Static and Dynamic Crossover in a Critical Polymer Mixture

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A model low-molecular-weight polymer mixture was studied as a function of temperature near the critical point by small-angle neutron scattering (SANS) and dynamic light scattering (DLS). SANS measurements reveal a crossover in the static susceptibility from mean-field to non-mean-field behavior at $T_x \cong T_c + 30\,°\mathrm{C}$, in quantitative agreement with the Ginzburg criterion. This crossover behavior is also reflected in the DLS experiments, which reveal mode-coupled critical dynamics far into the mean-field regime.

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It has long been appreciated that the equilibrium critical properties of binary mixtures of simple liquids fall into the Ising universality class. The dynamical critical properties have only been more recently established, with extensive theoretical and experimental evidence supporting the hypothesis that such mixtures belong to the same dynamical universality class as model H of Hohenberg and Halperin.[1] Key to the maturation of this field was the advent of mode-coupling theories[2] and the dynamical renormalization group.[3]

As was first appreciated by de Gennes,[4] binary mixtures (blends) of high-molecular-weight, flexible polymers also exhibit Ising-like static critical properties, although the long-ranged nature of the polymer-polymer interactions shrinks the Ising (i.e., non-mean-field) regime to a narrow range of reduced temperatures about the critical point,[4-6] $\epsilon \lesssim N^{-1}$. Here, N is the degree of polymerization of a symmetric polymer mixture and $\epsilon = (\chi_s - \chi)/\chi_s$, where $\chi = AT^{-1} + B$ represents the segment-segment interaction energy; A and B are system-specific constants, and χ_s corresponds to the thermodynamic stability limit. The existence of a Ginzburg parameter $\sim N^{-1}$ consistent with numerous experimental observations[7] of mean-field static exponents in high-molecular-weight polymer mixtures ($N \gtrsim 100$). Recently, however, Schwahn, Mortensen, and Yee-Madeira[8] have succeeded in observing the crossover in the static susceptibility from mean-field to Ising-like temperature dependence in a relatively high-molecular-weight ($N \sim 10^3$) polystyrene-polyvinylmethylether (PS-PVME) mixture, by conducting small-angle neutron-scattering (SANS) measurements near the critical point, $5 \times 10^{-4} \lesssim \epsilon \lesssim 3 \times 10^{-2}$.

The dynamical critical behavior of binary polymer blends, while largely unexplored experimentally, is potentially very rich.[9,10] Ultimately, on close approach to the critical point, the behavior should be that of model H, although the crossover to the nonclassical critical properties of model H can be quite complex. To discuss this crossover we focus on the collective (mutual) diffusion coefficient D_c, which can generally be written[1] as the ratio of an Onsager transport coefficient Λ to the concentration susceptibility $S(0)$: $D_c = \Lambda/S(0)$. The simplified description of a symmetric binary fluid embodied in model H highlights critical fluctuations of the order parameter (concentration field), as well as nonlinear interactions (mode couplings) of these fluctuations with fluctuations in the momentum density. Proper treatment of these fluctuations[1,3] leads to renormalizations of both Λ and $S(0)$. At high temperatures ($\epsilon \gtrsim 1$), however, such renormalizations are negligible and mean-field (Van Hove) theory applies. For polymer mixtures, the bare transport coefficient scales as[6,11] $\Lambda_0 \sim N_e/N$, where N_e is the number of segments between entanglements.[12] Hence, in the case of polymers sufficiently large to be well entangled, we have $\Lambda_0 \sim N^{-1}$, while for shorter chains obeying Rouse dynamics one sets $N \sim N_e$ to obtain $\Lambda_0 \sim 1$. Because the mean-field susceptibility of a blend scales as $N\epsilon^{-1}$, the expected behavior for $\epsilon \gtrsim 1$ is $D_{c,0} \sim N_e N^{-2} \epsilon$, which has recently been observed in high-molecular-weight mixtures.[13]

As the critical point is approached, singular contributions to Λ and $S(0)$ emerge, but not necessarily in the same range of reduced temperature. In particular, for $\epsilon \sim N^{-1}$ the susceptibility is expected to cross over to the Ising expression[14] $S(0) \sim N^{2-\gamma} \epsilon^{-\gamma}$, but the fluctuation contribution (Kawasaki approximation[1] with reptation estimate of the viscosity $\bar{\eta} \sim N^3/N_e^2$) to Λ is $O(N_e/N)$ smaller than Λ_0. Hence, in this regime D_c should scale as $N_e N^{\gamma-3} \epsilon^{\gamma}$. Note that for $\gamma = 1$ the mean-field expression $D_{c,0}$ is recovered. Finally, as ϵ is reduced to be of order $\epsilon \sim N_e^{(\gamma-\nu)^{-1}} N^{-(1+\gamma-\nu)/(\gamma-\nu)}$ the fluctuation contribution to Λ is expected to dominate and the following collective diffusion behavior is obtained (model-H behavior in Kawasaki approximation): $D_c = k_B T/6\pi\bar{\eta}\xi \sim N_e^2 N^{\nu-4} \epsilon^{\nu}$, where $\xi \sim N^{1-\nu} \epsilon^{-\nu}$ is the composition correlation length. In spite of arguments such as that outlined above, which suggest that the dynamical crossover behavior of polymer blends should be much richer than in simple fluid mixtures, we are not aware of any systematic studies to date. In the present Letter, we report on such a study of static and dynamic critical phenomena in a model polymer mixture.

The narrow-molecular-weight-distribution ($M_w/M_N < 1.05$) samples of polyisoprene (PI) and partially deuterium-labeled poly(ethylene-propylene) (PEP) were prepared and characterized using standard procedures; $N_{\mathrm{PI}} = 29$ and $N_{\mathrm{PEP}} = 73$, where N refers to the weight-average degree of polymerization. The associated binary phase diagram was approximated, based on cloud-point measurements as reported elsewhere.[15] To a close approximation the apex of the two-phase boundary, which we identify as the critical temperature, $T_c \cong 38\,°\mathrm{C}$, coincides with the predicted[9] (mean-field) critical volume fraction of PI, $\phi_c = 0.61$. All experiments discussed in this Letter were carried out at this (critical) composition. Also, N_e for PEP and PI are 23 and 74, respectively, so that $\langle N_e \rangle \cong \langle N \rangle$, where $\langle N \rangle = (N_{\mathrm{PI}} N_{\mathrm{PEP}})^{1/2}$.

Small-angle neutron-scattering (SANS) experiments were conducted on a low-q diffractometer (LQD) at the Manuel Lujan Jr. Neutron Scattering Center at the Los Alamos National Laboratory using a pinhole geometry. Descriptions of the LQD instrument and time-of-flight–SANS data-reduction methods are presented elsewhere.[16] The scattering specimen was prepared by injecting the homogeneous ($T > 40\,°\mathrm{C}$) mixture into a 1-mm-thick by 2-cm-diam cylindrical quartz cell, which was then sealed under vacuum. The sample temperature was controlled to within $0.15\,°\mathrm{C}$ and monitored with two thermocouples in contact with the quartz cell. The azimuthally symmetric SANS data were reduced to the one-dimensional form of intensity $I(q)$ versus scattering wave vector, $q = 4\pi\lambda^{-1}\sin(\theta/2)$, where λ and θ are the neutron wavelength and scattering angle, respectively, using established procedures.[16] Finally, the incoherent scattering contribution was subtracted from the total measured intensities based on the angle-independent scattering obtained from the pure PI and PEP components.

Dynamic-light-scattering measurements were conducted with a cylindrical cell that was immersed in a thermostated ($\pm 0.1\,°\mathrm{C}$) index-matching liquid. Scattered light ($\lambda = 488$ nm) was collected using a photomultiplier and analyzed with a Brookhaven BI2030 correlator. Intensity autocorrelation functions were obtained at various angles between 30° and 150° and as a function of temperature over the range from $38.2 < T < 170\,°\mathrm{C}$. Selected autocorrelation functions were analyzed by a Laplace inversion method, yielding spectra of decay rates, which established the existence of a single narrow component, proportional to q^2, at all temperatures. Accordingly, the correlation functions were modeled with single exponential functions from which we obtained decay rates $\Gamma = q^2 \Lambda(q)/S(q)$. For the present case [$q\xi < 1$ and in the mode-coupled regime (see below)],

$$\Gamma = q^2 k_B T/6\pi\bar{\eta}\xi = q^2 D_c\,. \tag{1}$$

We have measured the mixture shear viscosity $\bar{\eta}(T)$ on a Rheometrics RS800 fluids rheometer and modified Γ by the factor $\bar{\eta}(T)/T$ to isolate the critical-temperature dependence in $\Gamma\bar{\eta}/T$.

The temperature dependence of the static susceptibility, $S(0) \sim I(0)$, and correlation length ξ have been extracted from the SANS results based on the Ornstein-Zernike relationship,[9]

$$I(q) = I(0)(1 + q^2\xi^2)^{-1}\,, \tag{2}$$

where $I(0) \sim \epsilon^{-\gamma}$ and $\xi \sim \epsilon^{-\nu}$. Several representative

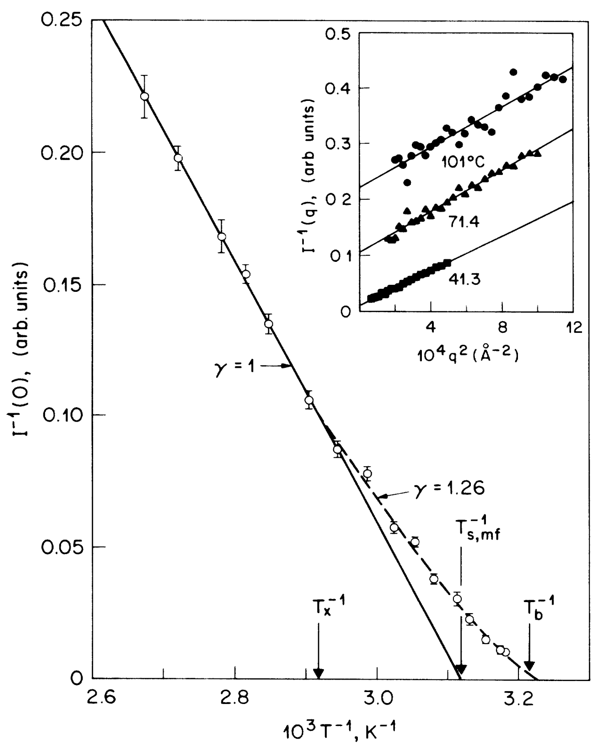

FIG. 1. Inverse susceptibility plotted vs inverse temperature. $I(0)$ values were obtained by extrapolating SANS data, assuming an Ornstein-Zernike form, as illustrated in the inset. Deviation from linearity at T_x^{-1} signifies the crossover from mean-field ($\gamma = 1$) to non-mean-field behavior. The dashed curve was fitted to the non-mean-field data by *assuming* an Ising ($\gamma = 1.26$) exponent and adjusting the stability temperature. T_b represents the independently determined binodal temperature and $T_{s,\mathrm{mf}}$ is the mean-field stability temperature.

SANS results are plotted as $I^{-1}(q)$ vs q^2 in the inset of Fig. 1. For the purpose of identifying the static crossover from mean-field to Ising behavior we presently focus our attention on the temperature dependence of $I(0)$; we note, however, that the same conclusions are derived from an analogous analysis of $\xi(T)$, where $28 \leq \xi \leq 122$ Å in the SANS experiments.

$I^{-1}(0)$ is plotted versus T^{-1} in Fig. 1 for $41 < T \leq 101\,°\mathrm{C}$; below 41 °C, ξ increases beyond the resolution of the SANS instrument, preventing the quantitative application of Eq. (2). For mean-field behavior ($\gamma=1$), $I^{-1}(0)$ should be linear with T^{-1}, while Ising (non-mean-field) behavior should result in a nonlinear dependence of the inverse susceptibility on inverse temperature. Both regimes are clearly evident in Fig. 1. For $T > T_x \cong 70\,°\mathrm{C}$, $I^{-1}(0) \sim T^{-1}$ from which we have determined[9] $\chi = 26.5T^{-1} - 0.0367$. Below T_x, $I^{-1}(0)$ systematically lies above the linear extrapolation from the high-temperature (mean-field) regime, in agreement with $I^{-1}(0) \sim (T_s^{-1} - T^{-1})^{1.26}$ where a best fit is obtained (assuming $\gamma = 1.26$) with $T_s = 36.6\,°\mathrm{C}$ as indicated by the dashed curve. The crossover temperature T_x is specified by the intersection of the solid and dashed curves.

Two additional temperatures are identified in Fig. 1. Extrapolation of the linear regime (mean-field) data to infinite susceptibility provides an estimate of the mean-field stability limit, $T_{s,\mathrm{mf}} = 48.1\,°\mathrm{C}$. The precise location of the equilibrium phase boundary or binodal temperature T_b for the SANS specimen was determined to be $T_b = 38.2 \pm 0.1$ using light-scattering measurements. Thus, extrapolation of the susceptibility data in the non-mean-field regime based on an Ising exponent ($\gamma = 1.26$) places the stability temperature slightly under the binodal temperature. As described below, the dynamic data indicate that within experimental error ($\pm 0.3\,°\mathrm{C}$) $T_s \cong T_b$, i.e., $\phi \cong \phi_c$. This implies that the non-mean-field static data should be modeled with a more complete crossover function, rather than the asymptotic Ising relationship, which would increase the extrapolated value of T_s. However, because the non-mean-field region for this system is so large, $T_x - T_c \cong 30\,°\mathrm{C}$, a more precise determination of the critical conditions is not necessary for accomplishing our present goals. The reduced crossover temperature based on $\chi(T)$ is $\epsilon_x = (\chi_{s,\mathrm{mf}} - \chi_x)/\chi_{s,\mathrm{mf}} = 0.11$.

Anticipating non-mean-field mode-coupled dynamics ($\Gamma \sim \epsilon^{\nu}$ with $\nu = 0.63$) for $T \lesssim T_x$, $(\Gamma\bar{\eta}/T)^{1/0.63}$ is plotted versus inverse temperature in Fig. 2. For $T \lesssim 50\,°\mathrm{C}$ the data are linear in these coordinates (see inset) and extrapolate to $T_s = (38.2 \pm 0.3)\,°\mathrm{C}$ in agreement with our independent measurement $T_b = (38.2 \pm 0.1)\,°\mathrm{C}$, indicating that the system lies close to the critical point (note that the dynamic data are grouped considerably closer to T_b than the static susceptibility data). Above 50 °C the experimental points systematically deviate from the extrapolated lower-temperature behavior. Using the mean-field stability temperature $T_{s,\mathrm{mf}}$ (see Fig. 1) we have plotted $\ln(\Gamma\bar{\eta}/T)$ vs $\ln(T^{-1} - T_{s,\mathrm{mf}})$ in Fig. 3 from which we obtain an exponent of 0.52 ± 0.03. Because this is consistent with a mode-coupled, mean-field regime ($\Gamma\bar{\eta}/T \sim \epsilon^{\nu}$, $\nu = 0.5$), the crossover from mode-coupled to non-mode-coupled dynamics must occur at $\epsilon > 0.5$ [based on our highest measurement temperature and $\chi(T)$ as determined by SANS]. This observation of mean-field mode-coupled dynamics is made possible by

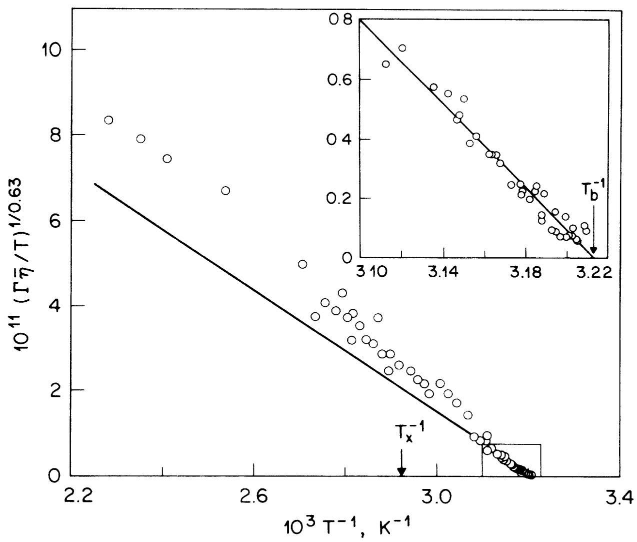

FIG. 2. Normalized decay rates obtained by dynamic light scattering for the critical PEP-PI mixture. Low-temperature behavior (inset) is consistent with non-mean-field mode-coupled dynamics.

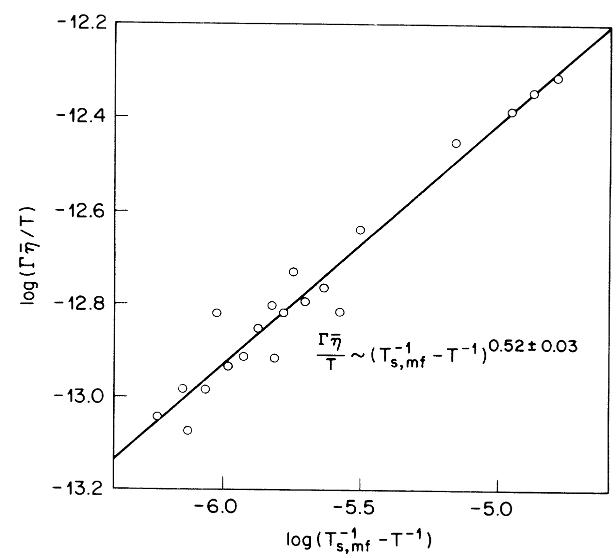

FIG. 3. Dynamic scaling of the normalized decay rate in the mean-field regime, $T > T_x$, where $T_{s,\mathrm{mf}}$ was determined as shown in Fig. 1. Scaling exponents (mean field) of 0.5 and 1.0 are predicted for mode-coupled and non-mode-coupled dynamics, respectively.

the design of a system where $N \lesssim N_e$; recall that the dynamical crossover scales as $N_e^{(\gamma-\nu)^{-1}} N^{-(1+\gamma-\nu)/(\gamma-\nu)}$.

Finally, we evaluate the Ginzburg criterion quantitatively. Schwahn, Mortensen, and Yee-Medeira[8] report $T_x - T_s = 2.4\,^\circ\mathrm{C}$ for a PS-PVME mixture. Based on a segment volume of $v_m = 1.3\times10^{-22}$ cm^3, the PS-PVME mean degree of polymerization is[8] $(N_{\rm PS}N_{\rm PVME})^{1/2} = 1647$; for our system $(N_{\rm PI}N_{\rm PEP})^{1/2} = 46$. At first glance the larger Ising-temperature range for the PI-PEP system might be attributed to a smaller degree of polymerization since one expects $\epsilon_x \sim N^{-1}$. However, using published data to estimate $\chi(T)$,[17] and $T_{s,\rm mf}$ as reported by Schwahn, Mortensen, and Yee-Medeira, we calculate $\epsilon_x = 0.12$ for the PS-PVME mixture, seemingly in violation of the Ginzburg criterion.

For mixtures of monodisperse asymmetric [$N_1 \neq N_2$ and/or $a_1 \neq a_2$, where $R_i = a_i (N_i/6)^{1/2}$] polymers, the appropriate Ginzburg criterion is[18]

$$\epsilon_x = C v_m^2 \frac{[N_1^{-1}\phi_1^{-3} + N_2^{-1}(1-\phi_1)^{-3}]^2}{[N_1^{-1}\phi_1^{-1} + N_2^{-1}(1-\phi_1)^{-1}][R_1^2 N_1^{-1}\phi_1^{-1} + R_2^2 N_2^{-1}(1-\phi_1)^{-1}]^3}, \tag{3}$$

where C is a system-independent constant; note that this expression reduces to $\epsilon_x \sim N^{-1}$ for $a_1 = a_2$ and $N_1 = N_2 \equiv N$. Using the independently measured (SANS) values $a_{\rm PI} = 6.9$ Å and $a_{\rm PEP} = 8.0$ Å, and $\epsilon_x = 0.11$, we obtain $C = 0.29 \pm 0.08$; the uncertainty in C is estimated from the combined uncertainties in a, N, and ϵ_x. A similar calculation based on published values for $a_{\rm PS}$ and $a_{\rm PVME}$ along with the results of Schwahn, Mortensen, and Yee-Medeira,[8] $\epsilon_x = 0.12$, leads to $C = 0.46$; here an accurate estimate of uncertainty cannot be made although it is undoubtably greater than for the PI-PEP calculation. Thus, Eq. (3) has reduced a nearly fortyfold disparity ($\epsilon_x \sim N^{-1}$) to agreement within experimental error.[19] To our knowledge this is the first such verification of the Ginzburg criterion.

In summary, we have quantitatively verified the Ginzburg criterion for the crossover from mean-field to non-mean-field critical behavior in binary polymer mixtures. Dynamic-light-scattering measurements also confirm a rich dynamical behavior for polymer mixtures near the entanglement molecular weight, which are characterized by mode-coupled dynamics well into the static mean-field regime.

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[19]A more quantitative comparison of these results probably requires the consideration of polydispersity effects.