Repulsive van der Waals Forces in Soft Matter: Why Bubbles Do Not Stick to Walls

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Measurements of nonequilibrium hydrodynamic interactions between bubbles and solid surfaces in water provide direct evidence that repulsive van der Waals forces of quantum origin control the behavior of liquid films on solids in air. In addition to being the simplest and most universal 3-phase system, the deformable air-water interface greatly enhances the sensitivity of force measurements compared with rigid systems. The strength of the repulsive interaction, controlled by the choice of solid, is sufficient to prevent coalescence (sticking) on separation due to hydrodynamic interactions.

The van der Waals force acts between all physical bodies due to the coupling of quantum fluctuations of electrical dipoles within materials [1,2]. An alternate but equivalent description is that the interaction is due to the change in the zero point energy of the electromagnetic field with separation between bodies of different dielectric materials [3–6]. In the vast majority of cases, the force is attractive and is responsible for many adhesion and coalescence processes in biological and colloidal systems [2]. However, for certain combinations of materials, repulsive interactions can also arise, as first proposed by Hamaker [7]. Previous demonstrations of such repulsions have involved equilibrium measurements using somewhat esoteric material combinations that have limited applications [2,8,9]. For instance, Hutter and Bechhoefer first found that by changing the intermediate solvent, the interaction force between a sharp, silicon nitride atomic force microscope (AFM) tip and mica surface could be switched from attractive to repulsive [10]. Repulsive van der Waals interactions have also been demonstrated between combinations involving solids such as gold, silica, and PTFE [poly(tetrafluoroethylene), Teflon^{TM}] when the intervening fluid is a nonpolar organic solvent [8,9,11].

In fact, the force is also of vital importance in wetting films: as predicted by de Gennes [12] and others, water films on solid substrates cannot be thinned past a critical thickness due to this repulsion, and whereas previous authors have noted that the van der Waals force may exist between particles and bubbles [13], as yet none have systematically demonstrated its presence, sign, or magnitude. Such repulsive interactions become most significant at nanometer separations, and hence are of great relevance in the development of essentially friction-free microfluidic and nanofluidic devices. However, there are relatively few techniques that possess sufficient sensitivity to directly measure the nonequilibrium interactions. These

are the surface forces apparatus [14], AFM [15], and total-internal-reflection microscope [16]. Although the van der Waals interaction is universal in that it exists between all bodies, its magnitude cannot be easily manipulated compared to electrical double-layer or steric forces, for instance. At larger separations, beyond 10 nm, electromagnetic retardation effects due to the finite speed of light in the coupling of fluctuations cause the magnitude of the interaction to fall away rapidly [1,2]. Whereas continuum models predict that the van der Waals interaction force per unit area between two semi-infinite half-spaces diverges as the inverse cube of the separation, in reality the natural molecular dimension of matter must moderate this behavior at very small separations.

This work presents the first direct demonstration of the combined effects of repulsive van der Waals forces and hydrodynamic flow on the nanoscale. This proof of principle suggests that smart surface coatings may be used to control fluid flows in ways far more advanced than was thought possible. We use nonequilibrium force measurements between a deformable bubble and a solid surface to quantify the role of repulsive van der Waals interaction in providing dynamic stability of aqueous films on solid surfaces such as mica, silica, and gold. The near-atomic smoothness of the substrates and the air-water interface of the bubble allow us to probe the limit of validity of continuum expressions of the van der Waals interaction. The interface of the bubble confers a novel advantage in significantly enhancing the sensitivity and accuracy of direct force measurements by being able to deform and hence increase the effective area of interaction. Atomic force microscopy using bubbles attached to cantilevers [17–20] has been shown to provide highly reproducible results for both film drainage and bubble-bubble coalescence. Significantly, a theoretical model for the dynamic drainage behavior in such systems has been developed with the

capability to give excellent quantitative agreement with these experimental data.

In this Letter, we report measurements using an AFM with a bubble attached to the cantilever to demonstrate and accurately quantify repulsive van der Waals forces in one of the simplest and most generically important systems possible: gas-liquid-solid, with the solid taking the form of a flat gold, silica, or mica surface. In the selection of substrates, gold is a material of particular interest because it represents an extremely high-energy surface (exemplified by the Hamaker constant for gold-vacuum-gold $A_{121} = 670 \times 10^{-21}$ J at small separations), which results in a significant van der Waals interaction for material combinations involving gold. Silica is extremely ubiquitous and of relevance to a vast array of processes and applications ranging from microelectronics to mineral processing, and freshly cleaved mica provides a surface that is atomically smooth and free of contamination. By using a "soft," deformable probe, substantial advantages are gained over solid sphere probes that are commonly used. Rigid probes have a fixed and small effective area of interaction and place a limit on the sensitivity of the measurement. Also at small separations, effects due to surface roughness can become dominant. The smooth air-water interface with its propensity to deform under force makes it possible to reliably obtain significantly larger areas of interaction which vastly improves the sensitivity in the measurement of short-ranged forces.

In our experiments, a bubble attached to the cantilever of an atomic force microscope was driven towards and away from gold, silica, and mica surfaces, and the force on the bubble was measured (Fig. 1). Bubbles were generated ultrasonically as described previously [19,20], on glass substrates modified by reaction with ethanol [21], to generate a slightly hydrophobic surface suitable for anchoring of bubbles (water contact angle 40°). Rectangular silicon AFM cantilevers ($450 \times 50 \times 2$ μm) were custom fabricated with a circular patch of gold (diameter 45 μm, thickness 20 nm—shown schematically in inset of Fig. 1) deposited ≈ 5 μm from the end [17,20]. A hydrocarbon layer was chemically linked to the gold area on the cantilever via a thiol bond to form a circular area that is energetically favorable for bubble attachment. Thus the contact area of the bubbles on the cantilever is known precisely. Bubble radii and substrate contact radii were measured by optical video microscopy (Nikon Ti2000). Cantilever spring constants K were determined by the method of Hutter and Bechhoefer [22]. The AFM measurements were performed on an Asylum MFP-3D AFM, equipped with linear variable differential transformer sensors, to allow direct detection of cantilever Z position during force measurements. This has been shown to be vital for accurate force-displacement measurements, as the nominal velocity of the piezomotor does not remain constant to within our required precision [17].

In these systems, the primary forces expected are due to hydrodynamics of water drainage in the film region, the
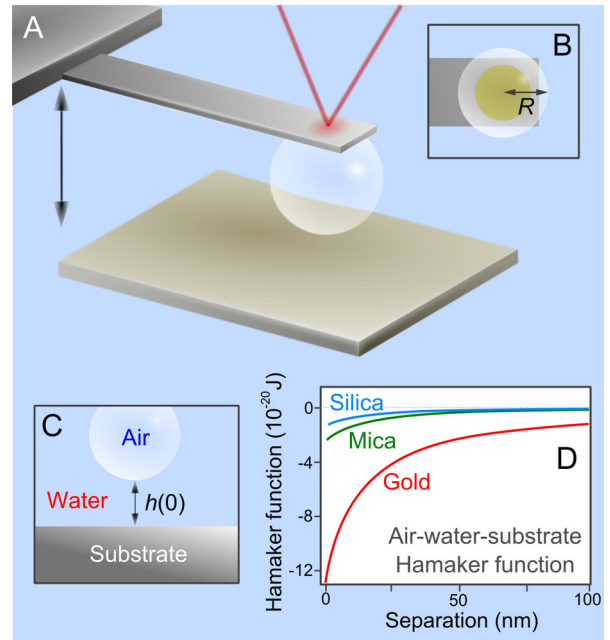

FIG. 1 (color online). (a) Schematic of the experimental AFM setup, (b) schematic bottom view of the bubble attached to the gold patch on the cantilever, (c) vertical-slice schematic showing the central film thickness at the symmetry axis of the bubble, (d) retarded Hamaker functions for the three material combinations calculated using Lifshitz theory.

van der Waals repulsion, and potentially short-range forces due to interactions between the surfaces and water molecules. The experiments were performed in aqueous solutions comprising Milli-Q water (minimum resistivity 18.4 MΩ cm) with 500 mM electrolyte of NaClO$_4$. This inert salt dissociates completely to give a Debye length of <0.5 nm; thus, electrical double-layer effects were sequestered. A short-range hydrophilic repulsion (the so-called "hydration repulsion") has been demonstrated for silica [23], but is limited to <3 nm in range. Additionally, for pure gold surfaces, which are known to be hydrophobic [24], a short-range hydrophobic attraction is expected over a similar range [25]. The theoretical framework used to predict the force versus time behavior of the AFM experiment [26,27] is capable of giving excellent agreement with the measured force curves without free parameters. In brief, a hydrodynamic (Stokes flow) lubrication model is used to treat the axisymmetric flow of the aqueous solution between the bubble and the solid substrate. Deformation of the bubble due to the repulsive van der Waals disjoining pressure and hydrodynamic pressure is described by the Young-Laplace equation. From this model, the total force and the evolution of the thickness $h(r, t)$ of the axisymmetric aqueous film can be calculated as the cantilever displacement is varied with time during the course of the nonequilibrium force measurements. From this model it is possible to infer that the repulsive van der Waals interactions are sufficiently strong that the water film between the bubble and surface never drops below 10 nm for

gold (or 6 nm for silica), and hence any short-range hydrophobic forces are not experienced by the bubble [Figs. 2(b) and 3(b)]. However, by performing the force measurement above a step defect on the gold-covered mica surface, the water film can become thin enough for the hydrophobic force to cause coalescence between the bubble and gold surface. It is important to note that no evidence for nanobubbles was detected on the pure gold surfaces, and no additional long-range forces were observed in the measurements. It has been shown that surface roughness [28] is of considerable importance when such thin films are generated, and that roughness on a similar scale to the film thickness may be exploited to access these short-range interactions. In this work, the surfaces used were all determined by AFM imaging studies to exhibit mean roughness below 1 nm, which is much less than the minimum thickness of the water film at any time. Hence, the only forces between the bubble and surface should be due to the repulsive van der Waals interaction and hydrodynamic effects.

The van der Waals interaction between macroscopic bodies is commonly characterized in terms of the dependence of interaction free energy per unit area, $E(h) = -A(h)/(12\pi h^2)$ between half-spaces of the same material upon the separation h, where $A(h)$ is the Hamaker function. The sign convention is that a repulsion corresponds to $E(h) > 0$ and hence $A(h) < 0$. The variation of the Hamaker function with separation is due to electromagnetic retardation effects that arise from the finite speed of light in the coupling of electromagnetic fluctuations

between the interacting bodies. At small separations, $A(h)$ tends to the Hamaker constant, but its magnitude decreases when the separation starts to exceed 5 nm. We have calculated Hamaker functions for the bubble-electrolyte-substrate systems using the full Lifshitz theory that includes retardation effects and electrolyte effects on the so-called zero-frequency term [1]. The results, presented in Fig. 1(d), indicate that a significantly greater repulsion should be present between a bubble and gold than either silica or mica. The air-water-solid Hamaker constants at vanishing separation for different substrates are: $A(0) = -148 \times 10^{-21}$ J (gold), -24×10^{-21} J (mica), and -12×10^{-21} J (silica). However, the effect of retardation and the inverse squared dependence of the interaction free energy upon separation means that the interaction is still relatively short ranged in all cases [see Fig. 1(d)].

The presence of hydrodynamic interactions means that, at high approach velocities, drainage from the film region retards the bubble's approach, and this effect manifests itself as a velocity-dependent repulsive force. Similarly, as the bubble is retracted from the surface, the resistance of water draining back into the film region causes a "suction" effect, which is apparent in the force or displacement curve as the hydrodynamic minimum or "well" seen in Fig. 2. This suction force is strongly dependent on, and is hence a sensitive probe of, the minimum film thickness attained during an approach-retract collision. Based on its dimensions, the bubble can be treated as being incompressible [27]. We also see that by varying the maximum load applied to the bubble [Fig. 2(a)] it is possible to control the corresponding minimum central film thickness $h(0, t)$
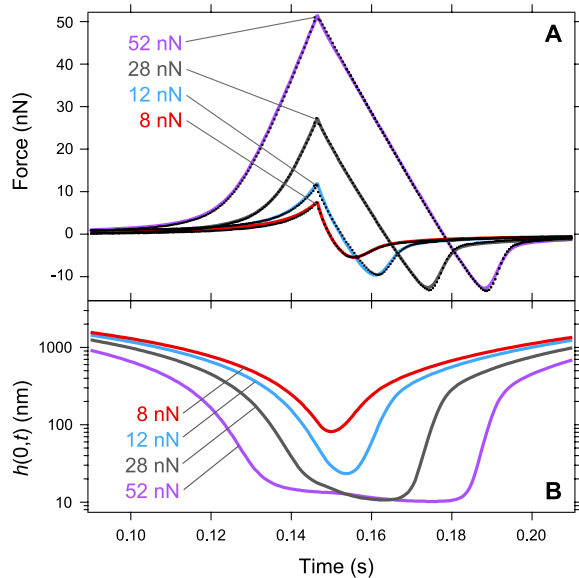

FIG. 2 (color online). (a) Force as a function of time for a bubble interacting with a gold surface in 500 mM $NaClO_4$ solution using different maximum force loadings. In all cases, the nominal approach and retract speeds were fixed at 20 μm/s. Black dots are experimental data points and solid lines are model fits. (b) Modeled central film thickness as a function of time for the bubble-gold interaction curves presented in (a).
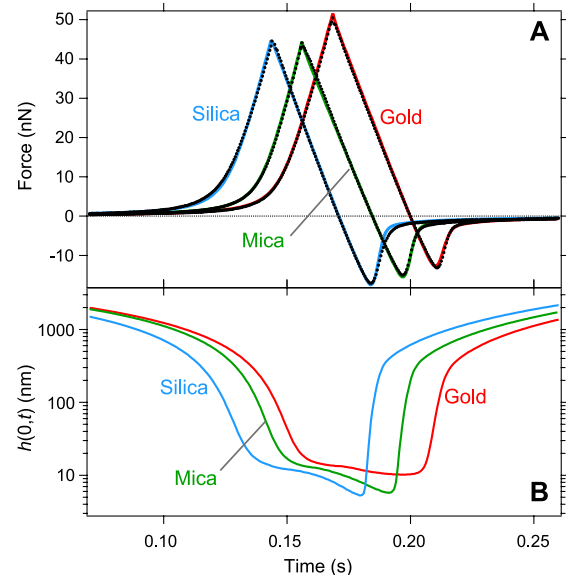

FIG. 3 (color online). (a) Experimental force as a function of time for a bubble interacting with gold, mica, and silica surfaces in 500 mM $NaClO_4$ solution. Nominal approach and retract velocity was 20 μm/s in each case. Solid lines are model fits to the data. (b) Modeled central film thickness as a function of time for the bubble-substrate interactions presented in (a).

[Fig. 2(b)] that can be reached in such nonequilibrium approach-retract collision experiments. The strength and form of the van der Waals repulsion controls the relation between the maximum load and the minimum thickness. The contribution from hydrodynamic pressure is negligible around the minimum of $h(0, t)$ as the film is no longer thinning. However, because the bubble can deform, the maximum magnitude of the van der Waals repulsive disjoining pressure that can be sampled with such experiments is the Laplace pressure of the bubble [26,27].

Figure 3(a) shows the interaction between a bubble and 3 different surfaces: gold, silica, and mica, for otherwise identical experimental parameters. It can be seen that for mica and silica the hydrodynamic minimum is considerably greater than for gold, which is rationalized by the significantly greater calculated repulsive force between the bubble and gold. This larger repulsion keeps the bubble further from the surface, and hence the equilibrium film generated is thicker for gold; the modeled film thickness [Fig. 3(b)] supports this. It can be seen that during approach (film thinning) the profile is relatively insensitive to the van der Waals force, as only minimal differences are seen between the three materials. It is only when the minimum thickness value is reached that significant resolution is obtained. Our nonequilibrium study provides an important capability in the study of repulsive interactions involving soft matter. For interactions at equilibrium, force measurements involving deforming bubbles (and drops) furnish little information about repulsive surface forces. The reason is that, when the bubble-substrate separation reaches that at which the repulsive disjoining pressure becomes equal to the Laplace pressure of the bubble, its interface will thereafter deform, while the separation will remain constant. From this point on, the experimental force-displacement data will simply reflect the deformation of the bubble rather than providing information on variations of the strength of interaction with the separation between the interfaces [26,27].

These results show conclusively that a repulsive van der Waals force exists between bubbles and flat gold, silica, and mica surfaces. The strength of this force can be controlled by the choice of materials, and it can further be expected that the force will exist with varying magnitudes between bubbles and virtually all solid surfaces in water. However, because of the ability of bubbles to deform, the water film thickness between the bubble and the substrates we used did not fall below 6 nm and, consequently, a continuum model could be used to calculate the repulsive van der Waals interaction. The quantitative success in the theoretical predictions of the measured nonequilibrium force curves indicates the validity of applying continuum classical fluid mechanics down to the nanoscale. This also demonstrates that repulsive van der Waals forces modulate behavior within many everyday systems and may guide the materials choice and design of future microfluidic and nanofluidic devices for transporting fluids with essentially no frictional forces.

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