Dynamic crossover to tricriticality and anomalous slowdown of critical fluctuations by entanglements in polymer solutions

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We have performed accurate dynamic light-scattering measurements near critical demixing points of solutions of polystyrene in cyclohexane with polymer molecular weight ranging from 200 000 to 11.4×10^6. Two dynamic modes have been observed, "slow" and "fast," which result from a coupling between diffusive relaxation of critical fluctuations of the concentration and viscoelastic relaxation associated with the entanglement network of the polymer chains. The coupling with the viscoelastic mode causes an additional slowdown of the critical mode on top of the uncoupled diffusion mode. By implementing crossover from the critical to the θ-point tricritical behavior for both static and dynamic properties, we are able to present a quantitative description of the phenomenon and obtain a scaling of the viscoelastic parameters as a function of the molecular weight.

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Critical phenomena in high-molecular-weight polymer solutions (PSs) differ from critical phenomena in simple fluids. In polymer solutions, the thermodynamic properties and the static correlations near the critical point of mixing are determined by a competition of two mesoscale lengths, namely, the correlation length of critical fluctuations of the concentration (tuned by the distance to the critical point) and the radius of gyration of the polymer molecules (tuned by the molecular weight) [1,2]. In the asymptotic vicinity of the critical point, the correlation length becomes much larger than the radius of gyration and the polymer solution exhibits Ising critical behavior. With the increase of the polymer molecular weight and, hence, of the radius of gyration, the range of asymptotic Ising critical behavior shrinks, ultimately yielding to θ-point tricritical behavior [2]. This competition of two mesoscales arises from a coupling between two different order parameters belonging to two different static universality classes, namely, one associated with phase separation and the other with self-avoiding-walk singularities of long polymer chains [3]. Such a competition of two mesoscales and, consequently, the crossover from critical to multicritical behavior are expected to be a general feature of phase transitions with coupled order parameters [4]. Hence, it is natural to expect that the dynamic critical behavior near the θ point will be affected by a coupling between two soft dynamic modes associated with the two order parameters [5].

In the present paper we report a study of dynamic correlations in near-critical solutions of polystyrene in cyclohexane at the critical volume fraction ϕ_c as a function of temperature and of polymer molecular weight, ranging from 200 000 to 11.4×10^6. Specifically, we have found that starting with a molecular weight of about 10^6, two effective dynamic modes emerge, which result from a coupling between two soft critical modes, a diffusion mode (association with the decay of critical fluctuations), and a viscoelastic mode (associated with entanglements of long polymer chains). Very close to the critical point, as expected, the slow mode becomes critical. However, we have found that this mode

being trapped by the entanglements, may become an order slower as compared to uncoupled critical slowdown. Moreover, the diffusivity, like static properties [2], exhibits a crossover from critical (Ising) to θ-point tricritical (mean field) behavior, becoming almost "classical" at the highest molecular weight. In fact, the coupling of two modes and the crossover to tricriticality are just two sides of the same physical phenomenon, caused by an interaction of two order parameters resulting in the emergence of a tricritical point.

Coupling between diffusion and entanglement has been discussed in the literature for a long time. It was predicted by Brochard and de Gennes [6] and was first detected with dynamic light scattering in noncritical polymer solutions by Adam and Delsanti [7] and later by Jian *et al.* [8] and Nicolai *et al.* [9]. Ritzl *et al.* [10] observed two dynamic modes near the demixing critical temperature in a polystyrene-cyclohexane solution with a polystyrene molecular weight $M_w = 0.96 \times 10^6$. Most recently, Tanaka *et al.* [5] observed two dynamic modes in near-critical solutions of high-molecular-weight nearly monodisperse polystyrene in diethyl malonate (explicitly shown for $M_w = 3.84 \times 10^6$ with a polydispersity index $M_w/M_n = 1.04$, where the subscripts w and n denote weight and number averaging). Our experiments reveal how the coupled critical dynamics in polymer solutions varies with increasing molecular weight. Moreover, making use of theoretical predictions previously developed for the static and dynamic crossover behavior from Ising to mean-field (tricritical) behavior, we are able to present a quantitative description of the phenomenon.

The original light-scattering setup as well as measurements for a moderate-molecular-weight sample PS1 ($M_w = 1.96 \times 10^5, M_w/M_n = 1.02, \phi_c = 0.066, T_c = 296.47$ K) have been described in a previous publication [11]. We have measured the intensity of scattering and the dynamic correlation function with a linear (PhotoCor-SP) [12] and a logarithmic (ALV-5000/E) correlator. The reduced distance of the temperature T to the critical temperature $T_c (T - T_c)/T$, varied from 0.1 to 10^{-5}. Four high-molecular-weight samples were
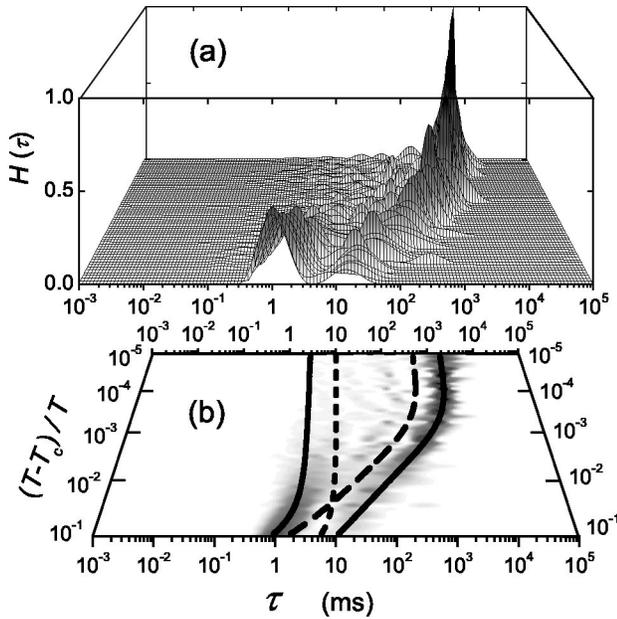
FIG. 1. (a) Equal-area representation of the relaxation-time distribution extracted from the intensity correlation function for the critical polystyrene-cyclohexane solution PS5 ($M_w = 11.4 \times 10^6, \theta = 30°$) as a function of the reduced temperature $(T - T_c)/T$. (b) Projection of the relaxation-time distribution plot. The solid curves represent the relaxation times τ_- and τ_+ of the effective modes as calculated from Eq. (2). The long-dashed curve represents the pure critical diffusion time τ_q as calculated from Eq. (3). The short-dashed curve represents the pure viscoelastic relaxation time τ_{ve}.

FIG. 2. Same as Fig. 1, but for PS4 ($M_w = 3.9 \times 10^6, \theta = 150°$).

studied: PS2, $M_w = 1.12 \times 10^6$ ($M_w/M_n = 1.06, \phi_c = 0.033, T_c = 303.09$ K); PS3, $M_w = 1.95 \times 10^6$ ($M_w/M_n = 1.04, \phi_c = 0.024, T_c = 304.31$ K); PS4, $M_w = 3.9 \times 10^6$ ($M_w/M_n = 1.05, \phi_c = 0.018, T_c = 304.80$ K); and PS5, $M_w = 11.4 \times 10^6$ ($M_w/M_n = 1.09, \phi_c = 0.011, T_c = 305.95$ K). The radii of gyration R_g of the polymers are 12 nm for PS1 (from a small-angle neutron scattering experiment [13]), 28 nm, 37 nm, 52 nm, and 89 nm for PS2, PS3, PS4, and PS5, respectively (extrapolated as $R_g \sim M_w^{0.5}$). We used two scattering angles, 30° and 150°, which correspond to the wave numbers $q = (4\pi n/\lambda)\sin^2(\theta/2)$ (n is the refractive index of the solution, λ is the wave length of light, and θ is the angle of scattering) equal to 7.27×10^{-3} nm^{-1} and 2.73×10^{-2} nm^{-1}, respectively. We have performed a Monte Carlo simulation [14] of the intensity of the multiple scattering for our samples and found that at $(T - T_c)/T > 10^{-5}$ double scattering accounts for almost the entire correction to static properties. The double-scattering correction to the dynamic correlation function at scattering angles of 30° and 150° is expected to be relatively small [15] and, therefore, has been neglected. The correlation function for PS1 was found to be a single exponential and no additional mode was detected [11]. For this sample the values of qR_g for the two scattering angles of 30° and 150° are 0.086 and 0.32, respectively. For all other samples with larger polymer molecules we have found the dynamic correlation function to be not a single exponential. The distributions $H(\tau)$ of decay times τ
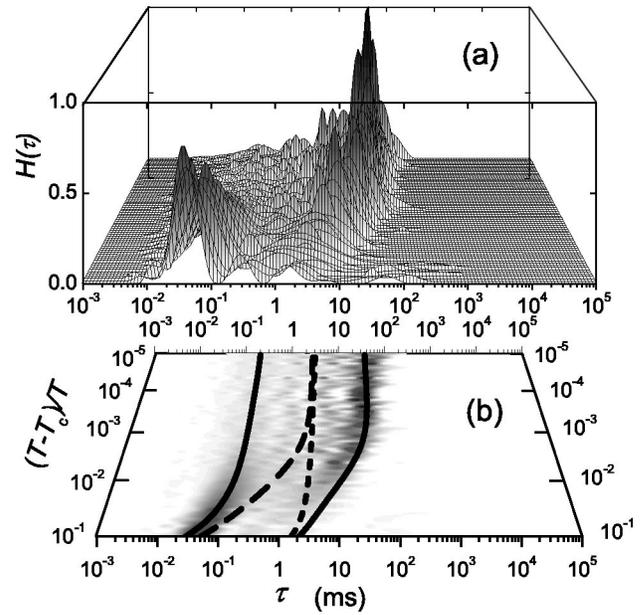
have been extracted from the correlation functions with the ALV-5000/E built-in regularization procedure.

We show in Fig. 1(a), as an example, a three-dimensional plot of this distribution for the sample PS5 and the angle of 30° ($qR_g = 0.65$) as a function of the distance to the critical temperature. All distributions are normalized by their integrals, thus the narrower the distribution, the higher the peak. One can clearly distinguish two modes that change significantly upon approach to the critical temperature. Far away from the critical temperature one can see a fast mode with a high peak and a slow mode with a low peak. Upon approaching the critical temperature, the intensity of the fast mode decreases and that of the slow mode rapidly increases. The shape of the corresponding dynamic correlation function in the near vicinity of the critical point is again close to a single exponential and the characteristic correlation time exceeds 1 s. Two other examples, PS4 at 150° ($qR_g = 1.42$) and PS5 at 150° ($qR_g = 2.43$), shown in Figs. 2(a) and 3(a), exhibit similar behavior with a more pronounced saturation of the intensity of the slow mode for larger qR_g.

We have interpreted these results quantitatively in terms of a coupling between two original soft modes, namely, a viscoelastic mode associated with entanglements of polymer chains and the diffusion mode associated with the relaxation of critical fluctuations. Neither of the two effective modes actually observed is a pure viscoelastic or a diffusion mode. Instead, the observed modes emerge as a result of the interaction of the original uncoupled modes. Following Tanaka *et al.* [5], we use the theory of Brochard and de Gennes [6] to represent the two effective dynamic modes with corresponding characteristic times: slow, τ_- and fast, τ_+. Then the normalized time-dependent intensity-correlation function $g_2(t)$ can be approximated as

$$g_2(t) = 1 + \left[f_+ \exp\left(-\frac{t}{\tau_+}\right) + f_- \exp\left(-\frac{t}{\tau_-}\right) \right]^2 \qquad (1)$$
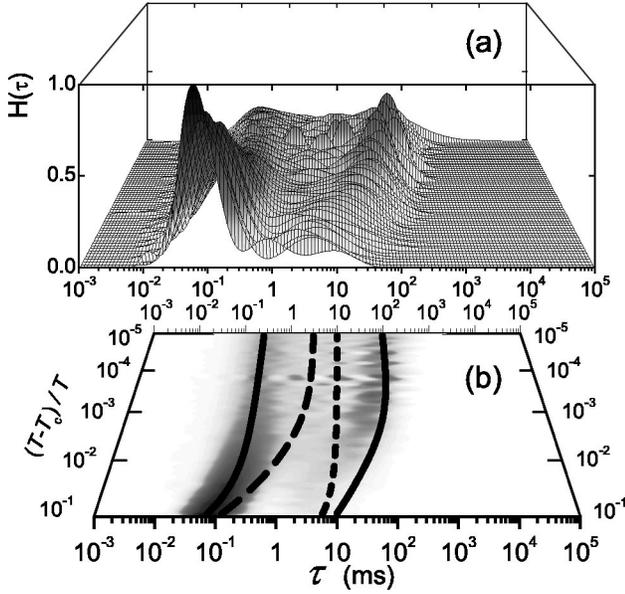
FIG. 3. Same as Fig. 1, but for PS5 ($M_w = 11.4 \times 10^6$, $\theta = 150°$).

with decay times

$$\frac{1}{\tau_\pm} = \frac{1 + q^2 \xi_{ve}^2 + \dfrac{\tau_{ve}}{\tau_q} \pm \sqrt{\left(1 + q^2 \xi_{ve}^2 + \dfrac{\tau_{ve}}{\tau_q}\right)^2 - 4\dfrac{\tau_{ve}}{\tau_q}}}{2\tau_{ve}} \quad (2)$$

and amplitudes $f_\pm = \pm[\tau_{ve}/\tau_\pm - (1 + q^2 \xi_{ve}^2)](\tau_{ve}/\tau_+ - \tau_{ve}/\tau_-)^{-1}$.

In Eq. (2), τ_{ve} is the q-independent viscoelastic relaxation time determined by entanglements of polymer chains, τ_q is the q-dependent diffusion relaxation time of critical concentration fluctuations, while ξ_{ve} is a mesoscopic viscoelastic length scale [16]. We have calculated the temperature dependence of the critical diffusion mode with the help of the dynamic scaling theory [17,18] accounting for a "background" (classical) contribution $D_0 q^2$ to the diffusion coefficient and for a crossover behavior of the "critical" (scaling) term

$$\tau_q^{-1} = \frac{k_B T}{6\pi\eta\xi} K(x) \left[1 + \left(\frac{x}{2}\right)^2\right]^{z_\eta/2} \Omega(q_D\xi) + D_0 q^2. \quad (3)$$

In Eq. (3) $K(x)$ is Kawasaki's function [17] $K(x) = 3/(4x^2)[1 + x^2 + (x^3 - x^{-1})\arctan(x)]$; $\Omega(q_D\xi)$ is a dynamic crossover function approximated as [19,20] $\Omega(q_D\xi) = 2/\pi \arctan(q_D\xi)$; and D_0 is the classical diffusion coefficient $D_0 = k_B T[1 + x^2](6\pi\eta_b q_D\xi^2)^{-1}$, where k_B is Boltzmann's constant, η is the viscosity of the solution, η_b is the regular part (background) of the viscosity; $x = q\xi$ with ξ being the static correlation length measured independently [2]; $z_\eta = 0.065$ is a universal dynamic scaling exponent; q_D is a characteristic cutoff wave number expected to be inversely proportional to the radius of gyration. It turned out that a good description of the experimental data is obtained if we adopt $q_D = \xi_{ve}^{-1}$, which indeed scales approximately as R_g^{-1}.
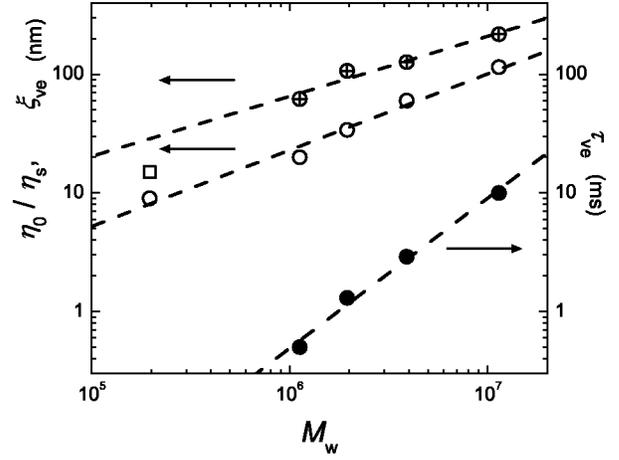

FIG. 4. Viscoelastic characteristic length ξ_{ve} (crossed circles, left axis), the background viscosity coefficient η_0 normalized by the solvent viscosity η_s (open circles, left axis; the square is from the measurements of Lao *et al.* [21]), and the relaxation time τ_{ve} (solid circles, right axis) as functions of the molecular weight M_w. The dashed lines show the slopes of 0.51, 0.64, and 1.3, respectively.

Asymptotically close to the critical temperature the classical term is negligible, the crossover function $\Omega(q_D\xi) \to 1$, and τ_q is described by the standard theory developed for simple fluids [17]. Incidentally, the static correlation length obeys the Ising asymptotic power law: $\xi \sim (T - T_c)^{-0.63}$ [2]. Further away from the critical temperature or with increase in the molecular weight, i.e., when R_g/ξ increases, $\Omega(q_D\xi)$ vanishes and τ_q is described by the classical diffusion term with the classical correlation length $\xi \sim (T - T_c)^{-0.5}$. We have found that accounting for crossover to tricriticality in Eq. (3) is necessary to obtain a quantitative description of the critical dynamics near the θ point. The shear viscosity η is expected to behave as $\eta \simeq \eta_0[(T - T_c)/T]^{-0.04}$ [17,18]. The coefficient $\eta_0(T)$ is proportional to $\eta_b(T)$ for which we assumed the same Arrhenius-type temperature dependence as that of the solvent, while treating $\eta_0(T = T_c)$ as an adjustable constant for each sample. With the crossover critical diffusion mode calculated from Eq. (3), we have obtained two q-independent parameters, namely, the viscoelastic time τ_{ve} and the viscoelastic length ξ_{ve}, by fitting two (experimentally obtained) dynamic modes to Eq. (2) simultaneously for both scattering angles.

The resulting temperature dependences of the characteristic times are shown in the projections of Figs. 1(a)–3(a) [denoted as Figs. 1(b)–3(b)]. As the viscoelastic time is proportional to η_s/T (η_s is the solvent viscosity) [22], it exhibits a slight temperature dependence. It is seen that neither the observed slow mode nor the observed fast mode can be associated with a pure critical diffusion mode or a pure viscoelastic mode. The assumption of a single relaxation time for the entanglements could be an oversimplification [6]. Indeed, in the range of strong coupling the observed modes are broadened. Nevertheless, it is clearly seen that far above the critical temperature the fast mode is closely associated with the diffusion, and the slow mode with the entanglements, but that near the critical point, the amplitude of the fast mode vanishes and the slow mode becomes critical. However, the

position of the slow mode is shifted to larger times with respect to the uncoupled critical diffusion as $\tau_- = \tau_q(1 + q^2 \xi_{ve}^2)$, whereas the position of the fast mode is shifted to shorter times with respect to the uncoupled viscoelastic time as $\tau_+ = \tau_{ve}(1 + q^2 \xi_{ve}^2)^{-1}$.

In Fig. 4, we have plotted the viscoelastic time τ_{ve}, the viscoelastic length ξ_{ve}, and the viscosity amplitude η_0 (normalized by the solvent viscosity η_s) as functions of the molecular weight. We have found that these parameters apparently diverge along the critical line in the limit of infinite molecular weight (θ-point limit) as approximately $M_w^{1.3}$, $M_w^{0.5}$, and $M_w^{0.6}$, respectively. We note that τ_{ve} scales with M_w weaker than the theoretical prediction, $M_w^{9/4}$, for the "disentanglement time" in θ solvents at overlap concentrations [6], while ξ_{ve} scales as the radius of gyration $R_g \sim M_w^{0.5}$ [3,13]. Experimental viscosity data are available only for $M_w = 1.96 \times 10^5$ [21]. The value of $\eta_0(T_c)$ obtained from our treatment of the light-scattering data is lower than that implied by the viscosity data. This fact, also reported in Ref. [11], requires further investigation.

The phenomenon of coupling of soft modes has also been observed in polymer blends [23] and in sheared polymer solutions [24]. In near-critical gas-liquid binary fluids, coupling of two diffusion relaxation modes associated with mass diffusivity and thermal diffusivity produce two effective dynamic modes, one of them becoming a critical mode [25]. The difference with polymer solutions is that in simple fluid mixtures the two original uncoupled modes belong to the same dynamic universality class. A more straightforward analog of the dynamic coupling in polymer solutions near the θ point is expected to appear in the ^{3}He-^{4}He mixture near its tricritical point.

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