Crossover to Strong Shear in a Low-Molecular-Weight Critical Polymer Blend

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Small-angle neutron scattering has been used to measure the influence of shear flow on a low-molecular-weight polymer blend near the critical point. When combined with light scattering measurements of the equilibrium ($\dot{\gamma}=0$) critical dynamics, these measurements reveal that the long-range critical fluctuations begin to break apart when the shear rate becomes comparable to the characteristic relaxation rate τ_c^{-1}, where τ_c is the equilibrium lifetime of the critical fluctuations. This effect is directly related to the decrease in the critical temperature caused by the flow, and the data are found to be in very good agreement with the theoretical predictions of Onuki and Kawasaki.

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The influence of shear flow on critical fluctuations in complex fluids is a topic that has received considerable attention lately [1]. For binary mixtures, it is interesting to ask how the large-scale concentration fluctuations near the critical point of unmixing respond to the mixing effect of the shear. The mode-coupling renormalization-group treatment of a simple binary fluid under shear, as formulated by Onuki and Kawasaki [2,3], has been used by a number of authors as a foundation for a description of polymer blends and solutions [4–7]. Some of the predictions of this complex theory have been confirmed in small-molecule critical mixtures [8,9]. For a high-molecular-weight critical polymer blend [10], small-angle neutron scattering (SANS) measurements appear to be consistent with a "mean-field" version of the Onuki-Kawasaki theory, where long-wavelength fluctuations are suppressed parallel to the flow, but there is no change in scattering intensity normal to the flow [11]. In this paper, we have used SANS to probe the influence of shear on a low-molecular-weight critical blend. The appeal of this study is that τ_c, the equilibrium ($\dot{\gamma}=0$) lifetime of the critical fluctuations, has been measured independently in the same material. Using the predictions of Onuki and Kawasaki, we have derived a simple expression that gives the shear response of the SANS structure factor in terms of the equilibrium structure factor, the shear rate $\dot{\gamma}$, and the equilibrium lifetime τ_c. The data are found to collapse onto a universal scaling curve that can be compared directly with theory without any free parameters. Displaying the data in this way also reveals a very intuitive interpretation of how the shear affects the critical fluctuations.

The binary mixture consisted of deuterated polystyrene (PSD) with a mean degree of polymerization $N_A \approx 9$ and polybutadiene (PB) with $N_B \approx 87$, both having narrow molecular-weight distributions (with polydispersity index less than 1.09). The equilibrium coexistence curve [12] is shown in the inset of Fig. 1. The observed maximum at $T_c = 41.2 \pm 0.1\,^{\circ}\mathrm{C}$ coincides closely with the Flory-Huggins critical PSD weight fraction of 0.75. All of the measurements described in this paper were carried out with samples taken from one large batch of blend prepared at this critical composition ϕ_c. The scattering measurements were conducted on the 8-m SANS instrument at the Cold Neutron Research Facility of the National Institute of Standards and Technology, with a shear apparatus that has been described in detail elsewhere [10]. The geometry of the shearing is in the x-y plane, with the flow in the x direction and the velocity gradient in the y direction. Neutrons of wavelength 9 Å, 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 small sectors both parallel and perpendicular to the flow to preserve any anisotropy that might be present. We are interested in the crossover from the "weak shear" limit, where $\dot{\gamma}\tau_c \ll 1$, to the "strong shear" limit, where $\dot{\gamma}\tau_c \gg 1$. Direct knowledge of τ_c provides an unambiguous distinction between these two limits.

We interpret our data using the theoretical description of the response of a binary fluid to shear proposed by Onuki and Kawasaki in Refs. [2] and [3]. Their description starts with the stochastic equations of motion for the order parameter $\psi(\mathbf{x},t)$ (the concentration) and the

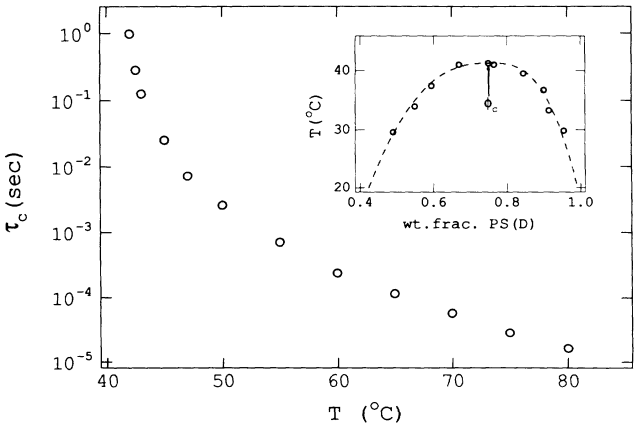

FIG. 1. The characteristic lifetime $\tau_c = \xi^2/D_c$ as a function of temperature. Inset: The measured equilibrium coexistence curve.

transverse part of the velocity field $\mathbf{v}(\mathbf{x},t)$,

$$\partial\psi/\partial t = -\dot{\gamma}y\,\partial\psi/\partial x - \rho_0\nabla\cdot(\psi\mathbf{v}) + \Lambda_0\nabla^2(\delta f/\delta\psi) + \theta\,,$$
$$\partial\mathbf{v}/\partial t = \eta_0\nabla^2\mathbf{v} - \rho_0\{\psi\nabla(\delta f/\delta\psi) + \mathbf{h}\}_\perp\,, \tag{1}$$

where $\{\}_\perp$ denotes the transverse part of the vector in brackets, η_0 is the zero shear viscosity, Λ_0 is the Onsager coefficient associated with ψ, and ρ_0 accounts for the hydrodynamic coupling between ψ and $\mathbf{v}$. The quantity f is the Ginzburg-Landau free energy [12],

$$f = f_0 + \int d^3x\{\tfrac{1}{2}a\psi^2 + \tfrac{1}{4}u\psi^4 + \tfrac{1}{2}\kappa|\nabla\psi|^2\}\,. \tag{2}$$

Here $a(T) = a_0(1 - T_c/T)$, where T_c is the critical temperature. The first term on the right-hand side of the equation of motion for ψ accounts for the shear, and leads to the stabilization of fluctuations in ψ along the direction of flow. The random noise sources θ and $\mathbf{h}_\perp$ have correlations related to Λ_0 and η_0 in the usual way via the fluctuation-dissipation theorem [2,3].

In equilibrium, the importance of critical fluctuations in both the statics and dynamics of this model is well understood, and the renormalization group has proved a powerful tool for calculating the expected behavior. In the case of low-molecular-weight polymer blends, the ψ^4 term in Eq. (2) leads to a crossover to Ising behavior in the static susceptibility and correlation length, $S(0)$ and ξ, respectively, as well as a "renormalization" of the critical temperature T_c [13–16]. For the blend considered here, $S(0)$ and ξ measured with equilibrium SANS show a crossover from mean-field to critical behavior as $T \to T_c$ [12]. Critical fluctuations are also important in the dynamics, where the nonlinear coupling between ψ and $\mathbf{v}$ in Eq. (1) causes a divergence in Λ_0 at the critical point [4,17]. Dynamic light scattering measurements of the equilibrium decay rate of the concentration fluctuations, $\Gamma_c = D_c q^2$, where q is the scattered wave vector, and the nature of the critical dynamics in this blend are described elsewhere [18]. The influence of critical fluctuations on the dynamics is apparent in the diffusion coefficient $D_c = \Lambda_0/S(0)$, and the characteristic lifetime $\tau_c = \xi^2/D_c$ is shown as a function of temperature in Fig. 1. The "critical slowing down" of the concentration fluctuations is evident as a dramatic divergence in τ_c near the critical point.

The treatment of Onuki and Kawasaki emphasizes the role of critical fluctuations in the response of the fluid to shear. Neglecting the nonlinear terms in Eq. (1), the structure factor $S(\mathbf{q},\dot{\gamma}) \sim \langle\psi_{\mathbf{q}}\psi_{-\mathbf{q}}\rangle$ is found to satisfy the mean-field equation [2,3]

$$[\Lambda_0 q^2(a + \kappa q^2) - \tfrac{1}{2}\dot{\gamma}q_x\partial/\partial q_y]S(\mathbf{q},\dot{\gamma}) = \Lambda_0 q^2\,. \tag{3}$$

In equilibrium ($\dot{\gamma}=0$), critical fluctuations renormalize $a(T)$ and $\kappa/a(T)$ to $S^{-1}(0)$ and ξ^2, respectively, and Eq. (3) reduces to the Ornstein-Zernike expression,

$$S(q) = S(0)[1 + \xi^2 q^2]^{-1}\,, \tag{4}$$

in agreement with the observed equilibrium behavior [12]. To account for critical fluctuations when $\dot{\gamma}\neq 0$, a renormalization-group analysis [2,3] of Eqs. (1) and (2) in the strong shear limit reveals that Eq. (3) remains valid if the parameters $a(T)$ and Λ_0 are renormalized in terms of the shear rate $\dot{\gamma}$ to first order in $\varepsilon = 4 - d$, where $d = 3$ is the spatial dimension of the system.

The second term on the left-hand side of Eq. (3) leads to strong anisotropy in $S(\mathbf{q},\dot{\gamma})$ for $q \to 0$. Even for strong shear, Eq. (3) predicts that $S(\mathbf{q},\dot{\gamma})$ will be isotropic at high q, and a useful solution can be found by treating the anisotropic term in Eq. (3) as a perturbation and solving for $S(\mathbf{q},\dot{\gamma})$ iteratively [2,3]. This approach gives $S(\mathbf{q},\dot{\gamma})$ as a power series in the shear rate $\dot{\gamma}$, and reduces to Eq. (4) when $\dot{\gamma}=0$. The first-order correction depends on $q_x q_y$, indicating that the anisotropy first appears in the x-y plane as q decreases. Since the projection of $S(\mathbf{q},\dot{\gamma})$ onto the x-z plane is what we measure ($q_y = 0$), this first trend toward anisotropy will not appear in our data. The first trace of anisotropy in the x-z plane comes from the second-order correction. For a given shear rate $\dot{\gamma}$, this contribution will be significant when

$$(\dot{\gamma}\tau_c)^2(q_x/q)^2[2\xi^2 q^2(1 + \xi^2 q^2)^3]^{-1} \sim 1\,. \tag{5}$$

The q range probed with SANS for this blend is $0.009 < q < 0.09$ Å^{-1}. At the highest shear rate used ($\dot{\gamma} = 223$ s^{-1}) in the vicinity of the equilibrium critical temperature, Eq. (5) predicts that the anisotropy will not emerge until $q < 0.01$ Å^{-1}. Thus any trend toward anisotropy would be difficult for us to see, and we expect $S(\mathbf{q},\dot{\gamma})$ to appear essentially isotropic over the q range used in this study.

The approximation that $S(\mathbf{q},\dot{\gamma})$ is isotropic over the q range in question simplifies the problem considerably, since we do not have to consider the shear renormalization of Λ_0. At temperatures where critical fluctuations are irrelevant ($T \gg T_c$), the structure factor is unchanged by the shear. At temperatures where critical fluctuations are important ($T \to T_c$), $S(\mathbf{q},\dot{\gamma})$ depends on $\dot{\gamma}$ through the shear dependence of the critical temperature only, and is given by Eq. (4) with $S(0)$ and ξ replaced by $S(0,\dot{\gamma})$ and $\xi(\dot{\gamma})$. The shear dependence of the critical temperature, $T_c(\dot{\gamma})$, follows from the strong shear renormalization of $a(T)$ described above, and is given in terms of the equilibrium critical temperature, henceforth denoted by $T_c(0)$, the equilibrium lifetime τ_c, and the shear rate $\dot{\gamma}$ as [2,3]

$$\frac{T_c(\dot{\gamma}) - T_c(0)}{T_c(0)} \approx -r[0.0832\varepsilon + O(\varepsilon^2)](\dot{\gamma}\tau_c)^{1/3\nu}\,, \tag{6}$$

where $r = 1 - T_c(0)/T$ is the equilibrium reduced temperature, and $\nu = 0.63$ is the Ising exponent describing the divergence of the correlation length at the critical point ($\xi \sim r^{-\nu}$). Although Eq. (6) is derived from the form of $a(T)$ predicted in the strong shear limit, it reduces to the correct equilibrium result for $\dot{\gamma}=0$. The shear depen-

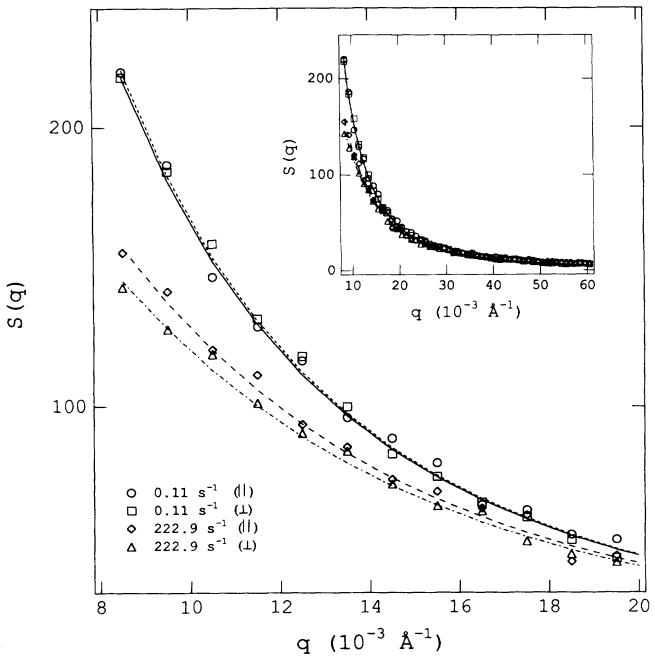

FIG. 2. The low-q structure factor $S(\mathbf{q},\dot{\gamma})$ measured along (∥) and normal (⊥) to the flow direction in both the weak and strong shear limits at $T=42.0\,^{\circ}$C. The lines are fits by Eq. (4). Over most of the q range, the scattered intensity (inset) is unaffected by the shear rates used in this study.

dence of $S(0,\dot{\gamma})$ and $\xi(\dot{\gamma})$ will be $S(0,\dot{\gamma})\sim[1-T_c(\dot{\gamma})/T]^{-2\nu}$ and $\xi(\dot{\gamma})\sim[1-T_c(\dot{\gamma})/T]^{-\nu}$ with $T_c(\dot{\gamma})$ given by Eq. (6). We have taken the susceptibility exponent γ to be equal to 2ν. The change in reduced temperature due to the shear can be written as

$$\Delta r/r \approx [0.0832\varepsilon + O(\varepsilon^2)](\dot{\gamma}\tau_c)^{1/3\nu}. \quad (7)$$

Figure 2 shows the measured structure factor $S(\mathbf{q},\dot{\gamma})$ as a function of q, parallel and perpendicular to the flow direction, for both strong ($\dot{\gamma}=222.9$ s^{-1}) and weak ($\dot{\gamma}=0.11$ s^{-1}) shear at $T=42.0\,^{\circ}$C. The lines are fits of the data by Eq. (4). Although the strong shear data in Fig. 2 appear to be slightly anisotropic, when all the shear rates and temperatures are examined, no trend toward any systematic anisotropy is evident, as expected. Figure 3 shows the susceptibility $S(0,\dot{\gamma})$ for $\dot{\gamma}=0$ and $\dot{\gamma}=222.9$ s^{-1}, both parallel and perpendicular to the flow, as a function of $T-T_c(0)$. The inset shows a similar plot of $\xi(\dot{\gamma})$. Both Figs. 2 and 3 reveal how the large-scale critical fluctuations become suppressed by the shear in the vicinity of the critical point. In Fig. 2 this is evident as a decrease in the low-q scattering intensity near $T_c(0)$. Similarly, Fig. 3 shows in detail how the flow decreases $S(0,\dot{\gamma})$ and $\xi(\dot{\gamma})$ in the vicinity of the equilibrium critical temperature. Further than 5 K away from $T_c(0)$, the structure factor is unchanged at the highest shear rates used in this study, which suggests that equilibrium critical fluctuations do not become significant until $T-T_c(0)\leq 5$ K.

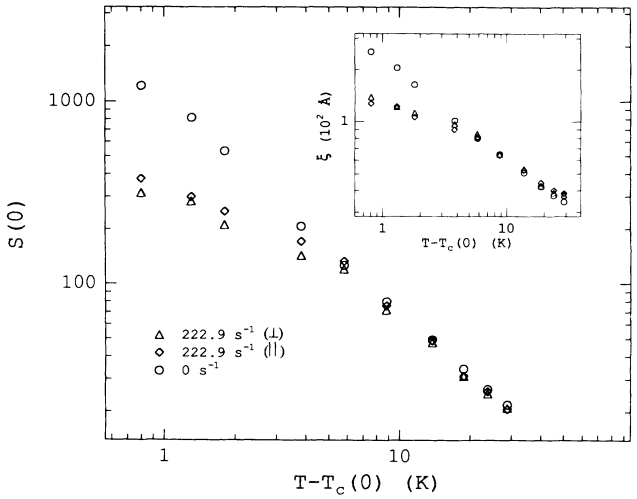

FIG. 3. $S(0,\dot{\gamma})$ for $\dot{\gamma}=0$ and in the strong shear limit, defined both parallel (∥) and perpendicular (⊥) to the flow direction, as a function of $T-T_c(0)$. Inset: A similar plot of ξ.

The breakup of the large-scale (low-q) critical fluctuations by the flow causes the suppression of the critical temperature described by Eq. (6). The mixing effect of the shear inhibits phase separation, leading to a drop in T_c. To relate the observed behavior of $S(0,\dot{\gamma})$ and $\xi(\dot{\gamma})$ described above to the prediction of Eq. (6), the susceptibility and correlation length can be written as $S(0,\dot{\gamma})\approx S(0)(1+\Delta r/r)^{-2\nu}$ and $\xi(\dot{\gamma})\approx\xi(1+\Delta r/r)^{-\nu}$, with $\Delta r/r$ given by Eq. (7). When $\dot{\gamma}\to 0$, these two quantities assume their equilibrium values $S(0)$ and ξ. Because $\Delta r/r$ becomes appreciable only for temperatures within 5 K of $T_c(0)$, the exponent $\nu=0.63$. The reduced susceptibility, $S_{\rm red}=S(0,\dot{\gamma})/S(0)$, and the reduced correlation length, $\xi_{\rm red}=\xi(\dot{\gamma})/\xi$, are then given in terms of the reduced shear rate, $\sigma=\dot{\gamma}\tau_c$, by

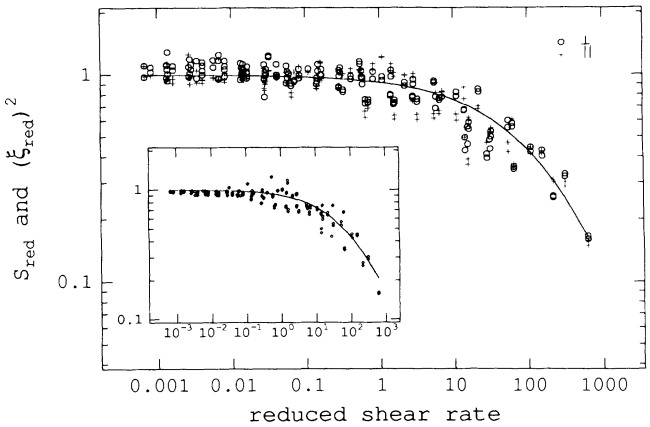

FIG. 4. The reduced correlation length squared and the reduced susceptibility as a function of reduced shear rate. The solid line is the behavior predicted to $O(\varepsilon)$, over six decades in reduced shear rate, with no free parameters. Inset: The same plot using a circular average of the scattering intensity, which is justified by the isotropic nature of the response.

$$S_{\text{red}} = \xi_{\text{red}}^2 \approx \{1 + [0.0832\varepsilon + O(\varepsilon^2)]\sigma^{1/3\nu}\}^{-2\nu}. \quad (8)$$

The quantities S_{red} and ξ_{red} are a measure of the influence of the shear. If the flow has no effect, S_{red} and ξ_{red} are both 1, as in equilibrium. When the flow starts to suppress the large-scale critical fluctuations, S_{red} and ξ_{red} begin to decrease, reflecting a drop in the low-q scattering intensity. In Fig. 4 we have plotted S_{red} and ξ_{red}^2 as a function of σ for all of the shear rates and temperatures used in this study. The line is the behavior predicted by the right-hand side of Eq. (8) to $O(\varepsilon)$ for $d=3$. Since S_{red}, ξ_{red}, and σ are all directly known, there are no free parameters in this fit. The agreement is very good over six decades in σ. Since the response is essentially isotropic, we can average the scattering intensity over the whole x-z plane, which slightly reduces the scatter in this plot, as shown in the inset of Fig. 4. The constant 0.0832 in Eq. (8) is a universal, system-independent number predicted by the $O(\varepsilon)$ renormalization-group analysis. A 20% change in this constant moves the theoretical curve well outside of the scatter in the data.

Besides lending strong support to the predictions of Onuki and Kawasaki applied to polymer blends, Fig. 4 reveals that the flow starts breaking up the long-range critical fluctuations when the shear rate becomes comparable to the equilibrium relaxation rate of these fluctuations. This is evidenced by the fact that S_{red} and ξ_{red}^2 begin to deviate from unity when the reduced shear rate $\sigma = \dot{\gamma}\tau_c$ becomes comparable to unity, or when $\dot{\gamma} \sim \tau_c^{-1}$. That the size of the critical fluctuations would be limited by the shear for $\dot{\gamma} \geq \tau_c^{-1}$ is very intuitive, since any component with an equilibrium lifetime greater than $\dot{\gamma}^{-1}$ will essentially be suppressed by the flow.

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