CPP 21: French-German Session: Simulation Methods and Modeling of Soft Matter III

Time: Tuesday 9:30–11:15 Location: ZEU/0255

Invited Talk CPP 21.1 Tue 9:30 ZEU/0255

Molecular modelling of gas solubility and free volume trends in Si-functionalized ionic liquids — •Kateryna Goloviznina[1,2], Eduards Bakis[3], Inês C. M. Vaz[2,4], Agilio Padua[2], and Margarida Costa Gomes[2] — [1]ICSM, University of Montpellier, CEA, CNRS, ENSCM, 30207 Bagnols-sur-Ceze, France — [2]Laboratoire de Chimie, ENS de Lyon and CNRS, 46 allée d'Italie, 69364 Lyon, France. — [3]Faculty of Chemistry, University of Latvia, Jelgavas 1, Riga, LV-1004, Latvia. — [4]CICECO, Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

Molecular dynamics (MD) simulation is a powerful technique that provides insight into the nanoscale structure and transport properties of liquids in bulk and at interfaces, explaining experimentally observed phenomena and contributing to the rational design. In the present work, we explored Si-functionalized imidazolium-based ionic liquids—low-density, low-viscosity systems—that are promising for gas capture and separation due to their enhanced free volume. [1] Using classical MD simulations with the CL&Pol polarizable force field, [2] we proposed a way to estimate free-volume trends and solubilities of simple gases (e.g., argon) without the need to perform costly experiments. The work was further extended to unsaturated C_2 hydrocarbons, for which we rationalized solubility trends via local structural analysis and estimated the contributions of van der Waals, electrostatic, and polarization terms to the solvation free energy.

[1] E. Bakis et al. Chem. Sci. 2022, 23, 9062.

[2] Goloviznina et al. J. Chem. Theory Comput. 2019, 15, 5858.

CPP 21.2 Tue 10:00 ZEU/0255

Classical DFT compared to AFM measurement of structural forces from confined electrolyte containing charged nanoparticles — •Simone Riva[1], Michael Ludwig[2], Regine von Kltizing[2], and Ofer Manor[1] — [1]Technion, Haifa, Israel — [2]Technische Universität Darmstadt, Darmstadt, Germany

We use classical density functional theory (DFT) to model colloidal-probe atomic force microscopy (AFM) force curves across an aqueous electrolyte containing charged solid nanoparticles. The charged AFM probe and substrate interact through a suspension of silica nanoparticles. The probe experiences oscillatory forces driven by the structuring of the charged nanoparticles, which can enhance the stability of the film. Structural forces are characterized by an alternation of repulsion due to steric and electrostatic nanoparticle interactions, and depletion attraction. We present a self-consistent theory of oscillatory forces in ionic systems. Moreover, we compare different DFT approaches and validate them against AFM measurements, to develop a theory that best fits the rich physics of experiments. We calculate structural and EDL forces by minimizing dedicated functionals. We adopt two types of weighted density functionals, disclosing their applicability in different concentration conditions. We propose a way to include electrostatic interactions between nanoparticles in an effective hard-sphere functional. We further confirm a general scaling law of the oscillation wavelength observed in experiments and connect it to nanoparticle packing structures. The theory agrees well with measurement in the absence of fitting parameters. Riva et al., JCIS 2026, 702, 138901.

CPP 21.3 Tue 10:15 ZEU/0255

Sc-cDFT: A Single-Chain Simulation Framework with Classical Density Functional Theory for Polymers — •Raju Lunkad[1], Alejandro Gallegos[2], Jianzhong Wu[3], and Marcus Müller[1] — [1]Institute for Theoretical Physics, Georg-August University, 37077 Göttingen, Germany — [2]Department of Chemical and Materials Engineering, New Mexico State University, Las Cruces, New Mexico 88001, United State of America — [3]Department of Chemical and Environmental Engineering, University of California, Riverside, CA, United States of America

We present Sc-cDFT, a combination of Single-Chain Simulation with classical Density-Functional Theory (cDFT), for modeling polymer solutions and brushes. In this approach, intramolecular correlations are explicitly treated using Monte-Carlo (MC) simulations, while intermolecular correlations are extracted from cDFT. In this way, we capture structural properties and thermodynamics of multi-chain systems while providing a segment-level description of the dynamic behavior. Importantly, this framework substantially reduces computational cost, enabling the simulation of significantly longer polymer chains that are often inaccessible to fully explicit particle-based simulations. We validate the Sc-cDFT framework for hard-sphere polymer solutions and brushes by comparing polymer configurations and the segmental density profiles with fully explicit particle-based simulations, showing quantitative agreement.

CPP 21.4 Tue 10:30 ZEU/0255

Adsorption Thermodynamics and Kinetics of Complex Fluids: Physical Modeling of Surface Saturation, Reservoir Depletion, Lateral Interactions, and Collective Effects — •Nada Ben Amor[1,2], Daniela Bauer[1], Benjamin Braconnier[1], and Benoit Coasne[2,3] — [1]IFP Energies nouvelles, 92852 Rueil-Malmaison, France — [2]Université Grenoble Alpes, CNRS, LIPhy, F-38000 Grenoble, France — [3]Institut Laue Langevin, F-38042 Grenoble, France

Adsorption at solid surfaces is considered a promising technique to capture and remove emerging pollutants such as PFAS from water. However, a major gap in the literature remains in modeling complex adsorption mechanisms. Three key factors were identified for modeling adsorption thermodynamics and kinetics: surface saturation, reservoir depletion, and lateral interactions. While the first is captured by the celebrated Langmuir model, reservoir depletion, which is crucial for assessing adsorption in batch and dynamic experiments, is often neglected in classical kinetic models. Lateral interactions are also important for pollutants like PFAS as they undergo cooperative adsorption. A 2D lattice gas model with two- and three-body lateral interactions is solved using mean-field and quasi-chemical approximations. The resulting thermodynamics lead to a phase diagram predicting complex adsorption isotherms in agreement with available experiments as well as a first-order dilute to dense phase transition. A mixed-order kinetic model including all three factors is proposed and both thermodynamic and kinetic models are successfully applied to experimental data.

CPP 21.5 Tue 10:45 ZEU/0255

Molecular Dynamics Insights into Thermodynamic and Structural Properties of Water Adsorbed Poly(Heptazine Imide) Zeolites — •Youssef Mabrouk[1], Akshey Suresh[2], Yizak Tzegazab[2], Lingli Ni[2], Martin Oschatz[2], Alexander Croy[1], and Stefanie Gräfe[1] — [1]Friedrich Schiller University of Jena, Insitute of Physical Chemistry, Lessingstraße 4, 07743 Jena, Germany — [2]Friedrich Schiller University of Jena, Institute for Technical Chemistry and Environmental Chemistry, Philosophenweg 7a, 7743 Jena, Germany

The recently reported reversible water adsorption of porous layered carbon nitrogen frameworks suggests their high potential as functional materials for energy storage and conversion applications specifically in view of the controlled crystallinity and polarity and water binding motifs these frameworks offer. Based on molecular dynamics simulations of pressure-controlled solid/gas equilibrium isotherms, the framework structure-dependent adsorption of water in poly(heptazine imides) is here investigated. Using minimal motifs of heptazine sheets in pressure-controlled water vapor environments, the load-dependent transition from monomolecular to condensation-limited adsorption is furthermore investigated. The hydrophilicity characterized by the isotherms agree with physiosorption experiments. The layer planarity and pore geometry-dependent crystallinity characterized by the structure factor and normal modes agree with x-ray diffraction and infrared spectroscopy experiments. Overall, our results contribute to identifying the relevance of each structural motif to adsorption.

CPP 21.6 Tue 11:00 ZEU/0255

Insights into phenylalanine self-assembly and its modulation by nucleotides from molecular dynamics simulations. — •Mattia Borriello — Ruhr-Universität Bochum

Phenylalanine (Phe) can aggregate in water into various fibrillar structures, which is relevant to diseases like phenylketonuria. The precise molecular structure of these aggregates is still unknown, and although they dissolve in the presence of nucleotides such as ATP, the mechanism behind this disassembly remains unclear. We use molecular dynamics simulations to gain new insights on Phe cluster structure, understand which interactions drive this process and how nucleotides can modulate it.

Parallel tempering simulations of Phe in water in zwitterionic form have been performed varying concentration and temperature. Analysis of the trajectories revealed a strong tendency to aggregate in two ordered structures. One is characterized by a tubular shape, while the other by an alternating motif. Cluster stabilization is mainly electrostatic for smaller aggregates, while apolar interactions become significant as the size of the clusters grows.

The same computational approach has been extended to systems containing Phe and NaCl or different nucleotides, such as ATP, ADP and AMP. While NaCl showed a limited influence on aggregation, nucleotides can inhibit cluster formation and disrupt pre-existing aggregates. Our findings provide molecular-level insight into both the structural organization of Phe assemblies and into the mechanisms through which nucleotides modulate their stability.