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Direct Measurement of Hydrophobic Forces: A Study of Dissolved Gas, Approach Rate, and Neutron Irradiation

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Theoretical interpretations of the, as yet, poorly understood long-range hydrophobic attraction are briefly reviewed. We report long-range hydrophobic attractive forces between silica surfaces made hydrophobic by adsorption of the cationic surfactants cetyltrimethylammonium bromide and cetylpyridinium chloride onto silica surfaces. The effects of dissolved gas, surface approach velocity, and neutron irradiation on the measured interaction have been studied in order to investigate possible non-electrostatic mechanisms for the long-range hydrophobic attraction. At large separations the presence of dissolved gas, neutron irradiation, and reduced approach velocities are, in each case, found to result in a stronger attraction between the hydrophobic surfaces. These results are consistent with mechanisms related to the metastability of the thin aqueous film separating the approaching hydrophobic surfaces.

Introduction

There are several theories in the literature that purport to explain the origin of long ranged "hydrophobic" attraction between surfaces.⁵³ The first is based on water structural effects propagating from the surfaces into the bulk liquid, due to enhanced hydrogen bonding of the water molecules close to the hydrophobic surfaces.¹ The resulting structural changes associated with dynamic ordering and disordering give rise to a force that decays exponentially with distance. However such a theory yields neither a value for the pre-exponential term nor for the decay length of the measured force. A decay length of 1–10 nm was required to fit the theory to the earliest experimental data depending on the system. Indeed the range of these forces has increased with time. Yet simulation studies yield surface correlation effects with a range of <0.5 nm.^{2,3}

Another suggestion is that the hydrophobic attraction is driven by the metastability of water films between hydrophobic surfaces with contact angles greater than 90°. Cavitation has been inferred or directly observed for hydrophobic surfaces in contact⁵ or just prior to contact,⁴ in SFA experiments. Theoretically, cavitation is predicted between surfaces at close separations (<1 nm), with a contact angle greater than 90°, and has been dealt with thoroughly by Yuschenko et al.^{6,7} Related to the metastable film and cavitation arguments are those of Yaminsky and Ninham,⁸ who postulate that the increased attraction

occurs as a result of the lateral enhancement of subcritical density fluctuations in the water film between the hydrophobic surfaces. Cavitation between poorly wetted surfaces has been investigated using Monte Carlo simulation.⁹ As the surfaces approach, an attraction is predicted prior to spinodal cavitation. This effect results in a monotonically increasing attractive force which the authors suggest could be the microscopic origin of the long-range hydrophobic interaction. The theory predicts a small increase in force with increasing electrolyte concentration and a force inversely proportional to the cube of the separation.

Explanations based on electrostatic fluctuations between neutral bodies give rise to an attractive force decaying exponentially with twice the Debye length. In the work of Podgornik, the attraction arises from specific interactions of mobile charges with the surface.^{10,11} Attard suggests density fluctuations occurring at the hydrophobic–aqueous interface give rise to an enhanced van der Waals type attraction or alternatively, for very low salt concentrations, the presence of microscopic domains can give rise to forces acting over similar lengths to the domain dimension.¹² Both these proposals require that the pre-exponential term is chosen to fit the data. Miklavic et al.¹³ have treated the interaction of heterogeneous surfaces theoretically. In systems where the surface charge distributions are free to migrate to lower the interaction energy, the force is found to always be attractive. However, the force is very much model dependent. The decay of the interaction is determined by the Debye length at high salt concentrations and the lattice spacing at low salt concentrations. Spalla and Belloni¹⁴ propose an electrostatic model similar to that of Podgornik,^{10,11} based on zero frequency ion–ion charge fluctuations inducing an

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attraction.¹⁵ The treatment is for colloidal particles and predicts a force that decays with twice the Debye length for large colloidal particles and with the square of the radius for very small particles.

Ruckenstein and Churaev¹⁶ propose a hydrodynamic origin for the hydrophobic attraction, whereby fluctuations of the water interface propagate via hydrodynamic motions from one interface to another. This requires the assumption that fluctuating vacuum gaps are present between the hydrophobic surface and the aqueous phase. Experiments on the flow of nonwetting liquids in capillaries offer some support for the existence of vacuum gaps at the water–hydrophobic surface interface.^{17,18} The attraction is expected to decay with the cube of the separation. Another interpretation due to Podgornik and Parsegian^{19,20} of the attraction measured between CTAB coated surfaces concludes that “.... there seems to be no need to postulate anything new or dramatic.” They attempt to explain the published results for this system in terms of classical electrostatics, with interaction driven adsorption changing the zero of separation for the vdW component of the interaction. This hardly explains the existence of much stronger hydrophobic interactions between systems that do not involve surfactants or charge. Most recently Yaminsky et al.²¹ attribute the attraction in CTAB systems to a charge regulation effect that is enhanced by cooperative surfactant adsorption at hydrophilic surfaces. As the surfaces approach, surfactant adsorption increases between the surfaces and is further enhanced by the onset of two-dimensional micellization, leading to the measured attraction. The thermodynamics of the attraction are described, but a description of how the surfaces interact at long range in high salt is not addressed.

It is clear from the previous discussion that the mechanisms of hydrophobic attraction are yet to be clearly elucidated. They will remain so until the effects and role of the many experimental variables are clarified. We have performed a variety of experiments with the aim of providing experimental evidence to support or eliminate some of the many proposed theories. The results of these experiments are presented here and the implications for proposed theories discussed.

Liquids supersaturated with dissolved gases or superheated both exhibit sensitivity to radiation.²² Clearly radiation is capable of providing one means by which a metastable system can overcome an energy barrier and thereby achieve an energetically more stable state. The formation of a cavity between hydrophobic surfaces with contact angles exceeding 90° requires that a considerable energy barrier be breached,⁶ and radiation may provide the energy required. However, as a mechanism for the hydrophobic attraction *direct effects* of radiation appear unlikely to be important. A high number of events per unit volume would be required to give rise to the forces measured, as very small volumes of solution are present between interacting surfaces. Also, measurements are generally reproducible from one approach to the next. Nonetheless, secondary effects of radiation are known to

be important in acoustic cavitation and may be of relevance to the hydrophobic attraction. Cavitation induced by sound waves arises from the growth of preexisting nuclei to visible size. These nuclei have been shown to arise from neutron radiation,²³ though an understanding of their stability is still to be realized.²⁴ In this work, the effect of neutron irradiation on the hydrophobic attraction has been investigated, motivated by the assumption that metastability of the aqueous film between hydrophobic surfaces is of importance to the hydrophobic attraction.

The threshold for cavitation of water in an ultrasonic field is critically dependent upon the gas content of the water,²⁵ suggesting that cavitation induced by other means may depend on the gas concentration. The simple observation that degassing produces an increased stability of oil in water emulsions^{26–28} supports this assertion. Since the oil droplets are destabilized via the hydrophobic attraction, the implication is that removal of the dissolved gas reduces this interaction. If indeed the hydrophobic attraction is driven by the metastability of the thin aqueous film between hydrophobic surfaces, then the time scale over which the film ruptures may be significant. Thus, the rate at which the surfaces approach may effect the interaction.

In this paper the effects of dissolved gas content, rate of surface approach, and prior neutron irradiation on the interaction forces between hydrophobic surfaces are investigated.

Materials and Methods

Experiments were conducted using a purpose built instrument, LLIFE, described in detail elsewhere.²⁹ This instrument employs the light lever technique to sense the deflection of a fine spring under the action of surface forces. With this instrument the rate of approach of the surfaces can be widely varied. Microfabricated³⁰ cantilever springs (Nanoscope, Digital Instruments) of two types were used to evaluate surface forces. The so-called stiff springs are a single beam of etched silicon crystal, trapezoidal in cross-section, with typical dimensions of 140 μm in length, thickness of 4.8 μm , and widths of 20 μm at the top and 45 μm at the base. These springs typically have a spring constant of the order of 50 N m^{-1} and are attached to a silicon stub. The weaker V-shaped springs have spring constants that vary from 0.02 to 0.7 N m^{-1} . A silica sphere was attached to the tip of the cantilever using Epikote glue according to the method developed by Ducker et al.³¹ This allows the radius of interaction to be determined. Forces are usually reported normalized by this radius (i.e. F/R), as this value may be related to the energy of interaction through the Derjaguin approximation.³² The geometric mean radius of the probes were measured, after the force experiment, using a Cambridge S360 scanning electron microscope.

In experiments with added electrolyte, analytical grade NaCl, further purified by roasting in air at 600 °C for 5 h, was used. Water used to prepare solutions was filtered and passed through activated charcoal and a reverse osmosis membrane, followed by distillation. All operations were carried out in a laminar flow cabinet. Glassware was soaked in 10 wt % NaOH solution and rinsed thoroughly with clean water. All fittings for the AFM

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fluid cell were washed thoroughly in distilled AR grade ethanol, rinsed in water, and finally boiled in water. The AFM fluid cell was cleaned using the same technique.

The silica flat and sphere were plasma treated (0.65 Torr H₂O, 0.10 Torr Ar, 10 W, 45 s) to ensure cleanness and complete hydroxylation of the silica surfaces. Additionally, the fluid cell was plasma treated under the same conditions. Silica spheres used were $\sim 20\ \mu\text{m}$ in diameter and supplied by Polysciences. Advancing and receding contact angles were measured by the sessile drop method on a flat silica surface.

Surface forces between silica surfaces immersed in solutions of cetyltrimethylammonium bromide (CTAB) and cetylpyridinium chloride (CPC) and 0.1 M NaCl were investigated. The CTAB was supplied by BDH, 98% pure. The CPC was supplied by Aldrich, 98% pure. Both surfactants were further purified by recrystallization from an ethanol–water mixture. Experiments were conducted at room temperature, which is a few degrees above the Krafft temperature for the CTAB solutions. Solutions containing gas in equilibrium with the atmosphere (gassed) and solutions from which the majority of dissolved gases had been removed (degassed) were used. Degassing was achieved over 1 h using a water jet pump while cooling the solution in an ice bath to minimize evaporation. The solution was either placed in a sonication bath or subjected to mechanical shocks in order to facilitate gas removal. Solutions were brought back to room temperature before use. Surface forces were measured using both weak and stiff springs for a range of approach rates. When measurements were conducted with a stiff spring, it was necessary to average the signal over several approaches in order to reduce instrumental noise.

The effect of neutron irradiation on the measured force was also studied. Some solutions were neutron treated over 1 h or more, prior to injection in the fluid cell. A radium–beryllium neutron source was used to irradiate solutions. Irradiation was ceased immediately prior to injection into the fluid cell, and measurements were conducted within 10 min.

Radium and beryllium do not naturally emit neutrons. Neutron emission is achieved by bombardment of the beryllium atoms with alpha radiation from the decaying radium source. The Ra–Be neutron source used emitted $60\ 000\ \text{neutrons s}^{-1}$. The emitted neutrons have a Gaussian distribution of energies with a maximum intensity at approximately 4 MeV.³³ Studies of the effect of neutrons on sonic cavitation have shown that water has an increased susceptibility to cavitation for some time after neutron irradiation has ceased.^{22,23,25} These investigations imply that possible effects of neutrons on hydrophobic interactions can be studied fairly easily, for neutron irradiation may be conducted immediately prior to injection of the solution and terminated prior to measurement. In this way, difficulties in achieving sufficient neutron irradiation of the small volume of fluid in the AFM cell and any direct effects of neutron irradiation may be avoided. Charging of the surfaces due to secondary ionising radiation is also then minimized or avoided.

Results

1. Effects of Dissolved Gas. An earlier study³⁴ on the effect of dissolved gas between polypropylene surfaces produced statistical evidence for a reduction in the measured attraction upon degassing. The forces in that study were only measurable to a distance of less than 30 nm. The very long range strongly attractive forces present between CPC coated surfaces³⁵ presents a system more suitable to the study of the effect of dissolved gas on the interaction, as the range and magnitude of the force are substantially larger. The anticipated change in pH upon removal of dissolved CO₂ is unlikely to be of any importance in the presence of 0.1 M electrolyte, which strongly screens electrostatic forces ($\kappa^{-1} < 1\ \text{nm}$). The measured interaction in a gassed and degassed CPC solution is shown in Figure

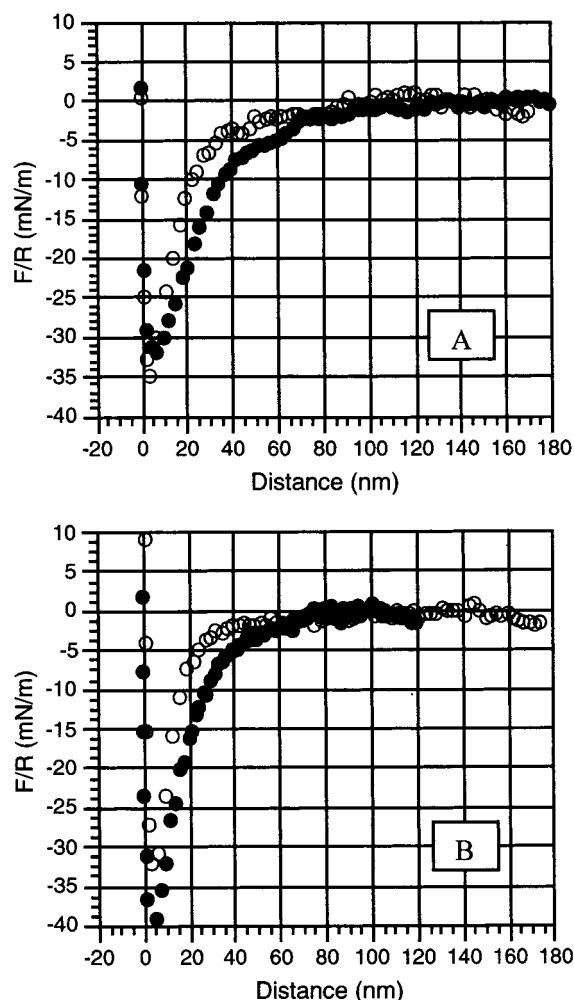


Figure 1. F/R versus separation distance between silica surfaces immersed in $5 \times 10^{-6}\ \text{M}$ CPC and 0.1 M NaCl measured using a stiff spring. The interaction measured in both gassed (filled circles) and degassed (open circles) is shown. The gassed curve was measured immediately prior to injection of degassed solution (A). Similar results were obtained in another experiment when the order was reversed (B). The curves were obtained with approach velocities of $1000\ \text{nm s}^{-1}$ and are averaged over 30 approaches.

1. The removal of dissolved gas is seen to diminish the force at large separations, but at very small separations, the magnitude of the attraction is very similar. This behavior was observed when the degassed interaction was measured prior to the gassed interaction. The experimental data can be fitted to a double exponential as shown in eq 1. The fitted parameters for the normal ($C_1 = -40$

$$F/R = C_1 \exp(-D/L_1) - C_2 \exp(-D/L_2) \quad (1)$$

mN/m, $L_1 = 16\ \text{nm}$, $C_2 = -10\ \text{mN/m}$, and $L_2 = 45\ \text{nm}$) and degassed ($C_1 = -45\ \text{mN/m}$, $L_1 = 11\ \text{nm}$, $C_2 = -8\ \text{mN/m}$, and $L_2 = 40\ \text{nm}$) interactions quantify the diminished range of the long-range component of the attraction for the degassed interaction.

The adhesion for both cases was measured to be $210\ \text{mN m}^{-1}$, which gives rise to a calculated³⁶ γ_{sl} value of between 17 and $22\ \text{mJ m}^{-2}$. The surface deformation resulting from this large adhesion is $\sim 0.8\ \text{nm}$. A solution of $5.0 \times 10^{-6}\ \text{M}$ CPC and 0.1 M NaCl gave an advancing

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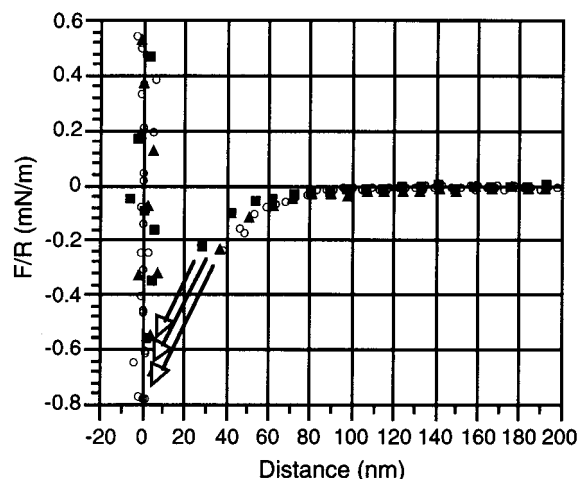


Figure 2. Effect of approach rate on the measured interaction: F/R versus separation distance for silica surfaces in 2.2×10^{-5} M CTAB solution. The attraction was measured at three different approach rates of 2830 nm s^{-1} (filled squares), 1700 nm s^{-1} (filled triangles), and 850 nm s^{-1} (open circles). Three successive approaches at 850 nm s^{-1} are shown to illustrate the reproducibility.

angle of 60° and a receding angle of 31° on a plasma-treated silicon surface.

2. Effects of Changes in Approach Rate. The interaction measured between silica surfaces in a solution of 2.2×10^{-5} M CTAB with varying rates of approach is shown in Figure 2. Upon increase of the rate at which the surfaces approach, the measured attraction diminishes. Three sets of data for the slowest approach rate are shown. It is evident that the variation in the measured force seen upon increasing the approach rate is considerably greater than the variability between repeat measurements obtained at the slower rate.

The effect of approach rate on the measured attraction was also investigated using CPC solutions. However, due to the weakness of the springs used, each interaction could here be characterized only in terms of a single parameter, the jump distance. In solutions where the attraction measured was very large, either a strong adhesion or the formation of a cavity resulted upon retraction of the substrate. Consequently, after each approach of the surfaces it was necessary to separate the surfaces manually. In solutions for which the jump distances were smaller, the adhesion was significantly less and the surfaces would separate upon retraction of the substrate with the piezo. For this reason a solution of 8.0×10^{-6} M CPC in 0.1 M NaCl was used. This was found to give moderate jump distances.

The jump distances are variable. Consequently a number of interactions were made at rates varying over 3 orders of magnitude to obtain firm statistics. The results are presented in Figure 3. The rates were varied from one measurement to the next, to avoid any systematic error resulting from a change in the interaction with time. Measurements were not conducted continuously. This procedure was adopted to minimize disruption to the adsorbed surface layers. The results suggest that the distance at which the interaction shows up is inversely related to the logarithm of the approach velocity. But due to the variation in the measured jump distances, the error bars are large and such an inference is not certain. To overcome this difficulty we have employed much stiffer cantilever springs. This permits the investigation of a greater range of interaction forces. Further, on separation, the stiffer spring allows the surfaces to separate within

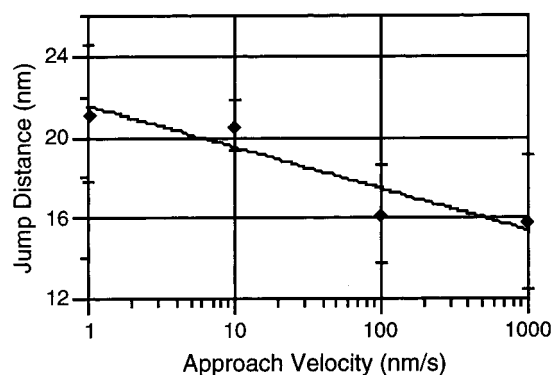


Figure 3. Interaction between silica surfaces immersed in a solution of 8.0×10^{-6} M CPC and 0.1 M NaCl characterized by a sudden jump into contact from approximately 18 nm . The jump distances measured at different approach rates from 26 curves were analyzed, and the average jump distance versus the approach velocity is shown. The error bars denote standard deviations.

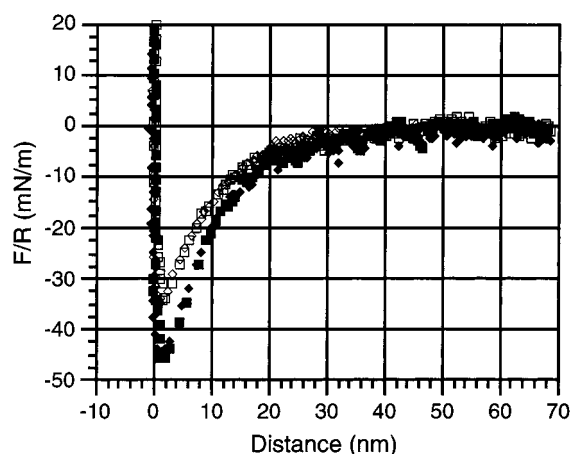


Figure 4. F/R versus separation distance between silica surfaces immersed in 6×10^{-6} M CPC and 0.1 M NaCl measured using a stiff spring. The curves were obtained with approach velocities of 1000 nm s^{-1} (open symbols) and 100 nm s^{-1} (filled symbols) and are averaged over 10 approaches. Two curves are shown for each velocity.

the range of the piezo travel, even for the most strongly attracting surfaces. This advantage with the use of stiff springs is offset by a reduction in sensitivity in the results. So the data need to be averaged over a number of approach runs to minimize errors. Results for interaction forces so measured between silica surfaces in 6.0×10^{-6} M CPC and 0.1 M NaCl with a stiff spring are shown in Figure 4. Here the effects of changes in approach velocity can be more easily seen. Again, an increase in approach velocity reduces the magnitude of the attractive force.

3. Effects of Neutron Irradiation. Neutron irradiation of the CTAB solutions immediately prior to injection was found to increase the magnitude of the attraction. This is demonstrated in Figure 5. The adhesion measured in the neutron treated solution at 27 mN m^{-1} was found to be slightly larger than that in the normal (untreated) solution (21 mN m^{-1}). However this difference is probably related to the forces with which the surfaces are pushed together, which were 3.8 and 3.2 mN m^{-1} , respectively.

The effect of neutron irradiation has also been studied for the CPC and 0.1 M NaCl solutions. An increased attraction was seen at large separations as shown in Figure 6. At a separation of $\sim 10 \text{ nm}$ the curves cross over and the attraction in untreated solution exceeds that of the treated solutions. Similar behavior is often seen when

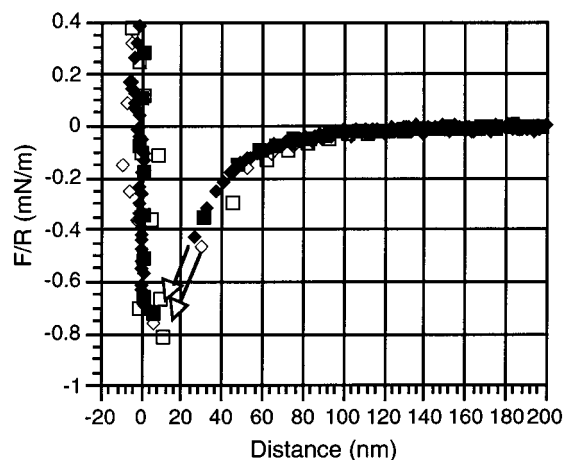


Figure 5. Effect of neutron treatment on the measured interaction: F/R versus separation distance for silica surfaces in 2.2×10^{-5} M CTAB solutions. The effect of neutron treatment prior to measurement has been studied. Interaction curves are shown for the untreated CTAB solution (filled symbols) and neutron-treated CTAB solution (open symbols). The neutron curves were obtained shortly after the normal curve, following injection of 2.2×10^{-5} M CTAB solution exposed to the Ra-Be neutron source for 55 min.

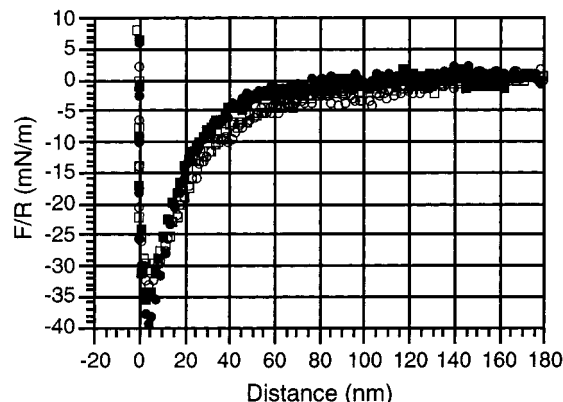


Figure 6. F/R versus separation distance between silica surfaces immersed in 5×10^{-5} M CPC and 0.1 M NaCl measured using a stiff spring. The interactions measured in both normal (filled symbols) and neutron-treated solutions (open symbols) are shown. Two sets of data are shown for each solution. The neutron curves were measured immediately prior to injection of the normal solution. Similar results were obtained on reversing the order of measurement. The curves were obtained with approach velocities of 600 nm s^{-1} and are averaged over 30 approaches.

comparing gassed and degassed solutions (see Figure 1). This suggests that the increase in the attraction seen between neutron-treated solutions may be related to the presence of microcavities of dissolved gas.

The data, if fitted to the double exponential form of eq 1, give parameters for the normal and neutron-treated solutions as $C_1 = -45 \text{ mN/m}$, $L_1 = 14 \text{ nm}$, $C_2 = -9 \text{ mN/m}$ and $L_2 = 35 \text{ nm}$ and $C_1 = -40 \text{ mN/m}$, $L_1 = 16 \text{ nm}$, $C_2 = -12 \text{ mN/m}$, and $L_2 = 50 \text{ nm}$, respectively. The longer range, and magnitude, of the long-range component of the attraction for the neutron treated interaction are apparent. The measured adhesive force was very similar for all four curves at $\sim 218 \text{ mN m}^{-1}$, with a calculated γ_{sl} value³⁶ of between 17 and 23 mJ m^{-2} .

Discussion

Regardless of whether all observations of the hydrophobic attraction are due to a single mechanism—in effect

capillary condensation in one form or another—it is clear that electrostatic theories alone, with or without charge regulation and hydrophobic association of adsorbed surfactant tails, cannot alone be responsible for many of the interactions measured with surfactants.^{27,37} Most theoretical notions that purport to account for hydrophobic attractions derive from the metastability of the water film between the hydrophobic surfaces. For strongly hydrophobic surfaces, those solids with contact angle greater than 90° , this metastability is manifest in the formation of a cavity upon separation.^{4,5,38} It is demanded by thermodynamics. Cavitation reflects a genuine phase transition. It can then be argued that this propensity to cavitate will show up through subcritical density fluctuations⁸ even for less hydrophobic surfaces for which cavitation proper is forbidden. The resulting surface-induced lowering of density of the film, which depends on separation, is then responsible for the strongly attractive force.⁸ The presence of dissolved gas in solution must influence the metastability of the liquid film between hydrophobic surfaces, as it can be expected to accumulate in excess in the aqueous region adjacent to a hydrophobic surface.³⁹ Indeed, cavitation due to sonication is greatly enhanced in the presence of dissolved gas.²⁵ So too is optical cavitation.⁴⁰

Dissolved Gas as a Factor. With this in mind, we have studied the effects of removing dissolved gas from solution on a particular class of hydrophobic attractions. A reduction in force upon removal of dissolved gas was observed (recall Figure 1). Clearly the attraction still exists when much of the dissolved gas is removed. How much gas is still present is not known, but at least 2.5% of the equilibrium dissolved gas concentration will remain in solution as the pressure in the evacuating vessel is approximately 0.025 atm.

But in any event, the range and magnitude of the interaction is reduced. That the effect is small is not too surprising. First, for at least one given hydrophobic surface the interaction is found to be largely independent of temperature.⁴¹ For another system it is unaffected by addition of low concentrations of other solvents³⁸ and, we argue,⁴² by electrolyte concentration. In other words, although these and other observations on hydrophobic interactions apply to a miscellany of different systems, taken together, they suggest that there is no obvious experimental parameter yet known that does not alter the interface but which strongly effects the attraction. Second, the complete removal of dissolved gas from solution was not possible with our procedures. Even if it were, prevention of readsorption of gas would not be possible with the experimental system used in this study.

Currently, we cannot say if the decrease in the attraction upon removal of dissolved gas is a result of an effect in bulk, a surface effect, or both. It might be argued that dissolved gas accumulates on the hydrophobic surface and by so doing increases the hydrophobicity of the surfaces—the vapor–water interface ($\gamma_{lv} \approx 72 \text{ mJ m}^{-2}$) is higher in energy than the hydrocarbon–water interface ($\gamma_{sl} \approx 50 \text{ mJ m}^{-2}$). No direct evidence to confirm such a proposition is available. The presence of macroscopic bubbles would

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have been detected by the FECO technique used in the surface forces apparatus. However very small gas bubbles of the order of tens of nanometers would not be detected. Evidence for the existence of such substructure in water is controversial but appears to be accumulating.^{25,47,52} A study of the refractive index between mica surfaces with adsorbed CTAB monolayers using the FECO technique found no effect on the refractive index within experimental error,⁴³ which suggests that any accumulation of gas that may occur is small. Alternatively, it may be argued that the presence of dissolved gas in bulk assists in the propagation of structural effects induced by the hydrophobic surface.⁸ If this is the case, it may provide an important clue to the mechanism of the hydrophobic attraction. Analysis of cavities formed on separation show that the cavities contain both water vapor and dissolved gas.³⁷ An inability to disentangle surface from bulk effects of dissolved gas precludes any definite conclusions to be drawn on mechanisms of interaction from dissolved gas studies alone.

Rates of Approach as a Factor. By comparison with the SFA method for measuring surface forces, the light lever technique enables greater approach rates to be studied. The maximum useful approach rate is limited by the onset of significant hydrodynamic forces. These are determined by the radius of the probe and the viscosity of the solution.⁴⁴ Using the equation for the hydrodynamic force derived by Chan and Horn,⁴⁴ it is found that, for the small radius probes used in this work, approach rates of 1 mm s^{-1} are required before the hydrodynamic forces become significant in water. The fastest approach rates used in this work are more than 2 orders of magnitude less than this. In most work on surface forces, the rate of approach of the surfaces has not been considered important. DLVO type interactions are unaffected at experimentally available approach rates. However, as the hydrophobic attraction is not of classical electrostatic origin, at least for some systems, a study of approach rates is warranted.

The approach rates of two systems using silica surfaces were studied. These were CPC in 0.1 M NaCl and CTAB,

at rates from 1 to 2830 nm s^{-1} . The effect of the approach rates upon the interaction are illustrated in Figures 2–4. The results given in Figures 2 and 3 were obtained using a weak spring. Hence, the full range of the interaction cannot be covered. For the CTAB system the interaction extends to more than 80 nm. It is measurable to at least 50 nm before the surfaces jump into contact. As the rate of approach is decreased, the attraction becomes larger for a given separation and the surfaces jump into contact from a greater distance. This variation is considerably larger than what is seen between measurements at the same rate. The change in force with approach rate is not attributable to any artifact associated with the operation of the LLIFE. It has been demonstrated previously²⁹ that the measured interaction in other systems using the LLIFE does not change as a function of the rate of approach.

The change in measured force with rate of approach is consistent with a mechanism that involves cooperative two-dimensional condensation of adsorbed surfactants, if one likes, hemimicelle formation, driven by double layer charge regulation, which is a highly nonlinear process. In the systems studied here, this is not a feasible explanation due to the near neutrality of the surfaces, and in the CPC system, this is not feasible due to the screening of electrostatic interactions by the high background salt concentration. Alternatively, it can be viewed as resulting from an increased probability that an event associated with the disruption of the metastable aqueous film may occur.

For the CPC system, the onset of the attractive force was so sudden that only a jump into contact was seen. In this case jump distances are variable and a good deal of caution has to be used in assessing the data. It might be argued that the true surface separation is changed by vibrations of the cantilever spring and that a slower approach rate increases the probability of the surfaces interacting when the true distance is less than the measured distance. The silica probe for this experiment was situated on the tip of a V-shaped cantilever spring of length $\sim 100 \mu\text{m}$ and spring constant 0.21 N m^{-1} . A force of only 1 nN acting on the tip of the spring will result in a 5 nm deflection at the tip. For this reason the effect of mechanical vibrations may have a considerable effect on the jump distance measured. If the variation in the baseline of the measured interaction is computed, and the assumption is made that all noise present is due to vibrations at the tip of the cantilever, a measure of the amplitude of spring vibrations can be made. Such a calculation yields a deflection of $< \pm 0.5 \text{ nm}$. This is an upper limit, as electronic noise will provide some contribution to the noise in the baseline. Clearly the measured variation in the jump distances is larger and cannot be attributed to spring vibrations. By using a stiffer spring, the interaction at smaller separations can be investigated and the effect of the approach rate can be evaluated with more certainty. A 10-fold decrease in the rate of approach results in an increase in the measured attraction as depicted in Figure 4. From these measurements we may conclude that a decrease in the measured attraction shows up with an increasing approach rate.

Relevance of Cavitation Phenomena. The major challenge in developing an understanding of the plethora of "hydrophobic" attractions is to elucidate how it is that "hydrophobic" surfaces communicate their proximity at separations of 100 nm and more.

Several observations from other fields that deal with the cavitation behavior of water may provide some clues. In the study of cavitation of supersaturated water, it is

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(53) In the discussion of this matter there is an immediate difficulty, usually ignored, for the word hydrophobic is impossible to define. The surface of solid paraffin with a contact angle greater than 90° is one thing. The surface of mica or silica "hydrophobized" by adsorption of cationic surfactants like CTAB at the point of zero charge, with a contact angle of 15° – 80° , is another. In the latter the contact angle arises from migration of surfactant across the three phase line and the surface density of surfactants at the solid–liquid interface one molecule every 100 or 700 \AA^2 (Yaminski, V. V.; Yaminskaya, K. B. *Langmuir* **1995**, *11*, 936; Yaminski, V. V.; Nylander, T.; Ninham, B. W. *Langmuir* **1997**, *11*, 936). Such a surface is mostly "hydrophilic". Both such surfaces give rise to long-ranged interactions, 10–100 times larger than any conceivable van der Waals forces. We include in this review the plethora of such forces to underline the complexity of the general phenomenon. Most "theoretical" treatments ignore details of the vastly different nature of the interacting surfaces and search for some universal decay length. This is of course absurd. Any universality in the phenomenon of "hydrophobic" interactions must lie—and this is our thesis—only within the unifying principles embraced by the term capillary condensation. This is directly coupled to metastability of the aqueous film, whatever the surfaces.

accepted that water contains long-lived micronuclei in the bulk of the fluid. These can be removed to some extent by degassing. But they can be removed with much greater efficiency by subjecting the water to several hundred atmospheres of mechanical pressure.⁴⁵ Thus the micronuclei can be crushed out of existence. In the field of sonochemistry it is also well established that free radicals are produced as a result of the growth of long-lived micronuclei during the negative pressure cycle of the sound wave.²⁵ These micronuclei are equally present in tap and distilled water and occur in the bulk of the liquid, well away from any surface. Recent controversial work has been interpreted as meaning that micronuclei in water (or bubstons) congregate, forming fractal structures large enough to scatter light.⁴⁶ Further the concentration of bubstons is higher near a hydrophobic surface in water.⁴⁷ Analysis of the flow of water in thin hydrophobic capillaries^{17,18} suggests that slip does not occur directly over the solid surface but over a gap between the liquid and the solid.

Theoretical estimates of the supersaturation required to induce cavitation in water range from 500 to 10 000 atm.²⁵ However, experimentally, values much lower, from 100 to 300 atm, have been realized.^{48–50} This is despite careful and elaborate efforts to remove nuclei. Ultrasonic measurements of the tensile strength of degassed water give values of 6–8 atm which are reduced to less than 1 atm for gassed water.²⁵ The effects of radiation have been studied for ultrasonically induced cavitation, and the results are somewhat surprising.

Neutron Radiation and Cavitation. Sette and Wanderlingh have clearly demonstrated that the micronuclei responsible for sonic cavitation are formed by cosmic neutron radiation.²³ Using an experimental arrangement that focuses the ultrasound, they were able to avoid the influence of interfaces and ensure that cavitation took place in the bulk of the fluid. The cavitation threshold was determined for distilled water surrounded by lead and paraffin screens of variable thickness and also when screens were not present. Further, the effect of a Ra–Be neutron source on the cavitation threshold was studied. The cavitation threshold is defined as the minimum sound intensity that gives rise to visually detectable cavities. The presence of a neutron shielding screen was found to increase the cavitation threshold of the water. Upon removal of the screens, the cavitation threshold dropped to the initial value. Alternatively, the screens could be left in place and the solution subjected to neutron radiation (from within the screens). The cavitation threshold was again found to drop to the initial value of untreated, unscreened distilled water. Earlier work using either a positron or neutron source was able to eliminate positron radiation as a source of micronuclei. It was concluded from this work that recoil oxygen or carbon nuclei from neutron collisions, rather than recoil protons, were the most probable nucleating agents for micronuclei.²²

The time for the cavitation threshold to vary by half the maximum variation possible was about 70 min. The Ra–Be source produced 1.5×10^5 neutrons with a maximum energy of 10 MeV, with a Gaussian energy distribution peaked around 4 MeV. The energy of neutrons entering the water could be attenuated using a paraffin shield. A shield that causes approximately 90% energy attenuation was used, and the cavitation threshold studied. No effect on the threshold was found. This suggests that only neutrons of sufficient energy are capable of forming nuclei. The indication is that energies between 1 and 10 MeV are necessary. Finch²⁵ reported similar results using degassed water, with a shorter time of 25 min for the cavitation

threshold to vary by half the maximum variation. In the work presented here experiments were carried out within 10 min of irradiation being ceased, to avoid complications associated with the decay of the effect.

Neutrons with energies in excess of 10 MeV are present in cosmic radiation. Their density at $2 \times 10^{-4} \text{ cm}^{-2} \text{ s}^{-1}$ ⁵¹ is considerably less than the neutron density due to the artificial Ra–Be neutron source, yet the effect on cavitation thresholds is similar. This observation may be rationalized in two ways. Either (i) there exists some limit to the number of nuclei that can exist in the liquid at any one time which is not determined by the neutron flux or (ii) only neutrons of sufficient energy are able to form nuclei, and only a small percentage of the neutrons emitted by the Ra–Be neutron source are of this energy. The second contention is supported by the work of Sette and Wanderlingh.²³ They estimate that oxygen recoil nuclei must possess an energy of ~ 2.5 MeV or greater in order to form cavitation nuclei, and neutrons of ~ 10 MeV or greater are required to produce oxygen recoil nuclei of these energies. This implies then that only the most energetic of neutrons from the Ra–Be source are able to create cavitation nuclei.

We can now reconsider our results. While removal of dissolved gases was found to reduce the attraction between hydrophobic surfaces, neutron treatment prior to measurement results in an increase in the attraction (cf. Figures 5 and 6). In addition to the formation of cavitation nuclei by oxygen recoil nuclei, neutron irradiation has other effects on the solution. Neutrons produce OH• free radicals along the path of the particle as it passes through water.³³ The emitted γ -rays produce H• free radicals distributed some 15 nm from the same path.³³ These will react to form many H₂ and O₂ molecules and occasionally may react with a surfactant molecule. Further the α radiation emitted may interact with the solution, but only very low levels of α particles will penetrate into the solution. Clearly neutron irradiation causes a complicated array of effects in solution that are not remotely understood.

Sonication studies would suggest that the increased attraction measured following neutron irradiation is associated with the production of micronuclei. However, a calculation of the concentration of micronuclei that could be formed from the neutron source due to recoiling oxygen nuclei is disconcerting. It reveals that an insufficient number are produced to explain an increase in the hydrophobic attraction between a small probe and a flat surface. An explanation associated with the production of radicals can also be discounted, as while many radicals are produced from each neutron, most will recombine to form water.⁵² If the micronuclei produced by neutron irradiation accumulate favorably at hydrophobic surfaces, then the increase in the attraction may be associated with their presence. Evidence for this accumulation has come recently from light scattering studies near hydrophobic surfaces.⁴⁷ Alternatively, a new, efficient unknown mechanism for micronuclei formation that creates many more nuclei per neutron would need to be invoked. Finally, we remark that nucleation of micronuclei from the dissolved gas already present in solution, and from gas formed by hydrolysis, may be responsible for an increased attraction.

Conclusion

The mechanism(s) responsible for long-range attractions between hydrophobic surfaces in aqueous solutions remains unresolved. However, the recent demonstration that the attraction remains in the presence of high salt⁴¹ and the demonstration here that it is (i) increased following

neutron irradiation, (ii) decreased upon the removal of dissolved gas, and (iii) decreased upon increasing the approach velocity of the surfaces strongly suggest that the attraction is related to the metastability of the thin aqueous film present between the interacting hydrophobic surfaces.

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