

DY 35: Modelling and Simulation of Soft Matter I (joint session CPP/DY)

Time: Wednesday 9:30–13:00

Location: ZEU 255

Invited Talk

DY 35.1 Wed 9:30 ZEU 255

Structure and dynamics of semiflexible polymers in bulk and confinement — ●ARASH NIKOUBASHMAN — Institut für Physik, Johannes Gutenberg Universität Mainz, Mainz, Deutschland

Semiflexible macromolecules are important constituents of living matter and also find various applications as versatile materials, in particular due to their possible liquid crystalline order. To better understand these systems, we employed coarse-grained molecular dynamics simulations to study lyotropic solutions of semiflexible polymers in the bulk as well as in confinement over a wide range of monomer densities, persistence lengths, and contour lengths. In bulk systems, we observed an isotropic-nematic transition and a nematic-smectic transition as the persistence length and monomer density were increased. Further, we found that semiflexible polymers exhibited a much lower diffusivity and higher shear viscosity compared to their flexible counterparts. Under spherical confinement, we discovered that densely packed semiflexible polymers could not anymore exhibit uniform nematic order when their contour length became of the same order as the sphere radius. Instead, confinement led to the emergence of topological defects on the sphere surface with competing ordering in the interior of the sphere. Each of the configuration variables including chain length, chain stiffness, packing density, and shell thickness uniquely affected the ordering, including the nature and relative orientation of the defects on the surface.

DY 35.2 Wed 10:00 ZEU 255

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).

DY 35.3 Wed 10:15 ZEU 255

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 growths 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 charac-

teristics 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.

DY 35.4 Wed 10:30 ZEU 255

Morphology on Reaction Mechanism Dependency for Twin Polymerization — ●JANETT PREHL¹, ROBIN MASSER¹, PETER SALAMON², and KARL HEINZ HOFFMANN¹ — ¹Institut für Physik, Technische Universität Chemnitz, Chemnitz, Germany — ²Department of Mathematics and Statistics, San Diego State University, San Diego, USA

Within this presentation we will present our latest results [1] on the 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 the 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 can identify key factors to adapt structural properties to fulfill desired requirements for possible applications. Hereby, we point out which implications these parameter changes have on the underlying chemical structure.

[1] 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

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

DY 35.5 Wed 10:45 ZEU 255

Effect of the Backbone Chemical Composition and Monomer Sequence on Phenylene Polymer Persistence Lengths — ●NANCY C. FORERO-MARTINEZ¹, BJÖRN BAUMEIER², and KURT KREMER¹ — ¹Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany — ²University of Technology, P.O. BOX 513-5600 MB, Eindhoven, The Netherlands

The study of the physical properties of phenylene polymer precursors used in the fabrication of graphene nanoribbons poses open questions whose answers will contribute to the design of more efficient synthesis protocols. Particularly, size-exclusion chromatography combined with persistence length measurements assigns both, semiflexible to semirigid structures depending on the molecular weight of the precursor. Surprisingly, these results suggest an apparent structural change upon increasing the length of the polymer. In this work, we use a generic model to build phenylene polymer chains as random walks that take into consideration the nature of the arene substitutions along the backbone. In addition to conformational changes, this model allows one to study the backbone contribution to the persistence length by modifying a small set of parameters controlling chemical content and structure. We consider the flexibility of polyphenylene precursors in a theta-like solvent in terms of chain composition by building both, chains that are purely composed by meta or para connected repeat units, and randomly mixed chains with a given composition. We find that systems with apparently the same chemistry have different persistence length due to different monomer mixing ratios and sequence along the chain.

DY 35.6 Wed 11:00 ZEU 255

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 .

15 min. break

DY 35.7 Wed 11:30 ZEU 255

Modeling Depletion Interactions in Blends of Branched and Linear Polymers — ●MARTIN WENGENMAYR^{1,2}, RON DOCKHORN¹, and JENS-UWE SOMMER^{1,2} — ¹Leibniz Institute of Polymer Research, Dresden, Germany — ²TU Dresden, Germany

Effective attractive interactions in colloidal systems are well understood and described by depletion potentials. Similar effective attractions have been found for a wide range of soft matter systems like brush coated particles and dendrimers as well. For colloidal particles the depletion potentials are deduced from volume exclusion layers around the hard particles, but this is not applicable for soft particles, which are interpenetrated by the depletant. In this work we present a mean field free energy approach modeling the origin of the soft matter depletion interactions by balancing the excess free energy between the soft particle and the depletant with the elastic repulsion between particles. This approach is adopted for a model system containing dendrimers as soft particles in the melt of linear polymer chains acting as depletant. From recent investigations [1] it is known that the dendrimers display so called crowded conformations that are compact but not fully collapsed and the dendrimers are strongly interpenetrated by linear chains. The mean field model is compared with coarse grained computer simulations applying the bond fluctuation model. This work contributes to the understanding of soft matter interactions and provides predictions for the occurrence of depletion interactions in experimental setups.

[1] Wengenmayr, Dockhorn, Sommer; *Macromolecules* **2019**, 52, 2616-2626

DY 35.8 Wed 11:45 ZEU 255

Role of preferential adsorption in cononsolvency — ●SWAMINATH BHARADWAJ and NICO VAN DER VEGT — Technische Universität Darmstadt, Germany

Cononsolvency is the phenomenon in which a polymer chain collapses in a mixture of good solvents. The solvation forces and interactions that drive this phenomenon however remain poorly understood. An important question which arises is whether the cononsolvency mechanism is generic. In this regard, studies have proposed simple and universal mechanisms depending on preferential cosolvent adsorption [1] and solvent-cosolvent clustering [2].

We demonstrate through computer simulations that cononsolvency is not a generic phenomenon driven by a universal interaction. We show that cononsolvency can occur with and without the preferential adsorption of the cosolvent and discuss the related experimental results [3]. We also discuss preliminary results on the role of attractive polymer-solvent/cosolvent interactions in cononsolvency. Our results highlight the need to understand the role of microscopic interactions in polymer solubility. The aforementioned generic models [1,2], though not universal, can still be employed on a case-by-case basis depending on the dominant underlying interactions.

[1]Mukherji, D., Marques, C. M. & Kremer, K. *Nat. Commun.* **5**, 4882 (2014).

[2]Zhang, G. & Wu, C. *J. Am. Chem. Soc.* **123**, 1376 (2001)

[3]Bharadwaj, S. & van der Vegt, N. F. A. *Macromolecules* **52**, 4131 (2019)

DY 35.9 Wed 12:00 ZEU 255

Mesoscopic modeling of disordered morphologies of blends and block-copolymers for light-emitting diodes — ●JIANRUI ZHANG, KURT KREMER, JASPER MICHELS, and KOSTAS DAOULAS — Max Planck Institute for Polymer Research, Mainz, Germany

Experiments have demonstrated [1] that the luminous efficiency of polymer light emitting diodes can be significantly increased by blending the semiconducting polymer with an insulator. However, the limited thermodynamic stability of the disordered phase in polymer blends motivates the consideration of alternatives, e.g. block-copolymers (BCPs) comprising semiconducting and insulating blocks. We choose as model systems blends and BCPs of poly(p-phenylene vinylene)

(PPV) and polyacrylates. Using a hybrid mesoscopic model, disordered morphologies of these blends and BCPs are obtained with Monte Carlo simulations. We study different compositions and vary the immiscibility to mimic annealing at different temperatures. We find that disordered blends and BCPs are heterogeneous because of fluctuations and local segregation. Local segregation is stronger in BCPs than in their equivalent blends, even though the strength of immiscibility, normalized by the mean-field spinodal, is the same. Using a qualitative charge-percolation model, we link the spatial distribution of PPV with electric conductance. We predict that the annealing temperature affects the electrical percolation in disordered BCPs much stronger than in blends. The observed differences between blends and BCPs are enhanced at high contents of insulator. [1] Abbaszadeh et al., *Nature Materials* **2016**, 15, 628.

DY 35.10 Wed 12:15 ZEU 255

Chemically-transferable structure-based coarse-grained models — ●KIRAN H. KANEKAL and TRISTAN BEREAU — Max Planck Institute for Polymer Physics, Mainz, Germany

An attractive feature of the popular Martini [1] coarse-grained force field is its chemical transferability. Multiple chemical fragments can be assigned to the same Martini representation based on their similar hydrophobicity, maintaining thermodynamic accuracy in the resulting simulations [2]. However, since the Martini force field was optimized in order to reproduce certain thermodynamic properties of various condensed phase systems in a top-down fashion, it does not accurately portray the internal structures of these systems when compared to results from corresponding simulations at atomistic resolutions. On the other hand, implementing bottom-up coarse-graining approaches results in highly accurate structural properties by construction, yet these methods are traditionally performed on a small set of compounds, limiting their chemical transferability. In this work, we establish a new technique for building chemically-transferable coarse-grained models with high structural accuracy by coupling bottom-up coarse-graining methods with unsupervised machine learning. We validate our results by comparing our new model to Martini and show how changing the resolution of our coarse-grained model affects these results. 1. Marrink, S. J. & Tieleman, D. P. *Chem. Soc. Rev.* **42**, (2013). 2. Menichetti, R., Kanekal, K. H. & Berau, T. *ACS Cent. Sci.* **5**, (2019).

DY 35.11 Wed 12:30 ZEU 255

Consistent representation of structural and dynamical properties from coarse-grained simulation models — ●JOSEPH RUDZINSKI — Max Planck Institute for Polymer Research, Mainz, Germany

“Bottom-up” coarse-grained models retain chemical specificity by targeting the reproduction of properties from a higher-resolution reference model. These models are inherently limited by the molecular representation, set of interaction potentials, and parametrization method. These limitations often result in an inaccurate description of cross-correlations between coarse-grained degrees of freedom, complicating the stabilization of hierarchical structures in soft matter systems. Perhaps more troubling, reduced molecular friction and softer interaction potentials obscure the connection to the true dynamical properties of the system. In this talk, I will discuss the relationship between these two problems and introduce methodologies for characterizing and improving the dynamical properties generated by coarse-grained simulation models.

DY 35.12 Wed 12:45 ZEU 255

Coarse graining of Bovine serum albumin (BSA) — ●FRANK HIRSCHMANN¹, HENDER LÓPEZ², and MARTIN OETTEL¹ — ¹University of Tübingen — ²Dublin Institute of Technology

The intercellular medium of living cells typically contains biomolecules (such as proteins) at high packing fractions, which directly affects diffusive and transport properties of the suspended components. Additionally, molecular shape plays a key role for interactions in crowded environments.

To treat these systems computationally, we present a coarse grained model of the globular antibody BSA, which neglects full atomistic details, but enables access to larger system sizes of hundreds to thousands of molecules. Using Brownian dynamics, we present static and dynamic properties of different implementations of our model. A particular emphasis is on the influence of molecule flexibility on diffusion coefficients. A comparison is made with an already existing coarse grained model of γ -Globulin (IgG), which is a significantly more flexible molecule.