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Interaction Forces between Hydrophobic Surfaces. Attractive Jump as an Indication of Formation of “Stable” Submicrocavities

Gleb E. Yakubov,^{†,‡} Hans-Jürgen Butt,[†] and Olga I. Vinogradova^{*,†,‡}

Institut für Physikalische Chemie, Universität Mainz, Jakob-Welder-Weg 11, 55099 Mainz, Germany, and Laboratory of Physical Chemistry of Modified Surfaces, Institute of Physical Chemistry, Russian Academy of Sciences, 31 Leninsky Prospect, 117915 Moscow, Russia

Received: February 3, 2000; In Final Form: February 28, 2000

We study the interaction between hydrophobized silica surfaces of defined contact angle in water using an AFM-related force measuring device. In all cases the attraction between surfaces leads to a jump into contact from separations larger than expected if only van der Waals forces were acting. The jump distance was found to vary dramatically for different pairs of interacting surfaces. For a given pair of interacting surfaces the jump-in distance is smallest for the first approach, then increases and reaches a steady-state value after measuring 3–10 force curves. This confirms that hydrophobic attraction is closely related to the formation of long-life submicrocavities in the gap between surfaces. These submicrocavities are formed due to the first contacts (separations) of surfaces. Their “stability” is probably a consequence of confinement between hydrophobic solids.

Introduction

The existence of a long-range attractive interaction between hydrophobic surfaces in water is by now well documented.^{1,2} It has already been inferred from dewetting experiments.³ Until recently, all direct measurements of the interaction between hydrophobic surfaces had been carried out with the surface force apparatus (SFA) between two crossed mica cylinders of typically 1–2 cm radius.⁴ The only exception was an investigation of the interaction between silica filaments of 0.5–2 mm radius.⁵ The mica substrate was rendered hydrophobic by adsorption of cationic surfactants,⁶ Langmuir–Blodgett deposition,^{7,8} and, finally, by chemical modification.⁹ The silica filaments were hydrophobized by a standard methylation technique. One of the results of the SFA hydrophobic force measurements was the phenomenon of cavitation observed.^{5,7} It seemed, however, that cavitation only occurred after the surfaces were first brought into contact, and not at any finite separation.^{1,5,7} It was, therefore, concluded that the hydrophobic attraction observed in an SFA is not a direct result of cavitation.^{1,7}

Recent years have seen an increase in the number of devices used for the measurement (such as, for example, a MASIF¹⁰), and the atomic force microscope (AFM) is now becoming an important tool for investigating the interaction between hydrophobic surfaces. In a typical AFM force experiment the interaction between a spherical particle of 2–20 μm diameter attached to the end of a microfabricated cantilever and a plane is measured.^{11,12} The advantage of the AFM is that one can measure the forces between hydrophobic polymers^{13,14} or silanated silica (or glass)^{15–18} and other surfaces.¹⁹ In the AFM technique solid surfaces are continually being brought into contact and separated. This does not readily allow the first interaction between surfaces to be measured. So, taking into

account the conclusions of the SFA experiment, one can suggest that the dynamic nature of the AFM technique may play a role in the effects observed.

The aim of this Letter is to compare the first, second, third etc. interactions between hydrophobic (silanated silica) surfaces measured with our homemade AFM related setup, which is capable of making single approaches to contact. The approach of surfaces was typically characterized by a jump into contact. The main result is that a smaller jump distance was found on the first approach. This suggests that the hydrophobic attraction observed in a usual AFM experiment could be a consequence of cavitation. The reasons for an apparent disagreement with the SFA observations are discussed.

Materials and Methods

Preparation of Surfaces and Water. Silica spheres (Bangs Inc., Carmel, USA) of 4.7 μm diameter were glued onto tipless cantilevers (Digital Instruments, California, V-shaped, 100 μm long, 0.6 μm thick) using a small amount of epoxy resin (Epikote 1004, Shell). Spring constants of each individual cantilever were determined as described before²⁰ and were typically ≈ 0.3 N/m. The particles were treated in O_2 plasma for 100 s and then hydrophobized by exposing them to a vapor of 1,1,1,3,3,3-hexamethyldisilazane (Aldrich, Germany, 99.9%) for 5 h at 70 $^\circ\text{C}$. A silanated silica plate was prepared by silanating a piece of an oxidized silicon wafer with the same procedure.

Water was purified using a commercial Milli-Q system containing ion-exchange and charcoal stages. The deionized water had a conductivity less than 0.1×10^{-6} S/m and was filtered at 0.22 μm . The Teflon cuvette was cleaned in concentrated hot nitric acid for several minutes, followed by thorough rinsing with high-purity water.

Experimental Setup. The experimental setup has been described in detail before.²¹ A silanated silicon wafer was placed onto the bottom of a Teflon cuvette. Then the particle was positioned few micrometers above the surface with a micrometer

* To whom correspondence should be addressed. E-mail: olgav@wintermute.chemie.uni-mainz.de, olvin@ium.ips.ras.ru.

[†] Universität Mainz.

[‡] Russian Academy of Sciences.

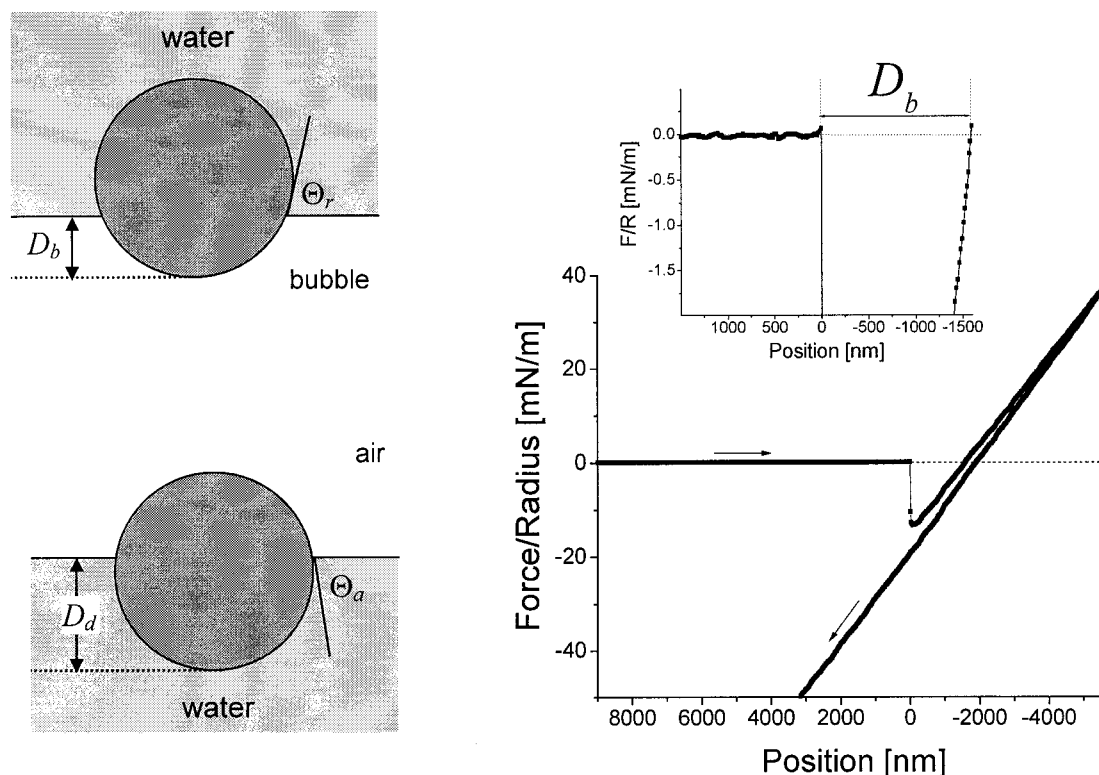


Figure 1. (Left) scheme showing the two types of contact angles measured. (Right) force vs position curve for the interaction measured between a hydrophobized silica sphere and an air bubble in water. The inset shows the part close to jump-in in more detail.

screw driven by a stepper motor (in height) and two micrometer screws of an X–Y-table (lateral position). This was done under optical control of a microscope with a long-distance lens (magnification 120) and a binocular. To measure force-versus-position curves, the cuvette was moved toward the particle with a 15 μm range piezoelectric translator (Queensgate, DPT-CS, England). This translator was equipped with integrated capacitance position sensors, which provided the position with an accuracy of 1 nm in closed-loop operation. During the movement the deflection of the cantilever was measured with an optical lever technique. Therefore, the light of a laser diode (1.5 mW, 670 nm) was focused onto the back of the gold-coated cantilever. After reflection by a mirror, the position of the reflected laser spot was measured with a position sensitive device (United detectors, active area $30 \times 5 \text{ mm}^2$).

Force curves were usually measured in 90 s. This leads to typical driving speeds of 0.3 $\mu\text{m/s}$. We assume that at such a speed the hydrodynamic contribution to the force curve can be ignored (although it is impossible to be absolutely certain of this²²). The height position of the solid surface and the deflection of the cantilever were recorded with a digital oscilloscope (12 bit effective resolution). After the data were transferred into a personal computer, the results were further analyzed. All experiments were done at room temperature without buffer. Hence, the pH was around pH 6.

Interpretation of Force Curves Obtained for Solid Surfaces. The result of a force measurement is a plot of the cantilever deflection Δz_c versus the height position of the piezo translator z . To obtain a total force-versus-distance curve from these data, Δz_c and z have to be converted into force and distance h according to $F = K\Delta z_c$ and $h = \Delta z_c + z$. We further assume that the total force measured is entirely due to a surface force acting.

Contact Angle Measurements. To determine the contact angle of microspheres, we used a method based on the

determination of the equilibrium position of a particle (zero net force) from the force vs position curves.^{23,24} To measure the receding contact angle, a bubble (approximate diameter 1–1.5 mm) was placed by a pipet onto the bottom of the silanated silica plate. The plate is moving toward a bubble. When the particle touches the air–water interface, a three-phase contact is formed and the capillary force pulls the particle into the bubble. When the bubble is moved further up at a certain position, no force is acting on the particle. This zero-force equilibrium position of the microsphere is characterized by the penetration depth D_b , which can be directly obtained from force vs position curve, because this is the difference between the jump-in point and the zero-force position (Figure 1). Then the receding contact angle is calculated from $\cos \theta_r = 1 - D_b/R$. Advancing contact angles of particles θ_a were obtained from a similar experiment with water drops (approximate diameter again 1–1.5 mm). From the penetration depth of the particle into the zero-force position of the drop surface D_d the advancing contact angle was calculated according to $\cos \theta_a = D_d/R - 1$.

Measurements on planar surfaces were done by observation of a sessile drop with a commercial setup (Krüss, G10, Hamburg, Germany) equipped by a stepper motor to drive the syringe that controls the drop volume. The estimated error is $\approx 1^\circ$.

Results and Discussion

Imaging the hydrophobized spheres and silicon wafers with a regular AFM tip revealed that 1,1,1,3,3,3-hexamethyldisilazane forms a smooth monolayer. Root-mean-square roughness over a $1 \mu\text{m} \times 1 \mu\text{m}$ area was in the range 0.5 nm for both an individual sphere and a wafer. No indications of larger asperities or peaks were detected (Figure 2).

Receding contact angles measured with different particles were highly reproducible and showed a variation of only $\pm 1^\circ$

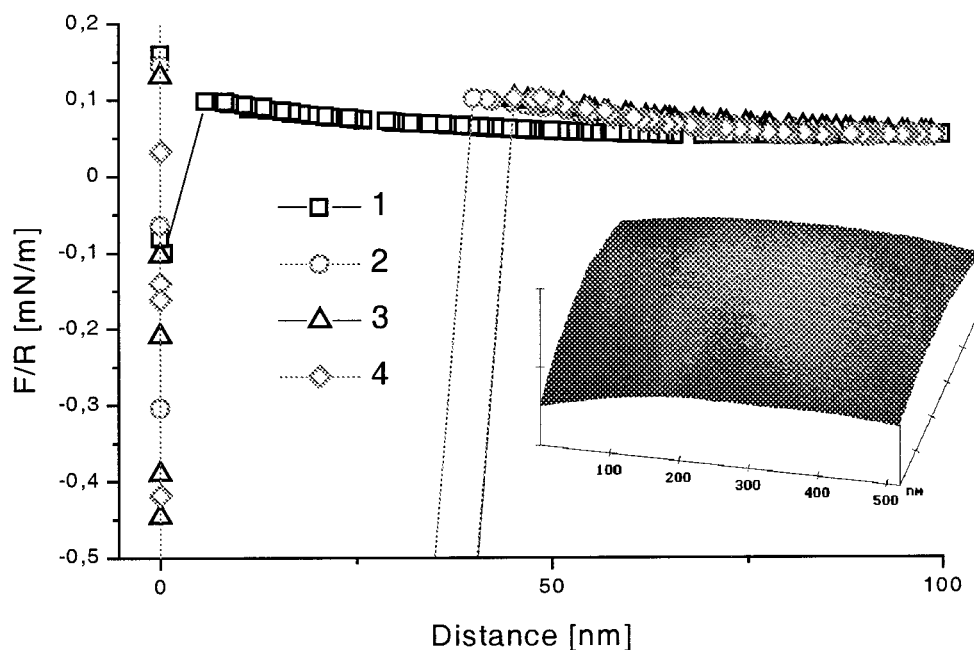


Figure 2. Typical force curves measured on 1st (1), 2nd (2), 5th (3), and 10th (4) approaches. The inset shows an AFM image of a silanated silica particle (z -scale 15 nm/div) taken in contact mode with a standard silicon nitride cantilever with integrated tip (Nanoscope 3, Digital Instruments, California) at scan speeds of 5–10 Hz.

from particle to particle. The average receding contact angle was $\theta_r = 81^\circ$, which is close to the receding contact angle $\theta_r = 83^\circ$ measured on a similarly prepared flat surface. The advancing contact angle of particles varied significantly more ($\pm 4^\circ$ from particle to particle). The average advancing contact angle was $\theta_a = 97^\circ$. This agrees with the advancing contact angle $\theta_a = 95^\circ$ on a planar surface.

Figure 2 shows typical force vs separation curves between a hydrophobic particle and a hydrophobic flat surface obtained on first and later approaches in water. All the force curves have the following features. At large separations there is a region of repulsion in which the force decays roughly exponentially. We, however, do not try to analyze the force at long range, because in water the Debye length is large and not well-defined. This causes problems in accurately fitting double-layer forces. There is always a maximum in the repulsive force. From the force maximum the surfaces are suddenly pulled into close proximity by an attractive force. The range of the attractive jump observed varied significantly (from 5 to 275 nm) from particle to particle (Figure 2), although the particles were prepared in an identical manner and had the same contact angle, which was controlled in situ after the force measurements. Figure 2 also shows that the jump-in distance is smallest for the first force curve (usually from 5 to 12 nm), increases after a separation from the first contact, and remains roughly constant for repeated force measurements (after several approaches) for any particular pair of surfaces. All previous AFM experiments showed late (after contact) interaction, and therefore almost certainly they resulted in higher jump-in distances than expected for a first approach. Our results suggest that to analyze properly the AFM force vs distance curves, we definitely have to distinguish between the first approach and the later ones. However, even for a first approach this jump is not due to a van der Waals force, which with $K = 0.3$ N/m would give the jump distances lower than 3 nm for the silanated silica particles. Also, this jump distance cannot, even partly, be accounted for by elastic deformation of surfaces. Our estimates with the JKR theory²⁵ suggest that in our conditions the deformation is less than 0.5 nm.

The questions now become: what could the physical origin of this phenomenon be, and why, in contrast to the SFA experiments, does the contact lead to an increase in the attractive force?

On purely thermodynamic grounds we should expect cavitation to occur between hydrophobic surfaces.²⁶ This should happen, however, only when the separation becomes very small (~ 1 nm). The size of the cavity at contact depends on the size of interacting surfaces. Therefore, the contact of surfaces in an SFA and an AFM should lead to different types of cavities, namely, microscopic or visible cavities and submicroscopic ones. In the SFA experiment cavities of microscopic size are formed and have been detected by refractive index measurements and through an optical microscope.^{1,5,7} A large attractive interaction was reproducibly measured in the absence of these visible cavities.⁷ (As for submicrocavities, the sensitivity of an SFA to the refractive index measurements does not allow such a structure to be studied.²⁷) The contact of surfaces in the AFM should lead to formation of cavities of submicroscopic size. Thus, the increase in the attractive jump distance after the first approach in the AFM indirectly confirms the hypothesis that the hydrophobic attraction, being not a consequence of formation of microscopic cavities, could be a direct result of submicrocavity formation.

This was suggested earlier,^{10,28} further supported by optical cavitation²⁹ and spectroscopic³⁰ studies, and now indirectly confirmed by our AFM force experiments.

Similar force curves (late interaction) and the variation in the jump distance from particle to particle were recently observed in an AFM experiments and interpreted in favor of trapped bubbles³¹ stabilized by chemical heterogeneity¹⁷ or roughness.³² Our results also indicate that the submicrocavities formed after the first approach do not dissolve immediately as predicted by simple theories^{33,34} and remain "stable" during the removal/approach cycles. However, we should definitely rule out the hypothesis that the submicron bubbles attached to the surface when it is first immersed in water could be responsible for a long-range attraction.^{10,31} The attractive jump distance is

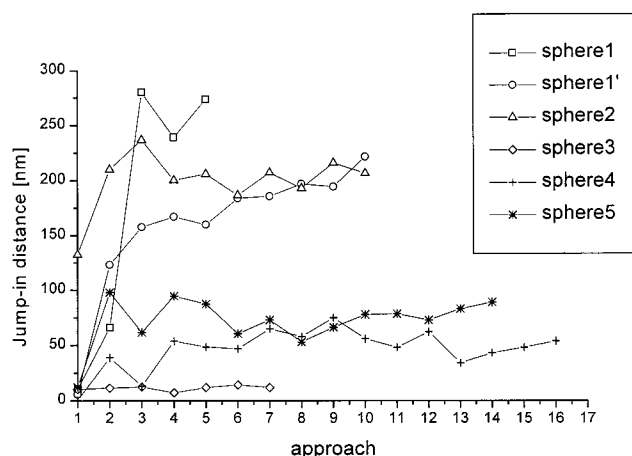


Figure 3. Onsets of instabilities for different approaches. Spheres 1, 4, and 5 give the typical distances of attractive jumps. Similar behavior was observed in many experiments. Sphere 2 illustrates an exceptional case where the distance of the first jump into a contact exceeded 100 nm; so does sphere 3 for which no long-range attraction was found. Sphere 1' is sphere 1 used again after the surfaces were kept in contact with bulk water for a few hours.

set by the size of submicrobubbles, and the first jump-in distances are very short. Taking into account that with the AFM technique one can detect lateral heterogeneity down to a scale ≈ 5 nm only, one can suggest that the first jump-in could probably be due to bubbles trapped between (lateral) asperities. An interesting observation is that the distance of our first jump-in coincides with that observed for dehydroxylated silica surfaces in repeat measurements.¹⁷ This is not surprising, because for dehydroxylated silica the contact angle is about 40° only. Hence, there should be no difference between the first and the late interactions of such dehydroxylated surfaces (contact cavitation does not occur). As discussed above, the submicrocavity formation, which leads to a large jump-in distance, is observed only after contact of the surfaces (only once we observed on the first approach a jump-in distance larger than 100 nm). On a scale above 5 nm our hydrophobic surfaces are smooth and laterally homogeneous. Hence, the observations of a large attractive jump are not implicated by roughness. The “stability” of the submicron bubbles could be due to chemical heterogeneities.¹⁷ To explore that in more detail, we repeated some of the experiments after our surfaces had been kept separated by 100 μm for 2 h. The subsequent experiment showed that the first approach again gave the smallest jump distance (equal to the preceding experiment) (Figure 3). This indicates that the submicrobubbles formed during the first experiment have been dissolved after being in contact with bulk water (and further confirms that they do not originate during the initial passage from air to water^{10,31}). One can, therefore, exclude the chemical heterogeneities as the possible reason for a “stability” of submicrocavities at the late interaction and suggest that the confinement between hydrophobic surfaces could be an important factor for “stability”.

Figure 3 also shows that the attractive jump distance sometimes remains constant and equal to the first jump-in distance for repeated force measurements. In other words, in this case for hydrophobic particles we observe some attraction, but of very short range. This is different from what people usually observe, but the absence of a strong attractive interaction before contact was detected in some early reports.³⁵

Acknowledgment. We acknowledge financial support from the Alexander von Humboldt Foundation (O.I.V.) and the

Deutsche Forschungsgemeinschaft under grant BU 701/11-1 within the priority program “Wetting and structure formation at interfaces” (G.E.Y.). Roger Horn is thanked for helpful discussions.

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