CPP 9: Modeling and Simulation of Soft Matter (joint session CPP/DY)

Time: Monday 15:00–17:45 Location: H39

CPP 9.1 Mon 15:00 H39

Machine Learning of consistent thermodynamic models using automatic differentiation — •David Rosenberger[1], Kipton Barros[2], Timothy Germann[2], and Nicholas Lubbers[2] — [1]Freie Universität Berlin, Berlin, Germany — [2]Los Alamos National Laboratory, Los Alamaos, NM, USA

Instead of fitting suitable analytical expressions to thermophysical data, we propose to combine automatic differentiation and artificial neural networks (ANNs) to obtain complex equations of state (EOS) for arbitrary systems. Rather than training directly on the properties of interest, we train an ANN on a model free energy whose partial derivatives match the thermophysical properties measured in experiment. We show that this method is advantageous over direct learning of thermodynamic properties, in terms of both accuracy and the exact preservation of the Maxwell relations. Furthermore, the method can implicitly solve the integration problem of computing the free energy of a system without explicit integration given appropriate data to learn from.

CPP 9.2 Mon 15:15 H39

Atomistic Machine Learning for Aqueous Ionic Solutions — •Philip Loche, Kevin K. Huguenin-Dumittan, and Michele Ceriotti — Laboratory of Computational Science and Modeling, IMX, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

Accurate modeling of matter at the atomic scale requires to simultaneously account for the quantum nature of the chemical bond - that usually manifests itself on short time and length scales - and long-range interactions, such as electrostatics and dispersion, that occur on a large scale and often result in phenomena with a long characteristic time. Electronic structure calculations provide an accurate description of both quantum and long-range effects, but are computationally demanding, and scale poorly with system size. Machine learning (ML) approaches have emerged as a very effective strategy to build surrogate models that provide comparable accuracy at a fraction of the cost, but the most widespread techniques base their efficiency and transferability on a local description of atomic structure, which makes them ill-equipped to deal with long-range effects.

Here, we are going to to connect local and long range physics in a data driven ML approach by applying the current ML techniques to, condensed-phase systems, involving the characterization of aqueous ionic solutions. We show that only a combination of a long and a short range approach is able to predict short distanced molecular vibrations as well a long ranged ionic screening lengths.

CPP 9.3 Mon 15:30 H39

Identification of glass transition temperature for polymer melts using data-driven methods — •Atreyee Banerjee, Hsiao-ping Hsu, Oleksandra Kukharenko, and Kurt Kremer — Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

On fast cooling, the dynamics of polymer melts slow down exponentially, leading to solid glassy states without any drastic change in the structural structure. We employ data-driven methods based on purely confomational fluctuations to identify the glass transition temperature for a coarse-grained weakly semi-flexible polymer model. More precisely, we used principal component analysis (PCA) to quantify the conformational fluctuations and identify a sharp change in fluctuation around the glass transition temperature. The first eigen value of PCA shows a clear difference below and above glass transition temperatures. The new method of glass transition temperature predicted from PCA considers local structural fluctuations and does not depend on any fitting parameters like the existing methods.

CPP 9.4 Mon 15:45 H39

Systematic parametrization of non-Markovian dissipative thermostats for coarse-grained molecular simulations with accurate dynamics — •Viktor Klippenstein and Nico F. A. Van Der Vegt — Eduard-Zintl-Institut für Anorganische und Physikalische Chemie, Technische Universität Darmstadt, 64287 Darmstadt, Germany

The Mori-Zwanzig theory, in principle, allows to derive an exact equation of motion for coarse-grained degrees of freedom based on the dynamics of an underlying fine-grained reference system.[1] Still, in practice the simultaneous representation of structural and dynamic properties in particle-based models poses a complicated problem, e.g. due to the non-linearity of the exact coarse-grained equation of motion.

A viable approximate approach is to start from a conservative coarse-grained force-field and to extend the standard Newtonian equation of motion used in molecular simulation with a linear generalized Langevin thermostat. We demonstrate how such a thermostat can be parametrized to correctly represent dynamic properties, both in a purely bottom-up approach[2,3] or by applying iterative optimization.[3] We consider the Asakura-Oosawa model as a simple test case.[3]
[1] V. Klippenstein, M. Tripathy, G. Jung, F. Schmid, and N. F. A. van der Vegt, The Journal of Physical Chemistry B 125, 4931 (2021).
[2] V. Klippenstein and N. F. A. van der Vegt, The Journal of Chemical Physics 154, 191102 (2021).
[3] V. Klippenstein and N. F. A. Van Der Vegt, The Journal of Chemical Physics under review (2022).

CPP 9.5 Mon 16:00 H39

Stretching biopolymers with fluctuating bending stiffness — •Panayotis Benetatos — Kyungpook National University, Daegu, South Korea

In many biopolymers, the local bending stiffness fluctuates. For example, DNA-binding proteins attach to and detach from DNA to regulate cellular functions, thus causing a change in the local bending stiffness of the polymer backbone. This could also happen due to internal conformational transitions, such as the DNA denaturation or the helix-coil transition in polypeptides. What all these cases have in common is that the change in the local flexibility is transient and reversible. In order to analyse the conformational and elastic behaviour of such biopolymers, we propose a minimal but encompassing model of a freely jointed chain with reversible hinges (rFJC). We show that the tensile response of a rFJC is remarkably different from that of the usual freely jointed chain (uFJC). At small stretching forces, the rFJC is more compliant than the uFJC and the size (mean square end-to-end distance) of the former is greater than that of the latter. At strong stretching forces, in contrast, the rFJC is much stiffer than the uFJC. In this talk, we also discuss a strongly stretched wormlike chain with fluctuating local bending stiffness. We show that, under certain conditions, we get significant ensemble inequivalence (Gibbs vs Helmholtz).

CPP 9.6 Mon 16:15 H39

Modulating internal transition kinetics of responsive macromolecules by collective crowding — •Nils Göth, Upayan Baul, Michael Bley, and Joachim Dzubiella — Applied Theoretical Physics—Computational Physics, Physikalisches Institut, Albert-Ludwigs-Universität Freiburg, 79104 Freiburg, Germany

Packing and crowding are used in biology as mechanisms to (self-) regulate internal molecular or cellular processes based on collective signaling. Here, we study how the transition kinetics of an internal "switch" of responsive macromolecules is modified collectively by their spatial packing. We employ Brownian dynamics simulations of a model of Responsive Colloids, in which an explicit internal degree of freedom–here, the particle size–moving in a bimodal energy landscape self-consistently responds to the density fluctuations of the crowded environment. The bimodal energy landscape is motivated by existing two-state behavior like in protein folding or hydrogels with bimodal volume transitions. We demonstrate that populations and transition times for the two-state switching kinetics can be tuned over one order of magnitude by "self-crowding". An exponential scaling law derived from a combination of Kramers' and liquid state perturbation theory is in very good agreement with the simulations.
[1] Upayan Baul, NG, MB, and JD, J. Chem. Phys. 155, 244902 (2021).

15 min. break

CPP 9.7 Mon 16:45 H39

Modelling process-structure-properties of polymer nanocomposites — •Janett Prehl, Constantin Huster, and Karl Heinz Hoffmann — TU Chemnitz, Chemnitz, Germany

Twin polymerization is a complex chemical reaction process leading to a broad range of organic-inorganic nano composite materials.

Within this presentation we will show our latest results [1] on the theoretical analysis of the structure formation process of twin polymerization via a previously introduced lattice-based Monte Carlo method, the reactive bond fluctuation model [2]. We analyze the effects of various model parameters, such as movability, attraction, or reaction probabilities on structural properties, like the specific surface area, the radial distribution function, the local porosity distribution, or the total fraction of percolating elements.

From these examinations, we may identify structural key factors and thus chemical properties of the underlying components that need to be adapted to fulfill desired requirements for possible applications.

[1] Prehl, J. and Huster, C., *polymers* **11** (2019) 878

[2] Hoffmann, K.H. and Prehl, J., *Reac. Kinet. Mech. Cat.* **123** (2018) 367-383; Huster, C., Nagel, K., Spange, S., and Prehl, J., *Chem. Phys. Lett.* **713** (2018) 145-148

CPP 9.8 Mon 17:00 H39

A cosolvent surfactant mechanism affects polymer collapse in miscible good solvents — •Swaminath Bharadwaj[1], Divya Nayar[1,2], Cahit Dalgicdir[1], and Nico van der Vegt[1] — [1]Technische Universität Darmstadt, Germany — [2]IIT Delhi, India

The coil-globule transitions of aqueous polymers are of profound significance in understanding the structure and function of responsive soft matter. In particular, the remarkable effect of amphiphilic cosolvents (which preferentially adsorb on the polymer surface) that leads to both swelling and collapse of stimuli responsive polymers is still hotly debated in the literature [1]. The predominant focus has been on the attractive polymer-(co)solvent interactions and the role of solvent-excluded volume interactions has been largely neglected. The solvent-excluded volume contribution to the solvation free energy corresponds to the formation of a repulsive polymer-solvent interface.

Using MD simulations, we herein demonstrate that alcohols reduce the free energy cost of creating a repulsive polymer-solvent interface via a surfactant-like mechanism which surprisingly drives polymer collapse at low alcohol concentrations. This hitherto neglected role of interfacial solvation thermodynamics is common to all coil-globule transitions [2], and rationalizes the experimentally observed effects of higher alcohols and polymer molecular weight on the coil-to-globule transition of thermoresponsive polymers [2]. This mechanism is generic and applicable to other solutions containing amphiphilic cosolvents or cosolutes.

References: [1] S. Bharadwaj et al., Soft Matter, 2022, 18, 2884. [2] S. Bharadwaj et al., Commun. Chem., 2020, 3, 165.

CPP 9.9 Mon 17:15 H39

Water transport in soft nanoporous materials: Impact of mechanical response on dynamics, slippage and permeance — •Alexander Schlaich[1,2], Matthieu Vandamme[3], Marie Plazanet[2], and Benoit Coasne[2] — [1]Stuttgart Center for Simulation Science (SC SimTech), University of Stuttgart, Germany — [2]Univ. Grenoble Alpes, CNRS, LIPhy, 38000 Grenoble, France — [3]Navier, Ecole des Ponts, Univ. Gustave Eiffel, CNRS, Marne-la-Vallee, France

Transport of water in soft porous materials is relevant to applications such as ultrafiltration and reverse osmosis processes, where polymeric membranes are employed in filtration/separation, or energy related processes. While water transport in hard porous materials such as porous silica glasses is well studied, the situation in soft matter is much more puzzling and remains unclear due to the combination of surface heterogeneity, the diffuse boundary location and pore deformations due to mechanical stresses.

In this work we study water in chemically realistic hydrophobic pores at different thermodynamic and mechanical conditions using atomistic molecular dynamics simulations. In detail, we analyze pore swelling, adsorption and confinement effects as well as microscopic diffusion mechanisms and transport effects due to pore size fluctuations. Strikingly, we find that hydrodynamic continuum models remain valid for planar flow of water even in monolayer confinement in soft pores.

CPP 9.10 Mon 17:30 H39

Solvation structure of polymer cathodes for Li/S batteries — •Diptesh Gayen[1], Yannik Schuetze[2], Sebastien Groh[1], and Joachim Dzubiella[1] — [1]Institute of Physik, University of Freiburg, Freiburg, Germany — [2]Helmholtz Zentrum Berlin, Berlin

Lithium-sulfur (Li/S) batteries are regarded as one of the most promising next-generation energy storage devices. Meanwhile, some challenges inherent to Li/S batteries remain to be solved, for instance, the polysulfide shuttle effect and the volume expansion of the cathode during discharge. To suppress the above-mentioned drawbacks, polymeric cathodes, e.g., based on poly(4-(thiophen-3-yl) benzenethiol) (PTBT) are considered sulfur host material (S/PTBT). Here, we use molecular dynamics (MD) computer simulations to study the structure and dynamics of a single PTBT chain at 300 K in different concentrations and compositions of dimethoxyethane (DME) and dioxolane (DOL) solvents. The force-field parameters for this polymer were constructed based on the OPLS database, with missing parameters newly developed by us by benchmarking to density-functional theory calculations. We report results on polymer conformational behavior, solvent-specific adsorption, and thermodynamic properties such as the partial molar volume. Our results show that DOL is more absorbed at the PTBT compare to DME. We find no significant effect of the solvent on the structure factor of the polymer. Our simulation model enables future systematic studies of PTBT in various solvent mixtures, in particular electrolytes, for the optimizations of modern Li/S batteries.