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Effects of Shear Flow and Viscosity Difference on Phase Separation[1]

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We discuss some salient features recently found in phase-separating fluids under shear. They are highly elongated, bicontinuous domain structures (string phase), hysteresis in the droplet distribution in the off-critical case, existence of the spinodal due to suppression of droplet formation in shear, and critical rheology. We also examine the condition of bicontinuity and the effective viscosity when the two phases have different viscosities.

KEY WORDS: near-critical fluids; phase separation; shear flow; rheology.

1. INTRODUCTION

Recently, effects of shear on phase transitions have been extensively studied in various fluid systems. The effects are particularly marked in the following cases. (i) First studies were focused on fluids with slowly relaxing fluctuations such as near-critical fluids [1, 2]. They are deformed by shear within their thermal lifetimes. (ii) If shear is applied to phase-separating fluids, domains grow and are eventually nonlinearly affected by shear, however small the shear rate is [3–9]. The observed effects are very different in the two cases of spinodal decomposition [3–7] and nucleation [8, 9]. (ii) Fluids with long-range order such as colloidal suspensions have also been studied extensively. They can often form layered structures with two-dimensional order in shear [10]. (iv) Fluids with mesoscopic structures are also very sensitively affected by shear [11]. They are liquid crystals [12], surfactant systems [13], block copolymers [14], and electrorheological (or ferromagnetic) fluids [15]. (v) Viscoelastic fluids such as entangled polymer solutions and blends behave like gels on relatively small spatial

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scales or on relatively short time scales [16]. Their responses to shear are very unique and dramatic. An example of such effects is shear-induced phase separation [6, 17], which arises from a dynamical coupling between stress and diffusion [16]. That is, shear produces stress disequilibrium in the presence of the composition fluctuations because they sensitively give rise to heterogeneities of the viscosity; it then leads to relative motion between the two components.

Most theoretical and experimental studies have thus treated near-critical fluids and a variety of complex fluids with large and/or complicated internal degrees of freedom. However, from the above criteria, interesting nonlinear effects of shear can also be expected in fluids near glass transitions, in which the relaxation of the density or composition fluctuations is extremely slow and viscoelasticity is apparent. Because this field is very diverse and still expanding, it is very difficult at present to write a paper reviewing all these aspects. In this paper, therefore, we review and comment on some recent findings in phase-separating fluids under shear in Section 2–5. In Section 6 we present a first theory of spinodal decomposition when the two phases have different viscosities.

2. STRING PHASE IN SHEAR

We bring a fluid mixture into the unstable region with a stationary shear S held fixed. It is known that the spinodal decomposition is stopped by shear when the two mechanisms of thermodynamic instability and flow-induced deformation are balanced, giving rise to dynamical stationary states [4, 7]. When the composition is at the critical value, previous light scattering experiments have detected very strong anisotropy (streak patterns) in the scattering intensity even in weak shear, $S\tau \ll 1$, where τ is the average relaxation time of the critical fluctuations [5, 7, 18]. Computer simulations have also shown strong deformations of bicontinuous domain structures just after quenching [19–21]. To investigate the ultimate bicontinuous morphology in shear, Hashimoto et al. have recently taken microscope pictures from a Newtonian ternary polymer solution undergoing phase separation [22]. In their system the interaction between two species of polymers is much weakened by a common solvent, and the viscosity is quite high (~ 1 poise), though the entanglement effect is not yet severe [7]. As a result the time scale of phase separation is dramatically slowed down ($\tau \sim 6$ s) even if the quench depth is not small. They have found that domains are elongated into extremely long cylinders in steady states except for extremely weak shear. For $S\tau < 1$ such stringlike domain structures still contain a number of random irregularities undergoing frequent breakup, interconnection, and branching, although the overall structure is kept stationary. For $S\tau > 1$ the continuity of the strings increases and extends even macroscopically in the flow direction while their diameter is less than $10\,\mu$m. This means that strong shear can suppress undulations of the interfaces, which would grow in the absence of shear. Finally, for very large shear S ($\gtrsim 10^2$ s), the diameter becomes of the order of the interface thickness, of the order of 500 A, and the contrast between the two phases vanishes, resulting in shear-induced homogenization.

It seems to be a general aspect in any two-phase state that domains are much more elongated in shear in the bicontinuous case than in the droplet case in which only one phase is percolated.

3. NUCLEATION IN SHEAR

Let us consider the situation in which the temperature T is slightly lowered below the coexistence temperature T_{cx} by $\delta T = T_{cx} - T$ in the off-critical case. To observe appreciable droplets of the phase, the critical droplet must not be torn by shear and hence we require $R_c < R^*$, where $R_c \sim \xi/\Delta$ is the critical radius and $R^* \sim \sigma/\eta S$ is the Taylor breakup size [3]. The Δ $[=\Delta(0)]$ is the initial supersaturation, much smaller than 1, and is related to δT and $\Delta T = T_c - T_{cx}$ by $\Delta \simeq \frac{1}{6}(\delta T/\Delta T)$ near criticality. Then, a necessary condition of observing noticeable droplets [8] is as follows:

$$S\tau < \Delta \tag{1}$$

This gives an upper limit of shear, $S^* \sim \Delta/\tau$, at each δT or a lower limit of the quench depth, $\delta T^* \sim S\tau(\Delta T) \propto S(\Delta T)^{1-3\nu}$, at each S in order to trigger nucleation. This simple criterion has been confirmed in binary mixtures under stirring [24] and uniform shear [9]. Let $\delta T_{\mathrm{BD}} \cong 0.15\Delta T$ be the classical Becker–Döring limit. Then $\delta T^* > \delta T_{\mathrm{BD}}$ close to the critical point and $\delta T^* < \delta T_{\mathrm{BD}}$ relatively far from the critical point. It is clear that δT must exceed δT_{BD} for growth of droplets in realistic observation times if there are no stable droplets ($R > R_c$) at the initial condition. On the other hand, if δT is decreased from a value larger than both δT^* and δT_{BD}, droplets preexist and are broken at $\delta T = \delta T^*$ from Eq. (1).

According to Eq. (1), a nearly stationary distribution of droplets is realized after a long relaxation time. Remarkably, the size distribution peaks at $R \cong R^*$ and, once such a distribution is established, further time development of the droplet distribution becomes extremely slow. Min and Goldburg [9] found by gradually increasing δT from zero that the supersaturation tends to a finite value $\Delta(S)$ dependent on S. Here the supersaturation can be determined because the droplet volume fraction is

$\phi = \Delta(0) - \Delta(S)$. Though such a state is nearly stationary, there is still a diffusive current onto each droplet from the surrounding metastable region. It will grow above R_c and break into smaller droplets, which will then start to grow again or dissolve into the metastable region depending on whether their radii are larger or smaller than R_c. Each droplet will also collide with another one on the time scale of $1/S\phi$ [5]. The evolution of the droplet distribution is therefore very complex and the observed quasistationarity is produced by a delicate balance among these processes. Alternatively, we may also start with an opaque state in which δT is sufficiently large and $\Delta(S) \cong 0$ [or $\phi \cong \Delta(0)$]. Then, by gradually decreasing δT at fixed S, a nearly stationary state will be obtained. Surprisingly, it has been found to be more opaque and has a larger droplet volume fraction (or a smaller supersaturation) than in the reverse case of increasing δT from zero [9]. Takebe et al. [6] also found similar hysteresis in an off-critical ternary polymer solution by increasing or decreasing S with δT fixed. There, however, the fluid is far from criticality and S is changed over very wide ranges. These steady states seem to be still slowly evolving, but it is not clear how the observed hysteresis depends on the waiting time at given δT and S (~ 10 min in both experiments [8, 26]).

4. SPINODAL IN SHEAR

So far we have assumed the very weak shear condition $S\tau \ll 1$ in the off-critical case. However, if $S\tau$ is larger than Δ and δT is increased, metastability will be suppressed, because localized droplets larger than R^* cannot be stable. In particular, if $S\tau \gtrsim 1$, the suppression is complete because R_c becomes of order ξ, and instability of plane-wave fluctuations will occur as spinodal decomposition. Remarkably, the spinodal can be well defined as the onset point of phase separation, whereas T has no definite meaning in quiescent fluids. This explains a part of data by Takebe et al. [26] (a branch of decreasing S). They decreased shear from very large values and detected a well-defined spinodal curve in strong shear. In the case $S\tau \lesssim 1$ the problem is delicate; however, we can well expect considerable enhancement of thermal fluctuations as δT and hence the supersaturation are increased. We finally mention experiments by Russian groups [27, 28]. They detected a peak in the specific heat well inside the coexistence curve in stirred off-critical fluids, where the peak height increased with increase in the degree of stirring. They claimed that the spinodal point can be reached in the presence of stirring. We need more experiments to clarify these points.

5. CRITICAL RHEOLOGY

In shear flow the fluctuations of the order parameter ψ give rise to the following additional shear stress [29]:

$$\Delta\sigma_{xy} = S\Delta\eta = -k_{B}T\left\langle \frac{\partial}{\partial x}\psi \frac{\partial}{\partial y}\psi \right\rangle \tag{2}$$

The fluctuation contributions to the normal stress differences are written as

$$\sigma_{xx} - \sigma_{yy} = k_{B}T\left\langle \left(\frac{\partial\psi}{\partial y}\right)^{2} - \left(\frac{\partial\psi}{\partial x}\right)^{2} \right\rangle \tag{3}$$

$$\sigma_{xx} - \sigma_{zz} = k_{B}T\left\langle \left(\frac{\partial\psi}{\partial z}\right)^{2} - \left(\frac{\partial\psi}{\partial x}\right)^{2} \right\rangle \tag{4}$$

In the one-phase region of near-critical fluids, the mode-coupling theory predicted that $\Delta\eta$ is nearly logarithmic as $\ln(\xi/\xi_0)$ in weak shear and as $\ln(1/k_c\xi_0)$ [30] in strong shear. In the $\varepsilon = 4 - d$ expansion of renormalization group theory [31] we obtain slightly different forms, $\sigma_{xy} \propto S\,|S|^{-\varepsilon/76}$ and $\eta \propto |S|^{-\varepsilon/76}$ to first order in ε in the strong-shear case $S\tau > 1$. The normal stress differences are proportional to $|S|^{1-\varepsilon/76}$ because they are even functions of S. For positive S the following ratios are universal in strong shear:

$$(\sigma_{xx} - \sigma_{yy})/\sigma_{xy} = 0.046\varepsilon[1 + O(\varepsilon)] \tag{5}$$

$$(\sigma_{xx} - \sigma_{zz})/\sigma_{xy} = 0.024\varepsilon[1 + O(\varepsilon)] \tag{6}$$

In the two-phase case, larger contributions arise from interface deformations. In particular, in weak shear, interfaces are sharp and Eqs. (2)-(4) yield a well-known expression [29, 32],

$$\Delta\eta = -\frac{1}{S}\sigma\int da\, n_x n_y \tag{7}$$

$$\sigma_{ii} - \sigma_{jj} = \sigma\int da\,(n_j^2 - n_i^2) \tag{8}$$

where σ is the surface tension, $n = (n_x, n_y, n_z)$ is the normal unit vector, da is the surface element, and the surface integral is within a unit volume. Note that Eqs. (7) and (8) are generally valid even for fluids far from the critical point. The are the sole excess contribution in two-phase states if the viscosities of the two phases are the same. If we suppose an assembly of spheroidal droplets near the breakup condition, $R \sim R^*$, we estimate $\langle -n_x n_y \rangle \sim 1$ and

$$\Delta\eta \sim \phi\sigma/SR \sim \phi\eta \tag{9}$$

where ϕ is the volume fraction. The normal stress differences behave as

$$\sigma_{xx} - \sigma_{yy} \sim \sigma_{xx} - \sigma_{zz} \sim |S|\, \phi\eta \tag{10}$$

In near-critical fluids these values are two orders of magnitude larger than those in the one-phase region given by Eqs. (5) and (6). Equations (9) and (10) were derived in Refs. 29 and 32.

Krall et al. have confirmed Eq. (9) in a near-critical binary mixture [33]. There, however, $\Delta\eta(t)$ slowly decreased to 0 after $t \gtrsim 20$ s at the critical composition. They ascribed this decay to the fact that in their viscometer shear oscillates and damps in time and cannot stop coarsening after a certain decrease of the oscillating amplitude. Here I point out that in the string phase discussed in Section 2.2 the interfaces are mostly parallel to the flow and $n_x \cong 0$ in Eq. (7), leading to $\Delta\eta \cong 0$. In fact, in a very recent experiment by Hamano et al., $\Delta\eta(t)$ decreased to zero very slowly after quenching in stationary shear [4]. This should arise from reorganization of domains from random to elongated shapes.

Takahashi et al. measured the first normal stress difference to confirm Eq. (10) in a viscous Newtonian polymer mixture in which the viscosity difference is small [35]. This is a marked effect because the normal stress differences are very small in the one-phase region and jump to large values after quenching. Note that the normal stress differences remain large even in the string phase, in contrast to the behavior of $\Delta\eta$.

6. SPINODAL DECOMPOSITION IN BINARY MIXTURES WITH DIFFERENT VISCOSITIES

In near-critical fluids the two phases have almost the same viscosity. However, the viscosity difference is not generally small far from the critical point and then the velocity fields in the two phases become asymmetric even for the same volume fraction of 50%. Thus the viscosity difference is a crucial factor determining the domain morphology as well as the volume fraction. In the following the viscosity and the volume fraction of the more viscous phase will be written as η_1 and ϕ_1, respectively, and those of the less viscous phase as η_2 and $\phi_2 = 1 - \phi_1$, respectively. Notice that the typical velocity gradients in the two phases, S_1 and S_2, satisfy

$$\eta_1 S_1 \sim \eta_2 S_2 \tag{11}$$

from the shear stress balance at the interfaces. That is, the velocity gradients in the first phase are smaller than those in the second phase by the factor η_2/η_1. This suggests that domains of the first phase tend to take closed shapes because those of the second phase are more easily deformed into extended shapes.

We first suppose a bicontinuous case in spinodal decomposition without applied shear. Here the second phase is compressed and extended simultaneously, while the first phase takes more isotropic shapes. In particular, in the limit $\eta_2 \ll \eta_1$, the second phase forms thin layers enclosing the first phase. Let R_1 be the typical domain size of the first phase. Then, because the second phase is compressed into layers, the distance between two neighboring domains of the first phase is equal to the layer thickness and is characterized by a smaller length R_2. The two lengths R_1 and R_2 are related to the volume fractions by

$$AR_1 \sim \phi_1, \qquad AR_2 \sim \phi_2 \tag{12}$$

where A is the surface area per unit volume. Here we note that the velocity fields in the two phases, $S_1 R_1$ and $S_2 R_2$, should both be of the order of the growth rate $\partial R_1/\partial t$ of the domains of the first phase,

$$S_1 R_1 \sim S_2 R_2 \sim \frac{\partial}{\partial t} R_1 \tag{13}$$

From Eqs. (11) and (13) we obtain

$$R_1/\eta_1 \sim R_2/\eta_2 \tag{14}$$

Furthermore, using Eq. (12), we find the following condition of bicontinuity:

$$\phi_1/\eta_1 \sim \phi_2/\eta_2 \tag{15}$$

The less viscous phase has a smaller volume fraction in the bicontinuous case, as ought to be the case. The above relation has been known as an empirical law for polymer mixtures in the engineering literature [36]. On the other hand, the growth law may be obtained by assuming that the shear stress $\eta_1 S_1 \sim \eta_2 S_2$ given in Eq. (11) is of the order of the surface tension foce density σ/R_1. It readily follows that

$$(\partial/\partial t) R_1 \sim \sigma/\eta_1 \qquad \text{or} \qquad R_1 \sim (\sigma/\eta_1) t \tag{16}$$

which is a generalized McMaster–Siggia law for the case of different viscosities [37, 38].

Next we apply a weak macroscopic shear to the system. The bicontinuity is realized in a wider parameter region than in the absence of macroscopic shear and high elongation of domains will be attained there as discussed in Section 2. We estimate the effective viscosity $\eta_{\rm eff}$ in such two-phase states. Note that we need not assume Eq. (15) and then Eqs. (13) and (14) are not necessarily correct, whereas Eqs. (11) and (12) remain valid. The macroscopic shear S is the following average of S_1 and S_2:

$$(R_1+R_2)S \sim R_1S_1+R_2S_2 \tag{17}$$

Using Eq. (11), we find

$$S \sim \phi_1 S_1+\phi_2 S_2 \tag{18}$$

The $\eta_{\rm eff}$ is equal to S divided by the shear stress, so Eqs. (10) and (17) yield the desired result,

$$1/\eta_{\rm eff} \sim \phi_1/\eta_1+\phi_2/\eta_2 \tag{19}$$

When $\eta_1 \gg \eta_2$, this relation means that even a small fraction of the second phase can drastically reduce $\eta_{\rm eff}$. Obviously, the second phase acts as a lubricant. We note that the surface contribution, Eq. (7), to $\Delta\eta$ has been neglected here, which is valid in the string phase. But in the transient process or in the droplet case, it holds that $\langle -n_x n_y \rangle \sim 1$; then, the surface contribution $\Delta\eta$ is of order $\sigma A/S \sim \sigma\phi_1/R_1 S$.

Very recently the rheology in two-phase states with viscosity difference has been studied theoretically [39]. The normal stress differences are predicted to be still proportional to $|S|$, but have a maximum around the bicontinuity condition as a function of the volume fraction.

7. SUMMARY

Although our examples treated here constitute only a fraction of those in the literature, they nevertheless show that the effects of shear are very diverse and sometimes even spectacular. This paper succeeds a recent short review paper by the present author [40], both shedding light on a facet of the unique problem of shear in condensed matter physics.

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