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Relation between bulk and interface descriptions of alloy solidification

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From a simple bulk model for the one-dimensional steady-state solidification of a dilute binary alloy we derive the corresponding interface description. Our derivation leads to exact expressions for the fluxes and forces at the interface and for the set of Onsager coefficients. The constitutive equations, connecting the crystallization and diffusion fluxes and forces, decouple in the low-velocity limit and there generate an occasionally negative, but nevertheless thermodynamically consistent friction coefficient. We, moreover, discover a continuous symmetry, which is independent of our model and allows to decouple the constitutive equations for the two components of the alloy for arbitrary growth velocities.

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I. INTRODUCTION

The interface kinetics at the solidification front of a growing dilute binary alloy has been described by Baker and Cahn [1] within the framework of linear irreversible thermodynamics. An apparent violation of the Onsager symmetries in their approach has led to several partly controversial discussions in papers by Caroli, Caroli, and Roulet [2], by Kaplan, Aziz, and Gray [3], and in the review [4] by Hillert. Another apparent paradox is the possible appearance of a negative friction coefficient in the crystallization flux-force relation. This unexpected effect has been observed in the phase-field approach by Karma and Rappel [5], and in Ref. [6] has been shown to be compatible with the principle of a positive entropy production. A thorough discussion of this point within a phenomenological interface description has recently also been presented by Brener and Temkin [7] considering the one-dimensional steady-state solidification of a pure material and of a binary alloy. A noteworthy question was posed in this treatment, concerning the origin of the off-diagonal Onsager coefficients in view of the fact that they apparently have no counterpart in standard phase-field models.

In the present paper we are going to create a clarifying picture of the situation by presenting a transparent exact derivation of an interface description from a bulk model for the case of solidification of a dilute binary alloy. Since we are mainly interested in kinetic effects rather than in curvature corrections at nonplanar interfaces, we focus, following Ref. [7], on the scenario of a one-dimensional steady-state motion of the solidification front. In our initially more microscopic model we will, however, allow values of the front velocity in the rapid-growth regime. Conceptually, our procedure utilizes the capillary-wave representation of a phase-field model, previously worked out in Ref. [6]. A convenience of this approach is that the artificial critical point, unavoidably appearing in phase-field models, is effectively shifted to infinite temperatures by projection to the soft modes of the system, which are the capillary waves of the interface and the bulk diffusion mode of the solute component. The freedom in the choice of the original phase-field model, furthermore, allows us to select a simple, nevertheless representative capillary-wave model.

Our result for the entropy production in the interface region suggests to define pairs of fluxes and of forces at the interface, which carry the full velocity dependence due to the solute trapping effect. The Onsager matrix, appearing in the constitutive equations connecting these pairs, is exactly calculated, and, remarkably, turns out to be velocity independent. One, in particular, observes that the off-diagonal Onsager coefficients derive from the coupling between the interface position and the solute concentration in the effective Hamiltonian of the system. As a consequence, they even appear in the absence of kinetic cross couplings in the original phase-field model. Such couplings have recently been proposed by Brener and Boussinot [8], but are absent in standard phase-field models, as emphasized by Bi and Sekerka [9].

We next map the chosen favored basis of fluxes and forces onto the more often used basis of crystallization and diffusion fluxes and forces. The Onsager matrix in this basis derives from the original one by a similarity transformation, which preserves its sign and symmetry properties. In the low-velocity limit of this description a two-parameter continuous symmetry is seen to arise, which does not change the constitutive equations and, consequently, also conserves the entropy production. The transformed set of kinetic coefficients, however, does in general not form an Onsager matrix due to the entrance of the two free parameters. By a convenient choice of the latter, a decoupled low-velocity form of the constitutive equations can be achieved, which, in a simple way, shows the existence of a sometimes negative, but nevertheless, thermodynamically consistent friction coefficient.

We, finally, consider the mapping from the basis of crystallization and diffusion fluxes and forces to the also frequently used basis of two-component fluxes and forces. The associated Onsager matrix again derives from the original one by a similarity transformation, once more preserving its sign and symmetry properties. Contrary to this, apparent violations of Onsager symmetries have been reported by the authors of Refs. [1,3]. Both papers, however, suffer from a conceptional mistake, which, deviating from the authors of Ref. [2], we uncover, using the example of a simple model, borrowed from Ref. [1]. Another issue, visible in the two-component representation, is the existence of a second more general symmetry, which applies to arbitrary values of the growth velocity in all approaches, dealing with a planar solidification front. This symmetry can again be used to decouple the constitutive equations, in which the two remaining diagonal coefficients turn out to have opposite signs. Due to this, the two driving forces have opposite orientations, a necessary premise of the solute-trapping effect.

II. CAPILLARY-WAVE MODEL

Based on a phase-field description, we have established in Ref. [6] a capillary-wave model for the solidification of a dilute binary alloy where the interface position $Z(\mathbf{x},t)$ enters as an extra field variable in addition to the solute concentration $C(\mathbf{r},t)$. In the one-dimensional case the effective Hamiltonian of our model reads

$$H = \frac{\kappa}{2}\int_{-\infty}^{+\infty} dz[C(z,t) - U(z - Z(t))]^2. \tag{1}$$

Here, in addition to the coupling constant κ, the function $U(z - Z)$ enters as an input quantity, which, following from the condition $\delta H/\delta C = 0$, means the equilibrium concentration of the solute. The equations of motion of the model are given by

$$\partial_t Z = -\Lambda\frac{\delta H}{\delta Z}, \quad \partial_t C = \partial_z D(z - Z(t))\partial_z \frac{1}{\kappa}\frac{\delta H}{\delta C}, \tag{2}$$

where Λ and $D(z - Z)$ are kinetic coefficients, measuring the mobility of the interface and the local diffusivity of the solute. Instead of including an external driving force in the first of these equations, as was done in Ref. [6], the solidification process will be activated, as in Ref. [7], by imposing appropriate boundary conditions on the second of the equations (2).

In a steady-state solidification process with constant growth velocity V in the z direction, the solute concentration in the comoving frame only depends on the variable

$$\zeta \equiv z - Vt. \tag{3}$$

As a result, the insertion of Eq. (1) into the first equation in Eqs. (2) yields

$$V = -\Lambda\kappa\int_{-\infty}^{+\infty} d\zeta\, U'(\zeta)\,[C(\zeta) - U(\zeta)]\,. \tag{4}$$

The second equation in Eqs. (2) can be integrated once, which, with the boundary condition

$$C(-\infty) = C_0, \tag{5}$$

leads to the first-order differential equation

$$[C_0 - C(\zeta)]V = D(\zeta)[C'(\zeta) - U'(\zeta)]. \tag{6}$$

Equation (4) can be rewritten in the form of the force-balance equation

$$-\frac{V}{\Lambda} + F + G(V) + \kappa\frac{(\Delta C)^2}{2} = 0, \tag{7}$$

where the first term has the form of a viscous-friction force. The contribution

$$F \equiv \kappa(\Delta C)(C_S - C_0) \tag{8}$$

acts as an external driving force where, in terms of the solute concentrations

$$C_S \equiv U(-\infty),\ \ C_L \equiv U(+\infty) \tag{9}$$

in the liquid and solid phases,

$$\Delta C \equiv C_L - C_S \tag{10}$$

means the miscibility gap. Evidently, F describes the effect of a quench from the equilibrium value C_S to some nonequilibrium value C_0, which for $C_S - C_0 \geqslant 0$ induces a growth rate $V \geqslant 0$. The contribution

$$G(V) \equiv -\kappa\int_{-\infty}^{+\infty} d\zeta\, U'(\zeta)[C(\zeta) - C_0] \tag{11}$$

is a drag force, generated by the comoving solute layer at the interface. Using the steady-state boundary condition

$$C(+\infty) = C(-\infty), \tag{12}$$

it can be rewritten, due to Eq. (6), in the form

$$G(V) \equiv -\kappa\int_{-\infty}^{+\infty} d\zeta\,\frac{D(\zeta)}{V}[U'(\zeta) - C'(\zeta)]^2, \tag{13}$$

which, for velocities $0 < V < \infty$, is negative and shows the appropriate behavior $G(V) \to 0$ for $V \to \infty$. In the limit $V \to 0$, corresponding to $C_0 \to C_S$, Eq. (7) implies $G(0) = -\kappa(\Delta C)^2/2$, elucidating the role of the last term in Eq. (7).

To derive the interface description, one needs an expression for the density of the entropy production, generated in the steady-state solidification process. Such an expression is provided by the authors of Ref. [9] in terms of a phase field $\Phi(\zeta)$. Assuming in the original phase-field model a linear coupling between the phase field and the solute concentration, one finds, following the authors of Ref. [6], the relation

$$U(\zeta) = \frac{C_L + C_S}{2} + \frac{\Delta C}{2}\Phi_E(\zeta), \tag{14}$$

where $\Phi_E(\zeta)$ is the equilibrium profile of the phase field at coexistence of the two phases, which, due to the settings in Ref. [6], obeys the normalization condition

$$\int_{-\infty}^{+\infty}\frac{d\zeta}{\xi}[\xi\partial_\zeta\Phi_E(\zeta)]^2 = 1. \tag{15}$$

Here ξ is a microscopic length scale of the order of the interface thickness. The insertion of Eq. (14) into the result for the entropy production, given in Ref. [9], leads, in accordance with the analogous procedure in Ref. [6], to the obviously positive expression

$$p(\zeta) = \frac{1}{T}\frac{V^2}{\Lambda}\left(\frac{2}{\Delta C}\right)^2\frac{1}{\xi}[\xi\partial_\zeta U(\zeta)]^2 + \frac{1}{T}\frac{D(\zeta)}{\kappa}\left(\partial_\zeta\frac{\delta H}{\delta C(\zeta)}\right)^2 \tag{16}$$

for the density of the entropy production at some fixed temperature T.

To explicitly evaluate Eqs. (6), (7), and (16), we now consider the specific model, defined by

$$U(\zeta) = C_S + \frac{1}{4\xi}(C_L - C_S) \times \begin{cases} 0 & \zeta < -2\xi \\ \zeta + 2\xi & -2\xi < \zeta < +2\xi \\ 4\xi & +2\xi < \zeta, \end{cases} \tag{17}$$

$$D(\zeta) = D_S + \frac{1}{4\xi}(D_L - D_S) \times \begin{cases} 0 & \zeta < -2\xi \\ \zeta + 2\xi & -2\xi < \zeta < +2\xi \\ 4\xi & +2\xi < \zeta. \end{cases} \tag{18}$$

Here, D_S and D_L are the diffusion coefficients of the solute in the solid and liquid phases, and the width 4ξ of the well-encompassed interface region has been chosen to ensure the normalization (15).

The usefulness of the concentration profile (17) can be substantiated by connecting it via Eq. (14) with standard phase-field models. There the function $\Phi_E(\zeta)$ appears as a kink profile, generated from a double-well potential of the phase field. The choice of this potential is a matter of convenience, except for the presence of two pronounced degenerate minima, representing the two phases of the material. Numerical simulations are frequently based on a Ginzburg-Landau phase-field potential, which leads to a tanh-like equilibrium-concentration profile, as shown by Löwen *et al.* in Ref. [10]. The analytical treatment by Löwen *et al.* in Ref. [11] is based on a two-parabola potential, producing a piecewise exponential profile.

A common feature of these profiles is the appearance of two shifted flat branches, which are connected by a link in the interface region. In the model equation (17) this property is realized by a piece-wise linear profile, which only in the tiny regions near the matching points $\zeta = \pm 2\xi$ deviates from the concentration profiles, deriving from standard phase-field models. In the same spirit the model equation (18) constitutes a representative specification of the space-dependent diffusion coefficient.

In Ref. [6] we have demonstrated that the model, given by Eqs. (17) and (18), leads in a few lines to the form of the velocity-dependent partition coefficient, established by Aziz in a discussion of the solute-trapping effect [12]. In an elaborate phase-field approach Ahmad *et al.* [13] have presented a numerical plot of this coefficient, which convincingly supports the Aziz formula. Another feature, obtained in Ref. [6] in a surprisingly simple way from our model, is the relation between the undercooling and the growth rate of a solidifying material. Our analytic result for this relation closely matches the respective plots in Refs. [10,13], and is almost identical to the findings by Umantsev [14] in a phase-field discussion of adiabatic solidification processes. In view of these experiences, we also expect to derive from our model generic expressions for the the forces and fluxes at the solidification front and for the set of Onsager coefficients.

In the special case $D_S = 0$ the solution of Eq. (6), subject to the boundary condition (12), has the simple form

$$C(\zeta) = C_0 + \frac{1}{4\xi}(C_L - C_S)\left(1 + 4\xi\frac{V}{D_L}\right)^{-1} \times \begin{cases} 0 & \zeta < -2\xi \\ (\zeta + 2\xi) & -2\xi < \zeta < +2\xi \\ 4\xi \exp\left[-\frac{V}{D_L}(\zeta - 2\xi)\right] & +2\xi < \zeta, \end{cases} \tag{19}$$

showing, due to the factor $(1 + 4\xi V/D_L)^{-1}$, the solute-trapping effect. Some properties of this solution have already been discussed in Ref. [6] and below will be used to establish the interface description of the solidification process.

The entropy production P, generated in the interface region per unit area, follows from Eq. (16) by integration along the interval $-2\xi < \zeta < +2\xi$. Taking into account Eqs. (1), (6), (7), (11), and (15), one obtains

$$\begin{aligned} P &\equiv \frac{V}{T}\left[F + G(V) + \frac{\kappa}{2}(\Delta C)^2\right] + \frac{V}{T}\int_{-2\xi}^{+2\xi} d\zeta[C_0 - C(\zeta)]\kappa[C'(\zeta) - U'(\zeta)] \\ &= \frac{V}{T}\left[F + \frac{\kappa}{2}(\Delta C)^2 - \frac{\kappa}{2}(C_+ - C_-)^2\right], \end{aligned} \tag{20}$$

where we have used the notation

$$C_\pm \equiv C(\zeta = \pm 2\xi), \tag{21}$$

and the identity

$$C_- = C_0, \tag{22}$$

implied by Eq. (19). By insertion of the solution (19) into the force balance (7) one, furthermore, finds the relation

$$C_0 = C_S - (\Delta C)\left(\frac{1}{V_C} - \frac{1}{V_D + 2V}\right)V, \tag{23}$$

written in terms of crystallization and diffusion velocities

$$V_C \equiv \kappa(\Delta C)^2\Lambda, \quad V_D \equiv \frac{D_L}{2\xi}. \tag{24}$$

According to the result (23), the limit $F \to 0$ of the driving force (8) not only is compatible with the behavior $V \to 0$, but also with the possibility $V \to (V_C - V_D)/2$. In the process of establishing the interface description, this observation leads us to take care of the full velocity dependence, appearing in the solution (19).

III. INTERFACE DESCRIPTION

The last expression in Eq. (20) can be written in the standard form

$$P = J_{\hat{C}}F_{\hat{C}} + J_{\hat{D}}F_{\hat{D}}, \tag{25}$$

where the fluxes $J_{\widehat{C}}, J_{\widehat{D}}$ and the related forces $F_{\widehat{C}}, F_{\widehat{D}}$ are exactly given by

$$\begin{aligned} J_{\widehat{C}} &\equiv \rho V, \quad F_{\widehat{C}} \equiv \frac{1}{T}\frac{F}{\rho}, \\ J_{\widehat{D}} &\equiv \frac{1}{2}(C_- - C_+ - \Delta C)V, \\ F_{\widehat{D}} &\equiv \frac{\kappa}{T}(C_+ - C_- - \Delta C), \end{aligned} \tag{26}$$

ρ meaning the density of the material.

The constitutive equations, connecting the fluxes and forces (26), are obtained by evaluating Eqs. (6) and (7) by means of Eqs. (17), (18), and (19). This leads to the result

$$\begin{pmatrix} F_{\widehat{C}} \\ F_{\widehat{D}} \end{pmatrix} = \frac{\kappa}{T V_D}\begin{pmatrix} R_{\widehat{C}\widehat{C}} & R_{\widehat{C}\widehat{D}} \\ R_{\widehat{D}\widehat{C}} & R_{\widehat{D}\widehat{D}} \end{pmatrix}\begin{pmatrix} J_{\widehat{C}} \\ J_{\widehat{D}} \end{pmatrix} \tag{27}$$

with the again exact expressions of the matrix elements

$$\begin{aligned} R_{\widehat{C}\widehat{C}} &= \left(\frac{V_D}{V_C} + 1\right)\left(\frac{\Delta C}{\rho}\right)^2, \quad R_{\widehat{D}\widehat{D}} = 4, \\ R_{\widehat{C}\widehat{D}} &= 2\frac{\Delta C}{\rho}, \quad R_{\widehat{D}\widehat{C}} = 2\frac{\Delta C}{\rho}, \end{aligned} \tag{28}$$

which obviously obey the basic properties

$$\begin{aligned} &R_{\widehat{C}\widehat{D}} = R_{\widehat{D}\widehat{C}}, \quad R_{\widehat{C}\widehat{C}} \geqslant 0, \\ &R_{\widehat{D}\widehat{D}} \geqslant 0, \quad R_{\widehat{C}\widehat{C}}R_{\widehat{D}\widehat{D}} - R^2_{\widehat{C}\widehat{D}} \geqslant 0 \end{aligned} \tag{29}$$

of general Onsager coefficients. We point out that the fluxes and forces (26) carry the full velocity dependence, reflecting the solute trapping effect, whereas the kinetic coefficients (28) turn out to be velocity independent.

In the limit $\Delta C \to 0$ the diagonal elements in Eqs. (28) approach, due to the definitions (24), the finite values $R_{\widehat{C}\widehat{C}} = V_D/(\kappa\rho^2\Lambda), R_{\widehat{D}\widehat{D}} = 4$ whereas the off-diagonal elements disappear. Simultaneously the expression (17) for $U(z - Z(t))$ approaches the constant value C_S, so that the coupling term between the basic field variables $Z(t)$ and $C(z,t)$ in the effective Hamiltonian (1) also vanishes. The appearance of finite off-diagonal Onsager coefficients, therefore, is caused by this coupling term in the Hamiltonian and, accordingly, is of thermodynamic rather than of kinetic origin. This statement solves the puzzle raised by Brener and Temkin in Ref. [7].

IV. CRYSTALLIZATION-DIFFUSION BASIS

Whereas the definitions (26) of fluxes and forces are naturally suggested by the expression (20) of the entropy production, the relations (4) and (6) suggest to define the crystallization and diffusion fluxes

$$J_C \equiv \rho V, \quad J_D \equiv (C_- - C_+)V. \tag{30}$$

The later of these derives from the left-hand side of Eq. (6) at $\zeta = +2\xi$, and from the identity (22).

In view of these definitions and the corresponding ones in Eqs. (26), one is led to the relations

$$\begin{pmatrix} J_C \\ J_D \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ X & 1 \end{pmatrix}\begin{pmatrix} J_{\widehat{C}} \\ J_{\widehat{D}} \end{pmatrix}, \tag{31}$$

$$\begin{pmatrix} F_C \\ F_D \end{pmatrix} = \begin{pmatrix} 1 & -X \\ 0 & 1 \end{pmatrix}\begin{pmatrix} F_{\widehat{C}} \\ F_{\widehat{D}} \end{pmatrix}, \tag{32}$$

where the matrix element X is given by

$$X \equiv \frac{1}{2\rho}(C_- - C_+ + \Delta C). \tag{33}$$

Equation (32) determines the crystallization force F_C, and is enforced by assuming that the entropy production has the canonical form

$$P = F_C J_C + F_D J_D, \tag{34}$$

The constitutive equations in the C,D basis read

$$\begin{pmatrix} F_C \\ F_D \end{pmatrix} = \frac{\kappa}{T V_D}\begin{pmatrix} R_{CD} & R_{CD} \\ R_{DC} & R_{DD} \end{pmatrix}\begin{pmatrix} J_C \\ J_D \end{pmatrix} \tag{35}$$

where the Onsager matrix is given by

$$\begin{aligned} &\begin{pmatrix} R_{CC} & R_{CD} \\ R_{DC} & R_{DD} \end{pmatrix} \\ &= \begin{pmatrix} 1 & -X \\ 0 & 1 \end{pmatrix}\begin{pmatrix} R_{\widehat{C}\widehat{C}} & R_{\widehat{C}\widehat{D}} \\ R_{\widehat{D}\widehat{C}} & R_{\widehat{D}\widehat{D}} \end{pmatrix}\begin{pmatrix} 1 & 0 \\ -X & 1 \end{pmatrix}. \end{aligned} \tag{36}$$

One easily verifies that the Onsager symmetry and sign conditions (29) also are valid in the C,D basis.

A noticeable simplification of Eqs. (35) occurs in the limit $V \to 0$ where, following from Eq. (19), the quantity X vanishes, so that the $\widehat{C},\widehat{D}$ and C,D representations become identical. Eqs. (30) then also imply the relation

$$(\Delta C)J_C = -\rho J_D, \tag{37}$$

which, independently of our model, leads us to establish the two-parameter continuous symmetry operation

$$\begin{pmatrix} \widetilde{R}_{CC} & \widetilde{R}_{CD} \\ \widetilde{R}_{DC} & \widetilde{R}_{DD} \end{pmatrix} = \begin{pmatrix} R_{CC} & R_{CD} \\ R_{DC} & R_{DD} \end{pmatrix} + \begin{pmatrix} S_{CC} & S_{CD} \\ S_{DC} & S_{DD} \end{pmatrix} \tag{38}$$

with matrix elements

$$\begin{aligned} S_{CC} &= \lambda\left(\frac{\Delta C}{\rho}\right)^2, \quad S_{DD} = \mu, \\ S_{CD} &= \lambda\frac{\Delta C}{\rho}, \quad S_{DC} = \mu\frac{\Delta C}{\rho}. \end{aligned} \tag{39}$$

The transformation (38) causes separate cancellations of the contributions containing the free parameters λ and μ in Eq. (35) and, consequently, also conserves the entropy production (34). It should be noticed that the matrix on the left-hand side of Eq. (38) is a proper Onsager matrix only in the domain

$$\lambda = \mu \geqslant 0, \tag{40}$$

where, however, it still depends on the single redundant parameter λ.

Generally, it is fairly allowed to ignore the constraint (40) and to choose in Eqs. (39) the values

$$\lambda = \mu = -2, \tag{41}$$

which leads to a diagonal form of the transformed matrix and, consequently, to the decoupled transport equations

$$\begin{aligned} F_C &= \frac{\kappa}{T}\left(\frac{\Delta C}{\rho}\right)^2\left(\frac{1}{V_C}-\frac{1}{V_D}\right)J_C, \\ F_D &= \frac{\kappa}{T}\frac{2}{V_D}J_D, \end{aligned} \tag{42}$$

which explicitly show that the coefficient, connecting F_C and J_C, can become negative. Simultaneously one finds the expression

$$P = \frac{\kappa}{T}\left(\frac{\Delta C}{\rho}\right)^2\left(\frac{1}{V_C}+\frac{1}{V_D}\right)J_C^2 \tag{43}$$

for the entropy production, which, in an impressively simple way, demonstrates the thermodynamic consistency of a possibly negative friction coefficient.

V. TWO-COMPONENT REPRESENTATION

The fluxes, associated with the two components of the solidifying alloy, are given by the relations

$$\begin{pmatrix} J_A \\ J_B \end{pmatrix} = \begin{pmatrix} 1-Y & -1 \\ Y & 1 \end{pmatrix}\begin{pmatrix} J_C \\ J_D \end{pmatrix}, \tag{44}$$

$$\begin{pmatrix} F_A \\ F_B \end{pmatrix} = \begin{pmatrix} 1 & -Y \\ 1 & 1-Y \end{pmatrix}\begin{pmatrix} F_C \\ F_D \end{pmatrix}, \tag{45}$$

where, by definition,

$$Y \equiv \frac{C_+}{\rho}. \tag{46}$$

In the entropy production

$$P = F_A J_A + F_B J_B, \tag{47}$$

arising from the similar expression (25), all Y-dependent terms cancel. The special choice (33), however, leads to the familiar relations

$$J_A = (\rho - C_-)V, \quad J_B = C_- V, \tag{48}$$

which are valid in all descriptions of solidification at a flat interface, ranging from Ref. [1] up to Ref. [7]. To establish the corresponding expressions for F_A and F_B, we insert the definition (8) for F into the second line of Eqs. (26), and introduce the chemical potentials

$$\begin{aligned} \mu_A(\zeta) &\equiv \frac{1}{\rho}\left[1 - C(\zeta)\frac{\partial}{\partial C(\zeta)}\right] f[C(\zeta)], \\ \mu_B(\zeta) &\equiv \frac{1}{\rho}\left\{1 + [\rho - C(\zeta)]\frac{\partial}{\partial C(\zeta)}\right\} f[C(\zeta)], \end{aligned} \tag{49}$$

where, in accordance with the Hamiltonian (1)

$$f[C(\zeta)] \equiv \frac{\kappa}{2}[C(\zeta) - U(\zeta)]^2 \tag{50}$$

is the free-energy density of the system. In terms of these quantities one is led to the again standard relations

$$\begin{aligned} F_A &= \frac{1}{T}[\mu_A(+2\xi) - \mu_A(-2\xi)], \\ F_B &= \frac{1}{T}[\mu_B(+2\xi) - \mu_B(-2\xi)]. \end{aligned} \tag{51}$$

By inversion of Eqs. (44) and (45) one also finds the relations

$$\begin{aligned} &J_C = J_A + J_B, \quad F_C = \left(1 - \frac{C_+}{\rho}\right)F_A + \frac{C_+}{\rho}F_B, \\ &J_D = \left(1 - \frac{C_+}{\rho}\right)J_B - \frac{C_+}{\rho}J_A, \quad F_D = F_B - F_A, \end{aligned} \tag{52}$$

which agree with the corresponding expressions, known from Ref. [1].

The constitutive equations, connecting the fluxes J_A, J_B with the forces F_A, F_B, read

$$\begin{pmatrix} F_A \\ F_B \end{pmatrix} = \frac{\kappa}{T V_D}\begin{pmatrix} R_{AA} & R_{AB} \\ R_{BA} & R_{BB} \end{pmatrix}\begin{pmatrix} J_A \\ J_B \end{pmatrix}, \tag{53}$$

where, according to Eqs. (27), (44), and (45), the matrix of the Onsager coefficients is given by

$$\begin{aligned} &\begin{pmatrix} R_{AA} & R_{AB} \\ R_{BA} & R_{BB} \end{pmatrix} \\ &= \begin{pmatrix} 1 & -Y \\ 1 & 1-Y \end{pmatrix}\begin{pmatrix} R_{CC} & R_{CD} \\ R_{DC} & R_{DD} \end{pmatrix}\begin{pmatrix} 1 & 1 \\ -Y & 1-Y \end{pmatrix}. \end{aligned} \tag{54}$$

One easily sees that this mapping conserves the Onsager symmetry and sign conditions (29).

The last statement seems to contradict a conclusion by Baker and Cahn [1], which later has been criticized by Caroli, Caroli, and Roulet [2] as a fallacy, resulting from the assumed absence of solute diffusion in the solid phase. Contrary to this claim, the erroneous conclusion in Ref. [1] is, to our mind, due to an conceptual mistake, which we here clarify, picking up from Ref. [1] a model, which has only diagonal elements in the inverse relation of Eq. (53),

$$J_A = L_{AA}F_A, \quad J_B = L_{BB}F_B. \tag{55}$$

From Eqs. (44), (45), and (55) one correctly obtains the first constitutive equation in the C,D basis,

$$J_C = (L_{AA} + L_{BB})F_C + [(1-Y)L_{BB} - Y L_{AA}]F_D. \tag{56}$$

To attain the second equation, which determines J_D, the authors of Ref. [1] just multiplied Eq. (56) by the ratio of the fluxes (30). This procedure, however, does not exhaust the full content of Eqs. (55), and as a result, their mapping from the A,B to the C,D basis is singular instead of being a one-to-one mapping. A similar mistake has led to an apparent violation of Onsager symmetries in the analysis of one of the models, discussed by Kaplan, Aziz, and Gray in Ref. [3], an issue, which later has also been criticized by Hillert [4].

The correct procedure to establish an equation for J_D, complementing Eq. (56), is, to adopt from Eqs. (44) the expression

$$J_D = (1 - Y)J_B - YJ_A, \tag{57}$$

which, together with Eqs. (45) and (55), yields

$$\begin{aligned} J_D = {} & [(1 - Y)L_{BB} - YL_{AA}]F_C \\ & + [(1 - Y)^2 L_{BB} + Y^2 L_{AA}]F_D. \end{aligned} \tag{58}$$

Comparing this with Eq. (56), one immediately observes that the diagonal matrix elements are positive and that the off-diagonal matrix elements are equal. It is an easy exercise, to verify that the determinant, formed with these matrix elements, also is positive, in accordance with our general statement below Eq. (54).

We finally point out that, on the basis of Eqs. (48), one can establish a symmetry operation, similar to that in the preceding chapter, which now, however, conserves the constitutive equations and the entropy production for arbitrary values of the growth velocity. In the present case the transformation reads

$$\begin{pmatrix} \widetilde{R}_{AA} & \widetilde{R}_{AB} \\ \widetilde{R}_{BA} & \widetilde{R}_{BB} \end{pmatrix} = \begin{pmatrix} R_{AA} & R_{AB} \\ R_{BA} & R_{BB} \end{pmatrix} + \begin{pmatrix} S_{AA} & S_{AB} \\ S_{BA} & S_{BB} \end{pmatrix}, \tag{59}$$

this time with matrix elements

$$\begin{aligned} S_{AA} &= \lambda \frac{C_0}{\rho}, \quad S_{BB} = \mu \frac{(\rho - C_0)^2}{\rho C_0}, \\ S_{AB} &= -\lambda \frac{\rho - C_0}{\rho}, \quad S_{BA} = -\mu \frac{\rho - C_0}{\rho}. \end{aligned} \tag{60}$$

Remembering the identity (22), one easily verifies that the symmetry transformation (59) again conserves the constitutive equations (53) and the entropy production (47). It is obvious, however, that the matrix on the left-hand side of Eq. (59) is in general not a proper Onsager matrix.

In the case of the special choice

$$\lambda = \mu = \frac{\rho}{\rho - C_0} R_{AB}, \tag{61}$$

the off-diagonal elements $\widetilde{R}_{AB}$ and $\widetilde{R}_{BA}$ vanish, so that the constitutive equations decouple in the form

$$F_A = \frac{\kappa}{TV_D} \widetilde{R}_{AA} J_A, \quad F_B = \frac{\kappa}{TV_D} \widetilde{R}_{BB} J_B. \tag{62}$$

Although this looks rather surprising, these equations are completely equivalent to Eqs. (53). The crucial point is that, pursuing the way from the initial Onsager matrix in Eq. (27) to the final one in Eq. (59), the coefficient $\widetilde{R}_{AA}$ turns out to be positive whereas the sign of the coefficient $\widetilde{R}_{BB}$ is determined by its lowest-order term in C_0/ρ, which is found to be negative. The corresponding signs of the driving forces F_A and F_B satisfy a necessary condition for the appearance the solute-trapping effect.

VI. CONCLUSION

The model, leading to the exact results (26)–(28) presumably is the simplest one, which can exactly be evaluated. We also have considered the case of a nonzero diffusion constant D_S in the model equation (18), which did not lead to any new substantial effects, as one might expect from the discussion in Ref. [2]. The only changes we noticed were slightly more complicated expressions for the Onsager coefficients.

A remarkable result of our analysis is the observation that the Onsager coefficients turn out to be independent of the growth velocity in the $\widehat{C}, \widehat{D}$ basis, which is the most natural basis, suggested by the underlying phase-field model. As a more important feature we have seen that the off-diagonal Onsager coefficients in this basis do not necessarily require the presence of kinetic cross couplings in the phase-field model. Such cross couplings have recently been proposed by Brener and Boussinot [8] and shown to generate additional terms in the Onsager coefficients.

Another crucial point in our treatment is the advice not to disregard, in the discussion of steady states, the possibility of a finite growth velocity, which, according to Eqs. (8) and (23), is clearly compatible with a small driving force. At low velocities these equations signal a possible change of sign of the driving force, which, in the low-velocity version (42) of the constitutive equations, leads to a thermodynamically consistent change of sign of the friction coefficient. The ultimate physical origin of this unexpected behavior is easily identified as the solute-drag component in the force balance (7).

We finally have shown that all approaches describing the steady-state motion of a planar solidification front are invariant under a continuous symmetry, unavoidably generating a redundancy in the kinetic coefficients. This redundancy can be used to eliminate the off-diagonal terms in the constitutive equations.

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