Effect of Dissolved Gas and Salt on the Hydrophobic Force between Polypropylene Surfaces

2 AUTHORS:

Laurence Meagher
Monash Institute of Medical Engineering. Mon…
61 PUBLICATIONS **1,472** CITATIONS

SEE PROFILE

Vincent S J Craig
Australian National University
101 PUBLICATIONS **4,057** CITATIONS

SEE PROFILE

Effect of Dissolved Gas and Salt on the Hydrophobic Force between Polypropylene Surfaces

Laurence Meagher[*,†] and Vincent S. J. Craig[†,‡]

Department of Chemistry, Faculty of Science, The Australian National University, Canberra, ACT 0200, Australia, and Department of Applied Mathematics, Research School of Physical Sciences and Engineering, The Australian National University, Canberra, ACT 0200, Australia

The hydrophobic interaction between polypropylene surfaces in NaCl solutions has been measured using a modified atomic force microscope (AFM). An attractive force of 30 nm range was measured. This is of much shorter range than that reported for Langmuir–Blodgett deposited surfactant films on mica. Removal of the gases dissolved in dilute NaCl solutions was found to reduce the range of the interaction. Increased NaCl concentration up to 1 M has little or no effect on the range of the interaction, within experimental error. The results have implications for the mechanism of the long range hydrophobic interaction.

Introduction

The hydrophobic nature of molecules often determines their solution properties and provides the driving force for phenomena such as molecular self-assembly of amphiphilic molecules (e.g. lipids and surfactants) into aggregates such as micelles, vesicles, and bilayers.[1] The extension of this effect to macroscopic surfaces, known as the hydrophobic interaction, is of great academic interest and is important in many areas such as froth flotation and wetting.

The first indication that the hydrophobic interaction between macroscopic surfaces was much longer ranged than that proposed for small molecules in water came from measurements of the film thickness between a gas bubble and methylated silica in aqueous solutions.[2] For hydrophilic silica the film is stabilized by electrostatic forces; however, for methylated silica (i.e. with a high water contact angle) destabilization of the film occurs at about 64 nm. In the early 1980s the first direct measurements of strong, attractive forces between macroscopic hydrophobic surfaces[3–5] were made. These measurements were obtained from the interaction between muscovite mica surfaces, coated with an adsorbed layer of the surfactant cetyltrimethylammonium bromide (CTAB), using the Israelachvili surface forces apparatus (SFA).[6] Forces of much longer range, up to about 30 nm,[7] were later measured between weakly charged hydrophobic surfaces prepared by the deposition of Langmuir–Blodgett (LB) monolayers onto mica. Measurement of purely attractive forces between neutral LB films deposited on mica showed that the range of the hydrophobic interaction was about 70 nm[8] and even larger (90 nm) for fluorocarbon

surfactants deposited in the same manner.[9] A long-range hydrophobic interaction has also been measured between crossed filaments of hydrophobized glass[10] and inferred from the coagulation of hydrophobized silica spheres.[11,12]

The effect of electrolyte has been studied. In one study,[15] after a reanalysis of their previous work,[13,16,17] the authors concluded that the exponential decay of the long range attraction was not substantially changed by electrolyte concentrations below about 0.01 mol dm^{-3}. The effect of dilute solutions of 1:1 and 2:2 electrolyte solutions on the range and magnitude of the hydrophobic interaction has also been investigated recently.[18] A strong dependence on concentration was observed and the effect of 2:2 electrolyte was found to be larger than that of 1:1 electrolytes.

The mechanism of the long range hydrophobic interaction has been a subject of speculation for about a decade. There are several theories in the literature concerning the origin of the hydrophobic interaction between surfaces. The first is based on water structural effects propagating from the surfaces into the bulk liquid.[19] Approach of the two surfaces further increases this dynamic water structuring, displacing water molecules from the interlayer region to bulk water and decreasing the free energy of the system. However, this theory is unlikely to be able to explain the long-range nature of the hydrophobic interaction since water structure effects would probably have decayed by about 5 water molecule diameters,[20] whereas

---

* Author to whom correspondence should be addressed.

† Department of Chemistry.

‡ Department of Applied Mathematics.

(1) Tanford, C. *The Hydrophobic Effect*; Wiley: New York, 1973.

(2) Blake, T. D.; Kitchener, J. A. *J. Chem. Soc., Faraday Trans 1* **1972**, *68*, 1435.

(3) Pashley, R. M.; Israelachvili, J. N. *Colloids Surf.* **1981**, *2*, 169.

(4) Israelachvili, J. N.; Pashley, R. M. *Nature* **1982**, *300*, 341.

(5) Israelachvili, J. N.; Pashley, R. M. *J. Colloid Interface Sci.* **1984**, *101*, 511.

(6) Israelachvili, J. N.; Adams, G. E. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 1525.

(7) Claesson, P. M.; Blom, C. E.; Herder, P. C.; Ninham, B. W. *J. Colloid Interface Sci.* **1986**, *114* (1), 234.

(8) Christenson, H. K.; Claesson, P. M. *Science* **1988**, *239*, 390.

(9) Claesson, P. M.; Christenson, H. K. *J. Phys. Chem.* **1988**, *92*, 1650.

(10) Rabinovich, Y. A. I.; Derjaguin, B. V. *Colloids Surf.* **1988**, *30*, 243.

(11) Xu, Z.; Yoon, R.-H. *J. Colloid Interface Sci.* **1990**, *134*, 427.

(12) Zhou, Z.; Wu, P.; Ma, C. *Colloids and Surf.* **1990**, *50*, 177.

(13) Claesson, P. M.; Blom, C. E.; Herder, P. C.; Ninham, B. W. *J. Colloid Interface Sci.* **1986**, *114*, 234.

(14) Christenson, H. K. *Modern Approaches to Wettability: Theory and Applications*; Schrader, M. E., Loeb, G., Eds.; Plenum Press: New York, 1992.

(15) Christenson, H. K.; Claesson, P. M.; Parker, J. L. *J. Phys. Chem.* **1992**, *92*, 6725.

(16) Christenson, H. K.; Claesson, P. M.; Berg, J.; Herder, P. C. *J. Phys. Chem.* **1989**, *93*, 1472.

(17) Christenson, H. K.; Fang, J.; Ninham, B. W.; Parker, J. L. *J. Phys. Chem.* **1990**, *94*, 8004.

(18) Tsao, Yi-H.; Evans, F.; Wennerstrom, H. *Langmuir* **1993**, *9*, 779.

(19) Eriksson, J. C.; Ljunggren, S.; Claesson, P. M. *J. Chem. Soc., Faraday Trans. 2* **1989**, *85*, 163.

(20) Lee, C. Y.; McCammon, J. A.; Rossky, P. J. *J. Chem. Phys.* **1984**, *80*, 4448.

the measured long-range hydrophobic interaction extends for some 300 water molecule diameters. Another suggestion is that the hydrophobic interaction is somehow driven by the metastability of water films between hydrophobic surfaces with contact angles greater than 90°.[8,9] Cavitation has been inferred or directly observed for hydrophobic surfaces in contact[21] or just prior to contact,[8,9] in SFA experiments. Theory predicts cavitation between surfaces at close separations, with a contact angle greater than 90°, and has been dealt with thoroughly by Yushenko et al.[22,23] Yet another proposal uses classical continuum electrostatics to illustrate how electrostatic correlations, arising from a surface induced perturbation in the fluid next to a hydrophobic surface, could give rise to a long range electrostatic force.[24,25] Related to the metastable film and cavitation arguments are those of Yaminsky[26] who postulates that the increased attraction is a result of the lateral enhancement of density fluctuations in the water film between the hydrophobic surfaces. Monte Carlo simulations of a fluid between two hard walls suggest that a separation induced phase change, the opposite of capillary condensation, can be induced.[27] This effect results in a monotonically increasing attractive force which the authors suggest could be the microscopic origin of the long-range hydrophobic interaction.

However, the precise mechanism still remains to be quantified. All theoretical approaches so far fail to predict the range of the interaction correctly. Recent AFM images and SFA measurements between neutral surfactant coated mica surfaces suggest that the long range nature of the hydrophobic interaction may be partially related to the crystalline state of the adsorbed layer.[28] However, these results are inconsistent with other SFA measurements which showed that long range forces were still observed between surfaces with disordered surfactant layers.[29]

The hydrophobic interaction has recently been measured between polystyrene surfaces using an atomic force microscope.[30] No long range tail was observed and the surfaces jumped to contact from about 25 nm. This observation is more in line with early measurements using surfactants adsorbed from solution. Measurements made with pure polymers are without some of the problems associated with surfactant coatings, such as the method of preparation and the different crystalline state of the layers. The effect of salt is also easily investigated at concentrations above 10^{-2} M. Salt concentrations higher than this affect the packing of the adsorbed hydrophobic layers[31] but not pure polymer surfaces.

When cavitation between hydrophobic surfaces was first observed,[21] the possibility of this being due to nucleation of dissolved gas was considered and rejected in favor of a vapor cavity. Since that time, discussion has followed the vapor cavitation model. However, the original reason for rejecting dissolved gas nucleation—that on separating
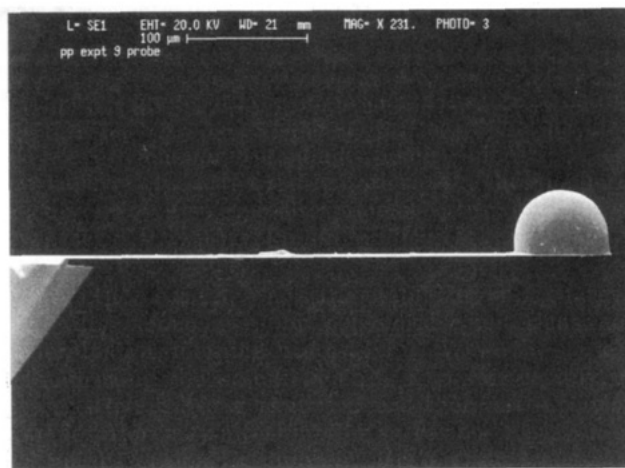

Figure 1. Scanning electron micrograph of a typical weak spring as viewed from the side. The approximately hemispherical polypropylene surface can be seen on the right-hand side of the image.

the surfaces the cavity rapidly disappeared—may have been invalid, since fine bubbles of gas may also rapidly redissolve on separating the surfaces. The main reason for reexamination of the dissolved gas model has come from recent work on the remarkable effects of salts on bubble coalescence[32,33] and, more directly, on the simple observation that degassing produces an increased stability of oil in water emulsions.[34] Since the oil droplets are destabilized via the hydrophobic interaction, the implication is that removal of the dissolved gas reduces this interaction. With these recent developments in view, we have examined the effect of the removal of dissolved gas (about 20 cm³/L of water at normal atmospheric pressures) on the hydrophobic interaction between polypropylene surfaces, measured using the AFM technique.

Methods and Materials

The forces between polypropylene surfaces were measured using a Nanoscope II atomic force microscope (Digital Instruments, Inc.) using the method developed by Ducker et al.[35] In this method, a colloidal particle is placed either on or around the pyramidal scanning tip on the microfabricated cantilever spring. For the present experiments, a polymer melt rather than a silica sphere was attached to the cantilever (see Figure 1). This provides a surface with known geometry and chemistry, in this case polypropylene. The deflection of this spring was monitored as a function of separation distance between the colloid particle and a flat surface mounted on a piezoelectric crystal. The cantilevers used for these measurements, purchased from Digital Instruments, Inc., were etched, single crystal silicon, rectangular beams.

In order to scale direct force measurements correctly, the spring constant must be known accurately. This value can be calculated or measured directly. Microfabrication of the cantilever springs used in AFM[36] has allowed imaging techniques to progress rapidly. Unfortunately this means that direct calibration for force measurement is difficult because of the physical size of the cantilever. Calibration methods reported so far in the literature require assumptions to be made on the mass of the cantilever[37] and/or of objects placed on the cantilever.[37,38] Calculation of the

(21) Pashley, R. M.; McGuiggan, P. M.; Ninham, B. W.; Evans, D. F. *Science* **1985**, *229*, 1088.

(22) Yuschenko, V. S.; Yaminsky, V. V.; Schukin, E. D. *J. Colloid Interface Sci.* **1983**, *96*, 307.

(23) Yaminsky, V. V.; Yuschenko, V. S.; Amelina, E. A.; Schukin, E. D. *J. Colloid Interface Sci.* **1983**, *96*, 301.

(24) Attard, P. *J. Phys. Chem.* **1989**, *93*, 6441.

(25) Podgornik, R. *J. Chem. Phys.* **1989**, *91*, 5840.

(26) Yaminsky, V. V.; Ninham, B. N. *Langmuir* **1993**, *9*, 3618.

(27) Berard, D. R.; Attard, P.; Patey, G. N. *J. Chem. Phys.* **1993**, *98*, 7236.

(28) Tsao, Y.; Yang, S. X.; Evans, D. F.; Wennerstrom, H. *Langmuir* **1991**, *7*, 3154.

(29) Christenson, H. K.; Parker, J. L.; Yaminsky, V. V. *Langmuir* **1992**, *8*, 2080.

(30) Karaman, M. E.; Meagher, L.; Pashley, R. M. *Langmuir* **1993**, *9*, 1220.

(31) Christensen, H. K.; Claesson, P. M.; Berg, J.; Herder, P. C. *J. Phys. Chem.* **1989**, *93*, 1492.

(32) Craig, V. S.; Ninham, B. W.; Pashley, R. M. *Nature* **1993**, *363*, 317.

(33) Craig, V. S.; Ninham, B. W.; Pashley, R. M. *J. Phys. Chem.* **1993**, *97*, 10192.

(34) Pashley, R. M.; Karaman, M. E., personal communication, 1993.

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

(36) Albrecht, T. R.; Akamine, S.; Carver, T. E.; Quate, C. F. *J. Vac. Sci. Technol. A* **1990**, *8* (4), 3386.

(37) Cleveland, J. P.; Manne, S.; Bocek, D.; Hansma, P. K. *Rev. Sci. Instrum.* **1993**, *64* (2), 1.

spring constant on the other hand, requires knowledge of Young's modulus for the material from which the spring is made and an accurate measurement of the dimensions of the spring, in particular the thickness. The use of literature values for the Young's modulus can be misleading, especially for vapor-deposited films like Si_3N_4,[37] as the film may vary in composition.[39] In addition, recent theoretical calculations have shown that the equation used to calculate the spring constant from literature material properties is inaccurate for the V-shaped cantilevers typically used.[40]

To resolve this essential difficulty, we have chosen to calibrate the spring using the method of Senden and Ducker.[37] Two or three tungsten spheres were attached to the cantilever spring.[35] The deflection of the spring was measured under the influence of this mass using the optical lever arrangement of the AFM. The compliance was also measured against hydrophobized mica (to eliminate capillary condensation of water from the atmosphere). This procedure provides a direct measure of the spring constant for an individual spring. Measurement of the dimensions using scanning electron microscopy then allows the Young's modulus for the material to be calculated using eq 1[41]

$$E = \frac{4kl^3}{wt^3} \quad (1)$$

where E is the Young's modulus, k the spring constant, l the length, w the width, and t the thickness of the spring. This gave an average value of 67.5 ± 13.2 GPa from five determinations using two springs. For comparison, calculation of the Young's modulus from literature elasticity constants[42] gave a value of 131–137 GPa depending on the plane of bending.[43]

In our case, since all the springs used were made in the same way[41] from the same material (i.e. etched from single crystal silicon), the Young's modulus calculated from the measured spring constant may then be applied to other springs of the same material, but of different dimensions, with some confidence. That the springs indeed had the same chemical composition was verified using scanned microprobe wavelength dispersive X-ray analysis.

The method used to prepare the polypropylene colloid probe is as follows. The cantilever was initially rendered hydrophilic by exposure to a water plasma (135 kHz, 10 W for 45 s, $P_{H_2O} = 4.0$ Pa and $P_{Ar} = 4.0$ Pa). The cantilever was then made oliophobic by gas phase reaction with (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-methyldichlorosilane for 2 h. A small piece of pure polypropylene (Memtec Pty Ltd.), approximately 100 μm in size, was placed at the tip end of the cantilever spring. This was heated to form a roughly spherical bead of molten polymer. The shape was retained on cooling. All operations were carried out in a glovebag, filled with dry, high-purity, oxygen-free N_2, in order to avoid oxidation of the polypropylene. The probe was stored in a N_2 atmosphere until use (no longer than 3–4 days). A SEM image of a typical example of the colloid probes used in these experiments is presented in Figure 1.

The flat polypropylene surface was made in the following way. A bead (3–4 mm in diameter) was placed between two freshly cleaved pieces of mica and heated while pressure was applied. This produced a flat, smooth disk which was then glued (Araldite) to a sample stub. The mica which adhered to the upper surface of the polypropylene disk was left in place until just before commencement of the force experiment. Again, melting of the bead was carried out in oxygen-free, high-purity N_2 and the samples were stored in a N_2 environment until required (no longer than 3–4 days). AFM images of these surfaces (181 × 181 nm region), obtained in 0.01 M NaCl, had a typical roughness (peak to trough) of 7.6 nm with a standard deviation of 1.3 nm. A typical AFM image is presented in Figure 2. The roughness in
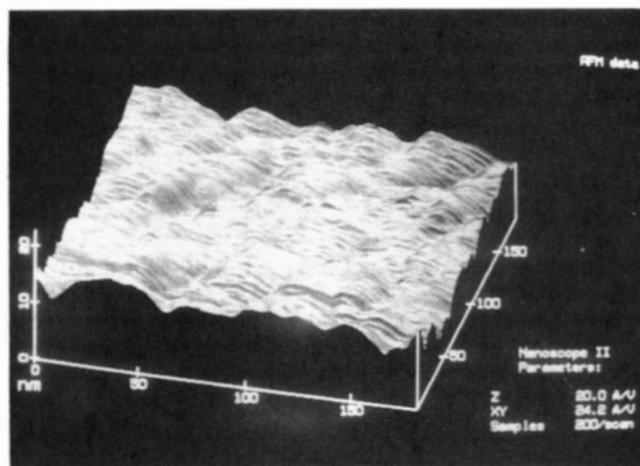
(38) Senden, T. J.; Ducker, W. A. *Langmuir* **1994**, *10*, 1003.
(39) Butt, H.-J.; Siedle, P.; Seifert, K.; Fendler, K.; Seeger, T.; Bamberg, E.; Weisenhorn, A. L.; Goldie, K.; Engel, A. *J. Microsc.* **1993**, *169*, 75.
(40) Sader, J. E.; White, L. *J. Appl. Phys.* **1993**, *74*, 1.
(41) Wolter, O.; Bayer, Th.; Greschner, J. *J. Vac. Sci. Technol. B* **1991**, *9* (2), 1353.
(42) Fukumoto, A. *Phys. Rev. B* **1990**, *42* (12), 7462.
(43) Wohlfarth, E. P., Ed. *Thermophysical Properties of Materials*; North Holland: Amsterdam, 1986.

Figure 2. Atomic force microscope image of a typical polypropylene flat surface as used in the experiments. The image was obtained in 0.01 M NaCl. The roughness is amplified in this image because the z range is much larger than the x and y ranges.

this image is amplified by the choice of vertical scale.

Analytical grade NaCl was further purified by roasting in air at 600 °C for 5 h. Water used to make up solutions was filtered and passed through an activated charcoal and a reverse osmosis membrane, followed by distillation. Final purification was carried out by the following procedure. The water obtained after the first distillation was stirred with coarse activated charcoal for 2 h, filtered through two 50 nm pore size Nucleopore, filters and finally distilled. All operations were carried out in a laminar flow cabinet. Glassware was soaked in 10 wt % NaOH solution and rinsed thoroughly with clean water. All fittings for the AFM fluid cell were washed thoroughly in redistilled AR grade ethanol and water and finally boiled in clean water. The AFM fluid cell was cleaned using the same technique.

The solutions were degassed for a minimum of 1 h using a vacuum pump and a liquid N_2 cold trap. With this arrangement, a vacuum of 10^{-3} Torr or better was obtained. The solution was then sealed and transferred to the AFM where it was injected into the fluid cell. Care was taken not to introduce any air into the cell.

The geometric mean radius of the polypropylene probe was measured after the force experiment using a Cambridge S360 scanning electron microscope, and this value was used to scale the measured forces.

Results and Analysis

Measurements of the contact angle between polypropylene and water or NaCl solutions of different concentration gave advancing angles between 103° and 111° and a receding angle of 90°.

The interaction force between two polypropylene surfaces was measured as a function of separation distance in NaCl solutions over a range of concentrations. The effect of dissolved gas on the range and magnitude of the interaction was also investigated. Springs with spring constants that differed by more than 2 orders of magnitude were used to investigate the interaction at both long and short range. A typical spring constant for the weaker spring was 0.30 N m^{-1}, whereas that of the stiffer spring was 59.5 N m^{-1}.

The results obtained by using the weak springs fall into two categories. The first consisted of a long range repulsion resulting from the interaction of diffuse double layers, followed by a jump into adhesive contact as the gradient of the attractive force exceeded the spring constant. This jump to contact occurred from various separation distances depending on the particular experiment, but always occurred from a distance substantially greater than that expected for the van der Waals interac-

tion between polypropylene surfaces. An adhesion between the two surfaces, as they were pulled apart, was always observed in these experiments. The second type of experimental result consisted of a long range repulsive force which was variable and could not be explained by electrostatic repulsion. No van der Waals jump or adhesion of the surfaces was observed under these conditions. We therefore attribute this type of result to contamination arising either from solutions, equipment, or glassware or from the polymer itself[44] (i.e. antioxidants or plasticizers) or to entrapment of an air bubble between the surfaces on injection. Experiments using hydrophobic surfaces in water are particularly sensitive to surface contamination.[45] The high interfacial energy favors adsorption of any suitable contaminant. In summary, repulsive forces with a decay length markedly different to the Debye length, with no jump to adhesive contact, were assumed to be due to contamination or entrapment of an air bubble and rejected.

All theoretical curves were calculated using a Runga-Kutta numerical solution to the nonlinear Poisson–Boltzmann equation[46] and a nonretarded Hamaker constant of 0.64×10^{-20} J. The Hamaker constant was calculated using an oscillator model[47] with the approximations that the UV spectral data for polypropylene could be represented by the first ionization potential for polymethylene[48] and the IR spectral data by that of $CH_3(CH_2)_{14}CH_3$.[49] The calculated Hamaker constant values were graphed and the value, extrapolated to zero distance, used in this work. Retardation of the van der Waals interaction in this system means that the Hamaker constant falls by about one-third by 30 nm. Thus the nonretarded value is an upper limit for the magnitude of the van der Waals force. A similar Hamaker constant for polypropylene across water was calculated by Gingell and Parsegian[48] using a more sophisticated representation for water than the one used here although they did not include a representation for the infrared region.

The interaction between two polypropylene surfaces was measured as a function of separation distance in 1.4×10^{-4} M NaCl using a weak spring. In these experiments NaCl solutions were studied under both gassed and degassed conditions. Figure 3 shows a typical curve obtained with gassed NaCl. As the surfaces approach each other, a repulsive force due to the overlap of diffuse double layers is observed at moderate separations. The surfaces then jump into contact at 21.7 nm due to a spring instability. The solid line is the theoretical force profile calculated using a constant potential of 45 mV which corresponds to a surface charge of 1.36×10^{-3} C m^{-2} (1 unit charge/117.7 nm²). The dashed line is the force profile calculated using the constant charge assumption for the same conditions. Quite clearly there is an additional attractive force present in these experiments not accounted for by DLVO theory, which would predict a jump distance of between 2.1 nm (constant charge) and 4.6 nm (constant potential). Since the jump distance observed on repeated force runs was somewhat variable, a total of 10 force curves were obtained by using gassed NaCl giving an average jump distance of 21.0 nm with a standard deviation of 5.2 nm.

Figure 3. *F/R* versus separation distance for polypropylene surfaces in gassed 1.4×10^{-4} M NaCl, measured using a weak spring. The fitted surface potential was 45 mV. The solid line is the fitted theoretical curve corresponding to the constant potential limit whereas the dashed line corresponds to the constant charge limit.

Figure 4. *F/R* versus separation distance for polypropylene surfaces in degassed 1.4×10^{-4} M NaCl, measured using a weak spring. The fitted surface potential was 38 mV. The solid line is the fitted theoretical curve corresponding to the constant potential limit whereas the dashed line corresponds to the constant charge limit.

Figure 4 shows a typical force curve obtained after injection of degassed NaCl. The features are similar to those in Figure 3 but in this case the fitted potential is 38 mV and the jump distance is 13.7 nm. The surface charge in this case was slightly lower at 1.11×10^{-3} C m^{-2} (1 unit charge/144.2 nm²). Again, jump to contact occurs from a distance much larger than that predicted by DLVO theory (2.4–4.8 nm), suggesting the presence of a large additional attractive force. The average jump distance from 25 force curves was 15.2 nm with a standard deviation of 4.2 nm. The measured force data prior to the jump appears to lie between the constant charge and constant potential limits for both gassed and degassed cases. This charge regulation behavior has been observed previously with mineral surfaces such as mica[50] and amorphous inorganic surfaces such as silica.[51]

Figure 5 compares the distribution of jump distances observed in both gassed and degassed 1.4×10^{-4} M NaCl. The data are plotted as a percentage of the total number of force runs (% frequency) versus the jump distance observed. Only those force profiles with similar fitted

(44) Morris, R. Memtec Pty Ltd., personnal communication, 1993.
(45) Israelachvili, J. N.; Pashley, R. M.; Perez, E.; Tandon, R. K. *Colloids Surf.* **1981**, *2*, 287.
(46) Chan, D. Y. C.; Pashley, R. M.; White, L. R. *J. Colloid Interface Sci.* **1980**, *77*, 283.
(47) Hunter, R. J. *Foundations of Colloid Science*; Clarendon Press: Oxford, 1987; Vol. 1.
(48) Gingell, D.; Parsegian, V. A. *J. Colloid Interface Sci.* **1973**, *44*, 456.
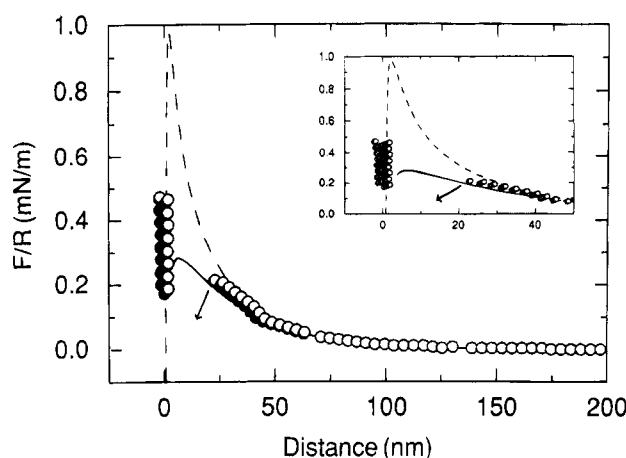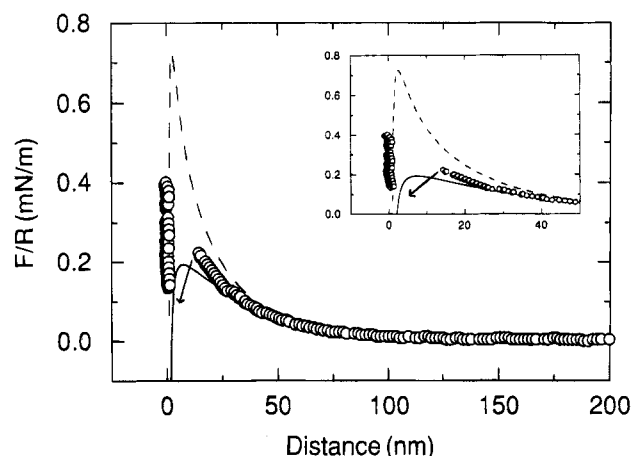(49) Hough, D. B.; White, L. R. *Adv. Colloid Interface Sci.* **1980**, *14*, 3.

(50) Pashley, R. M. *J. Colloid Interface Sci.* **1981**, *83* (2), 531.
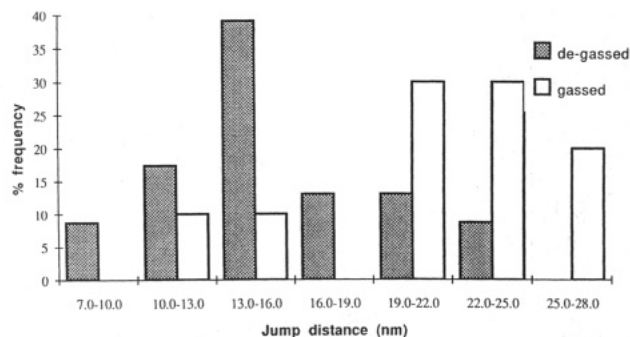(51) Ducker, W. A.; Senden, T. J.; Pashley, R. M. *Langmuir* **1992**, *8*, 1831.

Figure 5. Comparison of jump distances obtained from force profiles in both gassed and degassed 1.4×10^{-4} M NaCl, measured using a weak spring.
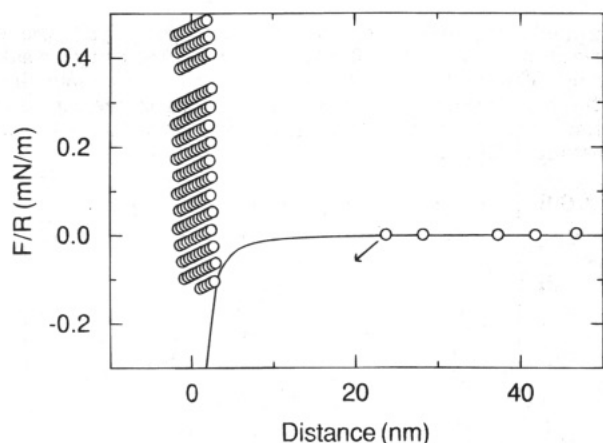

Figure 6. F/R versus separation distance for polypropylene surfaces in gassed 1.0×10^{-2} M NaCl, measured using a weak spring. The solid line is the theoretical prediction based on a van der Waals interaction alone. The unretarded Hamaker constant used in the calculation was 0.64×10^{-20} J.

Figure 7. F/R versus separation distance for polypropylene surfaces in gassed (J, ●; B, ■) and degassed (E, ○; G, □) 1.0×10^{-4} M NaCl, measured using a stiff spring. The solid line is the theoretical prediction based on a van der Waals interaction alone. The unretarded Hamaker constant used in the calculation was 0.64×10^{-20} J.

Figure 8. F/R versus separation distance for polypropylene surfaces in gassed 1×10^{-4} M (J, ●), 1×10^{-2} M (G, □), and 1.0 M (1, ×) NaCl solutions, measured using a stiff spring. The solid line is the theoretical prediction based on van der Waals interaction alone. The unretarded Hamaker constant used in the calculation was 0.64×10^{-20} J.

potentials were compared. It is clear that in gassed NaCl, the jump distance is nearly always larger than for the degassed case, suggesting that the range of the additional attractive force is larger in the case of gassed NaCl.

In 1.0×10^{-2} M NaCl solution, the electrical double layer was completely compressed and the surfaces jumped to an adhesive contact from an average distance of 24 nm (from 10 curves, std dev = 3.5 nm). A typical example, compared to that expected for van der Waals forces alone, is shown in Figure 6. The average jump distance in 1 M NaCl was found to be 22 nm (from 10 curves std dev = 5.0), substantially greater than that expected by van der Waals forces under conditions where the electrostatic double layer force is completely screened by the salt.

The results above, obtained by using a weak spring, do not tell us what the force profile looks like at surface separations below about 15 nm. In fact in 10^{-2} M NaCl, where there is no double layer repulsion, no significant force is observed until about 25 nm where the attraction increases very rapidly to exceed the spring constant and cause an instability. In order to obtain more information in the short range region, it is necessary to use a much stiffer spring even though a loss of sensitivity will result. A comparison of F/R verses separation distance is gassed and degassed 1×10^{-4} M NaCl is presented in Figure 7. These curves were obtained with a spring approximately $200\times$ stiffer than those presented in Figures 3 to 5. The interaction in both cases is purely attractive with a jump to contact as the force gradient exceeds the spring constant. A small double layer repulsion may be present; however it cannot be observed because of the large forces measured and error in selecting zero force. This zero force error
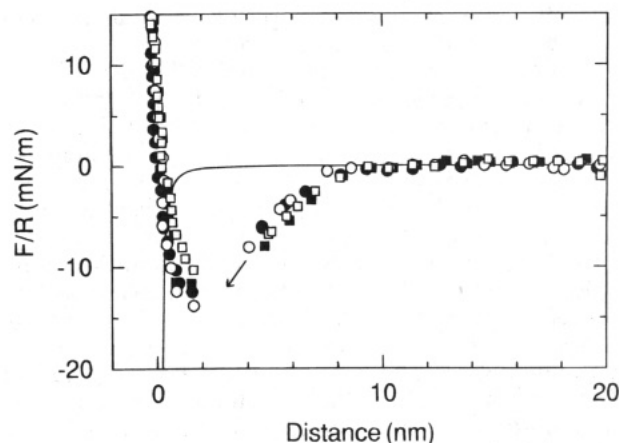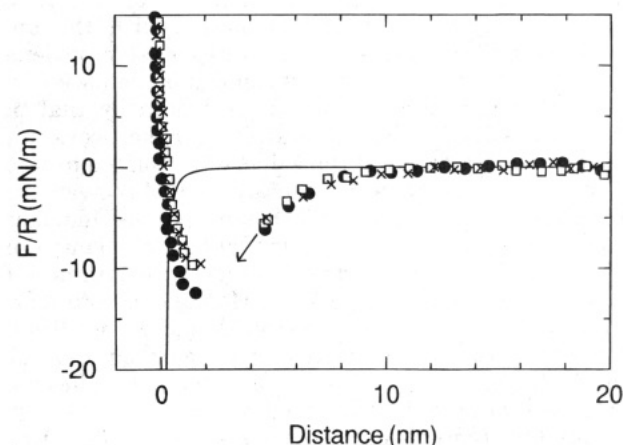
arises because of baseline variations in the AFM instrument. Also masked in this experiment is the long range behavior observed in the previous experiments with a weak spring. Thus there appears to be little difference in the force profile measured between polypropylene surfaces in gassed and degassed NaCl solution below about 10 nm separation, within the sensitivity of the measurement. Figure 8 compares the force profile obtained in gassed 1×10^{-4}, 1×10^{-2}, and 1.0 M NaCl. Again, within the sensitivity of the measurement, there appears to be no obvious relationship between the measured force and the ionic strength of the solution. There is certainly no trend with ionic strength which would suggest an electrostatic mechanism for the hydrophobic interaction.

A very short range repulsion is present in all of the force curves obtained with the stiff spring. This is most likely due to compression of suface asperities. That these polypropylene surfaces are rougher than Langmuir–Blodgett deposited surfactant layers on mica is clear from the AFM image presented in Figure 2. Certainly one would not expect a hydration type repulsion like that observed between mica[50] and silica surfaces[51] to be present on these very hydrophobic polymer surfaces. Similarly, an electrostatic origin can be ruled out also as this repulsion was present even in 1 M NaCl. Further, the
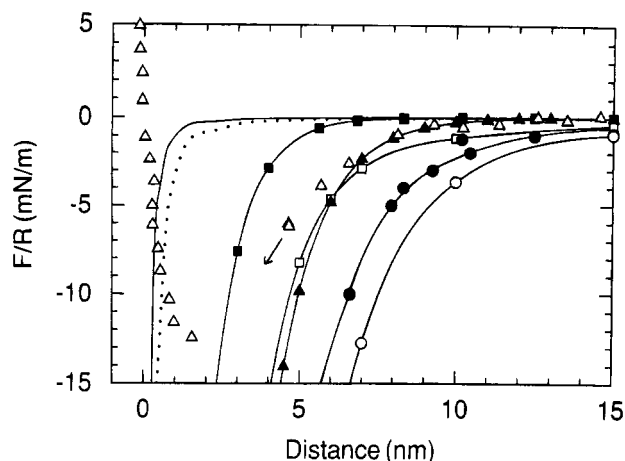
Figure 9. Comparison of the hydrophobic interaction in gassed 1.4×10^{-4} M NaCl, measured in this study (C, $\triangle$), with those measured by other workers: (B, ■) ref 5; (G, □) ref 7; (J, ●) ref 9; (H, ▲) ref 21; (E, O) ref 53. The solid line is the theoretical prediction based on van der Waals interaction for polypropylene alone ($A = 0.64 \times 10^{-20}$), whereas the dotted line is the theoretical prediction based on van der Waals interaction for mica with a thin layer of hydrocarbon ($A = 1.8 \times 10^{-20}$ J).

adhesion of the polypropylene surfaces measured in these experiments was approximately 35 mN m^{-1} and did not appear to be influenced by the ionic strength of the NaCl solution. It is well-known that surface roughness on the order of nanometers can significantly reduce adhesion.[52] The adhesion value measured in this study corresponds to an interfacial energy of approximately 2.8 mJ m^{-2}. This may be compared to other reported values in the range 11 mJ m^{-2} for CTAB surfaces[5] to 35 mJ m^{-2} for LB-coated hydrocarbon surfactants on mica.[9] A similar decompression curve was obtained as the surfaces were pulled apart.

Figure 9 compares the results in gassed NaCl obtained in this study with those obtained between hydrophobic surfaces by other workers.[5,7,9,18,53] The results obtained in this study fall between those obtained previously. Also plotted are the theoretical curves predicted for van der Waals interaction alone. The solid line is calculated for polypropylene, whereas the dotted line is calculated for mica with a thin layer of hydrocarbon.

Discussion

The surfaces used in this study are fundamentally different in nature to the surfactant-coated substrates used in earlier measurements of the hydrophobic interaction. That our results differ in some features from those might help shed some light on the mechanism involved in this long-range interaction, which has remained a mystery since the first measurements in 1981.[3] Before we consider the earlier experiments, let us examine the behavior of polymer surfaces in this and an earlier study.[30]

For both polypropylene and polystyrene surfaces, the hydrophobic interaction apparently extends only up to moderate distances (<30 nm) and appears to be largely unaffected by the addition of electrolytes. The situation for these polymer substrates is complicated by the observation of a residual and significant charge on polypropylene. This charge must arise due to both surface oxidation and, in the aerated solution, specific adsorption of bicarbonate[54] (or some other ion in solution). In both

cases, however, the surfaces are strongly hydrophobic ($\theta_A^{H_2O} = 106°$) and yet exhibit only a moderate range interaction. There is no evidence of a long range tail in the interaction as has been observed by other workers using both silanated and surfaces with LB deposited surfactant layers. The forces observed clearly fit into the range of results obtained previously (see Figure 9) but are closest to those measured between layers of the surfactant dihexadecyldimethylammonium acetate adsorbed from solution onto mica.[21] Also similar in magnitude are those between weakly charged dioctyldecyldimethylammonium bromide layers LB coated onto mica.[7]

An initial conclusion must follow that an attractive interaction between hydrophobic surfaces is quite general and can be detected between pure hydrocarbon surfaces, Langmuir–Blodgett, and adsorbed (equilibrium) layer hydrophobic surfaces. A second conclusion is that the presence of dissolved gas extends the magnitude and range of this interaction. A third conclusion should, perhaps, encompass the observation that the precise nature of the interaction is variable and related to the surface type and method of measurement. This follows from a rationalization of the results published in the literature. In general, forces between surfaces which have been formed from equilibrium adsorption of surfactant onto mica[3-5,21,55,56] are of short range (<10 nm). Forces between surfaces formed from nonequilibrium processes such as LB deposition[8,9,13,16,17,57] and silanation[58-60] are long ranged in nature (100–300 nm). The forces observed in the present study between polymer surfaces may then be described as a moderate ranged interaction (<30 nm). Surface charge density appears to have only a minor, if any, influence.

The novel observation presented here, that dissolved gases play some role, does not appear to offer any immediate resolution of the mechanism. It is not unreasonable that nonpolar (gas molecule) solutes will be adsorbed and hence accumulate in aqueous layers next to a hydrophobic surface.[61] This adsorption will be driven by the release to the bulk state of perturbed water surrounding the solute. However, it is not clear how this surface accumulation might influence the hydrophobic interaction. It is, however, interesting that cavitation by either vapor or dissolved gas (it is not clear which) does occur as two hydrophobic surfaces approach.[8,9,13,21] The problem remains that the accumulation of solute (dissolved gas) will only occur in the region of water already perturbed by the hydrophobic surface and hence it is unclear how this gas could extend the range of the hydrophobic interaction. An induced phase separation has been suggested for vapor cavitation[26,27] and the energies involved must be substantially reduced by the presence of dissolved gas. What is quite clear is that even though the presence of dissolved gas appears to extend the range of the hydrophobic interaction, it appears only to affect the long range tail of the force curve and not the short range strong interaction.

One major difference between these measurements and those obtained previously is the radius of the interacting surfaces. In these experiments, the radius is approxi-

(52) Israelachvili, J. N. *Intermolecular and Surface Forces*; Academic Press: New York, 1985; p 222.

(53) Tsao, Y.-H.; Evans, D. F.; Wennerstrom, H. *Science* **1993**, *262*, 547.

(54) Pashley, R. M.; McGuiggan, P. M.; Ninham, B. W.; Brady, J.; Evans, D. F. *J. Phys. Chem.* **1986**, *90*, 1637.

(55) Kekicheff, P.; Christenson, H. K.; Ninham, B. W. *Colloids Surf.* **1989**, *40*, 31.

(56) Parker, J. L.; Yaminsky, V. V.; Claesson, P. M. *J. Phys. Chem.* **1993**, *97*, 7706.

(57) Herder, P. C. *J. Colloid Interface Sci.* **1990**, *134*, 336.

(58) Parker, J. L.; Cho, D. L.; Claesson, P. M. *J. Phys. Chem.* **1989**, *93*, 6121.

(59) Parker, J. L.; Claesson, P. M. *Langmuir* **1994**, *10*, 635.

(60) Parker, J. L.; Claesson, P. M.; Attard, P. *J. Phys. Chem.*, in press.

(61) Beaglehole, D. *J. Phys. Chem.* **1987**, *91*, 5091.

mately 30 μm while previous measurements have used surfaces with a radius of 1–2 cm. This means that the difference in the area of interaction is roughly 5 orders of magnitude. The fact that a moderate range interaction was measured between the much smaller radius surfaces used in this study lends some support for a nucleation/cavitation mechanism for the long range tail of the hydrophobic interaction. Such an event is statistically much more likely to occur between the much larger radius surfaces used in the SFA. While the interacting surfaces used here are quite smooth (see Figure 2), it is unlikely that they are as smooth as say Langmuir–Blodgett deposited surfactant layers adsorbed onto mica. What effect this roughness may have on the range and magnitude of the measured interaction is unclear.

The observation that the hydrophobic interaction between some surfaces is quite strongly dependent on electrolyte[18] suggests an electrostatic mechanism, which has been considered before.[25] An electrostatic mechanism has the substantial advantage of offering a possible explanation for the long-range (up to 300 nm)[62] nature of the observed forces, which any known surface-induced, solvent structural model must fail to do. Although hydrophobic surfaces must perturb the structure of adjacent water layers, the effect should only extend to a few molecular layers.[20]

However, for the pure polymer surfaces, such as those used in this study and a previous one,[30] neither the short

or long range components of the hydrophobic interaction are substantially effected by the presence of electrolytes. Therefore it is unreasonable to look for an electrostatic mechanism for the hydrophobic interaction observed here. By comparison, this may not be the case for the long range hydrophobic interaction between surfactant-coated surfaces where a significant electrolyte effect is observed.[18] In fact, the observation of only a moderate range hydrophobic interaction in this study may result from the inability of a crystalline polymer, such as polypropylene, to develop regions of different surface charge which might lead to a correlated electrostatic attractive force between the surfaces. Regions of different charge cannot be ruled out for Langmuir–Blodgett deposited films on mica and have been suggested for surfactants adsorbed onto mica from cyclohexane.[53]

Given the variation in both the range and magnitude of the long range hydrophobic interaction reported in the literature, it is not surprising that a theory which can account for all the experimental results obtained so far has not been found. Indeed, the varying degree of attraction observed between hydrophobic surfaces prepared in different ways may in part be due to the presence of more than one mechanism.

(62) Kunihara, K.; Kato, S.; Kunitake, T. *Chem. Lett.* **1990**, 1555.