Investigating Odd-Even Behavior in Wetting by Molecular Dynamics Simulation

P. Srivastava[S] and W.G. Chapman
Department of Chemical and Biomolecular Engineering, Rice University, Houston, U.S.A.

P.E. Laibinis[C]
Department of Chemical Engineering, Vanderbilt University, Nashville, TN, U.S.A.
paul.e.laibinis@vanderbilt.edu

The macroscopic property of wettability is often the result of molecular-scale interfacial effects. Recent abilities to experimentally access molecularly tailored surfaces have revealed new insights into the molecular origins of wetting, however simulations to investigate these experimental results have been rare. This talk will describe the results of molecular dynamics (MD) simulations that explain the unexpected experimental observation that the wetting properties of some liquids on monolayers prepared using alkanethiols (CnSH) depend on whether the chain length (n) is odd or even. Fundamental information, that is not available experimentally, about whether these differences are due to surface reorganization events or to attributes of the near-surface liquid films, is provided by our simulations. To study this system, we performed MD simulations of systems that included a droplet of either 256 water molecules or 60 hexadecane molecules localized on a supported alkanethiol monolayer, which had either an even or odd chain length. We selected hexadecane and water as the liquids used in these simulations, because the former experimentally exhibits a large odd-even variation in wetting, while the latter displays none. In our simulations, the contact angles calculated for these nanoscopic droplets were consistent with observed macroscopic trends in wettability. MD simulations revealed that the effects of these solvents on the monolayer structure were restricted to the chain terminus, and had no effect on its inner structure. The density profiles for the liquids were different, in that the water displayed a significant depletion in its density in the near-surface region, while no such depletion occurred for hexadecane. This difference in the near-surface structure of the liquid (and not that of the reorganization events by the monolayer) appears to be responsible for the high sensitivity of hexadecane and the general insensitivity of water to the structural differences expressed by odd- and even-chained monolayer surfaces.