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Dynamics of the phase behavior of a polymer blend under shear flow

Tao Sun,[1] Anna C. Balazs,[1] and David Jasnow[2]
[1]*Chemical and Petroleum Engineering Department, University of Pittsburgh, Pittsburgh, Pennsylvania 15261*
[2]*Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh, Pennsylvania 15260*

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We study the dynamics of the phase behavior of a polymer blend in the presence of shear flow. By adopting a two-fluid picture and using a generalization of the concept of material derivative, we construct kinetic equations that describe the phase behavior of polymer blends in the presence of external flow. A phenomenological form for the shear modulus for the blend is proposed. The study indicates that a nonlinear dependence of the shear modulus of the blend on the volume fraction of one of the species is crucial for a shift in the stability line to be induced by shear flow. [S1063-651X(99)12501-7]

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I. INTRODUCTION

The dynamics of the phase behavior in polymer mixtures under external flow fields has aroused great interest over the last two decades [1–10]. The motivation for these studies is twofold. First, the effect of viscoelasticity on the phase behavior of polymer mixtures can be directly detected for some macroscopic flows. Secondly, many industrial processes, such as extrusion and painting processes, generate shear flow fields in polymer solutions and melts. In order to gain further insight into nonequilibrium phase transitions and to optimize these industrial processes, one must understand the phase behavior of polymer mixtures in the presence of a flow field. Experimentally, a number of groups have reported that the phase behavior of polymer mixtures can be dramatically changed by macroscopic flow fields. In particular, for polymer-solvent mixtures in the presence of a shear flow, a greatly enhanced turbidity has been observed at temperatures much higher than the equilibrium critical temperature [1–3]. To study the mechanism of the observed phenomenon in polymer solutions, a number of theoretical efforts have been made [5,8–10], and it is now understood that a nonlinear concentration dependence of the shear modulus is crucial for an upward shift of the phase separation temperature [10]. The temperature shift is proportional to the square of the shear strength in the regime of weak shear [8,10].

Although some experiments have been carried out for polymer blends under external flow [4], theoretically, one knows very little about the phase behavior of this system. Doi and Onuki first discussed the Langevin equations describing the dynamics of phase separation of a polymer blend [7]. However, to our knowledge, the full consequences of the equations have not been explored. Moreover, the original approach employed in the ground-breaking work of Doi and Onuki prevents these kinetic equations from reducing to the polymer-solution case. Here, we present an expanded derivation, in which the difference between the Lagrangian and Eulerian descriptions has been taken into account. Using a phenomenological form for the shear modulus of a polymer blend, we can carry out a linear stability analysis for the model and find that the equilibrium spinodal line can be shifted in a complicated fashion by the shear flow. The purpose of this paper is to report on these studies and describe the relevant techniques in detail.

The system consists of two kinds of polymers with different degrees of polymerization, N_A and N_B. The volume fraction of polymer A at space-time point (r,t) is denoted by $\phi_A(r,t)=\phi(r,t)$, and the volume fraction of polymer B is then $\phi_B(r,t)=1-\phi(r,t)$. We make the assumption that monomers of both species have the same specific volume, which can be expressed as [6–8]

$$\frac{\rho_A(r,t)}{\phi(r,t)}=\frac{\rho_B(r,t)}{1-\phi(r,t)}=\rho, \tag{1}$$

where ρ_A and ρ_B are the respective mass densities of polymers A and B and ρ is the total mass density, which is a constant. This assumption is consistent with the incompressibility of the system. In the two-fluid picture [6–9], the two species are moving with different velocities, so that both bulk flow of the fluid and mutual diffusion of the two species, accompanied by chain deformation, take place simultaneously. Our task is to study the effect of flow and chain deformation on the dynamics of the phase behavior of the system.

The paper is organized as follows. In Sec. II, we first discuss appropriate material derivatives and then derive the kinetic equations for the fluid velocity v and volume fraction ϕ. In Sec. III, we perform a linear stability analysis of the model, from which the effect of flow on the domain of linear stability can be obtained. Finally, our conclusions are briefly summarized in Sec. IV.

II. MODEL

A polymer blend is a viscoelastic system, sharing features of an elastic continuum and a viscous fluid. The system is elastic, but it only has a ''faded'' memory. The system is viscous, but it can bear deformation on some time scales. To derive the kinetic equations for such a system, one must call on familiar methods in studies of deformable media, as well as techniques for viscous fluids.

A. Material derivatives

In continuum mechanics, one uses both Lagrangian and Eulerian coordinates to describe the motion of a material element [11,12]. The Lagrangian coordinates, which can be denoted by $a=\{a_i\}, i=1,2,3$, are used to label the material elements or ''particles'' in a reference configuration (usually the undeformed state), while the Eulerian coordinates, denoted by $r=\{r_i\}, i=1,2,3$, are the coordinates of the particles in the current configuration. The two coordinates are related through the following equations:

$$r=r(a,t), \tag{2}$$

$$a=a(r,t). \tag{3}$$

The velocity of the material element that is currently located at the point r is defined as the time rate of change of its position,

$$v=\left(\frac{\partial r}{\partial t}\right)_a, \tag{4}$$

where the subscript a is used to emphasize the fact that the derivative is to be evaluated for a particular material element the Lagrangian coordinates of which are a. This is the usual material derivative. In the Eulerian description, the material derivative of any property pertaining to the particle labeled by the Lagrangian coordinate a is given by

$$\frac{D}{Dt}=\frac{\partial}{\partial t}+v\cdot\nabla, \tag{5}$$

where v is the velocity of the particle a at position r, given in Eq. (4). For small deformations in which the Lagrangian strain tensor and the Eulerian strain tensor have the same form, the strain tensor ϵ is the symmetric part of the displacement gradient tensor,

$$\epsilon=\tfrac{1}{2}[\nabla(\Delta r)+\nabla(\Delta r)^{\dagger}], \tag{6}$$

where $\Delta r=r-a$, and the dagger superscript stands for the transposition of tensors. Notice that ϵ is the total local strain of the composite material. This point will be discussed further, below. The material derivative of the strain tensor is given by [11],

$$\frac{D\epsilon}{Dt}=\tfrac{1}{2}(\nabla v+\nabla v^{\dagger}). \tag{7}$$

Finally, the principle of conservation of mass leads directly to the following well-known formula [11–13]

$$\frac{d}{dt}\int d^3r\rho(r,t)Q(r,t)=\int d^3r\rho(r,t)\frac{D}{Dt}Q(r,t), \tag{8}$$

where $Q(r,t)$ is any physical quantity per unit mass and $\rho(r,t)$ is the mass density of the material.

We now generalize the above concepts to the two-fluid picture of polymer blends. As usual, we choose the undeformed state as the reference configuration, in which each material particle is identified by its Lagrangian coordinates a. Since in the present situation there are two kinds of material particles moving with different velocities in the system, one should distinguish the Lagrangian coordinates for the two species. We denote the Lagrangian coordinates of the particles of polymers A and B by a_A and a_B, respectively. Then Eq. (4) can be generalized as

$$v_A=\left(\frac{\partial r}{\partial t}\right)_{a_A}, \tag{9}$$

$$v_B=\left(\frac{\partial r}{\partial t}\right)_{a_B}. \tag{10}$$

The physical meaning of Eqs. (9) and (10) is as follows. At each space-time point in the current configuration, there are two velocities, $v_A(r,t)$ and $v_B(r,t)$, which will be acquired by the material particles passing through this point, depending on the type of material particles. That is, particles of polymer A pass the point with velocity $v_A(r,t)$, while particles of polymer B pass the same point with velocity $v_B(r,t)$. The fluid velocity (average velocity) of this point is given by

$$v(r,t)=\phi(r,t)v_A(r,t)+[1-\phi(r,t)]v_B(r,t). \tag{11}$$

Naturally, corresponding to Eqs. (9) and (10), we may introduce two kinds of material derivatives in the system,

$$\left(\frac{D}{Dt}\right)_A=\frac{\partial}{\partial t}+v_A\cdot\nabla, \tag{12}$$

$$\left(\frac{D}{Dt}\right)_B=\frac{\partial}{\partial t}+v_B\cdot\nabla. \tag{13}$$

If we focus on particles of polymer A, the material derivative is given by Eq. (12); similarly, the material derivative for species B is given by Eq. (13). The essential point is that any difference between v_A, v_B, and the center of mass velocity is due to mutual diffusion. A constitutive relation is required to fix the diffusion flux or, equivalently, $v_A - v_B$. We will return to this point later.

It is easy to evaluate the two material derivatives for some basic physical quantities, such as the volume fraction ϕ and strain tensor ϵ. First, from the continuity equations for both species

$$\frac{\partial \rho_A(r,t)}{\partial t} + \nabla \cdot \rho_A(r,t) v_A(r,t) = 0, \tag{14}$$

$$\frac{\partial \rho_B(r,t)}{\partial t} + \nabla \cdot \rho_B(r,t) v_B(r,t) = 0, \tag{15}$$

we can obtain the expressions for the material derivatives of the volume fraction

$$\left[\frac{D\phi(r,t)}{Dt}\right]_A = -\phi(r,t)\nabla \cdot v_A(r,t), \tag{16}$$

$$\left[\frac{D\phi(r,t)}{Dt}\right]_B = [1-\phi(r,t)]\nabla \cdot v_B(r,t), \tag{17}$$

where Eq. (1) has been used. Note that, augmented by Eq. (1), the continuity equations lead directly to the incompressibility condition

$$\nabla \cdot v = \nabla \cdot \phi v_A + \nabla \cdot (1-\phi) v_B = 0. \tag{18}$$

Next, for small deformations, the total strain tensor of the polymer blend is still given by Eq. (6), but the material derivative of ϵ is generalized to the following equations:

$$\left(\frac{D\epsilon}{Dt}\right)_i = \tfrac{1}{2}(\nabla v_i + \nabla v_i^\dagger), \quad i = A,B. \tag{19}$$

Taking material derivatives defined in Eqs. (12) and (13) on both sides of Eq. (6), and noticing that for small deformation, $\nabla = \partial/\partial r \simeq \partial/\partial a$, Eq. (19) is obtained. As will be seen in the next section, Eqs. (16), (17), and (19) are useful in the evaluation of the dissipation rate of the total free energy of the system.

Finally, it follows from the principle of mass conservation that Eq. (8) still holds. But in the present situation, ρ is the total mass density $\rho = \rho_A + \rho_B$, which is a constant [see Eq. (1)], and v is the fluid velocity given in Eq. (11). Noticing the fact that the system is incompressible ($\nabla \cdot v = 0$), for a polymer blend Eq. (8) can be written as

$$\frac{d}{dt}\int d^3 r \rho Q(r,t) = \int d^3 r \rho \frac{\partial Q}{\partial t}. \tag{20}$$

Here, a boundary term has been ignored. Furthermore, since the masses of both species are also conserved individually, one has the following equations:

$$\frac{d}{dt}\int d^3 r \rho_i Q_i(r,t) = \int d^3 r \rho_i \left(\frac{D}{Dt}\right)_i Q_i(r,t), \quad i = A,B, \tag{21}$$

where $\rho_i Q_i$ is any physical quantity contributed by the i species. Note that only two of the three formulas for the time derivative of the volume integration are independent. In fact, summing up the two equations given in Eq. (21), one obtains Eq. (8).

B. Total free energy

We take into account three kinds of contributions to the total free energy of the system: The kinetic energy K of moving particles, the mixing free energy F_m of the two species, and the elastic free energy F_e of polymers due to chain deformation [8]. Thus, the total free energy of the system can be written as

$$F_t = K + F_m(\phi) + F_e(\phi,\epsilon). \tag{22}$$

Here, we have assumed that the mixing free energy is a function of ϕ only, while the elastic free energy depends on both ϕ and ϵ. The kinetic energy of the two kinds of moving particles can be expressed as

$$K = \int d^3 r \left(\tfrac{1}{2}\rho_A v_A^2 + \tfrac{1}{2}\rho_B v_B^2\right). \tag{23}$$

The mixing free energy can be written as

$$F_m(\phi) = \int d^3 r f_m(\phi), \tag{24}$$

where $f_m(\phi)$ is the mixing free energy density, which, for example, can be chosen to be the Flory-Huggins form. Our derivation for the kinetic equations is independent of the precise form of $f_m(\phi)$. In a similar way, the elastic free energy can be expressed as

$$F_e(\phi,\epsilon) = \int d^3 r f_e(\phi,\epsilon). \tag{25}$$

In the theory of linear elasticity, the elastic energy density due to chain deformation can be phenomenologically expressed as [8,14],

$$f_e(\phi,\epsilon) = G(\phi) f_e^*(\epsilon), \tag{26}$$

where $f_e^*(\epsilon) = \epsilon : \epsilon$, and the coefficient G is the shear modulus of the system, which, in general, depends on concentration only. Here, the notation $(:)$ stands for the scalar product of second rank tensors. Note that consistently with earlier work of Doi and Onuki on the two-fluid approach [7], the strain ϵ is the total local strain of the blend. The domain of applicability of Eqs. (22), (25), and (26) will be addressed at the end of this subsection.

Since in a polymer blend both species contribute to the elastic energy, we propose the following intuitive form for the shear modulus of the blend [15]

$$G = G_B^{(0)} + [G_A^{(0)} - G_B^{(0)}]\Delta(\phi), \tag{27}$$

where $G_i^{(0)}$ is the shear modulus of the i species before mixing (''bare'' shear modulus), and $\Delta(\phi)$ is an interpolating function describing the effect of blending. The condition that $G(\phi=0) = G_B^{(0)}$ and $G(\phi=1) = G_A^{(0)}$ requires that $\Delta(0)$

$=0$ and $\Delta(1)=1$. Then the simplest form of the interpolating function would be $\Delta(\phi)=\phi$, i.e., an ideal mixture approximation. More generally we suppose

$$\Delta(\phi)=\phi+\tilde{\Delta}(\phi) \tag{28}$$

with $\tilde{\Delta}(0)=\tilde{\Delta}(1)=0$. For use in Eq. (26), it is convenient to cast Eq. (27) into the form

$$G(\phi)=\phi G_A(\phi)+(1-\phi)G_B(\phi), \tag{29}$$

where $G_i, i=A,B,$ are the ''renormalized'' shear moduli of species A and B individually, which can be expressed as

$$G_A(\phi)=G_A^{(0)}\left[1+\frac{\tilde{\Delta}(\phi)}{\phi}\right], \tag{30}$$

$$G_B(\phi)=G_B^{(0)}\left[1-\frac{\tilde{\Delta}(\phi)}{1-\phi}\right]. \tag{31}$$

As we will see below, Eq. (29) is a reasonable approximation leading to a sensible result for the network velocity.

We return now to a discussion of the applicability of Eq. (22) with Eqs. (25) and (26). The polymer blend is a viscoelastic fluid (rather than a purely elastic system) so that at sufficiently long times stresses relax. Yet one uses in Eqs. (22) and (26) ideas from solid elasticity. One expects that Eq. (22) describes the physics within the time scales less than the relaxation time of the shear stress (usually referred to as the ''terminal relaxation time'') [18]. The elastic part of Eq. (22) represents a constrained free energy appropriate to prescribed order parameter (concentration) and strain distributions. As discussed elsewhere [14] such a constraint may be physically meaningful only on sufficiently short time scales. Note that for polymer blends, in general, both species contribute to the strain tensor and that the individual relaxation times of the two species can differ from one another in an asymmetric case. The relevant relaxation time is for the blend, and it will typically be controlled by the larger of the two relaxation times, which guarantees that Eq. (26) is meaningful. For time scales shorter than both relaxation times, both species contribute to effective elastic energy. In a situation in which one of the species relaxes much more quickly than the other, at an intermediate time scale, it is expected that only the species with the longer relaxation time contributes to the elastic free energy, while the second species (with the shorter relaxation time) does not contribute to the elasticity, but rather contributes to the viscosity of the system. This is precisely what happens in the case of a polymer solution in which case the elastic stresses reside in the polymer network. Equation (26) is not meaningful on exceptionally long time scales where the stress cannot be maintained.

C. Dissipation rate of total free energy

With the results presented in the previous two subsections, we are ready to discuss the dissipation rate of the total free energy of the system. First, using the formula given in Eq. (21), the evaluation of the time derivative of the kinetic energy is straightforward, and the result can be expressed as

$$\frac{dK}{dt}=\int d^3r\left\{\rho_A v_A\cdot\left(\frac{Dv_A}{Dt}\right)_A+\rho_B v_B\cdot\left(\frac{Dv_B}{Dt}\right)_B\right\}. \tag{32}$$

Next, since, in general, the mixing free energy $f_m(\phi)$ cannot be simply divided into contributions by particles A and B, it is convenient to use Eq. (20) to calculate the dissipation rate of the mixing free energy. Indeed, it is easy to obtain

$$\frac{dF_m}{dt}=\int d^3r\frac{\partial f_m(\phi)}{\partial t}=\int d^3r\frac{\partial f_m(\phi)}{\partial\phi}\frac{\partial\phi}{\partial t}. \tag{33}$$

Making use of the continuity equation (16) and integrating by parts, we have

$$\frac{dF_m}{dt}=\int d^3r v_A\cdot\phi\nabla\frac{\partial f_m(\phi)}{\partial\phi}=\int d^3r v_A\cdot\nabla\pi_m, \tag{34}$$

where π_m is the osmotic pressure associated with the mixing free energy, given by

$$\pi_m=\left(\phi\frac{\partial}{\partial\phi}-1\right)f_m(\phi). \tag{35}$$

Note that if the continuity equation (17) were used, a different expression for dF_m/dt would be obtained, but it will give the same final kinetic equations when the condition $\nabla\cdot v=0$ is taken into account.

Finally, we discuss the time derivative of the elastic free energy. In view of Eq. (29), we can write

$$f_e(\phi,\epsilon)=f_{eA}(\phi,\epsilon)+f_{eB}(\phi,\epsilon), \tag{36}$$

where $f_{ei}(\phi,\epsilon)=\phi_i G_i f_e^*(\epsilon), i=A,B$. Recall that ϵ is the total local strain tensor. Using Eq. (21), we have

$$\frac{dF_e}{dt}=\int d^3r\left\{\phi\left[\frac{D}{Dt}\phi^{-1}f_{eA}(\phi,\epsilon)\right]_A\right.$$
$$\left.+(1-\phi)\left[\frac{D}{Dt}(1-\phi)^{-1}f_{eB}(\phi,\epsilon)\right]_B\right\}. \tag{37}$$

Using the chain rule, the material derivatives of the free energies $f_{eA}(\phi,\epsilon)$ and $f_{eB}(\phi,\epsilon)$ can be expressed in terms of the material derivatives of ϕ and ϵ. Making use of Eqs. (16), (17), and (19), we obtain

$$\frac{dF_e}{dt}=\int d^3r\left\{-\pi_{eA}\nabla\cdot v_A-\pi_{eB}\nabla\cdot v_B\right.$$
$$\left.+(\nabla v_A):\frac{\partial f_{eA}}{\partial\epsilon}+(\nabla v_B):\frac{\partial f_{eB}}{\partial\epsilon}\right\}, \tag{38}$$

where π_{ei}, with $i=A,B$, are the ''elastic osmotic pressures,'' given by

$$\pi_{ei}=\left(\phi_i\frac{\partial}{\partial\phi_i}-1\right)f_{ei}(\phi,\epsilon),\quad i=A,B. \tag{39}$$

The stress tensor acting on the network can be defined as [16]

$$\tau = \frac{\partial f_e(\phi,\epsilon)}{\partial \epsilon}. \tag{40}$$

In view of Eqs. (26) and (36), it is easy to check that

$$\frac{\partial f_{eA}}{\partial \epsilon} = \phi \frac{G_A}{G}\tau, \tag{41}$$

$$\frac{\partial f_{eB}}{\partial \epsilon} = (1-\phi)\frac{G_B}{G}\tau. \tag{42}$$

Substituting Eqs. (41) and (42) into Eq. (38), the dissipation rate of the elastic free energy can be written as

$$\frac{dF_e}{dt} = \int d^3r \Bigg\{ v_A \cdot \left[\nabla \pi_{eA} - \nabla \cdot \phi \frac{G_A}{G}\tau \right] + v_B \cdot \left[\nabla \pi_{eA} - \nabla \cdot (1-\phi)\frac{G_A}{G}\tau \right] \Bigg\}, \tag{43}$$

after an integration by parts.

Combining Eqs. (32), (34), and (43), we obtain the dissipation rate of the total free energy

$$\frac{dF_t}{dt} = \int d^3r \Bigg\{ \rho_A v_A \cdot \left(\frac{Dv_A}{Dt} \right)_A + \rho_B v_B \cdot \left(\frac{Dv_B}{Dt} \right)_B + v_A \cdot \left[\nabla(\pi_m + \pi_{eA}) - \nabla \cdot \phi \frac{G_A}{G}\tau \right] + v_B \cdot \left[\nabla \pi_{eB} - \nabla \cdot (1-\phi)\frac{G_B}{G}\tau \right] \Bigg\}. \tag{44}$$

It should be understood that the partial derivative $\partial/\partial\phi$ is carried out at fixed ϵ and $\partial/\partial\epsilon$ is carried out at fixed ϕ.

D. Network velocity

In this subsection, we discuss the network velocity (or tube velocity in the reptation picture). Substituting Eqs. (41) and (42) into Eq. (38), the dissipation rate for the elastic free energy can be expressed as

$$\frac{dF_e}{dt} = \int d^3r \{ -\pi_{eA} \nabla \cdot v_A - \pi_{eB} \nabla \cdot v_B + G^{-1}[\phi G_A \nabla v_A + (1-\phi) G_B \nabla v_B] : \tau \}. \tag{45}$$

The last term in the above equation describes the time rate of change of the elastic energy purely due to the change of the strain tensor, so that the coefficient of the stress tensor τ can be identified as the gradient of the network velocity (or tube velocity in the reptation picture),

$$\nabla v_t = G^{-1}[\phi G_A \nabla v_A + (1-\phi) G_B \nabla v_B]. \tag{46}$$

As we now show, this expression is in agreement with a previously obtained result using a microscopic approach.

The network velocity v_t has previously been estimated from molecular theory [7,17] for a uniform system (ϕ is constant) with the result

$$v_t = \frac{\zeta_A v_A + \zeta_B v_B}{\zeta_A + \zeta_B}. \tag{47}$$

Here $\zeta_i, i=A,B$, are effective friction coefficients given by

$$\zeta_i = \nu_i \phi_i \frac{N_i}{N_i^e}\zeta_0, \quad i=A,B, \tag{48}$$

where ν_i is the number of chains of species i per unit volume, N_i^e is the average interval between two successive entanglement points along one chain, and ζ_0 is the phenomenological friction coefficient between the two species. On the other hand, when ϕ is independent of space, Eq. (46) can be solved with the result

$$v_t = G^{-1}[\phi G_A v_A + (1-\phi) G_B v_B], \tag{49}$$

where an integrating constant has been determined as zero from the condition that $v_t = v_A$, when $\phi = 1$. We may suppose that $G_{A,B}$ measure the densities of entanglement points, i.e., $G_i \propto T\phi_i / N_i^e$ [18]. Then Eq. (47) is recovered.

E. Kinetic equations

First we derive the equations for the two velocity fields v_A and v_B. These equations can be obtained by means of Rayleigh's variational principle [6,7]. Following Doi and Onuki [6,7], one can define a Rayleighian functional,

$$R = \frac{1}{2}W + \frac{dF_t}{dt}, \tag{50}$$

where F_t is the total free energy of the system and W is the dissipation function due to relative motion of the two polymers, which one assumes can be written as

$$W = \int d^3r c(r) \zeta (v_A - v_B)^2. \tag{51}$$

Here c is the monomer concentration of species A defined via $\phi = v_m c$ with v_m the monomer volume, and ζ is the friction constant, which, in general, is a function of ϕ [9]. The Rayleighian defined in Eq. (50) may be understood as the total energy dissipation rate of the system. The variational principle states that the velocities v_A and v_B are determined by the condition that they minimize the Rayleighian [6,7].

Substituting Eqs. (44) and (51) into Eq. (50), we have the Rayleighian for the polymer blend,

$$R = \int d^3r \Bigg\{ \rho_A v_A \cdot \left(\frac{Dv_A}{Dt} \right)_A + \rho_B v_B \cdot \left(\frac{Dv_B}{Dt} \right)_B + v_A \cdot \left[\nabla(\pi_m + \pi_{eA}) - \nabla \cdot \phi \frac{G_A}{G}\tau \right] + v_B \cdot \left[\nabla \pi_{eB} - \nabla \cdot (1-\phi)\frac{G_B}{G}\tau \right] + \tfrac{1}{2} c(r) \zeta (v_A - v_B)^2 \Bigg\}. \tag{52}$$

Since v_A and v_B are not independent variables due to the incompressibility condition (18), the functional R must be minimized under this condition. The conditional minimization of the functional R with respect to v_A and v_B leads to the following equations:

$$\rho_A\left(\frac{Dv_A}{Dt}\right)_A = -c\zeta(v_A - v_B) - (\nabla p)\phi - \nabla(\pi_m + \pi_{eA}) + \nabla\cdot\phi\frac{G_A}{G}\tau, \tag{53}$$

$$\rho_B\left(\frac{Dv_B}{Dt}\right)_B = c\zeta(v_A - v_B) - (1-\phi)(\nabla p) - \nabla\pi_{eB} + \nabla\cdot(1-\phi)\frac{G_B}{G}\tau, \tag{54}$$

where p is the Lagrange multiplier imposing the incompressibility condition. Equations (53) and (54) describe the motion of polymers A and B in the system.

Solving Eqs. (53) and (54) for v_A and then substituting the resulting expression into Eq. (16), we can obtain the diffusion equation for ϕ. Clearly this cannot be done exactly and some approximation must be applied [7]. Since the velocities relax much faster than ϕ, we can ignore the inertia terms in Eqs. (53) and (54) to obtain an explicit expression for v_A. After eliminating the p terms, we can express v_A as

$$v_A = v - \frac{\phi(1-\phi)^2}{c\zeta}\left\{\nabla\frac{\partial f}{\partial\phi} - \alpha[(\nabla\epsilon):\tau + \nabla\cdot\tau] - \beta\cdot\tau\right\}, \tag{55}$$

where $f = f_m + f_e$ and Eq. (11) has been used. In Eq. (55), we have introduced two parameters $\alpha(\phi)$ and $\beta(\phi)$ for convenience, which are given by

$$\alpha = G^{-1}[G_A - G_B], \tag{56}$$

$$\beta = \phi^{-1}\nabla\phi\frac{G_A}{G} - (1-\phi)^{-1}\nabla(1-\phi)\frac{G_B}{G}. \tag{57}$$

Substituting Eq. (55) into Eq. (16), we obtain

$$\frac{\partial\phi}{\partial t} + v\cdot\nabla\phi = v_m\nabla\cdot\frac{\phi(1-\phi)^2}{\zeta} \times\left\{\nabla\frac{\partial f}{\partial\phi} - \alpha[(\nabla\epsilon):\tau + \nabla\cdot\tau] - \beta\cdot\tau\right\}, \tag{58}$$

where the incompressibility condition has been used. This is the diffusion equation for ϕ.

It is convenient to describe the motion of the system using the fluid velocity v and relative velocity $u = v_A - v_B$. From Eqs. (53) and (54), it is easy to check that the kinetic equations for v and u can be written, respectively, as

$$\rho\left(\frac{\partial v}{\partial t} + v\cdot\nabla v + R_v\right) = -\nabla p - \nabla\pi + \nabla\cdot\tau, \tag{59}$$

$$\rho\phi\left(\frac{\partial u}{\partial t} + u\cdot\nabla u + R_u\right) = -\frac{c\zeta}{1-\phi}u - \phi\left\{\nabla\frac{\partial f}{\partial\phi} - \alpha[(\nabla\epsilon):\tau + \nabla\cdot\tau] - \beta\cdot\tau\right\}, \tag{60}$$

where $\pi = \pi_m + \pi_{eA} + \pi_{eB}$ is the total osmotic pressure, and R_v and R_u are couplings between v and u that can be expressed as

$$R_v = u\nabla\cdot\phi(1-\phi)u + \phi(1-\phi)u\cdot\nabla u, \tag{61}$$

$$R_u = u\cdot\nabla(v - \phi u) + (v - \phi u)\cdot\nabla u. \tag{62}$$

Equation (59) is the generalized Navier-Stokes equation for the fluid velocity. R_v is the correction due to coupling between bulk flow and relative motion. Equation (60) describes the relative motion between the two species.

The constitutive equation cannot be derived from the above formalism, because so far no ordinary viscosity effects have been included in the Rayleighian. We assume that the time evolution of the stress tensor is described by the upper convected Maxwell equation [7,10,19]

$$\lambda\left[\frac{\partial\sigma}{\partial t} + v_t\cdot\nabla\sigma - \sigma\cdot\nabla v_t - (\nabla v_t)^{\dagger}\cdot\sigma\right] + \sigma = G(\phi)\delta, \tag{63}$$

where λ is the relaxation time, v_t is the network velocity, and the stress tensor σ is related to τ through $\sigma = G\delta + \tau$. The network velocity v_t has been used here because the stress acts on the polymer network [7,20]. Since in polymer blends the fluctuations of concentration are small, and Eq. (46) cannot be solved explicitly, we will use Eq. (49) as an approximate expression for the network velocity v_t in the linear analysis. Using the expressions for v_A and v_B, we have finally

$$v_t = v - v_m\alpha\frac{\phi(1-\phi)^2}{\zeta}\left\{\nabla\frac{\partial f}{\partial\phi} - \alpha[(\nabla\epsilon):\tau + \nabla\cdot\tau] - \beta\cdot\tau\right\}. \tag{64}$$

Equations (58), (59), (60), and (63) describe the dynamics of phase behavior of a polymer blend under shear flow. Since u appears only in Eqs. (59) and (60), and in most cases R_v is negligibly small [7], one can ignore the R_v term in Eq. (59), and then the model reduces to three equations. In the extreme case where the B component represents small molecules, $G_B \sim 0, \alpha \simeq 1/\phi, \beta \simeq 0$, previous results for a polymer solution are recovered [8,10]. However, since features of solid elasticity have been used in the free energy expression, as has been discussed in the end of Sec. II B, taking this limit may not be fully justifiable.

Note that although the structure of our set of kinetic equations is similar to that given in Ref. [7], some important differences exist. First, the free energy density f in Eq. (58) is the total free energy density, i.e., $f = f_m + f_e$, while in Eq. (4.17) of Ref. [7], f is the mixing free energy only. That is, we have taken into account the fact that, in general, the elastic free energy can be ϕ dependent [through the shear modulus $G(\phi)$]. Second, two more terms $[\alpha(\nabla\epsilon):\tau]$ and $(\beta\cdot\tau)$ are generated in Eq. (58). The $\alpha(\nabla\epsilon):\tau$ term and the inclusion of f_e in the total free energy density f enable the kinetic equations to reduce *formally* to the solution case [see, however, the comment after Eq. (64)].

III. LINEAR ANALYSIS

Equations (58), (59), and (63) are nonlinear equations, so that a complete analysis is difficult. However, to study the effect of viscoelasticity on the phase boundary under shear, it is sufficient to carry out a linear analysis similar to that developed in Refs. [5,8]. In this formalism, we first iteratively solve Eq. (63) for σ to the ''second-order fluid'' level from which the stress tensor σ can be expressed in terms of ϕ and v [19]. Then we substitute this constitutive relation for $\sigma(v,\phi)$ into Eqs. (58) and (59). Setting

$$\phi=\phi_0+\phi_1, \tag{65}$$

$$v=v_0+v_1, \tag{66}$$

where ϕ_0 and v_0 are the overall average volume fraction and the fluid velocity, and ϕ_1 and v_1 are small deviations, we can solve the equations to linear order in ϕ_1 and v_1. In the case of shear flow, $v_0=Sye_x$, where S is the shear rate and e_x is the unit vector in the x direction. The expansion parameter is essentially the combination $S\lambda$, which limits the approximations to the regime of weak shear.

A. Iterations for σ and ϵ

We first solve the Maxwell equation iteratively [19]. Since our aim is to see how viscoelasticity changes the stability line for phase separation, it is sufficient to obtain a solution for σ in the long wavelength limit. It is easy to check by ''power counting'' that ϕ_1 and ∇v_1 are the leading order terms, and then $v-v_t \sim \nabla\phi+\nabla^2 v$ are higher order terms. Therefore, we can replace v_t by v in the Maxwell equation for the present purpose. Furthermore, since v and σ relax much faster than ϕ, we may ignore the inertia terms [5,8] and obtain

$$\lambda[-\sigma\cdot\nabla v-(\nabla v)^\dagger\cdot\sigma]+\sigma=G(\phi)\delta. \tag{67}$$

Directly iterating to the ''second-order fluid'' (i.e., to $O(|\nabla v|^2)$, we obtain

$$\sigma=G\delta+2\eta D+2\eta\lambda(D\cdot\nabla v+\nabla v^\dagger\cdot D), \tag{68}$$

where $\eta=\lambda G$ is the viscosity and D is the gradient tensor given by $2D=\nabla v+\nabla v^\dagger$. Note that, at this order, only leading order non-Newtonian terms are included. Finally, for later convenience, we write down the expression for the strain tensor ϵ,

$$\epsilon=\lambda D+\lambda^2(D\cdot\nabla v+\nabla v^\dagger\cdot D). \tag{69}$$

Now we have expressed σ in terms of ϕ and v. Our next task is to eliminate σ and ϵ using Eqs. (68) and (69) in Eqs. (58) and (59) and carry out a linear analysis for the remaining equations.

B. Navier-Stokes equation

Now we discuss the linear analysis of the Navier-Stokes equation. In a similar spirit to the treatment of the Maxwell equation, we ignore the inertia terms since fluid velocities relax much faster than ϕ [5,8]. Then the equation for v becomes simply

$$\nabla p+\nabla\pi-\nabla\cdot\tau=0. \tag{70}$$

We next find expressions for $\nabla\pi$ and $\nabla\cdot\tau$ linear in ϕ_1 and v_1. For later convenience, we introduce two parameters g and ξ through $G(\phi)=k_BTg(\phi)$ and $\eta(\phi)=k_BT\xi(\phi)$. It follows from the definition that $\pi=\pi(\phi,\epsilon)=\tilde{\pi}(\phi,v)$, and therefore we have

$$\nabla\pi=\left(\frac{\partial\tilde{\pi}}{\partial\phi}\right)_0\nabla\phi_1+(\nabla v_1)\cdot\left(\frac{\partial\tilde{\pi}}{\partial v}\right)_0, \tag{71}$$

where the subscript ''0'' indicates that the derivatives are evaluated at ϕ_0 and v_0. In view of Eq. (68), we can express $\nabla\cdot\tau$ in a similar way as

$$\nabla\cdot\tau=k_BT\nabla\cdot[2\xi D+2\xi\lambda(D\cdot\nabla v+\nabla v^\dagger\cdot D)]. \tag{72}$$

Substituting Eqs. (65) and (66) into Eq. (72) and keeping terms only linear in ϕ_1 and v_1, we have

$$\nabla\cdot\tau=k_BT[\xi_0\nabla^2 v_1+S\xi_0'(e_x\partial_y\phi_1+e_y\partial_x\phi_1)+O(S^2,Sv)], \tag{73}$$

where e_i with $i=x,y,z$ are unit vectors. Here the subscript 0 means that the values are evaluated at $\phi=\phi_0$, and primes indicate ϕ differentiation. To obtain the shift in the spinodal (stability line) to leading order in the shear rate $[O(S\lambda)^2]$, the $O(S^2,Sv)$ terms can be ignored at this stage.

Substituting Eqs. (71) and (73) into Eq. (70) and eliminating p via $\nabla\cdot v=0$, we can solve v to order $O(S)$ in Fourier space with the result

$$v_{1x}(k)=-iS\frac{\xi_0'}{\xi_0}\frac{k_y}{k^2}(2\hat{k}_x^2-1)\phi_1(k), \tag{74}$$

$$v_{1y}(k)=-iS\frac{\xi_0'}{\xi_0}\frac{k_x}{k^2}(2\hat{k}_y^2-1)\phi_1(k), \tag{75}$$

$$v_{1z}(k)=-2iS\frac{\xi_0'}{\xi_0}\frac{k_xk_yk_z}{k^4}\phi_1(k), \tag{76}$$

where $\hat{k}_i=k_i/k$. As we see, to this order, the solution for v is independent of the precise form of π. Note that the expressions given in Eqs. (74)–(76) are the same as those for polymer solutions [8,10]. That is, to leading order, the linear $\phi-v$ relations are the same for both polymer solutions and blends.

C. Shift in the stability line

We now discuss the linearization of the diffusion equation (58), from which the effect of viscoelasticity on the phase boundary can be studied. We choose the Flory-Huggins form for the mixing free energy [18],

$$f_m(\phi)=k_BT\left[\frac{\phi}{N_A}\ln\phi+\frac{1-\phi}{N_B}\ln(1-\phi)+\chi\phi(1-\phi)\right],\tag{77}$$

where χ is the Flory-Huggins interaction parameter, and use Eq. (26) for the elastic free energy. Substituting Eqs. (65) and (66) into Eq. (58) and making use of Eqs. (74)–(76), we can obtain the following linearized diffusion equation in Fourier space,

$$\left(\frac{\partial}{\partial t}-Sk_x\frac{\partial}{\partial k_y}\right)\phi_1(k)=-v_m\frac{k_BT}{\zeta}\phi_0(1-\phi_0)^2k^2 \times[\Psi_0+\Psi_1(\hat{k}_x,\hat{k}_y)]\phi_1(k).\tag{78}$$

Here Ψ_0 is an isotropic constant given by

$$\Psi_0(\phi_0)=\frac{1}{N_A\phi_0}+\frac{1}{N_B(1-\phi_0)}-2\chi+\kappa(\phi_0)(S\lambda_0)^2,\tag{79}$$

where $\lambda_0=\xi_0/g_0$ is the average relaxation time and the coefficient κ is given by

$$\kappa(\phi_0)=\frac{1}{2}g_0''-\frac{g_0'^2}{g_0}+\alpha_0g_0'.\tag{80}$$

Note that κ depends only on the shear modulus of the blend. The second term on the right-hand side of Eq. (78) produces an anisotropic modification of the scattering function [5] and is given by

$$\Psi_1=-2S\lambda_0(A_0+B_0)\hat{k}_x\hat{k}_y+(S\lambda)^2[4(C_0-2B_0)(\hat{k}_x\hat{k}_y)^2-2(A_0+B_0-D_0)\hat{k}_x^2+(C_0-B_0)\hat{k}_z^2],\tag{81}$$

where A_0, B_0, C_0, and D_0 are the constants

$$A_0=\alpha_0'g_0+\phi_0^{-1}g_{A0}+(1-\phi_0)^{-1}g_{B0},\tag{82}$$

$$B_0=\alpha_0g_0\frac{\xi_0'}{\xi_0},\tag{83}$$

$$C_0=g_0'\frac{\xi_0'}{\xi_0},\tag{84}$$

$$D_0=\alpha_0g_0'.\tag{85}$$

The zero-shear spinodal line (linear stability line) in the $\chi-\phi$ parameter space is determined by the first three terms of Ψ_0 [18]. The last term is the modification of the stability line arising from the dynamics of viscoelasticity; this shift is $O(S^2)$, where S is the shear rate.

The direction of the stability line shift is dependent on the sign of κ, which in turn depends on the details of the interpolating function $\Delta(\phi)$. When $\kappa>0$, the effective value of χ is reduced, and stability line in the $\chi-\phi$ plane is shifted to larger values of χ (lower temperatures). On the other hand, when $\kappa<0$, the stability line is shifted in the opposite manner. Since, in general, the shear moduli for the individual species A and B involve material parameters, the details of the shift in the stability line cannot be determined explicitly. In highly symmetric situations, the magnitude of any shift might be small, owing to the small value of the coefficient $[G_A^{(0)}-G_B^{(0)}]$. However, the shift in the linear stability should, according to the present analysis, correlate with measurements of the interpolating function for the blend, $\Delta(\phi)$. If $\Delta(\phi)=\phi,\kappa=0$ and there is no shift in stability.

IV. CONCLUSION

We have applied the general two-fluid approach of Doi and Onuki [7] to establish model equations for the study of the phase behavior, or more precisely, linear stability, of a polymer blend in the presence of shear flow. A phenomenological form of the shear modulus for a polymer blend is used, which can be experimentally determined. The modifications used here allow the kinetic equations to reduce *formally* to the solution case in the limit in which one of the species becomes a small (solvent) molecule. However, since features of solid elasticity have been used, taking the limit remains to be fully justified. Linear analysis of the model indicates that the equilibrium stability line is shifted by the effect of viscoelasticity when the dependence of the shear modulus of the blend on the volume fraction of one of the species is nonlinear. The direction of the shift is dependent on the material properties of the species and on the range of volume fraction, so that the nature of the temperature shift is more complicated than that in polymer solutions [8,10]. Physically, this feature of polymer blends can be attributed to the fact that both species have contributions to the elastic free energy.

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