Phase Inversion during Viscoelastic Phase Separation: Roles of Bulk and Shear Relaxation Moduli

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We simulate viscoelastic phase separation of polymer solutions by solving numerically Langevin equations of a "viscoelastic model" that newly includes the bulk relaxation modulus in addition to the shear relaxation modulus. The results reproduce almost all the essential features of viscoelastic phase separation observed experimentally: (i) The existence of a frozen period, the nucleation of the solvent-rich phase, (ii) the volume shrinking of the polymer-rich phase, (iii) the transient formation of a networklike structure, and (iv) the phase inversion in the final stage. Our simulations clearly indicate that the bulk stress is responsible for (i), (ii), and (iv), while the shear stress for (iii). [S0031-9007(97)03404-2]

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Phase-separation phenomena are widely observed in various kinds of condensed matter including metals, semiconductors, simple liquids, and complex fluids such as polymers, surfactants, colloids, and biological materials [1]. It has been an open question for a long time whether there are significant effects of internal dynamics of component molecules on critical phenomena and phase separation or not. From the concept of dynamic universality [2], there should not be such effects. However, de Gennes [3] noticed that there can be viscoelastic effects on the early stage of phase separation in polymer mixtures, and this problem has recently been studied by Kumaran and Fredrickson [4]. Since the effects are not so drastic and also limited only to the very early stage, they have not been considered seriously.

Recently we have shown that phase separation of a fluid mixture (such as a polymer solution) whose components have very different internal dynamics is essentially different from that of classical fluid mixtures [5,6]. We call this new type of phase separation "viscoelastic phase separation" since viscoelastic effects play important roles in phase separation in addition to diffusion and hydrodynamic effects. The "dynamic asymmetry" between the components of a mixture is a prerequisite to viscoelastic phase separation. To consider this problem theoretically, we need a basic model that can treat the motion of each component separately, since the description of the difference in elementary dynamics between the two components of a mixture is required: such a model, which is known as a "two-fluid model" [7–9], has recently been studied intensively [8,10–17] to understand the stress-diffusion coupling and also the unusual shear effects in polymer solutions.

Since the basic equations describing viscoelastic phase separation are very complicated, the analytical approach is quite difficult and the numerical simulations are required to gain physical insight into the problem. Very recently the first numerical simulation was reported by Taniguchi and Onuki [18] on the basis of a different set of the basic equations describing viscoelastic phase separation [13]. Although some features of viscoelastic phase separation have been clarified by their study, the quantitative studies have just been initiated and the situation is still far from complete understanding.

In this Letter, we study viscoelastic phase separation of polymer solutions numerically on the basis of the fundamental equations derived from Doi and Onuki [15] and Milner [16] with an essential modification, namely, the inclusion of bulk modulus as a controllable parameter [19]. The bulk relaxation modulus, which has been neglected (or, more strictly, not treated as an important physical factor) in previous theories [13,15,16], likely plays crucial roles in viscoelastic phase separation as in gel phase separation [19]. We focus our special attention on the comparison of the numerical results with our experimental results and also on the roles of bulk and shear relaxation moduli.

First we describe the basic equations describing viscoelastic phase separation of polymer solutions used in our simulation. They are based on a two-fluid model of a mixture of polymer p and solvent s [15,16]. Let $\vec{v}_p(\vec{r},t)$ and $\vec{v}_s(\vec{r},t)$ be the average velocities of polymer and solvent, respectively, and $\phi(\vec{r},t)$ be the volume fraction of polymer at a point $\vec{r}$ and time t. Here we assume that the two components have the same density ρ for simplicity. The volume average velocity $\vec{v}$ is given by $\vec{v} = \phi\vec{v}_p + (1-\phi)\vec{v}_s$. The free energy of the system F_{mix} is given by $F_{\mathrm{mix}} = \int d\vec{r}\{f(\phi(\vec{r})) + (C/2)[\nabla\phi(\vec{r})]^2\}$, where $f(\phi)$ is the free energy per unit volume of a mixture with the composition ϕ of polymer. Here we use the Flory-Huggins-type free energy [20] as $f(\phi)$: $f(\phi)/k_BT = (1/N)\phi\ln\phi + (1-\phi)\ln(1-\phi) + \chi\phi(1-\phi)$. In this study, however, we set $N=1$ and do not introduce any dependence of C on ϕ to pick up only the pure effect of dynamic asymmetry. Then, the basic equations are given by [15,16]

$$\frac{\partial\phi}{\partial t} = -\vec{\nabla}\cdot(\phi\vec{v}) + \vec{\nabla}\cdot\frac{\phi(1-\phi)^2}{\zeta}[\vec{\nabla}\cdot\mathbf{\Pi} - \vec{\nabla}\cdot\boldsymbol{\sigma}], \quad (1)$$

$$\vec{v}_p - \vec{v}_s = -\frac{1-\phi}{\zeta}[\vec{\nabla}\cdot\mathbf{\Pi} - \vec{\nabla}\cdot\boldsymbol{\sigma}], \quad (2)$$

$$\rho\frac{\partial v}{\partial t} \cong -\vec{\nabla}\cdot\mathbf{\Pi} + \nabla p + \vec{\nabla}\cdot\boldsymbol{\sigma} + \eta_s\nabla^2\vec{v}\,, \quad (3)$$

where ζ is the friction constant, p is a part of the pressure, and η_s is the solvent viscosity. Here $\vec{\nabla}\cdot\mathbf{\Pi} = \phi\nabla(\frac{\partial f}{\partial\phi} - C\nabla^2\phi)$ and $\mathbf{\Pi}$ is the osmotic tensor. $\boldsymbol{\sigma}$ is the total stress tensor, which is, in general, given by the constitutive equation of material. In a linear-response regime, the most general expression of σ_{ij} is formally written by introducing the time dependence of bulk and shear moduli in the theory of elasticity [21] as

$$\sigma_{ij} = \int_{-\infty}^{t} dt'[G(t-t')\kappa_p^{ij}(t') + K(t-t')\vec{\nabla}\cdot\vec{v}_p(t')\delta_{ij}], \quad (4)$$

where $\kappa_p^{ij} = \frac{\partial v_p^j}{\partial x_i} + \frac{\partial v_p^i}{\partial x_j} - \frac{2}{d}(\nabla\cdot\vec{v}_p)\delta_{ij}$ and d is the spatial dimensionality ($d = 2$ in our simulations). Here we use the fact that $\vec{v}_p$ is only the velocity relevant to the rheological deformation in polymer solutions [14–16]. $G(t)$ and $K(t)$ are material functions containing information on all the spatiotemporal history, which we call the shear relaxation modulus and bulk relaxation modulus, respectively. The second term in the above equation for σ_{ij} has been newly introduced to incorporate the effect of volume change into the stress tensor [19]. It should be stressed that its diagonal nature leads to the direct coupling with diffusion: note that the effective osmotic pressure is given by $\pi^{\mathrm{eff}} = (\phi\frac{\partial f}{\partial\phi} - f) - \int_{-\infty}^{t} dt'\,K(t-t')\vec{\nabla}\cdot\vec{v}_p(t')$.

In our simulation, we assume the Maxwell-type relaxation for both bulk and shear relaxation moduli for simplicity: $G(t) = M_S\exp(-t/\tau_S)$ and $K(t) = M_B\exp(-t/\tau_B)$. Further, we assume that M_S, M_B, τ_S, and τ_B are the functions of only $\phi(\vec{r})$. Under these assumptions on $G(t)$ and $K(t)$, we need to solve the following upper-convective equations instead of Eq. (4):

$$\frac{D\boldsymbol{\sigma}_w}{Dt} = \vec{\nabla}\vec{v}_p\cdot\boldsymbol{\sigma}_w + \boldsymbol{\sigma}_w\cdot(\vec{\nabla}\vec{v}_p)^T - \frac{1}{\tau_w}\boldsymbol{\sigma}_w + M_w(\vec{\nabla}\vec{v}_p + (\vec{\nabla}\vec{v}_p)^T)\,, \quad (5)$$

where $\frac{D}{Dt} = \frac{\partial}{\partial t} + \vec{v}_p\cdot\vec{\nabla}$, and $w = B$ and S indicate bulk and shear, respectively. We calculate the final shear stress $\boldsymbol{\sigma}_S^f$ as $\boldsymbol{\sigma}_S^f = \boldsymbol{\sigma}_S - \frac{1}{d}\mathrm{Tr}(\boldsymbol{\sigma}_S)\boldsymbol{I}$ ($\boldsymbol{I}$ is a unit tensor), while the final bulk stress as $\boldsymbol{\sigma}_B^f = \frac{1}{d}\mathrm{Tr}(\boldsymbol{\sigma}_B)\boldsymbol{I}$.

The above Langevin equations were solved numerically by the Euler method in two dimensions using periodic boundary conditions, under the incompressibility condition $\vec{\nabla}\cdot\vec{v} = 0$ and the quasistationary approximation $\partial\vec{v}/\partial t \cong 0$. The system size was 128×128. We choose the grid size $\Delta x = \Delta y = 1$ and time step $\Delta t = 0.02$ to ensure the stability. The stress tensor $\boldsymbol{\sigma}_w(\vec{r}, t + \Delta t)$ at a point $\vec{r}$ and time $t + \Delta t$ is calculated from $\boldsymbol{\sigma}_w(\vec{r}, t)$, using the following relation:

$$\boldsymbol{\sigma}_w(\vec{r}, t+\Delta t) = \boldsymbol{\sigma}_w(\vec{r}, t)\exp\left(-\frac{\Delta t}{\tau_w}\right) + M_w[\vec{\nabla}\vec{v}_p + (\vec{\nabla}\vec{v}_p)^T]\Delta t + \cdots\,, \quad (6)$$

where $\cdots$ represents the terms containing spatial derivatives. The numerical calculation of the memory effects based on the above relation has some technical advantage over that based on the differential equation (see, e.g., Ref. [18]) in that the former is stable even for $\Delta t \geq \tau_w$, but the latter is not. We assume $M_S = 0.5\phi^2$ and $M_B = 5.0\theta(\phi - \phi^*)$, where θ is a step function. In the following simulations, we set ϕ^* to be equal to the initial composition, for simplicity. This choice is one of the easiest ways to induce the strong asymmetry in bulk stress between a polymer-rich and a solvent-rich phase. We also assume that $\tau_S = 50\phi^2$ and $\tau_B = 10\phi^2$. Although there is no firm basis on the above relations assumed, the details of the dependencies of these quantities on ϕ do not affect the qualitative features of the simulated results. These parameters are chosen to illustrate the roles of bulk and shear moduli clearly.

The velocity field $\vec{v}$ in k space, $\vec{v}_k$, is calculated from the relation $\vec{v}_k = \boldsymbol{T}_k\cdot(-\vec{\nabla}\cdot\mathbf{\Pi} + \vec{\nabla}\cdot\boldsymbol{\sigma})_k$, where $\boldsymbol{T}_k$ is the Osceen tensor in k space given by $\boldsymbol{T}_k = \frac{1}{\eta_s k^2}(\boldsymbol{I} - \frac{\vec{k}\vec{k}}{k^2})$, where $(\,)_k$ denotes the Fourier component of k.

In the simulation, we set $k_BT = 1.3$, $\zeta = 0.1$, $\chi = 2.7$, and $\eta_s = 0.1$. This set of parameters guarantees that the coarsening behavior without $\vec{\nabla}\cdot\boldsymbol{\sigma}$ is quite similar to that simulated by using the fully scaled time-dependent Ginzburg-Landau equations of model H with ϕ^4 potential [1,2]. We introduce the Gaussian random noise of ϕ with the intensity of 10^{-3} into the initial composition distribution. We set the initial polymer composition to be 0.35. For $\chi = 2.7$, the equilibrium compositions are 0.107 and 0.893. Thus, the final volume fraction of the polymer-rich phase is 0.309.

Figure 1 shows the simulated pattern evolution dynamics of viscoelastic phase separation with bulk modulus and without shear modulus [1(a)], without bulk modulus and with shear modulus [1(b)], and with both bulk and shear moduli [1(c)]. All these simulations were done using the same parameters. Only when there is the bulk relaxation modulus [1(a) and 1(c)], we have phase inversion.

We stress that the simulation results with both bulk and shear moduli [see Fig. 1(c)] recover almost all the essential features of viscoelastic phase separation observed experimentally [5,6]: (i) The existence of an incubation time of nucleation of the solvent holes and their nucleation-growth-like appearance, (ii) the volume shrinking of the polymer-rich phase (see also Fig. 2), (iii) the resulting formation of a networklike structure, and (iv) the final relaxation of the pattern dominated by the elastic energy to that by interfacial tension, which leads to phase inversion.

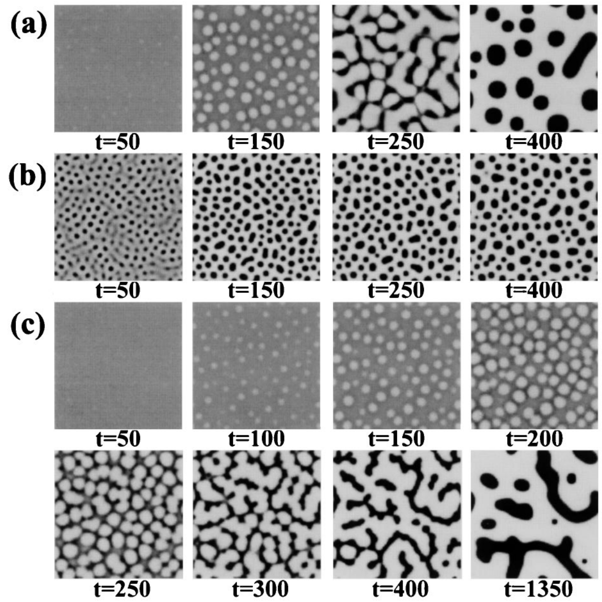

FIG. 1. Simulated pattern evolution during viscoelastic phase separation. (a) With bulk modulus and without shear modulus, (b) without bulk modulus and with shear modulus, and (c) with both bulk and shear moduli. Note that the darkness is proportional to ϕ.

Figure 2 shows the temporal change in the volume fraction Φ_p of a polymer-rich phase for all three cases. The temporal change in the darkness of a polymer-rich phase even after the formation of a sharp interface in Figs. 1(a) and 1(c) is another indication of volume shrinking. The volume shrinking behavior is observed only for the cases of the existence of the bulk stress. It is evident that bulk stress is a prerequisite to the volume shrinking behavior and the resulting phase inversion.

Figure 3 shows the temporal change in the average magnitudes per lattice of the three types of forces, namely, the thermodynamic force $\vec{F}_\phi = -\vec{\nabla} \cdot \mathbf{\Pi}$, the bulk mechanical force, $\vec{F}_B = -\vec{\nabla} \cdot \boldsymbol{\sigma}_B$, and the shear mechanical force, $\vec{F}_S = -\vec{\nabla} \cdot \boldsymbol{\sigma}_S$. Both $|\vec{\nabla} \cdot \mathbf{\Pi}|$ and $|\vec{\nabla} \cdot \boldsymbol{\sigma}_B|$ have the peaks at the same time of $t = 270$. This is natural since both quantities are directly related to $\vec{\nabla} \cdot \vec{v}_p$. In the initial stage, these two effects are canceled out and the diffusion is significantly suppressed. On the other hand, $|\vec{\nabla} \cdot \boldsymbol{\sigma}_S|$ has a peak at $t = 370$, retarded from the peaks of $|\vec{\nabla} \cdot \mathbf{\Pi}|$ and $|\vec{\nabla} \cdot \boldsymbol{\sigma}_B|$ by $\Delta t \sim 100$. Note that $\vec{\nabla} \cdot \boldsymbol{\sigma}_S$ is not directly coupled with diffusion coming from the diagonal part of $\mathbf{\Pi}$ and simply produces the mechanical force fields.

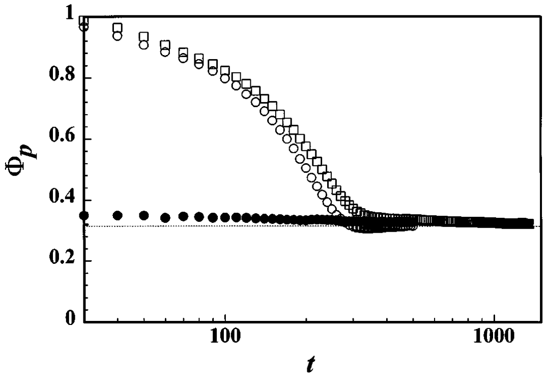

FIG. 2. Temporal change in the volume (area) fraction Φ_p of a polymer-rich phase. Open circles, filled circles, and open squares correspond to the cases of Figs. 1(a)–1(c), respectively. Dashed line gives the equilibrium value of $\Phi_p = 0.309$.

First we discuss the roles of the bulk relaxation modulus in viscoelastic phase separation. The bulk relaxation modulus likely suppresses the initial rapid growth of concentration fluctuations characteristic of spinodal decomposition [compare Figs. 1(a) and 1(c) with Fig. 1(b)], since $\vec{\nabla} \cdot \vec{v}_p$ is directly related to $\partial\phi/\partial t$ through the continuity equation [19]. The bulk relaxation modulus likely plays dominant roles in the initial stage of phase separation. The existence of the dark-contrast part surrounding the solvent holes [see, e.g., Fig. 1(c), $t = 200$] indicates the excess polymer concentration on the edge of the solvent holes (overshooting effects). This is likely caused by the effects of bulk relaxation modulus, which retard the diffusion in the polymer-rich phase selectively. The similar phenomena are also observed by the simulation of model *B* with a large composition dependence of the mobility [22]. This effect of the bulk stress that suppresses the growth of the composition fluctuations and the diffusion probably leads to the volume shrinking of a polymer-rich phase and the resulting phase inversion.

Next we discuss the roles of the shear relaxation modulus in viscoelastic phase separation. By comparing Fig. 1(a) with Fig. 1(c), we can learn that the shear relaxation modulus plays a significant role in the formation of a networklike structure. Although the stress fields around an isolated solvent hole have the spherical symmetry, the coupling of the diffusion fields around neighboring solvent holes induces the deformation of shear type. Thus, we expect that $|\vec{\nabla} \cdot \boldsymbol{\sigma}_S|$ increases, reflecting the increase in the coupling between the diffusion fields around solvent drops. This is quite consistent with the fact that $|\vec{\nabla} \cdot \boldsymbol{\sigma}_S|$ has a peak, retarded from the peaks of $|\vec{\nabla} \cdot \mathbf{\Pi}|$ and $|\vec{\nabla} \cdot \boldsymbol{\sigma}_B|$ (see Fig. 3). This retardation of the peaking of

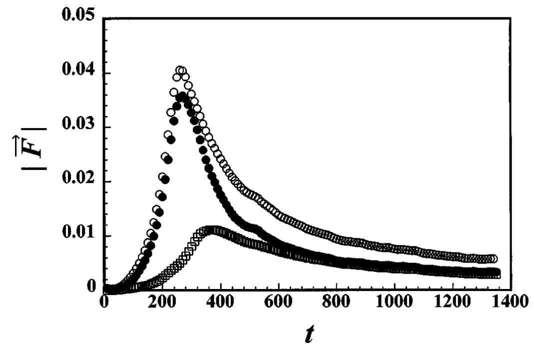

FIG. 3. Temporal changes in the average magnitudes of the three types of forces, $|\vec{F}|$. Open circles: $|\vec{F}_\phi|$, filled circles: $|\vec{F}_B|$, and open squares: $|\vec{F}_S|$.

the shear force plays a significant role in the enhancement of the network character of the pattern.

Further, the shear relaxation stress extremely slows down the shape relaxation process [compare Fig. 1(a) and 1(c)], since it inevitably accompanies the shear deformation. In the absence of the shear relaxation modulus $[G(t) = 0]$, the characteristic shape relaxation time for a domain of size R, τ_R, is given by $\tau_R \sim \eta_s R/\gamma$ (γ: interface tension). In the presence of $G(t)$, on the other hand, $\tau_R \sim \eta R/\gamma$, where $\eta = \int_0^\infty G(t)\,dt$. Using the fact that $\phi = 0.89$ in the polymer-rich phase and $G(t) = 0.5\phi^2 \exp(-t/50\phi^2)$, we obtain $\eta \sim 16$. Since $\eta_s = 0.1$, the shape relaxation time should be about 160 times longer for Fig. 1(c) than for Fig. 1(a), which is consistent with what is seen in Fig. 1.

Here we compare our results with those of Taniguchi and Onuki [18]. Very recently Taniguchi and Onuki have successfully demonstrated the network domain structure in viscoelastic phase separation by simulations. Their simulation is based on the model [12] in which the viscoelastic contribution is described by the so-called conformation tensor W_{ij}. The model used by us [15] is more phenomenological than theirs, but our model can be applied not only to polymers, but also to any material [19]. It should be noted that viscoelastic phase separation may be generally observed in a mixture of any material having dynamic asymmetry between its components [6,19]. The phenomenological constitutive equation corresponding to their model is given by

$$\sigma_{ij} = \int_{-\infty}^{t} dt'\, G(t - t') \left(\frac{\partial v_{pi}}{\partial x_j} + \frac{\partial v_{pj}}{\partial x_i} \right). \qquad (7)$$

This constitutive equation includes only one material function $G(t)$ in contrast to ours [see Eq. (4)]. The most crucial difference comes from the fact that we include both shear and bulk moduli as controllable variables. In their model, the bulk modulus is fixed to be $2/3$ of the shear modulus in three dimensions and the relaxation time is the same. It is probably this difference in the treatment of bulk modulus that is responsible for the fact that phase-inversion phenomena or volume-shrinking behavior characteristic to viscoelastic phase separation [5,6] is observed in our simulation, but not in theirs. Our results clearly indicate that the bulk modulus plays crucial roles in the suppression and retardation of growth of concentration fluctuations in the early stage of viscoelastic phase separation.

Finally we briefly discuss the physical reasons why the bulk relaxation modulus is important in the phase separation of polymer solutions [19]. The key point is that phase separation always occurs under a poor-solvent condition. The term associated with $\vec{\nabla} \cdot \vec{v}_p$ was dropped in the previous theories [13,15] or not treated as an important physical factor [12,16,18] since the standard theory of polymer solutions [23] tells us that the stress associated with $\vec{\nabla} \cdot \vec{v}_p$ decays very rapidly and it cannot be stored by polymer chains. However, the above standard theory that mainly focuses on the topological interactions between polymer chains cannot be applied to polymer dynamics in a poor solvent. Although there is no reliable theory on the polymer dynamics in a poor solvent, it is natural to consider that there exist attractive interactions between polymer chains, which lead to the formation of transient crosslinking points. Thus, we expect that polymer solutions behave as a physical gel in a short time scale. The existence of transient crosslinking points guarantees that polymer chains can store the bulk stress as a gel for a certain deformation rate. We need further studies for a deeper understanding of viscoelastic phase separation, including the study of polymer dynamics in a poor solvent.

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