

CPP 17: Transport and Confinement I

Time: Tuesday 9:30–12:45

Location: ZEU 260

Invited Talk

CPP 17.1 Tue 9:30 ZEU 260

Glassy dynamics of polymers in geometrical confinement: From nanometric layers to condensed isolated chains — ●FRIEDRICH KREMER — Institute of Experimental Physics I, University of Leipzig

The question on what length-scale molecular and especially glassy dynamics of polymers takes place is of fundamental importance and has multifold practical implications as well. Recent results based on Broadband Dielectric Spectroscopy for nanometric thin (>5 nm) layers of poly(styrene), poly(methylmethacrylate) and poly(cis-1,4-isoprene) will be presented, delivering the concurring result that deviations from glassy dynamics of the bulk never exceed margins of ± 3 K independent of the layer thickness, the molecular weight of the polymer under study and the underlying substrate. A further exciting perspective is the measurement of the dynamics of condensed isolated polymer chains. - The experiments lead to the conclusions that glassy dynamics takes place on the length-scale a few polymer segments (<0.5 nm) while the conformation of the chain as a whole is strongly modified due to geometrical confinement.

References: Tress, M. et al., *Science* 341, (6152) 1371-1374 (2013); Mapesa, E.U. et al., *Soft Matter* 9 (44), 10592-10598 (2013); Kremer, F., E.U. Mapesa, M. Tress, M. Reiche, "Molecular Dynamics of Polymers at Nanometric Length Scales: From Thin Layers to Isolated Coils" in: "Recent Advances in Broadband Dielectric Spectroscopy", Y. P. Kalmykov (Eds.), NATO Science for Peace and Security Series B: Physics and Biophysics, Chapter 12, Springer (2012)

CPP 17.2 Tue 10:00 ZEU 260

Direct measurement of thermophoretic forces — ●LAURENT HELDEN¹ und CLEMENS BECHINGER^{1,2} — ¹2. Physikalisches Institut, University of Stuttgart, Pfaffenwaldring 57, 70550 Stuttgart, Germany — ²Max Planck Institut for Intelligent Systems, Heisenbergstr. 3, 70569 Stuttgart, Germany.

Thermophoretic motion of colloidal particles is ubiquitous in nature where ever temperature gradients occur. In spite of this the exact mechanism of thermophoretic motion is not yet fully understood and even preminent features like the size dependence of Soret coefficient are still under debate.

In this context we present a new strategy to directly measure thermophoretic forces. Using total internal reflection microscopy (TIRM) we observe the motion of a single polystyrene particle in a narrow slit subjected to temperature gradients. With increasing gradient a preference of the cold side is observed. Implications for the theoretical description of thermophoresis are discussed.

CPP 17.3 Tue 10:15 ZEU 260

Anomalous Diffusion of Proteins in a Membrane due to Crowding and Trapping — ●MISLAV CVITKOVIĆ¹, TIMO BIHR^{1,2}, and ANA-SUNČANA SMITH¹ — ¹Institute for Theoretical Physics I and Cluster of Excellence: Engineering of Advanced Materials, Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany — ²II Institute for Theoretical Physics, University of Stuttgart, Germany

The transport of lipids and proteins in biological membranes is one of the most fundamental processes in living cells. Despite a wealth of experiments on related biological processes, the general biophysical principles underlying the complex diffusion in a membrane are still not well understood. Here we model anomalous diffusion in the crowded and multicomponent membrane environment where proteins acting as tracers bind and unbind from immobilised counter-partners (traps), the latter representing a functionalized scaffold. Using a self-developed Monte-Carlo simulation scheme that accounts for length scales from 1 nm to 1 μ m in the time domain from 1 μ s to 10 s, we explore the full parameter space spanned by the densities of the diffusing molecules and the traps, as well as the binding and unbinding rates. We find several regimes of diffusion and types of anomalous transport. We determine the effective diffusion constant within an analytical model based on scaling arguments that account for trapping, self-avoidance and cooperative effects in the long-time limits of all regimes. We find that this approach reproduces well the results of analogous single-particle-tracking experiments in supported scaffolding membranes.

CPP 17.4 Tue 10:30 ZEU 260

Confinement of DGEBA: molecular dynamics & macroscopic flow — ●ANNA DJEMOUR, JOERG BALLER, CARLO DIGIAMBATTISTA, and ROLAND SANCTUARY — Laboratory for the Physics of Advanced Materials, University of Luxembourg, 162A, Avenue de la Faiencerie, L-1511 Luxembourg

Glass formers in confinement have been extensively studied with differing results: shifting of T_g towards smaller/higher temperatures, no shift, broadening of the glass transition, even several T_g s. This strongly depends on the type of confinement, the materials involved and the confining surfaces and their treatment. These shifts can be used to determine the size of the cooperative rearranging regions aiding in the research into the nature of the glass transition. Additionally, there has been some work done on the influence of the confined matter on confining systems such as porous glasses (Ref. 1).

Both aspects were investigated for the low molecular weight epoxy resin DGEBA confined by a 3D porous network i.e. controlled pore glass with randomly oriented pores (native and silanized pores of pore sizes ranging from 4nm to 110nm). For native pores a large shift to higher temperatures was observed for the glass transition in small pores ($d \leq 20$ nm). Contributions from a layer adhered to the pore walls could be distinguished from a faster core layer of the glass former. We also observe a hitherto unreported hysteresis in heating and cooling measurements which we assume to be an effect of the macroscopic flow/transport of the glass former through the glass channels.

1. J. Koppensteiner et al, *Phys. Rev. B* 81 (2010) 024202.

CPP 17.5 Tue 10:45 ZEU 260

Hydrodynamic interactions induce anomalous diffusion under partial confinement — ●JOHANNES BLEIBEL^{1,2}, ALVARO DOMINGUEZ³, and MARTIN OETTEL¹ — ¹Institut für angewandte Physik, Universität Tübingen, Tübingen, Germany — ²Max-Planck-Institut für intelligente Systeme, Stuttgart, Germany — ³Física Teórica, Universidad de Sevilla, Sevilla, Spain

We consider a system of colloidal particles which are restricted to a plane, but surrounded by an unbound fluid. Examples for such a setup are colloids trapped at fluid-fluid interfaces or colloids trapped by laser fields. Although this partial confinement allows for motion of the particles only within the plane, their dynamics is influenced by hydrodynamic interactions mediated by the unconfined, three-dimensional flow of the embedding fluid. We demonstrate that this dimensionality mismatch induces a characteristic divergence in the collective diffusion coefficient of the colloidal subsystem. This result, independent of the specific interparticle forces in the monolayer, is solely due to the kinematical constraint on the colloidal particles, and it is different from the known divergence of transport coefficients in purely one or two-dimensional fluids. We study the consequences for two different setups: We find anomalous diffusion for an ideal-gas-like system of non-interacting colloidal particles and a significant speedup for the capillary induced collapse of a colloidal patch at a fluid interface.

15 min break

Invited Talk

CPP 17.6 Tue 11:15 ZEU 260

Molecular Dynamics simulations of the glass transition in 1,4-polybutadiene confined by graphite walls — ●WOLFGANG PAUL¹, MATHIEU SOLAR¹, and KURT BINDER² — ¹Institut für Physik, Martin-Luther-Universität, 06099 Halle — ²Institut für Physik, Johannes-Gutenberg-Universität, 55099 Mainz

We will discuss simulations of a chemically realistic representation of 1,4-polybutadiene (PBD) between graphite surfaces and discuss the influence of the walls on structure and dynamics in the polymer film. There have been many studies of polymers at interfaces and especially on the influence of interfaces on the glass transition in polymers, and with partially contradicting results. We will show that there are two influences of the wall on the structure in the adjacent melt. The first is a strong layering in the monomer density next to the wall, and the second is an orientation of the chains close to the wall and a layering in the centre of mass density of the chains.

Both structural effects give rise to significant modifications of the relaxation behaviour of the polymer next to the wall. We will discuss in detail how these can be identified in different experiments ranging from dielectric spectroscopy to nuclear magnetic resonance to neu-

tron scattering. Determining the glass transition temperature of the confined system from the dielectric relaxation, we find that for this realistic polymer wall model it is independent of the thickness of the film studied down to about 1 nm.

CPP 17.7 Tue 11:45 ZEU 260

Enhanced Dispersion by Elastic Turbulent Flow Through Porous Media — ●CHRISTIAN SCHOLZ¹, FRANK WIRNER¹, and CLEMENS BECHINGER^{1,2} — ¹2. Physikalisches Institut, Universität Stuttgart, Pfaffenwaldring 57, 70569 Stuttgart, Germany — ²Max-Planck-Institut für Intelligente Systeme, Heisenbergstraße 3, 70569 Stuttgart, Germany

We experimentally investigate hydrodynamic dispersion of micron-sized tracer particles in elastic turbulent flows of semi-dilute polymer solutions through a periodic porous medium at ultra low Reynolds numbers $Re < 5 \times 10^{-4}$. The asymptotic behaviour of the transversal mean squared displacement is linear and characterized by a dispersion coefficient D_{\perp} , that grows non-linearly with the Weissenberg number Wi and is several orders of magnitude larger compared to laminar flow. While the enhanced velocity fluctuations appear as Wi dependent noise, for Wi far away from the onset of elastic turbulence we observe a non-linear asymmetry in the flow field.

CPP 17.8 Tue 12:00 ZEU 260

Hydrodynamic dispersion of micron-sized colloids in micro-structured porous media — ●FRANK WIRNER¹, CHRISTIAN SCHOLZ¹, and CLEMENS BECHINGER^{1,2} — ¹2. Physikalisches Institut, Universität Stuttgart, Pfaffenwaldring 57, 70569 Stuttgart, Germany — ²Max-Planck-Institut für Intelligente Systeme, Heisenbergstraße 3, 70569 Stuttgart, Germany

The flow of liquids through porous media is of importance in many areas, such as groundwater pollution, secondary oil recovery or blood perfusion inside the body. The complex geometry of porous media can give rise to a combination of principal pathways, along which particles are transported by advection, and stagnant parts, wherein particles can only move slowly by diffusion. Especially in porous media with low porosities these stagnant parts may eventually dominate the transport properties of fluids and colloids. The mean sojourn time of a particle in a stagnant part, however, can easily exceed experimentally accessible time scales. Therefore, we investigate the effect of stagnant parts on the transit times of micron-sized particles in quasi-two-dimensional porous structures by a semi-experimental approach, which enables us to capture these rare events. The longest transit times can be related to the stagnant parts of the structure, whereby it might be possible to predict the amount of trapped fluid in porous media.

CPP 17.9 Tue 12:15 ZEU 260

Single water molecule confined in a nano-cavity of beryl

crystal lattice — ●MARTIN DRESSEL¹, E.S. ZHUKOVA^{1,2,3}, V.I. TORGASHEV⁴, V.V. LEBEDEV^{3,5}, G.S. SHAKUROV⁶, R.K. KREMER⁷, E.V. PESTRJAKOV⁸, V.G. THOMAS⁹, D.A. FURSENKO⁹, and B.P. GORSHUNOV^{1,2,3} — ¹1. Phys. Inst., Univ. Stuttgart — ²A.M. Prokhorov Gen. Phys. Inst., RAS, Moscow — ³Moscow Inst. Phys. Techn., Dolgoprudny — ⁴Fac. Phys., Southern Fed. Univ. Rostov-on-Don — ⁵Landau Inst. Theor. Phys., RAS, Chernogolovka — ⁶Kazan Phys.-Techn. Inst., RAS, Kazan — ⁷MPI Festkörperforschung, Stuttgart — ⁸Inst. Laser Phys., RAS, Novosibirsk — ⁹Inst. Geology Mineralogy, RAS, Novosibirsk

Using terahertz and infrared spectroscopy, we have studied the low-energy excitations of a single H₂O molecule confined within a nano-cage formed by ions of beryl (Mn:Be₃Al₂Si₆O₁₈) crystal lattice. At terahertz frequencies, for electric field of the probing radiation polarized perpendicular to the crystallographic *c*-axis ($E \perp c$) multiple resonances are discovered and assigned to librational and translational vibrations of the H₂O molecule that is weakly (via hydrogen bonds) coupled to the walls of the nano-cage. Only two water-related absorption peaks are seen for the second polarization $E \parallel c$. A model is presented that explains the resonances by taking into account the quantum tunneling between the H₂O states in the minima of a six-well potential felt by a molecule within the cage. We draw analogies with the electrodynamic spectra of liquid water and ice. Ref.: B.P. Gorshunov et al., J. Phys. Chem. Lett. **4**, 2015 (2013).

CPP 17.10 Tue 12:30 ZEU 260

Gold Nano-Structure Assisted Thermophoretic Trapping of Single Nano-Objects — ●MARCO BRAUN and FRANK CICHOS — Molecular Nanophotonics, Fakultät für Physik und Geowissenschaften Universität Leipzig, Deutschland

Single molecule spectroscopy has become indispensable in today's soft-matter sciences. Brownian motion scaling with the molecules hydrodynamic radius lets it quickly disappear from the observation volume, which is why the molecule of interest is typically immobilized in a polymer matrix or by chemical interactions, generally accepted due to a lack of alternatives. Here, we present an all-optical technique to trap single nano-objects in solution which exploits highly localized thermal fields. The so-called thermophoretic trap exploits thermophoretic forces that act on a particle placed in a temperature gradient, which e.g. locally distorts the screening of the surface charges and by that induces a particle drift. In our approach the temperature field is generated by an optically heated gold nano-structure. Due to the small dimensions of the heat sources, even a small temperature increase introduces large temperature gradients causing a strong thermophoretic drift by which the motion of a Brownian particles can be manipulated. In our experiment an appropriate gold structure is heated locally by a focused laser beam with feedback to the Brownian particles position.