The Impact of Confinement on Entropy and Liquid-State Dynamics: Thermodynamic Expectations and Experimental Trends

Jeetain Mittal
Department of Chemical Engineering, The University of Texas at Austin, TX 78712
Thomas M. Truskett
Department of Chemical Engineering and Institute for Theoretical Chemistry,
The University of Texas at Austin, 1 University Station, C0400, Austin, TX 78712

The dynamics of a liquid in the vicinity of an interface can be very different than that of a bulk sample. One commonly cited experimental manifestation is the confinement-induced shift of a material's glass transition to either higher or lower temperatures. Two factors are believed to play a role in determining the magnitude and the sign of this shift: (i) the spatial dimensions of the confined sample, and (ii) the nature of the confining interfaces. Unfortunately, because molecular-scale properties in highly inhomogeneous environments are difficult to resolve experimentally, a mechanistic picture for precisely how these factors impact dynamics has been slow to develop. In this talk, we will explore whether there are any basic trends in the dynamical properties of confined liquids that might be expected based on simple thermodynamic arguments.

For bulk liquids, there are two well-known and empirically successful (although still incompletely understood) correlations between the temperature dependencies of dynamics and thermodynamics. The first is Adam-Gibbs theory [J. Chem. Phys. **43**, 139 (1965)], which relates mean relaxation times in deeply supercooled liquids to their configurational entropy. The second is a scaling relationship proposed by Dzugutov [Nature (London) **381**, 137 (1996)] between the diffusion coefficient of liquids and their excess entropy. In this talk, we use three different statistical mechanical models to calculate how the entropy of the liquid state is affected by confinement. Our results, when viewed in the context of the Dzugutov and Adam-Gibbs relations, paint a coherent picture for what “thermodynamics” would predict about the possible consequences of confinement on diffusivity and the glass transition. We will describe that picture and how well it compares to experimental trends.