Cavitation in the Interaction Between Superhydrophobic Surfaces

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Motivation—The unique interaction of hydrophobic surfaces in water has been implicated in such diverse effects as protein folding, micelle assembly and the large-scale, ordered assembly of specifically functionalized components. In addition, there has been considerable debate over the last 20 or so years over the so called long-range hydrophobic force, which is often seen to decay exponentially with interfacial separation, is stronger by one or two orders of magnitude than that expected from the van der Waals force and ranges over several tens of nm. We have probed the interaction of Sandia-developed superhydrophobic (SH) surfaces in water with the Interfacial Force Microscope (IFM) in an attempt to shed light on this elusive force and have compared the results with state-of-the art calculations.

Accomplishment—The experiments consist of using the IFM to measure the force as a SH tip and surface approach. The SH surfaces are a porous silica gel functionalized to be hydrophobic. The several 100 nm scale surface roughness renders these surfaces superhydrophobic in a manner similar to a Gecko's foot pad or the Lotus leaf. Water contact angles near 170° indicate that water does not want to be near this surface. As the IFM tip approaches, we observe the sudden nucleation of a cavity (bubble) between the tip and sample creating a large attractive force on the tip (Fig. 1). Continuing the tip motion inward signals tip/substrate contact by the appearance of a rapidly increasing repulsive force. This allows the IFM to obtain the distance from contact over which the cavity nucleates. Surprisingly, this distance is often found to be larger then a micron, a fact which is hard to accept on the basis of simple surface tension arguments.

In order to try to get a better understanding of the process and the role of fluctuations, we have undertaken molecular dynamics simulations of cavitation. We studied cavitation in a slit-like pore with wall-fluid interactions chosen to produce a contact angle of zero degrees (complete wetting). To mimic the experiment an SH stripe was created on each wall. Two hemicylindrical vapor bubbles start to develop. Mechanical and chemical equilibrium conditions imply that these two new menisci must grow and adopt the same radius of curvature as the two outer vertical menisci. This process eventually leads to merging, i.e. cavitation. This phase transition is preceded by intense fluctuations that ultimately produces the rupture of the thin liquid film. The vapor pressure of the newly emerged vapor bridge is initially too high, and the system quickly restores mechanical equilibrium by simultaneously expanding the bubble and changing the curvature of the menisci to convex.

Significance—Although cavitation, or capillary evaporation as it is sometimes called, is expected to occur when two SH surfaces are brought closely together, the gap size for which this takes place in the IFM experiment is larger by several orders of magnitude than would be predicted on the basis of simple surface tension arguments. Although the vapor bridge connecting both surfaces may be the stable configuration when the gap is approximately micron-sized, one would ordinarily expect a configuration of the liquid film separating the two independent vapor regions to continue to be quite stable, indicative of the presence of a free energy barrier. The experimental observations suggest therefore that the liquid film must somehow be destabilized. Fluctuations are a likely candidate for this scenario, and this is substantiated by the MD results, albeit that the simulation represents a much smaller length scale. Visual observations also indicate significant density fluctuations just prior to cavitation.

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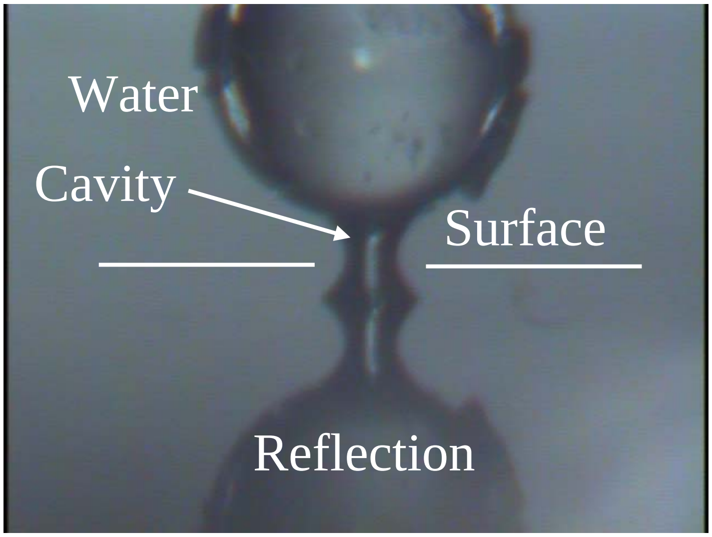

Figure 1. The IFM tip is shown at the top, while the SH surface is indicated by the horizontal lines. The tip and cavity reflection is shown at the bottom of the figure.

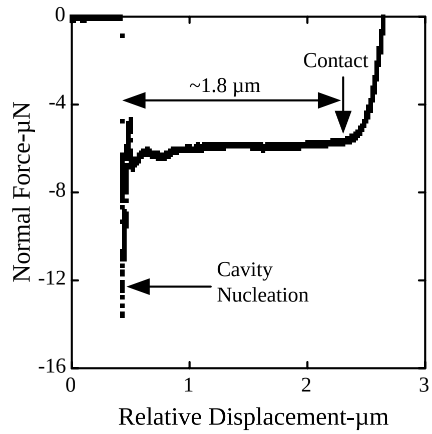

Figure 2. The IFM tip is approaching from the left and nucleates the cavity creating a large attractive (negative) force. It then moves an additional 1.8 μm before contacting the substrate.

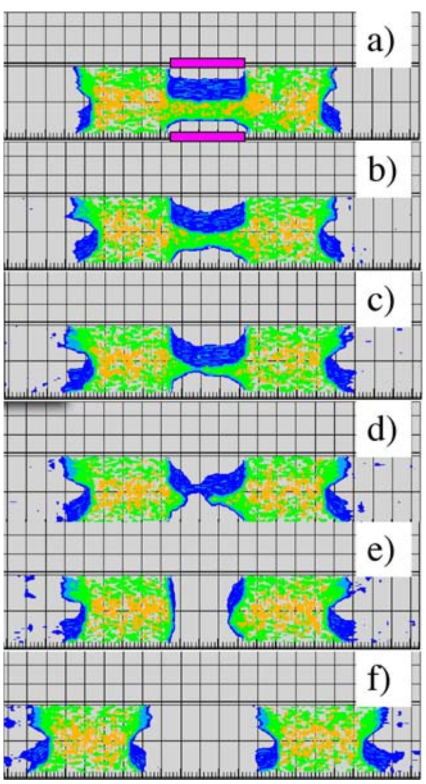

Figure 3.. Molecular dynamics results of cavitation inside a capillary slit. At time is zero a SH patch (indicated by purple bars) is created on the walls of an otherwise hydrophilic slit. The SH patch stimulates the growth of two vapor bubbles (a-c), separated by a thin liquid bridge. The liquid bridge ruptures (c-d) corresponding to cavitation. Panel (f) shows the final equilibrium state when all menisci have reached the correct curvature.