Dynamics of molecules at confined interfaces: viscous water and nano tumbleweed

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Abstract:

Molecules adsorbed on surfaces or confined between interfaces of nanoscopic separation are common to a large number of processes in chemical, physical, and biological processes. The motion of these molecules is hindered due to restrictions in spatial and conformational freedoms and interaction with the surface. We demonstrate dramatic consequences of this confinement effect using two examples. In the first example, we measure the viscosity of water adsorbed on hydrophilic surfaces. On the nanometer thickness scale, the adsorbed water (hydration layer) on hydrophilic molecular or solid surfaces has an effective viscosity which is over one million times greater than that of bulk water at room temperature. This viscous water layer corresponds to the "ice-like" or structured water layer suggested by vibrational spectroscopies. We propose that the unique properties of interfacial water is not due to ordering or increased hydrogen bond strength, but is simply a consequence of confinement. In bulk water, breaking a hydrogen bond costs little energy due to the nearly simultaneous formation of a new hydrogen bond. However, in a confined environment within the adsorbed water layer, breaking a hydrogen bond is hindered due to the lack of assistance by the formation of a new one. This may explain the much increased viscosity. In the second example, "*a nano tumbleweed*", we show the chemical consequence of noncovalent interaction with the local environment on a surface confined (tethered) macromolecule. We study the surface initiated polymerization of a hydrophilic polymer, hyperbranched polyglycidol (HPG), on a hydrophobic surface. We grow a self-assembled monolayer of a small percentage of –COOH terminatd alkanethiols in a matrix of–CH_3 terminated alkanethiols on Au. The hydrophilic –COOH groups serve as initiation sites for HPG growth. As each HPG molecule grows, it inevitably encounters unfavorable local environment of the hydrophobic (-CH_3) surface. We find using tapping-mode atomic force microscopy that the HPG molecules break away from the surface when they grow to certain size. Breaking a covalent bond to the surface becomes energetically favorable because a free HPG molecule can form a much larger number of hydrogen-bonds to other glycerol molecules in the liquid phase.