F. C., Yang, Q., Hu, S., Garaj, S., Nair, R. R., Geim, A. K., & Gopinadhan, K., Science, Size effect in ion transport through angstrom-scale slits (2017) 358(6362), 511–513.

[4] Bocquet, L., Nature Materials, Nanofluidics coming of age (2020), 19(3), 254–256.

FIGURE

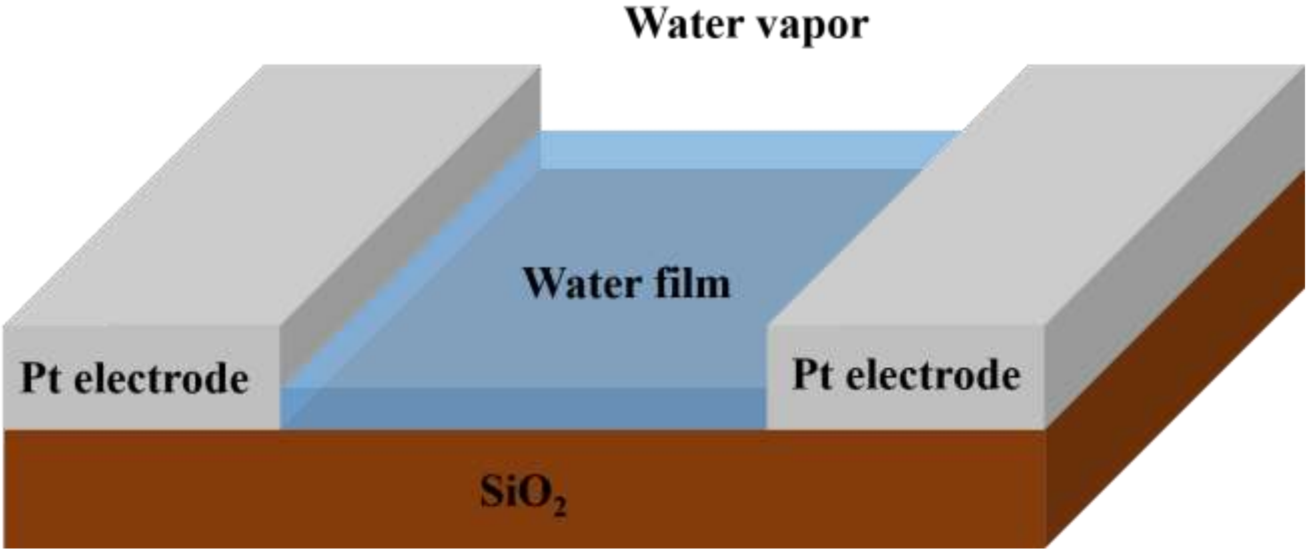

Figure 1: Schematic of the experimental setup

Structure of Aqueous Solutions of Heterocyclic Amines

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Heterocyclic amines, such as piperidine and N-methylpiperidine, and their hydrates aggregate in aqueous solutions due to hydrogen bonds between hydration water molecules. No such aggregation occurs in the mixtures of these amines with other hydrogen-bonded solvents, such as methanol or ethanol. This difference highlights the active role of water solvent in promoting the self-aggregation. However, the role of various contributions in thermodynamic functions due to specific interactions, van der Waals forces, and the effect of the size and shape of the molecules remains open. In the present communication we explore and discuss the family of solutions of pyrrolidine, piperidine, and their methylated counterparts in water and in methanol, as revealed by thermodynamic measurements as well as by direct visualisation of the mesoscopic stucture employing small-angle neutron scattering.

While the limiting partial molar enthalpies of solutions of pyrrolidine, N-methylpyrrolidine, piperidine, and N-methylpiperidine in methanol follow closely the trend assessed from theoretically calculated molecular interaction energies, their behavior is markedly different in water solutions, which require an empirical hydrophobic hydration term to be considered.

SANS evidenced that the aqueous amine solutions are microheterogeneous on the nanometer-order length scale [1]. Various models are considered for describing the structural arrangement of the hydrated amine molecules. The tendency of approaching phase separation increases in the order: N-methylpiperidine < N-methylpyrrolidine < piperidine < pyrrolidine [2].

REFERENCES

[1] W. Marczak, J.T. Hołaj-Krzak, P. Lodowski, L. Almásy, G.C. Fadda, Chem. Phys. Lett., 619 (2015) 77
[2] W. Marczak, M.A. Varfolomeev, I.T. Rakipov, P. Lodowski, K. Kowalska-Szojda, M. Łężniak, L. Almásy, A. Len, J. Phys. Chem. B 121 (2017) 3070

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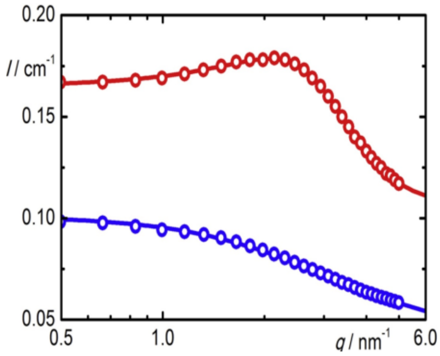

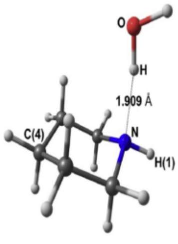

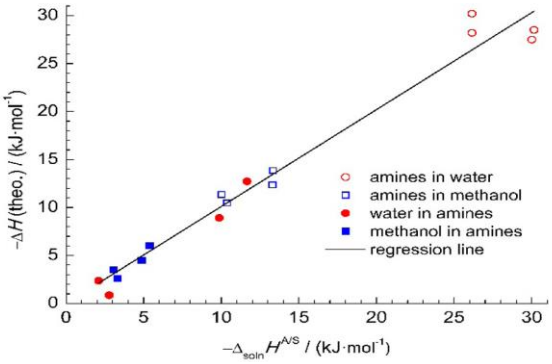

Nucleation of helium in molten lithium

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In the breeding blankets of nuclear fusion reactors tritium and helium (He) are produced in the same amount (mol-to-mol) from neutron capture reactions by lithium (Li) isotopes. The resulting He, which has a very low solubility in liquid metals (LM), may nucleate affecting the behavior of the BB (magneto-hydrodynamic flow and transport properties, electrical conductivity, etc.). Due to safety reasons, liquid lead-lithium (LiPb) eutectic alloy is preferred over pure Li as the breeding material. The molecular dynamics method is implemented, using both LAMMPS package [1] and Fortran codes, to simulate the phenomenon of He nucleation in pure molten Li as a first step to characterize its behavior in LiPb alloys. The most fundamental step to understand and describe our systems is finding the best choice of interatomic potentials. Starting from pure Lennard-Jones (LJ) interactions and other simple models [2-4], which reproduce the segregation of Li and He phases quite well (see, for instance, figure 1), but overestimate the Li-He repulsion, we have moved to more refined models: figure 2 shows the Toennies-Tang-Sheng (TTS) potentials [5,6] for He-He and Li-He, which have a softer repulsive region compared to the steep wall of LJ potentials but similar wells (both position and depth), while figure 3 presents both embedding function (electronic density contribution) and pair potential of Embedded Atom Models (EAM) [6-9] for the LM. We rely on the accuracy of radial distribution functions and thermo-physical properties (such as density and diffusion coefficients), compared to experimental data, to validate the chosen set of interatomic potentials. Other issues related to the potentials, such as the computational complexity, have also been considered. In addition, other properties such as surface tension of He bubbles have been studied. The onset of nucleation is studied by means of the Henry's constant. We explore moderate thermodynamic states in which temperature is below the boiling and above the melting points of both pure molten Li and LiPb eutectic and ambient-like pressures (typically of 843 K and 1 bar).

REFERENCES

[1] A. P. Thompson, H. M. Aktulga, R. Berger, D. S., Bolintineanu, W. M. Brown, P. S. Crozier, P. J. in 't Veld, A. Kohlmeyer, S. G. Moore, T. D. Nguyen, et al., Computer Physics Communications 271 (2022): 108171.
[2] R.A. Aziz, V.P.S. Nain, J.S. Carley, W.L. Taylor, and G.T. McConville., The Journal of Chemical Physics 70.9 (1979): 4330-4342.
[3] P. Dehmer, and L. Wharton, *The Journal of Chemical Physics,* 57.11 (1972): 4821-4835.
[4] M. Canales, L.E. González, J.À. Padró, *Physical Review E,* 50.5 (1994): 3656-3669.
[5] X. Sheng, J. P. Toennies, and K. T. Tang., *Physical Review Letters,* 125.25 (2020): 253402.
[6] X. W. Sheng, and K. T. Tang. "The development of a full range analytical interatomic potential." *Physical Chemistry Chemical Physics* 23.13 (2021): 7748-7757.
[7] D. K. Belashchenko, *Inorganic Materials*, 48.1 (2012): 79-86.
[8] D. K. Belashchenko, *Russian Journal of Physical Chemistry*, *A* 86.5 (2012): 779-790.
[9] D. K. Belashchenko, *High Temperature*, 57.6 (2019): 848-858.

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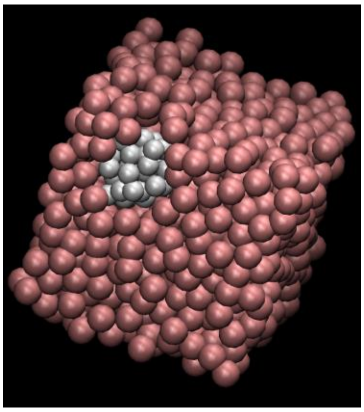

Figure 1: Snapshot of a cluster of 40 He atoms in a simulation box with 1000 Li.

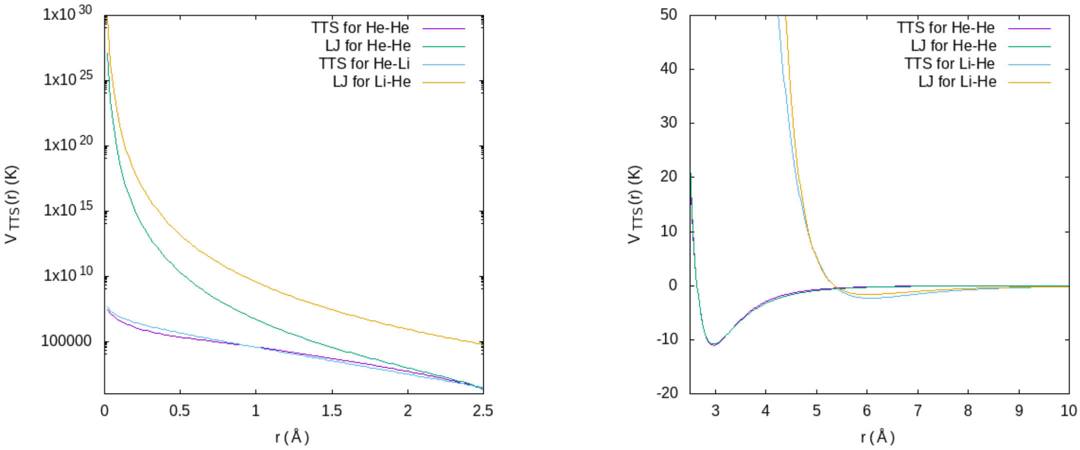

Figure 2: Comparison of LJ and TTS potentials for pair (helium-helium and helium-lithium) interactions. Both short (left, logarithmic scale for the y-axis) and long (right) ranges are represented.

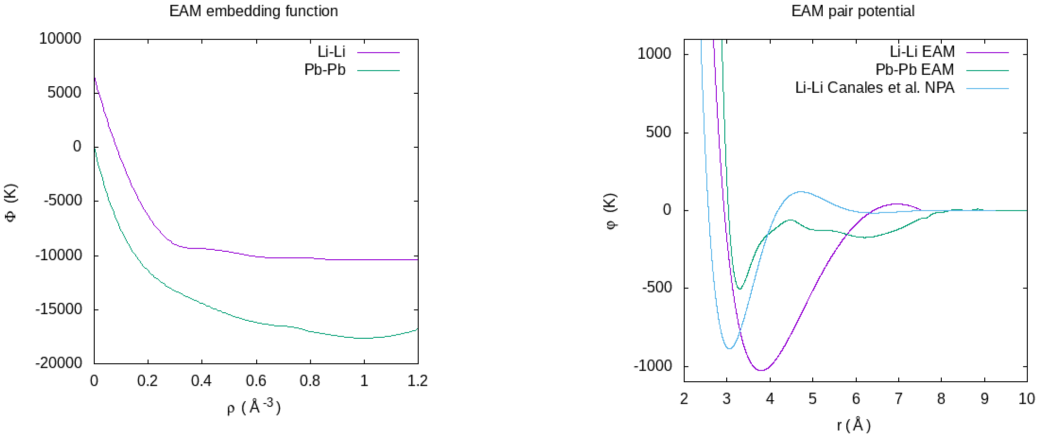

Figure 3: Embedding function and pair contribution of lithium-lithium and lead-lead (EAM) potentials.

Theory for Heterogeneous Water/Oil Separation

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Oil-polluted water is produced in large quantities in both domestic and industry utilities, which necessitate the development of new functional materials for fast and cheap phase separation [1-2]. It was shown in laboratory that membranes designed as hydrophilic or hydrophobic may separate oil/water mixtures [3-4]. The membrane pores possess specific affinity to water or oil, so that to favor the passage of the same phase through the pores and repeal the opposite phase away from the membrane.

We employ classical density functional theory (DFT) to elucidate the physical mechanisms governing the phase separation of water/oil emulsion near a membrane surface which possesses specific affinity to oil, at near-equilibrium. We capture emulsion concentration variations near the membrane surface while accounting for the finite volume of oil droplets in the emulsion's bulk and surface forces of molecular origin, i.e., hydrophobic, Van Der Waals (VDW), and electrical double layer (EDL) interactions, between the emulsion droplets.

We establish a clear connection between the size of drops, the surface forces between drops in the suspension and the variation in the concentration of droplets next to the membrane. We observe an increase in the concentration of oil droplets next to the lipophilic membrane surface at approximately 10 drop radii. Hence, pores in the membrane will support phase separation if their diameter corresponds to the length scale where the concentration of oil droplets near the solid is appreciably greater than the one in the liquid bulk. Moreover, we observe that the contribution of surface forces to the oil film (wetting the surface) thickness becomes appreciable for droplets smaller than 1 micron. Energy barriers to droplet attachment, which originate in surface forces, appear to increase the dense oil region volume next to the membrane.

REFERENCES

[1] R. K. Gupta, G. J. Dunderdale, M. W. England, and A. Hozumi, “Oil/water separation techniques: a review of recent progresses and future directions,” Journal of Materials Chemistry A, vol. 5, no. 31, pp.16 025–16 058, 2017.

[2] Y.-T. Hung, H. H. Lo, L. K. Wang, J. R. Taricska, and K. H. Li, “Powdered activated carbon adsorption,” in Advanced physicochemical treatment processes. Springer, 2006, pp. 123–153.

[3] A. Cambiella, E. Ortea, G. Rios, J. M. Benito, C. Pazos, and J. Coca, “Treatment of oil-in-water emulsions: Performance of a sawdust bed filter,” Journal of Hazardous Materials, vol. 131, no. 1-3, pp.195–199, 2006.

[4] X. Huang and T.-T. Lim, “Performance and mechanism of a hydrophobic–oleophilic kapok filter for oil/water separation,” Desalination, vol. 190, no. 1-3, pp. 295–307, 2006.

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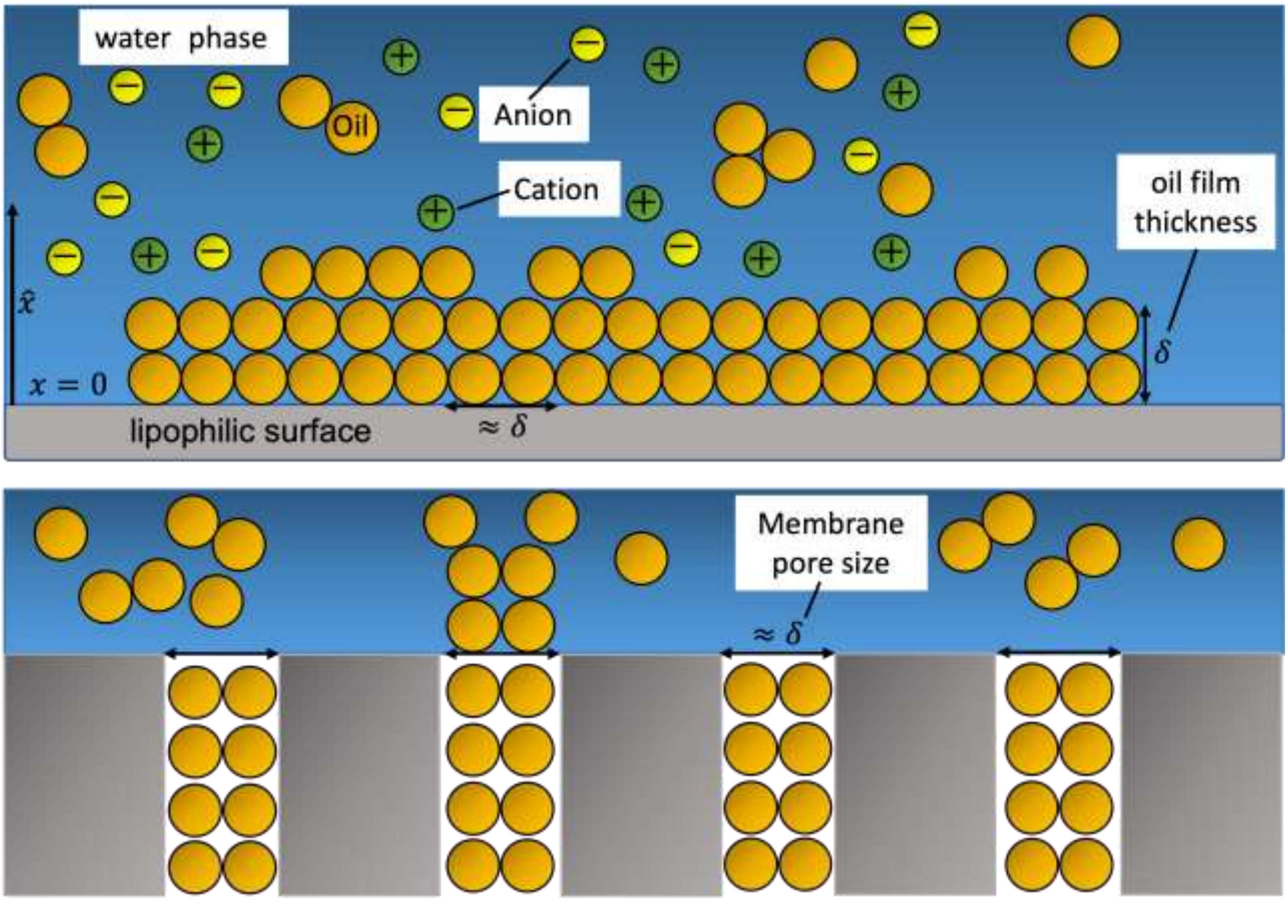

Figure 1: A semi-finite system with oil droplets (brown spheres) in water near a lipophilic solid surface (in gray). The oil droplets wet the membrane due to their chemical affinity to the lipophilic surface to form an oil film of thickness δ, which should be roughly equal to the pore size of a corresponding membrane to separate the mixture.

Water-methanol mixture segregation and separation under confinement

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Water pollution and renewable energy sources are a matter of broad concern, both environmental challenges for our society. For its applications in the chemical and pharmaceutical industry, production of synthetic fibers and plastic, and as a fuel additive, methanol attracts interest for how to model its properties when mixed with water. Here, we consider a minimalistic model for a water-methanol mixture confined between two parallel graphene nanosheets and analyze the diffusion coefficient of each component as the slit-pore's width δ increases. We find that layering in the hydrophobic pore induces segregation between the two components. The methanol apolar moiety segregates near the pore walls, while water populates more in the central layer away from the hydrophobic walls. Furthermore, both liquids have a diffusion coefficient that changes non-monotonically with δ, with water always diffusing faster than methanol. Changes in the pore width affect the two mixture components in different amounts, suggesting the possibility of an efficient method for methanol-water separation based on a physical procedure.

The Madrid-2019 force field for electrolytes in water: An extension to the ions F^-, Br^-, I^-, Rb^+ and Cs^+

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In this work, we present an extension of the Madrid-2019 force field [1]. We have added to this extension the cations Rb+ and Cs+ and the anions F−, Br−, and I−. These ions were the remaining alkaline and halogen ions, not previously considered in the Madrid-2019 force field. The force field, denoted as Madrid-2019-Extended [2], does not include polarizability and uses the TIP4P/2005 [3] model of water and scaled charges for the ions. A charge of ±0.85e is assigned to monovalent ions. This new force field developed provides an accurate description of aqueous solution densities over a wide range of concentrations up to the solubility limit of each salt studied. Good predictions of viscosity and diffusion coefficients are obtained for concentrations below 2 m. Structural properties obtained with this force field are also in reasonable agreement with the experiment. The number of contact ion pairs has been controlled to be low so as to avoid precipitation of the system at concentrations close to the experimental solubility limit. We also present a comprehensive comparison of the performance for aqueous solutions of alkaline halides of force fields of electrolytes using scaled and integer charges. This comparison will help in the future to learn about the benefits and limitations of the use of scaled charges to describe electrolyte solutions.

REFERENCES

[1] I. M. Zerón, J. L. F. Abascal and C. Vega, J. Chem. Phys., 151 (2020) 134504
[2] S. Blazquez, M. M. Conde, J. L. F. Abascal and C. Vega, J. Chem. Phys., 156 (2022) 044505
[3] J. L. F. Abascal and C. Vega, J. Chem. Phys., 123 (2005) 234505

Rules of thumb for creating useful reduced models: the case study of nanopores

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“All models are wrong, but some are useful.” said George Box in 1976. How true it is! This presentation is about how we can create useful reduced models. In a complex many-particle system, by reduced model we mean that some of the degrees of freedom are modeled explicitly, while some of them are modeled implicitly. The explicit degrees of freedom are the important ones that we handle with explicit particles in the model and in the associated computer simulations. The implicit degrees of freedom are the less important ones that are modeled by implicit response functions. By useful reduced models we mean models that can predict and explain the relationship between the input and output variables of a device. We call this relationship the device function. The art of creating good reduced models lies in distinguishing between the important and unimportant degrees of freedom. Here we present rules of thumb that we can apply in a procedure of constructing reduced models of nanopores that facilitate the controlled transport of ions through a membrane. This system is a device of basic importance both in biology (ion channels) and in technology. Controlling the ion transport depends on molecular level phenomena so using a molecular model is essential. In the case of nanopore, we balance between the need for molecular description (more detail) and the need for efficient computation of device behavior (less detail). This balance results in the useful reduced model. We show, for example, that basic device functions can be understood and reproduced by using the implicit-water framework where the effect of water molecules on ions are described by two response functions: their screening effect on electrostatic forces is described by a dielectric constant of a dielectric continuum, while their frictional effect on moving ions is described by a diffusion coefficient. Results are shown for selective ion channels and rectifying nanopores.

REFERENCES

[1] D. Boda, M. Valiskó, D. Gillespie. Modeling the device behavior of biological and synthetic nanopores with reduced models. *Entropy*, 22 (2020) 1259.

FIGURES

Figure 1: A typical reduced model that can reproduce device behavior.

Dynamics of water under confinement by *soft* and *hard* boundaries: a comparative analysis using all-atom MD simulations.

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Understanding the distinctive properties of water in confinement is important as a fundamental problem and also for potential applications in microfluidics such as in processes of filtration and separation of solutes [1]. It is known both from experiment and simulations that the dynamics of water is greatly affected when it is under confinement and that the nature of the confining walls can have a strong effect on the dynamics of interfacial water. In this contribution we perform a comparative analysis of the influence of confinement on the dynamical properties of water for soft and hard confining boundaries using molecular dynamics simulations. We use realistic all-atom models of a phospholipid membrane as the soft boundary and of a graphene plane as the hard boundary. We show that, although the effect of confinement hinders the dynamics of water molecules in both cases, the nature of the boundaries induces very distinctive behavior. On the one hand, the dynamics of water confined between phospholipid membranes monotonically slows down as the distance between the confining boundaries decreases [2]. In addition, both the diffusion and the rotational dynamics of water molecules are dramatically slowed down (by ~ 2 orders of magnitude) in high confinement due to the sluggish dynamics of water molecules which penetrate into the membrane. On the other hand, the dynamics of water confined by graphene planes exhibits a non-monotonic behavior as a function of the distance between the confining boundaries as a result of a more structured water interface [3,4]. The effect of pressure on the dynamics of water under confinement is also discussed.

REFERENCES

[1] R. K. Joshi, P. Carbone, F. C. Wang, V. G. Kravets, Y. Su, I. V. Grigorieva, H. A. Wu, A. K. Geim, R. R. Nair, RR. *Science*, 343 (2014) 752
[2] C. Calero, H. E. Stanley, G. Franzese. *Materials* 9.5 (2016) 319.
[3] C. Calero, Carles, G. Franzese. *Journal of Molecular Liquids* 317 (2020) 114027.
[4] F. Leoni, C. Calero, G. Franzese. *ACS nano* 15.12 (2021) 19864.

Hydrogen bonding in aqueous solutions of sulfuric and methanesulfonic acids: a computer simulation study

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Abstract

One of the current research topics in atmospheric physics is the study of the influence of sulphate aerosols in the atmospheric dynamics; particularly, in the acid rain or in the greenhouse effect. In many cases these aerosols are aqueous clusters of ionized sulfuric or methanesulfonic acids [1]. In the present study, we have performed a series of molecular dynamics simulations of aqueous solutions of sulfuric [2,3] and methanesulfonic [4] acids at different concentrations and temperatures. The dissociation of the acids has been explicitly considered. Calculations have been conducted using reliable force fields, with scaled ionic charges, which allow us to determine density and viscosity values in good agreement with available experimental data. A hydrogen bond analysis, involving only water molecules, has been carried out. To this end, the mean number of hydrogen bonds between water molecules and between ions and water molecules, the percentages of molecular species hydrogen bonded with a given number of water molecules, and the continuous and interrupted lifetimes have been calculated. We have observed that water molecules bonded to the anions are more labile than those bonded to other water molecules or to hydronium ions, the labilities increasing when the temperature rises. Moreover, the characteristic tetrahedral structure of water vanishes when the concentration or the temperatures increases.

REFERENCES

[1] K. Lehtipalo et al., Nat. Commun. 7 (2016) 11594.
[2] M. Canales, E. Guardia, J. Mol. Liq. 293 (2019) 111463.
[3] M. Canales, E. Guardia, J. Mol. Liq. 347 (2022) 118351.
[4] M. Canales, E. Guardia, *to be submited* (2022).

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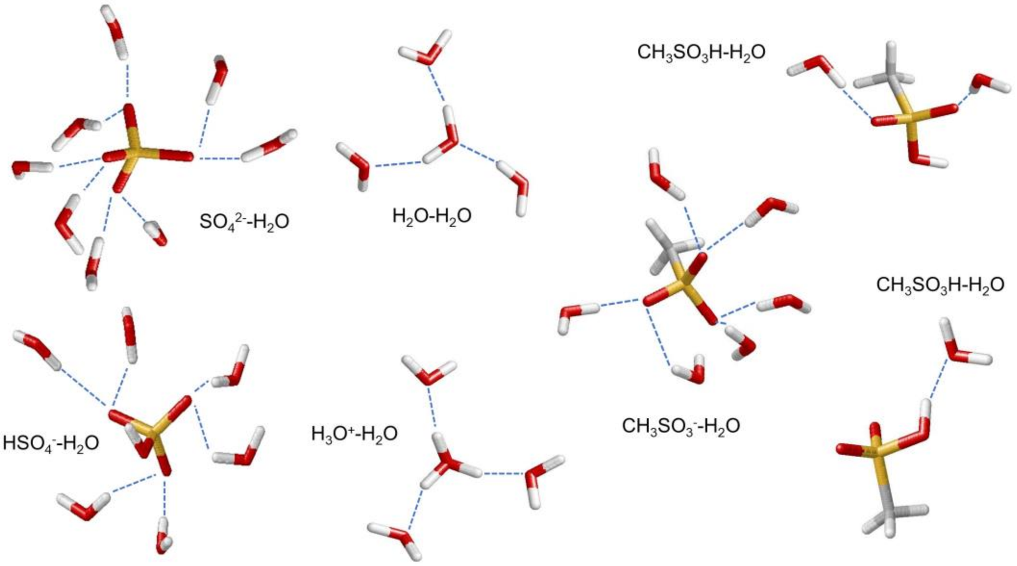

Figure 1: Representative snapshots of ion-water and water-water hydrogen bonds

Fluid phase equilibrium in confinement: effects of compressibility and wetting

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The liquid-vapor transition is affected by confinement. Even for water in sub-millimeter containers, the density of the liquid in equilibrium with its vapor differs from the bulk value, and the vapor becomes unstable before the liquid reaches the bulk equilibrium pressure [1-4]. I revisit this phenomenon with a fully analytic approach. A natural length emerges: the Berthelot-Laplace length $\lambda=2\gamma\kappa/3$, where γ and κ are the liquid-vapor surface tension and the liquid isothermal compressibility, respectively. This allows to easily determine the various regimes for any fluid, and to extend the results to the case where the liquid phase wets the container walls only partially. This has practical implications in the use of fluid inclusions in minerals for palaeotemperature reconstruction [2,5].

REFERENCES

[1] A. Fall, J. D. Rimstidt, and R. J. Bodnar, Amer. Mineralogist, 94 (2009) 1569.
[2] D. Marti, Y. Krüger, D. Fleitmann, M. Frenz, and J. Rička, Fluid Phase Equilib., 314 (2012) 13
[3] Ø. Wilhelmsen, D. Bedeaux, S. Kjelstrup, and D. Reguera, J. Chem. Phys., 141 (2014) 071103
[4] O. Vincent and P. Marmottant, J. Fluid Mech., 827 (2017) 194
[5] E. Guillerm, V. Gardien, D. Ariztegui, and F. Caupin, Geostand. Geoanal. Res., 44 (2020) 243

A quantitative water model for large-scale simulations at life-relevant conditions

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All-atom simulations of large-size biological systems with explicit water come at a tremendous computational cost. To overcome this problem, coarse-grained models aim to represent the system in a simplified manner but keep the essential properties relevant to its behavior. We consider the coarse-grained model initially introduced by Franzese and Stanley (FS) for water monolayers [1, 2]. The model describes the hydrogen bonds at the molecular level, explicitly accounting for the many-body interactions, but coarse-grains the molecular positions. It is analytically tractable [3] and can be equilibrated by efficient cluster Monte Carlo dynamics [4] for large systems (10^7 molecules) at extremely low temperatures (deep supercooling) in a wide range of pressures (both negative and positive) [5]. Here, we extend it to bulk and reparametrize it to quantitatively agree with the experimental water results for density and thermodynamic response functions around ambient conditions, a prerequisite for its use as a solvent in biological simulations. The region of the quantitative agreement extends up to 50 MPa, covering almost all pressure conditions allowing life on Earth in a temperature range that can be as large as 60 degrees around ambient conditions.

REFERENCES

[1] G. Franzese and H. E. Stanley, J. Phys.: Condens. Matter, 14 (2002) 2201-2209
[2] L. E. Coronas, O. Vilanova, V. Bianco, F. de los Santos, and G. Franzese, arXiv:2004.03646 (2020) IN PRESS
[3] G. Franzese, and H. E. Stanley, J. Phys.: Condens. Matter, 19 (2007) 205126
[4] V. Bianco, and G. Franzese, J. Mol. Liq. 285 (2019) 727-739
[5] V. Bianco, and G. Franzese, Sci. Rep. 4 (2014) 4440

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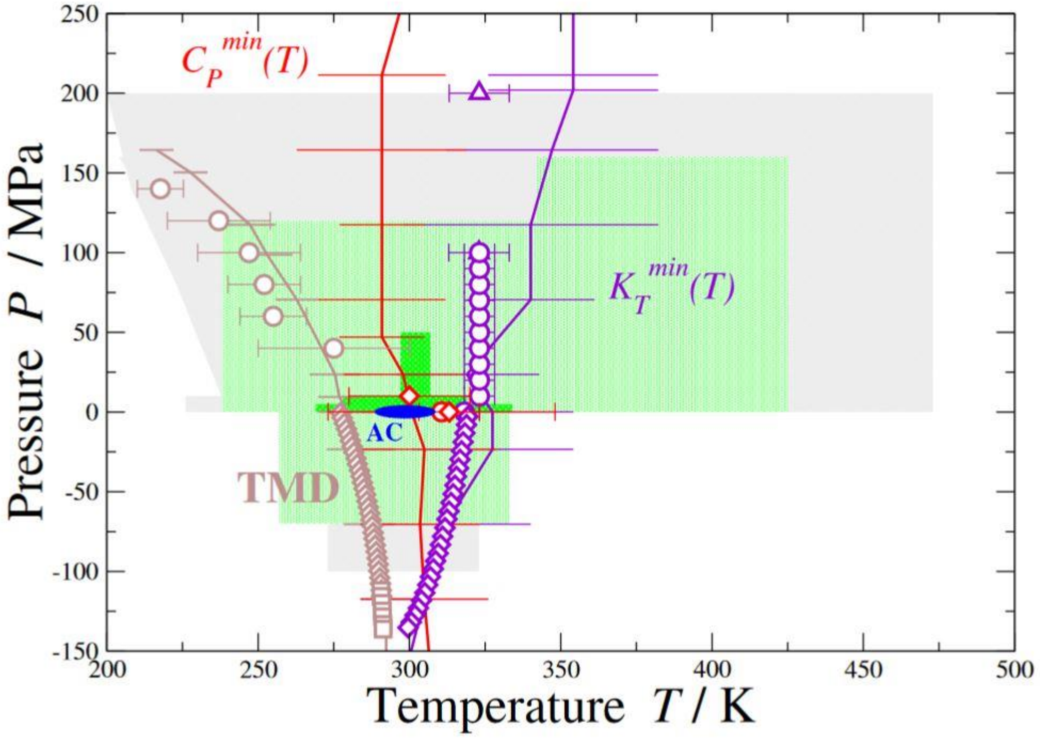

Figure 1: Pressure-Temperature phase diagram of liquid water from experiments (symbols) and the FS model (lines) around ambient conditions (300 K, 1 atm, blue ellipse). The dark-green area marks the thermodynamic region where the model has a complete quantitative agreement with the experimental density, the Temperature of Maximum Density (TMD) along isobars (maroon symbols), the response functions—specific heat (C_P), and isothermal compressibility (K_T)—and their loci of minima (red and violet symbols, respectively). The light-green region is where the model quantitatively agrees with the experimental density but describes the response functions only qualitatively. Experimental data are available only within the grey area.

Task-specific ionic liquids as smart additives for nanoparticles

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The increasing application of nanoparticles (NPs) in various fields has led to a search for more useful nanomaterials, and thus, the quality requirements for NPs are becoming more stringent. Unfortunately, the prevalent methods for fabrication of NPs do not meet the essential requirements set for modern (bio)materials and as such cannot be widely used in (bio)technology applications because these procedures are often uneconomical and contain toxic reagents. However, ionic liquids (ILs) are a pivotal option for the development of NPs with good morphology and bioapplicability. The synthesis of NPs in the presence of ILs is increasingly recognized as eco-friendly and more effective than prevalent methods.

Here, we focused on the use of task-specific ionic liquids (TSILs) to prevent the aggregation and agglomeration of the nanostructures. We have research TSILs that contain various functional group as follows: (*i*) pharmaceutical active anion, salicylate; (*ii*) component of natural origin in the cation part (–)-menthol; (*iii*) or alkoxymethyl substituent (Figure 1).

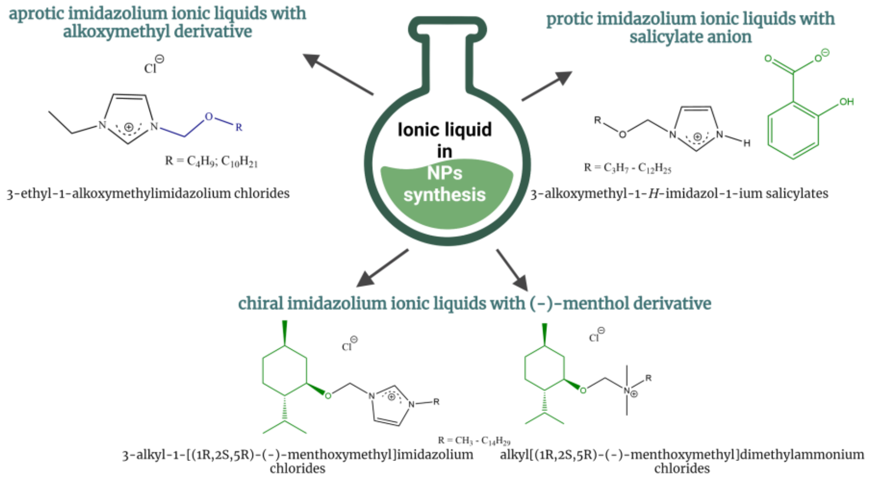

Figure 1: Type of task-specific ionic liquids use for stabilizing NPs

TSILs were used for the synthesis of nanoparticles (NPs) and acted as stabilizers for them as well as interface their shape and size. The precise control of NPs size distribution together with a better understanding of the chemical behaviour of those nanomaterials (NMs) are becoming progressively more essential to grow the utility of NPs in various applications. Morphology and particle size of the metal NPs are largely influenced by the factors affecting their stability. The particular advantages of using TSILs are mainly due to their mono-dispersive and non-agglomerative behaviours that could be possible through the stabilization of metallic NPs by cations and/or anions of ILs.

For instance, we have synthesized AgNPs using an aqueous extract of green tea Camellia sinensis and we have used 3-alkoxymethyl-1-*H*-imidazol-1-ium salicylates as silver nanoparticles (AgNPs) stabilizers. Optical characterization revealed that we have obtained small (40-75 nm) and stable for over 20 days AgNPs with the addition of protic ionic liquids compared to the unsterilised sample.

Using synthesized by us TSILs lead to prevent the aggregation and agglomeration of the nanostructures, and affect their specific features, including optical and structural what is crucial in (bio)technological applications.

The research was supported by the European project Horizon 2020 „Open innovation test bed for developing safe nano-enabled bio-based materials and polymer bionanocomposites for multifunctional and new advanced application" no 953206.

Anion-based magnetic ionic liquids: from non-polarizable to polarizable force fields

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Magnetic ionic liquids (MILs) are a new class of ionic liquids that contain a paramagnetic atom (e.g., iron, cobalt, dysprosium) in their cation or anion structure and yield a magnetic response in the presence of an external magnetic field. These compounds exhibit the same exceptional and tunable properties as ILs, such as negligible vapor pressure, low flammability, and high thermal and chemical stability.[1] In addition, the magnetic response enhances their transport properties, such as increasing ion diffusion and consequently reducing viscosity.[2] Moreover, experimental results show that MILs can be effortlessly recycled by magnetic separation, saving extraction steps, and reducing the use of organic compounds.[3]

Since 2004, MILs have been emerged for a wide range of applications such as gas capture, environmental remediation, PET depolymerization, food safety analysis, and biomedical needs.[1,3] However, there are few atomistic level studies due to the lack of force fields for these anion species.

The aim of this work is to establish a non-polarizable and a polarizable force field for (FeX_4)-based MILs, where X = Cl or Br atoms, and to investigate thermodynamic, transport and structural properties using molecular dynamics (MD) simulations (Figure 1). This study will help to propose a cost-effective design of MILs and their mixtures to boost their potential applicability and is the starting point for new insights into the nature of these magnetoactive substances.

REFERENCES

[1] K.D. Clark, O. Nacham, J.A. Purslow, S.A. Pierson, J.L. Anderson, Anal. Chim. Acta 934 (2016) 9-21

[2] C.I. Daniel. A.M. Rubio, P.J. Sebastiao, C.A.M. Afonso, J. Storch, P. Izak, C.A.M. Portugal, J.G. Crespo, J. Membr. Sci. 505 (2016) 36-43

[3] M. Varona, P. Eor, L.C.F. Neto, J. Merib, J. L. Anderson, TrAC 140 (2021) 116275

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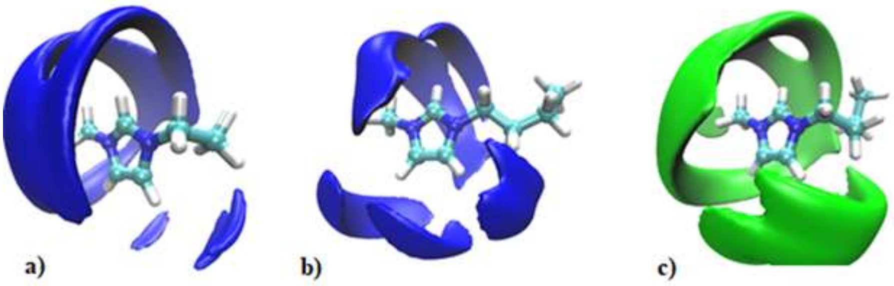

Figure 1: Spatial distribution functions of a) [Emim][$FeCl_4$], b) [Bmim][$FeCl_4$], and c) [Bmim][$FeBr_4$] describing the distribution of [$FeCl_4$] (blue) and [$FeBr_4$] (green) anion around the reference cation at 293.15 K.

Radial and unidirectional water pumping using zeta-potential modulated Nafion nanostructures

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Nowadays the development of micro/nanomachines which can move in a controlled way and perform useful tasks in a fluid environment is one of the most interesting challenges confronting nanoscience and nanotechnology. In addition to the difficulties associated to the involved nanofabrication processes, the struggle against the dominance of viscous forces and Brownian motion makes it necessary to develop efficient strategies to convert chemical energy into directed motion. In this context, different methods of self-propulsion have been investigated, such as catalytic reactions or bubble propulsion. Ion exchange constitutes an interesting alternative mechanism to achieve self-propulsion, with the potential advantages of using innocuous salts as fuels and working at biologically relevant conditions. In order to explore and harness the capabilities of this mechanism to drive micromotors, the use of micropumps becomes an interesting alternative. Micropumps are the immobilized counterparts of micro/nanomotors, sharing the same working principle, but driving the flow of the surrounding fluid instead of self-propelling in a fluid at rest [1]. Micropumps are also promising platforms for many applications such as mass transport, accumulation, and clearance, material patterning at precise locations, or in sensing applications.

Here, we report on a new and versatile self-driven polymer micropump fuelled by salt which can trigger both radial recirculating and unidirectional fluid flows [2]. The micropump is based on the well-known ion-exchanger Nafion, which produces chemical gradients with the consequent local generation of electric fields capable to trigger interfacial electro-osmotic flows [3]. By structuring Nafion in microarrays by means of new nanofabrication strategies in combination with fine tuning modulation of the surface zeta potentials it was possible to redirect electroosmotic flows into unidirectional pumping. The experimental data have been contrasted with numerical simulations accomplishing good agreement.

Nafion micropumps work in a wide range of salt concentrations covering more than four orders of magnitude, they are activated using different cations and can be regenerated for reusability. In particular, we demonstrate that they can work using heavy metal ions, such as the typical water-contaminant cadmium, *using the own capture of the contaminant ion as fuel to drive fluid pumping*. Thus, this novel system has shown its potentialities for effective and fast water purification strategies for environmental remediation, where the fluid motion triggered by the contaminant ions also speeds up the ion trapping in the polymer backbone. In addition, this study constitutes a very appealing proof of concept for a new generation of wireless micro/nanofluidic networks which can autonomously propel and steer material to certain locations and be useful for different applications.

REFERENCES

[1] M. J. Esplandiu, K. Zhang, J. Fraxedas, B. Sepúlveda, and D. Reguera, *Acc. Chem. Res.* 51 (2018) 1921.

[2] M. J. Esplandiu, D. Reguera, D. Romero-Guzmán, A. M. Gallardo-Moreno, and J. Fraxedas, *Nat. Commun.* 13, (2022) 2812.

[3] M. J. Esplandiu, D. Reguera, and J. Fraxedas, *Soft Matter* **16**, (2020) 3717.

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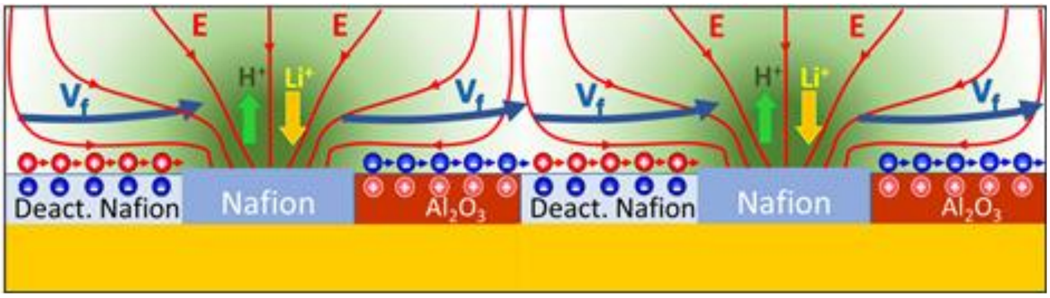

Figure 1: Unidirectional pumping. Scheme of the design of a pump based on the periodic repetition of a basic unit made of alternating strips of deactivated Nafion by electron beam lithography (negative zeta potential)/Nafion/Al2O3 (positive zeta potential) which leads to unidirectional fluid flow along the patterned surface. The Al2O3 patches accumulate negative counterions that in the presence of the tangential component of the electric field generated by the ion-exchange will move also to the right, dragging the fluid along to the next repeating unit, achieving unidirectional flow. The charged interface in the Nafion has been omitted for clarity.

Experimental and simulation results (using the extended Madrid-2019 force field) for the maximum in density of 1m salt solutions containing the cations Rb^+ and Cs^+: and the anions F^-, Br^- and I^-.

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We present the experimental validation of the temperature of the maximum in density (TMD) at constant pressure (1 bar) predicted by the recently proposed extension of the Madrid-2019 force field for electrolyte solutions containing F^-, Br^- and I^- anions and Rb^+ and Cs^+ cations [1]. To that aim the TMD for a number of salts comprising at least one of those ions have been measured by monitoring the temperature-dependent meniscus position in capillary glass tubes within the prescriptions reported in reference [2]. The experimental results are contrasted against Molecular Dynamics simulation in the isothermal-isobaric ensemble (NpT) results within the scale-charged framework provided by the extended Madrid-2019 force field. Drawbacks and future prospections are also projected.

REFERENCES

[1] S. Blazquez, M. M. Conde, J. L. F. Abascal and C. Vega, J. Chem. Phys., 156 (2022) 044505.
[2] L. F. Sedano, S. Blazquez, E. G. Noya, C. Vega and J. Troncoso, J. Chem. Phys. 156 (2022) 154502.

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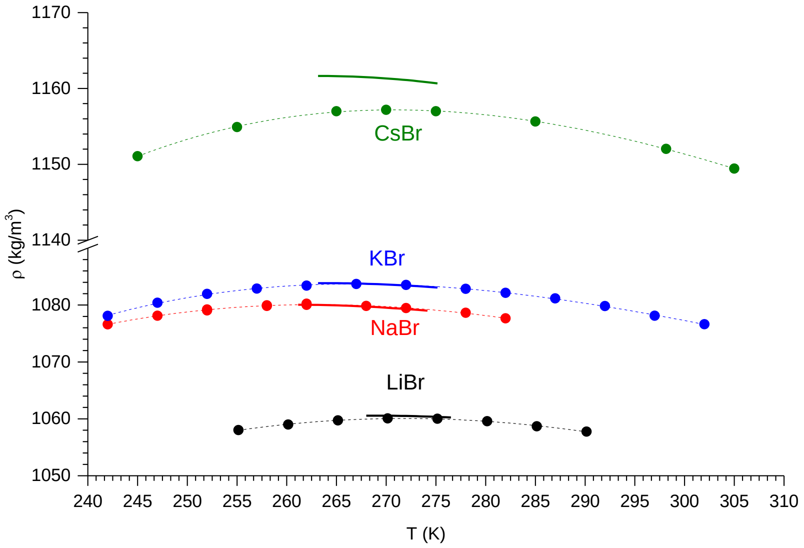

Figure 1: Experimental (continuous lines) and simulated (symbols) TMDs for alkaline bromides. Dashed lines stand for third order polynomial fitting to Molecular Dynamics results.

Solubility of methane in water and its connection to the hydrate nucleation

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Differently than in the case of the formation of ice, the process of the formation of a hydrate requires the presence of two different compounds – water and a guest molecule. Because of their low solubility in water, hydrophobic guest molecules are a limiting factor in the process of nucleation and growth of a hydrate. As a result, studies of these processes by the means of molecular dynamics can be challenging. In this work we shall determine the solubility of methane in water when in contact either with the hydrate or with the gas phase using two-phase direct coexistence simulations using TIP4P/Ice model for water and a single Lennard-Jones site model for the methane. The solubility will be computed at several temperatures along the 400 bar isobar. The impact of the curvature of the interface on the solubility of methane will be analyzed. The solubility curves obtained from two phase simulations (via a planar interface), where liquid solution of methane in water was in contact with either the methane gas phase or the hydrate phase, will be used in order to determine the triple point (T_3) at the studied pressure of 400 bar. This result will be then compared to the value of T_3 obtained by the three phase direct coexistence method – it will be shown that both results are in good agreement and give the value of T_3 of 295(3) K. The analysis of the impact of the curvature of the interface (either gas-liquid or solid-liquid) on the solubility of methane in water will also be presented. It will be shown that the concentration of methane in water can be increased above the solubility limit by introducing curved interfaces. In the last section, the change in chemical potential for the formation of the hydrate will be evaluated along the 400 bar isobar and it will be shown that the supersaturation of the solution increases the driving force for nucleation dramatically.

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Fingerprints of the crossing of the Frenkel and Melting Lines in high-pressure supercritical water

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Abstract

In previous studies [1,2], we performed a systematic analysis of a variety of thermodynamic, structural and dynamic properties of supercritical water in the pressure region of 0.12-11 GPa along the near-critical isotherm of $T=1.03\ T_c$ using molecular simulations. We provided for the first time a general picture of the structural behaviour of supercritical water in a wide pressure range. According to this picture, a near-critical isotherm can be divided in different domains where the system exhibits a very distinct behavior [2]. In the present work [3] , we use the two phase thermodynamic model to reveal novel fingerprints of the crossing of the Frenkel and melting lines in high-pressure water at $T=1.03\ T_c$. The crossing of the Frenkel line at about 1.17 GPa is characterized by the rotational and translational entropy ratio S^{rot}/S^{trans}, indicating a change in the coupling between translational and rotational motions which is also reflected on the shape of the rotational density of states. The first-order phase transition from a rigid liquid to a face-centered cubic plastic crystal phase at about 8.5 GPa is reflected on the discontinuous changes in the translational and rotational entropy, particularly on the significant increase of the ratio S^{rot}/S^{trans}. A noticeable discontinuous increase of the dielectric constant has also been revealed when crossing this melting line. The reorientational dynamics in the plastic crystal phase is faster in comparison with the 'rigid' liquid-like phase, but remains unchanged upon a further pressure increase in the range 8.5-11 GPa.

REFERENCES

[1] I. Skarmoutsos, E. Guardia, J. Samios, J. Supercrit. Fluids 130 (2017) 156.
[2] I. Skarmoutsos, A. Henao, E. Guardia, J.Samios, J. Phys. Chem. B 125 (2021), 10260.
[3] I. Skarmoutsos, J. Samios, E. Guardia, submittted (2022).

One hundred years for Enskog theory: application to fluids in porous media

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The theory proposed by D. Enskog [1] one hundred years ago was the first extension of the Boltzmann transport equation to higher densities. In this report, we present the extension of the Enskog theory for the description of the self-diffusion coefficients of hard sphere fluid and hard sphere mixture in disordered porous media. The theory includes the contact values of fluid-fluid and fluid-matrix pair distribution functions which are used as the input in the theory. In contrast to the bulk case they are modified to include the dependence from the so-called probe particle porosity in order to describe correctly the effects of trapping the fluid particles by a matrix [2]. Such semi-empirical improvement of the Enskog theory corresponds to SPT2b1 approximation for the description of thermodynamic properties and it predicts correct trends for the influence of porous media on the diffusion coefficient of a hard sphere fluid in disordered porous media. For hard-sphere mixture the generalisation is done on the bases of the revised version of Enskog theory developed in bulk case during the last decades. Good agreement with computer simulations is illustrated.

Finally, we present the extension of the Enskog theory for patchy colloidal fluids in disordered porous media. We present two different approaches. On the one of them [4] we modify the contact values of fluid-fluid and fluid matrix pair distribution functions due to clustering. In result the pair distribution functions include three terms. Namely, a hard sphere contribution, the depletion contribution connected to the cluster-cluster and cluster-matrix repulsion and the intermolecular correlation inside the cluster. It is shown that the last term leads to a remarkable decrease of the self-diffusion coefficient at a low fluid density. With a decreasing matrix porosity this effect becomes weaker. For intermediate fluid densities the depletion contribution leads to an increase of the self-diffusion coefficient in comparison with the hard sphere fluid. For a sufficiently dense fluid, the self-diffusion coefficient strongly decreases due to a hard-sphere effects. In other description we consider clusters, as additional particles and the description of patchy colloidal particles in disordered porous media reduces to the hard-sphere mixture in disordered porous media [5]..

REFERENCES

[1] D. Enskog. Kungl. Svenska Vet.-Akad. Handl., 1922, 63, No. 1, 1–44.
[2] M.F. Holovko, M.Ya. Korvatska, Condens. Matter Phys., 2020, 23, 23605.
[3] M. Korvatska, V. Shmotolokha, T. Patsahan, M. Holovko (in preparation).
[4] M.F. Holovko, M.Ya. Korvatska, Condens. Matter Phys., 2021, 24, 3.
[5] M. Korvatska, M. Holovko (in preparation).

Improved Data Analysis on Atomic Dynamics in Liquid CCl_4

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About two decades ago, we measured inelastic x-ray scattering (IXS) on liquid CCl_4 [1] to investigate longitudinal acoustic (LA) phonon dynamics in this molecular liquid. CCl_4 is considered as the simplest molecular liquid because the molecular species are almost isotropic and connected with a van der Waals interaction with each other like liquid rare gas. Thus, we analyzed the IXS spectra by using a damped harmonic oscillator (DHO) model [2] to obtain the excitation energies of LA phonons, and found that the microscopic sound velocity in the molecular level highly exceeds the ultrasonic one by about 37%.

Recently, we measured IXS on liquid acetone [3] and the obtained data were analyzed by using generalized Langevin formalism [4]. The generalized Langevin equation used in this study is described by a damped oscillation equation for the intermediate scattering function $F(Q,t)$, the time-Fourier transforms of the measurable dynamic structure factor, $S(Q,\omega)$, with a memory function. Here, the memory function was assumed to be composed of one thermal and two viscoelastic decay channels, where the fast and slow viscoelastic are called as microscopic μ-relaxation and structural α-relaxation processes, respectively. To avoid any interferences of parameters, we employed a simple idea of sparse modeling so that the parameters exhibit smooth changes with Q. For liquid acetone, we found that the $Q\to0$ limit of the fast μ-relaxation rate is about 60 fs, which is highly related to the vibrational dynamics of the dipoles of liquid acetone, and that of α-relaxation rate of 0.5-1.0 ps, being similar to the reorientation correlation time of 0.75 ps.

Based on this sophisticated analytical method for the IXS spectra, we revisit liquid CCl_4 to examine the feasibility of the generalized Langevin formalism and a sparse modeling. The left panel of Fig. 1 shows logarithmic plots of IXS spectra (circles) and their fitting results (solid curves) of liquid CCl_4 at selected Q values. Broad LA excitation modes are observed as shoulders at the both sides of the central quasielastic peaks. The mode energy of the LA excitations, ω_Q, is calculated as the maxima of the current-current correlation function, $J(Q,\omega) = \omega^2/Q^2\cdot S(Q,\omega)$. The model coincides well with the experimental data.

The middle upper panel of Fig. 1 shows the dispersion relation, and the dashed line indicates the hydrodynamic relation predicted by adiabatic sound velocity of v_s = 923.4 m/s [5]. As clearly seen in the figure, the mode excitation energies highly exceed the hydrodynamic prediction. The middle lower panel of Fig. 1 shows the dynamical sound velocity calculated as $v_Q = \omega_Q/Q$. The adiabatic sound velocity is also given as the dashed line. The v_Q value reaches about 1450 m/s, exceeding the v_s value by about 57%, which is much larger than the previous result of 37% [1] obtained from the DHO model.

The right panel of Fig. 1 shows the Q dependence of the fast μ- (upper) and slow α-relaxation rates obtained from the present generalized Langevin analysis. Although the data are rather scattered, both the values look to gradually decrease with increasing Q. The $Q\to0$ limit of are about 0.2 and 1.5 ps for the τ_μ and τ_α values, respectively. These values are larger than those of liquid acetone of 0.06 and 0.5-1.0 ps for τ_μ and τ_α values, respectively. These differences may be owing to the bonding origins between molecules, a van der Waals liquid for CCl_4 and a dipolar liquid for acetone.

Further analyses are now in progress to reduce the ambiguities of parameters in the generalized Langevin formalism. Detailed comparisons with macroscopic dynamic properties of liquid CCl_4, such as Raman data and rotational motions, are also just getting underway.

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REFERENCES

[1] T. Kamiyama, S. Hosokawa, et al., J. Phys. Soc. Jpn. 73 (2004) 1615.
[2] B. Fåk and B. Dorner, Physica B 234-236 (1997) 1107.
[3] S. Hosokawa et al., J. Mol. Liq. 332 (2021) 115825.
[4] J. P. Boon and S. Yip, Molecular Hydrodynamics (McGraw-Hill, New York, 1980).
[5] Y. S. Touloukian, Thermophysical properties of matter (Plenum Press, New York, 1970).

FIGURES

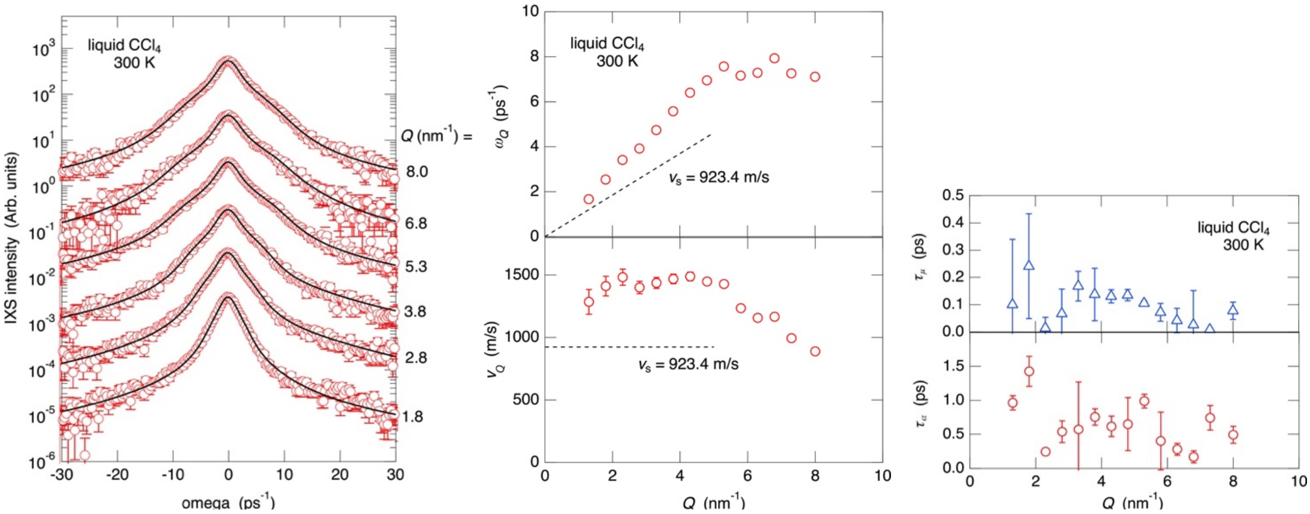

Figure 1: (Left) Logarithmic plots of IXS spectra of liquid CCl_4 at selected Q values. The solid curves represent the generalized Langevin fits. (Middle) The dispersion relation (upper) and dynamical sound velocities (lower) with Q. (Right) The fast (upper) and slow (lower) viscoelastic relaxation rates of the memory function in the generalized Langevin formalism.

The Crucial role of Mg^{2+} in conformational change of KRas

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KRas proteins plays an important role in various cellular events such as cell proliferation, differentiation, and survival[1]. KRas mutations impair both the intrinsic and GAP stimulated GTP hydrolysis activity[2], leading to hyperactivation of KRas signaling and ultimately cancer. As one of the important Ras cofactors, Mg^{2+} is coordinated in an octahedral arrangement with a high affinity on Ras proteins[3]. Mg^{2+} has been established essential for both guanine nucleotide binding and GTP-hydrolysis of Ras proteins. For instance, in HRas the difference in affinity between HRas and guanine nucleotide in the presence or absence of Mg^{2+} is ～500-fold[4]. However, HRas is rarely mutated in human cancers with ～10% rate found in only bladder and cervical cancers[5]. The mechanism of Mg^{2+} interaction with the most prevalent and oncogenic KRas has never been investigated yet. Herein, through long-time scale molecular dynamics simulations at all-atom level, we revealed that cofactor Mg^{2+} plays a crucial role in the conformational changes of KRas. The mutation of GLY12 on KRas, G12D, triggers a distinct shift in the interaction patterns between Mg^{2+} and KRas, makes the conformation of KRas(G12D) is more stable compared to wild-type and KRas(G12C) (Figure 1 and Figure 2).

REFERENCES

[1] J. M. Ostrem & K. M. Shokat, *Nat. Rev. Drug Discov.* **15** (2016), 771.
[2] B. E. Hall, D. Bar-Sagi & N. Nassar, *Proc. Natl. Acad. Sci. USA* **99** (2002), 12138.
[3] J. John, H. Rensland, I. Schlichting, et al. *J. Bio. Chem.* **268** (1993), 923.
[4] J. Tucker, G. Sczakiel, J. Feuerstein, et al. *The EMBO Journal* **5** (1986), 1351.
[5] A. R. Moore, S. C. Rosenberg, F. McCormick, et al. *Nat. Rev. Drug Discov.* 2021.

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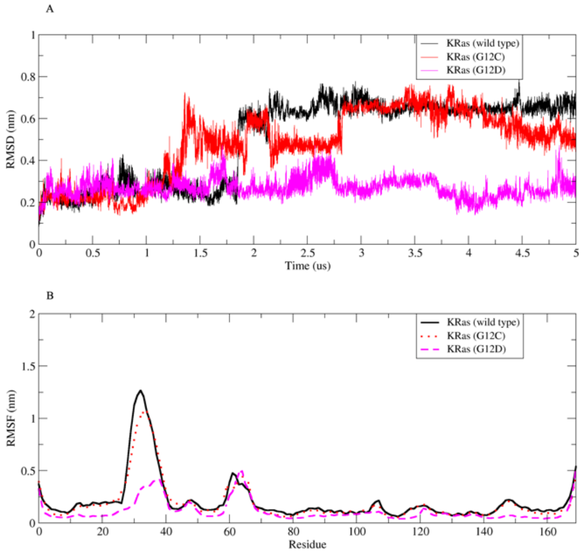

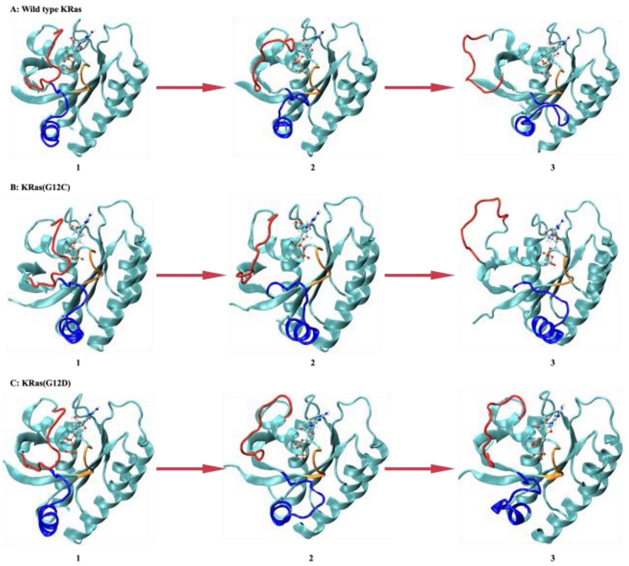

Figure 1: RMSD and RMSF information of different KRas conformational changes

Figure 2: Selected snapshot of different KRas conformational changes

The fragmentation of intermolecular interactions in a carboxyl-functionalized ionic liquid and its molecular mimic – Quantification of hydrogen bond strength

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We have studied the carboxyl-functionalized ionic liquid (IL) 1-(carboxymethyl)pyridinium bis(trifluoromethylsulfonyl)imide [HOOC-CH_2-Py] [NTf_2] and its molecular mimic phenylacetic acid to get a better understanding of the non-covalent interactions. The compounds were analyzed by IR spectroscopy in the Mid-IR region between 193 K and 413 K (Fig. 1) or 293K and 473 K, respectively. The IL shows the formation of three types of hydrogen bonding: The anticipated singly hydrogen bonds between anion and cation, and surprisingly single and even double hydrogen bonds between the cations, forming dimers between ions of like charge. The latter dimer is related to the structural motifs known for formic and acetic acid in the gas phase. [1,2]

We extended our investigation to X-ray crystallography, DFT calculations and thermodynamic methods to analyze and characterize all types of hydrogen bonding. The crystalline phase of the ionic liquid consists of doubly hydrogen bonded cyclic dimers between the cations (c=c). This binding motif, also present in the ionic liquid as well as in phenylacetic acid, successively opens with increasing temperature and is replaced by a linear species (c-c-a). Here, additionally to one remaining single cationic hydrogen bond an additional hydrogen bond between cation and anion is formed. We deconvoluted the spectra of both species in the carbonyl stretching region to get a better understanding of the temperature behavior (Fig. 2). The DFT calculations provide an insight into the assignment of the different vibrational bands. The derived transition enthalpies allow to expose the non-covalent interaction and to determine the hydrogen bond strength between ions of like charge. Finally, we were able to show, that the repulsive Coulomb interactions between two like-charged ions weakens the strength of the hydrogen bonds in comparison to the molecular species.

REFERENCES

[1] L. Al Sheakh, S. Fritsch, A. Appelhagen, A. Villinger, R. Ludwig, *Molecules*, 27 (2022), 366.
[2] M. Samsonowicz, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, 118 (2014), 1086.

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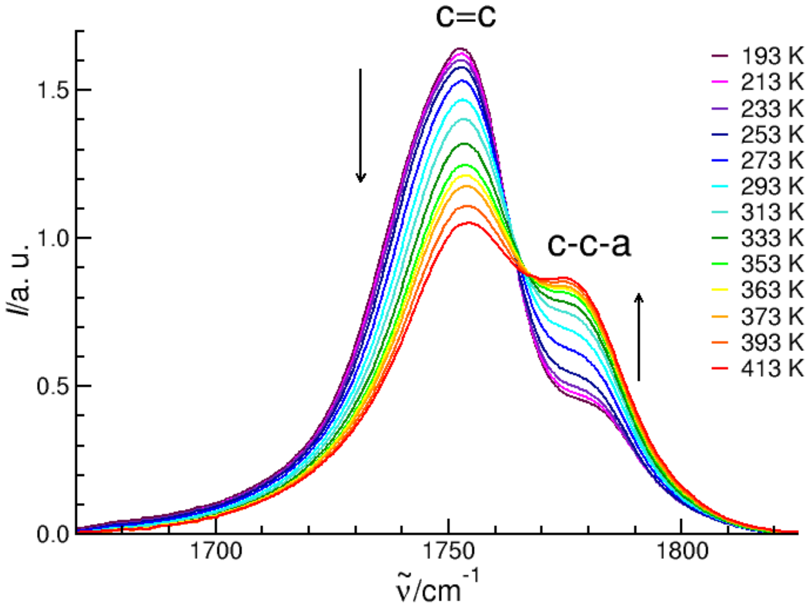

Figure 1: Temperature-dependent IR spectra of the C=O stretching region for the IL. Contributions from the cyclic dimer (c=c) decrease with increasing temperature and contributions from the linear dimer (c-c-a) increase with increasing temperature. The arrows indicate the changes in intensity with increasing temperature.

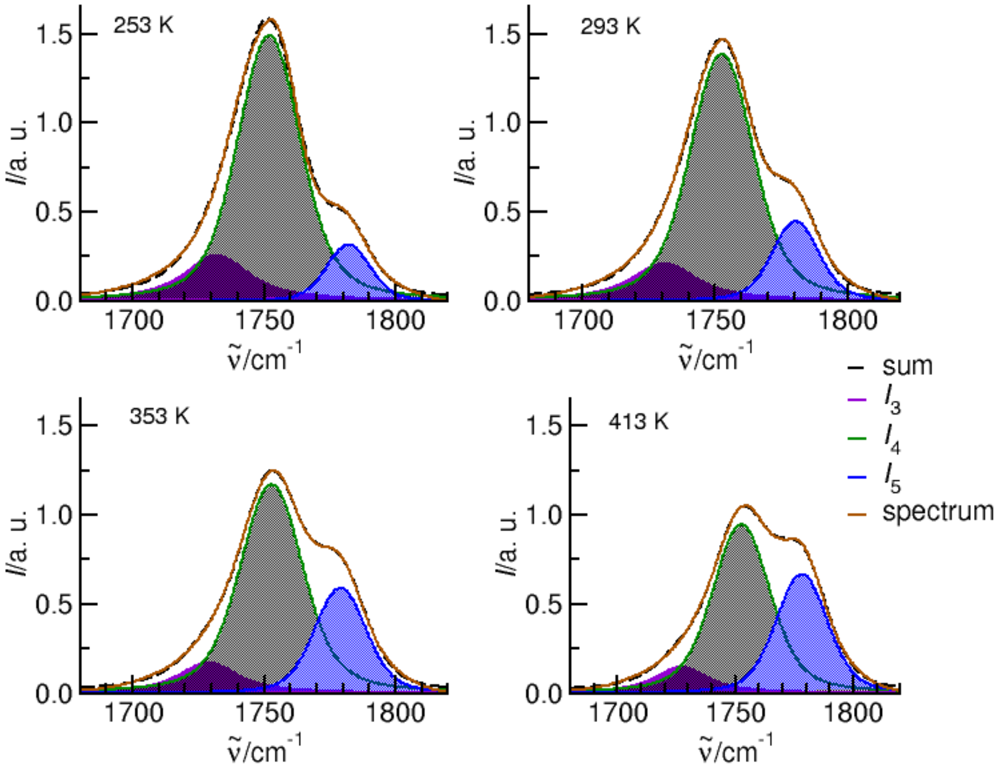

Figure 2: Deconvoluted IR spectra of the C=O stretching region for the IL at four different temperatures. The vibrational bands I_3 and I_4, assigned to the cyclic dimer, decrease with increasing temperature to the benefit of I_5, assigned to the linear dimer.

Characterizing electrospun 3D matrices for biomedical purposes

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Polymers are widely used in our everyday life, as well as for medical or pharmaceutical purposes. For that reason, natural and biocompatible polymers are getting more and more attention to use them in a harmless way. Technological advances made it possible to create micro-, and nanofiber based artificial matrices from these polymers to be used for simple filtration systems or mimic the extracellular matrix (ECM). These matrices look very close to ECM and can act like a scaffold for cell cultures as well. One of the methods to create fibers is the electrospinning technique. Varying the electrospinning parameters, we can influence the properties as well, to fine tune the system for a desirable outcome. To create a high porosity fibrous mesh for culturing cells in a suitable three-dimensional way, we need to step forward from conventional electrospinning. Our aim was to create and characterize 3D fiber structures from Poly(succinimide) with the help of electrospinning. Therefore, the effect of the presence of different inorganic salts (LiCl, $MgCl_2$, $CaCl_2$) and the effect of humidity on the fiber structures were investigated. By adding salt to the polymer solutions, the weight percent needed to create homogenous fibers were decreased along with the fiber diameter (from 25 to 20w/w%). The conductivity and infrared spectra of salt-solvent, polymer solution and the fibers were measured. Increasing the amount of $CaCl_2$ increased the tensile strength as well. A critical humidity level was defined as a threshold to create 3D fiber structures. The fiber diameter and surface roughness were analyzed and observed with the help of Scanning Electron Microscopy.

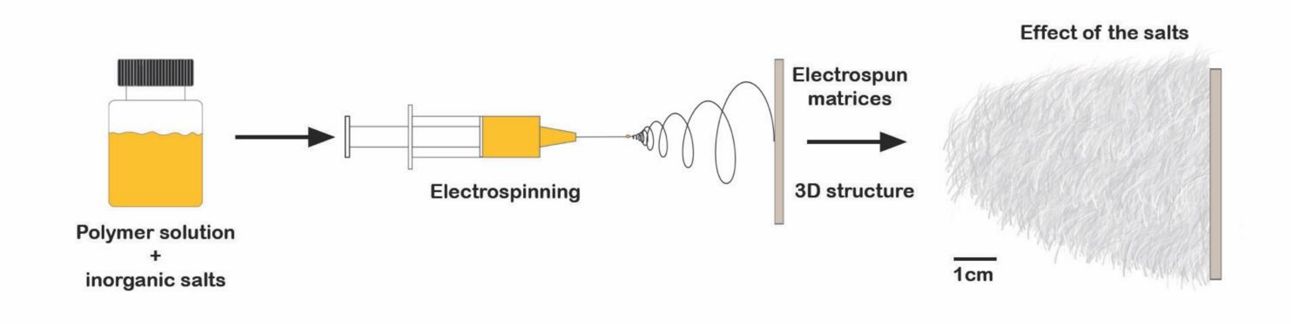

Figure 1: Different steps of creating a three-dimensional fiber structure

REFERENCES

[1] Juhasz, A. G., Molnar, K., Idrissi, A., & Jedlovszky-Hajdu, A. (2020). Salt induced fluffy structured electrospun fibrous matrix. Journal of Molecular Liquids, 312, 113478.

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Universality of two gigahertz-ranged cluster lifetimes in hydrogen bonding liquids and mixtures

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Hydrogen bonding liquids are know to form various patterns of short lived hydrogen bonded clusters. A typical example is that of short mono-ols such as methanol and ethanol, which form chain-like clusters of various shapes[1]. By studying the lifetime distribution of various Hbonded liquids and mixtures through Molecular Dynamics simulations, we put in evidence two universal lifetimes in the gigahertz frequency domain[2]. The first frequency, of 50Ghz, corresponds to a mean cluster vibrational mode, while the lower frequency of 20Ghz would correspond to the internal topology of the cluster (linear, chain, etc...) [2,3]. In addition to these two modes, an additional mode is found, which however depends strongly on the Hbonding distance criteria, and spans a lifetime range from 0 to 0.15ps with increasing distances from bonding oxygen atom contact ($r_c \approx 2.8\,\mathring{A}$) to approximatively $r_c \approx 3.5\,\mathring{A}$. In contrast to these universal very short time features, we find that the long time kinetics of the lifetimes are very strongly dependent the bonding distance r_c for a given density or concentration in case of a mixture[2], in line with this third cluster lifetime. These 2 findings, namely universality of atom-level lifetimes and microscopic details depending kinetics, are surprisingly in variance with the intuitive view of the kinetics of molecular association.

REFERENCES

[1] Aleksander Vrhovšek, Orsolya Gereben, Andrej Jamnik, Laszlo Pusztai: *Hydrogen bonding and molecular aggregates in liquid methanol, ethanol and 1-propanol*, J. Phys. Chem. B 2011, 115, 46, 13473 - 13488

[2] I. Jukić, M. Požar, B. Lovrinčević, A. Perera: *Universal features in lifetime distribution of clusters in hydrogen bonding liquids*, Physical Chemistry Chemical Physics 23 (35), 19537-19546

[3] I. Jukić, M. Požar, B. Lovrinčević, A. Perera: *Lifetime distribution of clusters in binary mixtures involving hydrogen bonding liquids*, Scientific Reports 12 (1), 1-9

Vibrational cooling dynamics of nitromethane

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Energy dissipation is of interest for the accurate generation and control of movement in micro and nano-particles. Thus, studying the relaxation of molecules after a vibrational excitation has potential applications in multiple fields.

We consider the nitromethane molecule, whose energy relaxation after vibrational excitation has already been studied in argon gas and for microcanonical excitations [1, 2]. We first test these previous works by performing individual mode excitations within the normal mode approximation. The obtained results suggests that the relaxation behaviour (shape, characteristic time, etc.) does not depend on the particular excitation in an Argon gas.

Prompted by the polar nature of the nitromethane molecule we study its relaxation in liquid water, based on the assumption that a polar solvent will present different behaviour than for a noble gas. We perform high energy excitations (200 kJ/mol) of individual modes and study their energy relaxation via all-atom molecular dynamics simulations.

Our results show that, as expected, some normal modes relax considerably faster than others. These faster modes have associated motions related to the nitro group of the nitromethane molecule, which is to be expected due to the hydrophilic nature of the functional group.

To get more insight into the relaxation mechanisms we also studied the work performed by the nitromethane molecule on the surrounding water molecules [3]. We divide surrounding molecules in two groups: the one on the nitro group side and the ones on the methyl group side.

Our main finding is that energy relaxation is remarkably asymmetric, favoring the nitro side (30% more work the work is performed to the nitro side than to the methyl side). Excitations to low frequency normal modes associated with the nitro group are significantly more asymmetric, again favoring the nitro side (between 10 and 20% more than for other excitations).

To our knowledge this is the smallest molecule for which a marked asymmetry has been found, irrespective of the excited mode.

REFERENCES

[1] Rivera-Rivera, L. A., Wagner, A. F., Sewell, T. D., and Thompson, D., J. Chem. Phys.142 (2015) 014303
[2] Rivera-Rivera, Luis A. and Wagner, Albert F. and Perry, Jamin W., J. Chem. Phys. 151 (2019) 034303.
[3] Rossend Rey and James T. Hynes, PCCP, 14 (2012) 6332

FIGURES

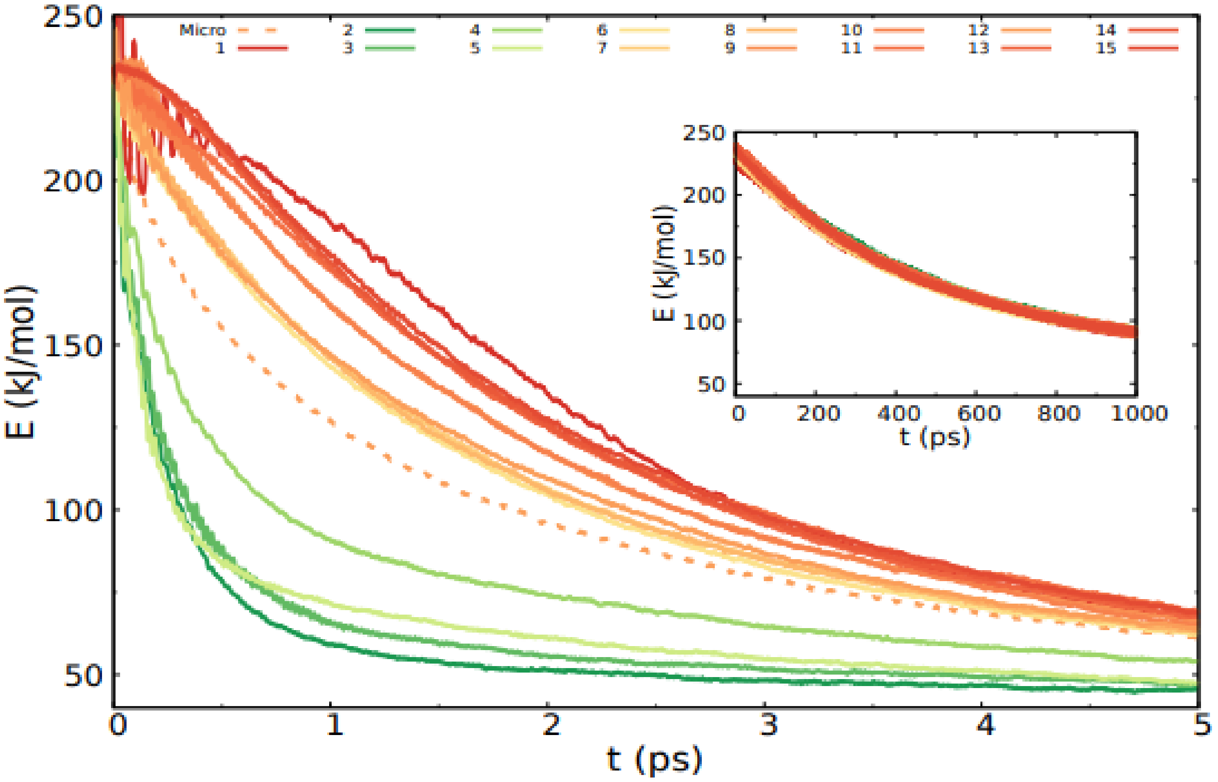

Figure 1: Total vibrational energy of a nitromethane molecule in liquid water after an excitation of 200 kJ/mol in a single normal mode, indicated by the key label. Results for argon are also shown on an inset.

Spectroelectrochemical and IR-photocatalytic investigations of manganese based CO_2-reduction-catalysts

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The application of spectroelectrochemical (SEC) and IR-photocatalytic methods for the investigation of electrocatalytic CO_2-reduction is a powerful tool to gain excellent insight into the mechanisms of such processes. We report the IR-spectroscopical investigation of different manganese-based CO_2-reduction-catalysts under reaction conditions. The ligand-framework of these catalysts, based on pyridine-thiazoline or pyridine-oxazoline networks, is easily to be obtained. [1,2,3] Catalytic systems similar to the investigated catalysts provide the electrochemical and photochemical ability to convert carbon dioxide into different products. [2,4,5] In this project cyclovoltammetric experiments show further evidence for the catalytic behaviour due to increased catalytic current under CO_2-atmosphere. Cyclovoltammetric and amperometric experiments in combination with IR-spectroscopic measurements have been conducted under argon and under CO_2 saturated conditions, respectively. Furthermore, in photocatalytic IR measurements the behaviour of these manganese- based catalysts could be examined as well. Here a Tensor 27 from Bruker is connected to a micro annular gear pump, purging the irradiated reaction solution through a liquid cell, while a series of IR spectra is recorded. Various intermediates have been observed during both IR-SEC and IR-photocatalytic measurements for different catalysts and have been assigned with the help of DFT-calculations. [4]

REFERENCES

[1] M. Trose et al., Green Chem., 2015,17, 3090.
[2] Kundan K. Singhet al., Organometallics, 2020, 39 (7), 988.
[3] T. Toyama et al., Chemistry Letters, 2017, 46:5, 753.
[4] C. Steinlechner et al., ACS Catalysis, 2019, 9 (3), 2091.
[5] R. Francke et al., Chem. Rev., 2018, 118 (9), 4631.

Computational screening of Transition metals doped on CdS photocatalyst for green hydrogen generation

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Hydrogen production and converting solar energy through photocatalysis into suitable fuels such as hydrogen has been established as an intriguing strategy to alleviate both energy crisis and environmental problems [1]. Several photocatalysts have been studied to assist solar visible-light during H_2O and H_2S photocatalysis processes [2]. In specific, cadmium sulfide (CdS), with a suitable band gap (around 2.4 eV) for visible light response, is the most widely studied experimentally for this purpose, whether as a pure photocatalyst or in conjunction with some suitable semiconductors. However, achieving higher quantum yields and selectivity still poses a great challenge in this field, making essential to understand how to improve the solar light utilization and conversion efficiency based on existing technologies and materials. Among these efforts, first principle Density Functional Theory (DFT) calculations can provide guidance to effectively select or design photocatalysts for improving hydrogen generation efficiency.

Therefore, in this contribution, we present and discuss results of the first computational screening study of single TM (TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ru, Rh, Pd, Ag, Os, Ir, Pt, and Au)-doped CdS (TM@CdS) and selected dual TMs-doped CdS (TM1-TM2@CdS) focused on their stability and activity for hydrogen evolution of both H_2O and H_2S splitting reactions. We have performed spin polarized DFT-D3 calculations to gain a quantum-level understanding of the hydrogen evolution mechanism in these different catalytic surfaces, validated with measurements obtained from experiments and thermochemical computational approaches, while evaluating the stability and electronic structures of different CdS surfaces, as well as calculating the adsorption capacity for H_2S adsorption/splitting [6]. Results demonstrate that doping of TMs promotes the reduction of energy band and enhancement of impurity d-states near the Fermi level, resulting in more efficient photocatalytic activity. Activity analysis places Pt, Rh and Pd as optimal single metal doped to be used in TM@CdS catalysts for both H_2O and H_2S splitting reactions, with the lowest Gibbs free energy change of hydrogen adsorption, outperforming pristine CdS surface. Moreover, the dual co-catalysts decorated CdS photocatalysts show even better performance for hydrogen generation. The insights obtained from this work provide robust guidance on the designing of optimal HER catalyst candidates based on CdS for green hydrogen production.

We acknowledge support for this work from Khalifa University of Science and Technology under project RC2-2019-007 (Research and Innovation Center on CO_2 and H_2, RICH Center). YL acknowledges a grant from China Scholarship Council (CSC).

REFERENCES

[1] A.P Bhirud, S.D. Sathaye, R.P. Waichal, L.K. Nikam, B.B. Kale, Green Chem. 14 (2012) 2790–2798.
[2] H. Wang, L. Zhang, Z. Chen, J. Hu, S. Li, Z. Wang, J. Liu, X. Wang, Chem. Soc. Rev. 43 (2014) 5234–5244.
[3] C. Lin, W. Qin, C. Dong, Appl. Surf. Sci. 387 (2016) 720–731.
[4] S.O. Akande, E.T. Bentria, O. Bouhali, F. El-Mellouhi, Appl. Surf. Sci. 532 (2020) 147470.
[5] M. Yu, W. Qu, S. Xu, L. Wang, B. Liu, L. Zhang, J. Peng, Comput. Mater. Sci. 153 (2018) 217–227.

[6] Y. Li, D. Bahamon, M. Sinnokrot, K. Al-Ali, G. Palmisano, L.F. Vega, J. Photochem. Photobiol. C Photochem. Rev. 49, (2021) 100456.

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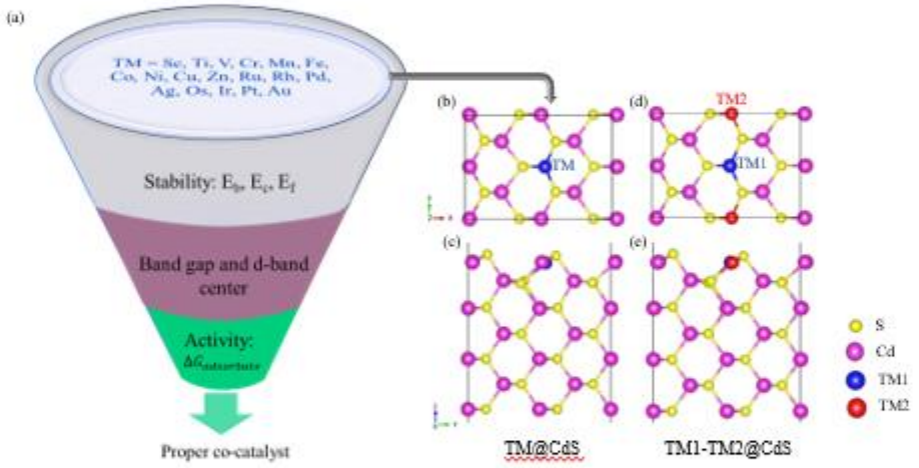

Figure 1: (a) Screening protocol for the discovery transition metal-doped CdS catalysts. (b) top view of an optimized TM@CdS configuration, (c) side view of an optimized TM@CdS configuration, (d) top view of optimized TM1-TM2@CdS configuration and (e) side view of optimized TM1-TM2@CdS configuration.

Spatio-temporal heterogeneity in octanol rich region: Revealing via time resolved fluorescence measurements

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Abstract

Neat 1-octanol and wet-octanol has been the subject of numerous studies due to their property of membrane mimics.[1-3] Interaction and dynamics as well as solution heterogeneity aspect pure octanol and water/octanol mixtures have been investigated via steady state and time-resolved fluorescence (TRF) measurements in the temperature range of $283 \leq T/K \leq 323$ with various mole fraction of water in the octanol rich region. Coumarin 153 (C153)[4], Coumarin 343 (C343)[5], trans-2-[4'-(dimethylamino)styryl]benzothiazole (DMASBT)[6] fluorophores have been employed as local reporters to investigate relaxation dynamics in this aqueous mixture in presence of reactive and non-reactive fluorophores. Excitation wavelength dependence of fluorescence emissions[7,8] suggest that the neat and aqueous binary mixtures, within the lifetime DMASBT ($< \tau_{life} >$ ~ 0.5 ns), are spatially heterogeneous.[9] Solute-medium frictional coupling in neat and wet-octanol have been further explored *via* time-resolved fluorescence anisotropy studies of the two non-reactive fluorophores, C153 and C343. Inspite of nearly similar size, rotational diffusion of C153 exhibits fractional viscosity dependence while C343 nearly follows the Stoke-Einstein-Debye model.[10] Dynamic fluorescence Stokes's shift registered by C153 and C343 report bimodal relaxation processes in these media. The inter and intra relationship between rotation and solvation process associated with solvation and rotation of the hydrophobic C153 differ from hydrophilic C343 which reflects their qualitatively different local environments scene these two probes due to their chemical nature.

REFERENCES

[1] S. E. Debolt, P. A. Kollman, *J. Am. Chem. Soc*. **1995**,117(19) 5316-5340.
[2] S. A. Best, K. M. Merz, C. H. Reynolds, *J. Phys. Chem*., B, **1999**, 103(4), 714-726 (1999).
[3] J. L. MacCallum, D. P. Tieleman, *J. Am. Chem. Soc*., **2002**, 124(50), 15085-15093.
[4] M. L. Horng, J. A. Gardecki, M. Maroncelli, *J. Phys. Chem. A* **1997**, *101* (6), 1030–1047.
[5] S. Koley, H. Kaur and S. Ghosh, *Phys. Chem. Chem. Phys*., **2014**, 16, 22352.
[6] M. Kondo, X. Li, M. Maroncelli, *J. Phys. Chem. B*, **2013**,117, 12224–12233.
[7] Z. Hu, C. J. Margulis, *PNAS*, **2006**, 103(4) 831-836.
[8] P. K. Mandal, M. sarkar, A. Samanta, *J. Phys. Chem*., B **2004**, 108(42), 9048-9053.
[9] M. D. Ediger, *Annu. Rev. Phys. Chem.* **2000**, *51*, 99–128.
[10] B. Guchhait, S. Daschakraborty, R. Biswas, J. Chem. Phys., **2012**, 136, 174503(1–16).

Can Machine Learning help us to systematically analyze the UV Resonance Raman Spectra of Glycoproteins absorbing on Nanoparticles?

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Abstract

We apply Gaussian Process (GP) regression to UV Resonance Raman (UVRR) Spectra of two glycoproteins, Fetuin and Asialofetuin, which differ only for the sialic acid end of their glycans. First, we collect their UVRR Spectra for temperatures ranging from 295 K to 359 K, at different concentrations, in bulk or with Carbon nanoparticles. Next, we characterize the spectra features under different conditions. Our findings show that GPs can reach state of the art in predicting the (noisy) experimental spectra, using suitable kernel functions depending on a few hyperparameters. More importantly, the GPs yield results amenable to sound physical interpretations that might lead to a novel machine learning protocol for a systematic analysis of UVRR spectra of proteins in the presence of nanoparticles.

Oncogenic K-Ras Proteins: Mechanisms of Activation by Guanine Exchange Factors

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Ras proteins work as GDP–GTP binary switches and regulate cytoplasmic signaling networks that are able to control several cellular processes, playing an essential role in signal transduction pathways which may turn on genes involved in cell growth, differentiation and survival and eventually leading to cancer [1]. Mutations in Ras genes are found in about 25% of human cancers so that identifying anti-Ras therapeutic strategies is very relevant for cancer treatments, but despite intense effort no general therapies have reached full clinical application [2]. One of the hardest challenges to face is that, with more than hundred different missense mutations found in cancer, mutation-selective therapeutic strategies are needed. In the present communication a mutated GDPase "Kirsten Rat Sarcoma" KRas-4B protein at the inactive state bound to the guanine exchange factor (GEF) "Son-of-Sevenless" SOS1 [3] has been simulated in aqueous solution by molecular dynamics at the all-atom level (Figure 1). The Gibbs free-energy landscape reveals stable configurations of the KRas-SOS1-GDP complex at given values of RMSD and gyration radius of the complex (Figure 2). A specific mechanism due to the binding of the SOS1 to KRas has been identified as the key for GDP extraction and consequent protein activation for signaling, so that such mechanism can be targeted by small-molecule drugs designed to block the release of GDP and its eventual substitution by GTP, i.e. to promote the inactive states of KRas.

REFERENCES

[1] S. Lu, H. Jang, S. Muratcioglu, A. Gursoy, O. Keskin, R. Nussinov, J. Zhang, *Chem. Rev.* **116** (2016), 6607.
[2] C. Sheridan, *Nat. Biotechnol.* **39** (2021), 1032.
[3] P. A. Boriack-Sjodin, S. M. Margarit, D. Bar-Sagi, J. Kuriyan, *Nature* **394** (1998), 337.

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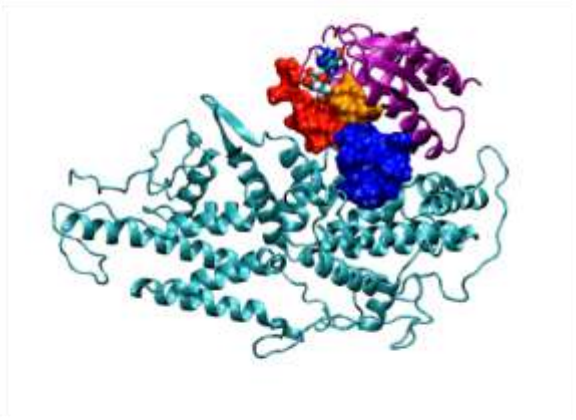

Figure 1: The KRas-SOS-GDP complex

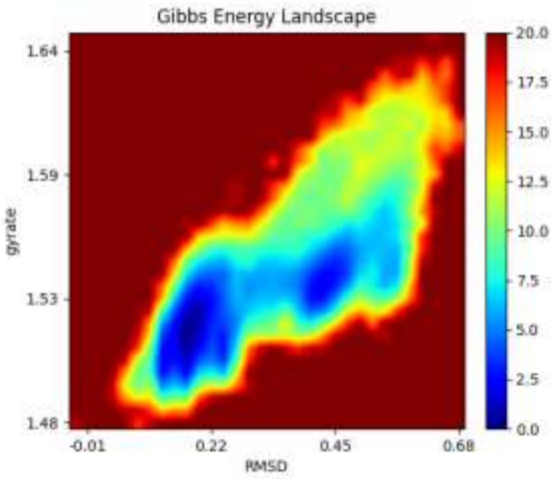

Figure 2: Gibbs free-energy landscape of KRas-SOS-GDP complex (left)

Hydrogen bonding and local structure of imidazolium-based ionic liquids in the water-rich domain

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Abstract

Since water has a high impact on the chemical-physical characteristics of Ionic Liquids (IL), both as a contaminant or as cosolvent, the detailed knowledge of the intermolecular interactions in IL/water solutions is a crucial step for understanding and predicting the range of properties of these non-conventional solvents for applications in many fields including electrochemistry, biochemistry, and synthesis [1-4]. In this work, aqueous solutions of a prototypical set of imidazolium (MIM)-based IL are investigated by UV Raman spectroscopy in the water-rich domain. Analysis of selected Raman signals in different wavenumber ranges provides insights into the local organization of cation-anion pairs as a function of the increasing amount of water in a wide range of concentrations. In particular, the high-frequency range of Raman spectra is analyzed by a differential method to extract from the OH stretching profile of water the solute-correlate (SC) spectra [5], which emphasize the molecular structuring of the interfacial water present in the hydration shells around the selected anions. Peculiar solvation behavior is observed for the different MIM-based systems in connection with the hydrogen bonding features of the hydrating water molecules. Related insights on the solvation properties of the ILs are obtained by analyzing specific signals of the MIM cation when different anions are considered. Interestingly, the ionic liquid [MIM]Cl seems most sensitive to hydration than [MIM]TfO even in an extremely hydrated regime.

REFERENCES

[1] Greaves, T. L.; Drummond, C. J, Chem. Rev. (2015), 115, 20, 11379–11448.
[2] Seddon, K. R.; Stark, A.; Torres, M., Pure Appl. Chem. (2000), 72, 2275−2287.
[3] Yao, Joseph G., Sze-yin Tan, Philip I. Metcalfe, Paul S. Fennell, Geoffrey H. Kelsall, and Jason P. Hallett., Environ. Sci. Technol. (2021), 55, no. 8: 5291-5300.
[4] Nasirpour, N., Mohammadpourfard M., and Zeinali Heris S., Chem. Eng. Res. Des. (2020), 160: 264-300.
[5] Bottari, C.; Almásy, L.; Rossi, B.; Bracco, B.; Paolantoni, M.; Mele, A. ., J. Chem. Phys. B (2022), 126: 4299-4308.

Temperature dependent dielectric relaxation measurement of an amino acid derivative based deep eutectic solvent: origin of timescales via experiment and molecular dynamics simulation

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Abstract

We report here temperature dependent ($303 \leq T/K \leq 343$) dielectric relaxation (DR) measurement of [Betaine+Urea+Water][1] deep eutectic solvent (DES)[2] in the frequency window from 20Hz to 50 GHz (with a gap from 10 MHz to 200 MHz). We also performed molecular dynamics simulation of DR in the above-mentioned temperature range employing General Amber Force Field (GAFF)[3] model interaction. Experimental DR measurement of this DES require multi-debye fits and produce well separated DR time scales that are spread over sub-10 picosecond to few nanoseconds (~3ns). A comparison between simulation predictions and the experimental DR data in the KHz-GHz frequency regime describes the well similarities of the dynamics(time-scales). A well correlation between the measured DR and simulated DR activation energies further revels the strong connection between the measured DR and the simulated $C_M(t)$ (dipole moment-moment autocorrelation function). The simulated single dipole reorientation dynamics also contributes to the collective polarization relaxation. Average experimental DR times exhibits fractional viscosity dependence. Deviation from hydrodynamic predictions confirms partial decoupling of the solute rotation from the medium frictional resistance exerted by the viscosity. Also, viscosity related activation energy (E_a=57 kJ/mol) is ~1.5 times larger than activation energy related to experimental average DR times (E_a=39 kJ/mol) which supports the fractional viscosity dependence of the medium dynamics.

REFERENCES

[1] E. Tarif, J. Mondal and R. Biswas, *J. Mol. Liq.*, **2020**, 303, 112451.
[2] A. P. Abbott, D. Boothby, G. Capper, D. L. Davies and R. K. Rasheed, *J. Am. Chem. Soc*. **2004**, 126, 9142−9147.
[3] J. Wang, R. M. Wolf, J. W. Caldwell, P. A. Kollman and D. A. Case, *J. Comput. Chem*. **2004**, 25, 1157−1174.

Equation of state of hard-disk fluids under single-file confinement

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We consider a fluid of hard disks of unit diameter confined between two parallel walls separated by a distance $w = 1 + \epsilon$, so that each disk can only interact with its two nearest neighbors (single-file configuration, see Figure 1). The equation of state for this system was originally obtained by Kofke and Post [1] following the transfer-matrix method. It reads

$$Z = 1 + p\,\frac{\int_{-\epsilon/2}^{\epsilon/2} dy_1 \int_{-\epsilon/2}^{\epsilon/2} dy_2\, e^{-a(y_1-y_2)p} a(y_1-y_2)\phi(y_1)\phi(y_2)}{\int_{-\epsilon/2}^{\epsilon/2} dy_1 \int_{-\epsilon/2}^{\epsilon/2} dy_2\, e^{-a(y_1-y_2)p} \phi(y_1)\phi(y_2)},$$

where p is the longitudinal pressure (in units of $k_B T$), $Z = p/\lambda$ is the associated compressibility factor (λ being the longitudinal number density), $a(s) = \sqrt{1-s^2}$ is the longitudinal separation between two hard disks at contact with a transverse separation s, and $\phi(y)$ is the solution to the eigenfunction problem

$$\int_{-\epsilon/2}^{\epsilon/2} dy'\, e^{-a(y-y')p} \phi(y') = \ell \phi(y),$$

ℓ being the associated (maximum) eigenvalue. In this framework, $|\,\phi(y)|^2$ represents the probability density in the transverse direction.

In this work, we present two alternative approximations to this exact solution, a *basic* and an *advanced* one, that avoid having to numerically solve the integral eigenfunction equation and yield more manageable tools to characterize the equation of state of the system. In the *basic* approximation, based on the low-pressure limit behavior where particle density does not change along the transverse direction, $\phi(y)$ is assumed to be constant. This approximation not only yields the exact second virial coefficient, but it also reproduces the asymptotic behavior in the close-packing limit, although it overestimates the amplitude. The *advanced* approximation is based on the high-pressure behavior of the system, where particles accumulate more and more near the walls in two symmetric layers. More specifically, we assume $\phi(y) \propto e^{-a(y-\epsilon/2)p} + e^{-a(y+\epsilon/2)p}$. Consequently, this advanced approximation correctly reproduces the behavior in the high-pressure limit and, since it reduces back to the basic one for low pressures, it also produces the exact second virial coefficient.

Comparisons between these two approximations to results coming from both the exact equation and Monte Carlo simulations [1,2] show a good agreement of the *basic* approximation under low-pressure and/or narrow-pore conditions and a very good agreement of the *advanced* approximation for all ranges of pressure and pore sizes (see Figure 2).

REFERENCES

[1] D. A. Kofke and A. J. Post, J. Chem. Phys. **98** (1993), 4853-4861.
[2] K. K. Mon, Physica A **556** (2020), 124833.

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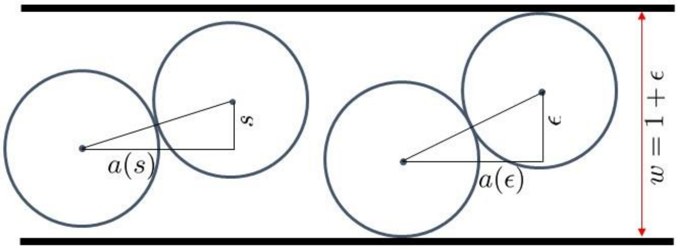

Figure 1: Schematic representation of the single-file hard-disk fluid.

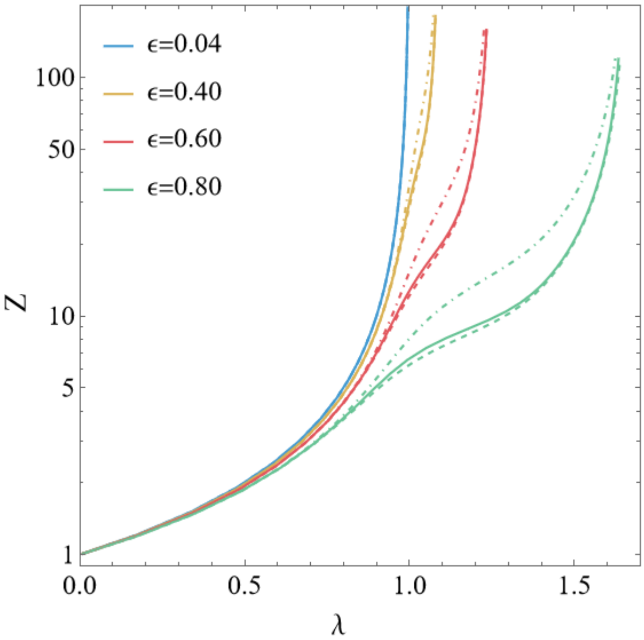

Figure 2: Equation of state for different values of the excess pore width ϵ for the exact solution (solid lines), the basic approximation (dash-dotted lines) and the advanced approximation (dashed lines).

Cluster Formation in Mixtures of [Li][NTf_2] and Triglyme

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The recent search for more environmentally-friendly energy conversion technologies is also accompanied by developments in energy storage devices. Lithium ion batteries offer great prospects regarding their high energy density and are therefore often a preferred choice. However, currently used electrolytes also often possess a high inflammability and other undesirable properties [1]. In order to study possible alternative electrolytes for lithium-ion batteries with hopefully less problematic properties, we have studied mixtures of [Li][NTf_2] and the glycol ether triglyme by means of molecular dynamics simulations. The added triglyme molecules coordinate to the lithium cations, thus separating cations and anions and improving the transport properties of the mixture significantly. However, the structure and thereby the physical properties of the mixtures are primarily dependent on the composition of the mixture. In particular, we observe an equilibrium of lithium being coordinated by either one or two triglyme molecules. By adding more triglyme to the lithium salt, this equilibrium is shifted towards a two-fold coordinated state leading to higher mobility (gauged through computed diffusion coefficients) and therefore lower viscosities, which is preferred for the application as an alternative electrolyte. As a consequence, a quasi-ionic liquid can be obtained, which could be used in battery research [2]. Simulated and observed transport properties are in good qualitative agreement for this system, and the simulations can give insights into the microscopic origin of the macroscopic properties.

REFERENCES

[1] K. Xu, Chem. Rev., 114 (2014) 11503-11618
[2] K. Yoshida, M. Tsuchiya, N. Tachikawa, K. Dokko, M. Watanabe, J. Phys. Chem. C, 115 (2011) 18384-18394

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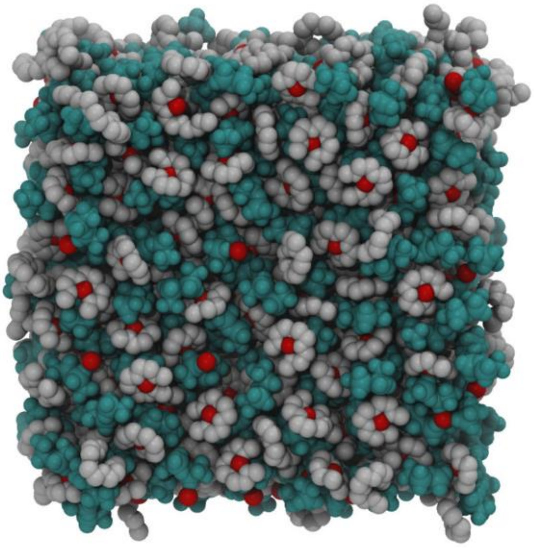

Figure 1: Snapshot taken from MD simulations of [Li-G3][NTf_2] system at $T = 300$ K. Lithium cations have a red colour, NTf_2 anions are coloured in cyan and triglyme molecules are shown in grey.

Vibrational SFG spectrum prediction from classical molecular dynamics simulations

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Interfaces attract a lot of scientific attention due to their ubiquitous occurrence in a wide range of natural and industrial environments, since the surface of any material is the principal pathway for its interaction with the surrounding environment. Interfaces induce inhomogeneous environment where numerous properties differ significantly from their homogeneous (bulk) values and intriguing phenomena take place. Experimental techniques such as X-ray scattering, neutron diffraction, adsorption measurements, surface titration, electrokinetic experiments, photoelectron emission spectroscopy, among others, provide invaluable information on phenomena occurring at liquid/vapor, liquid/liquid, or solid/liquid interfaces. During last decades, nonlinear optics experiments, namely Sum Frequency Generation (SFG), Second Harmonic Generation (SHG) and Second Harmonic Scattering (SHS), also referred to as hyper-Rayleigh scattering (HRS) as representatives of the second-order nonlinear optical techniques, became respected and powerful tools for exploring a variety of topics ranging from fundamental questions of molecular dynamics at liquid interfaces to more applied problems of material surfaces, polymer chemistry, environmental chemistry, electrochemistry, and life sciences. These techniques are highly suitable to study processes at surfaces and interfaces since the signal arises solely from the non-centrosymmetric regions at the interface. They provide direct information about the average orientation of the water molecules at the interface; monitor ion adsorption at the surface with micromolar sensitivity; infer interfacial electrostatic potentials, or even monitor the time-resolved evolution of interfacial processes. We present a simulation technique to predict vibrational SFG non-linear optics spectra from classical molecular dynamics simulations of solid-liquid and solid-air interfaces [1]. The method requires ab initio calculated parameterizations of change of dipole moment and polarization tensor of a water molecule upon its vibration. However, the trajectory to analyze is calculated by classical molecular dynamics simulations of non-polarizable flexible water models. This strongly reduces computation cost compared to ab initio calculations [2] and opens the possibility to study larger systems for long periods of time. The analysis allows detailed investigation of the origin of the SFG spectra, including contributions from water molecules differing in location at the interface. We successfully predict phase-resolved vibrational sum frequency generation (vSFG) spectra of air/water, fluorite (111)/water and α-alumina (0001)/water interfaces. The role of various water models on the predicted spectra, parameters affecting the calculation, as well as inclusion of so far often neglected cross-correlation terms in evaluation of the necessary time-correlation functions [3], will be discussed.

REFERENCES

[1] O. Kroutil, S. Pezzotti, M.-P. Gaigeot, M. Předota, Phase-Sensitive Vibrational SFG Spectra from Simple Classical Force Fields Molecular Dynamics Simulations, *J. Phys. Chem. C* **124** (2020) 15253–15263. https://doi.org/10.1021/acs.jpcc.0c03576

[2] S. Pezzotti, D. R. Galimberti, and M.-P. Gaigeot, Deconvolution of BIL-SFG and DL-SFG spectroscopic signals reveals order/disorder of water at the elusive aqueous silica interface, *Phys. Chem. Chem. Phys.* **21** (2019) 22188-22202. https://doi.org/10.1039/c9cp02766a

[3] Y. Nagata and S. Mukamel, Vibrational Sum-Frequency Generation Spectroscopy at the Water/Lipid Interface: Molecular Dynamics Simulation Study, *J. Am. Chem. Soc.* **132** (2010) 6434–6442. https://doi.org/10.1021/ja100508n

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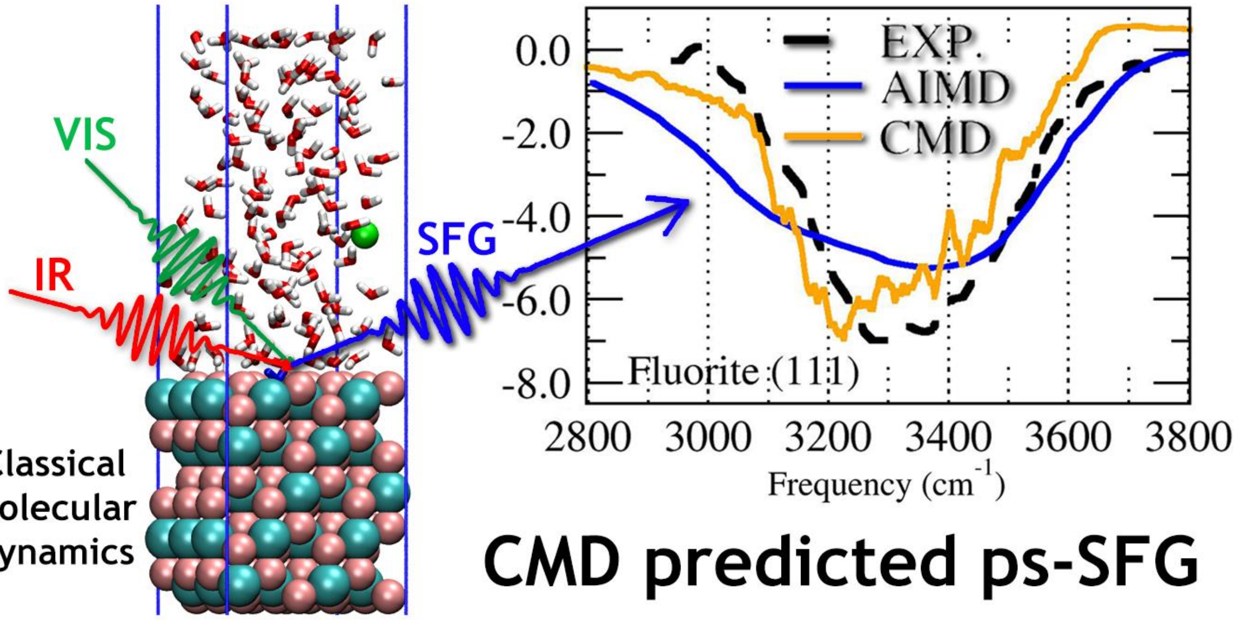

Figure 1: Schematics of the origin of SFG signal (left) and predicted imaginary part of second-order susceptibility $\chi^{(2)}$ for fluorite (111)/water interface from classical molecular dynamics (CMD), ab initio molecular dynamics (AIMD) and experiment.

Microscopic origins of the viscosity of a Lennard-Jones liquid

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In contrast with crystalline solids or ideal gases, transport properties remain difficult to describe from a microscopic point of view in liquids, whose dynamics results from complex energetic and entropic contributions at the atomic scale. Two scenarii are generally proposed: one pictures dynamics in a fluid as a series of energy barrier crossings, leading to Arrhenius-like laws, while the other one assumes atoms rearrange through collisions, as exemplified by the free volume model. To assess the validity of these two viewpoints, we computed with molecular dynamics simulations the transport properties of the Lennard-Jones fluid, and tested how well the Arrhenius equation and the free volume model describe the temperature dependence of the viscosity and of the diffusion coefficient at fixed pressure. Although both models reproduce the simulation results in a large range of pressure and temperature covering the liquid and supercritical states of the Lennard-Jones fluid, we found that the parameters of the free volume model can be estimated directly from local structural parameters, also obtained in the simulations. This consistency of the results gives more credibility to the free volume description of transport properties in liquids.

Farid Rizk, Simon Gelin, Anne-Laure Biance, Laurent Joly , Microscopic origins of the viscosity of a Lennard-Jones liquid , arXiv:2203.16156

Scaling for selectivity in uniformly charged selective nanopores

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Nanopores are nanoscale channels embedded in a membrane providing a controlled transport of ions between the two bulk phases on the two sides of the membrane. The nanopore's radius, *R*, is in the nanometer range, comparable to the Debye length, λ_{D}.

Charge patterns are chemically deposited on the inner wall of the engineered nanopore providing different output signals for different input parameters. From the relation of the input and output signals a device function can be generated. In the case of a uniformly (negatively) charged nanopore, the device function is (cation) selectivity defined as $S_+ = I_+/I$ where I_+ is the cation current and *I* is the total current. The scaling of the selectivity of the nanopore means that selectivity is a unique smooth and monotonic function of the a well defined scaling parameter.

The scaling parameter is constructed from the input parameters of the nanopore device. We showed [1] that the Dukhin number [2] defined as

$$\mathrm{Du} = \sigma / eRc = \sigma 8\pi l_{\mathrm{B}} \lambda_{\mathrm{D}}^2 / eR$$

is a suitable scaling parameter for the nanotube limit, namely, for the infinitely long nanopores ($H \to \infty$, where *H* is the length of the pore). In this formula, σ is the surface charge density and l_B is the Bjerrum length.

For the nanohole limit ($H \to 0$), we introduced [1] the modified Dukhin number defined as

$$\mathrm{mDu} = \mathrm{Du}\left(H/\lambda_{\mathrm{D}}\right) = \sigma 8\pi l_{\mathrm{B}} \lambda_{\mathrm{D}} H / eR$$

and show that it is an appropriate scaling parameter. A mixed scaling parameter can be used in between.

We use simple models based on the primitive model of electrolytes and study those models with the Nernst-Planck (NP) transport equation coupled either to the Local Equilibrium Monte Carlo method (NP+LEMC) [3] or the Poisson-Boltzmann theory.

The latter, known as the Poisson-Nernst-Planck (PNP) theory, is a mean-field theory. We show that scaling is fundamentally a mean-field phenomenon. We show that the NP+LEMC and PNP results agree for 1:1 electrolytes where ionic correlations are weak, while deviations are found from the mean-field scaling behavior for 2:1 and 3:1 electrolytes. Thus, scaling can be considered as a measure of the applicability of mean-field theories.

REFERENCES

[1] Zs. Sarkadi, D. Fertig, Z.Ható, M. Valiskó, D. Boda, *J. Chem. Phys.*, **2021**, 154(15):154704.
[2] L. Bocquet and E. Charlaix, *Chem. Soc. Rev.*, **2010**, 39(3):1073-1095.
[3] D. Boda and D. Gillespie, *J. Chem. Theory Comp.*, **2012**, 10(8):824-829.

FIGURES

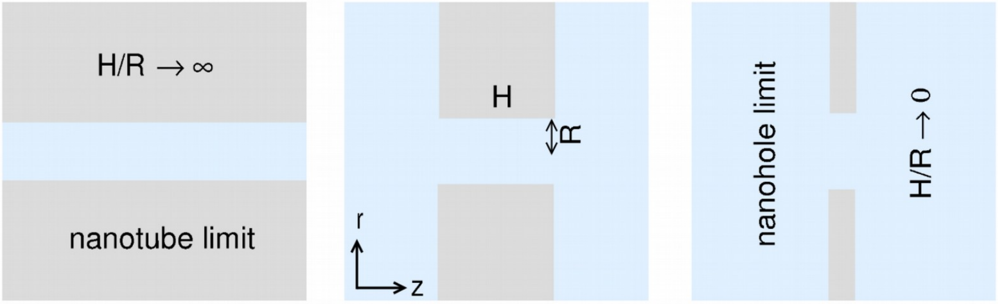

Figure 1: Pore geometries from the nanotube limit to the nanohole limit.

Quercetin in water, studied with molecular simulations

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Quercetin, or 3,3′,4′,5,7-Pentahydroxyflavone, is an important molecule in biological photochemistry [1,2], belonging to the class of flavonoids. Quercetin has five hydroxyl groups at different kind of sites that can interact with the water molecules around it. It is therefore interesting to study how the solvation around the four OH groups differ. Here we want to study the quercetin solvated in the aqueous environment. This system has been widely studied experimentally. We report atomistic simulations to investigate the solvation of quercetin in liquid water. Both models of microsolvation and full solvation in explicit water are used. We characterise the solvation dynamics and describe spectroscopic quantities obtained from the simulations, and compare these to the available experimental results.

REFERENCES

[1] Malgorzata Musialik, Rafal Kuzmicz, Tomasz S Pawłowski and Grzegorz Litwinienko, *"Acidity of Hydroxyl Groups: An Overlooked Influence on Antiradical Properties of Flavonoids"*, Journal of Organic Chemistry 74 (2009) 2699–2709; DOI: 10.1021/jo802716v

[2] Stefano Protti and Alberto Mezzetti, *"Any colour you like. Excited state and ground state proton transfer in flavonols and applications"* in *"Photochemistry: Specialistic Periodical Reports", Royal Society of Chemistry*, Edited by A Albini (2012); DOI: 10.1039/9781849734882

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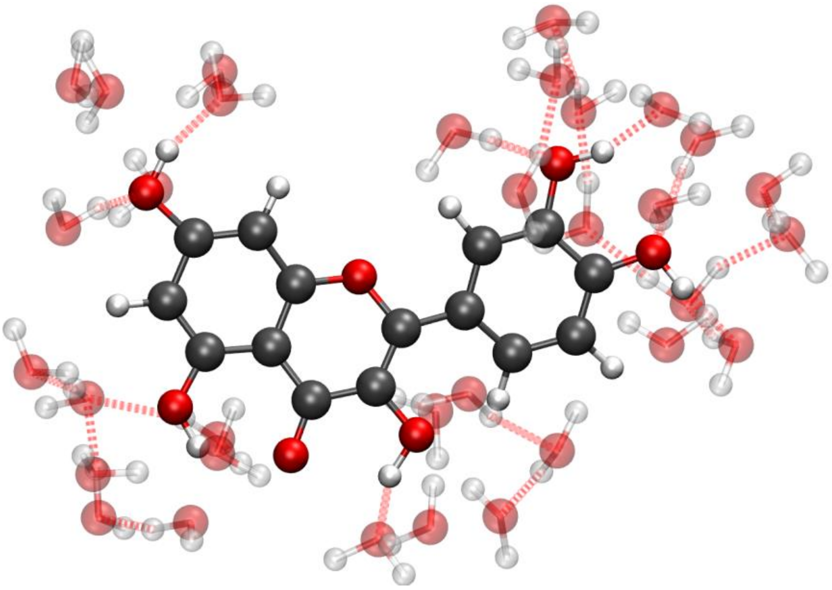

Tuning the Optical Properties of a Chromophore in a Nanoconfined Environment

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Abstract :

Organometallic complexes based on Ru(II)-polypyridine systems display electronic properties that are very sensitive to the local environment. A photoinduced charge transfer leads to reorganization dynamics that depend on the interactions with the solvent. We have shown that the transient electronic spectra reveal different mechanisms depending on the nature of the latter [1]. To this end, we developed a computational strategy that is based on an integrated multilevel approach providing an ad hoc intramolecular force field for the Ru complex ground and excited states to be used in classical molecular dynamics simulations. Such simulations are coupled with TD-DFT calculations of the optical properties of the chromophore in its local environment.

Nanoconfinement can lead to significant modifications of the dynamical, optical, and physicochemical properties of confined species, which can be exploited for a wide range of applications [2]. Layered double hydroxides (LDHs) are a class of claylike layered systems, the structure of which comprises positively charged mixed-metal hydroxides on the inorganic surface, with charge-compensating anions immersed in an aqueous environment, in the expandable interlayer space [3]. Some experimental work on ruthenium/LDH hybrids have shown that intercalating Ru complexes in LDHs leads to a significant improvement of their thermal and photo-stability [4]. However, a molecular interpretation of the role played by the confined environment, which is key to fine tuning the effect on intercalated compounds, is still missing.

We adapted and applied our computational approach to develop an ad hoc intramolecular force field for the Ru complex ground and excited states and model its interaction with the LDH. The influence of nanoconfinement on the absorption and fluorescence spectra of the chromophore will be discussed. In particular, we shall focus on the Ru complex – surface interactions and on the role of the surrounding water molecules. The effect of the specific confined environment of the LDH on water will be also analyzed.

REFERENCES

[1] G. Prampolini, F. Ingrosso, A. Segalina, S. Caramori, P. Foggi, M. Pastore, J. Chem. Theory Comput., 1 (2019) 529-545. G. Prampolini, F. Ingrosso, J. Cerezo, A. Iagatti, P. Foggi, M. Pastore, J. Phys. Chem. Lett. 11 (2019) 2885-2891.
[2] A.B. Grommet, M. Feller, R. Klajn, Nat. Nanotechnol., 4 (2020) 256–271.
[3] Wang, Q., O'Hare, D. Chem. Rev., 7 (2012) 4124–4155.
[4] F. N. Xiao, K. Wang, F. B. Wang, X. H. Xia., Anal. Chem. 8 (2015) 4530–4537.

The 2PT approach for a molecular dipolar liquid

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Abstract

The two-phase thermodynamic model (2PT) has been developed to calculate absolute entropy, free energy and other thermodynamic magnitudes in fluids by using relatively short Molecular Dynamics simulations [1]. In the approach, velocity autocorrelation functions and vibrational densities of states are modeled as combinations of a solid-like component and a gas-like one. The solid-like part is intended to reproduce the harmonic behavior of the fluid. The gas-like component, which is responsible for diffusion, includes anharmonic dynamic processes. The method requires the fluidicity fraction that characterizes the gas-like proportion in the overall functions. A revisited 2PT version, including a redefinition of the fluidicity parameter, outperforms the classical approach when tested in Lennard-Jones systems and liquid metals [2]. We have extended this modified version of the original 2PT methodology in order to evaluate thermodynamic properties of molecular systems. The solid part has been approximated by that of a set of harmonic oscillators, whereas a subset composed of rough hard spheres [3,4] has been considered for the gas part. In this new approach, molecules are rotating hard spheres that experience elastic collisions. Different fluidicity factors for rotation and translation have been introduced in the model. The technique has been tested on a system made up of diatomic molecules with a dipole moment at a wide range of temperatures, from the liquid to the supercooled state. Additionally, instantaneous normal modes (INM) have been evaluated for the system. Translation and rotation 2PT solid components of the overall spectra have been compared to the stable wing of the corresponding INM vibrational densities of states, which are commonly associated with the purely harmonic dynamics of the system. It has been obtained that the 2PT approach reasonably reproduces INM spectra at short frequencies, overestimates the function at intermediate frequencies and slightly underestimates the high frequency part. The proposed methodology provides accurate results for total entropy, potential energy reference and heat capacity [5].

REFERENCES

[1] S. T. Lin and M. Blanco and W. A.Goddard, J. Chem. Phys. 119 (2003) 11792-11806.
[2] T. Sun and J. Xian and H. Zhang and Z. Zhang and Y. Zhang, J. Chem. Phys. 147 (2017) 194505.
[3] D. Chandler, J. Chem. Phys. 62 (1974) 1358.
[4] J. W. Lycklema, Phys. A 96 (1979) 573; 96 (1979) 594.
[5] R. Palomar and G. Sesé, Phys. Chem. Chem. Phys. 23 (2021) 26524.

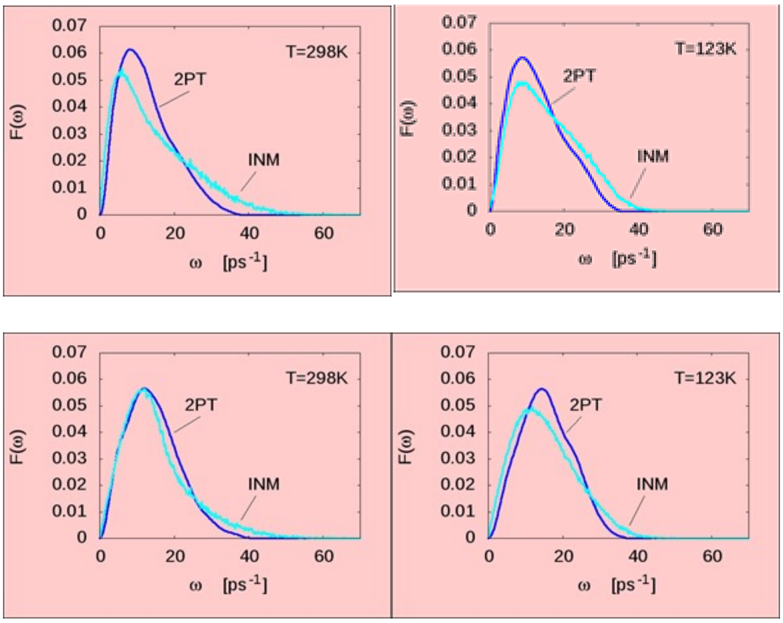

Figure 1: Solid components of vibrational densities of states evaluated within the 2PT approximation, compared with the harmonic instantaneous normal modes spectra (INM) associated with translation (up) and rotation (down) at liquid (298 K) and supercooled (123 K) states.

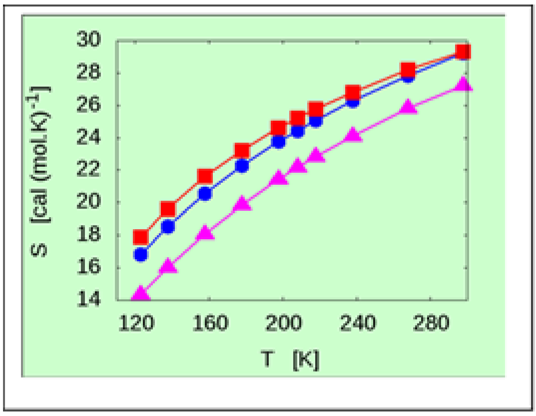

Figure 2: Entropy obtained by using the 2PT rough hard sphere approach (red squares) [5], and by considering the 2PT approach in [1] (pink triangles). Reference values are also shown (blue circles).

The role of surface ionisation in the hydration-induced swelling of graphene oxide membranes

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Graphene Oxide (GO) membrane are hydrophilic materials that swell in the presence of water either in humid environment or when in contact with liquid water and the magnitude and mechanism of the swelling is dependent on the degree of ionisation of the functional groups present on the surface of GO flakes. In this work, using Grand Canonical Monte Carlo and Molecular Dynamics simulations we investigate the effect that surface charge, resulting from the ionisation **[1]** process, has on both the amount of water **[2]** adsorbed in the membranes at various humidity conditions and the swelling of the membranes in contact with liquid water **(Figure 1)**. Three models with increasing surface charge from -63 mC/m^2 to -177 mC/m^2 and a neutral one is used **[3]**. We show that by incorporating ionised functional groups, the onset of adsorption **(Figure 2)** is shifted to a lower chemical potential and the internal membrane pressure **(Figure 3)** increases due to the repulsive interactions between the graphene flakes. We suggest that for a fairly ordered membrane as the ones modelled here a surface charge of -120 mC/m^2 is the upper limit before membrane delaminate. Our simulations also show that the presence of ions in the channel reduced the swelling due to screening effect but also increases the amount of water adsorbed when the membrane is immersed in liquid water. At low chemical potential, instead, the amount of water adsorbed is determined by the number of ionised groups. The charged model is able to qualitatively reproduce experimental data showcasing the importance of including surface charge in GO model to predict hydration and swelling mechanism. These findings are crucial in underpinning the future development of GO membranes in simulation and experimental study for aqueous separations since hydration-induced swelling is widely known to lead to significant deterioration in performances.

FIGURES

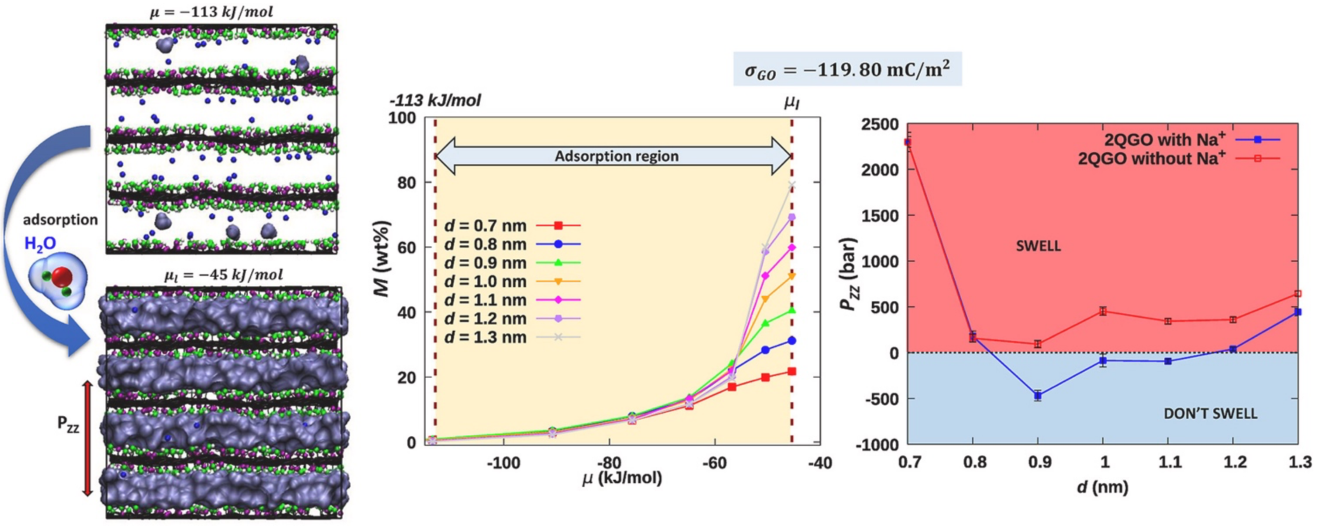

Figure 1: (a) Adsorption of water in a rigid charged GO membrane from low chemical potential to bulk liquid water chemical potential using Grand Canonical Monte Carlo simulation. (b) Amount of water adsorbed in GO membrane at different interlayer spacing (example on 2QGO model). (c) Pressure normal to plane of GO membrane, P_{ZZ} to check for swelling of GO membrane in liquid water (example on 2QGO model).

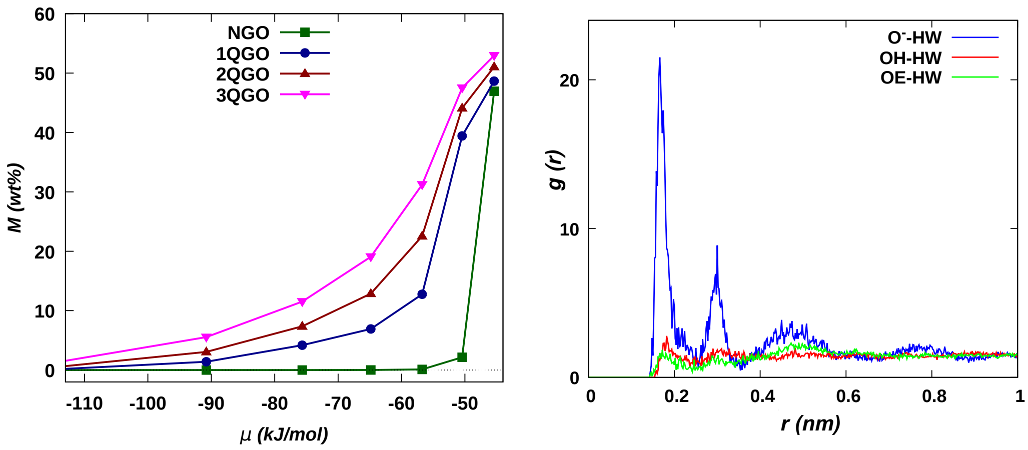

Figure 2: (a) Water adsorbed in GO membrane model NGO, 1QGO, 2QGO, 3QGO (d = 1.0 nm). (b) RDF between oxygen atom of ionised hydroxyl (O-), hydroxyl (OH) and epoxide (OE) with hydrogen of water molecules (HW).

SWELLING

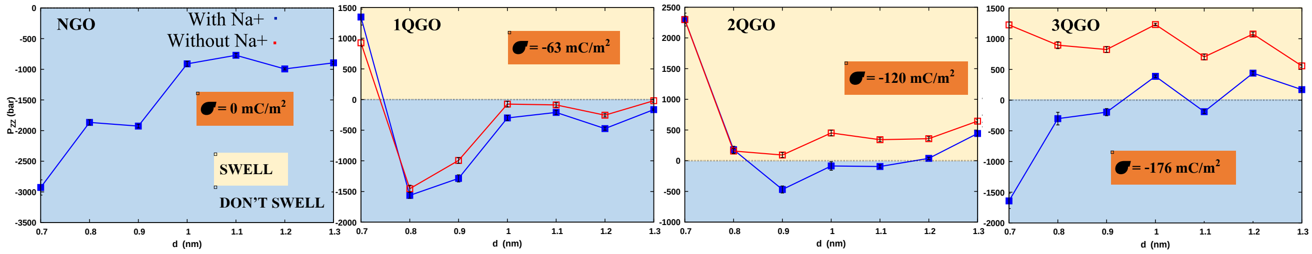

Figure 3: Pressure (P_{ZZ}) in (a) NGO, (b) 1QGO, (c) 2QGO, and (c) 3QGO. $P_{ZZ} > 0$ = swelling of GO membrane.

REFERENCES

[1] Mouhat, F., Coudert, F. and Bocquet, M., Nature Communications 11 (2020), 1566.
[2] Price, D. and Brooks, C., The Journal of Chemical Physics 121 (2004), 10096-10103.
[3] Williams, C., Carbone, P. and Siperstein, F., Nanoscale 10 (2018), 1946-1956.

Heterogeneous Electron Transfer Reactions inside Carbon Nanotubes: Molecular Dynamics Simulations

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Molecular details of the electron transfer (ET) elementary act in confined systems like nanopores, are interesting but challenging to obtain. Two recent attempts to elucidate the kinetics of simple redox couples in solvent-filled nanopores using molecular dynamics (MD) simulations [1, 2] led to contradictive results; an enhancement of the ET rate under nano-confined conditions was predicted in [1], whereas a rate decrease compared with bulk solution has been reported in [2].

We investigated systematically the heterogeneous kinetics of a $Fe^{3+/2+}$ redox couple in carbon nanopores in an aqueous environment. Conducting single-walled carbon nanotubes with diameters from 0.8 to 3.5 nm serve as a model of pores. Molecular dynamics simulations were performed using the LAMMPS program package [3]. The SPC/E model describes water while the CHARMM force field [4] and the $Fe^{3+}/^{2+}$–H2O potentials devised in [5] are used for the other interactions. We analyse primarily the solvent reorganization energy which is calculated at several ion-wall separations. This is performed by constructing two reaction free energy surfaces along the solvent coordinate. The influence of the image charge on the reorganization energy could be investigated after solving this electrostatic problem for a perfectly conducting cylinder. Axial and radial components of the static dielectric constant are also presented [6].

REFERENCES

[1] R.C. Remsing et al., J. Phys. Chem. Lett., (2015), 6, 4804-4808.
[2] Z.J.Li et al., J. Phys. Chem. Lett., 8 (2017), 1925-1931.
[3] Stevens M., J. Tranchida, C. Trott, S. J. Plimpton, Comp. Phys. Comm., 271 (2022) 10817.
[4] Alexiadis A., Kassinos S. Chem. Rev., 108 (2008), 5014-5034.
[5] L.A. Curtiss, J.W. Halley, J. Hautman, Rahman A. J. Chem. Phys., 86 (1987), 2319-2327.
[6] S. Shermukhamedov, et al., ChemElectroChem, 3 (2021), p. 563–569.

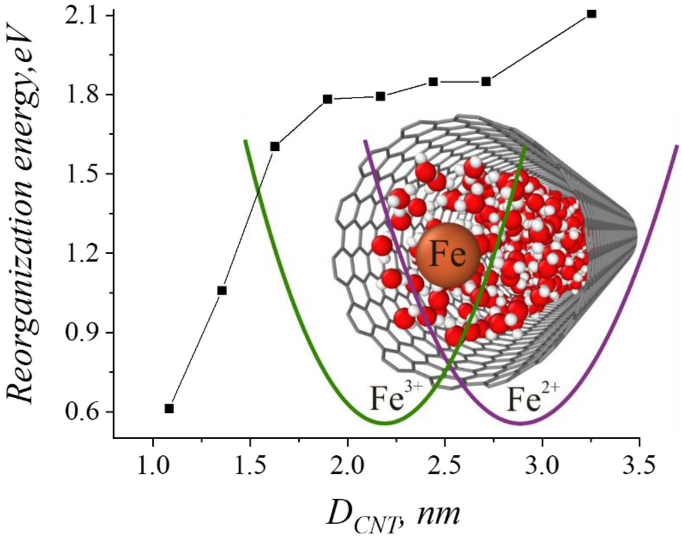

Figure 1: Reorganization energy calculated from free energy surfaces and visualization of the Gibbs energy surfaces for heterogeneous electron transfer along the solvent coordinate

Thermodynamics and structure of TIP4P/Ice supercooled water

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The existence of the liquid-liquid critical point (LLCP) [1] of water has been a long-discussed problem and the arguments that speak in favor of its existence are usually based on simulation data analysis. Standard ways to describe structural changes of the simulated system, like pair correlation function or the structure factor, have been proved to be not sensitive enough to describe the liquid-liquid transition. Therefore, a number of so-called local structure parameters were defined to identify structural changes around individual molecules. Most of these parameters were defined ad-hoc do describe only a specific level of structural order and thus results of certain parameters may be in contradiction with each other. They also very often depend on an ambiguous criterion like hydrogen bond or nearest neighbors definition [2]. Recently there was an attempt to overcome these criterion definitions by employing parameters based on properties of Delaunay triangulation applied to water molecules rather than investigate molecules themselves [3]. These parameters exhibit significant structural changes in the supercooled area but their physical explanation is problematic.

Thermodynamic and structural properties of TIP4P/ice [4] water have been studied in detail in the region of the expected occurrence of the second critical point. Various structure order parameters along with the Delaunay tessellation and density histogram have been used with a focus on their ability and mutual consistency to provide the necessary information. Whereas density histograms clearly show the bimodal distribution corresponding to the coexistence of two metastable density states, most of the standard structural parameters provided only information about the increase in the level of molecular order with lowered temperature. Only the parameter called the local structure index and parameters based on the Delaunay tesselation provided information consistent with the density histogram. The bimodality in these parameters has been connected to the anomalous behavior of the isothermal compressibility which increases in the supercooled region gaining the λ-shape form which a sign of the presence of the critical point.

REFERENCES

[1] O. Gallo, K. Amann-Winkel, Ch. A. Angell, M.A. Anisimov, F. Caupin, Ch. Chakravarty, E. Lascaris, T. Loerting, A. Z. Panagiotopoulos, J. Russo, J. A. Sellberg, H. E. Stanley, H. Tanaka, C. Vega, L. Xu, L. G. M. Pettersson, Chem. Rev. 116 (2016) 7463-7500 .
[2] E Duboué-Dijon and D. Laage, J. Phys. Chem. B, 119 (2015) 8406-8418
[3] J. Škvára, F. Moučka and I. Nezbeda, J. Mol. Liq. 261 (2018) 303-318
[4] J. L. F. Abascal, E. Sanz, R. García Fernández and C. Vega, J. Chem. Phys., 122 (2005) 234511

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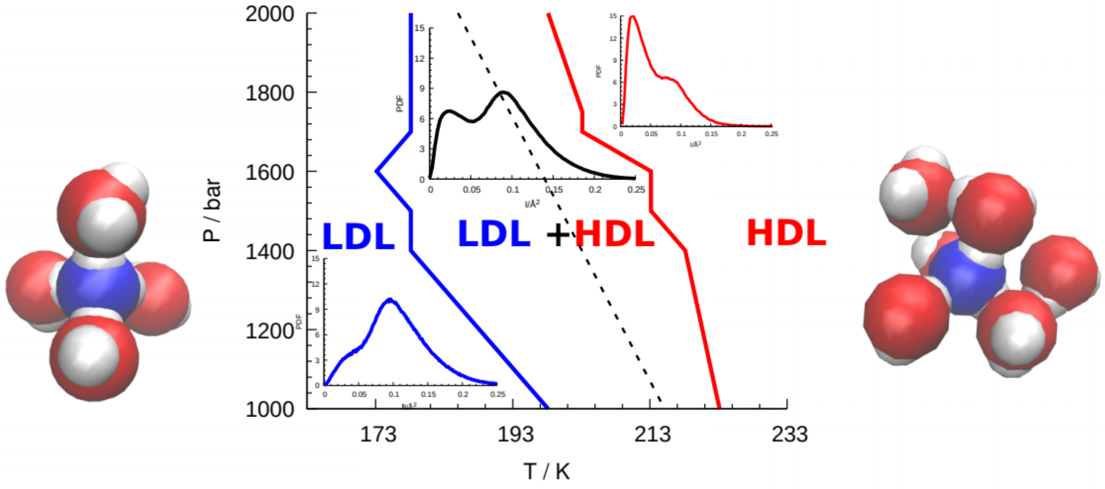

Figure 1: Illustration of changes in the structure of supercooled water at various thermodynamic conditions. Typical behavior of the local structural index is shown for each area..

Calculation of effective interaction between like-charged particles ; Integral equation theory of liquids and Monte Carlo simulation

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Abstract

Acidic proteins, which are negatively charged particles, show an interesting condensation behavior in an electrolyte solution if the electrolyte has multivalent cations[1]. As the electrolyte concentration increases, the state changes in order of dispersion, condensation, and re-dispersion. So, the effective interaction changes repulsive, attractive, and repulsive, in other words, an effective attraction between like-charged particles exhibits reentrant behavior to the electrolyte concentration. DNA also shows this behavior.

In our previous study, to explain this phenomenon, we calculated the effective interaction between anions by using the OZ-HNC theory, which is one of the integral equation theories of liquids[2]. These results reproduced the above experimental results qualitatively. We should note that the results given by the integral equation theory are based on an approximation, namely the HNC approximation. The confirmation using molecular simulation is important.
However, it is difficult that the concentration dependence of effective interaction is investigated by simulation. It is one of the results that the reentrant behavior had been reproduced by molecular simulations. Thus, we decided calculation parameters based on the results of HNC-OZ theory. And we calculate the effective interaction between anions by using the Monte Carlo simulation in the present study.

We carried out the modeling using the results of the OZ-HNC theory to survey the reentrant behavior. Here, we prepared the electrolyte solution which includes monovalent anion and multivalent cation. Additionally, in this system which strong coulomb interaction works, we predicted easy to fall into the local minimum. As a measure, we calculated with replica exchange method.

Some of the results are shown in Figure 1. The effective attraction of the OZ-HNC theory was a lot larger than simulation when the electrolyte concentration was low. So, the results of the OZ-HNC theory and simulation were different quantitatively because the OZ-HNC theory provides larger effective attraction. On the other hand, the simulation results indicated the reentrant behavior to the concentration. So, the results of the theory and simulation were qualitatively same. And these results indicated the HNC approximation emphasizes an effect of the mediation site between like-charged particles.

REFERENCES

[1] M. R. Fries, N. F. Conzelmann, L. G˙unter, O. Matsarskaia, M. W. A. Skoda, R. M. J. Jacobs, F. Zhang, F. Schreiber, Langmuir 37 (2021) 139.Authors, Journal, Issue (Year) page (Calibri 11)
[2] A. Suematsu, R. Akiyama, J. Chem. Phys. 154 (2021) 034902.

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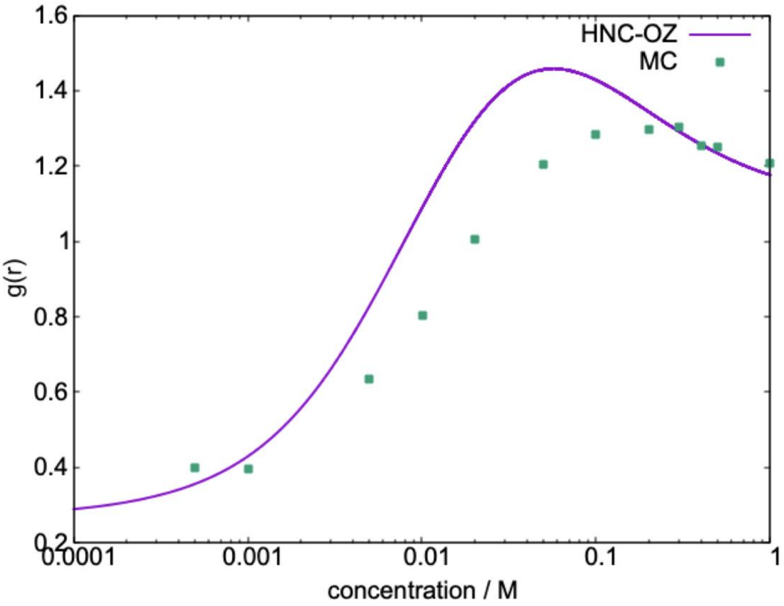

Figure 1: Anion-concentration dependence of the values of radial distribution function g(r) at a specified separation. The corresponding separations are 5.38 Å and 5.60 Å for the HNC-OZ theory and MC simulation, respectively.

The Mean Countershell Approximation for electrolytes: electrostatic correlations in the excess chemical potential

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An extension of the Mean Spherical Approximation (MSA) has been proposed [1] to take the electrostatic correlations (called electrostatic screening component) into account in the excess chemical potential (activity coefficient) for homogeneous electrolytes. The underlying model is the (not so) primitive model where ions are charged hard spheres immersed in a dielectric continuum. The new Mean Countershell Approximation (MCSA) is an analytic theory of the electrostatic screening correlations derived from physical arguments with no adjustable parameters. Comparisons to Monte Carlo simulations show the MCSA to be highly accurate. It also makes qualitative improvements over the MSA and its formulas are simpler. The theory is based on the interactions of the two clouds of screening ions around two distinct ions. This term provides a significant contribution to the energetics of an electrolyte especially at high concentrations and high ion size asymmetries. Simulations show that the MCSA is highly accurate also at the low dielectric constants of ionic liquids. Comparisons with MC data for various conditions are reported.

REFERENCES

[1] D. Gillespie, M. Valiskó, D. Boda. Electrostatic correlations in electrolytes: Contribution of screening ion interactions to the excess chemical potential. *J. Chem. Phys.* 155 (2021) 221102

Is TiO_2 cleaning our wastewater in the future?

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Humanity is polluting this planet in multiple ways. We are all aware of phenomenas like the ocean garbage patches, but not only plastic can be found in our waters. Likewise chemicals from industry, agriculture, pharmaceutics and everyday life products can be detected in our rivers and wastewaters [1,2].
To remove the chemicals that we release into the environment we need innovative technologies to clean our wastewaters. TiO_2 is known from experiments to act as a catalytic surface to degrade pollutants [3], but there is still the need for more knowledge about the degradation mechanism on the atomic level: What environmental conditions are favoring a degradation (i.e. pH value, TiO_2 phase)? Which pollutants can be removed by TiO_2? Which role does water play in the adsorption and splitting process? And what can we do to improve this process?
In this project we try to answer these questions by simulating different water pollutants on a TiO_2 slab in bulk water with a multi method approach (fig. 1) [4,5]. Starting with FF MDs of multiple molecules we get hints on how they are interacting with the surface. This allows us to sort the pollutants into categories: adsorption, no adsorption and clustering.
If adsorbing behavior can be identified, we simulate the corresponding molecule in the most prominent adsorption geometry in ab initio DFT methods to get more information about the splitting and possible water recombination processes. Since the presence of UV light supports the splitting procedure, TD-DFT simulations of a first excited state can help us interpret the previously obtained results [6].
When the pollutant shows clustering it can be assumed that the molecules rather interact with themselves than with the surface. The driving forces of this phenomenon can be multiple ones, i.e. hydrophobic collapses, hydrogenbond formation or salt bridges. We are performing MD and enhanced sampling simulations (MetaD) to further investigate the behavior of the clustering pollutants and their interaction with the aqueous environment as well as with the TiO_2 surface.

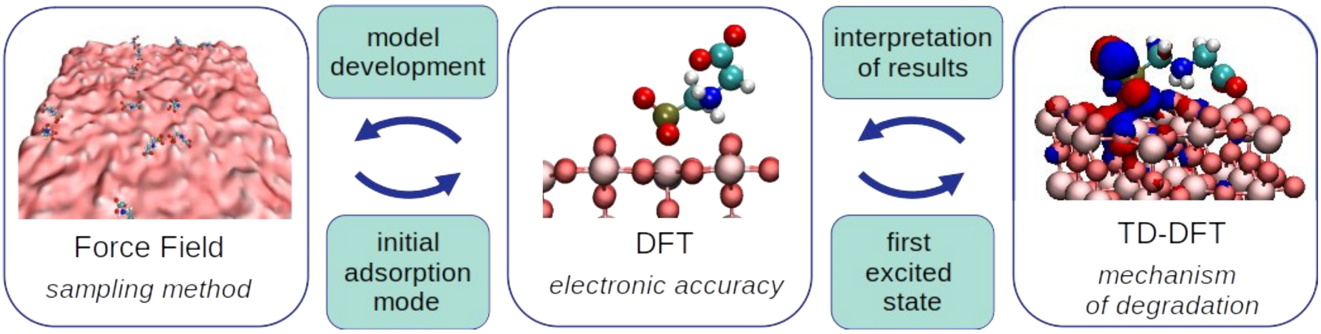

Figure 1: Multi method approach for adsorbing pollutants. The initial adsorption geometries are taken from the FF simulations as a starting model for DFT and TD-DFT simulations.

REFERENCES

[1] Dsikowitzky, L., Schwarzbauer, J., Kronimus, A., Littke, R., *Chemosphere*, 57, 10 (2004), 1275-1288.
[2] Caliman, F.A., Gavrilescu, M., *Clean*, 37, 4 – 5, (2009), 277 – 303.
[3] Zhu, X.-D., Wang, Y.-J., Sun, R.-J., Zhou, D.-M., *Chemosphere*, 92, 8 (2013), 925-932.
[4] Balzaretti, PhD Thesis (2021), University of Bremen, doi: 10.26092/elib/1495
[5] Romero, M., Bachelor Thesis (2018), University of Bremen.
[6] Balzaretti, F., von Einem, M., Gerhards, L., Dononelli, W., Stauch, T., Klüner, T., Köppen, S., Preprint (2021), doi: 10.26434/chemrxiv.14465436.v1

Wettability of graphite under 2D confinement

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The thermodynamics of solid/liquid interfaces under nanoconfinement has tremendous implications for liquid transport properties. Here using molecular dynamics, we investigate graphite nanoslits and study how the water/graphite interfacial tension changes with the degree of confinement. We found that, for nanochannel heights between 0.7nm and 2.6nm, graphite becomes more hydrophobic than in bulk, and that the value of the surface tension oscillates before eventually converging towards a constant value for larger slits. The value of the surface tension is correlated with the slip length of the fluid and explained in terms of the effective and interfacial density, hydration pressure and friction coefficient. The study clearly indicates that there is a critical channel height of 0.9nm (achievable experimentally[1]) at which the surface tension reaches its highest value, but the water diffusion across the channel is at its minimum. The structural analysis shows that for this pore size a transition between a 2D and 3D hydrogen bond network is accompanied by an abrupt increase in conformational entropy. Our results show that the wettability of solid surfaces can change under nanoconfinement and the data can be used to interpret the experimental permeability data.

REFERENCES

[1] Williams, C. D., Wei, Z., Shaharudin, M. R. bin & Carbone, P. A molecular simulation study into the stability of hydrated graphene nanochannels used in nanofluidics devices. *Nanoscale* **14**, 3467–3479 (2022).

FIGURES

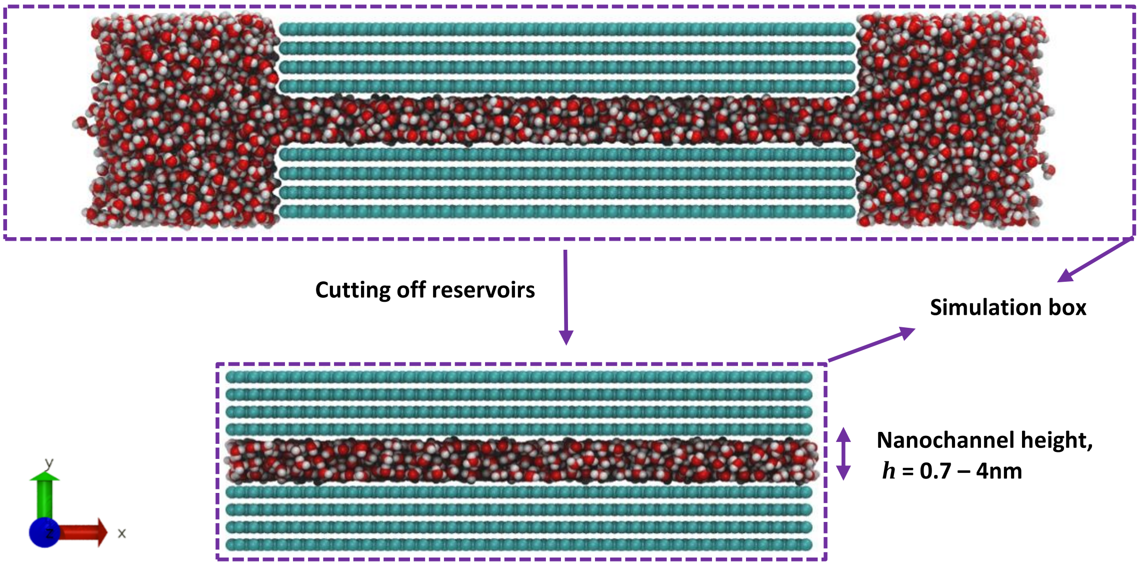

Figure 1: Side-view of water confined in a graphitic nanochannel of 1.2nm height: snapshot of the channel in contact with the two reservoirs after the water has filled the channel (top); snapshot of the channel after the reservoirs have been removed (bottom). The y-direction is normal to the graphite surface. Periodic boundary conditions are applied in all three directions. The surface area is defined by A = LxLz. The red, white, cyan spheres represent oxygen, hydrogen, and carbon atoms respectively.

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