

## Critical Dynamics of an Asymmetric Binary Polymer Mixture

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The critical dynamics near the consolute point of a relatively low molecular weight asymmetric critical binary polymer mixture is studied with dynamic light scattering. In contrast to a single exponential decay showing a critical slowing down, as has been reported for another low molecular weight polymer blend, we observe both a "fast" and a "slow" relaxation rate. The critical slowing down of the concentration fluctuations is seen to be contained in these two modes.

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The critical dynamics of small molecule binary mixtures has been studied in great detail, and the experimental results have been in remarkable agreement with the modern mode-coupling and renormalization-group theories of dynamic critical phenomena [1,2]. This work has demonstrated the crucial role played by the nondissipative coupling between the order parameter and the transverse part of the momentum density in the "critical slowing down" of the order-parameter fluctuations. The essential feature is that this coupling leads to a divergence in the order-parameter transport coefficient  $\Lambda_c$  very close to the critical temperature proportional to  $\xi^x$ , where  $\xi = \xi_0(T/T_c - 1)^{-\nu}$  is the static correlation length. The exponent  $x$  is both predicted and measured to be around 0.93, in contrast to the conventional Van Hove theory, where  $\Lambda_c$  is assumed to vary smoothly through the transition. The divergence of  $\Lambda_c$  will be apparent in the "softening" of the quantity  $D_c = \Lambda_c/S(0)$  near the critical point, where  $S(0)$  is the static susceptibility. In the asymptotic critical regime,  $D_c$  will scale as  $\xi^{-1.06}$ , while the conventional theory predicts  $D_c$  should scale as  $\xi^{-1.96}$  (Ref. [3]).

In contrast, the critical dynamics of binary polymer mixtures is a subject that is relatively new. It has been argued that for low molecular weight blends, the formalism for the binary fluid should remain valid, with the possibility of a crossover to dynamics dominated by conventional (non-mode-coupled) slowing down [4]. Dynamic light scattering (DLS) studies of low molecular weight polyisoprene/poly(ethylene-propylene) (PI/PEP) blends appear to agree with this prediction [5]. The composition fluctuation decay rate,  $\Gamma_c = D_c q^2$ , of the observed single exponential relaxation process gave values of the coefficient  $D_c$  that when reduced by the Kawasaki-Stokes form [6],  $D_c = k_B T / 6\pi\eta\xi^*$ , yielded a dynamic correlation length  $\xi^*$  that showed an increase near the transition temperature, in qualitative agreement with the behavior expected for the static correlation length  $\xi$ . Reducing  $D_c$  in this way amounts to ignoring the Van Hove background contribution to  $\Gamma_c$ , which has been shown to be small but present in small molecule binary liquids [2,7], and assuming that the Kawasaki-Stokes result, which is

predicted to hold only at temperatures close to  $T_c$ , is valid over the whole temperature range. When  $\xi^*$  was quantitatively compared with  $\xi$  as measured by small-angle neutron scattering (SANS), the values were only in agreement close to  $T_c$  (Ref. [5]), suggesting that  $D_c$  scales like  $\xi^{-1}$  only in the vicinity of the critical point, as expected. In all of these blends the mean degree of polymerization  $\langle N \rangle$  was roughly at or below the entanglement value  $N_e$  and the blends were fairly symmetric, with the critical composition  $\phi_c$  varying between 0.496 and 0.605.

In this paper we present DLS data for another relatively low molecular weight critical polymer mixture. The sample used in this study consisted of deuterated polystyrene (PSD) with  $M_w = 897$  and  $M_w/M_n = 1.09$ , and polybutadiene (PB) (20% vinyl, 80% 1,4) with  $M_w = 5.25 \times 10^3$  and  $M_w/M_n = 1.04$ . Mixtures of varying composition by weight were prepared and the phase diagram mapped using temperature jump light scattering [8]. The maximum in the measured coexistence curve at the transition temperature  $T_c = 41.2 \pm 0.1^\circ\text{C}$  coincides closely with the predicted critical PSD weight fraction of 0.75. A portion of the sample was used for SANS measurements of the static susceptibility and correlation length as a function of temperature. The details of these measurements are described elsewhere [8]. The measured correlation length as a function of temperature at the critical composition  $\phi_c$  is shown in Fig. 1 for reference. Both  $S(0)$  and  $\xi$  show typical mean-field behavior until roughly 10 K away from  $T_c$ , where the onset of a crossover to critical behavior is observed [8].

The scattering sample was sealed in a tube and placed in a quartz scattering cell containing an index matching fluid. The cell temperature was monitored with a calibrated platinum resistance thermometer and controlled to within  $\pm 50$  mK. Scattered laser light with a wavelength of 476 nm was collected with a photomultiplier tube at various scattering angles  $\theta$  ranging between  $30^\circ$  and  $120^\circ$ , corresponding to a scattered wave vector  $q$  between  $4.5 \times 10^4$  and  $2.3 \times 10^5 \text{ cm}^{-1}$ . Autocorrelation functions at various temperatures and angles were measured with a Brookhaven BI-2030 AT correlator and an ALV-5000 multiple tau digital correlator. The sample time and the

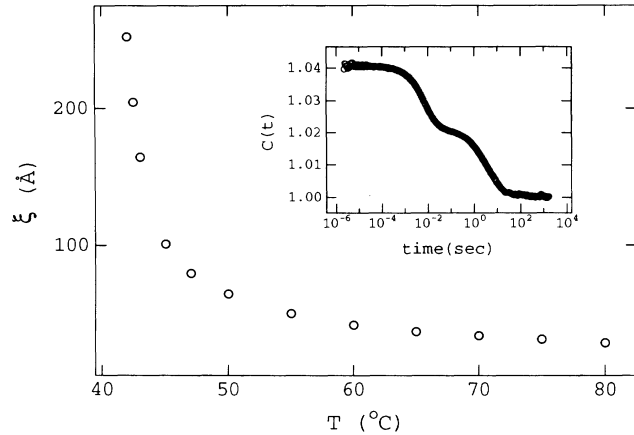


FIG. 1. The static correlation length as measured with SANS. Inset: The measured autocorrelation function vs  $\log(t)$  for  $T=70^\circ\text{C}$  at a scattering angle of  $100^\circ$ . The bimodality of the decay and the flat base line at long times are quite evident. Similar decays were observed at all temperatures and angles.

duration of each run were chosen such that a complete decay to a flat base line was observed in the long-time channels. The macroscopic viscosity  $\eta$  of the blend was measured as a function of temperature, controlled to within  $\pm 0.1$  K, and varied between 15 P at  $80^\circ\text{C}$  and 1500 P at  $41^\circ\text{C}$ , with a temperature dependence that was well described by the William-Landau-Ferry equation [9].

A striking feature of our data is the presence of two relaxation processes at all temperatures and scattered wave vectors. For a time-dependent structure factor of the form

$$S(q,t) = S_1(q,0)\exp[-\Gamma_1(q)t] + S_2(q,0)\exp[-\Gamma_2(q)t], \quad (1)$$

the normalized correlation function we obtain from the scattered light at a given temperature and scattering angle is

$$C(t) = 1 + \beta[S_1\exp(-\Gamma_1 t) + S_2\exp(-\Gamma_2 t)]^2. \quad (2)$$

A typical correlation function fit with Eq. (2) is shown in the inset of Fig. 1. The bimodality is quite evident, as is the flat base line at very long time. From the measured  $C(t)$  we identify both a “fast” and a “slow” mode, with the corresponding relaxation rates  $\Gamma_{\text{fast}}(q)$  and  $\Gamma_{\text{slow}}(q)$ . This is in marked contrast to the behavior reported in Ref. [5], where a single exponential decay was reported at all temperatures and scattering angles. The presence of these two modes is confirmed by DLS measurements on a hydrogenated polystyrene(PSH)/PB blend closely matched in molecular weight to the PSD/PB blend described here. We have ruled out the possibility that the slow mode is due to the presence of a mobile impurity such as dust, since the sample was carefully filtered, the decay rate is fairly monodisperse, and  $k_B T / 6\pi\eta D_{\text{slow}}$  is

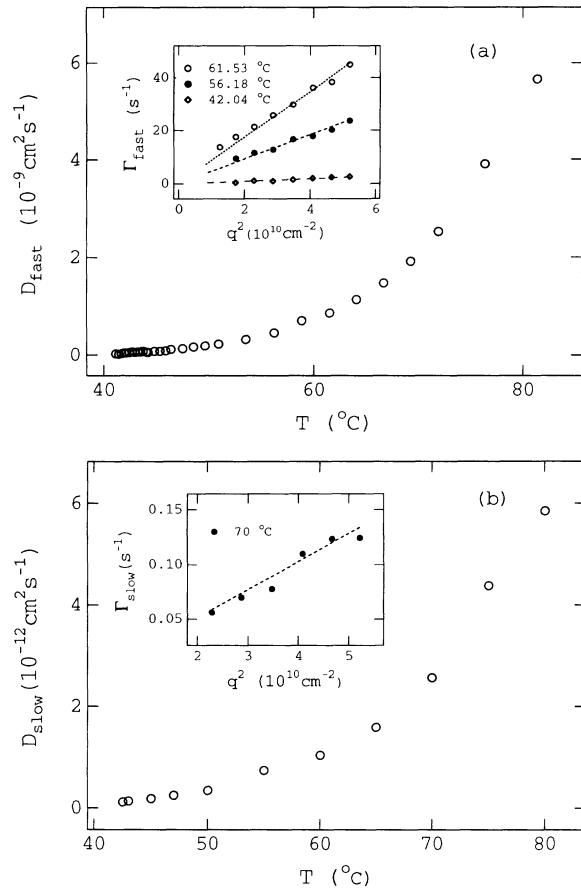


FIG. 2. (a) The temperature dependence of the fast diffusion coefficient  $D_{\text{fast}}$ . Inset to (a): The  $q$  dependence of the fast decay rate. (b) The temperature dependence of the slow diffusion coefficient  $D_{\text{slow}}$ . Inset to (b): The  $q$  dependence of the slow decay rate.

roughly 200 nm. The static structure factor  $S(q)$  measured with SANS is related to  $S_1$  and  $S_2$  in Eq. (1) by  $S(q) = S_1(q,0) + S_2(q,0)$ .

For a given temperature,  $C(t)$  was obtained at a number of different scattering angles to determine the  $q$  dependence of the two modes.  $\Gamma_{\text{fast}}$  as a function of  $q^2$  is shown in the inset of Fig. 2(a) for three different temperatures. A similar  $q$  dependence was observed at all temperatures, and to a good approximation a diffusion coefficient can be defined by the relation  $\Gamma_{\text{fast}} = D_{\text{fast}} q^2$ . The temperature dependence of  $D_{\text{fast}}$  determined from a linear least-squares fit of  $\Gamma_{\text{fast}}$  as a function of  $q^2$  (constrained to include the origin) is shown in Fig. 2(a). The  $q$  dependence of the slow mode is also well approximated by diffusive behavior, as shown in the inset of Fig. 2(b). The quantity  $D_{\text{slow}}$  was obtained in a similar manner as  $D_{\text{fast}}$ , and its  $T$  dependence is shown in Fig. 2(b). There was no significant change in  $D_{\text{fast}}$  or  $D_{\text{slow}}$  if the linear fit was not constrained to include the origin. Both  $D_{\text{fast}}$  and  $D_{\text{slow}}$  show a dramatic decrease as  $T$  decreases toward the

phase boundary. While most of this is due to the increase in the viscosity at lower  $T$ , the critical slowing down of the concentration fluctuations is also contained in these two coefficients.

In order to isolate the critical contribution, it is instructive to review the critical dynamics of a real binary fluid as outlined by Hohenberg and Halperin in Ref. [1], and Siggia, Halperin, and Hohenberg in Ref. [3]. The concentration fluctuations are described by the order parameter

$$c(\mathbf{x}) = [\langle \rho_A \rangle \rho_B(\mathbf{x}) - \langle \rho_B \rangle \rho_A(\mathbf{x})] / \langle \rho \rangle^2,$$

where  $\rho_A$  and  $\rho_B$  are the mass densities of the two species. The binary fluid has an additional long-wavelength diffusive mode  $u(\mathbf{x})$ , the "thermal fluctuation density," that is, a linear combination of  $\rho_A$ ,  $\rho_B$ , and the energy density  $e(\mathbf{x})$ . The quantity  $u(\mathbf{x})$  is orthogonal to  $c(\mathbf{x})$  in the sense that the equal-time cross correlation function of  $c$  and  $u$  vanishes. The static susceptibility matrix, with elements  $S_{ij}$  where  $i$  and  $j$  are either  $c$  or  $u$ , is then diagonal, with  $S_{cc}$  being the concentration susceptibility that diverges strongly at  $T_c$ . The "specific heat"  $S_{uu}$  has at most a very weak singularity near  $T_c$ . The two long-wavelength diffusive modes are the eigenvalues of the matrix  $\mathbf{D}q^2 = \Lambda \mathbf{S}^{-1} q^2$ , where  $\mathbf{D}$  is given by

$$\begin{pmatrix} D_c & D_1 \\ D_2 & D_u \end{pmatrix} = \begin{pmatrix} \Lambda_c & \Lambda' \\ \Lambda' & \Lambda_u \end{pmatrix} \begin{pmatrix} S_{cc}^{-1} & 0 \\ 0 & S_{uu}^{-1} \end{pmatrix}.$$

The quantity  $D_c = \Lambda_c / S(0)$  is the element that we seek to determine. The eigenvalues of  $\mathbf{D}$  are given by

$$\lambda^2 - (D_c + D_u)\lambda + D_c D_u - D_1 D_2 = 0, \quad (3)$$

with solutions  $\lambda_1 = D_{\text{fast}}$  and  $\lambda_2 = D_{\text{slow}}$ . Since the trace of  $\mathbf{D}$  is invariant under a change of basis, it follows that  $D_c = D_{\text{fast}} + D_{\text{slow}} - D_u$ , which relates the diffusion coefficient  $D_c$  to the measured fast and slow modes, and a background  $D_u$ . It also follows that  $S_1(q, 0)$  and  $S_2(q, 0)$  in Eq. (1) will be linear combinations of  $S_{cc}(q)$  and  $S_{uu}(q)$ , where the latter is taken to be independent of wave vector [3]. The total static structure factor  $S(q)$  measured with SANS is then proportional to a Lorentzian describing the concentration fluctuations with a constant background [8].

The coefficient  $\Lambda_u$  can be thought of as the "thermal conductivity" associated with the center-of-mass motion of the molecules. It will be extremely small compared to the "bulk" thermal conductivity of the blend, which will be dominated by the chain degrees of freedom. This represents a very fundamental difference between a small molecule binary fluid and a polymer blend. It is still reasonable to expect that  $D_u$ , like in a small molecule binary fluid [10], is essentially nonsingular at  $T_c$  and does not vary strongly with temperature. The value of  $D_u$  at  $T_c$  can be inferred from the fact that  $D_c$  should go to zero at  $T = T_c$ , and  $D_u(T_c) \approx D_{\text{fast}}(T_c) + D_{\text{slow}}(T_c)$  can be approximated from the values of  $D_{\text{fast}}$  and  $D_{\text{slow}}$  extrapolat-

ed to  $T = T_c$ , where we use the value of  $T_c$  measured carefully with temperature jump light scattering,  $T_c = 41.2^\circ\text{C}$ . We obtain  $D_u(T_c) \approx 3.75 \times 10^{-11} \text{ cm}^2/\text{s}$  in this way, and use the assumption that  $D_u$  does not depend strongly on  $T$  to deduce  $D_c$ .

From the fact that  $D_{\text{fast}} \gg D_{\text{slow}}$  and the form of the solutions to Eq. (3), it follows that  $D_{\text{slow}} \approx (D_c D_u - D_1 D_2) / (D_c + D_u)$ , and  $D_{\text{fast}} / D_{\text{slow}} \approx (D_c + D_u)^2 / (D_c D_u - D_1 D_2)$ . Although  $D_c$  is present in  $D_{\text{slow}}$  and will contribute to the slowing down of the slow mode, the contribution from off-diagonal terms makes it difficult to isolate the critical behavior in  $D_{\text{slow}}$ . The quantity  $D_{\text{fast}} / D_{\text{slow}}$  decreases as  $T \rightarrow T_c$ , as shown in the inset of Fig. 3(a). It is worth noting that the characteristic relaxation rates  $\Gamma_{\text{fast}}$  and  $\Gamma_{\text{slow}}$  separate into  $D_c q^2$  and  $D_u q^2$  only when the binary mixture is symmetric ( $\phi_c = 0.50$ ). If the mixture is asymmetric it is not possible, in general, to simply identify  $\Gamma_c = D_c q^2$  as the decay rate of a measured autocorrelation function. In our case, naively reducing  $D_{\text{fast}}$  or  $D_{\text{slow}}$  by the viscosity in an attempt to isolate the singular temperature dependence in the vicinity of  $T_c$  does not reveal any trace of the expected slowing down. In addition, although the dissipative coupling be-

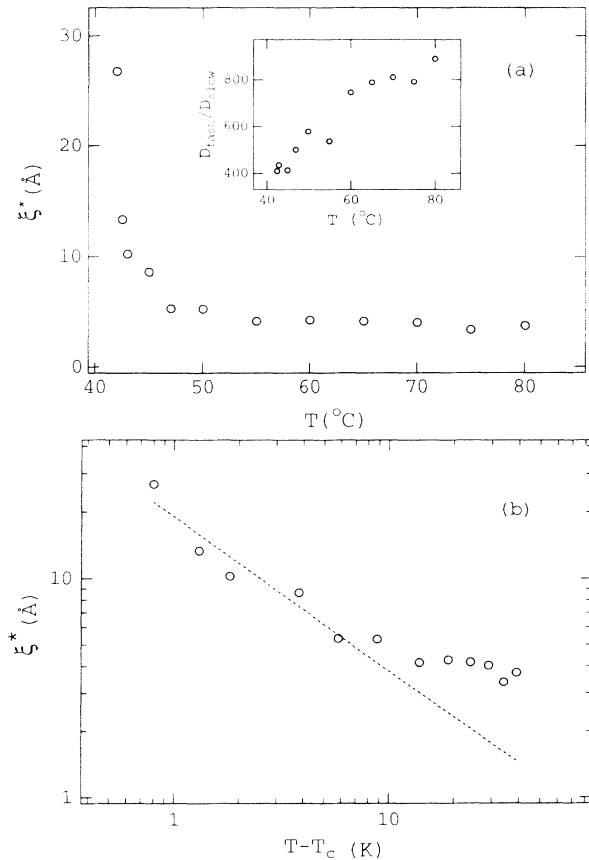


FIG. 3. (a) The quantity  $\xi^*$  as a function of temperature. Inset: The temperature dependence of  $D_{\text{fast}}/D_{\text{slow}}$ . (b) An asymptotic power-law fit of  $\xi^*$  vs  $T - T_c$ .

tween  $c$  and  $u$  is believed to have no effect on  $\Lambda_c$  in small molecule mixtures, the data suggest that  $(\Lambda')^2$  is roughly equivalent in size to  $\Lambda_c \Lambda_u$  in this case, and thus the influence of the coupling might need to be included [3].

The dynamic correlation length  $\xi^* = k_B T / 6\pi\eta D_c$  is shown in Fig. 3(a) as a function of temperature. The divergence as  $T \rightarrow T_c$  signals the critical slowing down of the concentration fluctuations. As can be seen by comparing Fig. 3(a) with Fig. 1,  $\xi^*$  is very different from the quantity  $\xi$  determined from SANS. This indicates that the experimental temperatures are still outside of the asymptotic scaling regime for the critical dynamics, and hence the Kawasaki prediction that  $D_c = k_B T / 6\pi\eta\xi$  is not yet valid. This is similar to what is found in Ref. [5], although in our case the disagreement is more pronounced. A fit of  $\xi^*$  by a power-law expression of the form  $(T/T_c - 1)^{-a}$  close to  $T_c$  [Fig. 3(b)] yields an exponent  $a = 0.7$ . True asymptotic critical behavior in the statics is in general only achieved for  $T/T_c - 1 < 10^{-3}$  (Ref. [11]), and this restriction is even more severe for the critical dynamics of binary fluids [2,12]. These observations suggest that the data are in a crossover regime between the Kawasaki mode-coupled prediction without corrections to scaling and the conventional Van Hove theory.

In summary, we have investigated the critical dynamics of an asymmetric critical polymer blend with dynamic light scattering. We observe two essentially diffusive decay rates, which we interpret as the "normal modes" of an asymmetric binary fluid [13]. The critical slowing down of the concentration fluctuations in the vicinity of  $T_c$  is consistent with a crossover between asymptotic mode-coupling and conventional behaviors. For blends of this type, however, our data suggest that the influence of the dissipative coupling between these two modes might need to be reconsidered.

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