

Modified models of polymer phase separation

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In this paper we discuss continuum models of phase separation in polymer solutions, with emphasis on the thermodynamic foundation of these models. We demand that these models obey a free energy dissipation relation, which in the present context plays the role of the second law of thermodynamics, since the system is isothermal. First, we derive a modified two-fluid model for viscoelastic phase separation from nonequilibrium thermodynamics. Then we study the special case when only diffusion is present, and hydrodynamic effects are neglected. Numerical results demonstrate that our models show better stability properties and at the same time reproduce the expected physical phenomena such as volume shrinking and phase inversion. Our findings suggest that these important phenomena are caused by a diffusional asymmetry of the constituent molecules.

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I. INTRODUCTION

The phenomena of phase separation have attracted a great deal of interest in recent years [1–4]. When a binary mixture is quenched from the miscible region into the immiscible two phase region in the phase diagram, phase separation occurs via mechanism of spinodal decomposition. Generally speaking, in the early stage, phase separation is controlled by concentration fluctuation and the decrease of bulk energy. At the later stage, phase separation is controlled by diffusion and coarsening, and the decrease of surface energy. It is established that the domain size $R(t)$ satisfies some scaling law: $R(t) \sim t^\alpha$ during the course of phase separation, where α is the growth exponent [5]. The dynamics and morphology of phase separation also depend on the particular systems. In small-molecule systems the morphology of phase separation is quite simple, and it is determined by the relative concentration in the mixture. In polymer systems, however, the morphology of phase separation can exhibit many unusual features such as volume-shrinking and phase inversion [6,7]. Much work has been done in order to understand the dynamics of polymer phase separation. It is now established that the internal dynamic asymmetry between component molecules of the mixture determines on the morphology and the dynamics during the phase separation process [3]. Jäckle and Sappelt introduced dynamic asymmetry through concentration-dependent mobility [8]. Then Ahluwalia carried out a study of phase separation in polymer solutions with a similar viewpoint [9]. Onuki, Doi, and Milner established a two-fluid model in which the dynamic asymmetry was reflected by the stress field [10,11,22]. Later on Tanaka and co-workers further developed the two-fluid model and extensively investigated viscoelastic phase separation both theoretically and experimentally [2–4,6,7].

In this paper we will follow the same philosophy, and focus on viscoelastic phase separation in polymer solutions

and the consequence of dynamic asymmetry. However, we will pay special attention to the thermodynamic foundation of the models, namely, we demand that the models should satisfy the energy dissipation relation which plays the role of the second law of thermodynamics. This should be a basic requirement for any physical models. But it is not satisfied by the existing two-fluid models. We will first derive our modified two-fluid model from nonequilibrium thermodynamics. Then we present two models in which the transport is only due to diffusion—hydrodynamic effects are neglected. Our numerical results demonstrate that these models can reproduce the overall features of phase separation in polymer solutions and at the same time have much better stability properties, compared with existing two-fluid models.

This paper is organized as follows. From Sec. II to Sec. IV, we present models and their corresponding numerical simulations. We also discuss briefly the energy dissipation relation. Section V contains some discussions and conclusions. The details of the energy dissipation relation of our models are given in the Appendix.

II. THE MODIFIED TWO-FLUID MODEL

A. Free energy of the polymer-solvent system

We describe the dynamics of phase separation through the Cahn-Hilliard-Cook theory [12–14]. The local volume fraction of the polymer molecules ϕ is chosen as the order parameter, which is a function of space and time. Due to the incompressibility condition, the local volume fraction of the solvent molecules is then $1 - \phi$. We use a simplified version of the free energy in a nonhomogenous isotropic system [12]

$$F[\phi, \nabla \phi] = \int d\vec{r} \left[f(\phi) + \frac{C_0}{2} |\nabla \phi|^2 \right] \quad (1)$$

with

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$$f(\phi) = \frac{1}{n_p} \phi \ln \phi + \frac{1}{n_s} (1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi), \quad (2)$$

where n_p and n_s are the molecular weight of the polymer and the solvent, respectively. χ is the effective Flory interaction parameter which decays with temperature. We assume that χ is inversely proportional to the temperature T :

$$\chi = \frac{\chi_0}{T}, \quad (3)$$

where χ_0 is a positive constant.

The gradient of the chemical potential as driving force is defined by

$$\nabla \mu = \nabla \left[\frac{\delta F}{\delta \phi} \right],$$

where μ is the chemical potential.

B. Tanaka's two-fluid model

We first recall the original two-fluid model equations given in Refs. [10,15].

$$\frac{\partial \phi}{\partial t} + \nabla \cdot (\phi \vec{v}_p) = 0,$$

$$\vec{v}_p - \vec{v} = -M_1(\phi) [\nabla \cdot \vec{\Pi} - \nabla \cdot \vec{\sigma}],$$

$$\frac{\partial \vec{v}}{\partial t} = -\nabla P + \nabla \cdot \vec{\sigma} - \nabla \cdot \vec{\Pi} + \eta \Delta \vec{v},$$

$$\nabla \cdot \vec{v} = 0,$$

where $\vec{\Pi}$ is the osmotic pressure tensor and $\vec{\sigma}$ is the stress tensor satisfying the following equations:

$$\vec{\sigma} = \vec{\sigma}_s - \frac{1}{d} \text{Tr}(\vec{\sigma}_s) \vec{I} + q \vec{I},$$

$$\begin{aligned} \frac{\partial \vec{\sigma}_s}{\partial t} + (\vec{v}_p \cdot \nabla) \vec{\sigma}_s &= (\nabla \vec{v}_p) \cdot \vec{\sigma}_s + \vec{\sigma}_s \cdot (\nabla \vec{v}_p)^T \\ &\quad - \frac{1}{\tau_s} \vec{\sigma}_s + M_s [\nabla \vec{v}_p + (\nabla \vec{v}_p)^T], \end{aligned}$$

$$\frac{\partial q}{\partial t} + \vec{v}_p \cdot \nabla q = -\frac{1}{\tau_B} q + M_B (\nabla \cdot \vec{v}_p),$$

where d is the spacial dimensionality and \vec{I} is the unit tensor. The stress $\vec{\sigma}$ consists of two parts [23,24]: one is the shear stress tensor $\vec{\sigma}_s$, the other is the bulk stress tensor $q \vec{I}$. The total energy of the above system should contain the free energy, the kinetic energy, and the viscoelastic energy of polymers and it should decay with time from thermodynamic viewpoints. However, it is quite easy to verify that this two-fluid model does not satisfy the expected energy dissipation relation

$$\frac{d}{dt} \left[F + \int \frac{1}{2} |\vec{v}|^2 + \int \frac{1}{2} q^2 + \int \frac{1}{2} (\text{Tr} \vec{\sigma}_s) \right] < 0.$$

Not only is this unsatisfactory from a physical viewpoint, it also sometimes results in numerical instability in simulations.

C. Derivation of model equations

We now derive the modified two-fluid model that does respect an energy dissipation relation. Following the standard procedures in nonequilibrium thermodynamics, we split the currents into a reversible and a nonreversible part. The reversible contributions can be obtained through the virtual work principle, while the irreversible contributions are obtained by analyzing the dissipative process. We start from the total energy which has the form

$$E = F + \int \frac{1}{2} |\vec{v}|^2 + \int \frac{1}{2} q^2 + \int \frac{1}{2} \text{Tr}(\vec{\sigma}_s).$$

The first term represents the free energy of mixture. The second term is the kinetic energy of the system. The third term derives from the chain conformational entropy of the polymer molecules which can be regarded as some penalty function since the migration of polymer molecules will cause much more decrease in entropy compared with the solvents. The last term is the elastic energy of polymer molecules. The underlying physics of this term comes from the well-known Hookean-dumbbell models of flexible polymers [16].

First we write down the general equations for variables ϕ , q , \vec{v} , and $\vec{\sigma}_s$. According to the continuity equation, the volume fraction ϕ should satisfy

$$\frac{\partial \phi}{\partial t} + \nabla \cdot (\phi \vec{v}_p) = 0,$$

namely

$$\frac{d\phi}{dt} = \frac{\partial \phi}{\partial t} + (\vec{v} \cdot \nabla) \phi = -\nabla \cdot [\phi (\vec{v}_p - \vec{v})],$$

where \vec{v}_p and \vec{v} are the velocity of polymer molecules and the volume-averaged velocity of fluid particles, respectively.

Next we deal with the constitutive equations of polymer molecules for q and $\vec{\sigma}_s$. They should obey relaxational dynamics

$$\frac{dq}{dt} = -\frac{1}{\tau} q + A,$$

$$\frac{D\vec{\sigma}_s}{Dt} = -\frac{1}{\tau_s} \vec{\sigma}_s + \vec{B},$$

where A and B remain undetermined at this stage. τ and τ_s are the relaxation time which take the form [3,17].

$$\tau = \tau_B^0 \phi^2, \quad \tau_s = \tau_s^0 \phi^2.$$

The time derivative $\frac{D}{Dt}$ is the upper-convected derivative.

The hydrodynamic equation for the incompressible system is given by

$$\frac{d\vec{v}}{dt} = -\nabla P + \nabla \cdot \vec{\sigma}_e + \nabla \cdot \vec{\sigma}_v,$$

$$\nabla \cdot \vec{v} = 0,$$

where \vec{v} is the volume-averaged velocity of polymer molecules and solvents. $\vec{\sigma}_e$ corresponds to the elastic stress, while $\vec{\sigma}_v$ is the viscous stress.

We first derive an expression for the reversible part $\vec{\sigma}_e$ in the above equations using the generalized virtual work principle [16]. The variation of the total free energy in response to the infinitesimal deformation can be identified through the work done by the elastic stress with respect to the deformation rate as follows:

$$\delta E_f = \int \vec{\sigma}_e : \nabla \vec{v} \delta t.$$

Namely

$$\begin{aligned} \delta E_f &= \delta \left[F + \int \frac{1}{2} q^2 + \int \frac{1}{2} \text{Tr}(\vec{\sigma}_s) \right] \\ &= \int \left[\frac{\partial F}{\partial \phi} \frac{d\phi}{dt} + \frac{\partial F}{\partial \nabla \phi} \cdot \frac{d\nabla \phi}{dt} + q \frac{dq}{dt} \right. \\ &\quad \left. + \frac{1}{2} \frac{d}{dt} \text{Tr}(\vec{\sigma}_s) \right] \delta t \\ &= \int \left[\frac{\delta F}{\delta \phi} \frac{d\phi}{dt} + q \frac{dq}{dt} + \frac{1}{2} \frac{d}{dt} \text{Tr}(\vec{\sigma}_s) \right] \delta t \\ &\quad - \int \left(\frac{\partial F}{\partial \nabla \phi} \otimes \nabla \phi \right) : \nabla \vec{v} \delta t \\ &= \int \left[\frac{\delta F}{\delta \phi} \frac{d\phi}{dt} + q \frac{dq}{dt} + \frac{1}{2} \text{Tr} \left(\frac{D}{Dt} \vec{\sigma}_s \right) \right] \delta t \\ &\quad + \int \left(\vec{\sigma}_s - \frac{\partial F}{\partial \nabla \phi} \otimes \nabla \phi \right) : \nabla \vec{v} \delta t. \end{aligned} \quad (4)$$

Here we only consider the reversible parts, thus we do not take account of relative motions between polymer molecules and solvents which correspond to the irreversible parts. In other words, we have

$$\vec{v}_p = \vec{v}_s = \vec{v}.$$

Therefore, we get the following expression through Eq. (4),

$$\delta E_f = \int \left(\vec{\sigma}_s - \frac{\partial F}{\partial \nabla \phi} \otimes \nabla \phi \right) : \nabla \vec{v} \delta t.$$

The elastic stress is obtained as

$$\vec{\sigma}_e = \vec{\sigma}_s - \frac{\partial F}{\partial \nabla \phi} \otimes \nabla \phi.$$

In the following we deal with the irreversible part which is related to the dissipation process. The first step is to construct the entropy source TS . Our derivation of the entropy

source follows rather closely the approach of de Groot and

Mazur for isotropic fluids [18]. The dissipation TS for an isothermal process is equal to the decrease in the total energy

$$\begin{aligned} TS &= -\frac{d}{dt} \left[F + \int \frac{1}{2} |\vec{v}|^2 + \int \frac{1}{2} q^2 + \int \frac{1}{2} \text{Tr}(\vec{\sigma}_s) \right] \\ &= -\int \left(\frac{\partial F}{\partial \phi} \frac{d\phi}{dt} + \frac{\partial F}{\partial \nabla \phi} \cdot \frac{d\nabla \phi}{dt} \right) - \int \vec{v} \cdot \frac{d\vec{v}}{dt} \\ &\quad - \int \left[q \frac{dq}{dt} + \frac{1}{2} \frac{d}{dt} \text{Tr}(\vec{\sigma}_s) \right] \\ &= -\int \frac{\delta F}{\delta \phi} \frac{d\phi}{dt} + \int (\vec{\sigma}_v : \nabla \vec{v}) - \int q \frac{dq}{dt} \\ &\quad - \int \frac{1}{2} \text{Tr} \left(\frac{D}{Dt} \vec{\sigma}_s \right) \\ &= \int \left[-\phi(1-\phi) \nabla \frac{\delta F}{\delta \phi} \right] \cdot (\vec{v}_p - \vec{v}_s) + \int (\vec{\sigma}_v : \nabla \vec{v}) \\ &\quad - \int qA - \int \frac{1}{2} \text{Tr}(\vec{B}) + \int \frac{1}{\tau} q^2 + \int \frac{1}{2\tau_s} \text{Tr}(\vec{\sigma}_s) \end{aligned} \quad (5)$$

Considering that there are only two freedoms among the strain rate $\nabla \vec{v}_p$, $\nabla \vec{v}_s$ and $\nabla \vec{v}$, we choose $\nabla(\vec{v}_p - \vec{v}_s)$ and $\nabla \vec{v}$ as independent variables. For small deformation case, we have the linear relationship between the stress and the strain rate. Therefore, we obtain the following expressions:

$$A = A_1 \text{Tr}[\nabla(\vec{v}_p - \vec{v}_s)] + A_2 \text{Tr}[\nabla \cdot \vec{v}],$$

$$\vec{B} = B_1 [\nabla(\vec{v}_p - \vec{v}_s) + \nabla(\vec{v}_p - \vec{v}_s)^T] + B_2 [\nabla \vec{v} + (\nabla \vec{v})^T].$$

Due to the incompressibility condition, we obtain

$$A = A_1 \text{Tr}[\nabla(\vec{v}_p - \vec{v}_s)],$$

$$\text{Tr}(\vec{B}) = B_1 \text{Tr}[\nabla(\vec{v}_p - \vec{v}_s) + \nabla(\vec{v}_p - \vec{v}_s)^T].$$

Since $\text{Tr}(\vec{\sigma}_s)$ is the spring energy and must remain positive, this will only hold when B_1 is zero. Therefore, we get

$$\begin{aligned} TS &= \int \left[-\phi(1-\phi) \nabla \frac{\delta F}{\delta \phi} \right] \cdot (\vec{v}_p - \vec{v}_s) + \int (\vec{\sigma}_v : \nabla \vec{v}) \\ &\quad - \int qA_1 [\nabla \cdot (\vec{v}_p - \vec{v}_s)] + \int \frac{1}{\tau} q^2 + \int \frac{1}{2\tau_s} \text{Tr}(\vec{\sigma}_s) \\ &= \int \left[-\phi(1-\phi) \nabla \frac{\delta F}{\delta \phi} + \nabla(A_1 q) \right] \cdot (\vec{v}_p - \vec{v}_s) \\ &\quad + \int (\vec{\sigma}_v : \nabla \vec{v}) + \int \frac{1}{\tau} q^2 + \int \frac{1}{2\tau_s} \text{Tr}(\vec{\sigma}_s). \end{aligned}$$

Noticing that the chain conformation entropy only induces

an extra pressure ∇q which can be absorbed by pressure P in the momentum equation, we can treat the viscous stress tensor $\vec{\sigma}_v$ as one proportional to the strain rate $\nabla \vec{v}$ in the newtonian case

$$\vec{\sigma}_v = \eta[\nabla \vec{v} + (\nabla \vec{v})^T].$$

Assuming that the linear friction law holds, we have

$$\vec{v}_p - \vec{v}_s = -M(\phi) \left[\phi(1-\phi) \nabla \frac{\delta F}{\delta \phi} - \nabla(A_1 q) \right], \quad (6)$$

where $M(\phi)$ is the mobility coefficient. Then we get the following dissipation relation:

$$\begin{aligned} T\dot{S} = \int \left[M(\phi) |\vec{v}_p - \vec{v}_s|^2 + \frac{\eta}{2} |\nabla \vec{v} + (\nabla \vec{v})^T|^2 + \frac{1}{\tau} q^2 \right. \\ \left. + \frac{1}{2\tau_s} \text{Tr}(\vec{\sigma}_s) \right]. \end{aligned}$$

In summary, our two-fluid model reads:

$$\begin{aligned} \frac{d\phi}{dt} &= \nabla \cdot \left\{ \phi(1-\phi) M(\phi) \left[\phi(1-\phi) \nabla \frac{\delta F}{\delta \phi} - \nabla(A_1 q) \right] \right\}, \\ \frac{dq}{dt} &= -\frac{1}{\tau} q - A_1 \nabla \cdot \left\{ M(\phi) \left[\phi(1-\phi) \nabla \frac{\delta F}{\delta \phi} - \nabla(A_1 q) \right] \right\} \\ \frac{\partial \vec{\sigma}_s}{\partial t} &+ (\vec{v} \cdot \nabla) \vec{\sigma}_s = (\nabla \vec{v}) \cdot \vec{\sigma}_s + \vec{\sigma}_s \cdot (\nabla \vec{v})^T - \frac{1}{\tau_s} \vec{\sigma}_s + B_2 [\nabla \vec{v} \\ &+ (\nabla \vec{v})^T], \\ \frac{d\vec{v}}{dt} &= -\nabla P + \nabla \cdot \{ \eta [\nabla \vec{v} + (\nabla \vec{v})^T] \} - \nabla \cdot \left(\frac{\partial F}{\partial \nabla \phi} \otimes \nabla \phi \right) \\ &+ \nabla \cdot \vec{\sigma}_s, \\ \nabla \cdot \vec{v} &= 0, \end{aligned} \quad (7)$$

where A_1 is the bulk modulus between the isotropic stress (induced by conformation entropy) and the strain rate.

D. Numerical results

Simulations are carried out in two dimensions for the above model. We use a forward Euler method in time and finite volume method in space to discretize the equations. The grid size is $\Delta x = \Delta y = 1$ and the system size is 128×128 . Periodic boundary conditions are used. The time step is chosen as $\Delta t = 0.025$. The parameters for the free energy in Eqs. (1)–(3) are chosen as $C_0 = 1, n_p = n_s = 1, \chi_0 = 2.8$. For this set of parameters, the phase diagram is calculated in Ref. [19]. Here we do not consider the molecular weight difference since we mainly care about viscoelastic effects of polymer which are pivotal to the morphology of phase separation.

The mobility coefficient $M(\phi)$ in Eq. (6) is given by

$$M(\phi) = \frac{1}{\zeta},$$

where ζ is the friction constant between polymer and solvent molecules and is chosen as $\zeta = 0.1$ in simulations. This form of $M(\phi)$ can be obtained from Fickian diffusion in ideal mixtures where the free energy only consists of entropic contributions.

The relaxation modulus B_2 in Eq. (7) is given by [3,17]

$$B_2 = M_s^0 \phi^2.$$

The bulk modulus A_1 in Eq. (7) is given by

$$A_1(\phi) = M_B^0 \left[1 + \tanh \left(\frac{\cot \pi \phi^* - \cot \pi \phi}{\epsilon} \right) \right] + M_B^1,$$

where $\epsilon \ll 1$ and is chosen as 0.01 in simulations. Therefore, A_1 changes rapidly from M_B^1 when ϕ is smaller than ϕ^* to its maximum value ($2M_B^0 + M_B^1$) when ϕ is larger than ϕ^* . Here ϕ^* is the critical concentration for the polymers to crosslink and we take ϕ^* as the initial uniform value ϕ_0 in simulations. The initial value of the volume fraction ϕ is the uniform concentration perturbed by uncorrelated noise distributed in the interval $[-0.001, 0.001]$ [15]. In the following, we will present the grey-scale map of the volume fraction. White stands for the solvent-rich region, and black stands for the polymer-rich region.

Figure 1 shows simulation results of the modified two-fluid model Eqs. (7). The whole viscoelastic phase separation process is exhibited more clearly for the case $T = 1.1, \phi_0 = 0.35$ shown in Fig. 2. We see that the morphology evolution in both figures is quite as similar as the experimental observations [6,7]. The simulation results will be explained at length in Sec. III for no hydrodynamic case since the model is more simple and easier to be understood.

Here we should point out that there is an important phenomenon which is called the ‘‘frozen state’’ and occurs in the very early stage of phase separation in polymer solutions. This indicates that the viscoelastic effects of polymer suppress the macroscopic phase separation in the initial stage [3]. In our model, this is manifested by the retardation of diffusion due to the presence of extra pressure ∇q . This extra pressure is active since we have chosen the bulk modulus smaller compared with zero bulk modulus in Tanaka’s model for the solvent-rich region [20]. In these simulations, we are able to use a time step size $\Delta t = 0.025$ which is much larger than the time step size (≈ 0.01) tolerated by Tanaka’s model. It shows that the model has better numerical stability properties. This is expected since the model satisfies the energy dissipation relation.

III. THE SIMPLIFIED MODEL

A. Dynamic model equations

We consider the modified two-fluid model in the special case where there is no hydrodynamic transport, in other words, we have

$$\vec{v} = \phi \vec{v}_p + (1 - \phi) \vec{v}_s = 0. \quad (8)$$

Thus a simplified model is obtained as

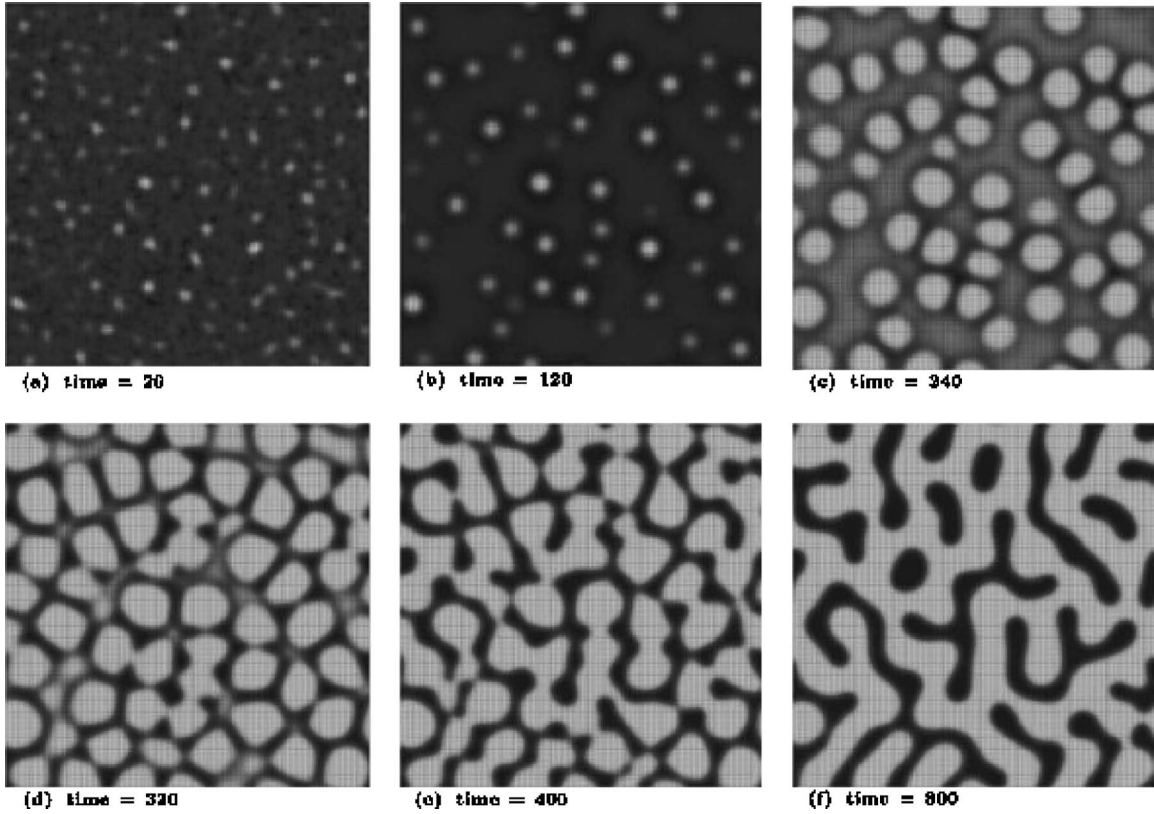


FIG. 1. Time evolution of phase separation after temperature quench with $T=1.1$, $\phi_0=0.4$ and $\tau_B^0=10$, $\tau_s^0=5$, $M_B^0=0.5$, $M_B^1=1$, $M_s^0=0.5$, at time=20, 200, 240, 320, 400, 800.

$$\begin{aligned} \frac{\partial \phi}{\partial t} &= \nabla \cdot \left\{ \phi(1-\phi)M(\phi) \left[\phi(1-\phi) \nabla \frac{\delta F}{\delta \phi} - \nabla(A_1 q) \right] \right\}, \\ \frac{\partial q}{\partial t} &= -\frac{1}{\tau} q - A_1 \nabla \cdot \left\{ M(\phi) \left[\phi(1-\phi) \nabla \frac{\delta F}{\delta \phi} - \nabla(A_1 q) \right] \right\}. \end{aligned} \quad (9)$$

Using Eqs. (6) and (8), we get the following linear relationship between the flux \vec{J} and the driving force

$$\vec{J} = \phi \vec{v}_p = -\phi(1-\phi)M(\phi) \left[\phi(1-\phi) \nabla \frac{\delta F}{\delta \phi} - \nabla(A_1 q) \right].$$

The thermodynamic driving force contains two parts: one is the gradient of chemical potential, the other is called the extra pressure which causes dynamic asymmetry between the polymer-rich and the solvent-rich region. We will see that this simple model can reproduce almost all experimental observations of viscoelastic phase separation and at the same time has the following energy dissipation relation:

$$\frac{d}{dt} \left[F + \int \frac{1}{2} q^2 \right] = - \int \frac{1}{(1-\phi)^2 M(\phi)} |\vec{v}_p|^2 - \int \frac{1}{\tau} q^2.$$

B. Numerical results

Figure 3 shows simulation results of the simplified model Eqs. (9). We will see that this model captures some physical

mechanism of viscoelastic phase separation. For ease of notation, we will use Ω_1 to represent the polymer-rich region and Ω_0 to represent the solvent-rich region. Due to the initial disturbance added to the system, and that the bulk modulus in Ω_0 is quite different from that in Ω_1 , we have an extra pressure ∇q with a direction pointing from Ω_1 to Ω_0 . This pressure ∇q has an opposite effect for the movement of polymer molecules since polymer molecules move from Ω_0 to Ω_1 . Therefore, ∇q makes it harder for the polymer molecules to aggregate than for the solvent molecules. As a result droplet phase forms in Ω_0 whereas Ω_1 remains a continuous matrix. These are shown in Figs. 3(a) and 3(b). Afterwards solvent molecules begin to aggregate and the solvent-rich region (shown in white) forms droplet phase, while the polymer-rich region (shown in black) forms a continuous phase. This is unusual compared with standard phase separation of small-molecule mixtures where the solvent-rich region forms continuous phase since it has a larger volume fraction.

In Figs. 3(c) and 3(d), the matrix-polymer-rich phase forms thin networklike structures. At the same time, the solvent-rich droplets grow and coagulate. The area of the polymer-rich phase keeps decreasing. This is the well-known volume-shrinking process in polymer phase separation [3]. It can be explained as follows. Since solvent molecules move faster, it is natural that the volume fraction in Ω_0 is close to the equilibrium value. Subsequently, the driving force for diffusion in Ω_0 becomes very small. However, the volume fraction in Ω_1 is still in the unstable state of the phase dia-

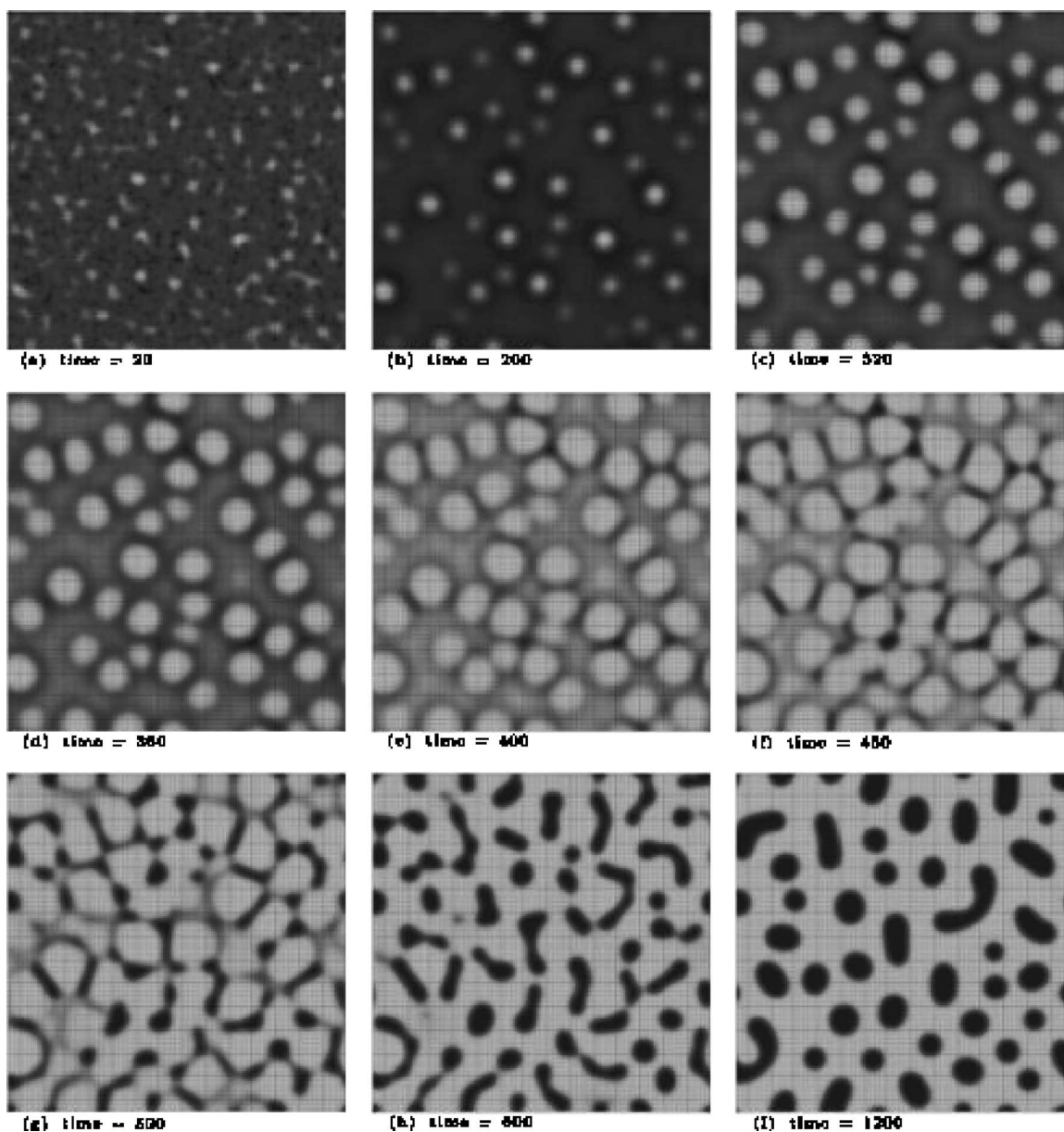


FIG. 2. Time evolution of phase separation after temperature quench with $T=1.1$, $\phi_0=0.35$ and $\tau_B^0=10$, $\tau_s^0=5$, $M_B^0=0.5$, $M_B^1=1$, $M_s^0=0.5$ at time=20, 200, 320, 360, 400, 450, 500, 600, 1200.

gram because of the slow down caused by the extra pressure ∇q . Therefore, the diffusion process in Ω_1 dominates the development of morphology in the intermediate stage. As solvent molecules are repelled from Ω_1 , the area fraction of Ω_1 decreases rapidly.

In the late stage which is shown in Figs. 3(d) and 3(f), polymer-rich networklike structures are broken and the polymer-rich phase changes from being continuous to being discontinuous. This process is called phase inversion. It can be explained as follows. After the volume-shrinking process is completed, the volume fraction of Ω_1 is also close to the equilibrium value. Therefore, diffusion driven by the gradient of chemical potential is weak in the whole system. The extra pressure ∇q becomes the main driving force in the system. Polymer-rich network structure is stretched by the solvent-rich droplets. This causes the network structure to

break and the polymer-rich region reduces to discontinuous phase. The morphology in Fig. 3 is almost the same as that in Figs. 1 and 2 except that phase inversion is observed more rapidly in the former. This is quite understandable since hydrodynamic flow accelerates domain coarsening.

IV. THE DIFFUSION MODEL

A. Dynamic model equations

In this section we will consider dynamic asymmetry through concentration-dependent mobility. The solvent molecules are smaller and easier to aggregate compared with the polymer molecules. Based on this, we establish another simple model that reproduces the volume-shrinking and phase inversion phenomena. To represent such asymmetry,

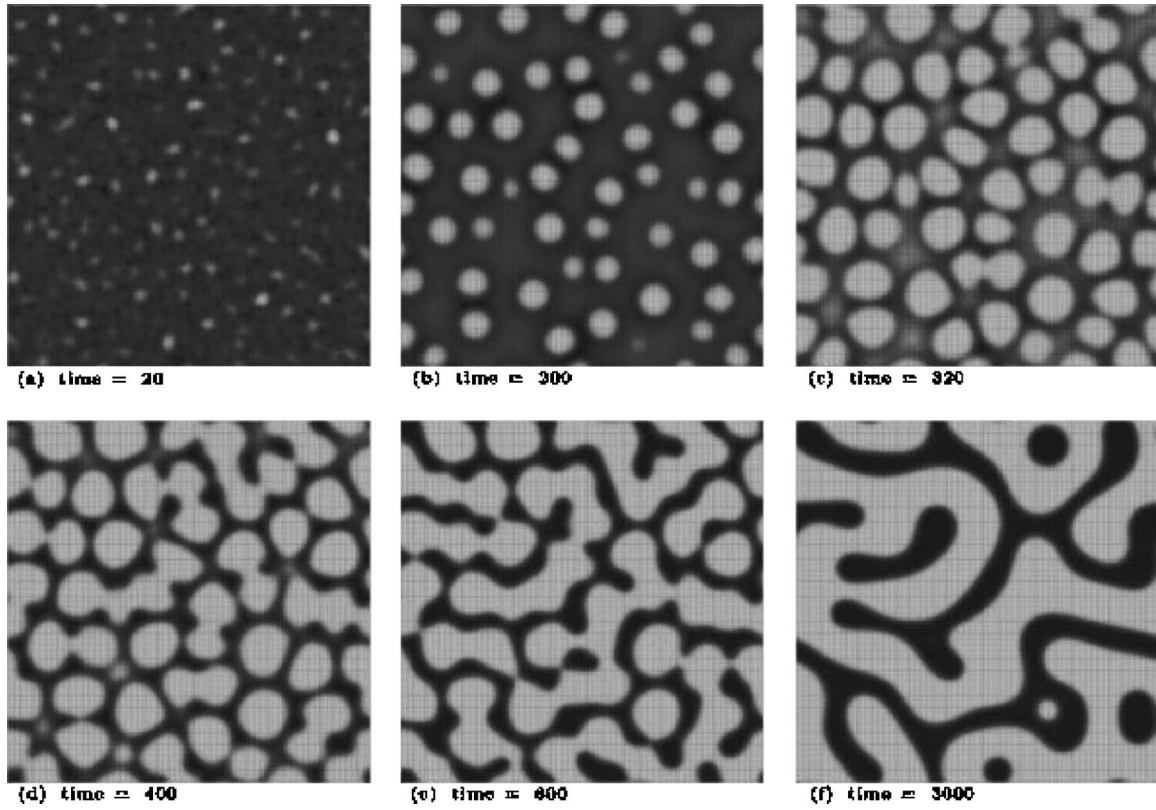


FIG. 3. Time evolution of phase separation after temperature quench with $T=1.1$, $\phi_0=0.4$ and $\tau_B^0=10, M_B^0=0.5, M_B^1=1$ at time =20, 200, 320, 400, 600, 3000.

we consider the system to be compressible [21,24]. The local volume fractions of polymer and solvent are denoted by ϕ_1 and ϕ_2 , respectively,

$$\phi_1 + \phi_2 < 1,$$

where $1 - \phi_1 - \phi_2$ can be regarded as the fraction of free volume. The free energy functional is given by

$$F[\phi_1, \phi_2, \nabla\phi_1, \nabla\phi_2] = \int d\vec{r} f(\phi_1, \phi_2) + \int d\vec{r} \left[\frac{C_1}{2} |\nabla\phi_1|^2 + \frac{C_2}{2} |\nabla\phi_2|^2 \right], \quad (10)$$

where

$$f(\phi_1, \phi_2) = \frac{1}{n_p} \phi_1 \ln(\phi_1) + \frac{1}{n_s} \phi_2 \ln(\phi_2) + (1 - \phi_1 - \phi_2) \ln(1 - \phi_1 - \phi_2) + \chi \phi_1 \phi_2. \quad (11)$$

The dynamic equations can be expressed as

$$\frac{\partial \phi_1}{\partial t} + \nabla \cdot (\phi_1 \vec{v}_1) = 0,$$

$$\frac{\partial \phi_2}{\partial t} + \nabla \cdot (\phi_2 \vec{v}_2) = 0,$$

$$\vec{v}_1 = -\frac{1}{\xi_p} (1 - \phi_1) \nabla \mu_1,$$

$$\vec{v}_2 = -\frac{1}{\xi_s} (1 - \phi_2) \nabla \mu_2, \quad (12)$$

where $\frac{1}{\xi_p}$ and $\frac{1}{\xi_s}$ are the mobility coefficient of polymer and solvents, respectively.

The gradient of the chemical potential $\nabla \mu_1$ and $\nabla \mu_2$ are defined through the relation

$$\nabla \mu_1 = \nabla \left[\frac{\delta F}{\delta \phi_1} \right],$$

$$\nabla \mu_2 = \nabla \left[\frac{\delta F}{\delta \phi_2} \right].$$

We show in the Appendix that the model satisfies the following energy dissipation relation:

$$\frac{dF}{dt} = - \int \frac{1}{\xi_p} \phi_1 (1 - \phi_1) |\nabla \mu_1|^2 - \int \frac{1}{\xi_s} \phi_2 (1 - \phi_2) |\nabla \mu_2|^2.$$

B. Numerical results

Simulations are carried out in two dimensions for this model. The parameters for the free energy in Eqs. (10) and (11) are chosen as $C_1=C_2=10, n_p=n_s=1, \chi_0=8.0$.

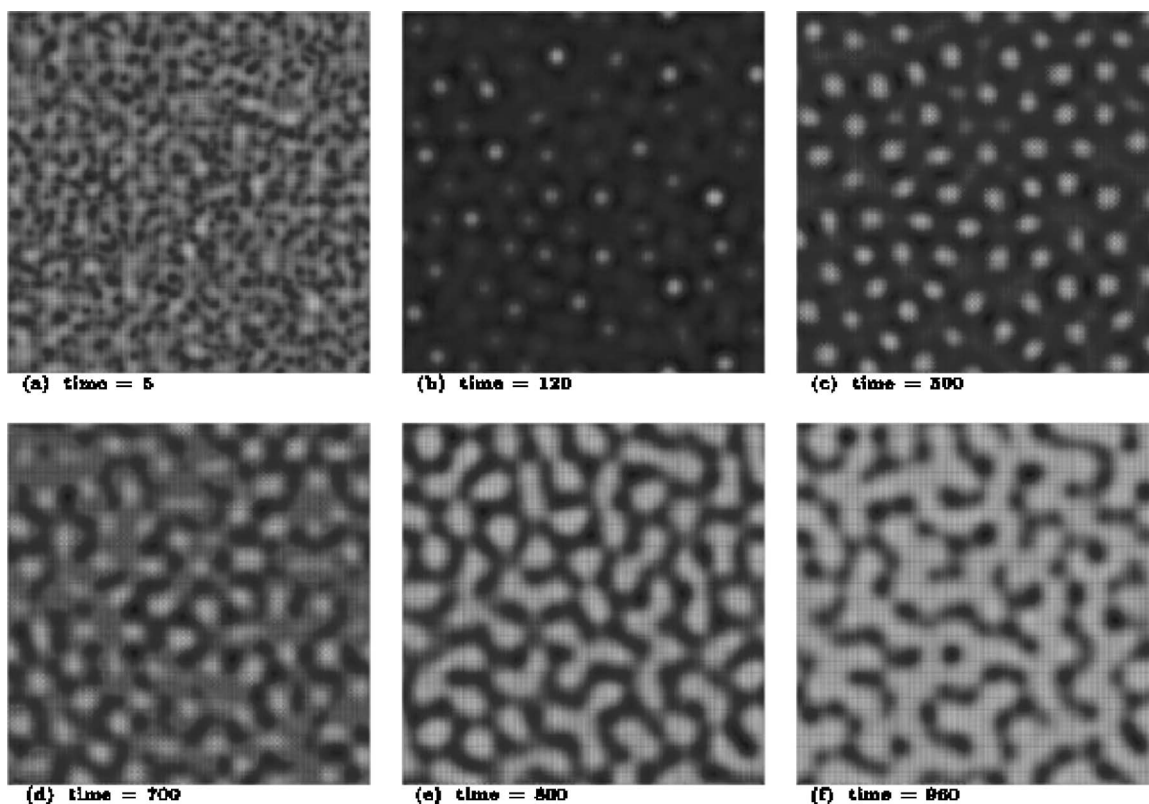


FIG. 4. Time evolution of phase separation after temperature quench with $T=1.1$, $\phi_1^0=0.35$, $\phi_2^0=0.5$ and $\xi_s=1$, $\zeta_1=40$, $\zeta_2=2$, $\epsilon=0.01$ at time=5, 120, 500, 700, 800, 960.

The mobility coefficient of polymer molecules $\frac{1}{\xi_p}$ is given by

$$\xi_p = \frac{\zeta_1 - \zeta_2}{2} \tanh\left(\frac{\cot \pi \phi^* - \cot \pi \phi_1}{\epsilon}\right) + \frac{\zeta_1 + \zeta_2}{2},$$

where ζ_1 is much larger than ζ_2 . Therefore, ξ_p chooses different value in polymer-rich ($\phi_1 > \phi^*$) and solvent-rich ($\phi_1 < \phi^*$) regions, and this reflects the dynamic asymmetry. ζ_1 and ζ_2 are chosen as $\zeta_1=40$, $\zeta_2=2$ in simulations. We take the critical concentration ϕ^* as the initial background value ϕ_1^0 .

Figure 4 shows simulation results of the diffusion model Eqs. (12). We see that volume shrinking and phase inversion phenomena are also well reproduced in these simulations. This model is established based on the diffusion asymmetry between molecules. Dynamic asymmetry is reflected through the mobility function. It is easy to understand that the friction coefficient of solvent molecules is much smaller than that of the polymer molecules. In solvent-rich region we suggest that the mobility coefficient of polymer molecules become large in order to promote the aggregation of the solvent molecules. In other words the polymer moves passively because of the movement of solvent molecules.

The underlying mechanisms are the same for the simplified model and the diffusion model. Recall that ϕ_0 is the initial volume fraction of polymer, ϕ_1 and ϕ_2 are the volume fraction of equilibrium values with ϕ_1 smaller than ϕ_2 . Diffusion is suppressed in the region where ϕ is larger than ϕ_0 . This causes the retardation of diffusion when ϕ approaches

to ϕ_2 . In contrast diffusion is fast in the region where ϕ is smaller than ϕ_0 , which makes ϕ approach to ϕ_1 quickly. This retardation is caused by the large size of the polymer, which makes polymer molecules move more difficult than small solvent molecules. And it is vital to the volume-shrinking process in the polymer-rich region and the subsequent phase inversion phenomenon.

V. CONCLUSION

We have discussed phase separation in quenched polymer solutions and have identified the dynamic diffusional asymmetry as being the origin of observed characteristics in polymer phase separation, mostly the volume shrinking and phase inversion. This is verified in both the diffusion model and the modified two-fluid model as we proposed. Our work on the two-fluid model is motivated by Tanaka's model. But we have gone one step for them by emphasizing the importance of not only reproducing experimental results in phase separation but also respecting the energy dissipation relation, which plays the law of entropy production in the model equations. The latter is absent in Tanaka's original model. Our model is numerically more stable and can be easily extended to studying phase separation in polymer blends and polymer-dispersed liquid crystal system.

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APPENDIX

In the following part (Subsections A–C), we prove that all the above model equations (the simplified model, the diffusion model, the modified two-fluid model) satisfy the energy dissipation relation.

1. Energy dissipation relation of the simplified model

The transport in this model is only through diffusion, therefore the energy of the system does not contain the kinetic energy. The entropy production of this isothermal system is given by

$$\begin{aligned}
 TS &= -\frac{d}{dt} \left[F + \int \frac{1}{2} q^2 \right] \\
 &= -\int \left(\frac{\partial F}{\partial \phi} \frac{\partial \phi}{\partial t} + \frac{\partial F}{\partial \nabla \phi} \cdot \frac{\partial \nabla \phi}{\partial t} \right) - \int q \frac{\partial q}{\partial t} \\
 &= -\int \left[\frac{\partial F}{\partial \phi} - \nabla \cdot \frac{\partial F}{\partial \nabla \phi} \right] \frac{\partial \phi}{\partial t} - \int (A_1 q) \nabla \cdot \left(\frac{\vec{v}_p}{1-\phi} \right) \\
 &\quad + \int \frac{1}{\tau} q^2 \\
 &= \int \frac{\delta F}{\delta \phi} \nabla \cdot (\phi \vec{v}_p) + \int \nabla (A_1 q) \cdot \frac{\vec{v}_p}{1-\phi} + \int \frac{1}{\tau} q^2 \\
 &= \int \frac{\vec{v}_p}{1-\phi} \cdot \left[-\phi(1-\phi) \nabla \frac{\delta F}{\delta \phi} + \nabla (A_1 q) \right] + \int \frac{1}{\tau} q^2 \\
 &= \int \frac{1}{(1-\phi)^2 M(\phi)} |\vec{v}_p|^2 + \int \frac{1}{\tau} q^2. \tag{A1}
 \end{aligned}$$

The above equation indicates that the polymer molecules will store energy once they crosslink. The total energy of the

system contains both free energy and the energy of the network (entropy loss). Dissipation is caused by diffusion and visco-elastic damping of the conformational entropy.

2. Energy dissipation relation of the diffusion model

Using Eqs. (12), we have

$$\begin{aligned}
 TS &= -\frac{dF}{dt} \\
 &= -\int \left(\frac{\partial F}{\partial \phi_1} \frac{\partial \phi_1}{\partial t} + \frac{\partial F}{\partial \nabla \phi_1} \cdot \frac{\partial \nabla \phi_1}{\partial t} \right) \\
 &\quad - \int \left(\frac{\partial F}{\partial \phi_2} \frac{\partial \phi_2}{\partial t} + \frac{\partial F}{\partial \nabla \phi_2} \cdot \frac{\partial \nabla \phi_2}{\partial t} \right) \\
 &= -\int \left(\frac{\delta F}{\delta \phi_1} \frac{\partial \phi_1}{\partial t} + \frac{\delta F}{\delta \phi_2} \frac{\partial \phi_2}{\partial t} \right) \\
 &= \int \left[\frac{\delta F}{\delta \phi_1} \nabla \cdot (\phi_1 \vec{v}_1) + \frac{\delta F}{\delta \phi_2} \nabla \cdot (\phi_2 \vec{v}_2) \right] \\
 &= \int \frac{1}{\xi_p} \phi_1 (1-\phi_1) |\nabla \mu_1|^2 + \int \frac{1}{\xi_s} \phi_2 (1-\phi_2) |\nabla \mu_2|^2.
 \end{aligned}$$

Therefore, dissipation in this model is caused by diffusion of both polymer molecules and solvent molecules.

3. Energy dissipation relation of the modified two-fluid model

In this case the transport is not only through diffusion but also through hydrodynamic flow. Therefore, the energy of the system should include both the kinetic energy and the total free energy

$$E = \int \frac{1}{2} |\vec{v}|^2 + F[\phi, \nabla \phi] + \int \frac{1}{2} q^2 + \int \frac{1}{2} \text{Tr}(\vec{\sigma}_s).$$

Using Eq. (7), we have

$$\begin{aligned}
 TS &= -\frac{d}{dt} \left[\int \frac{1}{2} |\vec{v}|^2 + F[\phi, \nabla \phi] + \int \frac{1}{2} q^2 + \int \frac{1}{2} \text{Tr}(\vec{\sigma}_s) \right] \\
 &= -\int \left(\vec{v} \cdot \frac{d\vec{v}}{dt} + \frac{\partial F}{\partial \phi} \frac{d\phi}{dt} + \frac{\partial F}{\partial \nabla \phi} \cdot \frac{d\nabla \phi}{dt} \right) - \int \left[q \frac{dq}{dt} + \frac{1}{2} \frac{d}{dt} \text{Tr}(\vec{\sigma}_s) \right] \\
 &= \int \frac{\eta}{2} |\nabla \vec{v} + (\nabla \vec{v})^T|^2 - \int \left[\frac{\partial F}{\partial \phi} \frac{d\phi}{dt} + \frac{\partial F}{\partial \nabla \phi} \cdot \nabla \left(\frac{d\phi}{dt} \right) \right] - \int (A_1 q) \nabla \cdot (\vec{v}_p - \vec{v}_s) + \int \frac{1}{\tau} q^2 + \int \frac{1}{2\tau_s} \text{Tr}(\vec{\sigma}_s) \\
 &= -\int \frac{\delta F}{\delta \phi} \frac{d\phi}{dt} + \int \nabla (A_1 q) \cdot (\vec{v}_p - \vec{v}_s) + \int \frac{\eta}{2} |\nabla \vec{v} + (\nabla \vec{v})^T|^2 + \int \frac{1}{\tau} q^2 + \int \frac{1}{2\tau_s} \text{Tr}(\vec{\sigma}_s) \\
 &= \int \frac{\delta F}{\delta \phi} \left[\nabla \cdot (\phi(1-\phi)(\vec{v}_p - \vec{v}_s)) \right] + \int \nabla (A_1 q) \cdot (\vec{v}_p - \vec{v}_s) + \int \frac{\eta}{2} |\nabla \vec{v} + (\nabla \vec{v})^T|^2 + \int \frac{1}{\tau} q^2 + \int \frac{1}{2\tau_s} \text{Tr}(\vec{\sigma}_s)
 \end{aligned}$$

$$\begin{aligned}
&= \int \left[-\phi(1-\phi) \nabla \frac{\delta F}{\delta \phi} + \nabla(A_1 q) \right] \cdot (\vec{v}_p - \vec{v}_s) + \int \frac{\eta}{2} |\nabla \vec{v} + (\nabla \vec{v})^T|^2 + \int \frac{1}{\tau} q^2 + \int \frac{1}{2\tau_s} \text{Tr}(\vec{\sigma}_s) \\
&= \int M(\phi) |\vec{v}_p - \vec{v}_s|^2 + \int \frac{\eta}{2} |\nabla \vec{v} + (\nabla \vec{v})^T|^2 + \int \frac{1}{\tau} q^2 + \int \frac{1}{2\tau_s} \text{Tr}(\vec{\sigma}_s).
\end{aligned}$$

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