

CPP 63: Polymer and Molecular Dynamics II

Time: Thursday 9:30–13:00

Location: C 264

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Local dynamics in polyelectrolyte multilayers and complexes — ●ULRICH SCHELER — Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Str 6, 01069 Dresden, Germany

Relaxation NMR can measure molecular mobility over a wide range of correlation times. The longitudinal relaxation time in the rotating frame ($T_{1\rho}$) is ideally suited for molecular chain motion in the range kiloHertz. If is detected in solid-state NMR with chemical shift resolution, the mobility can be attributed to individual functional groups and thus the mobility of polycation and polyanion in the multilayers or complexes are separated. Thus dynamic heterogeneity between PDADMAC and PSS in multilayers formed from high-salt solutions has been observed. This is compared to the local mobility in polyelectrolyte complexes formed from the same solutions and those formed from salt-free solutions, exhibiting more homogeneous mobility.

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Enhancing the Lithium Ion Transport in Polymer Electrolytes – Plasticization and Shuttling — ●DIDDO DIDDENS¹ and ANDREAS HEUER^{1,2} — ¹Helmholtz-Institut Münster, Ionics in Energy Storage (IEK-12), Forschungszentrum Jülich GmbH, Corrensstraße 46, 48149 Münster, Germany — ²Institut für physikalische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstraße 28/30, 48149 Münster, Germany

Solid polymer electrolytes consist of a salt dissolved in an amorphous polymer matrix, resulting in mechanically stable and flexible ion conductors. However, at ambient temperatures, their conductivity is still too low for an efficient use in modern energy storages. To overcome this deficiency, the addition of a low-molecular additive such as an ionic liquid (IL) has been proposed. We demonstrate by molecular dynamics simulations that the way in which the IL enhances the lithium mobility can in principle be twofold: First, the IL can act as a plasticizer, enhancing the dynamics of the polymer segments and thus also the motion of the attached lithium ions [1,2], and second, for IL molecules that directly coordinate to the lithium ions, the IL may serve as a *shuttle* detaching the lithium ions from the slow polymer chains [3], resulting in a much larger enhancement. In this contribution, we screen a large range of electrolyte compositions to identify molar ratios facilitating fast ion transport to serve as a guideline for electrolyte optimization.

- [1] D. Diddens, A. Heuer, *ACS Macro Lett.*, **2013**, 2(4), 322-326
 [2] D. Diddens, A. Heuer, *J. Phys. Chem. B*, **2014**, 118(4), 1113-1125
 [3] D. Diddens *et al.*, *J. Electrochem. Soc.*, **2017**, 164(11), E3225

CPP 63.3 Thu 10:00 C 264

Probing intramolecular energy transfer rates on the single molecule level — ●JAKOB SCHEDLBAUER¹, PHILIPP WILHELM¹, FLORIAN HINDERER², SIGURD HÖGER², JAN VOGELSANG¹, and JOHN M. LUPTON¹ — ¹Universität Regensburg, Universitätsstr. 31, 93053 Regensburg, Germany — ²Universität Bonn, Gerhard-Domagk-Str. 1, 53121 Bonn, Germany

Efficient excitation energy transfer (EET) is a key process in organic photovoltaic devices as well as in natural light harvesting complexes. Single molecule spectroscopy (SMS) has proved itself to be a powerful technique to probe the interactions between single isolated units or to visualize intramolecular energy migration. However, these EET processes take place on a timescale of a few picoseconds or even faster, which exceeds the temporal resolution of conventional SMS techniques. Here we present a new experimental approach to determine EET rates in a donor-acceptor-system on a single molecule level by influencing the photon statistic in a pump-pump like experiment. We excite the donor repetitively with a laser pulse train consisting of two pulses identical in terms of wavelength, polarization and power, separated by a variable time delay. After an excitation in the first pulse the donor moiety can only absorb a photon in the second pulse if it has decayed into the ground state by transferring its excitation energy to the acceptor. Using the technique of time correlated single photon counting (TCSPC) we can measure the probability for such a double excitation of our donor-acceptor system as a function of the time delay between the two pulses and therefore get access to the EET time constant.

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Hyperbranched PAMAM/ Kaolinite Nanocomposites: De-

coupling phenomenon and conductivity mechanism — ●SHEREEN OMARA^{1,2}, GAMAL TURKY², MONA H ABDEL REHIM², and ANDREAS SCHÖNHALS¹ — ¹Bundesanstalt für Materialforschung und- prüfung (BAM), Unter den Eichen 87, 12205 Berlin, Germany — ²National Research Centre (NRC), 33 El Behouth St., Dokki, Giza, P.O.12622, Egypt

Increasing demands of the daily life requires a continuous discovering of new and tailored properties of materials that can be utilized in covering the requirements in several fields. Hyperbranched polymers (HBPs) are macromolecules that are characterized by a highly branched structure and multiplicity of reactive end groups, which could be promising for numerous applications. Here, hyperbranched poly(amidoamine) (HPAMAM)/ Ka nanocomposites was prepared via an in-situ polymerization and an ex-situ method. The latter approach leads to a partly intercalated structure of the nanocomposites, while the former method results in an exfoliated morphology. A combination of different techniques such as broadband dielectric spectroscopy (DBS), SXAS, FTIR, TEM, and DSC are employed to study the prepared samples. For the HPAMAM/ Ka-DCA nanocomposites (an ex-situ samples), the results indicated that the dc conductivity is increased by 4 orders of magnitude, with increasing concentration of the Ka-DCA. As an interesting result is that a significant decoupling between the characteristic time for conductivity relaxation and the segmental dynamics was observed, which depends on the concentration of the nanofiller.

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Self-assembly of semiflexible polymers confined in thin spherical shells — ●MIHIR KHADILKAR and ARASH NIKOUBASHMAN — Institute of Physics, Johannes Gutenberg University Mainz, Staudingerweg 7, 55128 Mainz, Germany

Confinement effects are critical for stiff macromolecules in biological cells, vesicles, and other confined systems. Here, the competition between the packing entropy and the enthalpic cost of bending is further shaped by strong confinement effects. Through coarse-grained molecular dynamics simulations of a semiflexible bead-spring model we discovered a rich phase behavior, including nematic ordering with an accumulation of chain ends in the equatorial plane as well as the emergence of bipolar and quadrupolar topological defects on the surface [1, 2]. To better understand the complex interplay between confinement and nematization, we investigate the self-assembly of semiflexible polymers confined in thin spherical shells as a function of chain length, packing density, chain stiffness, and shell thickness. We explore the range of ordered structures exhibited as the system changes from a monolayer to multiple layers, approaching bulk behavior. Relevant order parameters elucidate the nature of orientational ordering in different parameter regimes.

- [1] Nikoubashman et al. *Phys. Rev. Lett.* 118, 217803 (2017)
 [2] Milchev et al. *J. Chem. Phys.* 146, 194907 (2017)

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Hierarchical excluded volume screening in solutions of bottlebrush polymers — ●JAROSLAW PATUREJ^{1,2} and TORSTEN KREER¹ — ¹Leibniz Institute of Polymer Research Dresden, Germany — ²University of Szczecin, Poland

Polymer bottlebrushes provide intriguing features being relevant both in nature and in synthetic systems. While their presence in the articular cartilage optimizes synovial joint lubrication, bottlebrushes offer pathways for fascinating applications, such as within super-soft elastomers or for drug delivery. However, the current theoretical understanding lacks completeness, primarily due to the complicated interplay of many length scales. During the talk analytical model will be presented demonstrating how structural properties of bottlebrushes depend on the concentration, ranging from dilute solutions to highly concentrated melts. The validity of our model is supported by data from extensive molecular dynamics simulations. We demonstrate that the hierarchical structure of bottlebrushes dictates a sequence of conformational changes as the solution concentration increases. The effect is mediated by screening of excluded volume interactions at subsequent structural parts of the bottlebrushes. Our findings provide important insights that should enable improved customization of novel materials based on the architectural design of polymer bottlebrushes.

15 min. break

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Conformational relaxation of chains in highly entangled polymer melts after a large step deformation — ●HSIAO-PING HSU and KURT KREMER — Max Planck Institute for Polymer Research

Anisotropic stress relaxation of strongly deformed polymer melts in a non-linear viscoelastic regime and the resulting anisotropic structures of chains after isochoric elongation are studied. Both the classical Doi-Edwards tube theory and refined GLaMM tube theory incorporating contour length fluctuation, and convective constraint release predict that the process of retraction in entangled linear chains sets in immediately after the deformation, while there exist contradictions between experiment and theory. Our results of radius of gyration in the direction perpendicular to the stretching direction indicate chain retraction in the initial relaxation process. Applying the harmonic spherical expansion approach to the 2D scattering function along the parallel and perpendicular to the stretching direction, the profiles of the first anisotropic term of scattering function also qualitatively agree with the theoretical prediction by GLaMM around Rouse time. The influence of finite-size effects is also investigated. Finally, applying the primitive path analysis to the deformed polymer melts, we also observe that there exists significantly delayed equilibration processes while deformed polymer melts are relaxing.

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Dissipation Controls the Relaxation Pathways of Collapse of a Polymer — ●SUMAN MAJUMDER, HENRIK CHRISTIANSEN, and WOLFHARD JANKE — Institut für Theoretische Physik, Universität Leipzig, Postfach 100 920, 04009 Leipzig, Germany

Variations in the nature of interactions with a solvent trigger various conformational transitions associated with macromolecules, e.g., the collapse of a polymer. Having this fact in hindsight, here, we investigate the kinetics of collapse of a model homopolymer in explicit solvent via a modified dissipative particle dynamics that allows qualitative tuning of the particle-velocity dissipation or in other words the solvent viscosity. As a generic phenomenon, the collapse follows a pathway characterized by the "pearl-necklace" picture (local clusters of monomers connected by strings of monomers) before eventually collapsing to a globule. However, as the viscosity increases, the time span of the "pearl-necklace" picture shortens and the dynamics appear to be dominated by de Gennes' "sausage-like" structures, which only in the long run approaches a compact spherical globule. We provide a novel way of separation of the time scales involving the "pearl-necklace" stage and the relaxation of the "sausage-like" structures based on cluster identification and shape factor analyses, respectively.

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Relaxation of Disentangled and Collapsed Polymer chains in a melt — ●MAJESH KUMAR SINGH, HSIAO-PING HSU, and KURT KREMER — Max Planck Institute for Polymer Research, Ackermannweg 10, 55128, Mainz, Germany

Entanglements dominate the rheological behavior of high molecular weight polymeric melts. Experimental studies [1] show that slow and careful melting of disentangled polymer crystals lead to formation of metastable melt exhibiting lower viscosity. With an objective of studying the non-linear rheological behavior of fully disentangled globules in a melt under elongation, we follow the similar strategies developed in Ref. [2], and perform standard bead-spring model based molecular dynamics simulations to our polymer melt systems. The system is prepared by first forming independent single globules of polymer chains. We observe that for short chains ($N \leq 200$) our melt systems of disentangled globules reach their entangled and fully equilibrated state at $t \approx \tau_{R,N}$ ($\tau_{R,N}$: the Rouse time for chains of size N) while for $N = 1000$, the system has not reached its equilibrated state even at $t \approx 10\tau_R$. Through the primitive path analysis [3], we show the development of entanglements during the relaxation process from disentangled globules to entangled states. [1] Rastogi, et al. *Nat. Mater.* 4, 635 (2005). [2] Vettorel, Kremer, *Macromol Theory Simul.* 19, 44 (2010). [3] Everaers, et al. *Science* 303, 823 (2004).

CPP 63.10 Thu 12:00 C 264

Transitions between diblock copolymer lamellar orientations in shear flow — ●LUDWIG SCHNEIDER and MARCUS MÜLLER — University of Göttingen, Institute of Theoretical Physics, Göttingen, Germany

Shear alignment of microphase-separated materials is a well known strategy to manipulate self-assembled samples towards macroscopic anisotropy. However, details about the exact mechanism of the reorientation towards equilibrium states, previously trapped in meta-stable states, remain an open research question.

A constant shear flow is applied to a melt of symmetric diblock copolymers. The subsequent transition between the unstable (parallel) and the stable (perpendicular) lamellar configuration is investigated. The hypothesis for the transition of an unstable lamellar grain in a stable matrix is either i) the rotation of the grain in the matrix, ii) a growth and shrink process extinguishing the unstable grain, or iii) a melting of the unstable grain with a subsequent reorientation of the stable orientation.

Using Molecular Dynamics simulation, we observe two different mechanisms as a function of shear rate: At high shear rate, none of the hypotheses apply. Instead, we observe a fast transition where the unstable grain loses its orientation order and disintegrates into a microemulsion-like state with a characteristic length scale. We believe that this scenario is realized in LAOS experiments. At low shear rate, the slow transition proceeds via the shrinking mechanism iii).

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Towards understanding three-body contributions to coarse-grained force fields — ●CHRISTOPH SCHERER and DENIS ANDRIENKO — MPIP, Mainz, Germany

CG is a systematic reduction of the number of degrees of freedom (DOF) used to describe a system of interest. CG can be thought of as a projection on the CG DOF and is therefore dependent on the number and type of CG basis functions. We present an extension of the two-body basis set with three-body basis functions of the Stillinger-Weber type with a flexible angular potential. The CG scheme is implemented in the VOTCA-CSG toolkit [1]. We show that naive extensions of the CG force-field can result in substantial changes of the two-body interactions making them much more attractive. This is related to the three-body basis functions having a significant two-body component which we examine in detail by decomposing the two-body potential of mean force (PMF). This interference can be alleviated by CG the two- and three-body forces separately which also helps to evaluate the importance of many-body interactions for a given system. The approach is illustrated on liquid water where three-body interactions are essential to reproduce the structural properties [2,3], and liquid methanol where two-body interactions are sufficient to reproduce the main features of the atomistic system. Our findings motivate to systematically extend the CG basis set in a way to clearly separate the many-body contributions of different order. [1] Rühle, Junghans, Lukyanov, Kremer, Andrienko, *JCTC*, 5, 3211 (2009); [2] Molinero, Moore, JPCB, 113, 4008 (2009); [3] Larini, Lu, Voth, *JCP*, 132, 164107 (2010)

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Molecular Dynamics Simulation of Twin Polymerization via SDAT-ReaxFF — ●JANETT PREHL¹, THOMAS SCHÖNFELDER¹, and JOACHIM FRIEDRICH² — ¹Institut für Physik, Technische Universität Chemnitz, Chemnitz, Germany — ²Institut für Chemie, Technische Universität Chemnitz, Chemnitz, Germany

Twin polymerization enables the formation of two different macromolecular structures from organic-inorganic hybrid materials in one single process step. To investigate in structure formation process on the atomic scale we utilize reactive molecular dynamics simulation via the SDAT-ReaxFF force field [1-3]. This recently developed extension of the ReaxFF force field is capable to cope with the complexity of the reaction mechanism of twin polymerization. The new feature of SDAT-ReaxFF is to define several atom types per chemical element instead of only one, as it is in the original ReaxFF.

In this presentation we introduce the SDAT-ReaxFF in the context of Twin Polymerization. We will show that we are able to model all partial reaction steps and the subsequent polymerization with this approach.

[1] T.Schönfelder et al., *Chem Phys* 440 (2014) 119–126[2] J.Prehl et al., *J Chem Phys C* 121 (2017) 15984–15992[3] K.H.Hoffmann, J.Prehl *Reac Kinet Mech Cat* DOI: 10.1007/s11444-017-1303-y

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Cononsolvency of PNIPAM in Aqueous Methanol Solutions — ●CAHIT DALGICDIR¹, FRANCISCO RODRÍGUEZ-ROPERO², and NICO F. A. VAN DER VEGT¹ — ¹Technische Universität Darmstadt, Darmstadt, Germany — ²Illinois Institute of Technology, Chicago, United

States of America

A polymer might dissolve in the pure forms of two different solvents but may precipitate in mixtures of these solvents. This interesting phenomenon is called cononsolvency and poly(N-isopropylacrylamide) (PNIPAM) in aqueous methanol solutions is an example of it. Although cononsolvency for PNIPAM in water/methanol solutions is well known, the underlying mechanism and the driving forces are still

under debate. Using extensive molecular dynamics simulations we find that the calorimetric enthalpy of the collapse transition shows a similar pattern compared to cononsolvency.[1] Polymer hydration is found to be the key factor for chain collapse where the hydrogen bonds between the water and the polymer amide are frustrated by methanol. [1]C.Dalgicdir, F.Rodríguez-Ropero, N.F.A. van der Vegt J. Phys. Chem. B, 2017, 121 (32)