

Coarse graining for the phase-field model of fast phase transitions

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(Received 15 August 2013; published 31 October 2013)

Fast phase transitions under lack of local thermalization between successive elementary steps of the physical process are treated analytically. Non-Markovian master equations are derived for fast processes, which do not have enough time to reach energy or momentum thermalization during rapid phase change or freezing of a highly nonequilibrium system. These master equations provide a further physical basis for evolution and transport equations of the phase-field model used previously in the analyses of fast phase transitions.

DOI: [10.1103/PhysRevE.88.042151](https://doi.org/10.1103/PhysRevE.88.042151)

PACS number(s): 05.70.Fh, 05.70.Ln, 64.60.My

I. INTRODUCTION

The phase-field model presents a useful and elegant tool for analysis of various free-boundary problems. A main idea of the model is to describe the dynamics of a system by conserved or nonconserved field variables, which change steeply but continuously differentiable in an interfacial region of finite width (diffuse interface) between transforming and final phases. The evolution of this field is obtained from the formalism of irreversible thermodynamics that makes the model flexible for the analysis and numerical modeling of various problems in materials physics, from solidification phenomena up to pattern formation in colloidal solutions [1].

To have a robust base for equations of motion a coarse-graining procedure is used in free-boundary problems. This procedure consists of dividing a system into mesoscopic cells and writing kinetic equations for the evolution of the atomic configurations in a cell. Normally, a special assumption is applied about a local equilibrium or full energetic thermalization in every cell at the characteristic time scale of the microstructure evolution. As an example, this procedure leads to a mesoscopic master equation where the driving force is derived from a coarse-grained free-energy functional of the Ginzburg-Landau type [2–5].

Several useful advances of the coarse-graining procedure were made for the phase-field equations, which describe the dynamics of local equilibrium systems. For instance, application of coarse-graining in time to the microscopic density field of molecular-dynamics simulations leads to the phase-field crystal model [6]. Moreover, a complete coarse-grained derivation of a phase-field model for precipitation and phase separation was presented by Bronchart *et al.* [7]. Their derivation leads to a mesoscopic nonlinear Fokker-Planck equation finally equivalent to a Cahn-Hilliard equation with noise and with definite expressions for the mobilities and the moments of the noise. Using the coarse-graining procedure in the phase-field theory allows for the obtention of a mesoscopic free energy to model properties of materials [8] or even nonequilibrium effects, such as solute trapping by a rapidly moving interface [9].

For a high driving force of phase transformation, fast phase transitions can be initiated, in which the phase boundaries move with velocities comparable with the atomic diffusion speed or with the speed of local structural relaxation [10]. Examples of such motion or transitions are known in transport of non-Newtonian fluids, viscoelastic bodies, rapidly solidifying alloys and systems, materials deeply quenched into the spinodal region, and, more generally, systems with memory [11,12]. Considering microscopic accessible states of particles (atoms or molecules), one should accept the absence of local equilibrium in fast phase transitions because the particles do not have enough time to sample all the phase space. The number of microstates accessible to each of them will be lower than in equilibrium; therefore, a local equilibrium hypothesis fails. Phenomenologically, fast phase transitions are described using memory kernels, which, in a simplest case of their exponential relaxation, provide a system of hyperbolic partial differential equations for dynamics of interface motion and transport of matter [13,14].

In this paper we generalize the analysis of Bronchart *et al.* [7] to fast phase transitions described by the phase-field model. One of the remarkable features of fast transitions is that the system lacks sufficient time for local thermalization between consecutive elementary steps of the process. We shall consider two different situations, namely, a lack of thermalization in the local energy distribution and in the local momentum distribution. Both these situations lead to non-Markovian processes, which in some conditions may be described at the mesoscopic level by means of a hyperbolic differential equation for a conserved parameter, the particle concentration. These derivations provide an explicit physical basis to the previous analysis of fast phase transitions using such hyperbolic equations that give satisfactory information for the short-time dynamics of processes such as the initial stages of spinodal decomposition, rapid solidification, etc., as well as for long-time dynamics [14].

The paper is organized as follows. Section II describes the system being considered. In Sec. III, a non-Markovian master equation is derived for fast phase transitions, which do not have enough time to thermalize the energy distribution. Atomic transport in phase transitions for systems with inertia, lacking time for momentum thermalization, is described in Sec. IV. The corresponding non-Markovian master equation

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is derived for analysis of very short periods of transitions (at the absence of momentum thermalization) as well as transitions under local thermodynamic equilibrium (upon momentum thermalization). Finally, Sec. V presents a discussion of the obtained results together with outcomes of the present work.

II. MARKOVIAN MASTER EQUATION AND DESCRIPTION OF THE SYSTEM

The system being considered is an alloy composed of A and B atoms in a line or a regular lattice. An instantaneous configuration of the alloy at a microscopic level is given by $C \equiv (p_1 \dots p_i \dots p_j \dots p_N)$, p_i being the probability of occupancy of an atom B to the site i , and $1 - p_i$ the probability of occupancy of an atom A to the site i . A configuration of the alloy evolves by the following master equation [5,7]:

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

Here, $P(C, t)$ is the probability distribution of finding configuration C at time t , $W(C, C^{ij})$ is the transition rate from configurations C to C^{ij} , where C^{ij} is a configuration identical to C , except that atoms at sites i and j have been mutually exchanged. The stars in the sums mean that Eq. (1) is restricted to first-neighbor exchanges.

The authors of Ref. [7] assumed that the time scale between successive atom exchanges, let us say the time t_0 , is long enough for thermalization of the system after the exchange. Namely, assume that in the jump at time t , a particle A previously at site j arrives to site i and a particle B previously at site i arrives at site j . Before the next jump, the system has time enough to thermalize in such a way that the energy probability distribution f_{eq} at sites i and j is the canonical one, namely,

$$f_{\text{eq}} \propto f_{\text{eq},i}^A f_{\text{eq},j}^B \propto \exp \{ \beta [h_i^A(C) + h_j^B(C)] \}, \quad (2)$$

where $\beta = (k_B T)^{-1}$ is the Boltzmann factor with the temperature T and the Boltzmann constant k_B , $h_i^A(C)$ is the interaction energy between site i and the rest of the system in configuration C when site i is occupied by an atom A . An analogous definition is true for $h_j^B(C)$. The hypothesis about full thermalization has been used in Ref. [7] to set the expression for the transition rates as

$$W(C, C^{ij}) \propto \theta' \delta(p_i) \delta(p_j - 1) f_{\text{eq}} = \theta' \delta(p_i) \delta(p_j - 1) \exp \{ \beta [h_i^A(C) + h_j^B(C)] \}, \quad (3)$$

with $\theta' = \theta \exp[-2\beta E_s]$, θ being a characteristic attempt frequency, and E_s the energy of the barrier that particles must surpass for the jump exchange of atoms between sites i and j to take place, and $\delta(p_i)$ are the Kronecker deltas related to the presence of A in i and B in j . Equation (3) has been used to describe precipitation in a binary mixture, where the process from a well-mixed initial state to a two-phase final state with components A and B forming two different regions takes place [7].

III. MASTER EQUATION IN THE LACK OF ENERGY THERMALIZATION

Our aim is to generalize the idea about coarse-grained derivation presented in Ref. [7] to fast phase transitions [14]. The main feature characterizing a fast transition in the present content is that the time t_0 elapsed between successive elementary steps of the physical process is not long enough to allow for a true thermalization of the system. Therefore, first, we consider the lack of energy thermalization for the elementary steps characterizing particle exchanges between sites i and j .

To describe the degree of thermalization we need an evolution equation for the local probability distribution (f) of energy. Here, for the sake of simplicity, we will consider the simplest relaxation time approximation:

$$\frac{\partial f}{\partial t} = -\frac{1}{\tau} (f - f_{\text{eq}}), \quad (4)$$

with τ the relaxation time characterizing the local thermalization of the energy, and f_{eq} the corresponding equilibrium distribution function. In Eq. (4) we refer to f_{eq} in general terms, namely, not directly referring to our system but rather to the generic expression of the usual relaxation-time approximation for the distribution function. In our system, for instance, Eq. (4) would apply to f_i , the energy distribution function at each i th site.

Thus, one has two microscopic characteristic times: the time t_0 between successive particle jumps and the local thermalization time τ . A slow transition occurs for $t_0 \gg \tau$ and fast transitions correspond to $t_0 \approx \tau$ or $t_0 < \tau$. For the diffusion process, this situation is considered in details in Ref. [15].

A. Evolution of the alloy's configuration

In the situation analyzed by Bronchart *et al.* [7], the energy distribution (f) of the system after a time t_0 following a jump of a particle A from j to i and of a particle B from i to j will be, according to Eq. (4),

$$f \propto f_i^A f_j^B \propto \{ \exp[\beta h_i^A(C)] [1 - \exp(-t_0/\tau_{A_i})] + \exp[\beta h_j^A(C)] \exp(-t_0/\tau_{A_j}) \} \times \{ \exp[\beta h_j^B(C)] [1 - \exp(-t_0/\tau_{B_j})] + \exp[\beta h_i^B(C)] \exp(-t_0/\tau_{B_i}) \}, \quad (5)$$

where $\tau_{A_{i,j}}$ and $\tau_{B_{i,j}}$ are the respective thermalization times of the system after the particle A (or B) arrives at site i (or j), respectively. The times τ_A and τ_B play the role of τ from Eq. (4), but refer to the distribution functions of particles A and B , respectively. For notational simplicity, we assume that this relaxation time is independent of the site i or j , but in general it could also depend on the site. Obviously, when $t_0 \gg \tau_A$ and $t_0 \gg \tau_B$, Eq. (5) simply reduces to Eq. (2).

The distribution function Eq. (5) leads to a new type of the master equation which, in fact, will be non-Markovian. This could be seen from the following argumentation.

Equation (5) takes explicitly into account that the energy distribution function of particle A (respectively, particle of B -sort) for times t not much longer than t_0 is not yet the Boltzmann equilibrium distribution function for A at its final

site i . The distribution function Eq. (5) tends to the equilibrium distribution exponentially [see the first term in the right-hand side of the first line of Eq. (5)], while it is “forgetting” exponentially the initial distribution function it had at site j [see the second term in the right-hand side of Eq. (5)]. Analogously, this is true for particle B [see the third and fourth lines of Eq. (5)]. In the following step, at $t = 2t_0$, the distribution function for A at the initial site of the second step will no longer be the Boltzmann distribution function at that site, but the expression given by the first and second lines of the right-hand side of Eq. (5), and so on (and analogously for B , of course). Thus, the actual distribution function f at any time t will be a complicated expression of the history of the system between the initial time (say, 0 or t') and the actual considered time t . In steady-state systems, the history will depend only on $t - t'$, but not on the particular initial time t' .

Nonequilibrium distribution Eq. (5) assumes that the initial state before the first jump exchange was a state of full equilibrium. This will not be the case after successive jumps. As this takes place, the transition rates Eq. (3) should use, instead of f_{eq} given by Eq. (2), the actual distribution function f as given by Eq. (5). Since f in Eq. (5) depends not only on t but it is in general a complicated function of $t - t'$ (t' being the initial time of the whole process), Eq. (1) with instantaneous transition rates depending only on the considered instant t , will become a generalized master equation with memory kernels dependent on $t - t'$. Hence, Eq. (1) takes the following generic form:

$$\begin{aligned} \frac{\partial P(\mathcal{C}, t)}{\partial t} &= \sum_{i,j}^* \int_0^t W(\mathcal{C}^{ij}, \mathcal{C}, t - t') P(\mathcal{C}^{ij}, t') dt' \\ &\quad - \sum_{i,j}^* \int_0^t W(\mathcal{C}, \mathcal{C}^{ij}, t - t') P(\mathcal{C}, t') dt'. \end{aligned} \quad (6)$$

In Eq. (6) we have taken the integration limits from 0 to t , because we assume that the process begins at $t = 0$. An alternative extreme possibility that is also often adopted would have been to assume that the process began at $t = -\infty$. Since, in fact, the relaxation times are relatively short compared to macroscopic observation times, these different expressions are essentially equivalent.

The generalized master Eq. (6) is analogous to well-known equations with memory as, for instance, the Mori functional equation (see Ref. [16] and Chapter 7 in Ref. [12]). The memory kernels $W(\mathcal{C}^{ij}, \mathcal{C}, t - t')$ and $W(\mathcal{C}, \mathcal{C}^{ij}, t - t')$ govern the current evolution of the alloy's configuration through its past relaxation of local states. For instance, in the case when the

time t_0 between successive steps is smaller than the relaxation times τ_A and τ_B , Eq. (5) for $t - t' = n_0 t_0$ (n_0 being the number of time steps of the system) would have the form

$$\begin{aligned} f(t - t') &\propto \exp[\beta h_j^A(\mathcal{C})] \exp(-n_0 t_0 / \tau_A) \\ &\quad \times \exp[\beta h_i^B(\mathcal{C})] \exp(-n_0 t_0 / \tau_B). \end{aligned}$$

In doing so, the corresponding transition kernels $W(\mathcal{C}, \mathcal{C}^{ij}, t - t')$ and $W(\mathcal{C}^{ij}, \mathcal{C}, t - t')$ would also have an exponential form in $t - t'$:

$$W(\mathcal{C}^{ij}, \mathcal{C}, t - t') = \tau^{-1} W_0(\mathcal{C}^{ij}, \mathcal{C}) \exp[-(t - t') / \tau].$$

In this exponential case, the master Eq. (6) becomes

$$\begin{aligned} \tau \frac{\partial^2 P(\mathcal{C}, t)}{\partial t^2} + \frac{\partial P(\mathcal{C}, t)}{\partial t} \\ = \sum_{i,j}^* W_0(\mathcal{C}^{ij}, \mathcal{C}) P(\mathcal{C}^{ij}, t) - \sum_{i,j}^* W_0(\mathcal{C}, \mathcal{C}^{ij}) P(\mathcal{C}, t). \end{aligned} \quad (7)$$

Equation (7) describes the evolution of probability for the whole configuration of the alloy. This equation represents the simplest non-Markovian generalization of Eq. (1). One should especially note that the alloy's configuration may strongly depend on the memory kernels $W(\mathcal{C}^{ij}, \mathcal{C}, t - t')$ and $W(\mathcal{C}, \mathcal{C}^{ij}, t - t')$ in Eq. (6). This is shown in consideration of the concentration evolution described in the next section (see Table I). As such, to describe realistic systems undergoing fast transition, the choice of the memory kernels for the concrete dynamics of conserved and nonconserved phase-field variables should be microscopically motivated.

B. Coarse-grained concentration

Using the arguments and coarse-graining procedure of Bronchart *et al.* [7], we now derive one of variants of the phase-field models for the system described by Eq. (6). In particular, we derive the phase-field for the phase separation with the diffusive interface, i.e., the Model B by classification of Hohenberg and Halperin [17].

Let us divide the system into cells of linear size d and assume that $N_d = (d/a)^3$ is the number of sites in each cell, where a is the characteristic distance between sites. Further, we define mesoscopic configuration $\vec{\mathcal{C}} = (c_1 \dots c_n \dots)$ with $c_n = N_d^{-1} \sum_{i \in n} p_i$ the average concentration of B atoms in cell n . The diffusion transport equation for $\vec{\mathcal{C}}$, which has been analyzed in the literature [5,7], may be generalized by taking into account the evolution prehistory and memory effects as

TABLE I. Memory kernels for different types of relaxation to local states with thermalization.

Type of the local relaxation dynamics	Memory kernel $\ell_{nm}(\vec{\mathcal{C}}, t - t')$
Dissipative propagation	$\ell_{nm}^{(1)}(\vec{\mathcal{C}}, t) \delta(t - t')$
Wave propagation	$\ell_{nm}(\vec{\mathcal{C}}, 0) \equiv \text{const}$
Exponential relaxation	$\tau^{-1} \ell_{nm}^{(0)}(\vec{\mathcal{C}}, t) \exp(-\frac{t-t'}{\tau})$
Dissipation with relaxation	$\ell_{nm}^{(1)}(\vec{\mathcal{C}}, t) \delta(t - t') + \tau^{-1} \ell_{nm}^{(0)}(\vec{\mathcal{C}}, t) \exp(-\frac{t-t'}{\tau})$
Exponential relaxation with oscillations	$\tau^{-1} \ell_{nm}^{(0)}(\vec{\mathcal{C}}, t) \exp(-\frac{t-t'}{\tau}) \cos[\Omega(t - t')]$

follows:

$$\frac{\partial c_n(t)}{\partial t} = \frac{\beta a^2}{d^2} \sum_m^{(n)} \int_0^t dt' \{ \ell_{nm}(\tilde{C}, t-t') \times [\mu_m(\tilde{C}, t') - \mu_n(\tilde{C}, t')] \} + \xi_n(t), \quad (8)$$

where n and m are adjacent cells. Here the average chemical potentials μ_n within cell n are given by

$$\mu_n(\tilde{C}) = g_n^B(\tilde{C}) - g_n^A(\tilde{C}), \quad (9)$$

with the functions

$$g_n^A(\tilde{C}) = (\beta N_d)^{-1} \sum_{i \in n} \ln \{ \delta [p_i(C)] \exp [\beta h_i^A(C)] \}_{C/\tilde{C}}, \quad (10)$$

$$g_n^B(\tilde{C}) = (\beta N_d)^{-1} \sum_{i \in n} \ln \{ \delta [p_i(C) - 1] \exp [\beta h_j^B(C)] \}_{C/\tilde{C}},$$

having the following transition kernels ℓ_{nm}

$$\ell_{nm}(\tilde{C}, t-t') = \theta' \exp(0.5\beta g_{n,m}),$$

$$g_{n,m} = g_n^A(\tilde{C}, t) + g_n^B(\tilde{C}, t) + g_m^A(\tilde{C}, t') + g_m^B(\tilde{C}, t'). \quad (11)$$

The noise $\xi_n(t)$ in Eq. (8) is characterized by

$$\langle \xi_n(t) \xi_n(t') \rangle = \frac{2}{N_d} \cdot \frac{a^2}{d^2} \sum_p^{(n)} \ell_{np}(\tilde{C}, t-t'), \quad (12)$$

$$\langle \xi_n(t) \xi_m(t') \rangle = -\frac{2}{N_d} \cdot \frac{a^2}{d^2} \ell_{nm}(\tilde{C}, t-t').$$

Without memory effects, the function $\ell_{nm}(\tilde{C}, t-t')$ from Eq. (12) is a δ -correlated function in time, i.e., $\ell_{nm}(\tilde{C}, t-t') = \ell_{nm}(\tilde{C}, t) \delta(t-t')$ [7]. In the presence of memory effects, the chemical potential Eqs. (9) and (10) should correspond to a nonequilibrated system in such a way that $g_n^A(\tilde{C})$ is related to the expression $\exp[\beta h_i^A(C)] [1 - \exp(-t_0/\tau_A)] + \exp[\beta h_j^B(C)] \exp(-t_0/\tau_A)$, which is commented on in Eq. (5). Further details of noise modifications arising from the fast character of transitions is given through the example of phase separation by the spinodal mechanism in Ref. [18].

The memory kernels $\ell_{nm}(\tilde{C}, t-t')$ in Eq. (8) characterize the type and intensity of relaxation to local thermalization. Table I shows various types of relaxation by the memory kernels. *First*, by choosing the memory kernel of the form of δ function (see the first line in Table I) pure diffusive dynamics takes place [as is given by Eq. (1)]. *Second*, if the memory kernel is given by the constant value (see the second kernel in Table I), undamped waves will propagate in the alloy's concentration. *Third*, for the exponential relaxation to local thermalization (see the third kernel in Table I, which is given by the so-called Maxwell's relaxation function), the concentration evolves through the diffusive and wave mechanisms. This evolution is given by the "telegrapher" equation, which predicts damped wave propagation by the hyperbolic differential equations. *Fourth*, when the memory is set by a more complicated kernel, namely, by the sum of δ -like and exponential functions (see the fourth line in Table I, which is given by the so-called Jeffreys relaxation function), the relaxation proceeds by damped waves together with gradient's temporal relaxation of the chemical potential

(see Ref. [19] for the concrete equation of fast transitions). Finally, *ffth*, by setting the memory kernel as the exponential relaxation with oscillations having the frequency Ω (see the fifth kernel in Table I), one can analyze the alloy's configuration by the equation with the third time derivative as well as including all the above mentioned processes (i.e., with damped waves and with the gradient's temporal relaxation of the chemical potential). It should be noted that the inclusion of memory effects (excluding, of course, the δ -like function from Table I) can essentially delay the concentration evolution and, therefore, the time for the system to thermalize might not suffice prior to the start of the fast phase transition.

In the particular case of the exponential memory kernel, $\ell_{nm}(\tilde{C}, t-t') = \tau^{-1} \ell_{nm}^{(0)}(\tilde{C}, t) \exp[-(t-t')/\tau]$ (see the third kernel in Table I), we may rewrite Eq. (8) as

$$\tau \frac{\partial^2 c_n(t)}{\partial t^2} + \frac{\partial c_n(t)}{\partial t} = \frac{\beta a^2}{d^2} \sum_m^{(n)} \ell_{nm}^{(0)}(\tilde{C}, t) [\mu_m(\tilde{C}, t) - \mu_n(\tilde{C}, t)] + \xi_n^*(t), \quad (13)$$

where the noise term $\xi_n^*(t)$ is characterized by

$$\langle \xi_n^*(t) \xi_n^*(t') \rangle = \frac{2}{N_d} \cdot \frac{a^2}{\tau d^2} \sum_p^{(n)} \ell_{np}^{(0)}(\tilde{C}, t) \exp\left(-\frac{t-t'}{\tau}\right), \quad (14)$$

$$\langle \xi_n^*(t) \xi_m^*(t') \rangle = -\frac{2}{N_d} \cdot \frac{a^2}{\tau d^2} \ell_{nm}^{(0)}(\tilde{C}, t) \exp\left(-\frac{t-t'}{\tau}\right).$$

Equation (13) describes the evolution of the coarse-grained concentration of the second component of the binary mixture. Introducing the memory effects and obtaining the hyperbolic Eq. (13) leads to the exponential temporal correlation of the noise as predicted by Eq. (14). Therefore, internal stochastic process influence the fast phase transitions in the form of colored noise but not in the form of δ -correlated or "white thermodynamic" noise (see also analysis in Ref. [18]).

An explicit form of the chemical potential from Eq. (13) can be written with the definition of the free energy. In fact, Bronchart *et al.* [7] find that the shape of the chemical potentials μ_n appearing in Eq. (13) depend significantly on the size of the coarse-graining cell d in such a way that there is not a well-defined univocal continuum limit to the coarse graining procedure. Here, following previous studies [5,7], we consider the free energy in the form of the discrete Ginzburg-Landau functional

$$F(T, p_i; d) = \sum_i f(T, p_i; d) + \frac{\epsilon(T, c_n; d)}{2} \sum_b (p_{i+b} - p_i)^2, \quad (15)$$

where the free-energy density f and stiffness ϵ are written explicitly in such a way that these mesoscopic quantities depend on the cell size d and summation over b means a sum over all nearest-neighbor sites. For example, the present coarse-graining procedure introduces the stiffness,

$$\epsilon = \frac{\epsilon_{AA}(T, c_n; d) + \epsilon_{BB}(T, c_n; d)}{2} - \epsilon_{AB}(T, c_n; d),$$

as the d -dependent energetic parameter of the free-energy Eq. (15) with ϵ_{AA} , ϵ_{BB} , and ϵ_{AB} being the interaction energies between pairs $A - A$, $B - B$, and $A - B$ (or $B - A$), respectively. In fact, we assume here that the interaction between A atoms (or B atoms) exists also for different cells, making some average on their separations, which change with the cell size d .

It was additionally observed by Bronchart *et al.* [7] that in spite of the fact that free energies, mobilities, and intensity of noise depend on the coarse-graining size d , three simulations carried out by them on the problem of precipitation in binary mixture (with values $d/a = 6, 8, 10$) yield approximately the same qualitative results for the volume fraction of precipitate as a function of time. Thus, the overall method proposed in Ref. [7] leads from the practical point of view to a consistent macroscopic formalism roughly independent on d .

The expression for the effective macroscopic (d -independent) free energy will depend on the system and the situation at hand. In particular, in our previous analyses [12,18,22], we have used an effective free-energy density of the form

$$f(T, p_i) = -\frac{z\epsilon_{AA}}{2}(1-p_i)^2 - z\epsilon_{AB}(1-p_i)p_i - \frac{z\epsilon_{BB}}{2}p_i^2 + \beta^{-1}[(1-p_i)\ln(1-p_i) + p_i\ln p_i], \quad (16)$$

where z is the coordination number of the lattice. Equation (16) is suitable in the limit $d \rightarrow a$, i.e., when d has the minimum possible value, which is not strictly zero but is equal to the distance a between atomic sites, and it is well defined, as a given value of d is specified. Thus, one can state that (a) the coarse-graining formalism leads to the d -dependence of the mesoscopic functions and parameters (free energy, stiffness, etc.); (b) the d -independent effective mesoscopic approach is qualitatively consistent with the coarse-graining description, and may be quantitatively satisfactory for a macroscopic description with the suitably chosen thermodynamic potentials, mobilities, and relaxation time.

The explicit expression for the chemical potential is obtained from the derivative of the free energy Eqs. (15) and (16) with respect to the local occupation probability as

$$\mu_i(\tilde{C}, t) \equiv \left. \frac{\partial F}{\partial p_i} \right|_T = \mu_i^{(\text{hom})} - \epsilon(T, c_n)\Delta_b p_i, \quad (17)$$

where

$$\mu_i^{(\text{hom})} = (1-p_i)\mu_A + p_i\mu_B + \beta^{-1} \ln \frac{p_i}{1-p_i} \quad (18)$$

is the contribution into the chemical potential from the particles (components A and B) and their mixing, $\Delta_b p_i = \sum_b (p_{i+b} - p_i)$ is the discrete Laplacian for the concrete lattice, and $\mu_A = z(\epsilon_{AA} - \epsilon_{AB})$ and $\mu_B = z(\epsilon_{AB} - \epsilon_{BB})$ are the chemical potentials of the atoms A and B , respectively.

The continuum limit would correspond to both d and a going to zero. In this case, the several differences between values of chemical potentials at different neighboring cells may be written in the form of gradients, as we will mention. The physical problem, however, may be found in the d -dependence of the free energy and the chemical potential, as mentioned above. Therefore, we consider the continuous limit $d \rightarrow 0$ and take the local (near-neighbor) approximation, $(\mu_m - \mu_n)/d$

tends to $(\mu_{n+1} - \mu_n)/d \rightarrow \nabla\mu$, into account, where μ is now a continuous function of spatial coordinates (instead of a function with values at discontinuous positions md , for m integer numbers). Analogously, $(\beta a^2/d)l_{nm}[(\mu_m - \mu_n)/d]$ tends to $(\beta a^2/d)l_{n+1}(\mu_{n+1} - \mu_n)/d \rightarrow \nabla \cdot [M_c(T, c)\nabla\mu]$, with $M_c(T, c)$ the mobility given by $\beta a^2 l_{n+1}$ with c the average local concentration. In fact, in the continuous limit one gets $a \rightarrow 0$ but the product $a^2 l_{n+1}$ should tend to a finite constant value. As a result, Eqs. (13)–(18) present the hyperbolic equation for the phase segregation by the spinodal mechanism:

$$\tau \frac{\partial^2 c}{\partial t^2} + \frac{\partial c}{\partial t} = \vec{\nabla} \cdot [M_c(T, c)\vec{\nabla}\mu] + \xi_n^*(t), \quad (19)$$

with the chemical potential

$$\mu \equiv \frac{\partial F}{\partial c} = \mu_{(\text{hom})}(T, c; d) - \epsilon(T, c; d)\nabla^2 c. \quad (20)$$

As for Eq. (15), we have written explicitly the d -dependencies of μ_{hom} and ϵ to remind that the mesoscopic quantities depend on the cell size d , although suitable phenomenological expressions independent on d are eventually useful from the practical view and consistent with the features of the results of microscopic simulations. Obviously, different forms of the free energy and of the chemical potential from Eqs. (13) and (19) may lead to different phase field models (see comments in Sec. V).

Hence, by application of the coarse graining procedure, Eq. (19) represents the hyperbolic equation for spinodal decomposition [13], which has been investigated mathematically with regard to existence and uniqueness of its solutions [20]. Physically reasonable solutions of this equation and their outcomes have been tested against experimental data [21]. In these tests, one of the important parameters of the first fast stages of spinodal decomposition is the relaxation time τ as introduced by Eq. (19). Its numerical values will define the duration of the transition stage to a purely dissipative regime of spinodal decomposition. To date, τ has been obtained only by fitting theoretical comparison to experimental data. For example, the relaxation time can be estimated in a wide range, $10^{-11}(\text{s}) < \tau < 10^{-7}(\text{s})$, as for a Co-Cu melt deeply quenched into the spinodal region or for the amorphous $\text{SiO}_2\text{-Na}_2\text{O}$ system under spinodal decomposition [21]. Using these values of τ , one may explain nonlinear behavior of characteristic functions of spinodal decomposition, namely, in the amplification rate and structure factor [18,22]. In addition to the present description using hyperbolic equation, an alternative analysis leading to qualitative explanation of experimentally observed nonlinearities in spinodal decomposition can also be given using mean-field kinetic equations [23].

IV. TRANSITIONS WITH INERTIA: LACK OF MOMENTUM EQUILIBRATION

Another situation in which a hyperbolic phase-field model is needed is the case of correlated jumps, analogous to correlated random walks [12,24]. In this case, it is assumed that if a particle has jumped in one direction, the probability that the next jump is in the same direction of the previous jump is higher than the probability of jumping in the opposite direction. This may also be seen as arising from a lack of complete

thermalization in the momentum space, because in that case the different directions of motion would be equivalent. To model this situation, one assumes that the transition rate $W(C, C^{ij})$ depends not only on the situation at time t but also on the previous jump exchange at time $t - t_0$. For instance, let us assume that C^{ij} means exchanging particle B at i and particle A at j . If $i < j$, this means that site i was more at left than site j as in a simple one-dimensional situation. Finally, this would mean that if particle B arrived to i from a previous jump from left to right, and particle A arrived to j from a previous jump from right to left, the rate $W(C, C^{ij})$ will be higher than in all the other possibilities.

Following the analogy with the correlated random walk [24], we split $p_i(t)$ as

$$p_i(t) = p_i^{(+)}(t) + p_i^{(-)}(t) + p_i^{(o)}(t),$$

where $p_i^{(+)}$, $p_i^{(-)}$, and $p_i^{(o)}$ are the probabilities to find particles of the sort B at site i , having arrived from the right (+) or from the left (-), or which were already at i th site (o). Here, for simplicity, we shall consider $p_i^{(o)}$ as a small quantity, i.e., most particles move at each step (one can also avoid this hypothesis at the price of more cumbersome expressions).

The transition rates, $W_{ij}(\alpha)$ and $W_{ij}(\gamma)$ [with $W_{ij}(\alpha) > W_{ij}(\gamma)$], are correlated (respectively, autocorrelated) with the former exchange, which is denoted by the indices α or γ . α means that the particle arrived at site i from the left (i.e., from some site i' with $i' < i$). γ means that the particle arrived at site i from the right (i.e., from some site $i' > i$). Furthermore, the transition rates W_{ij} are used namely for $W(C, C^{ij})$ to have shorter expressions for the probabilities, such that

$$\begin{aligned} & \frac{p_i^{(+)}(t + t_0) - p_i^{(+)}(t)}{t_0} \\ &= W_{i,i-1}(\alpha)p_{i-1}^{(+)}(t) - W_{i+1,i}(\alpha)p_i^{(+)}(t) \\ & \quad + W_{i,i-1}(\gamma)p_{i-1}^{(-)}(t) - W_{i-1,i}(\gamma)p_i^{(+)}(t), \\ & \frac{p_i^{(-)}(t + t_0) - p_i^{(-)}(t)}{t_0} \\ &= W_{i,i+1}(\alpha)p_{i+1}^{(-)}(t) - W_{i-1,i}(\alpha)p_i^{(-)}(t) \\ & \quad + W_{i,i+1}(\gamma)p_{i+1}^{(+)}(t) - W_{i+1,i}(\gamma)p_i^{(-)}(t). \end{aligned} \quad (21)$$

Note that the transitions from the site $i - 1$ to the site i for particles in i having arrived from the right in the former exchange have a higher transition rate $W_{i,i-1}(\alpha)$ than the transitions from the site $i - 1$ to the site i for the particles in site i that arrived from the left in the former exchange, which have the transition rate $W_{i,i-1}(\gamma)$. Analogously, one gets for the transitions from the site $i + 1$ to the site i for particles previously arriving from the right, $W_{i,i+1}(\alpha)$, or from the left, $W_{i,i+1}(\gamma)$.

Equations (21) may be rewritten as

$$\begin{aligned} & \frac{p_i^{(+)}(t + t_0) - p_i^{(+)}(t)}{t_0} \\ &= W_{i,i-1}(\alpha)p_{i-1}(t) - v_d p_i^{(-)}(t) - v_s p_i^{(+)}(t), \end{aligned}$$

$$\begin{aligned} & \frac{p_i^{(-)}(t + t_0) - p_i^{(-)}(t)}{t_0} \\ &= W_{i,i+1}(\alpha)p_{i+1}(t) - v_d p_{i+1}^{(+)}(t) - v_s p_i^{(-)}(t), \end{aligned} \quad (22)$$

with $v_d \equiv W_{i,i-1}(\gamma) - W_{i,i-1}(\alpha) = W_{i,i+1}(\gamma) - W_{i,i+1}(\alpha)$ and $v_s \equiv W_{i-1,i}(\gamma) + W_{i+1,i}(\alpha) = W_{i-1,i}(\alpha) + W_{i+1,i}(\gamma)$. In fact, the rate coefficients $W_{ij}(\alpha)$ and $W_{ij}(\gamma)$ could have general sets of values, though not necessarily satisfying these equations. A simple illustration can be provided as follows.

Summation of Eqs. (22) yields (neglecting the role of $p_i^{(o)}$ as it has been already noted)

$$\begin{aligned} & \frac{p_i(t + t_0) - p_i(t)}{t_0} = W_{i,i-1}(\alpha)p_{i-1}(t) + W_{i,i+1}(\alpha)p_{i+1}(t) \\ & \quad - v_d [p_i^{(-)}(t) + p_{i+1}^{(+)}(t)] - v_s p_i(t). \end{aligned} \quad (23)$$

Taking into account the equality

$$p_i(t - t_0) = p_{i+1}^{(+)}(t) + p_{i-1}^{(-)}(t),$$

Eq. (23) can be rewritten as

$$\begin{aligned} & \frac{p_i(t + t_0) - p_i(t)}{t_0} = W_{i,i-1}(\alpha)p_{i-1}(t) + W_{i,i+1}(\alpha)p_{i+1}(t) \\ & \quad - v_s p_i(t) - v_d p_i(t - t_0). \end{aligned} \quad (24)$$

Thus, the values of $p_i(t + t_0)$ depend on the values of p_i at the moments t and $t - t_0$ in such a way that the non-Markovian character is clearly seen. It is straightforward to show that Eq. (24) is approximated as

$$\begin{aligned} & v_d t_0^2 \frac{d^2 p_i}{dt^2} + (1 - v_d t_0) \frac{dp_i}{dt} \\ &= W_{i,i-1}(\alpha)p_{i-1}(t) + W_{i,i+1}(\alpha)p_{i+1}(t) - (v_d + v_s)p_i(t). \end{aligned} \quad (25)$$

Equation (25) is a hyperbolic master equation for description of the local probability of occupation of the i site by the B atom. Obviously, this equation also predicts the probability $(1 - p_i)$ of occupation of the i site by the A atom. Coming from consideration of the correlated jumps of particles, Eq. (25) seems to be important for the analysis of atomic transport and diffusion of defects (vacancies, microscopic imperfections, etc.) in phenomena of disorder trapping, solute trapping, and degeneration of solute drag appearing around a rapidly moving interface [10]. For vanishing correlations, $v_d = 0$ [i.e., for $W_{i,i-1}(\alpha) = W_{i,i-1}(\gamma)$ and $W_{i,i+1}(\alpha) = W_{i,i+1}(\gamma)$], Eq. (25) reduces to the known Markovian master equation.

V. FINAL COMMENTS AND CONCLUSIONS

Two physical situations concerning the fast phase transitions were studied. In the system of binary mixture we assumed lack of energy thermalization and a lack of complete thermalization in the momentum space of jumping particles (atoms, molecules). It is shown that the mesoscopic description of such processes requires going beyond the usual parabolic differential equations for the evolution of the concentration. This description requires hyperbolic transport equations in

phase transformations, which have indeed been known to provide a richer and more faithful description of several fast transitions, such as fast solidification fronts [25] or initial stages of spinodal decomposition [22].

Fast phase transitions are recognized as transitions having different temporal scales with changing slow thermodynamic variables (such as internal energy, chemical potential, concentration, etc.) and fast thermodynamical variables (such as fluxes of heat and substances, rate of phase-field change, etc.). For example, the atomic concentration and the diffusion flux of atoms are physically motivated to be slow and fast independent variables, respectively, in rapid solidification [25]. Also, reasonable incorporation of fast elastic relaxation and slower mass diffusion leads to the hyperbolic (modified) phase-field crystal equation [26]. Within this context, the evolution equations for the diffusion flux have been considered previously [14,15,22], which result in the hyperbolic evolution equation for the concentration directly. Even though the use of such formalism is efficient on quantitative and practical grounds [10], from the conceptual viewpoint it provides only a particular situation leading to hyperbolic equations. In the present paper, we have given two other different physical bases for hyperbolic equations of the phase-field model. They are not directly related to relaxation effects in diffusion transport but rather to nonequilibrium of internal energy and of linear momentum inbetween successive elementary steps of the corresponding physical process. A specific feature of the present particular derivation of hyperbolic differential equations is that the noise is not δ -correlated in time (so-called “white noise”) but it instead depends on prehistory of thermalization (known as “colored noise”) [18].

Following the treatments for the coarse-grained concentration, which lead to the hyperbolic transport Eq. (13) and its continuum limit Eq. (19), one can analyze the discrete distribution of atomic density—conserved variable used in the phase-field crystal model [27]. Indeed, considering now the probability p_i to find the atomic density of B atoms at site i , the free energy might be taken as

$$F(p_i, T) = \sum_i f(p_i, T) - r_1 \sum_b (p_{i+b} - p_i)^2 + \frac{r_2}{2} \left[\sum_b (p_{i+b} - p_i) \right]^2, \quad (26)$$

where the free-energy density $f(p_i, T)$ has the form of Eq. (16) and r_1 and r_2 are the parameters of the crystal model [28]. Equation (26) represents the discrete analog of the concrete free energy (see Ref. [29] and references therein) for the description of locally periodic states, which, in general, is given by the Brazovskii-Swift-Hohenberg functional [30]. Furthermore, just as Eq. (26), the free-energy with high-order nonlocal terms has also been analyzed by Rosenau [4] within the extension of the Ginzburg-Landau theory to high-gradient domains. Obviously, with $r_2 = 0$ and $r_1 = -\epsilon/2$, Eq. (26) transforms into the discrete Ginzburg-Landau functional Eq. (15). The explicit expression for the chemical potential is obtained from the derivative of the free-energy Eq. (26)

with respect to the local probability as

$$\mu_n(\tilde{C}, t) \equiv \frac{\partial F}{\partial p_i} = \mu_i^{(\text{hom})} + 2r_1 \Delta_b p_i + r_2 \Delta_b^2 p_i, \quad (27)$$

where $\Delta_b p_i = \sum_a (p_{i+b} - p_i)$ is the discrete Laplacian for the chosen concrete lattice, $\Delta_b^2 p_i = \sum_b (p_{i+b} - p_i)^2$ is the discrete analog for the squared Laplacian, and $\mu_i^{(\text{hom})}$ has the same form as Eq. (18). Applying the same analysis and analytical treatments, as is given for Eqs. (8)–(14), to the nonuniform periodic atomic density, the hyperbolic Eq. (19) with the continuum limit of chemical potential Eq. (27),

$$\mu \equiv \frac{\partial F}{\partial c} = \mu_{(\text{hom})} + 2r_1 \nabla^2 c + r_2 \nabla^4 c, \quad (28)$$

is obtained. Equations (19) and (28) describe the hyperbolic phase-field-crystal model as is previously introduced from various physically motivated situations [19,26,31]. Therefore, the use of coarse-graining procedures and various types of free energy have led to overcoming different phase-field models.

A few comments on the obtained non-Markovian master Eqs. (7) and (25), as well as the equation for coarse-grained concentration, Eq. (13), can also be outlined. Avoiding the restriction on the energy thermalization or momentum equilibration, these equations describe atomic transport in fast transitions under local nonequilibrium and slow transitions evolving under local equilibrium conditions. Such generalization leads to the appearance of memory effects in the equations describing non-Markovian kinetic processes, which can, however, be obtained from the other physically reasonable situations [32]. For instance, one can refer to a time-dependent diffusion coefficient, which is considered as an alternative way to introduce memory effects. Moreover, following the other alternative description, one can even eliminate the memory effects in the equations if a greater number of variables are taken into consideration. Indeed, one can get a typically Markovian equation for density by introducing density and its flux as thermodynamically independent variables. Similarly, the fast phase transition can be described by the Markovian equations if high-order diffusion fluxes are included [12].

With regard to coupled processes, such as atomic diffusion and phase-field dynamics (by classification of Hohenberg and Halperin [17] it could be “Model C”), one can state that, in the present work, we have considered just a single relaxation time for the internal equilibration. In addition to this, study of solute trapping by rapid solid-liquid front shows that the diffusion coupled with the phase-field dynamics in isothermal system requires introducing two characteristic times for the local equilibration [33]. These two times are related to a pair of characteristic speeds for disturbances propagation as is described by the hyperbolic model tested in atomistic simulations [34]. The values of τ depend on the concrete system. As an example of the relaxation time of the solute diffusion flux, one can estimate $\tau \sim 10^{-10}$ (s) for semiconductors [33] and one can get 10^{-11} (s) $< \tau < 10^{-7}$ (s) for binary alloy systems or inorganic solutions [14]. In general, a given spectrum of relaxation times for the internal equilibration of the different variables of the system should be taken into account. This would lead to more complicated but more faithful evolution equations.

ACKNOWLEDGMENTS

D.J. acknowledges support by the Direcció General de Investigaci3n of the Spanish Ministry of Economy and Competitiveness under Grant No. FIS 2012-32099 and of the

Generalitat of Catalonia under Grant No. 2009-SGR-00164. P.K.G. acknowledges the partial support within the framework of Program 07.08 “Research Investigations in Education,” Project No. 2.947.2011.

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