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Spinodal decomposition under shear

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We examine phase separation of immiscible fluid mixtures in shear flow. Far from the critical point there are two regimes depending on the Reynolds number of the velocity field induced by surface tension. Near the criticality, domains are strongly anisotropic in the strong shear case.

In a previous paper[1] a spinodal decomposition process of a critical binary mixture was considered in the presence of a stationary shear flow. There, strong anisotropy of the growing fluctuations was predicted. However, the theory was based on a linear approximation and on a decoupling scheme of Langer, Bar-on, and Miller.[2] Hence, it is applicable only to an initial stage of the decomposition process and no physical picture was presented for late stages. The aim here is to present such a picture.

The phenomenon has attracted little attention so far and might appear to be special and complicated. However, its study has already been recognized to be of great technological importance for polymer blends.[3,4] In such viscoelastic mixtures shear-induced domains can be sharply elongated and intricately percolated.

Previously, Beysens and Perrot realized a periodic spinodal decomposition of a critical binary mixture quenched below T_c by periodically tilting the capillary tube through which the fluid passed.[5] A spinodal ring appeared when the tube was horizontal and the shear was small. Then it changed into a sharp streak as the tilting angle was increased. Unfortunately, however, in their setup the fluid was turbulently mixed at the two ends of the tube. This makes the analysis not straightforward, although the observed phenomenon is very impressive.

Very recently Hashimoto's group at Kyoto University has performed a preliminary shear-flow experiment on a semidilute solution of polystyrene and polybutadiene.[6] They have found that, even if the fluid is initially in the two-phase state, the interface is broken in pieces and the fluid becomes homogeneous on application of a stationary shear using a setup explained in Ref. 7. At high shear they have observed a stationary sharp streak similar to the transient streak found by Beysens and Perrot. This result suggests that a shear can stop the decomposition process, giving rise to anisotropic domain structures which are dynamically stationary as a result of the balance of the thermodynamic instability and the breakup mechanism by shear. A similar effect has been supposed for the spinodal decomposition in turbulence.[8]

In this Rapid Communication analysis is restricted to binary mixtures of low molecular weights. The temperature T is slightly below the critical value T_c and the composition is at the critical value. Then there are two characteristic regimes, $S\tau_\xi < 1$ and $S\tau_\xi > 1$. Here S is the shear rate and $\tau_\xi \equiv 6\pi\eta\xi^3/k_BT$ is the characteristic time scale of the critical fluctuations, η being the shear viscosity and $\xi = \xi_0(1-T/T_c)^\nu$ being the correlation length.

First let us consider the very weak shear case $S\tau_\xi \ll 1$, for which usual hydrodynamic arguments are sufficient. Therefore the results are applicable even not close to the criticality if $1-T/T_c$ is regarded to be of order 1. A steady state is assumed to be established, in which sedimentation does not take place. Domain sizes will be much greater than ξ and then interfaces can be regarded to be sharp. Here note that a large domain can be easily torn by shear without strong elongation (when the viscosities inside and outside the domain are of the same order). This has been confirmed in the case of an isolated droplet in shear.[9] Let $R_\perp$ and $R_\parallel$ be the characteristic domain sizes perpendicular and parallel to the flow. Then the ratio $R_\parallel/R_\perp$ should not be so large, presumably, being of order $2\sim3$ from the analogy to the droplet case.

The gravity effect will be negligible if[10]

$$R_\parallel < (\sigma/g\Delta\rho)^{1/2} , \tag{1}$$

where g is the gravitational acceleration, σ is the surface tension, and $\Delta\rho$ $[\propto (T_c-T)^\beta]$ is the mass-density difference between the two phases.

If domains are much greater than ξ, the interfacial velocity is equal to the velocity field $\mathbf{u}(\mathbf{r},t)$ at the interfacial position. Here $\mathbf{u}(\mathbf{r},t)$ obeys

$$\rho\frac{\partial}{\partial t}\mathbf{u}+\rho(\mathbf{u}\cdot\nabla)\mathbf{u} = -\nabla p+\eta\nabla^2\mathbf{u} , \tag{2}$$

together with $\nabla\cdot\mathbf{u}=0$. The pressure p is discontinuous across the interface by the amount $\sigma\kappa$, κ being the curvature.

We first neglect the two terms on the left-hand side of (2) which represent the effect of inertia. Then $\nabla p \cong \eta\nabla^2\mathbf{u}$ and this is solved to give[9,11]

$$\mathbf{u}(\mathbf{r}) \cong Sy\mathbf{e}_x + \left(\frac{\sigma}{\eta}\right)\int da'\overleftrightarrow{T}(\mathbf{r}-\mathbf{r}')\cdot\mathbf{n}(\mathbf{r}')\kappa(\mathbf{r}') , \tag{3}$$

where the first term is the average flow, $\mathbf{e}_x$ being the unit vector along the x axis, $\int da'\cdots$ is the surface integral over the interfacial position $\mathbf{r}'$, $\mathbf{n}(\mathbf{r}')$ is the normal unit vector at the interface, and $\overleftrightarrow{T}(\mathbf{r})$ is the following tensor:

$$T_{\alpha\beta}(\mathbf{r}) = \frac{1}{8\pi}\left(\frac{1}{r}\delta_{\alpha\beta}+\frac{1}{r^3}r_\alpha r_\beta\right) . \tag{4}$$

The competition of the two terms in (3) should result in a stationary state. Hence, we are led to the following order estimation:

$$R_\perp \sim R_\parallel \sim \sigma/\eta S \ , \quad (5)$$

where coefficients of order unity are not written explicitly. We can verify $R_\perp \gg \xi$ using the relation $\sigma \sim 0.1 k_B T/\xi^2$.[12] Obviously, the distortion time by shear is of order $R_\parallel/SR_\perp$, whereas the deformation due the surface tension occurs on the time scale of $\eta R_\perp/\sigma$.[13] Equalization of these two times also readily yields (5).

On the basis of (5) the two terms on the left-hand side of (2) are estimated as

$$\rho \frac{\partial}{\partial t}\mathbf{u} \sim \rho(\mathbf{u}\cdot\nabla)\mathbf{u} \sim (\rho\sigma^2/\eta^3 S)(\eta\nabla^2\mathbf{u}) \ . \quad (6)$$

Namely, the Reynolds number is of order $\rho\sigma^2/\eta^3 S$. Thus, (3) and (5) are found to be valid only in the low-Reynolds-number case,

$$S > \rho\sigma^2/\eta^3 \text{ or } S\tau_\xi > \rho\sigma\xi/\eta^2 \ . \quad (7)$$

From (5) this condition can also be written as

$$R_\parallel < \eta^2/\rho\sigma \ . \quad (8)$$

As $T \rightarrow T_c$ we have $(\sigma/g\Delta\rho)^{1/2} \ll \eta^2/\rho\sigma$ except for some exceptional cases.[14] Then (8) [or (7)] is weaker than (1) and the effect of inertia can be safely neglected (before the gravity effect becomes dominant). In this case (5) holds in the following shear region:

$$1/\tau_\xi \gg S > (\sigma g \Delta\rho)^{1/2}/\eta \ . \quad (9)$$

For $S < (\sigma g\Delta\rho)^{1/2}/\eta$ the fluid will tend to a two-phase state.

On the other hand, far from T_c many systems seem to satisfy the reverse condition $(\sigma/g\Delta\rho)^{1/2} \gg \eta^2/\rho\sigma$. For such cases there emerges a shear region where we have $R_\parallel < (\sigma/g\Delta\rho)^{1/2}$, (1), and $S < \rho\sigma^2/\eta^3$, (7). Here the difference in the dynamic pressures exerted on opposite sides of domains is of order $\rho u^2 \sim \rho(SR_\perp)^2$. If this is balanced with the capillary pressure $\sigma/R_\perp$, we can determine the characteristic size of domains.[15] Assuming that $R_\perp$ and $R_\parallel$ are of the same order we find

$$R_\perp \sim R_\parallel \sim (\sigma/\rho S^2)^{1/3} \ . \quad (10)$$

This will hold for

$$(g\Delta\rho)^{3/4}/(\rho^2\sigma)^{1/4} < S < \rho\sigma^2/\eta^3 \ . \quad (11)$$

The Reynolds number is of order $\rho R_\perp^2 S/\eta \sim (\eta^3 S/\rho\sigma^2)^{-1/3} \gtrsim 1$. Within a domain there will be eddies smaller than $R_\perp$. However, they will not strongly affect the interface motion.[15] Note that Furukawa predicted the existence of a late stage with high Reynolds numbers in the normal spinodal decomposition process (without shear).[16,17] There, the domain size was supposed to grow as $R \sim (\sigma/\rho)^{1/3} t^{2/3}$ analogously to (10). The crossover from (5) to (10) and that of Furukawa should be detectable far from T_c rather than close to T_c.

Next we proceed to the strong shear case $S\tau_\xi > 1$, which can be realized only near the criticality.[18,19] There are two characteristic wave numbers, κ and k_c, defined by[1]

$$\kappa = \xi_0^{-1}(k_c\xi_0)^{(\gamma-1)/2\nu}(1-T/T_c)^{1/2} \ , \quad (12)$$

$$k_c = (16\eta S/k_B T)^{1/3} \ , \quad (13)$$

where T is the final temperature below T_c, γ and ν are the usual critical exponents, and ξ_0 is a microscopic length. Note that $l_0 \equiv \kappa/k_c \sim (S\tau_\xi)^{-1/6\nu} < 1$. For $k \gtrsim k_c$ the fluctuations are not much affected by shear and $I_{\mathbf{k}} \equiv \langle |c_{\mathbf{k}}|^2 \rangle \sim 1/k^2$, where $c_{\mathbf{k}}$ is the Fourier component of the order parameter. For $k \lesssim k_c$, neglecting nonlinear interactions, we obtain a linear equation for $I_{\mathbf{k}}(t)$,

$$\frac{\partial}{\partial t} I_{\mathbf{k}} = 2L_0 k^2 - 2L_0 k^2(k^2-\kappa^2) I_{\mathbf{k}} + S k_x \frac{\partial}{\partial k_y} I_{\mathbf{k}}, \quad (14)$$

where $L_0 \cong (k_B T/16\eta) k_c^{-1}$.

If $k_x = 0$, the last term of (14) vanishes and $I_{\mathbf{k}}(t)$ grows for $k < \kappa$ with the growth rate of order $L_0\kappa^4$. If $k_x \neq 0$, the last term serves to strongly suppress the growth. Here the distortion by shear occurs rapidly because

$$S/L_0\kappa^4 = (k_c/\kappa)^4 \sim (S\tau_\xi)^{2/3\nu} \gg 1 \ .$$

As a result the fluctuations can be enhanced only in a narrow wave-vector region given by

$$k_\perp \lesssim \kappa \text{ and } |k_x| \lesssim \kappa^5/k_c^4 \cong \kappa(S\tau_\xi)^{-2/3\nu} \ , \quad (15)$$

where $k_\perp = (k_y^2 + k_z^2)^{1/2}$. Integration of (14) also shows that the peak wave number decreases as $k_m = \kappa/St$ for $k_\perp = 0$, whereas $k_m = 2^{-1/2}\kappa$ for $k_x = 0$.

If either of the two inequalities in (15) does not hold, $I_{\mathbf{k}}$ relaxes to the steady-state intensity in the one-phase state:[18]

$$I_{\mathbf{k}} \sim 1/(k_\perp^2 + \text{const} \times k_c^{8/5} |k_x|^{2/5}) \ . \quad (16)$$

This is the mean-field intensity at $T = T_c$ valid for $k \lesssim k_c$. As $k \rightarrow 0$ it grows more weakly than in equilibrium due to the presence of the power $|k_x|^{2/5}$ in the denominator of (16). This ensures the validity of a mean-field theory for $d > 2.4$ in the one-phase steady state, d being the spatial dimensionality. Namely, the critical dimensionality is lowered to 2.4. Note that the anisotropic intensity in the one-phase region has been measured by light scattering.[19]

The small dimension of the region (15) much reduces the magnitude of the nonlinear interactions among the growing fluctuations. This makes the linear equation (14) applicable in a sizable time region $0 < t < t_c$ after the quench. Numerical calculations yield[1]

$$t_c \sim 6\ln(k_c/\kappa)/(L_0\kappa^4) \ . \quad (17)$$

At $t = t_c$ the fluid should be composed of anisotropic domains, which are presumably interconnected at the critical composition. The length perpendicular to the flow $R_\perp$ is not much larger than $1/\kappa$. The length along the flow $R_\parallel$ is of the following order:

$$R_\parallel \sim St_c/\kappa \sim [6\ln(k_c/\kappa)](S\tau_\xi)^{2/3\nu}\kappa^{-1} \ . \quad (18)$$

Reference 1 does not give a picture for $t > t_c$. I consider that the coarsening process is likely to be stopped at $t \sim t_c$. If domains with well-defined interfaces are rapidly elongated, the conservation law requires that the domain sizes perpendicular to the flow should soon be diminished to be less than the interface width $1/\kappa$. This should lead to fragmentation of domains. Then we expect that $R_\perp \sim 1/\kappa$ and $R_\parallel$ is given by (18) for $t \gtrsim t_c$. As a result the scattered light intensity should have a very thin streak in the region $|k_x| \lesssim 1/R_\parallel$ and $k_\perp \lesssim \kappa$. In the remaining regions the intensity is given by (16) for $k \lesssim k_c$ and by $1/k^2$ for $k \gtrsim k_c$. With further increasing shear the interfaces will become diffuse and the contrast between the two phases will be blurred.[20] We stress that these expectations for the late stage ($t \gtrsim t_c$) are at present only conjectures inferred from the analysis in Refs. 1 and 18.

In Fig. 1 we show different dynamic regimes on the $|k_x/k_c| - k_\perp/k_c$ plane for unstable, critical binary mixtures in the strong shear case. The fluctuations can grow to form anisotropic domains only in the region (I), outside which they are not affected by the quench. The regions (II) and (III) are divided by the curve $|k_x/k_c| = (k_\perp/k_c)^5$. In (II) the fluctuation variance is suppressed as $I_{\mathbf{k}} \sim k_c^{-8/5} |k_x|^{-2/5}$, while $I_{\mathbf{k}} \sim 1/k^2$ outside (I) and (II).

Our conclusions seem to agree qualitatively with the previous observations[5,6] and further experiments are very desirable. Also, note that the nucleation process can be drastically affected near the critical point by laminar shear even in the weak shear case $S\tau_\xi \ll 1$.[21] This is one of the future problems.

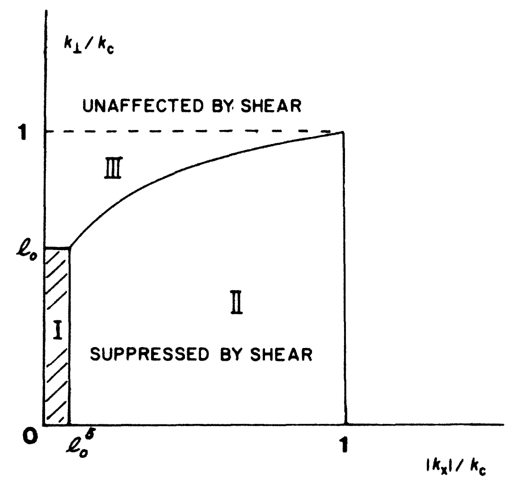

FIG. 1. Different dynamic regimes in the strong shear case. Here $l_0 = \kappa/k_c = (S\tau_\xi)^{-1/6\nu}$, (12) and (13).

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