

Shear suppression of critical fluctuations in a diluted polymer blend

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Small-angle neutron scattering has been combined with equilibrium dynamic light scattering to study shear-induced mixing in a diluted high-molecular-weight polymer blend. The data show an enhancement of critical fluctuations upon dilution and are found to collapse onto a universal scaling curve containing no free parameters. This scaling curve is motivated by the theoretical predictions of Onuki and Kawasaki for undiluted binary mixtures. The data also appear to suggest that ‘‘Fisher renormalization’’ is relevant in this diluted pseudobinary polymer mixture, consistent with a previous dynamic-light-scattering study. [S1063-651X(96)52005-2]

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The behavior of polymer blends under steady shear flow has important applications in chemical processing and manufacturing. As measured with small-angle scattering, the shear response also offers a direct probe of the couplings in order-parameter and velocity fluctuations that lead to interesting phenomena in these mixtures, the nature of which depends on the molecular weights of the polymers involved [1,2]. In the miscible phase of high-molecular-weight blends, the imposition of shear leads to a distortion of thermal composition fluctuations along the direction of flow, while the scattering perpendicular to the flow (vorticity) direction retains its equilibrium profile [1]. These observations are consistent with ideal mean-field type statics of phase separation. The details of this anisotropic response also suggest that hydrodynamic or mode-coupling effects are significant in such blends, which is consistent with equilibrium dynamic-light-scattering (DLS) studies [1,2]. In contrast, low-molecular-weight blends under steady shear show a true suppression of the critical temperature that arises from an interplay between mode-coupling and nonclassical critical behavior [1,3].

In this paper we use a combination of small-angle neutron scattering (SANS) and equilibrium DLS to study shear-induced mixing in a diluted high-molecular-weight polymer blend near its critical point. Treating the ternary system as a pseudobinary mixture [4], dilution of a high-molecular-weight polymer blend with a good solvent should lead to an enhancement of critical fluctuations [5]. This is because dilution serves to increase the volume of phase space readily available to thermal composition fluctuations, which effectively increases the so-called ‘‘Ginzburg number’’ of the transition. In small-molecule binary systems, dilution leads to a ‘‘Fisher renormalization’’ of the critical behavior in the ‘‘impure’’ or ternary system with respect to the pure binary mixture [6,7]. Past studies of this effect have focused on small changes in the critical exponents γ and ν as the stability limit is approached [7,8]. The existence of Fisher renormalization in diluted polymer blends is a question that is currently unresolved [8,9], although one could argue that it should be expected in any binary system for which T_c is modified strongly upon dilution [6].

The sample used for both the SANS and DLS measurements was a blend of monodisperse deuterated polystyrene (PSD) and polybutadiene (PB) dissolved in a solution of

dioctyl phthalate (DOP). The PSD had a molecular weight of $M_w=89\,000$ g/mol and a polydispersity of $M_w/M_n=1.03$. The PB (8% vinyl, 92% *cis* and *trans* 1,4) had a molecular weight of $M_w=22\,000$ g/mol and a polydispersity of $M_w/M_n=1.06$. Mixtures of varying composition were prepared at a constant total polymer concentration of 8% and the nominal coexistence curve for this upper-critical-solution-temperature (UCST) system was measured with temperature-jump light scattering [8]. Based on these measurements, the critical composition and critical temperature were determined to be $\phi_c=0.315$ volume fraction PSD and $T_c=40.9\pm 0.1$ °C. All of the measurements described here were performed on samples taken from a large batch prepared at the critical composition. A detailed DLS study of the equilibrium critical dynamics is described elsewhere [8] and suggests an exponent $a=0.68\pm 0.02$ for the divergence of the *dynamic* correlation length [$\xi^* \sim (1 - T_c/T)^{-a}$] in the vicinity of T_c .

SANS measurements as a function of temperature and shear rate ($\dot{\gamma}$) were carried out at the Cold Neutron Research

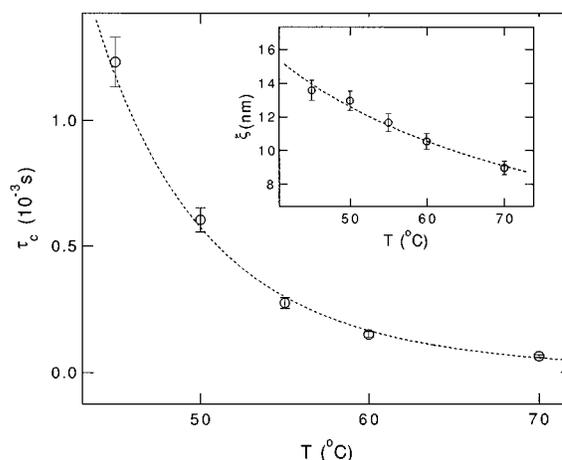


FIG. 1. The temperature dependence of the characteristic lifetime τ_c as deduced from SANS and DLS, and the correlation length ξ as deduced from SANS (inset). Both show a marked increase in the one-phase region as T_c is approached. The dashed lines are guides to the eye. A quantitative fit of these two quantities is complicated by the crossover to ‘‘critical’’ behavior in both the equilibrium statics and dynamics.

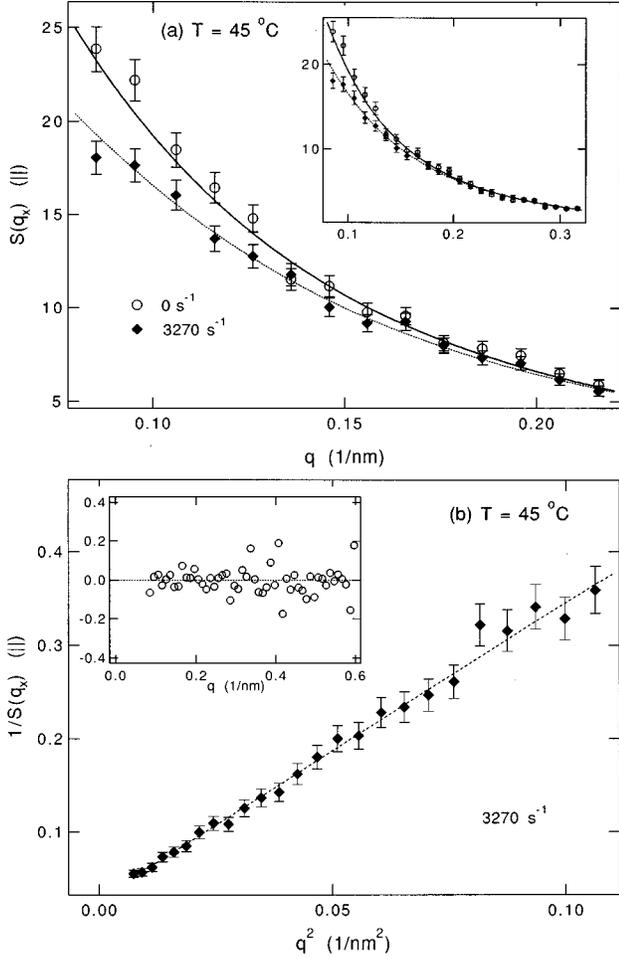


FIG. 2. (a) Suppression of thermal composition fluctuations along the direction of flow. Similar behavior was observed perpendicular to the flow. The lines are fits with the Ornstein-Zernike (Lorentzian) expression. (b) Zimm plot and (inset) fractional-deviation plot for the sheared data and fit shown in (a), supporting the validity of Eq. (1) under steady shear.

Facility at the National Institute of Standards and Technology. The details of the instrument and shear cell are described elsewhere [10]. The geometry of shearing is in the x - y plane with the flow in the x direction and the velocity gradient in the y direction. Neutrons incident along the y axis were scattered by the sample and a two-dimensional detector measured the scattering intensity in the x - z plane. The data were averaged over angular sectors both parallel (x direction) and perpendicular (z direction) to the flow so as to preserve any anisotropy that might be present in the data. The scattering contrast in this dilute binary system is sufficiently weak so that multiple scattering is negligible and the measured intensity, after background corrections, should be proportional to the structure factor $S(\mathbf{q}, \dot{\gamma}) \sim \langle \Psi_{\mathbf{q}} \Psi_{-\mathbf{q}} \rangle$, where the order parameter $\Psi(\mathbf{r})$ represents local fluctuations around ϕ_c .

Equilibrium ($\dot{\gamma}=0$) SANS measurements of the relatively low- q scattering intensity as a function of the scattered wave vector q were fitted with the Ornstein-Zernike expression

$$S(q) = \frac{S(0)}{1 + \xi^2 q^2} \quad (1)$$

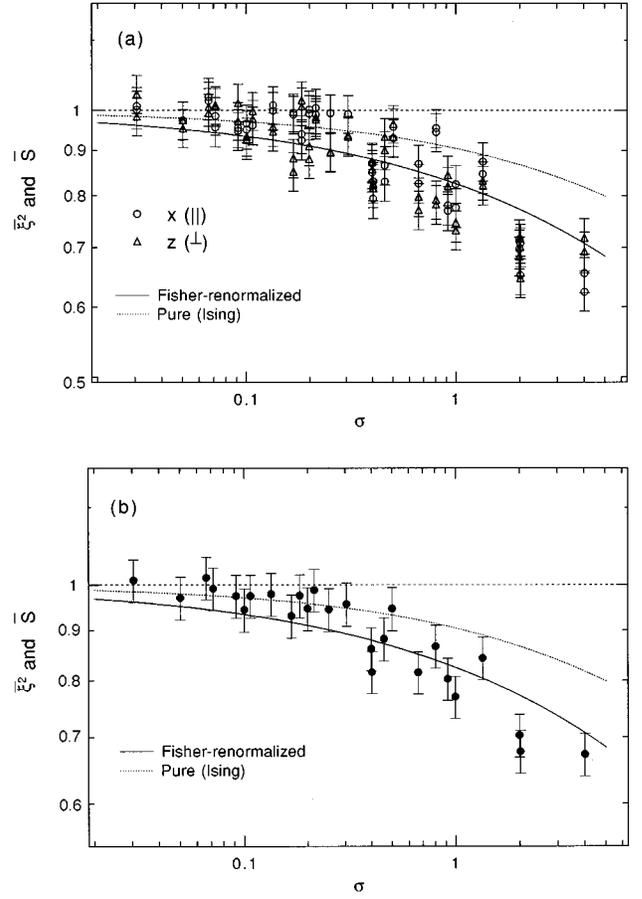


FIG. 3. (a) Log-log plot (base 10) of the reduced susceptibility and reduced correlation length squared as a function of the reduced shear rate both parallel (x) and perpendicular (z) to the direction of flow. Within the inherent scatter, the response is isotropic. (b) A similar plot with all parallel and perpendicular quantities averaged together. In both (a) and (b), the solid line is the predicted form of the ‘‘Fisher-renormalized’’ response and the dotted line is the predicted form of the ‘‘pure’’ or Ising response.

to deduce the correlation length ξ and the susceptibility $S(0)$. Combined with equilibrium DLS measurements of the cooperative-diffusion coefficient D_c , we obtain a characteristic order-parameter relaxation time:

$$\tau_c = \xi^2 / D_c. \quad (2)$$

The temperature dependencies of τ_c and ξ are shown in Fig. 1. Both exhibit a marked increase as the phase boundary is approached, consistent with the appearance of slow and extended coherent fluctuations in composition. Because these quantities are in a regime of crossover [1,8], quantitative fits are cumbersome, and the dashed lines are intended only as guides to the eye.

The error bars due to the relatively weak scattering of neutrons in this dilute system prevent a precise determination of the correlation-length critical exponent ν via an extrapolation of the apparent T_c from equilibrium SANS. Our interpretation is based on the shear response. The details of theoretical background are given elsewhere [1,3,5], and we only summarize the results here. Typically SANS probes length scales in the vicinity of a cutoff wave vector $q_c(\dot{\gamma})$ that

separates those thermal-fluctuation modes unaffected by the shear ($q > q_c$) from those that are suppressed by the shear ($q < q_c$). In the immediate vicinity of q_c , an *isotropic* decrease in scattering intensity indicates a true suppression of the critical temperature by the flow (shear-induced mixing), and is intimately linked to the presence of critical fluctuations. In this case the scattering profiles can be reasonably well described by Eq. (1) with a shear-dependent correlation length and susceptibility, $\xi(\dot{\gamma})$ and $S(0, \dot{\gamma})$, where the shear dependence is contained in the “modified” critical temperature, $T_c(\dot{\gamma})$.

Figure 2(a) shows the projection of the scattering intensity parallel to the flow direction at $T=45^\circ\text{C}$ for both $\dot{\gamma}=0$ and $\dot{\gamma}=3270\text{ s}^{-1}$. The lines are fits with Eq. (1). A weak decrease in the low- q intensity is clearly evident. Figure 2(b) shows a plot of $S^{-1}(q)$ vs q^2 for the nonequilibrium data in Fig. 2(a), and the inset shows the fractional deviation from the Ornstein-Zernike fit as a function of q . Similar behavior was observed at all temperatures and shear rates, both parallel and perpendicular to the flow direction. We found no evidence of shear-induced phase separation between either of the polymer components and the solvent. Within the scatter inherent to the data, the response appears isotropic, although anisotropy should become apparent at lower q . The shear response predicted by the mode-coupling renormalization-group theory of Onuki and Kawasaki [11] can then be cast in a compact form [1,3] by introducing the reduced (dimensionless) quantities $\bar{S}=S(0, \dot{\gamma})/S(0, \dot{\gamma}=0)$, $\bar{\xi}=\xi(\dot{\gamma})/\xi(\dot{\gamma}=0)$, and $\sigma=\dot{\gamma}\tau_c$. The data should then collapse onto the universal scaling curve given by

$$\bar{S}\bar{\xi}^2 = \{1 + A\sigma^{1/3\nu}\}^{-2\nu} \quad (3)$$

where $A\approx 1/2$ to leading order in $\varepsilon=4-d$ ($d=3$ is the spatial dimension) and $\nu=0.63$ for a pure (Ising) mixture. In Eq. (3), we have made the approximation $\gamma\approx 2\nu$. Previous measurements on an undiluted, low-molecular-weight PSD-PB blend are in remarkable agreement with this prediction [1,3].

Although a rigorous extension of the Onuki-Kawasaki theory to a Fisher-renormalized system is lacking, a heuristic modification of Eq. (3) for such a diluted mixture can be made as follows. The leading order contribution to the shear-

induced shift in the stability limit is proportional to the fixed point value of the critical (Ψ^4) coupling constant, u^* [11]. Based on the known shift in the critical exponents upon dilution and the relationship between these exponents and the coupling constant u^* , one can heuristically predict how the critical amplitudes should evolve under Fisher renormalization. This gives the estimated values $A\approx 1/7$ to go with $\nu=0.72$ in Eq. (3). Figure 3 shows a comparison of the observed x - z response with Eq. (3). Within the inherent scatter, the response appears isotropic, and Fig. 3(b) shows the same plot with an isotropic average of the experimental quantities. In both graphs, the solid line represents the Fisher-renormalization form of Eq. (3) ($A\approx 0.143$ and $\nu=0.72$) and the dashed line represents the usual Ising form of Eq. (3) ($A\approx 0.0832$ and $\nu=0.63$). Because all of the experimental quantities appearing in Eq. (3) have been directly measured, there are no free parameters in this comparison with theory. Previous light-scattering studies of the T_c shift in PS-PB-DOP under shear by Takebe *et al.* [4] gave an exponent $1/3\nu=0.50\pm 0.02$, which is consistent with our previous DLS estimate of ν [8], and which is lower than that observed in small molecule binary mixtures [12].

In conclusion, our data offer unambiguous evidence for the importance of critical fluctuations and a crossover to non-classical critical behavior in a diluted, pseudobinary polymer mixture of moderately high molecular weight. In addition, the agreement with the $O(\varepsilon)$ prediction of Onuki and Kawasaki (modified or unmodified) is quite good over more than two decades in reduced shear rate without any free parameters. Although our data can be interpreted as supporting an argument in favor of Fisher renormalization in such a diluted polymer blend, the size of the error bars prevents a truly rigorous distinction. Rather, the results obtained here suggest that further investigation of such effects in diluted polymer mixtures is very much warranted. It would be interesting to measure the viscosity anomaly in diluted blends [13], as the exponent and amplitude ratios should be strongly influenced by Fisher-renormalization effects.

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