Stress correlations in glass-forming liquids

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Background. Many liquids cooled to low temperature do not crystallize, but stay amorphous upon freezing. The amorphous solid is called “glass”. On cooling the liquid toward the glass, the viscosity of the liquid increases dramatically. Since the viscosity can be expressed as the time-integral of the shear relaxation modulus $G(t)$, the increase of the viscosity implies that the decay of $G(t)$ with time t strongly slows down. Within the framework of nonequilibrium statistical mechanics $G(t)$ can be defined by the auto-correlation function of the wave-vector ($\boldsymbol{q}$) dependent shear stress in the limit $q \to 0$. A more general quantity is therefore the wave-vector and time dependent correlation function $\boldsymbol{C}(\boldsymbol{q},t)$ of the shear stress. This function is tensorial in nature and encapsulates the intricate interplay of relaxation phenomena (via t) and structural correlations (via $\boldsymbol{q}$) of the local shear stress. For glass-forming liquids $\boldsymbol{C}(\boldsymbol{q},t)$ has attracted a lot of attention in the recent past (see e.g. [1–3]) because it is found that the slowing down of the dynamics upon cooling is accompanied by the emergence of elastic features, typical of solids. In particular, these solid-like features give rise to long-range spatial correlations that can be probed by $\boldsymbol{C}(\boldsymbol{q},t)$. This function is therefore an appealing candidate to unravel hidden spatio-temporal correlations underlying the transition from the liquid to the glass, a topical problem in current condensed matter physics.

PhD project. The project builds on recent and ongoing work in our group [3,6]: It will employ Monte Carlo (swap algorithm [4]) and molecular dynamics (MD) simulations of two-dimensional (2D) polydisperse Lennard-Jones (LJ) systems to explore the spatio-temporal correlations of $\boldsymbol{C}(\boldsymbol{q},t)$. Since the stress correlations are expected to be long-ranged, large systems must be studied, up to the largest sizes currently feasible [5]. While 2D systems allow for such large sizes, they have 2D-specific long-range correlations, first recognized by Mermin and Wagner in the 1960s (see e.g. [7]). These correlations need to be characterized [5] and disentangled from those of $\boldsymbol{C}(\boldsymbol{q},t)$. For small wave-vectors the theory of $\boldsymbol{C}(\boldsymbol{q},t)$ has been developed either using the Zwanzig-Mori projection operator formalism [1] or via the fluctuation-dissipation theorem (FDT) [3,6]. Both approaches express $\boldsymbol{C}(\boldsymbol{q},t)$ in terms of memory kernels that describe the impact of prior fluctuating forces on stress correlations at time t. While the memory kernels are formal objects in the projection operator formalism, our FDT-based approach suggests a method to determine them via an adapted force field in the MD simulations. This method shall be explored in the project. If successful, it would not only be a fascinating addition to the MD toolbox, but also contribute to the vibrant field to develop microscopically founded coarse-graining procedures for dynamic and transport properties.

Profile. The PhD project involves extensive computer simulations and data analysis based on advanced theoretical concepts. The candidate must have a disposition for numerical work and theory. A good background in statistical physics and in programming is required.

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