Diffuse-interface model for rapid phase transformations in nonequilibrium systems

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(Dated: March 23, 2022)

A thermodynamic approach to rapid phase transformations within a diffuse interface in a binary system is developed. Assuming an extended set of independent thermodynamic variables formed by the union of the classic set of slow variables and the space of fast variables, we introduce finiteness of the heat and solute diffuse propagation at the finite speed of the interface advancing. To describe the transformation within the diffuse interface, we use the phase-field model which allows us to follow the steep but smooth change of phases within the width of diffuse interface. The governing equations of the phase-field model are derived for the hyperbolic model, model with memory, and for a model of nonlinear evolution of transformation within the diffuse-interface. The consistency of the model is proved by the condition of positive entropy production and by the outcomes of the fluctuation-dissipation theorem. A comparison with the existing sharp-interface and diffuse-interface versions of the model is given.

PACS numbers: 05.70.Fh; 05.70.Ln; 64.60.-i; 83.20.Hn

I. INTRODUCTION

Arising from phase transformations, a classic free-boundary problem introduces a model of phase interface with zero thickness. Within this problem, a sharp discontinuity in properties or a jump of fluxes and thermodynamic functions occurs across the interface. The sharp-interface model has been a successful description of many physical phenomena in various systems [1]. However, the sharp-interface model has difficulties in describing situations when interfacial thickness becomes comparable with the characteristic length of the considered phenomenon, and when a topology of the interface becomes complicated or multiply connected. In order to avoid these difficulties in the sharp-interface model, an alternative model with a finite interfacial thickness was suggested for explaining phase transformations [2].

Historically, the first formulation of basic principles of diffuse interfaces was given by Poisson, Maxwell, and Gibbs [2], who suggested to consider interface as a region with finite thickness in which a steep but smooth transition of physical properties of phases occurs. Lord Rayleigh, van der Waals, and Korteweg [5] applied thermodynamical principles to develop gradient theories for the interfaces with non-zero thickness. Through the past century, ideas of diffuse interface given by these authors [5, 6] were refined and applied in many physical phenomena (see, e.g., overviews in Ref. [2]).

The diffuse-interface formalism has been widely applied to phase transformations in condensed media. Borrowing the formalism of the Landau theory of phase transitions [2], the first introduction of the diffuse interface into the theory of phase transformations was made by Landau and Khalatnikov [7], who labelled the different phases by an additional order parameter to describe anomalous sound absorption of liquid helium. In its well-known form, the formal variational approach was established by Ginzburg and Landau for phase transitions from the normal to the superconducting phase [8]. On the basis of this approach, diffuse-interface models with order parameters have been developed by Halperin, Hohenberg and Ma for the theory of critical phenomena [9], and by Allen and Cahn for antiphase domain coarsening [10].

The diffuse-interface model has been also developed for the description of phase transformations of the first order, especially, for the solidification phenomenon. The diffuse-interface model of solidification incorporates an order parameter in the form of a phase-field variable [11]. The phase-field \( \Phi \) has a constant value in homogeneous phases, e.g. \( \Phi = -1 \) for unstable liquid phase which is transforming into the solid phase with \( \Phi = +1 \). Between these phases in the interfacial region, the phase field, \( \Phi \), changes steeply but smoothly from \(-1\) to \(+1\). In numerical solutions, it allows one to avoid explicit tracking of the interface and locate the interface at \( \Phi = 0 \) [12]. As a particular case, the phase-field model is reduced to the sharp interface limits [13] and adopts the major models of sharp interface (such as Hele-Shaw type models, classical or modified Stefan problem, etc.). The phase-field \( \Phi \) is considered as an order parameter which is introduced to describe the moving interfacial boundary between the initially unstable phase and the final phase.

Several thermodynamically consistent phase-field models have been proposed [14, 15, 16, 17]. These include models for transformation in a pure system up to the rather general modelling of multiphase transformation in a multi-component system [18]. All of these
models assume local equilibrium in the system, being consistent with the basic hypothesis of the classic irreversible thermodynamics (CIT) \[18, 19\]. This assumption leads to the examination of a number of transport processes with small and moderate deviations from thermodynamic equilibrium and, as a consequence, relatively slow movement of the interface can be predicted. In principle, such an approach can be extended to the case when the condition of equilibrium is violated locally at the interface, e.g., as it has been made for solute trapping and kinetic effects \[20\]. However, the local equilibrium is missing both at the interface and within the bulk phases for rapid transformations such as rapid solidification \[21\]. In this case, the description of rapid phase transformations might be provided by the formalism of extended irreversible thermodynamics (EIT) \[22\] which gives a causal description of transport processes and abandons the assumption of local equilibrium. An extension of the phase-field methodology for rapid transformation, which is caused by significant deviations from thermodynamic equilibrium, has been made recently \[22\].

The main purpose of the present paper is to describe a thermodynamically consistent model for rapid phase transformation in a binary system under local nonequilibrium conditions. Using the phase-field methodology, we derive the governing equations compatible with the macroscopic formalism of EIT and the microscopic fluctuation-dissipation theorem.

The paper is organized as follows. In Sec. \[II\] a thermodynamic description of a considered system is given. We introduce the dissipative diffusion fluxes for heat and mass transport together with the phase-field rate of change as independent variables. In Sec. \[III\] the generalized Gibbs equation and entropy balance applicable to rapid advancing of the diffuse interfaces are given. As a starting point of the present phase-field model, an entropy functional is used in Sec. \[IV\]. The analysis of the present phase-field model leads to the governing equations for the hyperbolic system with dissipation. In Sec. \[V\] a generalization of the hyperbolic phase-field model is given using the flux relaxation functions as well as a variational principle. In Sec. \[VI\] the model equations are compared with the outcomes of the existing sharp-interface and diffuse-interface models. Finally, in Sec. \[VII\] we present a summary of our conclusions.

II. DESCRIPTION OF THE SYSTEM

A. Thermodynamic variables

Let us consider an isobaric binary system at nonuniform temperature \(T\) with no convective flow and given concentration of atoms \(A\) and \(B\). The local equilibrium hypothesis establishes that the local and instantaneous correlations among the properties of the system are the same as for the whole system at a global equilibrium. Describing the nonequilibrium system as an ensemble of small local volumes in internal equilibrium, CIT \[19\] is applicable to processes not too far from equilibrium. In addition to CIT, a local nonequilibrium formalism applicable to the strongly nonequilibrium systems has been developed in past two decades \[22, 24, 25, 26\]. As a phenomenological theory, this formalism is well-known as EIT \[22, 27\] which goes beyond the hypothesis of local equilibrium and avoids the paradox of propagation of disturbances with an infinite speed.

A fundamental problem in attempting to describe systems out of equilibrium is to select the relevant variables needed for a valid description of a nonequilibrium state. This problem has been intensively discussed in the literature (see references in bibliographic overview \[28\]). A selection of the basic state space with the inclusion of the dissipative fluxes is formulated in EIT \[22\] and tested against experimental data \[29\]. Accordingly, we extend the classic set of independent thermodynamic variables by the inclusion of dissipative fluxes as additional basic variables.

CIT is based on the local equilibrium hypothesis \[18, 19\] which assumes instant relaxation of fluxes to their steady-state values and describes the ensemble of atoms within local volumes by the Gibbs-Boltzmann statistics. In the standard formalism of the diffuse-interface using CIT, the set \(\{C\}\) of independent variables is assumed to consist of the conserved variables such as energy density \(e(\vec{r}, t)\) and concentration \(X(\vec{r}, t) = X_B/(X_A + X_B)\) of the \(B\) component in the system, and the non-conserved phase-field \(\Phi(\vec{r}, t)\) variable [where \(t\) is the time, and \(\vec{r}\) is the position-vector of a point within system]. This can be expressed formally as follows: \(\{C\} = \{e, X, \Phi\}\).

The extended space of independent variables \(E\) is formed by the union of the classical set \(\{C\}\) and the additional space \(\{F\}\) of the fluxes of heat \(\vec{q}\) and solute \(\vec{J}\), and also the rate of change \(\partial \Phi/\partial t\) of the phase-field variable, i.e. \(\{F\} = \{\vec{q}, \vec{J}, \partial \Phi/\partial t\}\). This yields

\[
E = \{C\} \cup \{F\} = \{e, X, \Phi\} \cup \{\vec{q}, \vec{J}, \partial \Phi/\partial t\}.
\]

Here \(\{F\}\) is the space of fast non-conserved thermodynamic variables.

There are, in fact, different possible choices of variables (fluxes in EIT, microstructural details in theories with internal variables), and the specific choice to be adopted depends on the aims of the description and on the problems to be analyzed. This does not mean that different choices of variables are incompatible with each other. For instance, in the study of flowing polymer solutions one may select as independent variables either the viscous pressure tensor or the conformation tensor describing the average microstructure of the macromolecules of the system; a Legendre transform exists which allows one to pass from one description to the other, in a similar way as it is possible, in equilibrium thermodynamics, to pass from a description using internal energy as independent variable to a description using absolute temperature as an independent variable \[30\].
Thus, our choice of the fluxes as variables does not exclude other possibilities. To justify our choice, we comment on the qualitative grounds, the meaning and the relevance of $\tilde{q}$, $\tilde{J}$, and $\partial\Phi/\partial t$ as variables. The fluxes $\tilde{q}$ and $\tilde{J}$ describe the exchanges of heat and matter between the interface and the neighboring bulk phases. The fluxes do not instantaneously follow by the classical Fourier and Fick laws, relating them with temperature and concentration gradients, it takes them some time (usually rather short) to reach the value predicted by the classical transport equations. Obviously, when the interface motion is fast enough, the delay effects in the dynamics of the fluxes may play a determining role. This happens, for instance, when the velocity $V$ of the interface becomes comparable or higher than $l/\tau$, $l$ being the mean-free-path of the particles and $\tau$ the relaxation time of the fluxes. Thus, in these circumstances, $\tilde{q}$ and $\tilde{J}$ behave as independent variables with their own dynamics, which has important consequences on the dynamics and stability of the interface.

The introduction of $\partial\Phi/\partial t$ as a further independent variable is motivated by similar, though slightly different consideration. Indeed, the space variation of $\Phi$ is related, among other factors, to the width of the interface. Thus, including $\partial\Phi/\partial t$ as an independent variable allows for a more detailed description of the internal kinetics and shape of the interface. In the same way as in Newtonian mechanics, where the initial position and velocity of a particle must be specified to determine their evolution, here we take both $\Phi$ and $\partial\Phi/\partial t$ as independent variables. If inertial effects are sufficiently low in comparison with dissipative effects, $\partial\Phi/\partial t$ will be directly determined in terms of $\Phi$ and its gradient by a dynamical equation. Otherwise, $\Phi$ and $\partial\Phi/\partial t$ will be independent and an equation for $\partial^2\Phi/\partial t^2$ must be found.

Consequently, with taking the above choice of variables, one may distinguish between the two sets of independent variables as it follows. The variables from the set $\{C\}$ are characterized as the slow variables, as their behavior is governed by conservation laws for energy and solute concentration plus the evolution of the phase-field, and as they decay slowly in time. In contrast, the independent space $\{F\}$ consists of non-conserved variables with relatively high rate of decay. The variables from $\{F\}$ differ from their classical value during intervals of the order of magnitude of the characteristic times $\tau_i$ for relaxation of the heat flux, solute diffusion flux, and rate of change of the phase-field variable. For time intervals much longer than these relaxation times $\tau_i$, the rate of variation of the fluxes can be ignored.

B. Relaxation times

Generally, the relaxation times $\tau_i$ represent physically reasonable time estimations for the spontaneous return of the system to the steady state after some sudden perturbation. The relaxation times $\tau_T$ and $\tau_D$ for the heat and solute can be considered as the times needed for smoothing of inhomogeneities of temperature and concentration, respectively, by diffusion. The time $\tau_\Phi$ of relaxation for the phase-field can be evaluated from the velocity of the diffuse interface moving through the local volume with the characteristic spatial length. Consequently, the rate of decay of the heat flux $\tilde{q}$, solute diffusive flux $\tilde{J}$, and phase-field rate of change $\partial\Phi/\partial t$ are estimated by the following characteristic times

$$
\tau_T = a/V_T^2, \quad \tau_D = D/V_D^2, \quad \tau_\Phi = l/V,
$$

(2)

where $a$ is the thermal diffusivity, $V_T$ the finite speed for heat diffusion (i.e. the speed of propagation of temperature disturbances), $D$ the solute diffusion constant, $V_D$ the finite speed for diffusion (i.e. the speed of propagation of concentration disturbances), $V$ the velocity of the diffuse interface, and $l$ the spatial length.

For instance, the time $\tau_T$ is defined by the phonon-electron and phonon-phonon interactions for heat diffusion in metallic systems and it is estimated in Ref. [33] to be in the range of $10^{-10} s < \tau_T < 10^{-11} s$. The time $\tau_D$ is defined by the time for diffusion jumps of particles, which varies within a wide interval: $10^{-11} s < \tau_D < 10^{-7} s$ in a binary alloy system or inorganic solution [34]. In addition to this, the time $\tau_\Phi$ might be evaluated numerically from Eq. (2) assuming that the length $l = W_0$ the width of the diffuse interface and the velocity $V$ is the characteristic velocity for rapid adiabatic transformations. Thus, for numeric evaluation of $\tau_\Phi$ in a pure system, one may accept the following expression

$$
\tau_\Phi = W_0\chi/(\mu_0Q),
$$

(3)

where $Q$ is the heat of transformation, $\chi$ is the heat capacity (so that relation $Q/\chi$ is considered as the characteristic temperature for adiabatic transformation), and $\mu_0$ the coefficient for atomic kinetics. Taking the values for pure nickel, e.g., $Q/\chi = 418 K$ [35], $\mu_0 = 0.52 m/(s-K)$ [36], and $W_0 = 5 \cdot 10^{-9} m$, one gets $\tau_\Phi = 2.30 \cdot 10^{-11} s$. This value for $\tau_\Phi$ fits well to the time of diffuse-interface kinetics which might be calculated from the “thin-interface” analyses of Karma and Rappel [37] extended by Bragard et al. [38].

It is also reasonable to evaluate the relaxation time for the phase-field in a binary system using outcomes of the phase-field model via “thin-interface” analyses of Karma and Rappel [37]. Namely, for the nonisothermal solidification of a binary system, Ramirez et al. [38] derived the time $\tau_\Phi$ for the phase-field as a function of $X$ and $\Phi$. It is described by

$$
\tau_\Phi = \frac{W_0^2}{\Gamma} \left( \frac{1}{\mu_0} + a_1 \frac{W_0}{a} \left[ \frac{DQ}{aX} + \frac{m(1-k)X}{1+k-(1-k)\Phi} \right] \right).
$$

(4)

For numeric evaluation, we accept the following material parameters for a Cu-Ni metallic system in Eq. (4): diffuse-interface width $W_0 = 1 \cdot 10^{-9} m$, Gibbs-Thomson coefficient $\Gamma = 1.3 \cdot 10^{-7} K \cdot m$, atomic...
kinetics coefficient \( \mu_0 = 0.24 \text{ m/(s·K)} \), constants \( a_1 = 0.8839 \) and \( a_2 = 0.6267 \), solute diffusion constant \( D = 3 \times 10^{-9} \text{ m}^2/\text{s} \), thermal diffusivity \( \alpha = 1.5 \times 10^{-5} \text{ m}^2/\text{s} \), adiabatic temperature (relation of latent heat and heat capacity) \( Q/\chi = 402 \text{ K} \), slope of the liquidus line \( m = 4.38 \text{ K/at.}\% \), solute partitioning coefficient \( k = 0.81 \). As a result following from Eq. (4), one gets \( \tau_p = 7.92 \times 10^{-11} \text{ s} \) for the values of \( X = 70 \text{ at.}\% \) and \( \Phi = 0.5 \).

The values for the relaxation times for some pure and binary systems are summarized in Table I. It can be seen, e.g., for metals and alloys, that even though the heat speed \( V_T \) is much larger than the solute diffusion speed \( V_D \), the relaxation times for \( \vec{q} \) and \( \vec{J} \) have the same order of magnitude, i.e., \( \tau \approx \tau_D \). Therefore, a front of the heat profile moves with a speed much higher than a front of the solute diffusive profile. However, due to the fast thermal diffusion, \( \alpha >> D \), the relaxation of the heat flux \( \vec{q} \) proceeds approximately at the same characteristic time as the relaxation for solute diffusion flux \( \vec{J} \).

### III. ENTROPY APPROACH

#### A. Generalized Gibbs equation

For the local nonequilibrium system described in Sec. II, we postulate the existence of a local generalized entropy density \( s \) whose set of variables is the extended space \( \mathbf{E} \) by Eq. (1). The generalized Gibbs equation for \( s \) is described by

\[
\begin{align*}
\dot{s}(e, X, \Phi, \vec{q}, \vec{J}, \partial \Phi/\partial t) &= \dot{s}_c(e, X, \Phi) \\
+ \dot{s}_{ne}(\vec{q}, \vec{J}, \partial \Phi/\partial t) &= \frac{\partial s_c}{\partial e} \dot{e} + \frac{\partial s_c}{\partial X} \dot{X} + \frac{\partial s_c}{\partial \Phi} \dot{\Phi} \\
+ \frac{\partial s_{ne}}{\partial \vec{q}} \cdot \dot{\vec{q}} + \frac{\partial s_{ne}}{\partial \vec{J}} \cdot \dot{\vec{J}} + \frac{\partial s_{ne}}{\partial (\partial \Phi/\partial t)} d \left( \frac{\partial \Phi}{\partial t} \right). 
\end{align*}
\]

(5)

In Eq. (5), \( \dot{e} \) is a local equilibrium contribution defined on the set \( \{C\} \) of the classic slow variables \( \{e, X, \Phi\} \), and \( \dot{s}_{ne} \) is a flux-dependent purely nonequilibrium part of the generalized entropy density defined on the space \( \{F\} \) consisting of the fluxes \( \{\vec{q}, \vec{J}, \partial \Phi/\partial t\} \) as the independent fast variables.

The derivatives of the entropy density with respect to classical variables and their fluxes appearing in Eq. (5) are described by

\[
\begin{align*}
\frac{\partial s_c}{\partial e} &= \frac{1}{T}, & \frac{\partial s_c}{\partial X} &= -\frac{\Delta \mu}{T}, \\
\frac{\partial s_c}{\partial \Phi} &= (1 - X) \frac{\partial s_A}{\partial \Phi} + X \frac{\partial s_B}{\partial \Phi}, \\
\frac{\partial s_{ne}}{\partial \vec{q}} &= -\alpha_q \vec{q}, & \frac{\partial s_{ne}}{\partial \vec{J}} &= -\alpha_J \vec{J}, \\
\frac{\partial s_{ne}}{\partial (\partial \Phi/\partial t)} &= -\alpha_\Phi \frac{\partial \Phi}{\partial t}. 
\end{align*}
\]

(6)

where \( \Delta \mu = \mu_A - \mu_B \) is the difference of the chemical potentials for components \( A \) and \( B \), respectively, and \( s_A \) and \( s_B \) are the entropies for pure components \( A \) and \( B \), respectively. The chemical potentials and entropies of components can be chosen for every concrete system (see, e.g., Refs. [15, 17]).

In Eqs. (6), the coefficients \( \alpha_i \) are scalars which do not depend on \( \vec{q}, \vec{J}, \) and \( \partial \Phi/\partial t \), and are assumed to be

\[
\begin{align*}
\alpha_q &= \left( \frac{\tau_T}{\kappa T^2} \right)_X, & \alpha_J &= \left( \frac{\tau_D}{TD} \frac{\partial (\Delta \mu)}{\partial X} \right)_T, \\
\alpha_\Phi &= \left( \frac{a_0 \tau D W_0 Q}{T \mu_0} \right)_T X, 
\end{align*}
\]

(7)

where \( \kappa \) is the thermal conductivity, \( a_0 \) a dimensionless factor (dependent on the model of the diffuse interface, specifically leading to the sharp-interface asymptotic limit), and \( Q \) the heat of the transformation.

After integration, Eq. (5) can be written in the form

\[
\begin{align*}
\dot{s}(e, X, \Phi, \vec{q}, \vec{J}, \partial \Phi/\partial t) &= s_c(e, X, \Phi) + s_{ne}(\vec{q}, \vec{J}, \partial \Phi/\partial t), \\
\dot{s}_{ne}(\vec{q}, \vec{J}, \partial \Phi/\partial t) &= -\frac{\alpha q}{2} \vec{q} \cdot \vec{q} - \alpha J \vec{J} \cdot \vec{J} - \alpha \Phi \left( \frac{\partial \Phi}{\partial t} \right)^2. 
\end{align*}
\]

(8)

Consequently, we arrive to a generalized entropy density given by an expansion around its local equilibrium value up to second-order in the fluxes. In the limit of infinite speeds \( V_T \to \infty, V_D \to \infty, \) and \( V \to \infty \), one gets \( \tau_T \to 0, \tau_D \to 0, \) and \( \tau_\Phi \to 0 \). In such a case, the term \( s_{ne} \) vanishes and Eq. (8) gives the entropy density \( s_c(e, X, \Phi) \) for local equilibrium system.

**TABLE I: Relaxation time for the fluxes of heat, solute diffusion, and phase-field**

| System                  | \( \tau_T \) (s) | \( \tau_D \) (s) | \( \tau_\Phi \) (s) |
|-------------------------|------------------|------------------|---------------------|
| Carbon tetrachloride    | \( 2.50 \cdot 10^{-13} \), Ref. [42] | —                | —                   |
| Benzene                 | \( 1.22 \cdot 10^{-13} \), Ref. [42] | —                | —                   |
| Nickel                  | \( 1.20 \cdot 10^{-11} \), Ref. [43] | —                | —                   |
| Diluted alloy Ni - 0.7 at.% B | —                | \( 1.54 \cdot 10^{-11} \), Ref. [45] | —                   |
| Concentrated alloy Cu - 30 at.% Ni | —                | \( 0.75 \cdot 10^{-11} \), Ref. [46] | \( 7.92 \cdot 10^{-11} \), Ref. [47] |
B. Entropy balance

For the system described by the extended set \(E\) of variables, Eq. (1), the local balance laws for the energy and concentration are given by

\[
\frac{\partial e}{\partial t} + \nabla \cdot \vec{q} = 0, \quad \frac{\partial X}{\partial t} + \nabla \cdot \vec{J} = 0,
\]

and the evolution of entropy density is defined by

\[
\frac{\partial s}{\partial t} + \nabla \cdot \vec{J}_S = \sigma_S. \quad (10)
\]

The change of the total entropy \(S\) in time \(t\) is described by

\[
\frac{dS}{dt} = \left(\frac{dS}{dt}\right)_{ex} + \left(\frac{dS}{dt}\right)_{in}, \quad (11)
\]

where

\[
\left(\frac{dS}{dt}\right)_{ex} = -\int_v \nabla \cdot \vec{J}_S dv = -\int_\omega \vec{J}_S \cdot \vec{n} d\omega, \quad (12)
\]

is the external exchange of entropy due to entropy flux \(\vec{J}_S\) and

\[
\left(\frac{dS}{dt}\right)_{in} = \int_v \sigma_S dv, \quad (13)
\]

is the internal production of entropy due to dissipation within the system. In Eqs. (12) and (13): \(\omega\) is the outer surface of sub-volume \(v\), \(\vec{n}\) the normal vector to the surface, and \(\sigma_S\) the local entropy production.

IV. HYPERBOLIC PHASE-FIELD MODEL

In this section, the important class of hyperbolic models with dissipation is considered. We work out the explicit evolution equations for the variables including the relaxation terms.

A. An entropy functional

Now we use an entropy functional of the following form

\[
S = \int_v \left[ s(e, X, \Phi, \vec{q}, \vec{J}, \partial \Phi/\partial t) - \frac{\varepsilon_e^2}{2} |\nabla e|^2 - \frac{\varepsilon_x^2}{2} |\nabla X|^2 - \frac{\varepsilon_\phi^2}{2} |\nabla \Phi|^2 \right] dv. \quad (14)
\]

Here \(\varepsilon_e, \varepsilon_x, \) and \(\varepsilon_\phi\) are constants for the energy, concentration, and phase-field, respectively. In the functional (14) the gradient terms \(|\nabla e|^2, |\nabla X|^2, \) and \(|\nabla \Phi|^2\) are used to describe spatial inhomogeneity within the fields according to previous diffuse-interface models [8, 10, 12].

It is logical to include gradient terms in Eq. (14) [of the so-called “Ginzburg-Landau form”] because, as stressed before, our interest is focused on interfaces with steep gradients. In addition, the extension (1) gives the entropy density \(s\) based also on the fluxes \(\vec{q}, \vec{J},\) and \(\partial \Phi/\partial t\) as independent variables.

To obtain the evolution of the entropy, Eq. (11), and consider the several parts of the entropy exchange, Eqs. (12)–(13), we differentiate Eq. (1) with respect to time. Combining the terms, after some algebra one obtains

\[
\frac{dS}{dt} = \int_v \left[ \frac{\partial s}{\partial e} \left(\frac{\partial e}{\partial t}\right) + \varepsilon_e^2 \nabla^2 e \right] dv + \int_v \left[ \frac{\partial s}{\partial X} + \varepsilon_x^2 \nabla^2 X \right] \left(\frac{\partial X}{\partial t}\right) dv + \int_v \left[ \frac{\partial s}{\partial \Phi} + \varepsilon_\phi^2 \nabla^2 \Phi \right] \left(\frac{\partial \Phi}{\partial t}\right) dv

+ \int_v \left[ \frac{\partial s}{\partial \vec{q}} \left(\frac{\partial \vec{q}}{\partial t}\right) + \frac{\partial s}{\partial \vec{J}} \left(\frac{\partial \vec{J}}{\partial t}\right) + \frac{\partial s}{\partial (\partial \Phi/\partial t)} \left(\frac{\partial^2 \Phi}{\partial t^2}\right) \right] dv

- \int_\omega \left[ \varepsilon_e^2 \left(\frac{\partial e}{\partial t}\right) \nabla_n e + \varepsilon_x^2 \left(\frac{\partial X}{\partial t}\right) \nabla_n X + \varepsilon_\phi^2 \left(\frac{\partial \Phi}{\partial t}\right) \nabla_n \Phi \right] d\omega, \quad (15)
\]

where \(\nabla_n\) is the gradient vector pointed by the normal vector \(\vec{n}\).
Now we substitute the balance laws for energy and concentration, Eqs. (9), into Eq. (15), and then use the theorem of divergence. One gets

$$
\frac{dS}{dt} = - \int_\omega \left\{ \varepsilon^2_c \left( \frac{\partial e}{\partial t} \right) \nabla_n e + \left( \frac{\partial s}{\partial e} + \varepsilon^2_e \nabla^2 e \right) q_n + \varepsilon^2_e \left( \frac{\partial X}{\partial t} \right) \nabla_n X + \left( \frac{\partial s}{\partial X} + \varepsilon^2_e \nabla^2 X \right) J_n + \varepsilon^2_e \left( \frac{\partial \Phi}{\partial t} \right) \nabla_n \Phi \right\} \, d\omega \\
+ \int_v \left\{ \bar{q} \cdot \nabla \left[ \frac{\partial s}{\partial e} + \varepsilon^2_e \nabla^2 e \right] + \frac{\partial s}{\partial \bar{q}} \frac{\partial \bar{q}}{\partial t} + \bar{J} \cdot \nabla \left[ \frac{\partial s}{\partial X} + \varepsilon^2_e \nabla^2 X \right] + \frac{\partial s}{\partial \bar{J}} \frac{\partial \bar{J}}{\partial t} + \frac{\partial \Phi}{\partial \bar{q}} \left[ \frac{\partial s}{\partial \Phi} + \varepsilon^2_e \nabla^2 \Phi \right] + \frac{\partial s}{\partial \bar{J}} \frac{\partial \bar{J}}{\partial t} \right\} \, dv,
$$

(16)

where $q_n$ and $J_n$ are the diffusion fluxes pointed by the normal vector $n$.

Using Eq. (16), the change of the entropy, Eqs. (11) - (15), is obtained from Eq. (16). This yields

$$
\frac{dS}{dt} = - \int_\omega J_S d\omega + \int_v \sigma_S dv,
$$

(17)

where

$$
J_S = \varepsilon^2_c \left( \frac{\partial e}{\partial t} \right) \nabla_n e + \left( \frac{\partial s}{\partial e} + \varepsilon^2_e \nabla^2 e \right) q_n \\
+ \varepsilon^2_e \left( \frac{\partial X}{\partial t} \right) \nabla_n X + \left( \frac{\partial s}{\partial X} + \varepsilon^2_e \nabla^2 X \right) J_n \\
+ \varepsilon^2_e \left( \frac{\partial \Phi}{\partial t} \right) \nabla_n \Phi
$$

(18)

is the projection of the entropy flux vector on the normal vector $n$, and

$$
\sigma_S = \bar{q} \cdot \left[ \nabla \left( \frac{\partial s}{\partial e} + \varepsilon^2_e \nabla^2 e \right) - \alpha_0 \frac{\partial \bar{q}}{\partial t} \right] \\
+ \bar{J} \cdot \left[ \nabla \left( \frac{\partial s}{\partial X} + \varepsilon^2_e \nabla^2 X \right) - \alpha_0 \frac{\partial \bar{J}}{\partial t} \right] \\
+ \frac{\partial \Phi}{\partial t} \left[ \frac{\partial s}{\partial \Phi} + \varepsilon^2_e \nabla^2 \Phi - \alpha_0 \frac{\partial^2 \Phi}{\partial t^2} \right] > 0
$$

(19)

is the local entropy production which has a bilinear form in the fluxes ($\bar{q}$, $\bar{J}$, and $\partial \Phi/\partial t$) and their respective conjugate forces (expressions inside the square brackets).

B. Governing equations and thermodynamic consistency

Relation (13) is well known from the phase-field model based on CIT (see, e.g., Ref. 17), whereas the entropy production (19) includes the additional terms $-\alpha_0 \partial \bar{q}/\partial t$, $-\alpha_0 \partial \bar{J}/\partial t$, and $-\alpha_0 \partial^2 \Phi/\partial t^2$ related to the nonequilibrium part of the generalized entropy. This is due to the special form for entropy, Eq. (8), and has a clear physical meaning: far from equilibrium, the dissipative fluxes provide ordering that leads to a decrease of the entropy production near a steady state as compared with the local-equilibrium state characterized by the same values of $e$, $X$, and $\Phi$.

The production $\sigma_S$ of the generalized entropy, Eq. (8), is positive due to the statement of the second law of thermodynamics. This condition implies a relation between fluxes and forces which, in the simplest cases, is assumed to be linear. For Eq. (16), it gives the following set of equations:

- evolution equations for heat and solute diffusion fluxes

$$
\begin{align*}
\bar{q} = (M) \left\{ \nabla \left( \frac{\partial s}{\partial e} + \varepsilon^2_e \nabla^2 e \right) - \alpha_0 \frac{\partial \bar{q}}{\partial t} \right\} \\
\bar{J} = (M) \left\{ \nabla \left( \frac{\partial s}{\partial X} + \varepsilon^2_e \nabla^2 X \right) - \alpha_0 \frac{\partial \bar{J}}{\partial t} \right\}
\end{align*}
$$

(20)

- evolution equation for the phase-field

$$
\frac{\partial \Phi}{\partial t} = M_\phi \left( \frac{\partial s}{\partial \Phi} + \varepsilon^2_\phi \nabla^2 \Phi - \alpha_0 \frac{\partial^2 \Phi}{\partial t^2} \right),
$$

(21)

where

$$
(M) = \begin{pmatrix} M_{ee} & M_{ex} \\ M_{xe} & M_{xx} \end{pmatrix}
$$

(22)

is the matrix of mobilities for thermal and solutal transport, and $M_\phi$ is the mobility of the diffuse interface.
Dependent on composition, the interface mobility is assumed to be
\[ M_\phi = (1 - X)M_\phi^A + XM_\phi^B > 0, \quad (23) \]
where \( M_\phi^A \) and \( M_\phi^B \) are the interface mobility for the transformation in pure systems consisting of \( A \) or \( B \) components, respectively. In various formulations of the phase-field model \([20, 21]\), the mobilities of \( M_\phi^A \) and \( M_\phi^B \) are proportional to the atomic interface kinetic coefficient \( \mu_0 \) and inversely proportional to the interface width \( W_0 \), so that \( M_\phi \sim \mu_0/W_0 \).

The matrix \([22]\) of transport and the interface mobility \([24]\) are assumed to be positively defined for the positive entropy production \( \sigma_S \). The matrix \([22]\) can be considered as symmetric, so that the matrix can be regarded as being positive with the inequality: \( M_{ee} M_{xx} > M_{ex}^2 \). Note that the linear phenomenological laws given by Eqs. \([20]\) and \([21]\) adopt the representation theorem of isotropic tensors \([18]\), according to which fluxes and forces of different tensorial rank do not couple as far as linear relations are involved (this independence of processes of different tensorial rank is also known as the Curie principle). In our case, the vectors of heat and solute diffusion fluxes cannot give rise to the flux of the scalar phase-field flux in a linear description. More complicated nonlinear relations between fluxes and forces consistent with positive entropy production in EIT are considered elsewhere \([22, 24, 27]\).

For simplicity, we ignore both kinds of “cross coupling” effects in Eq. \([20]\), so that \( M_{ee} = M_{xx} = 0 \). Then, substitution of the fluxes from Eq. \([20]\) into the balances \([9]\), respectively, gives
- the governing equation for energy density
\[ \tau_T \frac{\partial^2 e}{\partial t^2} + \frac{\partial e}{\partial t} = -\nabla \cdot \left[ M_{ee} \nabla \left( \frac{\partial s}{\partial e} + \varepsilon_e^2 \nabla^2 e \right) \right], \quad (24) \]
- the governing equation for solute concentration
\[ \tau_D \frac{\partial^2 X}{\partial t^2} + \frac{\partial X}{\partial t} = -\nabla \cdot \left[ M_{xx} \nabla \left( \frac{\partial s}{\partial X} + \varepsilon_x^2 \nabla^2 X \right) \right], \quad (25) \]
in which \( \tau_T = \alpha_q M_{ee} \) is the relaxation time for the heat diffusion flux, and \( \tau_D = \alpha_q M_{xx} \) is the relaxation time for solute diffusion (see Eqs. \([22]\) and Table \([1]\)). After simplifying the transformation, Eq. \([21]\) leads to
- the governing equation for the phase-field
\[ \tau_\Phi \frac{\partial^2 \Phi}{\partial t^2} + \frac{\partial \Phi}{\partial t} = M_\phi \left( \frac{\partial s}{\partial \Phi} + \varepsilon_\Phi^2 \nabla^2 \Phi \right), \quad (26) \]
where \( \tau_\Phi = \alpha_\Phi M_{ee} \) is the timescale of the phase-field kinetics. According to Eq. \([21]\), the acceleration \( \frac{\partial^2 \Phi}{\partial t^2} \) of the phase-field appears due to introduction of both \( \Phi \) and \( \partial \Phi/\partial t \) as independent variables and characterizes inertial effects inside the width of diffuse interface.

Equations \([23]\)-\([26]\) are the central outcome of our proposal [or, to mention a more complicated setting, we could also refer to equations \([20]\)-\([21]\)]. The role of the relaxation times is clear: they characterize the delay with which \( \bar{q} \) and \( \bar{J} \) reduce to their classical expressions (corresponding to classical transport equations), and the delay with which the inertial effects in the dynamics of the interfacial region are lost. The relaxation terms may be neglected in many circumstances, but become crucial in some important situations, leading, for instance, to a maximum possible value for the speed of advancement of the interface (in contrast to classic theory which allows for an infinite speed of propagation), and to the possibility of oscillatory phenomena in the width of the interface. Thus, the role of the new terms is not simply to add some new undetermined parameters (relaxation times) allowing for an improved fit of experimental results. These terms also play an important conceptual role, as they drastically change the possible kinds of behavior of the system.

Some comments on the consistency of our proposal can be outlined. First of all, we may refer to its internal consistency as a thermodynamic (macroscopic) theory. Second, one must check its consistency with microscopic descriptions based, for instance, on kinetic theory, or on linear response theory, or in other statistical (microscopic) theories. Finally, one must check its consistency with experimental results.

Here, we comment on the internal thermodynamic consistency and, in the next Section, we shall refer to its consistency with a statistical theory, based on the fluctuation-dissipation theorem. In this theoretical paper we do not refer to experimental results. We assume that a consistent nonequilibrium thermodynamic theory should satisfy two main conditions:

(i) the generalized or extended entropy must be maximum at equilibrium;
(ii) the entropy production must be positive.

To these two conditions one could add two more requirements:

(iii) the second differential of the entropy with respect to its basic variables (which is related to the dynamics of the variables) must be negative in order to lead to dynamically stable solutions;
(iv) the generalized equations of state obtained by differentiation of the generalized entropy must have a physical meaning consistent with experiments.

It can be seen immediately that the essential conditions (i) and (ii) are satisfied in our proposal. Indeed, the form \([5]\) and \([13]\) of the entropy guarantees that homogeneous equilibrium state has the maximum entropy as compared to nonequilibrium states with the same local values of \( e, X \) and \( \Phi \). Furthermore, introduction of the constitutive equations \([20]-[21]\) into the expression \([10]\) of the entropy production yields for the latter a definite positive expression:

\[ \sigma_S = \left( \frac{\bar{q}}{\bar{J}} \right) (M)^{-1} \left\{ \frac{\partial \Phi}{\partial \bar{q}} \right\} + M_\phi^{-1} \left( \frac{\partial \Phi}{\partial \bar{J}} \right)^2 > 0. \quad (27) \]
As we noted, the transport matrix \( (\mathcal{M}) \) and the interface mobility \( M_\phi \) are assumed to be positively defined for the positive entropy production, \( \sigma_S > 0 \). If one included higher-order nonlinear terms into the entropy \( S \) or in the constitutive equations \( (20)-(21) \), thermodynamic consistency would be more difficult to check than in our second-order approximation \( S \). This approximation is sufficient to deal with a wide range of physical problems.

We shall not deal with conditions (iii) and (iv), which are subtler and typically involve nonlinear effects. For an indication of their analysis in some situations involving only \( \vec{q} \) as nonequilibrium variables, the reader is referred to the monograph \( [24] \).

V. GENERALIZATION OF THE MODEL

The governing equations \( (24)-(26) \) present causal propagation of heat and mass signals and a dissipative-wave advancing of a diffuse interface. We generalize them into evolution equations which are nonlinear in time. First, equations of state are considered from the point of view of the relaxation functions for the fluxes. Second, nonlinear evolution equations of a general type are derived from a variational formulation.

A. Relaxation functions for the fluxes

Let’s take into consideration a prehistory of the change of the phase-field in a point of a system. Such a prehistory must be taken if the system is not in local equilibrium. We shall use a functional description with a memory function.

We use the entropy functional \( (14) \), as before, to derive the equations of the model. In the absence of local equilibrium, one may incorporate the prehistory of the diffusion process. Then, the connections between the fluxes, \( \vec{q}, \vec{J} \), and \( \partial \Phi / \partial t \), from the one side, and driving forces, \( \nabla (\delta S/\delta e) \), \( \nabla (\delta S/\delta X) \), and \( \delta S / \delta \Phi \), from the other side, are defined by the following integral forms:

- relaxation of the heat flux

\[
\vec{q}(\vec{r}, t) = \int_{-\infty}^{t} D_q(t - t^*) \nabla \frac{\delta S(t^*, \vec{r})}{\delta e} dt^*,
\]

(28)

- relaxation of the solute diffusion flux

\[
\vec{J}(\vec{r}, t) = \int_{-\infty}^{t} D_j(t - t^*) \nabla \frac{\delta S(t^*, \vec{r})}{\delta X} dt^*,
\]

(29)

- relaxation of the phase-field rate of change

\[
\frac{1}{M_\phi} \frac{\partial \Phi}{\partial t} = - \int_{-\infty}^{t} D_\phi(t - t^*) \frac{\delta S(t^*, \vec{r})}{\delta \Phi} dt^*,
\]

(30)

where \( D_R = \{ D_q, D_j, D_\phi \} \) are the relaxation kernels for the fluxes, and the variational derivatives are obtained from the following expressions

\[
\frac{\delta S}{\delta e} = \frac{\partial s}{\partial e} + \varepsilon^2 \nabla^2 e, \quad \frac{\delta S}{\delta X} = \frac{\partial s}{\partial X} + \varepsilon^2 \nabla^2 X,
\]

\[
\frac{\delta S}{\delta \Phi} = \frac{\partial s}{\partial \Phi} + \varepsilon^2 \nabla^2 \Phi.
\]

(31)

After substitution of expressions for the heat flux relaxation, Eq. \( (28) \), and the solute diffusion relaxation, Eq. \( (29) \), into the balance laws for energy and solute concentration, Eq. \( (10) \), respectively, one can get the following integro-differential equations

\[
\frac{\partial e(\vec{r}, t)}{\partial t} = - \nabla \cdot \int_{-\infty}^{t} D_q(t - t^*) \nabla \frac{\delta S(t^*, \vec{r})}{\delta e} dt^*,
\]

(32)

\[
\frac{\partial X(\vec{r}, t)}{\partial t} = - \nabla \cdot \int_{-\infty}^{t} D_j(t - t^*) \nabla \frac{\delta S(t^*, \vec{r})}{\delta X} dt^*.
\]

Together with relaxation of the phase-field, Eq. \( (30) \), the general system evolution during phase transformations is described by Eqs. \( (32) \).

When the relaxation functions \( D_R \) are specially defined, Eqs. \( (30) \) and \( (32) \) can be reduced to known models. Particularly, for the important class of dissipative and hyperbolic models, one can take the relaxation kernels in the following forms

\[
D_R = \begin{cases} D_R(0) \equiv \text{const}, & \text{wave propagation,} \\ D_R(0) \delta(t - t^*), & \text{dissipation,} \\ D_R(0) \exp\left( - \frac{t - t^*}{\tau} \right), & \text{wave and dissipation,} \end{cases}
\]

(33)

where \( D_R(0) = \{ D_q(0), D_j(0), D_\phi(0) \} \) are the relaxation kernels for the fluxes at present time \( t = t^* \), and \( \tau = \{ \tau_e, \tau_D, \tau_\Phi \} \) are the characteristic relaxation times for the fluxes.

The different transformations within the diffuse-interface are described by different kernels in the integrals \( (28)-(30) \). As it follows from Eq. \( (33) \), the relaxation functions \( D_R \) describe the memory of the system by assigning different weights to different moments in the past. Dissipation corresponds to a zero-memory transformation, i.e. the only relevant contributions are the ”last” ones. In contrast to this situation, the infinite memory transformation with \( D_R \equiv \text{const} \) leads to undamped wave propagation of the heat, solute, or the interface advancement. In between, the combination of the wave and dissipative regimes described by the exponential law can be observed during rapid phase transformations. This is the case of hyperbolic phase-field model described in Sec. \( IV \). For the latter case, the relevance of all contributions to the fluxes decreases as the system moves to the past.

In Sec. \( IV \) the model macroscopic consistency of the statements of EIT has been shown. Now, the consistency
of our macroscopic approach with a microscopic description is verified in relation to the outcomes following from the fluctuation-dissipation theorem.

The memory functions introduced in Eqs. (28)-(30) may be related to our analysis of the dynamics of the fluxes $\vec{q}$ and $\vec{F}$ and of $\partial \Phi / \partial t$ proposed by constitutive equations (20)-(21). To do this, first, we may consider the fluctuation-dissipation theorem relating response memory functions to the time-correlation function of the corresponding fluxes (see, e.g., Ref. [4]). This will allow us to show the consistency of our macroscopic formulation with the microscopic basis provided by the fluctuation-dissipation theorem.

The corresponding expressions are

$$D_q(t-t^*) = \frac{1}{k_BT} \langle \vec{q}(t)\vec{q}(t^*) \rangle_{eq},$$

$$D_j(t-t^*) = \frac{1}{k_BT} \langle \vec{J}(t)\vec{J}(t^*) \rangle_{eq},$$

$$D_\phi(t-t^*) = \frac{1}{k_BT} \langle \partial_t \Phi(t)\partial_t \Phi(t^*) \rangle_{eq}. \tag{34}$$

Here $k_B$ is Boltzmann’s constant, $\vec{q}$, $\vec{J}$, and $\partial_t \Phi$ stand for the microscopic operators for the heat flux, diffusion flux and the time derivative of $\Phi$, respectively, and $\langle \cdots \rangle_{eq}$ means an average over an equilibrium ensemble in statistical mechanics (as, for instance, the canonical one).

Relations (34) play an important role in modern statistical mechanics, and may be formally derived from the Liouville equation in the framework of linear-response theory or from information theory [10, 54]. However, from a practical point of view, the computation of the evolution of the microscopic operators for $\vec{q}$, $\vec{J}$ or $\partial_t \Phi$ on purely microscopic grounds is an overwhelming task exceeding actual capabilities. Such an evolution is either obtained by computer simulations, or tentatively given by a reasonable form inspired on phenomenological grounds. Thus, our evolution equations (20)-(21) for $\vec{q}$, $\vec{J}$ and $\partial_t \Phi$ may be considered as a macroscopic modelling of the evolution of the fluxes, which according to Eq. (34) is equivalent to proposing a form for the corresponding memory functions introduced in Eqs. (28)-(30). In general terms, it could be said that, according to Eq. (34), the study of the evolution of the fluxes around equilibrium is equivalent to the determination of the corresponding memory functions.

Constitutive equations (20)-(21) imply that fluctuations of $\vec{q}$ and $\vec{J}$ near a homogeneous equilibrium state will decay exponentially as $\vec{q}(t) = \vec{q}(0) \exp(-t/\tau_T)$ and $\vec{J}(t) = \vec{J}(0) \exp(-t/\tau_D)$. Introducing these expressions into Eq. (34) one obtains

$$D_q(t-t^*) = \frac{1}{k_BT} \langle \vec{q}(t)\vec{q}(0) \rangle_{eq} \exp\left(-\frac{t-t^*}{\tau_T}\right),$$

$$D_j(t-t^*) = \frac{1}{k_BT} \langle \vec{J}(0)\vec{J}(t) \rangle_{eq} \exp\left(-\frac{t-t^*}{\tau_D}\right). \tag{35}$$

which may be rewritten as

$$D_q(t-t^*) = D_q(0) \exp\left(-\frac{t-t^*}{\tau_T}\right),$$

$$D_j(t-t^*) = D_j(0) \exp\left(-\frac{t-t^*}{\tau_D}\right). \tag{36}$$

Indeed, when the microscopic expressions for $\vec{q}$ and $\vec{J}$ corresponding to an ideal gas are introduced into Eq. (35) and the equilibrium average is performed (over a Maxwell-Boltzmann distribution function), the results for the $D_q(0)$ and $D_j(0)$ are equivalent to those obtained from the kinetic theory of gases in the time-relaxation approximation [44].

Note, finally, that the usual transport coefficients (thermal conductivity, diffusion coefficient) may be obtained (when the relaxation time is sufficiently short) by integration of Eq. (34), as

$$\lambda = \frac{1}{k_BT} \int_{-\infty}^{\infty} \langle \vec{q}(t)\vec{q}(0) \rangle_{eq} dt,$$

$$D = \frac{1}{k_BT} \int_{-\infty}^{\infty} \langle \vec{J}(t)\vec{J}(0) \rangle_{eq} dt, \tag{37}$$

which are the well-known Green-Kubo formulae for transport coefficients [24, 49, 50]. Thus, our macroscopic formalism is consistent with the microscopic fluctuation-dissipation theorem. It provides, in fact, a phenomenological complement to the fluctuation-dissipation expressions, which are the formal expressions from which it is difficult to obtain on exact grounds the form of the memory functions.

B. A variational principle and Euler-Lagrange equations

We assume, as above, that the generalized entropy density $s$ is a continuous and differentiable function defined by the local equilibrium contribution $s_e$ and flux-dependent nonequilibrium part $s_{ne}$ with the total set of variables $\{e, X, \Phi\}$ and fluxes $(\vec{q}, \vec{J}, \partial \Phi / \partial t)$, and also by introducing general forms of the entropy flux $\hat{S}$ and the source $\sigma_S$ in Eq. (10). Depending on their own tensorial character, these are

$$\left( \frac{\partial s}{\partial e} \right)_q = \beta_1^s(e, I_q), \quad \left( \frac{\partial s}{\partial X} \right)_j = \beta_1^s(X, I_j),$$

$$\left( \frac{\partial s}{\partial \Phi} \right)_{\phi} = \beta_2^s(\Phi, I_{\phi}), \quad \left( \frac{\partial s}{\partial \phi} \right)_e = \beta_2^s(e, I_q)\phi.$$
\[
\left( \frac{\partial s}{\partial J} \right)_X = \beta_2^X (X, I_j) \vec{J},
\]
\[
\left( \frac{\partial s}{\partial (\partial \Phi / \partial t)} \right)_\Phi = \beta_2^\Phi (\Phi, I_\Phi) \frac{\partial \Phi}{\partial t},
\]
\[
\vec{J}_S = \beta_3^S (e, I_q) \vec{q} + \beta_3^X (X, I_j) \vec{J} + \beta_3^\Phi (\Phi, I_\Phi) \frac{\partial \Phi}{\partial t},
\]
\[
\sigma_S = \beta_4^S (e, I_q) + \beta_4^X (X, I_j) + \beta_4^\Phi (\Phi, I_\Phi),
\]
where
\[
I_q = \vec{q} \cdot \vec{q}, \quad I_j = \vec{J} \cdot \vec{J}, \quad I_\Phi = \left( \frac{\partial \Phi}{\partial t} \right)^2
\]
are the single scalar invariants of the extended set of variables, and \( \beta_i \) are the scalar functions depending on classic variables \((e, X, \Phi)\) and invariants \(I_i\). Then, utilizing Eqs. (38), the generalized Gibbs equation gives the time derivative of the entropy density as follows:
\[
\frac{\partial s}{\partial t} = \beta_1^i (e, I_q) \frac{\partial e}{\partial t} + \beta_2^i (e, I_q) \frac{\partial \vec{q}}{\partial t} + \beta_3^X (X, I_j) \frac{\partial \vec{J}}{\partial t} + \beta_4^\Phi (\Phi, I_\Phi) \frac{\partial \Phi}{\partial t} + \beta_5^\Phi (\Phi, I_\Phi) \frac{\partial^2 \Phi}{\partial t^2}.
\]
Locally, Eq. (40) is satisfied as a balance law and, for the entire system, one can postulate extremal condition in the Lagrangian form of \(L = \int_v (\partial s / \partial t + \nabla \cdot \vec{J}_S - \sigma_S)dv \rightarrow \text{extr} \), implying an extremal difference between the “kinetic” part \(\int_v (\partial s / \partial t + \nabla \cdot \vec{J}_S)dv\) and the “potential” part \(\int_v \sigma_Sdv\). Then, the entropy density satisfies the following variational principle
\[
\delta L = \delta \int_v dv \left( \frac{\partial s}{\partial t} + \nabla \cdot \vec{J}_S - \sigma_S \right) = 0,
\]
in which the variation \(\delta\) is carried out only on the nonconserved flux variables \(\vec{q}, \vec{J}, \) and \(\partial \Phi / \partial t\), i.e. \(\delta\) is taken only over the space \(\{F\}\) from the set \(\{\text{I}\}\) while the variables \(e, X, \) and \(\Phi\) from the set \(\{C\}\) remain constant during the variation. Also, during the variation, the tangent thermodynamic space [time and spatial derivatives from the set \(\{\text{I}\}\)] is fixed. From this it follows that Eq. (41) is a variational principle of a restricted type.

Using balance laws and substitution of Eqs. (35) and (40) into variational principle (41) leads to
\[
\delta \int_v dv \left[ (\beta_5^c - \beta_4^c) \nabla \cdot \vec{q} + \left( \beta_2^c \frac{\partial \vec{q}}{\partial t} + \nabla \beta_3^c \right) \cdot \vec{q} - \beta_4^c \right] + (\beta_3^X - \beta_4^X) \nabla \cdot \vec{J} + \left( \beta_2^c \frac{\partial \vec{J}}{\partial t} + \nabla \beta_3^X \right) \cdot \vec{J} - \beta_4^X
\]
\[
+ \beta_3^X \frac{\partial \Phi}{\partial t} + \beta_3^\Phi \frac{\partial \Phi}{\partial t} + \left( \beta_2^c \frac{\partial^2 \Phi}{\partial t^2} + \nabla \beta_3^\Phi \right) \frac{\partial \Phi}{\partial t} - \beta_4^c = 0.
\]
Variance of Eq. (42) is obtained by taking as constants the time derivatives, gradients and divergences. Since \(\delta I_q = 2 \vec{q} \cdot \delta \vec{q}, \delta I_j = 2 \vec{J} \cdot \delta \vec{J}\), and \(\delta I_\Phi = 2 (\partial \Phi / \partial t) \delta (\partial \Phi / \partial t)\) from Eq. (42) one gets
\[
\int_v dv \left[ 2 \left( \frac{\partial \beta_3^c}{\partial I_q} - \frac{\partial \beta_4^c}{\partial I_j} \right) \vec{q} \cdot \delta \vec{q} + \beta_5^c \frac{\partial \vec{q}}{\partial t} + \frac{\partial \beta_3^c}{\partial I_q} \frac{\partial \vec{q}}{\partial t} + \frac{\partial \beta_4^c}{\partial I_j} \frac{\partial \vec{q}}{\partial t} + \nabla \beta_3^c - 2 \frac{\partial \beta_4^c}{\partial I_j} \delta \vec{q} \right]
\]
\[
+ \int_v dv \left[ 2 \frac{\partial \beta_3^X}{\partial I_j} - \frac{\partial \beta_4^X}{\partial I_j} \right] \vec{J} \cdot \delta \vec{J} + \beta_3^X \frac{\partial \vec{J}}{\partial t} + \frac{\partial \beta_3^X}{\partial I_j} \frac{\partial \vec{J}}{\partial t} + \nabla \beta_3^X - 2 \frac{\partial \beta_4^X}{\partial I_j} \delta \vec{J} \right]
\]
\[
+ \int_v dv \left[ 2 \frac{\partial \beta_3^\Phi}{\partial I_\Phi} \left( \frac{\partial \Phi}{\partial t} \right)^2 + 2 \frac{\partial \beta_3^c}{\partial I_q} \frac{\partial \Phi}{\partial t} + \beta_5^c \frac{\partial^2 \Phi}{\partial t^2} + 2 \frac{\partial \beta_3^c}{\partial I_q} \frac{\partial^2 \Phi}{\partial t^2} + 2 \frac{\partial \beta_3^c}{\partial I_\Phi} \frac{\partial^2 \Phi}{\partial t^2} + 2 \frac{\partial \beta_3^\Phi}{\partial I_\Phi} \delta \left( \frac{\partial \Phi}{\partial t} \right) \right] = 0.
\]
\[
+ \left[ \left( \frac{\partial \beta_3^X}{\partial \mathbf{q}} \cdot \frac{\partial \beta_3^X}{\partial \mathbf{q}} \right) \nabla \cdot \mathbf{q} - \frac{\partial \beta_3^X}{\partial \mathbf{q}} \right] \mathbf{q} = -\frac{1}{2} \nabla \beta_3^X, \tag{44}
\]

- evolution equation for the solute diffusion flux
\[
\left( \frac{\partial \beta_3^X}{\partial \mathbf{q}} \cdot \mathbf{f} + \beta_3^X \mathbf{J} \right) \cdot \frac{\partial \mathbf{f}}{\partial t} + \left[ \left( \frac{\partial \beta_3^X}{\partial \mathbf{q}} - \frac{\partial \beta_3^Y}{\partial \mathbf{q}} \right) \nabla \cdot \mathbf{J} - \frac{\partial \beta_3^Y}{\partial \mathbf{q}} \right] \mathbf{J} = -\frac{1}{2} \nabla \beta_3^X, \tag{45}
\]

- evolution equation for the phase-field
\[
\left( \frac{\partial \beta_3^X}{\partial \mathbf{q}} \cdot \mathbf{f} + \beta_3^X \mathbf{J} \right) \cdot \frac{\partial \mathbf{f}}{\partial t} + \left[ \left( \frac{\partial \beta_3^X}{\partial \mathbf{q}} - \frac{\partial \beta_3^Y}{\partial \mathbf{q}} \right) \nabla \cdot \mathbf{J} - \frac{\partial \beta_3^Y}{\partial \mathbf{q}} \right] \mathbf{J} = -\frac{1}{2} \nabla \beta_3^X, \tag{46}
\]

where \( \mathbf{U} \) is the unit tensor of second rank.

Eqs. \((44)-(46)\) are nonlinear evolution equations for \( \mathbf{q}, \mathbf{J}, \) and \( \partial \mathbf{f}/\partial t \) and they are of the general form of evolution equations \((44)-(46)\). Indeed, the nonlinearity is clearly seen from the following form of these equations:

\[
\tau_T(e, \mathbf{q}) \frac{\partial \mathbf{q}}{\partial t} + \mathbf{q} = M_{ee}(e, \mathbf{q}) \nabla \beta_3^X,
\]

\[
\tau_D(X, \mathbf{J}) \frac{\partial \mathbf{J}}{\partial t} + \mathbf{J} = M_{xx}(X, \mathbf{J}) \nabla \beta_3^X,
\]

\[
\tau_f \left( \Phi \frac{\partial \Phi}{\partial t} \right) \frac{\partial^2 \Phi}{\partial t^2} + \frac{\partial \Phi}{\partial t} = M_{f} \left( \Phi \frac{\partial \Phi}{\partial t} \right) \nabla \beta_3^X \tag{47}
\]

VI. RELATION TO EXISTING MODELS

It is interesting to note that sharp-interface and diffuse-interface models with relaxation of fluxes have been used to describe transient processes in various nonequilibrium systems (see monograph \([52]\). Chapter 4). Therefore we synthesize here several previous and very recent results in comparison with the developed hyperbolic model (Sec. IV) and generalized model (Sec. V) of rapid phase transformation.

A. Superconductivity

Ginzburg and Landau established their variational principle for the continuous transition from the normal to the superconducting phase \([8]\). They used a free energy density with a gradient term which has been further used in many phenomena (e.g., in description of spinodal decomposition \([53]\) or crystal growth \([54]\)). As a logical extension, the transition between the normal and the superconducting phases can be described with the delay given by equations of the hyperbolic model [starting from the functional of the form \((14)\) or using generalized models with memory, Sec. V A].

Generally, equations \((21)-(24)\) are consistent with the generalized entropy density given by Eq. \((8)\). The equations are reduced to the classic equations from Refs. \([8, 52, 53]\) when the times \( \tau_T, \tau_D, \) and \( \tau_f \) tend to zero. Furthermore, the entropy density \((8)\) together with the evolution equations \((20)\) has been justified microscopically \([24, 20]\) for the one-component system and from Grad’s procedure for monatomic gases.

The choice of thermodynamic potential is important, as it governs the transition from metastable state to the stable one. Normally, the potential for transition is included in the expression for entropy density (or for free energy density) in the form of a double-well function or by a monotonically increasing function incorporating nonequilibrium conditions at the interface \([8, 12, 55]\). In the present paper, we do not give an explicit form of \( s_e \) in Eq. \((8)\) and present governing equations \((21)-(24)\) [or variational derivatives \((41)\) in a general form. The choice of the thermodynamic potential might be given for the problem under consideration.

B. Glass transition, structural relaxation and phase separation

Jäckle et al. \([55]\) considered isothermal phase transformation in the presence of additional slow structural relaxation variables. Considering the dynamics based on the relaxation chemical potential, these authors refer their model to systems with phase separation and to slow structural relaxation in polymeric solutions in the proximity of the glass transition temperature. The calculation has shown that, even at the early stages of phase separation, equation for chemical potential with memory may give pronounced deviations from the predictions of classic linear Cahn-Hillard’s model \([52]\).

Phase separation during spinodal decomposition may proceed under local nonequilibrium conditions in solute diffusion field offered by rapid quenching. As it has been demonstrated in computational modeling \([56]\), the rapidly quenched liquid mixtures under decomposition exhibit non-equilibrium patterns, evolving with universalities different from those extracted from the Cahn and Hillard’s model.

Local nonequilibrium separation in liquids can be de-
scribed in terms of EIT as a model for isothermal spinodal decomposition in a binary system [23], in conditions of large deviation from thermodynamic equilibrium. The dynamics of the diffusion flux \( \vec{J} \) as a fast variable from the set \( \{1\} \) is consistent with the characteristic time of local rearrangement of particles (atoms or molecules) or with the time of relaxation of diffusive flux to its local equilibrium steady-state value. The model equation for spinodal decomposition of a binary system is the generalized Cahn-Hilliard equation of the form of Eq. (25) for local nonequilibrium solute redistribution. In this case, the dynamics of rapidly quenched decomposition is described for short periods of time or large gradients of chemical composition.

C. Shear flow, viscoelastic fluids and diffusion-reaction systems

The system of coupled evolution equations (20)–(21) describes, in fact, a process of phase separation under shear if temperature is replaced by viscous pressure tensor. In this case, one may get the condition defining the spinodal line in non-equilibrium states [see monograph 31, Chapter 6]. As a reduced one, equation of type (20) or (25), endowed with homogeneous Dirichlet boundary conditions, has been introduced to model the behavior of certain viscoelastic fluids and to predict the velocity of flow [57].

In addition, equation of type (25) is used to predict a wavefront in time-delayed reaction-diffusion systems of the generalized Fisher’s equation [58]. The speed of the travelling wave depends on the relaxation time and therefore spreading of population in reaction-diffusion system might be predicted with great flexibility. One of the consequences of this equation, reduced to Eqs. (21) or (25) for modelling a hyperbolic reaction-diffusion system [with \( \varepsilon_x = 0 \) or \( \varepsilon_y = 0 \), respectively], might be considered in an exciting example suggested by Fort and Mendez in Ref. 59 for neolithic advancing of human groups across Europe. They have shown, in particular, that hyperbolic reaction-diffusion equations of type of Eqs. (21) or (25) predict the population spreading during the European past in agreement with the existing archaeological data.

D. Rapid solidification

At deep supercoolings in a solidifying system, or at high velocity of the solid-liquid interface, it is necessary to take into account local nonequilibrium effects in solute diffusion and to use a non-Fickian model for transport processes which is compatible with EIT [21, 41]. The problem of rapid solidification within the sharp-interface limit is described by generalized Stefan problem (so-called “self-consistent hyperbolic Stefan problem” [31, 32]) which takes into account local nonequilibrium both at the interface and within the bulk phases. In such a case, the spatio-temporal evolution of solute concentration is described by the partial differential equation (26) of a hyperbolic type [with \( \varepsilon_x = 0 \)] which takes into account the relaxation of solute diffusion flux to the local thermodynamical equilibrium in a rapidly solidifying system.

Advancing of the diffuse-interface with a higher velocity comparable with the solute diffusion speed is also described by the phase-field model with relaxation of the diffusion flux (26). It has been shown that choosing the concrete form of the entropy (as the thermodynamic potential), one may recover the existing models based on the CIT and analyze solidification under local nonequilibrium conditions.

E. Motion of antiphase domains

In the description of diffuse interface kinetics, Allen and Cahn [10] proposed a model for evolution of the non-conserved order field during antiphase domain coarsening. For isotropic interfaces, gradient flow gives the Allen-Cahn equation by taking \( \tau_\phi = 0 \) in Eq. (26). This equation is true in the case of low inertial effects in comparison with the dissipative effects. With finite relaxation time, \( \tau_\phi \), and finite acceleration, \( \partial^2 \Phi / \partial t^2 \), Eq. (26) predicts the evolution of coarsening with relaxation. It is reasonable to say that the generalized Allen-Cahn equation (26) is true for the case of significant inertial effects during the motion of antiphase domains.

As an advancing of the Allen and Cahn’s model, the process of the interface motion by mean curvature with delayed response has been analyzed recently. Rotstein et al. [60] developed the phase-field model based on equations similar to Eqs. (25) and (26). These authors described the first-order transition with the delayed response of the system due to slow relaxation of internal variables. Using the exponential relaxation function for wave and dissipative mode, Eq. (55), which leads to the hyperbolic phase-field model, the dynamics of the perturbed motion of interface by mean curvature has been considered. It has been shown in Ref. 60 that internal relaxing effects induce damped oscillations in the interfacial motion during crystalline coarsening. As opposed to the classic parabolic phase-field model, the hyperbolic phase-field model predicts these interfacial oscillations in qualitative consistency with the oscillations on the surface of quantum crystals [61] and in crystallization waves in helium [62]. From a mathematical viewpoint, a search for existence and uniqueness of the solution and some well-posedness results for the problem of motion by mean curvature using the phase-field model with memory are beginning to be presented (see Ref. [63]).
F. Complex (dusty) plasmas

Recent investigation into the field of complex (dusty) plasma physics show that this system exhibits a complicated behavior which depends on the behavior of its “subsystems” which are represented by electrons, ions, neutral gas, and charged dust particles. All of them have their own relaxation time to local equilibrium; therefore, interaction among them may lead to a delay of relaxation to local equilibrium in plasma. Moreover, in the electronic subsystem of plasma, local equilibrium does not exist, that stimulates development of theories beyond local equilibrium [64]. Interaction of different subsystems in complex (dusty) plasmas with missing local thermodynamic equilibrium in the electronic subsystem, makes the description of observed experimental data of this object rather complicated.

Experimental results of Morfill et al. [65] from plasma observations exhibit unusual behavior from weak collisionless interaction of gases to fluid flow with further possible crystallization of plasma. These results are described by means of molecular dynamic simulations [66]. The field approach, also, seems to be also applicable due to the fact that during transitions in plasma, the characteristic size of patterns is on the mesoscopic or even macroscopic scale. The field approach to a heat- and electronically-conducting fluid has been demonstrated in ionized gases [51] using equations of generalized type of Eqs. (44)-(46).

VII. CONCLUSIONS

The diffuse-interface model for rapid phase transformation in metastable binary systems has been presented. To describe the steep but smooth change of phases within the width of diffuse interface, we use the formalism of the phase-field model.

Rapid phase transformations may proceed under local nonequilibrium conditions. In our phenomenological macroscopic description, we extend the classic set of independent thermodynamic variables by inclusion of dissipative fluxes as additional basic variables. The evolution of the fluxes is characterized by their own dynamics with relaxation times \( \tau \) summarized in Table 1. Thus, the extended set \( \Pi \) of variables allows one to describe phase transformations with finite interface velocity that is comparable or even higher than \( l/\tau \), where \( l \) is the mean-free-path of particles (atoms).

The evolution equations for the hyperbolic phase-field model with dissipation are derived from an entropy functional \( I^{\Pi} \) based on the extended set \( \Pi \) of independent thermodynamic variables. This model yields a definite positive entropy production \( I^{\Pi} \) in consistency with the second law of thermodynamics.

Generalization of the model has been done by introducing memory functions and using a variational principle. As a result, the consistency of the macroscopic approach with the macroscopic fluctuation-dissipation theorem has been found for the phase-field with memory [Eqs. (34)-(37)] and nonlinear evolution equations [Eqs. (41)-(46)] are derived from the variational principle \( I^{\Pi} \).

The derived equations for the evolution of diffuse interface were correlated with existing models of nonequilibrium transport processes and for systems under phase transformation. Particularly, we compare our derivation to models of superconductivity, phase separation, viscoelastic or electronically-conducting fluids, interface motion by mean curvature, rapidly solidifying systems, and reaction-diffusion systems.

Acknowledgments

P.G. acknowledges financial support from the German Research Foundation (DFG - Deutsche Forschungsgemeinschaft) under the project No. HE 1601/13. He also acknowledges the support of the Administration of the Physical Statistics Group during his stay in Universitat Autonoma de Barcelona. D.J. acknowledges financial support from the Dirección General de Investigación of the Spanish Ministry of Science and Technology BFM 2003-06033 and the Direcció General de Recerca of the Generalitat de Catalunya under grant 2001 SGR-00186.
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