Effects of Hydrodynamics on Growth: Spinodal Decomposition under Uniform Shear Flow

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To investigate the interaction of hydrodynamics and domain growth in phase-separating fluids, the spinodal decomposition of a binary mixture subjected to a uniform and steady shear flow has been studied by light-scattering techniques. We find that the effects of hydrodynamics become important when the distortion produced by shear is faster than the growth of the domains. When this happens, the growth becomes anisotropic and new and unexpected features are detected. Finally, a steady state predicted by theory is observed and compared to the theory.

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In real fluid systems (e.g., liquid metals, fluids, binary mixtures, polymer blends, microemulsions, etc.), flows due to gravity[1] accelerate and modify the phase-separation process. This rapid growth could be an indication of a new growth mechanism in the presence of flows. We know very little about this mechanism but obviously it should depend on the form of the flows and presumably on the morphology of the phase-separating domains. In nucleation,[2] where the phase-separating domains are isolated droplets, flows might affect the growth through the shape and the coalescence of the droplets, and the concentration gradient around the droplet which is the source of the growth. For spinodal decomposition[2] the picture is far less clear. The phase-separating pattern is highly interconnected and essentially grows by capillary flows. Here the influence of external flows remains mostly unknown. Because of this complication, new growth phenomena might be observed.

However, since the gravity-induced flow varies rapidly spatially and temporally, it is difficult to understand the relationship between the growth and the hydrodynamics in such systems. In order to study this growth mechanism, we have performed an experiment in which the spinodal decomposition (SD) of a binary mixture subjected to a uniform and steady shear flow, with shear rate C, is investigated; this choice is the simplest nontrivial flow. Moreover, binary mixtures are well-studied systems; near their critical point, the properties of the mixtures (e.g., the surface tension) are scaled[2] and temperature variation allows these properties to be changed continuously. Different basic mechanisms of growth can also be obtained by varying the concentration: SD for critical concentration and nucleation for off-critical ones.

We stress that we are interested in the effect of hydrodynamic flow at the scale of the growing domains but not at the scale of the interfacial thickness (i.e., at the scale of the critical fluctuations). In the experiment described below, interfaces should remain well defined and modifications of critical behavior of the mixture by shear[3] are negligible. In this situation there are some theoretical predictions by Onuki[4] concerning only the steady state. We will refer to them below. A few related experiments[5] have already been reported but their results are difficult to interpret. No experiment has been reported with a constant uniform shear flow and this Letter is devoted to the first study under such conditions. Our main findings are that growth is accelerated by the shear flow in a certain direction but may be suppressed in another direction, where ultimately a remixing process might occur.

The shear was produced in a high-precision Couette cell made of Pyrex glass. This cell must be transparent and sealed to prevent any leaks. It is made up of a fixed outer cylinder with a radius of 26.5 mm and a concentric rotating inner cylinder giving a gap of 1.5 mm, whose axis (Z direction) is vertical. If one neglects end effects, the shear, directed radially, is constant along the length of the cell (17.5 mm). The cell is sealed by indium rings, and the gap filled with a binary mixture of isobutyric acid and water at the critical concentration (experimental uncertainty: $\pm 1\%$). To prevent leaks a magnetic driver was used. The cell is immersed in a water bath whose temperature is controlled to within ± 0.2 mK during the experiment. A beam from a He-Ne laser is directed through the gap along Z, that is, perpendicular to the flow (X) and the shear (Y) as shown in Fig. 1. The scattered intensity at low angles is detected with a screen and a video camera, connected to a tape and an image analysis system. The time dependence of the structure factor can thus be readily obtained, after a quench from the one-phase region (typical temperature $T_i = T_c + 2$ mK) to the two-phase region (typically $\Delta T = T_c - T_f = 1$-5 mK, where T_f is the final temperature). The time needed to perform the quench is about 15 s, and the results did not show any dependence on T_i, at least in the range $T_i - T_c = 2$–10 mK. Note that the shear rates that we considered were always in the range between 17.4×10^{-3} s^{-1} and 1.74 s^{-1} and therefore heating by shear was negligible. Finally, we list the constants of the mixture[6]: the critical concentration $c_c = 61$

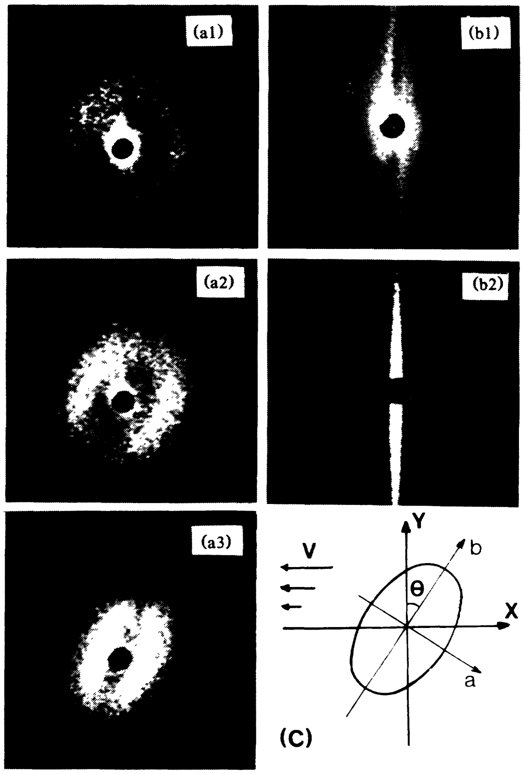

FIG. 1. Time evolution of the scattering pattern of a phase-separating system under shear, after a quench of 2 mK below T_c. (a) Shear rate 35×10^{-3} s^{-1}; (a1) $t=26$ s, (a2) $t=46$ s, and (a3) $t=96$ s. (b) Shear rate 1.74 s^{-1}; (b1) $t=15$ s and (b2) $t=284$ s. (c) The definitions relating to the geometry and symbols used in the text.

wt.% of water, the correlation length in the two-phase region $\xi^-=\xi^+/2=1.8(\epsilon)^{-\nu}$ (Å), the critical temperature $T_c=300$ K, the viscosity $\eta=0.025$ (cgs units), and the density difference of the two phases $\Delta\rho=5.3\times10^{-2}\epsilon^{\beta}$ (cgs units). The typical fluctuation lifetime can be estimated by $t_{\xi^-}=6\pi\eta(\xi^-)^3/k_BT_c$, where k_B is the Boltzmann constant. In order to estimate the surface tension (σ), we have applied two-scale-factor universality between σ and ξ^-,[7] $k_BT_c/\sigma=10.6(\xi^-)^2$. Here $\epsilon=1-T_f/T_c$ is the reduced temperature and $\nu=0.63$ and $\beta=0.325$ are universal exponents.

The parameters in SD are essentially time (t) and quench depth (ΔT). The study is generally made through the structure factor $S(\mathbf{K})$, which is radially symmetric for SD, and depends only on $|\mathbf{K}|$. Note that we have access with this technique only to the correlation function of the domains. The case of the SD under shear is more complex; the shear rate is another parameter, and the structure factor is no longer radially symmetric. It is helpful to start by briefly reporting the qualitative features of the light scattering pattern when both C and ΔT are varied:

(1) *Very low shear* (e.g., $C=35\times10^{-3}$ s^{-1}, $\Delta T=2$ mK).—In the early stage, $S(\mathbf{K})$ is symmetrical as in normal SD and is seen as a ring [Fig. 1(a1)]. As time proceeds, this ring becomes more intense and shrinks while anisotropy due to the effects of shear progressively takes place [Fig. 1(a2)]. Shear affects the ring in two ways: First by deforming it into an ellipse whose major axis, originally at 45° from the shear, rotates with time towards zero, and second by modifying the relative intensities along the axes of the ellipse. For instance, the intensity along the minor axis does not behave the same way as that along the major axis and after a while the scattered intensity looks like lines nearly parallel to the shear direction [Fig. 1(a3)]. During the typical time ($\frac{1}{2}$ h) of the experiment, no steady state is observed to be reached. This is probably due to the effect of gravity.

(2) *Higher shear* (e.g., $C=1.74$ s^{-1}, $\Delta T=2$ mK).—In the early stages, the scattering pattern is already very anisotropic, and comparable to the late stages of the very-low-shear case. It also exhibits a peaked structure and the intensity distribution is not simple [Fig. 1(b1)]. This pattern then collapses and after a few minutes a still more anisotropic figure forms, having no visible structure [Fig. 1(b2)]. Here a steady state is reached, where no clear phase separation can be detected, the influence of shear being such that it suppresses the effect of gravity. Note that one observes a continuous variation between cases (1) and (2) when C or ΔT is varied. For instance, a pattern similar to Fig. 1(b) can be reproduced with $C=1.74$ s^{-1}, $\Delta T=2$ mK or $C=0.07$ s^{-1}, $\Delta T=4$ mK.

Let us briefly review what can be obtained from $S(K)$ in SD. First the peak of $S(K)$ at K_m corresponds to a typical distance ($L_m=2\pi/K_m$) between domains, which appears to be also of the order of one domain size. Scaling arguments make it possible to remove the quench-depth influence; when K_m is expressed in scaled units $K_m^*=K_m\xi^-$, its behavior versus the reduced time $t^*=t/t_{\xi^-}$ becomes universal[2] and it can be approximated as

$$K_m^*=K_0^*t^{*\,-\phi}. \qquad (1)$$

The exponent ϕ ranges from about $\frac{1}{3}$ at early times ($t^*\leq10^2$) to unity at late times ($t^*\geq10^3$). K_0^* is an amplitude defined for the above two asymptotic cases. The same scaling arguments make the reduced structure factor time independent.[2]

Let us analyze now the results for shear SD:

(1) *Very low shear.*—The structure factor can be approximated by an ellipse with axes a and b as in Fig. 1(c), the major axis b making an angle θ with the shear direction. We have studied the time variation of the following parameters at different C and ΔT: (i) the positions (K_m^a and K_m^b) of the maxima of $S(\mathbf{K})$ along a and b; (ii) the angle θ; (iii) the intensity $S(K^a)$ along a.

(i) *Behavior of K_m^a and K_m^b.*—In Fig. 2 the time variations of these quantities are reported for a 2-mK quench

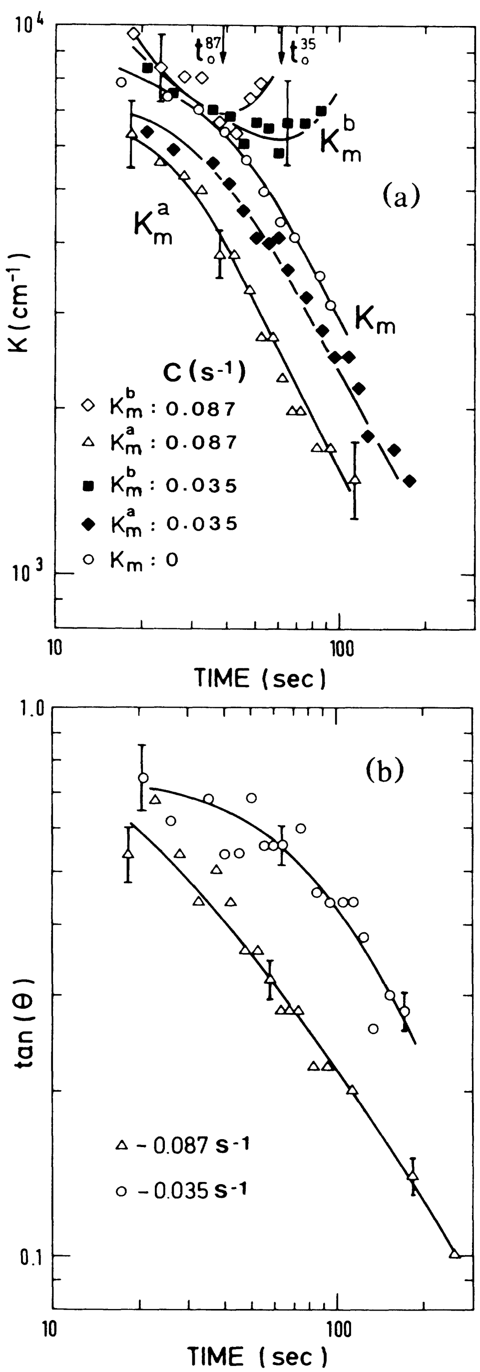

FIG. 2. Quench of 2 mK below T_c. (a) Time dependence of K_m^a and K_m^b at various shear rates (C). The typical time t_0^C corresponds to the moment when shear affects the growth (see text). Note that when shear is zero (normal SD), $K_m^a = K_m^b = K_m$. (b) Time dependence of the angle θ [see Fig. 1(c)] at two typical shear rates.

with the typical shears $C = 35 \times 10^{-3}$ s^{-1} and 87×10^{-3} s^{-1}. They are compared to normal SD at the same quench depth. It is striking that the behavior of K_m^a can also be described by Eq. (1); however, the amplitude K_0^* is shear dependent, and decreases with increasing shear, demonstrating that shear does increase the effective growth in the K_m^a direction. The behavior of K_m^b is comparable to normal SD at early times, where it does not exhibit any obvious shear dependence. However, the measurements cannot be performed a long time after the quench because the intensity in this direction becomes much weaker than in the other direction; this occurs typically after a characteristic time t_0. This suggests that after a growth during the time t_0 the correlations between domains are destroyed in the b direction.

The time t_0 corresponds to the moment when shear affects the growth. When the growth velocity (dL_m/dt) is smaller than the velocity difference (CL_m) acting on a domain, shear is expected to modify the growth. Making use of (1) to estimate the growth rate, we find that the condition is $Ct > \phi \simeq 1$. The typical time $t_0 \sim C^{-1}$ compares favorably with our measurements ($Ct_0 = 1$–3). Note that this time is only shear dependent; no influence of the quench depth is expected. This last point has been checked experimentally.

(ii) *Behavior of* θ.—Figure 2(b) shows the variation of $\tan\theta$ versus time for the experiments reported above. At early times the angle is nearly 45°, and decreases with time. Note that the shear flow as obtained in a Couette device consists of a pure straining motion with the principal axis of extension at 45° in the (X,Y) plane, and a solid-body rotation around the origin. A comparison can be made[8] with the deformation of a single droplet of radius (L_m), with surface tension σ, surrounded by a medium of the same viscosity η. When the capillary number $C_a = \eta D L_m/\sigma$ is much smaller than unity, the deformation of the droplet is elliptical, with the major axis at 45° from the flow. When C_a increases (via C), the equilibrium shape becomes more elongated and the major axis of the droplet tends to align in the flow direction. For higher shears ($C_a > 0.4$), the droplet bursts. This comparison remains, however, limited in the sense that here the domains are not independent (the domains are interconnected) and also that they are continuously growing.

(iii) *Scaling properties of* $S(\mathbf{K})$.—For times $t \ll t_0$ the structure factor is isotropic and behaves the same way as for normal SD. Scaling is approximately verified. For times $t \gtrsim t_0$ one can analyze only the intensity along the direction a $[S(K^a)]$. The intensity along b is vanishing as mentioned above. In this regime scaling is violated. In order to illustrate this point, a new scaled structure factor was constructed:

$$\tilde{S}(x^a,t) = \frac{S(K^a/K_m^a)}{S(K_m^a)}, \tag{2}$$

where $x^a = K^a/K_m^a$. It is similar to the one generally used in normal SD,[2] but it has the advantage of not requiring any integral evaluation. The latter is indeed very sensitive to the background level and to the noise, particularly

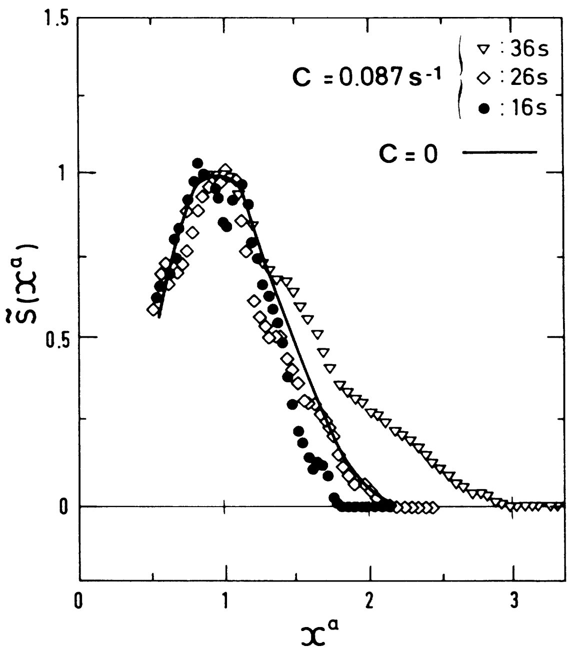

FIG. 3. Reduced structure factor along the direction a (see text) at various times, for a quench of 1 mK below T_c. The case without shear (normal SD) is shown for comparison.

important here because of the impossibility of making a circular averaging. In Fig. 3, a typical experiment ($\Delta T = 1$ mK, $C = 87\times 10^{-3}\ \mathrm{s}^{-1}$) is compared to a normal SD under the same temperature conditions. When $t < t_0$, the structure factor compares relatively well with that from normal SD, whereas for $t > t_0$ the difference is striking, especially the tail in K, which falls much more slowly than that of normal SD. This suggests that the interfaces between domains are less well defined and that a mixing process might have occurred here.

Finally, the violation of scaling for $t > t_0$ indicates that the usual units of length (ξ^-) and of time (t_{ξ^-}) have to be changed by other scales typical of the shear.

(2) *Higher shear.*—The large anisotropy of the structure factor [Fig. 1(b1)] indicates that the domains are strongly elongated in the flow direction. If one compares the size of the domains in this direction with that of the normal SD case, one realizes that the shear has greatly accelerated the effective growth in the flow direction. For example, the case of Fig. 1(b) corresponds to a speeding up of nearly a factor of 10. We could not investigate $S(\mathbf{K})$ further because a detailed study of the structure factor is not possible because of the resolution of the present experiment.

The steady state [Fig. 1(b2)] where shear counterbalances gravitational effects has been studied theoretically by Onuki.[4] In this regime the inequality $1/t_{\xi^-} \gg C \gg (\sigma g \Delta\rho)^{1/2}/\eta$ holds. This inequality is roughly satisfied in the experiment of Fig. 1(b), where $1/t_{\xi^-} = 2.5\ \mathrm{s}^{-1}$, $C = 1.74\ \mathrm{s}^{-1}$ and the right-hand side of the inequality is of order $0.3\ \mathrm{s}^{-1}$. The anisotropy was expected to be of the order 2–3 from Onuki's work; it seems that the observed value is much larger. The size of the domains, predicted to be of the order of $\sigma/\eta D \simeq 10^{-4}$ cm, is different from what is observed in the flow direction but is roughly consistent with the dimension of the stripe in the shear direction. More experiments are needed to fully understand this regime, but at present the high anisotropy prevents accurate measurements from being obtained.

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[1]T. Benda, P. Alpern, and P. Leiderer, Phys. Rev. B **26**, 1450 (1982); C. K. Chan and W. I. Goldburg, Phys. Rev. Lett. **58**, 674 (1987).

[2]See, e.g., J. D. Gunton, M. San Miguel, and P. S. Sahni, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J. L. Lebowitz (Academic, New York, 1983), and references therein.

[3]D. Beysens, M. Gbadamassi, and B. Moncef-Bouanz, Phys. Rev. A **28**, 2491 (1983).

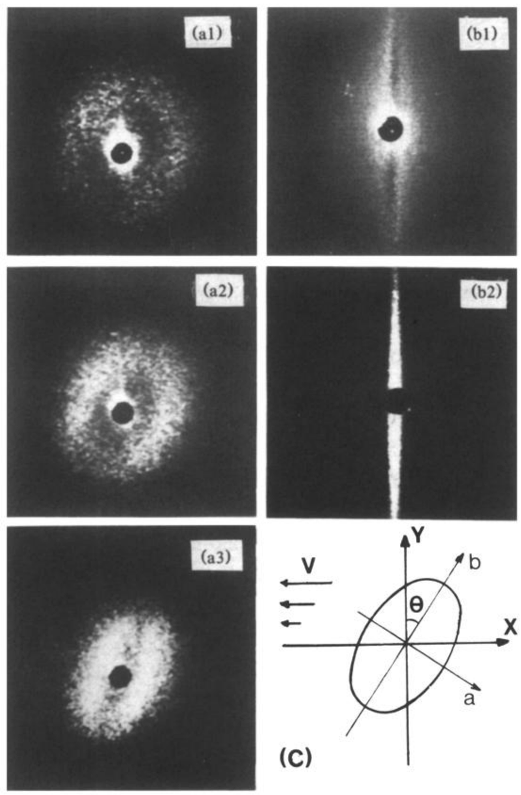
[4]A. Onuki, Phys. Rev. A **34**, 3528 (1986).

[5]C. Rangel-Nafaile, A. B. Metzner, and K. F. Wissbrun, Macromolecules **17**, 1187 (1984); D. Beysens and F. Perrot, J. Phys. (Paris), Lett. **45**, L31 (1984); D. J. Pine, N. Easwear, J. V. Maher, and W. I. Goldburg, Phys. Rev. A **29**, 308 (1984).

[6]D. Beysens, A. Bourgou, and G. Paladin, Phys. Rev. A **30**, 2866 (1984), and references therein.

[7]H. Chaar, M. R. Moldover, and J. W. Schmidt, J. Chem. Phys. **85**, 418 (1986).

[8]J. M. Rallison, Annu. Rev. Fluid Mech. **16**, 45 (1984).



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