Forces Measured between Hydrophobic Surfaces due to a Submicroscopic Bridging Bubble

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Atomic force microscopy on hydrophobic microspheres in water reveals a strong attraction with a range of 20–200 nm, following an initial steep repulsion at long range. The data are consistent with a single submicroscopic bubble between the surfaces, with the attraction due to its attachment and lateral spread, and the repulsion dependent on film drainage and the electric double layer. The results provide direct experimental evidence of the existence of long-lived submicron bubbles, and of their bridging as the cause of the measured long-range attractions between macroscopic hydrophobic surfaces. [S0031-9007(98)06357-1]

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In the early 1970s Blake and Kitchener [1] measured the rupture of the water film between a hydrophobic surface and an approaching bubble, and concluded that a long-ranged attraction existed. The force between two macroscopic hydrophobic surfaces has since been directly measured, and, although the quantitative details vary, the measurements confirm a strong attraction that is much larger than the van der Waals force (see Ref. [2]). The extreme range of the force (measurable at 300 nm [3]) challenges conventional theories of surfaces forces and the liquid state. Comparisons with polywater are not entirely uncalled for, following the early suggestion [4] that the force was due to extended, surface-induced, water structure.

Most consensus for the underlying physical mechanism has focused on long-range electrostatic forces, following the proposal by Attard [5] that the two surfaces coupled via correlated fluctuations. This idea and its various modifications [6–9] all predict a strong dependence on the electrolyte concentration, which experiments variously confirm [10–12] and refute [3,13–15].

Alternatively, it has been suggested [3,16] that the force is due to the presence of submicroscopic bubbles adhering to the surfaces (Harvey nuclei), with the attraction due to the attachment to the other surface and subsequent lateral spreading. The proposal was based on the observation of steps or discontinuities in the force data at large separations [3], which were taken to be due to the bridging of multiple bubbles. The idea is supported by the fact that the force tends to be more short ranged when measured in de-aerated water [15,17], and when measured between surfaces that had never been exposed to the atmosphere [17], presumably due to the attachment of bubbles to defects in the surfaces when they were taken through the air-water interface.

What is attractive about bridging bubbles as a mechanism for these long-ranged forces is that the range of the force is set by the physical size of the bubble, and one avoids a putative surface-induced structure in the liquid that extends over thousands of molecular diameters. The main difficulty with the proposal is that, according to macroscopic thermodynamics, bubbles are metastable [16]; the Laplace equation predicts a high internal gas pressure for submicroscopic bubbles that should make them dissolve [18]. In addition, the experimental evidence for bridging bubbles is somewhat indirect, since their submicroscopic size precludes direct visual observation.

Here we report measurements of long-ranged attractions between hydrophobic surfaces in water, which, when all of the features are considered in detail, provide the most direct evidence to date for bridging bubbles. The interpretation of our data is relatively straightforward because the microscopic particle that we use traps at most a single bubble in the contact region, whereas the macroscopic surfaces used in Ref. [3] showed the forces due to many bubbles. In addition we are able to establish unambiguously the zero of separation from the hard-wall contact, which could not be done in previous force measurements that involved macroscopic bubbles [19,20]. We use complementary optical microscopy to establish visually the existence of micron and submicron sized bubbles attached to the surfaces, which shows that the lifetimes of these metastable bubbles are at least comparable to the experimental time scales. This is a significant observation given the thermodynamic arguments discussed above, and is obviously a necessary precondition for the bridging bubble mechanism to be viable.

Force measurements were made with an atomic force microscope (Autoprobe LS, Park Scientific Instruments), and simultaneous visual observations were made with the attached high resolution optical microscope. The cantilever spring constant and the piezodriver were calibrated gravitationally and interferometrically, respectively. An oxidized silicon wafer was used as the substrate, and a glass microsphere (Duke Scientific Corp., CA) of radius $R = 10.3 \pm 0.7\ \mu\text{m}$ was attached to the cantilever spring. Both surfaces were hydrophobed by exposure to a fluorinated silane vapor (Tridecafluoro-1,1,2,2-tetrahydrooctyl)-methyldichlorosilane (United Chem. Tech., Bristol, PA) for ten minutes, and then heated to 120–150 °C for an hour in the absence of the silane, following Parker *et al.* [3,21].

This gives a smooth chemically robust hydrophobic surface with contact angle greater than 100° [3]. Electrolyte solutions, 0.1–100 mM, were prepared on the day of use from reagent grade sodium chloride and sodium perchlorate, using purified water (Milli-Q plus).

Using the high resolution optical microscope, we examined the hydrophobized surfaces *in situ* for the presence of bubbles. In a number of experiments we observed macroscopic, free floating bubbles, 1–4 mm in diameter, and on occasion we saw a large bubble bridging the surfaces following solution exchange. We also observed many microscopic bubbles attached to the surfaces, which we sized by comparison with the 20 μm particle simultaneously in view. We definitely observed bubbles ≤ 1 μm in diameter, attached to either the lower substrate or to the colloid particle. Force measurements were not made when a bubble was visible in the contact region, which obviously leaves open the possibility of smaller submicron bubbles. The bubbles likely originate during the initial passage from air to water of the surfaces following silanation, and also when the electrolyte was changed (by exchange using syringes). There was no marked decrease in the size or number of bubbles over the several hours of an experiment.

Figure 1 shows two examples of the measured force when there is no long-range attraction, as occurred in about a dozen of the few hundred measurements. This force in 0.11 mM NaCl is well fitted by a weak electric double layer repulsion (nonlinear Poisson-Boltzmann, constant area per surface charge of 326 nm^2), van der Waals attraction, and hydrodynamic drainage repulsion. The surfaces showed a strong adhesion with the pull-off force being 1–1.5 μN. The data at long range show the importance of the hydrodynamic drainage repulsion [22], $F_d = -6\pi\eta R^2\dot{h}/h$ ($\eta = 10^{-3}$ kg m^{-1} s^{-1} is the viscosity, h is the surface separation, and $\dot{h}$ is their mutual velocity), which is measurable beyond 200 nm at high driving velocities. The qualitative difference between the force measured in this case and those shown next shows that the long-range attraction between hydrophobic surfaces is very different from classic surface forces, which are always reproducible: Therefore it cannot be an intrinsic or molecular property of the surfaces or water. We interpret the particular data of Fig. 1 as representative of the case when no bubble is trapped in the contact region.

The long-range attractions evident in Fig. 2 typify the bulk of our measurements, and could be interpreted as *the* long-ranged hydrophobic attraction. One of the exhibited attractive regimes extends out to 140 nm, although 50 nm of the other case would be more typical. There are a number of features evident in these measurements that support our interpretation of a submicroscopic bubble in the contact region. First, of course, is the attraction itself, since it has been shown that a bubble bridging hydrophobic surfaces gives such an attraction [3,16]. The attraction arises from the lateral spreading of the bubble, which displaces unfavorable water-solid contact. Second is the suddenness of the onset of the attraction, which indicates that the attraction is not some exponentially decaying function from zero separation but rather occurs instantaneously, as one would expect of a bubble attaching to the other surface. Third, there is the variability in the range of the attraction, which is uncharacteristic of an equilibrium surface force, but which would be expected for bridging bubbles since different experiments and different contact positions will trap differently sized bubbles (or none at all, as in Fig. 1). We interpret the onset of the attraction as a measure of the radius of the bubble, typically 50–100 nm, since prior to the interaction it sits as a hemisphere on one of the surfaces

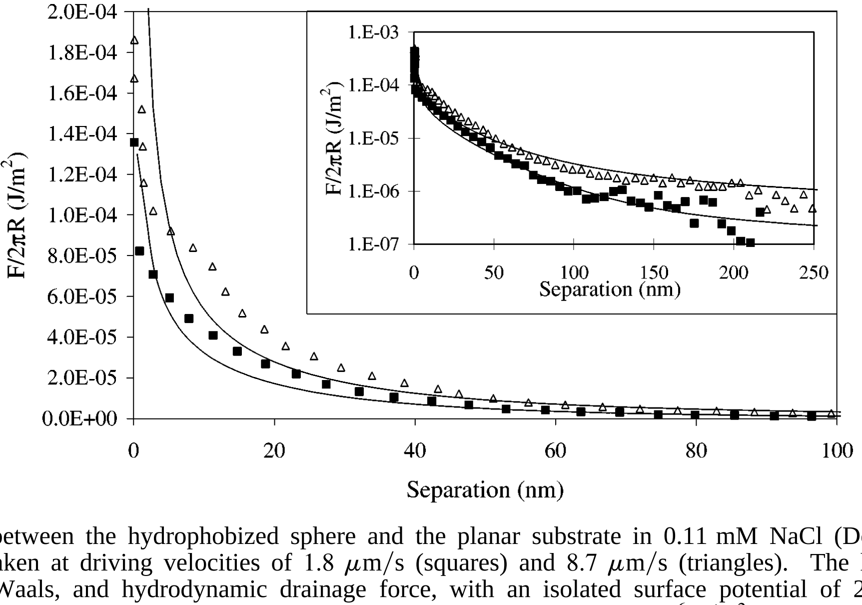

FIG. 1. The force F between the hydrophobized sphere and the planar substrate in 0.11 mM NaCl (Derjaguin scaling). The experimental data are taken at driving velocities of 1.8 μm/s (squares) and 8.7 μm/s (triangles). The lines are the combined double layer, van der Waals, and hydrodynamic drainage force, with an isolated surface potential of 20 mV and a Hamaker constant of 8×10^{-21} J. The force resolution of the device corresponds to about 10^{-6} J/m^2. The inset shows the data on a logarithmic scale.

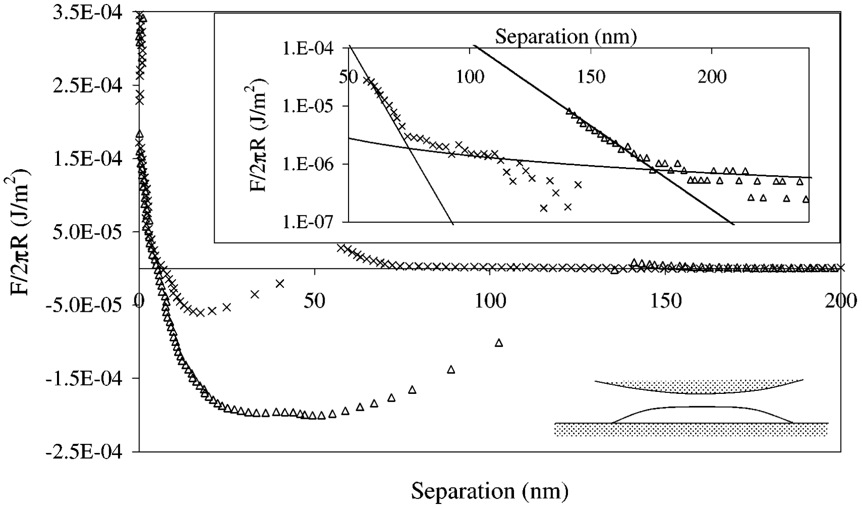

FIG. 2. Forces measured at 4.5 μm/s in NaCl at 0.19 mM (triangles) and 9.5 mM (crosses). The gaps in the data signify rapid jumps toward contact due to a strong attraction. The logarithmic inset shows the rather flat drainage repulsion and steeper linear exponential fits with decay lengths 15 and 6 nm.

[23]. Fourth, there is the steep increase in the repulsion just prior to the attraction, which has the character of an interaction between surfaces at much smaller separations. The particle-substrate drainage repulsion dominates the total force at large separations, (due to the relative size of the particle and the bubble), and it is only exceeded by the putative bubble-surface repulsion when the bubble-surface separation becomes quite small. Fifth, there is the soft repulsion prior to contact, which does not correlate with the Debye length. We attribute this regime to an enhanced hydrodynamic repulsion that arises from the increased drainage due to the displacement of water by the spreading bubble. It seems likely that the rate of spreading reaches a steady state due to the opposing hydrodynamic drag and drainage, which may account for the rather flat constant attraction regime, and the increasing repulsion at small separations.

We also measured the forces in sodium perchlorate (Fig. 3) but found little evidence for specific ion effects. The long-range attraction and soft contact are again prominent, and in one of the two cases shown the additional repulsion at long range is also clear. The steep repulsion was missing in 92 mM $NaClO_4$, but it was also less marked in high concentrations of NaCl. The attraction is measured in these cases at a range of about 50 Debye lengths, which confirms that it is not electrostatic in origin.

The decay length fitting the steep repulsion preceding the attraction decreased with increasing electrolyte concentration, ranging from 21 nm in pure water, to 12–15 nm in 0.2 mM NaCl, to about 6 nm in 10 mM electrolyte. The

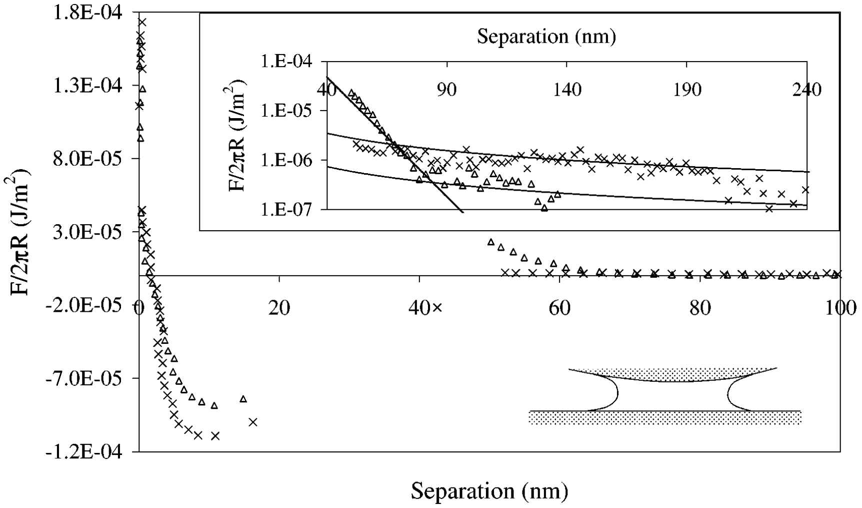

FIG. 3. Forces measured in $NaClO_4$ at 0.95 μm/s and 8.7 mM (triangles) and 4.5 μm/s and 92 mM (crosses). The curves in the inset are the drainage repulsion, and the straight line is an exponential fit with decay length 9 nm.

Debye length goes from about 100, to 22, to 3 nm over this range. Since surface deformation increases the nominal range of a repulsive interaction [24], we conclude that the additional repulsion cannot be a pure electric double layer repulsion between the bubble and the surface. The decay length was independent of driving velocity but the magnitude of the maximum repulsion (the peak prior to the jump) increased with increasing speed, which suggests contributions from film drainage. This peak also decreased with increasing electrolyte concentration, and in general appeared higher in $NaClO_4$ than in NaCl, which suggests that counterion dehydration may play a role. Finally, the van der Waals interaction is expected to be repulsive for the asymmetric bubble-water-surface system. We note that these mechanisms have been discussed in the context of the measured monotonic repulsions between a macroscopic bubble and a quartz particle [20].

The variability in the jump separation between experiments was taken to be due to different sized trapped bubbles. Series of consecutive measurements (presumably the same trapped bubble) showed that the jump-in distance decreased with increasing driving velocity, changing by up to a factor of 2 over the range $0.15-4.5\ \mu\mathrm{m/s}$. This may be due either to greater flattening of the bubble by the increased hydrodynamic repulsion or to the bubble attaching via a large amplitude capillary wave, which occurs with greater probability during the slower run. The jump-in distance did not appear to change systematically with electrolyte concentration.

In summary, we attribute the long-range attraction that we measure between a microscopic hydrophobic particle and a flat hydrophobic surface to a single submicroscopic bubble bridging between them. The evidence in support of this included the attraction itself, its sudden onset, its variability or even complete absence, the steeply increased repulsion prior to the attraction, and the soft repulsion prior to final contact [25]. In addition, we observed long-lived, submicroscopic bubbles attached to the surfaces *in situ*. We conclude that a class of the measured long-range attractions between macroscopic hydrophobic surfaces can be attributed to submicroscopic bridging bubbles, and that it is not necessary to invoke unusual water structure or enhanced electrostatic correlations to account for these. The results also have practical implications (such as the efficacy of de-aeration treatments, or the dynamics of bubble-particle attachment) and question the applicability of macroscopic thermodynamics on submicroscopic length scales.

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[1] T. D. Blake and J. A. Kitchener, J. Chem. Soc. Faraday Trans. 1 **68**, 1435 (1972).

[2] H. K. Christenson, in *Modern Approaches to Wettability: Theory and Applications,* edited by M. E. Schrader and G. Loeb (Plenum, New York, 1992).

[3] J. L. Parker, P. M. Claesson, and P. Attard, J. Phys. Chem. **98**, 8468 (1994).

[4] J. C. Eriksson, S. Ljunggren, and P. M. Claesson, J. Chem. Soc. Faraday Trans. 2 **85**, 163 (1989).

[5] P. Attard, J. Phys. Chem. **93**, 6441 (1989).

[6] R. Podgornik, J. Chem. Phys. **91**, 5840 (1989).

[7] Y. H. Tsao, D. F. Evans, and H. Wennerström, Langmuir **9**, 779 (1993).

[8] S. J. Miklavic, D. Y. C. Chan, L. R. White, and T. W. Healy, J. Phys. Chem. **98**, 9022 (1994).

[9] O. Spalla and L. Belloni, Phys. Rev. Lett. **74**, 2515 (1995).

[10] Ya. I. Rabinovich and B. V. Derjaguin, Colloids Surf. **30**, 243 (1988).

[11] H. K. Christenson, P. M. Claesson, J. Berg, and P. C. Herder, J. Phys. Chem. **93**, 1472 (1989).

[12] P. Kekicheff and O. Spalla, Phys. Rev. Lett. **75**, 1851 (1995).

[13] H. K. Christenson, J. Fang, B. W. Ninham, and J. L. Parker, J. Phys. Chem. **94**, 8004 (1990).

[14] H. K. Christenson, P. M. Claesson, and J. L. Parker, J. Phys. Chem. **96**, 6725 (1992).

[15] L. Meagher and V. S. J. Craig, Langmuir **10**, 2736 (1994).

[16] P. Attard, Langmuir **12**, 1693 (1996).

[17] J. Wood and R. Sharma, Langmuir **11**, 4797 (1995).

[18] Macroscopic thermodynamics may be inapplicable on these length scales. Taking into account molecular contributions to curvature will decrease the surface tension compared to a planar interface, and the proximity of the external liquid will increase the chemical potential of a gas compared to a bulk reservoir. Both effects tend to stabilize bubbles.

[19] W. A. Ducker, Z. Wu, and J. N. Israelachvili, Langmuir **10**, 3279 (1994).

[20] M. L. Fielden, R. A. Hayes, and J. Ralston, Langmuir **12**, 3721 (1996).

[21] A silanated silica probe and substrate has been used previously in atomic force measurements of the hydrophobic attraction by Ya. I. Rabinovitch and R.-H. Yoon [Colloids Surf. A: Physicochem. Eng. Aspects **93**, 263 (1994)].

[22] D. Y. C. Chan and R. G. Horn, J. Chem. Phys. **83**, 5311 (1985).

[23] An obtuse contact angle, bubble deformation, and off-axial placement all increase the estimate of the bubble size. It is also possible that, prior to bridging, the bubble exists on both surfaces as an apposite half-sized pair, although this arrangement has a higher Gibbs free energy than a single bubble.

[24] J. L. Parker and P. Attard, J. Phys. Chem. **96**, 10 398 (1992).

[25] R. Considine, R. A. Hayes, and R. G. Horn (to be published) have contemporaneously measured strikingly similar forces between hydrophobic latex particles, and similarly conclude that a bridging bubble is responsible. In addition, de-aeration experiments by these authors yield time scales of the order of hours for bubble regrowth, which is consistent with the stability of the bubbles observed in the present experiments.