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Stochastic generalization for a hyperbolic model of spinodal decomposition

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ABSTRACT

A model for diffusion and phase separation which takes into account exponential relaxation of the solute diffusion flux and its fluctuations is developed. The model describes a system undergoing phase separation governed by a partial differential equation of hyperbolic type. The analysis is done for the evolution of patterns in spinodal decomposition for the system supercooled below critical temperature. Analytical results show that relaxation processes of the solute diffusion flux lead to the selection of patterns with different wavenumbers. Considering spatial–temporal correlations of the flux fluctuations, we have found that the temporal correlations promote selecting large-period patterns, whereas the corresponding spatial correlations accelerate such processes.

1. Introduction

A process of phase separation evolving through spontaneous growth of fluctuations of concentration (as in liquid–liquid systems) or fluctuations of density (as in gas–liquid systems) is known as spinodal decomposition. It results in the separation of phases having equivalent symmetry and differing only in composition (density).

From the pioneering works of Cahn and Hilliard [1,2] and Cook [3], substantial progress has been made in the investigation of different materials undergoing phase separation by the spinodal mechanism [4–9]. As follows from experimental findings and the theoretical description of various functions characterizing spinodal decomposition [4–9], the amplification rate $\omega(\mathbf{k}, t)$ and structure factor $S(\mathbf{k}, t)$ as functions of the wavevector $\mathbf{k}$ and time t are used to characterize the growth of fluctuations and developing patterns. In spinodal decomposition, the amplification rate $\omega(\mathbf{k}, t)$ is the exponent of the faster growing mode and the structure factor $S(\mathbf{k}, t)$ is analyzed as an equal time concentration (density) correlation function which at equilibrium does not depend on time (for an overview of various other definitions, see [10]).

In its linear version, the Cahn–Hilliard–Cook (CHC) model [1–3] predicts (i) smooth behavior of $S(\mathbf{k}, t)$ with one characteristic peak in time t, and (ii) linear behavior for $\omega(\mathbf{k}, t)/k^2$ *versus* k^2. However, predictions (i)–(ii) contradict many experimental findings in which, particularly for $\omega(\mathbf{k}, t)/k^2$ *versus* k^2, a nonlinear behavior is clearly observed [4,5,7,8].

To describe the nonlinearity in the amplification rate $\omega(\mathbf{k}, t)$ of spinodal decomposition, several models have been developed in addition to the CHC model. One of them – the Langer–Baron–Miller model (LBM model) [11] – has been widely tested against experimental data. The LBM model predicts the behavior of functions $\omega(\mathbf{k}, t)/k^2$ and $S(\mathbf{k}, t)$ in reasonable agreement with experiment [8,12–14]; however, it is limited by the hydrodynamic approximation in which a local equilibrium exists at every moment of transformation. This approximation limits the description of very early stages

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of phase separation in spinodal decomposition and might fail in its description of evolving patterns in non-ergodic systems, e.g., in glasses [15].

Using extended irreversible thermodynamics [16], a model for fast spinodal decomposition has also been advanced for the case of local non-equilibrium solute diffusion [17,18]. In this model, the introduction of a kinetic contribution responsible for the purely non-equilibrium part of the entropy (or free energy) leads to a nonlinearity in the amplification rate for decomposition and to agreement with experimental data, at least for a spinodally decomposed binary glass [18]. The kinetic contribution changes a model based on a parabolic partial differential equation [1,3,11] to a model with memory [19]. As a result, the model is able to describe both the fast decomposition existing at the early stages and the slow spinodal decomposition occurring at the following and final stages. It can predict the process of rapidly quenched decomposition for short periods of time, large composition gradients or deep undercoolings into the spinodal region of the phase diagram. Thus, the model describes the earliest stages when the standard hydrodynamic approximation fails and gradually converges with the Cahn–Hilliard model at later stages of decomposition. In particular, the memory function for the diffusion flux in a form of exponential decay leads to a "hyperbolic model" described by a partial differential equation of the hyperbolic type [19].

In the present article, we concentrate on the stochastic generalization of the hyperbolic model for fast spinodal decomposition. As has been shown [18], the nonlinearity in the amplification rate $\omega(\mathbf{k}, t)/k^2$ is governed by atomic diffusion and interaction between decomposing phases. Also, computational modeling demonstrates that nonlinearity may be observed in the behavior of the structure factor [20]: a wave behavior for $S(\mathbf{k}, t)$ occurs at small t and large $\mathbf{k}$ at the initial stages of decomposition. These features are observed in a pure deterministic hyperbolic model and a possible noise contribution into the mechanism of fast spinodal decomposition has not yet been analyzed. Therefore, the role of stochastic processes in the form of white and colored noise is clarified in the present article.

The article is organized as follows. In Section 2, a model of fast spinodal decomposition proceeding under local non-equilibrium and with space–time-correlated noise in the atomic diffusion field is formulated. Section 3 deals with the derivation of the structure factor $S(\mathbf{k}, t)$ as one of the main functions responsible for pattern evolution in spinodal decomposition. Limiting cases are presented from the general expression on evolution of $S(\mathbf{k}, t)$. In particular, the limit of the white noise and limits of the colored noise separately in space and in time are found. Further, the analysis of the dynamics of $S(\mathbf{k}, t)$ is presented in Section 4. It is given for initial stages when the local non-equilibrium in the diffusion field (deterministic contribution) and the noise (stochastic contribution) may both have an essential influence on the rate of spinodal decomposition. We discuss the role of a fluctuating source on the system dynamics in Section 5. Finally, in Section 6, a brief summary of the results is presented.

2. The model

Let us consider an isothermal binary system $A_{\bar{c}}B_{1-\bar{c}}$ which begins to spinodally decompose at the critical concentration $\bar{c}$. The considered system is a binary alloy or mixture of chemical components in liquid or solid states free of imperfections, without the effect of coherency strain, shear flow or magnetic effects. Even though these effects contribute to the free energy density of the system and influence phase separation qualitatively and quantitatively [6,9,21,22], we exclude them from the statement of the present problem to simplify the analysis. As a result, the following main contributions to the free energy are taken into account:

- free energy density distinguishing between the separating phases;
- concentration gradient contribution due to surface energy between phases;
- local non-equilibrium effect in the form of atomic flux relaxation to its steady state;
- stochastic effects appearing from the presence of noise.

To describe the system behavior under the above contributions, let us also introduce the conserved order parameter in the form of the local concentration difference $x = c - \bar{c}$ described by the continuity equation

$$\frac{\partial x}{\partial t} = -\nabla \cdot \mathbf{J}, \tag{1}$$

where $\mathbf{J}$ is the diffusion flux which, generally, depends on the time t [16]. When there is a large driving force for phase separation (which usually occurs at initial stages of transformation, for short periods of time, high local concentration gradients, or deep supercooling into a spinodal region of phase diagram), the system undergoes fast spinodal decomposition [17–19]. It proceeds with the time evolution of atomic diffusion flux, which, in the presence of stochastic effects, is described by

$$\tau_D \frac{\partial \mathbf{J}}{\partial t} = -\mathbf{J} - M\nabla \frac{\delta \mathcal{F}[x]}{\delta x} + \sqrt{M}\zeta(\mathbf{r}, t). \tag{2}$$

Here, τ_D is the relaxation time for the atomic flux $\mathbf{J}$ to reach its steady state, M is the atomic mobility, and $\mathcal{F}$ is the free energy functional of the binary system. The quantity ζ is a Gaussian source to represent flux fluctuations which obeys the fluctuation dissipation relation. It is consistently introduced into the equation for flux for both cases [23]: the noise ζ corresponds to values relaxing in time scales shorter than or longer than τ_D. The statistical properties of ζ are given by

$$\langle \zeta(\mathbf{r}, t) \rangle = 0, \qquad \langle \zeta(\mathbf{r}, t)\zeta(\mathbf{r}', t') \rangle = 2\sigma^2 C(\mathbf{r} - \mathbf{r}'; t - t'), \tag{3}$$