Supporting Information (SI)

Measuring Forces and Spatiotemporal Evolution of Thin Water Films between an Air Bubble and Solid Surfaces of Different Hydrophobicity

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SI Experiment

AFM force measurement

Force measurement between an air bubble and a solid surface was conducted using an Asylum MFP-3D Atomic Force Microscopy (AFM) following a previously reported procedure.1-3

The aqueous solution used in the AFM experiments was prepared using sodium chloride (NaCl, Fisher Scientific) with highest purity and Milli-Q water (Millipore deionized) with a specific resistivity greater than 18.2 MΩ·cm.

Before force measurement, a custom-made glass pipette with an ultra-sharp end was used to inject air bubbles into an AFM fluid cell filled with the aqueous solution to be tested. The glass substrate of the fluid cell was mildly hydrophobized by immersing in 10 mM
octadecyltrichlorosilane (OTS, ACROS Organics) solution in toluene for a few seconds that led to a water contact angle of \(~50^\circ\) on the glass substrate for bubble immobilization. An air bubble with suitable size (typical radius \(R_0\) of 60-100 \(\mu m\)) was picked up with a custom-made rectangular tipless cantilever (400 \(\times\) 70 \(\times\) 2 \(\mu m\)) to form an AFM bubble probe, as shown in Figure S1. The tipless cantilever has a circular patch of gold (diameter 65 \(\mu m\), thickness 30 nm) at the end, which was strongly hydrophobized in 10 mM dedcanethiol solution in absolute ethanol overnight to facilitate secure and precise anchoring of the air bubble. The spring constant of the unloaded cantilever was determined using the Hutter and Bechhoefer thermal tune method\(^4\). The effective spring constant of the loaded cantilever was validated using force data for bubble-hydrophilic mica interactions at all drive velocities (see below) and then used for in all experiments with hydrophobized mica.

Force measurements were conducted by driving the cantilever-loaded air bubble towards the solid surface from a large initial separation until bubble attachment occurred or until a desired deflection of cantilever was detected whereupon the cantilever was then driven away from the surface. The driving velocity of the air bubble was controlled by a piezo-actuator of the AFM. Time variation of the cantilever deflection was recorded for each measurement, which could be converted to forces \(via\) the spring constant. The actual variation of the cantilever-substrate separation, \(X(t)\), with time \(t\), during a force measurement was measured and recorded with a linear variable differential transformer (LVDT) that is part of the AFM. This data was used in the theoretical model for calculation.
**Hydrophobization of mica surfaces**

Freshly peeled mica surfaces were hydrophobized by exposing to OTS vapor at room temperature (23 °C) under vacuum. Different surface hydrophobicity, characterized by the contact angle $\theta_w$ made a sessile drop on the surface, measured through the water, was achieved by varying the exposure time. A 1-hour treatment typically leads to a water contact angle of 45° and 48-72 hours treatment can lead to a water contact angle of 90°. Before each experiment, the hydrophobized mica surfaces were rinsed with toluene, ethanol and Milli-Q water to remove any physically adsorbed OTS molecules. AFM tapping mode imaging was applied to investigate the surface roughness of these hydrophobized mica surfaces that showed rms roughness of ~0.3 nm.

**Theoretical model**

The Stokes-Reynolds-Young-Laplace model$^{1-3}$ reported before was applied to describe the interaction between air bubble and solid surfaces. Reynolds lubrication theory with immobile boundary condition at both air/water and solid/water interfaces was applied to model the hydrodynamic drainage of the nanoscale water film of thickness, $h(r,t)$ between the air bubble and solid surface,

![AFM bubble probe with bubble radius of 60 µm.](image)

**Figure S1.** An AFM bubble probe with bubble radius of 60 µm.
\[
\frac{\partial h}{\partial t} = \frac{1}{12\mu r} \frac{\partial}{\partial r} \left( rh^3 \frac{\partial p}{\partial r} \right)
\]  

(S1)

where \(\mu\) is the dynamic viscosity of water, \(p(r,t)\) is the hydrodynamic pressure. The film is taken to be axisymmetric, and is a good approximation for the present experiments as can be seen from the symmetry of the interference fringes.

The deformation of the bubble surface in response to the hydrodynamic pressure \(p(r,t)\) and the disjoining pressure \(\Pi(h(r,t))\) is described by the augmented Young-Laplace equation

\[
\frac{\gamma}{r} \frac{\partial}{\partial r} \left( r \frac{\partial h}{\partial r} \right) = \frac{2\gamma}{R_0} - p - \Pi,
\]

(S2)

where \(\gamma\) is the air-water interfacial tension, \(R_0\) is the bubble radius.

The interaction force \(F(t)\) is calculated by integrating over \(p(r,t)\) and \(\Pi(h(r,t))\)

\[
F(t) = 2\pi \int_0^\infty \left[ p(r,t) + \Pi(h(r,t)) \right] r dr
\]

(S3)

The equations were solved in a suitable region \((0, r_{max})\), where the local separation \(h(r,t)\) at \(r > r_{max}\) was sufficiently large so that the contribution of disjoining pressure could be neglected.\(^2\) Hence, the interaction force can be calculated as

\[
F(t) = 2\pi \int_0^{r_{max}} [p(r,t) + \Pi(h(r,t))] r dr + 2\pi \int_{r_{max}}^\infty p(r,t) r dr
\]

(S4)

In general, the first integral on the right side of Equation (S4) makes the dominant contribution to the calculated force and the impact of the second integral is rather small. In our calculation, the value of \(r_{max}\) was also checked to ensure the calculated force was independent on its exact value.

The boundary conditions for \(h(r,t)\) and \(p(r,t)\) at \(r = 0\) are \(\partial h / \partial r = 0\) and \(\partial p / \partial r = 0\). The actual variation of cantilever displacement \(X(t)\) was incorporated in a boundary condition, equation S5,
which took in account the deformation of the air bubble during interaction and the pinned contact area of the air bubble on the cantilever

\[
\frac{\partial h(r_{\text{max}}, t)}{\partial t} = \frac{dX(t)}{dt} + \frac{dF(t)}{2\pi \gamma dt} \left( \frac{2\pi \gamma}{K} \ln \left( \frac{1 + \cos \theta}{1 - \cos \theta} \right) - \ln \left( \frac{r_{\text{max}}}{2R_0} \right) \right)
\] (S5)

Here \( K \) is the spring constant of the cantilever, \( \theta \) is the contact angle of the air bubble on cantilever. The hydrodynamic pressure \( p(r, t) \) decays as \( r^{-4} \) at \( r \to \infty \), leading to the boundary condition \( r(\partial p / \partial r) + 4p = 0 \) at \( r = r_{\text{max}} \). The initial condition for \( h(r, t) \) follows the undeformed spherical bubble shape.

The equations above were solved numerically with MATLAB after being non-dimensionalized with the scaling parameters: \( h_c = R_0 \text{Ca}^{1/2}, \ r_c = R_0 \text{Ca}^{1/4}, \ p_c = \gamma / R_0, \ t_c = \mu \text{Ca}^{-1/2} \), where \( \text{Ca} = \mu V / \gamma \) is the capillary number and \( V \) is the nominal drive velocity. Details of the numerical method are reported previously.

**Van der Waals interaction**

The VDW disjoining pressure during interaction is calculated using the full Lifshitz theory\(^5,6\) that includes the effects of electromagnetic retardation. Denoting the air bubble, solid surface and aqueous solution as 1, 2 and 3, the VDW disjoining pressure \( \Pi_{\text{VDW}}(h) \) between two half spaces at separation \( h \) can be calculated as:

\[
\Pi_{\text{VDW}}(h) = \Pi_{\text{VDW}0}(h) - \frac{kT}{\pi c^3} \sum_{n=1}^{\infty} \epsilon_3^{3/2} \xi_n^3 \int_1^{\infty} p^2 \left[ (\Delta_1 \Delta_2 e^{-x} - 1)^{-1} + (\Delta_1 \Delta_2 e^{-x} - 1)^{-1} \right] dp
\] (S6)

\[
\Pi_{\text{VDW}0}(h) = -\frac{kT}{2\pi} \int_0^{\infty} p \sqrt{p^2 + \kappa^2} (\Delta_0 - 1)^{-1} dp
\] (S7)
\[
\Delta_i = \frac{s_i + p\varepsilon_i / \varepsilon_3}{s_i - p\varepsilon_i / \varepsilon_3}, \quad \Delta_i = \frac{s_i + p}{s_i - p}, \quad s_i = \sqrt{\varepsilon_i / \varepsilon_3 - 1 + p^2}
\]

\[
\Delta_0 = \left(\frac{\sqrt{p^2 + \kappa^2 \varepsilon_1(0) + p\varepsilon_3(0)}}{\sqrt{p^2 + \kappa^2 \varepsilon_1(0) - p\varepsilon_3(0)}}\right) \left(\frac{\sqrt{p^2 + \kappa^2 \varepsilon_2(0) + p\varepsilon_3(0)}}{\sqrt{p^2 + \kappa^2 \varepsilon_2(0) - p\varepsilon_3(0)}}\right) \exp\left(2\sqrt{p^2 + \kappa^2}\right)
\]

\[x = 2p\xi_n\varepsilon_2^{1/2}h/c, \quad \xi_n = 2\pi nk_B T/h, \quad \varepsilon_k = \varepsilon_k(i\xi_n)\]

where \(c\) is the speed of light in vacuum, \(k_B\) is the Boltzmann constant, \(T\) is the temperature, \((2\pi h)\) is the Planck’s constant, \(\varepsilon_k = \varepsilon_k(i\xi_n)\) is the dielectric permittivity, and \(\kappa^{-1}\) is the Debye length. Due to screening by high salt concentration in this study, the effects of zero frequency \((n = 0)\) term \(\Pi_{VDW_0}(h)\) was highly suppressed. The dielectric permittivity of water at imaginary frequencies was taken from previous report\(^6\) and the dielectric permittivity of mica was constructed from Cauchy plot data taken from the literature\(^7\).

**RICM image analysis**

Monochromatic green light with wavelength \(\lambda = 546.1\) nm was used for RICM imaging. The RICM interference patterns were obtained by a Nikon Ti-U inverted microscope and were recorded with a video camera. The obtained images were processed with the *ImageJ* software (National Institutes of Health, USA).
Figure S2. Schematic model of non-planar RICM image formation

Construction of film thickness profile from RICM interference patterns was achieved by an improved mathematical approach\(^8\) that can accurately reconstruct convex object with arbitrary shape by approximating its surface as an ensemble of wedges, as shown in Figure S2. According to the non-planar model, in a system with single interference layer (Figure S3), the light intensity at position \(x\) due to interference of light rays \(I_1\) and \(I_2\) can be calculated as

\[
I(x) = I_1 + I_2 + 2\sqrt{I_1I_2} \cos \left( \frac{2\pi}{\lambda} \left( 2n_1h(x_\alpha) \frac{\cos^2(\theta_R)}{\cos(\alpha + \theta_R)} \right) + \delta \right) \tag{S8}
\]

where \(\alpha\) is the inclination angle of the air/water interface at \(x = x_\alpha\), \(\theta_R\) is the reflective angle at the air/water interface, \(h(x_\alpha)\) is the thin film thickness at \(r = x_\alpha\), \(\lambda = 546.1\) nm is the light wavelength, \(n_1 = 1.333\) is the refractive index of water and \(\delta\) is a phase shift due to reflection, which is 0 here.
since the refractive index of air is less than that of water. According to geometry, $x$ and $x_\alpha$ could be related as

$$x_\alpha = x - h(x_\alpha) \tan(\alpha + \theta_R)$$  \hspace{1cm} (S9)

A bijective mapping between $x$ and $x_\alpha$ in the interference region has been established and reported including the non-planar effects and effects of illumination and detection zones. To construct the film thickness profile, the Equation S8 is rewritten and a height value $h^P$ is first expressed as

$$h^P = h(x_\alpha) \frac{\cos^2(\theta_R)}{\cos(\alpha + \theta_R)} = \frac{\Delta h_f^P}{\pi} \cos^{-1}\left(\frac{A - I(x)}{B}\right)$$  \hspace{1cm} (S10)

where $A = (I_{\text{max}} + I_{\text{min}})/2$, $B = (I_{\text{max}} - I_{\text{min}})/2$, $\Delta h_f^P = \lambda / 4n_1$. $\Delta h_f^P$ characterizes the height difference between two consecutive fringes. It is noted that in the case of planar parallel interfaces and normal incident light, $h^P = h(x_\alpha)$. Then the inclination angle $\alpha$ and the measured increments of $\Delta h^P$ and $\Delta x$ can be related as

$$\sin(\alpha) \cos(\theta_R) = \frac{\Delta h_f^P}{\Delta x}$$  \hspace{1cm} (S11)

in an individual wedge (note the object is approximated as an ensemble of wedges). With the Equations S9-S11, the inclination angles $\alpha$ and reflective angles $\theta_R$ in the interference region can be accurately retrieved by associating $\Delta h^P$ and $\Delta x$, and thus a mapping between position $x$ and $\alpha$ (and $\theta_R$) can be constructed.

Then two different but complementary methods were applied for analyzing the light intensity data. For positions larger than the first extremum, where interference fringes exist, $\Delta x$ is
taken as the distance between the consecutive fringes and $\Delta h_f^p = \Delta h_f^p$. For the positions inside the first extremum, the light intensity were analysed and transformed so that the $\Delta x$ is constant and the $\Delta h_f^p$ was calculated based on Equation S10. To achieve high resolution, $\alpha$ and $\theta_R$ is defined as a function of $x$ and Equation S9 is transformed to a first-order ordinary differential equation as

$$\frac{dx_a}{dx} + x_a F(x) = G(x)$$

$$F(x) = -\frac{d(\tan(\alpha + \theta_R))/dx}{\tan(\alpha + \theta_R) + \tan^2(\alpha + \theta_R)\tan \alpha}$$

$$G(x) = \frac{\tan(\alpha + \theta_R) - x d(\tan(\alpha + \theta_R))/dx}{\tan(\alpha + \theta_R) + \tan^2(\alpha + \theta_R)\tan \alpha}$$

(S12)

The above equations can be solved numerically with MATLAB to construct the profile of the thin film. It is noted that the above more rigorous calculation$^{8-10}$ and a simplified approach with assumption of planar parallel interfaces$^{10-12}$ actually provide very similar results in this work, since the maximum inclination in our analysis is very small ($<10^\circ$).

A procedure to transform RICM interference pattern to thin film profile construction is shown in Figure S3. For the interaction of a bubble and hydrophoized mica surface, the maximum light intensity $I_{\text{max}}$, which indicates zero separation, was measured after bubble attachment. For interaction with hydrophilic mica surface, $I_{\text{max}}$ is not directly available since there is always a thin water film trapped between the air bubble and the mica surface. The $I_{\text{max}}$ in this case was obtained by scaling the experiment light intensity values to the variation of intensity with height which is calculated theoretically for stratified planar structures.$^8$
Figure S3. The conversion of the RICM interference pattern to the thin film profile. (A) Profile of light intensity. The open circle symbols are local intensity values and the dark green line has been drawn to guide the eye. The inset shows the interference pattern and the light green line shows the location of the drawn light intensity. (B) Calculated thin film profile from the intensity pattern where the open circular symbols are RICM experiment results and solid red line is the theoretical prediction from the Stokes-Reynolds-Young-Laplace model.
AFM images of mica and hydrophobized mica surfaces in 500 mM NaCl

**Figure S4.** AFM images of (A) freshly cleaved mica (B) mica-OTS-45 and (C) mica-OTS-90 surfaces in 500 mM NaCl.

Interference fringe patterns of thin water film between air bubble and hydrophobized mica surfaces during interaction corresponding to Figure 3 in the main text

**Figure S5.** Interference fringe patterns of thin water film between air bubble and (A) mica-OTS-45 and (B) mica-OTS-90 surfaces during interaction of Figure 3 in the main text.
Interaction between air bubble and hydrophilic mica surface at high velocity

When the air bubble is driven at high velocity, the effects of hydrodynamic interaction on the interaction force and thin film drainage process become more evident and cannot be neglected. Figure S6 shows the interaction between an air bubble with radius of 98 µm and hydrophilic mica surface, with a velocity of 10 µm/s. Compared with the force curve in Figure 2A (in the main text), the interaction force with higher velocity shows a much larger attraction during retraction due to the stronger hydrodynamic suction effects since the water has to be drawn back into the thin film. The RICM data and theoretical results of the evolution of the thin water film shown in Figure S6B indicated that the central part of the liquid film continues thinning even after retraction starts, which is a result of hydrodynamic suction effect, indicating bubble attachment could also occur during retracting due to this thinning behaviour.

Figure S6. Interaction between an air bubble and hydrophilic mica in 500 mM NaCl solution. The bubble radius is 98 µm. The nominal driving velocity of bubble is 10 µm/s. (A) Variation of the measured force with time measured with the AFM (open circles) and theoretical predictions
(line). (B) The film profile deduced from RICM (open circle) and theoretical predictions (solid lines). The arrows indicate the driving direction of the air bubble.

**Functional Form of Hydrophobic Interaction**

An acceptable functional form of hydrophobic interaction should be able to predict the measured interaction forces and film profiles under all experimental condition. In addition to the exponential form (Equation 1 in main text) of hydrophobic interaction, we have also considered a decaying power of the form

\[
\Pi_H(h) = -dW_H(h)/dh = -\frac{n\gamma(1-\cos\theta_w)}{D_H} \left(\frac{D_H}{h + D_H}\right)^{n+1}
\]  

(S13)

In this form, both the decay length \(D_H\) and the power law index \(n\) need to be determined. We found that this power law form for \(\Pi_H(h)\) cannot provide agreement with experimental results at all velocities. For example, as shown in Figure S7A, a decay length \(D_H = 1\) nm and \(n = 4\) could provide a good fit to the experimental force data between an air bubble and mica-OTS-90 surface at nominal velocity \(v = 1\) \(\mu\)m/s including the point of bubble attachment. However, the same parameters for \(\Pi_H(h)\) would give an incorrect bubble attachment time at a nominal velocity of \(v = 30\) \(\mu\)m/s (Figure S7B). With a decay length fixed at \(D_H = 1\) nm (Figure S7A), power law form with \(n = 3\) predicted a much earlier attachment, representing a much stronger hydrophobic interaction; whereas the form with \(n = 5\) predicted a delayed attachment. The power law form therefore cannot provide quantitative match with the experiment results.
Figure S7. Comparison between the exponential (Equation 1 in main text) and power law forms (Equation S13) of the hydrophobic disjoining pressure. The open circular symbols are experiment results and the solid lines are theoretical prediction with different forms for hydrophobic interaction. (A) Comparison between exponential form and power law form with varying $n$ and $D_H = 1$ nm, in the case of interaction between an air bubble ($R_0 = 81 \, \mu$m) and mica-OTS-90 surface at nominal velocity $v = 1 \, \mu$m/s; (B) Comparison between exponential form and power law form with $n = 4$ and $D_H = 1$ nm, in the case of interaction between an air bubble ($R_0 = 65 \, \mu$m) and mica-OTS-90 surface at nominal velocity $v = 30 \, \mu$m/s.

Reference


