Polymer-Induced Repulsive Forces: Exponential Scaling

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The polymer-induced repulsive interactions between the surfaces of a liquid film are measured for two systems using two force measurement techniques, in the case where the polymer is in a good solvent and adsorbs at the liquid surface. The force decays exponentially with the film thickness with a decay length proportional to the radius of gyration. The data are compared with a recent theoretical work which predicts a repulsive exponentially decaying force at large thicknesses.   [S0031-9007(98)05373-3]

Double layer forces are commonly used to induce repulsive interactions in colloidal systems. However, the range of electrostatic forces is strongly reduced by increasing the ionic strength of the continuous phase. This is an important drawback for many applications (biological) that involve highly salted media. Also, electrostatic effects are strong only in aqueous solutions, which is a severe restriction. An alternative way to create long range repulsions is to adsorb macromolecules at the interface between the dispersed and the continuous phases [1]. Polymer adsorption occurs if the monomers are attracted by the interface. The interaction between surfaces coated with polymers results from a subtle balance between attractive bridging forces and repulsive excluded volume forces; if the adsorption is irreversible, the force is in general repulsive in good solvent conditions [2]. Adsorbed polymer chains form on a surface a fluffy layer where they form loops and tails with a very broad distribution of sizes and extending in the continuous phase. Even in strong adsorption conditions, the thickness of an adsorbed polymer layer is thus much larger than the monomer size that would correspond to flat chains adsorbed on the surface. The repulsive forces between adsorbed polymer layers are due to the excluded volume interaction between the two layers when they overlap. An alternative way to form thick polymer layers is to use random copolymers where some monomers are attracted to the surface and the others form the loops that strongly repel each other [3]. The structure, the thickness, and the interactions generated by the presence of the adsorbed polymer layers have been extensively studied over the last few years [2–5]. In particular, the force between two polymer covered mica sheets in various solvency conditions has been probed with a surface forces apparatus [4,5]. The force is purely repulsive in a good solvent and becomes attractive as the solvent gets poorer. However, due to a technical limitation of the experiment, these studies concern only a regime of large interaction compared to the thermal excitation and are restricted to interactions between solid surfaces. Apart from a

pioneering experimental work of Lyklema and Van Vliet [6], only a few experiments have been performed on the weaker interactions that take place between two polymer covered liquid droplets or, more generally, liquid surfaces. In this paper, we report quantitative measurements of repulsive forces between liquid interfaces in the low force intensity regime (in our experiments $F \leq 10^{-11}$ N). We use two different force measurement techniques, i.e., the magnetic emulsion force distance and the film disjoining pressure measurement techniques. We have measured the interactions in the presence of successively two adsorbing polymers in various solvency conditions and for several molecular weights. The repulsive force shows an exponential decay with a characteristic length proportional to the radius of gyration of a free polymer chain in solution. This behavior is independent of the system and seems generic to the low force regime that we probe here. The results are interpreted qualitatively within the framework of the recent theory of Semenov and collaborators [7].

One of the polymers (further noted as PVA-Vac) is a statistical copolymer of vinyl alcohol (88%) and vinyl acetate (12%) of two different average molecular weights. The other polymer is a weak polyelctrolyte, polyacrylic acid (PAA) in aqueous solution at high ionic strength and low pH (concentrated NaCl solution). The PAA samples had a relatively narrow molecular weight distribution ($M_w/M_n < 1.4$). The radii of gyration and the overlap concentrations (C^*) were obtained from viscometric measurements [8]. All the experiments were performed in the dilute regime ($C \ll C^*$).

The force-distance measurement technique between liquid emulsion droplets has been described in a previous paper [9]; here we give only a brief description. A monodisperse ferrofluid (Fe_2O_3 in octane) emulsion was first prepared and calibrated to a radius of around 100 nm [10]. Upon the application of a magnetic field, the obtained monodisperse droplets form chains that align along the field direction. Within the chains, the droplets are regularly spaced; the equilibrium distance reflects the balance

between the magnetic attractive and the polymer-induced repulsive forces that exactly compensate at the equilibrium distance. The periodicity of the droplet positions gives rise to intense Bragg diffraction at a wavelength proportional to the interdroplet distance. From this length and the magnetic field strength, we deduce the repulsive force-distance profile between two droplets. The polymer stabilized emulsions have been prepared more than 20 h prior to any measurements to allow for the equilibrium adsorption.

The films disjoining pressure measurements were performed with the porous plate technique first introduced by Mysels and Jones [11] for soap film studies. Under the effect of the pressure difference ΔP between the box and a constant reference, a thin polymer film is formed at the center of a small hole (with a diameter of about 1 mm) drilled in the porous glass disk. The film stabilizes at a constant thickness h when the force per unit area π_d between the interfaces (the disjoining pressure) exactly balances the known applied pressure. ΔP is controlled (within ± 3 Pa) with a computer driven pump while the aqueous film thickness h is measured by interferometry at normal incidence.

The force (F)-distance (h) profiles between the ferrofluid droplets and the air-water films are displayed for the two molecular weights in good solvent condition for the vinyl alcohol monomers on Fig. 1(a). The transformation of the disjoining pressure π_d into a force was performed via the Derjaguin approximation. The two profiles are qualitatively similar and show a linear decay with the same slope on a semilogarithmic scale. However, the distances corresponding to equal forces are very different in the two experiments (they are much larger in the air-liquid film). We discuss this difference below. In the following, we write the force as a function of the distance as

$$F(h) = A \exp(-h/\lambda), \qquad (1)$$

where the decay length λ can be considered as the thickness of the adsorbed polymer layer on one of the interfaces. These exponentially decaying profiles are insensitive to the presence of electrolytes and cannot be attributed to a double layer repulsion that could exist if, for example, some parasitic charges were present at the interface. The force profiles are almost all identical when the adsorption proceeds from a dilute solution. If we now compare the profiles obtained with the two techniques for the two different molecular weights, we observe that the layer thickness increases with molecular weight and that the two experiments give similar values (between 9 and 11 nm for $M_w = 55\,000$ g/mol and 17.5 and 21.5 nm for $M_w = 155\,000$ g/mol) despite the fact that the interaction that drives the adsorption can be very different from one interface to the other. In both cases, the thickness λ is of the order of the radius of gyration of the chains in solution. Using a different polymer, we can show that this exponential behavior is not specific to PVA-Vac. We have performed a second set of experiments with a polyelectrolyte (PAA) in solutions of high ionic strength. The presence of salt ensures that any long range repulsion is not due to electrostatics. The sodium chloride concentration was 0.2 M corresponding to a Debye length κ^{-1} (≈ 0.7 nm) much smaller than the typical range of the repulsion observed in Fig. 1(b). Here also, we observe exponentially decaying profiles with characteristic distances varying with the molecular weight.

We have varied the polymer radius of gyration R_g by increasing the temperature closer to the PVA-Vac θ temperature (for PVA-Vac in water, the good solvent domain is at temperatures less than $\theta = 97\,^\circ$C). In Fig. 2, we show the evolution of the force profile as the temperature is increased from 20 °C to 80 °C, i.e., in a regime where the radius of gyration is significantly reduced
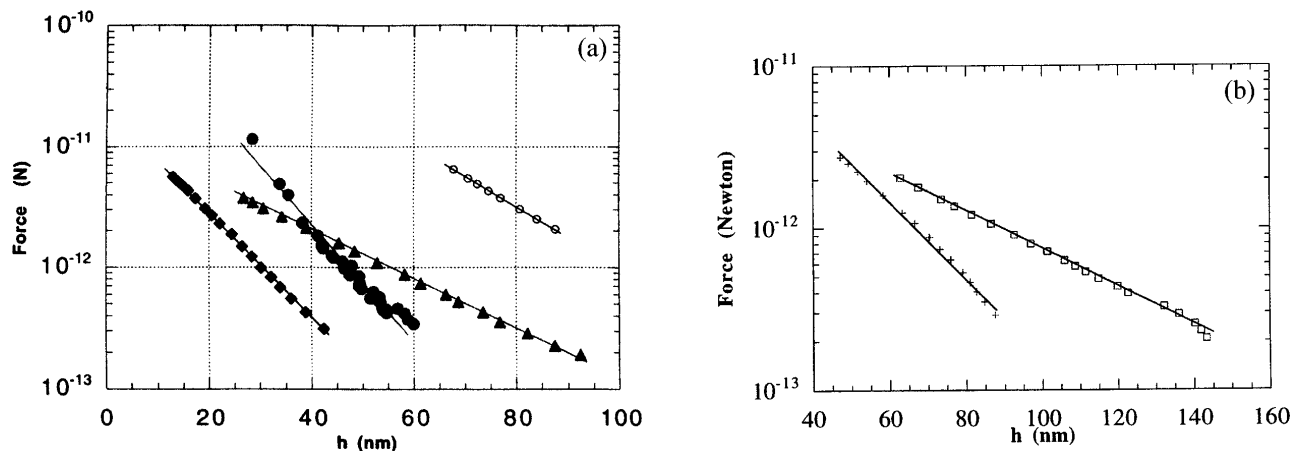

FIG. 1. Force-distance profile between liquid films in various polymer solutions and with various interfaces. The continuous lines are the best fits to our data using Eq. (1) in the text. (a) Forces in PVA-Vac solutions ($C_p = 0.5$ wt %). Oil-water interface: ◆, $M_w = 55\,000$ g/mol; ▲, $M_w = 155\,000$ g/mol. Air-water interface: ●, $M_w = 55\,000$ g/mol; ○, $M_w = 155\,000$ g/mol. (b) Forces in PAA solutions at the oil-water interface: $C_p = 0.1\%$; [NaCl] $= 0.2$ mol/1; pH $= 3$. +: $M_w = 100\,000$ g/mol; □: $M_w = 320\,000$ g/mol.
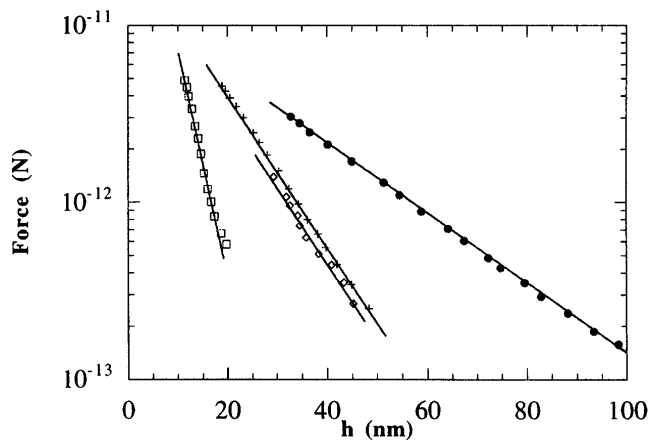
FIG. 2. Temperature effect. The continuous lines are the best fits to our data using Eq. (1) in the text. Force-distance profile between ferrofluid droplets in solutions of PVA-Vac ($C_p = 0.5\%$): $M_w = 55\,000$ g/mol; +: $T = 20\,°C$; □: $T = 80\,°C$. $M_w = 155\,000$ g/mol; ●: $T = 20\,°C$; ◇: $T = 80\,°C$.

but still in good solvent conditions. The profiles always remain exponential but the range decreases significantly. In Fig. 3, we have plotted the experimental adsorbed layer thickness λ as a function of the radius of gyration and we observe a variation that is reasonably linear for both PVA-Vac and PAA.

We have compared this result with the theoretical predictions obtained using both a mean field and a scaling approach by Semenov *et al.* The theory distinguishes the loop and tail sections of the adsorbed chains and involves three length scales, the adsorbed layer thickness λ, an adsorption length z^* that separates the regions where the monomer concentration is dominated by loops and by tails, and a microscopic length b inversely proportional to the adsorption strength. Two regimes must be distinguished depending on the strength of the adsorption measured by the ratio λ/b.

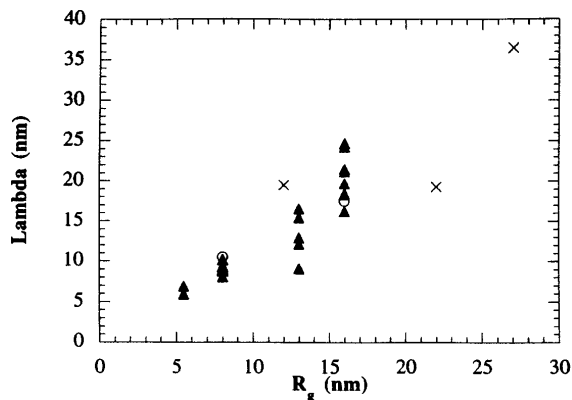In the strong adsorption limit ($\lambda/b \gg 1$) both a scaling and a mean field approach have been developed in

FIG. 3. Evolution of the characteristic length λ as a function of the polymer coil gyration radius R_g. Each point corresponds to a different experiment. ▲: PVA-Vac, oil-water interface; ×: PAA, oil-water interface; ○: PVA-Vac, air-water interface.

Ref. [7]. The expression of the adsorbed layer thickness λ, corresponding to the size of the largest loops or tails in the layer, reads in the mean field theory

$$\lambda = R_g/[\ln(1/\phi_0 \upsilon b^2)]^{1/2}, \qquad (2)$$

where υ is the Flory excluded volume parameter, and ϕ_0 the bulk polymer volume fraction. The adsorbed layer thickness is thus proportional to the chain radius of gyration and varies only weakly with the polymer concentration ϕ_0 and the adsorption strength b. The scaling theory in a good solvent leads to similar conclusions.

If the distance between the two surfaces is smaller than λ the polymer mediated interaction decays as a power law (h^{-4} in the mean field theory and h^{-3} in the scaling theory). The sign of the force depends, however, on the reversibility of the adsorption, and the force is repulsive at short distances only if the adsorption is irreversible. At distances larger than λ, the concentration is dominated by the tails, and the force is always repulsive and decays exponentially with the distance. Matching this exponential decay to the power law decay at smaller distances and using the Derjaguin approximation, we obtain, in the scaling theory, which is more appropriate to describe polymers in good solvents, the force between spherical droplets of radius R,

$$F(h) = (k_b T \pi R/\lambda^2) \exp(-h/\lambda), \qquad (3)$$

where k_B is the Boltzman constant and T the temperature. Note that this expression is valid only if λ is large enough (essentially larger than z^*) i.e., for a polymer adsorbed amount close to the saturation value. For smaller adsorbed amounts, the force may become attractive even in cases of irreversible adsorption.

The weak adsorption limit ($\lambda/b \ll 1$) has been studied less extensively. The only relevant length scale in this limit is the chain radius of gyration, and the adsorbed layer thickness is proportional to the radius of gyration. The force is proportional to the number of chains adsorbed at the interface, or to the polymer adsorbed amount Γ. In the crossover range between the weak and strong adsorption regimes one expects that the force increases (in an unknown way) with the polymer adsorbed amount.

The amount of polymer adsorbed (Γ, obtained from batch adsorption measurements) at the oil-water interface lies between 1.5 and 2 mg/m^2—a value that is typical for polymer at the plateau in the adsorption isotherm [3]. It is unknown at the air-water interface. However, we know from surface tension measurement that in both cases, the saturation of the adsorption occurs when the bulk polymer concentration exceeds roughly 0.5%, the concentration at which the measurements were performed. It thus seems that the adsorbed polymer amount is smaller than the saturation value.

The model in the strong adsorption limit seems to describe qualitatively the data. An estimation of the preexponential factor using $T = 300$ K, λ deduced from our data, and $R \approx 100$ nm leads to a value of $(k_b T \pi R/\lambda^2)$

between 6×10^{-12} and 10^{-11} N depending on λ. From the fit to the data of the ferrofluid emulsion, we obtain typically $A \approx 10^{-11}$ N while the other force measurement technique leads to values of about 10^{-10} N. The dependence of A with λ could not be observed due to a lack of precision. In order to test the variation of the force with Γ, we have introduced increasing quantities of a nonionic surfactant (nonylphenol oxyethylene NP10 of $CMC = 7 \times 10^{-5}$ M) that is known to adsorb preferentially at the interface and displace the polymer [12]. In Fig. 4, we show the evolution of the disjoining-pressure–distance profiles with increasing NP10 concentrations. The characteristic distance λ remains unchanged while the preexponential factor decreases with the polymer adsorbed amount. A similar behavior is observed at the oil-water interface. This variation of the force-distance profile with the adsorbed amount provides an explanation for the different equilibrium distances at identical repulsive forces observed in the two experiments. Another possibility is the contribution of the depletion attraction which might differ from one experiment to the other. These observations are in disagreement with the predictions of the theory (for $\lambda/b \gg 1$) in which both λ and the preexponential factor vary only weakly with the adsorption strength that controls the adsorbed amount. We believe that the polymer desorption that is driven by the NP10 concentration causes a change of regime from the large (for the lowest NP10 concentrations) to the weak adsorption limit (at high NP10 concentrations).

Our results are completely different from those obtained with the surface forces apparatus in similar conditions [13,14] probably because of the different nature of the involved interfaces and of the larger force range that is investigated with the SFA. Therefore, we most probably explore the low force part of the profile (first interactions between the polymer tails) while the SFA measurements explore the regime where the force decays as a power law.
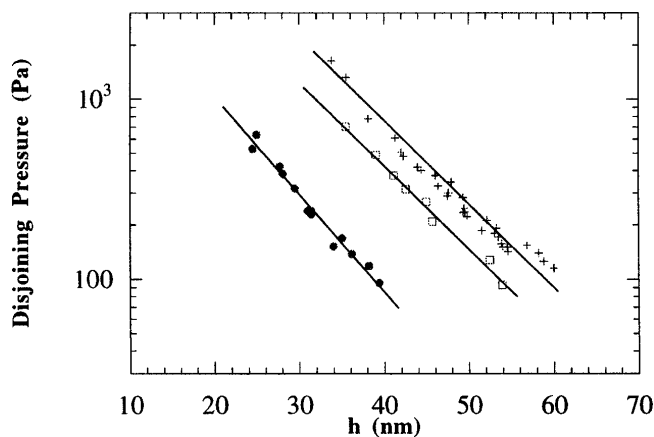
We believe that our results bring some new insights on the problem of polymer induced colloidal forces. The repulsion between liquid interfaces is exponentially decaying, with a characteristic length that is directly proportional to the radius of gyration of the free polymer chains in solution. This length is insensitive to the polymer bulk concentration and to the nature of the fluid-fluid interface. The force intensity is a direct—though unknown—function of the polymer adsorbed amount and thus depends on the nature of the interface. Our results compare reasonably well with the theory of Semenov and co-workers, and we believe that the observed discrepancies are mainly due to the fact that we probe a regime of intermediate adsorption strength that does not fully enter the theoretically treated weak and strong adsorption limiting cases.

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FIG. 4. Evolution of the force-distance profiles as a function of the nonylphenol ethoxylene (NP10) concentration in solutions of PVA-Vac ($C_p = 0.5\%$, $M_w = 55\,000$ g/mol), air-water interface. $+$: [NP10] $= 0$M; $\square$: [NP10] $=$ CMC/10; $\bullet$: [NP10] $=$ CMC.