Supporting Information for

Probing Hydrophobic Interaction between Air Bubble and Partially Hydrophobic Surfaces Using Atomic Force Microscopy

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1. Force measurements using deformable bubble probe, compared with solid colloid probe

Atomic force microscopy has been widely applied for topographic imaging and force measurements of various surfaces and materials.\textsuperscript{1,2,3} Our work focuses on the interaction between a deformable air bubble and partially hydrophobic substrates. The major differences in AFM force measurements using conventional solid colloid probe and deformable bubble probe are provided below.

Figure S1. Schematics of AFM force measurements and typical results (force vs. cantilever displacement, or force vs. separation) using (A) a solid colloid probe and (B) a deformable bubble probe.

Figure S1A and S1B illustrate the working principle of AFM in typical force measurements and interpretation of typical results using a solid colloid probe and a deformable bubble probe,
respectively. During a typical force measurement, the probe is first driven towards and then away from the sample surface, viz. the separation between cantilever and surface, first decreases and then increases. The cantilever displacement $\Delta X(t)$ is measured by a linear variable differential transformer. The force $F$ is determined using Hooke’s Law $F = K \Delta D$, where $K$ is the spring constant of cantilever and $\Delta D$ is the deflection or displacement of cantilever. During the measurement, the deflection of cantilever can be monitored with time, thus the evolution of the force and deflection of cantilever can be obtained. In AFM measurements, the precise separation between the probe and the sample surface cannot be directly measured (as different from force measurements using surface forces apparatus, SFA), but needs to be deduced indirectly from the data.

For a solid particle probe, upon contact with sample surface, the local deformation of the particle and the sample surface are generally considered much smaller and negligible as compared to the deflection of the cantilever, which can be considered as the “zero separation” (reference position of the cantilever). Therefore, by subtracting the deflection of the cantilever at the reference position from $X(t)$, the separation between the probe and the sample surface can be obtained, as shown in Figure S1A. For a deformable bubble probe, however, the bubble can be deformed in response to the external force and the deformation of the bubble cannot be neglected (particularly at short separation distance). Theoretical model is normally needed for the interpretation of the AFM results, which is discussed in Section 3. The AFM bubble probe allows the direct measurement of interaction involving deformable bubble, and has the following features as compared to solid colloid probe. First, the deformation of the bubble enlarges the effective interaction area to many times larger than that of a solid particle, which provides significantly enhanced sensitivity. Second, the surface of bubble is extremely smooth, far
smoother than the cleanest solid particle, and hence can provide reliable information, especially for force at small separations.\(^4\) The AFM bubble probe technique can also be extended to interactions between other deformable liquid drops.

2. Force measurement between bubble and substrate by AFM

During AFM measurements, the distance between the cantilever and the substrate, \(X(t)\), is controlled by a piezoelectric actuator, but the actual position of the cantilever is measured by a linear variable differential transformer (LVDT). The variation of \(X(t)\) as a function of time is monitored and used for data analysis.

2.1 Calibration of cantilever

The rectangular tipless cantilever (400 × 70 × 2 µm) with a circular gold patch of diameter 65 µm was custom fabricated. The circular gold patch was hydrophobized with 1-dodecathiol in absolute ethanol (10 mM) for bubble anchoring. The back side of the cantilever was coated with a layer of gold to enhance light reflection. The spring constant of the cantilever was determined using the Hutter-Bechhoefer method.\(^5\) The spring constants of the cantilevers used in the experiments were 0.3-0.4 N/m.

2.2 Force measurement

An AFM fluid cell was used for AFM experiments. The glass wall of the fluid cell was first boiled in absolute ethanol for 2h to achieve a water contact angle of \(~30^\circ\) for bubble immobilization and loading onto cantilever. After hydrophobization, \(~3\) ml aqueous solution was added to the fluid cell. Air bubbles were injected into the solution using a custom-made glass pipette of radius \(~10\) µm which were immobilized on the bottom glass wall of the fluid cell.
The sample substrate was then carefully added and immersed in the solution of the fluid cell, avoiding contact with the immobilized air bubbles.

During experiments, a bare cantilever was first driven towards the bottom glass wall of fluid cell to calibrate the deflection InVOLs, and its spring constant was determined using the Hutter-Bechhoefer method. Then the cantilever was positioned over an air bubble with diameter of 80-200 µm and was driven towards to pick up the air bubble. The hydrophobized gold patch (water contact angle of ~110°) was much more hydrophobic than the glass wall (water contact angle of ~30°) and the bubble would preferentially attach to the gold patch on the cantilever. The bubble probe was then positioned above the sample surface for force measurement.

3. Boundary conditions

Fig. S2 shows the comparison between experiment results and theoretical results with immobile and fully mobile boundary conditions for the interaction shown in Figure 4B (interaction between an air bubble with radius of 65 µm and mica-OTS-85 with velocity $v = 30$ µm/s)

The equation of lubrication theory with fully mobile/slip hydrodynamic boundary condition used here is as follows: 

$$\frac{\partial h}{\partial t} = \frac{1}{3\mu r} \frac{\partial}{\partial r} \left( rh^3 \frac{\partial p}{\partial r} \right)$$

which predicts a 4 times faster drainage rate than that with immobile boundary condition. It is clear that the forces calculated with the fully mobile boundary condition at the air-water interface
are too small compared to the experimental values whereas results using the no-slip/immobile are in excellent agreement with measured data.

**Figure S2.** Comparison between theoretical predictions with immobile and fully mobile boundary conditions of the interaction shown in Figure 4B (Interaction between air bubble with radius of 65 µm and mica-OTS-85 with velocity v = 30 µm/s). The open circle symbols are experiment results, and the solid red and blue lines are theoretical results with immobile and mobile boundary conditions respectively.

4. *Lifshitz-van der Waals force*

The calculated Hamaker function and disjoining pressure based on the full Lifshiz theory including the retardation effects are shown in Fig S3.
**Figure S3.** Calculated Hamaker function and van der Waals disjoining pressure profile between bubble and mica in 0.5 M NaNO₃ solution.

5. **Morphology of hydrophobized mica surfaces.**

The morphology of hydrophobized mica surfaces were investigated by AFM tapping mode imaging. Both surfaces show very low rms roughness ~0.3 nm.
Figure S4. AFM topography image of (A) mica-OTS-45 and (B) mica-OTS-85.

6. References:


