Phase Separation Dynamics under Stirring

A. M. Lacasta,[1,2] J. M. Sancho,[2,4] and F. Sagués[3]
[1]*Departament de Física Aplicada, Universitat Politècnica de Catalunya, Avenida Dr. Gregorio Marañon 50, E-08028 Barcelona, Spain*
[2]*Departament d'Estructura i Constituents de la Matèria, Universitat de Barcelona, Avenida Diagonal 647, E-08028 Barcelona, Spain*
[3]*Departament de Química Física, Universitat de Barcelona, Avenida Diagonal 647, E-08028 Barcelona, Spain*
[4]*Institute for Nonlinear Science, University of California at San Diego, 9500 Gilman Drive, Department 0402, La Jolla, California 92093-0402*
(Received 19 September 1994)

Phase separation dynamics in the presence of externally imposed stirring is studied. The stirring is assumed independent of the concentration and it is generated with a well-defined energy spectrum. The domain growth process is either favored or frozen depending on the intensity and correlation length of this advective flow. This behavior is explained by analytical arguments.

PACS numbers: 64.60.My, 47.27.Sd

Phase separation, following a quench of a binary mixture inside its coexistence curve, has become a model system for studying generic nonequilibrium dynamical features. The simplest realization of such a process neglects hydrodynamic interactions, as it corresponds to binary alloys, glasses, etc. In these situations one looks for some sort of universality reflected in the properties of the correlation and structure functions and in power laws governing the domain growth of macroscopic structures [1,2]. Phase separation of binary fluids has also been considered in the literature [3,4]. As an extension of this last problem, phase separation under externally imposed stirring is progressively receiving an increasing attention from both the theoretical [5–7] and experimental [8–10] points of view. Actually, mixing of domains under flow [11] has an intrinsic technological interest mainly associated with the expected distinctive rheological properties of phase separating binary fluids [6]. When stirring is present, the central question to analyze is the competition between the thermodynamic forces, leading to segregation, and local shear effects favoring droplet dissolution. Two nonequilibrium steady behaviors can then be envisaged, and have indeed been reported in the literature. Close to the critical point and under vigorous stirring, a regime of completely suppressed phase separation has been experimentally observed [8], in accordance with theoretical predictions [5] based on a linear stability analysis of the Cahn-Hilliard equation. On the contrary, and following a deep quench into the coexistence region, experimental work [10] evidences a scenario of continuously ruptured droplets once they have grown to sufficient size.

Motivated by the above experiments and restricting the situation where stirring preserves phase separation, we aim in this Letter to expand the perspectives of theoretical investigation in this field by proposing a new strategy based on the use of stochastic differential equations to model a random advective flow [12,13]. Stated in short, we will consider the kinetics of segregation of passive scalar phases that are stirred by a space- and time-dependent incompressible flow, here assumed independent of the concentration field. Although in this last respect we are not really facing the full hydrodynamical problem, the stirring mechanism will already introduce its own time and length scales to compete with those inherent to the underlying phase separation process. The chosen level of description of the stirring mechanism is purely statistical. In this sense its energy spectrum and spatiotemporal scales are fully defined in terms of the correlation tensor of the isotropic stochastic velocity field. Even with such a reduced description we will be able to evidence distinctive scenarios of domain growth, by appropriately varying the intensity and correlation length of the random advective flow. In particular, either a new regime of enhanced segregation or the previously commented steady-state situation of frozen growth will be characterized.

Our dynamical model for the phase separation process subjected to turbulent stirring is based on the well-known Cahn-Hilliard equation supplemented with the convective term [5]

$$\frac{\partial c}{\partial t} = \nabla^2(-c + c^3 - \nabla^2 c) - \boldsymbol{\nabla} \cdot (\mathbf{v}c), \tag{1}$$

where $c(\mathbf{r}, t)$ is the concentration field variable and $\mathbf{v}(\mathbf{r}, t)$ stands for the stochastic velocity field. We will take it divergence free (incompressible fluid) $[\boldsymbol{\nabla} \cdot \mathbf{v}(\mathbf{r}, t) = 0]$ and statistically isotropic, homogeneous and stationary, with zero mean, and, for simplicity, Gaussian correlation

$$\langle v^i(\mathbf{r}_1, t_1) v^j(\mathbf{r}_2, t_2)\rangle = R^{ij}(|\mathbf{r}_1 - \mathbf{r}_2|, |t_1 - t_2|). \tag{2}$$

These requirements, for two-dimensional flows, are satisfactorily assured by using a versatile approach that has proven to be useful for a variety of spectral realizations of well-behaved turbulent flows [12,13].

The simulation strategy appropriate to the model defined by Eqs. (1) and (2) can be summarized in the following two steps.

(i) According to the algorithms introduced in Refs. [12, 13] we generate a velocity field with correlation

$$R^{ij}(r,s) = u_0^2 \exp\left(-\frac{r^2}{4\lambda^2} - \frac{s}{\tau}\right) \times \left[\frac{r^2}{2\lambda^2} n^i n^j + \left(1 - \frac{r^2}{2\lambda^2}\right)\delta_{ij}\right], \qquad (3)$$

where n^i stands for the components of the unit vector in the $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ direction. The three basic statistical parameters identified in Eq. (3) are the spatial correlation length λ, the characteristic time correlation τ, and the effective intensity of the velocity field u_0^2. These three parameters together with the Gaussian property fully determine the statistical properties of the velocity field. The choice (3) corresponds to Kraichnan's turbulent spectrum [14] and is motivated by the fact that it reproduces a widely distributed band of excitations with a peak centered at a well-defined wave number $k_0 = (3/2)^{1/2}\lambda^{-1}$. This model generates eddies of typical size $l_0 \sim \sqrt{\pi}\,\lambda$. In this way, the random advective field introduces a characteristic length scale which competes with that of the phase separation process.

(ii) In a second step, Eq. (1) with a velocity field satisfying (3) has been simulated following standard procedures [12] in a two-dimensional lattice $L \times L$, with $L = 128$, a mesh size $\Delta x = \Delta y = 1$, and a time integration step $\Delta t = 0.025$. The initial quench is assumed to take place inside the off-critical region of coexistence in order to better detect the effects of the advective turbulent flow on the growth of segregated droplets. Triggering conditions for growth correspond to an initial seeding in a stationary configuration of the flow pattern with $c(\mathbf{r},0) = c_0 + \tilde{c}(\mathbf{r},0)$, c_0 being the mean concentration, $c_0 = 0.4$, and $\tilde{c}$ a random number uniformly distributed in the interval $[-0.1, 0.1]$. In all the simulations we take τ fixed ($\tau = 1$), whereas the effective intensity (u_0^2) and correlation length of turbulence (λ) will be considered as variable parameters.

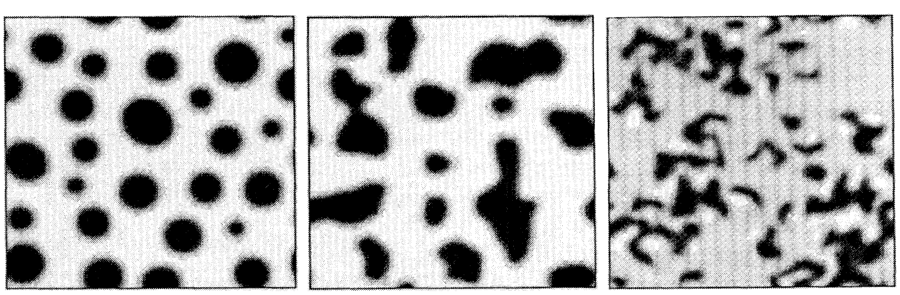
A snapshot corresponding to an instantaneous state of the phase separation process under random advection is presented in Fig. 1. Two characteristic behaviors are easily evidenced when comparing our simulation results here with those corresponding to a phase separation process in a quiescent medium [Fig. 1(a)]. Under the lower stirring intensities, configurations of larger although slightly distorted droplets are obtained [Fig. 1(b)]. However, in a more turbulent ambient [Fig. 1(c)], the domains appear largely corrugated under the stretching or thinning effects of the local turbulent shears. A better quantitative representation of the spatiotemporal dynamics in our phase separating system is provided by the pair-correlation function

$$G(\mathbf{r},t) = \left\langle \frac{1}{L^2} \sum_{\mathbf{r}'} [c(\mathbf{r} + \mathbf{r}', t)c(\mathbf{r}', t) - c_0^2] \right\rangle, \qquad (4)$$

or by its circularly averaged form $g(r,t) = N_r^{-1} \sum G(\mathbf{r},t)$, where the sum runs over a set of N_r points inside a corona of radii r and $r + \Delta r$. This quantity is depicted in Figs. 2 and 3.

Figure 2 shows the spatial structures corresponding exactly to the conditions of Fig. 1, whereas Fig. 3 reproduces the two distinctive dynamic scenarios already announced in the introductory remarks. Steadily phase separating conditions under low stirring correspond to the larger but still well-defined (Fig. 2; dashed line) and continuously growing domains (Fig. 3; discontinuous lines). In contrast, vigorous random advection results in a truly frozen phase separation dynamics as evidenced by the nonoscillatory and practically flat decay (Fig. 2; continuous line) of the stationary nonequilibrium correlation function $g(r,t)$ (Fig. 3; continuous lines joining symbols).

A more comprehensive representation of the whole dynamical process is displayed in Fig. 4, where we plot the time evolution of a characteristic droplet size $R(t)$ defined as the distance at which $g(R(t),t) = 0.2$. Before going into a more analytic discussion let us try to qualitatively describe the different scenarios reproduced in Fig. 4. We could consider two different and subsequent stages of the phase separation process depending on whether the characteristic main domain size $R(t)$ is smaller or larger than the correlation length of the stirring flow λ. When $R(t) < \lambda$ the apparent generic behavior corresponds to a faster growth as compared



(a) (b) (c)

FIG. 1. Concentration patterns at time $t = 2500$ for (a) $u_0^2 = 0$; (b) $\lambda = 4$, $u_0^2 = 0.015$; and (c) $\lambda = 4$, $u_0^2 = 0.25$.

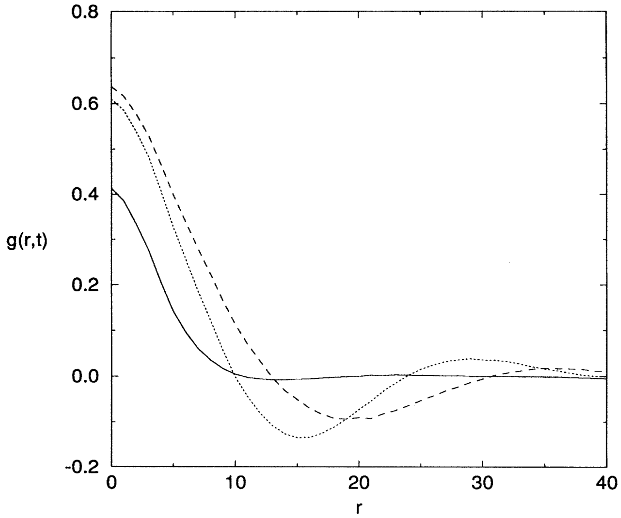


FIG. 2. Radial correlation function $g(r,t)$ for the same time and parameters showed in Fig. 1: $u_0^2 = 0$ (dotted line), $\lambda = 4$, $u_0^2 = 0.015$ (dashed line), and $\lambda = 4$, $u_0^2 = 0.25$ (solid line).

to the hydrodynamic-free situation. Actually the growth dynamics seems to approach a power law t^α with $\alpha \approx 1/2$ rather than the usual Lifshitz-Slyozov behavior ($\alpha = 1/3$). On the contrary when $R(t) > \lambda$ the system either goes through a crossover leading to the asymptotic growth mode $t^{1/3}$ or it is really trapped into a frozen phase separation stage whose characteristic domain size largely depends on λ. This is clearly depicted in Fig. 4 where we reproduce two cases of continuous growth, (b1) and (b2), and two cases of frozen phase separation, (c1) and (c2). The longer lasting regimen of droplet coalescence when increasing λ, under steady growth conditions, is evidenced when comparing (b1) and (b2). However, beyond their respective crossovers (marked by arrows), situations (b1) and (b2) get adjusted equally to the Lifshitz-Slyozov regime illustrated by the nonstirring case (a). On the other hand, the corresponding dependence on λ of the ruptured droplets under higher levels of stirring is apparent when comparing (c1) and (c2). Actually, this suppression growth mechanism turns out to be very effective as also evidenced in Fig. 4 where two routes, either a full time superimposed stirring or a situation of activated random advection at a late growth stage collapse into a unique pattern of frozen phase separation.

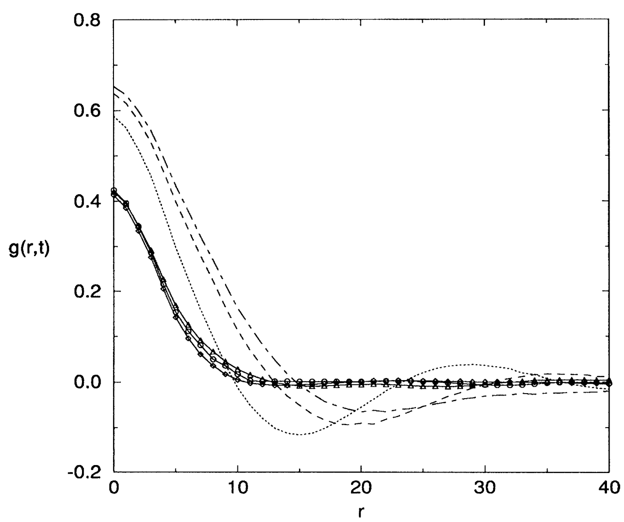


FIG. 3. Radial correlation functions for $\lambda = 4$ and two values of u_0^2: 0.25 (symbols) and 0.015 (lines), for times $t = 1000$ [(○) and dotted line], $t = 2500$ [(◇) and dashed line], and $t = 4000$ [(△) and dot-dashed line].

Two arguments may be relevant to interpret the scenarios just described. When the characteristic domain size is smaller than the correlation length of stirring, each individual droplet may be viewed as an independent Brownian particle immersed in the much more rapidly evolving superimposed random flow, relative to the much slower time scale of the coarsening process itself [2]. When two such droplets approach each other they would coalesce into a larger droplet. This process would continue until the mean distance between droplets, typically comparable to the average domain size, becomes of the order of the correlation length of the advective flow. Under the hypothesis of passive phases with stochastic stirring, one can define an effective diffusion constant D, independent of the droplet radius R, for the Brownian motion of the

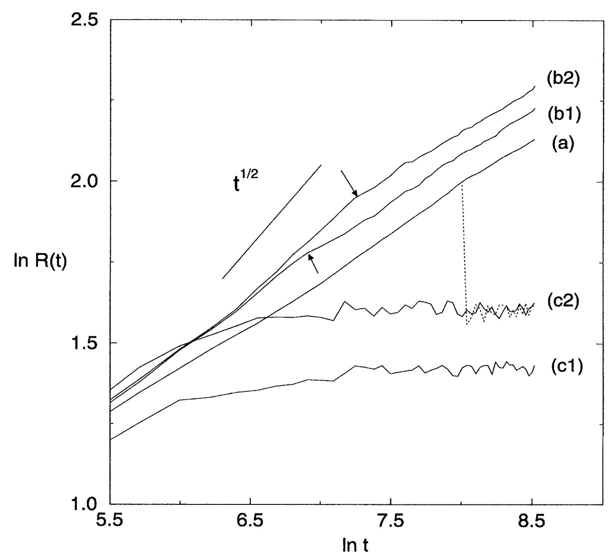


FIG. 4. Log-log plot of the time evolution of $R(t)$, for (a) $u_0^2 = 0$; (b1) $\lambda = 3$, $u_0^2 = 0.015$; (b2) $\lambda = 5$, $u_0^2 = 0.015$; (c1) $\lambda = 4$, $u_0^2 = 0.25$; and (c2) $\lambda = 6$, $u_0^2 = 0.25$. The results have been averaged over an ensemble of ten runs. The broken line illustrates the suppression of the growth once the stirring is plugged into the system with the parameter values of (c2). The straight line illustrates the 1/2 regime, and the arrows illustrate the crossover from the droplet coalescence regime to the Lisfshitz-Slyozov dynamics.

droplets. Under these asumptions, the mean free time between collisions is related to the radius of the droplets by $R^2 \approx D\Delta t$. Since each encounter increases the droplet radius by an amount of order R, we end up with a simple equation, $\Delta R/\Delta t \approx R/\Delta t \sim D/R$. From it the power law $R \sim t^{1/2}$ is trivially recovered. Once the droplets have attained the typical size of the random advective vortices their dynamics cannot be longer described according to the previous picture. Either they continue to grow or they burst apart under vigorous enough stirring. In the first regime, the random motion mechanism no longer applies for already largely segregated domains, but rather the Lifshitz-Slyozov (or evaporation-condensation) mechanism becomes dominant.

The remaining question consists precisely of predicting whether or not this sustained growth, versus a frozen dynamics, will take place. According to our simulations this would depend on the two statistical parameters of the random flow: the intensity and the correlation length. Actually, our numerical simulations indicate that, for each value of the stirring intensity, a critical correlation length λ_c appears to fix a threshold such that for values of λ below (above) λ_c a continuous (interrupted) growth mode is predicted. The argument behind this observation can only be based on the competition between the distorting effect (on large enough droplets) of the turbulent shear flow and the stabilizing effects of their surface tension. An approximate analytical argument is developed as follows. Let us assume a perturbing bump of lateral extent l_0 and vertical size $h(x,t)$, caused by an advective flow $\mathbf{v} = (0, v_y)$ of amplitude u_0, on a planar surface (very large droplet) along the x axis. In terms of the one-dimensional steady-state solution $c_0(y)$ of the equation without stirring ($-c_0 + c_0^3 - d^2c_0/dy^2 = 0$) we write this perturbation in the form

$$c(x,y) = c_0(y) + \eta_0(y)h(x), \qquad (5)$$

with $\eta_0(y) = dc_0(y)/dy$. Substituting Eq. (5) into Eq. (1), using Green's functions technique, and by going to Fourier space one can obtain the following relation for the perturbation $h_k(t)$

$$\frac{dh_k(t)}{dt} = -\frac{\sigma}{2}k^3h_k + u_0, \qquad (6)$$

where $\sigma = \int(dc_0/dy)^2 = 2\sqrt{2}/3$ is related with the surface tension. The first term of the right-hand side of Eq. (6) is the usual surface-tension mediated stabilizing mechanism. The second term represents the effect of the velocity field, which tends to deform the interface independently of h_k. Both effects will be equal when $h_k \sim 2u_0/\sigma k^3$. Considering that the break of the interface takes place for $h_k \sim l_0 = \sqrt{\pi}\,\lambda$, and taking into account that $k \sim \sqrt{\pi}\,\lambda^{-1}$, we can find the critical value for λ as

$$\lambda_c^2 \sim \frac{\pi^2}{2}\frac{\sigma}{u_0}. \qquad (7)$$

This equation allows us to understand the numerical results of Fig. 4. For $u_0^2 = 0.015$, Eq. (7) gives a $\lambda_c \sim 6$, so for the cases (b1) and (b2) of Fig. 4 with $\lambda = 3$ and $\lambda = 5$, respectively, we would expect a sustained growth process. Contrarily for $u_0^2 = 0.25$, Eq. (7) gives a $\lambda_c \sim 3$, and hence for the cases (c1) and (c2) with $\lambda > \lambda_c$ a situation of frozen growth would be predicted. Both conclusions are in agreement with the numerical results of Fig. 4.

In summary, we have discussed, by numerical simulations, dynamical aspects of segregating passive scalar phases subjected to random advective flows. Both situations of favored and frozen growth are predicted, depending on the statistical parameters of the superimposed flow. In this respect, the crucial competition between the intrinsic length of the stirring mechanism and that of the phase separation process itself is analytically discussed. In addition, a transient faster growth regime, different from the standard Lifshitz-Slyozov dynamics, has been found and interpreted in terms of a diffusionlike behavior applying to small size uncorrelated droplets immersed in a much more rapidly evolving advective flow.

We would like to thank J. Casademunt for helpful discussions. We acknowledge financial support of the Dirección General de Investigación Científica y Técnica (Spain) under Projects No. PB93-0769 and No. PB93-0759. We also acknowledge the Centre de Supercomputació de Catalunya (CESCA) for computing support.

[1] J.D. Gunton, M. San Miguel, and P.S. Shani, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J.L. Lebowitz (Academic, New York, 1983), Vol. 8, p. 267.
[2] H. Furukawa, Adv. Phys. **34**, 703 (1985).
[3] E.D. Siggia, Phys. Rev. A **20**, 595 (1979).
[4] N.C. Wong and C.M. Knobler, Phys. Rev. A **24**, 3205 (1981).
[5] J.A. Aronovitz and D.R. Nelson, Phys. Rev. A **29**, 2012 (1984).
[6] A. Onuki, Phys. Lett. **101A**, 286 (1984).
[7] A. Onuki and S. Takesue, Phys. Lett. **114A**, 133 (1986).
[8] D.J. Pine, N. Easwar, J.V. Maher, and W.I. Goldburg, Phys. Rev. A **29**, 308 (1984).
[9] C.K. Chan, W.I. Goldburg, and J.V. Maher, Phys. Rev. A **35**, 1756 (1987).
[10] K.J. Min, J. Stavans, R. Piazza, and W.I. Goldburg, Phys. Rev. Lett. **63**, 1070 (1989); K.J. Min and W.I. Goldburg, Phys. Rev. Lett. **70**, 469 (1993).
[11] J.M. Ottino, *The Kinematics of Mixing: Stretching, Chaos and Transport* (Cambridge University Press, Cambridge, 1989).
[12] A. Careta, F. Sagués, and J.M. Sancho, Phys. Rev. E **48**, 2279 (1993).
[13] A. Careta, F. Sagués, and J.M. Sancho, Phys. Fluids **6**, 349 (1994).
[14] R.H. Kraichnan, Phys. Fluids **13**, 22 (1970).

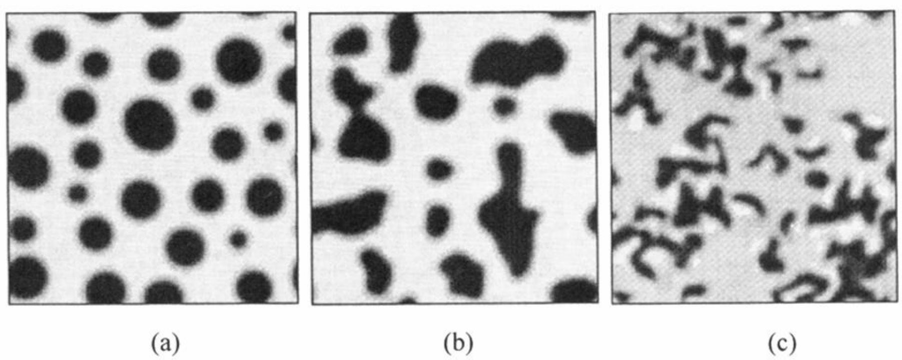


FIG. 1. Concentration patterns at time $t = 2500$ for (a) $u_0^2 = 0$; (b) $\lambda = 4$, $u_0^2 = 0.015$; and (c) $\lambda = 4$, $u_0^2 = 0.25$.