Universal Growth Exponent at the Early Nonlinear Stage of Spinodal Decomposition

Vlad Mitlin

3Com Corporation, 10329 Azuaga st., Suite 263, San Diego, CA 92129, USA

Summary: The nonlinear Cahn's model of spinodal decomposition is considered within the framework of the Langer's 'mean-field approximation'. It is argued that a universal growth exponent of ¼ characterizes the early nonlinear stage of spinodal decomposition, regardless of the space dimensionality and the spectral characteristics of the gradient energy matrix. This is a contrary to our earlier predictions made for isotropic and anisotropic decomposition (Mitlin, 1989, 1990). The temporal dependence of the magnitude of the structure factor follows a power law with the exponent of *d/2* (*d* is the space dimensionality). The temporal dependence of the semi-width of the structure factor follows a power law with the exponent of -¼ (with logarithmic corrections).

Introduction

Spinodal decomposition is a general phase transition phenomenon. Due to large relaxation times, spinodal decomposition is easier observable in polymer systems compared to simple fluids. An asymptotic analysis of the Cahn's nonlinear model of spinodal decomposition[1] was presented in .[2] That analysis was performed within the framework of so-called 'mean-field approximation' proposed by Langer.[3] As shown in molecular dynamics simulations (see, for example, [4-6]), the 'mean-field approximation' does not accurately describe the late nonlinear stage of the process. It properly captures the main features of the early nonlinear stage of spinodal decomposition (including the motion of the maximum of the structure factor to the long-wave region and a power law for the growing spatial scale of spinodal structures).[5-8] Our analysis showed that a simple power law could describe the growth of decomposition structures at the early nonlinear stage of the process. The exponent in this asymptotic law was found to depend on the space dimensionality, d. Namely, at $d=1$ the exponent was ½, and at $d=2$ and $d=3$ it was ¼ .[2] Later that approach was extended to describing the growth of structures in anisotropic solid solutions.[9, 10] In that case the exponent in the power law of structures growth was found to depend both on the space dimensionality and the degeneracy m of the minimum eigenvalue λ_1 of the gradient energy matrix. Particularly, at $d=3$ and $m=1$ (a strongly anisotropic solid solution) the exponent was found to be ½, while at $d=3$ and $m=3$ (an isotropic solution) the value of ¼ was

 CCC 1022-1360/00/$ 17.50+.50/0

obtained again.

Some time ago I was pointed out that the exponent of ½ has not been observed in the molecular dynamics simulations based on the Cahn model.[11] A subsequent analysis revealed that one asymptotic solution was missed in [2, 9] while another solution yielding an exponent of ½, was physically unreasonable. This analysis is presented below, and it yields an important conclusion that a universal growth exponent of ¼ characterizes the early nonlinear stage of spinodal decomposition described by the Cahn's equation. This value of the exponent is observed regardless of the space dimensionality and, in case of an anisotropic solution, of the degeneracy of the minimum eigenvalue of the gradient energy matrix. The asymptotic behavior of the structure factor is also discussed. It is found that the temporal dependence of the magnitude of the structure factor follows a power law with the exponent of *d/2*, regardless of the spectral characteristics of the gradient energy matrix. The temporal dependence of the semi-width of the structure factor follows a power law with the exponent of -¼ (with logarithmic corrections). The results obtained in this paper bring a desired consistency in the mathematical description of the early nonlinear stage of spinodal decomposition.

Isotropic Model

The isotropic model of spinodal decomposition is presented by the following equations [2, 12]:

$$\frac{\partial \varphi}{\partial t} = \nabla \Lambda \nabla \frac{\delta F}{\delta \varphi} \tag{1}$$

$$F = \int \left[F_0(\varphi) + \kappa (\nabla \varphi)^2 \right] d\vec{r} \tag{2}$$

where φ is the fraction of a component of the binary mixture, F is the free-energy functional in units of k_BT, Λ is the Onsager coefficient, and κ is the gradient energy coefficient.

In [2] Eqs.(1) and (2) were analyzed using the 'mean-field approximation'.[3] As a result, the following equation describing the evolution of the spatial scale of spinodal structures, was derived (see details in [2]):

$$\frac{\exp\left(\nu^2 \tau\right) \nu^{(d-2)/2}}{\tau^{1/2}} = Y\left(\left(\nu \tau\right)' \right) > 0 \tag{3}$$

$$\nu = q_*^2 / q_M^2 ,\ \tau = 2\kappa \Lambda q_M^4 t \tag{4}$$

Here q_M is the wavelength corresponding to the maximum growth mode at the initial (linear) stage of decomposition; q_* is the wavelength corresponding to the maximum growth mode at the time *t*, and *Y* is a positive function of the time derivative, $(\nu\tau)'$. If $(\nu\tau)'$ is an asymptotically rising function of time the spatial scale of spinodal structures will decrease with time. If $(\nu\tau)'$ tends to a constant then the spatial scale tends to a non-zero constant too which is also meaningless. The only case of physically reasonable behavior of q_*^2 at large times corresponds to an asymptotic vanishing of the time derivative on the r. h. s. of Eq. (3).[2] But then at large times one should have:

$$\frac{\nu^{(d-2)/2}\exp(\nu^2\tau)}{\tau^{1/2}} = y, \quad y = Y(0) \tag{5}$$

Equation (5) does not contain time derivatives.

At *d =2* Equation (5) has an exact solution

$$\nu^2 = \ln(\tau y^2)/2\tau \tag{6}$$

At *d=3* introducing a new variable

$$g = 4\nu^2\tau \tag{7}$$

yields:

$$g\exp g = 4y^4\tau^3 \tag{8}$$

Equation (8) has the following solution at large times [13]:

$$g = \ln(4y^4\tau^3) - \ln\ln(4y^4\tau^3) + O\left(\frac{\ln\ln(4y^4\tau^3)}{\ln(4y^4\tau^3)}\right) \tag{9}$$

At *d=1* one has the following equation for the variable defined in Eq. (7):

$$\frac{\exp g}{g} = \frac{y^4\tau}{4} \tag{10}$$

Equation (10) can be presented as

$$g - \ln g = \ln(y^4\tau/4) \tag{11}$$

Applying the method described in Ref. [13], p. 51, yields the following solution of Eq. (11):

$$g = \ln(y^4\tau/4) + \ln\ln(y^4\tau/4) + O\left(\frac{(\ln\ln(y^4\tau/4))^2}{\ln(y^4\tau/4)}\right) \tag{12}$$

Note that in [2] the solution presented by Eq. (12) was missed. Instead, the following solution of Eq. (10) was constructed using the Burmann-Lagrange series:

$$g = \sum_{n=1}^{\infty} \left(\frac{4}{y^4 \tau} \right)^n \frac{n^{n-1}}{n!}$$

or

$$g = \frac{4}{y^4 \tau} + O\left(\frac{1}{\tau^2} \right) \tag{13}$$

Equation (13) is another asymptotic solution of Eq. (10); however, it yields an asymptotic vanishing of the maximum of the structure factor

$$\Gamma(q_*) = \frac{\delta\varphi(q_*,t)\delta\varphi(-q_*,t)}{\delta\varphi(q_*,0)\delta\varphi(-q_*,0)} = \exp(2v^2\tau) \tag{14}$$

(refer to Eq. (43) in [2]). This is physically unreasonable (the magnitude of fluctuations of the order parameter should increase in the process of spinodal decomposition); that is why the solution given by Eq. (13) has to be ignored in favor of the solution given by Eq. (12).

Equations (6), (9), and (12) show that the evolution of the spatial size $\xi = 2\pi / q_*$ of spinodal structures is described by a power law (with logarithmic correction), i.e.

$$\ln \xi = \frac{\ln \tau}{4} \left[1 + O\left(\frac{\ln \ln \tau}{\ln \tau} \right) \right] \tag{15}$$

The exponent in this power law is ¼ regardless of the space dimensionality *d*.

Anisotropic Model

Spinodal decomposition in anisotropic solid solutions can be described using the following generalization of the free energy functional (1)[9]:

$$F = \int \left[F_0(\varphi) + (K\nabla\varphi, \nabla\varphi) \right] d\vec{r} \tag{16}$$

where ***K*** is the symmetric gradient energy matrix. The quadratic form in Eq. (16) is positive-definite, i.e. all eigenvalues of ***K*** are real and positive. It was shown that the most general long-wavelength form of the anisotropic model for a diffusion–controlled phase transition in a system with one order parameter reduces to Eqs. (1) and (16).[9, 10]

As described in,[9] the dynamics of the system described by Eqs. (1) and (16) is stipulated by the spectrum of the matrix ***K***. It was shown that in the case of general position (when all eigenvalues are different, i.e. their degeneracy equals 1) the eigenvector corresponding to the minimum eigenvalue of ***K*** determines the most favorable spatial direction of decomposition. In the process of spinodal decomposition the micro-lamellation happens preferentially in that direction. The evolution of spatial scale of spinodal structures in that direction is determined from the following equation[9]:

$$\frac{\exp\left(v^2\tau\right)}{\left(v\tau\right)^{d/2}} = y \tag{17}$$

where $v = q_*^2 / q_M^2$, $\tau = 2\lambda_1 \Lambda q_M^4 t$. Equation (17) can be rewritten as,

$$\frac{\exp g}{g} = \frac{d\, y^{4/d}\tau}{4}, \quad g = \frac{d\, v^2 \tau}{4} \tag{18}$$

The solution of Eq. (18) has the same form that Eq. (12):

$$g = \ln\left(d\, y^{4/d}\tau/4\right) + \ln\ln\left(d\, y^{4/d}\tau/4\right) + O\left(\frac{\left(\ln\ln\left(d\, y^{4/d}\tau/4\right)\right)^2}{\ln\left(d\, y^{4/d}\tau/4\right)}\right) \tag{19}$$

Again, it is possible to construct a different form of asymptotic solution of Eq. (18), the result being:

$$g = \frac{4}{d\, y^{4/d}\tau} + O\left(\frac{1}{\tau^2}\right) \tag{20}$$

The solution (20) was presented in [9] but, as Eq. (13) in the isotropic case, it yields an asymptotic vanishing of the maximum of the structure factor; thus it is physically unreasonable.

For an arbitrary degeneracy of the minimum eigenvalue of ***K***, one obtains a generalization of Eq. (17) [9, 10]:

$$\frac{\exp\left(v^2\tau\right)}{v^{(d-2m+2)/2}\tau^{(d-m+1)/2}} = y \tag{21}$$

When *m=d* (the only one eigenvalue with the degeneracy *d*) one obtains the isotropic case presented by Eq. (5). When *m=1* one recovers the anisotropic case of general position presented by Eq. (17). As in the isotropic case, there are three cases existing in solving Eq. (21).

At *d-2m+2=0* Eq. (21) is solved exactly:

$$v^2 = \ln\left(\tau y^{4/d}\right) d / 4\tau \tag{22}$$

At *d-2m+2>0* let us present Eq. (21) in the form:

$$\frac{\exp g}{g} = \frac{(d-2m+2)\, y^{4/(d-2m+2)}\tau^{d/(d-2m+2)}}{4}, \quad g = \frac{4v^2\tau}{d-2m+2} \tag{23}$$

The solution of Eq. (23) is (only the terms not vanishing at large times are shown):

$$g = \ln\left((d-2m+2)y^{4/(d-2m+2)}\tau^{d/(d-2m+2)}/4\right) + \ln\ln\left((d-2m+2)y^{4/(d-2m+2)}\tau^{d/(d-2m+2)}/4\right) \qquad (24)$$

Again, it is possible to construct a different form of asymptotic solution of Eq. (23). Similarly to Eq. (20), the result is [9]:

$$v^2 = y^{-4/(d-2m+2)}\tau^{-(2d-2m+2)/(d-2m+2)},$$

and again it yields an asymptotic vanishing of the maximum of the structure factor.

At *d-2m+2<0* let us present Eq. (21) in the form:

$$g\exp g = \frac{4\, y^{4/(2m-d-2)}\tau^{d/(2m-d-2)}}{2m-d-2}, \quad g = \frac{4v^2\tau}{2m-d-2} \qquad (25)$$

The solution of Eq. (25) is

$$g = \ln\left(4y^{4/(2m-d-2)}\tau^{d/(2m-d-2)}/(2m-d-2)\right) - \ln\ln\left(4y^{4/(2m-d-2)}\tau^{d/(2m-d-2)}/(2m-d-2)\right) \qquad (26)$$

Equations (19), (22), (24), and (26) show again that the evolution of the spatial size of spinodal structures is described by a power law (with logarithmic correction), i.e. one obtains Eq. (15). Again, the exponent in this power law is ¼ regardless of the space dimensionality d and the spectral characteristics of ***K***.

Evolution of the Structure Factor

Other important characteristics of spinodal decomposition are the maximum and the width of the structure factor,

$$\Gamma(\vec{q}) = \frac{\delta\varphi(\vec{q},t)\delta\varphi(-\vec{q},t)}{\delta\varphi(\vec{q},0)\delta\varphi(-\vec{q},0)}, \qquad (27)$$

determined in scattering experiments. Specifically, the maximum of the structure factor is given by the following expression [2, 10]:

$$\mu = \Gamma(\vec{q}_*) = \exp(2v^2\tau) \qquad (28)$$

The semi-width of the structure factor is [2, 10]:

$$\delta = q_M v^{1/2} = q_* \qquad (29)$$

In the anisotropic case the semi-width presented by Eq. (29) is measured in the most favorable direction of decomposition, $\vec{q}_*$. Introducing expressions obtained in Section 3 into Eqs. (28) and (29) yields

$$\mu \sim \tau^{d/2}\left(1 + O\left(\frac{\ln\tau}{\tau^{d/2}}\right)\right) \qquad (30)$$

and

$$\delta \sim \left(\frac{\ln \tau}{\tau}\right)^{1/4}\left[1 + O\left(\frac{1}{(\ln \tau)^{1/4}}\right)\right] \tag{31}$$

Equation (30) shows that the temporal dependence of the magnitude of structure factor follows a power law with the exponent of *d/2* that does not depend on the spectral characteristics of ***K***. Equation (31) shows that the semi-width of the structure factor decreases as $\tau^{-1/4}$ (with logarithmic corrections). A similar (in a power-law form) decrease in the width and increase in the magnitude the structure factor have been observed in molecular dynamics simulations of spinodal decomposition.[6, 14, 15]

Conclusion

A power law (with logarithmic corrections) characterizes the growth of structures at the early nonlinear stage of spinodal decomposition described by the mean-field approximation of the Cahn's model. The exponent in this law is ¼, and it does not depend on the space dimensionality *d* and (for general anisotropic model) on the spectral properties of the gradient energy matrix. This result agrees with Langer's numerical calculations,[3] as well as with molecular dynamics simulations.[5-8] The magnitude of the structure factor increases as $\tau^{d/2}$. The semi-width of the structure factor decreases as $\tau^{-1/4}$ (with logarithmic corrections). One has to outline that the analysis presented describes the early nonlinear stage of decomposition; at late stages the Langer approximation is not applicable and the Lifshitz-Slyozov [16] growth exponent of 1/3, is observed.[4-6]

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