55d Density Fluctuations, Interparticle Attractions, and the Dynamics of Simple and Complex Fluids

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Simple liquids get progressively more sluggish when cooled and, if they can avoid crystallization, form a glass when their temperature becomes low enough that intermolecular attractions substantially outweigh the thermal energy (~kT). These liquids, like suspensions of hard spheres, can also vitrify if they are isothermally compressed to high volume fractions. Suspensions of colloidal particles with both hard-core repulsions and short-range attractions, on the other hand, can show very different dynamical behaviors [1]. These systems can display diffusivity maxima at constant particle packing fraction as a function of the strength of their intermolecular attractions (relative to kT) [2]. In fact, they can even form two different types of glasses (a “repulsive glass” and an “attractive glass”) at the two extremes of the interparticle energy spectrum. While there has been a surge of interest in this latter type of colloidal suspension, both the microscopic origins of its unusual dynamic behavior and its connection to simpler liquids are still incompletely understood.

In this talk, we show that the diffusivity behaviors of hard spheres, simple liquids, and complex colloidal fluids can all be predicted from, and understood within, a common framework. In particular, we introduce a model that relates the self-diffusion coefficients of these fluids to (i) the reversible work required to create a “free path” for a particle of lengthscale greater than the localization length of the material and (ii) the time scale required for the particle to traverse this path. We use our model to analyze and understand molecular dynamics simulation results for the three aforementioned systems. The predictions provide new insights into the connections between thermodynamics and dynamics in these systems under static conditions and suggest future extensions for understanding the behaviors of liquids and colloidal suspensions under shear.

[1] F Sciortino, Nature Materials, 1 (2002) 145.

[2] AM Puertas, M Fuchs, ME Cates, Phys. Rev. E, 67 (2003) 031406.