Stratification Kinetics of Polyelectrolyte Solutions Confined in Thin Films

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We have studied free horizontal liquid films made with semidilute polyelectrolyte solutions. A stratification phenomenon is observed during film thinning, with a step size close to the mesh size of the polymer network: dark domains nucleate and expand, the outer polymer layer dewetting a thinner film. The kinetics of dark spot expansion is not simply related to bulk viscosity and becomes faster when the film thickness decreases, suggesting an increase of the chain mobility of the confined polymer chains. These findings are similar to recent ones for other confined liquids and are the first reported so far for freely standing films.

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The dynamic behavior of confined liquids and, in particular, the description of viscous dissipation in thin water or polymer films are presently actively investigated fields. Israelachvili *et al.* [1] used the surface force apparatus to study polystyrene (PS) films and found that the viscosity increases with decreasing film thickness (of the order of nanometers), which suggests an increase of the entanglement density. Neutron scattering and x-ray absorption (EXAFS) experiments on thin PS films showed on the contrary a decrease of the entanglement density with decreasing film thickness [2] and faster molecular motions [3]. However, in the surface force experiments, both interfaces of the films are constrained by hard substrates, whereas in the neutron scattering and EXAFS experiments, the films had a free surface. Masson and Green [4] have studied dewetting of PS films on silicium substrates, and have shown that the viscosity decreases with decreasing film thickness, consistent with these results. Valignat *et al.* [5] studied dewetting of another polymer, polydimethylsiloxane (PDMS), and showed that the viscosity is independent of the polymer molecular weight, in a range where the bulk viscosity varies by a factor of 50. The few existing experimental results tend therefore to show that local viscosity is smaller than bulk viscosity if the film surfaces are free to move (nonadsorbing case) and larger if the polymers stick to the film surfaces (adsorbing case). Recent experiments on water in porous media led to similar conclusions, in agreement with numerical simulations [6,7].

In this Letter, we report a study of freely standing films that offer a different configuration, with two free surfaces. We have used polyelectrolyte aqueous solutions, and controlled the surface conditions by adding small amounts of surfactant: surfactant of the same charge as the polymer will repel the polymer chains and create nonadsorbing conditions, whereas surfactants of opposite charge will create adsorbing conditions. We have used different polymer concentrations (which affect bulk viscosity) and show the consequences on film thinning. We have reported previously the variation of the disjoining pressure Π of these films versus thickness h:Π is the force between film surfaces counted per unit area, and is an oscillatory function of h, with a period close to the polymer network mesh size ξ [8]. The origin of the oscillatory forces in polymer films has been explained earlier [9] and is essentially due to electrostatic interactions between polymer chains. When the film thins under the influence of an external pressure, the film thickness changes discontinuously between the different branches of the disjoining pressure curve. Circular domains of smaller thickness nucleate, expand, and cover the whole film area (see insets of Fig. 3 below). This process is a particular case of dewetting. We describe here the domain time expansion, and relate it to existing dewetting models in order to access the local viscosity.

The films were made from mixed solutions of a polyelectrolyte, carboxy-methylcellulose (CMC) and of sodium dioctyl sulfosuccinate (AOT), a surfactant with the same charge, thereby working in nonadsorbing conditions. CMC is from Aqualon and AOT from Sigma Aldrich. The AOT concentration was fixed to 0.1 mM, more than 10 times smaller than the critical micellar concentration above which micelles form. All experiments were made at room temperature (21 ± 1 °C).

We have measured the surface tension and compression viscoelasticity of the solutions with an oscillating drop tensiometer. The results show that these properties are not significantly affected by the presence of the polymer, confirming that no polymer-surfactant complexes are formed at the surface. The shear viscosity η of the solutions was measured with a rheometer (PAAR Physica, MRC 300) at different shear rates ranging from 10 to 500 s^{-1}. The results are displayed in Fig. 1 in the concentration range studied. The viscosity decreases when shear rate increases, a classical shear thinning behavior for semidilute solutions of polyelectrolytes. The viscosities measured with and without surfactant are the same within experimental error.

We have used a version of the porous-plate technique [10,11]. The film is formed in a small hole (diameter ~1 mm) drilled into a porous glass disk onto which a glass capillary tube is fused. The free end of the capillary tube is

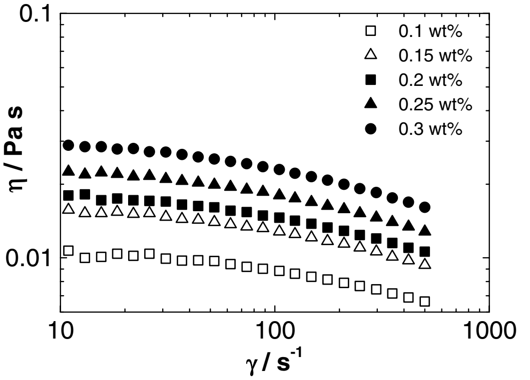

FIG. 1. Log-log representation of bulk viscosity versus applied strain rate for the different polymer solutions used.

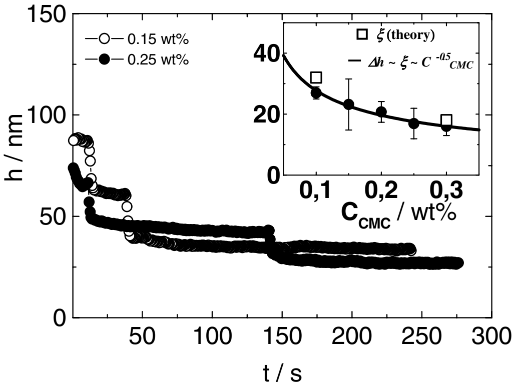

FIG. 2. Typical film thickness variation with time. Inset: dependence of the strata thickness versus polymer concentration together with a fit with $\Delta h \sim C_p{}^{-0.5}$ and calculated mesh sizes ξ.

at atmospheric pressure and the disk is enclosed in a pressurized cell. The pressure is regulated by a syringe pump, which allows us to change the pressure ΔP applied to the film; ΔP is measured by transducers covering various pressure ranges. Once formed, the film thins because of the applied pressure, flattens, and eventually reaches an equilibrium thickness, at which ΔP is compensated by the disjoining pressure Π. The film thickness h is measured by using a microinterferometric method. The whole film area is imaged by a video camera and the images recorded on a computer. The image analysis has been done with two types of software, IDL 6.0 and SCION IMAGE.

The disjoining pressure measurements described in [8] were made by using disks with small porosities (average pore size 40 μm), in order to have a slow film drainage. In these conditions, the film pressure at which the thickness transitions occur is different and depends on polymer concentration. The velocity of drainage V_d depends on ΔP and is given by [11]

$$V_d = -dh/dt = h^3[\Delta P - \Pi(h)]/(3\eta R^2), \qquad (1)$$

where R is the film radius; V_d also depends on the disk porosity, because of the pressure drop in the disk. We observed that the velocity of dark spot expansion also varies with ΔP, so we have decided to use a disk with a high porosity (100 μm), inside which the pressure drop is negligible. We have then fixed the applied pressure to 100 Pa. In these conditions, the film thickness reaches a quasiequilibrium before the jumps (Fig. 2), and several thickness jumps can be observed at the same pressure, 100 Pa.

The drainage velocity does not appear to depend on the bulk viscosity η, although Eq. (1) predicts that $V_d \sim 1/\eta$. However, the presence of the jumps did not allow us to make a precise enough analysis. Let us recall that, in semidilute solutions, the mesh size of the polyelectrolyte network ξ is such that $\xi = (AC_p)^{-1/2}$, where C_p is the polymer concentration as A is the distance between charges along the chain, provided A is smaller than the Bjerrum length l_b ($l_b = 7$ Å and $A = 4$ Å for the CMC used) [12]. This leads to ξ values indeed comparable with the jump size Δh which also varies as $C_p{}^{-1/2}$ as shown in the inset of Fig. 2. The total film thickness is close to an integer multiple of ξ:$h_n \sim n\xi$. The smallest observed film thickness corresponds to one mesh size. The film thicknesses before each transition are given in Table I.

A typical time dependence of the domain radius $r(t)$ is shown in Fig. 3. Here, a rim is formed during domain expansion, which becomes unstable at a critical radius (r_c) and breaks into droplets surrounding the domain (Rayleigh type of instability). This behavior is observed for all the films. Before the instability, $r(t)$ scales as $t^{1/2}$, and after the instability, $r(t)$ increases linearly with time. A similar behavior was observed by Reiter and co-workers during dewetting of PDMS layers [13]. We have analyzed at least seven sets of experimental data for each polymer concentration, and the results for h_n and r_c are reported in Table I. We also give the values of the exponents ν such as $r(t) \sim t^\nu$, the effective diffusion coefficients D and the velocities V such as $4D = dr^2/dt$ ($r < r_c$) and $V = dr/dt$ ($r > r_c$). Above 0.2 wt %, the rim instability begins at short times ($t < 0.30$ s), and we did not have enough points to perform a reliable analysis of the diffusive behavior.

Let us first discuss the diffusive behavior. In previous papers [8,14], we have compared the value of the effective diffusion coefficients with an expression derived by de Gennes for similar diffusivelike behavior observed during wetting of stratified drops [15]:

$$D_w = -\frac{h^3}{3\eta}\frac{\partial \Pi}{\partial h}. \qquad (2)$$

The relation between D and D_w is nontrivial [16], but as D, D_w is inversely proportional to the bulk viscosity η. The local shear rate can be estimated as $(dr/dt)/h$ and is of the order of 200 s^{-1}. For these shear rates, the viscosities vary

TABLE I. Film thicknesses, critical radii, exponents for $r(t)$, and effective diffusion coefficients for the different thickness transitions studied.

C_p (wt %)	h_3 (nm)	h_2 (nm)	h_1 (nm)	r_c (μm)	$r \sim t^{\nu}$		D (μm^2/s)
					$\nu_{r<rc}$	$\nu_{r>rc}$	
0.1		57.2 ± 0.8	30 ± 8	32 ± 3	0.65 ± 0.03	1.0 ± 0.03	464
0.15		53.4 ± 1.5	34 ± 2	23 ± 7	0.59 ± 0.04	1.01 ± 0.07	416
0.2		42 ± 3	24 ± 5	12 ± 1	···	0.94 ± 0.03	
0.25		42 ± 3	26 ± 0.8	11 ± 2	···	0.95 ± 0.05	
0.3	56 ± 2	38 ± 1		30 ± 2	0.57 ± 0.01	1.08 ± 0.04	317
		38 ± 1	23.5 ± 1	9 ± 1	···	1.10 ± 0.04	

by a factor of about 2.5 between $C_p = 0.1$ and 0.3 wt % and are still about 10 times larger than water viscosity (Fig. 1). The experimental values of D are, nevertheless, similar (Table I).

Let us now discuss the regime of constant velocity. Similar regimes are found in pure surfactant films for the expansion of very thin domains ($h \sim 5$ nm, Newton black film) on a thicker film ($h \sim 10$–50 nm, common black films) [14], and were described theoretically by de Gennes [17]. The rate of time entropy increase (counted per unit length) due to the friction at the contact line between the films containing n and $n + 1$ layers is $TdS/dt = k^{-1}\eta V^2/\theta$, where θ is the contact angle between the two films, $V = dr/dt$ is the velocity of the contact line (velocity of domain expansion), and k is a constant ($k \sim 1/60$). This entropy source is also equal to the work of the surface force per unit time and length: $TdS/dt = 2\gamma(\cos\theta - \cos\theta_e)V$, where θ_e is the equilibrium contact angle. In the case of small contact angles, the expansion velocity is then given by

$$V = k\gamma(\cos\theta - \cos\theta_e)\theta/\eta \sim k\gamma({\theta_e}^2 - \theta^2)\theta/\eta. \qquad (3)$$

Here θ_e is such that $\gamma_n = \gamma_{n+1}\cos\theta_e$. The surface tension σ_n of a film of thickness h_n is related to the disjoining pressure by [18]

$$\sigma_n = 2\gamma_n = 2\gamma_0 + \int_0^{\Pi(h_n)} h d\Pi, \qquad (4)$$

γ_0 being the bulk liquid surface tension and γ_n the air-film surface tension. The integral is a very small contribution to σ_n and $\gamma_n \sim \gamma_0$. One also has $\Delta\gamma = \gamma_n - \gamma_{n+1} \approx \Pi\Delta h/2$. Because this is a extremely small surface tension difference, θ_e is indeed small and such that $\Delta\gamma \sim \gamma_n(1 - \cos\theta_e) \sim \gamma_0{\theta_e}^2/2$. Therefore ${\theta_e}^2 \sim \Pi\Delta h/\gamma_0 \sim 5 \times 10^{-5}$, so that $\theta_e \sim 7 \times 10^{-3}$. The actual contact angles (dynamic contact angles) were measured by image analysis, and found to be smaller and similar for all samples: $\theta \sim 2 \times 10^{-3}$. By using these numbers and Eq. (3), we find $V \sim 0.01$ μm/s, much smaller than the measured velocities (see Fig. 4). It is to be noted that the appearance of the constant velocity regime coincides with the onset of rim instability. This suggests that the driving force is not the uncompensated Young force $\gamma(\cos\theta - \cos\theta_e)$, but the force linked to the gain in surface area after the instability, also proportional toγ: $dS/dt = 2\gamma\alpha V$, where $\alpha = (\text{rim surface-spheres surface})/\pi r^2$. In the classical Rayleigh instability, the ratio of rim radius to sphere radius is about 4/9, and the surface of the spheres is about half the surface of the rim [19]. If we assume that the difference between rim surface and spheres surface is similar here,

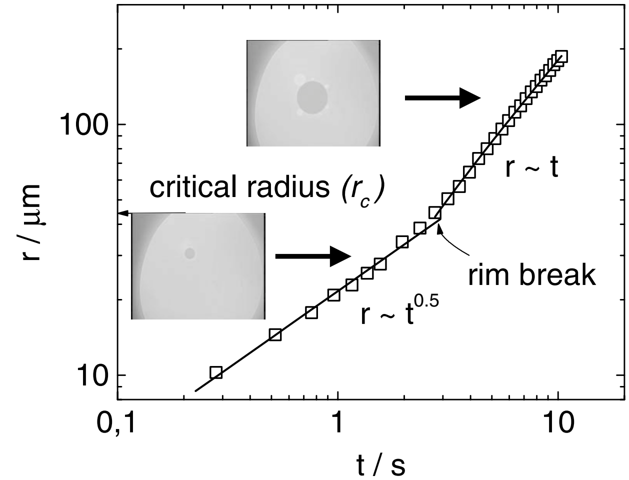

FIG. 3. Typical time dependence of the radius of domains; $C_p = 0.15$ wt %.

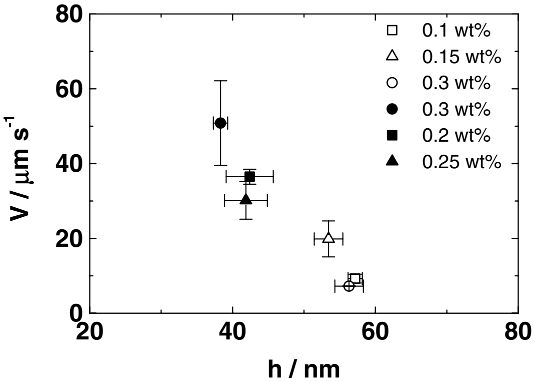

FIG. 4. Expansion velocity of the stratification domains for different film thicknesses and polymer concentrations.

and if we use typical observed values for the domain radius of 30 μm and for the drop diameter of 3 μm (at the onset of formation), we find a value of α of about 10^{-2} (for a number of spheres of a few unities). If we further assume that the viscous friction of the spheres on the film is small (pointlike friction) compared to the friction at the frontier between thin and thick film (wedge friction), we can evaluate the velocity by $V = k\gamma_0\theta\alpha/\eta$. We then find $V \sim 2\ \mu\text{m/s}$, much closer to the experimental values. Of course, our assumptions are very crude, but they account for the simultaneity of the regime change and the appearance of the rim instability.

Figure 4 shows that the velocity does not depend on bulk viscosity and increases when the film thickness decreases. These features cannot be explained unless one assumes that the local viscosity decreases and becomes close to that of water. In this way, we estimate rim velocities of the order of 20 μm/s, in agreement with the measured values.

Let us mention that the above discussion applies to the case where the films' surfaces do not move. When slippage occurs, the velocity is predicted to decrease with time: $r \sim t^{2/3}$ [13]. Here, ν is slightly larger than 0.5 in the initial regime (Table I). However, it is hard to conceive that a layer containing essentially water could slip on another water layer.

Let us finally compare our results with the earlier ones obtained with surfactants of charge opposite to the polymer (adsorbing conditions) [8]. In this case, the constant velocity regime was never observed, possibly because the surface tension in these systems is smaller than here. The diffusion coefficients are much smaller and depend on both the surfactant chain length and concentration: D is in the range 0.2–20 $\mu\text{m}^2/\text{s}$. This is equivalent to a local viscosity much larger than in nonadsorbing conditions.

In conclusion, our results suggest that the local viscosity in a thin film made from polymer semidilute solutions differs from the bulk viscosity. These films exhibit a stratification phenomenon, and the kinetics is seemingly not affected by the polymer concentration. One possibility is that the network cannot be formed when confined to a thickness of only a few times ξ, the network mesh size. The chains parallel to the film surface can be accommodated easily, but not those perpendicular to it. Because the mesh size is also the mean distance between polymer chains and is dictated by electrostatic interactions, the thickness of the film strata would not change under confinement, and the observation of the stratification is therefore not proof that the network is still present. Below a critical radius r_c, we found that the stratification kinetics is *diffusivelike,* and that, above r_c, the radius $r(t)$ of the dark spots grows *linearly* with time, a process accompanied by rim instability. We could explain the simultaneous occurrence of these features by surface energy considerations.

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