

CPP 50: Glasses and Glas Transition II

Time: Thursday 12:15–13:00

Location: ZEU 255

CPP 50.1 Thu 12:15 ZEU 255

Analysis of glass transition for polymer melts using data-driven methods — ●ATREYEE BANERJEE, HSIAO-PING HSU, KURT KREMER, and OLEKSANDRA KUKHARENKO — Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

Upon cooling, the dynamical properties of most polymer melt slow down exponentially leading to a glassy state without any drastic change in structure. While determining glass transition temperature and understanding the glass transition are important topics of current physical research, the properties in the glassy state are crucial for their general applicability. The conventional ways to calculate glass transition temperature from simulation data of polymer melts rely on the fitting of high- vs. low-temperature branches of macroscopic properties such as volume or density and are sensitive to the choice of parameters. We propose a new data-driven approach based on the information about structural fluctuations in the chains to identify the glass transition temperature. Our data-driven approach utilizes high-resolution details accessible through molecular dynamics simulations and considers the structural information of individual chains. The method was tested for coarse-grained weakly semi-flexible polymer model simulations [1]. It is also applied to the all-atom acrylic polymer simulations with different lengths of side-chain residues.

[1] Atreyee Banerjee, Hsiao-Ping Hsu, Kurt Kremer, and Oleksandra Kukharenko, arXiv:2211.14220 (2022)

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Roughness Induced Rotational Slowdown near the Colloidal Glass Transition — BEYBIN ILHAN, MICHEL DUTS, and ●FRIEDER MUGELE — University of Twente, Physics of Complex Fluids group

Rotational diffusion of colloidal spheres has been studied rarely, in spite of its importance in the kinetics of many processes involving friction. While for smooth hard spheres, rotational diffusion gets impeded only weakly with increasing volume fraction, the picture changes drastically when surface roughness is introduced. We show this for a system of undeformable all-silica colloidal raspberries, studied with time-resolved 3D Confocal Scanning Laser Microscopy (CSLM).

We find that the strong surface roughness leads to a significantly lower maximum volume fraction, preceded by a broad concentration range in which the rotational Brownian motion changes signature from

high-amplitude diffusive to low-amplitude rattling. This strong rotational slowdown occurs at significantly higher concentrations than for the translations, thus presenting a second glass transition.

In the regime where the Mean Squared Angular Displacement (MSAD) is subdiffusive, significant correlations are found between the translational and rotational motions. The drastic rotational slowdown occurs when the particle intersurface distance becomes comparable to the surface roughness amplitude. Concurrently, the number of contacts exceeds a critical value. This picture is supported by observations in a densely packed layer of raspberries at a smooth wall: here significant rotational motions are found while the translations are almost completely frozen.

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When molecular heterogeneities matter: thermal expansion and relaxation time in polyalcohols — ●MARTIN TRESS¹, JAN GABRIEL², and FRIEDRICH KREMER¹ — ¹Universität Leipzig, Leipzig, Germany — ²Roskilde University, Roskilde, Denmark

Structural relaxation in liquids is considered to depend directly on the available free volume. Many theoretical concepts of liquid dynamics and the glass transition approximate this molecular quantity using macroscopic density. However, particularly hydrogen (H-) bonding liquids defy proper description by these approaches (e.g. the failure of density-scaling in such materials). To study densification on molecular scale, we use infrared spectroscopy on a series of polyalcohols. By analyzing specific molecular vibrations and correlating them with interatomic bond lengths, the thermal expansion of several types of intramolecular covalent bonds and intermolecular H-bridges is quantified. Pronounced differences between intra- and intermolecular expansion verify the dominance of the latter. Surprisingly, the overall thermal expansion (i.e. cube root of inverse density) is even bigger than that of the strong H-bridges. This suggests that weak H-bridges dominate thermal expansion while strong ones must control structural relaxation, i.e. the glass transition. The method is validated by successfully describing the density of water based on extracted H-bridge lengths. Consequently, inhomogeneities on intra- and intermolecular scale can play distinct roles in densification and orientational relaxation and require a careful consideration in a comprehensive theoretical description. [Gabriel, Tress et al. J Chem Phys 154 (2021) 024503]