

CPP 8: Polymer and Molecular Dynamics, Friction and Rheology

Time: Monday 15:00–16:00

Location: H 0107

CPP 8.1 Mon 15:00 H 0107

Viscoelastic response of cross-linked epoxy using non-affine lattice dynamics: Bridging the timescale gap — ●VINAY VAIBHAV¹, TIMOTHY W. SIRK², and ALESSIO ZACCONE¹ — ¹Department of Physics "A. Pontremoli", University of Milan, Via Celoria 16, 20133 Milan, Italy — ²Polymers Branch, U.S. Army Research Laboratory, Aberdeen Proving Ground, MD 21005, USA

There is a vast timescale disparity, at least six orders of magnitude, at which mechanics can be probed in simulations compared to experiments. The theoretical approach, known as Non-affine Lattice Dynamics (NALD), developed by solving the equation of motion for the non-affine displacement in a disordered environment [1], has been promising in predicting the mechanics of amorphous solids at lower frequencies, making it possible to access the experimental timescales. We use large-scale computer simulations to model an epoxy system comprised of diglycidyl ether of bisphenol A (DGEBA) cross-linked by poly(oxypropylene) diamine [2], and calculate the viscoelastic response using NALD at different frequencies and also via molecular dynamics simulations for the oscillatory shear. The NALD calculations of modulus at ultra-low frequencies match with experimental data, thus, opening a new paradigm in the field of polymer viscoelasticity research to bridge the timescale gap between experiments and theory.

[1] R. M. Elder, A. Zaccone, T. W. Sirk, ACS Macro Letters, 8(9), 1160 (2019) [2] T. W. Sirk, K. S. Khare, M. Karim, J. L. Lenhart, J. W. Andzelm, G. B. McKenna, R. Khare, Polymer 54(26), 7048 (2013)

CPP 8.2 Mon 15:15 H 0107

Relating Fractional Viscoelastic Models to Relaxation Time Spectra — ●ROBERT FRANZ SCHMIDT¹, HORST HENNING WINTER², and MICHAEL GRADZIELSKI¹ — ¹Stranski-Laboratorium, Institut für Chemie, TU Berlin, Berlin, Germany — ²Chemical Engineering and Polymer Science & Engineering, University of Massachusetts Amherst, Amherst, MA, USA

Soft matter materials frequently exhibit power-law viscoelastic responses due to a broad range of relaxation times. Classical viscoelastic models, based on series-parallel arrangements of springs and dashpots, predict exponential relaxation behavior and therefore have difficulty reproducing experimental data from power-law materials. Fractional viscoelastic models represent a second class of models that incorporate derivatives of fractional order in time. They naturally predict power-law behavior and provide an excellent description of experimental data. However, physical interpretation of the model parameters is challenging due to fractional units of time.

To elucidate the meaning of the fractional parameters, we analyze the dynamic moduli of poly(ethylene oxide) (PEO) solutions using both classical and fractional viscoelastic models. We find that the Fractional Maxwell Model provides excellent description of the experimental data with only four parameters. We derive an analytical ex-

pression for the relaxation time spectrum as a function of the fractional parameters. By relating the elusive fractional parameters to tangible relaxation time spectra, our work helps to combine the advantages of both classes of models.

CPP 8.3 Mon 15:30 H 0107

Polymer dynamics and transport of energy and matter studied by rheological NMR — ●ULRICH SCHELER — Leibniz-Institut für Polymerforschung Dresden e.V

The effect of external shear on transport properties and polymer dynamics are studied by rheological NMR in a Searle cell. Nanoemulsions as phase-change materials are used for storage of thermal energy. A hysteresis of melting of the oil phase is observed following the fraction of the liquid signal from the oil. This is accompanied by a transition from Newtonian flow to shear banding determined by low NMR imaging. With the more flexible and deformable droplets a deviation from a linear flow profile is seen. That is accompanied by a variation of the concentration distribution as detected by spatially resolved NMR spectra in the gap. The chain dynamics in entangled polymer melts and solutions is effectively monitored by the spin-spin relaxation time T₂ that is most sensitive to slow motions like chain segment motion. In polymer melt with a chain length above the entanglement length the dominating effect is the loss of entanglements. This effect sets in only at deformation rates in excess of 1000 s⁻¹. The behavior of solutions of polyelectrolytes depends on concentration and ionic strength. Entanglement effects are observed above the entanglement concentration only. They are enhanced when the polyelectrolytes become more flexible by screening the electrostatic interaction by the addition of salt.

CPP 8.4 Mon 15:45 H 0107

Chilling alcohol on the computer: isothermal compressibility and the formation of hydrogen-bond clusters in liquid propan-1-ol — ●ROBIN CORTES-HUERTO, LUIS A. BAPTISTA, MAURICIO SEVILLA, and KURT KREMER — Max-Planck-Institut für Polymerforschung, Mainz, Deutschland

Molecular dynamics simulations have been performed to compute the isothermal compressibility κ_T of liquid propan-1-ol in the temperature range 200 - 300 K. A change in behaviour, from normal (high T) to anomalous (low T), has been identified for κ_T at 210 < T < 230 K. The average number of hydrogen bonds (H*bond) per molecule turns to saturation in the same temperature interval, suggesting the formation of a relatively rigid network. Indeed, simulation results show a strong tendency to form H*bond clusters with distinct boundaries, with the average largest size and width of the size distribution growing upon decreasing temperature, in agreement with previous theoretical and experimental studies. These results also emphasise a connection between the behaviour of and the formation of nanometric structures.