PHYSICAL REVIEW E VOLUME 56, NUMBER 4 OCTOBER 1997

Viscoelastic model of phase separation

Hajime Tanaka
Institute of Industrial Science, University of Tokyo, Minato-ku, Tokyo 106, Japan

(Received 26 November 1996; revised manuscript received 16 June 1997)

We show here a general model of phase separation in isotropic condensed matter, namely, a *viscoelastic model*. We propose that the bulk mechanical relaxation modulus that has so far been ignored in previous theories plays an important role in viscoelastic phase separation in addition to the shear relaxation modulus. In polymer solutions, for example, attractive interactions between polymers under a poor-solvent condition likely cause transient gel-like behavior, which makes both bulk and shear modes active. Although such attractive interactions between molecules of the same component exist universally in the two-phase region of a mixture, the stress arising from attractive interactions is asymmetrically divided between the components only in dynamically asymmetric mixtures such as polymer solutions and colloidal suspensions. Thus the interaction network between the slower components, which can store the elastic energy against its deformation through bulk and shear moduli, is formed. This unique feature originates from the difference in mobility between two components of a mixture. It is the bulk relaxation modulus associated with this interaction network that is primarily responsible for the appearance of the sponge structure peculiar to viscoelastic phase separation and the phase inversion: It suppresses short-wavelength concentration fluctuations in the initial stage, and causes the volume shrinking of a more viscoelastic phase. We also propose a simple general law of the stress division between the two components of a mixture, as a straightforward extension of that obtained in polymer mixtures. We demonstrate that a viscoelastic model of phase separation including this new effect is a general model that can describe all types of isotropic phase separation including solid and fluid models as its special cases without any exception, if there is no coupling with additional order parameters. We show that this feature leads to a phenomenon of ''order-parameter switching'' during viscoelastic phase separation, even if it is driven by a single thermodynamic driving force. The physical origin of volume shrinking behavior during viscoelastic phase separation and the universality of the resulting spongelike structure are also discussed.
[S1063-651X(97)13510-3]

PACS number(s): 61.41.+e, 64.75.+g, 61.25.Hq, 05.70.Fh

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, colloids, and biological materials. The phenomena play key roles in the pattern evolution of immiscible multicomponent mixtures of any material. Thus phase-separation dynamics has been intensively studied in the past two decades from both experimental and theoretical viewpoints [1]. From the concept of dynamic universality, phase-separation phenomena have been classified into various theoretical models by Hohenberg and Halperin [2]: For example, phase separation in solids is known as the ''solid model (model B),'' while phase separation in fluids is known as the ''fluid model (model H)'' [2]. For the former the local concentration can be changed only by material diffusion, and for the latter by both diffusion and flow. It has been established that within each group the behavior is universal, and does not depend on the details of the material [1,2].

In all conventional theories of critical phenomena and phase separation, however, the same dynamics for the two components of a binary mixture, which we call ''dynamic symmetry'' between the components, has been implicitly assumed [1,2]. However, such an assumption of dynamic symmetry is hardly valid in various mixtures, especially in a material group of ''complex fluids.'' Recently we found that in mixtures having intrinsic ''dynamic asymmetry'' between its components (e.g., polymer solutions composed of long chainlike molecules and simple liquid molecules), a critical concentration fluctuation is not necessarily only the slow mode of the system and, thus, we have to consider the interplay between critical dynamics and the slow dynamics of the material itself [3–6]. In addition to solid and fluid models, thus, we need a third general model for phase separation in condensed matter, which we call a ''viscoelastic model'' [5,6].

To describe the difference in the elementary dynamics between the two components of a mixture, we need a basic model that can treat the motion of each component separately: such a model is known as a ''two-fluid model.'' The basic dynamic equations of the viscoelastic model have been derived to understand the coupling between the stress and diffusion [7–9] and also the unusual shear effects in polymer solutions [9–14], which are known as ''Reynolds effects,'' on the basis of a two-fluid model [7,15,16].

In this paper, we propose that we need some essential modification to the ''viscoelastic model'' of phase separation described above: We believe [17] that the bulk relaxation modulus, which has been neglected (or, more strictly, not treated as an important physical factor) in previous theories [12,13], plays as important a role in viscoelastic phase separation as in gel phase separation. This modified viscoelastic model can describe any kind of phase separation in mixtures of isotropic condensed matter without any exception, if there is no coupling with an additional order parameter. In Sec. II,

© 1997 The American Physical Society

we review the theoretical derivation of a viscoelastic model based on a two-fluid model. In Sec. III, we discuss the internal modes of the material itself, and the resulting stress and how the stress is partitioned between the two components. In Sec. IV, we describe the basic equations of a viscoelastic model. In Sec. V, we discuss the origins of asymmetric stress division, using a few examples. We also propose a general rule of stress division that is independent of the material. In Sec. VI, we discuss the generality of a viscoelastic model, and demonstrate that all the models of phase separation in isotropic condensed matter are special cases of a viscoelastic model. In Sec. VII, we discuss the viscoelastic suppression of local concentration fluctuations in polymer solutions, focusing on the roles of a bulk relaxation modulus. In Sec. VIII, we demonstrate that characteristic features of viscoelastic phase separation can be explained by a simple concept of ''order-parameter switching,'' which originates from the general nature of the viscoelastic model. In Sec. IX, we discuss the universal nature of spongelike morphology characteristic of a dynamically asymmetric mixture containing a fluid as its component. In Sec. X, we conclude our work. In the Appendix, we briefly mention the applications of viscoelastic phase separation to material science.

II. VISCOELASTIC MODEL BASED ON A TWO-FLUID MODEL

Here we review how a viscoelastic model can be derived on the basis of the two-fluid model [11–13] (see Ref. [12] for the details of the theoretical method). The model was originally derived to describe phase separation in polymers [12,13], but we believe that the viscoelastic model should describe phase separation in any dynamically asymmetric mixture, irrespective of the microscopic details of a system [5,6]. Thus here we focus special attention on how the most general version of the viscoelastic model can be derived. Let us consider a two-fluid model of a mixture of components 1 and 2. Let $\vec{v}_1(\vec{r},t)$ and $\vec{v}_2(\vec{r},t)$ be the average velocities of components 1 and 2, respectively, and $\phi(\vec{r},t)$ be the volume fraction of the component 1 at point $\vec{r}$ and time t. Here we assume for simplicity that the two components have the same density ρ. Then the conservation law gives

$$\frac{\partial \phi}{\partial t}=-\vec{\nabla}\cdot(\phi\vec{v}_1)=\vec{\nabla}\cdot[(1-\phi)\vec{v}_2]. \tag{1}$$

The volume average velocity v is given by

$$\vec{v}=\phi\vec{v}_1+(1-\phi)\vec{v}_2. \tag{2}$$

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

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

where $f(\phi)$ is the free energy per unit volume of a mixture with the concentration ϕ of component 1. The form of $f(\phi)$ depends upon the system; for example, it is given by the Flory-Huggins free energy [18] for polymer mixtures. Its time derivative can be written as

$$\begin{aligned}\dot{F}_{\rm mix}&=\int\left[\frac{\partial f}{\partial\phi}-C\nabla^2\phi\right]\dot{\phi}d\vec{r}\\&=-\int\left[\frac{\partial f}{\partial\phi}-C\nabla^2\phi\right][\vec{\nabla}\cdot(\phi\vec{v}_1)]d\vec{r}\\&=\int(\vec{\nabla}\cdot\mathbf{\Pi})\cdot\vec{v}_1d\vec{r},\end{aligned} \tag{4}$$

where $\vec{\nabla}\cdot\mathbf{\Pi}=\phi\nabla[(\partial f/\partial\phi)-C\nabla^2\phi]$ and $\mathbf{\Pi}$ is the osmotic tensor. We also assume here that the forces $\vec{F}_i$ acts on the component i. Thus the Rayleighian to be minimized is

$$R=\int d\vec{r}\left[\tfrac{1}{2}\rho\frac{\partial}{\partial t}\vec{v}^2+\tfrac{1}{2}\zeta(\phi)(\vec{v}_1-\vec{v}_2)^2+(\vec{\nabla}\cdot\mathbf{\Pi})\cdot\vec{v}_1-p\vec{\nabla}\cdot\vec{v}\right.$$
$$\left.-\vec{v}_1\cdot\vec{F}_1-\vec{v}_2\cdot\vec{F}_2\right]. \tag{5}$$

In the above, the term containing the pressure p is added to guarantee the incompressibility condition

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

The condition that the functional derivatives of the Rayleighian with respect to $\vec{v}_1$ and $\vec{v}_2$ be zero gives the following equations of motion:

$$\rho\frac{\partial(\phi\vec{v}_1)}{\partial t}=-\vec{\nabla}\cdot\mathbf{\Pi}-\zeta(\vec{v}_1-\vec{v}_2)+\phi\nabla p+\vec{F}_1, \tag{7}$$

$$\rho\frac{\partial[(1-\phi)\vec{v}_2]}{\partial t}=\zeta(\vec{v}_1-\vec{v}_2)+(1-\phi)\nabla p+\vec{F}_2. \tag{8}$$

Thus the average velocity $\vec{v}$ obeys

$$\rho\frac{\partial\vec{v}}{\partial t}=-\vec{\nabla}\cdot\mathbf{\Pi}+\nabla p+\vec{F}_1+\vec{F}_2. \tag{9}$$

In the quasistationary condition, the velocity difference between the two components, on the other hand, obeys

$$\vec{v}_1-\vec{v}_2=-\frac{1}{\zeta}[(1-\phi)\vec{\nabla}\cdot\mathbf{\Pi}-(1-\phi)\vec{F}_1+\phi\vec{F}_2]. \tag{10}$$

III. COUPLING OF INTERNAL MODES OF MATERIAL WITH DEFORMATION AND THE DIVISION OF THE RESULTING STRESS

A. Origins of stress

To obtain the form of the forces $\vec{F}_i$ explicitly, we need to understand how the stress is partitioned between the two components, and also to have the microscopic expression of the stress tensor of the material. The macroscopic total force $\vec{F}$ should be related to $\vec{F}_1$ and $\vec{F}_2$ as

$$\vec{F}=\vec{\nabla}\cdot\boldsymbol{\sigma}=\vec{F}_1+\vec{F}_2. \tag{11}$$

Here $\boldsymbol{\sigma}$ is the total stress tensor, which is, in general, given by the constitutive equation of material. In a linear-response regime, the most general expression of σ_{ij} is formally written by introducing the time dependence of bulk and shear moduli in the theory of elasticity [19] as

$$\sigma_{ij}=\int_{-\infty}^{t} dt'\{G(t-t')\kappa_r^{ij}(t')+K(t-t')[\vec{\nabla}\cdot\vec{v}_r(t')]\delta_{ij}\}, \tag{12}$$

where

$$\kappa_r^{ij}=\frac{\partial v_r^j}{\partial x_i}+\frac{\partial v_r^i}{\partial x_j}-\frac{2}{d}(\vec{\nabla}\cdot\vec{v}_r)\delta_{ij}. \tag{13}$$

Here $\vec{v}_r$ is the velocity relevant to the rheological deformation, and d is the spatial dimensionality. $G(t)$ and $K(t)$ are material functions, which we call the shear and bulk relaxation modulus, respectively. Here it should be noted that $K(t)$ does not contain the bulk osmotic modulus, $K_{\rm os}=\phi^2(\partial^2 f/\partial\phi^2)$. We have the relation $\eta=\int_0^\infty G(t)dt$, where η is the viscosity of the material.

The second term of Eq. (12) is newly introduced to incorporate the effect of volume change into the stress tensor [20,21]. In a two-component mixture, the mode associated with $\vec{\nabla}\cdot\vec{v}_r$ can exist as far as $\vec{v}_r\neq\vec{v}$, even if the system is incompressible. It should be stressed that its diagonal nature leads to the direct coupling with diffusion: note that the effective osmotic pressure is given by $\pi^{\rm eff}=[\phi(\partial f/\partial\phi)-f]-\int_{-\infty}^{t}dt'K(t-t')\vec{\nabla}\cdot\vec{v}_r(t')$. We believe, thus, that this term is important even in the case of polymer solution, as described below, although this term has so far been ignored (or, more strictly, not treated as an important physical factor) in the previous theories [11–14].

B. Estimation of the stress division parameter α_k

Here we consider the physical meaning of $\vec{v}_r$. In a linear-response regime, the rheological velocity $\vec{v}_r$ is generally given by the linear combination of $\vec{v}_1$ and $\vec{v}_2$ [12,14]:

$$\vec{v}_r=\alpha_1\vec{v}_1+\alpha_2\vec{v}_2. \tag{14}$$

Then the next problem is how the stress is partitioned between the two components. Since $\vec{F}\cdot\vec{v}_r$ should be equal to $\vec{F}_1\cdot\vec{v}_1+\vec{F}_2\cdot\vec{v}_2$ in the Rayleighian, we have the following stress division:

$$\vec{F}_1=\alpha_1\vec{F},\quad \vec{F}_2=\alpha_2\vec{F}. \tag{15}$$

Here $\alpha_1+\alpha_2=1$ from Eq. (11).

C. Direct estimation of $\vec{F}_k$

Here we consider the meaning of the forces from a different viewpoint. The forces acting on the component k are (i) the friction between the component k and the other component due to their relative motion, and (ii) the rheological coupling between the component k and the surrounding rheological environment including the component k itself. This can be easily understood by considering a gel that is composed of a polymer network and a solvent, as an example: The motion of polymer is affected by the two forces, namely, the friction force against the solvent and the elastic force due to the network deformation. Thus *it is natural to think that $\vec{F}_k$ $(k=1,2)$ corresponds to the force of type (ii), namely, the force acting on the component k by the motion of the component k ($\vec{v}_k$) itself,* and not by that of the other component. Thus we assume that $\vec{F}_k$ is linear in $\vec{v}_k$:

$$\vec{F}_k=\vec{\nabla}\cdot\boldsymbol{\sigma}^{(k)}, \tag{16}$$

$$\sigma_{ij}^{(k)}=\int_{-\infty}^{t} dt'\{G^{(k)}(t-t')\kappa_k^{ij}(t')+K^{(k)}(t-t')[\vec{\nabla}\cdot\vec{v}_k(t')]\delta_{ij}\}, \tag{17}$$

where

$$\kappa_k^{ij}=\frac{\partial v_k^j}{\partial x_i}+\frac{\partial v_k^i}{\partial x_j}-\frac{2}{d}(\vec{\nabla}\cdot\vec{v}_k)\delta_{ij}. \tag{18}$$

Here the unknown factors become the functional shapes of $G^{(k)}(t)$ and $K^{(k)}(t)$ for the motion of the component k, instead of α_k.

Using the stress division parameters α_k, we obtain the following relations between G and $G^{(k)}$ and also between K and $K^{(k)}$:

$$G=\frac{G^{(1)}G^{(2)}}{\alpha_2^2G^{(1)}+\alpha_1^2G^{(2)}}, \tag{19}$$

$$K=\frac{K^{(1)}K^{(2)}}{\alpha_2^2K^{(1)}+\alpha_1^2K^{(2)}}. \tag{20}$$

These functions $G^{(k)}$ and $K^{(k)}$ express the rheological properties of the material responding to the velocity $\vec{v}_k$. The fact that $\vec{v}_1$ and $\vec{v}_2$ are coupled with each other makes the estimation of the rheological functions difficult.

D. α_k or $\vec{F}_k$

The estimation of the stress division of $\vec{F}$ into $\vec{F}_1$ and $\vec{F}_2$, which is given by the stress division parameter α_k, formally looks simpler than the direct estimation of the above rheological functions, $G^{(k)}$ and $K^{(k)}$; this is true for a nearly symmetric stress division, as in the case of a polymer mixtures: More strictly speaking, when the dynamics of both components is governed by the same mechanism, α_k is useful to estimate the stress division.

However, the physical meaning of the latter is clearer than the former in a case of a strongly asymmetric stress division: In polymer solutions, for example, the mechanism of polymer dynamics is essentially different from that of solvent dynamics; and, thus, the rheological functions $G^{(k)}$ and $K^{(k)}$ are more useful than α_k (see Sec. V).

IV. BASIC EQUATIONS OF A VISCOELASTIC MODEL

Here we summarize the basic equations describing a viscoelastic model:

$$\frac{\partial \phi}{\partial t} = -\vec{\nabla}\cdot(\phi\vec{v}) - \vec{\nabla}\cdot[\phi(1-\phi)(\vec{v}_1-\vec{v}_2)], \tag{21}$$

$$\vec{v}_1-\vec{v}_2 = -\frac{1-\phi}{\zeta}\left[\vec{\nabla}\cdot\mathbf{\Pi} - \vec{\nabla}\cdot\boldsymbol{\sigma}^{(1)} + \frac{\phi}{1-\phi}\vec{\nabla}\cdot\boldsymbol{\sigma}^{(2)}\right], \tag{22}$$

$$\rho\frac{\partial v}{\partial t} \cong -\vec{\nabla}\cdot\mathbf{\Pi} + \nabla p + \vec{\nabla}\cdot\boldsymbol{\sigma}^{(1)} + \vec{\nabla}\cdot\boldsymbol{\sigma}^{(2)}. \tag{23}$$

We also need Eqs. (2), (6), and (17), and the information on the stress division. Here it should be noted that we need phenomenological or microscopic theories describing the forms of $G(t)$ and $K(t)$, or those of $G^{(k)}$ and $K^{(k)}$. Since we derive the above basic equations, relying only upon a two-fluid model, *they should be independent of types of material and quite general*.

V. ASYMMETRIC STRESS DIVISION

Here we focus on some specific problems to gain deeper insight into the origins of stress, and how the resulting stress is partitioned between the two components of a mixture. Then we consider some general features of asymmetric stress division.

A. Examples of asymmetric stress division

1. Polymer solutions: cases of good and θ solvents

In this case, the stress division has already been given in the literature [11–14]: $\alpha_1 \cong 1$ and $\alpha_2 \cong 0$, provided that the component 1 is a polymer and 2 is a solvent. However, this division itself is based indirectly on the estimation of $G^{(k)}$, since the stress division parameters cannot be determined precisely. It should be stressed that there is no direct way to determine α_1 and α_2 from the first principle. Thus there is no firm basis for $\vec{v}_r = \vec{v}_1$ in a polymer solution, as pointed out by Doi and Onuki [12], although it appears physically natural. In this case, we believe that Eq. (17) is more useful and physically easier to understand than Eq. (12), as described in Sec. III D.

The topological entanglement can be ''felt'' only by polymers, and never by solvent molecules. Then $G^{(1)}(t)$ is approximately given by the existing polymer-solution theory [22] [$G^{(1)}(t) \cong G(t)$] and $K^{(1)}(t) \sim 0$ [11–13], *if the solvent is not poor*. On the other hand, $G^{(2)}(t)$ is an extremely fast decay function and, thus, the solvent viscosity η_2 is obtained as $\eta_2 = \int_0^\infty dt G^{(2)}(t)$. Since the solvent has no large internal degrees of freedom, we can safely assume that $K^{(2)} = 0$.

2. Polymer solutions: a case of a poor solvent

It should be stressed that the phase separation of a polymer solution always occurs in a poor solvent, and, thus, the case of a poor solvent is extremely important when we consider critical phenomena and phase-separation phenomena. Unfortunately, however, there do not exist any established theories that describe quantitatively the polymer dynamics in a poor solvent. In a poor solvent, we need to consider the attractive interactions between polymer chains seriously. Thus the most natural model is a transient gel model [20,21] in which the interpolymer attractive interaction produces the temporal contact point (cross linking) between polymer chains. If we assume that the lifetime of the temporal contact between chains is τ_x, we expect that the bulk relaxational modulus $K^{(1)}(t)$ has a relaxation time of the order of τ_x. τ_x likely obeys the Arrhenius-type law: $\tau_x = \tau_x^0 \exp(E/k_B T)$ (k_B is the the Bolzmann constant). Here the bonding energy E is likely proportional to $T_\theta - T$ (T_θ is the θ temperature) near T_θ, and also dependent upon the distance and orientation of the relevant segments. Even in polymer solutions, thus, we expect that $K^{(1)}(t)$ plays an important role in viscoelastic phase separation, in contrast to the previous theories [11–14]: *The transient network of topological origin itself (entanglement effects) might not lead to the bulk relaxation mode, while the transient network formed by attractive interactions does clearly make the bulk relaxation mode active.* We believe that it is this mode that is primarily responsible for the volume shrinking behavior of a more viscoelastic phase observed in our experiments [5,6]. The characteristic decay time of $G^{(1)}(t)$ is likely longer than τ_x, since reptationlike motion is additionally required for the polymer motion under the temporal network formed by the attractive interaction. We need further theoretical studies to find quantitative expressions of $G(t)$ and $K(t)$ in a poor solvent.

Relating to the above transient gel model, we speculate that a polymer solution behaves as a physical gel *universally* at least at a high polymer concentration under a strongly poor-solvent condition. The existence of special junction points is not a prerequisite for the formation of such a transient gel. The transient pairing of any parts of two chains can be regarded by a temporal cross linking. Any pair of segments of polymer chains can form a temporal cross linking point, irrespective of interchain or intrachain interaction. The probability of its formation is determined by the balance between the intersegment attractive interaction depending upon the geometrical configuration of chains and the thermal energy. Thus the most probable candidate for the contact point is an entanglement point. The sol-gel transition can be given simply by the criterion that the transient network formed by interpolymer attractive interaction is percolated at any moment. A polymer chain having at least two contact points with other different polymers plays the role of a junction point of a usual physical gel. If we assume simply that the topological entanglement point is the only candidate for a temporal cross linking point, the criterion for physical gelation is given by

$$\frac{N}{N_e}\exp(E/k_B T) \geqslant 2, \tag{24}$$

where N is the degree of polymerization of the polymer, and N_e is the degree of polymerization between entanglement points. Further quantitative studies along the above line are highly desirable.

3. Polymer mixtures

In the case of a mixture of polymers 1 and 2, whose degrees of polymerization are N_1 and N_2, respectively, the stress produced by the motion of polymer 1 can be different from that produced by the motion of polymer 2. Intuitively, the motion of a longer chain causes stronger stress than that of a shorter chain does. Following the Brochard theory on mutual polymer diffusion [23], which is based on a reptation theory that mainly deals with the effect of topological constraints (tube) on entangled polymer chains, Doi and Onuki [12] explained how the stress should be divided by the two polymers with different lengths. According to them,

$$\vec{v}_r=\vec{v}_T=\alpha_1\vec{v}_1+\alpha_2\vec{v}_2, \tag{25}$$

$$\alpha_k=\frac{\zeta_k}{\zeta_1+\zeta_2}=\frac{\phi N_k}{\phi N_1+(1-\phi)N_2}, \tag{26}$$

where $\vec{v}_T$ is the tube velocity. Here ζ_k is the friction of the component k with the tube surrounding it. ζ_k is given by $\zeta_k=\phi_k(N_k\zeta_0/N_e)$ [12], where ϕ_k is the volume fraction of the component k, ζ_0 is the microscopic friction constant, and N_e is the average degree of polymerization between the entanglement points. The resulting stress division is given by $\vec{F}_k=\alpha_k\vec{\nabla}\cdot\boldsymbol{\sigma}$ [12]. Here it should be stressed that ζ_k *is the very essential quantity in the sense that it represents the coupling strength between the component k (the volume fraction of* ϕ_k*) and the surrounding rheological environment.*

Near and below a critical point T_c, however, we also have to consider the role of the attractive interactions between the same kind of polymers, which increases the rheological coupling, namely, ζ_k. For example, this leads to a slower diffusion constant than that predicted by a reptation theory which concerns only topological effects and neglects energetic interactions between polymers. The inclusion of energetic interactions is a prerequisite to a more precise description of polymer dynamics. However, the following fact should be mentioned: High-molecular weight polymer mixtures often mix at a lower temperature, and demix at a higher temperature. In such a case, energetic interactions likely play more important roles in polymer dynamics in the one-phase region rather than in the demixing region.

4. A mixture of components having very different glass-transition temperatures (T_g)

In this case, we also expect an asymmetric stress division, since the two kinds of component molecules are expected to ''feel'' very differently the rheological environment as in the case of polymer mixtures, even if the mean-field rheological environment surrounding them is the same. We have actually observed viscoelastic phase separation in a mixture of polymers having very different T_g's, whose behavior is essentially the same as that of polymer solutions [6]. It is easy to imagine that a high-T_g component has less friction with the local rheological environment than a low-T_g component. Recent theoretical studies on supercooled binary liquids [24], based on the mode-coupling approximation, support such a picture. If we formally introduce the coupling strength ζ_k for the component k that is proportional to ϕ_k, the stress division can be expressed by the same relation as in the above case of polymer mixtures. The mean-field rheological environment in this problem of a glass transition is the so-called ''cage'' [25]. *The concept of a ''cage'' in the glass transition is quite similar to the concept of a ''tube'' in polymer mixtures.* The escape time of a molecule from a ''cage'' or ''tube'' gives a relaxation time of $G(t)$ in both cases. Unfortunately, we do not have a reliable theoretical basis even for a simple liquid-glass transition, and, thus, it is difficult to find specific quantitative expressions for ζ_k at present. Phenomenologically, however, it is known that $G(t)=G_0\exp[-(t/\tau)^\beta]$ and $\tau\sim\tau_0\exp[B/(T-T_0)]$, where β is the stretching parameter $(0\leqslant\beta\leqslant1)$ and T_0 is the so-called Vogel-Fulcher temperature. It should be stressed again that we have to take into account the effects of attractive interactions between the same species on their dynamics below T_c [26].

5. Colloidal suspensions

It is well known that the addition of enough of nonabsorbing polymer to an otherwise stable colloidal suspension can induce phase separation *via* the depletion mechanism. Colloidal suspensions form a transient gel state in the initial stage of phase separation [27] in much the same way as polymer solutions do. We believe that the essential features of colloid phase separation can also be well described by our viscoelastic model. The dynamic asymmetry in colloidal suspensions simply comes from the size difference between colloids and solvent molecules.

B. Physical origin of asymmetric stress division

Here we consider the problem of what is the most basic physical factor that is responsible for asymmetric stress division, on the basis of intermolecular or interparticle interactions. The network of attractive interaction is universally formed when a mixture is quenched into its metastable or unstable state, since there exist attractive interactions between the same components. In dynamically symmetric mixtures, the interaction network always relaxes in its equilibrium state much faster than the phase-separation process. In dynamically asymmetric mixtures, however, the relaxation time of the interaction network is different between the two components because of the mobility difference. This consideration, based on microscopic interactions, leads to the conclusion that *the dynamic asymmetry between the components of a mixture is the essential origin of asymmetric stress division*. Thus the phase-separation behavior of any dynamically asymmetric mixtures including the above [Secs. V A 1–V A 5] should be essentially the same and described by Eqs. (21)–(23).

C. A general rule of stress division

On the basis of the above examples, we discuss a general rule of the stress division in viscoelastic matter. Here we do not consider elastic matter where the elastic coupling plays an important role in addition to the friction. In the preceding discussion, we obtained the general relation given by [Eq. (14)], $\vec{v}_r=\alpha_1\vec{v}_1+\alpha_2\vec{v}_2$, with $\alpha_1+\alpha_2=1$. For the relative motion of the component k having a velocity of v_k, to the mean-field rheological environment having a velocity of $\vec{v}_r$, the friction force is given by $\zeta_k(\vec{v}_r-\vec{v}_k)$, where ζ_k is the average friction of the component k and the mean-field rheological environment at point $\vec{r}$, where the volume fraction of k component is $\phi_k(\vec{r})$. Here $\zeta_k=\phi_k\zeta_k^m$ and ζ_k^m is proportional to the friction between an individual molecule of the component k and the mean-field rheological environment, which we call the generalized friction parameter. Because of the physical definition of the mean-field rheological environment, the two friction forces should be balanced. This fact guarantees that the rheological properties can be described only by $\vec{v}_r$ as in Eq. (12). Thus we have the following relation, in general:

$$\zeta_1(\vec{v}_r-\vec{v}_1)+\zeta_2(\vec{v}_r-\vec{v}_2)=0. \tag{27}$$

From Eqs. (14) and (27), we obtain the general expression of the stress division parameter α_k:

$$\alpha_k=\frac{\phi_k\zeta_k^m}{\phi_1\zeta_1^m+\phi_2\zeta_2^m}. \tag{28}$$

The above relation is consistent with a simple physical picture in which the friction is only the origin of the coupling between the motion of the component molecules and the rheological medium. The above relation is a straightforward extension of the stress division in polymer mixtures [12], where $\vec{v}_r$ is the tube velocity $\vec{v}_T$. We expect that this relation holds, irrespective of the microscopic details of rheological models, and, thus, we can apply it to a mixture of any material, the motion of both of whose components is described by a common mechanism. However, it should be stressed that *this relation is not useful for mixtures whose components have essentially different mechanisms of molecular motion as in the case of polymer solutions*: In polymer solutions, for example, the motion of polymers is essentially different from that of solvent molecules in the mechanism. In the standard rheological theory of polymer solutions, $G(t)$ itself is estimated as the sum of the polymer contribution and the solvent contribution. Thus the stress division cannot be simply described by Eq. (28). In such cases, Eq. (17) is more useful, as mentioned in Sec. III D.

VI. GENERALITY OF A VISCOELASTIC MODEL

Next we briefly discuss the generality of the above viscoelastic model described by Eqs. (21), (22), and (23) [20]. This model including the bulk volume relaxation mode is quite a general model, as shown below. We describe below how the viscoelastic model reduces to various models under some assumptions.

A. Elastic solid model

If we assume that $G(t)=\mu(\phi)$ (μ is the shear modulus) and $K(t)=K_b(\phi)$ (K_b is the bulk modulus) and $\vec{v}=0$, this model reduces to the model of an elastic solid model [28]. Since the time integration of the velocity becomes the deformation u, the stress is given by

$$\sigma_{ij}=\mu(\phi)\left[\frac{\partial u_j}{\partial x_i}+\frac{\partial u_i}{\partial x_j}-\frac{2}{d}(\vec{\nabla}\cdot\vec{u})\delta_{ij}\right]+K_b(\phi)(\vec{\nabla}\cdot\vec{u})\delta_{ij}. \tag{29}$$

Thus the basic kinetic equation is given by

$$\frac{\partial\phi}{\partial t}=\vec{\nabla}\cdot\frac{\phi(1-\phi)^2}{\zeta}\left[\vec{\nabla}\cdot\mathbf{\Pi}-\vec{\nabla}\cdot\boldsymbol{\sigma}^{(1)}+\frac{\phi}{1-\phi}\vec{\nabla}\cdot\boldsymbol{\sigma}^{(2)}\right]. \tag{30}$$

In this case, the softer phase forms a networklike phase because the deformation of the softer phase costs less energy than that of the harder phase [28]. It should be stressed that the force balance condition plays no roles in determining the morphology. This fact causes the striking difference in morphology between an elastic solid model and an elastic gel or asymmetric viscoelastic model [5]: In the former the softer phase forms the networklike structure, while in the latter the harder phase does.

B. Solid model

If we assume dynamic symmetry (no dependence of μ and K_b on ϕ) further, it reduces the solid model (model B [2]). This is because we have a symmetric stress division of $(1-\phi)\vec{F}_1=\phi\vec{F}_2$. Here it should be noted that the condition $\mu=K_b=0$ is unnecessary, and only symmetry in elastic properties between the two components is required. In this case, the basic equation becomes the simplest diffusion equation

$$\frac{\partial\phi}{\partial t}=\vec{\nabla}\cdot\frac{\phi(1-\phi)^2}{\zeta}[\vec{\nabla}\cdot\mathbf{\Pi}]. \tag{31}$$

C. Symmetric viscoelastic model

If we assume only dynamic symmetry between the two components of a mixture, it reduces to a new ''symmetric viscoelastic model.'' In this case, we have a trivial stress division $\vec{F}_1=\phi\vec{\nabla}\cdot\boldsymbol{\sigma}$ and $\vec{F}_2=(1-\phi)\vec{\nabla}\cdot\boldsymbol{\sigma}$. That is, $\alpha_1=\phi$ and $\alpha_2=1-\phi$. The rheological functions $G^{(k)}$ can be estimated as $G^{(1)}(t)=\phi G(t)$ and $G^{(2)}(t)=(1-\phi)G(t)$. In this particular case, $\vec{v}_r=\vec{v}$, and, accordingly, there should be no contribution of the bulk relaxation modulus under the incompressibility condition ($\vec{\nabla}\cdot\vec{v}=0$). The basic kinetic equations are given by

$$\frac{\partial\phi}{\partial t}=-\vec{\nabla}\cdot(\phi\vec{v})+\vec{\nabla}\cdot\frac{\phi(1-\phi)^2}{\zeta}\vec{\nabla}\cdot\mathbf{\Pi}, \tag{32}$$

$$\rho\frac{\partial v}{\partial t}\cong-\vec{\nabla}\cdot\mathbf{\Pi}+\nabla p+\vec{\nabla}\cdot\boldsymbol{\sigma}. \tag{33}$$

Since $\vec{v}_r=\vec{v}$, the gross variables describing the dynamics are only ϕ and $\vec{v}$. Here it should be stressed that the rheological function $G(t)$ does not depend upon the location $\vec{r}$ because of the dynamic symmetry. Using the relation $\vec{\nabla}\cdot\vec{v}=0$, thus,

$$\vec{F}=\nabla\cdot\boldsymbol{\sigma}=\int_{-\infty}^{t}dt'G(t-t')\nabla^2\vec{v}(t'). \tag{34}$$

We also have the relation

$$\vec{v}_1-\vec{v}_2=-\frac{1-\phi}{\zeta}[\vec{\nabla}\cdot\mathbf{\Pi}], \tag{35}$$

although it is unnecessary for solving the problem.

This model describes the dynamics of dynamically symmetric polymer mixtures. It should be stressed that this model is different from the fluid model (model *H*) described below. Thus there remains a possibility that there is a new polymer effect relating to this model: For example, we expect an unusual feature in the initial stage of phase separation where the deformation rate is large. The polymer effect corresponding to this was first pointed out by de Gennes [29], and was very recently studied in detail by Kumaran and Frederickson [30].

D. Fluid model

If we assume that the deformation is much slower than the internal rheological time of the material for the above model, we further have the relation $\vec{\nabla}\cdot\boldsymbol{\sigma}=\eta\nabla^2\vec{v}$. Thus the model reduces to the fluid model (model *H* [2])

$$\frac{\partial\phi}{\partial t}=-\vec{\nabla}\cdot(\phi\vec{v})+\vec{\nabla}\cdot\frac{\phi(1-\phi)^2}{\zeta}\vec{\nabla}\cdot\boldsymbol{\Pi}, \tag{36}$$

$$\rho\frac{\partial v}{\partial t}\cong-\vec{\nabla}\cdot\boldsymbol{\Pi}+\nabla p+\eta\nabla^2\vec{v}. \tag{37}$$

E. Elastic gel model

If we assume only $G=\mu(\phi)$ and $K=K_b(\phi)$, it reduces to the elastic gel model [31,32] that describes phase separation in elastic gel. The basic equations are essentially the same as those of viscoelastic phase separation in a polymer solution [Eqs. (21), (22), and (23)], except that the stress tensor is given by

$$\sigma_{ij}^{(1)}=\mu(\phi)\left[\frac{\partial u_1^j}{\partial x_i}+\frac{\partial u_1^i}{\partial x_j}-\frac{2}{d}(\vec{\nabla}\cdot\vec{u}_1)\delta_{ij}\right]+K_b(\phi)(\vec{\nabla}\cdot\vec{u}_1)\delta_{ij},$$

$$\sigma_{ij}^{(2)}=\eta_2\left[\frac{\partial v_2^j}{\partial x_i}+\frac{\partial v_2^i}{\partial x_j}-\frac{2}{d}(\vec{\nabla}\cdot\vec{v}_2)\delta_{ij}\right].$$

In this case, when the elastic energy overcomes the mixing free energy, phase separation stops and the coarsening of domains is pinned.

F. Generality and intrinsic nonuniversality

Since any phase separation in all isotropic condensed matter can be classified into solid, elastic solid, elastic gel, symmetric and asymmetric viscoelastic, and fluid models, the above viscoelastic model (see Sec. IV), including both shear and bulk relaxation stresses, should be a universal model describing phase separation and critical phenomena in isotropic matter without any exception.

However, this model is not universal in the usual sense of critical phenomena, since it requires some microscopic theories describing the rheological properties of the matter. In the extreme limit of strong dynamic asymmetry, the elementary slow dynamics (internal mode) of material affects the critical fluctuation even near the critical point, in contrast to the concept of the dynamic universality [2]. Thus there is a possibility that we cannot experimentally approach a critical regime where the order parameter dynamics is only the slow mode in the system [4,5].

Viscoelastic effects can be parameterized by the so-called viscoelastic length $\xi_{\rm ve}\sim(D_\xi\tau_t)^{1/2}$ originally introduced by Brochard and de Gennes [7], where τ_t is the characteristic time of rheological relaxation and D_ξ is the diffusion constant. For length scales longer than $\xi_{\rm ve}$, concentration fluctuations decay by diffusion, while for length scales shorter than $\xi_{\rm vc}$, viscoelastic effects dominate [7,12,13]. This is a simple mapping of the dynamic crossover in which, on a time scale longer than τ_t, diffusion dominates concentration fluctuations, while on a time scale shorter than τ_t viscoelastic effects dominate. The critical regime is, thus, described by the condition $\xi\gg\xi_{\rm ve}$, where ξ is the correlation length of concentration fluctuations. This condition can also be written as $\tau_\xi\gg\tau_t$, where τ_ξ is the characteristic time of the critical concentration fluctuations. Thus we need to consider whether we can easily approach the critical regime that is defined by the above criterion, in a viscoelastic system. A more detailed consideration of this problem of *intrinsic nonuniversality* will be described elsewhere.

VII. VISCOELASTIC SUPPRESSION OF LOCAL CONCENTRATION FLUCTUATIONS IN POLYMER SOLUTIONS

A. Fluctuation suppression due to bulk relaxation modulus

According to the continuity equation, Eq. (1), we have the relation

$$\frac{\partial\phi}{\partial t}=-\nabla\phi\cdot\vec{v}_1-\phi\vec{\nabla}\cdot\vec{v}_1. \tag{38}$$

Here we assume that component 1 is a polymer and that component 2 is a solvent. In the above equation, the first term on the right-hand side simply describes the translational transport of polymers to a point $\vec{r}$ by the locally uniform velocity field $\vec{v}_1$, while the second one describes polymer diffusion toward or from a point $\vec{r}$. Thus the first term is associated only with the change in the spatial pattern of the concentration distribution, while the second term is responsible for the change in the concentration distribution itself. In the initial stage of phase separation, the major process is the diffusion process leading to the change in the concentration distribution itself, and there are few changes in the spatial pattern of the concentration distribution. Neglecting the first term in Eq. (38), thus, we have the relation

$$\frac{\partial\phi}{\partial t}/\phi\cong-\vec{\nabla}\cdot\vec{v}_1. \tag{39}$$

The left-hand side of the above equation is inversely proportional to the characteristic time of the concentration change, τ_ϕ. On the other hand, the bulk relaxation modulus $K(t)$, that is directly coupled with $\vec{\nabla}\cdot\vec{v}_1$, has a characteristic decay time of τ_x, which is related to the characteristic time of the transient crosslinking between polymer chains in a poor-solvent condition. If $\tau_x\gg\tau_\phi$, the rapid growth of concentration fluctuations characteristic of spinodal decomposition is suppressed severely and may even be prohibited. If $\tau_x\ll\tau_\phi$, on the other hand, there are few elastic effects, and the concentration fluctuations can grow as in typical spinodal decomposition.

B. Spinodal decomposition vs nucleation and growth

If the above mechanism of the suppression of concentration fluctuations works efficiently, spinodal decomposition cannot proceed further after the crossover between τ_x and τ_ϕ. Thus the type of phase separation switches from spinodal decomposition to nucleation and growth. More strictly speaking, the concentration fluctuations grow only locally in the solvent-rich region where τ_x is short and diffusion takes place easily. Such behavior is actually observed in our experiments [5]. The crossover from an initial fluid state to a transient gel state likely takes place almost immediately after the temperature quench, since the long-range diffusion or motion of molecules is not required for the formation of a transient network (see also Sec. VIII C.). After the formation of a transient gel state, the ‘‘mechanical instability’’ that is a universal feature of the ‘‘soft’’ network of attractive interactions leads to nucleation-growth-like behavior. In the following, we discuss the concept of ‘‘order-parameter switching’’ resulting from the crossover between the characteristic phase-separation time and the internal rheological time.

VIII. ORDER-PARAMETER SWITCHING

A. Order-parameter switching between composition and deformation tensor

Here we consider the dynamic process of viscoelastic phase separation on the basis of the viscoelastic relaxation phenomena described by Eq. (12). The quantitative feature of the dynamics can be understood on the basis of a concept of ‘‘order-parameter switching’’ [20]. Phase separation is usually driven by a 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 [1] [in other words, there are more than two kinds of thermodynamic forces (order parameters)], a phase-separation process is usually characterized by a single order parameter. In the viscoelastic model, on the other hand, the phase-separation mode can be switched between a ‘‘fluid mode’’ and an ‘‘elastic gel mode.’’ This switching is likely caused by a change in the coupling between stress fields and velocity fields, which is described by Eq. (12): Equation (12) tells us that these two ultimate cases, namely, (i) the fluid model [$\kappa_{ij}^{p}, \vec{\nabla}\cdot\vec{v}_r \sim \text{const}$] and (ii) the elastic gel model [$G(t), K(t) \sim \text{const}$], correspond to $\tau_{ts} \gg \tau_d$ and $\tau_{ts} \ll \tau_d$, respectively. Here τ_d is the characteristic time of deformation, and τ_{ts} is the characteristic rheological time of the slower phase. There can be two types of τ_{ts}: One is associated with the characteristic decay time of $G(t)$, and the other with that of $K(t)$. We think that the former is generally longer than the latter in polymer solutions, as mentioned in Sec. V A 2. As described in Sec. VII, we believe that the latter plays an important role in the suppression of concentration fluctuations in the initial stage.

For $\tau_d \gg \tau_{ts}$ the primary order parameter is the composition in usual classical fluids, while for $\tau_d \ll \tau_{ts}$ 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 written only by the deformation tensor d_{ij} as $f(d_{ij})$. Thus, we can say that the order-parameter switching is a result of the competition between two time scales characterizing domain deformation τ_d and the rheological properties of domains τ_{ts}. This is a kind of *viscoelastic relaxation* in pattern evolution.

B. How does order-parameter switching occur?

We next consider how τ_{ts} and τ_d change with time during phase separation. In the initial stage, the velocity fields grow as $v \sim (k_B TK/3\eta\xi)\Delta\phi^2$, where $\Delta\phi$ is the composition difference between the two phases and ξ is the correlation length, or the interface thickness. Since $\Delta\phi$ approaches $2\phi_e$ (ϕ_e is the equilibrium composition) with time, this expression of v reduces to the well-known relation $v \sim \gamma/\eta$ (γ is the interface tension) in the late stage [note that $\gamma \sim k_B TK(2\phi_e)^2/3\xi$]. Thus the characteristic deformation time τ_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, and, accordingly, τ_d decreases rapidly. On the other hand, τ_{ts} increases steeply with an increase in $\Delta\phi$, reflecting the increase in the polymer concentration in a polymer-rich domain. Thus τ_{ts} becomes comparable to τ_d in the intermediate stage of phase separation. Once $\tau_d < \tau_{ts}$, the slower phase cannot follow the deformation speed 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, τ_d ($\sim R\eta/\gamma$) increases with an increase in R, while τ_{ts} becomes almost constant. Thus τ_d again becomes longer than τ_{ts}. In short, $\tau_d \gg \tau_{ts}$ in the initial stage, $\tau_d \ll \tau_{ts}$ 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. This is the first case of ‘‘order-parameter switching’’ during an ordering process driven by a single thermodynamic driving force, to our knowledge.

C. Further consideration on $G(t)$ and $K(t)$: Kinetics of transient gel formation

Here we briefly consider the viscoelastic functions $G(t)$ and $K(t)$, which are dependent upon the material. In the above discussion, τ_{ts} is assumed to be a function of $\Delta\phi$. However, this picture is not necessary true. In polymer solutions and colloidal suspensions, for example, the transient gel-like structure is likely formed very quickly after the quench. This is because the diffusion of polymers or colloidal particles over a large length scale is not required to form the interaction network. The diffusion length scale l is of the order of polymer or particle size a near the critical composition (ϕ_c); thus the time required to form a network is $\sim a^2/D_a$, where D_a is the diffusion constant of a polymer or particle. In such a case, τ_{ts} very rapidly increases to the order of τ_x, within a time of $\sim a^2/D_a$ after the quench. In such a case, the first order-parameter switching from composition to deformation tensor occurs within a very short period ($\sim a^2/D_a$) after the quench: The system enters into an elastic regime just after the quench.

The diffusion length scale l increases with a decrease in polymer or colloid concentration ϕ. If a percolated network cannot be formed within a sufficiently short time, a quasihomogeneous transient gel state is not realized due to phase separation, and, thus, a networklike phase-separated pattern is not formed; instead, a droplet pattern is formed [5]. This criterion may cause the threshold composition between droplet and network phase separation.

Finally, it should be stressed that to describe this network formation process and the resulting change in viscoelastic functions, $G(t)$ and $K(t)$, we need a microscopic model of each system.

D. Volume shrinking behavior: Absence of self-similar pattern growth in viscoelastic phase separation

Because of the order-parameter switching, there is no self-similarity in the pattern evolution of viscoelastic phase separation. In the elastic regime, further, the volume ratio between the two phases changes with time [5,6,20], and, thus, there is no proportionality between interdomain distance and domain size. This behavior even leads to phase inversion when the more viscoelastic phase is a slightly minority phase in equilibrium: in the initial stage a less viscoelastic phase forms droplets, while in the final stage a more viscoelastic phase does. This means that there are at least two length scales that change differently with time. This is also related to the absence of any characteristic length scale in elastic deformation.

Here we make a rough estimate of volume shrinking kinetics. The elastic regime should be analogous to the volume shrinking of gel. The characteristic shrinking time τ_{shrink} is likely dependent upon the characteristic length scale L as L^2/D (D is the gel diffusion constant [8]). It should be noted that only the length scale in this problem is the length scale associated with the ''mechanical instability,'' that is, the characteristic distance between solvent holes, L_{hole}. Neglecting the time dependence of L_{hole}, we obtain a very rough estimation of the volume shrinking time as $\tau_{\mathrm{shrink}} \sim L_{\mathrm{hole}}^2/D$, which can be a very long time. The estimation of L_{hole}, including its time dependence, requires a stability analysis under the influence of phase separation. We need further study on this problem.

E. Pattern selection: elastic energy vs interface energy

Since the deformation tensor intrinsically has a geometrical nature, the pattern in the elastic regime is essentially different from that of usual phase separation in fluid mixtures. The domain shape during viscoelastic phase separation is determined by whether the elastic or interface energy is more dominant. Roughly, the elastic energy is estimated as $\mu e^2 R^d$ (e is the strain and d is the spatial dimensions) for a domain of size R, since it is the bulk energy. On the other hand, the interface energy is estimated as γR^{d-1}. For macroscopic domains, thus, the elastic energy is much more important than the interface energy in the intermediate stage where $\tau_d \leqslant \tau_{ts}$. Accordingly, the domain shape is determined by the elastic force balance condition ($\vec{\nabla} \cdot \boldsymbol{\sigma}^{(n)} \sim 0$), which leads to networklike or spongelike morphology. In the initial and late stages of phase separation where $\tau_d \gg \tau_{ts}$, on the other hand, the interface energy dominates the domain shape, since $\mu \sim 0$.

IX. UNIVERSALITY OF SPONGE MORPHOLOGY CHARACTERISTIC OF A MIXTURE HAVING BULK COMPRESSION MODES

A. Universality of sponge morphology

Here we discuss the universal nature of a spongelike morphology (or the formation of a continuous structure by a minority phase) and its physical origin. It is known that gel undergoing a volume-shrinking phase transition forms a bubblelike structure [31,33,34]. The competition between phase separation and gelation or a glass transition also causes a spongelike morphology [35–37]. The physical origin of the appearance of a honeycomb structure in plastic foams (e.g., polystyrene foam and urethane foam) is also similar to ours. All these processes have a few common features. (i) A mixture contains a fluid as a component. (ii) Holes of a less viscoelastic fluid phase (gas in plastic foam, water in gel, solvent in polymer solution, and so on) are nucleated to minimize the elastic energy associated with the formation of a heterogeneous structure in an elastic medium. (iii) Then, a more viscoelastic phase decreases its volume with time. This volume shrinking process is dominated by the transfer (diffusion or flow) of a more mobile component under stress fields, from a more viscoelastic phase to a less viscoelastic phase. The above picture suggests the possibility that a spongelike structure is the *universal morphology* for phase separation in systems in which only one component asymmetrically has elasticity stemming from either topological connectivity or attractive interaction.

We also point out [6] the similarity of these patterns in condensed matter to the spongelike structure of the universe (the large-scale galaxy distribution) [38]. We speculate that the gravitational attractive interaction, which is stronger between heavier matter, may play a role similar to the elastic network in producing the spongelike large-scale structure. This explanation seems to be consistent with a standard picture of the universe evolution (a gravitational-instability model) that such a heterogeneous structure develops by gravitational amplification of density fluctuations.

This universal appearance of sponge structures in the phase separation of these systems originates from the volume phase transition, or, more strictly, the elastic phase separation of a *dynamically asymmetric mixture that is composed of a network-forming component and a fluid (such as a liquid and a gas)*. The elastic network can be a real one as in gels (permanent network), and polymer solutions (transient network), or a virtual one due to attractive interactions. In the former, a real structure having large internal degrees of freedom can store the elastic energy for bulk compression, while in the latter the virtual network due to attractive interactions can also store the elastic energy. In this sense, we can conclude that the existence of both the component having a bulk (relaxation) modulus and the fluid component is a prerequisite for the formation of a spongelike structure due to the volume shrinking of one phase.

For example, such phenomena are never observed in solid mixtures, except for the case where the mobility is strongly dependent upon the composition [39]. Phase separation of elastic solid mixtures (e.g., metal alloys) does not accompany a drastic volume change of each phase if there is no strong composition dependence of mobility. This difference causes a marked contrast between elastic phase separation in solid mixtures and viscoelastic phase separation; in the former, a softer phase always forms a continuous phase to minimize the total elastic energy [14], in contrast to the latter.

B. Physical origin of volume shrinking

We briefly discuss the physical meaning of the above criteria for the formation of a sponge structure, or relative volume shrinking of a more viscoelastic phase. This is related to the fact that in a two-fluid model $\vec{\nabla}\cdot\vec{v}_k$ needs not be zero even under the incompressible condition $\vec{\nabla}\cdot\vec{v}=0$ for the average velocity. There are three important factors in this problem: (i) whether or not the component k is compressible in a mixture, (ii) whether or not $\vec{\nabla}\cdot\vec{v}_k$ is large enough, and (iii) whether or not the change in $\vec{\nabla}\cdot\vec{v}_k$ is properly coupled with the stress.

Condition (i) is usually satisfied, since we can change the spatial configuration of one component arbitrarily in a two-component mixture, in general. Condition (ii) is satisfied only for a system containing a fluid as its component. Finally, condition (iii) is satisfied only when there exist attractive interactions between the components. In a simple fluid mixture, for example, $\vec{\nabla}\cdot\vec{v}_k$ is not coupled with the elastic stress even if there is a difference in viscosity between the two components. In relation to this problem, we consider the case of a mixture whose components have different glass transition temperatures as an example. If only one component becomes viscoelastic, the deformation of this component, which is described by $\kappa_{ij}^{(k)}$ and $\vec{\nabla}\cdot\vec{v}_k$, causes the elastic stress. Thus the more viscoelastic phase becomes the matrix phase and forms the spongelike structure, as experimentally observed [6]. To prevent usual spinodal decomposition from taking place, the bulk modulus should be sufficiently large: The initial growth of the concentration fluctuation has to be suppressed mainly by $\vec{\nabla}\cdot\vec{v}_k$. For example, this is realized by the formation of a transient interaction network.

We believe that the bulk mechanical relaxation modulus $K(t)$ plays an essential role in fluctuation suppression and volume shrinking, while the bulk osmotic modulus K_{os} does not play a primary role. The interactions can have any origin, including entropic and energetic ones. The long-range nature of the elastic interaction in a more viscoelastic phase is directly related to how efficiently the fluctuation is suppressed, and the volume of the relevant phase can be changed and, thus, its ability to form a spongelike structure.

In relation to the above, it should be mentioned that the strong composition dependence of the mobility has a similar effect [39], since it slows down the diffusion process in the slow-component-rich region selectively. Thus a similar behavior of the phase inversion has been observed even in the framework of a solid model (model B) [39]. As discussed in Sec. V B, the physical factor responsible for the asymmetric stress division in a fluid mixture is dynamic asymmetry between the two components of a mixture. This strongly indicates that the most essential physical origin of volume shrinking behavior and the resulting phase inversion is the coexistence of ''asymmetry in mobility between the two components of a mixture'' and ''attractive interactions,'' irrespective of whether a mixture is solid or fluid.

C. Roles of shear relaxation modulus on the formation of a networklike structure

We have already discussed the roles of the bulk relaxation modulus, namely, the suppression of the homogeneous growth of concentration fluctuations. Here we focus our attention on the roles of the shear relaxation modulus. An important fact is that the bulk relaxation modulus is closely related to the diffusion while the shear relaxation modulus is not: The bulk stress gradient $\vec{\nabla}\cdot\boldsymbol{\sigma}_B$, is usually (at least in the initial stage) in the same orientation as the osmotic stress gradient $\vec{\nabla}\cdot\boldsymbol{\Pi}$, since both are related to the diagonal part of the deformation velocity $\vec{\nabla}\cdot\vec{v}_r$, as described above. On the other hand, the shear stress gradient $\vec{\nabla}\cdot\boldsymbol{\sigma}_S$ is usually not in the same orientation as $\vec{\nabla}\cdot\boldsymbol{\Pi}$, since it is related to the off-diagonal part of the deformation velocity. Thus we believe that the shear relaxation modulus plays a dominant role in the formation of a networklike structure in the intermediate stage of viscoelastic phase separation: The overlapping of stress fields having spherical symmetry around spherical solvent holes induce a deformation of shear type. This initial spherical symmetry of the stress field is characteristic of bulk stress fields coupled with $\vec{\nabla}\cdot\overrightarrow{v_r}$. The shear deformation causes shear stress fields through the shear relaxation modulus. Thus the thin part of a more viscoelastic phase can support the shear stress and be elongated further. In other words, the existence of a shear relaxation modulus is responsible for the formation of a networklike pattern composed of highly elongated thin structures [21]. We believe that without the shear relaxation modulus, the networklike pattern with threadlike structures can never be formed.

D. Difference in elastic effects between solid and fluid systems

Here we discuss the difference in phase-separation morphology between elastically asymmetric solid mixtures [28] and dynamically asymmetric fluid mixtures. In the diffusion-dominated process, the system approaches the final equilibrium state to reduce the total free energy including the elastic energy [see Eq. (30)]. As a result, the morphology that minimizes the elastic energy is selected. This is the case of solid mixtures having only elastic asymmetry but no dynamic asymmetry. In relation to this, it should be noted that the solid mixture having dynamic asymmetry behaves entirely differently (see e.g., Ref. [39]).

In the flow-dominated process, on the other hand, the force balance condition plays an essential role in pattern selection [see Eq. (23)]. As a result, the morphology itself is determined by the force balance condition. The asymmetric stress division leads to a spongelike structure, where the more viscoelastic phase forms a continuous networklike structure to support the stress. Further, the two-fluid nature makes the volume change of phases possible. Thus we can say that dynamic asymmetry is a prerequisite to the phase inversion, irrespective of whether material is solid or fluid.

X. CONCLUSION

In summary, we obtain a general model of viscoelastic phase separation on the basis of a two-fluid model: We demonstrate that the bulk relaxation modulus plays an important role in viscoelastic phase separation even in polymer solutions. Our recent simulations based on the viscoelastic model indicates the importance of this bulk mode [21]. Inclusion of this effect makes a viscoelastic model quite general: The viscoelastic model can describe phase separation or critical phenomena in any isotropic condensed matter without any exception, if there is no coupling with additional order parameter.

Although the viscoelastic model is a quite general model of critical phenomena and phase separation, the critical behavior of this model may be intrinsically nonuniversal in the sense that internal slow modes of the material can affect the critical dynamics even near the critical point. This problem needs further studies to check whether the dynamic universality practically breaks in a mixture having strong dynamic asymmetry between its components, or not [5].

As a straightforward extension of the stress division in polymer mixtures [12], we also propose a simple relation describing how the stress is divided by the two components, on the basis of the idea that the mechanical coupling between a component and the mean-field rheological environment is only due to the friction between them. We also point out that the relation is not useful for a mixture whose components have different mechanisms of the molecular motion.

We also show that the characteristic features of viscoelastic phase separation can be well explained by the concept of ‘‘order-parameter switching’’ between composition and deformation tensor.

We discuss the universal features of spongelike structures observed in various materials, and demonstrate that there is a common physical origin that is explained by the framework of our viscoelastic model of phase separation. It is concluded that the most essential physical origin of volume shrinking behavior, and the resulting sponge structure, is the coexistence of ‘‘asymmetry in mobility between the two components of a mixture’’ and ‘‘attractive interactions,’’ irrespective of whether a mixture is solid or fluid. In relation to this, we would like to point out that phase inversion is also observed in a recent simulation of model B, including the strong composition dependence of the mobility [39]. We believe that this is the only way to introduce dynamic asymmetry into a solid model. The relation between our model and their model and the underlying physics of their similar behavior [21,39] will be discussed in detail elsewhere.

ACKNOWLEDGMENTS

The author is grateful to Professor A. Onuki and Professor M. Doi for valuable discussions. He also thanks Professor J. Jäckle for discussions on the roles of asymmetric mobility and those of bulk relaxation modulus. This work was partly supported by a Grant-in-Aid from the Ministry of Education, Science, Culture, and Sports, Japan.

APPENDIX: COMMENTS ON APPLICATIONS OF VISCOELASTIC PHASE SEPARATION IN MATERIAL SCIENCE

We briefly discuss the application of the spongelike morphology observed in viscoelastic phase separation. Although a spongelike structure appears only transiently in viscoelastic phase separation, this structure can be frozen by suitable methods: (i) simultaneous evaporation of a solvent for a polymer solution during phase separation, (ii) a further quench of a system below T_g, and (iii) a combination of other processes such as cross linking reaction. We believe that the spongelike structures reported in the literature [35–37,40,41] are induced primarily by the mechanism described here. In relation to this, we point out that some sponge phases have periodic structures (see, e.g., Ref. [41]), while others do not, as in our case. This can be explained by the manner of nucleation of solvent holes: only when nucleation is heterogeneously induced with a high density in a short period can a periodic sponge structure be formed by the long-range elastic interaction between solvent holes (correlated nucleation). We also point out that polymerization-induced phase separation may lead to a networklike structure of a minority phase if there is a certain degree of dynamic asymmetry induced by the polymerization of a component.

In the common sense view of conventional phase separation, a minority phase never forms a continuous phase, and forms only an isolated phase [1]. However, our present study indicates the possibility that we can intentionally form a spongelike continuous structure of the minority phase of a more viscoelastic phase for any dynamically asymmetric mixture.

---

[1] J. D. Gunton, M. San Miguel, and P. Sahni, in *Phase Transition and Critical Phenomena*, edited by C. Domb and J. H. Lebowitz (Academic, London, 1983), Vol. 8.
[2] P. C. Hohenberg and B. I. Halperin, Rev. Mod. Phys. **49**, 435 (1976).
[3] H. Tanaka and T. Nishi, Jpn. J. Appl. Phys., Part 2 **27**, L1787 (1988); H. Tanaka, Macromolecules **25**, 6377 (1992).
[4] H. Tanaka and T. Miura, Phys. Rev. Lett. **71**, 2244 (1993).
[5] H. Tanaka, Phys. Rev. Lett. **71**, 3158 (1993); J. Chem. Phys. **100**, 5253 (1994).
[6] H. Tanaka, Phys. Rev. Lett. **76**, 787 (1996).
[7] F. Brochard and P. G. de Gennes, Macromolecules **10**, 1157 (1977); F. Brochard, J. Phys. (France) **44**, 39 (1983).
[8] T. Tanaka and D. J. Filmore, J. Chem. Phys. **70**, 1214 (1979).
[9] E. Helfand and G. H. Fredrickson, Phys. Rev. Lett. **62**, 2468 (1989).

[10] A. Onuki, Phys. Rev. Lett. **62**, 2427 (1989).

[11] M. Doi, in *Dynamics and Patterns in Complex Fluids*, edited by A. Onuki and K. Kawasaki (Springer, New York, 1990), p. 100.

[12] M. Doi and A. Onuki, J. Phys. (France) II **2**, 1631 (1992).

[13] S. T. Milner, Phys. Rev. E **48**, 3674 (1993).

[14] A. Onuki, J. Non-Cryst. Solids **172-174**, 1151 (1994).

[15] P. G. de Gennes, Macromolecules **9**, 587 (1976); **9**, 594 (1976).

[16] M. Doi, J. Chem. Phys. **79**, 5080 (1983).

[17] H. Tanaka (unpublished).

[18] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, NY, 1979).

[19] L. D. Landau and I. M. Lifshitz, *Theory of Elasticity* (Pergamon, Oxford, 1970).

[20] H. Tanaka, Prog. Theor. Phys. Suppl. **126**, 333 (1997).

[21] H. Tanaka and T. Araki, Phys. Rev. Lett. **78**, 4966 (1997).

[22] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon, Oxford, 1986).

[23] F. Brochard, in *Molecular Conformation and Dynamics of Macromolecules in Condensed Systems*, edited by M. Nagasawa (Elsevier, Amsterdam, 1988), p. 249.

[24] J. Bosse and Y. Kaneko, Phys. Rev. Lett. **74**, 4023 (1995).

[25] See, e.g., *Disorder Effects on Relaxational Processes*, edited by R. Richert and A. Blumen (Springer-Verlag, Berlin, 1994).

[26] H. Tanaka, J. Chem. Phys. **105**, 9375 (1996).

[27] W. C. K. Poon, A. D. Pirie, and P. N. Pusey, Faraday Discuss. Chem. Soc. **101**, 65 (1995).

[28] See, e.g., J. W. Cahn, Acta Metall. **9**, 765 (1961); A. Onuki, J. Phys. Soc. Jpn. **58**, 3065 (1989); A. Onuki and H. Nishimori, Phys. Rev. B **43**, 13 649 (1991); C. Sagui, A. M. Somoza, and R. C. Desai, Phys. Rev. E **50**, 4865 (1994).

[29] P. G. de Gennes, J. Chem. Phys. **72**, 4756 (1980).

[30] V. Kumaran and G. H. Frederickson, J. Chem. Phys. **105**, 8304 (1996).

[31] K. Sekimoto, N. Suematsu, and K. Kawasaki, Phys. Rev. A **39**, 4912 (1989).

[32] A. Onuki, in *Advances in Polymer Sciences* (Springer, Berlin, 1993), Vol. 109, p. 63.

[33] E. S. Matsuo and T. Tanaka, J. Chem. Phys. **89**, 1695 (1988).

[34] Y. Li, C. Li, and Z. Hu, J. Chem. Phys. **100**, 4637 (1994).

[35] R. M. Hikmet, S. Callister, and A. Keller, Polymer **29**, 1378 (1988); S. Callister, A. Keller, and R. M. Hikmet, Makromol. Chem. **39**, 19 (1990).

[36] C. L. Jackson and M. T. Shaw, Polymer **31**, 1070 (1990).

[37] J. Arnauts, H. Berghmans, and R. Koningsveld, Makromol. Chem. **194**, 77 (1993); S. Berghmans, J. M. Mewis, H. Berghmans, and H. Meijer, Polymer **36**, 3085 (1995).

[38] See, e.g., M. J. Geller and J. P. Huchra, Science **246**, 897 (1989).

[39] D. Sappelt and J. Jäckle, Europhys. Lett. **37**, 13 (1997); J. Jäckle (private communication).

[40] S. W. Song and M. Torkelson, Macromolecules **27**, 6390 (1994); C. K. Haas and J. M. Torkelson, Phys. Rev. Lett. **75**, 3134 (1995).

[41] G. Widawski, M. Rawiso, and B. Francois, Nature (London) **369**, 387 (1994).