

## CPP 42: Polymer Physics IV

Time: Friday 10:30–13:00

Location: ZEU 160

CPP 42.1 Fri 10:30 ZEU 160

**A Molecular Dynamics Study of Polymers in Confinement** — ●JULIA ZABEL and ALEXANDER BLUMEN — Albert-Ludwigs-Universität Freiburg, Deutschland

The spin coating technique is a common method to produce thin polymer films. Experimental physicists are concerned that the extremely fast evaporation of the solvent leaves the polymers in an unequilibrium state. The behavior of these films in dewetting experiments leads to the assumption that the chains are under residual stress. Using Molecular Dynamics simulations we study the effects of confinement on polymer entanglement and the interdiffusion for two chains in a box. We also look at different geometric confinements such as pores and study the influence of the geometry on the dynamics. These results grant us a deeper understanding of the residual stress postulated by dewetting experiments with spin coated films.

CPP 42.2 Fri 10:45 ZEU 160

**Investigations of Chain Dynamics of Polymers Confined into Nanopores** — ●SALIM OK<sup>1</sup>, FABIAN VACA CHAVEZ<sup>2</sup>, MARTIN STEINHART<sup>1</sup>, and KAY SAALWÄCHTER<sup>2</sup> — <sup>1</sup>Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle, Germany — <sup>2</sup>Institute of Physics - Martin-Luther-University Halle-Wittenberg, Betty-Heimann-Str.7, 06120 Halle, Germany

Gaining better understanding of the nature of polymeric interphases in nanocomposites is still challenging. We show that self-ordered nanoporous anodic aluminum oxide (AAO) containing arrays of cylindrical channels with high aspect ratio and sharp diameter distribution is an ideal model system for the study of polymeric interphases in a well-defined anisotropic geometry. The chain dynamics of polybutadiene infiltrated into AAO was probed by Nuclear Magnetic Resonance (NMR) [1]. The mobility of polymer chains in nano-pores increased as a function of temperature systematically. However, comparing the bulk transverse relaxation ( $T_2$ ) data with  $T_2$  data in confined geometry shows that the mobility of the polymer molecules in the nano-pores is lower than the ones in the bulk. The less mobility is attributed to the smaller volume of the AAO nano-pores, restricting motion and entanglement of the polymer chains. The explanation is \*corset effect\*, defined as combined effect of impenetrable pore walls, the mutual uncrossability of polymer chains and the low compressibility of polymer chains [2].

[1] Saalwächter, K., *Prog. NMR Spectroscopy*, **51**, 1 (2007) [2] Fatkullin, N. *et al.*, *New Journal of Physics*, **6**,1 (2004)

CPP 42.3 Fri 11:00 ZEU 160

**Determination of local mobilities in polymer electrolytes - concepts and simulations** — ●DIDDO DIDDENS<sup>1,2</sup>, ANDREAS HEUER<sup>1,2</sup>, and ARIJIT MAITRA<sup>1,2</sup> — <sup>1</sup>Institut für physikalische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstraße 30, 48149 Münster, Germany — <sup>2</sup>NRW Graduate School of Chemistry, Corrensstraße 36, 48149 Münster, Germany

In polymer electrolytes based on poly(ethylene oxide) (PEO) one observes a local slowing down of the polymer motion due to attached ions. We study this effect by MD simulations of an electrolyte composed of PEO and LiBF<sub>4</sub>. It is, however, difficult to quantify locally slowed down polymer dynamics in MD simulations within established polymer theories like the Rouse model, as it describes the motion by nonlocalized modes. Additionally the short timescale dynamics in MD simulations do not obey the Rouse model but are strongly influenced by the local chemical structure. We provide a new statistical method to determine the relative mobilities of slow and fast regions from MD simulation data using the Langevin equation. In addition, Brownian dynamics simulations of various model chains that resemble polymer chains with heterogeneous friction coefficients are analyzed. By comparing molecular dynamics with the ideal Rouse dynamics the timescale for the validity of the Rouse model can be extracted.

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**Coexistence of Melting and Growth during Heating a Semi-crystalline Polymer: a MD simulation** — ●CHUANFU LUO and JENS-UWE SOMMER — Leibniz Institute of Polymer Research Dresden, Dresden, Germany

We present molecular dynamics (MD) simulations of the cool-

ing/heating of semi-crystalline polymers. Using a highly parallelized code we are able to study chains up to a length of 1000 repeat units using a coarse grained polymer model [1,2]. It is the first time that a clear multi-stage melting process during the heating of a semi-crystalline polymer is analyzed by MD simulations. The step-by-step melting of different sized micro-crystalline-domains (MCDs) can explain the multiple peaks in the curve of specific heat ( $c_p$ -T). However, melting is not a simple stepwise 'melting-recrystallization-melting' process. The averaged stem length (lamella thickness) is increasing during the melting of smaller MCDs, and the main contribution originates from orientational correlations in the semi-melted regions and not only from local trans-trans conformations. We can interpret this a slackening of the stems which increases their mobility in reorganization processes.

[1] H. Meyer and F. Müller-Plathe, *J. Chem. Phys.* **115**, 7807 (2001).  
[2] C. Luo and J.-U. Sommer, *Comp. Phys. Comm.* (in press)

CPP 42.5 Fri 11:30 ZEU 160

**Solid-solid transitions of flexible polymers** — ●STEFAN SCHNABEL, MICHAEL BACHMANN, and WOLFHARD JANKE — Institut für Theoretische Physik, Universität Leipzig, Postfach 100920, D-04009 Leipzig, Germany

Solid-solid transitions of Lennard-Jones clusters including non-icosahedral conformations are a challenging subject for computational research [1]. Applying a new extension to the multicanonical method we successfully analyzed similar transitions for a flexible off-lattice homopolymer model with FENE (finitely extensible nonlinear elastic) bond potential and intramonomeric Lennard-Jones interaction [2,3]. As a result we gain a detailed insight into the polymer crystallization process and the behavior within the solid phase. The transition between icosahedral and decahedral conformations was investigated for different system sizes (e.g.  $N = 75, 102$ ) as well as the transition to the tetrahedral ground state for  $N = 98$ . Small peaks in the specific heat as well as changes in geometrical quantities indicate the cross-over.

[1] V. A. Sharapov and V. A. Mandelshtam, *J. Phys. Chem. A* **111**, 10284 (2007).

[2] S. Schnabel, T. Vogel, M. Bachmann, and W. Janke, *to be published*.

[3] S. Schnabel, M. Bachmann, and W. Janke, *to be published*.

CPP 42.6 Fri 11:45 ZEU 160

**Scaling and scattering analysis for bottle-brush polymers in solutions** — ●HSIAO-PING HSU, WOLFGANG PAUL, and KURT BINDER — Institut für Physik, Johannes Gutenberg-Universität Mainz, Staudinger Weg 7, D-55099 Mainz, Germany

Bottle-brush polymers with a rigid backbone and flexible side chains are studied in a good solvent and a theta solvent by extensive Monte Carlo simulations. Varying the side chain length, backbone length, and the grafting density, the scaling behavior of the radius of gyration, end-to-end distance, radial density profiles of monomers and side chain ends are estimated and checked with the previous theoretical predictions [1]. In order to compare our results with experimental scattering data, the structure factors describing the scattering from a single side chain and from the total bottle-brush polymer are also estimated. Our simulations include two sets of data: (1) To describe the structure of a very long bottle-brush polymer, a periodic boundary condition along the backbone is used. (2) To describe effects due to the finiteness of the backbone, free ends of the backbone are considered in our simulations. In the latter case, the inhomogeneity of the structure in the direction along the backbone is carefully investigated. A detailed analysis of radial density profile and the total scattering of a bottle-brush are given [2].

[1] H.-P. Hsu, W. Paul, and K. Binder, *Macromol. Theory & Simul.* **16**, 660 (2007).

[2] H.-P. Hsu, W. Paul, and K. Binder, *J. Chem. Phys.* **129**, 204904 (2008).

CPP 42.7 Fri 12:00 ZEU 160

**Monte Carlo simulations of dendrimers** — ●JAROSLAW KLOS and JENS-UWE SOMMER — Leibniz Institute of Polymer Research, Dresden, Germany

We inspect star-burst dendrimers by means of Monte Carlo simulations based on the Bond Fluctuation Model. Each molecule is modeled as

a collection of monomers connected with bonds so as to form a tree-like structure on a cubic lattice. The simulations are athermal since merely the excluded volume interactions between the monomers and bond constraints are considered. Through a variation of dendrimers' generation number  $G$  and spacer length  $S$  we focus on their mean instantaneous shape, size and radial distributions of monomers and terminal groups. The calculations show that the shape of dendrimers changes monotonously from oblate to spherical as the increase in their molecular weight  $N$  is caused by an increase in  $G$ , while for fixed  $G$  it is hardly affected by variations of  $S$ . The obtained data lead to the conclusion that the radius of gyration obeys satisfactorily the scaling prediction  $R_g \sim (SG)^{2/5} N^{1/5}$  with  $G$  and  $S$  treated as two independent variables. Moreover, our simulations support the dense-core picture of dendrimers due to a substantial decrease of monomer densities with the radial distance from the dendrimers' centre of mass. The decrease is strictly monotonous for low generation molecules, whereas for ones with higher  $G$  there is either a local maximum or relatively broad plateau in the density profiles that correspond to the dendrimers' domain. The interior of dendrimers is also penetrated by the terminal groups due to finite values of the end-group densities in that area.

CPP 42.8 Fri 12:15 ZEU 160

**Chain conformations in bidisperse blends of linear chains** — ●MICHAEL LANG and JENS-UWE SOMMER — Leibniz Institut für Polymerforschung Dresden

Bidisperse polymer melts containing a small fraction of  $N$ -mers in a matrix of  $P$ -mers were studied using the bond fluctuation model. For mono-disperse melts ( $N = P$ ) we find deviations from ideal chain conformations in melt similar to previous studies [e.g. J.P. Wittmer, P. Beckrich, H. Meyer, A. Cavallo, A. Johner, J. Baschnagel, PhysRevE 76, 011803 (2007)] including long range correlations of bond vector orientations. The excluded volume screening in a dense melt according to the random phase approximation is controlled by the scaling variable  $N^{1/2}/P$ . For the case  $N^{1/2} > P$ , the  $N$ -mers should follow again the excluded volume statistics and the ratio  $R^2/N$  (R-extension of the  $N$ -mers) should scale as  $(P^2/N)^\alpha$  with  $\alpha \approx 1 - 2\nu \approx -0.176$ . Similar to experimental studies [Landry, Macromolecules 30, 7500 (1997)] we find an effective  $\alpha \approx -0.09 \pm 0.01$ . Possible reasons for the observed deviation to the theoretical prediction are discussed.

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**Static and Dynamic Properties of Hyperbranched Polymers Modelled by Generalized Vicsek Fractals** — ●TOBIAS PARDOWITZ<sup>1</sup>, MARTIN OLIVER STEINHAUSER<sup>2</sup>, and ALEXANDER BLUMEN<sup>1</sup> — <sup>1</sup>University of Freiburg, Freiburg, Germany — <sup>2</sup>Fraunhofer Ernst-Mach-Institut for High-Speed Dynamics, Freiburg,

Germany

We study the properties of hyperbranched polymers modelled by generalised Vicsek fractals (GVF) in dilute solution. Due to their fractal (self similar) structure one expects the static as well as the dynamic properties to exhibit typical power law behaviour. Both equilibrium as well as non-equilibrium Brownian dynamics simulations of dilute GVF polymer solutions are performed. Of special interest in both cases is the influence of the excluded volume (EV).

We find the static scaling in good solvent to differ significantly from previous results obtained by a generalised Flory argument. Thus we put forward a different expression for fractal polymers which enables us to explain the simulation data as well as recent experimental observations.

Studying non-equilibrium situations such as micromanipulations and polymers under shear we obtain results in very good agreement with predictions made in the generalised Gaussian structure (GGs) framework. We are furthermore able to establish the influence of the EV on dynamical quantities, effects which are beyond the range of the GGS approach.

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**Semi-flexible hydrogen-bonded and non-hydrogen bonded lattice polymers** — ●KRAWCZYK JAROSLAW<sup>1</sup>, PRELLBERG THOMAS<sup>2</sup>, and ALEKSANDER L. OWCZAREK<sup>3</sup> — <sup>1</sup>Technische Universität Dortmund — <sup>2</sup>School of Mathematical Sciences, University of London, UK — <sup>3</sup>The University of Melbourne, Australia

We investigate the addition of stiffness to the lattice model of hydrogen-bonded polymers in two and three dimensions. We find that, in contrast to polymers that interact via a homogeneous short-range interaction, the collapse transition is unchanged by any amount of stiffness: this supports the physical argument that hydrogen bonding already introduces an effective stiffness. Contrary to possible physical arguments, favouring bends in the polymer does not return the models behaviour to that comparable with the semi-flexible homogeneous interaction model, where the canonical  $\theta$ -point occurs for a range of parameter values. In fact, for sufficiently large bending energies the crystal phase disappears altogether, and no phase transition of any type occurs. We also compare the order-disorder transition from the globule phase to crystalline phase in the semi-flexible homogeneous interaction model to that for the fully-flexible hybrid model with both hydrogen and non-hydrogen like interactions. We show that these phase transitions are of the same type and are a novel polymer critical phenomena in two dimensions. That is, it is confirmed that in two dimensions this transition is second-order, unlike in three dimensions where it is known to be first order.