Depletion Attraction versus Steric Repulsion in a System of Weakly Adsorbing Polymer—Effects of Concentration and Adsorption Conditions

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ABSTRACT: Interaction forces were measured between surfactant-coated mica surfaces in tetradecane containing polyethylene−propylene. Two molecular weights, $M_w = 5800$ and 33 000 g/mol, were studied on two different surfactant layers at 15, 25, and 35 °C. At low polymer concentration, the force curves exhibited two maxima and two minima. On approach, a very weak repulsion at a separation of $D = 6-10R_g$ was followed by an attractive regime down to a minimum at $D \approx R_g$, where R_g is the radius of gyration. At smaller separations we found a second repulsive maximum, followed by a second attractive minimum at a separation of a few polymer segment widths. At the overlap concentration, a similar force profile, but with an additional depletion attraction, was measured under partial adsorption conditions, while equilibrium adsorption gave a monotonic steric repulsion for both M_w. Only monotonic repulsion was measured in tetradecane containing a polyethylene−propylene with an amino end group, which appeared to have bound to the underlying substrate by penetrating through the physisorbed surfactant layer. The effects of time, temperature, and water content were also investigated.

Introduction

The interaction forces between two surfaces across polymer solution depend mainly on whether the polymer is attracted (adsorbed) to or repelled (depleted) from the surfaces and on whether the interaction occurs at "true" or "restricted" thermodynamic equilibrium.[1,2] Theoretically, it has been suggested that at full equilibrium a monotonic attraction should arise between two surfaces being brought together in homopolymer solutions, where the polymer between the surfaces can equilibrate (exchange) with polymer in the bulk solution at all surface separations. This attraction due to bridging or depletion (which will be discussed further below) should exist independently of the solvent quality and of whether the polymer is attracted to or repelled from the surfaces (which can give rise to bridging or depletion attraction, respectively[1,2]) and is expected to extend over the whole interaction distance regime except for the last one or two segment widths in the case of strongly physisorbed chains,[1] where the short range interaction is likely to be oscillatory.

Another equilibrium situation, restricted equilibrium, arises when the adsorbed amount of polymer is kept constant as two surfaces are brought toward each other. The adsorbed polymer remains kinetically trapped between the two approaching surfaces, resulting in a repulsion at small separations due to the unfavorable entropy of confinement.[1,2] The interactions at larger separations may be attractive due to a combination of bridging, depletion, or, in poor solvents, intersegment attraction.[1,3] It has also been suggested that under good solvent conditions restricted equilibrium would give rise to only monotonic repulsion.[2]

In systems containing high concentration of nonadsorbing polymer, the difference in solute concentration in the bulk and between the surfaces at separations smaller than approximately the polymer coil diameter, i.e., when the polymer has been squeezed out from the gap between the surfaces, may give rise to an attractive osmotic force (depletion attraction).[4−13] However, if the polymer coils become initially compressed as the surfaces approach each other, this can give rise to a repulsion (depletion stabilization) at large separations.[10]

Bridging occurs when segments of one polymer chain, already adsorbed to one surface, are able to reach over and adsorb to an opposing surface. This can occur whenever there are adsorption sites available on the other surface,[1] either due to incomplete coverage (low adsorption density) or as sites become exposed during the dynamic adsorption−desorption process. Since the bridging chains could gain conformational entropy if the separation between the surfaces decreased, bridging gives rise to an attractive force. Some recent theoretical work suggests that a weak repulsion due to tail interactions may precede the attractive regime.[14]

Theoretical models for restricted equilibrium interactions assume that the amount of polymer in the gap between two surfaces remains fixed after each incremental approach of the surfaces, i.e., that the confined polymer is allowed to find its equilibrium conformation within the whole volume between the surfaces, instead of belonging to separate, approaching layers. Although experimental results from direct measurements of polymer interactions compare well with modern theories of restricted equilibrium,[1−3,8,10,12,15−17] a number of issues have remained unresolved.

(i) As mentioned above, for interactions between adsorbed polymer layers in a good solvent under restricted equilibrium conditions, some theories predict a monotonic repulsion at all separations,[2] which has been observed experimentally for some systems,[3] while others[1] predict an initial attraction due to bridging before the repulsion closer in, which also has been observed in experiments.[3,18−20]

(ii) While most direct measurements of forces across polymer solutions[3] have been carried out under some

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restricted equilibrium condition, it is not obvious whether equilibration of the confined polymer, initially associated with either surface, has occurred across the gap or not. Under such even more restricted conditions, the range of the repulsive interactions observed at small distances also depends on the approach rate. For example, in systems where the polymer adsorbs to the surfaces, bridging of chains from one surface to the other will give rise to an attraction under restricted equilibrium conditions, but especially at high coverage, any restriction to fully equilibrate across the gap will give rise to a long-ranged steric repulsion.

The question whether an interaction is occurring at full or partial adsorption equilibrium, or at full or partial restricted equilibrium, has been difficult to define as well as to establish during direct force measurements. It is also often difficult to distinguish between attractions due to depletion, bridging, segment−segment, and van der Waals forces, which in some systems can give rise to contributions of similar magnitudes.

(iii) The weakness of the depletion force in systems with nonadsorbing polymers has not allowed for a measurement of the full force law. Theoretically, a monotonically attractive force is expected, having a range of about R_g,[10,12] $2R_g$,[4−7,9,11,13] or $3R_g$,[8] where R_g is the radius of gyration. Since the force is of osmotic origin, it should increase in magnitude with increasing size (excluded volume) and number density of the polymer coils in solution,[4−13] as well as with negative deviations from ideal solution behavior for the polymer (e.g., the polymer coil being more expanded than in an ideal case).

(iv) Experimentally, a maximum in the destabilizing effect of free polymer on surfactant-coated colloid particles has been observed in the semidilute regime, while at high polymer concentration, stabilization was observed.[7,9] The destabilizing effect, which was dependent on the molecular weight and the volume fraction of the polymer, was ascribed to depletion, while the stabilization was explained as being due to strong overlap of polymer coils, giving a homogeneous segment density throughout the medium separating the particles. The theoretical basis[10,13] for this phenomenon has not, however, been fully clarified.

The issues above arise because most experiments have involved high molecular weight polymers, since these are often used to stabilize colloidal dispersions. High molecular weight polymers adsorb very easily to solid surfaces, and even though the adsorption process is highly dynamic, the probability of complete desorption is very low once a few polymer segments along a chain have become attached, even when the adsorption energy is very weak.[2] For such systems, both the times needed for the polymer to reach full adsorption equilibrium and to relax and desorb during a compression−decompression can be very long, usually much longer than the times of the experiments. Since depletion attraction increases both with R_g and with number concentration (which is inversely proportional to the volume occupied by polymer, $1/V_{coil}$, i.e., to $1/R_g^3$), it is also not possible, in practice, to produce a strong depletion force in a high molecular weight system.

This study focuses on low molecular weight polymer that does not interact strongly with the surfaces or with the solvent. We have chosen a pure, saturated hydrocarbon polymer, polyethylene−propylene (PEP); a hydrocarbon solvent, *n*-tetradecane, which is a good solvent for PEP; and hydrocarbon surfaces (adsorbed surfactant monolayers) that expose $-CH_2-$ and CH_3 groups. Since PEP is not expected to adsorb on hydrocarbon surfaces from this solvent, a purely attractive depletion force is expected for this system. Previous light-scattering experiments on surfactant-coated particles in decane containing PEP have showed an attractive interaction linearly proportional to the concentration of PEP in the solution and of a magnitude as expected for depletion forces.[21]

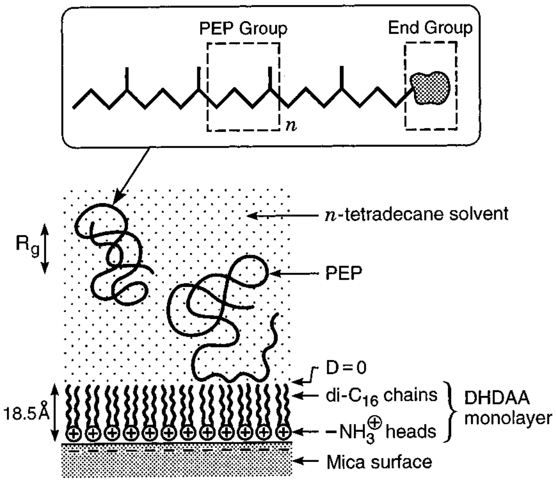

Figure 1. (Top) Molecular structure of the polyethylene−propylene (PEP) chain, with or without a terminal amino end group. The experimental results presented in Figures 2−7 are for unfunctionalized PEP, and the results in Figure 8 for functionalized PEP-amine. (Bottom) The investigated system of dissolved unfunctionalized polymer in the vicinity of one of the confining surfactant surfaces.

The times to reach adsorption and interaction equilibrium in this system are expected to be short, since the polymer chains are relatively short (~80−500 segments) and the binding energies are small. The interactions should therefore be accessible to direct force measurements with the surface forces apparatus technique. This type of system is also of practical interest: many lubricating oils and oil-based paints consist of low molecular weight polymers dissolved in hydrocarbon solvents containing surfactant-coated colloidal particles. In such systems, the affinities of the polymer, solvent, and surface groups for each other are often similar. The colloidal properties (stability, rheology, etc.) of such systems is thus delicately balanced and can go in different directions when one of the properties or experimental conditions is slightly changed, for example, the solvent quality, temperature, polymer backbone structure, molecular weight and concentration, surfactant type and colloid size.

Materials and Methods

The polymers used were two samples of unfunctionalized PEP: $-[CH_2CH(CH_3)CH_2CH_2]_n-$, with $M_w = 5800$ and 33 000 g/mol, synthesized by hydrogenating monodisperse, linear 1,4-polyisoprene prepared according to the anionic polymerization scheme described in ref 22. A sample of $M_w = 30\ 000$ g/mol PEP with one cationic tertiary amino end group, $N(CH_3)_2^+$, was also prepared according to the procedure in ref 23. PEP is an amorphous polymer with a T_g (glass transition temperature) of ca. −60 °C, and at room temperature these polymers are viscous liquids. The samples were kept in a refrigerator when not in use.

The structure of the polymer and the surface−solution configuration in a typical experiment is shown schematically in Figure 1. (The polyethylene−propylene backbone is in reality a mixture of *trans* and *gauche* configurations.) The radius of gyration can be determined from the relation $R_g = a(n/6)^{0.5}$, where n is the number of segments and a the segment length.[24] For the polymers in this study, $n \approx 83$ and 471, respectively, and $a = 4.5-5$ Å. In a good solvent, the expected "expanded" radius of gyration is larger by a factor $(n/6)^{0.6}/(n/6)^{0.5} = (n/6)^{0.1}$.[25] This equation is, however, strictly applicable only to polymers with large n, and it is known that short-chained polymers, as we have here, are often more expanded than the theoretical value. The calculated expanded values of the radius of gyration in a good solvent are slightly smaller than the experimentally determined values of 30 Å and 81 Å for $M_w = 5800$ and 33 000 g/mol, respectively.[26] The measured values will be used in any calculations involving R_g.

The solvent was n-tetradecane, $C_{14}H_{30}$ (Fisher, 99.9%), which was distilled under nitrogen immediately before use.

One of the surfactants used was dihexadecyldimethylammonium acetate, $DHDA^+Ac^-$, which was ion exchanged from the bromide, $DHDA^+Br^-$ (obtained from Sogo Pharmaceutical Co., Japan), according to the procedure in ref 27. $DHDA^+$ is a double-chained C_{16} surfactant with a cationic $N(CH_3)_2^+$ head group that attaches strongly to the anionic surface of mica.[28] The other surfactant was L-α-dipalmitoylphosphatidylethanolamine, DPPE (Avanti), a zwitterionic double-chained lipid that also forms a strongly bound monolayer on mica.[28] The monolayer depositions were done on previously back-silvered mica sheets, glued on silica disks with a thermosetting epoxy glue (Epon 1004F, Shell). Monolayers of $DHDA^+Ac^-$, (hereafter called DHDAA) were adsorbed by self-assembly from 7×10^{-5} M aqueous solution at room temperature, giving a monolayer which is in the fluid-to-amorphous state with a mean molecular area of 75 Å^2 and a thickness of 18.5 Å.[28] DPPE monolayers were prepared by Langmuir–Blodgett deposition at a surface pressure of 35–38 mN/m at 25 °C, giving a layer which is solid–crystalline at room temperature, with a mean thickness of 25 Å and a molecular area of 42 Å^2.[29]

PEP was dissolved in distilled n-tetradecane at concentrations of 8.9% (by weight) of $M_w = 5800$ g/mol and 3.46% of $M_w = 33\,000$ g/mol. These concentrations give number densities of $\rho = 7.1 \times 10^{24}$ m^{-3} for $M_w = 5800$ g/mol (which is 20% below the overlap concentration, c^*, based on the experimentally determined R_g above) and $\rho = 4.8 \times 10^{23}$ m^{-3} for $M_w = 33\,000$ g/mol (which is 10% above the c^* for this molecular weight). These concentrations were chosen to produce the maximum depletion force without complicating the interaction by entanglements, which would increase the viscosity (affecting the accuracy of the force measurement) or, at small separations, lead to slower relaxations in the trapped polymer layers. Solutions of functionalized PEP ($M_w = 30\,000$ g/mol) at a concentration of 3.4 wt % and lower concentrations, $0.01c^*$ and $0.1c^*$, of the unfunctionalized PEPs above were also prepared by weighing.

The interaction forces were measured by means of a standard Mark III surface forces apparatus (SFA 3), equipped with a low volume chamber (total volume ca. 25 mL). A more detailed account of the experimental method is given elsewhere.[30,31] The spring constant of the force-measuring spring was chosen in the range $k = 1.2-1.5 \times 10^5$ mN/m. In a typical experiment, the surfactant-coated surfaces were first installed in the apparatus. The chamber was then closed and sealed, and its atmosphere purged with dry nitrogen gas overnight. The contact calibration of the FECO fringes was done at monolayer–monolayer contact in dry nitrogen, which represents zero distance ($D = 0$) in the force curves shown. Polymer solution was added by filling the chamber with solution for the lower concentrations or, close to the overlap concentration, by injecting a droplet (ca. 0.25 mL) of the concentrated solution between the surfaces through a flush-cleaned Millipore Acrodisc PTFE filter (pore size 0.2 μm) to remove possible particles. To assure that no contamination was introduced by the filtering, control experiments were done in pure tetradecane injected through a filter, showing interaction forces similar to results in literature for similar systems.[32,33] In addition, some polymer solutions were not filtered, but ultracentrifuged at ~20 000 rpm for 1.5–2 h to remove particles. The results for the filtered solutions were identical to the ones for the unfiltered and centrifuged solutions.

The interactions between the surfaces were measured at 25 °C in solutions close to the overlap concentration, c^*, and at two additional concentrations, $0.01c^*$ and $0.1c^*$. Experiments were done both by increasing and decreasing the concentration (by adding polymer solution or solvent, respectively) during the experiment and at temperatures of 15 and 35 °C. At the lower concentrations, the polymer was allowed to adsorb from solution for 15 h with the surfaces kept at a separation of 1.5–2 mm. At the overlap concentration, the interaction forces were found to be dependent on the adsorption time and conditions: in the experiments presented as examples of "partial adsorption" conditions, the surfaces were brought together to a separation of 2 μm or closer after only 1–2 h of equilibrating (after injecting the solution), while for the "equilibrium adsorption", the surfaces were kept separated to 1.5–2 mm to let the polymer adsorb for at least 5 h for $M_w = 5800$ g/mol and overnight for $M_w = 33\,000$ g/mol.

Results

Forces between DHDAA Monolayers across Pure Tetradecane (No Polymer). The forces between various surfactant-coated surfaces across different hydrocarbon liquids, including tetradecane, but containing no polymer, have been measured previously.[32,33] The results were later shown to be quantitatively well-correlated with light-scattering data obtained on an analogous colloidal system[34] and also qualitatively consistent with earlier stability studies of colloidal particles in hydrocarbon solvents.[35,36] For amorphous monolayers, these forces typically exhibit a short-ranged attractive regime extending from a separation of ~30 Å down to ~10–15 Å, at which separation there is a weak adhesive minimum of depth $F/R = -(0.5-1.5)$ mN/m,[32,33] where F is the force and $R \approx 1$ cm is the radius of the surfaces. At smaller separations (2–4 times the solvent chain diameter, which for unbranched alkanes is ca. 4 Å), there is a "hard-wall" repulsion. The measured force curve for DHDAA monolayers across tetradecane is shown as an inset in Figure 2a.

The measured adhesion between DHDAA monolayers, $F/R \approx -1$ mN/m at $D \approx 10-15$ Å in pure tetradecane, is significantly more attractive than can be accounted for by the van der Waals–Lifshitz attraction between the monolayer-covered mica surfaces (calculated for a five-layer system[37] of mica/surfactant/tetradecane/surfactant/mica), which at a monolayer–monolayer separation of $D \approx 15$ Å would be approximately $F/R = -0.25$ mN/m. It was previously suggested[36] that an additional bridging attraction operates between surfaces across liquids composed of short-chain molecules. Computer simulations have shown that different regions of chain molecules have different affinities for surfaces and that certain groups, especially the end groups of alkanes[38] or short-chained polymers,[39,40] are found close to inert surfaces. This occurs because it is entropically more favorable to have an end group at the surface, compared to having a segment of the chain (with its neighboring segments) close to the surface. The end groups therefore can act as effective functional groups that may weakly bind to and bridge two surfaces below a separation corresponding to the chain length. The resulting equilibrium bridging attraction could thus be responsible for the additional short-range ($D < 25$ Å) monotonic attraction that has been repeatedly measured between surfactant-coated surfaces in liquid alkanes.[32,33] Furthermore, such an adsorption-dependent bridging mechanism would also be consistent with the shorter-ranged "steric" repulsion at $D < 10$ Å, corresponding to about one effectively "bound" chain on each surface. This end-effect in alkanes would be expected to vanish as the

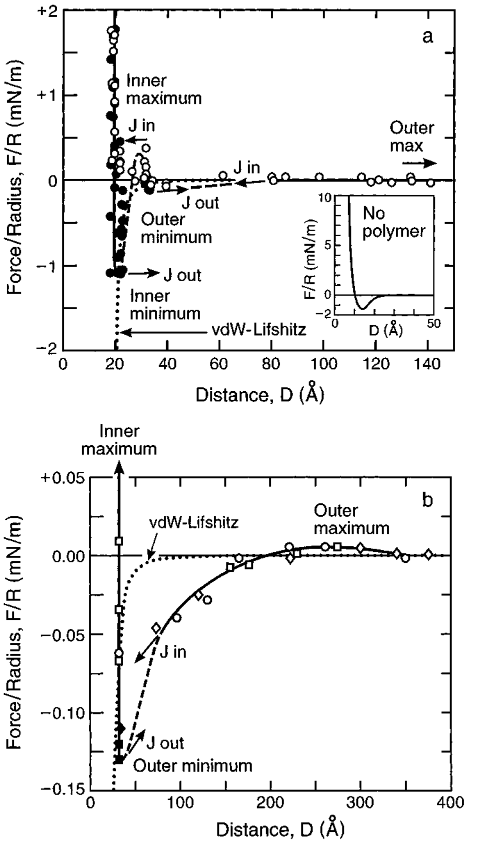

Figure 2. (a) Interactions between DHDAA monolayers in 0.1 and 1.0 wt % PEP with $M_w = 5800$ g/mol in tetradecane at 25 °C. Equilibration time 15 h. Open symbols denote approach and filled symbols separation of the surfaces in this and all following figures. $D = 0$ is at monolayer−monolayer contact, as indicated in Figure 1. A repulsive maximum is found at $D = 32−35$ Å, and a hard-wall repulsion at $D = 19$ Å. The van der Waals−Lifshitz attraction for a five-layer system consisting of mica/[18.5 Å DHDAA + 9 Å PEP]/tetradecane/[9 Å PEP + 18.5 Å DHDAA]/mica is shown as a dotted line. (Inset) the interactions between DHDAA monolayers in pure tetradecane (no polymer). (b) The small outer maximum at $D = 200−300$ Å for $M_w = 5800$ g/mol, shown together with the outer minimum and van der Waals interaction indicated in part a. Different symbols represent different force runs: open symbols denote approaching surfaces, filled symbols denote separating surfaces.

molecular weight increases (because fewer ends would be present per interacting area), but a similar end-induced adsorption mechanism may still occur for polymers with branches or effective “end groups” along the chain.

On a more close-packed monolayer such as DPPE, the hydrocarbon solvent molecules order in a layered structure and the forces are found to be oscillatory with a period corresponding to the width (~4 Å) of the molecules[32] (shown in the inset in Figure 7).

Force Curve for Unfunctionalized PEP at Low Concentration. Figure 2 shows the forces measured between two DHDAA-coated mica surfaces in tetradecane containing PEP of $M_w = 5800$ g/mol at two concentrations, $0.01c^*$ and $0.1c^*$ (0.1 and 1 wt %, respectively), at 25 °C. The forces, which were identical for these two concentrations, were measured after allowing the surfaces to equilibrate with the polymer solution at a separation of 1.5−2 mm for 15 h. The force is not monotonically attractive, as might be expected for a pure depletion force; instead, the force curve is characterized by two maxima, two minima, and a final short-range repulsion at small separations, indicating that the polymer adsorbs on the surfactant surface. The weak outer maximum is shown separately in Figure 2b. The interactions in the absence of polymer are shown in the inset in Figure 2a. The van der Waals−Lifshitz attraction, calculated for a five-layer system, assuming an average dielectric constant and refractive index for the surfactant monolayer and the compressed adsorbed polymer layer, is indicated by the dotted line in Figure 2.

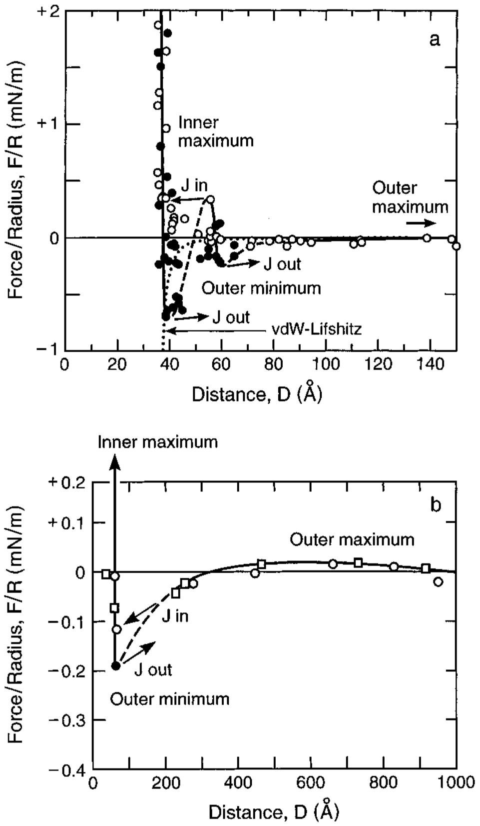

Figure 3. (a) Effects of molecular weight: interactions between DHDAA monolayers in 0.03 wt % PEP with $M_w = 33\,000$ g/mol in tetradecane at 25 °C. The van der Waals−Lifshitz attraction, shown as a dotted line, was calculated for a five-layer system similarly to the one in Figure 2, but with a PEP layer thickness of 17 Å on each monolayer surface. (b) The small outer maximum at $D = 400−800$ Å for $M_w = 33\,000$ g/mol, shown together with the outer minimum indicated in part a. Different symbols represent different force runs: open symbols denote approaching surfaces, filled symbols denote separating surfaces.

The force profile of Figure 2 was found to be typical for the forces measured at low concentrations and also for the higher molecular weight (33 000 g/mol) PEP at a concentration of $0.01c^*$, shown in Figure 3. This force curve thus appears to be generic for this system.

Effect of Molecular Weight. Figure 3 shows the forces measured across a solution containing the higher molecular weight PEP ($M_w = 33\,000$ g/mol) after similar equilibration times and conditions as for the lower M_w in Figure 2. An adsorbed polymer with higher molecular weight is expected to extend further into the solution, and with the higher M_w, the range of the outer maximum and long-range attraction are both about 2−3 times farther out than with the lower M_w, which scales with their R_g. In addition, the positions of the inner and outer minima for the higher molecular weight are found at slightly larger surface separations of 40 and 60 Å, respectively. The magnitude of the adhesive force in these minima are similar to those measured for the

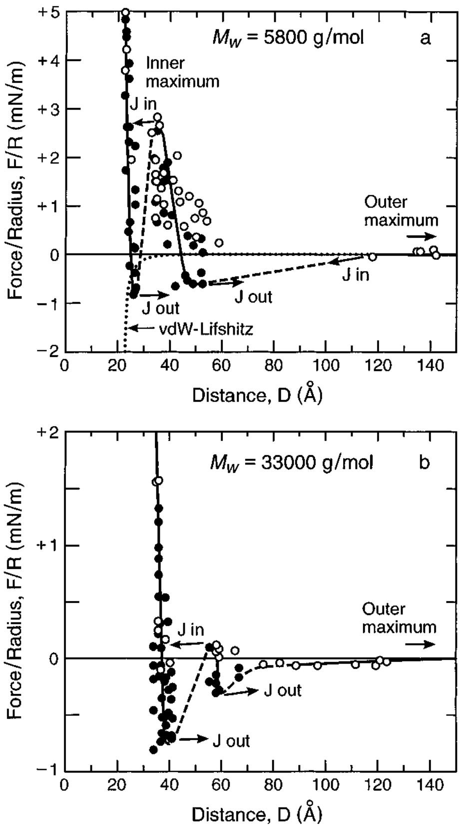

Figure 4. Interactions at polymer concentrations close to the overlap concentration, c^*: if the surfaces were brought to a separation of < 2 μm within 1−2 h after injecting the solution (see text), and kept at this or closer separation, the forces measured were reproducible for several days. The interactions at true adsorption equilibrium are, however, different (shown in Figure 5). (a) Interactions in 8.9 wt % PEP, M_w = 5800 g/mol, showing an increased adhesion at the outer minimum of $\Delta F/R$ = −0.5 mN/m compared to Figure 2a. The inner maximum, the position of which depended on the approach rate (see text), increased relative to the situation at low concentration, while the hard-wall separation at ~22 Å and the outer maximum (not shown) remain similar. The van der Waals−Lifshitz interaction, shown as a dotted line, was calculated as in Figure 2, but with a polymer layer thickness of 11 Å. (b) Forces between M_w = 33 000 g/mol PEP layers (adsorbed at low concentration, 0.03 wt %) after the concentration was increased to 3.46 wt %. The outer maximum and the hard-wall thickness were not significantly altered. The inner maximum decreased slightly. The difference in adhesion at $D \approx 60$ Å compared to Figure 3a was $\Delta F/R$ = −0.1 mN/m. Open symbols denote approaching surfaces, filled symbols denote separating surfaces.

lower molecular weight. The inner force maximum is, however, lower than for the lower M_w. Since the "hard-wall" repulsion occurs at a larger separation than in the case of M_w = 5800 g/mol, a larger amount of polymer is presumed to adsorb at higher M_w.

Effect of Concentration. At PEP concentrations close to c^* for each molecular weight, the interactions observed (Figure 4) depended strongly on the adsorption time and surface separation during adsorption. If the surfaces are brought in to a separation closer than a few microns within 1−2 h after the concentrated solution was injected between the surfaces and kept at a small separation throughout the experiment, there is little difference in the structure or thickness of the adsorbed layer compared to the situation at low concentrations for the lower molecular weight (shown in Figure 2a), except that a stronger attraction/adhesion is observed at the outer minimum at $D \approx R_g$ (Figure 4a). The inner maximum is also higher, but the magnitude of the force at the inner maximum was dependent on the approach rate and varied between the values shown for the low concentration in Figure 2a and the maximum value shown in Figure 3a. The effects of approach rate are discussed further below.

For the higher molecular weight, a similar effect of concentration on the outer minimum was observed if the polymer layer was first adsorbed at low concentration (as in Figure 3) and the solution concentration then increased to c^*, as shown in Figure 4b. The change in magnitude of the adhesion was, however, smaller than for the lower molecular weight. The outer maxima shown in Figures 2b and 3b remained the same at higher concentration.

It was possible to recover the interactions at low polymer concentrations, shown in Figures 2 and 3, by diluting the concentrated solution.

If the adsorption occurred from the high molecular weight PEP solution directly, without any previous adsorption at low concentration, the amount adsorbed within a few hours was *smaller* than in Figure 4b, and no inner maximum was observed. Instead, the surfaces jumped in from 100 Å to hard-wall contact at 20 Å. However, if these surfaces were then left well-separated overnight, the adsorbed amount increased and the hard-wall moved out to $D \approx 32$ Å, which is similar to the thickness adsorbed at low concentration. No inner minimum or inner maximum was observed. After 2−5 h of adsorption onto surfaces at a separation of 1.5−2 mm, the adhesion at D = 20 Å was −1.2 mN/m, and after additional adsorption overnight, the adhesion at the new hard-wall separation, D = 32 Å, was −0.9 mN/m. The adsorbed amount and conformation of the higher molecular weight PEP appears to thus depend on the adsorption time, but it may also be affected by compression during a force measurement. No such differences in thickness with time were observed with the lower molecular weight polymer, which adsorbed within 10−15 min (shorter times were not investigated) to give interactions identical to the ones shown in Figure 4a and which did not change over several days as long as the surfaces were kept close.

If the surfaces were kept at a large separation (1.5−2 mm) during the adsorption from c^* solution, the conformation of the adsorbed polymer was different, and only a monotonic, steric repulsion starting at a separation of ca. 300 Å was observed for both molecular weights (Figure 5). The repulsive force was proportional to $D^{-1.75}$ for 50 Å < D < 300 Å. Theoretically, the force between two layers of randomly adsorbed homopolymer is expected to scale as D^{-2}.[2] The amount of adsorbed polymer (estimated by comparing the thicknesses of the layers at the hard-wall repulsion) is higher than for adsorption at low concentration (Figures 2 and 3) or at partial adsorption conditions (Figure 4). The time needed for this adsorption to reach equilibrium at large separations was less than 5 h for the lower M_w and a few days for the higher. In contrast to the situation at partial adsorption (Figure 4), the interactions at the low concentrations in Figures 2 and 3 could *not* be recovered once a layer with this structure had adsorbed; instead, the steric repulsion in Figure 5 remained upon dilution.

Effects of Time and Compression. Given the likelihood that nonequilibrium or restricted equilibrium processes may be occurring in this system, we studied the effects of approach rate and equilibration time on

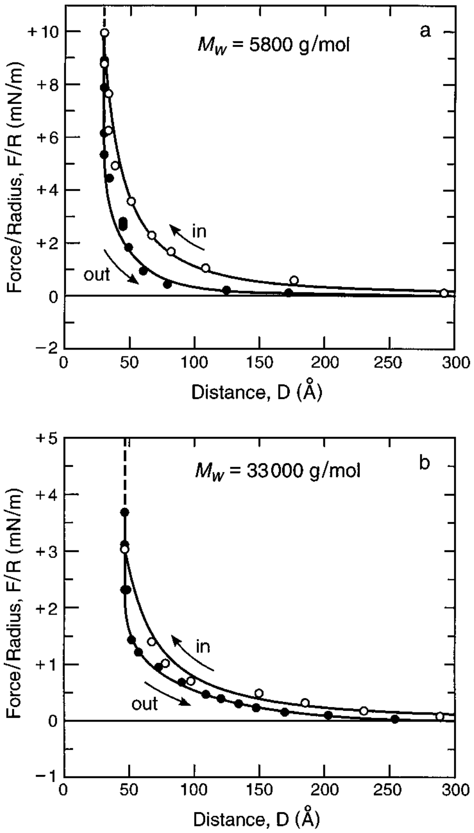

Figure 5. Forces measured at equilibrium adsorption of PEP at concentrations close to c^* (as in Figure 4), showing a monotonic repulsion on approach and separation. The curve through the open symbols (repulsion on approach) was obtained by fitting $F/R = aD^b$, where a and b are constants, while the curve through the filled symbols (separation) is drawn as a guide only. $b = -1.75$ for both molecular weights (theoretically[2] expected, $b = -2$). (a) $M_w = 5800$ g/mol and (b) $M_w = 33\,000$ g/mol.

different regions of the force curves. Figure 6 is a schematic representation of the findings.

For both M_w, the forces at the outermost maxima at $6-10R_g$ (point A in Figure 6) appeared to be insensitive to the approach rates used to measure them. In addition, they were also independent of the concentration and of the number of previous compressions.

The range of onset of the attraction closer in was not dependent on the rate of approach, nor were the times needed for the jumps in ("J in" in Figures 2−4) sensitive to the time spent at a larger separation before the approach or to the time in contact during the previous compression. The jumps in from the outer maximum to the repulsive wall at the outer minimum and the jumps out from both minima in 8.9 wt % PEP required ca. 30 s, while the same jumps at lower concentrations took only ~5 s. On compression, the jumps in from the highest points on the inner maxima to the hard-walls occurred within less than 1 s at all concentrations and M_w.

It is possible that the outer minimum (at $D = 30-35$ Å for the lower M_w and 55−60 Å for the higher) is not at true equilibrium but merely reflects a transient state of collapsed coils which become kinetically trapped between the two surfaces immediately after they have been pulled together after a jump in. Thus, the *inner* minimum, which is deeper, would represent the lower energy configuration of the coils between the two surfaces after they have been allowed to relax and reorder from their less favorable, intermediate state in the outer minimum. To test this quantitatively, time-dependent force measurements were carried out in two different ways: first, the adhesion forces were measured after the surfaces were kept in adhesive contact in either of the minima for different time periods; second, the adhesion forces were measured after different times after a separation.

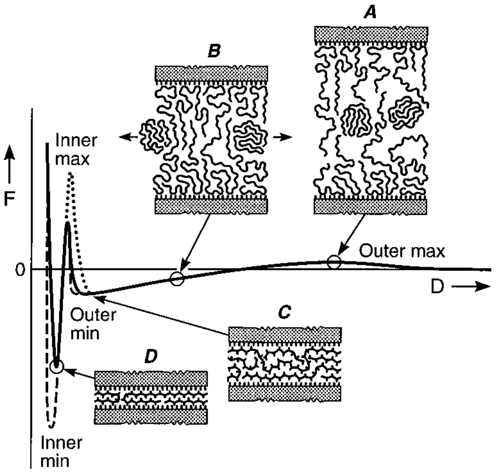

Figure 6. Schematic figure of the effects of compression rate and time in contact on different regimes of the force curve: The outer maximum (A) at $D \approx 6-10R_g$ and the attractive regime (B) were not affected by the rate of compression or time in contact. The outer minimum at $D \approx R_g$ (at C) and the repulsive force barrier ("inner maximum") were found at slightly larger separations (dotted line) when the approach rate was increased from ~0.1 Å/s (solid line) to ~0.5 Å/s. At the faster rate the inner maximum was also ~0.2−0.5 mN/m larger. The "outer minimum" at C moved ~5 Å toward smaller separations during 10 min or more in contact (dashed line), without any significant increase in adhesion. The surface separation at the inner minimum (D) (separation from which the jump out occurred) decreased by 2−3 Å as a result of strong compression to $F/R \approx 20-50$ mN/m, as well as after ca. 30 min or more in contact at the hard-wall separation at $F/R \approx 1-3$ mN/m. In both cases, the adhesion in the inner minimum increased by 2−5 mN/m (dashed line). We attribute these increased adhesions to a better ordering of the confined polymer. (The thickness of the monolayer is not drawn to scale with the width of the polymer).

The surface separation at the outer minimum (C in Figure 6) decreased somewhat with the time the surfaces were left at this minimum, but the magnitude of the attraction was not affected by the time in contact at any polymer concentration (dashed line). The magnitude and position of the inner force maximum, i.e., the force barrier that had to be overcome to take the surfaces from the outer to the inner minimum, were, however, highly dependent on the approach rate. For example, a 1 mN/m higher barrier, shifted by ~5 Å to larger separation, was measured during a fast approach (dotted line) compared to a slow approach. The inner minimum (at D) became deeper with increasing time in contact and also, independently, with increasing applied load for the same time in contact, as indicated by a dashed line in Figure 6. In both cases, the increase in adhesion (2−3 mN/m) was accompanied by a slight decrease in separation (2−5 Å) at the jump out. The measured adhesion was still consistent with the calculated van der Waals attraction at the new (smaller) separation and is thus probably due to an increased flattening and/or ordering of the confined layer.

Adhesion measurements were also done at different temperatures. The results showed that while the time to reach a steady state adhesion value decreased as the temperature increased, there was no evidence that the two minima were tending to coalesce into one with time (up to 5 h, and in a few cases the surfaces were left in contact overnight). Similar results were obtained with the higher molecular weight PEP. The results indicate that if the trapped coils are indeed in a nonequilibrium configuration, they cannot easily change as long a they remain confined by the close proximity of the two adhering surfaces. Finally, the force curve with an inner maximum (i.e., two minima) is also immediately recovered after a separation from the inner minimum, regardless of the previous compression or time in contact. However, as stated, the magnitude of the force barrier between these two states does depend on the compression rate.

Effects of Temperature. In addition to the experiments presented, which were all done at 25 °C, experiments were also done at 15 and 35 °C with both molecular weights. These small changes in temperature had no effect on the overall shapes of the force profiles or on the magnitudes of the forces measured. However, the time for the adhesive *inner* minimum to reach its maximum equilibrium adhesion value (a 2−3 mN/m larger adhesion than in Figures 2−4) decreased as the incubation temperature was increased, so the maximum adhesion was reached after a contact time of 5 min at 35 °C compared to 30 min at 25 °C. No effect of temperature on the magnitudes of the outer maxima and outer minima was seen at any concentration. The effects of temperature on the size of the polymer coil (R_g) are negligible in this narrow range of temperatures,[26] but in their dried state, the DHDAA monolayers are known to be amorphous at 25 °C and liquidlike at 35 °C,[41] and there could possibly be an effect of temperature in this range on the monolayers also in an inert liquid, even though no effect in range or adhesion was detected in our experiment.

Effects of Surfactant Monolayer. Figure 7 shows the effect of replacing the loose-packed, amorphous DHDAA monolayers by close-packed, crystalline monolayers of DPPE. The rigid DPPE layers have little or no surface fluctuations and no openings for the penetration of solvent or polymer molecules, and the forces in tetradecane in the absence of polymer are of shorter range and oscillatory,[32,33] as shown in the inset in Figure 7. The effect of DPPE on the forces in 1 wt % PEP solution (M_w = 5000 g/mol) was to shift the whole force curve toward smaller distances and magnify the extrema, i.e., increase the height of the inner maximum and the depth of the adhesive inner minimum (Figure 7). The adhesion in the outer minimum was similar to the adhesion measured for the same conditions in the DHDAA system (Figure 2). At small separations (<30 Å) the force profile appears to be approaching the oscillatory profile expected for rigid hydrocarbon surfaces interacting across pure hydrocarbon liquids.[32,33] The shorter range with DPPE than with DHDAA monolayers is indicative of less solvent and polymer penetration into the DPPE monolayers and less thermal fluctuations of the DPPE−solution interface.

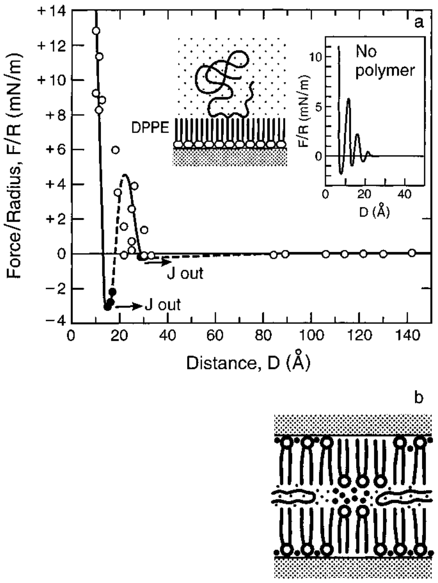

Figure 7. (a) Interactions between close-packed crystalline DPPE monolayers across 1 wt % M_w = 5000 g/mol PEP in dry tetradecane at 25 °C. The force curve is shifted to smaller separations, and the magnitude of the inner maximum and minimum are larger than for the corresponding experiment with loose-packed amorphous DHDAA monolayers. The outer maximum and minimum are similar to the results for DHDAA. The inset shows the oscillatory interactions between DPPE layers in pure tetradecane. (b) Schematic figure of the formation of capillary bridges of water (the water molecules are shown as larger black dots) at the hydrophilic head groups of overturned DPPE molecules in tetradecane containing PEP polymer and trace amounts of water.

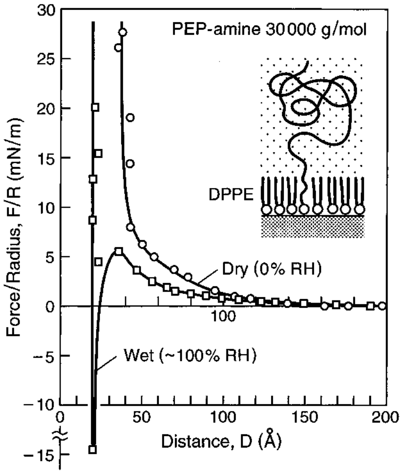

Figure 8. Forces between DPPE monolayers in tetradecane containing 3.4 wt % end-functionalized PEP (PEP-amine, M_w = 30 000 g/mol). The interaction in dry solvent is a monotonic, exponentially decaying repulsion. In tetradecane containing water, capillary condensation causes strong attraction at small separations.

Interactions with End-Adsorbed PEP. Figure 8 shows the force curve between two DPPE-coated surfaces in tetradecane containing 3.4 wt % PEP-amine (M_w = 30 000 g/mol) at 25 °C. No attraction was measured in this system under dry solvent conditions (relative humidity = 0). The interaction was purely repulsive with a shorter range ($\sim 2R_g$) compared to the forces at equilibrium adsorption of unfunctionalized PEP with a M_w of 33 000 g/mol.

The purely monotonic repulsion is consistent with previous light scattering studies of surfactant-coated colloidal particles in decane, where experiments with unfunctionalized PEP showed depletion attraction,[21] while amine-functionalized PEP rendered the colloid stable to aggregation.[42,43] Both these and our results suggest that the PEP-amine adsorbs strongly to the surfaces, so any bridging or depletion attraction is overwhelmed by the steric repulsion, as expected theoretically for end-adsorbing polymer at high concentrations in good solvents.[25,44–46] For the PEP-amine, the force curve in Figure 8 has an exponential shape for 50 Å < D < 200 Å, as expected for the interactions between end-adsorbed polymer at low adsorption densities.[44,45] Theoretically, the decay length is expected to be R_g,[45] but in the PEP-amine system we found that the decay length was 30−40 Å or about $^1/_2R_g$, that is, the force decayed more rapidly than expected. At high adsorption density, the force is expected to be proportional to $1/D^{5/3}$.[25,46] The adsorption density of PEP-amine is not known for our system, but we found that the magnitude of the force measured corresponded more closely to that expected at high adsorption density,[25,46] even though the shape of the force curve was found to be exponential.

It is most likely that the attachment occurs via the positively charged amine group to the negatively charged mica through the surfactant monolayer, as illustrated in the inset in Figure 8. To achieve this, exchange would have to occur with some of the surfactant molecules. We note that even solid, crystalline physisorbed monolayers such as DPPE are known to have sufficient mobility to partially overturn ("flip-flop") over time periods of minutes.[29] Chemisorbed monolayers would not be expected to undergo such changes and thus behave differently.

Effects of Small Amounts of Water in the Solution. In previous studies of monolayer-coated surfaces in oils, it was found that even small amounts of water or polar components such as alcohols in the oils can have a significant effect on the interactions, usually increasing the strength of the short-range adhesion forces.[29,32,34] This was also found to occur in the PEP system. In tetradecane which was saturated with water (∼100 ppm) the short-range adhesion force in the inner minimum between two DPPE-coated surfaces across 1 wt % unfunctionalized PEP of $M_w = 5000$ g/mol solution increased by a factor of 3, while the longer-ranged part of the force (beyond 30 Å) was unaffected. This is qualitatively similar to the effect of water on the interactions between monolayer-covered surfaces in various liquid alkanes.[29] The enhanced short-ranged attraction is probably due to the overturning of the surfactant molecules, which renders the surfaces locally hydrophilic, thereby allowing water molecules to condense around them and form adhesive capillary bridges, as illustrated in Figure 7b.

The effect of water on the interactions in the functionalized PEP-amine system is indicated in Figure 8. When water is introduced into the tetradecane solution, the long-ranged interaction measured is not significantly different, but the short-ranged force becomes strongly attractive, with a similar attraction as the unfunctionalized PEP in a water-saturated solvent.

Discussion

The results show that even a system consisting of inert surfaces immersed in an inert solvent containing an inert polymer may exhibit very complex interaction forces. The system we have studied is not expected to exhibit any strong surface−surface interactions other than a weak depletion attraction similar to the light-scattering results of Tong et al.,[21] obtained for surfactant-covered colloidal calcium carbonate particles (R = 50 Å) in decane containing 1.5−3% PEP with M_w = 26 000 g/mol.

The force curves reveal that PEP adsorbs to surfactant-coated surfaces at all concentrations, but the system also exhibits a relatively long-ranged attraction which is significantly affected by a high concentration of polymer, especially for low molecular weights and after short adsorption times. At low concentrations, the complex force curve appears to represent restricted equilibrium interactions at adsorption equilibrium, at least during the time of the experiment (1 week). The development of a monotonic steric repulsion at high concentration and longer adsorption times (Figure 5) show that the similar, complex shape of the force curve in Figure 4 in that case represents a nonequilibrium adsorption state. The interactions at this partial adsorption were, however, stable over several days, so long as the surfaces were kept at a small separation.

Polymer Adsorption and Adhesion to the Monolayer. The assumption that ethylene−propylene segments are not attracted to each other in tetradecane does not, however, preclude that the PEP molecule can be attracted to a hydrocarbon *surface*. As discussed earlier, it has been suggested[38−40] that in polymer melts or short-chain hydrocarbon liquids, the entropic constraints of chain confinement at a surface or between two surfaces cause the end groups to be preferentially located close to the surfaces. This is in contrast to the opposite case for polymers adsorbed from dilute solution, where it is entropically more favorable for the tails to dangle out into the solution, although this situation may be different for short chains at high concentrations. In addition to these entropic effects, any anisotropy in the PEP molecule or its segments will generate an anisotropic interaction which is known to affect the surface energies of polymer[47,48] and the interfacial energies and contact angles of liquids on polymer surfaces.[49] In PEP, the chemical asymmetry of the ethylene−propylene group favors a preferential attraction of the exposed CH_3 group on each segment to the hydrocarbon surfaces, which also expose mainly CH_3 groups. This mechanism is based on the like-attracts-like rule that applies to van der Waals dispersion forces (cf. ref 50). Specifically, CH_3 and $-CH_2-$ groups have surface energies of $\gamma = 24$ and 31 mJ/m^2, respectively.[47] This difference manifests itself in the immiscibility of polymers differing only in their $CH_3/-CH_2-$ ratio, and it also determines their interfacial energy.[47] Theoretically, if only van der Waals dispersion forces are considered, the maximum interfacial energy of a $CH_3/-CH_2-$ interface (which is equal to the energy of two CH_3 surfaces interacting across a liquid of $-CH_2-$ groups) is given by the following approximate equation:[50]

$$\gamma_i = \gamma_A + \gamma_B - 2\sqrt{\gamma_A\gamma_B} = (\sqrt{\gamma_A} - \sqrt{\gamma_B})^2 \approx 0.45\ \text{mJ/m}^2 \quad (1)$$

In hydrocarbon solvents and in systems containing adsorbing polymer, there is a final repulsion arising from the confinement of molecules at small surface separations which acts to decrease the adhesion force calculated above. This van der Waals attraction could, however, give rise to adsorption of PEP to the monolayer surfaces, even though the interaction energy per CH_3 group is only ∼0.02−0.05kT. The weak adsorption might explain why the polymer layer easily returns to the configuration with an inner maximum even after a strong compression.

A totally different explanation for the observed short-range repulsive forces is that the polymer in the solution becomes kinetically trapped between the two surfaces as they approach each other; i.e., the measured interaction is only due to the fact that insufficient time was given for the polymer to leave the gap during the force measurement. These measurements were obviously done at so-called "restricted equilibrium", when polymer remains between the surfaces, as are most measurements of polymer interaction. "True equilibrium" would be the situation when adsorbing or nonadsorbing polymer is given the time to leave the contact region, the time needed for such equilibration in a system of weakly adsorbed polymer could be very long. While we cannot exclude the possibility of PEP in the solution being trapped and pressed onto the surfaces, we note that in hydrophilic systems containing similar concentrations of *nonadsorbing* polymer (polyethylene oxide) of similar M_w,[51] the polymer is totally expelled from the gap and $D = 0$ is immediately reached on approach at similar rates as in the measurements presented above. Our results on PEP thus suggest that PEP adsorbs onto the two surfaces before they are brought in contact.

Long-Range Attraction. The long-range attraction may be due to (i) van der Waals forces, (ii) segment–segment interactions between adsorbed polymer chains, (iii) bridging, (iv) depletion, or some combination of the above.

(i) The theoretically expected van der Waals–Lifshitz attraction between the surfaces across tetradecane is shown as dotted lines in Figures 2 and 3. This curve was calculated for a five-layer system[37] consisting of (1) mica, (2) a combined layer of surfactant and adsorbed polymer with an average refractive index of 1.47, (3) tetradecane, (4) another combined layer of surfactant and polymer, and (5) mica. At low PEP concentrations (Figures 2 and 3) the observed adhesion in the inner minimum is in good agreement with the van der Waals–Lifshitz attraction calculated by assuming a 9 Å layer of PEP on each 18.5 Å monolayer for $M_w = 5800$ g/mol and a 17 Å PEP layer for the higher M_w (estimated from the hard-wall thickness of the maximally compressed layers at $F/R \approx 2$ mN/m). This calculation, assuming a maximally compressed PEP layer, obviously does not account for the interaction between the more expanded layers at the outer minimum. An estimate of the van der Waals attraction between two mixed layers across tetradecane, where each layer is assumed to consist of hexagonally ordered PEP chains in 50% tetradecane, was obtained by averaging the dielectric constants of the components in the mixed layer. The resulting van der Waals adhesion force between two such layers across 5 Å of tetradecane is −(0.15−0.20) mN/m, in good agreement with the measured adhesion in the outer minima at low concentrations (cf. Figures 2 and 3).

At the highest concentration, c^*, and partial adsorption (Figure 4), the force estimated above from van der Waals–Lifshitz theory, is too small to account for the measured attraction in the outer minimum, especially for the lower molecular weight.

(ii) The additional long-ranged attraction is unlikely to be due to favorable segment–segment interactions between the adsorbed polymer chains because tetradecane is a good solvent for PEP.

(iii) Since the polymer adsorbs, albeit weakly, to the surfaces, the long-range attraction could be due to bridging. The contribution of bridging to the attraction cannot be excluded; it should however be noted that bridging would be expected to be stronger at lower polymer concentrations, where the adsorbed polymer layer is slightly thinner, while the increased attraction was observed at higher concentration.

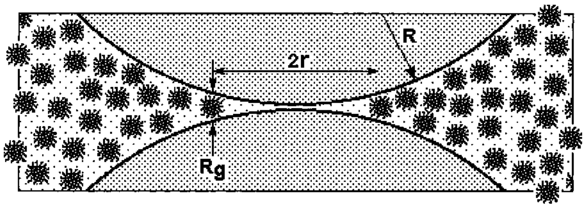

Figure 9. Local geometry of two cylindrically curved surfaces of radius R (equivalent to a single sphere of radius R near a flat surface) near contact in a liquid containing noninteracting polymer, giving rise to the attractive depletion force given by eq 2.

(iv) The increased attraction with increasing PEP concentration, and the vanishing of this attraction on dilution, suggests that a depletion attraction is acting between the surfaces. For the present system involving two cylindrically curved macroscopic surfaces of radius $R \approx 1$ cm, the maximum adhesive depletion force, F_{dep}, is expected to occur when the two surfaces are in contact (schematically illustrated in Figure 9) and is given by multiplying the depletion (osmotic) pressure, $P_{dep} = \rho kT$, by the contact area, πr^2, where r is given by the "chord theorem": $r^2 = (2R - R_g)R_g \approx 2RR_g$. Thus, the normalized theoretical depletion force is[4,5]

$$F_{dep}/R = -2\pi R_g \rho kT \tag{2}$$

where ρ is the concentration or number density (strictly, the activity) of the polymer in the bulk solution. For the present system, inserting $R_g = 30$ Å and $\rho = 7.1 \times 10^{24}$ m^{-3} at the overlap concentration for $M_w = 5800$ g/mol at 8.9 wt %, and $R_g = 81$ Å and $\rho = 4.8 \times 10^{23}$ m^{-3} for $M_w = 33\,000$ g/mol at 3.47 wt %, we obtain F_{dep}/R of −0.55 and −0.10 mN/m, respectively, at 25 °C. These values are in excellent agreement with the attractive forces measured in the outer minima (after subtracting the van der Waals contribution measured at low concentration), viz., $\Delta F/R \approx -0.5$ and −0.1 mN/m, respectively (cf. Figure 4a,b).

Further support for a depletion mechanism comes from the light-scattering measurements[21] on an analogous colloidal system containing 50 Å spheres coated with a monolayer of calcium alkylbenzenesulfonate in decane, which yielded data in excellent quantitative agreement with a depletion mechanism for the attractive force between the dispersed particles. The fact that the polymer also adsorbs to the surfaces may appear to be inconsistent with a depletion mechanism which usually assumes that the polymer must be repelled from the surfaces. However, short-ranged depletion attraction can occur even between surfaces containing adsorbed species, as occurs in micellar solutions.[52,53] Indeed, the oscillatory "solvation" force between two surfaces approaching each other in a liquid may be thought of as reflecting the succession of purely entropic attractive and repulsive (steric) regimes, which finally ends with a deep "depletion" energy minimum at contact, the magnitude[50] of which is formally identical to the expression for the polymer depletion force above (eq 2). In the case of adsorbed polymers, the adsorbed layer may simply constitute the new (although less well-defined) surface, which experiences a depletion force with another, similarly covered, surface.

It was interesting to note that the increased attraction at higher concentration only occurred at partial adsorption. This immediately raises the issue of adsorption from a confined or "starved" solution that is not at diffusional equilibrium with the surrounding, more concentrated bulk solution.[54] However, the amount of polymer present in a 2 μm thick gap of 8.9 wt % PEP solution is orders of magnitude larger than the amount found on the surfaces after equilibrium adsorption (from a larger gap). Thus, the reason for the relatively stable partial adsorption cannot be a low concentration of polymer in the gap (which would also eliminate the depletion force) but is more likely to be due to long equilibration times in confined geometries, although the mechanism for this is not clear.

The onset of attraction at ca. 120 Å for $M_w = 5800$ g/mol, and 200 Å for $M_w = 33\,000$ g/mol at c^* is approximately $2R_g$ if the hard-wall separation, which represents the interacting surfaces in a depletion attraction, is subtracted from the distance measured between the monolayer surfaces. This is consistent with the theoretically expected range of $2R_g$.[4–7,9,11,13]

Asymptotic Long-Range Form of the Force Curve. All force curves for the unfunctionalized PEP at low concentrations and also when measured at nonequilibrium adsorption exhibited a very weak repulsion at ca. $6-10R_g$. This repulsion could be due to one or a combination of the following two mechanisms.

(1) Depletion Stabilization. If depletion is occurring in the system, the PEP coils may initially prefer to be compressed rather than forced out of the confining gap between the surfaces, and this will give rise to an initial repulsion. This effect would be analogous to the alternating attractive and repulsive forces measured across simple liquids[55,56] and concentrated micellar solutions.[52,53] Feigin and Napper[10] were the first to suggest that polymer depletion attraction is preceded by a weak repulsion. However, this repulsion is expected to increase with increasing polymer concentration, which was not observed in our experiments. Unless the polymer coils are kinetically held by entanglement with the surface of already adsorbed polymer, the effect at low concentrations ($0.1c^*$) should have been too small to be detected.

(2) Steric Repulsion. The outermost repulsion could arise from the initial overlap and entropic confinement of the outermost segments of the adsorbed chains. This effect could occur at large separations where bridging attraction cannot yet occur because the polymer cannot yet extend all the way from one surface to the other across the gap. For an entropic–steric repulsion between the segments, the polymer chains need to extend only to the center of the gap, and the steric repulsion could thus occur at a larger surface separation than needed for bridging. Such a repulsion is predicted in recent work by Semenov and Joanny,[14,17,57] who suggest that the tail-dominated regime of the adsorbed layer (for *high* molecular weights) occurs at distances above an^{ν}, where a is the segment length (5 Å) and ν the Flory exponent (0.6 in a good solvent), which for our polymers is at distances larger than ca. 70 and 200 Å from each surface for $M_w = 5800$ and 33 000 g/mol, respectively. Experimentally, the repulsive outer maxima were observed at surface separations larger than 200 and 400 Å, respectively, which is within this distance regime dominated by tails.

Depletion attraction is generally considered to occur in systems of nonadsorbing polymers,[4–6,8,11–13] but the possibility of depletion forces arising in a system containing both free polymer in solution and adsorbing polymer filling all adsorption sites on the surfaces (to exclude bridging) has been considered by Feigin and Napper.[10] In their calculation, the combination of depletion attraction, depletion stabilization, and steric stabilization results in a steric repulsion starting at the range of steric interactions in a system without depletion, followed by an attractive depletion force, and ending with a final hard-wall repulsion due to the adsorbed polymer. These predictions of a repulsion–attraction–repulsion on approach are qualitatively very similar to our experimental results.

Implications for Colloidal Behavior. The existence of two stable or long-lived metastable minima has important implications for colloidal particle interactions. Thus, while the outer minimum may be responsible for weak adhesion and flocculation, the presence of a deeper inner minimum, separated from the outer by an energy barrier, could lead to slow aging effects as colloidal particles slowly overcome this barrier and fall into the deeper minimum. The forces, $F(D)/R$, measured between two cylindrically curved macroscopic surfaces (illustrated in Figure 9) can be related to the interaction energy or pair-potential, E, between two spherical colloidal particles of radius r at the same separation D by

$$E \approx \frac{F(D)}{R}\frac{Dr}{2} \tag{3}$$

Thus, for spherical colloidal particles with a radius of 50 Å (as studied in the experiment by Tong et al.[21] for PEP $M_w = 26\,000$ g/mol), the magnitude of the interaction energy in the outer minimum is around $0.5kT$ at low concentrations, $1.5kT$ at c^* in $M_w = 5800$ g/mol PEP solution, and approximately $0.5kT$ at both concentrations studied for $M_w = 33\,000$ g/mol. This is not sufficient to induce coagulation. The force barrier between the outer and inner minima is around $1-2kT$, and 50 Å particles could possibly be coagulated in the inner minimum, which for the results shown in Figures 2–4 implies an interaction energy of only $\sim 2kT$, but at longer contact times, a larger adhesion is produced to give a sphere–sphere interaction energy of approximately $6-8kT$. Larger particles would be more effectively coagulated; also, a higher polymer concentration should give a larger depletion force.

Our results show that the forces with functionalized polymer are quite different from those with unfunctionalized polymer, even when the surfaces are "protected" by a strongly physisorbed surfactant layer. The presence of water in the oils should have a significant effect on the competitive polymer–surface and surfactant–surface interactions and coagulation rates (Figures 7 and 8), as should more tightly packed (Figure 7) or chemisorbed monolayers. From our study, it appears that a physisorbed monolayer does not necessarily prevent a colloidal surface from adsorbing low molecular weight hydrocarbon polymer. In particular, our results show that forces may be very different in the cases of unfunctionalized and end-adsorbing polymer of similar molecular weight. Most likely the PEP-amine penetrates through the monolayer, as shown schematically in the inset in Figure 8. The resulting interaction is monotonically repulsive with an exponential shape in contrast to the equilibrium interactions at similar concentration of unfunctionalized PEP, where the repulsion had a longer range and decayed as a power law. These types of repulsive interactions are expected theoretically for end-adsorbed[25,44,45,46] and randomly adsorbed[2] polymer, respectively. At short adsorption times and at small surface separations (which is equivalent to high concentration of colloidal particles in a solution), unfunctionalized polymer may give rise to attractive interactions.

The results are in good agreement with the results of Tong et al.[21,42,43] We propose that the long-range attraction [down to the first (outer) energy minimum] observed for unfunctionalized PEP at concentrations close to c^* is due to depletion. Closer in, the inner adhesive minimum is likely to be due to van der Waals and molecular structural forces between the adsorbed segments, although it is uncertain whether both the outer and inner minima represent true equilibrium states in the interaction potential. Two important conclusions for these relatively short-chained polymers in good solvents are (1) that tails play an important role in generating long-range forces, and (2) that it may take a very long time (several hours or even days) to reach adsorption and interaction equilibrium.

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