

Abstract

Fluid molecules confined between solid surfaces separated by a few nanometers are of considerable interest in nanoscience and nanotechnology as they undergo structural and dynamical transitions absent in their corresponding bulk counterparts. The underlying microscopic structure and dynamics can be probed using molecular dynamics simulations both at experimental conditions as well as under extreme confinement which are difficult to assess in experiments. The phase state of octamethylcyclotetrasiloxane (OMCTS), a molecular liquid confined between two mica surfaces which is predominantly studied in surface force experiments had been a long-standing controversial debate. In this thesis, we examine the structure and dynamics of OMCTS confined between two infinite mica surfaces considering a fully atomistic model using molecular dynamics simulations. We present a strong evidence for a fluid undergoing dynamical slowdown characteristic of glassy dynamics at experimental conditions. The self-diffusion coefficient and the α relaxation time of the self-intermediate scattering function are in accordance with the scalings predicted by the mode-coupling theory. A distinct discontinuity in the Helmholtz free energy, potential energy, and a sharp change in the local bond order parameter, Q_4 , was observed for a five-layered system at 35 K below the bulk melting point of OMCTS, indicative of a first-order transition. These dynamical signatures indicate that confined OMCTS undergoes a slowdown akin to a fluid approaching a glass transition upon increasing confinement, and freezing under confinement would require substantial subcooling below the bulk melting point of OMCTS.

The above study was extended for a pure component, monatomic Lennard-Jones (LJ) fluid confined between mica surfaces. Lennard-Jones fluids are excellent representations of spherical soft-sphere fluids, small non-polar molecules and monatomic inert gases. A Lennard-Jones fluid has no glass transition temper-

ature by itself and can undergo freezing under extreme confinement. However, the presence of a structured wall can manifest structural and dynamical heterogeneities for a spherical molecule to a greater extent than that observed for anisotropic polyatomic molecular fluids such as OMCTS, cyclohexane and dodecane. We show that a LJ fluid can exhibit multiple relaxation dynamics with signatures of a strong glass former when confined in a specific range of surface separations at a constant temperature without supercooling.

Lastly, our understanding of the dynamics of fluids at interfaces have been extended to investigate biological systems. Pore forming toxins (PFT's) are a special class of proteins secreted by bacteria as water soluble monomers. When bound to the cell membrane, they self assemble and undergo significant conformational changes and form membrane bound oligomers. PFT's are classified as α -PFT and β -PFT depending on the dominant structure in the transmembrane domain of the lipid bilayer. The dynamics of the lipid molecules constituting the 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC) bilayers was investigated for two classes of completely oligomerized PFT's bounded on the lipid bilayers (i) Cytolysin-A (α -PFT) and (ii) α -Hemolysin (β -PFT). We show that α -PFT perturbs the lipid molecules of the upper leaflet to a greater extent than the β -PFT. Interestingly, the lipid molecules in the lower leaflet were more fluidic for the α -PFT bound lipid bilayer than the β -PFT bound lipid bilayer.

Together, our study provides a molecular understanding of dynamics unravelling the structure property relationship for various systems on a molecular level.