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Structural Forces in Thin Films Made from Polyelectrolyte Solutions

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We have studied thin liquid films made from semidilute polyelectrolyte solutions. The disjoining pressure (due to interaction between film surfaces) has been measured as a function of the film thickness. We observe pressure oscillations, corresponding to film stratification. The oscillations become sharper as the polymer concentration c increases, and disappear when salt is added. The period of the oscillations scales as $c^{-1/2}$. We propose that the observed stratification is related to the polymer network and the size of the steps to the mesh size ξ. [S0031-9007(97)03399-1]

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The behavior of polymers near surfaces and in confined environments has been the subject of many studies, both fundamental and applied [1]. Indeed, it is important to understand this behavior for the control of separation processes (filtration, gel chromatography, osmosis, etc.), oil recovery processes (drilling muds with added polymers, viscosity control of injected water) among others. From the fundamental point of view, it is interesting to describe how the polymer coils or the polymer networks are affected by the confinement. When the polymers are confined between two surfaces, and when the surfaces are close enough, surface forces arise. Their origin is steric most of the time: repulsion due to the overlap of chains adsorbed on each surface [2]. The knowledge of these forces is important to control colloid stabilization or flocculation. Polymers are extensively used, in particular, in nonaqueous media, where electrostatic forces are not effective [3]. Numerous measurements with the surface force apparatus (SFA, mica surfaces) have been reported in the literature for polymers that adsorb on the surfaces [2]. In addition to the usual steric repulsion, small attractive forces have been evidenced when the chains are in a bad solvent. These attractive forces are due to monomer-monomer interactions and in part to bridging of the surfaces, when the polymer surface coverage is low. Little is known for the case of nonadsorbed polymers, where depletion layers and depletion forces are expected. Depletion forces have been measured in solutions of polymerlike micelles that do not adsorb at the mica surfaces (coated with surfactant of the same charge sign than that of the micelles) [4]. Oscillatory forces have been recently observed with an atomic force microscope in polyelectrolyte solutions. These forces were attributed to the formation of a crystal of coils stabilized by long range electrostatic forces [5]. In the present paper, we report the existence of oscillatory forces in semidilute polyelectrolyte solutions, together with an explanation of their origin. In this work, the forces are measured with a different method, by using freely suspended polymer films.

The films are formed with a modified version of the porous plate technique first introduced by Mysels for the study of foam films [6,7]. A thin porous glass disk is fused on the side to a capillary tube (3 mm inner diam). A small hole is drilled in the center of the disk (diam of about 1 mm). The liquid solution fills the disk, part of the capillary, and a thin horizontal liquid film is formed across the hole. The disk is enclosed in a 200 cm^3 hermetically sealed Plexiglass box, with the capillary tube exposed to a constant reference pressure. Under the effect of the pressure difference ΔP between the box and the reference, the film thins and eventually stabilizes at a thickness h if the surface force per unit area Π balances the applied pressure. Π is a function of h and is called disjoining pressure after Derjaguin [8]. The pressure difference is controlled within ± 3 Pa with a computer driven pump. The thickness h is measured by monitoring the light reflectivity at normal incidence, and by using classical interferometric formulas. Here, film thicknesses are always much larger than the thickness of the monolayers stabilizing the film, and the bulk solutions are dilute enough so that we can use the refractive index of water for the thickness calculations. The film can also be observed by videomicroscopy; in this way, when oscillatory forces are present, spots of different thicknesses can be visualized on the film. This is the case for thin films made from micellar and latex spheres solutions [7,9].

We have studied mixed aqueous solutions of surfactant (DTAB, dodecyltrimethylammonium bromide, from Aldrich) and polyelectrolyte (random copolymer of acrylamide AM and acrylamido-methyl-propane sulfonate AMPS, from SNF Floerger). The surfactant was recrystallized three times before use and the polymer was purified by ultrafiltration (20 000 cutoff unit). Two molecular weights were used, 2.2×10^6 and 4×10^5, with a polydispersity $M_W/M_n \sim 1.5$ and a fraction of charged monomers of 25% (each AMPS monomer bears one elementary charge, AM being neutral). The surfactant concentration is 0.05 mM, well below the concentration at which mixed polymer-surfactant aggregates form in the bulk (1 mM) [10]. Part of the surfactant is concentrated at the film surfaces where it forms a mixed monolayer with the polymer, the polymer chains being stretched along the surface: The monolayer thickness is around 3 nm, as measured with ellipsometry [10]. This surface

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layer confers a good stability to the thin film: Without the polymer, the film breaks almost immediately. Several polymer concentrations were used: $75 < c < 4000$ ppm. At these concentrations, the polymer alone does not adsorb at the film surfaces (surface tension equal to that of water). Because the polyelectrolyte chains dimensions are large, the solutions are expected to be in the semidilute range. We have checked that this was the case by measuring the viscosity of the polymer solutions with a capillary viscosimeter. In the shear range explored (0.01 to 1 s^{-1}) the solutions are Newtonian. The reduced viscosity $\eta_r = (\eta - \eta_0)/\eta_0 c$ varies as $c^{-1/2}$ (see Fig. 1), as usual for semidilute polyelectrolyte solutions [11].

The disjoining pressure variations with film thickness are shown on Fig. 2 for different polymer solutions ($M_W = 4 \times 10^6$). At small thicknesses, a repulsive force is observed which can be fitted with an exponential form $\exp(-\kappa h)$, as expected for screened electrostatic repulsion; κ is close to the calculated inverse Debye length in the solution (see Table I),

$$\kappa^2 = 4\pi l_B \sum Z_i^2 n_i \qquad \text{with } l_B = e^2/4\pi\varepsilon kT$$
$$\text{and} \qquad n_i = Nc_i/M_i\,, \tag{1}$$

where l_B is the Bjerrum length, n_i the number concentration of the ionic species i, c_i its concentration by weight, M_i its molecular weight, Z_i its valency, N the Avogadro number, e the electron charge, ε the dielectric constant of the solution, and kT the thermal energy. For water at room temperature, $l_B \sim 0.7$ nm.

When the polymer concentration is increased, additional branches appear [12]. It should be noted that repulsive forces only can be measured with this technique, at the difference of the SFA. When ΔP increases, h decreases, and when the top of a given branch is reached, the thickness jumps to a smaller value on the next branch. When ΔP is decreased, the different branches are obtained back (although not the jumps). However, it must be pointed out that the equilibration times are much larger when the pressure is decreased (5 to 6 h instead of 1 or 2 h). The hysteresis of the equilibrium times might be due to the reorganization of the surface layers as in other polyelectrolyte systems [13]. At the pressures where jumps occur, spots of different thicknesses can be observed on the film (Fig. 3). The number of spots depends on the pressure jump used to nucleate the thinner spots on the film. When the number of spots is small, the spots expand with a radius proportional to the square root of time. This is as observed for micellar solutions [9,14]. Further work is currently under way to extract from this time evolution information about the viscosity in the polymer films.

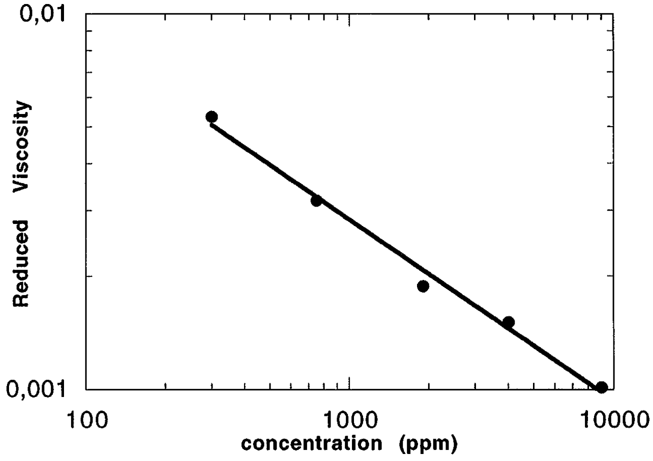

FIG. 1. Reduced viscosity of the polymer solutions vs polymer concentration. The slope of the line is −0.5.

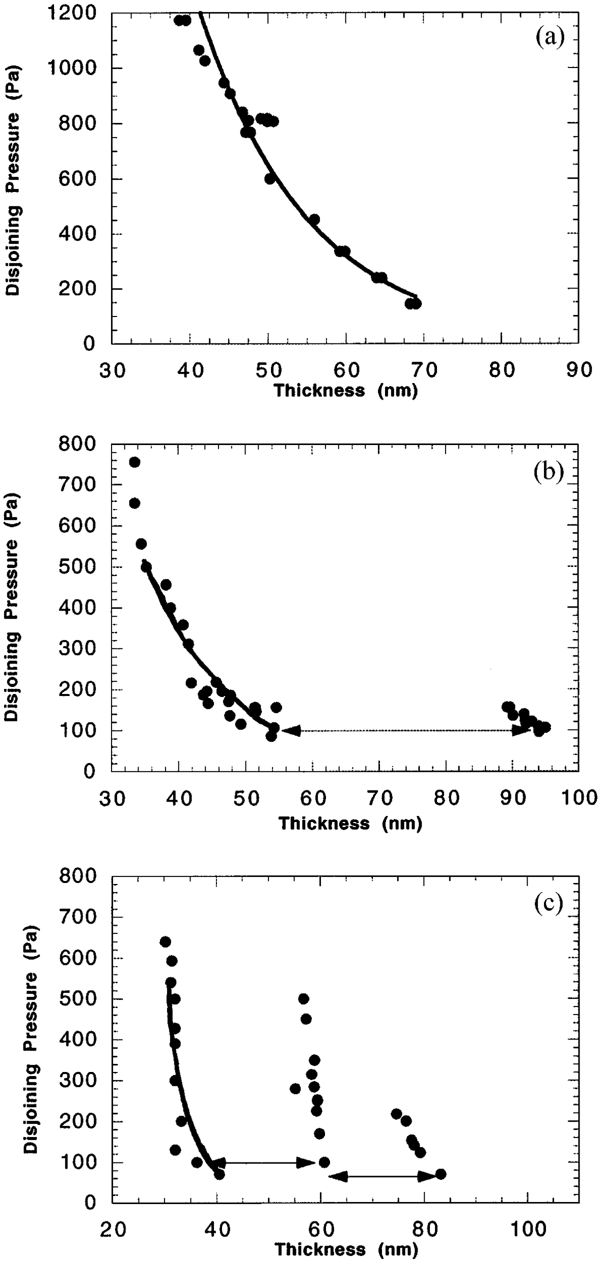

FIG. 2. Disjoining pressures vs film thickness for different polymer concentrations. The lines are exponential fits; (a) $c = 80$ ppm, (b) $c = 750$ ppm, and (c) $c = 1900$ ppm.

The distance between the branches of the curves of Fig. 2 are the same (when more than two branches are

TABLE I. Polymer concentration c, jump size d, theoretical mesh size ξ [Eq. (2) with $a = 3$ Å], experimental and calculated [Eq. (1)] Debye length κ^{-1}.

c (ppm)	d (nm)	ξ (nm)	$\kappa_{\mathrm{exp}}^{-1}$ (nm)	$\kappa_{\mathrm{th}}^{-1}$(nm)
80	⋯	⋯	18	23
300	70	59	12	11
750	40	37	10	7.4
965	29	33	6.6	6.6
1900	24	23	3	4.7
4000	19	16	2.5	3.2

observed). Experiments done with the larger molecular weight ($M_W = 2.2 \times 10^6$) for $c = 750$ ppm show that the distance between the branches is the same for the two molecular weights. This distance d is plotted in Fig. 4 as a function of polymer concentration: One sees that $d \sim c^{-1/2}$. Numerically, d is about 4 times larger than the Debye length κ^{-1}. Finally, we have checked the effect of added salt (sodium chloride). The effect of increasing salt concentration is similar to the effect of decreasing polymer concentration (Fig. 2): First, the outer branches disappear, and one is left with a single branch consistent with the electrostatic repulsion $\exp(-\kappa h)$ when the salt concentration becomes comparable to the polymer counterion concentration.

Attractive forces in thin polymer films can be due to monomer-monomer attraction in the case of bad solvents [2]. This is not the case here, since water is a good solvent, even for the uncharged polymer. The effect of depletion and of the bridging of the two surfaces by the polymer was investigated in the case of polyelectrolytes by numerical simulations [15]. Bridging occurs when the polymer chains adsorbed at one surface can have segments adsorbed at the opposite surface. This gives rise to attractive interactions, and a force minimum is obtained at a distance of the order of the distance between the charges on the polymer backbone. Here this distance is of the order of 1 nm, clearly much smaller than the position of our force minima. Depletion is more subtle, but as in the above cases, it can only produce one minimum, and cannot explain the occurrence of oscillatory forces. On the other hand, the period of the oscillations is closer to the expected mesh size of the polymer network.

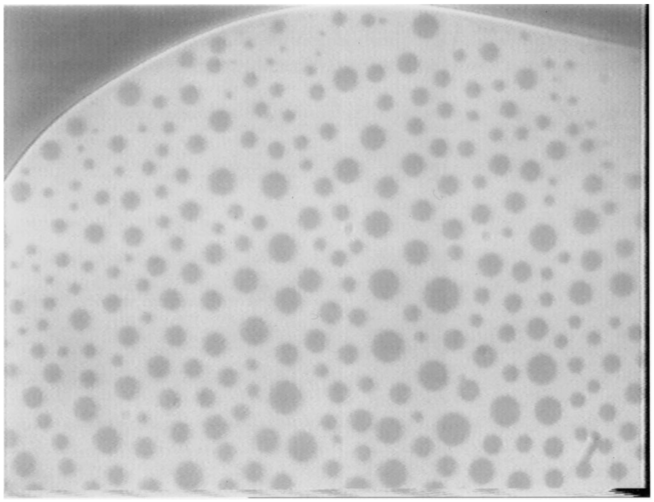

FIG. 3. Images of the liquid film showing spots of thicknesses smaller than the background.

Let us recall briefly the present state of understanding of semidilute solutions of flexible polyelectrolytes [16]. If the distance between charges on the chain is smaller than the Bjerrum length l_B, there is a counterion condensation (Manning condensation). In our case, the polymer is weakly charged, and no condensation is expected to occur [17]. The polyelectrolyte chain is flexible enough: The intrinsic persistence length, i.e., not due to charge effects, is comparable to the monomer size. In such a case, the chain starts to coil until the electrostatic repulsion energy becomes larger than kT. The coil size is then ξ_e, and up to the overall persistence length l_p, the chain can be viewed as a rod of electrostatic blobs ξ_e. Here, ξ_e is small and made from a few monomer units only [18]. In the semidilute regime, the rods form a mesh of size ξ, the average distance between rods overlap points. Small angle x-ray and neutron scattering experiments have evidenced the presence of a peak at a wave vector q^* corresponding to a characteristic distance that varies with polymer concentration as $c^{-1/2}$ and that has been identified to the mesh size [11,17]. The peak disappears when salt is added around a concentration comparable to that of the polymer ions. The scattering data and, in particular, the structure factor can be Fourier transformed to obtain the pair correlation function $g(r)$. A peak in the structure factor leads to oscillations in $g(r)$. When the polymer is confined between two surfaces, and when the distance h is comparable to the period of the oscillations of $g(r)$, oscillatory forces between the surfaces are expected. These oscillations have been observed on simple fluids made of spherical molecules in the SFA apparatus [19]. They do not arise because the molecules tend to structure into semiordered layers at surfaces, but because of the disruption or change of this ordering during the approach of the second surface. A

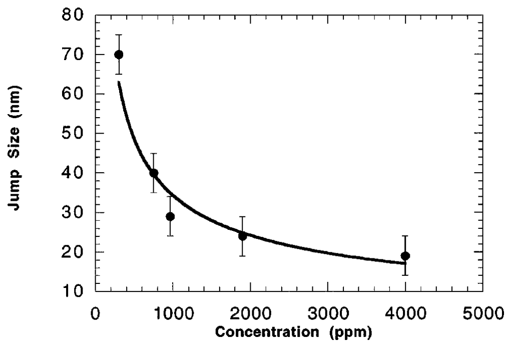

FIG. 4. Distances d between the branches of the disjoining pressure curves vs polymer concentration.

similar interpretation has been given for the oscillatory forces in micellar solutions [20]. Recently, they have been predicted to exist for polyelectrolyte solutions [21]. Clearly our data confirm that such structural forces do exist in semidilute polyelectrolyte solutions. We have compared the distance between branches d to the theoretical mesh size ξ [22],

$$\xi = \frac{a}{(a^3 n)^{1/2}}\left(\frac{l_B}{a}\right)^{-1/7} f^{-2/7} = \frac{\alpha}{c^{1/2}}, \qquad \text{with } \alpha = a^{-1/2} M^{1/2} N^{-1/2}\left(\frac{l_B}{a}\right)^{-1/7} f^{-2/7}, \tag{2}$$

where a is the monomer size and f the fraction of charged monomers. The agreement between d and ξ is remarkable: see Table I. The data also support the fact that the mesh size is somewhat larger than the Debye length. It was already found from indirect interpretation of viscosity data [23], and it was confirmed recently by numerical simulations [24] that the persistence length is also significantly larger than the Debye length. This result is not surprising since according to Odjik, the electrostatic energy between two consecutive pieces of the chain of size κ^{-1} is $kT/\kappa l_B$, i.e., much larger than kT [25]. Our data are also consistent with the disappearance of the scattering peak by the addition of salt, with its sharpening with increasing polymer concentration, and with the absence of dependence upon polymer molecular weight. Let us note that no oscillations were observed with a neutral polymer, polyethylene oxide, in thin films made from mixed solutions with sodium dodecyl sulfate [26]. Finally, it is likely that the observations reported in Ref. [5] are also due to the above proposed mechanism, instead of the coils crystal model of the author.

In conclusion, we have studied thin liquid films made from semidilute polyelectrolyte solutions. Small amounts of oppositely charged surfactant were added to stabilize the film. A mixed surfactant-polymer monolayer is formed at the two free surfaces of the film, but no mixed polymer-surfactant aggregates are present in the bulk. We have measured oscillatory forces, likely to be structural forces associated with the polymer mesh structure. A film stratification is observed, with a strata thickness corresponding to the mesh size ξ, distance between overlap points of two polymer chains. These oscillatory forces are particular to polyelectrolytes and disappear when the electrostatic forces are screened with salt. The present experiments give new useful insights into the structure of semidilute polymer solutions which are presently the object of numerous speculations. They allow one to probe concentration regimes inaccessible to scattering experiments because of poor contrast conditions, but who are the topic of most theories.

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[1] G. J. Fleer, J. M. H. M. Scheutjens, M. A. Cohen-Stuart, T. Cosgrove, and B. Vincent, *Polymer at Interfaces* (Chapman and Hall, London, 1993).
[2] S. S. Patel and M. Tirrel, Annu. Rev. Phys. Chem. **40**, 597 (1989).
[3] D. H. Napper, *Polymeric Stabilization of Colloïdal Dispersion* (Academic Press, London, 1983).
[4] P. Kékicheff, F. Nallet, and P. Richetti, J. Phys. II (France) **4**, 735 (1994).
[5] A. J. Milling, J. Phys. Chem. **100**, 8986 (1996).
[6] K. J. Mysels and M. N. Jones, Discuss. Faraday Soc. **42**, 42 (1966).
[7] V. Bergeron and C. J. Radke, Langmuir **8**, 3020 (1992).
[8] B. V. Derjaguin, N. V. Churaev, and V. M. Muller, *Surface Forces* (Consultant Bureau, New York, 1987).
[9] A. D. Nikolov and D. T. Wasan, J. Colloid Interface Sci. **133**, 1 (1989).
[10] A. Asnacios, D. Langevin, and J. F. Argillier, Macromolecules **29**, 7412 (1996).
[11] S. Förster and M. Schmidt, Adv. Polym. Sci. **120**, 51 (1995).
[12] The existence of two branches was already reported in V. Bergeron, A. Asnacios, and D. Langevin, Langmuir **12**, 1550 (1996).
[13] M. A. G. Dahlgren, Thesis, Univ. Stockholm, 1995.
[14] A. A. Sonin and D. Langevin, Europhys. Lett. **22**, 271 (1993).
[15] M. A. G. Dahlgren, A. Waltermo, E. Blomberg, P. M. Claesson, L. Sjostrom, T. Akesson, and B. Jönsson, J. Phys. Chem. **97**, 11 769 (1993); M. A. G. Dahlgren and F. Leemakers, Langmuir **11**, 1996 (1995).
[16] J. L. Barrat and J. F. Joanny, Adv. Chem. Phys. **94**, 1 (1996).
[17] W. Essafi, Thesis, Univ. Paris, 1996.
[18] For a polyelectrolyte in a good solvent, $\xi_e \sim a^{10/7}(f^2 l_B)^{-3/7}$.
[19] J. Israelachvili, *Intermolecular and Surface Forces* (Academic Press, London, 1992), 2nd ed.
[20] M. L. Pollard and C. J. Radke, J. Chem. Phys. **101**, 6979 (1994).
[21] X. Châtellier and J. F. Joanny, J. Phys. II (France) **6**, 1669 (1996).
[22] A. R. Kokhlov and K. A. Kachaturian, Polymer **23**, 1742 (1982). The polymer studied here is soluble in water, even for a zero degree of charge. Water is therefore a good solvent, contrary to most polyelectrolytes. The expressions of Ref. [20] have therefore been changed accordingly.
[23] M. Tricot, Macromolecules **17**, 1698 (1984).
[24] U. Micka and K. Kremer, Phys. Rev. E **54**, 2653 (1996).
[25] T. Odjik, J. Polym. Sci **16**, 477 (1977).
[26] O. Krichevski and J. Stavans, Physica (Amsterdam) **200A**, 743 (1993); Phys. Rev. Lett. **73**, 696 (1994).