

CPP 22: Polymer Networks and Dynamics II: Structure and Dynamics

Time: Tuesday 9:30–12:45

Location: ZEU 250

CPP 22.1 Tue 9:30 ZEU 250

Local orientational mobility in regular fractal networks — ●MAXIM DOLGUSHEV^{1,2}, DENIS A. MARKELOV^{3,4}, FLORIAN FÜRSTENBERG¹, and THOMAS GUÉRIN⁵ — ¹Institute of Physics, Uni Freiburg, Germany — ²Institut Charles Sadron, Strasbourg, France — ³St. Petersburg State University, Russia — ⁴ITMO University, St. Petersburg, Russia — ⁵LOMA, CNRS UMR 5798, Talence, France

This contribution presents the study of the local orientational dynamics of single bonds in fractal networks with the focus on the location of the bonds [1]. In contrast to studies on overall or structurally averaged dynamics, which typically need only the eigenvalues of the dynamical matrix, the investigation of the local dynamics requires the calculation of the coefficients from the eigenvectors of this matrix. To overcome this difficulty we provide iterative methods for calculation of such coefficients. The suggested procedure allowed us to treat very large structures (which would not be accessible by naive brute force diagonalization procedures) and to investigate the corresponding scalings for the dielectric relaxation. We show that the local dynamics can be vastly different from the structure averaged one. Indeed, the dynamics of the core segments (which are most remote from the periphery) has a scaling behavior, which differs from the dynamics obtained after structural average. Moreover, we analyze the most relevant processes of single segment motion and provide a well performing analytic approximation for the corresponding relaxation times.

[1] M. Dolgushev, D. A. Markelov, F. Fürstenberg, T. Guérin, Phys. Rev. E. 94, 012502 (2016).

CPP 22.2 Tue 9:45 ZEU 250

Dynamics of internally functionalized dendrimers — ●JONAS GRIMM¹ and MAXIM DOLGUSHEV^{1,2} — ¹Institute of Physics, Uni Freiburg, Germany — ²Institut Charles Sadron, Strasbourg, France

Recently, new types of dendrimers have been synthesized; among them the internally functionalized dendrimers are of a particular interest. We analyze the dynamics of such functionalized dendrimers that have additional functional units, which do not branch out further.

The dendrimers are modeled in the framework of semiflexible tree-like polymers [1], where their topology is described through beads connected by springs (bonds) and semiflexibility is taken into account by constraining the bonds' orientations. The dynamics of the structures is described by a set of Langevin equations. The spectrum of the dynamical matrix appearing in these equations is fundamental for the dynamical properties. In particular, the additional functional beads clearly leave their fingerprints in the eigenvalue spectrum of the dynamical matrix: We find a group of eigenvalues which does not exist for homogeneous dendrimers [2]. This part of the spectrum leads to an additional process in the intermediate frequency region of the imaginary part of the complex dielectric susceptibility. The presence of functional beads is clearly manifested in the local dynamics of the non-functionalized segments on intermediate frequencies [2].

[1] M. Dolgushev and A. Blumen, J. Chem. Phys. 131, 044905 (2009).

[2] J. Grimm and M. Dolgushev, Phys. Chem. Chem. Phys. 18, 19050 (2016).

CPP 22.3 Tue 10:00 ZEU 250

Glassy dynamics in one- and two-dimensional nanometric confinement - a comparison — ●FRIEDRICH KREMER and WYCLIFFE K. KIPNUSU — Institute of Experimental Physics I, University of Leipzig, 04103 Leipzig, Germany

Glassy dynamics of polymers (e.g. poly(methylphenylsiloxane) (PMPS) or poly(cis-1,4-isoprene) (PI)) is studied by broadband dielectric spectroscopy (BDS) in one-(1D)- and two-(2D)-dimensional nanometric confinement; the former is realized in thin layers having thicknesses down to 5 nm, the latter in unidirectional (length 50 m) nanopores with diameters varying between 4-8 nm. Based on dielectric measurements carried out in a broad spectral range at widely varying temperatures glassy dynamics is analyzed in detail in 1D and in 2D confinement. All the findings can be comprehended by considering the density of the polymer; in 1D it is assumed to be the same as in the bulk, hence the dynamic glass transition is not altered, in 2D it is reduced due to a frustration of packaging resulting in a higher free volume, as proven by ortho-positronium annihilation lifetime spec-

troscopy. [1] “Dynamics in Geometrical Confinement”, F. Kremer (Ed.), Springer (2014) [2] Kipnusu, W.K. et al., “Glassy dynamics of polymethylphenylsiloxane in one- and two-dimensional nanometric confinement-a comparison”, submitted 2016 [3] Kipnusu, W.K., “Confinement for More Space: A Larger Free Volume and Enhanced Glassy Dynamics of 2-Ethyl-1-hexanol in Nanopores” J. Phys. Chem. Lett. 6, 3708-3712 (2015) [4] Kipnusu, W.K., et al. “Structure and Dynamics of Asymmetric Poly(styrene-*b*-1,4-isoprene) Diblock Copolymer under 1D and 2D Nanoconfinement” ACS Appl. Mater. Interfaces, 7, 12328-12338 (2015) [5] Mapesa, E.U., et al. “Molecular dynamics of poly(cis-1,4-isoprene) in 1- and 2-dimensional confinement” in: “Dynamics in Geometrical Confinement”, F. Kremer (Ed.), Springer (2014)

CPP 22.4 Tue 10:15 ZEU 250

Tuning polymer dynamics by chain-end association — ●MARTIN TRESS¹, KUNYUE XING¹, PENGFEI CAO², SHIWANG CHENG², TOMONORI SAITO², VLADIMIR NOVIKOV¹, and ALEXEI SOKOLOV^{1,2} — ¹University of Tennessee Knoxville — ²Oak Ridge National Laboratory

Functional end groups in polymers are a molecular tool to reversibly connect and disconnect chains to combine properties of both short polymer and large supramolecular structures. The topology of the latter - and in turn the respective properties - can be tuned by the choice of the functional group. This is shown in a series of polydimethylsiloxanes (PDMS) of different molecular weight (MW) which are terminated by amino and carboxylic (-COOH) groups, respectively. Differential scanning calorimetry and dielectric spectroscopy measurements reveal that segmental dynamics are identical for the chains with two different end groups. In contrast, rheology unravels a mechanical reinforcement for PDMS-COOH and a rise in viscosity by ~ 2 decades. This is accompanied by a 2nd Tg and a corresponding dielectric relaxation process which indicates phase separation of the end groups in clusters forming a physically crosslinked network. As a consequence, the viscoelastic properties can be tuned from common short polymer chains at high temperatures to highly entangled or even crosslinked systems at T close and below the 2nd Tg. This suggests a promising route to combine easy processibility of low MW polymers with the desired mechanical performance of high MW polymers or even crosslinked networks.

CPP 22.5 Tue 10:30 ZEU 250

Cross-link fluctuations in entangled networks — ●MICHAEL LANG — Leibniz-Institut für Polymerforschung, Hohe Straße 6, 01069 Dresden, Germany

Cross-link fluctuations affect the instantaneous and time average bond orientations in entangled networks that are measured as birefringence or by Nuclear Magnetic Resonance respectively. In order to develop a quantitative model for cross-link fluctuations, computer simulation data on junction fluctuations in end-linked model networks are analyzed using the framework of the constrained junction model and the slip tube model of entangled networks. We discuss an analytical expression for cross-link fluctuations that compares well with simulation data on elasticity and residual bond orientations. As a consequence, cross-link fluctuation data can be used to estimate the tube diameter.

CPP 22.6 Tue 10:45 ZEU 250

A novel route towards entropic polymer separation — ●PAOLO MARGARETTI — Max Planck Institute for Intelligent Systems, Heisenbergstr. 3 70569 Stuttgart Germany

Many biological processes such as viral infection, DNA transport through membranes and gene transferring between bacteria involve the translocation of bio-polymer through nano-channels and nano-pores. Moreover, technological applications such as polymer separation, DNA sequencing, and protein sensing, rely on the translocation of polymer through restrictions.

Up to now, much attention has been paid to the case of polymers translocating through pores whose half-section is comparable to the monomer size. In contrast to this, we are concerned with the case of a polymer translocating through channels, whose cross section is larger than the size of a single monomer, yet comparable to the size of the overall gyration radius of the polymer.

In such a regime a novel dynamical scenario occurs and it appears a non-monotonous dependence of polymer translocation velocity as a

function of polymer size, a feature that can be exploited for polymer separation. I will show that these numerical results can be rationalized on the basis of a simplified model that reduces the problem of polymer translocation through varying-section channels to that of a point-like particle under the action of an effective potential.

15 min break

Invited Talk CPP 22.7 Tue 11:15 ZEU 250
Structure/dynamics interplay in interfacial layers: how adsorption influences thermal glass transition and segmental relaxation — ●SIMONE NAPOLITANO — Université Libre de Bruxelles (ULB), Brussels, Belgium

Growing experimental evidence shows that the behavior of thin polymer layers strongly depends on the degree of adsorption, the number density of monomers pinned onto the supporting substrate. Several groups have independently observed that properties as wettability, viscosity and thermal expansion are affected by prolonged annealing in the liquid state, even at timescales exceeding the equilibration time of a bulk melt.

In this talk, after introducing the physics behind the mechanisms of irreversible adsorption, I shall review some of these observations, focusing on those related to the thermal glass transition and to the segmental dynamics. Based on the information collected on different polymers, I will discuss on different models that could explain the origin of the striking correlation between the value of the glass transition temperature of 1D confined polymers and the degree of adsorption.

After presenting new results on the interplay between segmental dynamics and formation of adsorbed layers, I will demonstrate that, differently than what currently speculated, the transformation materials undergo during adsorption does not mimic physical aging.

CPP 22.8 Tue 11:45 ZEU 250
Polymer films deposited on solid surfaces studied with mesoscopic and microscopic models — JIANGUO ZHANG, DEBASHISH MUKHERJI, KURT KREMER, and ●KOSTAS DAOULAS — Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

Polymer films deposited on solid substrates are interesting for basic polymer physics and have numerous industrial applications. Here, to study these systems, we develop [1] a special particle-based model where polymers are represented as worm-like chains, while non-bonded interactions are defined [2] via a simple density functional. To specify the functional and the associated parameters, certain thermodynamic properties known from experiments are taken into account. Films of poly(methyl methacrylate) adsorbed onto silica surfaces are chosen as test cases. To validate the mesoscopic model we perform a direct comparison with smaller scale simulations, based on a generic microscopic model representing the same system. The comparison is performed considering observables such as chain-shape, structure of adsorbed layer, statistics of loops, tails, and trains. The two models are found to be consistent with each other. Certain deviations in poly-

mer conformations and structure of adsorbed layer can be rationalized by the simplified description of polymer-surface interactions and liquid structure in the mesoscale model. [1] Zhang et al, EPJ SP 2016. [2] Daoulas and Müller, JCP 2006.

CPP 22.9 Tue 12:00 ZEU 250
EMC: A monte carlo scheme with energyconservation applied to a soft, coarse-grained model of polymers — ●MARCEL LANGENBERG — Institut für Theoretische Physik, Georg-August-Universität Göttingen, Deutschland

Coarse-graining reduces the number of degrees of freedom (DoF) and the integrated out DoF gives rise to friction and noise and the coarse-grained beads are endowed with an internal energy. We derive the universal form of the internal energy-entropy relation in the limit of large molecular weight. Motivated by the idea of eDPD we developed an energy Monte-Carlo scheme, which locally conserves energy and momentum and does not suffer from discretization errors [1]. This simulation technique allows us to study thermal transport in diblock copolymer nanocomposites. Our coarse-grained model captures the difference between inter- and intramolecular transport and can address large Lewis numbers, which are characteristic for polymers. We investigate the Kapitza resistance of interfaces and study its dependence on the molecular architecture.

[1] M. Langenberg and M. Müller, EMC: A monte carlo scheme with energyconservation, EPL 114, 20001 (2016).

Invited Talk CPP 22.10 Tue 12:15 ZEU 250
Molecular-level framework for the dynamic mechanical response and yielding of polymer glasses — ●ALESSIO ZACCONE¹, VLADIMIR PLYULIN¹, CHRIS NESS¹, ROBERT ELDER², RICO MILKUS¹, and TIMOTHY SIRK² — ¹University of Cambridge, UK — ²US Army Research Laboratory, USA

Understanding the mechanical response of polymer glasses is currently one of the biggest challenges in polymer physics and soft matter. The deformation of polymer glasses has a considerable non-affine component at the monomer-unit level, meaning that every unit within every chain undergoes an additional displacement on top of the displacement imposed by the strain tensor [1]. We used theoretical and computational approaches, based on the non-affine molecular-level dynamics and on the vibrational density of states. A mechanistic assessment is obtained of how chemistry-dependent many-body angular constraints along the chain and cross-linking constraints affect: 1. the value of T_g (as parameterized also by the critical number of total nearest-neighbour units at the transition, z^* [2]), 2. the rate-dependent elasticity/rigidity component of response, 3. the rate-dependent energy-absorption and ductility, and 4. the yielding transition [3]. This theoretical description poses the basis of a new chemical-design platform for linking polymer chemistry to mechanical performance in advanced polymer-based functional materials. [1] A. Zaccone & E.M. Terentjev, Phys. Rev. Lett. (2013). [2] A. Lappala, A. Zaccone, E.M. Terentjev, Soft Matter (2016). [3] V. Palyulin, C.J. Ness, R. Milkus, R. Elder, T. Sirk, A. Zaccone, in preparation.