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"Shift" in Polymer Blend Phase-Separation Temperature in Shear Flow

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ABSTRACT: Recent experimental studies of polymer blends in simple shear flow have indicated large "shifts" of the apparent phase-separation temperature. These shifts are examined within the context of a nonequilibrium hydrodynamic theory of phase separation developed by Onuki and Kawasaki. A mean-field version of the hydrodynamic theory indicates that *no true shift* of the critical temperature T_c should be observed in high molecular weight polymer blend melts. However, the hydrodynamic theory indicates a large "apparent shift" $\Delta_{\parallel}T_c(\dot{\gamma})$ parallel to the flow direction, $\Delta_{\parallel}T_c(\dot{\gamma}) \sim \dot{\gamma}^{8/15}$, if the scattering data naively fit to the Ornstein–Zernike function. This spurious "shift" should not be observed in scattering data along the normal to flow direction. These predictions accord qualitatively with experiments on sheared melt blends by Nakatani et al. The apparent shift of T_c in high molecular weight polymer melt blends is coincidentally similar to the true shift of T_c observed in small-molecule binary mixtures where $\Delta T_c(\dot{\gamma}) \sim (\dot{\gamma})^{1/3\nu}$, $\nu(\text{Ising}) = 0.63$, is obtained from mode-coupling renormalization group theory. It is argued that a true shift of T_c should be observed in sufficiently *diluted* polymer blends in low molecular weight solvents because of a crossover from mean-field to Ising critical behavior upon dilution.

1. Introduction

The tendency of polymer solutions to become cloudy or clear when disturbed has long been recognized,[1–3] but the systematic study of this important phenomenon is recent.[4–10] This neglect is understandable given the complexities of developing a molecular theory of polymer solution rheology and the developments in statistical mechanics required for the study of nonequilibrium "phase separation" under flow conditions. The growing theoretical interest in phase separation in flowing polymer solutions is a natural outgrowth of recent advances in understanding phase separation and the transport properties of small-molecule liquids near their critical point.[11–14] Development is also driven by the need to control manufacturing processes involving flowing polymer solutions.[15]

Reviews of the effect of flow on polymer phase separation by Rangel-Nafaile et al.[16] and Nakatani et al.[10] indicate that a variety of factors could be important in determining the observed phase stability of flowing polymer solutions—flow geometry (type of flow field), shear rate, excluded-volume interactions, concentration, molecular weight ("entanglement" effects), etc. In semidilute polymer solutions the hydrodynamic interactions could also play an important role in the shear-induced turbidity phenomenon[3,16,17] (see section 4).

There is a diversity of theoretical approaches to phase separation under flow conditions. Many of the proposed theories are based on the original physical arguments of Silberberg and Kuhn[1] which suggest that the free energy of a polymer solution increases with flow in much the same fashion as a rubbery solid upon deformation.[3,16,18–22] Unfortunately, there is no unambiguous means of estimating "energy storage" in a flowing non-Newtonian liquid, and this interesting notion is avoided in the present paper, except for a speculative discussion in section 4 regarding flow-induced turbidity in semidilute polymer solutions.

The mode-coupling renormalization group (MCRG) approach to the nonequilibrium steady-state shear of critical fluids offers the prospect of a fundamental description of polymer phase separation under flow. The predictions of the MCRG theory are impressively confirmed in experiments on small-molecule critical mixtures with shear.[4,5] Helfand and Fredrickson,[23a] Onuki,[24] and Milner[25] have sought to generalize the classical MCRG calculations of Onuki and Kawasaki[6,7] to polymer solutions. Fredrickson and Bates have discussed the application of the mode-coupling theory to polymer blends.[23b]

High molecular weight polymer melt blends provide a natural starting point for studying shear effects on polymer phase separation. The equilibrium phase separation of polymer melt blends is rather well described by mean-field theory[26,27] since many polymers are in the sphere of influence of a given chain. We can then expect to have some success with a *mean-field model* of the dynamical critical properties of high molecular weight polymer blends.[6,28] It should also be instructive to compare melt blend data[10] with semidilute blend solution data since mean-field theory does not necessarily apply upon dilution of the polymer blend in a low molecular weight solvent.[29,30]

The discussions of the dynamics of critical fluctuations and the effect of shear on phase separation in high molecular weight blends in the present paper are greatly facilitated by previous studies of the dynamical critical properties of binary liquids within the mean-field approximation.[6,28] These mean-field calculations provided a stepping stone to the more sophisticated MCRG calculations and were not intended to apply to any real physical system. A primary contribution of the present work is to point out the relevance of these mean-field calculations to the description of high molecular weight blends and to discuss recent apparently contradictory observations on the effect of shear on the scattering function of polymer blends in terms of this available theoretical framework.

There are many experimental studies on the effect of shear on polymer blend phase separation which are based on the measurement of turbidity. Recent experiments by Hashimoto et al.[8,9] and Nakatani et al.[10] have examined the anisotropic scattering of sheared blends using light and neutron scattering. As in former turbidity studies,[16,18] the apparent critical temperature T_c in sheared blends is "shifted" by shear. Curiously, Nakatani et al.[10] observe a shift of the apparent critical temperature along the flow direction, but they observe *no shift* normal to the flow direction in a high molecular weight deuterated polystyrene (DPS) and poly(vinyl methyl ether) (PVME) melt blend. Hashimoto et al.[8,9] observe a significant "shift" *normal* to the flow direction (scattering data for the structure factor projection along the flow direction are not presented) in a high molecular weight blend of PS and polybutadiene (PB) diluted to a semidilute polymer concentration in dioctyl phthalate (DOP). Both Nakatani et al. and Hashimoto et al. claim agreement of the observed "shift" with the prediction of MCRG calculations,[6,7] despite their rather different observations.

In section 2 the experiments of Nakatani et al.[10] and Hashimoto et al.[8] are examined within the context of the nonequilibrium theory of phase separation with shear developed by Onuki and Kawasaki.[6,7] Since the static critical behavior of high molecular weight blends is accurately described by mean-field theory,[26,31] a corresponding mean-field hydrodynamic theory[6,28,32] is compared to the melt blend data. This particular mean-field theory indicates some rather striking predictions for the effect of shear on the phase separation of polymer blend melts. For example, the theory[6] indicates that there is *no shift* in the critical temperature with shear, although an "apparent shift" along the direction of flow is indicated because of a suppression of fluctuations along the flow direction. The absence of an observed shift in the critical temperature in the direction normal to flow in the data of Nakatani et al.[10] indicates there is *no real shift* of the critical temperature in the DPS/PVME blend. The paradoxical result of having a different critical temperature along the flow and normal to the flow direction is indicated to be an artifact of fitting scattering data to the Ornstein–Zernike functional form. It should be noted that Nakatani et al. are cautious in their interpretation of the "shift".

On the other hand, the limited data of Hashimoto et al.[8,9] for a semidilute blend solution seem to be consistent with a *true shift* in the critical temperature with shear and these results are discussed in section 3. The existence of this shift is rationalized by a crossover from mean-field to Ising critical behavior upon dilution. A variety of properties which should be sensitive to the conjectured mean-field to Ising crossover are summarized. Some speculative discussion regarding shear-induced turbidity is included in the discussion section since this effect is also likely to be relevant in sufficiently diluted blends.

2. Polymer Blend Melts

The mode-coupling approach[6,7] to phase separation with shear is a continuum hydrodynamic theory which makes no direct reference to the existence of molecules. All the details of the molecular interaction are absorbed into the phenomenological critical temperature and other hydrodynamic parameters. Once the universality class of liquid–liquid phase separation is specified (Ising, mean field) we should be able to apply the predictions of these calculations to small-molecule liquids as well as to polymer solutions. These calculations assume that the only effect of shear on the critical temperature is to suppress fluctuation interactions. Experiments[4,5] on small-molecule phase separation with shear seem to support the MCRG approach of Onuki and Kawasaki[6,7] remarkably well.

Following Onuki and Kawasaki[6,7] we schematically review the *mean-field* calculation of the structure function $S(\mathbf{q},\dot{\gamma})$ for a critical fluid mixture in steady plane Couette flow. A Langevin equation with a shear drift term is introduced to describe the effect of shear on critical concentration fluctuations, and this leads to a linear partial differential equation for "fluctuation variance" $S(\mathbf{q},\dot{\gamma})$. Solution of this equation in the mean-field approximation can be formally obtained by the method of characteristics, but closed form expressions for $S(\mathbf{q},\dot{\gamma})$ require some approximation. Onuki and Kawasaki[6,7] indicate a simple approximate expression[6] for $S(\mathbf{q},\dot{\gamma})$ for "strong shear" (see below)

$$[S(\mathbf{q},\dot{\gamma})]^{-1} \propto \tau + c[q_c(\dot{\gamma})]^{8/5}|q_x|^{2/5} + q^2 \qquad (2.1a)$$

$$c = (5/2)^{2/5}/\Gamma(3/5), \quad \tau \propto T - T_c \qquad (2.1b)$$

q_x, q_y, and q_z denote the components of the scattering wavevector $\mathbf{q}$, where the x-axis is the flow direction, y is the flow gradient direction, z is the "vorticity axis". τ measures the distance of the solution temperature from the critical temperature T_c; Γ is the gamma function. The constant of proportionality in (2.1) for $\dot{\gamma} \to 0$ is conventionally given a "molecular" interpretation for polymer blends based on RPA theory[33] (see Nakatani et al.[10] for a discussion). Before summarizing the implications of (2.1), we review the physical situation associated with critical fluctuations to define a characteristic critical fluctuation relaxation time which is necessary to define the limit of strong shear and to define a characteristic scale $q_c(\dot{\gamma})$ describing the suppression of fluctuations by shear.

When a fluid approaches a critical point, there is a "clustering" of the fluid components which is mathematically described in terms of order parameter (concentration or density) fluctuations.[14] These "clusters", where the order parameter locally differs from its average value,[14] persist to longer and longer times and grow to larger and larger scales as the critical point is approached from the one-phase region. Given the large scale of these transient critical clusters, which are subject to direct visual observation,[14b] it becomes appropriate to describe the dynamically fluctuating fluid by a hydrodynamic model.

Application of shear disrupts the cluster structures[6,7] which are larger than a scale q_c^{-1}. This cutoff wavevector can be estimated from the time scale τ_ξ for cluster Brownian motion.[34]

$$\tau_\xi = f\xi^2/k_B T \qquad (2.2a)$$

ξ is the correlation length describing the spatial extent of the concentration fluctuations[6,7,11]

$$\xi = \xi_0 \tau^{-\nu} \qquad (2.2b)$$

where ξ_0 is a system-specific constant and ν is the Ising correlation length exponent. An estimate of the cluster friction coefficient f is obtained by assuming an idealized spherical cluster of radius ξ

$$f = f_d \eta_0 \xi^{d-2}, \quad f_d = [d/(d-1)][4\pi^{d/2}/\Gamma(d/2-1)] \qquad (2.2c)$$

$$f = 6\pi\eta_0\xi, \quad d = 3 \qquad (2.2d)$$

where η_0 is the zero-shear viscosity, Γ denotes the gamma function, and d is the spatial dimension. Calculations[14,28,34,35] of the Rayleigh line width Γ of a binary fluid of small molecules near its critical point verify the heuristic estimate of τ_ξ in (2.2a), $\Gamma(T \to T_c;\ q = \xi^{-1}) = 1/\tau_\xi$.

For "weak shear", $\dot{\gamma}\tau_\xi \ll 1$, there should be hardly any effect of shear on the structure factor $S(\mathbf{q},\dot{\gamma})$, but for strong shear, $\dot{\gamma}\tau_\xi \gg 1$, the critical clusters of sufficient size ($q < q_c$) are highly distorted.[6] The shear-dependent scale q_c^{-1}

is estimated as[6,34]

$$\tau_\xi(\xi=q_c^{-1})\dot{\gamma} \approx 1 \qquad (2.2e)$$

which combined with (2.2a) gives

$$q_c \approx (f_d\dot{\gamma}/k_BT)^{1/d} \qquad (2.2f)$$

$$q_c \approx (6\pi\eta_0\dot{\gamma}/k_BT)^{1/3}, \quad d = 3 \qquad (2.2g)$$

Equations 2.1 and 2.2 indicate a number of striking predictions for the critical scattering of high molecular weight blends subject to strong shear, $\dot{\gamma}\tau_\xi \gg 1$:

(1) The scattering function is distorted by shear and is completely *separable* along the flow and normal to flow directions. Scattering normal to flow direction is unaffected by shear.

(2) The critical temperature T_c is *unaffected* by shear.[6] Moreover, the hydrodynamic theory also predicts that the critical concentration is unaffected by shear, even in "Ising" (non-mean-field) critical mixtures.[6,7,36]

(3) The projection of the structure function $S(\mathbf{q},\dot{\gamma})$ along the flow direction

$$[S(q_x,\dot{\gamma})]^{-1} \propto \tau + c[q_c(\dot{\gamma})]^{8/5}|q_x|^{2/5} + q_x^{\,2}, \quad \dot{\gamma}\tau_\xi \gg 1 \qquad (2.3a)$$

has a slowly varying nonanalytic component $|q_x|^{2/5}$ for intermediate q_x. Taking $|q_x|^{2/5} \approx D$, where D is a constant, gives the approximation

$$S(q_x,\dot{\gamma})^{-1} \approx [S_\parallel(q_x,\dot{\gamma})]^{-1} \propto \tau + cDq_c^{\,8/5} + q_x^{\,2} \qquad (2.3b)$$

for q_x not too small. Equations 2.3b and 2.2a indicate that an Ornstein–Zernike "fit" to $S(q_x,\dot{\gamma})$ for intermediate q_x should lead to an apparent variation of $S(q_x=0;\dot{\gamma})$ and the "correlation length" along the flow direction $\xi_\parallel$ as

$$S_\parallel(q_x=0;\dot{\gamma})^{-1} \sim \tau + \Delta\tau, \quad \xi_\parallel \sim (\tau + \Delta\tau)^{-1/2} \qquad (2.3c)$$

$$\Delta\tau \sim q_c^{\,8/5} \sim \dot{\gamma}^{8/15} \sim \dot{\gamma}^{0.53} \qquad (2.3d)$$

It is stressed that the apparent shift $\Delta\tau$ of T_c along the flow direction is due to a purely hydrodynamic effect owing to a faster regression of fluctuations along the flow direction.[6] The apparent shift in the critical temperature indicated by (2.3d) should not be confused with the *true shift* in the critical temperature indicated for small-molecule critical mixtures[4-7]

$$\Delta T_c(\dot{\gamma})/T_c(\dot{\gamma}=0) = 0.08\epsilon(\dot{\gamma}\tau_\xi)^{1/d\nu} + O(\epsilon^2) \sim \dot{\gamma}^{0.53}, \quad d = 3 \qquad (2.4)$$

$$\nu(d=3) \approx 0.63, \quad \epsilon = 4 - d, \quad \tau_\xi = \tau_\xi\,(\xi=\xi_0) \qquad (2.5)$$

where ν is the Ising critical exponent[11-13] [see (2.2b)]. The similarity of (2.4) to the apparent shift indicated in (2.3c) is a consequence of the approximate relation ν (Ising) $\approx$ $^5/_8$ in three dimensions.[37] Extensive experiments by Beysens et al.[4,5,38] on small-molecule mixtures support the shear rate dependence indicated by (2.4) where order of magnitude agreement with the $O(\epsilon)$ estimate of the prefactor is obtained. Higher order ϵ-expansion calculations should improve the situation. The main implication of (2.4) for the present discussion is that the scattering *both* along and normal to the flow direction must be carefully examined to differentiate a true from an apparent shift of the critical temperature. Turbidity measurements are not adequate for determining such a shift.

The growth of transient clusters as the critical point is approached is accompanied by local velocity fluctuations. Molecular motions within a cluster are highly correlated in much the same fashion as the monomers within a flexible polymer chain. In the "decoupled mode" theory of Ferrell[28] the velocity and concentration fluctuations are assumed to be uncorrelated random processes and the Ornstein–Zernike (mean-field) approximation is used to describe the equilibrium concentration fluctuations. This decoupled mode theory is evidently a variety of dynamical mean-field theory, and it is suggested that this theory should apply to high molecular weight blends[35] over the wide range of temperatures to which static mean-field theory applies. There are significant differences between the transport properties of Ising and mean-field fluids which should allow their discrimination.

The distinction between mode-coupling and decoupled mode theories can be somewhat confusing since the original mode-coupling calculations of Kawasaki[14] involve approximations which are *equivalent* to the decoupled mode theory.[28] Although the decoupled mode theory neglects the *cross correlation* between concentration and velocity fluctuations, the theory accounts for the physical coupling of concentration and velocity fluctuations which affects mass transport.[28] Nonlinear contributions to the free energy density of Ising-type fluids cause a cross correlation between concentration and velocity fluctuations; these corrections to the leading order decoupled mode theory can be calculated by ϵ-expansion RG methods or by higher order mode-coupling calculations.[6,7,14] The term mode-coupling theory will be reserved for calculations which include the cross correlation of velocity and concentration fluctuations.

The mode-coupling and dynamical RG theories include the nonlinear coupling of the velocity and concentration fluctuations which arise in Ising binary fluids. These couplings give rise to a diverging zero-shear viscosity in the vicinity of the critical point[6,7,12]

$$\eta_0 \sim \xi^{x_\eta} \qquad (2.6a)$$

Mode-coupling calculations in $d = 3$ and ϵ-expansion RG estimates of x_η give[39]

$$x_\eta = 0.065 \text{ (mode-coupling, } d = 3) \qquad (2.6b)$$

$$x_\eta = \epsilon/19 + 0.018\epsilon^2 + O(\epsilon^3) \text{ (}\epsilon\text{-expansion RG)} \qquad (2.6c)$$

Estimates of x_η from the temperature dependence of the zero-shear viscosity η_0 [see (2.2b)] yield

$$\eta_0 \sim |T - T_c|^{-x_\eta\nu}, \quad |T - T_c| \to 0^+ \qquad (2.6d)$$

where $x_\eta\nu$ (Ising) = 0.041.[40] The first and second normal forces of a critical binary (Ising) fluid are also predicted to diverge at the critical point in a fashion similar to η_0 in (2.6d).[41] The divergence of η_0 as $T \to T_c$ causes the characteristic relaxation time τ_ξ to become longer. Inserting (2.6a) into (2.2) yields the scaling relation

$$\tau_\xi \sim \xi^z, \quad z(\text{Ising}) = d + x_\eta \qquad (2.6e)$$

This slowing down of relaxation due to correlations between mode fluctuations is directly reflected in the Rayleigh line width Γ as $T \to T_c$. Careful measurements of Γ by Burstyn and Sengers[42] for a near-critical 3-methylpentane/nitroethane mixture indicate that $\Gamma \sim \xi^{-z}$ where $z = 3.063 \pm 0.024$ is in excellent agreement with the recent $d = 3$ mode-coupling theory estimate (2.6b).

The viscosity $\eta(\dot{\gamma})$ of a critical Ising binary fluid exhibits a characteristic "shear thinning" in the vicinity of the critical point. In the limit of strong shear the critical clusters responsible for the divergence of the zero-shear viscosity [see (2.6a)] η_0 are disrupted, and in the limit of infinite shear the clusters are broken up altogether so that η_0 is independent of ξ.[41] An approximation for the shear viscosity $\eta(\dot{\gamma})$ is obtained which reflects this physics by noting that $\eta(\dot{\gamma})$ is an even function of shear[43,44]

$$\eta_r(\dot{\gamma}) = \eta_r(\dot{\gamma}\to 0^+)[1 + A_\epsilon(\dot{\gamma}\tau_\xi)^2]^{-x_\eta/2z} \tag{2.7a}$$

$$\eta_r = \eta(\dot{\gamma})/\eta_b \tag{2.7b}$$

$$\eta_r(\dot{\gamma}\tau_\xi \gg 1) \sim \dot{\gamma}^{-x_\eta}, \quad \dot{\gamma}\tau_\xi \gg 1 \tag{2.7c}$$

Equation 2.7 assumes $\eta(\dot{\gamma})$ is analytic in $\dot{\gamma}$, and the exponent is determined in (2.7a) by requiring that $\eta_r(\dot{\gamma})$ is independent of ξ for $\dot{\gamma} \to \infty$. This scaling argument is consistent with the *exact* strong shear result (2.7c) of Onuki and Kawasaki.[41] In (2.7b) the viscosity η_b is the "background" viscosity (see Sengers[12] and Berg[40]), which is analogous to the solvent viscosity in dilute polymer solution theory, and A_ϵ is a constant which is expected to be universal. Measurements of $\eta(\dot{\gamma})$ in critical small-molecule liquids are qualitatively consistent with (2.7), but the data are too limited for quantitative comparison.[45,46] There are some limited $\eta(\dot{\gamma})$ data for polystyrene in cyclohexane near the critical point.[40]

The absence of a coupling between velocity and concentration fluctuation interactions in the mean-field decoupled mode theory implies a rather different behavior of critical transport properties. There is *no divergence* in the zero-shear viscosity as $T \to T_c^+$ and thus no shear thinning arising from critical point fluctuations. Further, the dynamical index z describing the order parameter relaxation time $\tau_\xi \sim \xi^z$ is exactly equal to d [see (2.2)], and Kawasaki's and Ferrell's expression for the Rayleigh line width $\Gamma(q)$ becomes *exact*.[14,28] There are evidently a number of independent measurements which can be employed to test the hypothesis that high molecular weight polymer blends are described by the mean-field decoupled mode theory.[47]

Recently Nakatani et al.[10,48] provided small-angle neutron scattering data for high molecular weight polymer blends under shear which can be compared to the mean-field calculation of $S(\mathbf{q},\dot{\gamma})$ in (2.1) and the transport properties summarized above. These data indicate a decoupling[10,48] of $S(\mathbf{q},\dot{\gamma})$ along the flow q_x and the normal to flow directions (q_y, q_z) in accord with (2.3). The apparent critical temperature and the scattering along the normal to flow direction were found to be *independent* of shear within experimental error. This striking observation accords exactly with the mean-field hydrodynamic theory. An Ornstein–Zernike fit of the projection of $S(\mathbf{q},\dot{\gamma})$ along the flow direction (see Figures 5 and 6 of Nakatani et al.[10]) indicates a shift of $S(\mathbf{q},\dot{\gamma})$ and the correlation length $\xi_\parallel(\dot{\gamma})$ along the flow direction. The apparent shift of the critical temperature with $\dot{\gamma}$ along the flow direction corresponds to an exponent of about $^1/_2$ in (2.3d).[10] Another striking verification of the hydrodynamic theory is indicated in Figure 17 of Nakatani et al. The critical wavevector $\mathbf{q}_c$, obtained by observing the value of q_x at which the projection of $S(\mathbf{q},\dot{\gamma})$ along the flow direction first deviates from the zero-shear projection,[10] obeys (2.2g) over a wide range of shear rates and temperature. Both the prefactor and exponent z appear to agree *quantitatively* with (2.2a). The prediction (2.2b) for the critical shear rate for strong shear suppression of fluctuations has not been checked yet, and further experiments will be required to test the mean-field decoupling theory. Certainly the main qualitative features of high molecular weight blend phase separation with shear seem to be well described by the decoupling theory without modification. Thus, there seems to be some support for the suggestion above of using the decoupled mode theory as an appropriate mean-field model of polymer blend melt dynamics. This could have important implications for the description of spinodal decomposition in polymer blends. The previous mode-coupling calculations of the Rayleigh line width Γ by Fredrickson and Bates[23b] for polymer blends involve approximations equivalent to the decoupled mode theory.

The hydrodynamic theory also provides important insight into the origin of apparent shifts in the critical temperatures in a variety of condensed polymer systems subject to an applied field which can suppress or enhance fluctuations along the field direction. Such fields can lead to a mistaken impression of a shift in critical temperature which depends on the field direction. As a further example, recent SANS data indicated different spinodal temperatures parallel and normal to deformation in deformed mixtures of cross-linked DPS and linear PVME (see Figure 10 of Bauer et al.[49]). In this instance the apparent value of $S(0)$ along the parallel to stretch direction is found to be *lower* than that in the normal direction. The projection of $S(0)$ normal to the direction of stretch is insensitive to deformation. By analogy with the sheared blend we expect that in fact there is *no true shift* of the spinodal and that increased fluctuations along the stretch direction are being registered as an apparent shift of the critical temperature.

3. Blends in Semidilute Solution

Fluctuation effects should become increasingly important upon dilution in a small-molecule solvent. This effect is evident in experimental estimates of the Flory–Huggins χ-parameter which becomes strongly molecular weight dependent[50] under dilute and semidilute conditions (see de Gennes[29]). A crossover from mean-field to Ising phase separation might also be expected upon dilution of a blend to low polymer concentrations in a low molecular weight solvent because of the increased influence of fluctuation effects. I am unaware of any specific evidence for such a crossover, however. The critical temperature of the diluted blend depends very strongly on solvent concentration, and large shifts of T_c on the order of 50 °C can easily be achieved, a very impressive effect which deserves study.

Given the increased prevalence of fluctuation effects upon dilution, we can expect a rather different response of a high molecular weight blend to shear upon dilution. Hashimoto et al.[8,9] consider the effect of shear on a 3% polybutadiene/polystyrene blend dissolved in dioctyl phthalate (DOP) which can be contrasted with experiments of Nakatani et al.[10] Scattering intensity *normal* to the flow direction is found to depend strongly on shear rate, giving rise to a very large apparent shift in the critical temperature[8,9]

$$\Delta T_c(\dot{\gamma})/T_c(\dot{\gamma}=0) = K(\dot{\gamma})^{0.50\pm0.02} \tag{3.1}$$

$$K = (2.6 \pm 0.6) \times 10^{-3}$$

The constant K is about 3000 times larger than previous estimates of K for small-molecule liquids.[8,9] Hashimoto et al.[8] indicate that (2.4a) gives the correct order of magnitude for the apparent shift of the critical temperature given in (3.1) where ξ_0 is assumed to be on the order of the chain radius of gyration. The existence of such a shift is consistent with Ising mixture phase separation and with the *conjectured* crossover between mean-field to Ising critical phase separation in blends indicated above. The MCRG theory[6,7] indicates further that the structure factor projection normal to the flow direction should be described well by the Ornstein–Zernike form where the critical temperature is shear dependent. The tentative interpretation of Hashimoto et al.[8,9] of the observed shear homogenization in terms of a true shift of the critical temperature seems quite reasonable. The preliminary data also indicate no detectable shift of the critical concentration with shear, in accord with MCRG theory for Ising binary fluids.[6,36] Scattering data for $S(\mathbf{q},\dot{\gamma})$ projected along the flow direction are needed to further check the consistency of the MCRG theory with shear experiments on diluted blends. A complementary neutron scattering study of diluted blends would be helpful, since the scattering could be studied starting from the single-phase quiescent state. Measurement of the shear-dependent transport properties should also be helpful in discriminating mean-field versus Ising critical behavior. In summary, application of the MCRG theory to diluted blends looks promising.

Shear suppresses fluctuation interactions which shift the critical temperature from its mean-field value. This would seem to imply that only a finite shift of the critical temperature should be possible and that the temperature shift in (3.1) should "saturate" at a finite value related to the mean-field critical temperature for $\dot{\gamma} \to \infty$. Evidently (3.1) is applicable to a finite range of shear rates, and some effort should be made to see if such a saturation effect is observed at high shear rates for polymer blends.

4. Conclusion

Recent experimental studies of polymer blends in simple shear flows have indicated large apparent shifts of the temperature for phase separation.[8,10] Nakatani et al.[10] observe a large shift along the flow direction but *no detectable shift* normal to the flow direction in a relatively high molecular weight blends of DPS/PVME. In contrast, Hashimoto et al.[8,9] observe a large shift normal to flow in a diluted (DOP solvent) blend of PS/PB. Both studies observe an apparent "shear stabilization" with shear and claim agreement with the MCRG theory[6,7] of Onuki and Kawasaki[6,7] for the shear dependence of the critical temperature shift. These experimental studies raise a number of interesting theoretical questions. Most importantly, how is it possible for the critical temperature to differ along the flow and normal to flow directions? Experiments on a deformed blend[49] of cross-linked DPS and linear PVME also indicate a similar phenomenon—no shift of the phase-separation temperature along the direction normal to stretch while indicating a large apparent shift along the stretch direction. The mean-field hydrodynamic theory[6,7,28] of phase separation explains the origin of this phenomenon rather clearly in the case of the sheared blends. If there is no shift of the critical temperature along the normal to flow direction, then there simply is no shift of the critical temperature. However, fluctuations along the flow direction are suppressed by shear and can lead to an apparent shift of the phase-separation temperature [see (2.3)]. The agreement of the shear dependence of the apparent shift along the flow direction[10] with the MCRG estimate (eq 2.4a) claimed by Nakatani et al. is simply a coincidence. There is no shift of the phase-separation temperature in the mean-field hydrodynamic theory of a critical binary fluid.

The diluted blends of Hashimoto et al.[8,9] respond to shear rather differentially than the melt blends of Nakatani et al., and this difference raises other interesting issues. Hashimoto et al.[8,9] observe a shift of the apparent phase-separation temperature normal to the shear direction, and the agreement of the order of magnitude of this shift with the MCRG expression (eq 2.4a) suggests that a shift similar to that in small-molecule liquids is being observed. The difference between the observations of Hashimoto et al.[8] and Nakatani et al.[10] can be rationalized by assuming a crossover from mean-field to Ising critical behavior in these blends upon dilution. Of course, further experiments will be necessary to check this conjecture. Such a crossover should also be obtained upon lowering the molecular weight of the blend components. Various experimental measures are listed which could be used to distinguish the mean-field critical behavior, as predicted from the decoupled mode theory, as opposed to Ising critical behavior. Finally, we make some observations on the flow-induced turbidity phenomenon because of its likely relevance to sufficiently diluted blends.

High molecular weight polymers dissolved in low molecular weight solvents often exhibit turbidity when sheared. Evidently some modification of the conventional hydrodynamic theory is necessary to explain this phenomenon. Helfand and Fredrickson,[23] Onuki,[24] and Milner[25] have recently developed models to describe the enhanced turbidity of flowing polymer solutions based on the mode-coupling theory pattern, and Rangel-Nafaile et al.[16] have presented interesting alternative arguments for shear-induced phase separation based on thermodynamic arguments.

I believe that some qualitative insight into the flow-induced turbidity phenomenon can be obtained by combining the hydrodynamic theory of phase separation with an estimate of the "free-energy storage" with flow in a non-Newtonian fluid. In practice, rather crude estimates of energy storage in flow are introduced based on idealized models of polymer solutions (dumbbell,[51] Rouse model,[52] ...). Bernstein et al.[53] have developed a formal nonequilibrium theory which defines free-energy change under flow conditions in the case of "simple" fluids. Further theoretical efforts will evidently be necessary to more precisely define the concept of free-energy storage under flow conditions, and at the present time the heuristic approach of Silberberg and Kuhn,[1] Philippoff and ver Strate,[3] and Rangel-Nafiele et al.,[16] which estimates the free-energy storage from the second normal force,[3,51,54] provides a useful *model* whose implications are worth exploring. Combining the normal force measurements with the Flory–Huggins model, a major approximation in itself at semidilute polymer concentrations, yields a rough estimate of the shift of T_c due to shear in non-Newtonian liquids.[16] In Newtonian fluids the first normal force vanishes, so there is no contradiction with the conventional hydrodynamic theory of phase separation which assumes a Newtonian fluid.[6,7] Combining this model of $T_c(\dot{\gamma})$ with the hydrodynamic theory [see (2.1)] leads to predictions that accord in some qualitative ways with the measurements of Hashimoto and Fujioka[17] for sheared solutions of high molecular weight PS dissolved in DOP. These experiments indicate shear-induced turbidity with *enhanced* scattering *normal* to the flow direction, as indicated by the simple model.[16] However, the model *does not* seem to explain the mysterious narrow "dark streak" in the scattering along the normal to flow direction.[17,55] Such an effect would be consistent with a small negative exponent replacing the $^2/_5$ exponent in (2.1). Physically such a term would reflect a suppression of long wavelength fluctuations along the flow direction due to elastic effects in a fashion analogous to block copolymers and cross-linked blend networks. A comparison of the model and experiment is intended once more complete experimental data are available.

The most provocative aspect of the phenomenological estimate of $T_c(\dot{\gamma})$, based on normal force measurements, is the connection it indicates between shear-induced turbidity and the concentration dependence of the steady shear compliance $J(\dot{\gamma})$. The steady shear compliance of high molecular weight polymer solutions often exhibits a maximum[16,56] in the semidilute concentration regime which is the origin of the estimated T_c shift.[16] An understanding of this maximum then offers the prospect of understanding the molecular origin of shear-induced turbidity.

The position of the maximum in $J(\dot{\gamma})$ seems to coincide with the critical concentration for entanglement.[16,56] Such a maximum in the zero-shear compliance $J_e = J(\dot{\gamma}\rightarrow 0^+)$ is expected as a consequence of hydrodynamic screening (the compliance is a Rouse chain is about twice that of a chain estimated within the preaveraged Rouse–Zimm chain with strong hydrodynamic interaction[57]). The rapid decrease of J_e at higher concentrations is associated with the phenomenon of entanglement.[57,58] Onuki[24] does not seem to appreciate this variation of J_e with concentration in his criticism of the work of Rangel-Nafaile et al.[16] Accepting our phenomenological estimate of $T_c(\dot{\gamma})$ in non-Newtonian liquids implies that the physical origin of shear-induced turbidity is a complicated interplay of hydrodynamic and entanglement interactions. Experiments on low molecular weight and high molecular weight polymer solutions subject to shear should be made to characterize the role of entanglement and concentration effects in shear-induced turbidity. A correlation of the apparent shift in T_c and $\dot{\gamma}\tau_T$, where τ_T is the terminal relaxation time[57] $\tau_T \sim O(\eta_0 J_e)$, should be considered. The critical shear rate for shear-induced turbidity is found to have a very strong molecular weight dependence in the preliminary measurements of Hashimoto and Fujioka,[17] and it suggested that the critical shear rate $\dot{\gamma}_c$ should scale as $\dot{\gamma}_c \sim 1/\tau_T$.

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$$(T_c - T_{co})/T_{co} \approx (\phi_c - \phi_{co})/\phi_{co}$$

(T_{co}, ϕ_{co}) denotes the unperturbed consulate point. Jacobs considers a variety of perturbations (impurities, deuterium labeling, pressure) and suggests that a shift in T_c should be universally correlated with a shift in ϕ_c.

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$$\nu(\text{Ising}) = (d+2)/4(d-1), \quad 2 \le d \le 4$$

$$\nu(d{=}3) = 5/8 = 0.625; \quad \nu = {}^1/_2, d > 4$$

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