

## Relaxation Dynamics of Langmuir Polymer Films: A Power-Law Analysis

Francisco Monroy,\* Hani M. Hilles, Francisco Ortega, and Ramón G. Rubio

*Departamento de Química Física I, Facultad de Química, Universidad Complutense,  
Ciudad Universitaria s/n, E28040 Madrid, Spain*

(Received 30 May 2003; published 29 December 2003)

We report an experimental study on the mechanical relaxation of Langmuir films of a flexible polymer: polyvinylacetate, a good example of a two-dimensional polymeric system at good-solvent conditions. This study allows us to explore the dependence of the relaxation times and the surface viscosity on the concentration. In the semidilute regime, both dynamical properties follow well-defined power laws, which are in quantitative agreement with 2D reptation.

DOI: 10.1103/PhysRevLett.91.268302

PACS numbers: 83.10.Kn, 62.40.+i, 68.18.-g, 83.60.Bc

Reptation theory was proposed 30 years ago by de Gennes [1,2]. Since then, reptation has been one of the most successful concepts in explaining polymer dynamics in different contexts: physics, chemistry, and biology (see Ref. [3] for a modern review). The key concept underlying this theory is that a polymer chain diffuses in a dense network of entanglements formed by the surrounding chains. This motion takes place along a tube defined by the topological constraints imposed by the entanglements, resulting in a “snake-like” motion of each chain along a path that follows its own contour [1–3]. A huge experimental and theoretical effort has been devoted to understand the effect of entanglements and the true existence of tube reptation in 3D systems [3–5]. Many of the experimental results have been found to be consistent with the predictions of the reptation theory [3]. However, little attention has been paid to the dynamics of flexible polymers confined to two dimensions (2D) [6], e.g., Langmuir polymer films at good-solvent conditions. In this case, the chains adsorbed at the air/water interface (A/W) are assumed to be in a flat “pancake” conformation with most monomers adsorbed at the interface. Even though the dynamics of Langmuir polymer films is relevant to important practical processes (film deposition, lubrication, emulsion, and foam stability) [7], or in mimic systems of biological processes (transmembrane transport [8], breathing [9]), this particular surface dynamics is still poorly understood in their microscopic grounds. Moreover, the existence of entanglements in Langmuir polymer films is still today a matter of controversy and thus also the adequacy of the reptation model. Recent studies on the surface shear viscosity of Langmuir polymer films of poly(vinyl octanal acetal) measured by a canal viscometer [10] and of polyisoprene by an oscillating rheometer [11] show scaling when the chain size  $N$  is increased,  $\eta_s \sim N^1$ . Although this result is compatible with isolated chain Rouse-like self-diffusion, it must be due to the rather limited range of studied  $N$  and that the A/W interface is a poor solvent for both polymers. Recently, Granick *et al.* have analyzed the diffusion dynamics of isolated chains of polyethyleneglycol (PEG;

$M_w$  ranging from 2200–30 500 g/mol,  $N \sim 100$ –700) adsorbed onto a solid surface [12,13]. These experiments, performed by fluorescence correlation, reveal a power-law scaling of the center-of-mass diffusion coefficient,  $D \sim N^{-3/2}$ . This scaling exponent is compatible with reptation dynamics and stronger than the Rouse-like relation  $D \sim D_{\text{Rouse}} \sim N^{-1}$  observed for charged, and strongly adsorbed, semiflexible DNA chains obeying excluded volume statistics [14]. However, as early recognized by de Gennes [15], this simple scaling law is not itself a definitive piece of evidence of reptation in 2D systems. Other possible dynamical transport models, as *sticking reptation* or, more generally, reptation with interactions, or less cooperative scenarios, as are the amoebalike or the hovercraft motion of more or less individual pancakes, can also lead to the same mathematical result (see Ref. [13] for a recent review). It is in this context where the concentration dependence of the transport coefficients appears as a useful piece of information to discriminate between these different transport mechanisms. In fact, strong concentration dependencies are usually obtained for highly cooperative motions such as chain reptation with hydrodynamic interaction in good solvents [13,15]. However, if the excluded volume interactions are screened, the diffusion of a self-avoiding walk (SAW) chain through a distance comparable to its own size  $R_g$  takes place during the Rouse time,  $\tau_{\text{Rouse}} = R_g^2/D_{\text{Rouse}}$ , independently of the polymer concentration  $\Gamma$ . In the semidilute regime, and if chain entanglements are present, reptation motion emerges; the characteristic time depends then on both,  $N$  and  $\Gamma$ , following a remarkably simple scaling law independent of the dimensionality  $d$  [15]:

$$\tau_{\text{rep}}(\Gamma) \sim N^3 \Gamma. \quad (1)$$

The famous  $N^3$  law, hypothesized by de Gennes for polymer solutions of very long molecules ( $N \rightarrow \infty$ ) is still today a subject of controversy [3]. Most experimental work in 3D confirms stronger dependencies of the terminal relaxation times,  $\tau_{\text{rep}} \sim N^{3.4}$ , due to finite size effects, sliding entanglements, and interactions [3,15]. For 2D

systems, and, in particular, for Langmuir polymer films, it is customary to use power-law analysis to explain experimental equilibrium [16–18] and dynamic [19] results. These power laws are interpreted as an indirect signature of the existence of a correlation length  $\xi$  related to the size of the pancake segments between entanglement points, the blobs in 3D systems [7,16–19]. In fact, scaling is based on the notion that a meshlike network of entangled chains is characterized by a length scale  $\xi$  which represents the mean distance between entanglements, i.e., the size of a blob, or a pancake segment in 2D. For polymers long enough, this characteristic length of the semidilute state is independent on the chain length  $N$  ( $N \geq 100$ ) [3]. Furthermore, it decreases with the film polymer concentration  $\Gamma$  following a scaling law with the Flory exponent  $\nu$  [at  $d = 2$  and good-solvent conditions:  $\nu = 3/(d + 2) = \frac{3}{4}$ ] [1]:

$$\xi \sim \Gamma^{-\nu/(d\nu-1)} \sim \Gamma^{-3/2}. \quad (2)$$

It should be stressed that a finite thickness  $h$ , comparable to the pancake size but smaller than the chain size ( $h \sim \xi \ll R_F$ ), is necessary in order to have entanglements in semidilute Langmuir monolayers, i.e., strictly speaking, the considered polymeric system is not 2D, but quasi-2D. From a dynamical point of view, polymer motion in the semidilute regime is viewed as the surface diffusion of a chain. Two time scales appear in this scenario: a *short time scale* characterized by  $\tau_{\text{Rouse}}$ , i.e., the characteristic scale over which an unconstrained pancake of size  $\xi$  equilibrates, and a *long time* or *reptation scale* characterized by the reptation time,  $\tau_{\text{rep}}$ , over which the center of mass of the polymer chain diffuses through the tube. At this long-time scale, the whole chain moves a mean distance comparable to its radius of gyration  $R_G \sim aN^\nu$  ( $a$  being the monomer size). In the primitive model, de Gennes states that this cooperative motion takes a time  $\tau_{\text{rep}} = R_G^2/D_{\text{rep}}$ , governed by  $D_{\text{rep}}$ , the cooperative diffusion coefficient for the reptation motion. Surprisingly, the above-mentioned experimental results obtained by Granick's group for the diffusion dynamics of isolated pancakes of PEG at good-solvent conditions ( $D \sim N^{-3/2}$ ) seem to support the validity of the  $N^3$  law in two dimensions. Specifically, since  $R_G \sim N^{3/4}$  for the considered 2D-PEG system, it follows that  $\tau = R_G^2/D \sim N^3$ . The reptation picture must be modified if hydrodynamic interactions are considered [15]. In this case, the monomer mobility decreases and, as a consequence, the characteristic time for reptation motion strongly increases with polymer concentration. Now, for 2D chains at good-solvent conditions and if the  $N^3$  dependence is assumed, the  $\Gamma$  dependence of  $\tau_{\text{rep}}$  is given by [12,15,20]:

$$\tau_{\text{rep}}(\Gamma) \sim N^3 \Gamma^3. \quad (3)$$

Now, the strong dependence  $\tau_{\text{rep}} \sim \Gamma^3$  is in clear contrast with the weaker dependence  $\tau_{\text{rep}} \sim \Gamma$  predicted for SAW chains moving without hydrodynamic interaction [see Eq. (1)].

Therefore, in order to test for the  $\Gamma$  dependence of the relaxation dynamics of two-dimensional polymer solutions at good-solvent conditions, we report in this Letter an experimental study on the mechanical relaxation of Langmuir films of atactic polyvinylacetate (PVAc, Polysciences, Germany,  $M_w = 90\,000$  g/mol,  $N = 1045$ ,  $M_w/M_n \sim 1.04$ ). A few  $\mu\text{l}$  of a chloroform solution of the polymer (ca. 1 mM) were spread at the A/W interface with a Hamilton syringe.  $\Gamma$  is changed by subsequent additions of this solution. Times ranging 5–50 min were allowed for solvent evaporation and equilibration. Figure 1 summarizes the equilibrium properties of this system. The A/W interface has been found to be a good solvent for this polymer at room temperature ( $\nu = 0.78 \pm 0.03$  as obtained from the  $\Pi \sim k_B T / \xi^2 \sim \Gamma^{2\nu/(2\nu-1)}$  dependence in the semidilute regime), i.e., the system is viewed as a 2D solution of flexible chains in extended conformation [21,22]. The overlapping concentration was found at  $\Gamma^* = 0.15$  mg/m<sup>2</sup> ( $\Pi^* = 0.5$  mN/m), corresponding to the crossover between dilute and semidilute regimes. Since  $\Gamma^* = M_w / N_{av} \pi R_g^2$ , one obtains  $R_g = 18$  nm, in rough agreement with the value obtained from the Flory formula ( $2R_g = R_F = aN^{3/4} \sim 42$  nm with  $N = 1045$  and  $a = 0.23$  nm [23]). The semidilute regime extends from  $\Gamma^*$  to  $\Gamma^{**} = 0.95$  mg/m<sup>2</sup> ( $\Pi^{**} = 17$  mN/m), where the concentrated regime is entered (the film becomes a polymeric melt). Surface rheology has shown relatively low values of the elasticity modulus ( $\varepsilon \sim 0$ –25 mN/m) and very high values of the dilational viscosity  $\kappa$  in the semidilute regime [24]. These parameters are characteristic of a very viscous 2D gel. This behavior makes this gel-like polymeric system suitable to study chain relaxation from mechanical deformation experiments. The experiments were performed in a Langmuir trough (KSV, Finland; total area  $A_0 = 243.8$  cm<sup>2</sup>). The stress relaxation  $\sigma(t)$  is recorded as a function of time  $t$  after a sudden uniaxial in-plane compression is performed with the barriers

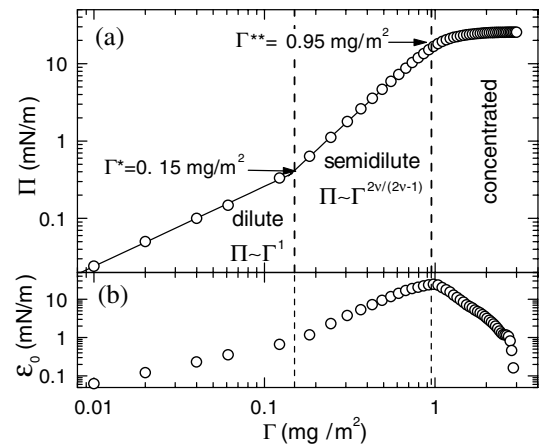


FIG. 1. (a) Equilibrium surface pressure  $\Pi$ - $\Gamma$  isotherm of PVAc spread in a Langmuir film at  $T = 25.00 \pm 0.01$  °C. (b) Equilibrium elasticity  $\varepsilon_0 = \Gamma(d\Pi/d\Gamma)_T$  as obtained from the  $\Pi$ - $\Gamma$  isotherm plotted in (a).

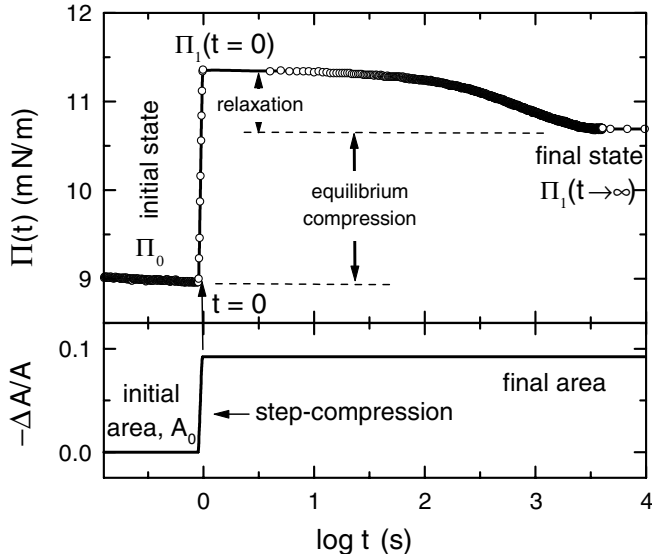


FIG. 2. Relaxation of the surface pressure in a typical step-compression experiment of a Langmuir film of PVAc ( $\Gamma = 0.5 \text{ mg/m}^2$  at  $25^\circ\text{C}$ ; surface dilation:  $-\Delta A/A = \Delta\Gamma/\Gamma = 0.092$ ). Any relaxation curve whose final state  $\Pi_1(t \rightarrow \infty)$  was different than the one corresponding to the equilibrium isotherm in Fig. 1(a) was rejected.

[24,25]:

$$\sigma(t) \equiv \Delta\Pi(t) = \Pi_1(t) - \Pi_0. \quad (4)$$

Here, the surface pressure (after the compression)  $\Pi_1(t) = \gamma_0 - \gamma$  ( $\gamma$  being the surface tension and  $\gamma_0$  that of the bare subphase) relaxes with respect to its initial value in the unperturbed state  $\Pi_0$  (see Fig. 2). Since ca. 2 s are necessary to perform a compression, the  $\sigma(t)$  measurements are limited to  $t > 5$  s. The compression ratio was adjusted at a 9.2% of the initial area  $A_0$ . It was checked that, at this strain, the viscoelastic response is linear [26] and the signal-to-noise ratio of the recorded signal high enough (see Fig. 2).

We have performed relaxation experiments at 20 different surface concentrations  $\Gamma$  ranging from the dilute regime to the concentrated one. No stress relaxation was observed in the dilute regime [ $\sigma(t) = \text{const}$  at  $\Gamma < \Gamma^* = 0.1 \text{ mg/m}^2$ ]. This points out that no slow *collective* motions exist when the polymer chains remain isolated. At higher  $\Gamma$  ( $\geq \Gamma^*$ ) a nice exponential-like relaxation is observed:

$$\sigma(t) = \sigma_0 e^{-t/\tau}. \quad (5)$$

In this equation,  $\tau$  is the relaxation time, and  $\sigma_0$  is the amplitude of the relaxation, which can be obtained from the raw  $\Pi(t)$  data (see Fig. 2) as  $\sigma_0 = \sigma(t=0) = \Pi_1(t=0) - \Pi_1(t \rightarrow \infty)$ .

Figure 3 shows the exponential character of three of the experimental relaxation curves, as expected from the linear-response theory of viscoelastic fluids at small strains.

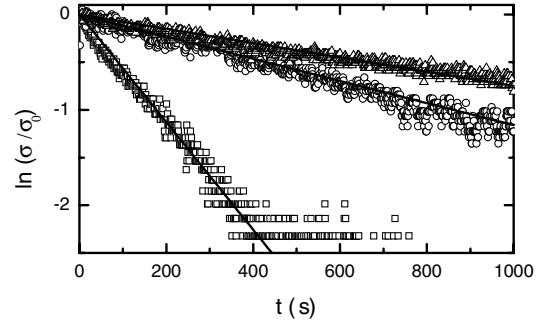


FIG. 3. Stress-relaxation curves of PVAc monolayers at  $T = 25^\circ\text{C}$  and at  $\Gamma = 0.3$  ( $\square$ ),  $0.6$  ( $\circ$ ), and  $0.8 \text{ mg/m}^2$  ( $\triangle$ ). The relaxation times  $\tau$  are obtained from the slopes of these linearized  $\ln(\sigma/\sigma_0)$  vs time plots.

From the slope of these plots, the relaxation times can be easily obtained. The viscoelastic moduli  $\varepsilon$  and  $\kappa$  can be also calculated as [25]:

$$\varepsilon = -\frac{\sigma_0}{\Delta A/A}, \quad \kappa = -\frac{\sigma_0}{\Delta A/A} \tau = \varepsilon \tau. \quad (6)$$

Here, the dilational elasticity  $\varepsilon$  represents the instantaneous elastic response of the film, and the dilational viscosity  $\kappa$  is the responsible of its friction delay.

Figure 4 shows the  $\Gamma$  dependencies of the relaxation time and the dilational viscosity. These plots show a crossover from an individual-like behavior to a strong  $\Gamma$  dependence just at  $\Gamma = \Gamma^*$ . The mechanical-relaxation time follows a power-law  $\tau \sim \Gamma^{3.20 \pm 0.01}$ , in very good

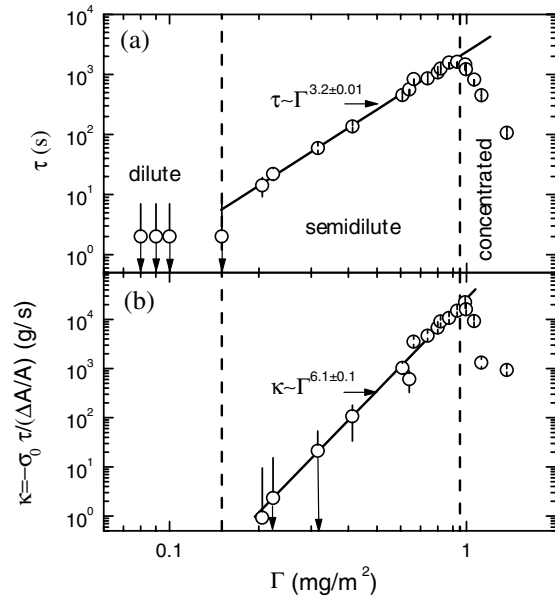


FIG. 4. (a) Power-law behavior of the experimental relaxation times obtained from the mechanical relaxation experiments of the PVAc films. Arrows indicate that there is no experimental accuracy for the relaxation times lower than some seconds; the true value could be lower yet. (b) Power-law behavior of the dilational viscosity as obtained from the relaxation times and amplitudes [see Eq. (7)].

agreement with the theoretical prediction for 2D reptation in semidilute solutions at good-solvent conditions [see Eq. (3)]. The molecular mobility at  $\Gamma^*$  is expected to be  $D_0^* = k_B T B = k_B T / 6\pi\eta_0 R_F \sim 10^{-8}$  cm<sup>2</sup>/s ( $R_F = 2R_g = 36$  nm,  $D_{\text{Rouse}} \sim D_0^*/N \sim 10^{-11}$  cm<sup>2</sup>/s), thus the relaxation time of one individual chain moving a distance equal its own size is  $\tau^* = R_F^2/D_{\text{Rouse}}^* \sim 1$  s, also in rough agreement with the data in Fig. 4(a). The dilational viscosity [Fig. 4(b)] is below the experimental sensitivity in the dilute regime. In the semidilute regime, it strongly grows as  $\kappa_0 \sim \Gamma^{6.1 \pm 0.1}$ , in good quantitative agreement with the scaling prediction at good solvents [15] (for  $d = 2$ ):

$$\kappa_0 \sim \varepsilon \tau_{\text{rep}} \sim \frac{k_B T}{\xi^2} \tau_{\text{rep}} \sim N^3 \Gamma^6. \quad (7)$$

It must be stressed that other less cooperative scenarios than reptation in good-solvent conditions, such as ideal reptation or amoebalike motion, lead to weaker  $\Gamma$  dependencies of the viscosity; note that from Eq. (1), one has  $\kappa_0 \sim \varepsilon \tau \sim N^3 \Gamma^4$ .

As a final comment, we must remark that, in the concentrated regime, both the relaxation time and the dilational viscosity decrease strongly. Here, and as a consequence of the decrease of  $\xi$  with  $\Gamma$ , the blob size probably falls below a critical value to support enough entropic elasticity [see Fig. 1(b)]. As a consequence, the blob mobility increases, and both  $\tau$  and  $\kappa$  decrease [27]. From the present data, a general conclusion can be stated: The self-consistent set of power laws for the  $\Gamma$  dependence of the dynamical parameters  $\tau$  and  $\kappa_0$  derived from the reptation theory of semidilute 2D-polymer solutions at good-solvent conditions is compatible with the mechanical-relaxation behavior observed in Langmuir films of a flexible polymer, such as PVAc. This was the main and general objective stated in the introduction of this Letter: to find a piece of evidence for the compatibility of the polymer film dynamics with the  $\Gamma$  dependencies expected from the de Gennes theory. It is necessary, however, to clarify the scaling behavior of the dynamical properties in terms of the molecular weight and it will be the subject of future work.

This work was supported in part by MCyT under Grants No. BQU2000-786, No. BQU2003-1556, and No. MAT2003-1517, by UCM (Grant No. PR48/01-9886), and by CAM (Grant No. 07N/0028/2002). The authors have greatly benefited from discussions with D. Langevin and C. Radke on the existence of entanglements in 2D. H. M. Hilles is grateful to AECI for support.

\*Author to whom correspondence should be addressed.

Electronic address: monroy@quim.ucm.es

[1] P.G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, NY, 1979); *Phys. Today* **36**, 33 (1983).

- [2] M. Doi and S.F. Edwards, *The Theory of Polymer Dynamics* (Clarendon, Oxford, 1986).
- [3] H. Watanabe, *Prog. Polym. Sci.* **24**, 1253 (1999).
- [4] T.T. Perkins, D.E. Smith, and S. Chu, *Science* **264**, 819 (1994).
- [5] J. Kas, H. Strey, and E. Sackmann, *Nature (London)* **368**, 226 (1994).
- [6] S. Granick, *Physics of Polymer Surfaces and Interfaces*, edited by I. Sanchez (Manning, New York, 1993).
- [7] D. Langevin, *Adv. Colloid Interf. Sci.* **88**, 209 (2000); J.E. Valentini *et al.*, *Ind. Eng. Chem. Res.* **35**, 434 (1996); E. Dickinson, *J. Chem. Soc. Faraday Trans.* **94**, 1657 (1998).
- [8] M. Heim and S. Jensen, *Nature (London)* **388**, 526 (1997).
- [9] R. Herold, R. Dewitz, S. Schürch, and U. Pison, in *Drops and Bubbles in Interfacial Research*, edited by D. Möbius and R. Miller (Elsevier, Amsterdam, 1998).
- [10] N. Sato, S. Ito, and M. Yamamoto, *Macromolecules* **31**, 2673 (1998).
- [11] C. Luap and W.A. Goedel, *Macromolecules* **34**, 1343 (2001).
- [12] S.A. Sukhishvili *et al.*, *Nature (London)* **406**, 146 (2000); S.C. Bae, F. Xie, S. Jeon, and S. Granick, *Curr. Opin. Solid State Mater. Sci.* **5**, 327 (2001).
- [13] S.A. Sukhishvili, Y. Chen, J.D. Müller, E. Gratton, K.S. Schweizer, and S. Granick, *Macromolecules* **35**, 1776 (2002).
- [14] B. Maier and O. Rädler, *Phys. Rev. Lett.* **82**, 1911 (1999).
- [15] P.G. de Gennes, *Macromolecules* **9**, 587 (1976); **9**, 594 (1976).
- [16] R. Vilanova and F. Rondelez, *Phys. Rev. Lett.* **45**, 1502 (1980).
- [17] M.W. Kim, S.N. Liu, and T.C. Chung, *Phys. Rev. Lett.* **60**, 2745 (1988).
- [18] M. Kawaguchi, *Prog. Polym. Sci.* **18**, 341 (1993).
- [19] R.A.L. Jones and R.W. Richards, *Polymers at Surfaces and Interfaces* (Cambridge University Press, Cambridge, England, 1999).
- [20] From the scaling analysis of the primitive reptation model  $\tau_{\text{rep}} \sim R_F^d (\Gamma/\Gamma^*)^m \sim N^{vd+m(vd-1)} \Gamma^m$ . If the excluded volume interaction is assumed to be screened out within each blob, the former law can be compared with Eq. (1)  $\tau_{\text{rep}} \sim N^3$ , and then  $m = (3 - vd)/(vd - 1)$ . Thus, the  $\Gamma^m$  exponent is really tied to a particular  $N$  exponent.
- [21] K.H. Yoo and H. Yu, *Macromolecules* **22**, 4019 (1989).
- [22] F. Monroy, M.J. Esquinas, F. Ortega, and R.G. Rubio, *Colloid Polym. Sci.* **276**, 960 (1998).
- [23] *Polymer Handbook*, edited by J. Brandrup, E.H. Immergut, and E.A. Grulke (Wiley, New York, 1999), 4th ed.
- [24] F. Monroy, F. Ortega, and R.G. Rubio, *Phys. Rev. E* **58**, 7629 (1998).
- [25] N.W. Tschoegl, *The Phenomenological Theory of Linear Viscoelastic Behaviour* (Springer-Verlag, Berlin, 1989).
- [26] Nonlinear or shear-thinning-like effects have been observed only at surface dilations higher than 40% of the initial surface area,  $-\Delta A/A > 0.4$  (unpublished results).
- [27] Also note the absence of viscous drag at the concentrated regime, where solvent is fully excluded of the film.