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Long-Time Relaxation Dynamics of Langmuir Films of a Glass-Forming Polymer: Evidence of Glasslike Dynamics in Two Dimensions

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We have carried out an experimental study on the mechanical relaxation of Langmuir films of a glass-forming polymer, poly-(4-hydroxystyrene), a good example of a two-dimensional system made of condensed polymer coils (at poor-solvent conditions). This study allows us to explore the response functions of the film and the temperature and density dependencies of the relaxation time. The dynamical properties show glasslike features (non-Debye mechanical response and non-Arrhenius relaxation times) reconcilable within the frame of the mode-coupling model.

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Glasses have been produced by humans for more than 3500 years, but despite the technological significance of glass-forming materials, the glass transition (GT) still remains an open question in condensed matter physics (see Ref. [1]). For temperatures well above the glass transition one T_g, the material is a fluid with Arrhenius-like viscosity. As T is decreased approaching T_g from above viscosity increases dramatically. Recent experiments have shown rather that both the temperature and density play relevant roles in controlling the GT [2]. The mode-coupling (MC) model of Ngai [3] appears to be a general approach for describing the behavior of systems wherein the motion of the basic units is constrained by mutual interactions. The cooperative rearrangement region (CRR) concept [4], was introduced as a measure of the spatial scale in which the system shows dynamic homogeneity. It is largely accepted that the size of the CRR's is the order of $l \sim 1$ nm. Thus, samples with at least one dimension comparable to this size may lead to finite-size effects on GT. Such a situation could even prevent the existence of the GT, the system remaining in the fluid state at T lower than the bulky T_g.

Thin polymer films represent an attractive choice for testing these finite-size effects since their size in the z axis is of the order of a few nm (see Ref. [5] for a recent review), and the size of a CRR in that direction can become smaller than R_g (R_g being the radius of gyration of the molecule). In fact, a strong decrease of $T_g(h)$ well below the bulk glass transition $T_g(3\text{D}; h \to \infty)$ caused by thickness reduction has been reported in thin polymer films supported in nonadsorbing substrates, and in freely standing polymer films [5]. The T_g decrease seems to indicate that the presence of the interface increases the mobility of the polymer segments. The limiting case of extremely thin films ($h < R_g$) that is represented by polymer Langmuir films remains today as an experimental challenge, and also as a matter of theoretical controversy [6].

Recent work has provided evidence of 2D-glassy structural characteristics in colloid systems adsorbed on a solid [7]. Also some glasslike rheological features have been pointed out on polymer Langmuir films: emerging shear elasticity [8] and nontrivial divergence of the surface viscosity [9]. However, only the dependence of T_g with the films thickness has been extensively studied. To the best of our knowledge, this is the first work in which the dispersion function and the relaxation time are studied as a function of T and of the system's density. This is important since the most significant features common to glassy systems are related to their dynamical-mechanical properties, which can be easily obtained from experiments on the mechanical response after a small perturbation. In particular near T_g two important features are usually found in 3D systems: (i) non-Debye linear response functions and, (ii) non-Arrhenius T dependence of the relaxation times.

In order to test for glasslike dynamics in 2D we report in this Letter an experimental study on the mechanical-stress relaxation of Langmuir films of an amorphous glass-forming polymer: poly-(4-hydroxystyrene) (P4HS, Polysciences, Germany. $M_w = 10\,000$ g/mol; polydispersity $M_w/M_n = 2$; $T_g(3\text{D}) = 115\,^\circ\text{C}$, as determined by differential scanning calorimetry). In order to form a monolayer in the Langmuir balance (KSV MiniTrough, Finland), small aliquots (20 μL typically) of a tetrahydrofuran—benzene (5:1) solution of the polymer (ca. 1 mg/ml) were spread at the air/water (AW) interface. The aqueous subphase (distilled and deionized water from a Milli-Q-RG unit) was acidified at $p\text{H} = 2$(HCl Normex, Carlo Erba). The surface pressure Π ($= \gamma - \gamma_0$, γ being the surface tension of the monolayer, and γ_0 that of the bare subphase) was recorded as a function of the surface concentration, Γ. The temperature of the system was controlled by flowing water through the bottom of the trough. Figure 1 summarizes the equilibrium behavior of these films at the lowest temperature experimentally

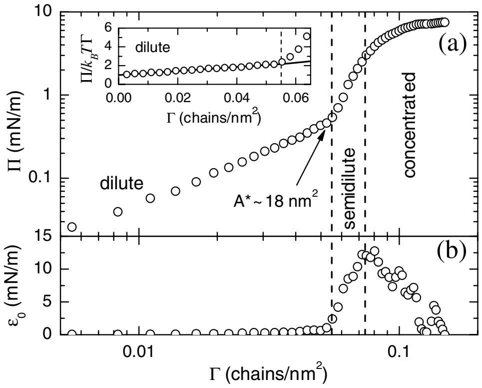

FIG. 1. (a) Equilibrium surface pressure Π-Γ isotherm of P4HS spread in a Langmuir film at $T = 6.84\,^\circ\mathrm{C}$. (b) Equilibrium elasticity $e_0 = \Gamma(d\Pi/d\Gamma)_T$ as obtained from the Π-Γ isotherm plotted in (a).

accessible, $T = 6.84$ C. Three different regimes are clearly shown: in the dilute region a virial coefficient equation describes the data (see inset at the bottom of Fig. 1). The semidilute regime can be described by a scaling law, with a value of the Flory exponent $\nu = 0.52 \pm 0.03$ (calculated from the $\Pi \sim \Gamma^{2\nu/(2\nu-1)}$ dependence of the isotherm in the semidilute regime) [10], which indicates that the A/W interface is found to be a poor-solvent for this polymer, i.e., each individual chain repeals the others, and adopts a condensed-coil conformation ($R_g \sim N^\nu \sim aN^{0.52}$, a being the monomer size, ca. 0.2 nm; $R_g \sim 2.4$ nm).

Film thickness in the semidilute and in the concentrated regimes (measured by ellipsometry) were found to be similar to the size of an isolated chain ($h \sim R_g \sim$ 2–3 nm) [11]. Thus, the Π–Γ isotherm in Fig. 1(a) can be interpreted as the concentration dependence of the osmotic pressure of a 2D distribution of P4HS disks—with radius $R_g = 2.4$ nm. At low Π ($\Gamma < \Gamma^* = 0.055$ chains/nm^2) the film behaves as a 2D diluted nonideal solution; here, the osmotic compressibility factor $Z = (\Pi/k_BT\Gamma)$ [inset in Fig. 1(a)] can be described by $Z = 1 + B_2(T)\Gamma$, with perfect-gas behavior at the zero density limit, $Z(\Gamma \rightarrow 0) = 0.998 \pm 0.002$, and a positive "repulsive" term with a second virial coefficient $B_2(T) = 21.5 \pm 0.5$ nm^2/chain. Concerning the equilibrium elasticity modulus, ε_0 [Fig. 1(b)], which determines the mechanical behavior of the film, it remains essentially zero at $\Gamma < \Gamma^*$, i.e., a quasiperfectly compressible 2D system where most space is *free space*. This two-body behavior lasts until $\Gamma = \Gamma^*$, where the system enters the semidilute regime. At this overlapping concentration, the pancakes touch each other; in fact, the value of the area occupied by each one at Γ^*, A^* defined as $A^* = (\pi R_g^2) = 1/\Gamma^* = 18$ nm^2 is equal to the value calculated from the coil dimensions, $\pi R_g^2 \sim 18$ nm^2. In the semidilute regime, many-body interactions become important, and a scaling description of the osmotic pressure, $\Pi \sim \Gamma^{2\nu/(2\nu-1)}$ is now possible. Also, collective entropic elasticity emerges, thus ε_0 increases up to a maximum value ca. 12 mN/m at $\Gamma = \Gamma^{**} = 0.072$ chains/nm^2. At $\Gamma > \Gamma^{**}$ the system becomes concentrated, i.e., the "surface solvent" is excluded of the film which becomes pure polymeric. At this state, and as a consequence of the strong decrease of the available free area, and of the conformational degrees of freedom of the coils, ε_0 monotonously decreases down to zero, i.e., the system supports less and less entropic elasticity. Therefore, it seems plausible to describe this system as a percolating 2D network of semirigid solid disks, which might start to become glassy at $\Gamma > \Gamma^*$. Because the solid disks are not monodisperse, noncrystalline solid arrangements are expected. Since the system is elastic, but not very rigid ($\varepsilon_0 \leq 15$ mN/m), it seems suitable to study chain relaxation from mechanical deformation experiments [11]. The experiments were performed in a Langmuir trough (KSV, Finland; total area $A_0 = 243.8$ cm^2). The stress-relaxation $\sigma(t)$ is recorded as a function of time t after a sudden uniaxial in-plane compression of the Langmuir film is performed with the barriers of the trough. The surface stress is defined as $\sigma(t) \equiv \Delta\Pi(t) = \Pi_1(t) - \Pi_1(t \rightarrow \infty)$ [11]. Here, after compression of the film the surface pressure relaxes with respect to its value in the final equilibrium state $\Pi_1(t \rightarrow \infty)$. The surface dilation was fixed at $-\Delta A/A_0 = -(A_0 - A)/A_0 = \Delta\Gamma/\Gamma = 0.092$, i.e., the film area A was rapidly reduced by 9.2% of the initial area A_0. It was checked that at this strain, the viscoelastic response is linear and the signal-to-noise ratio of the recorded signal high enough. At long enough times the system always recovers a final equilibrium state compatible with the equilibrium isotherm [Fig. 1(a)], i.e., $\Pi_1(t \rightarrow \infty) = \Pi_{\mathrm{eq}}(\Gamma_1 = 1.092\,\Gamma_0)$.

Since ca. 2 s are necessary to perform a compression with the barriers, the $\sigma(t)$ measurements are limited to $t > 2$ s. We have performed relaxation experiments at different surface concentrations ranging from the dilute regime to the concentrated regime and temperatures in the 6–60 °C range. No stress-relaxation was observed in the dilute regime at any temperature [$\sigma(t) =$ constant at $\Gamma < \Gamma^*$], pointing out that no-collective motions exist when the polymer coils remain isolated floating at the A/W interface. Figure 2 shows relaxation at higher Γs ($\geq \Gamma^*$). In practice the final equilibrium state is less than 60 min for this system. The relaxation curves can be fitted to a stretched exponential, the Kohlrausch-Williams-Watts (KWW) function

$$\sigma(t) = \sigma_0 \exp[-(t/\tau)^\beta], \tag{1}$$

where t is the relaxation time, σ_0 the amplitude of the relaxation; $\sigma_0 = \sigma(t = 0) = \Pi_1(t = 0) - \Pi_1(t \rightarrow \infty)$, and the stretching exponent β is related to the coupling parameter n of the coupling model by $\beta = 1 - n$ [3]. It lies within the range $0 \leq n \leq 1$ depending on the strength and *cooperativity* of the intermolecular interactions [3].

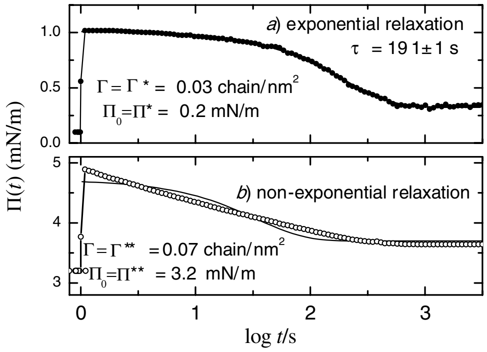

FIG. 2. Π-relaxation curves of P4HS films at $T = 6.84\,^\circ$C: (a) at the upper limit of the diluted regime, (b) at a concentrated state where connectivity between spheres is expected to be high. Negative values of the x scale correspond to the initial equilibrium state before compression of the film, Π_0. Straight lines represent best fits to an exponential relaxation Eq. (2).

Figure 2(a) clearly shows the existence of a near-exponential relaxation ($\beta = 1$) at the low density states ($\Gamma \sim \Gamma^*$). However, strong deviations of this Debye-like relaxation are observed at higher densities, $\Gamma > \Gamma^*$ [see Fig. 2(b) as a representative example]. Nonlinear fits of the experimental stress-relaxation curves to the KWW function were performed by the Marquardt-Levenberg algorithm with the amplitude σ_0 fixed at the experimental values. Figure 3 shows some representative results of these fits, the adequacy of Eq. (1) is confirmed by the linearized plot (see inset of Fig. 3). The nonexponential character of the relaxation curves at $\Gamma > \Gamma^*$ is clearly pointed out as an increasing curvature of the $\ln(\sigma/\sigma_0)$ vs t plot as Γ (or Π) increases. This result itself is very conclusive: to our knowledge, it is the first experimental evidence of nonexponential stress-relaxation of the long-time dynamics of Langmuir polymer films. Considering that the studied monolayer is a good candidate for 2D vitrification, this non-Debye mechanical response is a piece of experimental evidence of a typical glasslike dynamical feature in a 2D system.

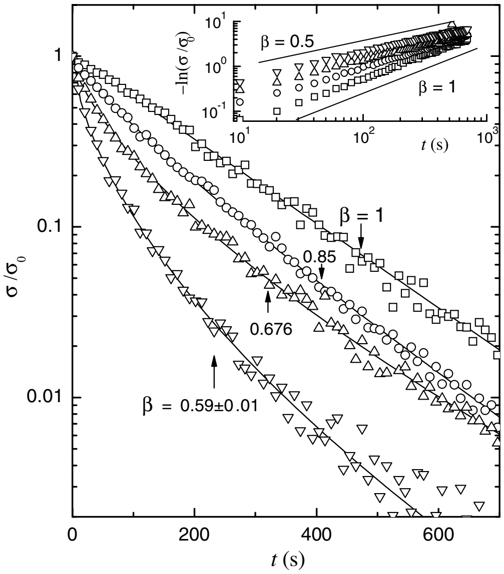

FIG. 3. Reduced stress-relaxation plots of Langmuir films of P4HS at $T = 6.84\,^\circ$C at $\Pi = \Pi^* = 0.2$ (□);1.0 (○); 2.0 (△); and 3.0 (▽) mN/m. The lines are the fits to a KWW function. The inset represents the linearized version of Eq. (1). The slopes of the straight lines give β, which decreases from $\beta = 1$ to a value close to 0.5 as the polymer density is increased.

Figure 4(a) shows that at low T the coupling parameter n continuously increases from a near-zero value at low densities up to a value of ca. 0.5, dealing with high cooperative motions ($\beta \sim 0.5$) at pressures corresponding to the concentrated regime ($\Pi > \Pi^{**} \sim 3$ mN/m), where the *molecular connectivity* is high enough. It is possible to draw about the parallelism between the osmotic pressure and the *molecular interaction strength* of the coupling model, where n increases as the strength does [3] [see Fig. 4(a)]. However, a Debye-like response ($n \sim 0$; $b \sim 1$) is always observed at higher temperatures ($T > 30\,^\circ$C).

The relaxation time τ decreases monotonously with Π following a simple power law $\tau \sim \Pi^{-1/2}$ [12]. Since the diffusive relaxation of an isolated coil of radius $R_g \sim 2.4$ nm is given by $t_{\text{dif}} = R_g^2/D \sim 0.1$ ms [13], the observed relaxation times ($\tau > 10\ \text{s} \gg t_{\text{dif}} \sim 1$ ms) must underlay some cooperativity, mainly at low T. Earlier experiments on the high-frequency viscoelastic relaxation of the system considered here ($\omega > 100$ Hz), pointed out a fast exponential-like motion [11]. As in this work, and also as a consequence of the increase of the restoring force of the percolating network of disks, in Ref. [11] τ also decreased with increasing Π ($\tau^* = 1.6$ ms at $\Pi^* \sim 0.2$ mN/m; $\tau^{**} = 0.15$ ms at $\Pi^{**} \sim 3$ mN/m). Within the perspective of the MC model, two relaxation times must exist in the glass: a microscopic one, τ_0, related to noncooperative motions of the CRR, and τ, the macroscopic cooperative time of the CRR's moving together. The first motion relaxes in a Debye-like fashion, while the macroscopic one follows the KWW function. Both time scales cross over at a time t_c; the continuity of the relaxation function at t_c leads to [3]:

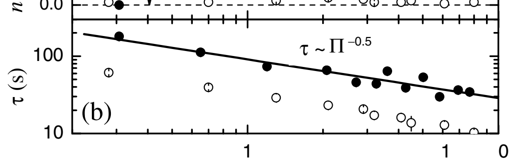

FIG. 4. Π dependence of (a) coupling parameter and (b) relaxation times of P4HS films at a low temperature state, (●) $T = 6.84\,^\circ$C; (○) at a high temperature one, $T = 49.1\,^\circ$C.

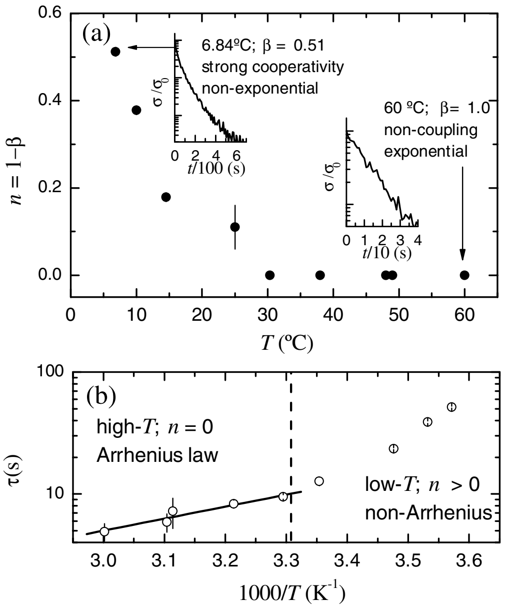

FIG. 5. (a) T dependence of the coupling parameter n of P4HS films at Γ^*. (b) Arrhenius plot of the stress-relaxation time.

$$t_c/\tau_0 = (t_c/\tau)^\beta = (t_c/\tau)^{1-n}. \qquad (2)$$

Considering that $\beta \sim 0.5$ and $\tau \sim 50$ s at $\Gamma \sim \Gamma^{**}$, and if one assumes $\tau_0 \sim \tau^{**} \sim 0.15$ ms as the relaxation time of an individual CRR at Γ^{**}, the calculated value of the crossover time would be of the order of $t_c \sim 2 \times 10^{-10}$ s [3], which explains why dynamical crossover is not observed in the present long-time relaxation experiments.

Finally, and in order to check for the effect of increasing cooperativity on the system dynamics, we performed relaxation experiments at constant Π ($\sim \Pi^{**} \sim 3$ mN/m) but increasing T (up to 60 °C), approaching T_g from below [remember that $T_g(\text{3D}) \sim 115\ °\text{C}$]. Stress-relaxation curves similar to those plotted in Fig. 3 were obtained, i.e., with higher curvature (smaller $\beta = 1 - n$) at lower T's [see insets in Fig. 5(a)]. Figure 5(a) shows that the coupling parameter monotonously decreases from a cooperativelike value $n \sim 0.5$ at low T (ca. 6 °C) down to $n \sim 0$ at about 30 °C, remaining close to zero, within the experimental uncertainty, at higher T's. Surprisingly, a break in the T dependence of the relaxation times is observed at the same temperature (see bottom of Fig. 5). In fact, an Arrhenius-like dependence of the relaxation time $\tau \sim \exp(E_a/RT)$ has been found at $T > 30\ °\text{C}$. The fitted value of the activation energy $E_a = 8.2$ kJ/mol ($\pm 16\%$) is relatively low ($\sim 3RT$), corresponding to a noncooperative motion ($n = 0$ at $T > 30\ °\text{C}$). When T decreases below 30 °C, $n > 0$ and a strong slowing down is shown by the relaxation time, which increases in a non-Arrhenius fashion [with apparent average $E_a \sim 40$ KJ/mol ($\sim 20RT$)]. For the present 2D-system, the two glasslike dynamical features appear together at $T \sim 30\ °\text{C}$, which can be interpreted as a signature of a two-dimensional T_g well below the corresponding T_g (3D).

To conclude, the present Letter presents several pieces of experimental evidence on glasslike long-time dynamics in Langmuir films of a glass-forming polymer. The reduced dimensionality (2D) promotes molecular mobility with respect to the bulk material yielding a finite reduction in T_g. Thus, 2D vitrification, appears as a reliable scenario for amorphous matter in 2D arrangements at temperatures low enough. The glassy state can be reached both by increasing Γ at constant T; or by decreasing the T at constant Γ.

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[12] For a compressed arrangement of spheres, the osmotic pressure Π can be conceived as the restoring force for internal motions. Naturally, collective dynamics becomes faster as Π increases.
[13] From the Stokes-Einstein relationship the self-diffusion coefficient of a bare sphere of radius R_g holds, $D = k_B T/6\pi\eta R_g \sim 10^{-9}$ cm^2/s.