CPP 49: Polymer Dynamics I

Time: Thursday 17:00–18:15 Location: ZEU 260

CPP 49.1 Thu 17:00 ZEU 260

Modeling high-molecular weight polymer melts: equilibration and rheological properties — •Livia Moreira, Guojie Zhang, Torsten Stuehn, Kostas Daoulas, and Kurt Kremer — Max Planck Institute for Polymer Research, Mainz

A modeling strategy is developed for studying rheological properties of high-molecular weight polymer melts described with microscopic detail. The microscopic model is generic but retains hard excluded volume interactions and realistic densities. Equilibrated configurations are generated by a backmapping strategy using a coarse-grained (CG) model representing polymer chains as strings of fluctuating blobs [1,2]. Each stands for one subchain of N_b microscopic beads. Varying N_b, a hierarchy of CG models with different resolutions is obtained. Within this hierarchy, CG configurations equilibrated at low-resolution are sequentially fine-grained into melts of higher resolution. Microscopic details are then introduced modifying the scheme of *Auhl et al* [3]. Backmapping involves only local polymer relaxation, thus the method is independent of chain length. This strategy is implemented to equilibrate melts with different persistence lengths and polymerization degrees up to 55 entanglement lengths, N_e. The N_e is quantified using primitive path analysis and effects of finite system-size and chain length are discussed. A master curve for the estimating N_e for different chain lengths and persistence lengths is provided. We comment on alternative estimations of N_e, e.g., from plateau modulus analysis. [1] Vettorel et al, Soft Matter (2010) 6, 2282 [2] Zhang et al, Macromol. Chem. Phys. (2013) 214, 214 [3] Auhl et al, J. Chem. Phys. (2003) 119, 12718

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Viscoelastic hydrodynamic interactions and anomalous CM diffusion in polymer melts — •Hendrik Meyer, A.N. Semenov, and Jean Farago — Institut Charles Sadron, Université de Strasbourg, CNRS UPR22, France

We have recently discovered that anomalous center-of-mass (CM) diffusion occurring on intermediate time scales in polymer melts can be explained by the interplay of viscoelastic and hydrodynamic interactions (VHI). The theory has been solved for unentangled melts in 3D [1] and 2D [2] and excellent agreement between theory and simulation is found. The physical mechanism considers that hydrodynamic interactions are time dependent because of increasing viscosity before the terminal relaxation time. We show that this mechanism is generally active and relevant in melts including entangled systems, rings or stars.

[1] PRL 107, 178301 (2011); PRE 85, 051807 (2012). [2] PRL 109, 248304 (2012); Soft Matter 9, 4249 (2013).

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Local Langevin Dynamics in Polymeric Materials — •Diddo Diddens[1] and Andreas Heuer[2] — [1]Institut Charles Sadron, Université de Strasbourg, 23 Rue du Loess, 67034 Strasbourg, France — [2]Institut für physikalische Chemie, Universität Münster, Corrensstraße 28/30, 48149 Münster, Germany

We present an in-depth analysis of the local segmental dynamics in various polymeric materials on the basis of MD simulation data. To this purpose, we employ a Langevin-like, stroboscopic picture of the local chain motion, comprising a systematic, a random and a frictional compound. This concept allows us to extract information about all these individual contributions, thus providing additional insights as compared to conventional observables such as the mean squared displacement. Moreover, due to the entirely local, mode-free approach, this scheme is especially suitable for non-linear polymer architectures or polymers in heterogeneous environments. As a starting point, we compare model systems with different levels of complexity, and assess the influence of the individual parameters. Based on these insights, we turn to simulation data of realistic polymers, and discuss the benefits of our method for a few selected issues in polymer science.

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Modeling Twin Polymerization processes by ReaxFF — •Thomas Schönfelder[1], Joachim Friedrich[2], Steffen Seeger[1], Janett Prehl[1], and Karl Heinz Hoffmann[1] — [1]Department of Physics, Computational Physics, TU Chemnitz — [2]Department of Chemistry, Theoretical Chemistry, TU Chemnitz

Twin polymerization is a new synthesis concept which enables the formation of two different macromolecular structures from organic-inorganic hybrid materials in one single process step [1]. It is characterized by two main process types - electrophilic substitutions contributing to the organic network formation and condensation reactions building the inorganic structure for the reviewed monomer 2,2*-spirobi[4H-1,3,2-benzodioxasiline]. To understand the formation process we develop a first-principles-based ReaxFF reactive force field for C/O/H/Si(S,F,Ti,...).

In this work we focus on the required parameters to model the twin-monomer structure and the electrophilic substitution leading to implications on the force field. After extending the ReaxFF model accordingly we are able to present the first steps of the twin polymerization process by molecular dynamics simulations.

[1]: Nanocomposites Prepared by Twin Polymerization of a Single-Source Monomer. S. Grund, P. Kempe, G. Baumann, A. Seifert, S. Spange, Angew. Chem. Int. Ed. 2007, 46, 628-632. DOI: 10.1002/anie.200504327

CPP 49.5 Thu 18:00 ZEU 260

Combined methods in Rheology: Rheo-SAXS, Rheo-NMR and Rheo-Dielectric to bridge length and time scales — Thomas Meins[1], Kyu Hyun[1,2], Karl Ratzsch[1,3], Christian Friedrich[3], Bernd Struth[4], and •Manfred Wilhelm[1] — [1]KIT, Karlsruhe, Germany — [2]Pusan University, Korea — [3]Universität Freiburg, Germany — [4]Desy, Hamburg, Germany

Rheology as the science of flow and deformation of matter measures in general forces (torque and normal forces) and displacement of materials. Rheology wants to establishment the interplay of molecular structure and mechanical properties. Both quantities often differ in their internal length scale starting from 10-9 m to 10-2 m and time scales covering 10-8 s to 10+2 s. Furthermore mechanical deformation e.g. shear can lead to oriented structures or crystallization if non-linear shear is applied. Consequently there is a need to conduct in-situ molecular characterization techniques during rheological measurements if non-linear shear, e.g. large amplitude oscillatory shear in combination with FT-Rheology is applied.

Within this presentation we would like to present three recent developments within our group to investigate short length scale dynamic measurements (< 1-2 nm) via Rheo-NMR, molecular size (Rg) measurements (ca. 10 * 50 nm) via Rheo-dielectric and structural correlations via Rheo-SAXS measurements. The experimental realization and first experiments will be presented in detail.