Viscoelastic phase separation in soft matter: Numerical-simulation study on its physical mechanism

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Abstract

Viscoelastic phase separation is a new type of phase separation, which may be universal to any dynamically asymmetric mixture composed of slow and fast components. Dynamic asymmetry can arise from (i) a large size disparity between the components and (ii) a large difference in glass-transition temperature. Origin (i) often exists in the so-called soft matter, while origin (ii) can exist in any material including oxide, metallic, and molecular glass formers. For case (i), phase separation generally leads to the formation of a long-lived “interaction network” (transient gel) of the slow components, if the concentration is high enough and attractive interactions between them are strong enough. This new type of phase separation allows us to form a network structure of the minority slow-component-rich phase, contrary to the conventional wisdom on phase separation. This has a significant technological impact on the morphological control of multi-component materials. Here we review our numerical simulation studies on viscoelastic phase separation. Effects of transient gelation on phase-separation kinetics are studied by numerical simulations based on the coarse-grained two-fluid model. We find that the bulk mechanical stress originating from connectivity of the slow components of a mixture plays a crucial role in pattern evolution of viscoelastic phase separation. We also discuss how we can control the phase-separation morphology by controlling the viscoelastic properties of component materials. This coarse-grained model cannot describe how a transient gel itself is formed. Thus, to study the formation process of a transient gel in colloidal suspensions, we develop a new simulation method (“fluid particle dynamics (FPD) method”), which can properly treat interparticle hydrodynamic interactions. This new method can be applied to various fields of colloidal science, where hydrodynamic interactions play important roles. Our FPD simulations of colloidal aggregation clearly indicate that hydrodynamic interactions play crucial roles in the formation of a transient gel. We emphasize that the percolation threshold is crucially affected by hydrodynamic interactions. We point out that viscoelastic phase separation should be universally observed in not only polymer solutions and mixtures but also colloidal suspensions, emulsions, and protein solutions.

Keywords: Viscoelastic phase separation; Hydrodynamic interaction; Polymer solution; Colloidal suspension; Numerical simulation

1. Introduction

Phase-separation phenomena are widely observed in various kinds of condensed matter including metals, semiconductors, superconductors, simple liquids and complex fluids such as polymers, surfactants, colloids, emulsions, and biological materials (Binder, 1992; Hashimoto, 1993; Onuki, 2002). The phenomena play key roles in the pattern evolution of immiscible multi-component mixtures of these materials (Utracki, 1990). Phase separation in condensed matter has so far been classified into solid and fluid models. For a solid model only diffusion is responsible for material transport, while for a fluid model diffusion and hydrodynamic flow are responsible for it. Contrary to the common belief that phase separation of all condensed matter can be classified into either a solid or a fluid model, we recently found a new type of phase separation, which can be explained by neither of these models, in polymer solutions (Tanaka and Nishi, 1988; Tanaka, 1992, 1993, 1994, 1996). It was also found that critical dynamics of dynamically asymmetric mixtures such as...
polymer solutions are significantly affected by viscoelastic effects (Tanaka and Miura, 1993; Tanaka, 1994; Tanaka et al., 2002; Kostko et al., 2002; Furukawa, 2003a,b). Early-stage kinetics of viscoelastic phase separation was also studied both theoretically and experimentally for polymer mixtures (Onuki and Taniguchi, 1997; Toyoda et al., 2001; Takenaka et al., 2003) and colloidal suspensions (Verhaegh et al., 1996; Tanaka, 1999, 2000). Since in the above new type of phase separation viscoelastic effects play a crucial role, we named it "viscoelastic phase separation" (Tanaka, 1993, 1994). We believe that viscoelastic phase separation should be universal to any dynamically asymmetric mixture, which is composed of fast and slow components (Tanaka, 1996, 1997, 1999, 2000). Such "dynamic asymmetry" can be induced by either the large size difference or the difference in a glass-transition temperature between the components of a mixture. The former often exists in soft matter (or complex fluids), such as polymer solutions, micellar solutions, colloidal suspensions (Tanaka, 1999), emulsions, and protein solutions (see Fig. 1). The latter, on the other hand, exists in a mixture of any materials such as oxide glasses, metallic liquids, and molecular liquids, in principle (Tanaka, 1996, 2000).

For a dynamically asymmetric mixture with size disparity, phase separation generally leads to the formation of a long-lived "interaction network" (transient gel) of slow component molecules (or particles), if attractive interactions between them are strong enough and the concentration is high enough (Tanaka, 2000). Then, fast-component-rich droplets are selectively nucleated in a transient gel and grow with time. Contrary to a common sense that a minority phase forms droplets, even a minority phase can form a network-like interconnected structure in viscoelastic phase separation. In this regime, domain shape is determined by the elastic force balance condition. We emphasize that the self-induced mechanical stress in a transient gel plays a crucial role in pattern evolution. Differently from the case of a permanent (or chemical) gel, where the bulk and the shear modulus are not independent of each other, they can be rather independent in a transient gel. This is because in a transient gel bonds may be reconnectable for shear deformation, while not for bulk (volume) deformation. Furthermore, the loss of the connectivity transforms a transient gel into an ordinary viscoelastic fluid. This feature is absent for physical and chemical gels. Thus, the variety of pattern can be formed during phase separation, depending upon the magnitude of bulk and shear moduli and their relaxational characteristics.

Here we consider the roles of bulk and shear stresses on the pattern evolution on the basis of our numerical studies. We also discuss mechanisms of network formation in colloidal suspensions by studying its elementary process. To elucidate the physical mechanisms of viscoelastic phase separation, we have performed two types of simulations: coarse-grained two-fluid simulations (Tanaka and Araki, 1997; Araki and Tanaka, 2001) and colloid simulations (Tanaka and Araki, 2000). In the following, we demonstrate the results of numerical simulations and discuss the physical mechanism of viscoelastic phase separation.

2. What is viscoelastic phase separation?

First we show how viscoelastic phase separation looks like by presenting the pattern evolution observed in two different types of dynamically asymmetric mixtures: polymer solutions of polystyrene (PS) and diethyl malonate (DEM) and a polymer blend of PS and poly(vinyl methyl ether) (PVME). The strong dynamic asymmetry comes from the large difference in molecular size and topology between the components for the former, while it is from the large difference in glass-transition temperature for the latter. The compositions are near their critical compositions in both cases. Here we focus our attention only on the pattern evolution and the volume change of each phase to extract the most fundamental features of viscoelastic phase separation.

2.1. Polymer solution

We study the phase-separation process of mixtures of PS and DEM, which are known as ideal polymer solutions. One solution is a mixture of PS (molecular weight: $3.55 \times 10^5$; polydispersity ratio: 1.02) and DEM. The composition was 6.78 wt% PS, which is the critical composition, and the phase-separation temperature was 16.5°C. Another solution was a mixture of PS (molecular weight: $1.90 \times 10^5$; polydispersity ratio: 1.04) and DEM. The composition was 8.53 wt% PS, which is also the critical composition, and the phase-separation temperature was 11.6°C. The phase-separation behavior was observed with phase-contrast microscopy. The sample was sandwiched between two cover glasses to form a thin film of a thickness of about 8 μm. We confirm that the wetting effects do not affect the coarsening seriously, particularly when the viscoelastic effects play significant roles.
2.1. Pattern evolution

Figs. 2 and 3 show the pattern evolution during the phase separation of two polymer solutions. In both cases, the sample first becomes cloudy just after the quench; then after some incubation time (several seconds), small solvent holes start to appear. We call this incubation period a “frozen period” (Tanaka, 1993). The number and the size of solvent holes increase with time [see (b)–(d)]. The polymer-rich matrix phase becomes networklike with the growth of solvent holes. The thin parts of the networklike structure are elongated and eventually broken up [see (e) and (f)]. In this stage, the pattern is dominated by the elastic force balance condition. In the final stage the networklike structure relaxes to the structure of rounded shape and the domain shape starts to be dominated by the interface tension as in usual fluid–fluid phase separation [see (g) and (h)]. During the period of (b)–(f), the volume of the polymer-rich phase keeps decreasing with time and the contrast of that phase becomes darker and darker with time, reflecting the increase in the polymer composition in the matrix phase. We can notice the clear phase inversion during phase separation. This phase inversion is a unique feature of viscoelastic phase separation.

2.1.2. Coarsening dynamics

Fig. 4 shows the temporal change in the peak wavenumber \( q_p \) of the structure factor for the two polymer solutions. The structure factor \( S(q) \) was numerically calculated from a real-space image by two-dimensional Fourier transformation as described earlier (Tanaka et al., 1986, 1989). For the polymer solution of higher molecular weight (see Fig. 2) the slope of the coarsening curve is small, while for that of lower molecular weight (see Fig. 3) it is large. The time region of the steep decrease in \( q_p \) in the latter coincides well with that of the steep decrease in the volume of the PS-rich phase (see Fig. 5). We call this regime an “elastic regime”. As described above, the coarsening behavior is strongly dependent upon the molecular weights of PS and the quench conditions.
There is no universal feature in the coarsening behavior. This is also confirmed by other experiments on mixtures of several different molecular weights under various quench conditions. However, there is a general feature that should be mentioned: With an increase in the quench depth and the molecular weight of PS, the slope of $q_p$ in the growth regime decreases. This point will be discussed in detail elsewhere.

In relation to this, it should be noted that the period of the initial frozen state directly affects the time exponent of $q_p$ that is determined from the slope of the log–log plot: Even when the growth rate of domain is the same, the long frozen period (time offset) apparently increases the slope simply because the length on the log-scale time axis corresponding to the period of a certain time decreases with an increase in the absolute time. Furthermore, the domain size is also dependent upon how many nuclei appear in the initial stage: the smaller number of nuclei leads to the larger domain size. As can be seen from these arguments, it is evident that the conventional analysis of the behavior of $S(q)$ and $q_p$, based on the scaling argument is not so useful for viscoelastic phase separation.

### 2.1.3. Volume shrinking behavior

Fig. 5 shows the temporal changes in the area fraction of polymer-rich domains, $\Phi_{\text{area}}$, and the number density of the solvent-rich droplets, $n$, which are obtained by the black and white operation of digital image analysis (Tanaka et al., 1986). $\Phi_{\text{area}}$ steeply decreases with time in the intermediate stage, contrary to the conventional wisdom that after the formation of a sharp interface between the coexisting phase (namely, in the so-called late stage) the concentration of each phase almost reaches the final equilibrium one and, thus, there is no change in the volume and concentration of each phase. As pointed out previously (Tanaka, 1992, 1993, 1996), the volume decrease of the more viscoelastic phase with time after the formation of the sharp interface is essentially the same as the volume shrinking of gels during volume phase transition. The physical reason of this similarity to gel will be discussed later. After several hundred seconds, the volume of each phase approaches the final equilibrium one determined from the equilibrium phase diagram and thus stops changing.

The number of the solvent-rich phase, on the other hand, initially increases with time, reflecting the nucleation of the solvent-rich domains. Then it starts to decrease since the walls between the solvent-rich domains are broken by the large elastic deformation in the late stage (see Fig. 3). Finally, $n$ should become 1/area in the very late stage, reflecting the phase inversion; that is, the solvent-rich phase transforms from the droplet phase to the matrix phase.

Finally we consider the effects of wetting (Tanaka, 2001). The wetting effects can also cause the apparent decrease in the volume of the less wettable phase during phase separation. Since our experiments were done in the confined geometry, the phase separation may be affected by wetting. We can say, however, that wetting effects do not play a primary role in the observed phase-separation behavior because of the following reasons: (i) Wetting does not alter the nature of phase separation itself and there should be no change in the composition between the two phases after the formation of the sharp interface. Accordingly, there should be no significant temporal change in the contrast of a phase-contrast image between the two phases. In our case, however, the contrast is changing with time. More importantly, we directly confirm that the volume of the polymer-rich phase indeed decreases with time by 3D observation. (ii) Wetting itself does not cause the retardation of phase separation. In our case, however, we have a clear frozen period where there are no visible domains. (iii) We have preliminary results indicating that we have the same behavior even in three dimensions (3D).

### 2.2. Polymer mixtures only one of whose components has a slow dynamics associated with the glass transition

Another system studied was a mixture of PS and PVME, whose phase diagram is shown schematically in Fig. 1 of
Tanaka (1996). The weight-averaged molecular weights of PS and PVME were $1.01 \times 10^5$ and $9.4 \times 10^6$, respectively. The polydispersity ratios $M_w/M_n$ were 1.01 and 1.5 for PS and PVME, respectively. The critical composition was 30 wt% PS and the critical temperature was 122 °C. This mixture is one of the most often-used polymer mixtures for the study of the phase-separation kinetics. Phase separation of this mixture has so far been believed to be typical of usual phase separation of binary liquid mixtures that is classified into a fluid model. This is supported by many previous experiments (Tanaka and Nishi, 1987). It is likely true for a shallow quench for which a difference in the rheological property between the two phases is small because of a small difference in the concentration between them. It should be noted that the difference in the degree of polymerization $N$ itself is too small to cause dynamic asymmetry stemming from $N$-dependent molecular dynamics (Tanaka, 1993, 1994) between the two coexisting phases. However, this polymer mixture can have strong dynamic asymmetry stemming from slow dynamics associated with glass-transition phenomena especially for a deep quench because of the following reasons: (1) The characteristic rheological time $\tau_r$ and the diffusion coefficient $D$ of a phase with the composition of $\phi_{PS}$ are proportional to $\exp(-A/(T - T_g(\phi_{PS})))$ ($A$, constant; $T_g$, PS composition), according to the Vogel–Fulcher law. (2) $T_g(\phi_{PS})$ is strongly dependent upon $\phi_{PS}$ since $T_g$ of PS ($T_g(1) \sim 100$ °C) is very different from that of PVME ($T_g(0) \sim -26$ °C). Thus, $\tau_r$ of the PS-rich phase can be much longer than that of the PVME-rich phase for a large temperature jump, which causes the large composition difference between the two coexisting phases. This dynamic asymmetry can play a dominant role in the phase separation.

The sample was sandwiched between two cover glasses to form a thin film of a few μm thickness. Since the experiment was done under the confined geometry, we cannot completely rule out the possibility that the wetting effects affect the pattern evolution, as in the case of polymer solutions. However, we believe that the basic characteristics of the phase-separation process are not affected by wetting effects (Tanaka, 2001) since the minority PS-rich phase is less wettable to glass: the drastic wetting effects are observed only when the minority phase is more wettable than the majority phase for usual fluid mixtures.

2.2.1. Pattern evolution

We observed the phase-separation process of a mixture having the composition of 20 wt% PS with phase-contrast microscopy. Fig. 6 shows the morphological evolution observed at 143 °C. The system phase separates as a usual fluid mixture and becomes cloudy in the initial stage. Then, there is no significant coarsening for a certain period and, accordingly, no macroscopic domains are formed. As in the case of polymer solutions, we call this stage ($t < \sim 800$ s) a “frozen period” (Tanaka, 1996). After this frozen period, macroscopic holes (PVME-rich domains) appear and grow in their size. This process is characteristic of a metastable state and can be interpreted as the nucleation of holes overcoming the elastic energy barrier. Then, the PS-rich phase starts to shrink with time and transforms into a sponge-like pattern. The transition in the phase-separation behavior around 800 s can be explained as follows: The enhancement of the concentration fluctuations makes the PS-rich phase much more viscoelastic than the PVME-rich one and this increase in dynamic asymmetry strengthens the coupling between the velocity and stress fields. In the elastic regime ($\sim 800$ s < $t < \sim 2000$ s), a domain shape is determined by the mechanical balance of elastic forces and the interfacial tension plays few roles in determining the domain shape. Namely, the elastic energy dominates phase separation and the system behaves like an elastic gel. In the late stage of phase separation ($t > \sim 2000$ s), on the other hand, the system approaches its final equilibrium state; accordingly, the deformation rate of domains slows down, which leads to the weakening of the resulting stress fields. Thus, the PS-rich phase eventually behaves as a fluid, and the domain shape transforms into a shape of the lowest interfacial energy per unit volume (sphere) as in usual phase separation. The spongolike structure becomes unstable in the absence of stress fields and, thus, the interconnectivity is lost (tube hydrodynamic instability): A thickness difference along a tube of the PS-rich phase causes the internal pressure difference and produces a hydrodynamic flow. Thus, a thin part becomes thinner and eventually breaks, while a thick junction part becomes thicker and finally forms an isolated droplet. The shape relaxation from a thin thread to a sphere is characterized by a time of $\eta R/\sigma$ ($R$: domain size; $\eta$: viscosity; $\sigma$: interface tension). The disruption of the network structure leads to a significant decrease in the coarsening rate, because only slow growth mechanisms such as evaporation–condensation and Brownian-coagulation mechanisms can work for this isolated-domain morphology.

2.2.2. Coarsening behavior

Fig. 7 shows the temporal change in the peak wavenumber $q_p$ and the peak intensity of the structure factor, $S(q_p)$. The shape change in $S(q_p)$ during phase separation was reported in Fig. 3 of Tanaka (1996). The scattering intensity grows with time in the early stage, while it decreases in the late stage. This unusual feature is partly caused by the volume shrinking of the PS-rich domains (see the following discussion on the volume shrinking dynamics). For viscoelastic phase separation, there are two competing factors affecting the scattering intensity oppositely: (i) the increase in the amplitude of the concentration fluctuations and (ii) the decrease in the volume fraction of domains. Another possible cause of the decrease in $S(q_p)$ in the late stage is the technical one related to the principle of phase-contrast microscopy: For a large domain, the microscopy does not produce the contrast that is proportional to the difference in the refractive index, due to the diffraction effects. It should be noted...
Fig. 6. Pattern-evolution process in phase separation of the PS–PVME mixture observed by video phase-contrast microscopy. The time shown in the figure is an elapsed time after the temperature jump.

Fig. 7. Temporal change in the peak wavenumber $q_p$ (filled circle) and the scattering peak intensity $S(q_p)$ (open circle). The gray solid and dashed lines are a guide for the eye.

Here that the scattering function has a multiple-peak structure, which likely stems from the geometrical characteristics of the spongelike structure (see Fig. 3 in Tanaka, 1996).

The wavenumber $q_p$ of the main peak, on the other hand, rapidly decreases with time as $q_p \sim t^{-3/2}$ ($t < 1500$ s) in the elastic regime (see Fig. 7), reflecting the fast growth of the PVME-rich holes. Such a steep decrease in $q_p$ is also observed in Fig. 4. The physical origin of this unusually large exponent is not clear at present. The value is apparently the same as that found in phase separation under wetting effects (Tanaka, 2001), but we believe that it is not due to wetting effects because of the following reasons: (i) As mentioned previously, our experimental situation is likely free from the drastic wetting effects. (ii) For wetting effects, we should not have such a long frozen period (see Fig. 6) where there is no coarsening of domain size. For viscoelastic phase separation, the exponent is not universal and is strongly dependent upon the quenching condition, as already described. As pointed out previously, the conventional analysis of the behavior of $S(q)$ and $q_p$ based on the scaling argument is almost meaningless for viscoelastic phase separation because of the absence of self-similarity in pattern evolution, which is apparent in Figs. 2, 3, and 6. This point will be discussed later. In the hydrodynamic regime, on the other hand, it almost becomes constant with time (see Fig. 7) ($t > 2000$ s), reflecting the very slow coarsening after the disruption of the networklike structure.

2.2.3. Volume shrinking behavior

Fig. 8 shows the decrease in the area fraction $\Phi_{area}$ of the more viscoelastic (PS-rich) phase with time. Since the phase-separation pattern is essentially two-dimensional especially after 1200 s, we can obtain the volume fraction from this area fraction. This unusual behavior, which is one of the most striking characteristics of viscoelastic phase separation (Tanaka, 1993), is quite similar to that in Fig. 5. The phase-separation process can be divided into three regimes.
(see Fig. 8): the initial diffusive regime, the intermediate elastic regime, and the final hydrodynamic regime. Only in the elastic regime, the volume fraction steeply decreases with time. As discussed before, this volume shrinking is partly responsible for the decrease in the peak intensity of the structure factor in the late stage, which is supported by the fact that both processes have nearly the same characteristic time. Since the concentration must be conserved, this volume change tells us that the concentration of each phase changes with time by the diffusional transport of PVME from the PS-rich phase to the PVME-rich one through the phase boundary. This violates the well-accepted view of the late-stage phase separation that after the formation of the sharp interface the two phases are almost in equilibrium and the volume fraction is almost constant. Since the absence of the concentration change after the formation of the sharp interface is prerequisite to self-similar growth, our experimental result indicates that there is no self-similarity in pattern evolution for viscoelastic phase separation. This volume shrinking process of the PS-rich phase should be very similar to the bulk phase-separation process of chemical gel, which itself has also been largely unexplored so far.

2.3. Common features of pattern evolution in the above two systems

The pattern evolution observed in the above polymer solution and polymer blend is essentially the same and there is no qualitative difference between the two cases. This suggests the universal nature of viscoelastic phase separation in dynamically asymmetric fluid mixtures, irrespective of the origin of dynamic asymmetry.

The characteristic feature of the pattern evolution process is schematically summarized in Fig. 9. In the initial regime, the usual growth of concentration fluctuation occurs because of very weak dynamic asymmetry. However, the viscoelastic effects (especially, the bulk stresses) likely prevent rapid growth of composition fluctuations characteristic of spinodal decomposition from proceeding further, and the system becomes the frozen state [see (a)]. Then, the phase of slower dynamics becomes more and more viscoelastic with time, and the system eventually behaves as an elastic body. Reflecting the viscoelastic relaxation, the system changes the way of phase separation from a fluid mode to a gel mode. Then, the less viscoelastic phase starts to appear as holes, which grow with time [see (b)]. In the elastic regime [see (c) and (d)], the elastic force balance dominates the morphology instead of the interface tension, which leads to the anisotropic shape of the domain. The matrix phase of slower dynamics forms the networklike structure. In the final stage [see (e) and (f)], the phase separation becomes from gellike to fluidlike, reflecting the slowing down of the characteristic deformation of the phase separation. This slowing down is simply due to the fact that the compositions of both phases approach their final equilibrium ones. In the switching process stemming from the viscoelastic relaxation, a domain shape becomes spherical again since the interface energy overcomes the elastic energy. Since domains are isolated with each other, the coarsening rate becomes extremely slow after the disconnection of a networklike structure.

The most striking feature is the phase inversion during the phase separation and the volume shrinking of the more viscoelastic phase even after the formation of the sharp interface. The pattern evolution process can be clearly divided into the three distinct regimes: the initial, intermediate, and late stages. The transition between these regimes can be explained by viscoelastic relaxation in pattern evolution and the resulting switching of the primary order parameter, as described below.

To reveal the physical mechanisms responsible for unique pattern evolution of viscoelastic phase separation, we have performed numerical simulations. In the following, we review our numerical simulation study in detail.

3. Coarse-grained two-fluid model of viscoelastic phase separation

3.1. Two-fluid model

3.1.1. Brief history of two-fluid model of phase separation

Dynamic coupling between stress and diffusion was first noticed by de Gennes and Brochard (Brochard and de Gennes, 1977; de Gennes, 1979; Brochard, 1983) when they considered the dynamics of concentration fluctuations in polymer solutions. The original form of a two-fluid model was derived from the intuitive physical consideration. They introduced the concept of viscoelastic (or magic) length $\xi_{ve}$. It is defined as $\xi_{ve} \sim (D_e \tau_f)^{1/2}$ (Brochard and de Gennes, 1977; Brochard, 1983), where $\tau_f$ is the characteristic time of rheological relaxation and $D_e$ is the diffusion constant. For the length scale longer than $\xi_{ve}$, concentration fluctuations decay by diffusion, while in the length scale shorter than $\xi_{ve}$ viscoelastic effects dominate (Brochard, 1983). The key idea of the two-fluid model is that we need two velocities, polymer velocity and solvent velocity, to properly describe (a) viscous drag effects and (b) viscoelastic nature of polymer chains.

Later, the two-fluid model was developed into a more formal theory that describes critical phenomena, phase-separation kinetics, and shear effects on them. Helfand, Ji, and Frederickson applied a dynamic coupling mechanism to sheared polymer solutions (Helfand and Fredrickson, 1989; Ji and Helfand, 1995). Onuki, Doi, and Milner developed a two-fluid model, which is a viscoelastic Ginzburg–Landau scheme with a conformation tensor as a new independent variable (Onuki, 1990; Doi and Onuki, 1992; Milner, 1993). The two-fluid model was intensively studied to understand the so-called shear-induced phase separation found in polymer solutions. The current form of the two-fluid model of polymer solutions and polymer melts...
was derived by Doi and Onuki (1992) and later by Milner (1993). The success of the two-fluid model in shear-induced phase separation was recently reviewed by Onuki (1997) in detail. Very recently, the two-fluid model has been further developed to incorporate the coupling between the transverse parts of the viscoelastic force and the velocity fluctuations (Furukawa, 2003a,b).

3.1.2. Kinetic equations of concentration and velocity fields

Here we explain the two-fluid model of polymer solution that is used by us to simulate viscoelastic phase separation. The mixing free energy functional is expressed by the local volume fraction of polymer \( \phi(\vec{r}, t) \) at position \( \vec{r} \) and time \( t \) as

\[
F_{\text{mix}}(\phi, T) = \int d^3r \left\{ f_{FH}(\phi, T) + \frac{C}{2} \left| \nabla \phi \right|^2 \right\}.
\]  

(1)

Here \( f_{FH}(\phi, T) \) is the so-called Flory–Huggins-type free energy functional (de Gennes, 1979) given by

\[
f_{FH}(\phi, T) = k_B T \left[ (1/N_p) \phi \ln \phi + (1 - \phi) \ln(1 - \phi) + \chi(T) \phi(1 - \phi) \right],
\]  

(2)

where \( k_B \) is the Boltzmann factor, \( T \) is the temperature, \( N_p \) is the degree of polymerization of polymer, and \( \chi(T) \) is the interaction parameter. Here \( C \) is the coefficient that is known to be a function of \( \phi \). In this study, however, we set \( N_p = 1 \) and neglect the \( \phi \) dependence of the coefficient of the gradient term \( C \) in order to pick up only the effects of viscoelastic stresses on the phase-separation kinetics and neglect all the other effects originating from size disparity.

The kinetic equations are given by

\[
\frac{\partial \phi}{\partial t} = -\nabla \cdot (\phi \vec{v}_p) + \theta.
\]  

(3)

\[
\vec{v}_p - \vec{v}_s = -\frac{1 - \phi}{\zeta} [\nabla \cdot \vec{\Pi} - \nabla \cdot \sigma],
\]  

(4)

\[
\rho_0 \frac{\partial \vec{v}}{\partial t} \cong -\nabla \cdot \vec{\Pi} + \nabla \cdot \sigma - \nabla \rho + \eta_s \nabla^2 \vec{v},
\]  

(5)

where \( \theta \) represents the coarse-grained thermal concentration fluctuations, \( \zeta \) is the friction constant between polymer and solvent, \( \rho_0 \) is the density, and \( \eta_s \) is the viscosity of the solvent. We assume the same density for the two components. Here \( \vec{v} \) is the averaged velocity field of the solution and is given by \( \vec{v} = \phi \vec{v}_p + (1 - \phi) \vec{v}_s \). \( \vec{\Pi} \) is a part of pressure, which is determined to satisfy the following incompressible condition:

\[
\nabla \cdot \vec{v} = 0.
\]  

(6)

For simplicity, we assume that both polymer and solvent have the same density \( \rho_0 \). \( \vec{\Pi} \) is the thermodynamic osmotic stress tensor and related to the mixing free energy \( F_{\text{mix}} \) as

\[
\nabla \cdot \vec{\Pi} = \phi \nabla \nabla \cdot F_{\text{mix}} = \phi \nabla \left( \frac{\partial F_{FH}}{\partial \phi} - C \nabla^2 \phi \right).
\]  

(7)

The temporal change of \( \phi \) and \( \vec{v}_p \) are slow in our system so that the inertia term in Eq. (5) can be neglected. Thus, we assume

\[
\rho_0 \frac{\partial \vec{v}}{\partial t} \approx 0.
\]  

(8)

Under the incompressible [Eq. (6)] and quasi-stationary [Eq. (8)] conditions, Eq. (5) reduces to

\[
\vec{v}(\vec{r}) = \int d\vec{r}' T(\vec{r} - \vec{r}') \cdot \{ \nabla \cdot (-\vec{\Pi}(\vec{r}') + \sigma(\vec{r}')) \}.
\]  

(9)
Here \( T(\vec{r}) \) is the Oseen tensor given by \( T(\vec{r}) = (1 / 8 \pi \eta \mu r) \{ I + \vec{r} \vec{r} / r^2 \} \) (\( I \) being a unit tensor). Thus, \( \vec{v}_p \) is obtained from Eqs. (4) and (9) as

\[
\vec{v}_p(\vec{r}) = \left( 1 - \frac{\phi(\vec{r})}{\zeta} \right)^2 \nabla \cdot \left[ -\Pi(\vec{r}) + \sigma(\vec{r}) \right]
+ \int \vec{d} \vec{r} T(\vec{r} - \vec{r}') \cdot \nabla \cdot \left[ -\Pi(\vec{r}') + \sigma(\vec{r}') \right].
\] (10)

3.2. Constitutive equation

To close the above set of equations, we need the constitutive equation that is specific to material. This material-specific feature is the origin of intrinsically nonuniversal nature of viscoelastic phase separation (Tanaka, 1997, 2000). \( \sigma \) is the viscoelastic stress tensor, which should be supported solely by the polymers and not by the solvent molecules. Thus, the associated deformation can be expressed only by \( \vec{v}_p \). Although only the shear part of viscoelastic stress was considered in the original two-fluid model (Doi and Onuki, 1992) for polymer solutions, we newly introduced the bulk stress in addition to the shear one (Tanaka, 1997, 2000) and demonstrated (Tanaka and Araki, 1997) that the bulk part of viscoelastic stress plays an important role in the phase-separation process as in the case of the volume phase transition of gels (Onuki, 2002). Thus, the total stress is given by

\[
\sigma = \sigma_B + \sigma_S.
\] (11)

Here the suffices \( B \) and \( S \) mean the bulk and shear stresses, respectively. Note that the bulk stress \( \sigma_B \) stems from the motion of polymers itself. Thus, it intrinsically has the mechanical origin. In other words, \( \sigma_B \) cannot be included in \( \Pi \). For simplicity, we assume that viscoelastic relaxation of each stress is single relaxational (or Debye-type). For such a case, it is known that the shear stress obeys the following upper-convective Maxwell equation,

\[
\frac{D}{Dr} \sigma_S = \sigma_S \cdot \nabla \vec{v}_p + (\nabla \vec{v}_p)^T \cdot \sigma_S - \frac{1}{\tau_S(\phi)} \sigma_S
+ G_S(\phi) \{ \nabla \vec{v}_p + (\nabla \vec{v}_p)^T \},
\] (12)

where \( D/Dr = \partial / \partial t + \vec{v} \cdot \nabla \). Here \( \tau_S \) and \( G_S \) are a relaxation time and a modulus of the shear stress, respectively. Note that \( (\nabla \vec{v}_p)_{ij} = \partial_i v_{pj} \). Since the shear stress is a traceless tensor, we calculate the final form of shear stress as \( \sigma_S = \sigma_S - (1 / d) \text{Tr} \sigma_S I \), where \( I \) is a unit tensor and \( d \) is the space dimensionality. Hereafter, the shear stress \( \sigma_S \) means this final form \( \sigma_S \). On the other hand, since the bulk stress is isotropic, it can be expressed by a scalar variable, namely, \( \text{Tr} \sigma_B \). Thus, the bulk stress obeys the following equations:

\[
\frac{D}{Dr} \bar{\sigma} = - \frac{1}{\tau_B(\phi)} \bar{\sigma} + G_B(\phi) \nabla \cdot \vec{v}_p,
\] \( \sigma_B = \bar{\sigma} I \). (14)

Here, \( \tau_B \) and \( G_B \) are the relaxation time and the modulus of the bulk stress, respectively. Note that \( \bar{\sigma} = (1 / d) \text{Tr} \sigma_B \).

For the shear mode, some theories such as the reputation model and the scaling relation (de Gennes, 1979) predict the behaviors of \( \tau_S \) and \( G_S \). They are known to depend on the concentration field \( \phi \) in good and/or theta solvents as follows:

\[
G_S \propto \phi^\gamma,
\] \( \tau_S \propto \phi^\alpha \). (16)

However, the values of \( \gamma \) and \( \alpha \) for a poor solvent condition, where phase separation occurs, are not available. In our study, thus, we assume that \( \gamma = 2 \) and \( \alpha = 2 \) for simplicity.

It is quite difficult to make any theoretical prediction on the exact form of bulk stress. From both experimental observation and physical consideration, however, we argue that a polymer solution transiently behaves as a gel just after the temperature quench and the destruction of this transient gel is the process of the selective nucleation of a solvent-rich phase (Tanaka, 2000). Thus, we express the formation and relaxation of a transient gel by using the following form for the bulk stress:

\[
G_B \propto \Theta(\phi - \phi_0),
\] \( \tau_B \propto \phi^2 \). (18)

where \( \Theta \) is a step function. This step function represents the fracture-like characteristics of the bulk stress originating from connectivity: Once connectivity is lost, the bulk stress disappears. The physical relevance of the above form of the bulk stress was discussed elsewhere in detail (Tanaka, 1997, 2000).

3.3. Dynamic asymmetry: origin of viscoelastic phase separation

We propose to group viscoelastic phase separation into two types, type A and B, in terms of the origin of the dynamic asymmetry (Tanaka, 2000). Type A is specific to a mixture of large size asymmetry, which is composed of large molecules (or large particles) and small liquid ones. For this type, only the slow component can support the elastic stress, while the fast (liquid) one cannot. In other words, the perfect stress division is expected. For type B, on the other hand, the stress division is asymmetric, but both components can support the mechanical stress. Type B is common to a mixture having the strong \( \phi \)-dependent mobility. Here we point out two examples of type B: (i) a mixture of long and short polymers and (ii) a mixture of two liquids, whose glass-transition temperatures are quite different. We stress that this second case can exist for any type of material including oxide glasses (e.g., a mixture of SiO2 and Na2O), molecular liquids, and metallic glass formers. The details of dynamic asymmetry and the resulting asymmetric stress division were discussed in Tanaka (1997, 2000).
3.4. Dynamic phase diagram and roles of bulk stress

First we theoretically consider the viscoelastic effects on the early-stage phase-separation behavior and construct a dynamic phase diagram, which tells us the dynamic characteristics of phase separation.

It is known that the external shear flow affects the position of the spinodal line of a polymer solution (Onuki, 1997). There are intensive studies on the shear-induced phase separation in polymer systems. Similarly to this problem, velocity fields induced by phase separation itself may affect the kinetics and the way of phase separation significantly. In the shear problem, the bulk stress does not play any important role, since shear flow does not involve the deformation of bulk type ($\nabla \cdot \vec{v}$). The concept of the bulk stress is newly introduced to express the unique mechanical properties of a transient gel (Tanaka, 1997). So it is meaningful to reveal the roles of shear and bulk stresses in the early-stage phase separation. Here we reconsider the concept of the "effective" phase diagram and dynamic symmetry line (Tanaka, 1994) on a more quantitative basis.

In the early stage of phase separation, the viscoelastic stress can be approximated from Eqs. (12) and (13) as

$$\sigma_{ij} = \int_0^t dt' \left[ G_B(\phi) e^{-t'-t/\tau_B(\phi)} \hat{\epsilon}_{k} u_{pk} \hat{\delta}_{ij} + G_S(\phi) e^{-t'-t/\tau_S(\phi)} \times \left\{ \hat{\epsilon}_{i} v_{pj} + \hat{\epsilon}_{j} v_{pi} - \frac{2}{d} \hat{\epsilon}_{k} u_{pk} \delta_{ij} \right\} \right].$$

(19)

When the temporal change of $\vec{v}_p$ is faster than the relaxation time, Eq. (19) reduces to

$$\sigma_{ij} = G_B(\phi) \hat{\epsilon}_{k} u_{pk} \hat{\delta}_{ij} + G_S(\phi) \left\{ \hat{\epsilon}_{i} u_{pj} + \hat{\epsilon}_{j} u_{pi} - \frac{2}{d} \hat{\epsilon}_{k} u_{pk} \delta_{ij} \right\},$$

(20)

where $\vec{u}_p = \int_0^t dt' \vec{v}_p(t')$ is the displacement vector of polymers. In this case, the viscoelastic stress behaves elastically. In the limit that $\tau_B$ and $\tau_S \to \infty$, thus, the viscoelastic model reduces to the gel model (Tanaka, 1997).

It is reasonable to assume that the motion of polymer $\vec{v}_p$ is faster than the relaxation of the viscoelastic stresses in the early stage of phase separation [Eq. (20)]. Thus, the time development equation of the concentration field around the initial concentration $\phi_0$, $\delta \phi(\vec{r}, t) = \phi(\vec{r}, t) - \phi_0$, is approximated, up to the second order of $\delta \phi$, as

$$\frac{\partial \delta \phi}{\partial t} \approx \nabla^2 \{ a(\phi_0, \chi) - C' \nabla^2 \} \delta \phi + b(\phi_0, \chi) \delta \phi^2 + O(\delta \phi^3),$$

(21)

$$a(\phi_0, \chi) = \frac{1}{\xi} \left[ k_B T \left\{ \phi_0 (1 - \phi_0) + \left( \frac{1}{N_p} - 1 \right) \times \phi_0 (1 - \phi_0)^2 - 2 \chi \phi_0^2 (1 - \phi)^2 \right\} + (1 - \phi_0)^2 \left\{ G_B(\phi_0) + \left( 2 - \frac{2}{d} \right) G_S(\phi_0) \right\} \right],$$

(22)

$$C' = C \phi_0^2 (1 - \phi)^2 / \xi.$$

(23)

Here the relation $\delta \phi \approx -\phi_0 \nabla \cdot \vec{u}_p$ is used.

The first term on the right-hand side (r.h.s.) of Eq. (21) corresponds to Cahn’s linearized theory. The coefficient of this term includes the mechanical stresses in the form of the longitudinal modulus, $G_B(\phi_0) + (2 - 2/d) G_S(\phi_0)$. This appearance of the longitudinal modulus is natural since spinodal decomposition is described by the superposition of the plane waves. Since the spinodal line is effectively shifted to the low temperature due to the bulk and the shear stresses in the early stage of phase separation, spinodal decomposition is suppressed and the phase separation proceeds in the nucleation-growth-like mechanism.

Here we consider how the viscoelasticity affects the selection of the domain morphology. The second term of the r.h.s. of Eq. (21) is the lowest even-order term of $\delta \phi$ and plays an important role in determining which phase becomes a majority one. Generally, the condition $[b(\phi_0, \chi) = 0]$ gives the composition symmetry line, where the two phases occupy equal volume, or the pattern is symmetric against the exchange of the phase of $\delta \phi > 0$ with that of $\delta \phi < 0$. If we assume that a nucleated droplet has a spherical shape, the coefficient of the second term is given by

$$b(\phi_0, \chi) = \frac{k_B T}{\xi} \left\{ \frac{5}{2} \left( 1 - \frac{1}{N_p} \right) \frac{\phi_0}{N_p} + \left( \frac{4}{N_p} - 1 \right) \phi_0 - \frac{3}{2N_p} \right\} \times \left[ \frac{(1 - 3\phi_0)}{2\phi_0} G_B(\phi_0) - (1 - \phi_0) \frac{\hat{\epsilon}}{\partial \phi} G_B(\phi_0) \right].$$

(24)

Because for a spherical domain the shear mode is effectively decoupled to the bulk stress and does not affect the diagonal part of the osmotic tensor, the contribution of the shear stress can be neglected in calculating Eq. (24). Of course, we must consider the contribution of the shear stress for the other shapes of droplets. For example, the coefficient depends on $G_B + \frac{1}{d} G_S$ for a cylindrical domain, while it depends on $G_B + \frac{1}{d} G_S$ for a lamellar structure. The possibility of the anisotropic shape of nuclei will be considered later. For the analytical argument, however, we assume a spherical shape for simplicity. For this case, the term $(\hat{\epsilon} / \partial \phi) G_B(\phi_0)$ determines the composition symmetry line. It can be regarded as a measure of the dynamical asymmetry. Thus, we conclude that the composition symmetry line shifts toward the solvent-rich side and the solvent-rich phase nucleates selectively even when this phase is a majority one.
In connection to this, it should be noted that Onuki studied the effects of shear stress on nucleation of a spherical polymer-rich droplet in a metastable semidilute polymer solution (Onuki, 2002). The growth process of the droplet was mainly studied and it was demonstrated that the viscoelastic shear stress decelerates the droplet growth. In the above, we do not take the shear stress into account, provided that the droplets are spherical. For a case of the nucleation and growth of droplets, however, this assumption cannot be so easily justified by analytical arguments; thus, we cannot completely deny the possibility that the shear stress may affect which phase is nucleated. In order to answer this difficult question, we make numerical simulations of phase separation with only shear stress of a step-function form (see Section 4) instead of the form of Eq. (15). We confirm that for this case the solvent-rich phase is not selectively nucleated. This leads us to the conclusion that the shear stress does not affect the selectivity of the phase. However, the strong dependence of the shear modulus on the concentration \(\langle \dot{\gamma} / \dot{\gamma} \rangle G_S(\phi)\) may affect the shape of nucleated domains. For example, when we set \(G_S = (d/2) G_B(\Theta(\phi - \phi_0))\), the nucleated domain is found to be not spherical, but rather oblate. This anisotropic shape of domains may be realized to reduce the total deformation energy of the polymer-rich matrix phase. Note that these anisotropic nuclei are made of a solvent-rich phase even for this case. This problem may be related to the anisotropic crack pattern formation in an elastic medium such as gels. Further analytical and numerical studies are necessary for clarifying how bulk and shear stresses affect the early stage of viscoelastic phase separation.

In the late stage of phase separation, both mechanical stresses relax and we can neglect the viscoelastic contributions there. The coefficients of the first- and second-order terms become

\[
a' = -\frac{k_B T}{\zeta} \left\{ \phi_0 (1 - \phi_0) + \left( \frac{1}{N_p} - 1 \right) \phi_0 (1 - \phi_0)^2 \right. \\
- 2\chi \phi_0^2 (1 - \phi_0)^2 \} ,
\]

\[
b' = \frac{k_B T}{\zeta} (1 - 2 \phi_0) \left\{ 1 + \left( \frac{1}{N_p} - 1 \right) (1 - \phi_0) \right. \\
- 4\chi \phi_0 (1 - \phi_0) \} .
\]

Fig. 10 schematically shows the effective phase diagrams for the early stage (gel regime) and the late stage (fluid regime) of phase separation. The phase diagram of the former is determined by Eqs. (22) and (24), while that of the latter is determined by Eqs. (25) and (26). If the system is quenched to the region (B) between the two lines determined by [Eq. (24)] \([b(\phi_0, \chi) = 0]\) and [Eq. (26)] \([b'(\phi_0, \chi) = 0]\), the polymer-rich phase transforms from the majority phase to the minority one with time for such a case; thus, phase inversion takes place. The moving droplet phase and the spongelike phase should be observed in regions (A) and (C), respectively (Tanaka, 1994, 2000).

4. Numerical simulations based on the coarse-grained two-fluid model of phase separation

There are some numerical simulation studies on viscoelastic phase separation based on asymmetric diffusion (Sappelt and Jäckle, 1998; Ahluwalia, 1999), the two-fluid model (Taniguchi and Onuki, 1996; Tanaka and Araki, 1997; Okuzono, 1997; Araki and Tanaka, 2001; Zhan et al., 2001; Nakazawa et al., 2001), and molecular dynamics (Bhattacharaya et al., 1998). Here we show the results of our numerical simulations based on the above model (Tanaka and Araki, 1997; Araki and Tanaka, 2001). The basic equations described in Section 3 are numerically solved by discretizing time and space using the periodic boundary condition. To calculate Eq. (3), we employ the explicit Euler method and set a grid size to \(\Delta x = 1\) and a time increment to \(\Delta t = 0.01\). We solve Eq. (9) using the fast Fourier transformation method. To reduce the computational cost, we solve the time development equations except for Eq. (9) without updating velocity field by skipping \(N_{\text{skip}}\) cycles for 3D simulations. In this study, we set \(N_{\text{skip}} = 10\). We confirm that there are no meaningful differences between the simulations with \(N_{\text{skip}} = 10\) and those with \(N_{\text{skip}} = 1\).

The stress tensors of the shear [Eq. (12)] and the bulk [Eq. (13)] modes are calculated by using the following relations (Tanaka and Araki, 1997):

\[
\sigma_S(\vec{r}, t + \Delta t) = \sigma_S(\vec{r}, t) \exp \left( -\frac{\Delta t}{\tau_S} \right) + [ -\vec{v}_p \cdot \nabla \sigma_S \\
+ \sigma \cdot \nabla \vec{v}_p + (\nabla \vec{v}_p)^T \cdot \sigma_S \\
+ G_S [\nabla \vec{v}_p + (\nabla \vec{v}_p)^T] ] \Delta t , \tag{27}
\]

\[
\tilde{\sigma}(\vec{r}, t + \Delta t) = \tilde{\sigma}(\vec{r}, t) \exp \left( -\frac{\Delta t}{\tau_B} \right) + [ -\vec{v}_p \cdot \nabla \tilde{\sigma} + G_B \nabla \cdot \vec{v}_p ] \Delta t . \tag{28}
\]

This method coincides with the usual Euler method up to the order \(\Delta t\), and has a significant advantage over it on the
Table 1
The $\phi$-dependence of bulk and shear moduli and their relaxation time used in our 2D simulations

<table>
<thead>
<tr>
<th>Case</th>
<th>$G_B(\phi)$</th>
<th>$\tau_B(\phi)$</th>
<th>$G_S(\phi)$</th>
<th>$\tau_S(\phi)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>B</td>
<td>$5.0\theta(\phi - \phi_0)$</td>
<td>$10.0\phi^2$</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>C</td>
<td>—</td>
<td>—</td>
<td>$\phi^2$</td>
<td>$50.0\phi^2$</td>
</tr>
<tr>
<td>D</td>
<td>$5.0\theta(\phi - \phi_0)$</td>
<td>$10.0\phi^2$</td>
<td>$\phi^2$</td>
<td>$50.0\phi^2$</td>
</tr>
<tr>
<td>E</td>
<td>$5.0\theta(\phi - \phi_0)$</td>
<td>$10.0\phi^2$</td>
<td>$5.0\theta(\phi - \phi_0)$</td>
<td>$10.0\phi^2$</td>
</tr>
</tbody>
</table>

following point. This method is free from numerical instabilities even for $\Delta t \geq \tau_B$ and/or $\tau_S$. In other words, it allows us to treat a very wide range of the stress relaxation time without suffering from the numerical instability problems.

The system sizes used were $128 \times 128$ for 2D while $64 \times 64 \times 64$ for 3D.

4.1. 2D simulation of viscoelastic phase separation

First we describe the results of 2D simulations. To investigate the effects of bulk and shear stresses on pattern evolution, we perform five types of simulations: (A) without any stress, (B) with bulk stress only, (C) with shear stress only, (D) with bulk and shear stress (only bulk stress has a step-function-like dependence on $\phi$), and (E) bulk and shear stress, both of which have the step-function-like dependence on $\phi$. The parameters for these simulations are listed in Table 1. The other parameters are commonly set as follows: $k_B T = 1.3$, $\chi = 2.7$, $C = 1.0$, $\eta_s = 0.10$, and $\zeta = 0.10$. We set the initial composition as $\phi_0 = 0.35$. The equilibrium volume fraction of the polymer-rich phase is approximately $30.9\%$. To initiate phase separation, we introduce the Gaussian noise of $\Delta \phi = 1.0 \times 10^{-3}$.

4.1.1. Pattern evolution and the roles of viscoelastic stresses

Fig. 11 shows the pattern evolution behavior simulated without any viscoelastic effects [case (A)], which is the same as normal fluid phase separation (model H). This phase-separation behavior is well known and typical of droplet spinodal decomposition. The polymer-rich phase, which is the minority phase, forms droplets, which coarsen with time by repeating collision and coalescence and also by evaporation-condensation mechanism. It should be noted that the pattern evolution process is self-similar.

Fig. 12 shows the phase-separation behavior of case (B), which includes only bulk stress. The behavior is entirely different from case (A). After some incubation time, the solvent-rich phase, which is the majority phase, forms droplets, which grow with time ($t \lesssim 200$). The droplet growth is caused by neither collision-coalescence nor evaporation-condensation mechanisms, but each droplet itself grows and increases its size. These solvent-rich droplets already have the final equilibrium concentration. We can say that the growth of droplet is induced by the solvent expelled from the shrinking polymer-rich phase. As a result, the polymer concentration in the polymer-rich phase increases with time and reaches its equilibrium value around $t \approx 350$ and, thus, the concentration distribution function itself stops changing there. During the volume-shrinking process, the minority phase forms the networklike structure instead of a droplet structure. However, this network structure is not stable: It breaks up soon after the volume shrinking stops, and transforms into the droplet structure around $t = 400$. For this case, the bulk stress induces the phase inversion, but does not produce the well-developed network structure, which was observed experimentally. This phase separation observed for case (B) very much resembles that observed by simulations of Sappelt and Jäckle (1998) and Ahluwalia (1999), which are based on the solid model with strongly $\phi$-dependent diffusion constant. This is natural in the sense that bulk stress suppresses concentration diffusion asymmetrically in the polymer-rich region (see also the previous section).

Fig. 13 shows the pattern evolution for case (C), where only shear stress is included. Phase separation proceeds by spinodal decomposition as in case (A). The minority polymer-rich phase forms droplets, which coarsen with time by collision-coalescence and evaporation-condensation mechanisms. However, careful comparison with Fig. 11 tells us that the coarsening rate is slower than case (A) and droplets often have ellipsoidal shape. This anisotropic shape is due to slow shape relaxation induced by the shear stress. For case (A), the characteristic shape relaxation time $\tau_R$ is estimated as $\tau_R \approx \eta_t R / \gamma$ (interface tension). For case (C), where $\sigma_s$ affects the shape relaxation, $\tau_R \approx \eta_R / \gamma$, where $\eta = \int_0^\infty dt \ G(t)$. Since the composition of the polymer-rich phase is estimated as $\phi \approx 0.89$, we obtain $\eta \approx 31$. On noting $\eta_t = 0.1$, thus, the shape relaxation should be about 300 times slower for case (C) than case (A).

Fig. 14 shows the pattern evolution observed for case (D), where both bulk and shear stresses are included. In the initial stage, the solvent-rich phase appears as droplets after some incubation time and then droplets grow with time. This behavior is essentially the same as that of case (B). The polymer-rich phase shrinks while expelling the solvent into the solvent-rich droplets and thus its volume decreases with time ($t \lesssim 350$). It forms the well-developed network structure during the volume shrinking process. The network structure is much more stable than in case (B) due to the effects of the shear stress, which make the shape relaxation time very long. Thus, the network structure is long-lived. After a long time, the network structure eventually transforms into the droplet structure. This pattern evolution captures all the essential features of pattern evolution experimentally observed in viscoelastic phase separation of a polymer solution (see Section 2).

Fig. 15 shows the pattern evolution of case (E), which includes the bulk stress as well as the shear stress that is given by Eq. (17) and not by Eq. (15). By including the bulk stress, which is characterized by $\tau_B = \tau_S$ and
$G_B = (d/2)G_S$, we use the following form of the mechanical stress:

$$\sigma_{ij} \approx \int_0^t dt' G(\phi(t'))e^{-(t-t')/\tau(\phi(t'))}\{\dddot{\epsilon}_{ij}v_{pj} + \dddot{\epsilon}_{ji}v_{pj}\}.$$  \hspace{1cm} (29)
(chainlike alignment of droplets) (see the pattern at $t = 250$) and leads to the formation of anisotropic cracklike domains (see the pattern at $t = 400$). This anisotropic domain formation may occur to minimize the elastic deformation energy of the polymer-rich phase around droplets. The late stage of pattern evolution is similar to that in case (D).

### 4.1.2. Volume shrinking kinetics and its relation to bulk stress

Fig. 16 shows the temporal change in the volume (strictly speaking, area) fraction of the polymer-rich phase $\Phi_p$ for various cases. $\Phi_p$ is the fraction of lattices having $\phi > 0.34$. The dashed line indicates the final equilibrium fraction $\Phi_p^\infty = 0.309$. For cases (A) and (C) (without bulk stress), $\Phi_p$ starts to decrease immediately after the initiation of phase separation and reaches the final equilibrium value $\Phi_p^\infty$ at $t \approx 40$, at which the sharp interface is formed. For cases (B) and (D) (with bulk stress), it takes a long time for $\Phi_p$ to reach $\Phi_p^\infty$. This result indicates that it is the bulk stress that is responsible for the volume shrinking behavior of the polymer-rich phase.

Here we consider the physical mechanism of this behavior. The effective osmotic pressure in viscoelastic phase separation is given by

$$\begin{align*}
\pi^\text{eff}(t) \approx \left( \phi \frac{\partial f_{FH}}{\partial \phi} - f_{FH} \right) & - \int_0^t dt' G_B(\phi(t')) \times e^{-\frac{(t-t')}{\tau_B}} \nabla \cdot \vec{v}^B(t') \\
& \approx \left( \phi \frac{\partial f_{FH}}{\partial \phi} - f_{FH} \right) + G_B(\phi) \frac{\phi - \phi_0}{\phi_0} \exp(-t/\tau_B).
\end{align*}$$

Here we use the relation $\nabla \cdot \vec{v}^B \sim -\partial \phi/\partial t/\phi$. The volume fraction at $t = \infty$ is determined by the Flory–Huggins free energy and should be equal for cases (A)–(E). The volume fraction at a finite time $t$ should roughly be determined from Eq. (30). This tells us that the increase in $\tau_B$ leads to the slowing down of the relaxation of $\Phi_p$. We also confirm by simulations that the characteristic volume relaxation time is dependent on $\tau_B$, but not on $G_B$. In relation to this, we note that for a case of gel where $\tau_B = \infty$, $\Phi_p^\infty$ is determined by $G_B$. Finally, we emphasize that this volume shrinking behavior is not dependent on the shear stress, which is natural on noting the deformation mode involved in volume shrinking is of bulk-deformation type.

### 4.1.3. Order-parameter switching between composition and deformation tensor

Here we consider the dynamic process of viscoelastic phase separation on the basis of viscoelastic relaxation phenomena. The quantitative feature of the dynamics can be understood on the basis of the concept of “order-parameter switching” (Tanaka, 1996, 1997). Phase separation is usually driven by the thermodynamic force and the resulting ordering process can be described by the temporal evolution of the relevant order parameter associated with the thermodynamic driving force. The primary order parameter describing phase separation of a binary mixture is a composition difference between the two phases. Besides exceptional cases where phase separation and other ordering processes such as superfluidization, gelation, liquid crystallization, and crystallization simultaneously proceed (in other words, there are more than two kinds of order parameters), the phase-separation process is usually characterized by the single order parameter, composition. In the viscoelastic model, on the other hand, the phase-separation mode can be switched between “fluid mode” and “elastic gel mode”. This switching is caused by the change in the coupling between stress and velocity fields, which is described by Eqs. (12) and (13): Eqs. (12) and (13) tell us that the two ultimate cases, namely, (i) fluid model ($\kappa_{pij}, \nabla \cdot \vec{v}_p \sim \text{const}$) ($\kappa_{pij}$ being the shear deformation tensor) and (ii) elastic gel model ($G_S(t), G_B(t) \sim \text{const}$), correspond to $\tau_{ts} \gg \tau_d$ and $\tau_{is} \ll \tau_d$, respectively. Here $\tau_d$ is the characteristic time of deformation and $\tau_{is}$ is the characteristic rheological time of the slower phase.

For $\tau_d \gg \tau_{is}$ the primary order parameter is the composition in usual classical fluids, while for $\tau_d \lesssim \tau_{is}$ it is the deformation tensor ($d_{ij} = \partial u_j/\partial x_i + \partial u_i/\partial x_j$) as in elastic...
gels. In the elastic regime, the force terms can be included in the Hamiltonian as in the case of gel. Then the free energy functional is formally expressed only by the deformation tensor $d_{ij}$ as $f(d_{ij})$. Thus, we can say that the order-parameter switching is the result of the competition between the two time scales characterizing domain deformation $\tau_d$ and the rheological properties of domains $\tau_{ts}$. This is a kind of viscoelastic relaxation in pattern evolution.

Next we consider how $\tau_{ts}$ and $\tau_d$ change with time during phase separation (Tanaka, 1996, 1997). In the initial stage, the velocity fields grow as $v \sim (k_BT/C/\beta \eta \zeta)\Delta \phi^2$, where $\Delta \phi$ is the composition difference between the two phases and $\zeta$ is the correlation length, or the interface thickness. Since $\Delta \phi$ approaches $2\phi_e$ (the equilibrium composition) with time, this expression $v$ reduces to the well-known relation $v \sim \gamma/\eta$ ($\gamma$ being the interface tension) in the late stage. Note that $\gamma \sim k_BT/C(2\phi_e)^2/3\zeta$. Thus, the characteristic deformation time $\tau_d$ changes with time as $\tau_d \sim R(t)/v(t) \sim R(t)/\Delta \phi(t)^2$. In the initial stage, the domain size does not grow so much with time while $\Delta \phi$ rapidly increases with time. Thus, $\tau_d$ decreases rapidly. On the other hand, $\tau_{ts}$ increases steeply with an increase in $\Delta \phi$, reflecting the increase in the polymer concentration in a polymer-rich domain. Thus, $\tau_{ts}$ becomes comparable to $\tau_d$ in the intermediate stage of phase separation. Once $\tau_d < \tau_{ts}$, the slower phase cannot follow the deformation speed created by phase separation itself and behaves as an elastic body: The elastic energy dominates the coarsening process in the intermediate stage. Next we consider the late stage. Since $\Delta \phi$ approaches $2\phi_e$ and becomes almost constant in the late stage, $\tau_d$ ($\sim R(t)/v(t)$) increases with an increase in $R$ while $\tau_{ts}$ becomes almost constant. Thus, $\tau_d$ becomes longer than $\tau_{ts}$ again. In short, $\tau_d \gg \tau_{ts}$ in the initial stage, $\tau_d \leq \tau_{ts}$ in the intermediate stage, and $\tau_d \gg \tau_{ts}$ in the late stage again. Accordingly, the order parameter switches from the composition to the deformation tensor and then switches back to the composition again. Such switching behavior is indeed observed in our numerical simulation of case (D) (see Fig. 17). This is a rare case of “order-parameter switching” during an ordering process driven by a single thermodynamic driving force.

4.1.4. How to control the morphological characteristics of a network structure formed in viscoelastic phase separation

Here we consider how pattern evolution is affected by the value of $\tau_B$. Fig. 18 shows the dependence of pattern evolution on $\tau_B$. $\tau_B$ used in the simulations are $\tau_B = 5.0 \phi_e^2$, $10.0 \phi_e^2$, $20.0 \phi_e^2$. All the other parameters except $\tau_B$ are the same as in case (D) (see Fig. 14). With decreasing $\tau_B$, the volume relaxation rate becomes faster and thus the phase inversion takes place at an earlier time. Fig. 18 indicates that the decrease in $\tau_B$ makes the bulk stress effects of suppressing the growth of concentration fluctuations weaker, which results in the increase in the nucleation frequency. This increase in the nucleation frequency makes the network structure finer and more homogeneous (or regular) [see, e.g., Fig. 18(a) ($t = 150$)]. The longer $\tau_d$, on the other hand, reduces the nucleation frequency and thus individual nuclei grow rather independently before elastic interactions come into play. Thus, the network becomes coarser and more random with increasing $\tau_d$, as can be seen in Fig. 18. The phase-separation kinetics is slower for larger $\tau_B$. The characteristic feature of the network pattern is basically determined by the nucleation frequency, the growth speed of droplets, and the anisotropy factor. We expect that the fine network pattern in Fig. 18(a) can be stabilized for a longer period of time by increasing $\tau_S$.

4.1.5. Viscoelastic effects on the temporal change in the concentration distribution function

Fig. 19(a) and (b) show the temporal change of a concentration distribution function $P(\phi)$ for a system without viscoelastic stress (case (A)) and that with both bulk and shear stress (case (D)). For case (A), $P(\phi)$ has a single peak at $\phi \approx \phi_0$ in the beginning of phase separation but it becomes broader with time. Then, $P(\phi)$ becomes bimodal and around $t \approx 40$ the concentrations of the two peaks reach the equilibrium ones, $\phi_e \approx 0.1$ and 0.9 [see Fig. 19(a)]. At this time, thus, $\Phi_p$ reaches $\Phi_p^\infty$ (see Fig. 16) and the phase separation enters the so-called late stage. Finally, the peaks become sharper with time. This behavior of $P(\phi)$ clearly demonstrates that the phase separation is spinodal-decomposition type and not nucleation-growth type (Tanaka and Nishi, 1987).

The behavior of case (D) [see Fig. 19(b)] is quite different from that of case (A). The initial peak at $\phi \approx \phi_0$ broadens with time, but this process is quite slow due to the viscoelastic suppression of the growth of concentration fluctuations. The broadening of the peak at $\phi = \phi_0$ is asymmetric and faster for the solvent-rich side ($\phi < \phi_0$) (see the curve at $t = 100$). According to Fig. 16, the volume fraction becomes $\Phi_p = 0.5$ around $t \approx 200$ for case (D). Around this time, the shape of $P(\phi)$ is already quite different from that for case (A). Then, a peak appears at $\phi \approx 0.1$, reflecting
Fig. 18. Dependence of pattern formation on $\tau_B$. (a) $\tau_B = 5.0\phi^2$, (b) $\tau_B = 10.0\phi^2$, and (c) $\tau_B = 20.0\phi^2$.

Fig. 19. Effects of mechanical stress on the temporal change of $P(\phi)$: (a) case (A) and (b) case (D).

4.1.6. Roles of bulk and shear stresses on pattern formation

Here we consider how bulk and shear stresses affect the pattern formation for case (D). Fig. 20 shows the temporal change in the strength of osmotic, bulk, and shear stress forces, which are, respectively, expressed as $\nabla \cdot \Pi$, $\nabla \cdot \sigma_B$, and $\nabla \cdot \sigma_S$. In the initial stage, the bulk stress force follows the osmotic one. In Eqs. (4) and (9), these two forces appear as $\Pi - \sigma$. This indicates that the bulk stress acts against and cancels the osmotic stress and thus the growth of concentration fluctuations is strongly suppressed. Here we note that since the bulk stress is induced by the polymer motion driven by the osmotic stress itself, $v_p$, the bulk stress never exceeds the appearance of the solvent-rich droplet phase. This peak becomes sharper with time, reflecting the volume shrinking of the polymer-rich phase and the resulting growth of the solvent-rich phase. At $t \approx 350$, the volume shrinking stops and the system reaches the final equilibrium state and thus $P(\phi)$ has the two peaks at the equilibrium compositions for $t > 400$.

Fig. 20. Temporal change in the strength of the forces due to $\Pi$, $\sigma_B$, and $\sigma_S$ for case (D).
the osmotic one irrespective of the values of $G_B$ and $\tau_B$. As mentioned before, both osmotic and bulk stress are related to the deformation of type $\nabla \cdot \vec{v}_p$. This indicates that the bulk stress has a role similar to the strongly $\phi$-dependent diffusion constant, which is introduced by Sappelt and Jäckle (1998) and Ahluwalia (1999). However, this is limited to the effects on concentration diffusion. The roles of mechanical stresses in material deformation and flow (see below) cannot be reproduced by the strongly $\phi$-dependent diffusion constant (Tanaka, 2000).

The osmotic and bulk stress forces become maximum at $t \approx 270$. The shear stress, on the other hand, has the maximum at $t \approx 410$, when the network starts to break up and the deformation rate becomes maximum. The time difference in the peak position ($\delta t \approx 140$ for the above case) depends on $\tau_S$. The larger $\tau_S$ is, the larger $\delta t$ is, which results in the longer lifetime of the network structure. Here we note that since the shear stress is induced by the interface tension originating from the off-diagonal terms of the osmotic stress, it can never exceed the osmotic stress irrespective of the value of $G_S$ and $\tau_S$. In the late stage, the following force balance condition should be satisfied:

$$\delta_{ij} \left[ C \left\{ \delta_i \phi \delta_j \phi - \frac{1}{d} (\delta_i \phi)(\delta_j \phi) \delta_{ij} \right\} - \sigma_{Sij} \right] = 0. \quad (31)$$

It is this force balance condition that controls the network morphology.

Fig. 21 shows the spatial distribution of (a) $\sigma_B$ and (b) $\sigma_S$ for the phase-separation process shown in Fig. 14. The darkness represents the strength of $|\nabla \cdot \sigma_B|$ and $|\nabla \cdot \sigma_S|$. As can be seen from Fig. 20, the bulk stress starts to increase with time immediately after the initiation of phase separation. The shear stress is, on the other hand, very weak even after the formation of the solvent-rich droplet ($t \lesssim 200$). The bulk stress further increases as the volume shrinking proceeds. When the deformation of the polymer-rich phase is initiated, the shear stress starts to increase around $t \approx 300$. The bulk stress decays when the volume shrinking process is finished, and eventually disappears at $t \gtrsim 400$. The shear stress, on the other hand, becomes strongest when the deformation associated with the breakup of the network structure becomes maximum. It keeps affecting the pattern evolution ($t \gtrsim 400$) even after the bulk stress disappears. At $t \approx 400$, the bulk stress is stronger at the periphery of the polymer-rich domain than in its inside, while the shear stress rather homogeneously distributes in the polymer-rich domains (it is slightly stronger in their middle). This reflects the fact that the bulk stress is induced by the diffusion taking place through the interface, while the shear stress is induced by the deformation of domain shape.

### 4.1.7. Roles of mechanical stresses upon the mixing process of domains

In the above, we have discussed how the viscoelastic stress affects phase-separation behavior. Here we briefly discuss the roles of the mechanical stress on the reverse process, namely, the dissolution process. Fig. 22 shows how the phase-separated pattern at $t = 2000$ for case (D) dissolves with time after a temperature jump into a one-phase region ($\chi = 2.7 \rightarrow 1.0$): (a) concentration field $\phi$, (b) $|\nabla \cdot \sigma_B|$, and (c) $|\nabla \cdot \sigma_S|$. The other parameters are the same as those of case (D) (see Fig. 14). Just after a temperature jump, the system allows to be mixed but the bulk stress tends to prevent mixing. Compared to the ordinary dissolution process without viscoelastic stresses, the interface remains rather sharp for a longer period of time. The process is asymmetric and regarded as polymer dissolution into solvent rather than simple intermixing. After the decay of the bulk stress, the two phases start to mix. Note that shear stress does not affect the process.

In the limit of $\tau_B \rightarrow \infty$, the process can be regarded as the swelling process of gel. For this case, when the bulk stress is balanced with the osmotic stress, the swelling stops. The shear stress, on the other hand, affects the shape of the gel for this case.
Fig. 22. Effects of viscoelastic stress on dissolution process: (a) \( \phi \), (b) \( |\nabla \cdot \sigma_B| \), and (c) \( |\nabla \cdot \sigma_S| \).

Table 2
The \( \phi \)-dependence of \( G_x \) and \( \tau_x \) \((x = B \text{ or } S)\)

<table>
<thead>
<tr>
<th>Case</th>
<th>( G_B(\phi) )</th>
<th>( \tau_B(\phi) )</th>
<th>( G_S(\phi) )</th>
<th>( \tau_S(\phi) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>5.0(\Theta(\phi - \phi_0))</td>
<td>10.0(\phi^2)</td>
<td>0.2(\phi^2)</td>
<td>10.0(\phi^2)</td>
</tr>
<tr>
<td>b</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>c</td>
<td>—</td>
<td>—</td>
<td>0.2(\phi^2)</td>
<td>50.0(\phi^2)</td>
</tr>
<tr>
<td>d</td>
<td>5.0(\Theta(\phi - \phi_0))</td>
<td>10.0(\phi^2)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>e</td>
<td>5.0(\Theta(\phi - \phi_0))</td>
<td>10.0(\phi^2)</td>
<td>0.2(\phi^2)</td>
<td>50.0(\phi^2)</td>
</tr>
<tr>
<td>f</td>
<td>—</td>
<td>—</td>
<td>7.5(\Theta(\phi - \phi_0))</td>
<td>10.0(\phi^2)</td>
</tr>
<tr>
<td>g</td>
<td>5.0(\Theta(\phi - \phi_0))</td>
<td>10.0(\phi^2)</td>
<td>7.5(\Theta(\phi - \phi_0))</td>
<td>10.0(\phi^2)</td>
</tr>
</tbody>
</table>

4.2. 3D simulations of viscoelastic phase separation

Here we describe the results of our 3D numerical simulations, focusing on the following points: How can we characterize the topology of the 3D phase-separated structure produced by viscoelastic phase separation? What are the characteristics of a 3D network structure?

Seven cases are studied here (see Table 2): (a) with both bulk and shear stresses, (b) without any stress, (c) with only shear stress, (d) with only bulk stress, (e) with bulk and shear stress \((\text{long } \tau_S)\), (f) with steplike shear stress, and (g) with bulk and shear stress (both are steplike). The initial composition is \( \phi_0 = 0.3 \) and Gaussian noise with an amplitude of \( \delta \phi = 0.1 \) was introduced at \( t = 0 \). All the other parameters are the same as those used in 2D simulations. The volume fraction of the polymer-rich phase at equilibrium was about 24.5\%, which is located in the unstable region inside the mean-field spinodal line.

4.2.1. Pattern-evolution kinetics

Fig. 23 shows the pattern evolution observed for case (a). The bright surface represents the solvent-rich side, while the dark one represents the polymer-rich side. Note that the real sharp interface is formed at \( t \approx 300 \). We can see that there is no self-similarity in pattern evolution. The solvent-rich phase nucleates after a frozen period at \( t \approx 100 \) despite this phase being thermodynamically the majority one. Then, these droplets grow in size and at the same time the polymer-rich phase decreases its volume fraction while keeping the connectivity. As a result, the well-developed continuous networklike structure of the polymer-rich phase is formed \((t \approx 700)\) even though it is thermodynamically the minority phase. In the late stage, the viscoelastic stresses relax, which makes this networklike structure unstable and breaks it up into polymer-rich droplets due to the hydrodynamic tube instability \((t \approx 1400)\) (Tanaka, 1994, 1997, 2000). The behavior is essentially the same as that in 2D (see Fig. 14).

The pattern evolution in 3D simulations (Araki and Tanaka, 2001) is essentially the same as that of our previous
2D simulations (Tanaka and Araki, 1997). Reflecting the difference in the dimensionality, however, both phases are continuous in the networklike morphology for 3D. In other words, the networklike structure is bicontinuous. Differently from ordinary spinodal decomposition, the bicontinuous structure can be formed in viscoelastic phase separation even at an asymmetric composition. We also note that the phase connectivity is more easily realized for 3D than for 2D. We can intentionally produce the networklike structure of the thermodynamically minority phase, through which the fluid phase can be transported freely. Thus, the structure can be used as a filter. Since the viscoelastic properties of a system are dominated by the connectivity of the more viscoelastic phase, the networklike structure transiently formed during viscoelastic phase separation should be much more viscoelastic and stronger than the final droplet structure. This point should be quite important for industrial applications.

For comparison, we made simulations for a system without any stress [case (b)]. Note that the simulation without any stresses [case (b)] corresponds to usual phase separation of a fluid model (model H) (Tanaka, 1997). The resulting pattern evolution is shown in Fig. 24. For this case, the well-known behavior is observed: The droplets of the minority phase (the polymer-rich phase) emerge just after the temperature quench and the droplets grow in time by the Lifshitz–Slyozov mechanism and/or the collision–coalescence mechanism (Onuki, 2002). This is also essentially the same as that in 2D (see Fig. 11).

Fig. 25 shows the pattern evolution of case (c), where only the shear stress is included. Although the behavior of case (c) is essentially the same as that of case (b), the coarsening rate of case (c) is a bit slower than that of case (b), because of the higher viscosity of a polymer-rich phase. In the late stage, the viscosity of the polymer-rich phase is \( \eta = \int_0^\infty dt \, G_3 e^{-t/\tau_3} \approx 6.3, \) which is about 60 times larger than that of the solvent. A larger number of non-circular droplets are observed in case (c) than in case (b). This is because the shear stress slows down the shape-relaxation process. However, since the limiting process is interdroplet collision, which is controlled primarily by the viscosity of the solvent-rich phase, the coarsening kinetics itself does not so drastically slow down.

Fig. 26 shows the pattern evolution of case (d), where only the bulk stress is included. For this case, the solvent-rich phase nucleates and the polymer-rich phase shrinks as in chemical gels. The early-stage pattern evolution in case (d) is quite similar to that in case (a). However, there is a large difference in the late-stage process between them: In case (d) the networklike structure breaks up and the polymer-rich phase becomes spherical at the time when the volume shrinking is finished, while in case (a) the network structure continues to exist even after that time. Accordingly, the well-developed networklike structure is never formed in case (d).

Fig. 27 shows the pattern evolution of case (e), where both bulk and shear stresses are included as in case (a) but \( \tau_S \) is longer than that in case (a). The behavior of case (e) is similar to that of case (a) in the early stage, as expected. However, the pattern relaxation from the network to the droplet structure after the volume shrinking is much more retarded even compared to that in case (a) because the relaxation time of the shear stress is longer for case (e) than for case (a). The final morphological transition to a droplet structure is not observed in our simulations simply due to the limitation of the computational time. The late-stage patterns for case (e) resemble the scanning electron microscope (SEM) images of fibril structures observed in the phase separation of polymer solution (Aubert, 1990). In relation to this, we note that the dynamical asymmetry, which is characterized by the difference in the viscoelastic properties between the two phases, may be much stronger in real polymer solutions than in our simulations.

We also studied cases (f) and (g) to compare the corresponding case of 2D. We confirm that the behavior is essentially the same as that in 2D, although the results are not presented here.

The above simulation results for various cases clearly demonstrate the roles of bulk and shear stress. The bulk stress is responsible for the selective nucleation of the solvent-rich phase and the gel-like volume-shrinking behavior in the early and intermediate stages, while the shear stress is responsible for the formation of the well-developed networklike bicontinuous structure. We confirm that the roles of viscoelastic stresses are essentially the same as those in 2D.

### 4.2.2. Temporal change in the scattering function

Fig. 28 demonstrates the evolution of the scaled scattering function for viscoelastic phase separation [case (a)] and normal phase separation [case (b)]. The scaled scattering function \( \hat{S}(q, t) \) is calculated by using 3D Fourier transformation as

\[
S(q, t) = \frac{\int_{|q'|=q} dq' S(q', t)}{\int_{|q'|=q} dq' \tilde{q} S(q', t)}, \tag{32}
\]

\[
\hat{S}(q, t) = \frac{S(q, t)}{\int dq' \tilde{q} S(q', t)}, \tag{33}
\]

\[
\langle q(t) \rangle = \frac{\int dq' \tilde{q} S(q', t)}{\int dq' \tilde{q} S(q', t)}. \tag{34}
\]

Fig. 28(b) shows that for a fluid model [case (b)] the scaled scattering function is independent of time except for the small wavenumber region. In this case, the following dynamical scaling laws are satisfied:

\[
\hat{S}(q, t) = \langle q(t) \rangle^{-d} F(q/\langle q(t) \rangle), \tag{35}
\]

\[
\langle q(t) \rangle \propto t^{-\beta}, \tag{36}
\]
Fig. 24. 3D pattern evolution for case (b).

Fig. 25. 3D pattern evolution for case (c).

Fig. 26. 3D pattern evolution for case (d).

Fig. 27. 3D pattern evolution for case (e).

Fig. 28. Temporal change in the scaled scattering function for viscoelastic phase separation (a) and normal fluid phase separation (b).
especially, the relaxation time of the shear stress, the exponent depends on the viscoelastic parameters (scaling relation [Eq. (35)] does not hold in this case and transition [case (a)] is about 0.27. However, since the dynamic exponent $\gamma$ of fluid–fluid phase separation, severely break down for viscoelastic phase separation. The absence of self-similarity is even obvious in Fig. 23.

We show the temporal change in the characteristic wavenumber calculated by Eq. (34) in Fig. 29. The growth exponent $\beta$ in the late stage of viscoelastic phase separation [case (a)] is about 0.27. However, since the dynamic scaling relation [Eq. (35)] does not hold in this case and the exponent depends on the viscoelastic parameters (especially, the relaxation time of the shear stress, $\tau_S$), it is not so meaningful to discuss the value of the exponent. We note that the power-law behavior is only apparent and there is no physical justification for it without self-similarity of pattern evolution.

For cases (a) and (d), in which phase inversion occurs, the characteristic wavenumber suddenly decreases at the time of phase inversion. This time coincides with the end of the volume shrinking, which indicates that the drastic change of the domain pattern, i.e., phase inversion, takes place just after the completion of the volume shrinking. The characteristic length right after the volume shrinking is primarily determined by the spatial distribution of the solvent-rich droplets nucleated in the early stage. If the bulk stress suppresses concentration fluctuations more strongly, the probability of the nucleation of solvent-rich droplets becomes smaller. Thus, the distance between the solvent-rich droplets, which is one of the characteristic lengths of phase separation, should become larger (see Fig. 18 for the 2D case).

Finally, it should be noted that pattern evolution should in principle become self-similar in the very late (asymptotic) regime, where phase separation should be described by a fluid model (model H). However, this regime is rather difficult to observe either experimentally or numerically, since it takes an extremely long time to reach this asymptotic regime.

### 4.2.3. Topological change of domain morphology during phase separation: analyses of the interface curvature and the Euler characteristics

We also analyze the mean and Gaussian curvatures of the interface to study the topological characteristics of the phase-separated structure (Mecke and Wagner, 1991; Jinnae et al., 1995; Aksimentiev et al., 2002). To do so, we first define the interface as follows. We define $\Phi$ at each lattice point $(x, y)$ so that $\Phi = 1$ for $\Phi > \Phi_0$ while $\Phi = 0$ for $\Phi < \Phi_0$. Then we introduce the interface function $d(x, y)$ so that $d = 1$ when $\Phi(x, y, z) = 1$ and $\prod_{l=\pm 1.0} \prod_{m=\pm 1.0} \prod_{n=\pm 1.0} \Phi(\alpha + l, \beta + m, \gamma + n) = 0$; otherwise, $d = 0$. Thus, the interface $\Sigma$ is defined by a group of points, where $d(x, y, z) = 1$. Then we calculate at all the lattice points the quantities

$$\bar{H} = \bar{c}_i n_i / 2,$$

$$\bar{K} = (\bar{c}_i n_i) (\bar{c}_j n_j) / 2,$$

where $\bar{n} = \nabla \phi / |\nabla \phi|$. These quantities $\bar{H}$ and $\bar{K}$ on the interface $\Sigma$ can be regarded as the mean and Gaussian curvatures $H$ and $K$, respectively. Then the average mean and Gaussian curvatures, $\langle H \rangle$ and $\langle K \rangle$, are, respectively, calculated as

$$\langle H \rangle = \sum_{x, y, z} \bar{H}(x, y, z) / \sum_{x, y, z} d(x, y, z),$$

$$\langle K \rangle = \sum_{x, y, z} \bar{K}(x, y, z) / \sum_{x, y, z} d(x, y, z).$$

In Fig. 30 the temporal changes in the averaged mean and Gaussian curvatures are presented for cases (a)–(e). Since our method to calculate the curvatures requires the sharp interface dividing the two phases, we cannot analyze the behaviors of the early stage (the shaded region in Fig. 30) properly. For cases without bulk stress [(b) and (c)], the polymer-rich droplet structure, which has negative $\langle H \rangle$ and positive $\langle K \rangle$, is formed and then coarsens with time. Reflecting this coarsening process, their absolute values gradually decrease with time. For cases with bulk stress [(a),(d) and (e)], on the other hand, the averaged mean curvature has a positive value in the early stage in contrast to the above cases (b) and (c). Then, its sign becomes negative. This change in the sign of the averaged mean curvature is the result of the phase inversion. On the other hand, the averaged Gaussian curvature changes its sign twice, namely, from positive to negative and then from negative to positive, for cases (a) and (d). The first change reflects the morphological change from the nucleated solvent-rich droplet structure, which is characterized by positive $K$, to the bicontinuous pattern with saddlelike structures, which is characterized by negative $K$. The second one reflects that this asymmetric bicontinuous structure breaks up and transforms into the polymer-rich droplet structure, which is characterized by positive $K$. Since the relaxation time of the shear stress $\tau_S$ is long for case (e),
the breakup of the network structure and the resulting morphological change to the droplet structure are not observed within the computation time. So, the averaged Gaussian curvature remains negative in the late stage and does not yet change its sign for case (e).

Fig. 30 shows that when the averaged Gaussian curvature has the minimum value, the averaged mean curvature changes its sign. This time \( t \sim 300 \) also coincides with the time when the volume fraction is nearly 50%. From the direct observation of Fig. 23, the structure at this time is quite similar to the bicontinuous structure observed in normal phase separation and the sponge phase in microemulsions. As time goes on, the averaged mean curvature has the minimum value at \( t \sim 340 \). Then, it approaches zero asymptotically, reflecting the decrease in the mean curvature due to the coarsening process in the late stage. This time \( t \sim 340 \) corresponds to the end of gellike volume shrinking of the polymer-rich phase.

Almost at the same time, the averaged Gaussian curvature enters into a plateau regime for cases with bulk and shear stresses [cases (a) and (e)]. This plateau is related to the stabilization of the network structure by the shear stress, which is supported by the fact that the plateau is not observed for case (d). Interestingly, it is shown for case (e) that although the absolute value of the averaged mean curvature decreases, the plateau is quite flat for \( t > 400 \). Note that this behavior is also observed in case (a) although it is not so pronounced. According to the Gauss–Bonnet theorem, the integrated value of the Gaussian curvature on the whole interface is topologically invariant. Namely, the integrated Gaussian curvature is not changed unless the events of the breakup of the network and/or the coagulation of droplets occur. However, the Gaussian curvature, which is shown here, is the averaged value. Thus, the behavior observed in case (e) does not necessarily mean that the structure coarsens without any topological change. Actually, the breakup of the network is observed even for \( t > 400 \). We speculate that this absence of the temporal change in the averaged Gaussian curvature in the late stage is due to the balance between two competing effects, the breakup of a network structure into a droplet one and the decrease in the total amount of the interface due to the domain-shape relaxation driven by the interface tension. This point will be discussed below, based on the behavior of the Euler characteristics.

As described above, when the volume shrinking stops, the structure is bicontinuous for case (a). It is believed that for an ordinary dynamically symmetric system a bicontinuous structure is observed when the volume fraction of one of the separated phases is almost equal to that of the other. In such a structure, the averaged mean curvature \( \langle H \rangle \) is nearly zero (Jinnai et al., 1995). For viscoelastic phase separation, on the other hand, a very asymmetric bicontinuous structure, in which the averaged mean curvature has a non-zero value \( \langle H \rangle < 0 \), can be observed: For this structure, both phases are percolated even for a small volume fraction of a polymer-rich phase.

Next we analyze the topological change during viscoelastic phase separation in terms of the Euler characteristic \( \chi_E \). Fig. 31 shows the temporal change in \( \chi_E \) for normal phase separation [case (b)] and viscoelastic phase separation [case (e)].
which is calculated as

\[
\chi_E^{(1)} = \frac{1}{2\pi} \int_S K dS = \frac{1}{2\pi} \sum_{x,\beta,\gamma} \hat{K}(x, \beta, \gamma) d(x, \beta, \gamma).
\] (41)

The other is the topological method: First we express the domain structure by polygons on the domain interface. Since we use the cubic lattice in this study, the interface is presented by squares. Then \(\chi_E\) can be obtained as

\[
\chi_E^{(2)} = F + V - E,
\] (42)

where \(F\), \(V\), and \(E\) are the number of faces, vertices, and edges of all polygons, respectively (Aksimentiev et al., 2002). According to the Gauss–Bonnet theorem, \(\chi_E^{(1)}\) should be equal to \(\chi_E^{(2)}\). We confirm that the relation \(\chi_E^{(1)} \approx \chi_E^{(2)}\) holds well in the late stage, which supports the validity of our analysis. The slight difference between \(\chi_E^{(1)}\) and \(\chi_E^{(2)}\) in the early stage \((t < 300)\) may stem from the uncertainty in the definition of the interface in calculating \(\chi_E^{(1)}\).

For case (b), \(\chi_E\) monotonically decreases, reflecting the decrease in the number of droplets. Note that for a droplet structure the number of droplets is given by \(\chi_E/2\). For case (c), on the other hand, the behavior of \(\chi_E\) is similar to that of the averaged Gaussian curvature \(\langle K \rangle\) [see Fig. 30(b)]. By definition, the time when the sign of \(\chi_E\) becomes negative should coincide with that of the averaged Gaussian curvature. At \(t \sim 300\), \(\chi_E\) has the minimum value and this large negative value of \(\chi_E\) means that the domain structure is highly interconnected. Note that this time again corresponds to the time when \(\langle K \rangle\) is minimal. However, the behavior of \(\chi_E\) in the late stage of case (c) is different from that of \(\langle K \rangle\). Namely, the value of \(\chi_E\) becomes half from \(t = 500\) to \(t = 1000\) (see Fig. 31), while the value of \(\langle K \rangle\) of case (c) is almost constant, or it fluctuates within \(\sim 5\%\) there. This strongly indicates that the topological feature of the networklike structure is changing with time, reflecting the breakup of the polymer-rich network. This supports the above discussion based on the curvature analysis.

Finally, it may be worth noting that these topological features can hardly be obtained from the \(q\)-space analysis, as mentioned in Section 4.2.2. The breakdown of the self-similarity is shown much more clearly by the topological analysis in real space than that by \(q\)-space analysis. Thus, we conclude that the curvature analysis and the analysis of the topological measure are quite powerful for characterizing the pattern evolution of viscoelastic phase separation.

4.3. Summary of simulations of viscoelastic phase separation based on the coarse-grained two-fluid model

In the above, we reviewed our simulation studies based on the coarse-grained two-fluid model and discuss how phase separation is affected by viscoelastic stresses, or dynamic asymmetry. Our numerical study has revealed that the bulk stress originating from the connectivity of “interaction network” plays a crucial role in the volume-shrinking behavior of a polymer-rich phase and the resulting phase inversion, while the shear stress does in the formation of a well-developed network structure. The former originates from the fact that bulk stress is directly coupled to diffusion. Topological characteristics are shown to be quite powerful for quantitative studies of the phase-separation structure formed by viscoelastic phase separation. We also demonstrate how to control the characteristics of the network pattern by controlling the viscoelastic relaxational functions. Such information may be useful for intentional design of the morphology of multiphase materials.

To elucidate the microscopic origin of the bulk stress, we need to understand how a transient gel is formed upon phase separation of a dynamic asymmetric mixture. Hereafter we consider this challenging problem by using the case of colloidal suspensions as an example.

5. Colloid simulations: process of transient gelation

The dynamic behavior of colloidal suspensions is quite important from both the scientific and the industrial viewpoints (Russel et al., 1989; Larson, 1999). It includes many fundamental problems, e.g., rheological behavior of colloidal systems under shear fields and kinetics of colloidal aggregation, phase separation, gel formation, and crystallization. If we try to attack these problems either theoretically or numerically, the most difficult problem arises from hydrodynamic interactions between solid particles. The nonlocal nature of hydrodynamic interactions is a key physical factor that makes this problem so rich, but at the same time so difficult to deal with either theoretically or numerically. It is known that for the creeping-flow regime, truncating the hydrodynamic interactions beyond some critical distance causes serious errors because of the intrinsically long-range nature of the interactions. This situation is physically very similar to the problem of interacting charged particles, where spherical truncation of the Coulomb interaction between ions leads to large errors. If we explicitly treat the solid–fluid boundaries of colloid particles thus, enormous calculations are required for simulations of many-body problems. A number of approximation methods are proposed to reduce the calculation time while keeping the important effects of hydrodynamic interactions (Brady et al., 1988; Koelman and Hoogerbrugge, 1993; Ladd, 1994; Ball and Melrose, 1997). These considerable improvements of methods and recent advances of computers now make numerical simulations a powerful and popular means to study the dynamics of suspensions. However, hydrodynamic interactions between particles are still serious obstacles for our understanding of the dynamics of colloidal suspensions. Thus, one of the main goals of colloidal science is to reveal the physical nature of long-range interparticle hydrodynamic interactions in a dense particle system.

There are a number of interesting problems, where interparticle hydrodynamic interactions may play crucial roles. For example, colloidal phase separation, aggregation, and
gel formation have recently attracted considerable attention. Phase separation in such a system has been found to have many unusual features including a long-lived transient gel formation upon phase separation (Verhaegh et al., 1997, 1999; Poon, 2002). For a deep quench, for example, the initial growth of the concentration fluctuations is followed by the formation of a transient gel, and the coarsening process apparently stops for a while. This transient gel state lasts for a long time, and then the gel eventually collapses under gravity (Poon, 2002). Phase separation of emulsion also has similar features (Bibette et al., 1992; Dickinson and Golding, 1997). Since these phenomena take place in dense colloidal suspensions, hydrodynamic interactions should play quite important roles.

Many simulation studies have so far been performed to understand these interesting, but mysterious phenomena. In most of these studies, the so-called Brownian dynamics simulations are employed to save the computation time (Whittle and Dickinson, 1997; Lodge and Heyes, 1998; Soga et al., 1999). The hydrodynamics is free draining there and thus hydrodynamic interactions between particles are completely ignored. However, there is a high possibility that hydrodynamic interactions between the particles play a crucial role in the structural formation during aggregation or phase separation and seriously affect it. This is indeed the case, as demonstrated below. To our knowledge, there are few simulations that include interparticle hydrodynamic interactions on the problem of phase separation and aggregation. This may be largely due to the difficulty in dealing with many-body hydrodynamic interactions in a dense colloidal suspension. So an efficient simulation method properly handling hydrodynamic interactions in a colloidal suspension is highly desirable.

In previous simulations, colloidal suspensions are usually treated as a mixture of solid particles and a simple liquid. This is quite natural since it reflects the reality. However, this type of approach inevitably suffers from the solid–fluid boundary conditions on the surface of colloidal particles, which make simulations very complicated and accompany the problem of the singularity associated with the squeezed flow (Ball and Melrose, 1995). Here we demonstrate a new simulation method, which is essentially different from the conventional ones in that we view colloidal suspensions as a mixture of viscous undeformable fluid particles and a nonviscous simple liquid, instead of treating colloids as solid particles. We call this new method a “fluid particle dynamics (FPD)” method. We apply this simulation method for studying phase-separation dynamics of colloidal suspensions while including hydrodynamic interactions (Tanaka and Araki, 2000).

5.1. Fluid particle dynamics method

5.1.1. Simulation method

The key idea of our method is to treat a solid colloid particle as an undeformable fluid particle, whose viscosity \( \eta_c \) is much higher than that of the surrounding liquid \( \eta_s \). This makes us free from the solid–fluid boundary condition, which makes the problem quite complex. In our method, the viscous dissipation inside a colloidal particle \( \eta_c (\nabla \bar{v})^2 \) goes to zero in the limit of \( R = \eta_c / \eta_s \to \infty \). In this limit, the flow field becomes homogeneous within a particle, which coincides with that of a solid particle with a non-slip boundary condition. Our numerical simulation is a hybrid method combining (a) the lattice simulation for obtaining \( \bar{v}(\vec{r}) \) by solving the Navier–Stokes equation and (b) the off-lattice one for solving the motion of the center of mass of a particle.

Our new method is hinted from model H simulations of fluid phase separation, whose hydrodynamics is also described by the Navier–Stokes equation. Note that since our simulation is based on the particle dynamics, coalescence between particles is, of course, not allowed, differently from model H simulations. This method allows us to avoid the discontinuity of flow fields at the interface. Namely, it enables us to apply the Navier–Stokes equation to our problem without suffering from solid–fluid boundary conditions. Thus, the singularity associated with the squeezed flow produced by two approaching particles can, for example, be avoided automatically. It is extremely simpler in its mathematical structure than the conventional methods. The accuracy of our approximation for colloidal suspensions increases with the increase in the viscosity ratio \( R \). For emulsions, in which fluid particles are suspended in a simple liquid, our method should be even more realistic.

Now we explain the details of our method (Tanaka and Araki, 2000). Here we consider suspensions of monodisperse spherical particles. Let us express the coordinate of the center of mass of particle \( x \) as \( \vec{r}_x \) and define the concentration field \( \phi_s(\vec{r}) \) representing a spherical particle as

\[
\phi_s(\vec{r}) = \frac{\tanh((a - |\vec{r} - \vec{r}_x|)/\zeta) + 1}{2},
\]

where \( a \) is the radius of a particle and \( \zeta \) is the effective colloid–fluid interface. \( \phi_s(\vec{r}) \) is 1 inside the particle and 0 outside. To regard this fluid particle as a solid one, the following two conditions are to be satisfied: \( R = \eta_s / \eta_c \to \infty \) and \( \zeta / a \to 0 \). In principle, the latter limit can be pursued by setting the spatial increment of simulation \( \Delta x \) quite small. Since \( \zeta \) is the minimum length unit in our model, setting \( \Delta x \) much smaller than \( \zeta \) costs too much computational time, which is usually not practical.

By using \( \phi_s(\vec{r}) \), we can express the spatial change of the viscosity reflecting the spatial distribution of particles as

\[
\eta(\vec{r}) = \eta_s + \sum_x \Delta \eta \phi_s(\vec{r}),
\]

where \( \Delta \eta = \eta_c - \eta_s \). The force field can also be defined as

\[
\vec{F}(\vec{r}) = \sum_x \frac{\vec{F}_s \phi_s(\vec{r})}{\int d\vec{r}' \phi_s(\vec{r}')}. \tag{45}
\]
\( \vec{F}_x \) represents the force acting on particle \( x \), which is composed of interparticle potential force and thermal noise force produced by solvent molecules as

\[
\vec{F}_x(t) = -\sum_{\beta \neq x}^N \frac{\partial}{\partial \vec{r}_x} U(|\vec{r}_x - \vec{r}_\beta|) + \vec{F}_x^B(t).
\]  

(46)

In this study, we employ the (12–6) Lennard-Jones (LJ) potential, simply because it is widely used for the problem of colloidal aggregation:

\[
U(r) = 4\varepsilon \left\{ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right\},
\]

(47)

where \( \varepsilon \) is the depth of LJ potential and \( \sigma \) is the characteristic length of particle. The potential has a minimum at \( r = \bar{r} \approx 1.122\sigma \). Both \( \sigma \) and \( \alpha \) are related to the particle size, and here we set \( \sigma = 2a \) for simplicity. Here we note that we can employ any type of potential in our method. The thermal noise force \( \vec{F}_x^B \) should satisfy the following fluctuation–dissipation theorem:

\[
\langle \vec{F}_{x2}(t)\vec{F}_{x2}(t') \rangle = 2\xi k_B T \delta_{x\beta} \delta(t - t').
\]

(48)

Using viscosity field \( \eta(\vec{r}) \) and force field \( \vec{F}(\vec{r}) \), we solve the following Navier–Stokes equation:

\[
\rho \left( \frac{\partial \vec{v}}{\partial t} + \vec{v} \cdot \nabla \right) \vec{v} = \vec{F} - \nabla p + \nabla \cdot [\eta(\nabla \vec{v} + (\nabla \vec{v})^T)].
\]

(49)

Here \( \rho \) is the density and we assume that there is no density difference between colloids and the surrounding liquid, for simplicity. \( p \) is a part of the pressure and determined so that the incompressibility condition \( \nabla \cdot \vec{v} = 0 \) is satisfied. From \( \nabla \cdot \vec{v} = 0 \), we obtain

\[
\nabla \cdot [\vec{F} - \nabla p + \nabla \cdot (\eta(\nabla \vec{v} + (\nabla \vec{v})^T)) - \rho(\vec{v} \cdot \nabla)\vec{v}] = 0.
\]

(50)

In the \( \vec{q} \) space,

\[
[p]_\vec{q} = -i \vec{q} \cdot [\vec{F} + \nabla \cdot (\eta(\nabla \vec{v} + (\nabla \vec{v})^T))] - \rho(\vec{v} \cdot \nabla)\vec{v}]_\vec{q} = i q^2 \vec{q} \cdot \nabla \eta(\vec{q}) + \frac{\partial}{\partial t} [\vec{q}]_\vec{q}.
\]

(51)

where \( [\cdots]_\vec{q} \) represents the Fourier transformation about \( \vec{q} \). Eq. (49) becomes

\[
\rho \frac{d}{dt} [\vec{v}]_\vec{q} = T_{\perp}(\vec{q}) \cdot (\vec{F} + \nabla \cdot (\eta(\nabla \vec{v} + (\nabla \vec{v})^T)) - \rho(\vec{v} \cdot \nabla)\vec{v})_\vec{q}.
\]

(52)

Here \( T_{\perp}(\vec{q})_{ij} = \delta_{ij} - q_i q_j/q^2 \) is the transverse projection tensor. By making inverse-Fourier transformation of Eq. (52), we calculate the time development of \( \vec{v}(\vec{r}) \) by the explicit Euler method. Here we note that we can also solve Eq. (49) without using Fourier transformation. We set \( \Delta t = 0.02 \) and \( \Delta x = 1 \). By using the flow field \( \vec{v}(\vec{r}) \), we calculate the center-of-mass velocity of a particle from the relation

\[
\frac{d}{dt} \vec{r}_x = \frac{\int d\vec{r} \vec{v}(\vec{r}) \phi_x(\vec{r})}{\int d\vec{r} \phi_x(\vec{r})}.
\]

(53)

Thus we obtain a new position of \( x \) particle \( \vec{r}_x \) in continuous space. We map the new particle positions on the lattice.

Here we summarize the practical procedures of FPD.

1. By using the coordinate of particles at time \( t \), \( \vec{r}_x(t) \), we obtain \( \vec{F}_x(t) \) from Eq. (46).
2. By using the particle coordinate \( \vec{r}_x(t) \), we obtain \( \phi = \sum_x \phi_x(\vec{r}, t) \) from Eq. (43).
3. By using the concentration field \( \phi(\vec{r}, t) \), we calculate the viscosity field \( \eta(\vec{r}, t) \) and the force field \( \vec{F}(\vec{r}, t) \) from Eqs. (44) and (45), respectively.
4. By using \( \eta(\vec{r}, t) \), \( \vec{F}(\vec{r}, t) \), and \( \vec{v}(\vec{r}, t) \), we calculate the flow field \( \vec{u}(\vec{r}, t + \Delta t) \) from Eq. (49).
5. From Eq. (53), we obtain a new particle position \( \vec{r}_x(t + \Delta t) \).
6. We repeat the procedure from step (1) using a new particle coordinate set \( [\vec{r}_x(t + \Delta t)] \).

5.1.2. Flow field around a particle

To check the validity of our FPD method, we investigate the steady flow field around a particle which is driven by a constant force. Fig. 32 shows the steady flow field produced around a particle for \( R = 1 \) (a) and \( R = 50 \) (b). The simulation was performed for a 2D system (64 × 64) under a periodic boundary condition. The force exerted on a particle is \( f = 0.1 \) and the particle radius is \( a = 8 \) (\( \xi = 1 \)).

As can be seen in Fig. 32, the flow field enters inside the particle since the viscosity is the same for \( R = 1 \). For \( R = 50 \), on the other hand, the flow does not enter inside the particle so much and thus the flow pattern resembles that around a solid cylinder, as expected.

Fig. 33 shows how the strength of the residual internal flow field inside a particle depends on the viscosity ratio \( R = \eta_i/\eta_s \). The viscosity of the surrounding fluid is fixed to \( \eta_s = 0.5 \). The strength of the residual flow fields inside a particle is characterized by

\[
\langle |\vec{v} - \vec{v}_0| \rangle = \frac{\int d\vec{r} \vec{v}(\vec{r})\phi(\vec{r})}{\int d\vec{r} \phi(\vec{r})} - \left( \frac{\int d\vec{r} \vec{v}(\vec{r})\phi(\vec{r})}{\int d\vec{r} \phi(\vec{r})} \right)^2. \tag{54}
\]

The other parameters are the same as those in Fig. 32. As can be seen in Fig. 33, the strength of the internal flow
field \(\langle |\vec{v} - \vec{v}_0|^2 \rangle\) decreases with an increase in \(R\). For \(R \geq 3\), we obtain the empirical relation \(\langle |\vec{v} - \vec{v}_0|^2 \rangle \propto R^{3/2}\). This indicates that for larger \(R\) we can regard the fluid particle as the more solidlike one, which supports the basic idea of the FPD method.

5.1.3. Einstein–Stokes relation

The results shown in Figs. 32 and 33 are obtained for 2D. For 3D, it is known that a spherical particle moving in fluid with a constant velocity experiences the resistive force proportional to its velocity. The proportional constant, namely, the friction coefficient, is given by

\[
\zeta_0 = 6\pi\eta a \frac{1 + 2/3 R^{-1}}{1 + R^{-1}}.
\]  

Eq. (55) reduces to the well-known Einstein–Stokes relation \(\zeta = 6\pi\eta a\) for a solid particle (for \(R \to \infty\)), while \(\zeta = 5\pi\eta a\) for a particle made of a fluid having the same viscosity as the surrounding fluid (for \(R = 1\)).

We made simulations in 3D to investigate how the friction constant depends on the particle size, the system size, \(\Delta x\), and \(R\) and compare the results with the prediction of Eq. (55). It turns out that the result is quite different from the prediction for a small system size: It is strongly dependent on the system size. Since we are using a periodic boundary condition, the smaller ratio between the system size and the particle size means a smaller interparticle distance, which effectively leads to the larger friction coefficient than the prediction of Eq. (55). Eq. (55) is for an infinite system, but for a finite system the velocity gradient becomes larger than for an infinite one with a decrease in the system size and thus a particle experiences the larger resistive force. Fig. 34 shows how \(\zeta\) depends upon \(L\) for two values of \(R\). We scale the friction constant and the system size, respectively, by \(\zeta_0\), which is given by Eq. (55), and the particle radius \(a\). For either value of \(R\), \(\zeta/\zeta_0\) tends to 1 with an increase in \(L\). For larger \(R\), the \(L\) dependence of \(\zeta\) is stronger. This is because the velocity gradient inside the particle becomes smaller for larger \(R\), which leads to the larger velocity gradient in the fluid surrounding the particle. To confirm the validity of our FPD method on a more quantitative level, we also need to study the dependence of the behavior on \(\zeta\) and \(\Delta x\). However, we would like to emphasize that the behavior described above is physically quite reasonable: It is caused by the long-range nature of hydrodynamic interactions and not by numerical problems. Thus, the above result supports the validity of our method. We also note that this finite-size effect becomes weaker for many particle systems since long-range hydrodynamic interactions are screened by the other surrounding particles.

5.1.4. Rotational motion of a particle under a shear field

In our FPD method, we consider only the translational motion of the center of mass of a particle \(\langle \vec{R}_c \rangle\) and do not consider its rotational motion explicitly. However, our method expresses the rotational motion quite naturally since all types of fluid motion are properly described by the Navier–Stokes equation. Here we investigate, by applying the shear flow field, how the rotational motion is introduced in our method. Fig. 35 indicates the flow field around a particle under a shear field for \(a = 20\) (\(\zeta = 1\)) and its dependence on \(R\). Here we employ the Lees–Edwards boundary condition. We set the shear rate as \(\gamma = 0.02\) and the system size is \(64 \times 64\) (2D).
As can be seen from Fig. 35, there are no effects of shear field for $R = 1$ (a). For $R = 50$ (b), on the other hand, the force field reflecting the viscosity difference acts on the particle surface, which induces the rotation of a particle. This can be interpreted as follows: For large $R$, the flow field is produced to minimize the viscous dissipation under the shear field.

Fig. 36 shows the off-diagonal component of the velocity gradient tensor $\hat{\sigma}_{xy} + \hat{\sigma}_{yx}$ for a particle with $a = 8$ under the shear field and its dependence on $R$. The brightness represents the strength of $|\hat{\sigma}_{xy} + \hat{\sigma}_{yx}|$ and the black color means $|\hat{\sigma}_{xy} + \hat{\sigma}_{yx}| = 0$. As in the case of Fig. 35, there is no change for $R = 1$ (a). For $R = 50$ (b), on the other hand, $|\hat{\sigma}_{xy} + \hat{\sigma}_{yx}|$ is almost zero inside a particle (note that it should be zero for the rotation of a solid sphere), but the force field is produced around a particle to induce the rotation of the particle. This is the so-called Stokeslet $S$, which leads to the increase of the viscosity of colloidal suspensions.

As shown above, the rotation of a particle is naturally induced by shear fields for our FPD method to avoid the slip at the surface of a particle.

5.1.5. Flow field for two approaching particles due to attractive interaction

Fig. 37 shows flow fields produced when two particles interacting with LJ potential approach each other. The particle radius is $a = 8$ ($\xi = 1$), and the interaction parameters are $\varepsilon = 0.25$ and $\sigma = 16$. The approaching velocity is smaller for $R = 50$ (b) than for $R = 1$ (a). The flow field inside a particle is more homogeneous for $R = 50$, which leads to the larger velocity gradient in the region between the particles when the interparticle distance becomes smaller.

Fig. 38 shows how the interparticle distance between two particles in Fig. 37 approaches its final value by plotting the deviation of the interparticle distance from its final value $\Delta r$ and its dependence on $R$. With increasing $R$, the approaching velocity becomes slower. The oscillation seen for small $R$ is due to the inertia term of the Navier–Stokes equation. The effects of the inertia term can be removed by employing the Stokes approximation. As explained above, the increase in $R$ causes the increase in the velocity gradient in the fluid between the particles, which causes the larger resistive force. For larger $R$, thus, the approaching velocity becomes slower and the oscillatory behavior becomes weaker. For a solid particle, the diffusion constant decreases in proportion to the interparticle distance, which is known as the lubrication effect. This indicates that it takes an infinite time for the direct contact of two solid particles. In our FPD method, $R$ is larger, the behavior of a single particle becomes more solidlike; for example, Eq. (55) tells us that $\zeta \approx 5.96\eta a$.

Fig. 36. Velocity gradient strength $|\hat{\sigma}_{xy} + \hat{\sigma}_{yx}|$ around a particle under shear flow: (a) $R = 1$ and (b) $R = 50$.

Fig. 37. Flow field produced when two particles interacting with LJ potential approach each other: (a) $R = 1$ and (b) $R = 50$.

Fig. 38. Temporal change in $\Delta r$, which is the deviation of the interparticle distance from its final value, for various values of $R$. 

Fig. 38. Temporal change in $\Delta r$, which is the deviation of the interparticle distance from its final value, for various values of $R$. 

Fig. 38. Temporal change in $\Delta r$, which is the deviation of the interparticle distance from its final value, for various values of $R$. 

Fig. 38. Temporal change in $\Delta r$, which is the deviation of the interparticle distance from its final value, for various values of $R$. 

for \( R = 50 \). Although there is no divergence in the friction coefficient for particle collisions even for \( R = 50 \), the slowing down of the approaching speed itself is well reproduced. The absence of the singularity has a practical merit in simulations.

Our FPD method has some advantages over other methods of colloidal simulations in studying the particle collision process. In usual Brownian dynamics simulations, the hydrodynamics is free draining and thus it cannot describe the hydrodynamic interactions upon particle collision. In Stokesian-dynamics simulations, the hydrodynamic interaction between particles can be in principle described by including two-body, three-body, and higher-body interactions sequentially. However, this is not practically easy due to theoretical difficulties and computational costs. We also note that the Stokesian-dynamics method cannot include the inertia effects and nonlinear convective term in the Navier–Stokes equation. Thus, hydrodynamic interactions are basically included only on the two-body level, which is expressed by connecting the relations for particular ranges of interparticle distance analytically. Our FPD method can include the effects of many-body hydrodynamic interactions among particles as well as the rotational motion naturally.

### 5.1.6. Many-body hydrodynamic interactions studied by the FPD method

To investigate many-body hydrodynamic interactions in the process of colloidal aggregation, we compare FPD with BD for three initial particle configurations shown in Fig. 39(A), (B), and (C). Configuration (A) in Fig. 39 is to study two-body interactions, configuration (B) is to study the collision of the third particle to a pair of particles in contact, and configuration (C) is to study particles on a hexagonal lattice. For each case, the initial interparticle distance is set to be \( r = 3a \). Fig. 40 shows the temporal change in \( \Delta r \) for three cases (A)–(C) simulated by FPD (a) and BD (b). The parameters used in FPD simulations are \( \eta_\nu = 0.5, R = 50, a = 3.6 (\zeta = 1.0), \epsilon = 0.25, \) and \( \sigma = 7.2 \). The system size is \( 64 \times 64 \). For BD simulations, the following equation of motion is solved:

\[
m \frac{d^2 \vec{r}_s}{dt^2} = \vec{F}_s - \zeta \vec{v}_s,
\]

where \( m \) is the mass of a particle and \( \zeta \) is the friction coefficient. The parameters for the LJ potential are the same as those used in FPD, and we set \( m = 1.0 \) and \( \zeta = 2.5 \). These values are chosen so that binary collision [see Fig. 39(A)] exhibits similar behavior for FPD and BD. The time required for two LJ particles initially separated by distance \( r = 3a \) to approach the final distance \( r = 21/6 \) is estimated as follows for BD: By neglecting the inertia and noise terms in Eq. (56), we obtain \( \frac{dr}{dt} = -U'(r)/\zeta \). Assuming \( \sigma = 2a \) and the Einstein–Stokes relation \( \zeta = 6\pi\eta_\nu a \), we obtain

\[
t_0 = (\pi\eta_\nu a^3/\epsilon) \int_{3/6}^{3/2} dx/(x^{-6} - 2x^{-12}) \approx 83.62\eta_\nu a^3/\epsilon.
\]

For BD [see Fig. 40(b)], there is little difference in the behavior for three configurations (A)–(C). Slightly faster kinetics in configuration (B) is simply due to the fact that the force acting on the particle is slightly stronger since the two particles are in contact already in the initial configuration. For FPD [see Fig. 40(a)], on the other hand, it takes more than 10 times longer for particles to collide for configuration (C) than for configuration (A). This fact reflects stronger hydrodynamic interactions since channels between particles for fluid drainage are narrower for (C) than for (A). This plays a quite important role, for example, when particles form a hexagonal crystalline structure. Here we should note that the hydrodynamic interactions are stronger in 2D than in 3D, since there is no escape dimension for flow in 2D. We also note that the process is slightly slower for (B) than (A).

### 5.1.7. Applicability of FPD to various problems

In the above, we have shown the validity of FPD for a few test problems, in which interparticle hydrodynamic interactions play crucial roles. Here we mention physical problems to which our FPD method can be applied. Since FPD is based on the phase-field model, it is compatible to various types of phase-field models describing the ordering of fluid and the variety of interactions. We are now applying our FPD method to the problems of colloidal particles dispersed in liquid crystal, where nematohydrodynamics should play crucial roles. Here we should note that the hydrodynamic interactions are stronger in 2D than in 3D, since there is no escape dimension for flow in 2D. We also note that the process is slightly slower for (B) than (A).

### 5.2. Aggregation process of colloidal particles

#### 5.2.1. Effects of hydrodynamic interactions on aggregation of colloidal particles

To study the roles of hydrodynamic interactions, we compare the difference in the behavior between FPD and BD. Fig. 42 shows the aggregation process observed in
simulation using FPD. The system size is $256 \times 256$ and $N_p$ is 400. The parameters used are $a = 3.6$ ($\zeta = 1.0$), $\eta_s = 0.5$, $R = 50$, $\varepsilon = 0.25$, and $\sigma = 7.2$. The volume fraction of particles is about 27.9%. Fig. 43, on the other hand, shows the aggregation process observed in simulation by BD without hydrodynamic interactions. We use Eq. (56) with the same interaction parameters as those used in Fig. 42. We set $m = 9.8168$ and $\zeta = 0.1179$. These values are chosen so that the single particle behavior is the same between FPD and BD.

The initial state is prepared by moving the randomly distributed 400 particles interacting with repulsive interaction $U(r) = 4\varepsilon[(\sigma/r)^{12} + (\sigma/r)^6]$ by BD simulation. After preparing the initial state, we neglect thermal noises and set $F^B = 0$. Both initial condition and interaction potential are the same between the two simulations. Thus, the difference in time development stems solely from hydrodynamic interactions.

For the case without hydrodynamic interactions (see Fig. 43), on the other hand, particles form compact clusters, which coarsen with time by collision and coalescence mechanism. For the case with hydrodynamic interactions (see Fig. 42), particles form linear chainlike strings instead of compact clusters and then they form the network structure.
Fig. 43. Aggregation process in colloidal suspensions simulated by the BD method without hydrodynamic interactions. Volume fraction is 27.9% and $T = 0$.

Fig. 44. Effects of hydrodynamic interactions on $P(\theta)$: (a) FPD and (b) BD.

Fig. 45. Temporal change in $\Phi_2/\Phi_6$ for FPD and BD.

Both simulations are started from the same initial particle configuration and there are no force noises imposed. Thus, the above differences should stem solely from hydrodynamic interactions between the particles. Without hydrodynamic interactions, particles have a tendency to aggregate into a compact structure, as often reported in Brownian dynamics simulations. Now it can be concluded that the formation of clusters with “open” structures in Fig. 42 is due to interparticle hydrodynamic interactions. This clearly demonstrates that hydrodynamic interactions crucially affect the pattern evolution and kinetics of aggregation, gel formation, and phase separation in colloidal suspensions.

To characterize the difference in the structure, we consider particle position correlation in more detail. First we consider the angular correlation. Fig. 44 shows the angular correlation of three neighboring particles $P(\theta) = \langle \delta(\theta_{\alpha\beta\gamma} - \theta) \rangle_{\alpha\beta\gamma}$ for $t = 200$ (a) and $t = 5000$ (b). Here $\theta_{\alpha\beta\gamma}$ is the angle between two vectors $\vec{r}_{\alpha} - \vec{r}_{\beta}$ and $\vec{r}_{\beta} - \vec{r}_{\gamma}$, and $\langle \cdot \cdot \cdot \rangle_{\alpha\beta\gamma}$ means the average for all the cases where $\alpha$ and $\beta$ particles are in contact with $\gamma$ particle. We regard particles to be in contact when the interparticle distance is closer than $1.2r_0$ ($r_0 = 2^{1/6}\sigma$). In the initial stage ($t = 200$), where only a few particles form clusters, $P(\theta)$ has peaks at $\theta = \pi/3$ and $5\pi/3$ for BD, while it has a broad peak at $\theta = \pi$ for FPD. The latter means that the third particle does not attach to the lowest-energy position of the pair of particles [see Fig. 39(b)], but forms a 1D chainlike configuration. In the late stage of the aggregation process [see Fig. 44], on the other hand, peaks develop at $\theta = n\pi/3$ ($n = 1, 2, 3, \ldots$), reflecting the hexagonal crystalline packing of particles for both FPD and BD. The fact that peaks at
Fig. 46. Temporal change in $g(r)$: (a) with hydrodynamic interactions and (b) without hydrodynamic interactions.

The peaks at $\theta = \pi/3$ and $5\pi/3$ are larger than the other peaks reflect that not all particles have six nearest neighbors.

Fig. 45 plots the ratio of two-fold symmetry to the six-fold one in the angular dependence, $\Phi_2/\Phi_6$, as a function of time $t$. We calculate the $p$-fold symmetry component as $\Phi_p = \int_0^{2\pi} d\theta \cos(p\theta) \langle \delta(\theta_{2\beta,\gamma} - \theta) \rangle_{\beta,\gamma}$. For BD, it approaches the final value in the rather early stage ($t \sim 400$). This means that even small clusters formed in the early stage have hexagonal order and only their size grows while keeping the same symmetry. For FPD, on the other hand, the two-fold symmetry component is more dominant than the six-fold one for a longer period of time, which means the network structure is kept for a longer time.

Next we check the radial distribution function $g(r)$. Fig. 46 shows the temporal change of $g(r)$ for FPD (a) and BD (b). $g(r)$ is calculated as

$$g(r) = \sum_{x > \beta} \delta(|\vec{r}_x - \vec{r}_\beta| - r)/g_0.$$ (57)

Here $g_0$ is the normalization factor to satisfy $g(r \to \infty) = 1$. In both cases, the peaks indicative of the crystalline structure are seen at $r/r_0 = 1, \sqrt{3}, 2, \ldots$. This is natural since for $F_B^0 = 0$ ($T = 0$) a system should crystallize into a hexagonal lattice. From Figs. 46(a) and (b), we can notice that the peak at $r/r_0 = \sqrt{3}$ is much weaker for (a) than for (b) at $t = 500$.

Here we focus on the growth of the peak at $r/r_0 = \sqrt{3}$. Fig. 47 shows the temporal change of $h(\sqrt{3})/h(2)$. Here

$$h(x/r_0) = \int_0^\infty r' dr' g(r') e^{-(r'-x)^2/d^2} / \int_0^\infty r' dr' e^{-(r'-y)^2/d^2},$$

where $d = 0.1$. Except for the initial stage ($t \leq 300$), this ratio decays with time for the case without hydrodynamic interactions, while it grows with time for the case with hydrodynamic interactions. The peak at $r/r_0 = \sqrt{3}$ reflects hexagonal configuration, while that at $r/r_0 = 2$ reflects 1D chainlike configuration. Thus the behavior seen in Figs. 46 and 47 also indicates that particles tend to form chainlike structures for FPD.

Here we consider why colloidal particles tend to form 1D chainlike open structure when hydrodynamic interactions are included (Tanaka and Araki, 2000; Tanaka et al., 2003). To reveal the physical mechanisms, let us consider the hydrodynamic effects on the elementary motion of particle pairs. When two particles are approaching each other, neighboring particles are moved away by the squeezed flow produced, as shown in Fig. 48(a). Without hydrodynamic interactions, they approach each other mainly by the translational motion and the rotational motion is only weakly induced before their contact. There are also no effects of the squeezed flows for this case. With hydrodynamic interactions, on the other hand, there are two mechanisms, which try to align the pair of paired particles in the same direction during their approach. One is the rotation of a particle pair toward the direction of the translational motion. This is induced by its anisotropic shape to minimize the viscous dissipation and can be explained by a simple symmetry argument.
If the third particle is not on the symmetric axis as shown in Fig. 40(a), the particle pair tends to rotate as indicated in Fig. 48(c). The other is due to hydrodynamic interactions between the particle pairs: When a particle approaches the pair of particles in contact [see Fig. 48(b)], the path indicated by ○ is kinetically more probable than that indicated by × due to lubricant effects, despite the fact that the latter is energetically more favorable. The flow fields induced by the motion of a particle pair also rotate the other particle pair. These mechanisms significantly increase the probability of the formation of a chainlike open structure. The hydrodynamic interactions (more specifically, squeezed-flow effects) also make the approaching speeds of particles considerably slower compared to the case without hydrodynamic interactions, which also helps the formation of chainlike structures. Furthermore, as indicated in Fig. 48(d), a particle pair has a tendency to move along its long axis due to hydrodynamic interactions. Its mobility perpendicular to the long axis is lower than that along it. This effect is more enhanced for a longer chain, which further helps the formation of chainlike structures. It should be emphasized that the percolation threshold for colloidal aggregation is crucially affected by hydrodynamic interactions. How to bridge the microscopic simulations on the formation of a transient gel with the macroscopic constitutive equation used in the coarse-grained two-fluid model (how to express the concept of mechanical connectivity in the phenomenological model) remains a future problem.

5.3. Summary of simulations on the aggregation kinetics accompanying transient gel formation in colloidal suspensions

Our numerical study suggests that the elementary coarsening process of phase-separating colloidal suspensions, which is characterized by stress accumulation and the resulting breakup of the network structure (see Fig. 49), can be regarded as viscoelastic phase separation and it is essentially the same as that observed in polymer solutions. This strongly supports that phase separation of colloidal suspensions should be classified into viscoelastic phase separation (Tanaka, 1999). Our numerical simulations of colloidal suspensions provide us with a hint at understanding how a transient gel is formed with a help of hydrodynamic interactions. How to bridge the microscopic simulations on the formation of a transient gel with the macroscopic constitutive equation used in the coarse-grained two-fluid model (how to express the concept of mechanical connectivity in the phenomenological model) remains a future problem.
6. Concluding remarks

In this paper, we review our numerical simulation studies on viscoelastic phase separation. We study the dynamic process of viscoelastic phase separation by numerically solving the coarse-grained two-fluid model. We also develop a new method (FPD) of colloid simulations and demonstrate its validity. The importance of interparticle hydrodynamic interactions in aggregation, gel formation, and phase separation of colloidal suspensions is demonstrated. Our simulations strongly suggest that phase separation of colloidal suspensions should be classified into viscoelastic phase separation. Dynamically asymmetric fluid mixtures universally take a new kinetic pathway, a transient gel state, upon their phase separation (see Fig. 49). A transient gel is defined as a state, where the characteristic deformation rate produced by phase separation itself is faster than the characteristic rheological relaxation rate. We argue that the basic features of viscoelastic phase separation, which originate from transient gel formation, should be common to any “dynamically asymmetric” fluid mixtures having large size disparity between the components, such as polymer solutions, emulsions, colloidal suspensions, and protein solutions (see Fig. 1). Further studies are highly desirable to check this universality.

Finally, we point out that there are a number of examples of pattern formation in material science, which may be explained by viscoelastic phase separation. On these examples, please refer to our recent review (Tanaka, 2000). We hope that viscoelastic phase separation will be intentionally used as a basic principle to form network or sponge structures in material science and technology.

Note added in proof

Network-forming phase separation have recently been observed in colloidal suspensions (Tanaka, H., Nishikawa, Y., Koyama, T., 2005. Network-forming phase separation of colloidal suspensions. Journal of Physics: Condensed Matter 17, L143-L153). This indicates that phase separation in colloidal suspensions may also belong to viscoelastic phase separation.

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