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Citation: *The Journal of Chemical Physics* **114**, 8124 (2001); doi: 10.1063/1.1365954

View online: <http://dx.doi.org/10.1063/1.1365954>

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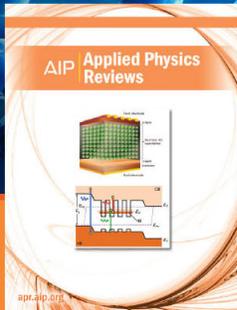
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Forces between polystyrene surfaces in water–electrolyte solutions: Long-range attraction of two types?

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(Received 28 November 2000; accepted 23 February 2001)

A great deal of effort has recently been focused on the experimental studies of the phenomenon of long-ranged attraction between identically charged colloidal (polystyrene) particles immersed in an electrolyte. The theoretical validation suggested the need for revision of the existing and established colloidal theories assuming the observed attraction is of electrostatic origin. We, however, demonstrate that for a number of reasons (first of all hydrophobicity and roughness of particles) the Derjaguin–Landau–Verwey–Overbeek (DLVO) behavior should not be expected for polystyrene surfaces. Indeed, the force measurements with an atomic force microscope-related set-up suggest that even within one pair of the interacting surfaces, attractive interaction of various types can be observed. There is usually a difference between the first approach and the later ones. The first approach is characterized by a short-range jump into a contact. Depending on conditions (electrolyte concentration, previous contacts of surfaces, etc.) there exists a late attraction of two types between polystyrene surfaces. The force of the first type is characterized by an abrupt jump from the maximum of a repulsive force, which is typically of longer-range than on the first approach. This is most likely due to submicroscopic bubbles trapped and/or formed due to previous contacts (and separation) of the surfaces. The attraction of the second type is weak and exponentially decaying.

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I. INTRODUCTION

Polystyrene lattices have been widely used for a variety of industrial purposes. They include the manufacture of water-based coatings, calibration of electron microscopes, pore size measurements of filters and membrane, packing material in chromatographic columns and more. Besides that, they are often used as models in colloid studies, mostly because they are easy to prepare as monodisperse spheres.¹ It is well known that latex colloids in water–electrolyte solutions are charge-stabilized. That is probably why some recent experiment with (submicroscopic and microscopic) polystyrene spheres interpreted in favor of a long-range attraction^{2–4} (not described by a simple Derjaguin–Landau–Verwey–Overbeek, or DLVO, model^{5,6}) led to the conclusion that some of the key principles of the modern theory of stability of colloids are wrong and that the like-charged colloids attract! These observations have caused an enormous theoretical activity devoted to a search for an explanation of net attraction between like-charged colloids (see, for example Refs. 7,8), giving rise to hot debates.^{9–11}

In the present paper we do not attempt to interfere with the theoretical discussion, or to analyze the force (potential) measuring technique. Instead, we suggest looking at the sys-

tem under experimental investigation, and to sound a note of caution here.

Study of the stability of latex suspensions is an indirect way to obtain information about the forces between surfaces. Direct force measurements between the surfaces of polymers were previously impossible. The surface force apparatus (SFA), that has been the main experimental technique, allowed only (macroscopic) transparent surfaces to be investigated.¹² Recent years have seen an increase in the number of devices used for the force measurements (such as, for example, a MASIF), and the atomic force microscope¹³ (AFM) has now become a standard tool for investigating surface interactions.^{14,15} In a typical AFM force experiment the interaction between a (microscopic) spherical particle and a plane is measured. The use of an optical lever technique to measure separation allows one to deal with opaque surfaces, such as polymers, for example.

The aim of the present work is the direct force measurement between two polystyrene surfaces immersed in water–electrolyte solution. In many of the force measuring devices used, surfaces are always brought into contact once before force vs separation data are collected, and a measurement on the first interaction is not possible, or at least very difficult. This applies in particular to experiments with the AFM, and this is usually not discussed in the published materials. Here we use our homemade setup which is capable of making single approaches to contact. We demonstrate that in general

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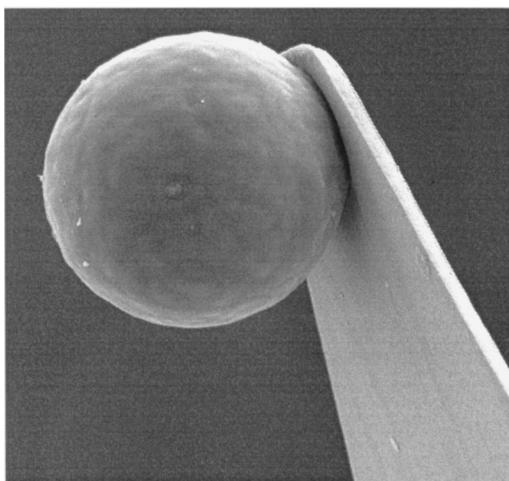


FIG. 1. Typical scanning electron micrograph of a polystyrene particle sintered onto the end of an AFM cantilever.

the simplest DLVO potential is indeed not observed for the polystyrene surfaces immersed in water–electrolyte solution, and a rather long range attractive force is found already on the first approach. The subsequent interaction between such surfaces is characterized by an attraction of two types. While the attraction of the first type is probably due to coalescence of long-lived surface submicrobubbles, the origin of the attraction of the second type remains unclear. We speculate that the reason for both types of long-range attraction could be the combined effect of hydrophobicity and roughness of the polystyrene particles. However, in the case of interaction of the second type the attraction of electrostatic origin cannot be excluded.

II. EXPERIMENT

A. Materials

We study the interaction between a polystyrene sphere and a flat polystyrene surface. Polystyrene spheres (Bangs Inc., Carmel, USA) of radius 1.8, 3.05, and 4.38 μm were rinsed with water to remove surfactants added during the synthesis to stabilize a dispersion. The radii of spheres was determined from optical and scanning electron microscopy. After washing, particles were removed from a filter onto a glass plate and dried in vacuum. In the last step polystyrene particles were fixed to tipless cantilevers (Digital Instruments, Santa Barbara, California, V-shaped, 100 or 200 μm long, 0.6 μm thick, spring constants about 0.12 N/m and 0.06 N/m) by sintering for 200–240 s (depending on the size of a sphere) at 120 $^{\circ}\text{C}$ (Fig. 1). The polystyrene plates were prepared in the following way. The polystyrene granules (purchased from Aldrich, Germany) were placed on a silicon wafer heated to 150 $^{\circ}\text{C}$ and pressed by a hand press with a Teflon piston (the load is about 0.5 kg for several sec).

A Teflon cuvette was cleaned in concentrated hot nitric acid for several minutes, followed by thorough rinsing with high-purity water. 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 . We have also used

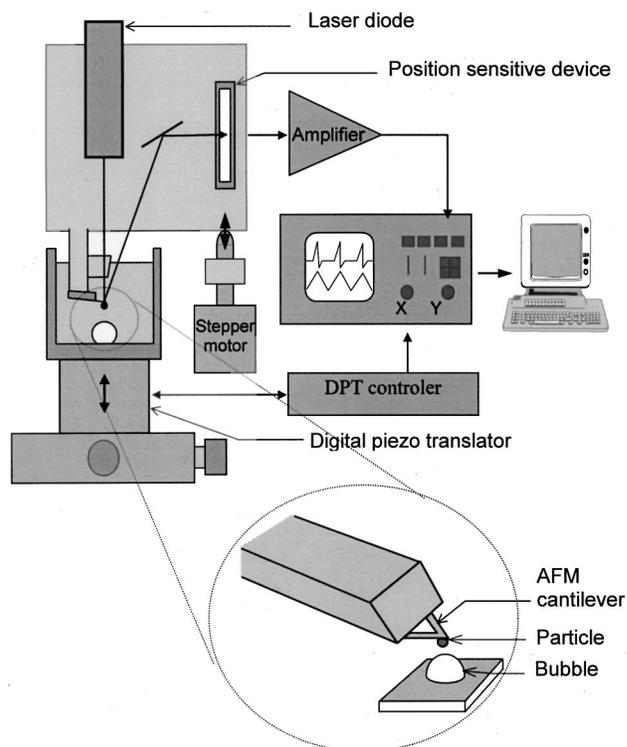


FIG. 2. Scheme of the homemade AFM-related setup.

10^{-4} – 10^{-2} M KCl solutions. All experiments were done at room temperature without buffer. Hence, the pH was around 6.

B. Force measurements

The main experimental set-up has been described in detail before^{16,17} (Fig. 2). The polystyrene plate was placed onto the bottom of a Teflon cuvette. Then the polystyrene particle was positioned a few μm above the surface with a micrometer 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). To measure force-vs-position curves the cuvette was moved towards the particle with a 15 μm range piezoelectric translator (Physics Instruments, Germany). This translator was equipped with integrated capacitance position sensor, which provided the position with an accuracy of 0.3 nm in closed-loop operation. During the movement the deflection of the cantilever was measured with an optical lever technique in which 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, UK, 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 $\mu\text{m}/\text{s}$. 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 this^{18,19}). The height position of the solid surface and the deflection of the cantilever were recorded with a digital oscilloscope (12 bit effective resolution). The

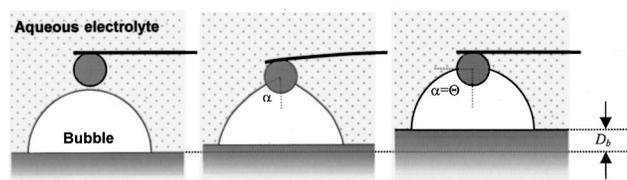


FIG. 3. Scheme showing interaction of a polystyrene particle with a bubble. To measure the contact angle of an individual particle a bubble is moved towards a particle. Before a TPC is established and in the absence of long-range forces the cantilever is not deflected (left). After a TPC line has been formed the bubble is deformed and a capillary force is acting on the particle. This leads to a deflection (middle). When the bubble is moved further towards the particle, at some point no force is acting on the cantilever (right). At this position the bubble is again not significantly deformed. The difference in the sample height between the position just before a TPC is established and the zero-force position is the parameter D_b , which was used to calculate a value we call receding contact angle.

result of a force measurement is a plot of the cantilever deflection Δz_c vs the height position of the piezotranslator 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 $F = K \cdot \Delta z_c$ and $h = \Delta z_c + z$. We further assume that the total force measured is entirely due to a surface force acting.

In order to explore the properties of the “constant compliance line,” some of the measurements were done with a commercial AFM (NanoScope III, Multimode, Digital Instr., California), and the speed was varied up to 200 $\mu\text{m/s}$. In these experiments only 100 μm cantilevers were used.

C. 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.^{16,20} To measure the receding contact angle a bubble (approximate diameter 1–1.5 mm) was placed by a pipette onto the bottom of the silanated silica plate. The plate is moving towards a particle attached to the cantilever. When the particle touches the air–water interface a three phase contact (TPC) is formed and the capillary force pulls the particle into the bubble. After a TPC has been formed, the capillary force dominates in the force balance, because the contribution from gravity and Laplace pressure is negligibly small²⁰

$$F = 2\pi R \gamma \cdot \sin \alpha \cdot \sin(\theta_r - \alpha),$$

where θ_r is the receding contact angle, and a parameter α characterizes the position of a particle at the interface (Fig. 3). On moving the bubble further up, there is a certain position at which no force is acting on the particle. This happens at $\alpha = \theta_r$, because the particle size is much smaller than the capillary length.^{21,22} 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 (Fig. 4). 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

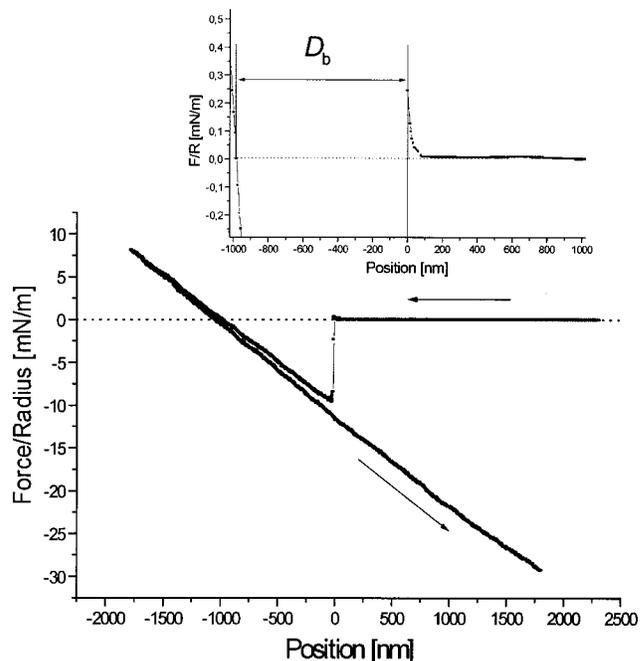


FIG. 4. Force-vs-position curve for the interaction measured between a polystyrene sphere and an air bubble in aqueous medium containing 1 mM KCl. The insert shows the part close to the jump-in in more detail.

the zero-force position of the drop surface D_d the advancing contact angle was calculated according to $\cos \theta_a = D_d/R - 1$. For every particle the contact angle was determined as a result of measurements of 15–20 force curves, subsequent determination of D_b (or D_d) for each interaction curve and its average value, and calculation of the contact angle with the above expressions.

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

III. RESULTS

A. Surface morphology

Imaging the polystyrene plate with a regular AFM tip revealed that it is smooth. Root mean square roughness over a $1 \mu\text{m} \times 1 \mu\text{m}$ area was in the range 0.3 nm. The polystyrene spheres were found to be significantly rougher (Fig. 5). The root-mean-square roughness was in the range 3–5 nm and the maximum peak-to-valley height difference was less than 20 nm.

B. Interaction of a polystyrene sphere with a liquid–gas interface

Typical force vs separation curves between a polystyrene particle and a bubble are shown in Fig. 4. At large distances no interaction was detected. When the particle approaches the air–water interface a small repulsive, exponentially decaying, component was usually observed. It is probably an electrostatic double-layer repulsion. As air bubbles bear a negative surface charge,²³ this result suggests that the

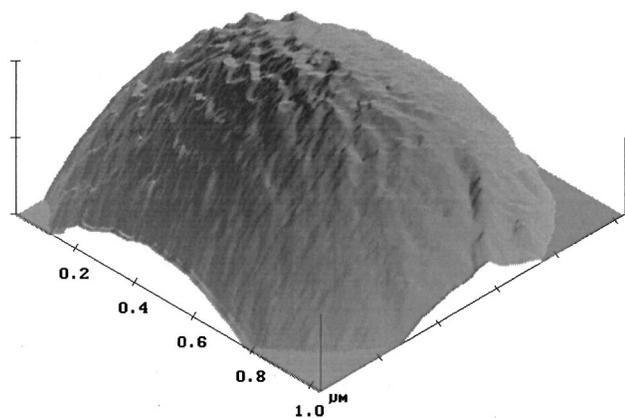


FIG. 5. AFM images of the surface of a polystyrene particle (z -scale 20 nm/div). Images were taken in contact mode with standard silicon nitride cantilevers with integrated tips (Nanoscope 3, Digital Instruments, California) at a scan speed of 5–10 Hz.

polystyrene particle is slightly negatively charged, or it contains some submicroscopic bubbles attached.^{24,25} From the repulsive barrier the particle jumps into the air bubble and also vice versa; the bubble snaps around the particle. When decreasing the position further at a certain point no force is acting on the particle.

The force vs position curve for an interaction with a drop in air was similar to that for an interaction with a bubble. In this case we also observed an electrostatic repulsion before a jump.

C. Contact angles

Receding contact angles measured with different polystyrene particles varied by $\pm 4^\circ$ from particle to particle (Fig. 6). The average receding contact angle were $\Theta_r = 82^\circ$, 70° , and 67° for particles of 1.8, 3.05, and $4.38 \mu\text{m}$ radius, respectively. This agrees with the receding contact angle measured on the polystyrene planar surface of 70° . The average advancing contact angles were $\Theta_a = 89^\circ$, 87° , and 84° , re-

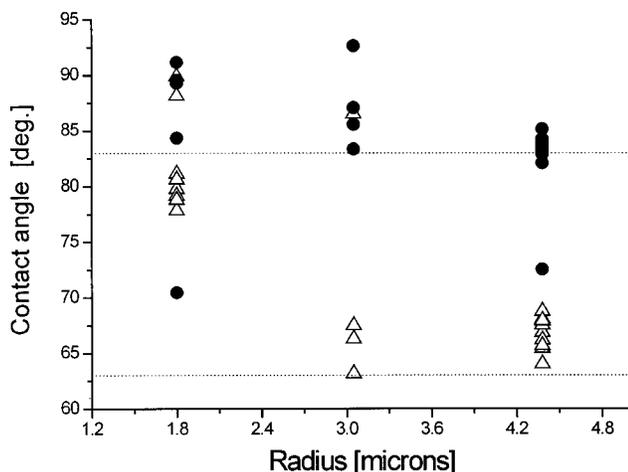


FIG. 6. Advancing (filled circles) and receding (open triangles) contact angles for polystyrene spheres. Dashed lines represent the results for polystyrene plates (upper line corresponds to the advancing, lower line to the receding contact angle).

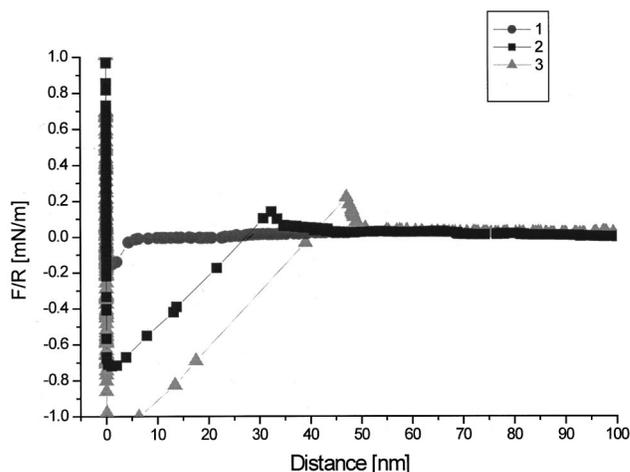


FIG. 7. A set of the typical force curves on 1st (1), 2nd (2), and 5th (3) approaches illustrating the late interaction of the first type (curves 2 and 3).

spectively. These were slightly lower than the advancing contact angle measured on the planar surface of 90° .

D. Surface interactions

The new feature of our experiment is that our setup allows not only measurement of the contact angle of microparticles (due to a large z -range of a piezotranslator), but also was capable of making single approaches to contact. The dynamic nature of the AFM force measurements is such that solid surfaces are continually being brought into contact and separated. As we have shown earlier,¹⁷ the late interaction of hydrophobic surfaces should, in general, be different from the first.

Figures 7 and 8 show typical force vs separation curves between a polystyrene sphere and a polystyrene flat surface.

All force curves on the first (before contact) interaction have the following features. At large separations there is a region of repulsion in which the force decays roughly exponentially. There is always a maximum in the repulsive force.

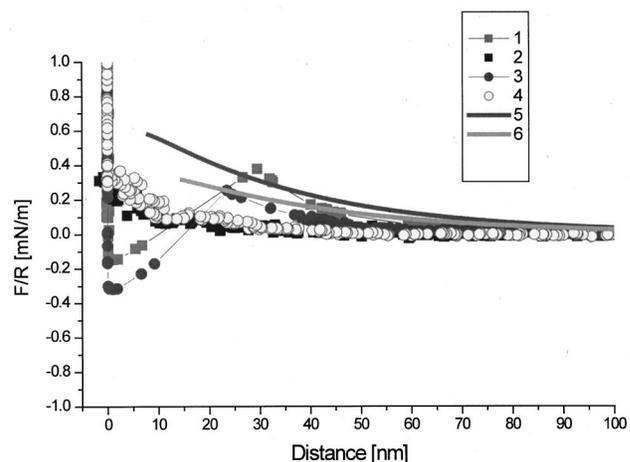


FIG. 8. A set of the typical force curves measured on 1st (1), 2nd (2), 6th (3) and 7th (4) approaches illustrating the late interaction of the second type (curves 2 and 4). The DLVO interaction with (constant) surface potentials -70 vs -65 mV (5) and -60 vs -50 mV (6).

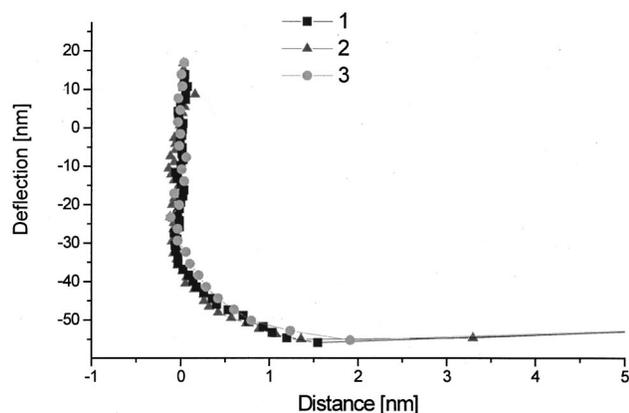


FIG. 9. Contact lines for polystyrene surfaces obtained at driving speeds of 3.5 (1), 10.5 (2), and 158.7 (3) $\mu\text{m/s}$.

From the force maximum the surfaces are suddenly pulled into close proximity by an attractive force. No correlation between the magnitude of the force maximum and the surface separation at which it occurs was found. The range of this attractive jump varied significantly (from 5 to 30 nm) from particle to particle, although the surfaces had roughly the same contact angle, which was measured *in situ* after the force measurements.

Late (after contact) interaction revealed force vs distance curves of two types.

Curves of the first type (Fig. 7) were similar to the force curves obtained for the first approach. The jump-in distance increases after separation from the first contact, and remains roughly constant for repeated force measurements (after several approaches) for any particular pair of surfaces. All the previous AFM experiments with polystyrene surfaces^{25,26} showed late (after contact) interaction and therefore almost certainly they resulted in higher jump-in distances than that expected for a first approach. The range of the late attractive jump varied (from 30 to 60 nm) from particle to particle. This conclusion is similar to that we first made for hydrophobed silica surfaces.¹⁷

For curves of the second kind no jump into contact was observed (Fig. 8). The net force is repulsive. An important point to note is that in the case of such an interaction, no variation in strength and range of F/R from particle to particle was observed (within the accuracy of our experiment) despite the fact that particles of different size had different contact angles.

In case of concentrated (10^{-2} M and 10^{-3} M) electrolyte solutions, for all the approaches we have observed only curves of the first kind. In case of pure water and a dilute (10^{-4} M) water–electrolyte solution force curves of both the first and the second types were observed.

No correlation between the type of force curve and the size of a particle and/or the value of the contact angle was found.

In all cases the “constant compliance line” has a slightly concave form, which suggests a short-range repulsion (Fig. 9). This indicates that the surfaces are somewhat compressible. The range of the repulsion is about 2 nm. This is much less than was observed before.²⁵

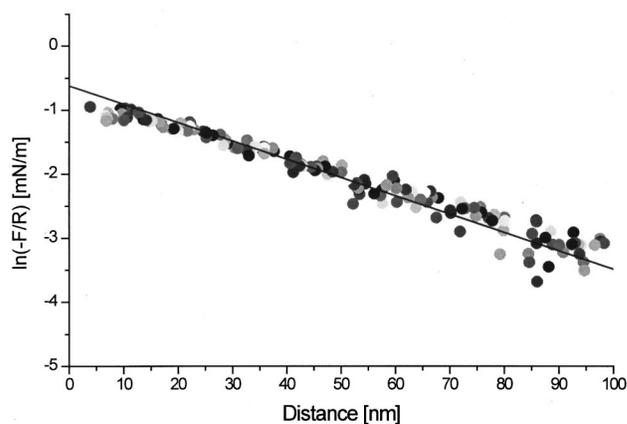


FIG. 10. Attraction of the second type plotted on a semilogarithmic scale. The attractive force (black circles) is calculated from the data of Fig. 8 as the difference between experiment (curves 2 and 4) and minimum theoretical predictions (curve 6). The results from similar experiments (other filled circles) giving the late interaction of the second type are also included. Solid line is computed by doing a least squares fit of the data.

IV. DISCUSSION

In the case of pure water we do not try to analyze the force of the first type (Fig. 7) at long range, because in water the Debye length is large and not well defined. This causes problems in accurately fitting double-layer forces. In the case of water–electrolyte solutions this decay length was close to the Debye length. If we take the force maximum as defining a position of the effective surface of charge and assume that the double layer forces are associated with this surface,²⁵ then the curves are fitted with a simple DLVO model with potentials around -30 to -60 mV. These potentials are comparable to zeta potentials measured for a bubble surface.²³

To make a DLVO fit in the case of interaction of the second type (Fig. 8) we used the results for the polystyrene flat surfaces and polystyrene spheres from literature.^{27–30} In this procedure we make an assumption that the pseudosurface of charge is smooth and equal to the “hard-wall” contact. The surface charge density of polystyrene plates depends on conditions of polymerization and the method of polymer film formation. However, to our knowledge the zeta potential of a smooth polystyrene film^{27,28} measured at 10^{-4} M KCl was always confined between -100 and -70 mV. The zeta potential of similar polystyrene latex spheres at 10^{-4} M KCl is usually in the interval -80 ± 15 mV. The use of these values allows one to estimate a minimum (-70 vs -65 mV) and a maximum (-100 vs -95 mV) DLVO force (the Hamaker constant is estimated³¹ as $0.95 \cdot 10^{-20}$ J) expected in our system. The calculations were made with the Chan–Pashley–White algorithm,³² assuming that the surface potentials are constant. Figure 10 shows that the experimental data for this particular pair of surfaces are well below the lowest limit for the DLVO interaction expected in our system. Similar results were found for different pairs of interacting surfaces. We also tried to make a fit by choosing the surface potentials by adjustment of the long-range part of the experimental force–distance curve of the second type. In this case, we made an assumption that for some reason the sur-

face potentials could be lower than the measured zeta potentials for polystyrene. We found that the potentials -60 against -50 mV can provide a good fit of the long-range part of the force-distance curve. However, with these potentials the theoretical DLVO fit is still above our experimental curves. Therefore, one can suggest that the force of the second type also contradicts the DLVO predictions.

Thus, we have made clear observations that typically the DLVO theory is an incomplete description of the interaction between two polystyrene surfaces. In other words, we have clear evidence for a non-DLVO attraction between them. From that point of view our conclusion is similar to that made in the AFM and MASIF work.^{25,33} It has previously been suggested that the attraction between two polystyrene surfaces could be because of (i) trapped gas due to roughness of polystyrene;²⁵ (ii) elastic deformation due to a van-der-Waals attractive force.³³ An attraction was also reported in the polystyrene latex stability studies,^{2,4} which led to speculation that two similar charges attract.⁴ Our observations are not entirely consistent with all these ideas.

As was stressed above, to analyze the AFM force experiment properly we have to distinguish between first and later approaches of the surfaces. Hence, first we focus on the first interaction of polystyrene surfaces. It has to be stressed that even for a first approach this jump is often not consistent with a van der Waals attraction, which with our spring constants would give jump distances lower than 5 nm for the largest polystyrene particles we have used. The surface separation is not measured directly in our set-up. However, it is clear that the jump distance cannot, even partly, be accounted for by plastic deformation of polystyrene,^{34,35} which would lead to a rate-dependent contact line and jump-in.³⁶ Such behavior was not observed (Fig. 9) which suggests that our deformation is elastic. Strictly speaking, our small sphere size suggests that we are in the center of the transition zone between theories by Johnson *et al.*³⁷ (JKR) and Derjaguin *et al.*³⁸ (DMT). However, it has recently been shown³⁹ that the JKR equations give good predictions of compliance even in conditions well outside the expected JKR zone. Estimates using the JKR theory show that for our conditions the central displacement is less than 3–4 nm. Hence, the measured force is also not entirely consistent with a van der Waals attraction provided that the surface deformation is considered. Even with the unrealistic assumption of the absence of double-layer forces, this would give an attractive jump distance less than 8–9 nm. Sometimes our jump distance was much larger, sometimes not. One can therefore suggest that on the first approach we could indeed observe a force consistent with the DLVO model, provided that the elastic deformation is considered.³³ On the other hand, sometimes, there exists an attractive force on the first approach, and that it is likely to be due to submicroscopic gas bubbles attached to the polystyrene surface and anchored by or trapped between asperities.¹⁷ Thus, our observations both agree and disagree with the earlier results^{25,33} for late interaction. Some disagreement with the MASIF results³³ can be connected with the fact that they have used macroscopic and smooth surfaces. That is why the effect of deformation dominated, but there was no data to support (or disprove) a hypothesis of

submicrobubble coalescence in their results. On the other hand, the experimental observation of an attractive force³³ which is two times less than the expected central displacement seems like an impossibility. It is very likely that something has not been considered properly in this work.

The long-range late interaction is discussed below.

The long-range attraction of the first type can be understood assuming that it is a direct result of submicrocavity formation. The contact of surfaces leads to formation of cavities of larger size. This explains the increase in the attractive jump distance after the first approach in some of our experiments. Such a model has been suggested before.^{24,40,41} AFM measurements of forces between two polystyrene surfaces were reported earlier.^{25,26} The (late) interaction between a polystyrene latex particle and a fused polystyrene block reported²⁶ is characterized by a jump into contact from a separation of 30 nm. Similar force curves (again late interaction) and the variations in the jump distance from particle to particle (from 20 to 400 nm) were recently observed in the AFM experiment with two spheres.²⁵ The jump distance we found is of longer range than in Ref. 26. In contrast to this work, our jump-in distance is of variable strength and range. To understand properly the reasons for some disagreement between our results and previous reports^{25,26} smoothness and hydrophobicity need to be considered. Unfortunately, in Ref. 26 no details of the attractive forces were presented, and no information about the particles was given. There are also no data about the roughness of the surfaces. Therefore, it is impossible to comment on the reasons for the differences between our results. On the other hand, we have observed much less variability in the jump-in distance than other authors.²⁵ It was tempting to infer that the highly variable jump observed earlier is the consequence of the AFM experiment between two colloidal particles, which inevitably leads to a “noncoaxiality” of the interaction (see Appendix). A thermal drift in the lateral direction causes some difficulties of finding an apex of the sphere as well as causing its shift during the continuous interactions. However, our estimates suggest that this could give a change of jump distance of up to a few nm only. One can surmise that the surfaces used in Ref. 25 were more hydrophobic than ours. Indeed, for smooth, but more hydrophobic silanated silica surfaces we have previously observed that the attractive jump varies significantly from particle to particle.¹⁷ Unfortunately, Ref. 25 (and Ref. 26) does not contain any information about precise contact angles of the polystyrene particles to support or disprove our hypothesis.

The long-range attraction of the second type is exponentially decaying $F/R \approx A \exp(-h/B)$ and can be fitted assuming $A \approx -0.6$ mN/m, and $B \approx 30$ nm (Fig. 10). Of course, this conclusion is valid only within the assumptions we have made about the smooth pseudosurface of charge for our rough surface. It has recently been suggested that the presence of asperities leads to a reduction in the DLVO interaction energy between a rough sphere and a smooth plate.⁴² The tendency we observe, i.e., the experimental results scattered well below the lowest DLVO limit, qualitatively agrees with the predictions,⁴² although they were made for very

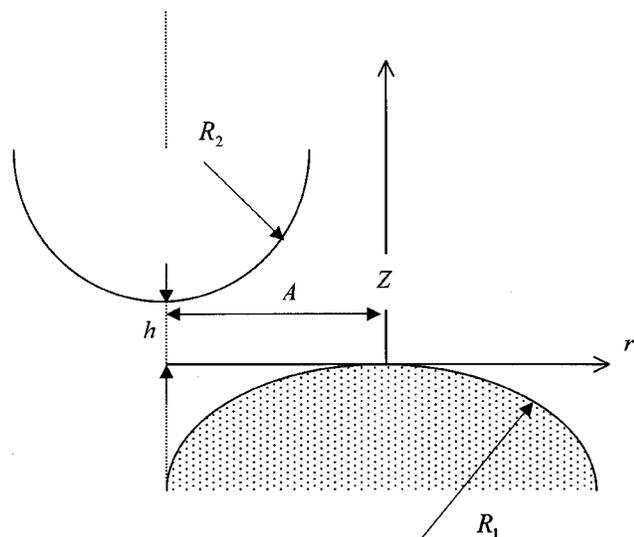


FIG. 11. A scheme of “noncoaxial” interaction of two spheres.

different situation, i.e., much smaller size of a sphere, as well as much larger relative size of asperities (peak-to-valley height difference) compared with the particle radius. So, the effect of roughness can contribute to, but cannot be entirely responsible for, the effect we observe.

A very long-range, exponentially decaying attraction has been measured in a variety of hydrophobic systems, mostly with the Langmuir–Blodgett films on mica,⁴³ sometimes with methylated silica or mica,⁴⁴ and with the adsorbed surfactants.^{45,46} The decay length of the attractive non-DLVO interaction we found for our polystyrene surfaces is very large and roughly equal to the Debye length of the electrolyte solution. Therefore, its possible electrostatic nature cannot be excluded. On the other hand, this force in the case of polystyrene is much weaker (i.e., the pre-exponential factor is smaller) than was previously observed for different systems. The category of long-range, exponentially decaying attraction includes the most puzzling results. The origin of the force we observed also remains unclear.

To finish this section, we recall that such a force was randomly observed only at relatively low concentration of electrolyte. This could indicate that the submicroscopic cavities responsible for the interaction of the first type remain less stable in more concentrated electrolyte solutions. This observation is consistent with the earlier ideas that the small bubbles could remain stable because of electrostatic stabilization.^{24,47}

V. CONCLUSION

The results reported above suggest strongly that, as a rule, there is an attractive force acting between polystyrene surfaces in water–electrolyte solutions, and that no single mechanism can account for the diversity of behavior observed with similarly prepared polystyrene surfaces in the AFM force experiment. In an attempt to classify the results according to the type of interaction measured, we divided them into two categories, namely, a force on first approach and a force on late approach. The latter type has been further

subdivided into a long-range attraction of variable strength and range, due to the presence of submicroscopic bubbles, and an exponentially decaying force. In concentrated solutions we deal with an interaction of “submicrobubble” type only, while in dilute solutions forces of both types are operating between the same pair of polystyrene surfaces.

ACKNOWLEDGMENTS

This work was started while we were at the Institute für Physikalische Chemie of the University of Mainz. We thank the Alexander von Humboldt Foundation (O.I.V.) for financial support of the initial stage of this study. We are grateful to Roger Horn for comments on the paper.

APPENDIX: THE INTERACTION OF TWO APPROACHING SPHERES

When dealing with the interaction between colloidal spheres it is often the case that its range is such that they do not interact significantly until the gap is small compared with the smaller of their radii. Under these circumstances, a very useful approximate expression for the interaction energy of the bodies is given by Derjaguin.⁴⁸ This is based on the recognition that the interaction of two bodies is equivalent to an interaction of an effective elliptic paraboloid with a plane⁴⁹ (or an equivalent sphere and a plane in the case of interaction of two spheres).

One of the main assumptions of the Derjaguin approximation is that bodies approach along the line connecting their centers. However, this condition can be violated in the AFM force experiment with two spheres.

We consider the interaction of two spherical particles with radii R_1 and R_2 . The axis system is chosen with z axis along the inward normal to sphere 1 and the r plane as shown in Fig. 11. The particle approach is in the direction of the axis z , and let A be a distance between z and the parallel axis which crosses the center of sphere 2. The gap profile is then given by

$$H = h + \frac{(r-A)^2}{2R_2} + \frac{r^2}{2R_1}. \quad (\text{A1})$$

In order to exclude the linear term from the equation for an effective surface, a new system of coordinates is defined with the relation $r = r' + t$. Substitution into Eq. (A1) gives

$$H = h + \frac{r'^2}{2R_e} + 2r' \left[\frac{t-A}{2R_2} + \frac{t}{2R_1} \right] + \frac{(t-A)^2}{2R_2} + \frac{t^2}{2R_1}, \quad (\text{A2})$$

with $R_e = R_1 R_2 / (R_1 + R_2)$. Therefore, $t = R_1 A / (R_1 + R_2)$ is the required shift of coordinates, and the *apparent* shift in separation can then be found by substitution of the expression for t into the expression for a free term in Eq. (A2). It follows that the “noncoaxial” approach of two spheres is equivalent to an interaction of a sphere of an equivalent radius R_e with a shift of t in the direction r and of $A^2 / [2(R_1 + R_2)]$ towards z . The shift along r does not play any role in the calculation of force (or energy), so that the effect of noncoaxiality of the interaction is equivalent to a change (increase) in minimum separation.

Assuming that thermal drift can cause a lateral shift of the two interacting spheres of up to 200 nm (this is the maximum value we observed in our experiment), with a sphere of size of roughly 3 μm we get a change in separation of 3–4 nm. This cannot be responsible for the variations in jump distance observed in Ref. 25.

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