Short-Range Hydrophobic Repulsion Revealed by FM-AFM

Uri Sivan* and Itai Schlesinger

Department of Physics and the Russell Berrie Nanotechnology Institute, Technion – Israel Inst. of Technology, Haifa 32000, Israel

**phsivan@tx.technion.ac.il*

Most studies of the hydrophobic interaction between two surfaces were carried out using a static AFM or a Surface Force Apparatus. The force curves indicate attraction commencing at distances shorter than 3-10 nm. However, both instruments suffer from mechanical instability at shorter distances when the gradient of the attractive force exceeds the instrument rigidity. As a result, data pertaining to distances shorter than 2-3 nm are scarce and the sign of force, let alone its form are unknown. Here, we report measurements of the hydrophobic interaction using a Frequency Modulation AFM (FM-AFM) that utilizes 2-3 orders of magnitude stiffer cantilevers that grant it stability over the entire distance range. At long distances, where traditional instruments are stable, the FM-AFM results reproduce the known attraction but at distances shorter than 1-2 nm, where traditional methods are blind, FM-AFM reveals that the attraction turns into pronounced repulsion. This striking deviation from the expected attraction helps rejecting various published explanations of the hydrophobic interaction.

The force measured between a silicon wafer coated with FDTS (114^0 contact angle) and a 40 N/m spring constant silicon cantilever coated with hydrophobic diamond-like carbon (DLC, 65^0-80^0 contact angle) is depicted in Fig. 1, together with a force curve taken with static AFM and a 0.3 N/m cantilever. The instability at ~3.2nm and jump to the repulsive regime are clearly observed in the latter.

The individual force curves all show clear attraction at long distances, turning into short-range repulsion. The experimental attraction is clearly larger than the vdW one, indicating a different origin. Integration of the force over the entire interaction range suggests hydrogen-bond physics. The inset depicts the cantilever dissipation judged from the excitation power needed for maintaining a constant cantilever oscillation amplitude. The dissipation is two orders of magnitude higher compared with hydrophilic surfaces or theoretical calculation (black solid line) of the hydrodynamic drag, suggesting that the medium between the tip and the sample is different from incompressible water (possibly, vapour or air-rich water). As disclosed by the figure, dissipation starts at the same distance as attraction, indicating that the same mechanism leads to the conservative and dissipative components of the force.

In the talk, we will offer a potential explanation for the observed repulsion and the anomalous viscosity.

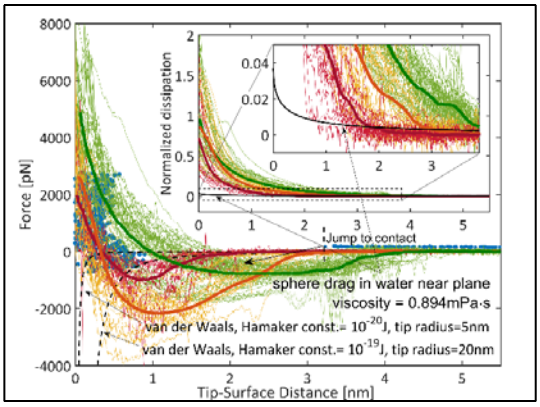

Figure 1: Main Panel - Thin lines depict individual force vs. distance curves taken with FM-AFM. Thick lines - averages over the individual curves. Black dashed lines - van der Waals attraction for the nominal tip (5 nm tip radius and 10^{-20} J Hamaker constant) and upper bound (20 nm radius and 10^{-19} J Hamaker constant). Blue dots – force curve taken with static AFM and soft cantilever. Inset: Normalized dissipation compared with calculation for a 5nm radius sphere in water, including the effect of surface under non-slip condition (black solid line).