I. RESEARCH INTERESTS

Our basic assumption is that complexity has an underlying set of simple explanations. Whether the complexity arises from the formation of extended networks as in micelles or fibrils, or local networks such as in the case of the clusters found in liquid water, or the the structural frustration and particle entrapment as found in glasses, presumably nature approached these issues with a simple algorithm. Over the last decade, our focus has been to try to understand what is a minimalist model for any of the above, aware that some issues may or may not surrender to a theme of reductionism. To begin, we think of processes as energy- or entropy-driven. Energy-driven processes are clearly those involving self assembly, whereas when structural confinement is the primary concern, as in a glass, we think of the process as entropy-driven.

A. Self assembly and energy-driven processes

Self assembly simply implies the non-catalytic formation of network fluids. A good example is the formation of a micelle at the cmc (critical micelle concentration). Above the cmc, we have aggregates, below the cmc we have a broad distribution of $n-$mers, where n ranges form 1 to 100. Our focus on self assembly starts from the point of view that each associating monomer has a small set of attractive spots on its otherwise hard spherical exterior. The arrangement of attractive spots defines the connectivity of the network, whereas the extension of the network is determined by temperature and fluid density. Network formation is clearly an energy-driven process. By means of the point-attraction models, we have been able address a few aspects of the thermodynamics of liquid water, fibrils, and polymers. For these varied systems, exact solutions of the PY integral equations are possible, as we have calculated coordination numbers, radial distribution functions, as well as the usual thermodynamic properties, heat capacities, enthalpies, compressibilities.

Hydrogen bonded fluids have interesting dynamics as well. The dynamics of bond-breaking, molecular rotation and translation were addressed using models based on an intermolecular potential for water being comprised of a hard spherical surface with tetrahedral H-bond attractive sites.

The collective lessons learned from our work emphasizes the bounds on what simple models can and can not do. Our studies have ignored the dipole moments of water as well as the attendant dielectric constant! Our cavalier attitude has consequences, e.g., the derived heat capacity is only sixty percent of the true heat capacity. Simplicity has a price.

B. Supercooled liquids and entropy-driven processes

Super cooled liquids and their limit, glasses, are complicated thermodynamic (or non-thermodynamic) states. Experimental evidence of Sillescu and Ediger suggests that the venerable Stokes-Einstein law (relating shear viscosity to self diffusion coefficient) breaks down as a liquid approaches a glass. On the approach to a glassy state, nearly all molecular time correlation functions lose their exponential or at times, diffusional long time decays, and become power law with fractional, non-rational exponents. Further, thermodynamic and transport properties adopt non-Arrhenius temperature dependence. Glassy behavior is non-universal in many ways, some organic glass formers, are fragile (i.e., its viscosity drops like a stone on heating the glass) whereas others, like silicates are strong, showing a gradual Arrhenius decay of its viscosity. Our focus on supercooled has been the the linear and angular velocity time correlation functions, relevant for self and rotational diffusion, respectively, and the Stokes-Einstein and Stokes-Einstein-Debye relations.

Specifically, we re-derived the Stokes-Einstein relation for fluids of hard spheres, hard ellipsoids, nematic liquid crystals and for fluids of hard spheres with a thin appended square well. For hard spheres, we have used a combination of correlated collision kinetic theory with hydrodynamic modelling of the memory functions to construct the SE relation. For non-spherical bodies, we have used so-called Enskog theory which looks at the uncorrelated collision limit. For the soft sphere case, we constructed the appropriate two-, three- and four-body correlation functions necessary to emulate the force correlation functions, needed for self diffusion, and the stress correlation functions, needed for the shear viscosity.

At this moment, the picture emerging from all of the above is the following. The jagged landscape of nearly frozen fluids demands a complex free energy. Particle entrapment is long in duration and the events leading to relaxation are rare. Particles are entropically trapped, but if their energy is sufficiently high, they can squeeze through tight openings. The issue then is how to implement the rugged free energy landscape,

coupled with the infrequent crossing of potential barriers that governs all transport properties properties in a fluid. Further, since all properties are limited by the same aspects of entrapped frustrated trajectories, then all transport properties should behave similarly. This is one direction for future research.

C.   Overview

Generally, future research will be concerned with the implementation of the proper free energy into the equations of motion that predict the dynamics of the system. Be it the dynamics of freezing, phase separation, glass formation and micelle kinetics, one would hope that a proper free energy can be found, tailored of course to the relevant physics, that will capture the fluctuations around the equilibrium as well as the transition to new minima on the free energy landscape.