Force Trace Hysteresis and Temperature Dependence of Bridging Nanobubble Induced Forces between Hydrophobic Surfaces

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ABSTRACT An atomic force microscope and the colloidal probe technique are used to probe the interaction between a hydrophobic particle and a hydrophobic surface in water. The characteristics of the observed force curves strongly suggest that a gas bubble is formed when the particle is moved toward the surface and that the bubble ruptures when the particle subsequently is retracted from the surface. We demonstrate that this type of interaction is not unique for hydrophobic surfaces in water since the interaction between hydrophilic surfaces in air provides very similar force curves. However, the interaction between hydrophobic surfaces vanish if water is replaced by an organic solvent with low polarity. The bridging bubble model is employed to explain the hysteresis observed between approach and retraction force traces and experimental conditions where the hysteresis can be almost eliminated are identified. Finally, it is demonstrated that the hydrophobic interaction is strongly temperature dependent and this dependence can be attributed mainly to the decreasing solubility of air in water with increasing temperature.

KEYWORDS: AFM · colloidal probe · hydrophobic interaction · bubbles · hysteresis · temperature dependence · fluorocarbon

The hydrophobic effect is of crucial importance for many life processes such as protein folding and self-assembly of lipids and surfactants. The driving force for hydrophobic assembly is mainly of entropic origin and is related to the unique properties of water. On the molecular level the widely accepted explanation is that hydrophobic molecules lower the entropy of the surrounding water molecules by restricting the number of configurational microstates of the hydrogen bonding network. However, this mechanism has been questioned and may not provide the full picture as discussed recently by Ball.[1] Similar to the assembly of hydrophobic molecules, hydrophobic colloids or macroscopic hydrophobic surfaces have been observed to attract each other in aqueous media. However, this interaction occurs on length scales which are much larger than the molecular scale. Although the underlying reason might be the same as for molecular entities, namely, that the hydrophobic interface perturbs the hydrogen bonding network in water, the direct mechanism for the interaction must be different. The explanation for the observed attraction between extended hydrophobic surfaces has been a great puzzle for many years, and a large number of different models have been proposed.[2−5] In many cases, compelling evidence indicates that the interaction is a consequence of the formation of nanoscopic or even microscopic gas bubbles that are bridging the surfaces. Today it is widely believed that this is the main mechanism for the observed attraction between macroscopic hydrophobic surfaces.

Hydrophobic interactions due to the formation of bridging gas bubbles are also the topics of the study presented in this paper. By using an atomic force microscope (AFM) and the colloidal probe technique[6] where a well-defined micrometer-sized spherical particle is attached to the end of an AFM cantilever, it has been possible to perform direct studies of the interaction between such a hydrophobic particle and a planar hydrophobic surface in water. This geometry is well-defined and also has the advantage that it is mathematically equivalent to the geometry employed in the surface force apparatus (SFA) which measures forces between two crossed cylinders. Even though interactions due to bridging bubbles between hydrophobic surfaces previously have been reported,[7−11] many details regarding this phenomenon still call for an explanation. In the following we have focused on three issues: First, to characterize the distinct features in the approach and

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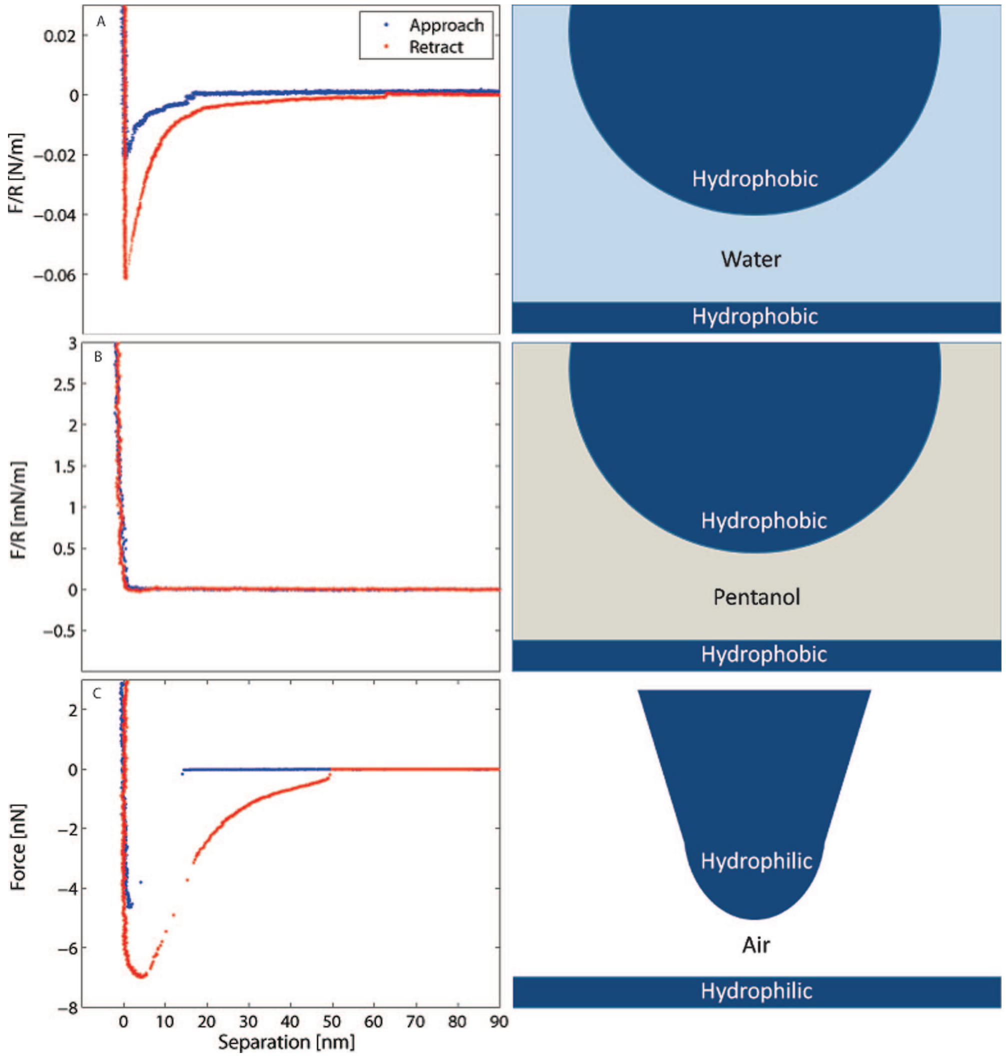

Figure 1. Approach and retraction curves for three different situations. (A) Interaction in 10 mM NaCl between a hydrophobized silica colloidal probe and a hydrophobized silica surface. (B) Interaction in pentanol between a hydrophobized silica colloidal probe and a hydrophobized silica surface. (C) Interaction obtained in air between an uncoated (hydrophilic) silicon AFM tip and an uncoated (hydrophilic) silica surface.

retraction force curves and their dependence on local surface properties. Second, to investigate the mechanism behind the observed hysteresis between approach and retraction curves. Third, to investigate the impact of a variation in the temperature on the force curve characteristics.

RESULTS AND DISCUSSION

We have measured the interaction in aqueous solution between a hydrophobized silica surface and a hydrophobized colloidal silica particle mounted on an AFM cantilever. In Figure 1A is shown typical approach and retraction force curves for this set of hydrophobic surfaces immersed in 10 mM NaCl. In some previous studies performed with AFM and with the SFA, a continuous long-range attraction was observed during approach.[12−15] However, such a continuous long-ranged attraction is not seen in the approach force curve for this system. Instead, at a surface separation of approximately 15 nm a discontinuous jump to an attractive force is observed. The first jump is followed by another jump where after the attractive force gradually increases until the probe and the surface repel each other in contact. Both the specific jump-in separation as well as the actual number of discrete jump events is observed to vary between individual force curves. When the probe subsequently is retracted from the surface, we initially observe a strong adhesion followed by a jump-out. After the jump-out a long-range attraction persists that decreases gradually out to a separation of 60−75 nm, where after the force suddenly drops to zero. If the aqueous solution is substituted by pentanol, none of these effects were observed (see Figure 1B). The effect of changing the solvent is thus an important control observation since it clearly demonstrates that the jump-in is a consequence of the hydrophobicity of the two surfaces and that the long-range attraction is mediated specifically by water rather than being a result of an interaction between molecules protruding from the two surfaces.

The behavior seen in the approach and retraction force curves in Figure 1A is attributed to the formation of a submicroscopic bubble bridging the two surfaces. To gain more insight into this phenomenon, it is useful to compare the force curve features with a force curve measured in an inverse setup where two hydrophilic surfaces in a humid atmosphere are pulled together by a capillary bridge of water. In this case the interfacial pull is known to be responsible for the attraction between the surfaces. With this purpose, we have measured the interaction in air between a hydrophilic AFM tip on a cantilever (standard tapping mode cantilever) and a clean glass surface (see Figure 1C). Upon retraction the interaction follows a characteristic trend, with a decreasing attractive force, out to a separation of 50 nm where the capillary bridge ruptures. The attraction observed when extending a capillary bridge is supposed to follow the force law

$$F = 4\pi R\gamma_{L} \cos\theta / (1 + D/d) \tag{1}$$

where R is the radius of the probe, γ_L is the surface tension, θ is the contact angle, D is the separation, and d is the thickness of the condensed water film.[16] In this particular case, several of these parameters are unknown. However, the retraction force curve in Figure 1C at least qualitatively follows this force law, which clearly shows that the attraction indeed is controlled by the interfacial pull. Although there are clear difference between the two systems, *e.g.*, that a thin film of water exist on the hydrophilic surface while a film of gas with the same thickness is unlikely to exist at the hydrophobic surface, the similarity between panels A and C of Figure 1 provides further support for the hypothesis that a bubble of gas is formed between the hydrophobic colloidal particle and the hydrophobic surface and that interfacial tension governs the attractive interaction. Alternatively, such a behavior could be attributed to hydrophobic contaminants accumulated at the surface as previously suggested by McKee and Ducker.[17] However, great care was taking in rinsing the surfaces after they were hydrophobized, and further a similar behavior has been seen for a number of very different systems.[9−11] Thus, we do not find contaminants to be a likely explanation in this case.

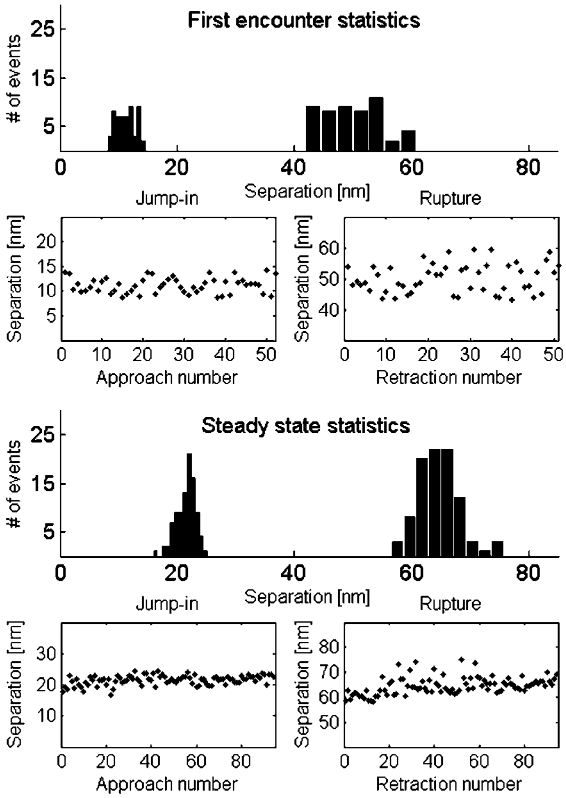

Figure 2. Histograms of jump-in and rupture separations obtained at 25 °C. The upper figures contain values measured during the first encounter while the lower figures contain values obtain in repeated steady-state measurements. Neither the first encounter statistics nor the steady-state statistics display any systematic change with time during the measurements.

Formation and Rupture of a Bridging Bubble. The following experiments were conducted using two different methods. First, a number of force curves were obtained where each approach−retraction cycle was performed at a new lateral position on the surface by using the (x,y)-offset function on the AFM. This generates the *first encounter* statistics. Second, a number of force curves were obtained at the same surface position by setting the AFM to perform continuously repeated approach−retraction cycles. This generates a *steady state* statistics. In both cases the jump-in separations from the approach force curves and rupture separations from the retraction force curves were recorded. In Figure 2 histograms of jump-in separations from two such series of experiments are shown. As seen, the average jump-in separation in the first encounter is around 10 nm while in the steady-state cycles it is increased to over 20 nm. If we assume that the jump-in is due to the formation of a bubble, it means that the bridging bubble is created at larger interface separations in the steady-state force curves compared to the first encounter. A similar behavior has previously been interpreted as indications that a bubble is formed on the first encounter, and when the bubble subsequently ruptures during retraction, it is leaving a bubble on the surface.[8,9,18,19] On the subsequent approach this bubble persists and is leading to a new bridging bubble between the two surfaces at a larger separation. When the bubble is extended during retraction, it ruptures at a characteristic separation where the bridge becomes unstable. The histograms of rupture lengths for the two experiments are shown in Figure 2. Similar to the jump-in separations, it is observed that the average rupture separation is shorter at the first encounter than at steady state which is consistent with previous studies.[20,21] Further, it is seen that the distribution is broader when a new position is probed at each ap-

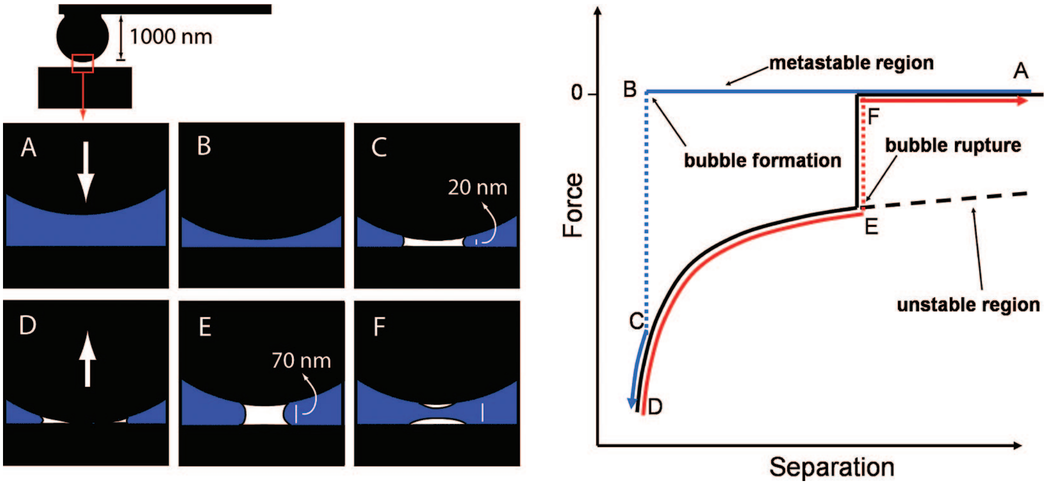

Figure 3. Conceptual model for bubble formation and rupture between a hydrophobic colloidal probe and a hydrophobic surface. The left panel shows how a bubble forms during approach (A−C) and ruptures during retraction (D−F). The right panel shows a schematic diagram of the force *vs* separation relationship during approach (blue line) and retraction (red line). Starting at panel A, the particle is approached toward the surface with no bubble bridging to the surface. At panel B a bubble is spontaneously formed and the system jumps to panel C and moves continuously into contact at panel D. Upon retraction the system goes through panel C to panel E where the bubble becomes unstable and ruptures which leaves a smaller bubble on the surface. It is suggested that the system follows the most stable route during retraction (given by the black solid line) while the system is follows a metastable route upon approach.

proach. From Figure 2 it is also clear that there is no systematic trend with time in the jump-in and bubble rupture separation during both series of measurements. These results indicate that the size of the bubble does not change from the second force curve to the end of the experiment, implying that not much additional gas is collected over time. Thus, the formation of the bubble appears to be a local phenomenon where most gas in the bubble is collected from an area in proximity to the contact area during the very first encounter. Small local variations in the distribution of gas close to the surface result in broader distributions of jump-in and bubble rupture separations in the first encounter statistics.

Force Trace Hysteresis. In addition to characterizing the jump-in and rupture phenomena, one should also pay attention to the hysteresis between approach and retraction force curves. Upon approach, the bubble is formed at a separation of 10−30 nm, while upon retraction it is stable out to a separation of 60−75 nm. This hysteresis is not unique for the situation with the bridging bubble. As already shown, a qualitatively similar observation is made for the interaction between a hydrophilic tip and a hydrophilic surface in air (Figure 1C). The hydrophilic tip jumps into contact at a separation of 10−15 nm even though during retraction the capillary bridge is stable out to a separation of approximately 50 nm. In this case the interpretation is straightforward: The capillary bridge cannot be formed before the tip gets close to the liquid film on the surface even though the formation of a capillary bridge can exist at larger separations as seen during retraction. One possible explanation is that an unformed capillary bridge constitutes a metastable state, separated from the most favorable state by an energy barrier of a height given by the energy needed to raise the water bridge against the surface tension.

As already discussed, this system has some parallels and some deviations from the case of a bridging bubble between hydrophobic surfaces in water. In the latter system, the bridging bubble is the most stable state out to a separation of approximately 60−75 nm. However, during approach the bubble is not formed before the surfaces are in much closer contact simply because the energy barrier the system must overcome for the bridging bubble to form is too high. In the case of hydrophilic surfaces in air, the barrier vanishes when the tip reaches the liquid film and it jumps into contact whereas in the case of hydrophobic surfaces in water the mechanism which leads to the jump into contact must be different. Theoretical studies suggest a drying transition when hydrophobic surfaces come close to contact.[22−24] A minor vacuum or water vapor cavity formed between the surfaces could fill up with dissolved gas and thereby form a larger bubble between the surfaces. However, such a cavity will not spontaneously form at a separation of 10 nm or more, and thus smaller preformed nanobubbles or a gaseous layer in proximity to the surface must be involved in the phenomenon. Furthermore, the fact that the jump-in phenomenon occurs in steps is another strong indication that preformed bubbles are involved. The conceptual model used to rationalize the approach−retraction data is summarized in Figure 3.

The hysteresis described above has the consequence that the long-range attraction only occurs when the surfaces have already been in close contact. However, if one imagines a situation where a bubble is bridging the surface both during approach and retraction, the behavior is expected to be very different. If the bubble model is correct and the attractive force observed during retraction is caused by an interfacial pull, the force curves should display absence of hysteresis for a certain separation range: When a bubble bridges the surfaces, the long-range attraction should be independent of the direction the two surfaces move relative to each other. This means that the force traces during approach and retraction should be completely reversible if the colloidal probe is first retracted while a bubble is bridging the surfaces and then subsequently approached before the bubble has ruptured. This prediction is confirmed in an approach–retraction cycle where we continuously decreased the maximum separation the probe was retracted from the surface. By this procedure we could reach a separation where the probe could be approached and retracted several times without breaking the bridging bubble. The typical outcome of this experiment is shown in Figure 4 where it is seen that the approach and retraction force curves superimpose at separation larger than 20 nm (Figure 4C). This means that the force trace is indeed reversible after the particle has jumped out of hard contact and reached a certain separation. In relation to Figure 3 this means that the system can follow the stable route between panel D and panel E during both approach and retraction as long as the bubble has not ruptured. However, at small surface separations (below 20 nm) the approach and retractions curves do not follow the same force trace. Although the results in Figure 4 are logical if one considers the attraction solely in terms of an interfacial pull, it should be mentioned that our results partly contradict results from previous studies.[7,10] Yaminsky and Ohnishi[10] have conducted an experiment with the surface force apparatus where two hydrophobic surfaces were brought into contact and a cavity was formed. Subsequently the surfaces were separated by 1200 nm and then brought back to contact without breaking the bubble. In that case nothing similar to our results outlined in Figure 4 was observed. Instead a hysteresis behavior where a much stronger force observed during retraction than during approach was explained in terms of contact angle hysteresis. A very similar observation from an experiment performed with a different kind of surface force apparatus (MASIF) has been reported by Parker et al.[7] However in the latter case the absolute distance between the surfaces was not measure during the retraction–approach loop. Important differences between these experiments and the experiments reported here are the size of the bubble and the relative length the bubble is extended in the retraction–approach loop. In ref 10 it is mentioned that a microscopic (visible) bubble was formed during contact and a retraction force curve which is qualitatively similar to Figure 1A shows that the bubble does not rupture before the surfaces have reached a separation of 49 μm. This illustrates a difference between results obtained by a different surface force method which is not corrected for by the Derjaguin approximation. The bridging bubble observed in a colloidal probe AFM experiment is much smaller and thus ruptures at a smaller separation than a bubble studied with the sur-

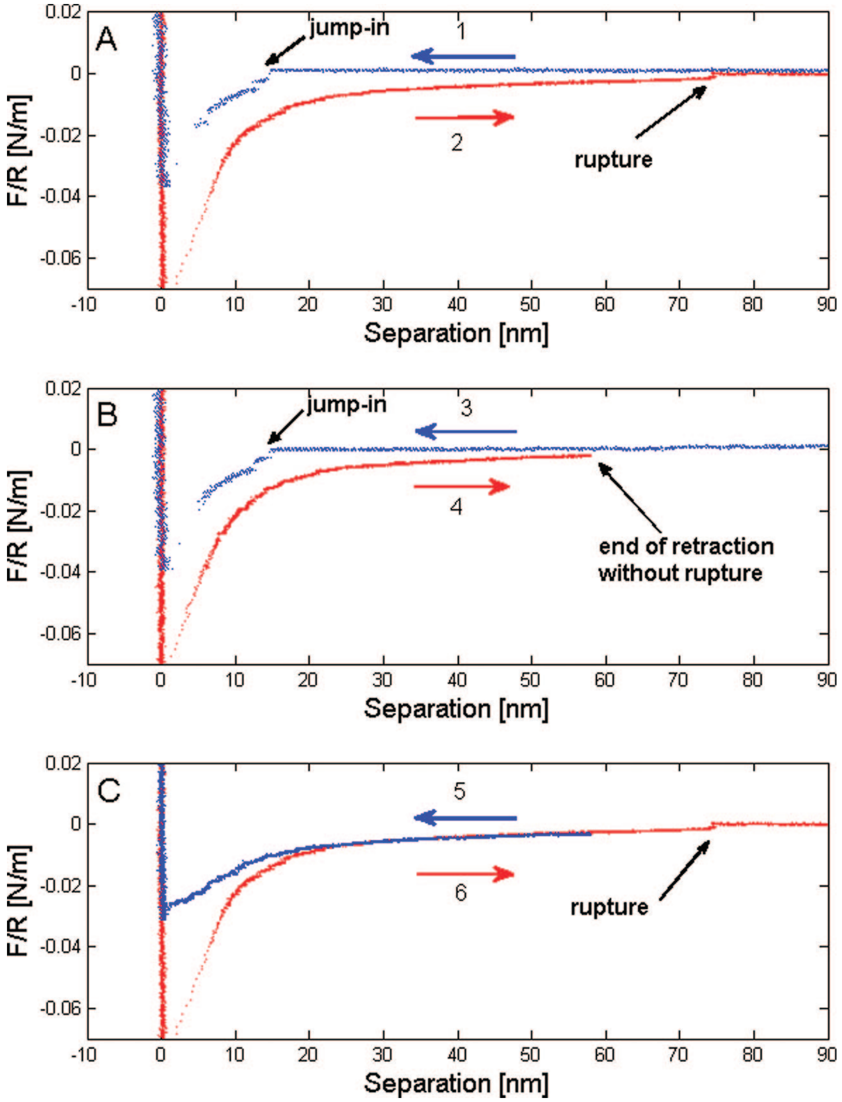

Figure 4. (A) Investigation of hysteresis effects in hydrophobic interactions. The colloidal probe is initially moved toward the surface and jumps into contact when a bubbles forms (1) and thereafter retracted to a separation where the bridging bubble has ruptured (2). (B) The probe is again approached (3) and then retracted, but now only to a separation where the bridging bubble remains intact (4). (C) The probe is approached with the bubble still bridging the surfaces and a long-range attraction is observed (5). Finally the probe is retracted until the bubble ruptures (6).

face force apparatus. Thus, in this case not only the magnitude of the force but also the range of the force needs to be somehow corrected for by the dimensions of the surfaces. If the results in refs 7 and 10 are scaled to our system where the bubble typical ruptures at a separation of 60–75 nm, it should be compared to retraction–approach loop of only a few nanometers. This actually compares well to our results where we observe a hysteresis behavior at small separations while no hysteric behavior is observed at larger separations. On the basis of these observations, we suggest that the interaction is completely dominated by the interfacial pull when the bubble is fairly extended. However, at smaller separation where the bubble has to spread laterally over the surface and thereby change its contact area with the surface, contact angle hysteresis seems to play a significant role.

We expect the observation that the approach force trace depends on the starting separation to be important for the aggregation process of a suspension of hydrophobic colloids in an aqueous media. If the density of colloids is high, the long-range attraction will always be present since the average separation between particles will be shorter than the bubble rupture separation. On the other hand, if the density of colloids is low, no long-range attraction will be present and the aggregation will thus solely be controlled by diffusion.

Effect of Changing Temperature. The results described above are reproducible when probing different spots on the same surface and when probing different samples prepared in the same manner. However, the hydrophobic interaction forces are sensitive to many additional physical parameters. For example, a change in contact angle which will make the surface more or less hydrophobic has already been shown to have a large effect on hydrophobic interactions.[9,18,25] However, even for the same set of hydrophobic surfaces, the interaction will be sensitive to changes in chemical or physical environment. Here we have studied the effect of changing the temperature in an interval between 20 and 40 °C, and the results of these experiments are summarized in Figure 5. The interval between 20 and 40 °C was partly chosen for practical reasons. In our experimental setup the temperature is easiest to control and keep stable in a relatively narrow interval around room temperature. However, we believe that the investigated temperature interval is highly relevant. Most previous AFM experiment have been performed at room temperature (20–30 °C), and due to heating from the laser, the temperature in the liquid cell will typically be 5–7 °C higher. Thus, the chosen temperature interval covers the typical experimental conditions. Furthermore, in biology most processes occur in this temperature interval and any changes in the interaction within this temperature interval will thus be of relevance for hydrophobic interactions in biological systems.

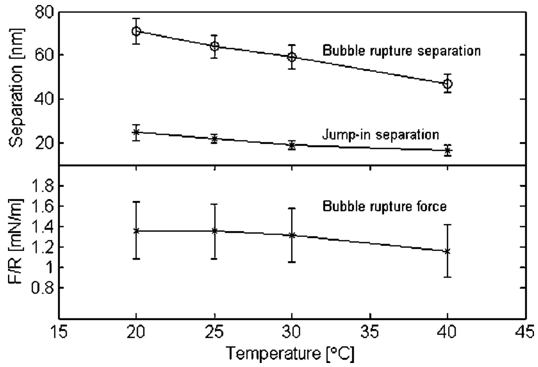

Figure 5. Temperature dependence of the jump-in separation determined from approach force curves and bubble rupture separation and rupture force determined from retraction force curves. Each point represents the average of results from minimum of 94 force curves obtain during steady-state measurements, and the error bars indicate the standard deviation in each case.

By increasing the temperature, we observe a significant and approximately linear decrease in the jump-in separation during approach and in the bubble rupture separation during retraction. Over this temperature range the decreases in jump-in separation and bubble rupture separation follow each other with a total decrease of approximately 33%. The change in the force level prior to rupture, F_{rupture}, is less pronounced, and the values are less accurate due to the limitation in the force resolution. However, we also find an approximately 15% decrease in bubble rupture force when changing the temperature from 20 to 40 °C. A decreased jump-in separation is an indication of a reduction in bubble size while a decrease in bubble rupture separation can be due to either a reduction in bubble size or a decreased stability of the extended bubble. An increase in temperature leads to a slight decrease in surface tension which will increase the stability of a bubble and also lower the energy cost for extending a bubble. However, an increase in temperature will also lead to a reduction in the solubility of air in water. This is important since we have used a liquid cell with an open design (see Materials and Methods) and thus expect the liquid to be in gas equilibrium at all temperatures. The decrease in solubility of air will therefore decrease the reservoir of (dissolved) air in proximity to the surface and thus lead to smaller bubbles between the probe and the surface. The observed decreases in both jump-in and bubble rupture separation suggest that the decrease in solubility of air is the most important effect while the small decrease in bubble rupture force could be an effect of a lower surface tension. Oppositely, one could argue that if the bubble is mainly consisting of water vapor and not trapped air, an increase in temperature should lead to a more long-range force since the energy penalty for forming a cavity will decrease. Since such an effect is not observed, it suggests that it is indeed air and not water vapor which dominates the pressure in the bridging bubble. However, it should be mentioned that in a previous study by Parker *et al.*,[7] an increase in the jump-in distance was observed when the temperature was increased from 20 to 40 °C. Although no statistics were provided to confirm if the trend was consistent, the fact that they used a closed system could possibly explain the difference. Consider a liquid cell where the liquid is saturated with air at 20 °C and the temperature subsequently is increased to 40 °C. If, the system is not allowed to release dissolved air to reach a new gas equilibrium with the atmosphere, either the water will be supersaturated with air or the surplus of air will be accumulated at the hydrophobic surface. A decrease in the solubility of air can thus have the opposite effect in a system which is not allowed to equilibrate.

CONCLUSION

The results presented in this paper enhance the general understanding of the physical chemistry of hydrophobic surfaces interacting in water. In particular, important details concerning the formation and rupture of a bridging bubble have been examined and discussed. We have shown how the force traces between hydrophilic surfaces in a humid atmosphere carry similarities with the force traces between hydrophobic surfaces in water. Hydrophilic surfaces in air connected by a capillary bridge of water correspond qualitatively to the inverse geometry of two hydrophobic surfaces in water connected by a bridging gas bubble, and both systems are kept together by an interfacial pull. The similarities between the force traces are thus strong evidence for the bubble model summarized in Figure 3. The interaction among hydrophobic surfaces is known to be strongly dependent on measurable surface properties such as the contact angle. In the present study we have further shown how the interaction forces between a specific set of surfaces correlate strongly with their chemical and physical environments. We have demonstrated how attractive interactions between hydrophobic surfaces vanish when the aqueous medium is substituted by an organic solvent such as pentanol, and we have shown that the spatial range of the interaction decreases significantly with increasing temperature. To our knowledge, there are only two other studies with the surface force apparatus where the effects of the temperature on hydrophobic interactions have been investigated.[7,26] However, all previous AFM studies, measuring bridging-bubble forces, have been performed at room temperature and no temperature control has been applied. We have also shown that the interaction depends not only on the environment and the surface properties but also on the detailed way the surface is probed. The jump-in separation during approach depends on whether the particle has previously encountered the same position on the surface or not. More importantly we have shown that the direction-dependent force trace can be turned into an almost reversible and hysteresis-free force trace if the particle after one approach is not retracted beyond the bubble rupture separation. On the basis of this observation we suggest that the attractive force is almost entirely determined by the interfacial pull when the bridging bubble is fairly extended while contact angle hysteresis might come into play when the two hydrophobic surfaces are in close contact. Increasing our knowledge of the hysteresis behavior between approach and retraction force curves not only is important for understanding the force traces measured by AFM or related techniques, but also can also be of practical importance for the stability of suspensions of hydrophobic colloids in aqueous solutions and in technical processes such as flocculation.

MATERIALS AND METHODS

Surfaces and AFM Probes. For the experiments a hydrophobic surface and a hydrophobic colloidal probe AFM cantilever were prepared. The substrate used was a microscope cover glass (Menzelgläser directly into our AFM liquid cell. The cover glass was cleaned in hot piranha solution (30% by volume H_2O_2 and 70% by volume H_2SO_4) for 15 min followed by extensive cleaning in water and by plasma treatment using a Harrick extended plasma cleaner at full effect for 20 min. After being cleaned, the surface was from an AFM image determined to have a rms (root mean square) roughness, $S_{RMS} = 0.543$ nm. Colloidal probe cantilevers were rinsed in water and ethanol followed by plasma treatment. Surfaces and colloidal probe cantilevers were made hydrophobic by a self-assembled monolayer (SAM) of trichloro(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silane (Aldrich, 97%) prepared by leaving surfaces and cantilevers in a closed container with a couple of droplets of the SAM agent for a few minutes. The short incubation time provided flat homogeneous surfaces ($S_{RMS} = 0.566$ nm) with a high water contact angle of approximately 110° while longer incubation time gave a more rough surface with clusters of aggregated material. Afterward, surfaces and cantilevers were washed carefully in heptane → isopropanol → ethanol → 1/1 ethanol−water → water and finally dried in a desiccator under low pressure where it was also stored until use. The hydrophobic surface and colloidal probe were used less than 24 h after preparation.

Force Measurements. Force measurements were carried out on a JPK NanoWizard (JPK Instruments, Berlin, Germany) in a temperature-controlled liquid cell (BioCell) from JPK Instruments. Rectangular cantilevers (NSC12 C-lever, MicroMasch) with attached silica particles of size $D = 1$ μm were purchased from Novascan Technologies (Ames, IA). The spring constants of the cantilevers were determined by the Hutter and Bechhoefer method and by the Sader method as described elsewhere.[27,28] All force curves presented in this study were recorded with a constant approach and retraction velocity of 500 nm/s, except for the force curves shown in Figure 4 which were recorded at an approach and retraction velocity of 30 nm. Experiments were performed in 10 mM NaCl solution to screen any electrostatic contributions to the force curve. Solutions were degassed immediately prior to the experiments. This was mainly done to avoid nucleation of microscopic air bubbles on the sample surface when the aqueous solution was introduced to the AFM liquid cell. However, our liquid cell has an open design where the liquid can exchange gas with the atmosphere during the course of the experiment. Further, since the system is left for temperature equilibration between each set of measurements, we expect the solution to be saturated with air at all temperatures.

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REFERENCES AND NOTES

1. Ball, P. Water as an Active Constituent in Cell Biology. *Chem. Rev.* **2008**, *108*, 74–108.
2. Christenson, H. K.; Yaminsky, V. V. Is the Hydrophobic Attraction Related to the Mobility of Hydrophobic Surface Groups? *Colloids Surf., A* **1997**, *129−130*, 67–74.
3. Attard, P. Nanobubbles and the Hydrophobic Attraction. *Adv. Colloid Interface Sci.* **2003**, *104*, 75–91.
4. Christenson, H. K.; Claesson, P. M. Direct Measurements of the Force between Hydrophobic Surfaces in Water. *Adv. Colloid Interface Sci.* **2001**, *91*, 391–436.
5. Meyer, E. E.; Rosenberg, K. J.; Israelachvili, J. Recent Progress in understanding Hydrophobic Interactions. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *103*, 15739–15746.
6. Ducker, W. A.; Senden, T. J.; Pashley, R. M. Direct Measurements of Colloidal Forces Using an Atomic Force Microscope. *Nature* **1991**, *353*, 239–241.
7. Parker, J. L.; Claesson, P. M.; Attard, P. Bubbles, Cavities, and the Long-Ranged Attraction between Hydrophobic Surfaces. *J. Phys. Chem.* **1994**, *98*, 8468–8480.
8. Carambassi, A.; Jonker, L. C.; Attard, P.; Rutland, M. W. Forces Measured between Hydrophobic Surfaces Due to a Submicroscopic Bridging Bubble. *Phys. Rev. Lett.* **1998**, *80*, 5357–5360.
9. Ishida, N.; Kinoshita, N.; Miyahara, M.; Higashitani, K. Effect of Hydrophobizing Methods of Surfaces on the Interaction in Aqueous Solutions. *J. Colloid Interface Sci.* **1999**, *216*, 387–393.
10. Yaminsky, V.; Ohnishi, S. Physics of Hydrophobic Cavitation. *Langmuir* **2003**, *19*, 1970–1976.
11. Thormann, E.; Simonsen, A. C.; Hansen, P. L.; Mouritsen, O. G. Interactions between a Polystyrene Particle and Hydrophilic and Hydrophobic Surfaces in Aqueous Solutions. *Langmuir* **2008**, *24*, 7278–7284.
12. Israelachvili, J. N.; Pashley, R. M. Measurement of the Hydrophobic Interaction between 2 Hydrophobic Surfaces in Aqoues-Electrolyte Solution. *J. Colloid Interface Sci.* **1984**, *98*, 500–514.
13. Pashley, R. M.; McGuiggan, P. M.; Ninham, B. W.; Evans, D. F. Attractive Forces between Uncharged Hydrophobic Surfaces - Direct Measurements in Aqueous-Solution. *Science* **1985**, *229*, 1088–1089.
14. Craig, V. S. J.; Ninham, B. W.; Pashley, R. M. Study of the Long-Range Hydrophobic Attraction in Concentrated Salt Solutions and its Implications for Electrostatic Models. *Langmuir* **1998**, *14*, 3326–3332.
15. Craig, V. S. J.; Ninham, B. W.; Pashley, R. M. Direct Measurement of Hydrophobic Forces: A Study of Dissolved Gas, Approach Rate, and Neutron Irradiation. *Langmuir* **1999**, *15*, 1562–1569.
16. Israelachvili, J. N. *Intermolecular and Surface Forces*; Academic Press, Inc.: San Diego, 1992; pp 330−334..
17. McKee, C. T.; Ducker, W. A. Refractive Index of Thin, Aqueous Films between Hydrophobic Surfaces Studied Using Evanescent Wave Atomic Force Microscopy. *Langmuir* **2005**, *21*, 12153–12159.
18. Mahnke, J.; Stearnes, J.; Hayes, R. A.; Fornasiero, D.; Ralston, J. The Influence of Dissolved Gas on the Interactions between Surfaces of different Hydrophobicity in Aqueous Media Part I. Measurement of Interaction Forces. *Phys. Chem. Chem. Phys.* **1999**, *1*, 2793–2798.
19. Tyrrell, J. W. G.; Attard, P. Atomic Force Microscope Images of Nanobubbles on a Hydrophobic Surface and Corresponding Force-Separation Data. *Langmuir* **2002**, *18*, 160–167.
20. Ishida, N.; Sakamoto, M.; Miyahara, M.; Higashitani, K. Attraction between Hydrophobic Surfaces with and without Gas Phase. *Langmuir* **2000**, *16*, 5681–5687.
21. Yakubov, G. E.; Butt, H.-J.; Vinogradova, O. I. Interaction Forces between Hydrophobic Surfaces. Attractive Jump as an Indication of Formation of “Stable” Submicrocavities. *J. Phys. Chem. B* **2000**, *104*, 3407–3410.
22. Lum, K.; Luzar, A. Pathway to Surface-Induced Phase Transition of a Confined Fluid. *Phys. Rev. E* **1997**, *56*, 6283–6286.
23. Lum, K.; Chandler, D. Phase Diagram and Free Energies of Vapour Films and Tubes for a Confined Fluid. *Int. J. Thermophys.* **1998**, *19*, 845–855.
24. Lum, K.; Chandler, D.; Weeks, J. D. Hydrophobicity at Small and Large Length Scales. *J. Phys. Chem. B* **1999**, *103*, 4570–4577.
25. Rabinovich, Y. I.; Yoon, R.-H. Use of Atomic-Force Microscope for the Measurements of Hydrophobic Forces. *Colloids Surf.* **1994**, *93*, 263–273.
26. Tsao, Y.-h.; Yang, S. X.; Evans, F. Interactions between Hydrophobic Surfaces. Dependence on Temperature and Alkyl Chain Length. *Langmuir* **1991**, *7*, 3154–3159.
27. Hutter, J. L.; Bechhoefer, J. Calibration of Atomic-Force Tips. *Rev. Sci. Instrum.* **1993**, *64*, 1868–1873.
28. Sader, J. E.; Chon, J. W. M.; Mulvaney, P. Calibration of Rectangular Atomic Force Microscope Cantilevers. *Rev. Sci. Instrum.* **1999**, *70*, 3967–3969.