Spinodal Decomposition of Binary Mixtures in Uniform Shear Flow

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(Received 27 May 1998)

The spinodal decomposition of binary mixtures in uniform shear flow is studied in the context of the time-dependent Ginzburg-Landau equation, approximated at one-loop order. We show that the structure factor obeys a generalized dynamical scaling with different growth exponents $\alpha_x = 5/4$ and $\alpha_y = 1/4$ in the flow and in the shear directions, respectively. The excess viscosity $\Delta\eta$ after reaching a maximum relaxes to zero as $\gamma^{-2}t^{-3/2}$, γ being the shear rate. $\Delta\eta$ and other observables exhibit log-time periodic oscillations which can be interpreted as due to a growth mechanism where stretching and breakup of domains cyclically occur. [S0031-9007(98)07467-5]

PACS numbers: 47.20.Hw, 05.70.Ln, 83.50.Ax

The kinetics of the growth of ordered phases as a disordered system is quenched into a multiphase coexistence region has been extensively studied in the past years [1]. The main features of the process of phase separation are well understood. Typically, domains of the ordered phases grow with the law $R(t) \sim t^{\alpha}$, where $R(t)$ is a measure of the average size of domains. The pair correlation function $C(r,t)$ verifies asymptotically a dynamical scaling law according to which it can be written as $C(r,t) \simeq f(r/R)$, where $f(x)$ is a scaling function. In particular, in binary liquids, the existence of various regimes characterized by different growth exponents α is well established [2]. In this Letter we study the process of phase separation in a binary mixture subject to a uniform shear flow. When a shear flow is applied to the system, the growing domains are affected by the flow and the time evolution is substantially different from that of ordinary spinodal decomposition [3]. The scaling behavior of such a system is not clear. Here we show the existence of a scaling theory with different growth exponents for the flow and the other directions. For long times, in the scaling regime, the observables are modulated by *log-time periodic* oscillations which can be related to a mechanism of storing and dissipation of elastic energy. The behavior of the excess viscosity and other rheological indicators reflects this mechanism and is also calculated.

The problem is addressed in the context of the time-dependent Ginzburg-Landau equation for a diffusive field coupled with an external velocity field [3]. The binary mixture is described by the equilibrium free-energy

$$\mathcal{F}\{\varphi\} = \int d^dx \left\{ \frac{a}{2}\varphi^2 + \frac{b}{4}\varphi^4 + \frac{\kappa}{2}|\nabla\varphi|^2 \right\}, \tag{1}$$

where φ is the order parameter describing the concentration difference between the two components. The parameters b, κ are strictly positive in order to ensure stability; $a < 0$ in the ordered phase. The Langevin equation for the evolution of the system is

$$\frac{\partial\varphi}{\partial t} + \vec{\nabla}(\varphi\vec{v}) = \Gamma\nabla^2 \frac{\delta\mathcal{F}}{\delta\varphi} + \eta, \tag{2}$$

where η is a Gaussian stochastic field representing the effects of the temperature in the fluid. The fluctuation-dissipation theorem requires that

$$\langle \eta(\vec{r},t)\eta(\vec{r}',t')\rangle = -2T\Gamma\nabla^2\delta(\vec{r}-\vec{r}')\delta(t-t'), \tag{3}$$

where Γ is a mobility coefficient, T is the temperature of the fluid, and the symbol $\langle\cdots\rangle$ denotes the ensemble average. We consider the simplest shear flow with velocity profile given by

$$\vec{v} = \gamma y \vec{e}_x, \tag{4}$$

where γ is the spatially homogeneous shear rate [3] and $\vec{e}_x$ is a unit vector in the flow direction.

In the process of phase separation the initial configuration of φ is a high temperature disordered state and the evolution of the system is studied in model (2) with $a < 0$. It is well known that in this case, also without the velocity term, the model (2) cannot be solved exactly [2]. In this Letter we deal with the nonlinear term of Eq. (2) in the one-loop approximation [4,5]. In this approximation the term φ^3 appearing in the derivative $\delta\mathcal{F}/\delta\varphi$ is linearized as $\langle\varphi^2\rangle\varphi$. It is also called the large-n limit. Indeed, in the case of a vector field $\vec{\varphi}$ with n-components the term $(\vec{\varphi}^2)\vec{\varphi}$ reduces to $\langle\varphi^2\rangle\varphi$ in the $n \to \infty$ limit [6]. The validity and the limitations of this approximation, due to the acquired vectorial character of the order parameter, are discussed in literature [7].

Before presenting our results it is useful to summarize the known behavior of a phase separating mixture under shear flow. The shear induces strong deformations of the bicontinuous pattern appearing after the quench

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[3,8,9]. When the shear is strong enough stringlike domains have been observed to extend macroscopically in the direction of the flow [10]. In experiments a value $\Delta\alpha = \alpha_x - \alpha_y$ in the range 0.8–1 for the difference of the growth exponents in the flow and in the shear directions is measured [11,12]. Two dimensional molecular dynamic simulations find a slightly smaller value [13]. We are not aware of any existing theory for the value of α_x, α_y. The shear also induces a peculiar rheological behavior. The breakup of the stretched domains liberates an energy which gives rise to an increased viscosity $\Delta\eta$ [14,15]. Experiments and simulations show that the excess viscosity $\Delta\eta$ reaches a maximum at $t = t_m$ and then relaxes to smaller values. The maximum of the excess viscosity is expected to occur at a fixed γt and to scale as $\Delta\eta(t_m) \sim \gamma^{-\nu}$ [8,11]. Simple scaling arguments predict $\nu = 2/3$ [8], but different values have been reported [11].

We study the time evolution of the structure factor

$$C(\vec{k}, t) = \langle \varphi(\vec{k}, t)\varphi(-\vec{k}, t)\rangle , \tag{5}$$

where $\varphi(\vec{k}, t)$ is the Fourier transform of the field $\varphi(\vec{x}, t)$ solution of Eq. (2). The excess viscosity is defined in terms of $C(\vec{k}, t)$ by

$$\Delta\eta(t) = -\gamma^{-1}\int_{|\vec{k}|<q}\frac{d\vec{k}}{(2\pi)^D}\, k_x k_y C(\vec{k}, t) , \tag{6}$$

where q is a phenomenological cutoff. In the one-loop approximation the dynamical equation for $C(\vec{k}, t)$ is

$$\frac{\partial C(\vec{k}, t)}{\partial t} - \gamma k_x \frac{\partial C(\vec{k}, t)}{\partial k_y} = -k^2[k^2 + S(t) - 1] \times C(\vec{k}, t) + k^2 T , \tag{7}$$

where

$$S(t) = \int_{|\vec{k}|<q}\frac{d\vec{k}}{(2\pi)^D}\, C(\vec{k}, t) . \tag{8}$$

The parameters Γ, a, b, and κ have been eliminated by a redefinition of the time, space, and field scales. We solve Eq. (7) numerically in two dimensions. A first-order Euler scheme is implemented with an adaptive mesh, due to the peaked character of the solution. The initial condition chosen for the function $C(\vec{k}, 0)$ is a constant value, which corresponds to the disordered state with $T = \infty$. The typical evolution of $C(\vec{k}, t)$ is shown in Fig. 1 for the particular case $T = 0$ and $\gamma = 0.001$. At the beginning the function $C(\vec{k}, t)$ evolves forming a circular volcano structure, as usual in the case without shear. This is the early-time regime when well-defined domains are forming. Then shear-induced anisotropy effects become evident in the elliptical shape of $C(\vec{k}, t)$ and in the profile of the edge of the volcano, as can be seen in Fig. 1 at $\gamma t = 0.05$. Similar elliptical patterns of $C(\vec{k}, t)$ are usually observed in experiments. The dips

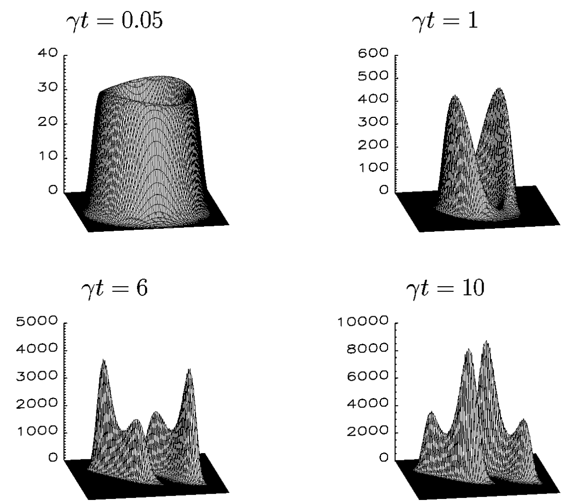

FIG. 1. The structure factor at consecutive times for $\gamma = 0.001$. The k_x coordinate is on the horizontal axis and assumes positive values on the right of the pictures, while the k_y is positive towards the upper part of the coordinate plane. The support of the function $C(\vec{k}, t)$ shrinks towards the origin. For a better view of $C(\vec{k}, t)$, in the last two pictures, we have enlarged differently the scales on the k_x and k_y axes. The actual angle between the direction of the foils of $C(\vec{k}, t)$ and the k_y axes is $\theta = 21°$ and $\theta = 13°$ in the last two pictures.

in the edge of the volcano develop with time until $C(\vec{k}, t)$ becomes separated into two distinct foils, as $\gamma t \simeq 1$. This explains the disappearance of the peak corresponding to the major axis of the ellipse observed in experiments [12]. During this evolution the support of $C(\vec{k}, t)$ shrinks towards the origin with different scales for the shear and the flow directions. At later times in each foil of $C(\vec{k}, t)$ two peaks can be distinguished and the relative heights of these peaks change in time. In Fig. 1 at $\gamma t = 6$ the peak characterized by $|k_y| \gg |k_x|$ dominates, while the other peak with $|k_y| \simeq |k_x|$ prevails successively. The oscillations between the two peaks have been observed to continue in time and characterize the steady state.

A quantitative measure of the size of domains is given by $R_x(t) = 1/\sqrt{\langle k_x^2\rangle}$, where $\langle k_x^2\rangle = \int d\vec{k}\, k_x^2 C(\vec{k}, t)/\int d\vec{k}\, C(\vec{k}, t)$, and the same for the other directions. The evolution of R_x, R_y is plotted in Fig. 2. The growth exponents in the shear and in the flow direction are $\alpha_y \simeq 1/4$ and $\alpha_x \simeq 5/4$. The value $\alpha_y = 1/4$ is the same as in models with a vectorial conserved order parameter without shear; this corresponds to the Lifshitz-Slyozov exponent $\alpha = 1/3$ for scalar fields. A growth exponent α_y unaffected by the presence of shear is also measured in experiments [11]. We see in Fig. 2 that the amplitudes of R_x, R_y oscillate periodically in logarithmic time. This behavior can be related to the oscillations of the peaks of $C(\vec{k}, t)$ previously observed and will be discussed later in relation to the behavior of the excess viscosity.

In order to study analytically the behavior of the model for arbitrary space dimensionality d we resort to a scaling ansatz [16]. For the structure factor we then assume

$$C(\vec{k},t) = \prod_{i=1}^{d} R_i(t) F[\vec{X}, \tau(\gamma t)] \qquad (9)$$

for long times, where $\vec{X}$ is a vector of components $X_i = k_i R_i(t)$, F is a scaling function and the subscript i labels the space directions with $i = 1$ along the flow. We also allow an explicit time dependence of the structure factor through $\tau(\gamma t)$; notice that, since $C(\vec{k},t)$ scales as the domains volume below the critical temperature, τ must not introduce any further algebraic time dependence in $C(\vec{k},t)$. We then argue that F is a periodic function of τ, as suggested by the oscillations observed numerically in the physical observables. Inserting this form of $C(\vec{k},t)$ into Eq. (7) we obtain

$$\gamma X_1 F_2 = R_1 R_2^{-1} \left\{ \dot{\tau} \partial F/\partial \tau + \sum_{i=1}^{d} \left[R_i^{-1} \dot{R}_i (F + X_i F_i) + R_i^{-2} X_i^2 \left(\sum_{k=1}^{d} R_k^{-2} X_k^2 - 1 + S \right) F \right] \right\}, \qquad (10)$$

where $F_i = \partial F/\partial X_i$ and a dot means a time derivative. Since the left-hand side of Eq. (10) scales as t^0, one has the solution $R_i(t) \sim \gamma^{\delta_i} t^{\alpha_i}$, $\tau(\gamma t) \sim \log \gamma t$, $S(t) = 1 - t^{-\beta}$, with $\delta_1 = 1$, $\delta_i = 0$ $(i = 2, d)$, $\alpha_1 = 5/4$, $\alpha_i = 1/4$ $(i = 2, d)$, and $\beta = 1/2$. In this way we recover the growth exponents previously found. Actually the exponents found numerically are slightly smaller then the predicted powers due to logarithmic corrections [16].

We now turn to the analysis of the rheological behavior of the mixture and, in particular, of the excess viscosity. The previous theoretical arguments can be used to establish the scaling properties of $\Delta\eta$. Inserting the form (9) into Eq. (6), we obtain $\Delta\eta(t) \sim \gamma^{-1} R_1(t)^{-1} R_2(t)^{-1} g(\tau) \sim \gamma^{-2} t^{-3/2} g(\tau)$, where $g(\tau) = \int X_1 X_2 F[\vec{X}, \tau(t)] d\vec{X}$ is a periodic function of $\tau(\gamma t)$. Therefore, in the scaling regime, for each value of γt, the functions $\Delta\eta$ corresponding to different values of γ collapse on each other if rescaled as $\Delta\eta \to \gamma^{1/2} \Delta\eta$. A similar analysis can be done for the normal stress which is defined as $\Delta N_1 = \int \frac{d\vec{k}}{(2\pi)^D} [k_y^2 - k_x^2] C(\vec{k},t)$ and scales as $t^{-1/2}$.

The behavior of $\Delta\eta$ at all times, calculated by the numerical expression of $C(\vec{k},t)$, is shown in Fig. 3 for the case $\gamma = 0.001$. $\Delta\eta$ reaches a maximum at $\gamma t \simeq 3.5$, then it decreases with the power law $t^{-3/2}$ modulated by a periodic oscillation in logarithmic time. A comparison with Fig. 2 shows that the asymptotic scaling regime starts when the excess viscosity reaches its maximum at $t = t_m$, as found also in experiments [11]. The occurrence of the predicted scaling of $\Delta\eta$ with γ is verified numerically with great accuracy for long times. However, since t_m is a time at the onset of scaling, an effective exponent somewhat larger then 1/2, ($\nu \simeq 0.6$) is measured for $\Delta\eta(t_m)$, due to preasymptotic corrections.

The periodic oscillations of $\Delta\eta$ are due to the competition between the different peaks of $C(\vec{k},t)$. A local

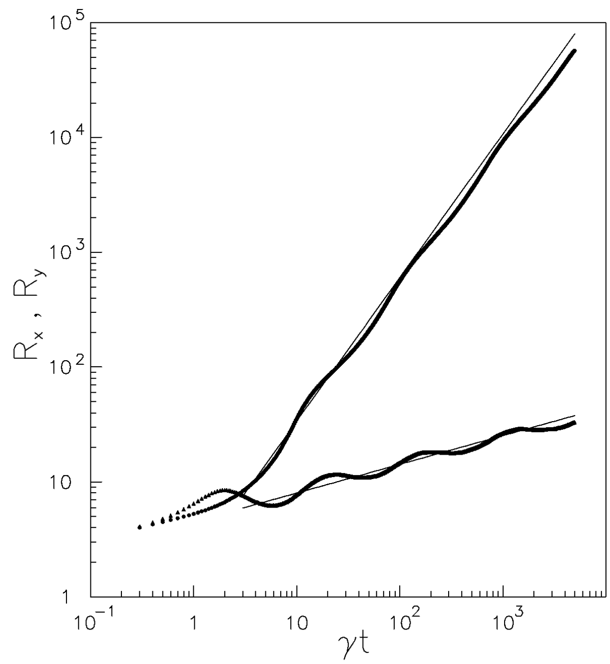

FIG. 2. The average size of domains in the x and y directions as a function of the strain γt. The two straight lines have slopes 5/4 and 1/4.

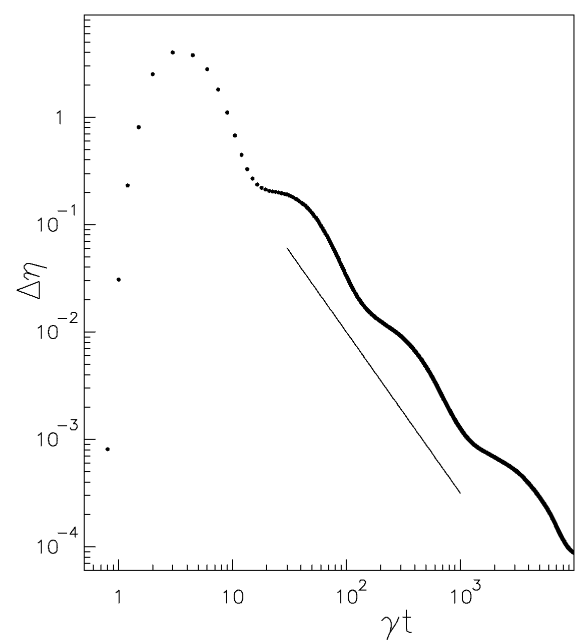

FIG. 3. The excess viscosity as a function of the strain γt. The slope of the straight line is $-3/2$.

maximum of $\Delta\eta$ occurs for a situation similar to that of Fig. 1 at $\gamma t = 6$, when the peak with $|k_y| \gg |k_x|$ dominates and the difference between the height of the two peaks is maximal. The minima of $\Delta\eta$ correspond to the opposite situation, as in Fig. 1 at $\gamma t = 10$. The oscillations can be explained in the following way: The elongation of the domains in the flow direction produces an increase of $\Delta\eta$. Stretched domains are characterized by $R_y \ll R_x$ and, therefore, are represented by the peak of $C(\vec{k}, t)$ with $|k_y| \gg |k_x|$, which dominates in this time domain. As time passes, however, domains are deformed to such an extent that they start to burst, dissipating the stored energy. As a consequence, $\Delta\eta$ decreases and more isotropic domains are formed. These are characterized by similar values of R_x and R_y and correspond to the other peak of $C(\vec{k}, t)$. This peak starts growing faster than the other until it prevails. Later on, a minimum of $\Delta\eta$ is observed. Then elongation occurs again and this mechanism reproduces periodically in time with a characteristic frequency. To our knowledge, the existence of this periodic behavior has never been discussed before [17].

In conclusion, we have studied the phase separation of a binary mixture in a uniform shear flow. Dynamical scaling holds for this system. Domains grow along the flow as $R_x(t) \sim t^{5/4}$ while in the other directions the exponent of the diffusive growth is the same as without shear. The difference $\Delta\alpha$ between the growth exponents is 1, a result which is consistent with real experiments. The excess viscosity after the maximum relaxes to zero as $\gamma^{-2} t^{-3/2}$. The amplitudes of physical quantities are decorated by oscillation periodic in logarithmic time. It would be interesting to study these phenomena in direct simulation of the Langevin equation and also to see the effects of hydrodynamics on this system.

We thank Julia Yeomans for helpful discussions. F. C. is grateful to M. Cirillo for hospitality at the University of Rome. F. C. acknowledges support by the TMR Network Contract No. ERBFMRXCT980183.

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