

Dynamics of phase separation in polymer solutions under shear flow

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(Received 14 August 1996; revised manuscript received 13 February 1997)

We present a general model for the dynamics of phase separation in polymer-solvent mixtures under shear flow, which unifies previous phenomenological theories. For the dilute case, the model can be derived in the absence of hydrodynamic interactions via the appropriate Smoluchowski equation. Linear analysis shows that the shear flow does not change the equilibrium phase boundary. We then generalize the model to the semidilute case, and find that the phase separation temperature is indeed shifted by the shear flow. The results indicate that a nonlinear concentration dependence of the modulus is necessary for a shift in the phase separation temperature. [S1063-651X(97)50306-0]

PACS number(s): 61.25.Hq, 47.10.+g, 62.10.+s

The dynamics of phase separation in polymer mixtures under shear flow has generated a great deal of interest over the last two decades [1–8]. A number of groups have reported that the phase separation of polymer-solvent mixtures can be dramatically changed by macroscopic flow fields. Indeed, a greatly enhanced turbidity is observed in flowing polymer solutions at temperatures much higher than the equilibrium critical temperature [1–3]. However, the mechanism of the observed phenomenon is not completely clear as current theoretical models provide conflicting explanations. Helfand and Fredrickson (HF) argued that the observed phenomenon is not a real phase separation, but is only a result of large-scale fluctuations in the monomer concentration induced by the shear flow [4]. On the other hand, Onuki suggested that the equilibrium phase boundary is shifted to higher temperatures by the shear flow [6]. Both groups are correct, and we believe the divergence in views may be attributable to the fact that the two groups used different models [7]. A key to resolving this issue is to develop a more fundamental theory that will account for the complexity of the system, and this is what we report here.

In the dynamics of phase separation, the basic stochastic variable is the monomer concentration $\phi(r,t)$, which describes the coarse-grained configuration of the system. However, in the presence of shear flow, $\phi(r,t)$ must couple with the fluid velocity $v(r,t)$, and the stress tensor $\sigma(r,t)$ of the deformed polymer chains. Since in general, the strain tensor w and σ are not independent variables, the stress tensor is chosen as the independent variable. The state of the system can then be described by a set of collective variables $\{\phi, v, \sigma\}$. The dynamics of the system is determined by a set of coupled Langevin equations governing the time evolution of the state $\{\phi, v, \sigma\}$. The time evolution of v is to be described by the Navier-Stokes equation. One must construct the Langevin equations for ϕ and σ .

In principle, the Langevin equations for ϕ and σ can be projected out of the equation describing the evolution of the full probability distribution [9]. While seminal work has already been carried out along this line [4,7], and some general features of the equation for ϕ were derived [4,7], one knows little about the equation for the stress tensor σ . A systematic approach to this problem, which can be carried out in the

dilute regime, combined with a synthesis of phenomenological approaches [4–6] leads us to propose the following set of equations to describe phase separation of polymer-solvent mixtures under shear:

$$\frac{\partial \phi}{\partial t} + v \cdot \nabla \phi = \zeta^{-1} \nabla \cdot \left[\phi \nabla \left(\frac{\delta F}{\delta \phi} \right)_w - \nabla w : \left(\frac{\delta F}{\delta w} \right)_\phi - \nabla \cdot \tau \right] + \theta_\phi, \quad (1)$$

$$\rho \left(\frac{\partial v}{\partial t} + v \cdot \nabla v \right) = -\nabla p + \eta_s \nabla^2 v + \nabla \cdot \tau + (\nabla \phi) \left(\frac{\delta F}{\delta \phi} \right)_w + \theta_v, \quad (2)$$

$$\lambda(\phi) \left[\frac{\partial \sigma}{\partial t} + \tilde{v} \cdot \nabla \sigma - \sigma \cdot \nabla \tilde{v} - (\nabla \tilde{v})^\dagger \cdot \sigma \right] + \sigma - \frac{b^2}{12} \nabla^2 \sigma = G(\phi) \delta. \quad (3)$$

In these equations, a linear stress-strain relation $\sigma = Gw$ is adopted with scalar modulus G , $F(\phi, w)$ is the free energy functional; $\tilde{v} = v - k_B T u(\nabla \phi) / \zeta$, $\tau = \sigma - G \delta$, with δ the unit tensor; λ is the relaxation time, and the constants u , ζ , η_s , ρ , and b are the excluded volume interaction parameter, the friction coefficient, the solvent viscosity, the solvent density, and the effective bond length, respectively. Note that, in general, ζ is ϕ dependent, and \tilde{v} has the interpretation of the polymer velocity in a two-fluid picture [10]. As usual, the incompressibility condition $\nabla \cdot v = 0$ is adopted, and is enforced by choice of the pressure p . Equation (2) is the generalized Navier-Stokes equation, and together with Eq. (1), constitutes a generalized Model H (in the terminology of the critical dynamics literature) [11], which has been used previously [4,6]. The stress tensor σ is treated as a dynamical variable satisfying Eq. (3), which is referred to as the upper-convected Maxwell equation [12]. Our method shows that the polymer velocity \tilde{v} enters Eq. (3), the Maxwell equation [10] and yields, from a microscopic starting point, contributions to the Maxwell equation arising from order-parameter gradients and involving the excluded volume interactions.

First we show that if hydrodynamic interactions are neglected (“NHI-dynamics”) [13], Eqs. (1) and (3) can be derived for a dilute system using the constrained distributions projected out of the full distribution function [9]. The state of polymer-solvent mixtures in the presence of shear flow can be described microscopically by a fluid velocity field v and a set of monomer position vectors $\{R\} = \{R_1, R_2, \dots, R_N\}$. The velocity v obeys the Navier-Stokes equation (2), while the configuration of $\{R\}$ is determined by its probability distribution functional $\Psi(\{R\}, t)$, which is governed by the Smoluchowski equation [14]

$$\frac{\partial \Psi(\{R\}, t)}{\partial t} = \frac{\partial}{\partial R_{ni}} \left\{ -v_i(R_n) + L_{nm}^{ij}(\{R\}) \times \left[k_B T \frac{\partial}{\partial R_{mj}} + \frac{\partial U}{\partial R_{mj}} \right] \right\} \Psi(\{R\}, t), \quad (4)$$

where L_{nm}^{ij} is the mobility matrix, $v(R_n)$ is the fluid velocity at position R_n , U is the Edwards Hamiltonian [14], and repeated indices imply summations ($i, j = x, y, z$, and $n = 1, \dots, N$). (Our results may be easily generalized to allow U to contain any two-body, three-body . . . interactions among the monomers. More general interactions among the monomers will just change the form of \tilde{v} .) When hydrodynamic interactions are ignored, the mobility matrix $L_{nm}^{ij} = \zeta^{-1} \delta_{ij} \delta_{nm}$, and one has what we have termed, for compactness, NHI dynamics [13]. When hydrodynamic interactions are taken into account, L_{nm}^{ij} is given by the Oseen tensor, and one has the Zimm model [14]. In either case, this approach based on Eq. (4) is limited to dilute systems [14].

For a given microscopic configuration $\{R\}$ of the system, the molecular expressions for $\phi(r)$ and $\sigma(r)$ can be written as $\hat{\phi}(r) = \int_0^N dn \delta(r - R_n)$, and $\hat{\sigma}(r) = (3k_B T / b^2) \int_0^N dn \delta(r - R_n) (\partial R_n / \partial n) (\partial R_n / \partial n)$. The probability distribution functional of the state $\{\phi, \sigma\}$ at time t can be expressed as $g(\phi, \sigma; t) = \int \mathcal{D}R \delta(\phi - \hat{\phi}) \delta(\sigma - \hat{\sigma}) \Psi(\{R\}, t)$.

For the equilibrium state, Ψ reduces to $\Psi_e(\{R\}) = \exp[-U(\{R\})/k_B T]$. Then, $g(\phi, \sigma)$ reduces to the constrained partition function $g_e(\phi, \sigma)$, which gives the constrained free energy of the system, $F(\phi, w) \equiv -k_B T \ln g_e(\phi, \sigma(w))$. Note that the independent variable of the free energy is w [15], so the stress-strain relation is needed to obtain $F(\phi, w)$. Our perturbation result (similar in spirit to the familiar random-phase approximation [14]) for the free energy to Gaussian order can be written as [16]

$$F(\phi, \pi) = k_B T \int dr \left\{ \frac{1}{2} \left(u + \frac{1}{N \phi_0} \right) \phi^2 + \frac{b^2}{36 \phi_0} (\nabla \phi)^2 + \frac{1}{4k_B T G(\phi_0)} \pi : \pi \right\}, \quad (5)$$

where ϕ_0 is the average concentration, π is a new stress tensor introduced for convenience and given by $\sigma = k_B T [\phi \delta + (b^2/6) \nabla \nabla \phi] + \pi$, and G is the shear modulus given by

$$G(\phi) = \frac{3}{2} G_0(\phi) \left(u \phi + \frac{1}{N} \right), \quad (6)$$

with $G_0(\phi) = k_B T \phi$ the “ideal gas” pressure. For a θ solvent, $u \phi$ should be replaced by $w \phi^3$ because the leading interaction term is the three-body interaction. From the form of Eq. (5), the free energy can be expressed as $F(\phi, \pi) = F_{\text{gl}}(\phi) + F_{\text{el}}(\phi, \pi)$, where F_{gl} is the usual Ginzburg-Landau form and F_{el} is the elastic contribution, $F_{\text{el}}(\phi, \pi) = \frac{1}{4} \int dr G^{-1}(\phi) \pi : \pi + O((\phi - \phi_0) \pi^2, \dots)$. The form of the elastic free energy was proposed phenomenologically by Onuki [6].

The Fokker-Planck (FP) equation necessary for deriving the dynamical equations can be derived by taking the time derivative of $g(\phi, \sigma)$

$$\frac{\partial g(\phi, \sigma; t)}{\partial t} = \int \mathcal{D}R \delta(\phi - \hat{\phi}) \delta(\sigma - \hat{\sigma}) \frac{\partial \Psi(\{R\}, t)}{\partial t}. \quad (7)$$

Substituting Eq. (4) into Eq. (7) and applying the local equilibrium approximation introduced by Kawasaki and Sekimoto [9], we obtain

$$\begin{aligned} \frac{\partial g(\phi, \sigma; t)}{\partial t} \simeq & \int \mathcal{D}R \delta(\phi - \hat{\phi}) \delta(\sigma - \hat{\sigma}) \\ & \times \frac{\partial}{\partial R_{ni}} \left\{ -v_i(R_n) + L_{nm}^{ij}(\{R\}) \right. \\ & \times \left. \left[k_B T \frac{\partial}{\partial R_{mj}} + \frac{\partial U}{\partial R_{mj}} \right] \right\} \\ & \times \Psi_e(\{R\}) \frac{g(\hat{\phi}, \hat{\sigma}; t)}{g_e(\hat{\phi}, \hat{\sigma})}. \end{aligned} \quad (8)$$

Following the procedures developed in Ref. [9] and using the properties of δ functions, this FP equation can be written as

$$\begin{aligned} \frac{\partial g(\phi, \sigma; t)}{\partial t} = & \int dr dr' \\ & \times \sum_{a,b} \frac{\delta}{\delta a(r)} \cdot \left\{ \Lambda_{rr'}^a + \Lambda_{rr'}^{ab} \cdot \left[k_B T \frac{\delta}{\delta b(r')} \right. \right. \\ & \left. \left. + \frac{\delta F}{\delta b(r')} \right] \right\} g(\phi, \sigma, t), \quad a, b = \phi, \sigma, \end{aligned} \quad (9)$$

where F is the free energy and the projected Onsager coefficients are given by

$$\Lambda_{rr'}^a = - \left\langle \delta(r' - R_n) \frac{\partial \hat{a}(r)}{\partial R_{ni}} v_i(r') \right\rangle_{g_e}, \quad (10)$$

$$\Lambda_{rr'}^{ab} = \left\langle \frac{\partial \hat{a}(r)}{\partial R_{ni}} L_{nm}^{ij}(\{R\}) \frac{\partial \hat{b}(r')}{\partial R_{mj}} \right\rangle_{g_e}. \quad (11)$$

Here the averages are over the equilibrium probability distribution function $g_e(\phi, \sigma)$. Note that Λ^{ϕ} , and $\Lambda^{\phi\phi}$ are scalars, Λ^{σ} , $\Lambda^{\phi\sigma}$, and $\Lambda^{\sigma\phi}$ are second-rank tensors, and $\Lambda^{\sigma\sigma}$ is a fourth-rank tensor. In Eq. (9), the dot products stand for “full scalar products.” For example, $\phi \cdot \Lambda^{\phi}$ means $\phi \Lambda^{\phi}$, $\sigma \cdot \Lambda^{\sigma}$ means $\sigma : \Lambda^{\sigma}$, and so on.

From the FP equation (9), we can obtain the Langevin equations for ϕ and σ , respectively:

$$\begin{aligned} \frac{\partial \phi(r,t)}{\partial t} = & - \int dr' \left\{ \Lambda_{rr'}^{\phi} + \Lambda_{rr'}^{\phi\phi} \frac{\delta F}{\delta \phi(r',t)} \right. \\ & + \Lambda_{rr'}^{\phi\sigma} \frac{\delta F}{\delta \sigma(r',t)} - k_B T \left[\frac{\delta}{\delta \phi(r',t)} \Lambda_{rr'}^{\phi\phi} \right. \\ & \left. \left. + \frac{\delta}{\delta \sigma(r',t)} \Lambda_{rr'}^{\phi\sigma} \right] \right\}, \end{aligned} \quad (12)$$

$$\begin{aligned} \frac{\partial \sigma(r,t)}{\partial t} = & - \int dr' \left\{ \Lambda_{rr'}^{\sigma} + \Lambda_{rr'}^{\sigma\sigma} \frac{\delta F}{\delta \sigma(r',t)} + \Lambda_{rr'}^{\sigma\phi} \frac{\delta F}{\delta \phi(r',t)} \right. \\ & \left. - k_B T \left[\frac{\delta}{\delta \sigma(r',t)} \Lambda_{rr'}^{\sigma\sigma} + \frac{\delta}{\delta \phi(r',t)} \Lambda_{rr'}^{\sigma\phi} \right] \right\}. \end{aligned} \quad (13)$$

Note that the above derivation is independent of a specific form of L_{nm}^{ij} , so that Eqs. (12) and (13) are valid even with the inclusion of hydrodynamic interactions.

To further simplify the Langevin equations for ϕ and σ , one needs to calculate the projected Onsager coefficients. If hydrodynamic interactions are neglected, five of the coefficients can be obtained exactly. We list the first four expressions here

$$\Lambda_{rr'}^{\phi} = -v_i(r') \phi(r') [\nabla_{r'l} \delta(r-r')] , \quad (14)$$

$$\begin{aligned} (\Lambda_{rr'}^{\sigma})_{ij} = & -v_l(r') [\nabla_{r'l} \delta(r-r')] \sigma_{ij}(r') \\ & + v_i(r') [\nabla_{r'l} \delta(r'-r)] \sigma_{lj}(r) \\ & + v_j(r') [\nabla_{r'l} \delta(r'-r)] \sigma_{li}(r) , \end{aligned} \quad (15)$$

$$\Lambda_{rr'}^{\phi\phi} = \zeta^{-1} [\nabla_r \cdot \nabla_{r'} \delta(r-r') \phi(r')] , \quad (16)$$

$$\begin{aligned} (\Lambda_{rr'}^{\phi\sigma})_{ij} = & \zeta^{-1} \{ [\nabla_r \cdot \nabla_{r'} \delta(r-r')] \sigma_{ij}(r') \\ & + [\nabla_{ri} \nabla_{r'l} \delta(r-r')] \sigma_{lj}(r') \\ & + [\nabla_{rj} \nabla_{r'l} \delta(r-r')] \sigma_{li}(r') \} . \end{aligned} \quad (17)$$

The expressions for $\Lambda_{rr'}^{\phi\phi}$ and $\Lambda_{rr'}^{\phi\sigma}$ have been obtained previously [7]. The sixth Onsager coefficient $\Lambda_{rr'}^{\sigma\sigma}$ cannot be calculated exactly. However, starting with the definition of $\Lambda_{rr'}^{\phi\phi}$ and $\Lambda_{rr'}^{\sigma\sigma}$ given in Eq. (11), we can derive the following relations in the absence of hydrodynamic interactions:

$$\begin{aligned} - \int dr' \left\{ \Lambda_{rr'}^{\phi\phi} \frac{\delta F}{\delta \phi(r')} + \Lambda_{rr'}^{\phi\sigma} \frac{\delta F}{\delta \sigma(r')} \right. \\ \left. - k_B T \left[\frac{\delta}{\delta \phi(r')} \Lambda_{rr'}^{\phi\phi} + \frac{\delta}{\delta \sigma(r')} \Lambda_{rr'}^{\phi\sigma} \right] \right\} \\ = \zeta^{-1} \left[k_B T \nabla^2 \left(\phi + \frac{1}{2} u \phi^2 \right) - \nabla \cdot \nabla \cdot \sigma \right] , \end{aligned} \quad (18)$$

$$\begin{aligned} - \int dr' \left\{ \Lambda_{rr'}^{\sigma\phi} \frac{\delta F}{\delta \phi(r')} + \Lambda_{rr'}^{\sigma\sigma} \frac{\delta F}{\delta \sigma(r')} \right. \\ \left. - k_B T \left[\frac{\delta}{\delta \phi(r')} \Lambda_{rr'}^{\sigma\phi} + \frac{\delta}{\delta \sigma(r')} \Lambda_{rr'}^{\sigma\sigma} \right] \right\} \\ = \frac{k_B T}{\zeta} \left\{ \frac{12}{b^2} (k_B T \phi \delta - \sigma) + \nabla^2 \sigma + u [\nabla \cdot (\nabla \phi) \sigma \right. \\ \left. - (\nabla \nabla \phi) \cdot \sigma - \sigma \cdot (\nabla \nabla \phi)] \right\} . \end{aligned} \quad (19)$$

Note that Eq. (18) is exact, just dependent on the form of the Edwards Hamiltonian. Eq. (19) involves a familiar decoupling approximation, in which averages over many bond displacements are replaced by products of pairwise averages [17].

Substituting Eqs. (14), (16), and (17) into Eq. (12), carrying out the integral over r' , and adding the noise term θ_ϕ , one obtains

$$\begin{aligned} \frac{\partial \phi}{\partial t} + v \cdot \nabla \phi = & \zeta^{-1} \left\{ \nabla \cdot \phi \nabla \left(\frac{\delta F}{\delta \phi} \right)_\sigma + \nabla \cdot \left[\nabla \left(\frac{\delta F}{\delta \sigma} \right)_\phi \right] : \sigma \right. \\ & \left. - 2 \nabla \nabla : \left[\sigma \cdot \left(\frac{\delta F}{\delta \sigma} \right)_\phi \right] \right\} + \theta_\phi . \end{aligned} \quad (20)$$

Using the linear strain-stress relation, one can express $(\delta F / \delta \phi)_\sigma$ in terms of $(\delta F / \delta \phi)_w$ and $(\delta F / \delta w)_\phi$ in Eq. (20) and find that, using $G \propto \phi$ appropriate to the dilute case, Eq. (1) is recovered. Next, substituting Eqs. (15) and (19) into Eq. (13), and carrying out the integral over r' , we readily arrive at Eq. (3) with the dilute-system identifications $\lambda(\phi) = \zeta b^2 / (12k_B T)$, and $G(\phi) = G_0(\phi) = k_B T \phi$. Note that a ‘renormalized’ G as suggested by Eq. (6) should appear in a more complete derivation. We will discuss this point in greater detail in a subsequent paper concerning the statics of deformed polymer systems [16]. Here the decoupling approximation [17] noted above only yields the trivial ‘ideal gas’ pressure on the right-hand side of Eq. (3). This completes our derivation of Eqs. (1) and (3) for the dilute case.

We now perform a linear analysis of this model. For a dilute system with no hydrodynamic interactions, one can start with Eqs. (20) or (1). However, as we now show, the Langevin equation for ϕ can be obtained exactly without having an explicit form for the constrained free energy, $F(\phi, \sigma)$. Substituting Eqs. (14) and (18) into Eq. (12), and performing the integrals over r' , we find directly

$$\frac{\partial \phi}{\partial t} + v \cdot \nabla \phi = \zeta^{-1} [k_B T \nabla^2 (\phi + \frac{1}{2} u \phi^2) - \nabla \cdot (\nabla \cdot \sigma)] + \theta_\phi . \quad (21)$$

This is essentially the equation proposed by HF [4]. [Excluded volume interactions have been included; more complicated interactions among the monomers introduce straightforward modifications of the Laplacian term.] Equations (2), (3), and (21) describe phase separation in dilute solutions, in the absence of hydrodynamic interactions. Performing a similar analysis to HF [4] and Onuki [6], we first solve Eq. (3) for σ to the ‘second-order fluid’ level using

the retarded motion expansion method [12], from which the stress σ can be expressed in terms of ϕ and v [18]. At this order only the leading non-Newtonian terms ($O(|\nabla v|^2)$) are included. Then we substitute this constitutive relation for σ into Eqs. (21) and (2). Finally, by setting $\phi = \phi_0 + \phi_1$ and $v = S y e_x + v_1$, where S is the shear rate, we can solve the equations for ϕ and v to linear order in ϕ_1 and v_1 . The result shows that the phase separation temperature is not shifted by the shear flow in the dilute case in agreement with HF [4].

For the semidilute case, we assume that the Langevin equations (1)–(3) remain valid. This is reasonable since Eqs. (1) and (2) can be constructed phenomenologically [5,6], while Eq. (3) is the Maxwell equation, which is used phenomenologically in studies of viscoelasticity [5]. Hence we assume the concentration can be increased somewhat, retaining the structure of Eqs. (1)–(3), and that the only difference from the dilute regime is the concentration dependence of some parameters, such as the modulus $G(\phi)$ and $\lambda(\phi)$. Hence the more general Langevin equations (1)–(3) may reasonably be taken to describe semidilute dynamics. Scaling analysis [6] and our random-phase-approximation result (5) show that at mean-field level for the semidilute case, $G(\phi) \sim \phi^\alpha$, with $\alpha=2$ for good solvent and $\alpha=3$ for a θ solvent. With this assumption, substituting Eq. (5) into Eqs. (1) and (2) and performing the linear analysis, we find that the phase boundary is indeed shifted. The temperature shift is proportional to the square of the shear strength: $(\Delta T)_s = \frac{1}{4} A_s (T_\theta - T_c) (\phi_0 / \phi^*) [S \lambda(\phi_0)]^2$, where $A_s = \alpha(\alpha$

$-1)G(\phi_0)/(k_B T \phi_0^3)$, $\phi^* = 1/\sqrt{N}$, and T_θ and T_c are the theta and critical temperatures, respectively. That is, phase separation is induced by the shear flow. From the expression of $(\Delta T)_s$, we see that as long as $\alpha > 1$, the phase separation temperature is shifted. That is, a nonlinear concentration dependence of the modulus is crucial for the temperature shift. When $\alpha=3$, the expression for $(\Delta T)_s$ is exactly the same as that obtained by Onuki [6].

From a microscopic starting point, we developed a general model for the dynamics of phase separation in polymer solutions in the presence of shear flow. For the dilute case, the diffusion equation for ϕ and the Maxwell equation for σ are derived from the Smoluchowski equation, showing that viscoelastic behavior of polymeric solutions can be obtained from that starting point. Linear analysis shows that the equilibrium phase boundary is not shifted by the shear flow for the dilute case, while the phase separation temperature is indeed shifted upward for the semidilute case. Now it is clear that concentration effects are crucial for a shift in the phase boundary. These conclusions agree with available experimental data [3], and unify previous phenomenological theories [4,6].

T.S. wishes to thank S. A. Patlazhan and R. Bhagavatula for useful discussions. We also thank Professor T. Ohta for his interest and suggestions. This work was supported by the ONR, through Grant No. N00014-91-J-1363 (to A.C.B.) and the NSF, through Grant No. DMR-92-17935 (to D.J.).

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- [17] In deriving Eq. (19), besides $\hat{\phi}$ and $\hat{\sigma}$, some other operators appear. Langevin equations generate a hierarchy that we close, using a familiar decoupling [14].
- [18] We have assumed that v and σ relax rapidly to the forms dictated by the local concentration pattern, so that $\partial/\partial t$ and $\tilde{v} \cdot \nabla$ terms can be ignored in Eqs. (2) and (3) [4]. Note also that the ‘‘second-order fluid’’ approximation is valid only for weak shear ($S\lambda \ll 1$).