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**PHASE SEPARATION IN BINARY MIXTURES  
AT LOW TEMPERATURES**

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**ABSTRACT**

Dynamical scaling during the late stages of phase separation in a binary mixture are studied for different values of the volume fraction  $\phi$  of the minority component. We have performed a numerical integration of the deterministic time-dependent Ginzburg-Landau equation with a variable-dependent diffusion coefficient. The forms of the pair-correlation function and the structure function are independent of temperature but dynamics are slower at low temperatures. A crossover between interfacial diffusion and bulk diffusion mechanisms is observed in the behaviour of the characteristic domain size. This effect is explained theoretically in terms of an equation of motion for the interface.

**1. Introduction**

Pattern formation during phase separation is an interesting nonlinear, non-equilibrium problem<sup>1</sup>. This situation appears, for example, when a binary mixture, initially in a homogeneous equilibrium state, is suddenly quenched into the two-phase coexistence region. Then, the system evolves spontaneously by generating macroscopic domains towards a new two-phase equilibrium state.

The classical theory makes a distinction between nucleation and spinodal decomposition, depending on whether the system reaches equilibrium from a metastable or unstable state. However, it is known that there is no sharp distinction between the two processes. Rather, there is a gradual transition in the dynamic behaviour. The position of the quench modifies the amount of each phase, and therefore the morphology of the patterns formed. By increasing the degree of asymmetry between the volume fraction of the two components, the shape of the domains varies from an interconnected structure, characteristic of spinodal decomposition, to a distribution of circular clusters of the minority phase in a background of the other phase.

From a theoretical point of view, apart from microscopic models, these phase separation processes have usually been described by a time-dependent Ginzburg -

Landau equation for the concentration  $\bar{c}$  :

$$\frac{\partial}{\partial \tau} \bar{c}(\vec{r}, \tau) = \nabla \left( \Gamma \nabla \frac{\delta F(\{\bar{c}\})}{\delta \bar{c}} \right) + \eta(\vec{r}, t), \quad (1)$$

where the mobility  $\Gamma$  is a constant and  $\eta(\vec{r}, t)$  is the thermal noise.  $F(\{\bar{c}\})$  is the Ginzburg-Landau free energy

$$F(\{\bar{c}\}) = \frac{1}{2} \int d\vec{r} \left\{ -r\bar{c}^2 + \frac{u}{2}\bar{c}^4 + k(\nabla\bar{c})^2 \right\}, \quad (2)$$

where  $r$ ,  $u$  and  $k$  are positive phenomenological coefficients.

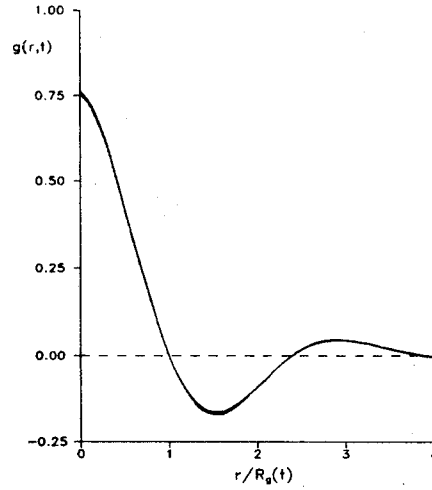


Figure 1: Radial Correlation Function versus the scaled variable  $r/R_g(t)$ , for  $\phi = 50\%$  and five values of  $a$ . The curves have been taken at times:  $t = 1200$  for  $a = 0$ ;  $t = 1400$  for  $a = 0.2$ ;  $t = 2000$  for  $a = 0.6$ ;  $t = 3000$  for  $a = 0.8$  and  $t = 5800$  for  $a = 1$ .

Computer simulations of this model for critical<sup>2-4</sup> and off-critical<sup>5-6</sup> quenches suggest that the late time behavior is well described in terms of a scaling with a characteristic length  $R(t)$ , which shows a power-law growth in time with an exponent  $1/3$ .

Recently, some authors<sup>7-10</sup> have argued the necessity of modifying the usual Ginzburg-Landau equation by considering a concentration-dependent diffusion coefficient for adequate modelling of a deep quench. This coefficient has been postulated to be

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

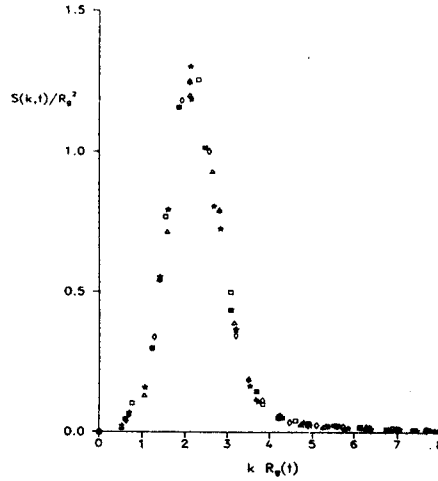


Figure 2: Scaled radial structure function versus the scaled variable  $kR_0(t)$ , for  $\phi = 50\%$  and two values of  $a$ :  $a = 0$  black symbols and  $a = 0.8$  white symbols. The points have been taken at times: 5000(★), 8000(■), 10000(▲), 12000(◆), 9000(☆), 12000(□), 15000(△), 18000(○).

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

In this contribution we focus on the effects of a concentration-dependent diffusion coefficient on the dynamics of phase separation<sup>10-11</sup>. Since we are interested in low temperatures and late stages of the evolution, the noise term is neglected.

## 2. Model and Numerical Results

Our macroscopic continuous model can be written in the dimensionless form:

$$\frac{\partial c}{\partial t} = \nabla \cdot ((1 - ac^2)\nabla(-c + c^3 - \nabla^2 c)) \quad (4)$$

where  $a = (\bar{c}_{st}(T)/\bar{c}_0)^2$  is the only relevant parameter in our study. Its values go from 0 to 1 as temperature is reduced,  $a = 1$  for  $T = 0$ , and we recover the usual G.L. equation for  $a = 0$ . Now the bulk equilibrium values of the variable  $c$  are  $c_{st} = \pm 1$ .

We have numerically integrated Eq. (4) in a square lattice of size  $L = 120$  and periodic boundary conditions, using Euler's method with mesh size  $\Delta x = 1$  and time step  $\Delta t = 0.025$ . We have studied quenches corresponding to three volume fractions of the minority phase:  $\phi = 50\%$  (critical case)<sup>10</sup>,  $\phi = 30\%$  and  $\phi = 5\%$  (both off-critical cases)<sup>11</sup>. We have selected different values for  $a$ , and the results have

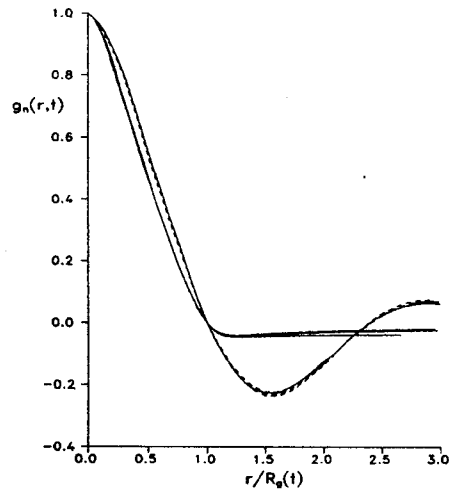


Figure 3: Radial and normalized correlation function, versus the scaled variable  $r/R_g(t)$ . The dashed lines correspond to the curves obtained for volume fraction  $\phi = 30\%$ , and three values of  $a$  (0, 0.8 and 1). The solid lines represent the case  $\phi = 5\%$  and the same three values of  $a$ . We have also represented by a solid line the function obtained for the critical case ( $\phi = 50\%$ ).

been averaged over 10 runs. The system was initially prepared by assigning to each point a concentration  $c(\vec{r}, t) = c_0 + \tilde{c}(\vec{r}, t)$ , where  $c_0 = 1 - 2\phi$  is the mean concentration and  $\tilde{c}$  is a random number uniformly distributed in the interval  $(-0.05, 0.05)$ .

In order to study the dynamics of the domain growth we introduce the pair-correlation function

$$G(\vec{r}, t) = \langle \frac{1}{L^2} \sum_{\vec{x}} (c(\vec{r} + \vec{x}, t)c(\vec{x}, t) - c_0^2) \rangle \quad (5)$$

where the brackets mean average over initial conditions. The Fourier transform of  $G(\vec{r}, t)$  is the structure function  $S(\vec{k}, t)$ .

As our system is isotropic, we introduce the circularly-averaged pair correlation function

$$g(r, t) = \frac{1}{N_r} \sum G(\vec{r}, t) \quad (6)$$

and the circularly-averaged structure function

$$s(k, t) = \frac{1}{N_k} \sum S(\vec{k}, t) \quad (7)$$

where the sums run over the set of points inside the 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.

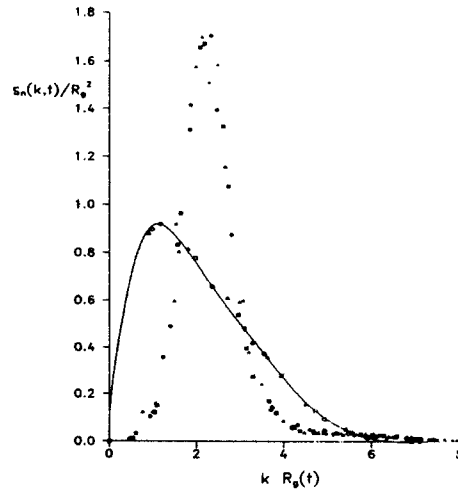


Figure 4: Scaled radial and normalized structure function versus the scaled variable  $kR_g(t)$ , for  $\phi = 5\%$  (white symbols) and  $\phi = 30\%$  (black symbols), and three values of  $a$  ( $a = 0$  ( $\square$ );  $a = 0.8$  ( $\circ$ );  $a = 1$  ( $\square$ )). The stars correspond to the values obtained for  $\phi = 50\%$ .

The dynamical scaling hypothesis for the pair-correlation function and the structure function states that

$$g(r, t) = g(r/R_g(t)) \quad (8)$$

$$s(k, t) = R_g(t)^2 s(kR_g(t)) \quad (9)$$

where  $R_g(t)$  is a relevant length defined as the first zero of the pair-correlation function.

First, we have tested that our numerical scheme reproduces the well-known results of the scaling regime for  $a=0$ . At late stages, the scaling pair-correlation and structure functions are time-independent, and their form depends strongly on  $\phi$ .

We find that, for different values of  $a$ , the scaling regime is reached for long enough times. The dynamics are slower and so the scaling regime is reached later, as  $a$  is increases from 0 to 1. In Fig.1 we present results for the pair-correlation function for the critical case and five values of  $a$ . We can see that the form of this scaling function (Eq. (8)) is independent of temperature. In Fig.2, we show the structure function for the critical case, two values of  $a$ , and some different times. We find that the scaling function (Eq. (9)) is independent of time and temperature, within our numerical accuracy. In Fig. (3) and Fig. (4), we present the normalized correlation function and the normalized structure function for the three different

| $a$ | $n(\phi = 30\%)$ | $n(\phi = 50\%)$ |
|-----|------------------|------------------|
| 0.0 | 0.32             | 0.33             |
| 0.8 | 0.26             | 0.28             |
| 1.0 | 0.20             | 0.22             |

Table 1: Exponents  $n$  obtained for a fit  $R_g(t) = \beta_2 + \beta_1 t^n$ , for the volume fractions  $\phi=50\%$  and  $\phi=30\%$ .

volume fraction values studied. We observe that for  $\phi=30\%$  the form of these functions is identical to that obtained for  $\phi=50\%$ , but the shape is different for  $\phi=5\%$ .

As to the behaviour of the characteristic domain size, the main effect of considering a non-zero value for  $a$  is that  $R_g$  exhibits a crossover from  $1/4$  to  $1/3$  power law as a function of time. This crossover appears at longer times for lower temperatures. In Table 1 we present the effective exponents  $n$  obtained from a fit of the form  $R_g(t) = \beta_2 + \beta_1 t^n$  for two volume fractions. The crossover behaviour can be understood in terms of the equation describing the motion of the interface<sup>9-10</sup>,

$$v(s, t) = \frac{1}{4}(1-a)\sigma \int ds' W(r(s), r(s'))K(s, t) + a\nabla^2 K(s, t) \quad (10)$$

where  $(u, s)$  are curvilinear coordinates,  $v(s, t)$  is the normal velocity of the interface,  $\sigma$  is the surface tension,  $K(s, t)$  is the local curvature and  $W$  is defined by the following equation

$$\int ds'' G(r(s), r(s''))W(r(s''), r(s')) = \delta(s - s') \quad (11)$$

where  $G(r(s), r(s''))$  is the Green function solution of

$$\nabla^2 G(\vec{r}, \vec{r}') = \delta(\vec{r} - \vec{r}') \quad (12)$$

The first term of Eq. (10) contains the usual bulk diffusion, responsible for the  $1/3$  power law, and it dominates for long times. The second term contains an interfacial mechanism that is associated with the presence of a tangential flux at the interface, which is the responsible for a  $1/4$  power law. From Eq. (10) it seems natural to propose the following equation for the characteristic domain size  $R(t)$ ,

$$\frac{dR(t)}{dt} = (1-a)\frac{C_2}{R^2} + a\frac{C_3}{R^3} \quad (13)$$

We obtain  $1/4$  power law for  $a = 1$  and  $a = 1/3$  power law for  $a = 0$ . For intermediate values of  $a$  there is a crossover behaviour between these two values in accordance with the numerical results.

### 3. Conclusions

We have studied both numerically and analytically the effects of a concentration-dependent diffusion coefficient on the domain growth dynamics of a deterministic time-dependent Ginzburg-Landau model. We find that the form of the scaling

functions  $g(z)$  and  $s(z)$  is independent of temperature. For  $\phi=50\%$  and  $\phi=30\%$  the form of these functions seems to be identical whereas for  $\phi=5\%$  they are clearly different. We obtain that the characteristic domain size presents a crossover from  $1/4$  to  $1/3$  power law as a function of time. This effect can be explained theoretically by means of an equation of motion for the interface, and it can be understood in terms of a reduction in the bulk diffusion mechanism that induces a greater role of interfacial diffusion for short time.

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