

New Coarse-Grained Derivation of a Phase Field Model for Precipitation

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We present the first derivation of the phase field equations using a coarse-graining procedure on a microscopic master equation. The procedure leads to a mesoscopic nonlinear Fokker-Planck equation equivalent to a Cahn-Hilliard equation supplemented with a noise, but with specific prescriptions for the mobilities and the noise term. All the ingredients (chemical potentials, mobilities, stiffness coefficient) depend on the coarse-graining size. Finally, we show the ability of the phase field equations to describe a precipitation kinetics involving a nucleation and growth mechanism.

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An important issue in physics is to predict and control macroscopic properties of materials. This quest inevitably requires a multiscale approach in order to bridge the gap between physics at the atomic scale and the mesoscopic scale at which systems self-organize. In materials science, where most of the engineering materials consist in a mixture of several phases, a very active and promising route toward this goal is the use of coarse-grained models in the spirit of Landau out-of-equilibrium thermodynamics. Seminal works along this line have been pioneered in solid-solid phase transformations by Cahn [1] and in solidification by Langer [2]. The development of these so-called phase field methods is presently the subject of numerous studies and their applicability has been extended to many different domains such as plasticity [3], fracture [4], etc. However, until now, no rigorous quantitative method has been proposed to derive comprehensive dynamic equations at the mesoscale. This is precisely the aim of this Letter, where we propose, starting from a microscopic kinetic model, the first rigorous derivation of a phase field model for precipitation.

One of the basic ingredients of a phase field model of microstructural evolution in alloys is the introduction of continuous fields (concentration, long-range order parameters) that describe the local state of the alloy. These fields have a meaning only at a mesoscopic scale, because their definition requires some spatial averaging procedure. As a consequence we can treat much larger systems than with microscopic methods such as Monte Carlo or molecular dynamics simulations. Another important consequence is that the basic ingredient is a *mesoscopic* free energy density which incorporates the short wavelength fluctuations. In the spirit of the Ginzburg-Landau approach, the usual way is to use a phenomenological free energy density whose form is dictated by general symmetry arguments. It is easy to write this phenomenological free energy density, for any phase transition, in the form of a polynomial expansion as a function of the concentration and long-range order parameter fields. It is also generally easy to fix the coefficients of this expansion to reproduce a given experimental phase diagram.

However, this approach does not give any reliable physical meaning, for example, to the metastable branches of the free energy density. This has important consequences, in particular, when the microstructural evolution begins by a nucleation and growth process, because the free energy barriers that the system should overcome through thermal fluctuations depends on these metastable free energies. The aim of this work is precisely to analyze the status of the mesoscopic free energy densities that are used in phase field theories and, simultaneously, to clarify the form that the phase field equations should adopt.

The starting point is a microscopic master equation,

$$\frac{\partial P(\mathcal{C})}{\partial t} = \sum_{i,j}^* W(\mathcal{C}^{ij}, \mathcal{C})P(\mathcal{C}^{ij}) - \sum_{i,j}^* W(\mathcal{C}, \mathcal{C}^{ij})P(\mathcal{C}), \quad (1)$$

where $\mathcal{C} = (\dots p_i \dots p_j \dots)$ is an alloy configuration (p_i is the occupancy of B atoms and $1 - p_i$ that of A atoms) and $P(\mathcal{C})$ is the probability of configuration \mathcal{C} . $W(\mathcal{C}, \mathcal{C}^{ij})$ is the transition rate between configurations \mathcal{C} and \mathcal{C}^{ij} , where \mathcal{C}^{ij} is identical to \mathcal{C} , except that sites i and j have been exchanged. The stars in the sums mean that we restrict the kinetics to first neighbor exchanges. The two parts of the right-hand side of Eq. (1) are usually referred to as the gain and loss terms. We consider a kinetic model based on a saddle point mechanism,

$$W(\mathcal{C}, \mathcal{C}^{ij}) = \theta' \delta(p_i) \delta(p_j - 1) \exp \beta (h_i^A(\mathcal{C}) + h_j^B(\mathcal{C})),$$

where $h_i^A(\mathcal{C})$ is the interaction energy between site i and the rest of the system if i is occupied by an A atom (and a similar definition for $h_j^B(\mathcal{C})$) and where $\theta' = \theta \exp(-2\beta E_s)$. θ is a characteristic attempt frequency, $\beta = 1/kT$, and E_s is the energy of a particle when it sits on the saddle point. Without lack of generality, we consider here a simple cubic lattice and we note a the first neighbor distance.

We now divide the system into cells of linear size d and define mesoscopic configurations $\tilde{\mathcal{C}} = (\dots c_n \dots)$ where c_n is the concentration of B atoms in cell n ,

$$c_n = \frac{1}{N_d} \sum_{i \in n} p_i,$$

where $N_d = (d/a)^3$ is the number of sites in each cell. By definition, the probability of the mesoscopic configuration \tilde{C} is given by

$$P(\tilde{C}) = \text{Tr}_{C/\tilde{C}} P(C),$$

where the sum runs over all the microscopic configurations C compatible with the mesoscopic configuration \tilde{C} .

We suppose that the evolution of \tilde{C} is still a Markov process. More precisely, we suppose that the cells are large enough so that the boundary exchanges do not significantly alter the cell concentration on the time scale within which the cell thermalizes. Under this assumption, the probability of the microscopic and mesoscopic configurations are linked by the following equation:

$$P(C) \simeq P(\tilde{C}) \frac{\exp[-\beta H(C)]}{\text{Tr}_{C_1/\tilde{C}} \exp[-\beta H(C_1)]}.$$

Consequently, the evolution of $P(\tilde{C})$ is given by

$$\frac{\partial P(\tilde{C})}{\partial t} = - \sum_{n,m}^* \sum_{i \in n, j \in m}^* \tilde{W}_{ij}(\tilde{C}) P(\tilde{C}) + (\text{gain term}), \quad (2)$$

where the stars in the sums mean that the first one runs over first neighbor cells and the second one over first neighbor sites,

$$\tilde{W}_{ij}(\tilde{C}) = \theta' \langle \delta(p_i(C)) \delta(p_j(C) - 1) e^{\beta h_i^A(C)} e^{\beta h_j^B(C)} \rangle_{C/\tilde{C}},$$

and the quantity $\langle X \rangle_{C/\tilde{C}}$ is defined by

$$\langle X(C) \rangle_{C/\tilde{C}} = \frac{\text{Tr}_{C/\tilde{C}} X(C) \exp[-\beta H(C)]}{\text{Tr}_{C/\tilde{C}} \exp[-\beta H(C)]}.$$

$\tilde{W}_{ij}(\tilde{C})$ is the average transition rate that governs the exchange between an A atom on site i and a B atom on site j , where sites i and j are first neighbors and belong to adjacent cells. This coarse-grained transition rate is of course a complex function of the mesoscopic configuration $\tilde{C} = \{\dots c_n \dots c_m \dots\}$. We suppose that it may be factorized as follows:

$$\tilde{W}_{ij}(\tilde{C}) \sim \theta' \exp(\beta g_i^A(\tilde{C})) \exp(\beta g_j^B(\tilde{C})), \quad (3)$$

where the functions $g_i^A(\tilde{C})$ and $g_j^B(\tilde{C})$ are defined by

$$\begin{aligned} g_i^A(\tilde{C}) &= kT \ln \langle \delta(p_i(C)) \exp[\beta h_i^A(C)] \rangle_{C/\tilde{C}}, \\ g_j^B(\tilde{C}) &= kT \ln \langle \delta(p_j(C) - 1) \exp[\beta h_j^B(C)] \rangle_{C/\tilde{C}}. \end{aligned} \quad (4)$$

In fact, in the framework of statistical mechanics, these two equations are nothing other than the expressions of the chemical potentials (per atom) of atomic species A and B on sites i and j , respectively. Equation (2) then becomes

$$\frac{\partial P(\tilde{C})}{\partial t} = -\theta' \sum_{n,m}^* \sum_{i \in n, j \in m}^* e^{\beta g_i^A(\tilde{C})} e^{\beta g_j^B(\tilde{C})} P(\tilde{C}) + (\text{gain term}). \quad (5)$$

This equation is not suitable for any expansion because the exponents, i.e., the chemical potentials $g_i^A(\tilde{C})$ and $g_j^B(\tilde{C})$, are not small. Therefore, we modify this equation and single out the spatial derivatives of the chemical potentials. But first we introduce the alloy chemical potential on site i , defined by $\mu_i(\tilde{C}) = g_i^B(\tilde{C}) - g_i^A(\tilde{C})$. The introduction of $\mu_i(\tilde{C})$ in Eq. (5) leads to

$$\begin{aligned} \frac{\partial P(\tilde{C})}{\partial t} &= -\theta' \sum_{n,m}^* \sum_{i \in n, j \in m}^* e^{\beta/2(g_i^A(\tilde{C}) + g_i^B(\tilde{C}) + g_j^A(\tilde{C}) + g_j^B(\tilde{C}))} \\ &\times e^{\beta/2(\mu_j(\tilde{C}) - \mu_i(\tilde{C}))} P(\tilde{C}) + (\text{gain term}). \end{aligned} \quad (6)$$

This equation still involves physical quantities (chemical potentials) defined at the atomic scale. We then define average chemical potentials within cells as follows:

$$g_n^X(\tilde{C}) = \frac{1}{N_d} \sum_{i \in n} g_i^X(\tilde{C}), \quad \mu_n(\tilde{C}) = g_n^B(\tilde{C}) - g_n^A(\tilde{C}), \quad (7)$$

where $X = A$ or B . If the spatial variations of the chemical potentials are slow enough, we may write

$$\begin{aligned} g_i^X(\tilde{C}) + g_j^X(\tilde{C}) &\simeq g_n^X(\tilde{C}) + g_m^X(\tilde{C}), \\ \mu_i(\tilde{C}) - \mu_j(\tilde{C}) &\simeq \frac{a}{d} (\mu_n(\tilde{C}) - \mu_m(\tilde{C})), \end{aligned}$$

where i and j are first nearest neighbor sites belonging to the adjacent cells n and m , respectively. With these approximations, Eq. (6) does not depend anymore on atomic quantities:

$$\begin{aligned} \frac{\partial P(\tilde{C})}{\partial t} &= -N_d \frac{a}{d} \left[\sum_{n,m}^* l_{mn}(\tilde{C}) e^{(\beta/2)(a/d)(\mu_m(\tilde{C}) - \mu_n(\tilde{C}))} P(\tilde{C}) \right. \\ &\quad \left. - \sum_{n,m}^* l_{mn}(\tilde{C}_{nm}) e^{(\beta/2)(a/d)(\mu_n(\tilde{C}_{nm}) - \mu_m(\tilde{C}_{nm}))} P(\tilde{C}_{nm}) \right], \end{aligned} \quad (8)$$

where the notation \tilde{C}_{nm} refers to a mesoscopic configuration identical to \tilde{C} , except that the concentrations in cells n and m are equal to $c_n - 1/N_d$ and $c_m + 1/N_d$, respectively. The functions $l_{mn}(\tilde{C})$ are defined by

$$l_{mn}(\tilde{C}) = \theta' e^{(\beta/2)(g_n^A(\tilde{C}) + g_n^B(\tilde{C}) + g_m^A(\tilde{C}) + g_m^B(\tilde{C}))}. \quad (9)$$

In Eq. (8), we can identify a term which depends only on the spatial variation of the alloy chemical potential and, therefore, which plays the role of the driving force for the kinetic process. The remaining terms define collectively the mobilities. Note that, contrary to the analysis proposed in [5,6], all the ingredients of the mesoscopic master equation (8) are explicitly connected to the microscopic description of the system.

A standard procedure consists in simplifying the master equation (8) using a well-known Fokker-Planck approximation [7] with respect to a small parameter, here identified as $1/N_d$. However, the latter is still a deterministic equation that represents the evolution of the probability distribution $P(\tilde{C})$, i.e., of an ensemble of systems. In a phase field method, we are rather interested in the evolution of a particular system. Hence we must derive the dynamical equations that govern the kinetics of the mesoscopic field $\tilde{C} = (\dots c_n \dots c_m \dots)$, and that are statistically equivalent to the Fokker-Planck equation. This can be done using the well-known equivalence between a Fokker-Planck equation and a Langevin formulation [7]. Using the Itô calculus for the noise terms, it gives

$$\frac{\partial c_n}{\partial t} = \frac{a^2}{d^2} \frac{1}{kT} \sum_m^{(n)} l_{nm}(\tilde{C})(\mu_m(\tilde{C}) - \mu_n(\tilde{C})) + \xi_n(t), \quad (10)$$

where the subscript (n) means that the sum runs over the first neighbor cells of cell n . $\xi_n(t)$ is a centered Gaussian noise whose second moments are given by

$$\begin{aligned} \langle \xi_n(t) \xi_n(t') \rangle &= \frac{2}{N_d} \frac{a^2}{d^2} \sum_p^{(n)} l_{np}(\tilde{C}) \delta(t - t'), \\ \langle \xi_n(t) \xi_m(t') \rangle &= \frac{-2}{N_d} \frac{a^2}{d^2} l_{nm}(\tilde{C}) \delta(t - t'), \end{aligned} \quad (11)$$

where n and m are adjacent cells. The Langevin equation (10) is nothing other than a Cahn-Hilliard-type equation supplemented with a noise term. Note however that this equation has several important characteristics. First, the mobilities $l_{nm}(\tilde{C})$ are concentration dependent. This property has already been proposed on a more phenomenological basis [8], and also using a single site mean field approach without fluctuations [9]. As a result, the amplitude of the correlations of the Langevin noise depends on the local concentrations. This type of equation is referred to as a nonlinear Langevin equation with a multiplicative noise. Second, the alloy chemical potential, whose discrete gradient is the kinetic driving force, depends on the size d of the cells. More precisely, the chemical potentials $g_n^A(\tilde{C})$ and $g_n^B(\tilde{C})$, and thus the alloy chemical potential $\mu_n(\tilde{C})$, should be computed using the coarse-graining procedure outlined in Eqs. (4) and (7).

In all generality, g_n^A , g_n^B , and μ_n are functions of all the concentrations $\{c_n\}$. These general dependences may be formally written as a sum of a homogeneous term that depends only on the local concentration and an inhomogeneous term that depends explicitly on the spatial variations. More specifically, we may write, to the leading order in spatial variations,

$$g_n^X(\tilde{C}) = g_{\text{homo}}^X(c_n) + H(c_n) \|\hat{\nabla} c_n\|^2 + K(c_n) \hat{\nabla}^2 c_n + \dots,$$

where $X = A$ or B , H and K are functions of the local concentration, and where $\hat{\nabla}$ and $\hat{\nabla}^2$ are the discrete version

of the gradient and Laplacian operators. An important point is that, provided the cell size is large enough, the role of these inhomogeneous contributions can be neglected in the mobility term (9). Indeed, the amplitudes of these terms decrease as the cell size increases, whereas the homogeneous contributions converge to a finite value. The situation is totally different for the alloy chemical potential $\mu_n(\tilde{C})$ because it enters Eq. (10) through a discrete gradient: The homogeneous and inhomogeneous parts act now through their spatial variations, which are of the same order of magnitude for any cell size. In brief, if the cells are large enough, the inhomogeneous components of g_n^A and g_n^B can be neglected in the mobilities, but not in the alloy chemical potential μ_n .

For a numerical implementation of Eqs. (10) and (11), we need to express the chemical potentials as explicit functions of the mesoscopic variables c_n . We first compute the homogeneous components $g_{\text{homo}}^A(c_n)$ and $g_{\text{homo}}^B(c_n)$ for a discrete set of concentrations using a Widom method [10] implemented in a Monte Carlo simulation of the canonical ensemble in a single cell, and interpolate the discrete data points with an analytical form. These expressions are then used in the mobility terms and provide also the homogeneous part $\mu_{\text{homo}}^d(c)$ of $\mu_n(\tilde{C})$. As for the inhomogeneous components, we use the fact that we expect $\mu_n(\tilde{C})$ to be equal to the functional derivative $(1/N_d)[dF_{\text{tot}}(\tilde{C})/dc_n]$ of a mesoscopic free energy which, to the lowest order in spatial variations, reads

$$F_{\text{tot}}(\tilde{C}) = N_d \sum_n \left[f_{\text{homo}}^d(c_n) + \frac{1}{2} \lambda^d(c_n) \|\hat{\nabla} c_n\|^2 \right], \quad (12)$$

where, in all generality, the stiffness coefficient $\lambda^d(c_n)$ should be made c dependent and where the subscript d has been added to stress the fact that all the mesoscopic quantities depend on the cell size. $\lambda^d(c)$ controls the correlations between neighboring cells, i.e., the fluctuations of wavelength larger than the cell size d . We computed $\lambda^d(c)$ using Monte Carlo simulations on a large system by a statistical analysis of the equilibrium fluctuations. More precisely, the simulation box is subdivided into cells of size d and we analyze the spatial fluctuations of the cell concentrations. If the fluctuations are small, the Fourier modes of the fluctuations can be analytically linked to $\lambda^d(c)$ and to the alloy chemical potential $\mu_{\text{homo}}^d(c)$.

As example, we present the result of the coarse-graining procedure for a simple cubic lattice of size a with repulsive first neighbor interactions $J_1 < 0$. The chemical potential $\mu_{\text{homo}}^d(c)$ obtained for the coarse-graining size $d = 8a$ is presented in Fig. 1. As can be seen, the equilibrium concentration c_{eq} differs from the minimum of the free energy density c_{min} , as it should, because this difference is related to the asymmetric fluctuations of the concentration field driven by the Langevin noise. Of course, as in [11,12], we also find (not shown here) that the shape of $\mu_{\text{homo}}^d(c)$ varies significantly with d . Then, we computed the value of $\lambda^d(c)$

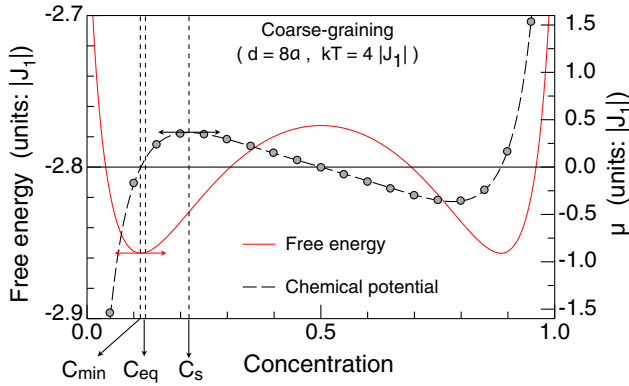


FIG. 1 (color online). Coarse-grained chemical potential $\mu_{\text{homo}}^d(c)$ measured using Monte Carlo simulations (circles) and corresponding free energy $f_{\text{homo}}^d(c)$. Specific concentrations are indicated: the minimum of the homogeneous free energy $c_{\min} = 0.11$, the solubility limit $c_{\text{eq}} = 0.125$, and the spinodal $c_s = 0.218$.

and we found that it varies significantly with the cell concentration c . This c dependence is incorporated in the phase field formalism through an analytical form. As we consider here a situation which is symmetric with respect to $c = 0.5$, $\lambda^d(c)$ is, to the lowest order, of the form $A + Bc(1 - c)$. The fit of our data gives $A = 0.77|J_1|$ and $B = -2.47|J_1|$. So, at $kT/|J_1| = 4$, the stiffness coefficient is about 3 times smaller in interfaces than in bulk domains.

We now present an analysis of the precipitation process using Eqs. (10) and (11). Our aim here is to test the ability of the phase field method to reproduce quantitatively a precipitation process when the kinetics is driven by thermal fluctuations. Thus, the overall concentration of the system has been chosen inside the “nucleation and growth” window, i.e., between the solubility limit $c_{\text{eq}} = 0.125$ and the spinodal concentration $c_s = 0.218$ (see Fig. 1). Therefore, the first stage of the precipitation is driven by concentration fluctuations that should overcome the free energy barrier of the critical nucleus. The results obtained for the overall compositions $c = 0.16$, $c = 0.165$, $c = 0.17$ are presented in Fig. 2. As expected, the incubation time increases when the supersaturation decreases. We mention that the numerical phase field analysis presented in Fig. 2 is more than 3 orders of magnitude less computationally demanding than the Monte Carlo implementation of the microscopic master equation (1). Therefore, the present phase field approach makes it possible to study the nucleation process for very small supersaturations, whereas it is out of reach of a microscopic modeling. Finally, as a stringent test of the theory, we analyze the influence of the coarse-graining size d on the nucleation process. The precipitate volume fraction $\tau(t)$ obtained for $c = 0.17$ with $d = 6, 8$, and $10a$ is presented in Fig. 2. We note that the three simulations lead approximately to the same evolutions. Thus, even

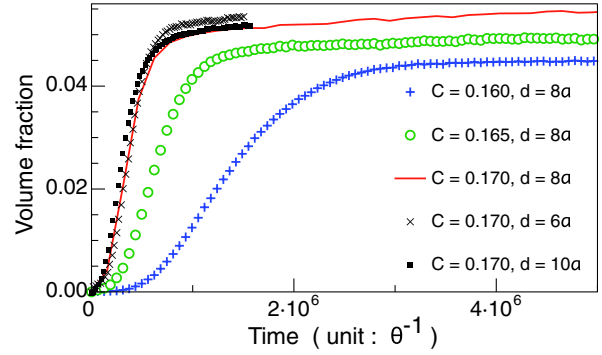


FIG. 2 (color online). Volume fraction of the precipitates as a function of time for $kT/|J_1| = 4$ on a lattice of dimensions $64d \times 64d \times 64d$. The phase field simulations have been done for three different compositions $c = 0.16$, $c = 0.165$, and $c = 0.17$ with a coarse-graining size $d = 8a$. For the composition $c = 0.17$, the results obtained with $d = 6, 8$, and $10a$ are compared.

though the metastable free energy branches, the mobilities and the amplitude of the noise all depend strongly on the mesoscopic coarse-graining size d , the overall procedure leads to a macroscopic behavior independent of d . It means that the method proposed above to derive the phase field equations relies on sound foundations.

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