

CPP 17: Theorie and Simulation - organized by Jens-Uwe Sommer (Leibniz-Institut für Polymerforschung Dresden, Dresden) (joint session CPP/DY)

Time: Wednesday 9:00–14:40

Location: CPPb

Invited Talk

CPP 17.1 Wed 9:00 CPPb

Data-driven methods in polymer physics: exploring the sequence space of copolymers — ●MARCO WERNER — Institut Theorie der Polymere, Leibniz-Institut für Polymerforschung Dresden, Germany

Automated experiments and computer simulation on highly parallel machines push the limits of available data in the field of soft matter. For long polymer chains, however, any data set can cover only a marginal fraction of the giant chemical space and conformation space involved. In this talk, data-driven strategies are discussed that allow to trace hidden physical patterns in both giant spaces by machine learning algorithms. The discussion is centered on the example of hydrophilic / hydrophobic copolymers and their interaction with lipid membranes. A neural network has been trained to predict the free energy landscape near a membrane as a function of the copolymer sequence. The information learned in the hidden neural layers showed that the neural network compressed the sequence space into physically meaningful latent variables. The learned semantics was transferable between simulation data with different levels of coarse-graining, and allowed for a physics-informed inverse search for the copolymer sequence leading to the smallest translocation time through the membrane.

CPP 17.2 Wed 9:40 CPPb

Prediction of iSCFT chemical potentials via machine learning — ●LUCIA MILENA WESENBERG, LUDWIG SCHNEIDER, and MARCUS MÜLLER — Institute for Theoretical Physics, Georg-August University Göttingen, Friedrich-Hund Platz 1, 37077 Göttingen

We explore the use of machine learning to enhance the simulation of polymeric nanostructures. Self-assembly of symmetric diblock copolymers is the chosen testing system for this purpose. Such polymers consist of two equally long blocks of different monomer types. As the two monomer types are incompatible but linked in the center of each polymer, microphase separation occurs.

Simulations of such systems often pose a challenge for particle-based models as large systems and concomitantly long time scales need to be simulated. Thus, continuum models are employed, where the dynamics can be conceived as the relaxation towards the local minimum of a free-energy basin and jumps between such basins. These models reduce the degrees of freedom by integrating out the molecular degrees of freedom. The most detailed continuum model investigated here is the Self-Consistent Field Theory (SCFT). Unfortunately, dynamic SCFT requires the chemical potential of a non-equilibrium morphology that is computationally expensive to obtain. The SCFT potential calculation is an iterative process, and the stability of the algorithm depends heavily on the starting conditions. Our machine learning approach provides suitable initial conditions for the algorithm. The predicted starting conditions reduce the computational effort considerably.

CPP 17.3 Wed 10:00 CPPb

Machine Learning Inter-Atomic Potentials Generation Driven by Active Learning: A Case Study for Amorphous and Liquid Hafnium dioxide — ●ANAND NARAYANAN KRISHNAMOORTHY^{1,2}, GANESH SIVARAMAN³, MATTHIAS BAUR¹, CHRISTIAN HOLM¹, CHRIS BENMORE⁶, MARIUS STAN⁴, GABOR CSANYI⁵, and ÁLVARO VÁZQUEZ-MAYAGOITIA⁷ — ¹Institute for Computational Physics, University of Stuttgart — ²Helmholtz Institute Muenster — ³Leadership Computing Facility, Argonne National Laboratory - USA — ⁴Applied Materials Division, Argonne National Laboratory, USA — ⁵Department of Engineering, University of Cambridge, UK — ⁶X-ray Science Division, Argonne National Laboratory, USA — ⁷Computational Science Division, Argonne National Laboratory, USA

We propose a novel active learning scheme for automatically sampling a minimum number of uncorrelated configurations for fitting the Gaussian Approximation Potential (GAP). We apply this scheme to a Hafnium dioxide (HfO₂) dataset generated from a melt-quench ab initio molecular dynamics (AIMD) protocol. Our results show that the active learning scheme, with no prior knowledge of the dataset is able to extract a configuration that reaches the required energy fit tolerance. Further, molecular dynamics (MD) simulations performed using this active learned GAP model on 6144-atom systems of amorphous and liquid state elucidate the structural properties of HfO₂ with near

ab initio precision and quench rates (ie 1.0 K/ps) not accessible via AIMD.

40 min. meet the speakers - break

CPP 17.4 Wed 11:00 CPPb

BoltzmaNN: Heuristic inverse design of pair potentials using neural networks — ●FABIAN BERRESSEM, MIHIR KHADILKAR, and ARASH NIKOUBASHMAN — Institute of Physics, Johannes Gutenberg University Mainz, Germany

In this work, we investigate the use of neural networks (NNs) to devise effective equations of state from a given isotropic pair potential using the virial expansion of the pressure. We train the NNs with data from molecular dynamics simulations, sampled in the NVT ensemble at densities covering both the gas- and liquid-like regime. We find that the NNs provide much more accurate results compared to the analytic estimate of the second virial coefficient derived in the low density limit. Further, we design and train NNs for computing the potential of mean force from the radial pair distribution function, $g(r)$, a procedure which is often performed for coarse-graining applications. Here, we find that a good choice for the loss function is crucial for an accurate prediction of the pair potentials. In both use cases, we study in detail how providing additional information about forces and the density impacts the performance of the NNs. We find that including this additional information greatly increases the quality of the predictions, since more correlations are taken into account. Further, the predicted potentials become smoother and are in general much closer to the target potential.

CPP 17.5 Wed 11:20 CPPb

PolyEC - an event-chain framework — ●TOBIAS A. KAMPMANN, DAVID MÜLLER, and JAN KIERFELD — TU Dortmund University, Germany

PolyEC is a MC event chain framework suitable for simulation of various colloidal systems. We focus on modularity and extensibility to simulate heterogeneous systems. In event-chain simulations only one particle is active and interactions can be treated independently by factorization, which allows for a highly modular approach for particle-based simulations. Albeit ECMC is a monte-carlo method, a single event-chain is deterministic (although there are modifications where this is not true). One crucial feature of this method is that each state a piece-wise deterministic event-chain visits between events are properly (Boltzmann-) weighted. This opens the possibility to measure observables like pressure or the distribution of energy on the fly. As examples we show needle-colloid mixtures and an active particle system.

Invited Talk

CPP 17.6 Wed 11:40 CPPb

Structure formation in drying films and droplets — ●ARASH NIKOUBASHMAN¹, MICHAEL HOWARD², MICHAEL KAPPL³, and HANS-JÜRGEN BUTT³ — ¹Johannes Gutenberg University Mainz, Mainz, Germany — ²Auburn University, Auburn (AL), USA — ³Max Planck Institute for Polymer Research, Mainz, Germany

Drying complex liquids are encountered in many technologies, including painting, manufacturing polymer LED displays, and spraying pesticides. Here, colloids and/or polymers are typically initially dispersed in a solvent such as water, which then evaporates, leaving behind a dried residue. Our recent simulations and experiments of drying bidisperse suspensions revealed that sufficiently fast evaporation could induce spatial segregation of the two species, with the smaller ones accumulating at the liquid-air interface followed by a homogeneously mixed region of small and big particles. To understand this counterintuitive behavior, we conducted particle-based simulations and dynamic density functional theory calculations, with and without hydrodynamic interactions. According to our model calculations, this drying-induced segregation occurs due to a local increase of the solute concentration near the film-air interface, resulting in a chemical potential gradient for both species; typically, this gradient is steeper for the larger particles, leading to a stronger force pushing them away from the liquid-air interface. Segregation then occurs if the mobility of the larger particles decreases slower than the driving force increases. Comparing the

various simulations and experiments, we found that including hydrodynamics can decrease or even completely suppress the segregation.

CPP 17.7 Wed 12:20 CPPb

Structure of bottlebrush polymers end-grafted to a planar surface — ●JAROSLAW PATUREJ¹, PAUL JUNGSMANN², JENS-UWE SOMMER³, and TORSTEN KREER² — ¹University of Silesia, Katowice, Poland — ²IPF, Dresden, Germany — ³Johannes Gutenberg Universität, Mainz, Germany

Polymer brush is a hybrid material composed of a solid substrate coated with end-grafted polymers. We conducted coarse-grained molecular dynamics simulations and scaling theory of the equilibrium structure of planar brushes formed by bottlebrush polymers. Bottlebrushes are branched macromolecules consisting of densely spaced linear side chains grafted along a central (linear) backbone. We elucidate the relationship between bottlebrush architecture, surface coverage σ and polymer brush thickness H . We study the impact of three length scales on the brush height H : D_0 , the cross-section radius of bottlebrushes determined by the degree of polymerization of side chains N_{sc} , R_0 the (overall) size of bottlebrushes controlled by the degree of polymerization of backbone N_{bb} and d the distance between nearest-neighbor tethering sites. The latter quantity provides a measure of molecular coverage σ of a substrate defined as the number of bottlebrush polymers per unit surface area $\sigma \propto 1/d^2$. Our theoretical analysis identifies three conformational regimes for the height H , which gradually establish upon increasing substrate coverage and stem from interplay between relevant length scales: d , D_0 and R_0 .

CPP 17.8 Wed 12:40 CPPb

Thermal conductivity of commodity plastics: From conventional to smart polymers — ●DEBASHISH MUKHERJI — Stewart Blusson Quantum Matter Institute, University of British Columbia, Vancouver Canada

Polymers are an important class of soft matter whose properties are dictated by large fluctuations. Because of this reason commodity polymers are ideal for the flexible design of advanced materials. However, applications of polymers are often hindered by their low thermal conductivity κ . While low κ values are desirable for thermoelectric materials, they create severe problems when used under the high temperature conditions. Going from the polymers dictated by weak Van der Waals to hydrogen-bonded interactions, κ varies between 0.1-0.4 W/Km. Using molecular dynamics simulations we study thermal transport and its links to the elastic response of polymers. We find that there exists a maximum attainable stiffness, thus limiting an upper bound of κ . The specific chemical details and the glass transition temperature play no role in controlling κ , especially when the microscopic interaction is hydrogen bonded. These results are consistent with the minimum thermal conductivity model and experiments.

[1] D. Mukherji, C. M. Marques, K. Kremer, Annual Review of Condensed Matter Physics 11, 271 (2020). [2] D. Bruns, T. E. de Oliveira, J. Rottler, D. Mukherji, Macromolecules 52, 5510 (2019). [3] C. Ruscher, J. Rottler, C. Boott, M. J. MacLachlan, D. Mukherji, Physical Review Materials (accepted) (2019).

60 min. meet the speakers - break

CPP 17.9 Wed 14:00 CPPb

Polymer Architectures by Chain Walking Catalysis - Theory, Simulations, and Experiments — ●RON DOCKHORN¹, LAURA PLÜSCHKE^{1,2}, ALBENA LEDERER^{1,2}, JAN MERNA³, and JENS-UWE SOMMER^{1,2} — ¹Leibniz-Institut für Polymerforschung Dresden e.V., D-01069 Dresden, Germany — ²Technische Universität Dresden, Institute for Theoretical Physics, D-01069 Dresden, Germany — ³University of Chemistry and Technology Prague, CZ-16628 Praha, Czech Republic

Recently developed chain walking catalysis is an elegant approach to synthesize branched polyethylenes (CWPE) with controllable structure and properties. The catalyst is able to walk along the polymer and to polymerize ethylene and α -olefines into complex topologies depending on pressure, temperature, and olefine concentration introducing branch-on-branch structures. Coarse-grained Monte Carlo simulations utilizing the bond fluctuation model of the CWPE are performed to investigate the influence of the walking mechanism on the polymer architecture. For slow walking rates the structure grows with linear chain extensions, whereas fast walking rates promote dendritic growth of the polymer. The crossover regime is characterized by linear global features and dendritic local substructures contrary to randomly hyperbranched systems. Indeed, the obtained CWPE systems have characteristics of dendritic bottle brushes and the degree of branching can be adjusted by the walking rate of the catalyst. These findings are aimed to understand the physical properties of the CWPE structures and to improve the synthesis of a new class of hyperbranched molecules.

CPP 17.10 Wed 14:20 CPPb

Mechanics of shape-shifting droplets — ●IRETH GARCIA-AGUILAR¹, PIERMARCO FONDA¹, ELI SLOUTSKIN², and LUCA GIOMI¹ — ¹Instituut-Lorentz, Universiteit Leiden, The Netherlands — ²Department of Physics and Institute of Nanotechnology & Advanced Materials, Bar-Ilan University, Ramat-Gan, Israel

It has been long understood that dispersed liquid droplets are spherical in order to minimize the tension at their interface. Surprisingly, oil emulsion droplets in water have been observed to spontaneously deform into polyhedral shapes when cooling down the system. The equilibrium shape of a droplet at some temperature depends on its initial volume but all deformations take place below the freezing point of the surfactant monolayer, while the bulk oil and water remain liquid. The frozen interface forms a hexagonal lattice which is topologically constrained to accommodate defects. These produce large stresses that induce in and out-of-plane deformations in the crystal which in turn are opposed by the interfacial tension between oil and water. Initially, it was thought that this competition determines the droplet shape; however, this alone can not explain the size dependence of the deformations. By modeling the interface as a 2D elastic surface and studying its equilibrium geometry, we found a mechanism that explains the size-scaling behaviour. Interestingly, crystalline defects are not the only peculiarity playing a role in shaping the droplets.