Two-Scale Competition in Phase Separation with Shear

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The behavior of a phase separating binary mixture in uniform shear flow is investigated by numerical simulations and in a renormalization group approach. Results show the simultaneous existence of domains of two characteristic scales. Stretching and cooperative ruptures of the network produce a rich interplay where the recurrent prevalence of thick and thin domains determines log-time periodic oscillations. A power-law growth $R(t) \sim t^{\alpha}$ of the average domain size, with $\alpha = 4/3$ and $\alpha = 1/3$ in the flow and shear direction, respectively, is shown to be obeyed.

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The application of a shear flow to a disordered binary mixture quenched into a coexistence region greatly affects the phase-separation process [1]. A large anisotropy is observed in typical patterns of domains which appear greatly elongated in the direction of the flow [2]. This behavior has consequences for the rheological properties of the mixture. A rapid strain-induced thickening followed by a gradual thinning regime is observed [3]. Various numerical simulations confirm these observations [4–6]. These studies, however, were carried out on rather small systems so that an accurate resolution of their spatial properties, which is usually inferred from the knowledge of the structure factor, is not available yet. A different theoretical approach has been considered in [7], where the phase-separation kinetics has been studied in a time-dependent Ginzburg-Landau model where nonlinear terms are accounted for in a self-consistent approximation, also known as large-N limit. Within this approach the existence of a scaling regime characterized by an anisotropic power-law growth of the average size of domains was established. The segregation process, however, cannot be fully described by this technique because interfaces are absent for large N [8].

In this Letter the ordering process is investigated by numerical simulation of large scale systems and the structure factor is then computed at a fine level of resolution. We undercover a much richer scenario than what is usually realized, characterized by the simultaneous existence of *two* length scales for the thickness of the growing domains. The competition between these scales produces an oscillatory phenomenon due to the cyclical prevalence of one of the two lengths. The scaling properties of the kinetics are investigated also in a renormalization group (RG) approach where a power-law growth $R(t) \sim t^{\alpha}$ of the average domain size, with $\alpha = 4/3$ and $\alpha = 1/3$ in the flow direction and the shear direction, respectively, is obtained.

In the following we consider a binary mixture in shear flow described by a model with a simple coupling between a diffusive field φ, representing the concentration difference between the two components of the mixture, and a shearing motion. This approach neglects hydrodynamic effects which generally play an important role in fluid mixtures. For weakly sheared polymer blends with large polymerization index and similar mechanical properties of the two species, however, the present model is expected to be satisfactory in a preasymptotic time domain when velocity fluctuations are small [8].

The fluid is described by the Langevin equation

$$\frac{\partial \varphi}{\partial t} + \vec{\nabla} \cdot (\varphi \vec{v}) = \Gamma \nabla^2 \frac{\delta \mathcal{F}}{\delta \varphi} + \eta . \qquad (1)$$

The equilibrium free energy can be chosen as

$$\mathcal{F}\{\varphi\} = \int d^d x \left\{ \frac{a}{2} \varphi^2 + \frac{b}{4} \varphi^4 + \frac{\kappa}{2} |\nabla \varphi|^2 \right\}, \qquad (2)$$

where $b, \kappa > 0$, and $a < 0$ are in the ordered phase. $\vec{v}$ is an external velocity field describing plane shear flow [1] with profile $\vec{v} = \gamma y \vec{e}_x$, where γ is the shear rate and $\vec{e}_x$ is the unit vector in the x direction [9]. η is a Gaussian white noise, representing thermal fluctuations, with mean zero and correlation $\langle \eta(\vec{r}, t) \eta(\vec{r}\,', t') \rangle = -2T\Gamma \nabla^2 \delta(\vec{r} - \vec{r}\,') \delta(t - t')$, where Γ is a mobility coefficient, T is the temperature of the fluid, and $\langle \dots \rangle$ denotes the ensemble average.

Equation (1) has been simulated in $d = 2$ by a first-order Euler discretization scheme. Periodic boundary conditions have been used in the flow direction; in the y direction we adopt the Lees-Edwards boundary conditions used in other contexts for simulation of shear flow [10]: the point at (x, y) is identified with the point at $(x + \gamma L \Delta t, y + L)$, where L is the size of the lattice and Δt is the time discretization interval [11]. The initial configuration of φ is a high temperature disordered state and the evolution is studied with $a < 0$. Parametrization invariance of (1) allows [12] one to set $\Gamma = |a| = b = \kappa = 1$. The structure factor is $C(\vec{k},t) = \langle \varphi(\vec{k},t)\varphi(-\vec{k},t)\rangle$, where $\varphi(\vec{k},t)$ are the Fourier components of φ. Lattices with $L = 1024, 2048, 4096$ [13] and space discretization $\Delta x = 0.5, 1$ were used. Results will be shown for the case $\gamma = 0.0488, T = 0, L = 4096, \Delta x = 1, \Delta t = 0.01$, $\langle\varphi\rangle = 0$. Similar results have been obtained for other sets of parameters and temperatures in the range $0 \le T \le 4$.

A sequence of configurations at different values of the strain γt is shown in Fig. 1. After an early time, when domains are forming, the usual bicontinuous structure starts to be distorted for $\gamma t \gtrsim 1$. The growth is faster in the flow direction and domains assume the typical striplike shape aligned at an angle $\theta(t)$ with the direction of the flow which decreases with time. As the elongation of the domains increases, nonuniformities appear in the system: Regions with domains of different thickness can be clearly observed at $\gamma t = 11$. The evolution at still larger values of the strain is shown for $\gamma t = 20$. The domains with the smallest thickness eventually break up and burst with the formation of small bubbles.

A systematic existence of two scales in the size distribution of domains is suggested by the behavior of the structure factor, shown in Fig. 2. At the beginning (see the picture at $\gamma t = 0.2$) $C(\vec{k},t)$ exhibits an almost circular shape, corresponding to the early-time regime without sharp interfaces. Then shear-induced anisotropy becomes evident, $C(\vec{k},t)$ is deformed into an ellipse, changing also its profile and, for $\gamma t \gtrsim 1$, four peaks can be clearly observed [14]. The position of each peak identifies a couple of typical lengths, one in the flow and the other in the shear direction. The peaks are related by the $\vec{k} \rightarrow -\vec{k}$ symmetry so that, for each direction, there are two physical lengths. This corresponds to the observation of domains with two characteristic thicknesses, made in Fig. 1.

The dips in the profile of $C(\vec{k},t)$ develop with time until $C(\vec{k},t)$ is separated in two distinct foils at $\gamma t \simeq 4$. The evolution of the system until this stage is well described by the solution of the linear part of (1) (letting $b = 0$):

$$C(\vec{k},t) = C_0 \exp^{-\int_0^t k^2(s)[k^2(s)-1]\,ds}, \qquad (3)$$

where $\vec{k}(s) = \vec{k} + \gamma s k_x \vec{e}_y$ and C_0 is the structure factor at the initial time. Then nonlinear effects become essential in producing the patterns shown in Fig. 2 at $\gamma t = 11, 20$. At $\gamma t = 11$ we evaluate the positions of the peaks at $(k_x, k_y) = (0.015, 0.107)$ and $(k_x, k_y) = (0.038, 0.23)$.

This gives a value of around two for the ratio between the characteristic sizes of domains; the same value is found for the ratio between the positions of the two peaks in the hystogram of the domain size distribution. The relative height of the peaks in one of the foils of $C(\vec{k},t)$ is better seen in Fig. 3 where the two maxima are observed to dominate alternatively at the times $\gamma t = 11$ and $\gamma t = 20$.

The competition between two kinds of domains is a cooperative phenomenon. In a situation like that at $\gamma t = 11$, the peak with the larger k_y dominates, describing a prevalence of stretched thin domains. When the strain becomes larger, a cascade of ruptures occurs in those regions of the network where the stress is higher and elastic energy is released. At this point the thick domains, which have not yet been broken, prevail and the other peak of $C(\vec{k},t)$ dominates, as at $\gamma t = 20$. In the large-N limit the prevalence of one peak or the other has been shown to continue periodically in time [7]. Here

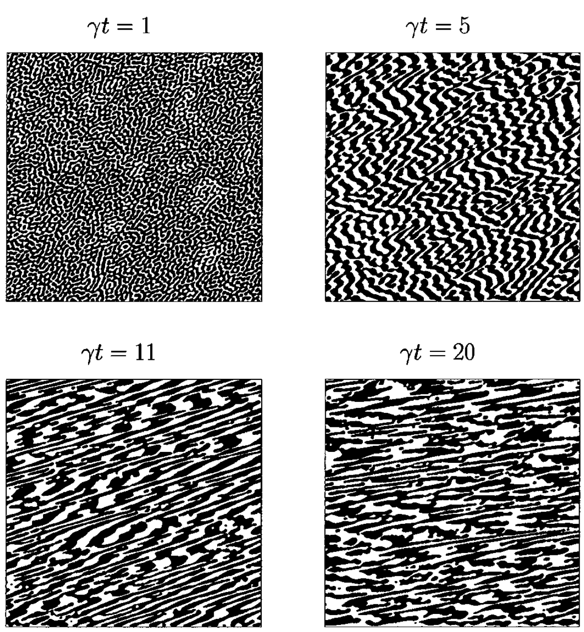

FIG. 1. Configurations of a portion of 512×512 sizes of the whole lattice are shown at different values of the strain γt.

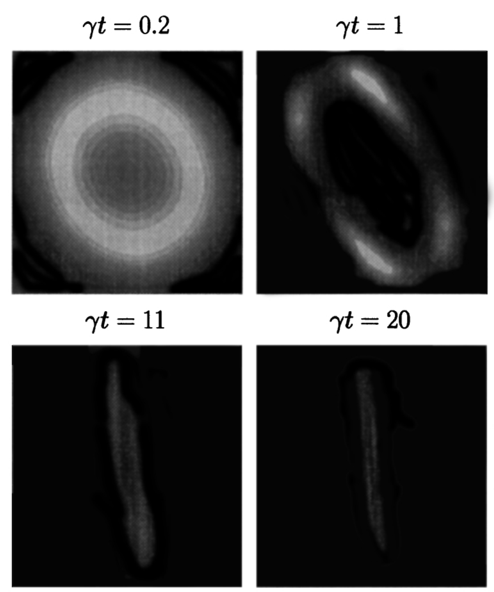

FIG. 2. The structure factor is shown at different values of the strain γt.

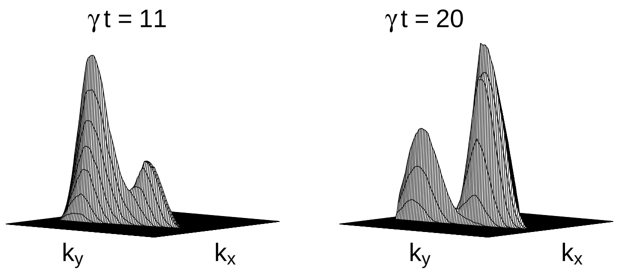

FIG. 3. The same structure factor of Fig. 2 at $\gamma t = 11, 20$ in a three-dimensional plot.

we have an indication of a similar behavior, although the observation of the recurrent dominance of the peaks on longer time scales is hardly accessible numerically.

The hallmarks of this dynamics are found in the behavior of the average size of domains, $R_x(t)$ and $R_y(t)$, in the flow and shear directions. These quantities have been calculated through $R_x(t) = [\int d\vec{k}\, k_x^2 C(\vec{k},t) / \int d\vec{k}\, C(\vec{k},t)]^{-1/2}$, and analogously for $R_y(t)$; their behavior is shown in Fig. 4. Because of the alternative dominance of the peaks of $C(\vec{k},t)$, R_x and R_y increase oscillating. The latter reaches a local maximum at the characteristic times t_n, when $C(\vec{k},t)$ is of the form of Fig. 2 at $\gamma t = 20$ and thick domains are more abundant. The time interval $\tau_n = t_{n+1} - t_n$ between two cascades of ruptures increases exponentially as the segregation proceeds so that the oscillations appear to be periodic on a logarithmic time scale. This is expected because domains are growing and longer and longer times are required to break them. The following argument simply illustrates the origin of the log-time periodic oscillations: The breakup of an elongated domain is caused by the shear flow, which enters Eq. (1) through the last term on the left hand side, whose magnitude we infer to be proportional to τ_n^{-1}. For a sharp interface exposed with an angle $\theta(t)$ to the flow this term is proportional to $\gamma \sin\theta(t) \simeq \gamma\theta(t) \sim \gamma R_y(t)/R_x(t)$, where the asymptotic smallness of $\theta(t)$ has been taken into account. The RG argument developed below shows that $\gamma R_y(t)/R_x(t) \sim 1/t$, so that $\tau_n \sim t_n$ and hence $\ln t_n \sim n + \text{const}$: The rupture events occur periodically in $\ln t$.

Stretching of domains requires work against surface tension and burst of domains dissipates energy resulting in an increase $\Delta\eta$ of the viscosity [3,15]. We calculate the excess viscosity as $\Delta\eta(t) = -\gamma^{-1} \int \frac{d\vec{k}}{(2\pi)^d} k_x k_y C(\vec{k},t)$ [1]. Starting from zero $\Delta\eta$ grows oscillating up to global maximum at $\gamma t \simeq 12$. Then the excess viscosity relaxes to zero in a similar way to what was observed in previous simulations [4]. The relative maxima of $\Delta\eta$ are found in correspondence of the minima of R_y when the domains are maximally stretched.

In the case without shear the asymptotic kinetics is characterized by scale invariance, which is reflected by a power-law growth $R(t) \sim t^\alpha$ of the average size $R(t)$ of domains [8]. The value of the exponent α is related to the mechanism operating in the separation process

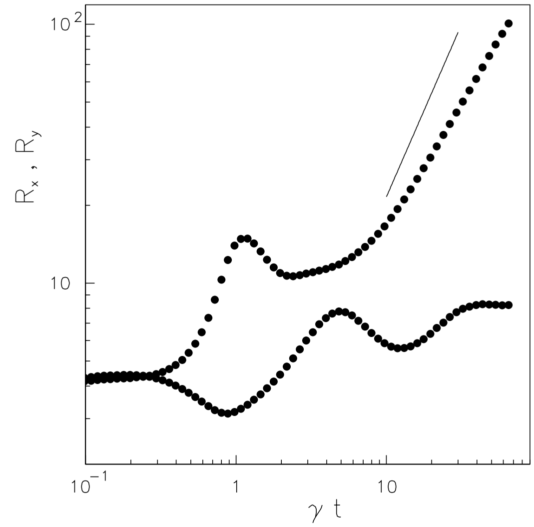

FIG. 4. Evolution of the average domain size in the shear (lower curve) and flow (upper curve) directions. The straight line has slope 4/3.

being $\alpha = 1/3$ for diffusive growth. In the case with shear the existence of a similar behavior has not been clearly assessed. A stationary state with domains of finite thickness is generally observed in experiments [16]. Only in some experimental realizations the existence of a regime with power-law growth has been shown [17,18].

The self-consistent solution of Eq. (1) shows [7,19] that a generalized scaling symmetry holds when a shear flow is applied and different exponents are found for the power-law growth of $R_x(t)$ and $R_y(t)$. However, these exponents are correct for vectorial models and do not directly apply to the case of a binary mixture [20]. The existence of a scaling symmetry and the actual value of the exponents could not be obtained by our simulations because the fast growth in the x direction makes finite size effects relevant before a full realization of the scaling regime occurs [21]. Moreover, the oscillatory behavior of $R_x(t)$ and $R_y(t)$ prevents a straightforward computation of the growth exponents. Therefore, in order to infer the actual value of the growth exponents we resort to a RG analysis.

As usual, we define the RG transformation for the Fourier components $\varphi_{\vec{k}}(t) = 1/\sqrt{V} \int d\vec{r}\, \varphi(\vec{r},t) e^{i\vec{k}\cdot\vec{r}}$ of the field $\varphi(\vec{r},t)$. They verify the equation

$$\frac{\partial \varphi_{\vec{k}}(t)}{\partial t} - \gamma k_x \frac{\partial \varphi_{\vec{k}}(t)}{\partial k_y} = -\Gamma k^2 \frac{\delta \mathcal{F}}{\delta \varphi_{-\vec{k}}(t)} + \eta_k(t) \quad (4)$$

with $\langle \eta_k(t) \eta_{k'}(t') \rangle = 2T\Gamma k^2 \delta(t - t') \delta(\vec{k} + \vec{k}')$. Taking into account the anisotropic growth of domains, we generalize the RG scheme of [22] by considering the change of scale and the field transformation:

$$k_x \to k_x' = k_x b^{\alpha_x}, \qquad k_y \to k_y' = k_y b^{\alpha_y},$$
$$t \to t' = t b^{-1}, \qquad \varphi_{\vec{k}}(t) = b^{\zeta} \varphi'_{\vec{k}'}(t'), \quad (5)$$

where b is the rescaling factor. The basic idea of the RG approach is to associate the scaling behavior with the existence of a fixed point of Eq. (4) under the transformations (5), meaning that the domain structure at time $t' > t$ is statistically similar to the one at time t apart from an anisotropic scale transformation with factors b^{α_x} and b^{α_y} along the two axes. This implies that α_x, α_y are the growth exponents. By dimensional analysis the structure factor can be written in scaling form as $C(\vec{k}, t) = R_x(t) R_y(t) f(x, y)$, where $x = k_x R_x(t)$ and $y = k_y R_y(t)$ are invariant quantities. Form invariance of $C(\vec{k}, t)$ with respect to the transformations (5) leads to $\zeta = (\alpha_x + \alpha_y)/2$. In the isotropic case [22] one makes the phenomenological ansatz that the free energy, being proportional to the surface area of the domains, scales as $b^{\alpha(d-1)}$ at the fixed point. In the present case, since the main contribution to the free energy is due to the interfaces in the direction of the flow, it appears straightforward to assume $\mathcal{F}[b^{\zeta}\varphi^{l}_{\vec{k}'}(t')] = b^{\alpha_x}\mathcal{F}[\varphi^{l}_{\vec{k}'}(t')]$ [23]. This property, inserted into (4) together with (5), gives a Langevin equation similar in form to (4) with rescaled parameters

$$\Gamma' = \Gamma b^{1+\alpha_x - 2\zeta - 2\alpha_y}, \; \gamma' = \gamma b^{\alpha_y - \alpha_x + 1}, \; T' = T b^{-\alpha_x}. \tag{6}$$

A fixed point of the above recursions with $\Gamma, \gamma \neq 0$ is obtained when $\alpha_y = 1/3$, $\alpha_x = \alpha_y + 1$, with the temperature being not relevant for the process of phase separation. We observe that a difference between the growth exponents $\Delta\alpha = \alpha_x - \alpha_y$ in the range $0.8 \div 1$ has been measured in [17,18]. Moreover, the above analysis suggests that, for a constant value of the strain γt, the excess viscosity scales as $\Delta\eta \sim \gamma^{-\beta}$ with $\beta = 1/3$ [24].

In conclusion, we have studied the phase-separation kinetics of a binary mixture in a uniform shear flow by direct numerical simulation of the constitutive equations and in a RG approach. Results show the simultaneous existence of domains of two characteristic sizes in each direction [25]. The two kinds of domains alternatively prevail, because the thicker are thinned by the strain and the thinner are thickened after cascades of ruptures in the network. This mechanism produces an oscillation which decorates the expected power-law growth $R(t) \sim t^{\alpha}$ of the average size of the domains, with $\alpha = 4/3$ and $1/3$ in the flow direction and the shear direction, respectively. The oscillations occur on logarithmic time scales as in models describing propagation of fractures in materials subject to an external strain where the releasing of elastic energy is measured [26]. Finally, it would be interesting to evaluate by extensive simulations [27] the effects of hydrodynamics [28] on the picture described in this Letter.

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