

## DEVELOPMENT OF STRUCTURAL DESCRIPTORS FOR THE MOBILITY OF GLASS FORMING LIQUIDS

Understanding the mechanism behind the extreme slowdown of liquids as they transition to glass has eluded scientists for over a century. In amorphous condensed matter the mobility, defined as the reciprocal of the main relaxation time, drops over several orders of magnitude as the material approaches the glass transition via cooling. Once in the glassy state, mobility can be increased in two primary ways: by heating back into liquid state or isothermally by applying a large deformation past the yield point, which makes the material flow. Although the dynamic effects are clear, understanding into the structural origin of the mobility change due to either temperature or deformation is still an open question.

Historically there have been efforts to develop a physically significant structural descriptor which captures both the temperature and deformation dependence of the mobility. Some phenomenological models, such as the VFT equation, can capture the temperature dependence, but say nothing of the deformation. Conversely, several models phenomenologically describe the rise in mobility with increasing strain rate or stress, but are silent on the effect of temperature. The free volume model is the most popular model that attempts to unify both the temperature and deformation dependence. It states that the mobility is driven by the amount of available free volume, i.e., the total volume minus the hard-core volume. The free volume model has multiple challenges, however. First, as temperature is decreased, the glass transition can occur isochorically. Second, compression experiments on materials lead to flow after the yield point and a significant increase in mobility despite a decrease in the specific volume.

Since the advent of computing there have been attempts to use molecular dynamic (MD) simulations to tackle the problem of the glass transition and glassy state. For historical reasons, there has been an artificial divide in the MD field, where simple model systems have been used to study the temperature effects and the polymeric models to study the deformation effects. In this work MD simulations are performed on three model systems, a binary mixture of Lennard-Jones spheres, a single component system of Lennard-Jones dumbbells, and a trimer representing a coarse-grained version of orthoterphenyl, an experimentally well-known molecular glass former. For the first time, both temperature and deformation effects are studied on the same systems. Simulation provides several advantages over real experiments, first of which is that system in a simulation box, unlike real-life molecular glasses, does not experience macroscopic failure. Second, the structural descriptors which have been analyzed in the simulation are not experimentally accessible. Comparing the deformation of molecular glasses to that of the polymeric glasses allows for the deconvolution of the generic glassy effects and the polymeric effects.

The relaxation times are extracted from the decay of the self-intermediate scattering function (SISF). For an isotropic i.e., undeformed case there is a single SISF. For a uniaxially deformed system there are two different SISF in the direction of deformation and in the orthogonal direction. A method has been developed for analyzing the SISF in the deformed case, where two different relaxation times are extracted.

Finding the descriptor which unifies the temperature and deformation effects has been an overarching goal of this project. Multiple candidates were tested. The mean squared force per molecule was the first considered, where it was found that the mean squared force is able to capture the temperature dependence of the relaxation time. However, in case of the deformation the extra force due to macroscopic deformation is orders-of-magnitude too weak to affect the

molecular forces and, hence, does not predict the large change in mobility. Other candidates that proved inadequate included the mean and the variance of the molecular Voronoi volume.

The energy landscape has been used as an explanatory concept for the dynamics of glass forming systems for decades. The idea is that the interatomic potential of the system defines a landscape in high-dimensional configurational space that is a collection of crests and basins. The inherent structure energy is the depth of an energy landscape basin which is determined via gradient descent. The system is thought to constantly transition from the basin it is currently in to an adjacent basin, and at low temperatures the relaxation time would be related to the energy barrier between the basins. From the perspective shared to date by the research community, the inherent structure energies are unimportant whereas the barriers are. Decades of pursuing this idea have not yielded the description of the relaxation time as a function of temperature and deformation. In this work we show that, contrary to the previous beliefs, the inherent structure energy is the long-sought descriptor that unifies the temperature and deformation behavior. The result is demonstrated across the systems analyzed. Discovery of this unification represents a significant step forward in describing the glassy state.

Another result with significant implications to the theory of glass is related to the effect of deformation on not just the longest relaxation time but the relaxation time spectrum as whole. It has been long assumed that breadth of the spectrum in glass forming material is due to the dynamical heterogeneity – an experimentally established phenomenon. Then the narrowing of the spectrum observed in polymeric glasses under deformation is taken as a consequence of decrease in heterogeneity. In our simulation of molecular systems, it is found that specifically under uniaxial compression the narrowing of the spectrum is complete where it becomes exactly single-exponential. As it is inconceivable that the nanometer scale dynamical heterogeneities are eliminated in compression but not in extension, the prevailing hypothesis is severely challenged. Alternative mechanism connecting the relaxation time spectrum to the tortuosity of the path a molecule in condensed matter must follow has been proposed.