

Viscoelastic model of phase separation in colloidal suspensions and emulsions

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We propose a simple physical model of phase separation of colloidal suspensions and emulsions, which we call the “viscoelastic model.” On the basis of this model, we consider two poorly understood phenomena: (i) phase separation accompanying the formation of a transient gel, and its collapse, and (ii) shear effects on composition fluctuations and phase separation. These phenomena can be explained by “asymmetric stress division” between the components of a mixture due to their size difference; the interaction network of particles can store elastic energy, while a fluid component cannot. The importance of the bulk stress stemming from an interaction network is discussed, using a concept of self-induced elastic constraint due to connectivity. We argue that there are common features to polymer solutions, colloidal suspensions, emulsions, and possibly protein solutions. They originate from dynamic asymmetry between the components and the resulting interaction network of the slower component of a mixture, which leads to the formation of a transient gel. [S1063-651X(99)01106-X]

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I. INTRODUCTION

Phase-separation phenomena are widely observed in various kinds of condensed matter including metals, semiconductors, simple liquids, and complex fluids such as polymers, surfactants, and colloids [1]. Recently it was found [2–5] that the addition of nonabsorbing polymers to a colloidal suspension can cause phase separation due to polymer-induced depletion attraction between colloidal particles [6]. When colloids are close enough, there is an overlap of the depletion zone from which polymers are sterically excluded. The resulting unbalanced osmotic force causes attractive interactions between colloidal particles.

Depending upon the sizes of polymers and colloids and their compositions, a variety of phase separation behaviors is observed [7–10], including (i) fluid-fluid phase separation, (ii) gel-like phase separation, and (iii) phase-separation-induced crystallization. For example, when colloidal suspensions are brought shallowly into an unstable region [case (i)], the early stage of phase separation cannot be described by the standard Cahn’s linear theory and the transport coefficient apparently has a strong q dependence [8,9]. For a deep quench [case (ii)], on the other hand, the initial growth of the concentration fluctuations are 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 [7–9]. Three-dimensional microscopic observation reveals that large holes are slowly created in a transient gel during the above process [9]. Its final state can be well described by the thermodynamic phase diagram. The quite similar phenomena are also observed in phase separation of other types of colloidal suspensions [11], and also that of emulsions [12,13]. The study of these interesting phenomena just began recently, and the situation is still far from being completely understood.

Recently we found similar phenomena in the phase separation of polymer solutions [14]. This is characterized by the appearance of a transient gel, the formation of a spongelike structure, the breakup of this structure, and the resulting phase inversion. We called this type of phase separation “viscoelastic phase separation,” since viscoelastic effects play key roles in phase separation in addition to diffusion and hydrodynamic effects. “Dynamic asymmetry” and the resulting “asymmetric stress division” are the essential physical origins of viscoelastic phase separation. Thus we argued that viscoelastic phase separation should be universal to a mixture whose components have “dynamic asymmetry” [15,16]. The appearance of a transient gel is reminiscent of viscoelastic phase separation [14–17]. Thus it is quite natural to expect a common physical mechanism to these phenomena.

In this paper, we focus our attention on the similarity of phase-separation behavior among colloidal suspensions, emulsions, protein solutions, and polymer solutions, and aim at a universal description of phase separation in dynamically asymmetric mixtures. Hereafter we focus on “colloidal suspensions,” but we believe that the same model can be applied to “emulsions” and “protein solutions” after some modifications.

II. SIMILARITY AND DIFFERENCE BETWEEN COLLOIDAL SUSPENSIONS AND POLYMER SOLUTIONS

A. Interaction network: A transient gel

Colloidal suspensions and polymer solutions are similar in the sense that both are two-component liquids with a large size difference between the components. Thus they have intrinsic “dynamic asymmetry” between their components. This feature leads to their interesting rheological properties including the strong composition dependence of the viscosity, η . Despite their similarities, however, these fields have developed rather independently, partly because they are topologically quite different. This topological difference leads

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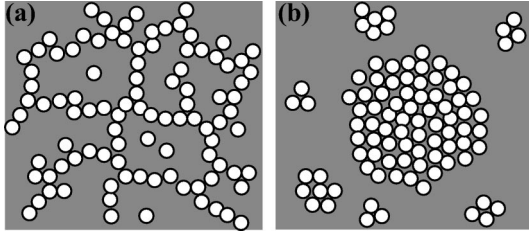


FIG. 1. Change in particle configuration from the open tenuous structure (a) to the compact structure (b) for colloidal suspensions. An open structure corresponds to a transient gel.

to a difference in the type of particle or molecular motion. Further, polymers have large internal degrees of freedom, while colloids do not. The large internal degrees of freedom allows even individual polymer chains to bear mechanical stress under strain fields. This can be an origin of asymmetric stress division. In contrast, individual colloidal particles cannot bear any stress because they are “rigid” particles (soft gel particles are exceptions). This difference makes colloidal gels much more fragile than polymer gels, which may cause crucial differences in their nonlinear rheology. Thus it is not so obvious whether phase separation of colloidal suspensions can be explained by the same mechanism as that of polymer solutions. Here we argue that the “interaction network” of colloidal particles can bear mechanical stress via topological and energetic interactions, even though individual particles cannot. Thus the essential features of phase separation in colloidal suspensions should be described by the viscoelastic model of phase separation [16].

We stress the importance of the concept of the interaction network in understanding viscoelastic phase separation of any material. Note that in a two-phase region, attractive interactions between like species win the entropic driving force of mixing. Thus components having a larger size (colloids) form their own interaction network. An important point is that the characteristic relaxation time of larger sized components is much slower than that of liquid components having a smaller size.

B. Morphological relaxation from open tenuous to compact structure

For colloid phase separation, a particle network has a rather open, or tenuous, structure initially because of the random sticking process of particles, and then slowly becomes more compact, or more dense, to lower the free energy (see Fig. 1). Note that compact aggregates are characterized by a large number of nearest neighbors. This change of particle configuration in colloidal suspensions just corresponds to a transition from a transient gel state to the final equilibrium state in the viscoelastic phase separation of polymer solutions.

For polymer solutions, we can speculate a few different situations: (i) Just after a temperature quench, a coil-globule transition takes place in individual polymers. A globule may be composed of parts of more than two chains. In this case, the junction point of a transient gel can be a globule. (ii) If a globule is composed of a single chain, on the other hand, the situation is very similar to colloidal suspensions. (iii) The other extreme is a gel similar to a chemically crosslinked gel,

which is composed of polymers without globules. We think that case (i) is the most probable. Since the situation is selected purely kinetically, however, it is dependent upon the molecular weight and concentration of polymers. Since this problem is beyond the scope of this paper, it will be discussed elsewhere.

III. TWO-FLUID MODEL OF COLLOIDAL SUSPENSIONS

A. Basic dynamic equations

On the basis of the above physical picture, we describe the basic equations for phase separation of colloidal suspension, which is a mixture of colloids c and liquid l . We coarse grain a system and do not treat colloidal particles as individual particles. After the coarse graining, the relevant order parameter is the local volume fraction of colloids, ϕ . For convenience, we introduce the effective temperature T^e as $T^e = -\Phi_p^R$ (Φ_p^R is the volume fraction of polymer in the reservoir) [4]. This allows us to map an unconventional phase diagram of colloidal suspensions, whose phase separation is induced by adding polymers instead of changing the temperature, to a conventional ϕ - T phase diagram. For simplicity, we do not explicitly treat the third component added to induce phase separation such as polymers, proteins, or surfactants; we regard the system as a quasibinary mixture, and assume that the polymer composition Φ_p affects only T^e . Then we use a “two-fluid model” [18] that can treat the motion of each component separately. This model was recently studied intensively to understand the stress-diffusion coupling [18,19] and unusual shear effects in polymer solutions [20–26].

Let $\mathbf{v}_c(\mathbf{r}, t)$ and $\mathbf{v}_l(\mathbf{r}, t)$ be the average velocities of colloids and liquid, respectively, and $\phi(\mathbf{r}, t)$ be the volume fraction of colloids at a point \mathbf{r} and time t . The average density is expressed by using density of a colloid, ρ_c , and that of a liquid, ρ_l , as $\rho(\phi) = \phi\rho_c + (1 - \phi)\rho_l$. The density difference is $\Delta\rho = \rho_c - \rho_l$. Under gravity (g is the gravitational acceleration), thus, this causes the relative motion of colloids and liquid. We represent the direction of gravitational force by a unit vector \hat{i}_z . In the following, we assume that $\Delta\rho$ is small enough to have the simple form of the incompressibility condition $\nabla \cdot \mathbf{v} = 0$.

The conservation law gives

$$\frac{\partial \phi}{\partial t} = -\nabla \cdot (\phi \mathbf{v}_c) = \nabla \cdot [(1 - \phi) \mathbf{v}_l]. \quad (1)$$

The volume average velocity \mathbf{v} is given by

$$\mathbf{v} = \phi \mathbf{v}_c + (1 - \phi) \mathbf{v}_l. \quad (2)$$

The free energy of the system F_{mix} is given by

$$F_{\text{mix}} = \int d\mathbf{r} \left[f[\phi(\mathbf{r})] + \frac{C}{2} [\nabla \phi(\mathbf{r})]^2 \right], \quad (3)$$

where $f(\phi)$ is the free energy per unit volume of a mixture with the concentration ϕ of colloids. Its time derivative can be written as

$$\begin{aligned}
\dot{F}_{mix} &= \int \left[\frac{\partial f}{\partial \phi} - C \nabla^2 \phi \right] \dot{\phi} dr \\
&= - \int \left[\frac{\partial f}{\partial \phi} - C \nabla^2 \phi \right] [\nabla \cdot (\phi \mathbf{v}_c)] dr \\
&= \int (\nabla \cdot \mathbf{\Pi}) \cdot \mathbf{v}_c dr, \tag{4}
\end{aligned}$$

$$R_a = \int dr \left[\frac{1}{2} \frac{\partial(\rho \mathbf{v}^2)}{\partial t} + \frac{1}{2} \zeta(\phi) (\mathbf{v}_c - \mathbf{v}_l)^2 + W_l^{(nl)} - p \nabla \cdot \mathbf{v} + (\nabla \cdot \mathbf{\Pi}) \cdot \mathbf{v}_c - (\nabla \cdot \boldsymbol{\sigma}_c + \mathbf{F}_c) \cdot \mathbf{v}_c - \mathbf{F}_l \cdot \mathbf{v}_l \right], \tag{5}$$

where $\zeta(\phi)$ is a friction coefficient per unit volume, and $\zeta(\phi) = \eta_l / \xi_H(\phi)$ [$\xi_H(\phi)$ is the hydrodynamic screening length]. The friction term is the local part of dissipation [27], while $W_l^{(nl)}$ represents its nonlocal parts: $W_l^{(nl)} = \eta_l \nabla \mathbf{v} : \nabla \mathbf{v}$. $\boldsymbol{\sigma}_c$ is the mechanical stress acting on colloidal particles. Thus the second line of Eq. (5) represents the work done by the thermodynamic and mechanical forces acting on the colloids and liquid. In the above, the term containing the pressure p is added to guarantee the incompressibility condition

$$\nabla \cdot \mathbf{v} = 0. \tag{6}$$

The condition that the functional derivatives of the Rayleighian with respect to \mathbf{v}_c and \mathbf{v}_l be zero gives the following equations of motion:

$$\begin{aligned}
\rho \frac{\partial(\phi \mathbf{v}_c)}{\partial t} &= -\nabla \cdot \mathbf{\Pi} - \nabla \cdot \boldsymbol{\sigma}_c - \zeta(\mathbf{v}_c - \mathbf{v}_l) \\
&\quad + \phi \nabla p + \phi \eta_l \nabla^2 \mathbf{v} + \mathbf{F}_c, \tag{7}
\end{aligned}$$

$$\begin{aligned}
\rho \frac{\partial[(1-\phi)\mathbf{v}_l]}{\partial t} &= \zeta(\mathbf{v}_c - \mathbf{v}_l) + (1-\phi) \nabla p \\
&\quad + (1-\phi) \eta_l \nabla^2 \mathbf{v} + \mathbf{F}_l. \tag{8}
\end{aligned}$$

Thus the basic kinetic equations are given by

$$\frac{\partial \phi}{\partial t} = -\nabla \cdot (\phi \mathbf{v}) + \nabla \cdot \frac{\phi(1-\phi)^2}{\zeta_R(\phi)} [\nabla \cdot \mathbf{\Pi} - \nabla \cdot \boldsymbol{\sigma}_c - \Delta \rho g \mathbf{i}_z], \tag{9}$$

$$\mathbf{v}_c - \mathbf{v}_l = -\frac{1-\phi}{\zeta_R(\phi)} [\nabla \cdot \mathbf{\Pi} - \nabla \cdot \boldsymbol{\sigma}_c - \Delta \rho g \mathbf{i}_z], \tag{10}$$

$$\rho \frac{\partial \mathbf{v}}{\partial t} = -\nabla \cdot \mathbf{\Pi} - \nabla \cdot \boldsymbol{\sigma}_c + \nabla p + \eta_l \nabla^2 \mathbf{v} + \rho(\phi) g \mathbf{i}_z, \tag{11}$$

where ζ_R is the effective friction constant after coarse graining [28]. The derivation of ζ_R requires the relevant microscopic theory, which can properly deal with hydrodynamic interactions between colloids. This problem, although it is important, remains for the future.

where $\nabla \cdot \mathbf{\Pi} = \phi \nabla [(\partial f / \partial \phi) - C \nabla^2 \phi]$, and $\mathbf{\Pi}$ is the osmotic tensor. $F_\phi = -\nabla \cdot \mathbf{\Pi}$ is the thermodynamic force conjugate to the order parameter ϕ .

Here we also consider the effects of gravitational force \mathbf{F}_i , which directly acts on the component i ($i=c$ and l): $\mathbf{F}_i = \rho_i \phi_i g \mathbf{i}_z$. Then, the Rayleighian to be minimized is

$\boldsymbol{\sigma}_c$ is the stress tensor, which is, in general, given by the constitutive equation of colloidal suspensions. Thus we need a knowledge of the constitutive equation relevant to the rheology of colloidal suspensions. Unfortunately, however, the constitutive equation of colloidal suspensions is not so well established compared to that of polymer solutions. We argue that the relevant velocity describing the rheology in colloidal suspensions is the colloidal velocity \mathbf{v}_c . This is justified by the fact that although the surrounding liquid produces hydrodynamic interactions between colloidal particles, the liquid cannot bear any mechanical stress on a long time scale, and only colloidal particles can bear it via topological and energetic interactions. Then we argue that the rheology of colloidal suspensions, in which we are interested, can basically be described by Maxwell-type relaxation as in the case of polymer solutions, although there are some essential differences between colloidal suspensions and polymer solutions, as will be discussed below. This is supported by various experimental evidence of such relaxation phenomena in colloidal suspensions [2]. Further, the theory of the dynamics of Brownian suspensions based on the mode-coupling closure of a system of generalized hydrodynamic equations [29–31] suggests the relevance of a Maxwell-type relaxation model to the rheology of Brownian suspensions. The Maxwell-type relaxation for the shear and bulk relaxation modulus can be written as $G_j(\phi, t) = G_j(\phi) \exp[-t/\tau_j(\phi)]$ (τ_j is the stress relaxation time). $j=S$ stands for shear, and $j=B$ for bulk. Here $G_j[\phi(\mathbf{r})]$ is the local elastic plateau modulus at \mathbf{r} (after coarse graining). $\boldsymbol{\sigma}_c$ is composed of shear stress $\boldsymbol{\sigma}_c^S$ and bulk stress $\boldsymbol{\sigma}_c^B$ as $\boldsymbol{\sigma}_c = \boldsymbol{\sigma}_c^S + \boldsymbol{\sigma}_c^B$. Then $\boldsymbol{\sigma}_c^j$ obeys the following upper-convective equation:

$$\begin{aligned}
\frac{\partial \boldsymbol{\sigma}_c^j}{\partial t} + (\mathbf{v}_c \cdot \nabla) \boldsymbol{\sigma}_c^j &= \mathbf{D} \cdot \boldsymbol{\sigma}_c^j + \boldsymbol{\sigma}_c^j \cdot \mathbf{D}^T - \frac{\boldsymbol{\sigma}_c^j}{\tau_j(\phi)} \\
&\quad + G_j(\phi) (\mathbf{D} + \mathbf{D}^T), \tag{12}
\end{aligned}$$

where $\mathbf{D} = \nabla \mathbf{v}_c$ is the gradient tensor of the colloid velocity \mathbf{v}_c . Finally, we redefine $\boldsymbol{\sigma}_c^S$ as $\boldsymbol{\sigma}_c^S = \boldsymbol{\sigma}_c^S - (1/d) \text{Tr}(\boldsymbol{\sigma}_c^S) \mathbf{I}$, while $\boldsymbol{\sigma}_c^B$ as $\boldsymbol{\sigma}_c^B = (1/d) \text{Tr}(\boldsymbol{\sigma}_c^B) \mathbf{I}$.

If we neglect the transportation and rotation of the stress tensor $\boldsymbol{\sigma}_c$, it can then be written as

$$\boldsymbol{\sigma}_c = \int dt' \left[G_B \exp\left(\frac{t-t'}{\tau_B}\right) \nabla \cdot \mathbf{v}_c + G_S \exp\left(\frac{t-t'}{\tau_S}\right) \left(\frac{\partial v_c^j}{\partial x_i} + \frac{\partial v_c^i}{\partial x_j} - \frac{2}{3} (\nabla \cdot \mathbf{v}_c) \delta_{ij} \right) \right]. \quad (13)$$

The constitutive equation is well established for shear deformation, but not for volume deformation. Further, it should be stressed that there is no *reliable* theory for the constitutive equation in a two-phase region. Thus we need a more careful consideration of the latter, which will be described in Sec. IV B 1. We propose that Eqs. (9)–(12) are the basic equations describing phase separation or critical dynamics of colloidal suspensions.

B. Beyond the above model

The above phenomenological model has a crucial deficiency: The constitutive equation shown above can describe colloidal suspensions in a one-phase region, but cannot do so in a two-phase region. For example, it cannot describe the formation of a transient gel and the resulting temporal change in the modulus, $G_j(\phi)$. This process should be described by a microscopic model, which deals with colloids as individual particles. This situation is similar to that of a polymer solution. To describe these phenomena, thus, we need a mesoscopic or hybrid model which can bridge between a microscopic model of colloidal suspensions and the above phenomenological one. Further studies in this direction are highly desirable.

Here we propose a simple phenomenological description of the formation of a transient gel on the basis of an intuitive physical picture. The important points of a transient gel are summarized as follows: (i) A transient gel is formed immediately after a temperature quench when ϕ is larger than a certain threshold ϕ_{tg} . (ii) It is easily broken under the deformation, which stretches an energetic bond. Once the network is broken, there is no elastic energy stored there.

Fact (ii) is a unique feature of transient gels. This causes a crucial difference between (chemically cross-linked) permanent gels and transient gels: The former remains elastic even when the stress-strain relation is not linear, whereas in the latter the linearity (the Hooke's law) ceases when the deformations are no longer elastic. In our previous study of viscoelastic phase separation using numerical simulation [17], in order to express fact (ii) on a phenomenological level, we chose a special composition dependence of G_B as $G_B(\phi) = G_B^*(\phi) \theta(\phi - \phi_{\text{th}})$, where G_B^* is a smooth function of ϕ [e.g., $G_B(\phi) \propto \phi$], θ is a step function, and ϕ_{th} is a threshold composition, below which a transient gel is broken. We supposed that ϕ_{th} is close to an initial homogeneous composition, ϕ_0 [17]. Although this choice of $G_B(\phi)$ is a bit artificial and not supported by firm theory, it may be worth explaining why we made such an assumption. The reasons are as follows: (a) We conjecture that the network is already fully stretched at the beginning since it is formed under strong attractive interactions between colloids and tries to shrink. Thus, it should easily be broken whenever it is strongly stretched to a further degree. This can be understood naturally by the help of the following spring model. We suppose the attractive interaction between colloids or segments

to be E . Then the bond probability is given by $\exp[-(E - k\Delta x^2/2)/k_B T]$, where k is a spring constant and Δx is an increment of the spring length from its natural one. The relation $\phi_{\text{th}} \sim \phi_0$ means that $E - k\Delta x^2/2 \sim k_B T$ at ϕ_0 . For larger E or smaller k , ϕ_{th} is lower than the initial composition ϕ_0 . This deviation of ϕ_{th} from the initial composition ϕ_0 may be less significant for colloidal suspensions than for polymer solutions, because of the more fragile nature of colloidal gels. The fragile nature may come from large k . (b) A nucleation of a liquid-rich phase is thermodynamically favored. Thus the breakup of the network is helped by the formation of a liquid-rich phase, and vice versa.

Further, the above functional form of $G_B(\phi)$ can also express fact (i) qualitatively, since concentration fluctuations immediately switch on the bulk stress. In this way, $G_B(\phi)$ can express the sudden change of G to that of a transient gel, G_{tg} , after a quench (see Fig. 4) on a qualitative level. However, it is evidently artificial, and the relevant microscopic theory of the transient-gel formation is highly desirable. The physical origin of the bulk stress will be considered in more detail in Sec. IV.

IV. UNIVERSALITY OF A TRANSIENT GEL AND ROLES OF BULK MODULUS: CONCEPT OF ‘‘TOPOLOGICAL CONSTRAINT FOR DIFFUSION’’

In the above, we introduced the bulk stress $\boldsymbol{\sigma}_c^B$. Below, we explain why the bulk stress is necessary to describe the phase-separation kinetics and critical dynamics of colloidal suspensions.

A. Universality of a transient gel

Here we point out a special feature of phase separation in *dynamically asymmetric mixtures*. It is the formation of a transient gel just after a quench into a two-phase region. A transient gel is the most direct appearance of the ‘‘interaction network,’’ which is originated from strong attractive interactions between like species that may universally exist in the two-phase region of an dynamically asymmetric mixture. Actually, it was ‘‘commonly’’ observed in phase separation of polymer solutions [14], polymer blends [15], colloidal suspensions [7–9], and emulsions [13]. Thus the appearance of a transient gel should be quite universal for phase separation of dynamically asymmetric mixtures [16].

In polymer solutions, the relaxation time τ was conventionally believed to be the reptation time under purely topological interactions [20,24–26,32]. As proposed by us recently [16,17], however, this should be the relaxation time of an interaction network of polymers (or a transient gel) itself under a poor-solvent condition. Similarly, the slow dynamics of colloidal suspensions should be due to both topological and energetic origins. Although colloidal particles have no internal degrees of freedom in contrast to polymers, the motion of particles is affected by both topological (cage effects) and energetic traps due to attractive interactions. In colloidal

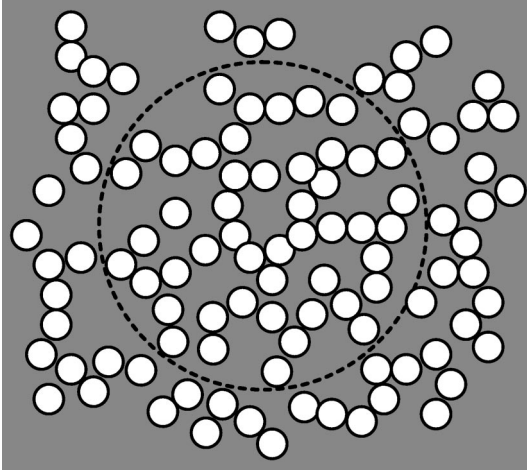


FIG. 2. Schematic figure explaining the concepts of an interaction network (transient gel) and a bulk relaxation modulus. The dashed circle represents a membrane through which liquid molecules pass where colloidal particles (white balls) cannot. When we try to reduce or increase the local volume surrounded by the membrane at a speed faster than the relaxation rate of the bulk modulus, the membrane “feels” not only the osmotic stress but also the bulk mechanical stress. There are three physical origins of the bulk mechanical stress for colloidal suspensions: (i) the elasticity of the interaction network under the constraint of connectivity, (ii) a topological constraint for particle motions, which originates from the connectivity of the interaction network, and (iii) a topological constraint due to the excluded-volume effect of individual particles and hydrodynamic interactions. Origin (iii) plays few roles in polymer solutions. The necessity of cooperative motion of particles causes slow dynamics (large τ_B and τ_S) especially near a glass transition.

phase separation, thus, τ should also be the characteristic relaxation time of the interaction network itself (a transient gel for a deep quench). Note that τ is formally given by $\tau(\phi, E) = \eta(\phi, E)/G(\phi, E)$, where E is the well depth of the depletion attraction, and $E/k_B T = -(3R\Phi_p/2R_p)$ (R is the radius of colloids and R_p is the effective radius of polymers).

B. Why is the interaction network responsible for bulk relaxation stress? Topological constraint

Figure 2 schematically shows the situation of a transient gel formed in a colloidal suspension. When we try to reduce or increase the volume occupied by some colloidal particles forming an interaction network by using a membrane through which only liquid molecules can pass and colloids cannot, the membrane should “feel” not only the osmotic pressure but also the bulk mechanical stress, when it moves faster than the characteristic relaxation rate τ_B . This originates from “elasticity of network” or “topological constraint for diffusion;” that is, the network has to move in keeping with its connectivity. It is easy to imagine that this process, which is characterized by τ_B , is very slow. This will be explained in more detail below.

Before discussing a situation in a two-phase region, it is worth noting the difference in longitudinal viscosity between polymer solutions and colloidal suspensions in a one-phase region. Reptation theory [33] tells us that the bulk stress originating from polymers decays very quickly in polymer

solutions in a “good-solvent” condition. Thus we need not consider bulk stress due to polymers, as far as we consider slow dynamics. For colloidal particles, it is known that there can exist a longitudinal viscosity even for a homogeneous system in a one-phase region [29–31]. This originates from “topological constraint” via repulsive interactions and/or hydrodynamic interactions.

Here we consider both similarities and essential differences among permanent gels, polymer solutions, and colloidal suspensions in a two-phase region, and intuitively explain why the interaction network is responsible for bulk relaxation stress. For colloidal suspensions, there can be three physical origins of the bulk mechanical stress (see Fig. 2): (i) The elasticity of interaction network itself. (ii) The topological constraint for the motion of particles coming from the connectivity of the interaction network. (iii) The topological constraint for the motion of individual particles due to excluded-volume effects and strong hydrodynamic interactions. Note that origins (i) and (ii) also exist for polymer solutions and gels, while origin (iii) does not.

1. Elasticity of network

The elasticity effect can naturally be explained by a conventional theory of elasticity, if we pay special attention to the constraint coming from the connectivity of an elastic network. Suppose that we have an infinite percolated network. Now the interaction network far from equilibrium tries to decrease its effective volume in order to lower the free energy. However, any nonuniform deformation of the network costs the elastic energy. This causes bulk mechanical stress. What is behind this intuitive explanation is a self-induced constraint due to the connectivity of the elastic network. *This constraint is mathematically equivalent to the following boundary condition for a finite system: the network velocity \mathbf{v}_n at the boundary is zero.* This is automatically satisfied whenever the network is interconnected and not isolated. Note that osmotic stress, or diffusion, tries to create and enhance inhomogeneity during phase separation. Thus this bulk stress effect against diffusion should universally exist whenever the interaction network exists during phase separation. This can be explained by the following force density acting on the elastic network:

$$F_n = -\nabla \cdot \Pi + \nabla \cdot \sigma. \quad (14)$$

A gel upon shrinking or swelling from a relaxed state, or a transient gel, always tries to avoid deformation. In other words, a transient gel is in a state of marginal balance where the osmotic force tries to reduce the effective network volume by diffusion to lower the free energy, but the bulk stress force tries to cancel it. Accordingly, the total net force acting on the network is strongly suppressed. This is an effect of the connectivity of the interaction network, as explained above. This picture intuitively explains the role of bulk stress. The above argument also justifies the method used in Eqs. (12) and (13) to introduce bulk; that is, we should take the natural length of a spring as the length of a spring just after the formation of a transient gel. It is the connectivity that prevents a network from collapsing.

There are two types of pattern evolution, depending upon a size of a (transient) gel: (a) to shrink homogeneously, or (b)

to shrink inhomogeneously under the strong influence of mechanical stress. Process (a) may occur only when a system size L is so small that the characteristic diffusion time $\tau_D = L^2/D$ (D is a diffusion constant) is shorter than the characteristic bulk mechanical relaxation time τ_B . In other words, the viscoelastic length ξ_{ve} is larger than L [34]. This condition ensures that a gel is free from constraint from interconnectivity. In this case, the mechanical instability (or nucleation) may be avoided. This means that there is a critical size of a gel, below which the gel can shrink rather homogeneously without mechanical instability. It is interesting to check this experimentally for chemically cross-linked permanent gels.

In all other cases, process (b), or mechanical instability, inevitably occur. The competition between osmotic stress and bulk stress plays a key role in pattern evolution during phase separation. The elasticity of the network does not favor any deformation. Thus the only way to achieve deformation during phase separation is to localize the deformation at the interface (or boundary) of domains. This leads to a suppression of the normal diffusion. A diffusion mode whose wavelength is shorter than ξ_{ve} is always strongly suppressed. Thus the diffusion process must accompany the volume shrinking of a more elastic phase to avoid the inhomogeneous deformation of a network. The localization of bulk stress at the periphery of a more elastic phase and the volume shrinking are confirmed in our simulation [17].

The local stretching caused by the shrinking of a transient gel leads to a stress concentration on the stretched part of a domain, and leads to its breakup, which further enhances the inhomogeneous stress distribution. Thus the process of phase separation accompanying the shrinking of interaction network can be viewed as the *mechanical instability of a network formed by nonlinear springs*.

2. Topological constraint for diffusion due to the connectivity of particles

Origin (ii) stems from the topological constraint for diffusion. This cannot be distinguished from origin (i) for polymer solutions. The connectivity of colloidal particles gives an additional constraint for the motion of particles, due to their excluded-volume effects. Particles must move in keeping with a network structure, which produces not only the elasticity effect [origin (i)], but also the topological constraint for diffusion due to the excluded-volume effects of connected particles and many-body interactions. The latter also produces bulk stress in addition to the former; in other words, it slows down the diffusion of particles forming a chain or network, since the reconfiguration of the network is sometimes required for its shrinking. This effect has not been properly recognized so far. We argue that it may play a crucial role in viscoelastic phase separation for colloidal suspensions. This effect can also be included naturally in the bulk stress, although we need a more quantitative theory to describe this effect on the microscopic basis. Since colloidal gels are not so deformable as polymer gels, origin (ii) may play a more important role than origin (i) for colloidal suspensions.

3. Excluded-volume effects and hydrodynamic interactions

Origin (iii) is a unique feature of colloids, which has strong excluded-volume effects and hydrodynamic interactions.

Even without a transient gel, this plays an important role in slow dynamics for large ϕ . Actually, the glassy behavior of colloidal suspensions is due to these effects. We believe that they can also be included into the bulk stress.

C. Roles of bulk stress

The interaction network can bear bulk stress against its volume deformation $\nabla \cdot \mathbf{v}_c$, which we believe dominates a transient gel stage of viscoelastic phase separation [16]. The bulk relaxation modulus, which produces stress fields under a coupling to the volume deformation $\nabla \cdot \mathbf{v}_c$. Since $\partial\phi/\partial t = -\nabla \cdot (\phi \mathbf{v}_c)$, it tries to suppress the diffusion when the diffusion rate exceeds the characteristic relaxation time τ_B of the interaction network for volume deformation. In other words, the topological-constraint effect discussed above has the effect of decreasing the diffusion constant of network-forming components. The bulk relaxation modulus is responsible for the long incubation time of macroscopic phase separation and the volume shrinking of the more viscoelastic phase during phase separation [17]. Thus it plays the most essential role in viscoelastic phase separation [16].

D. Bulk stress or the ϕ -dependent diffusion constant

Here we consider a naive problem, namely, whether we should include the above effects into the ϕ dependence of $\zeta(\phi)$ [35] or into the bulk stress [16]. Both apparently cause similar effects [16]. In the spirit of a two-fluid model, it is more natural to include the effects of origins (i) and (ii), as the bulk stress rather than as the ϕ dependence of ζ . Usually, the friction between colloidal particles and liquid per volume, ζ , should simply depend upon ϕ , reflecting the probability of contacts between colloids and liquid per volume and the hydrodynamic interactions. In a two-fluid model of polymer solutions, for example, even the effect of the chain connectivity of polymer itself (entanglement effects) is included in the stress tensor via the constitutive equation of polymer solution. All the topological information can, thus, be expressed by the mechanical stress term in a two-fluid model.

Although we may put the topological information, e.g., the connectivity of the interaction network of colloidal particles, into the friction term, there are two serious fundamental problems for such an approach: (i) It is not straightforward to include the dynamic effect into the diffusion constant. Note that the network tries to suppress diffusion only when the deformation rate exceeds τ_B . (ii) The friction term is introduced as a local term [see Eq. (5)], but the connectivity produces ‘‘nonlocal effects.’’ Thus we believe that our approach, based on the bulk stress, is physically more natural than an approach based on the ϕ -dependent diffusion constant to express the relaxational nature of a transient gel [origins (i)–(iii)].

V. PHASE SEPARATION

In this section, we neglect the effects of gravity ($\Delta\rho=0$ or $g=0$) and consider only viscoelastic effects.

A. Phase-separation kinetics under a shallow quench: A viscous fluid regime

First we consider viscoelastic effects for a case of a shallow quench ($T > T_c > T_{lg}$), where a transient gel is never

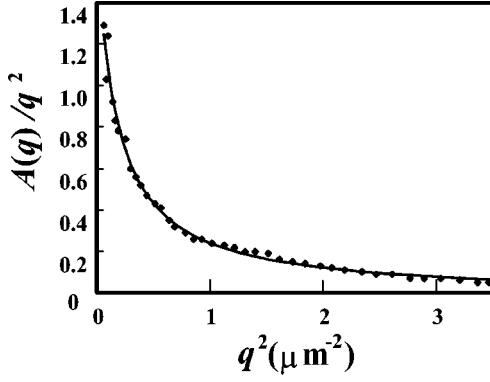


FIG. 3. Fitting of Eq. (16) to the experimentally observed growth rate of the concentration fluctuations, $A(q)$. The solid curve represents a theoretical curve. The data were taken from Ref. [8].

formed and the characteristic deformation rate is slower than the viscoelastic relaxation rate ($\sim 1/\tau$). Here we assume $\tau_B = \tau_S = \tau$ just for simplicity. We do not consider the difference in the relaxation time between shear and bulk stress. Using the relation $\nabla \cdot \mathbf{v}_c = -(1/\phi)(\partial\phi/\partial t)$, we obtain the linearized equation for $Z_q = [\nabla \cdot \nabla \cdot \boldsymbol{\sigma}_c]_q$:

$$\frac{\partial Z_q}{\partial t} \cong -\frac{Z_q}{\tau} + \frac{2G}{\phi} q^2 \frac{\partial \phi_q}{\partial t},$$

where $G = G_B + \frac{4}{3}G_S$. Here ϕ_q is the Fourier component of the deviation from the initial composition ϕ_0 , and it obeys, to linear order [23,36]

$$\frac{\partial \phi_q(t)}{\partial t} \cong -\Gamma_q \phi_q(t) - \frac{2LGq^2}{\phi^2} \int_0^t dt' e^{-(t-t')/\tau} \frac{\partial \phi_q(t')}{\partial t'}. \quad (15)$$

Here we use $f = k_B T [(r_0/2)(\phi - \phi_c)^2 + (u/4)(\phi - \phi_c)^4]$. This form of the free energy is reasonable as long as we concern only a shallow quench near a critical point. $\Gamma_q = Lq^2(r_\phi + Cq^2)$, where $L = \phi^2(1 - \phi)^2/\zeta(\phi)$, is the decay rate in the absence of the viscoelastic coupling. $r_\phi = r_0 + 3u(\phi_0 - \phi_c)^2$, where $r_0 = a(T^e - T_c^e)$ (a is a positive constant) and T_c^e and ϕ_c are the critical temperature and composition, respectively. The correlation length is given by $\xi = [C/|r_\phi|]^{1/2}$. For a case when the time scale of ϕ_q is slower than τ , we can set $\partial \phi_q(t')/\partial t' = \partial \phi_q(t)/\partial t$ in Eq. (15) and, thus, the growth rate of ϕ_q is given by

$$A(q) = L|r_\phi|q^2(1 - \xi^2q^2)/(1 + \xi_{ve}^2q^2), \quad (16)$$

where $\xi_{ve} = (2\eta L/\phi^2)^{1/2}$ is the so-called viscoelastic length [18,23,24]. This ξ_{ve} gives us the length scale above which dynamics is dominated by diffusion and below which by viscoelastic effects. Without viscoelastic coupling, the relation $A(q) = L|r_\phi|q^2(1 - \xi^2q^2)$ should hold as Cahn's linear theory [1] predicts. As shown in Fig. 3, the above relation [Eq. (16)] well explains the unusual q -dependence of $A(q)$ experimentally observed in colloid phase separation [8], with $\xi_{ve} \sim 10\xi \sim 2.4 \mu\text{m}$. This suggests the relevance of our model to colloidal phase separation, or the importance of viscoelastic effects.

B. Phase-separation kinetics under a deep quench: Transient gel regime

Next we consider phase separation accompanying the formation of a transient gel for a deep quench. If we consider only the topological effects, rheological theories of colloidal suspensions [37] without energetic interactions tell us that $\eta \sim \eta_l(1 - \phi^*)(1 - \phi/\phi^*)^{-2}$, where ϕ^* is a critical volume fraction separating a fluid and a glassy state, and, thus, the viscoelastic length ξ_{ve} can become much longer than ξ only for large ϕ near $\phi^* \sim 0.58$. As mentioned above, however, we also have to consider energetic interactions between particles at the same time [16]. Their effects change the above argument even qualitatively, and lead to a completely different physical picture. With an increase in E , the population of bonded colloidal particles and the lifetime of bonds both increase rapidly in proportion to $\exp(E/k_B T)$. This leads to the formation of a transient gel for $\phi > \phi_{tg}^e$ under a deep quench ($T^e < T_{tg}^e$, or $E > E_{tg}$). Here ϕ_{tg}^e , T_{tg}^e , and E_{tg} are, respectively, the threshold values of composition, effective temperature, and E that separate a liquid and transient gel state.

The ϕ_{tg}^e , T_{tg}^e , and E_{tg} can be estimated as follows. According to the diffusion-limited cluster aggregation (DLCA) model [38], the mean cluster size scales as $s \sim \phi t/\tau_R$, where $\tau_R \sim (R^2/D_R)$ ($D_R = k_B T/6\pi\eta R$) and the radius of gyration of a cluster as $R_{cluster}/R \sim s^{1/d_f}$, where d_f (~ 1.8) is the fractal dimension. The gelation occurs when $\phi(R_{cluster}/R)^{3-d_f} \sim 1$. The gel time is then given by $\tau_{gel} \sim \tau_R \phi^{-3/(3-d_f)}$. Whether a transient gel is formed or not is dependent upon the competition between cluster growth and phase separation. ϕ_{tg} can, thus, be estimated from the relation $\tau_{gel} \sim \tau_\xi$, where $\tau_\xi = \xi^2/D_\xi$ ($D_\xi = k_B T/6\pi\eta_l\xi$) is the characteristic time of composition fluctuations. It is worth noting that Hayward, Heermann, and Binder [39] studied the problem of dynamic percolation induced by phase separation of a short-range Ising lattice gas model, and estimated the dynamic percolation threshold as $0.16 < \phi_{tg} < 0.2$ by a Monte Carlo analysis, which is close to the percolation threshold of randomly packed spheres ($\phi_p \sim 0.16$). This ϕ_p is the upper bound of ϕ_{tg} , since the relation $\phi_{tg} \sim \phi_p$ means instantaneous gelation ($\tau_{gel} \sim \tau_R$). The T_{tg}^e (E_{tg}^e) is, on the other hand, estimated from the relation $-E_{tg}^e/k_B T \sim 1$ as $T_{tg}^e \sim -2R_p/3R\alpha(\phi)$, where $\alpha(\phi)$ is the volume fraction of free volume (see Refs. [4,5] on its functional form), and a decreasing function of ϕ .

C. Classification of phase-separation types

Here we discuss the possible types of phase separation, using the above estimation of ϕ_{tg} and T_{tg}^e . Figure 4 schematically explains how the way of phase separation depends upon the initial composition and the quench depth. If we bring a system into a transient gel region from a one-phase region, the plateau modulus of a system changes drastically from $G(\phi)$ to $G_{tg}(\phi)$, as shown in Fig. 4, reflecting the formation of a transient gel. This picture, which is supported by the direct rheological measurements of phase-separating emulsions [13], explains the transition from apparently ordinary fluid-fluid phase separation to a transient gel behavior around T_{tg}^e [7–9]. It should be noted that a similar transitional behavior is observed in polymer solutions [14]. Such a

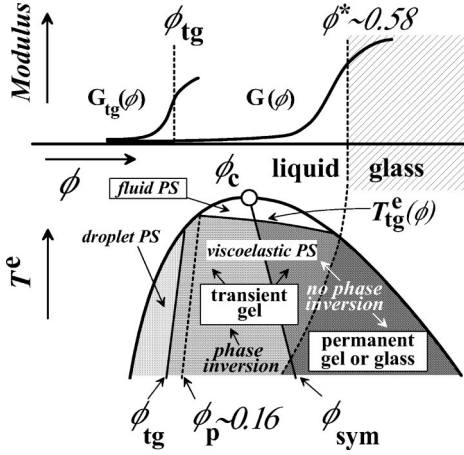


FIG. 4. Schematic equilibrium and transient modulus (an upper figure), and the corresponding dynamic phase diagram of a colloidal suspension (a lower figure) predicted by our model. PS stands for phase separation. The upper figure represents a rapid change in the mechanical properties of a mixture, which is induced by the formation of a transient gel after a deep quench.

deep quench induces a large jump in ξ_{ve} within a time scale of τ_{gel} , and ξ_{ve} can be quite macroscopic after the formation of a transient gel; in other words, the elastic effects are switched on. In a permanent gel, for example, it is known that when the bulk osmotic modulus K_{os} is negative but $K_{os} + G_B > 0$, only a single macroscopic mode becomes unstable against homogeneous volume change without enhancement of small-scale fluctuations [40]. This is because in such a gel $\xi_{ve} \sim L$ (L is the macroscopic size of a gel). We argue that the characteristic length of phase separation of a transient gel should be characterized by ξ_{ve} , which gives the average distance between nuclei of the dilute phase. This causes spatially correlated nucleation, which explains the existence of a peak at a finite wave number in the scattering function [14,15].

This leads to the following picture of phase separation: Initially spinodal decomposition proceeds by diffusion; however, it cannot proceed any more after the formation of a transient gel because its way of decomposition with the length scale of $\sim \xi$ costs too much elastic energy; in other words, the spinodal line is largely shifted down to T^e satisfying $K_{os}(T^e) + G_{tg}^B = 0$ (G_{tg}^B is the bulk modulus of a transient gel) from that satisfying $K_{os}(T^e) = 0$. This conclusion can be directly obtained from our dynamic equation [Eq. (9)]. When the diffusion rate ($\phi_0^{-1} \partial \phi / \partial t \cong -\nabla \cdot \mathbf{v}_c$) is faster than $1/\tau_B$ and $1/\tau_S$,

$$\begin{aligned} \sigma_c^{ij} \sim & G_B \int dt' \nabla \cdot \mathbf{v}_c \\ & + G_S \int dt' \left(\partial_i v_c^j + \partial_j v_c^i - \frac{2}{3} (\nabla \cdot \mathbf{v}_c) \delta_{ij} \right). \end{aligned}$$

Using the relation $\nabla \cdot \mathbf{v}_c \cong -\phi_0^{-1} \partial \phi / \partial t$, we obtain

$$\nabla \cdot \nabla \cdot \sigma_c \sim - \left(G_B + \frac{4}{3} G_S \right) \phi_0^{-1} \nabla^2 \phi = - \frac{G}{\phi_0} \nabla^2 \phi.$$

On the other hand,

$$\nabla \cdot \nabla \cdot \Pi \sim \phi_0 r_0 \nabla^2 \phi - \phi_0 C \nabla^2 \nabla^2 \phi + \dots$$

In the linear regime, thus,

$$\nabla \cdot \nabla \cdot [\Pi - \sigma_c] \sim \phi_0^{-1} [(r_\phi \phi_0^2 + G) - \phi_0^2 C \nabla^2] \nabla^2 \phi. \quad (17)$$

Since $K_{os} \sim r_\phi \phi_0^2$, the spinodal line is given by the condition $K_{os} + G = 0$. Phase separation initially tries to proceed as spinodal decomposition since $K_{os} < 0$, but immediately after the quench elastic effects come into play, reflecting the formation of a transient gel. In this way, the viscoelastic effects switch the way of phase separation from spinodal decomposition (SD) to nucleation and growth (NG). The liquid-rich phase appears by the NG mechanism and grows with time, even in the unstable region of the equilibrium phase diagram ($K_{os} < 0$). The appearance of a dilute phase as a hole in a transient gel of a colloidal suspension was actually observed with optical microscopy [9], which supports this picture.

It is not clear whether the condition of absolute instability $K_{os} + G < 0$ is realized for a deep quench or not: If G increases more rapidly than $|K_{os}|$ upon cooling, such an unstable situation may never be realized.

It is worth mentioning here that the above condition of instability has a very different meaning from that for permanent gels, reflecting the difference between transient and permanent gels. Note that a transient gel is formed by phase separation itself, and G is determined by the ‘‘dynamics’’ of deformation during phase separation.

VI. GEL COLLAPSING UNDER GRAVITY

Next we consider the phenomenon of a gel collapsing under gravity. This is important when $\Delta \rho \neq 0$. For usual colloidal suspensions $\Delta \rho > 0$, while for oil-in-water emulsions $\Delta \rho < 0$.

Note that the major effects of gravity appear in Eq. (11), which directly produces the hydrodynamic transport of material. The gravitational term in Eq. (9), which affects the diffusion via the composition-dependent diffusion constant, is negligible. In the initial stage, the majority phase is the colloid-rich phase that forms a transient gel. However, $G_{tg}(\phi)$ relaxes to $G(\phi)$ slowly (see Fig. 4). The lifetime of a transient gel can roughly be estimated as $\tau_r \sim \xi_{ve}^2 / D_\xi$. Since ξ_{ve} increases with an increase in Φ_p or E , τ_r should increase with an increase in a quench depth (or Φ_p). This is consistent with experimental results [8,9]. After τ_r , a transient gel state starts to lose its elastic nature, since the diffusional effects start to win over the viscoelastic effects. Thus a transient gel can no longer support the gravitational force $\Delta \rho g \hat{z}$. This leads to the collapse of the gel. In other words, the viscoelastic relaxation of a transient gel can be the origin of the gel-collapsing phenomena. After the relaxation, the volume fraction of the colloid-rich phase should simply be determined by the equilibrium phase diagram.

The collapsing process of gel may be simulated by solving our kinetic equations, including gravity effects [Eqs. (9)–(11)], numerically. This is now under investigation.

For $\phi_{tg} < \phi < \phi_{sym}$ (ϕ_{sym} is a symmetric composition where the two phases have an equal volume), thus, phase inversion takes place during phase separation, while for ϕ

$> \phi_{\text{sym}}$ it does not (see Fig. 4). For $\phi < \phi_{\text{tg}}$, on the other hand, a system cannot form an infinite network and, thus, isolated, compact spherical droplets are immediately formed by SD. In this case, there is no mechanism preventing colloids from falling down under the gravity, and sedimentation of drops begins immediately after the formation of droplets. We point out that the above case of $\phi_{\text{tg}} < \phi < \phi_{\text{sym}}$ the most drastic gel collapsing should be observed because there is a phase inversion during the phase separation.

VII. SHEAR-INDUCED COMPOSITION FLUCTUATIONS AND DEMIXING

Finally, we point out that shear-induced composition fluctuations and demixing (or flocculation) [2] may occur by a mechanism similar to that of polymer solutions [20,24–26]. Shear-induced composition fluctuations are induced by the increase of η with ϕ , which is commonly observed in colloidal suspensions. Shear-induced demixing, on the other hand, requires a certain mechanism to store elastic energy under shear. This causes the modification of the effective free energy functional that includes dynamic effects and leads to the shift of a phase diagram. This phenomenon is known as “shear-induced demixing” in polymer solutions under shear [20]. The mechanism to store elastic energy under shear is essentially different between colloidal suspensions and polymer solutions. The shear effects may be less pronounced for colloidal suspensions than for polymer solutions.

In the following, we briefly discuss shear effects on colloidal suspensions [41] on an intuitive level. The more detailed discussion, including the effects of long-range hydrodynamic interactions, will be presented elsewhere.

A. Linear regime

Under thermal fluctuations, local shear stress is stored inhomogeneously due to the strong nonlinear and asymmetric dependence of $G_S(\phi)$ on ϕ . Note that the stress relevant to a shear problem is the “shear” stress σ_c^S . Linear theory tells us that this enhances composition fluctuations along the extension axis of the flow, since this stress moves colloidal particles toward a more concentrated region.

This linear Newtonian regime is given by the condition $\dot{\gamma}\tau_S \leq 1$, where $\dot{\gamma}$ is the shear rate. Under this condition, σ_c is given as

$$\sigma_c \sim \eta(\phi)(\mathbf{D} + \mathbf{D}^T) \sim \eta(\phi)\dot{\gamma}. \quad (18)$$

Then one can straightforwardly obtain the following expression for the relaxation rate of the composition fluctuations convected by shear flow [20]:

$$\Gamma_{\text{eff}} = L \left[q^2(r_0 + Cq^2) - 2 \frac{\partial \eta}{\partial \phi} \phi^{-1} \dot{\gamma} q_x q_y \right] / [1 + \xi_{\text{ve}}^2 q^2]. \quad (19)$$

It is important to note that if $\partial \eta / \partial \phi > 0$, Γ_{eff} can be negative even for positive r_0 for $\dot{\gamma} > \dot{\gamma}_c$, indicating the growth of

fluctuations even in a thermodynamically stable region. Compare this equation with Eq. (16). The critical shear rate $\dot{\gamma}_c$ is obtained as

$$\dot{\gamma}_c \sim r_0 \phi / (\partial \eta / \partial \phi). \quad (20)$$

It should be noted that this enhancement occurs only in the limited region of q space [20,24]. We expect such shear-induced enhancement of fluctuations for colloidal suspensions in a one-phase region near a critical point (see Fig. 4).

It is worth noting that for adhesive spheres with stickiness $1/\kappa$, the following relation is known for $\eta(\phi)$ [2]:

$$\eta(\phi) = \eta_l \left[1 + 2.5\phi + \left(6.0 + \frac{1.90}{\kappa} \right) \phi^2 + O(\phi^3) \right]. \quad (21)$$

B. Nonlinear regime

In a nonlinear regime, the effects of normal stress may further strongly enhance the heterogeneity [20]. Our generalized diffusion equation [Eq. (9)] tells us that composition fluctuations grow when the typical value of the shear stress $\sigma_{c,xy}$ exceeds the osmotic modulus K_{os} . Because of the lack of reliable theories describing the non-Newtonian regime of colloidal suspensions, we cannot make definitive arguments. However, we can at least say that fluctuation enhancement is not expected when interactions between colloidal particles are repulsive where $K_{\text{os}} \gg G$, while it might be observed when $K_{\text{os}} \sim G$. Shear effects on colloidal suspensions in a nonlinear regime need further studies to be clarified.

VIII. SUMMARY

We recently proposed that phase separation of condensed matter can be classified into three types: solid, fluid, and viscoelastic phase separations [14–16]. In this paper, we show the possibility that the phase separation of colloidal suspensions, emulsions, and protein solutions can be described by the same viscoelastic model of phase separation [16]. This is based on the fact that the stress is divided quite asymmetrically between colloidal particles and the liquid: The liquid cannot support any mechanical stress, while the “interaction network” of colloidal particles can support it. This interaction network can bear bulk stress upon a change of $\nabla \cdot \mathbf{v}_c$. We conjecture that this is primarily the result of the “elasticity of interaction network” and the “topological constraint for diffusion” of colloidal particles: they have to move in keeping with the topology of the network, and this constraint produces the bulk stress. The self-induced constraint from the connectivity of the elastic network may be responsible for the bulk stress. Strong dynamic asymmetry between components of a mixture is a necessary condition for viscoelastic phase separation and the formation of a transient gel. This idea leads to simple explanations for two poorly understood phenomena: (i) phase separation accompanying the formation of a transient gel and its collapsing under gravity, and (ii) shear effects on composition fluctuations and phase separation.

In this paper, we focus on the similar features of phase separation between colloidal suspensions and polymer solutions, which originate from a “dynamic asymmetry” be-

tween components of a mixture. However, there are important differences between them. The effects of long-range hydrodynamic interactions between colloids, which are characteristic of colloidal suspensions, are much less significant in polymer solutions. This effect should be included properly in our model. Another crucial difference between polymer solutions and colloidal suspensions is their nonlinear rheology. For example, colloidal gels are much more fragile than polymer gels. It is quite important to clarify how this difference affects their phase-separation behavior. The inclusion of nonlinear rheology into a two-fluid model may be required, which is also necessary to understand the shear effects on composition fluctuations in a nonlinear regime.

There also remains a quite fundamental problem common to any dynamically asymmetric mixtures. In this paper, the effects of a transient gel on phase separation are discussed on a qualitative or phenomenological level, focusing on its physical significance. Accordingly, the discussion is rather speculative. We need a microscopic theory to describe the formation of a transient gel and the resulting change in moduli on a more quantitative level. Then we need to develop a mesoscopic or hybrid model to bridge the microscopic model with our phenomenological model. Further theoretical and experimental studies are highly desirable to check the validity of our phenomenological model, and to gain a deeper understanding of these phenomena. Numerical simulations would also play a quite important role in an understanding of these phenomena.

Concerning the relation between viscoelastic phase separation and shear effects on critical fluctuations and phase

separation, it is worth mentioning the following points: (a) For phase separation free from shear, the deformation rate is determined by the self-induced velocity fields during phase separation. Since it is diffusion that is responsible for phase separation and bulk stress is directly coupled to it, the bulk stress plays a much more essential role than the shear stress does, especially in the early stage. (b) For phase separation under steady shear, on the other hand, the deformation rate is determined by the shear rate $\dot{\gamma}$, and the shear stress plays a major role.

Finally, we suggest two simple experiments to check our model: (i) observe the phase separation in colloidal suspensions with microscopy, and check our dynamic phase diagram (Fig. 4), including phase inversion; and (ii) measure a light-scattering pattern of colloidal suspensions in a one-phase region near a critical point under a weak shear, to check the shear-induced enhancement of fluctuations.

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- [41] It is worth noting here that shear-induced flocculation can be irreversible. The mechanism of irreversible shear-induced aggregation [see, e.g., J. W. Goodwin and J. D. Mercer-Chalmers, in *Modern Aspects of Colloidal Dispersions*, edited by R. H. Ottewill and A. R. Rennie (Kluwer, London, 1998), pp. 61–75] is usually discussed in terms of the competition between interparticle interactions and stress applied by the shear fields. According to the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, a particle interaction from another particle encounters some barrier before it feels strongly attractive. The shear stress helps a particle to pass this barrier especially along the compression axis. Once a particle comes close to another particle passing the barrier, the pair becomes very stable. This apparently leads to irreversible flocculation, when the barrier height $\Delta \gg k_B T$. Here we do not discuss such an irreversible flocculation, which is beyond the scope of this paper. Thus we consider only a homogeneous colloidal suspension near its two-phase region.