

## Effects of domain morphology in phase-separation dynamics at low temperature

A. M. Lacasta

*Departament de Física Aplicada, Universitat Politècnica de Catalunya, C/Jordi Girona Salgado 31, E-08034 Barcelona, Spain  
and Departament d'Estructura i Constituents de la Matèria, Facultat de Física, Universitat de Barcelona, Av. Diagonal,  
647, E-08028 Barcelona, Spain*

J. M. Sancho and A. Hernández-Machado

*Departament d'Estructura i Constituents de la Matèria, Facultat de Física, Universitat de Barcelona, Av. Diagonal,  
647, E-08028 Barcelona, Spain*

R. Toral

*Institut d'Estudis Avançats i Departament de Física, Universitat de les Illes Balears—Consejo Superior de Investigaciones Científicas, E-07071 Palma de Mallorca, Spain*

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We present numerical results of the deterministic Ginzburg-Landau equation with a concentration-dependent diffusion coefficient, for different values of the volume fraction  $\phi$  of the minority component. The morphology of the domains affects the dynamics of phase separation. The effective growth exponents, but not the scaled functions, are found to be temperature dependent.

Pattern formation and domain growth in binary systems that are suddenly quenched to a point within the coexistence region provide interesting examples of nonlinear and nonequilibrium problems.<sup>1–22</sup> The classical theory of Cahn and Hilliard<sup>21</sup> identifies two mechanisms of evolution depending on whether the system evolves toward equilibrium from a metastable or unstable initial state. The first case corresponds to the situation in which the volume fraction of one of the components is sufficiently small. Then, evolution proceeds by nucleation and growth of the resulting spherical nuclei. In the case of an unstable quench, a deeply interconnected pattern develops and coarsens. This last mechanism is known as spinodal decomposition. The classical theory predicts clear separation (the so-called spinodal line) between evolution by nucleation and spinodal decomposition. However, it is known that there is no sharp distinction between these two processes. In this sense, for off-critical quenches, even near the critical concentration, domains evolve to circular shapes.

Many theoretical<sup>2–4</sup> and numerical<sup>5–8</sup> studies have been carried out to understand the role of the morphology in the growth process. The theory of Tokuyama, Enomoto, and Kawasaki,<sup>3</sup> valid in three dimensions, predicts a strong dependence of the form of the scaling correlation function on the volume fraction of the minority phase  $\phi$ , at least for small values of  $\phi$ . Numerical studies in two dimensions<sup>5–8</sup> indicate that for small volume fractions, the shape of the scaling functions depends strongly on  $\phi$  whereas for larger volume fractions, the scaling functions seem to be independent of  $\phi$  and are identical to those obtained for spinodal decomposition.

These phase-separation processes have usually been described by a time-dependent Ginzburg-Landau equation for the concentration field with constant diffusion. Recently, some authors<sup>9–15</sup> have noted the necessity of modifying this equation by considering a concentration-

dependent diffusion coefficient for a correct modeling of a deep quench. This assumption is also necessary when external fields, like gravity, are present.<sup>11,15</sup> We have previously studied the effects of this modification on the scaling dynamics for a critical quench.<sup>13</sup>

In this paper, our aim is to study the effects of a concentration-dependent diffusion coefficient on the dynamics of an off-critical quench. We have performed a numerical simulation of the Ginzburg-Landau equation for different values of the volume fraction of a component. We have compared the numerical data for the correlation and structure functions and effective growth exponents. We obtain much slower dynamics for an off-critical quench. Furthermore, the effective growth exponents, but not the scaled functions, are temperature dependent. To justify this result, we have used the equation of motion for the interfacial profile that was derived in Ref. 13. From this equation, two different mechanisms of growth, associated with interfacial and bulk diffusion, are clearly identified. When these general results are applied to an off-critical quench one finds, apart from the simple reduction of bulk diffusion due to the low temperature, that the morphology of domains affects the role of the growth mechanisms. The reason is that by increasing the degree of asymmetry between the volume fraction of each component, the shape of the domains varies from interconnected structures, characteristic of a critical quench, to a distribution of rather circular droplets of the minority phase against a background of the majority phase. Then, owing to this circular shape of domains in the off-critical quench, the interfacial diffusion is strongly suppressed giving rise to much slower dynamics.

The modified dynamic equation of motion for the concentration field  $\bar{c}$  can be written as follows:<sup>13</sup>

$$\frac{\partial}{\partial \tau} \bar{c}(\mathbf{r}, \tau) = \nabla \Gamma(\bar{c}) \cdot \nabla \frac{\delta F(\{\bar{c}\})}{\delta \bar{c}} \quad (1)$$

where  $F(\{\bar{c}\})$  is the Ginzburg-Landau free energy,

$$F(\{\bar{c}\}) = \int d\mathbf{r} \left[ -\frac{r\bar{c}^2}{2} + \frac{u\bar{c}^4}{4} + \frac{\kappa(\nabla\bar{c})^2}{2} \right], \quad (2)$$

and the concentration-dependent diffusion coefficient  $\Gamma(\bar{c})$  has been postulated using phenomenological arguments as<sup>9-11</sup>

$$\Gamma(\bar{c}) = \Gamma_0(\bar{c}_0^2 - \bar{c}^2). \quad (3)$$

$\Gamma_0$  is a constant,  $\bar{c}_0 = \bar{c}_{st}(T=0)$  and  $\bar{c}_{st}(T)$  is the equilibrium value at temperature  $T$ .

By defining the new scaled variables time  $t$  and concentration  $c$ , Eq. (1) can be written in the dimensionless form<sup>13</sup>

$$\frac{\partial c}{\partial t} = \frac{1}{2} \nabla(1-ac^2) \cdot \nabla \left[ -\nabla^2 c + \frac{df}{dc} \right], \quad (4)$$

$$f(c) = -\frac{c^2}{2} + \frac{c^4}{4}, \quad (5)$$

where  $a = [\bar{c}_{st}(T)/\bar{c}_0]^2$  is a relevant parameter in our study. Its values range from 0 to 1 as the temperature is reduced, so that  $a=1$  for  $T=0$ . The bulk equilibrium values of the variable are now given by  $c_{st} = \pm 1$ . The original Cahn-Hilliard equation is recovered by setting  $a=0$ . The role of temperature will be considered only through the dependence of the parameter  $a$  on  $T$ . In this paper, we are not considering the effect of thermal fluctuations. However, one should notice that a larger noise strength would also imply a slower dynamics as has been proven in previous studies.<sup>6</sup>

Our previous numerical study<sup>13</sup> indicates that, for a critical quench ( $\phi=50\%$ ) the scaled correlation functions remain unchanged at low temperatures ( $a > 0$ ) as compared to those for  $a=0$ . The main effect of considering a nonzero value for  $a$  is that the dynamics are slowed down, so that the characteristic domain size exhibits a crossover from a  $\frac{1}{4}$  to a  $\frac{1}{3}$  power law as a function of time. This crossover, which appears at longer times for lower temperatures, could be interpreted<sup>13</sup> in terms of the equation describing the motion of the interface between the two phases.

In this paper, we extend the results of Ref. 13 by studying off-critical quenches at two different volume fractions,  $\phi=30\%$  and  $\phi=5\%$ . Three different temperatures, corresponding to the values  $a=0, 0.8$ , and  $1$  have been considered.

We have numerically integrated Eq. (4) in a square lattice of size  $L^2=120^2$  and periodic boundary conditions. We have used Euler's method with spacial steps  $\Delta x = \Delta y = 1$  and time step  $\Delta t = 0.025$ . The results have been averaged over ten runs corresponding to different initial conditions.

The system is initially prepared by assigning to each point a concentration,

$$c(\mathbf{r}, 0) = c_0 + \bar{c}(\mathbf{r}, 0), \quad (6)$$

where  $c_0 = 1 - 2\phi$  is the mean concentration and  $\bar{c}$  is a random number uniformly distributed in the interval  $(-0.05, 0.05)$ .

At this point, a comment is required regarding the initial conditions for the concentration in the case of  $\phi=5\%$  and the different values of  $a$ . In this case, the quench places the system in a metastable state and large fluctuations are necessary to form initial nuclei. For  $a=0$ , we choose the initial configuration to be a Gaussian distribution centered at  $c_0=0.9$  with variance 5. A very small time step is necessary to ensure the stability of the numerical integration in the early stages. So, initially, we have chosen  $\Delta t = 0.001$  up to  $t=100$ . For  $t > 100$  we use  $\Delta t = 0.025$ . However, a problem appears for  $a \neq 0$ , since the large values, which the initial concentration can take at some points, would produce a negative value of the diffusion coefficient. To avoid this spurious fact, the concentration must be limited, according to Eq. (4), by the condition,

$$1 - ac^2 \geq 0. \quad (7)$$

However, a variance obeying Eq. (7) is too small to produce any initial center of nucleation. To avoid this problem, we have taken as an initial configuration for  $a \neq 0$ , the distribution of small clusters obtained for  $a=0$  at time  $t=100$ .

To study the dynamic behavior of the domain growth we define the pair-correlation function

$$G(\mathbf{r}, t) = \left\langle \frac{1}{L^2} \sum_{\mathbf{r}'} [c(\mathbf{r}+\mathbf{r}', t)c(\mathbf{r}', t) - c_0^2] \right\rangle, \quad (8)$$

and its Fourier transform, the structure function  $S(\mathbf{k}, t)$ . As our system is isotropic we introduce the circularly averaged and normalized pair-correlation function,

$$G_n(r, t) = \frac{1}{N_r} \frac{\sum G(\mathbf{r}, t)}{\langle c^2(t) \rangle - \langle c \rangle^2} \quad (9)$$

and the circularly averaged and normalized structure function

$$S_n(k, t) = \frac{1}{N_k} \frac{\sum S(\mathbf{k}, t)}{\langle c^2(t) \rangle - \langle c \rangle^2}. \quad (10)$$

The sums in Eqs. (8) and (9) run over a set of points inside coronas of radii  $r$  and  $r + \Delta r$  or  $k$  and  $k + \Delta k$ , respectively.  $N_r$  and  $N_k$  are the number of points inside such coronas.

In Fig. 1, we present, for two volume fractions, the scaled correlation function

$$g(r/R_g(t)) = G_n(r, t), \quad (11)$$

where  $R_g$  is a relevant length of the problem, defined as the smallest value of  $r$  at which  $G_n$  becomes zero.

Furthermore, in Fig. 2 we also present the results for the scaled structure function

$$F(kR_g(t)) = R_g(t)^{-2} S_n(k, t). \quad (12)$$

For the two volume fractions and the three different values of  $a$  studied, we have reached a time regime in which the scaled functions are independent of time. Similar to what happened in the case of critical concentration ( $\phi=50\%$ ), we find that the dynamics are slowed down as  $a$  increases from 0 to 1 and, consequently, the

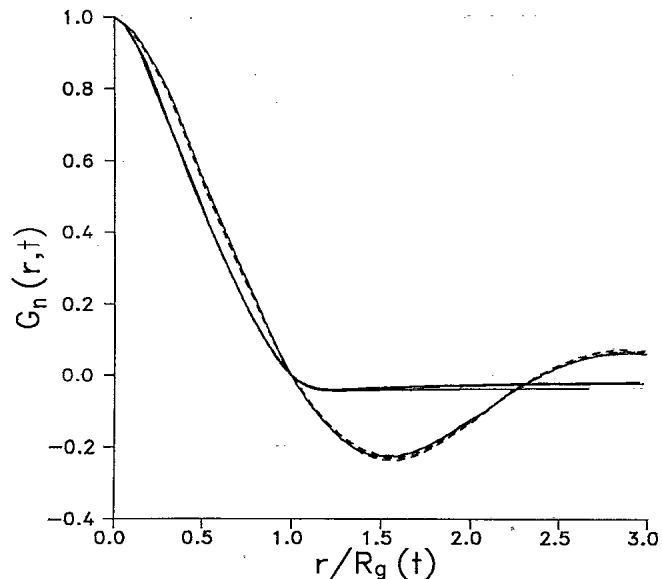


FIG. 1. Scaled correlation function [Eq. (11)] vs the scaled variable  $r/R_g(t)$ . The dashed lines correspond to the curves obtained for volume fraction  $\phi=30\%$ , and three values of  $a$  (0, 0.8, and 1). The solid lines represent the case  $\phi=5\%$  and the same three values of  $a$ . We have also represented by a solid line the function obtained for the critical case ( $\phi=50\%$ ) and  $a=0$ .

scaling regime is reached later.

Furthermore, we also find that the form of the scaled functions  $g(x)$  and  $F(x)$  is independent of  $a$ , as in the critical case.<sup>13</sup> In this sense, we remark that patterns with different  $a$  but the same characteristic size are similar. We observe that for  $\phi=30\%$  and  $\phi=5\%$ , the shape

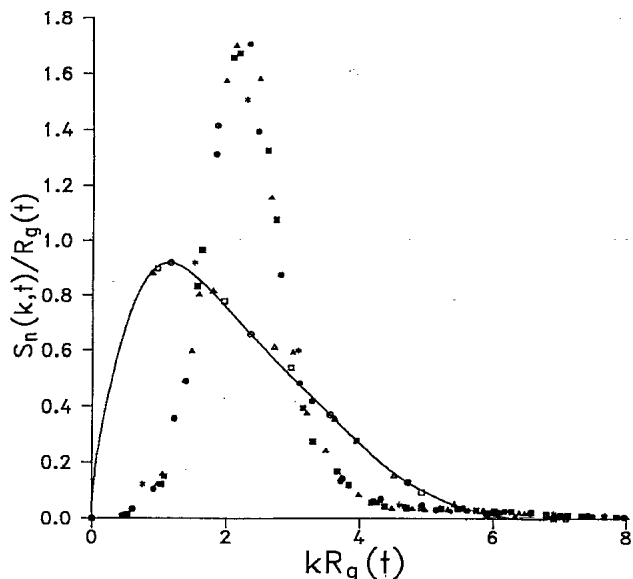


FIG. 2. Scaled structure function [Eq. (12)] vs the scaled variable  $kR_g(t)$ , for  $\phi=5\%$  (open symbols) and  $\phi=30\%$  (filled symbols), and three values of  $a$ :  $a=0$  ( $\Delta$ ),  $a=0.8$  ( $\circ$ ),  $a=1$  ( $\square$ ). The stars correspond to the values obtained for  $\phi=50\%$  and  $a=0$ . The solid line is a guide to the eye.

of these functions is independent of  $a$ . Then, we obtain that for  $\phi=30\%$ , the shape is similar to those obtained for the critical quench, although the shape is different for  $\phi=5\%$ .

Nonetheless, there is an interesting difference in the dynamics between the critical and off-critical quench, due to the different morphology of domains associated with them. This could be understood in terms of the role of two different growth mechanisms present during evolution, which explicitly appears in the interfacial equation describing the evolution of the domains:<sup>13</sup>

$$4v(s, t) = (1-a)\sigma \int ds' W[r(s), r(s')] K(s', t) + 4a \nabla^2 K(s, t), \quad (13)$$

where  $v$  is the normal velocity,  $K$  is the local curvature, and  $W$  is the inverse of the Green's function. The first term of the right-hand side of Eq. (13) contains the usual bulk diffusion, responsible for the  $\frac{1}{3}$  power law, and the second term contains an interfacial mechanism that is associated with the presence of a tangential flux at the interface, which is responsible for a  $\frac{1}{4}$  power law. In the derivation of the first term of Eq. (13), we have neglected any arbitrary function that satisfies  $\nabla^2 h(r, t) = 0$ . This factor, which is determined by the conservation condition of  $c(r, t)$ , is not usually included in the analysis because it does not affect the dimensional arguments.<sup>12</sup>

For  $\phi=50\%$ , when  $a=0$  the bulk diffusion mechanism dominates, but when  $a=1$  this mechanism is inhibited and the interfacial diffusion will be dominant. The presence of strong interfacial diffusion introduces crossover effects that manifest themselves in the fact that the observable power-law exponents differ from their theoretical asymptotic values. This crossover appears later at lower temperatures, but the long-time behavior is finally dominated by bulk diffusion in accordance with Lifshitz-Slyozov theory.<sup>22</sup>

Now, we study the modifications introduced in this picture when an off-critical quench is considered. We find that, as for a critical quench, bulk diffusion is reduced at low temperatures. However, the most interesting effect appears related to the interfacial mechanism. As one can see from Eq. (13), in general, interfacial diffusion is induced by the presence of differences in the curvature of the domains, and then, for an off-critical quench, this mechanism is reduced because the droplets are practically circular. These new effects of the off-critical quench could be observed in the values of the effective exponents. In Table I, we present the effective exponents  $n$  for a nonlinear fit of the form

TABLE I. Exponents  $n$  obtained for a fit  $R_g(t) = A_2 + B_1 t^n$ , for the volume fractions  $\phi=50\%$  and  $\phi=30\%$ .

$a$	$n$	
	$\phi=30\%$	$\phi=50\%$
0.0	$0.32 \pm 0.01$	$0.33 \pm 0.01$
0.8	$0.26 \pm 0.01$	$0.28 \pm 0.01$
1.0	$0.20 \pm 0.01$	$0.22 \pm 0.01$

$R_g(t) = A + Bt^n$ , obtained by minimizing the  $\chi^2$  function, for the off-critical quench at  $\phi=30\%$  and for the critical one. We obtain that the exponents seem to be smaller for the off-critical evolution. However, because the difference between them are within the numerical error, we include the results for an effective exponent defined by

$$n_{\text{eff}}(\alpha) = \frac{\ln[R_g(\alpha t)/R_g(t)]}{\ln \alpha} \quad (14)$$

In Fig. 3 we plot  $n_{\text{eff}}(4)$  vs  $1/R_g$  for  $\phi=30\%$  and  $\phi=50\%$ . The effective exponents  $n_{\text{eff}}$  for the off-critical case seem also to lie below the exponents for the critical case. For  $a=1$ , the bulk diffusion mechanism is also suppressed and we expect that the values of the effective exponents would be very far from  $\frac{1}{3}$ , as appears in Fig. 3. One should notice that these exponents are continuously changing in time but they give a quantitative measure of the importance of the correction to the asymptotic law.

For  $\phi=5\%$ , due to the presence of a small number of droplets in the temporal regime of interest, the statistics are lower than for  $\phi=30\%$ . For this reason, we have obtained the effective exponents in two different ways. First, we have used the same method as for 30%. Furthermore, we have focused on the growth of only one droplet, the biggest, in a larger lattice of size  $L^2=256^2$ . Our conclusion from both results is that the exponents are very similar to the case of  $\phi=30\%$ .

In summary, we have studied the effect of a concentration-dependent mobility coefficient on the time evolution of a system governed by a conserved Ginzburg-Landau equation. We have found that the scaled correlation and the scaled structure functions are independent of the values of the parameter  $a$ . The dependence on the volume fraction if any, is numerically indistinguishable for  $\phi=50\%$  and  $\phi=30\%$ , whereas the corresponding scaled functions for  $\phi=5\%$  are clearly different. This is in agreement with what is described in the case  $a=0$ . The main effect of considering  $a \neq 0$  is a slowing down of the dynamics. This effect is quantified in

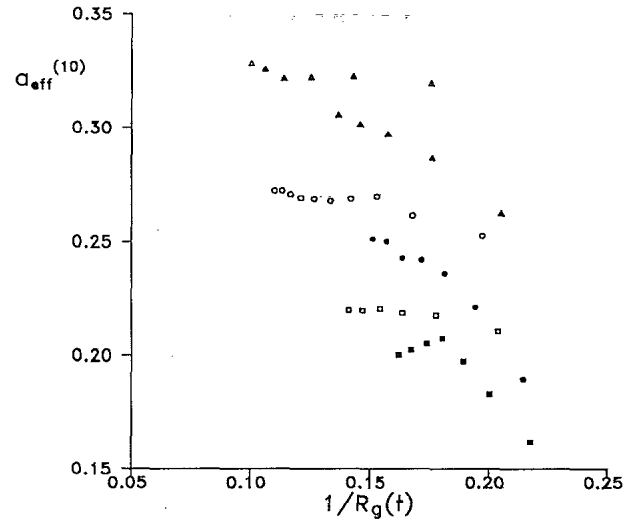


FIG. 3. Effective exponents, defined in Eq. (14) vs  $1/R_g(t)$ , for  $\phi=50\%$  (open symbols) and  $\phi=30\%$  (filled symbols), and three values of  $a$ :  $a=0(\triangle)$ ,  $a=0.8(\circ)$ ,  $a=1(\square)$ .

two ways: the time needed to reach the scaling regime increases and the corrections to the asymptotic Lifshitz-Slyozov law are more important. The effective exponents of the characteristic domain size are, for a given time, smaller in the case of the smaller volume fraction. The main reason for this is related to the reduction of surface diffusion due to the change in the morphology of domains when going from a critical to an off-critical quench. This could help to explain some of the small values for the effective exponents obtained in experiments.

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