Interaction Forces between Water Droplets and Solid Surfaces across Air Films

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Supporting Information

ABSTRACT: Wetting of solid surfaces occurs when the intervening air film between a water droplet and a solid surface ruptures. Although this rupturing phenomenon is well known, the underlying mechanism has not yet been well understood. In this work, the rupture of intervening air films is systematically studied by measuring the spatiotemporal thickness profiles of the air films between droplets of deionized water and flat solid surfaces using a synchronized triwavelength reflection interferometry microscope. It has been shown that the critical rupture thickness of the air film \(h_c\) depends on the surface hydrophobicity of solid surfaces. The \(h_c\) value was increased from 50 nm on a hydrophobic surface having an equilibrium water contact angle \(\theta_w\) of 96° to 1.42 μm on a hydrophilic surface having a \(\theta_w\) of 25°. In addition, an increase in the critical rupture thickness with decreasing surface hydrophobicity was found to be applicable not only to chemically treated quartz surfaces but also to a variety of natural mineral surfaces. By determining the pressure within the air films, we have shown that a strong attractive force is present between water droplets and hydrophilic surfaces, thereby accelerating the draining of air films. The measured forces might be of electrostatic origin, and the forces become less attractive with increasing hydrophobicity of solid surfaces. The present result provides a fundamental insight into the rupture of air films from the perspective of surface forces.

1. INTRODUCTION

The impact of water droplets on solid surfaces is not only important from a fundamental perspective, but also relevant to many technological applications, including dust control, spray coating, and pesticide control. On superhydrophobic surfaces, falling water drops bounce off the surfaces. On hydrophilic surfaces, water drops wet the surfaces readily. Depending on the nature of the applications, wetting processes may or may not be beneficial. For dust suppression, it is desirable to have dust particles wetted by liquid so that they settle to the ground. The drop impact phenomena were first studied by Worthington. Since then, numerous research efforts have been devoted to tracking the impact dynamics of drops. Impact of a liquid drop on a solid surface and/or a free surface is a complex process, as it involves splashing, crown formation, spreading, and bouncing. During the impact, an air film is formed between the water droplet and the solid surface. The presence of the intervening air film has significant effects on the impact dynamics of liquid drops. The draining of the intervening air film builds up pressure within the air layer, flattening the bottom of the droplet prior to coalescence. This leads to a delay in the wetting/merging process. During the later stage of the impact, the intervening air film collapses, resulting in a spreading of liquid drops on solid surfaces, or a merging of two free surfaces.

Despite of numerous investigations into impacts of drops on surfaces, very few studies were devoted to directly measuring the thickness profile of the air films during impact. Previous studies have been focused on the instability of thin liquid films (TLFs). It has been found that the rupture thicknesses of TLFs are on the order of 100 nm. The rupture thickness of the air film was found to be larger on the order of a few hundreds of nanometers, up to a few micrometers. The thickness of the air film has been previously measured using interferometry and total internal reflection microscopy. Using these techniques, it has been found that the air film ruptures at a thickness of 200−500 nm when two free silicon oil surfaces are brought closely together. The authors claimed that at this distance or below, the van der Waals force becomes dominant and is responsible for the film rupture. For a water droplet impacting on a microscope glass slide, the critical rupture thicknesses of the air films are in the range of 250−400 nm. Follow-up studies indicate that the critical rupture thickness remains the same regardless of the

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hydrophobicity of solid surfaces and surface tensions of aqueous liquid drops.37 The exact value of the critical rupture thickness depends on the size of surface irregularities.

The rupture of the air films might be attributed to several mechanisms. Intermolecular force may be considered the major driving force for the film rupture.37 In this case, the film rupture occurs when the separation distance is within the acting range of attractive intermolecular forces. There might be two types of forces acting within the air gap between the two surfaces. The van der Waals force is monotonically attractive, which might be responsible for bringing the two surfaces into a contact.36 Another type of attractive force leading to the film rupture might be an electrostatic interaction between two oppositely charged surfaces. Other mechanisms/factors might include surface asperity,37 which effectively reduces the actual distance between the free water surface and the solid surface. However, no research has been conducted to accurately determine the intermolecular force between water droplets and solid surfaces across air films. The mechanism leading to the breakup of the air film is still elusive.

An accurate determination of the spatiotemporal thickness profile of a fast-evolving air film is a prerequisite to characterize the dynamics of air film draining and subsequently, to determine the intermolecular force between two surfaces. This analysis involves a determination of the order of each interference pattern. The authors of the present work previously improved the dual-wavelength interferometry technique by including a third synchronized and high-speed camera that recorded interference fringes at a third wavelength.41 The synchronized triwavelength reflection interferometry microscopy (STRIM) technique improves the accuracy of film thickness measurements to 10 nm or better over the range of 0–4 μm, which is suitable to investigate highly unstable air films. Coupled with high-speed cameras, the synchronized triwavelength reflection interferometry microscope is able to reconstruct the spatiotemporal thickness profiles of the air films.

In the present work, measurements have been carried out on polished solid surfaces of varying hydrophobicity by bringing water droplets toward flat solid surfaces at an approaching speed of approximately 600–1000 nm/s. During the course of approaching, the spatiotemporal thickness profiles of the air films are determined from the fast-evolving interference fringes. The film profile data are then analyzed to determine the critical rupture thickness and the kinetics of the approach. From the kinetics data, the interaction force is determined. To further test the hypothesis that the water–solid interaction is sensitive to surface hydrophobicity, experiments are carried out on the basal surfaces of various layered minerals. These mineral surfaces exhibit varying surface hydrophobicity, and they are all atomically flat. The force results are discussed in the context of electrostatic forces.

2. RESULTS

2.1. Water Versus Quartz. Figure 1 shows both a side view (a) and a bottom view (b) of the interaction between a water droplet and a flat solid surface in air. The bottom view was shown as a set of the interference fringes recorded at λ = 460, 527, and 620 nm, respectively (Figure 1b). In one experiment, a water droplet was brought toward a flat hydrophobic quartz surface by an external drive at a nominal velocity of approximately 600 nm/s. When the two surfaces were brought in a close proximity on the order of 100 nm to a few micrometers, the water droplet plunged onto the solid surface manifested by a rupture of the air film. The rupture of the air film was followed by a spreading of the three-phase contact line. The spreading process occurred within a few milliseconds or less, and a finite contact angle was formed as shown from the side-view images (Figure 1a).

The obtained three-wavelength interference fringes were analyzed to determine the separation distance. Figure 2 shows the spatiotemporal thickness profile of the air film between a water droplet and a hydrophobic quartz surface having a θw of 96° and the difference (Δh) between the experimental data and the polynomial fit.
fitted curves matched with the experimental data well. The difference \((\Delta h)/\text{error}\) between the experimental data and the polynomial fit is shown in Figure 2. The maximum \(\Delta h\) is 20 nm and the root mean square (rms) error is 5.93 nm. The profile shows that the water droplet maintained a spherical shape during the interaction with the solid surfaces, validating the approach taken to determine the interaction force as described in the Materials and Experiments section. On the hydrophobic quartz surface of \(\theta_w = 96^\circ\), the critical rupture distance was found to be 45 nm.

Figure 3 compares the spatiotemporal profiles of the separation distances on quartz surfaces having different surface hydrophobicities. These quartz substrates exhibited water contact angles of \(96^\circ\), \(65^\circ\), \(35^\circ\), and \(25^\circ\), respectively. The lines shown in the profiles are polynomial fits to the spatial thickness profile data. The \(t = 0\) is when the closest separation distance is 4 \(\mu m\). As shown, the critical rupture distance \((h_c)\) was found to be 226 nm on the weakly hydrophobic quartz surface having a \(\theta_w\) of \(65^\circ\). The \(h_c\) values were increased to 865 and 1428 nm on quartz surfaces having \(\theta_w = 35^\circ\) and \(25^\circ\), respectively. Our statistical study conducted on over 50 substrates shows that the \(h_c\) values increased with decreasing surface hydrophobicity of solids, confirming the accuracy of the experimental data reported in this work (see the Supporting Information).

Note that the critical rupture distance was found to be above 2 \(\mu m\) on very hydrophilic surfaces having \(\theta_w < 20^\circ\). At this distance or above, the interference fringes were barely visible and therefore, a determination of the rupture thickness became challenging. In this communication, the result obtained on very hydrophilic surfaces will not be discussed.

Other characteristics of the spatiotemporal profiles include the kinetics of approach. The two adjacent spatial profiles were collected at an interval of 1 s. As shown in Figure 3, the water droplet accelerated toward the hydrophilic solid surfaces as reflected by a wider gap between two adjacent spatial profiles obtained on the hydrophilic surfaces than those obtained on the hydrophobic surfaces. To further quantify the kinetics of approach, Figure 4 shows the effect of surface hydrophobicity on both the kinetics of approach \((h vs t)\) and the approaching velocity \((V vs t)\). The result shows that the approaching velocity remained constant on hydrophobic surfaces of \(\theta_w = 96^\circ\) during the course of approaching. The kinetics of approach was decelerated as the two surfaces were brought closer together. On the hydrophilic surface having \(\theta_w = 25^\circ\), however, the kinetics were accelerated with a maximum velocity of approximately \(-3800\) nm/s. This result suggests that the distance \((h_c)\), critical rupture velocity \((\Delta V_c)\), and critical rupture time \((t_c)\). The critical rupture velocity is defined as the difference between the terminal approaching velocity and the external driving velocity prior to film rupture, as \(\Delta V_c = V_t - dh_c/\text{dt}\). The \(\Delta V_c\) value is influenced dominantly by the interaction force between the two surfaces. It has been found that the \(\Delta V_c\) was increased by reducing surface hydrophobicity of the solid surfaces. The negative value obtained on the hydrophobic surface having \(\theta_w = 96^\circ\) might be associated with

![Figure 4](image-url). Effect of hydrophobicity on the kinetics of film thinning (a) and approaching velocity (b).

Table 1 summarizes several characteristics of the rupture of air films, including water contact angle \((\theta_w)\), critical rupture time \((t_c)\), critical rupture distance \((h_c)\), and the root mean square (rms) error of the experimental data.

| \(\theta_w\) (deg) | \(t_c\) (s) | \(h_c\) (nm) | \(\Delta V_c\) (nm/s) |
|------------------|-------------|-------------|----------------------|
| 96               | 7.07        | 45          | -133                 |
| 65               | 6.30        | 226         | 58                   |
| 50               | 4.52        | 679         | 312                  |
| 35               | 2.99        | 865         | 1800                 |
| 25               | 2.36        | 1428        | 3200                 |

Table 1. Characteristics of the Rupture of Air Films Formed between the Water Droplet and Solid Surfaces
repulsive electrostatic forces (Coulombic force), which will be discussed in detail in the following paragraphs.

The critical rupture time \( t_c \) is defined as the total time spent from the initial closest separation distance of 4 \( \mu \)m to the critical rupture distance. As shown, the critical rupture time decreases with decreasing surface hydrophobicity. The reduced \( t_c \) with the decreasing \( \theta_w \) might be attributed to two reasons: (1) an increase in critical rupture thickness, and (2) an accelerated kinetics of approaching. Evidently, all characteristics signify an increase in attraction forces between water drops and solids with decreasing surface hydrophobicity.

To better understand the underlying mechanisms involved in faster thinning kinetics observed on hydrophilic surfaces, the interaction force was determined using eq 7. In eq 7, \( \mu = 1.825 \times 10^{-5} \) kg/m\( \cdot \)s at 20 °C, the radius of curvature \( (a) \) was determined by fitting individual spatial profiles using eq 4, and \( \Delta h/dt = -600 \) nm/s. Figure 5 shows the interaction forces of the air films are relevant to the surface hydrophobicity rather than surface functional groups, the second part of this work is to study the interaction forces between water droplets and natural mineral surfaces. A variety of layered minerals were used as the model surfaces, including muscovite mica, molybdenite, and talc. These mineral surfaces exhibit different degrees of surface hydrophobicities. Mica is naturally hydrophilic, while molybdenite and talc are naturally hydrophobic. The measurements were conducted on the basal planes of mineral surfaces which were atomically flat.

Figure 6 shows the spatiotemporal profiles obtained when water droplets approach three mineral surfaces at a nominal approaching velocity of 1000 nm/s. As shown, the water droplet steadily approached a talc surface and plunged onto the surface at a closest separation distance of 43.5 nm. The critical rupture distance was determined to be 1767 and 288 nm on mica and molybdenite surfaces, respectively.

Also shown from the spatiotemporal profiles (Figure 6) is the kinetics of approach. It has been shown that the kinetics was faster on mica surfaces than obtained on molybdenite and talc surfaces. Figure 7 compares the kinetics of approach obtained on three different mineral surfaces. The external driving velocity was 1000 nm/s. As shown, the kinetics curve was linear on talc surfaces with no significant accelerations during the course of approach. On molybdenite surface, acceleration occurred at a closest separation distance of below 2000 nm. On mica surface, which is very hydrophilic, an accelerated approaching was evident at a distance of above 3000 nm.

2.2. Water Versus Minerals. To further test the hypothesis that both the interaction and the rupture thickness between water drops and solid surfaces having different water contact angles. The result shows that the interaction force is attractive with hydrophilic quartz surfaces. The force becomes less attractive with increasing surface hydrophobicity of the quartz substrates. On hydrophobic surfaces having \( \theta_w = 65^\circ \), the interaction force becomes almost zero, with a weak attraction at a distance of below 500 nm. The interaction force becomes net repulsive on very hydrophobic surfaces \( (\theta_w = 96^\circ) \). Evidently, the result on interaction forces between water droplets and solid surfaces across air films is consistent with the result for kinetics of approach.

Figure 5. Effect of surface hydrophobicity on the interaction forces between water droplets and silica surfaces across air films.

Figure 6. Spatiotemporal profiles of water droplets against layered mineral surfaces.

Figure 7. Thinning kinetics of air films between water droplets and mineral substrates.
Table 2 summarizes several characteristics of natural mineral systems, including \( \theta_w, h_c, t_c, \) and \( \Delta V_c \). The result suggests that

(1) the \( h_c \) value decreases with increasing surface hydrophobicity (\( \theta_w \)), and (2) the kinetics of approach increases with decreasing \( \theta_w \). All data signify that the results obtained with natural mineral surfaces coincide with that obtained with chemically functionalized quartz surfaces, indicating that the water–solid interaction is sensitive to the surface hydrophobicity of solids rather than the surface functional groups. Figure 8 shows the interaction forces between water droplets and mineral surfaces. The results were determined from the spatiotemporal profiles shown in Figure 6 using eq 7. As shown, the interaction force was weakly attractive between water droplets and talc surfaces and became more attractive on less hydrophobic surfaces such as molybdenite and mica. The interaction force result is in a good agreement with the surface hydrophobicity data, as the intermolecular force became more attractive with decreasing the surface hydrophobicity of mineral surfaces.

3. DISCUSSION

As presented in the Results section, the critical rupture thickness of the air film between a water droplet and a solid surface increases exponentially with decreasing surface hydrophobicity. This finding was also found to be applicable to natural mineral surfaces regardless of surface functional groups. For instance, chemically hydrophobized quartz surfaces expose hydrocarbon when immersed in water. The basal surface of talc is composed of a silicon–oxygen tetrahedral, with magnesium–oxygen/hydroxyl octahedral in between. The basal surface does not contain hydroxyl groups which render the surface hydrophobic. The basal plane of Molybdenite has sulfur elements exposed on its surface. When immersed in water, the basal surface of molybdenite exhibits natural hydrophobicity. All of these hydrophobic surfaces exhibit a critical rupture distance of less than 300 nm when in close proximity to a water droplet.

The increase in the critical rupture thickness with decreasing surface hydrophobicity of solid surfaces might be explained using the thermodynamic principle and the mechanical mechanism. Thermodynamically, the free energy change (\( \Delta G \)) associated with the wetting of solid surfaces by water is given as

\[
\Delta G = \gamma_d - \gamma_c - \gamma_v
\]

where \( \gamma_d, \gamma_c, \) and \( \gamma_v \) are the interfacial tensions between solid and water, between solid and air, and between liquid and air, respectively. Using Young’s equation, it might be modified to

\[
\Delta G = -\gamma_v \left( 1 + \cos \theta \right)
\]

where \( \theta \) is the water contact angle of solid surfaces. According to eq 2, the free energy change (\( \Delta G \)) becomes more negative when decreasing the surface hydrophobicity of solid surfaces (i.e., increasing \( \cos \theta \)), indicating that hydrophilic surfaces can be wetted by water more easily than hydrophobic surfaces. The free energy change reaches a maximum of \(-2\gamma_v\) on hydrophilic surfaces with \( \theta_w = 0^\circ \). This thermodynamic analysis provides perspectives on the critical rupture distance.

Mechanically, the wetting of solid surfaces by water might occur when the gradient of the interaction force exceeds the spring constant or effective elastic constant of a free water film. For the case of drops, the spring constant is proportional to surface tension of liquid. Prior to the rupture of an air film, the elastic force balances the interaction force, maintaining the water droplet spherical. When the attractive force exceeds a critical value, the air film ruptures followed by spreading of water on a solid surface. Both Figures 5 and 8 suggest that the rupture of air films might occur when the gradient of interaction force exceeds in the range of 9.7 and 20 mN/m for water droplets having radii of 400–550 \( \mu \)m. For very hydrophobic surfaces (\( \theta > 80^\circ \)), we have shown that the rupture of air films occurred at a closest separation distance of below 100 nm, where the total force might be slightly attractive or repulsive. At this distance or below, the bridging of water droplets and solid surfaces might be attributed to additional factors, for example, surface asperity, despite of great efforts to minimize surface contaminations during the surface preparation.

Another characteristic of the water–surface interaction is the kinetics of approach. It was found that the kinetics of approach increases with decreasing surface hydrophobicity of the substrates. The fast approach kinetics observed on hydrophilic surfaces is attributed to a strong attractive force. Figures 5 and 8 show the total interaction force between water droplets and flat solid surfaces that have different degrees of hydrophobicity. The total force is consisted of surface force and hydrodynamic force. The viscosity of air is two orders smaller than that of water (\( \mu = 1.825 \times 10^{-5} \) kg/m/s at 20 °C), and therefore, the hydrodynamic force between two surfaces in air at a low approach speed (i.e., 600–1000 nm/s) is considerably negligible. In this regard, the measured force is mainly contributed from surface forces.

The calculated forces are fitted to an \( F = c/h \) function, where \( c \) is a constant and \( h \) is the separation distance. Figure 9 shows the fitting result with \( c \) values listed. It was found that the use
of a \( c/h \) function fits the force data well, indicating that the measured surface force between two surfaces might be an electric force following Coulomb’s law. These water droplets might carry opposite charges from hydrophilic solid surfaces, while the hydrophobic surfaces might carry similar charges as water droplets.

Water drops used in this study were formed by passing DI water from a syringe through a microsized stainless steel needle. Electrical double layers are formed when DI water flows through a metal needle. Because the inner surfaces of the stainless steel tubing are negatively charged, this results in positive charges on the surfaces of water droplets. The carried charges by the water droplet are achieved because of the charge separation when a water droplet is released from a stainless-steel needle to the quartz plate (i.e., an insulator). In this regard, the water droplet might carry excess hydrated protons on the surfaces of water droplets in the formation of \( H_2O_4^+, H_2O_6^+, \) or \( H_2O_8^+ \), causing the droplets to carry charges up to \( 4.5 \times 10^{-6} \) C/m².

Negative charges on hydrophilic surfaces might be attributed to the adsorption of water molecules on their surfaces. Under ambient conditions, water molecules might adsorb on solid surfaces to form pitches or islands with a few nanometers in thickness. The adsorption of water molecules renders the solid surfaces negatively charged because of the \( OH^- \) ion transfer. We have also shown that the negative charges on solid surfaces decrease with increasing the hydrophobicity of solids. Hydrophobic surfaces have difficulty adsorbing water molecules; however, the mechanism for which the hydrophobic surfaces carrying positive charge is still not clear.

4. CONCLUSIONS AND SUMMARY

In this work, we have studied the kinetics of thinning and rupture of air films formed between liquid droplets of DI water and mineral surfaces using the newly developed STRIM technique. The spatiotemporal thickness profiles of the air film during the interaction between water droplets and flat solid surface were determined with a 10 nm resolution over a distance of 0–4 μm. The effect of surface hydrophobicity on the critical rupture thickness of the air film was studied. By determining the evolution of the pressure within the air gap, we have determined the interaction force between water droplets and solid surfaces across an air film for the first time.

The results showed that water droplets spread on solid surfaces spontaneously, regardless of the surface hydrophobicity. The critical rupture thickness of the air films increases exponentially with decreasing the surface hydrophobicity of solid surfaces. The critical rupture thickness was found to be above 2 μm on a very hydrophilic quartz surface having a water contact angle of below 20°.

An acceleration of approaching was found between water droplets and hydrophilic solid surfaces. The acceleration in the film thinning was attributed to the presence of attractive surface forces. These interactions were strongly attractive on hydrophilic surfaces, and became less attractive with increased hydrophobicity of the surfaces. These attractive forces might be electric forces. The charging status was found to be more relevant to the hydrophobicity of surfaces, indicating that the charges on solid surfaces might be associated with the adsorption of water molecules on surfaces. This work provides fundamental insights into the wetting of solid surfaces by water drops, and the surface forces revealed between water droplets and solid surfaces across an air film are new additions to the field of surface forces.

5. MATERIALS AND EXPERIMENTS

5.1. Materials. Polished fused quartz plates were used as substrates in this study and were obtained from Technical Glass Product. The rms roughness of the quartz plates was less than 0.3 nm. Prior to the hydrophobization process, the substrates were cleaned in a freshly prepared piranha solution (\( H_2SO_4/H_2O_2 = 3:1 \), by volume) at a temperature of 80 °C for 15 min. The substrates were then cleaned with amounts of DI water to remove acid residue on surfaces and dried in an ultrapure \( N_2 \) stream. The obtained quartz plates were free of contaminants, hydrophilic, and could be wetted by water completely. Mineral samples, including molybdenite, mica, and talc, were obtained from various sources. These mineral samples were well crystallized. A freshly exposed surface was prepared on each of the minerals by peeling off the top layer with an adhesive tape. DI water was supplied by a Barnstead water purification system (Thermo Fisher). The resistance of the DI water was above 18.2 MΩ·cm.

Hydrophobic quartz surfaces were prepared through a methylation process. Methyltrichlorosilane (95%) and octade-cytrichlorosilane (OTS, 95%) were used as the chemicals. In this experiment, cleaned and dried quartz plates were immersed in a freshly prepared silane-in-toluene solution. The surface hydrophobicity was controlled by varying the concentrations of chemicals and immersion times. The hydrophobized quartz plates were taken out of the toluene solution and were cleaned with chloroform followed by isopropanol solutions in an ultrasonic cleaner for 0.5 h to remove residual chemicals on surfaces. The plates were then dried in an ultrapure \( N_2 \) stream in a fume hood and stored temporarily in a clean glass container. All chemicals used were of ACS grade. The toluene solution was dehydrated using 3 Å molecular sieves (Alfa Aesar) before use.

5.2. Experimental Setup. Figure 10 shows a schematic diagram of the experimental set-up used for studying the interaction between water droplets and solid surfaces. In this experiment, a water droplet is brought toward an upper interaction between water droplets and solid surfaces. In this experiment, cleaned and dried quartz plates were immersed in a freshly prepared silane-in-toluene solution. The surface hydrophobicity was controlled by varying the concentrations of chemicals and immersion times. The hydrophobized quartz plates were taken out of the toluene solution and were cleaned with chloroform followed by isopropanol solutions in an ultrasonic cleaner for 0.5 h to remove residual chemicals on surfaces. The plates were then dried in an ultrapure \( N_2 \) stream in a fume hood and stored temporarily in a clean glass container. All chemicals used were of ACS grade. The toluene solution was dehydrated using 3 Å molecular sieves (Alfa Aesar) before use.
which reflects the dynamics of water droplets under the influence of surface and hydrodynamic forces. In addition, a side-view camera is used to capture the contact angle images as well as the evolution of the moving contact line. Experiments are conducted under ambient conditions (70 °F and 30–55% humidity).

In using the STRIM technique, colored light beams are generated using three high-power color LEDs. These colored light beams are collimated and combined using beam combiners. A 20X infinity-corrected long working distance objective (Mitutoyo) is used. The incident light beam illuminates and then gets reflected at two adjoining interfaces of an air layer between the water droplet and the solid surface. The two reflected beams interfere and form a “Newton rings” pattern. The fringe pattern exits the microscope and is separated by dichroic mirrors to the interference patterns of different wavelengths. Three cameras are synchronized to capture images simultaneously at a rate of 150 frames per s. Short-pass optical filters are placed at the front of each camera to create a monochromatic image.

Image processing of the interference fringes is conducted using a self-programmed MATLAB code based on the principle of interferometry.

5.3. Experimental Procedure. In each experiment, a water droplet is placed on a polished fused quartz plate. The water droplet is created using a gas-tight micro-syringe with a stainless steel micro-needle. The radii of the water droplets are in the range of 440–570 μm. To form a hemispherical droplet on the surface, the quartz surface is rendered hydrophobic by immersing the substrates in a 10−3 M OTS-in-toluene solution for 1–3 h. The hydrophobized quartz plate is rinsed with chloroform followed by isopropanol to remove residue chemicals on its surface. The hydrophobized quartz plate exhibits a water contact angle of above 90°. The quartz plate sits on a customized piezo-controlled z-stage, with a 1.5 in. ID aperture. This configuration allows light beams to pass through a piezoelectric z-stage and illuminate the air film directly. The piezo stage can travel at a maximum of 7 μm at a nominal velocity of 0–2 μm/s.

A series of experiments are conducted by bringing a water droplet toward a flat mineral surface across an air film. Initially, the mineral surface is lowered manually to a closest separation distance of 5–10 μm. At this distance or below, the interference fringe becomes slightly visible. This is followed by bringing the water droplet toward the upper surface at a nominal velocity of 600–1200 nm/s, while recording three-colored fringes simultaneously. Each experiment generates three sets of monochromatic fringe images at λ = 460, 527, and 620 nm, respectively. The images are processed to determine spatiotemporal profiles, which can be used to determine the interaction forces using the method described in the following paragraphs.

5.4. Force Calculation. The interaction force between a water droplet and a flat surface across an air film is determined by solving the pressure distribution in the thin gap formed between the two surfaces. The pressure gradient within the gap is governed by the Reynolds lubrication equation

\[ \frac{dp}{dr} = \frac{6\mu}{h^3} \frac{dh}{dt} \]  

where \( \mu \) is the viscosity of air, \( h \) is the separation distance, \( r \) is the radial position, and \( t \) is time. The water droplet remains spherical during the process as reflected by the experimentally obtained spatiotemporal profiles, and therefore, the separation distance can be represented as

\[ h(r, t) \approx h_0 + \frac{r^2}{2a} = h_0(1 + s^2) \]  

where \( h_0 \) is the closest separation distance, \( a \) is the radius of curvature, and \( s = r/(2ah_0)^{1/2} \). By substituting eq 4 into eq 3, one obtains

\[ \frac{dp}{ds} = \frac{12\mu a}{h_0^2} \frac{dh_0}{dt} \frac{s}{(1 + s^2)^3} \]  

By integrating eq 5, one obtains the pressure distribution along the radial position under one boundary condition \( p = p_\infty \) at \( r = a \)

\[ p(s, t) - p_\infty = -\frac{3\mu a}{h_0^2} \left( \frac{dh_0}{dt} - \frac{dh_s}{dt} \right) \frac{1}{(1 + s^2)^2} \]  

where \( dh_s/dt \) is the approaching velocity at the outer region \( r = a \). The \( dh_s/dt \) is equal to the external approaching velocity. Therefore, the forces due to the interaction between two surfaces can be determined by integrating the pressure distribution over the total area.
\[
F = \int_{\infty}^{\infty} \left( p - p_0 \right) 2\pi (2a h_0) s \, ds = -\frac{6\eta u^2}{h_0} \left( \frac{dh_0}{dt} - \frac{dh_s}{dt} \right)
\]  
(7)

In eq 7, both \( h_0 \) and \( \frac{dh_0}{dt} \) can be determined from the spatiotemporal profiles obtained experimentally from interference fringes. The \( \alpha \) value can be determined using eq 4. The force data are presented as a function of the closest separation distance \( h_0 \).

**ASSOCIATED CONTENT**

2 Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02646.

Statistical results on critical rupture thicknesses of air films between water droplets and quartz surfaces of different hydrophobicities (PDF)

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Notes
The authors declare no competing financial interest.

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