Structural and Mechanical Properties of Glassy Water in Nanoscale Confinement

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Poster (2:20 PM)

Thin water films are prevalent in nature and engineering applications. Understanding the behavior of confined water is an important aspect in many areas such as the origin of the induced attraction between hydrophobic protein surfaces (i.e. the hydrophobic effect), the preservation of biomolecules in glassy carbohydrate-water matrices, and in the development of wet "lab on a chip" technologies. Complications from the confining geometry and surface chemistry often alter the thermodynamic and kinetic behavior compared to the bulk. Examples include wetting phenomena, shifts in phase transitions, and the formation of interfacial layers with decreased mobility and sluggish dynamics.

We investigate the structure and mechanical properties of glassy water confined between silica-based surfaces with continuously tunable hydrophobicity and hydrophilicity. Minimum energy, mechanically stable configurations (inherent structures) [1] and glasses formed from quenches are analyzed. The structured silica substrate imposes long-range order on the first layer of water molecules under hydrophobic confinement at high density ($\rho > 1.0$ g/cm^3). This proximal layer is also structured in hydrophilic confinement at very low density ($\rho \approx 0.4$ g/cm^3). The ordering of water next to the hydrophobic surface greatly enhances the mechanical strength of thin films (0.8 nm). This leads to a substantial stress anisotropy; the transverse strength of the film exceeds the normal strength by 500 MPa. The large transverse strength results in a minimum in the equation of state of the energy landscape [2] that does not correspond to a mechanical instability, but represents disruption of the ordered layer of water next to the wall. In addition, we find that the mode of mechanical failure is dependent on the type of confinement. Under large lateral strain, water confined by hydrophilic surfaces preferentially forms voids in the middle of the film and fails cohesively. In contrast, water under hydrophobic confinement tends to form voids near the walls and fails by loss of adhesion [3].

[1] Stillinger, F.H., and Weber, T.A., *Physical Review A*, *25*, 978, 1982.
[2] Debenedetti, P.G., Stillinger, F.H., Truskett, T.M., and Roberts, C.J., *Journal of Physical. Chemistry B*, 103, 7308, 1999.
[3] Shah, P., and Truskett, T.M., *Mechanics of Materials*, 38, 924, 2006.