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Dynamics of Phase-Separated Fluids Under External Fields[1]

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Phase separation in external fields has attracted much attention recently. The reason is twofold. Since kinetics of phase separation and morphology of growing domains can be controlled by external fields, it is of technological importance. The other is that existence of mesoscale domains causes curious dynamical properties in fields, which provides us with a fundamental statistical dynamic problem. One example is a phase separation of binary fluids under shear flow. Phase-separated domains are deformed under the field, which causes burst, fusion, and reconnection of domains so that extra energy dissipation occurs in these processes. Because of this large deformation of domains, the system exhibits quite unusual rheological behavior. The kinetics of phase separation of binary fluids is also influenced by an external electric field when the new phases have different dielectric constants. Deformation and interaction of domains in an electric field are investigated by means of an interfacial approach.

KEY WORDS: binary fluid; dielectric constant; domain rheology; electric field; normal stress difference; phase separation; shear flow.

1. INTRODUCTION

After a binary system is quenched below a phase-separation temperature, domains of the ordered phases form and grow. If we apply some external fields such as flow and electric fields, we can control the kinetics and morphology of growing mesoscopic domains. This is of technological importance, and a substantial number of experiments has been carried out recently. On the other hand, from a theoretical point of view, dynamics of domains in fields provides us with fascinating unsolved fundamental problems. Domain deformation under the field causes burst, fusion, and

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reconnection of domains so that extra energy dissipation occurs in these processes. Thus, the response of the system to the fields easily enters a nonlinear regime, so that anomalous effects are expected.

In this paper, we discuss mainly two subjects. One is the domain rheology under steady shear flow. The other is the domain deformation and interaction under external electric field.

The former subject was studied by Doi and Ohta [1]. It was predicted that anomalous rheological behavior appears even in weak shear. One of the characteristic features of a phase-separating fluid is that there is no intrinsic length (and time) scale. This causes asymptotically large deformation of domains under a steady shear flow. Thus the stress–shear rate relation becomes nonlinear and therefore the system exhibits a non-Newtonian behavior. In fact, the above prediction has been observed in recent experiments of polymer blends by Takahashi *et al.* [2, 3]. In Section 2, we briefly describe these developments.

In a system where the dielectric constant of domains is different from that of the surrounding matrix, one can control the domain morphology by applying an electric field. In fact, there are several experimental studies of phase separation under an external electric field. In a polymeric material, Adachi *et al.* [4] and Krause and her co-workers [5] have explored domain deformation and instability by changing the magnitude of the electric field.

In Section 3, starting with the model equations for binary critical fluids, we derive the interface equation of motion for the phase-separating process. We assume that the dielectric constant depends on the local order parameter so that this constant has a different value in each ordered phase.

As a special case, we study, in Section 4, deformation of a single domain in an electric field based on the interface equation of motion. The interaction between two polarized domains mediated by both the electrothermodynamic and the hydrodynamic effects is also obtained from our interface equation of motion. In Section 5, we discuss the results obtained and make a concluding remark.

2. DOMAIN RHEOLOGY

In a phase-separating process, domains of low-temperature phases appear and grow. When the volume fraction is 1/2, the domains constitute a randomly interconnected structure. If we apply a shear flow, these domains undergo deformation, burst, and recombine. This is responsible for the excess macroscopic stress. Because domains in fluids are easily deformable, a nonlinear effect is expected to emerge even in a relatively weak shear. A phenomenological theory of this problem was proposed in Ref. 1. Here we describe the essential part of the theory.

First, we emphasize that the relevant characteristic time scale of deformed domains is not a relaxation time of the local order parameter but a relaxation time associated with interface motion. In the absence of flow, the relaxation rate Γ_D due to the concentration diffusion across the domains is given by

$$\Gamma_D = \frac{L}{\xi} \frac{1}{l^3} \tag{1}$$

where L is an Onsager coefficient and ξ the interface width. The characteristic domain size is denoted by l. We have assumed $l \gg \xi$. In fluids, there is another relaxation mechanism due to the hydrodynamic interaction. The relaxation rate Γ_H is given by

$$\Gamma_H = \frac{\sigma}{\eta} \frac{1}{l} \tag{2}$$

where σ is the interfacial tension and η is the shear viscosity. For simplicity, we have assumed that the shear viscosity has the same value in the two phases.

Here we make two remarks about the above relaxation rates. First, it is noted that the characteristic size l of domains is not a material constant but is a dynamical quantity increasing with time in the ordering process. Second, in polymeric materials, the shear viscosity is so large that the hydrodynamic effect is not important in the early stage of the phase separation. Comparing Eqs. (1) and (2), however, one notes that the hydrodynamic relaxation eventually dominate the diffusional relaxation in the later stage, where l is sufficiently large.

We are concerned with this situation where the hydrodynamic effect is relevant. Thus the steady shear rate $\dot{\gamma}$ should be compared with Γ_H. From this dimensional analysis we have a characteristic length l^* of the problem,

$$l^* = \frac{\sigma}{\eta} \frac{1}{\dot{\gamma}} \tag{3}$$

Here we again emphasize that (3) is the only quantity which has a dimension of length constructed from the parameters of the system.

The macroscopic stress tensor Π due to domains has the dimension [1, 6]

$$[\Pi] = \frac{[\text{interfacial tension}]}{[\text{length}]} \tag{4}$$

Substituting Eq. (3) into Eq. (4) we obtain

$$\Pi = c\eta\dot{\gamma} \tag{5}$$

where the positive constant c may depend on the average volume fraction.

At first sight, Eq. (5) looks trivial. However, we should emphasize that we have not assumed any linearity between the stress and the shear rate in the derivation of Eq. (5). Equation (5) is a consequence of absence of any intrinsic length scales (and time scales) in the system and therefore is quite general. This unusual property will be clearer by noting that the above argument predicts the normal stress difference N to be proportional to the shear rate:

$$N \propto |\dot{\gamma}| \tag{6}$$

Equations (5) and (6) were also derived in Ref. 6 in a restricted condition based on a disconnected-droplet picture.

Quite recently, Takahashi *et al.* [2, 3] have performed viscoelastic experiments of immiscible polymer blends. They have indeed confirmed the anomalous relations expressed by Eqs. (5) and (6). Figures 1 and 2 show their results [3] for the shear stress and the normal stress difference, respectively. The system is a mixture of a polydimethylsiloxane (PDMS) and a polybutadiene (PB). The volume-fraction dependence is also seen in

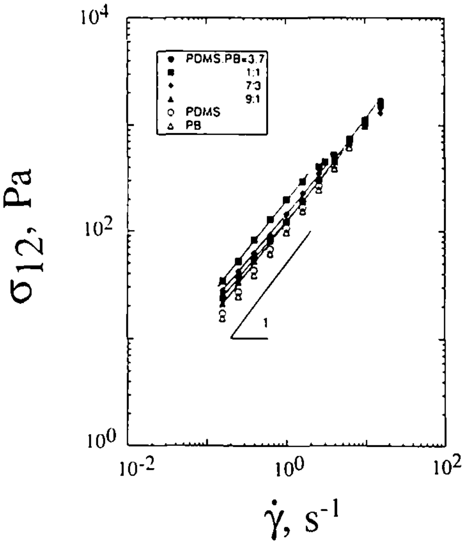

Fig. 1. Shear stress σ_{12} versus shear rate $\dot{\gamma}$ for several different volume fractions and for a pure PDMS and a pure PB system [3].

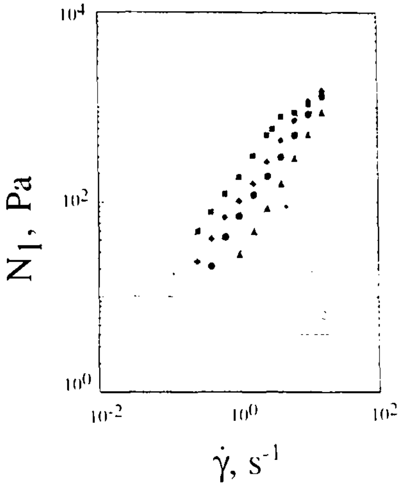

Fig. 2. Normal stress difference N_1 versus shear rate $\dot{\gamma}$ [3]. The meaning of the symbols is the same as in Fig. 1.

Figs. 1 and 2. In particular, the usual Newtonian behavior is evident in each pure system. This clearly indicates that the singularity in the normal stress difference Eq. (6) is attributed to the interfacial effects.

3. INTERFACE EQUATION OF MOTION

In this section, we derive an interface equation of motion for growing domains subjected to an external electric field. We start with the model equations for critical fluid mixtures [7]. The order parameter S is the local volume fraction of one of the components. When the static electric field is imposed on the system, the Ginzburg–Landau free energy functional $H\{S\}$ takes the following form:

$$H\{S\} = \int d\mathbf{r} \left[\frac{1}{2} (\nabla S)^2 + g(S) - \frac{1}{8\pi} \varepsilon(S) \mathbf{E}^2 \right] \tag{7}$$

where $g(S)$ has degenerate local minima at $S = 0$ and 1. The last term in Eq. (7) is the electrostatic energy. The local electric field is denoted $\mathbf{E}$. Here we assume that the electric field is so weak that it does not alter quantitatively the equilibrium phase diagram. The dielectric constant ε is assumed to depend on S such that

$$\varepsilon(S) = \varepsilon_M + (\varepsilon_D - \varepsilon_M) S \tag{8}$$

The time evolution of the local order parameter is coupled with the local-velocity field $\mathbf{v}$. These are governed by the following set of equations:

$$\frac{\partial S}{\partial t} + \nabla \cdot (\mathbf{v} S) = \nabla^2 \frac{\delta H}{\delta S} \tag{9}$$

$$\frac{\partial \mathbf{v}}{\partial t} = (\nabla S) \frac{\delta H}{\delta S} + \eta \nabla^2 \mathbf{v} \tag{10}$$

where the system has been assumed to be incompressible $\nabla \cdot \mathbf{v} = 0$. For simplicity, we do not consider the case where the shear viscosity η has a different value at each phase.

When the system has no free charges, the electric field $\mathbf{E}$ obeys

$$\nabla \times \mathbf{E} = 0, \qquad \nabla(\varepsilon \mathbf{E}) = 0 \tag{11}$$

These equations are to be solved for a given domain configuration and under the condition $\mathbf{E} = \hat{\mathbf{z}} E_{\mathrm{ex}}$ at infinity where $\hat{\mathbf{z}}$ is the unit vector in the z direction and E_{ex} is the magnitude of the external field.

We can derive the interface equation of motion in a manner similar to that in Ref. 8. Since the relaxation of the velocity field $\mathbf{v}$ is much faster than that of the order parameter S, we may put $\partial \mathbf{v}/\partial t = 0$ in Eq. (10). Hence the local velocity $\mathbf{v}$ can be expressed in terms of $\{S\}$. On the other hand, the interface relaxation due to the hydrodynamic effect given by Eq. (2) is larger than that of the diffusion effect given by Eq. (1). Therefore we may ignore the right-hand side of Eq. (9). This means that the normal velocity of an interface is equal to the local velocity $\mathbf{v}$ at that point. In this way, we obtain the equation of motion as

$$\begin{aligned} V(a) = {} & \int da' \sum_{ij} n_i(a)\, T_{ij}(\mathbf{r}(a) - \mathbf{r}(a'))\, n_j(a') \\ & \times \left[\sigma K(a') - \frac{1}{8\pi} \int dn'\, \mathbf{E}(a', n')^2 \frac{\partial \varepsilon}{\partial n'} \right] \end{aligned} \tag{12}$$

where $V(a)$ is the normal component of the interface velocity at point a on the interface, K the mean curvature, and n_i the ith component of the unit normal $\mathbf{n}$. The Oseen tensor is denoted T_{ij}; its Fourier component is given by

$$T^{\alpha\beta}(\mathbf{k}) = \frac{1}{\eta} \left(\delta_{\alpha\beta} - \frac{k^\alpha k^\beta}{k^2} \right) \frac{1}{k^2} \tag{13}$$

We have introduced the local curvilinear coordinates (a', n'), where n' stands for the axis normal to the interface. The integral over a' runs over all of the interfaces.

If the difference of the dielectric constants $\varepsilon_D - \varepsilon_M$ is small, the Maxwell equations, Eq. (11), can be solved perturbatively. Up to first order, the solution is readily obtained as

$$E^{\alpha}(\mathbf{k}) = \sum_{\beta} \left[\delta_{\alpha\beta}\delta(\mathbf{k}) - \frac{\varepsilon_D - \varepsilon_M}{\varepsilon_M} \frac{k^{\alpha}k^{\beta}}{k^2} S_{\mathbf{k}} \right] E^{\beta}_{\mathrm{ex}} \tag{14}$$

where $E^{\alpha}(\mathbf{k})$ and $S_{\mathbf{k}}$ are the Fourier components of $E^{\alpha}(\mathbf{r})$ and $S(\mathbf{r})$, respectively. Substituting Eq. (14) into the last term in Eq. (7), the electrostatic energy can be written in terms of S as

$$-\frac{1}{8\pi} \int d\mathbf{r}\, \varepsilon(S)\mathbf{E}^2 = +\frac{1}{8\pi} \frac{(\varepsilon_D - \varepsilon_M)^2}{\varepsilon_M} \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{1}{k^2} (\mathbf{k} \cdot \mathbf{E}_{\mathrm{ex}})^2 S_{\mathbf{k}} S_{\;\mathbf{k}} \tag{15}$$

By means of Eq. (15), the last term in Eq. (12) can be written in a more convenient form:

$$\frac{1}{4\pi} \frac{(\varepsilon_D - \varepsilon_M)^2}{\varepsilon_M} \int da'' \left[\mathbf{E}_{\mathrm{ex}} \cdot \nabla' G(\mathbf{r}(a'), \mathbf{r}(a'')) \right] \mathbf{E}_{\mathrm{ex}} \cdot \mathbf{n}(a'') \tag{16}$$

where $-\nabla^2 G(\mathbf{r}', \mathbf{r}'') = \delta(\mathbf{r}' - \mathbf{r}'')$.

Here we make a remark about Eq. (15). If we regard $\mathbf{E}_{\mathrm{ex}}$ as a uniaxial external stress, Eq. (15) is equivalent with an increase in the elastic energy in solids. Hence Eq. (9) with $\mathbf{v} = 0$ is a model for phase separation of binary solids under external load [9]. In the present problem, however, both the electrothermodynamic and the hydrodynamic coupling are relevant and therefore the dynamics of domains is entirely different from that in a solid system.

4. INTERACTION AMONG DOMAINS

By applying an electric field, domains are elongated in the direction of the field. When the field is weak, each domain takes an elliptic form. As in Ref. 4, we introduce the deformation parameter D:

$$D = \frac{a - b}{a + b} \tag{17}$$

where a and b are the major and minor semiaxes of the ellipsoid, respectively. The equation for D for a single domain deformed around a sphere with radius R can be derived from Eq. (12). The result is given by

$$\frac{dD}{dt} = -\frac{16}{35}\frac{\sigma}{\eta R}D + \frac{9}{35}\frac{1}{4\pi}\frac{\varepsilon_{\mathrm{M}}(\varepsilon_{\mathrm{D}}-\varepsilon_{\mathrm{M}})^2}{(\varepsilon_{\mathrm{D}}+2\varepsilon_{\mathrm{M}})^2}\frac{E_{\mathrm{ex}}^2}{\eta} \tag{18}$$

This is consistent with the known result [4] and provides a verification of the validity of the interface equation of motion given by Eq. (12).

The interaction between two domains can also be obtained. We assume that the domains are spherical with radii a_1 and a_2 for a weak electric field. The center of gravity is denoted $\mathbf{X}_i$ ($i = 1, 2$). Under the condition that the distance between the domains is much larger than the radii, we obtain from Eq. (12) with Eq. (14),

$$\begin{aligned}\frac{dX_1^\alpha}{dt} = -\frac{1}{4\pi}\frac{(\varepsilon_{\mathrm{D}}-\varepsilon_{\mathrm{M}})^2}{\varepsilon_{\mathrm{M}}}\bigg\{&\frac{E_{\mathrm{ex}}^2}{\eta}\frac{4}{15}V_2 a_1^2\frac{\partial}{\partial X_1^\alpha}\frac{\partial^2}{\partial X_1^\zeta\,\partial X_2^\zeta}G(\mathbf{X}_1-\mathbf{X}_2)\\ &+E_{\mathrm{ex}}^2 V_1 V_2\sum_\beta T^{\alpha\beta}(\mathbf{X}_1-\mathbf{X}_2)\frac{\partial}{\partial X_2^\beta}\frac{\partial^2}{\partial X_1^\zeta\,\partial X_2^\zeta}G(\mathbf{X}_2-\mathbf{X}_1)\bigg\}\end{aligned} \tag{19}$$

where V_i is the volume of ith sphere. The first term is dominant at long distance and it shows that the interaction is attractive for the configuration such that $\mathbf{X}_1-\mathbf{X}_2$ is parallel to the field direction, whereas it is repulsive for $\mathbf{X}_1-\mathbf{X}_2$ perpendicular to this direction.

5. DISCUSSION

Domain growth in fluids under shear flow and in an electric field has been investigated. The prediction of anomalous rheological behavior [1] is in a good agreement with experiments [2, 3]. However, the theory is essentially a dimensional analysis. It is not easy to develop a quantitative theory to describe burst and recombination of domains under flow. In fact, the phenomenological theory [1] does not succeed in reproducing, in full detail, the time dependence of stress relaxation observed in experiments [2]. Thus there is plenty of room for improving the theory.

In the case of fluid mixtures in an electric field, we have derived the interface equation of motion in a closed form when the difference of the dielectric constants is small. The problem is more difficult compared to solid systems because the domain motion is caused by the hydrodynamic effect as well as the electrothermodynamic one. When the strength of the external field is small, we are able to deal with these interactions analytically and derive the equation of motion for spherical domains. This interfacial approach together with computer simulations of Eqs. (9), (10), and (11) would be useful for further understanding kinetics of domain growth under fields.

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