

CPP 32: Focus: Stress Relaxation in Polymers - From single molecules to biological cells (joint focus with BP)

The session provides a synopsis of stress relaxation in polymeric materials, ranging from synthetic to biological polymers and from single molecule studies to network properties and their relevance for live cells and tissues. (Organizers: R. Magerle, K. Kroy)

Time: Thursday 9:30–12:30

Location: C 243

Invited Talk

CPP 32.1 Thu 9:30 C 243

Stress relaxation and chain dynamics in entangled polymer melts — ●RALF EVERAERS — Laboratoire de Physique, ENS Lyon, 46 allée d'Italie, F-69364 Lyon, France

High molecular weight polymeric liquids display remarkable viscoelastic properties. Contrary to glassy systems, their macroscopic relaxation times are not due to slow dynamics on the monomer scale, but arise from the chain connectivity and the restriction that the chain backbones cannot cross. We use a combination of analytical theory and computer simulations to arrive at a quantitative description of the complex relaxation scenario expected from current versions of the tube model. Our data for the stress relaxation in equilibrium and step-strained bead-spring polymer melts allow us to explore the chain dynamics and the shear relaxation modulus, $G(t)$, into the plateau regime for chains with $Z = 40$ entanglements and into the terminal relaxation regime for $Z = 10$. We have performed parameter-free tests of several different tube models using the known (Rouse) mobility of unentangled chains and the melt entanglement length determined via the primitive path analysis of the microscopic topological state of our systems. We find excellent agreement for the Likhtman-McLeish theory using the double reptation approximation for constraint release, if we remove the contribution of high-frequency modes to contour length fluctuations of the primitive chain. In particular, we rationalize the onset of entanglement constraints in polymeric liquids via an analysis of the short-time dynamics of (primitive) chains.

CPP 32.2 Thu 10:00 C 243

Direct stress measurements in nonequilibrium thin polymer films. — ●KATHERINE THOMAS¹ and ULLRICH STEINER² — ¹Max Planck Institute for Dynamics and Self-Organisation, Goettingen, Germany — ²Department of Physics, University of Cambridge, UK

Residual stresses in polymer films often arise from the solution deposition protocol. The origin of stresses in polymer films is easily justified: film formation by solvent evaporation steadily increases the polymer concentration, raising the glass transition temperature of the solution. When T_g reaches the ambient temperature the polymer vitrifies, suppressing further equilibration of the chains. Due to the entangled nature of the polymer network, evaporation of the remaining solvent induces substantial biaxial tensile stresses. Stresses in thin films are not, however, easy to measure and can often only be deduced indirectly.

Here stresses were quantitatively determined by measuring the deflection of cantilevers cut from film-covered SiN membranes using a focused ion beam. Spin-cast films showed notably high residual stresses, far greater than the bulk polymer tensile strength. Stress relaxation via thermal annealing suggests two relaxation mechanisms, both much faster than the reptation time. The fast relaxation indicates that the stress arises from segmental deformations of the chains, rather than entropic effects. Comparison of these data with EHD film stability experiments, suggests the same relaxation mechanisms, providing further evidence for the existence of a thin, highly stressed layer at the surface of the film. These experiments show the utility of our method for the systematic examination of non-equilibrium thin film properties.

CPP 32.3 Thu 10:15 C 243

Mechanical stress relaxation in polymers followed by low-field NMR — UTE BÖHME and ●ULRICH SCHELER — Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Germany

Low-field NMR provides information on molecular mobility over a wide range of rates of motion. In-situ low-field NMR has been applied on polymers under uniaxial stress [1]. Strongest stress-induced effects have been observed in T2 (indicative for slow motion) and T1rho (indicative for motion of rates of kilohertz) both indicating restrictions in the motion of polymer segments. In elastomers the changes are reversible after release of the external stress. Time-dependent experiments at constant extension on semicrystalline polymers show a return of both relaxation times to the values of the non-stressed sample. However, the

time constant of that return is significantly longer than that observed in mechanical stress-relaxation experiments.

[1]Böhme, U.; Gelfert, K.; Scheler, U. Solid-state NMR of polymers under mechanical stress AIP conference proceedings 1330 (2011) 109

CPP 32.4 Thu 10:30 C 243

Stress Induced Single Molecule Reorientation Motion in Elastomeric Polypropylene — ●STEFAN KRAUSE, MARTIN NEUMANN, MELANIE BIBRACH, ROBERT MAGERLE und CHRISTIAN VON BORCZYKOWSKI — Fakultät für Naturwissenschaften, TU Chemnitz, D-09107 Chemnitz

The fluorescence of a single molecule (SM) is a very sensitive probe for its environment and changes of the fluorescence lifetime, emission wavelength, and polarization can report spatial and temporal variations in the surrounding structure of the fluorescent dye. Here we report on SM microscopy and spectroscopy studies of stress relaxation in thin films of elastomeric polypropylene (ePP), a semicrystalline polymer with a complex microstructure of crystalline and amorphous regions on the nanometer scale. The films are stretched using a micro tensile testing setup. Simultaneously, perylene-3,4,9,10-tetracarboxylic diimide dyes functionalized with hexadecane were embedded in the ePP film and report via their molecular dynamics changes within their local environment. Orientation fluctuations were investigated via SM polarization dependent microscopy. This experiment allows for insights into dynamical processes within the amorphous regions of ePP which are not accessible using other microscopy techniques.

Invited Talk

CPP 32.5 Thu 10:45 C 243

Slow stress relaxation in recoiling polymers — ●ULRICH F. KEYSER — Cavendish Lab, University of Cambridge, JJ Thomson Ave, Cambridge, CB3 0HE, UK

The internal dynamics of semi-flexible chains in response to external forces is an important problem in soft matter, polymer and biological physics. Here, we describe a novel method to experimentally determine the relaxation of a single DNA molecule with one free end. The electric field in a nanopore[1] or nanocapillary[2] is used to apply a controlled force to one end of a DNA molecule while the other end is held in an optical trap[3,4]. High-speed video tracking of the colloidal particle[5] allows for a direct measurement of the relaxation in the recoiling DNA upon release from the nanopore. We show and discuss our single-molecule experiments for a range of forces and find that stress relaxation and recoiling is much slower than expected from the simple worm-like chain model. Our results pave the way towards investigating the nonlinear dynamics of semiflexible polymer relaxation and test recent theories[6] on propagation and relaxation of backbone tension in DNA.

[1] Keyser et al., Nature Physics 2, 473 (2006) [2] Steinbock et al., Nano Letters 10, 2493 (2010) [3] Steinbock et al., J. Phys. Cond. Mat. 23, 184114 (2010) [4] Otto et al., Rev. Sci. Instr. 82, 086102 (2011) [5] Otto et al., Optics Express 18, 22722 (2010) [6] Hallatschek et al., Phys. Rev. E 75, 031906 (2007)

CPP 32.6 Thu 11:15 C 243

Non-Equilibrium Relaxation in Polymer Solutions — ●CHIEN-CHENG HUANG, GERHARD GOMPPER, and ROLAND G. WINKLER — Theoretical Soft Matter and Biophysics, Institute of Complex Systems and Institute for Advanced Simulation, Forschungszentrum Jülich, 52425 Jülich

Individual DNA molecules in shear flow exhibit large conformational changes due to tumbling motion. A polymer continuously undergoes stretching and compression cycles with a characteristic frequency, which depends on the shear rate. To characterize the tumbling behavior, we perform large-scale non-equilibrium mesoscale hydrodynamic simulations of semidilute polymer solutions, which combine molecular dynamics simulations and the multiparticle collision dynamics approach. The non-equilibrium polymer end-to-end vector relaxation

times in the stationary state exhibit the shear rate dependence $\dot{\gamma}^{-2/3}$. In the dilute limit, the relaxation times for the various spatial directions are identical. For semidilute solutions, screening of hydrodynamic interactions leads to a slower and faster relaxation in the vorticity and gradient directions, respectively. The relaxation times are equal to the tumbling times extracted from cross-correlation functions of fluctuations of radius-of-gyration components. Furthermore, we find a memory effect in the tumbling dynamics, which causes an oscillatory relaxation along the flow and gradient directions. This memory effect decreases with increasing polymer length and is believed to be less pronounced or even absent for long polymers.

CPP 32.7 Thu 11:30 C 243

Stress relaxation through crosslink unbinding in biopolymer assemblies — •CLAUS HEUSSINGER — Institute for theoretical physics, University Göttingen

The cytoskeleton is a complex meshwork of long elastic filaments coupled together with the help of numerous, rather compact crosslinking proteins. An important aspect of a cytoskeletal polymer network is its dynamic nature, which allows it to react to external stimuli and adapt its internal structure and mechanical properties according to the needs of the cell. The reversible nature of crosslink binding is an important mechanism that underlies these dynamical processes.

In this contribution we devise a simple model polymer network to study the effect of network deformation on the crosslink binding processes. We evidence a discontinuous and sudden rupture transition after which the network is no longer able to resist the external load. By combining MC simulation with a necklace-type model (M. Fisher, J. Stat. Phys. (1984)) we discuss the role of the mechanical stiffness of the crosslinks and the fluctuation properties of the filaments. This allows to address the interplay of strain stiffening inherent in the entropic response of individual polymers, and strain softening due to crosslink unbinding.

CPP 32.8 Thu 11:45 C 243

Thermorheology of single living cells — •TOBIAS R. KIESSLING, ANATOL W. FRITSCH, ROLAND STANGE und JOSEF KÄS — Universität Leipzig, Institut für Experimentelle Physik I, Physik der weichen Materie, Linnéstr. 5, 04103 Leipzig

Within reasonable temperature ranges, many biological functions are known to undergo modulations, like myosin motor activity, CO₂ uptake of cultured cells or sex determination of several species. As mechanical properties of living cells are considered to play a key role for plenty of cell functions ranging from stem cell differentiation to cancer progression, it is surprising that only little is known on how their rheology is affected by temperature. Using an Optical Stretcher, thousands of single cell experiments were performed to systematically assess the effect of temperature on cell deformability. The impact of slow temperature changes occurring on a scale of about 30 minutes is compared to the influence of defined heat shocks in a range of milliseconds. Differences of thereby revealed temperature dependencies are discussed and compared to findings from in vitro rheological studies on polymer solutions.

Invited Talk

CPP 32.9 Thu 12:00 C 243

Cytoskeletal stress in collective cell migration — •XAVIER TREPAT — Institute for Bioengineering of Catalonia, Barcelona, Spain

For a group of living cells to migrate cohesively, it has long been suspected that each constituent cell must exert physical forces not only upon its extracellular matrix but also upon neighboring cells. I will present the first comprehensive maps of these distinct force components. These maps reveal an unexpectedly rich physical picture in which the distribution of physical forces is dominated by heterogeneity, both in space and in time, which emerges spontaneously propagates over great distances, and cooperates over the span of many cell bodies. Both in epithelial and endothelial cell sheets, these heterogeneous forces are mechanically linked to cell velocities through a newly discovered emergent mechanism of innately collective cell guidance: plithotaxis.