

Interactions between a Polystyrene Particle and Hydrophilic and Hydrophobic Surfaces in Aqueous Solutions

Esben Thormann,* Adam C. Simonsen, Per L. Hansen, and Ole G. Mouritsen

MEMPHYS, Department of Physics and Chemistry, University of Southern Denmark, Campusvej 55, DK-5230 Odense M, Denmark

Received February 17, 2008. Revised Manuscript Received April 21, 2008

The interaction between a colloidal polystyrene particle mounted on an AFM cantilever and a hydrophilic and a hydrophobic surface in aqueous solution is investigated. Despite the apparent simplicity of these two types of systems a variety of different types of interactions are observed. The system containing the polystyrene particle and a hydrophilic surface shows DLVO-like interactions characteristic of forces between charged surfaces. However, when the surface is hydrophobized the interaction changes dramatically and shows evidence of a bridging air bubble being formed between the particle and the surface. For both sets of systems, plateaus of constant force in the force curves are obtained when the particle is retracted from the surface after being in contact. These events are interpreted as a number of individual polystyrene molecules that are bridging the polystyrene particle and the surface. The plateaus of constant force are expected for pulling a hydrophobic polymer in a bad (hydrophilic) solvent. The plateau heights are found to be of uniform spacing and independent of the type of surface, which suggests a model by which collapsed polymers are extended into the aqueous medium. This model is supported by a full stretching curve showing also the backbone elasticity and a stretching curve obtained in pentanol, where the plateau changes to a nonlinear force response, which is typical for a polymer in a good or neutral solvent. We suggest that these polymer bridges are important in particular for the interaction between polystyrene and the hydrophilic surface, where they to some extent counteract the long-range electrostatic repulsion.

Introduction

Polystyrene particles belongs to the family of latex particles that are used for a large variety of industrial products and biological assays. Bare latex particles are, for example, used as binders of pigment in paint and in the process of paper coating.^{1,2} Surface-modified polystyrene particles are used as stabilizers for water-soluble proteins and as drug carriers.^{3,4} For such systems an understanding of the interparticle interactions as well as particle-surface interaction is important. However, the reason for studying the interaction between polystyrene particles and surfaces with different physical and chemical properties is two-fold. Besides the direct importance for technical systems containing polystyrene and polystyrene-like particles, these particles also serve as model systems for more complex surfaces. For example, it is of fundamental interest to improve our understanding of interactions between biological surfaces such as cell membranes. These surfaces are extremely complex due to charged lipids and proteins, hydrophobic patches, and a number of steric forces originating from collective thermal motions and from proteins and polysaccharides protruding from the surface.

Although much simpler, the polystyrene particles contain some important features that resemble biological surfaces. Polystyrene particles are known to work as charge regulators and to be slightly charged in aqueous solution.⁵ In addition, a polystyrene-coated

surface also acts as a hydrophobic surface with a contact angle to water of approximately 85°. Further, the surface of a polystyrene particle is not a smooth surface but has a soft interface consisting of loosely bound and dangling polymers.⁶ As will be clear from the results presented in this paper, the different features of this system lead to a variety of different types of interactions with a surface. The relative magnitudes of the interactions are strongly dependent on the physical and chemical properties of the surface and the solvent. Therefore, an understanding of this model system can advance our understanding of more complex systems.

By using an atomic force microscope (AFM) and the colloidal probe technique,⁸ where a polystyrene particle is attached to the end of an AFM cantilever, it has been possible to perform direct studies of the interaction between a polystyrene particle and a surface. Here, we have chosen to study various features of the interaction between a polystyrene particle and a simple hydrophilic silica surface as well as a hydrophobic octadecyltrichlorosilane-coated silica surface. These interactions include DLVO forces, hydrophobic interactions, and polymer bridges.

Materials and Methods

Surface Preparation. For the experiments two different surfaces were prepared: a pure clean hydrophilic silica surface and a hydrophobic surface. The substrate used was in both cases a smooth microscope cover glass (Menzel-gläser) that fits directly into our AFM liquid cell. The cover glass was cleaned in hot piranha solution (30 vol % H₂O₂ and 70 vol % H₂SO₄) for 15 min followed by extensive cleaning in water and plasma cleaning using a Harrick Extended Plasma Cleaner (PDC-002, Harrick Plasma, Ithaca, NY) at full effect for 20 min.

* To whom correspondence should be addressed. Current address: Department of Chemistry, Surface Chemistry, Royal Institute of Technology, Drottning Kristinas Väg 51, SE-100 44 Stockholm, Sweden. Fax: +46 8208998. E-mail: esben.thormann@surfchem.kth.se.

(1) Chinga, G.; Helle, T. *Nord. Pulp Pap. Res. J.* **2002**, *17*, 307–312.
(2) Ibrahim, K.; Salminen, A.; Holappa, S.; Kataja, K.; Lampinen, H.; Lofgren, B.; Laine, J.; Seppala, J. *J. Appl. Polym. Sci.* **2006**, *102*, 4304–4313.
(3) Wittemann, A.; Haupt, B.; Ballauff, M. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1671–1677.
(4) Blunk, T.; Hochstrasser, D. F.; Sanchez, J. C.; Müller, B. W.; Müller, R. H. *Electrophoresis* **1993**, *14*, 1382–1387.
(5) Vinogradova, O. I.; Yakubov, G. E.; Butt, H.-J. *J. Chem. Phys.* **2001**, *115*, 8124–8131.

(6) Kajiyama, T.; Tanaka, K.; Takahara, A. *Macromolecules* **1997**, *30*, 280–285.

(7) Li, Y.; Pham, J. Q.; Johnston, K. P.; Green, P. F. *Langmuir* **2007**, *23*, 9785–9793.

(8) Ducker, W. A.; Senden, T. J.; Pashley, R. M. *Nature* **1991**, *353*, 239–241.

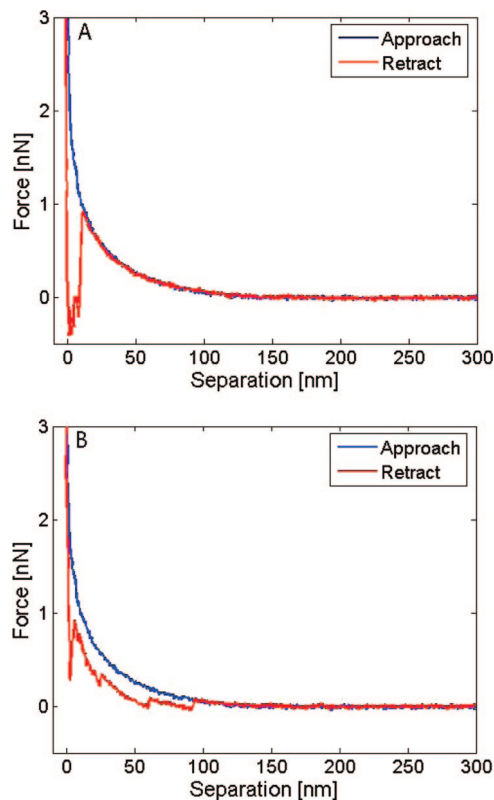


Figure 1. Force curves showing the interaction between a $4.5\ \mu\text{m}$ polystyrene particle and a glass surface in water. (A) In the approach force curve is seen a long-range repulsive force and in the retraction force curve, in addition to this repulsion, is observed an adhesion force. (B) Same as part A, but besides the primary adhesion, three secondary adhesion events are seen in the retraction force curve.

The hydrophobic surface was prepared by immersing the clean cover glass into a 0.05% v/v solution of octadecyltrichlorosilane (OTS, Sigma-Aldrich) in heptane for 8 h. Hereafter, the cover glass was carefully and repeatedly washed in heptane \rightarrow 2-propanol \rightarrow ethanol \rightarrow 1/1 ethanol–water \rightarrow water and finally dried under low pressure, where it was also stored until use. The hydrophobic surface was used less than 24 h after preparation.

Force Measurement. Force versus distance measurements were carried out using an atomic force microscope (JPK NanoWizard, JPK Instruments, Berlin, Germany), in a commercial liquid cell from JPK Instruments. Cantilevers with attached polystyrene particles of size $D = 1$ and $4.5\ \mu\text{m}$ were purchased from Novascan Technologies (Ames, IA) and were used as received after careful cleaning in ethanol and water. The spring constants of the cantilevers were determined by both the Hutter and Bechhoefer method and the Sader method as described elsewhere.^{9,10} The possible dependence of approach and retraction velocities on force traces was examined in the range from 50 nm/s to $5\ \mu\text{m/s}$, but no such dependence was found. All force curves shown in this paper were then recorded at a constant approach and retraction velocity of 500 nm/s. Milli-Q water and NaCl solutions were degassed immediately prior to the experiments.

Results

Interactions between a Polystyrene Particle and a Hydrophilic Surface. Interactions in aqueous solution between a bare silica surface and a colloidal polystyrene particle attached to an AFM cantilever were studied. In Figure 1 are shown two typical force curves for the interaction between a polystyrene

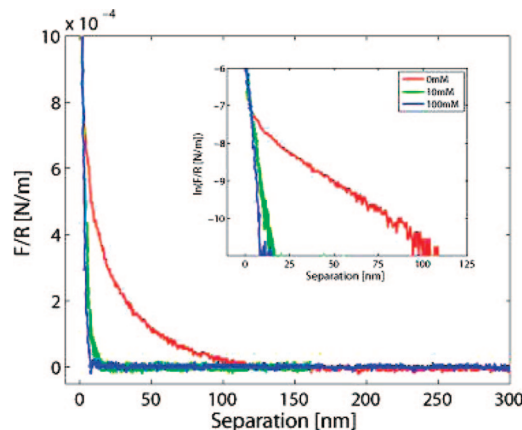


Figure 2. Normalized approach force curves in no salt and 10 and 100 mM NaCl, respectively. The inset shows the force on a logarithmic scale, and from the slope of the curves the Debye length is found to be 31 nm and 2.8 and 1.6 nm, respectively.

particle ($D = 4.5\ \mu\text{m}$) and a clean glass surface in pure water. Upon approach, a repulsive force with an onset at a separation of approximately 100 nm is observed. In the retraction force curve one observes that a force is needed to bring the surfaces out of contact. In some of the retraction force curves, secondary adhesion events laying on top of the repulsive force are also observed (see Figure 1B).

A long-range repulsive force is often observed between surfaces in water and is attributed to the electrostatic double layer repulsion. In Figure 2 is shown how the force curves change in the presence of salt. Going from no salt to 10–100 mM NaCl changes the Debye screening length from approximately 200 nm to 3–1 nm. This explains why the interaction is almost completely screened in 10 and 100 mM NaCl. From the slopes of straight lines fitted to the data in the inset in Figure 2, the Debye lengths are determined to be 31 nm and 2.8 and 1.6 nm, respectively. These values fit very well to the expectation for the high-salt conditions and reasonably well for the case of pure water.¹¹ A complete description of the interaction is however not straightforward due to the asymmetry of the system and the nonrigid polymer surface.^{12,13}

In the retraction force curve the primary adhesion is the first subject of interest. By repeating the measurements a histogram of adhesion forces can be constructed. These repeated measurements were performed in two different ways. First, a number of force curves were obtained where each approach–retraction cycle was performed at a new position on the surface by using the (x,y)-offset function on the AFM. Second, a number of force curves were obtained at the same position on the surface by setting the AFM to perform continuously repeated approach–retraction cycles. These measurements were all performed in 10 mM NaCl to avoid the repulsive contribution from the electrostatic double layer force. In Figure 3A,B histograms of adhesion forces for the two series of measurements are shown. The insets in the figures show that the adhesion force is not changing systematically in the course of the experiment. It is seen that measuring the adhesion force at a new position on the surface each time or

(11) For ultrapure water at pH 7, the Debye length is 961 nm, but due to absorption of CO_2 from the laboratory atmosphere, leading to a decrease in pH, the Debye length in Milli-Q water is assumed to be reduced to approximately 200 nm. However, even a very small amount of impurities will dramatically decrease the Debye length. A Debye length of 31 nm corresponds to less than 0.1 mM salt in the system.

(12) Mc Cormack, D.; Carnie, S. L.; Chan, D. Y. C. *J. Colloid Interface Sci.* **1995**, *169*, 177–196.

(13) Sjöström, L.; Åkesson, T. *J. Colloid Interface Sci.* **1996**, *181*, 645–653.

(9) Hutter, J. L.; Bechhoefer, J. *Rev. Sci. Instrum.* **1993**, *64*, 1868–1873.

(10) Sader, J. E.; Chon, J. W. M.; Mulvaney, P. *Rev. Sci. Instrum.* **1999**, *70*, 3967–3969.

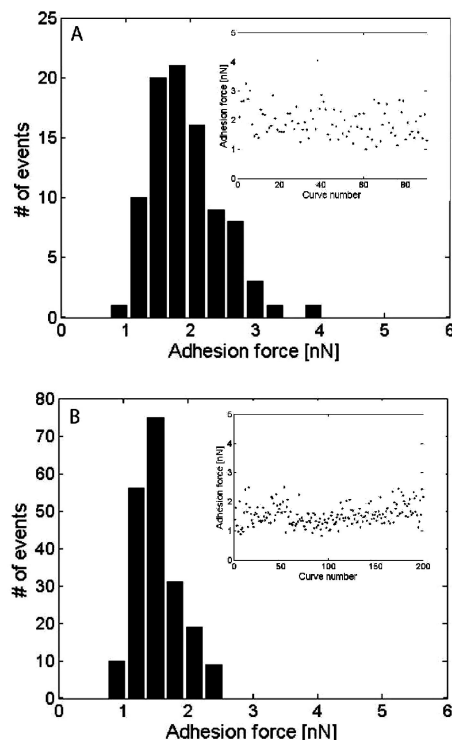


Figure 3. Histograms of adhesion forces between a $4.5\ \mu\text{m}$ polystyrene particle and a glass surface in 10 mM NaCl. (A) Measurements performed on different positions on the surface. (B) Measurements performed on the same position on the surface. The insets show that the values of the adhesion force are not changing systematically during the sequence of experiments.

measuring continuously at the same position are giving similar results. However, measuring at the same position on the surface gives a narrower distribution and in this case also a slightly lower average adhesion force. Repeating this experiment at a new position on the surface leads to a narrower distribution but with a slightly shifted maximum (data not shown). The shift in adhesion force between different positions on the surface explains why we observe a broader distribution when the position is shifted between each measurement and it indicates that local surface conditions have a small but discernible effect on the adhesion force.

In previous studies, the adhesion between a polystyrene particle and a flat silica substrate in a dry atmosphere¹⁴ and the adhesion between two polystyrene particles in water¹⁵ were investigated. In both cases it was found that the simple JKR theory¹⁶ fails to provide a reliable prediction of the adhesion force, and it was suggested that this failure was due to surface roughness and to plastic and viscoelastic deformations of the polystyrene particles. In Figure 4 are shown two histograms of adhesion forces where the surfaces are kept in contact at a constant applied load ($F/R = 10\ \text{mN/m}$) for 5 and 10 s, respectively, before the separation. It is clearly seen that the adhesion force increases with increasing contact time and it further appears as if the adhesion force is increasing during the experiments. Similar to the observations reported in ref 14, this indicates that the response of the polystyrene particle is not purely elastic at this applied load. Hence, the conditions for applying the JKR theory are not fulfilled.

Beside the primary adhesion, several secondary adhesion events are observed in many of our retraction force curves. In the presence

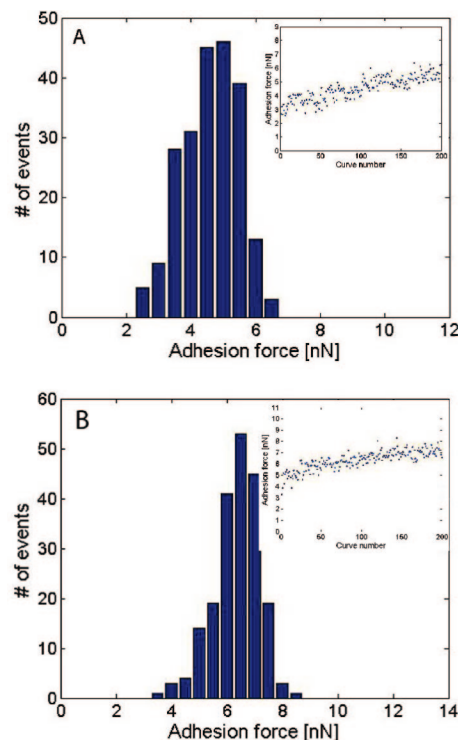


Figure 4. Histograms of adhesion forces between a $4.5\ \mu\text{m}$ polystyrene particle and a glass surface in water. (A) The particle is kept in contact for 5 s at a constant applied load ($F/R = 10\ \text{mN/m}$). (B) The particle is kept in contact for 10 s at a constant applied load ($F/R = 10\ \text{mN/m}$). The insets show how the adhesion force is changing during the sequence of experiments.

of salt, where the long-range repulsive electrostatic double layer force is screened out, these secondary adhesion events manifest themselves as plateaus of constant force but of varying length and height. These secondary adhesion events are ascribed to loosely bound polystyrene molecules protruding from the probe that are bridging to the surface. In Figure 5A, a number of retraction force curves obtained in 10 mM NaCl are shown, and in these force curves, plateaus of varying height and length are observed. If the curves are plotted on top of each other as in Figure 5B, it is seen that the forces are quantized such that the plateaus only exist at certain discrete force values. A similar behavior has been observed in a number of studies of polymers, and the plateaus are attributed to either pulling polymers from a good solvent to a bad solvent or to unzipping of polymers adhered to a surface.^{17–19} In the work by Scherer et al.,¹⁹ polymers were pulled out of a polymer film deposited on a cover glass and the observed nonuniform spacing between the plateaus was very convincingly explained by a mechanism where a bundle of polymers were pulled out of the polymer film rather than a number of individual polymers (see Figure 6A,B). By analyzing a large number of force curves, the plateau heights can be determined with high accuracy. The result of such an analysis is shown in Figure 5C, and the plateau heights are determined to have an almost uniform spacing with $F_{\text{plateau}} = 52 \pm 4, 102 \pm 6, 154 \pm 6, 205 \pm 7, \text{ and } 262 \pm 6\ \text{pN}$. This means that the plateaus in this case must represent individual polymers being pulled into the aqueous phase (see Figure 6B). If each of these polymers is

(14) Reitsma, M.; Craig, V. S. J.; Biggs, S. J. *Adhes.* **2000**, *74*, 125–142.

(15) Hodges, C. S.; Cleaver, J. A. S.; Ghadiri, M.; Jones, R.; Pollock, H. M. *Langmuir* **2002**, *18*, 5741–5748.

(16) Johnson, K. L.; Kendall, K.; Roberts, A. D. *Proc. R. Soc. London* **1971**, *324*, 301–313.

(17) Friedsam, C.; Bécares, A. D. C.; Jonas, U.; Seitz, M.; Gaub, H. E. *New J. Phys.* **2004**, *6*, 9.

(18) Friedsam, C.; Seitz, M.; Gaub, H. E. *J. Phys.: Condens. Matter* **2004**, *16*, S2369–S2382.

(19) Scherer, A.; Zhou, C.; Michaelis, J.; Brauchle, C.; Zumbusch, A. *Macromolecules* **2005**, *38*, 9821–9825.

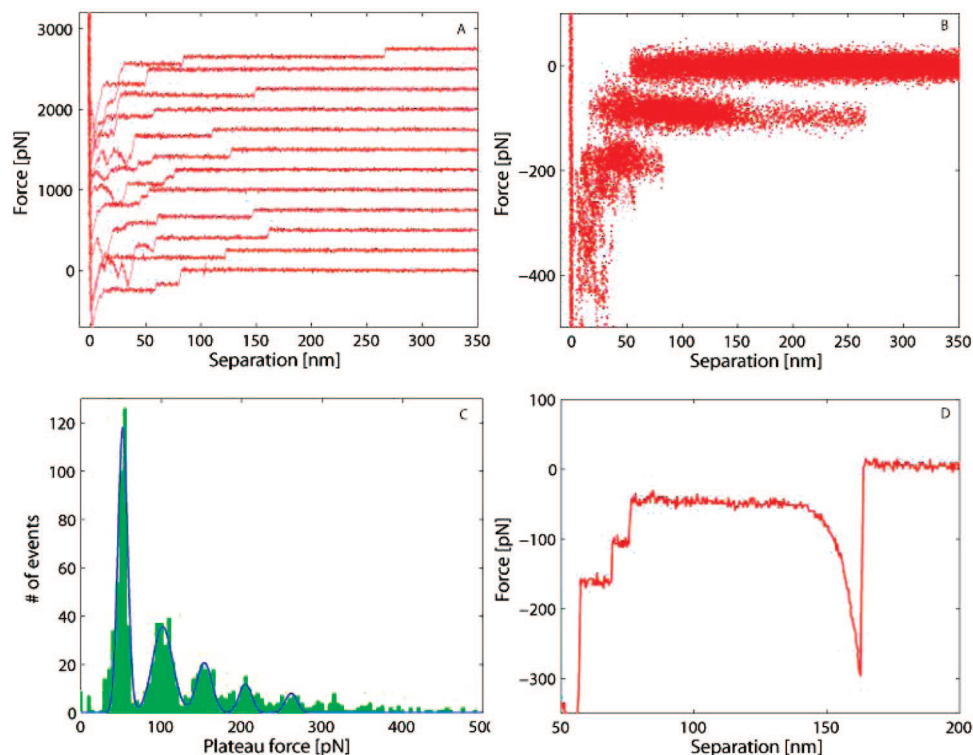


Figure 5. (A) Twelve force curves showing plateaus in the force during retraction. The zero-point of the force is offset to make the individual curves distinguishable. (B) The same curves as in A plotted on top of each other. It is seen that the force only assumes discrete values. (C) Histogram of plateau forces found by analyzing 922 different force curves. It is seen that the plateaus have an almost uniform spacing of approximately 50 pN. (D) A force curve showing not only plateaus in the force but also providing evidence for a single polymer with a contour length of approximately 160 nm being stretched to a length close to its full extension.

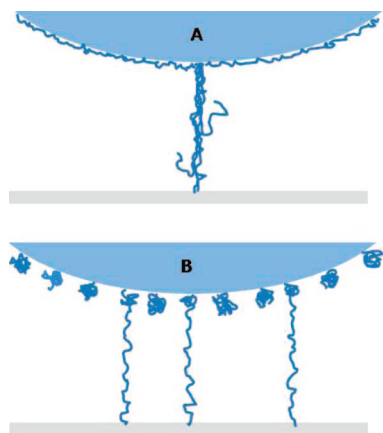


Figure 6. Two different scenarios that can lead to plateaus of constant force in the retraction force curves. (A) A bundle of polymers is pulled loose from the polystyrene particle. (B) Several individual collapsed polystyrene molecules attached to the particle are pulled into the aqueous phase. The uniform spacing between plateaus seen in Figure 5 suggests that the scenario sketch in part B is the correct in this case.

treated as a cylinder with an effective radius, r , the spacing between each plateau should be given as $F_{\text{plateau}} = 2\pi r\gamma_{\text{sv}}$. Using the macroscopic value for the surface energy of the polystyrene–water interface, $\gamma_{\text{sv}} = 30 \text{ mJ m}^{-2}$,²⁴ and a plateau height of 52 pN gives an effective radius of 2.8 Å. This corresponds approximately to the length of two C–C bonds and is a reasonable number for the average radius of a polystyrene chain.

Again, a plateau of constant force is a simple sign of the change in surface energy from having a polymer in a collapsed state or adhered to the surface to having the polymer chain exposed to the aqueous phase. However, if the polymer is not free to be

pulled into the aqueous phase but is constrained due to, for example, entanglement with other polymers, it will also be stretched against an entropic and enthalpic restoring force similar to what is seen for polymers in a good solvent.^{20–23} More precisely, in such a case the constant force plateau should turn into a region of increasing restoring force as the polymers are stretched to a length that is close to the contour length of the nonconstrained part of the polymer. Since this is not seen in Figure 5A, it must be because the polymer adhered to the glass surface jumps off before that length is reached. However, in a few cases a nonconstant force response is actually observed. An example of this is shown in Figure 5D, where three force plateaus are observed. In the end of the third plateau, a nonconstant restoring force onsets due to stretching of a strongly attached polymer. This observation is a nice example of a full stretching curve of a polymer in a bad solvent where both the solvent interactions and the backbone elasticity are important and is thus another indication of the fact that the plateaus are due to individual polymers and not a bundle of polymers. However, it should again be pointed out that the length of each plateau is in general not related to the length of the nonconstrained part of each polymer. Thus, a statistical treatment of the distribution of plateau lengths does not reveal any information of the underlying polymer structure.

(20) Hugel, T.; Grosholz, M.; Clausen-Schaumann, H.; Pfau, A.; Gaub, H.; Seitz, S. *Macromolecules* **2001**, *34*, 1039–1047.

(21) Oesterhelt, F.; Rief, M.; Gau, H. E. *New J. Phys.* **1999**, *1*, 6.16.11.

(22) Li, H.; Zhang, W.; Xu, W.; Zhang, X. *Macromolecules* **2000**, *33*, 465–468.

(23) Thormann, E.; Evans, E. R.; Craig, V. S. J. *Macromolecules* **2006**, *39*, 6180–6185.

(24) Schmitt, F. J.; Ederth, T.; Weidenhammer, P.; Claesson, P.; Jacobasch, H. J. *J. Adhes. Sci. Technol.* **1999**, *13*, 79–96.

At first sight it might seem a bit surprising that individual polymers are pulled loose from the surface rather than a bundle of polymer, since this would correspond to a lower cost in surface energy. However, this simply indicates that the bridging polymers are far apart. We have a large contact region between the probe and the surface, but still we only observe a couple of plateaus in each retraction curve. This suggests that most polymers stay at the polystyrene particle when it is separated from the surface. Hence, from a statistical point of view, the polymers bridging the particle and the surface will be far apart.

Interaction between a Polystyrene Particle and a Hydrophobic Surface. Next, the interaction between the same polystyrene particle and a silica surface coated by a hydrophobic self-assembled monolayer of octadecyltrichlorosilane (OTS) was investigated. In Figure 7A is shown typical approach and retraction force curves for the interaction between the polystyrene particle and the hydrophobic surface in pure water. Compared to Figure 1, the most conspicuous differences are the lack of a long-range repulsion in the approach force curve and a much stronger adhesion force in the retraction force curve.

In Figure 7B the approach force curve is shown for small separations where several differences from the interaction with the pure glass surface are observed. First, the lack of a long-range repulsive double layer force is not surprising, since the charge density is expected to be much lower on the OTS-coated surface than on the glass surface. On the other hand, a short-range repulsive force with an onset at approximately 20 nm is observed. At a separation of approximately 10 nm, the polystyrene particle suddenly jumps into contact. Before the jump-in, no indication of an attractive force acting between the polystyrene particle and the surface is observed.

While a soft cantilever such as the one used for the experiments presented in Figures 1, 2, and 5 is suitable for measuring soft interactions, the retraction force curve in Figure 7A (because of the strong adhesion and hence large jump-out distance) does not provide any information about the interaction at separations smaller than approximately 200 nm. We have thus conducted an experiment where the interaction between the OTS-coated surface and a smaller 1 μm sized polystyrene particle mounted on a stiffer cantilever was measured. The smaller particle has given rise to a smaller adhesion force while the stiffer cantilever has increased the mechanical stability of the system. The combination of these two effects reduced the jump-out distance to approximately 20 nm, which thus allowed us to get more information about the interaction during retraction. An example of typical approach and retraction force curves obtained under these experimental conditions is shown in Figure 7C. After the jump-out, a long-range attraction is observed that decreases gradually out to a separation of 70 nm, where the force suddenly goes to zero. A similar behavior has previously been reported and was attributed to the formation of a microscopic bubble bridging the two surfaces.^{25–28} In these previous studies, the bubble formed between highly hydrophobic silanized hydrocarbon surfaces, while the present study shows that the same phenomenon occurs between a silanized surface and a polystyrene particle. Briefly, during approach a bubble forms between the probe and the surface leading to the jump-in at approximately 10 nm. Upon retraction, the bubble, now bridging the probe and the surface, is elongated,

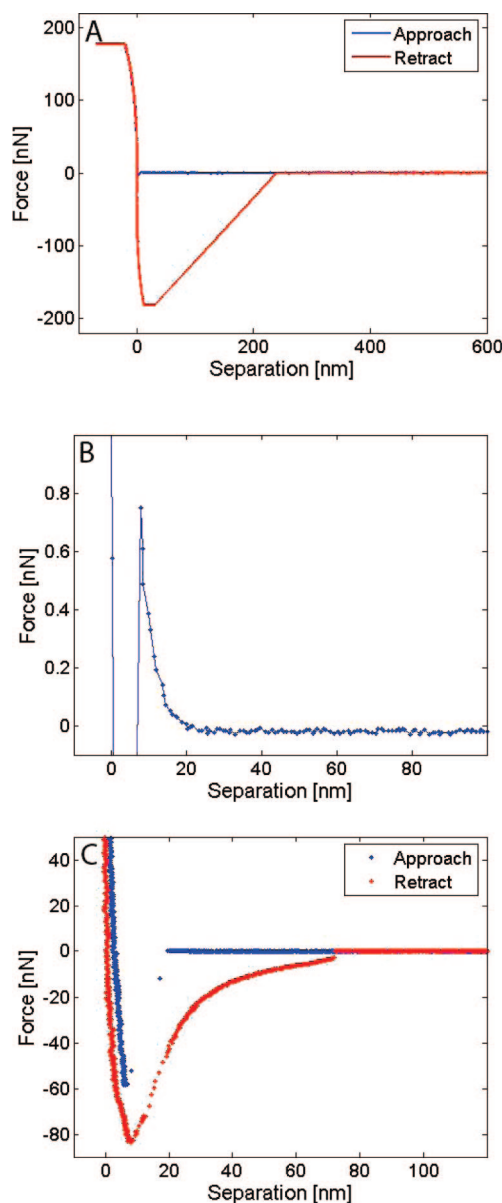


Figure 7. Force curves showing the interaction between a polystyrene particle and an OTS-coated surface in water. (A) Approach and retraction force curves obtained for experiment with a 4.5 μm particle mounted on a soft cantilever. The large jump-out distance observed in the retraction force curve is due to a combination of the strong adhesion and the use of a soft cantilever. (B) Close up look at the short-range repulsive force seen during approach. (C) Approach and retraction force curves obtained for an experiment with a 1 μm particle mounted on a stiff cantilever.

which leads to the long-range restoring force. At a certain separation, the bubble becomes unstable and ruptures. In this case, it happens at a separation of approximately 70 nm.

Studies of the adhesion force between a polystyrene particle and an OTS-coated surface did not give reproducible results, in contrast to the case with the studies of the adhesion between a polystyrene particle and a bare glass surface. In the latter case, the adhesion force seems to vary significantly between different positions on the surface as well as over time. However, the result shows in all cases that the average adhesion is stronger when the same position on the surface is probed continuously than if a new position on the surface is probed in each approach. In Figure 8 is shown an example of a series of adhesion measurements. The figure shows how the magnitude of the adhesion force change during 150 measurements in a case where the same position on

(25) Ishida, N.; Kinoshita, N.; Miyahara, M.; Higashitani, K. *J. Colloid Interface Sci.* **1999**, *216*, 387–393.

(26) Yaminsky, V.; Ohnishi, S. *Langmuir* **2003**, *19*, 1970–1976.

(27) Ishida, N.; Sakamoto, M.; Miyahara, M.; Higashitani, K. *Langmuir* **2000**, *16*, 5681–5687.

(28) Ishida, N.; Sakamoto, M.; Miyahara, M.; Higashitani, K. *J. Colloid Interface Sci.* **2002**, *253*, 112–116.

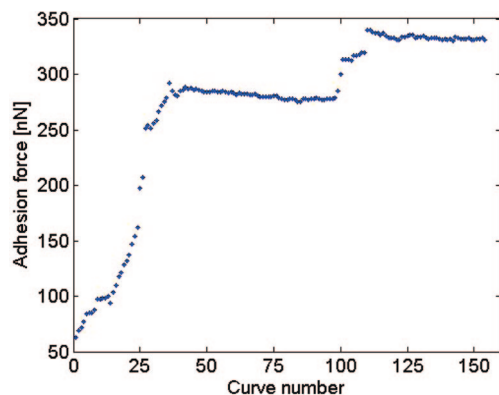


Figure 8. The change in the magnitude of the adhesion force over a range of 150 measurements, where the same position on the surface was probed repeatedly. It is seen that the magnitude of the adhesion force changes during the experiment in an irregular manner.

the surface was probed repeatedly. Interestingly, it looks as though the adhesion force increases over a number of measurements and then levels out at an almost constant value for a period before it again increases. The physical mechanism behind this behavior is not clear, but a possible explanation could be that preformed nanobubbles on the surface are joining up with the bubble formed between the polystyrene particle and the surface. Nanobubbles on hydrophobic surfaces have been reported in a number of studies^{27,29–31} and such nanobubbles randomly distributed on the surface could also explain why the adhesion force measured continuously over time are not the same for series of measurements performed at different positions on the surface.

Similar to the interaction between the polystyrene particle and the bare glass surface, plateaus in the retraction force curves are also observed for the polystyrene OTS interaction. Examples of such events are shown in Figure 9A, and the result of an analysis of the step height is shown in Figure 9B. Due to the large jump-out distance in these experiments, a smaller number of plateaus are observed compared to what was seen in Figure 5C. However, two distinct populations of plateaus with $F_{\text{plateau}} = 56 \pm 4$ and 106 ± 10 pN are identified. The similarity between these values and the values given in relation to Figure 5C support the hypothesis that the plateaus are due to single polymers that are being pulled loose from the polystyrene particle. Thus, the plateau height has nothing directly to do with the physical chemistry of the surface (bare silica or OTS-coated silica) but is only due to the polymer–solvent interaction.

Finally, we have substituted the aqueous medium with pentanol. An example of approach and retraction force curves from such an experiment is shown in Figure 10. A number of observations are noteworthy from these force curves. First, no jump-in is seen during approach and no long-range attraction is seen during retraction. The phenomena observed in Figure 7C were ascribed to the formation of a bubble bridging the surface and the polystyrene particle and such a bubble does clearly not form in the nonaqueous solvent. Second, it is seen that the adhesion force completely vanishes in pentanol. The reason for this is of course that the surface energies of the OTS surface and the polystyrene particle are much lower in pentanol than in water. Third, no plateaus of constant force are observed in the retraction

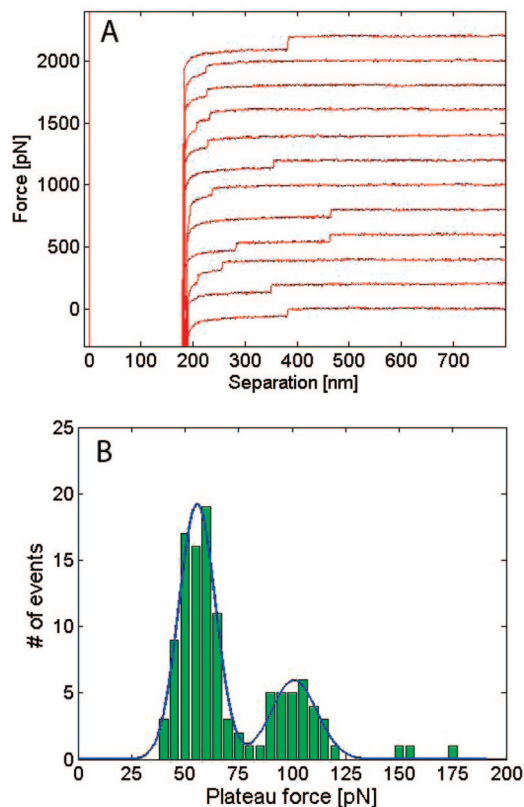


Figure 9. (A) Examples of retraction force curves showing plateaus. (B) Histogram of plateau forces. The analysis shows two populations of plateaus at approximately 56 and 102 pN.

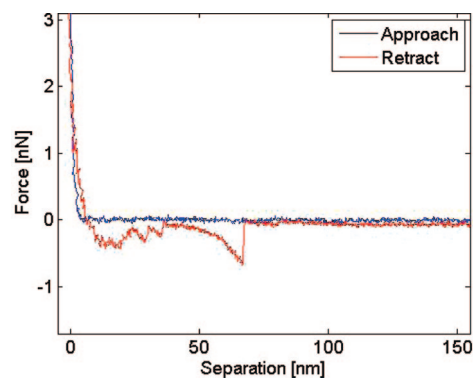


Figure 10. Approach and retraction force curves for the interaction between a polystyrene particle ($D = 4.5 \mu\text{m}$) and a hydrophobic OTS-coated silica surface in pentanol. None of the characteristic features observed in the aqueous medium are present here. Further, stretching a polymer bridging the probe and the surface now gives rise to a nonlinear force response, which is characteristic for stretching a polymer in a good or neutral solvent.

curve, since single polystyrene molecules are no longer stretched in a bad solvent. Instead, a nonlinear force response that is characteristic for stretching a polymer in good or neutral solvent is observed. These three observations demonstrate the importance of the solvent quality.

Conclusion

We have investigated the different kinds of interactions that occur between a polystyrene particle and a hydrophilic and a hydrophobic surface, respectively. Interestingly, it is found that the particle interacts very differently with the two kind of surfaces. In the case of the hydrophilic surface, the interaction is typically

(29) Parker, J. L.; Claesson, P. M.; Attard, P. *J. Phys. Chem.* **1994**, 98, 8468–8480.

(30) Simonsen, A. C.; Hansen, P. L.; Klösgen, B. *J. Colloid Interface Sci.* **2004**, 273, 291–299.

(31) Zhang, X. H.; Maeda, N.; Craig, V. S. *J. Langmuir* **2006**, 22, 5025–5035.

DLVO-like with a long-range repulsive force that can be regulated by addition of salt. In the case of the hydrophobic surface, the interaction is similar to the interaction observed between two identical highly hydrophobic surfaces, which are interpreted as being due to formation of a bridging air bubble. For both surfaces, a force response due to polymers bridging the surface and the probe is observed. These events manifest themselves as plateaus of constant force in the retraction force curves. The height of the plateaus are entirely given by the cost in surface energy of pulling a polymer from the polystyrene surface into the aqueous medium and thus does not depend on whether the opposite surface is hydrophilic or hydrophobic. However, these secondary adhesion events have different implications for the two types of surfaces. For the hydrophilic surface, where the primary adhesion to the polystyrene particle is weak, the bridging polymers give rise to

long-range attraction which effectively will anchor the particle to the surface after contact. For the interaction with the hydrophobic surface, this effect is less significant, since the retraction force curve is dominated by a strong and long-range restoring force due to a bridging air bubble. Finally, an experiment where the aqueous media is substituted by pentanol demonstrates the importance of solvent quality. In the case of the hydrophobic surface, it appears that the hydrophobic interaction vanishes and the plateau of constant force changes to a nonlinear force response, which is characteristic for stretching a polymer in a good or neutral solvent.

Acknowledgment. MEMPHYS—Center for Biomembrane Physics is supported by the Danish National Research Foundation.

LA8005162