

Extended thermodynamical analysis of a motion of the solid-liquid interface in a rapidly solidifying alloy

Peter Galenko*

Institute of Space Simulation, German Aerospace Center, Cologne 51170, Germany

(Received 12 October 2001; revised manuscript received 24 January 2002; published 27 March 2002)

On the basis of extended irreversible thermodynamics [D. Jou, J. Casas-Vazquez, and G. Lebon, *Rep. Prog. Phys.* **51**, 1005 (1988); **62**, 1035 (1999)] an analysis of the solid-liquid interface motion is presented. In addition to the formalism of the classic irreversible thermodynamics of Onsager and Prigogine, a space of independent thermodynamic variables is extended by introducing the solute diffusion flux in consistency with the extended thermodynamic approach to local nonequilibrium processes. Considering the rapid solidification front motion, when the crystal growth velocity is of the order or even greater than the speed for solute diffusion, a local nonequilibrium at the solid-liquid interface and inside bulk liquid is adopted by the model. Taking into account the solute diffusive speed at the phase interface and the finite speed of solute diffusive propagation in bulk system, the equations for thermodynamical fluxes, conjugated driving forces, the Gibbs free energy change on solidification, and liquidus line slope are derived. A discussion of the outcomes predicted by the present model and a comparative analysis of the model predictions with experimental data are made.

DOI: 10.1103/PhysRevB.65.144103

PACS number(s): 05.70.Ln, 05.70.Fh, 81.10.Aj, 81.30.Fb

I. INTRODUCTION

Considerable study has been given in past decades to the thermodynamic description of rapid phase transformations in various materials and processes.¹ Some first attempts to create thermodynamic models of rapid nonequilibrium transformations were successfully made in the pioneering works of Borisov,² Aptekar and Kamenetskaya,³ generalized by Baker and Cahn,⁴ and developed further in following works.⁵ In these studies special attention is paid to the definition of the Gibbs free energy change as a driving force of transformation, response functions at the phase interface (temperature, velocity, and chemical composition), and solute trapping and solute drag effects acting in a rapid nonequilibrium phase transformation. A recently published overview on these topics is presented by Hillert in Ref. 6. In order to describe the transfer processes, the models developed in Refs. 2,4, and 5 are based on the classical irreversible thermodynamics of Prigogine⁷ and can consider a shift from local equilibrium due to kinetic effects at the phase interface.

Special attention to nonequilibrium processes at the phase interface has been paid in previous studies of rapid solidification of alloys.^{8–10} In this analysis, thermodynamically consistent models for the solidification of binary alloys are developed. Describing the nonequilibrium process as a whole due to macrogradients of temperature and substance, the authors propose a view of classic irreversible thermodynamics in accordance with which every local volume is solidified in consistency with the diagram of an alloy phase state (so-called “quasiequilibrium solidification”) and they extend this formalism to local nonequilibriumness at the interface due to solute trapping and kinetic effects.^{8–10}

As is well known, Fick’s first law for transport processes can be obtained on the basis of classic irreversible thermodynamics which assumes propagation of concentration disturbances with an infinite velocity and with local equilibrium

in the bulk phases. Local equilibriumness can be characterized by the statistical distribution function given by the first order term of its expansion.¹¹ However, for a high-velocity solidification front, the time for crystallizing of a local volume can be of the order of the time for relaxation of the diffusion flux to its steady-state value.¹² In such a case, the approximation of local equilibrium may become unacceptable for a description of the diffusion process in rapid solidification.¹² Solidification of undercooled alloys can be so fast that the interface velocity V is of the order or even greater than the diffusive speed V_D in bulk liquid which is the maximum speed of propagation of the diffusion profile in the system and defined as $V_D = (D/\tau_D)^{1/2}$, where D is the diffusion coefficient and τ_D is the time of relaxation of diffusion flux to its local equilibrium value. For metal alloys, the diffusion speed can be of the order of $V_D \sim 0.1\text{--}10$ (m/s), and in modern experiments the interface velocity approaches¹³ $V = 10\text{--}100$ m/s. Therefore, the undercooling in melts is enough for detecting solidification with the front velocity comparable with the diffusion speed. In this case, local equilibrium is absent in the bulk phases and the solute flux cannot be described by the classical Fick’s first law. Thus one should take into account the deviations from local equilibrium in phases which affect both the solute diffusion and the interface kinetics.¹⁴ The description of nonequilibrium rapid solidification is provided by the formalism of extended thermodynamics¹⁵ which gives a causative description of transport processes and abandons the requirement of local equilibrium. Therefore, in the present article, we extend the thermodynamical formalism for rapid solidification front motion which is caused by significant deviations from local thermodynamic equilibrium.

We shall analytically investigate the influence of local nonequilibrium both at the interface and in the bulk phases on the motion of a planar solidification front in a binary alloy. Using the results of recently developed models,¹² one

can find that when the interface velocity V is of the order of the diffusive speed V_D , the solute propagates by a joint diffusion and wave mechanism.¹⁶ When $V \geq V_D$, the solute propagates by the wave mechanism only,¹⁷ and the concentration in the undercooled liquid becomes equal to the initial concentration of the melt.¹⁴ As has been obtained analytically for planar and nonplanar configurations of the solidification fronts,¹⁸ a complete solute trapping occurs with $V \geq V_D$.¹⁹ In this case, there is no solute diffusion in the liquid and rapid solidification cannot be controlled by the solute redistribution ahead of the interface with $V \geq V_D$. Consequently, first, we assume that local nonequilibrium in the bulk phases plays a significant role in rapid solidification¹⁴ and extend the previous thermodynamical analysis for the description of the solid-liquid interface motion. And, second, we shall evaluate the degree of local nonequilibrium by the relation of the interface velocity V to the diffusion speed V_D .

The paper is organized as follows. In Sec. II we describe the basic assumptions and general equations of the model. In addition to the thermodynamic theory developed in previous investigations,^{2-4,8-10} we introduce the dissipative diffusion flux as an independent variable in accordance with extended irreversible thermodynamics (EIT).^{15,20,21} In Sec. III we present a treatment of the driving forces for kinetics and diffusion by taking into account deviations from local equilibrium at the interface and solute diffusion in the bulk system. A derivation of the expressions for the interface temperature-velocity relationship and for the slope of the nonequilibrium liquidus line in the kinetic phase diagram of an alloy solidification is given. In Sec. IV, using the limit for a dilute alloy, we compare the derived function for the interface temperature with the available experimental results obtained on a Si-As alloy solidification. Finally, in Sec. V we present a summary of our conclusions. Appendixes A and B clarify the details of the extended thermodynamics applicable for local nonequilibrium diffusion in rapid solidification of a binary system.

II. MODEL

A. Model characteristics

To describe the rapid solidification process, we examine a model with the following characteristics.

(i) An isothermal two-phase system with a sharp solid-liquid planar interface is under study. Pressure is constant in the system.

(ii) The system consists of a chemically inert binary alloy that solidifies like a solid solution.

(iii) Solidification of an alloy melt can be so fast that the interface velocity V is of the order of the speed of the solute diffusive propagation in the liquid.

(iv) Convection in liquid, diffusion in solid, and effects of crossed-boundary transport processes are negligible.

Under these assumptions, the process is deemed to be controlled by both mass transfer and the kinetics of the interface. Particularly, from system characteristic (iii) it follows that one should take into account the finiteness of the speed of solute diffusive propagation in liquid and deviations from local equilibrium at the interface.¹⁴ Thus, a description

of the system is to be obtained by consideration of the local nonequilibrium solute diffusion and kinetics at the interface. In order to describe local nonequilibrium processes we shall use the formalism of EIT which has fueled much interest during the last several decades.^{15,21} An initially general view of such formalism which might be applied successfully to the problem of local nonequilibrium solute diffusion in rapid processes is reviewed in the Appendix of the present article.

B. General equations

For systems out of equilibrium, a general set of independent variables should be extended and can include the gradients of corresponding thermodynamical potentials used in rational thermodynamics,²² thermodynamic fluxes used in EIT,²³ or internal variables related to the structural peculiarities of the system.²⁴ Following EIT,^{15,21,23} we include dissipative mass flux in the set of basic independent variables of a solidifying system (see Appendix A). Starting from this idea, EIT provides a causative description of nonequilibrium processes and, for the case of rapid nonequilibrium solidification, leads to the non-Fickian diffusion problem described by the evolution equation for the mass flux. For solute diffusion, such an approach gives rise to a partial differential equation of a hyperbolic type which takes into account the finite speed for solute diffusive propagation (see Appendix B). Using this approach and the above model characteristics (i)–(iv), we form the space of independent thermodynamical variables for the isothermal binary system which consists of the concentrations and dissipative mass fluxes. In such a case, the local change of entropy at the solid-liquid interface is described by

$$T dS = - \sum_{p=L,S} \sum_{q=A}^B (\mu_p^q dx_p^q + \alpha_q^p J_p^q dJ_p^q). \quad (1)$$

Here T is the temperature, dS is the change of the irreversible entropy per unit area of the interface, $q=A,B$ is the index of a number of alloy components ($= A$ or B component), index p is related to the liquid phase ($p=L$) or the solid phase ($p=S$), μ_p^q is the chemical potential, x_p^q is the mole fraction of the alloy component, J_p^q is the diffusion flux of the x_p^q component (the dimension of J_p^q is m/s), and α_q^p is the coefficient defined by

$$\alpha_q^p = \frac{1}{\omega (V_p^q)^2} \frac{\partial \mu_q^p}{\partial x_p^q}, \quad (2)$$

where ω is the unit area of the interface, V_p^q is the diffusive speed of the q component in p phase. Note that the change dx_p^q in Eq. (1) occurs through the unit area ω of the interface. Equation (1) is the generalized Gibbs equation for the non-equilibrium entropy near the solid-liquid interface. Also, the function $T dS/dt$ described by Eq. (1) can be examined as generalized dissipative function for nonequilibrium isothermal solidification of an alloy. In the limits $V_p^q \rightarrow \infty$ and $\alpha_q^p \rightarrow 0$, Eq. (1) transforms into the Gibbs equation for local equilibrium mass transfer in isothermal binary system.⁷

The diffusive speed V_p^q is one of the most important parameters of solute diffusive propagation and it can have different values at the interface and in bulk phases. In the present description one can estimate the characteristic length λ_D for diffusion as follows:

$$\lambda_D = \Omega \omega^{-1}, \quad (3)$$

where Ω is the atomic volume. Using Eq. (3), the diffusion times that are equal to the characteristic times for relaxation of the diffusion fluxes to their steady-state values are described by

$$\tau_p^q = \frac{\lambda_D}{V_p^q}, \quad V_p^q = \left(\frac{D_p^q}{\tau_p^q} \right)^{1/2}. \quad (4)$$

The values of V_p^q are different from the value of an interface diffusive speed V_{DI} introduced in the continuous growth model with the nonequilibrium condition at the interface.¹⁰ From the definition it follows that V_{DI} is the speed for an atomic jump over the interatomic distance λ_I at the interface, i.e., $V_{DI} = \lambda_I \nu$, where ν is an attempt frequency for surmounting barriers and is of the order of an atomic vibrational frequency.^{10,25} The diffusive speeds V_p^q in the phases are the speeds for diffusion front propagation and these are defined by $V_p^q = \lambda_D / \tau_p^q$, where λ_D is the distance for a diffusion jump of bulk atoms. For atoms in a majority of metallic systems and intermetallic compounds, the interface atoms are packed more densely than in the bulk liquid, so the inequality $\lambda_I < \lambda_D$ obtains. If we consider a situation where atoms diffuse in the vicinity of the interface, then we also can have that $\lambda_I \cong \lambda_D$. The time for atomic vibration at the interface is of the order of time for diffusion relaxation in the bulk liquid, $\nu^{-1} \cong \tau_p^q$. Hence, from this it follows that $V_{DI} \leq V_p^q$. These inequalities have been formulated in Ref. 26 and gave a satisfactory comparison with experimental data on rapid dendritic solidification in undercooled binary alloys.²⁷

For a binary alloy the total mole fractions of the alloy components in the phases are

$$x_L^A + x_L^B = 1, \quad x_S^A + x_S^B = 1. \quad (5)$$

Neglecting diffusion fluxes in the solid phase (see Sec. II A), from Eqs. (1) and (5) it follows an equation for irreversible entropy production. This yields

$$T \frac{dS}{dt} = -\Delta\mu_A \frac{dx_S^A}{dt} - \alpha_A^L J_A \frac{dJ_A}{dt} - \Delta\mu_B \frac{dx_S^B}{dt} - \alpha_B^L J_B \frac{dJ_B}{dt}. \quad (6)$$

Here $\Delta\mu_A = \mu_A^S - \mu_A^L$ and $\Delta\mu_B = \mu_B^S - \mu_B^L$ are the differences of the chemical potentials within the solid S and the liquid L phases of A and B atoms, respectively, and the fluxes J_A and J_B are related to the liquid phase at the interface. The total entropy production $dS/dt \geq 0$ which takes into account local nonequilibrium diffusion, Eq. (6), can be treated as a sum of the local equilibrium part

$$\left(\frac{dS}{dt} \right)_E = -\frac{1}{T} \left(\Delta\mu_A \frac{dx_S^A}{dt} + \Delta\mu_B \frac{dx_S^B}{dt} \right) \quad (7)$$

and local nonequilibrium part

$$\left(\frac{dS}{dt} \right)_{NE} = -\frac{1}{T} \left(\alpha_A^L J_A \frac{dJ_A}{dt} + \alpha_B^L J_B \frac{dJ_B}{dt} \right), \quad (8)$$

so that

$$\frac{dS}{dt} = \left(\frac{dS}{dt} \right)_E + \left(\frac{dS}{dt} \right)_{NE} \geq 0. \quad (9)$$

With the local equilibrium limits $V_p^q \rightarrow \infty$ and $\alpha_p^q \rightarrow 0$ [see Eq. (2)], one obtains $(dS/dt)_{NE} \rightarrow 0$ and the entropy production, Eq. (6), includes the local equilibrium part only. The production dS/dt of the generalized entropy, Eqs. (7)–(9), is non-negative due to the statement of the second law of thermodynamics. It is evidenced in Ref. 15 for theories consistent with the formalism of EIT.

We define the atomic fluxes I_A and I_B across the interface as the number of A and B atoms per unit area of the interface per unit time. The atomic fluxes are^{10,28}

$$\Omega I_A = \Omega \frac{dx_S^A}{dt} = (1 - x_S) V, \quad (10)$$

$$\Omega I_B = \Omega \frac{dx_S^B}{dt} = x_S V, \quad (11)$$

where V is the velocity of the interface, and x_S is the mole fraction of B atoms in the solid. A connection between the atomic and diffusion fluxes is described by the equations^{10,28}

$$\Omega I_A = \Omega \frac{dx_S^A}{dt} = (1 - x_L) V - J_A, \quad (12)$$

$$\Omega I_B = \Omega \frac{dx_S^B}{dt} = x_L V - J_B, \quad (13)$$

where x_L is the mole fraction of B atoms in the liquid phase. From Eqs. (10)–(12) it follows that the crystallization flux J_C and the total diffusive flux J_D are described by

$$J_C = V\Omega^{-1}, \quad -J_A = J_B = \Omega J_D, \quad (14)$$

$$J_D = (x_L - x_S) V / \Omega. \quad (15)$$

Expressions (10)–(13) were used in various problems for the description of alloy transformations (see Refs. 4,6,10 and 28).

Taking into account Eqs. (10)–(13), a linear transformation of the entropy production, Eq. (6), to the new reference frame (see also Ref. 4) leads to the following expression:

$$T \frac{dS}{dt} = \sum J_i F_i = J_D F_D + J_C F_C = -\frac{dG}{dt} \geq 0, \quad (16)$$

where G is the Gibbs free energy dissipated by irreversible processes per unit area of the interface. Note that Eq. (14) establishes two equivalent thermodynamic requirements for

isothermal processes: necessity of non-negative entropy production and the nonincreasing of the Gibbs free energy in time.

In Eq. (14) the expressions for fluxes J_i and forces F_i are described by

$$J_D = x_L I_A - (1 - x_L) I_B, \quad J_C = I_A + I_B, \quad (15)$$

$$F_D = F_A - F_B, \quad (16)$$

$$F_A = -\Delta\mu_A + \Omega\alpha_A^L \frac{dJ_A}{dt},$$

$$F_B = -\Delta\mu_B + \Omega\alpha_B^L \frac{dJ_B}{dt}, \quad (17)$$

$$F_C = (1 - x_L) \left(F_A - \Omega\alpha_A^L \frac{dJ_A}{dt} \right) + x_L \left(F_B - \Omega\alpha_B^L \frac{dJ_B}{dt} \right). \quad (18)$$

Here F_D is the driving force of the diffusion defined by the difference between the driving forces F_A and F_B for the diffusion of A and B atoms, respectively, and $F_C = -(1 - x_L)\Delta\mu_A - x_L\Delta\mu_B$ is the crystallization driving force. Using Eqs. (10)–(13), a simple substitution of Eqs. (15)–(18) for Eq. (14) gives the initial equation for the irreversible entropy production, Eq. (6). Note that the obtained system of equations for fluxes and driving forces, Eqs. (15)–(18), differs from those predicted by classic irreversible theory.¹⁰ In addition to the previous analysis,¹⁰ the driving force F_D for diffusion takes into account the relaxation terms $\alpha_A^L dJ_A/dt$ and $\alpha_B^L dJ_B/dt$. As $V_p^q \rightarrow \infty$, the coefficients α_A^L and α_B^L tend to zero [see Eq. (2)] and Eqs. (15)–(18) describe fluxes and driving forces under a local equilibrium approximation in accordance with classic irreversible thermodynamics.

The requirements of the second law given by the non-negative function of entropy production, Eq. (9), imply a relation between fluxes and conjugate driving forces which, in a simple case, is assumed to be linear.¹⁵ For Eq. (14) this fact can be expressed by the following linear relation: $J_i = L_{ij} F_j$, where the indexes i or j are related to the indexes D or C respectively, and L_{ij} is a mobility matrix of kinetic coefficients. Using Eqs. (15)–(18), neglecting effects of the crossed-boundary influence of crystallization and diffusion processes, $L_{DC} = L_{CD} = 0$, and also neglecting effects of the crossed-boundary influence of atoms of one sort on another (see Sec. II A), one can obtain

$$J_D = L_{DD} F_D$$

$$= L_{DD}^A F_D^A - L_{DD}^B F_D^B$$

$$= -L_{DD}^A \left(\Delta\mu_A - \Omega\alpha_A^L \frac{dJ_A}{dt} \right) + L_{DD}^B \left(\Delta\mu_B - \Omega\alpha_B^L \frac{dJ_B}{dt} \right), \quad (19)$$

$$J_C = L_{CC} F_C = -L_{CC}^A (1 - x_L) \Delta\mu_A - L_{CC}^B x_L \Delta\mu_B, \quad (20)$$

where

$$L_{DD}^A = V_L^A \left(\frac{\partial\mu_A^L}{\partial(1-x_L)} \right)^{-1}, \quad L_{DD}^B = V_L^B \left(\frac{\partial\mu_B^L}{\partial x_L} \right)^{-1} \quad (21)$$

are the kinetic coefficients for diffusion of A and B atoms, respectively, L_{CC}^A and L_{CC}^B are the kinetic coefficients for crystallization, and $x_L^A + x_L^B = (1 - x_L) + x_L = 1$. The evolution equation (19) for diffusion flux and equation (20) for crystallization flux are compatible with the non-negative character of the entropy production, $dS/dt \geq 0$, as given by Eq. (14).

To define the coefficients α_q^p and L_{DD}^q [see Eqs. (2) and (21)], we assume a model in which the equilibrium part of chemical potentials are given by Henry's law. These are

$$\mu_q^p = \mu_q^{p0}(T) + RT \ln(\gamma_q^p x_q^p), \quad (22)$$

where $q = A$ or B , $p = L$ or S , γ_q^p are the coefficients of activity of atoms of sort A and B , and $\mu_q^{p0}(T)$ are the standard chemical potentials which depend on the temperature T . In such a case, substituting Eq. (22) for Eqs. (2) and (21) one can obtain α_q^p and L_{DD}^q . In the liquid these are described by

$$\alpha_q^L = \frac{RT}{\omega x_L^q (V_L^q)^2}, \quad L_{DD}^q = \frac{x_L^q V_L^q}{RT}. \quad (23)$$

As follows from Eqs. (3), (4), and (23), the combination of the coefficients α_q^L and L_{DD}^q gives the time for diffusion relaxation, i.e., $\Omega\alpha_q^L L_{DD}^q = \tau_q^L$, consistent with the general analysis of the fluxes and driving forces for non-Fickian diffusion (see, e.g., p. 289 in Ref. 23).

III. INTERFACE TEMPERATURE AND SOLIDIFICATION VELOCITY

Turnbull²⁹ suggested a relationship between the free energy change ΔG , interface temperature T_I , and the velocity V . This yields

$$V = fV_0 [1 - \exp(\Delta G/RT_I)]. \quad (24)$$

Here f is the fraction of sites at the interface at which growth can occur and V_0 is the upper limit of interface advance. In the present description we assume that the atomic attachment kinetics at the interface are collision limited. In such a case, the prefactor V_0 corresponds to the value comparable to the speed of sound as an ultimate upper limit of crystal growth velocity³⁰ and, therefore, we have³¹ $V_0 \gg V$.

For alloys, the total free energy change ΔG is interpreted as a sum of the driving free energy ΔG_{DF} for the transformation and driving force ΔG_K for the kinetics of atomic attachment to the interface, so that

$$\Delta G = \Delta G_{DF} + \Delta G_K. \quad (25)$$

Following the previous works^{4,8-10} and using the above treatments (see Sec. II B), one can calculate the total change of free energy, ΔG , in rapid solidification of an alloy. With this

aim, one should express Eq. (14) in terms of the free energy per mole of the alloy solidified.

From now on we consider a dilute alloy approximation in which we shall take only the diffusion process of atoms B for diffusion flux J_D in Eq. (19). Also, we shall imply for simplicity that $V_L^B = V_D$ is the diffusive speed of B atoms in bulk liquid. Then, after multiplying Eq. (14) by $-J_C^{-1}$ and using Eqs. (13) and (15)–(18), we find the driving free energy for transformation, $\Delta G_{DF} = J_C^{-1} dG/dt$, in the form

$$\begin{aligned}\Delta G_{DF} &= \Delta G_D + \Delta G_C \\ &= \Delta G_D^E + \Delta G_D^{NE} + \Delta G_C, \quad V < V_D, \\ \Delta G_{DF} &= \Delta G_C, \quad V \geq V_D,\end{aligned}\quad (26)$$

where

$$\Delta G_D = \Delta G_D^E + \Delta G_D^{NE} \quad (27)$$

is the driving free energy for diffusion,

$$\begin{aligned}\Delta G_D^E &= (x_L - x_S)(\Delta \mu_A - \Delta \mu_B), \quad V < V_D, \\ \Delta G_D^E &= 0, \quad V \geq V_D,\end{aligned}\quad (28)$$

is the solute-drag free energy that takes into account the finite speed of solute diffusive propagation,

$$\begin{aligned}\Delta G_D^{NE} &= (x_L - x_S)\Omega \alpha_B \frac{dJ_B}{dt}, \quad V < V_D, \\ \Delta G_D^{NE} &= 0, \quad V \geq V_D,\end{aligned}\quad (29)$$

is the change of free energy for local nonequilibrium part of diffusion, and

$$\Delta G_C = (1 - x_L)\Delta \mu_A + x_L\Delta \mu_B \quad (30)$$

is the crystallization free energy. Note that in Eqs. (26)–(30) we have used one of the results of the solution of the generalized Stefan problem on solidification under local nonequilibrium diffusion.¹⁴ In accordance with this solution, a source of concentrational perturbations, i.e., the solid-liquid interface, moving at the velocity V equal to or higher than the maximum speed V_D of these perturbations, cannot change the concentration or create the concentration profile ahead of itself. As a result, one obtains $x_L = x_S = x_0$ at $V \geq V_D$ (x_0 is the initial concentration of an alloy). Therefore, in Eqs. (26)–(30) we have found that $\Delta G_D^E = 0$, $\Delta G_D^{NE} = 0$, and $\Delta G_D = 0$ with $V \geq V_D$.

From Eqs. (26)–(30) one can obtain an expression for the driving free energy ΔG_{DF} for transformation. This yields

$$\begin{aligned}\Delta G_{DF} &= (1 - x_S)\Delta \mu_A + x_S\Delta \mu_B + (x_L - x_S)\Omega \alpha_B^L \frac{dJ_B}{dt}, \\ &V < V_D, \\ \Delta G_{DF} &= (1 - x_S)\Delta \mu_A + x_S\Delta \mu_B, \quad V \geq V_D.\end{aligned}\quad (31)$$

A part of the driving free energy ΔG_{DF} which is equal to the two first terms on the right-hand side of Eq. (31) can be obtained as (see Refs. 4,8 and 32)

$$\frac{(1 - x_S)\Delta \mu_A + x_S\Delta \mu_B}{RT} = x_L \left\{ k_e - k \left[1 - \ln \left(\frac{k}{k_e} \right) \right] \right\},$$

where

$$k(V) = \frac{x_S(V)}{x_L(V)} \quad (32)$$

is the solute partitioning function which depends on the solidification velocity V , and k_e is the equilibrium coefficient of the solute distribution at $V \rightarrow 0$. To define in Eq. (31) the local nonequilibrium part of ΔG_{DF} which equals $(x_L - x_S)\Omega \alpha_B^L dJ_B/dt$ we shall use a relation between the flux J_D and conjugated driving force F_D [see Eqs. (19)–(21)]. Using Eq. (23) and Eqs. (3) and (4), one gets the equation for solute diffusion flux from Eq. (19). This yields

$$\tau_L^B \frac{dJ_B}{dt} + J_B = \frac{V_D x_L}{RT} \Delta \mu_B, \quad (33)$$

where τ_L^B is the time for diffusion relaxation of the flux J_B to its steady-state value. Equation (33) is the simplest evolution equation for the flux J_B compatible with the formalism of EIT [see Eqs. (A6) and (A7) in Appendix A] and gives non-negative entropy production, Eq. (14), for the binary system. Using the result from the analysis of Baker and Cahn⁴ that $\Delta \mu_B = RT \ln(k/k_e)$ and also using mass balance, Eq. (13), we substitute Eq. (33) into a local nonequilibrium part of ΔG_{DF} in Eq. (31). As a result, one obtains $(x_L - x_S)\Omega \alpha_B^L dJ_B/dt = (x_L - x_S)RT [\ln(k/k_e) + (1 - k)V/V_D]$. Thus, assuming $T = T_I$, Eq. (31) has the form

$$\begin{aligned}\frac{\Delta G_{DF}}{RT_I} &= x_L \left\{ k_e - k \left[1 - \ln \left(\frac{k}{k_e} \right) \right] \right\} + (x_L - x_S) \left\{ \ln \left(\frac{k}{k_e} \right) \right. \\ &\quad \left. + (1 - k) \frac{V}{V_D} \right\}, \quad V < V_D, \\ \frac{\Delta G_{DF}}{RT_I} &= x_0(k_e - 1 - \ln k_e), \quad V \geq V_D.\end{aligned}\quad (34)$$

The driving force ΔG_K in Eq. (25) is described by³²

$$\frac{\Delta G_K}{RT_I} = \frac{1 - k_e}{m_e} (T_e + m_e x_L - T_I), \quad (35)$$

where T_e is the equilibrium temperature of solidification of the alloy main component and m_e is the liquidus line slope in the equilibrium diagram of an alloy phase state. Since $V < V_0$ for collision-limited growth kinetics,^{30,31} Eqs. (24) and (25) can be rewritten as

$$\frac{V}{fV_0} = - \frac{\Delta G_{DF} + \Delta G_K}{RT_I}. \quad (36)$$

Substituting Eqs. (34) and (35) in to Eq. (36) one obtains an equation for the temperature at the interface as a response function of the interface velocity and solute concentration. This yields

$$T_I = T_e + m(V)x_L - \frac{m_e V}{(1-k_e)fV_0}, \quad (37)$$

where

$$m(V) = \frac{m_e}{1-k_e} \left\{ 1 - k \left[1 - \ln\left(\frac{k}{k_e}\right) \right] + (1-k) \left[\ln\left(\frac{k}{k_e}\right) + (1-k) \frac{V}{V_D} \right] \right\}, \quad V < V_D, \\ m = \frac{m_e \ln k_e}{k_e - 1}, \quad V \geq V_D, \quad (38)$$

is the slope of the nonequilibrium liquidus line in the kinetic phase diagram of alloy solidification.

Thus, we have found the slope $m(V)$, Eq. (38), of the nonequilibrium liquidus line as a function of nonequilibrium solute partitioning $k(V)$ and interface velocity V . In the limits $V_D \rightarrow \infty$ (i.e., $V/V_D \rightarrow 0$), Eq. (38) reduces to a solution which incorporates local equilibrium in the solute diffusion and a deviation from equilibrium at the interface due to kinetic effects.¹⁰ As a whole, Eq. (38) reflects the fact that with $V < V_D$ the slope $m(V)$ of the liquidus line deviates from its equilibrium value m_e due to both local nonequilibrium at the interface, $(m_e/(1-k_e))\{1-k[1-\ln(k/k_e)]\}$ (see Refs. 8–10), and combined shifts from local equilibrium at the interface and in the solute diffusion, $[m_e(1-k)/(1-k_e)] \times \{\ln(k/k_e) + (1-k)V/V_D\}$. The slope $m(V)$ has a constant value, Eq. (38), due to the absence of the diffusion process ahead of the interface at finite velocity, $V \geq V_D$, when complete solute trapping occurs in alloys, $x_L = x_S = x_0$ [i.e., $k(V) = 1$, Eq. (32)].

IV. DISCUSSION AND COMPARISON WITH EXPERIMENTAL DATA

An interface kinetic model developed within the framework of the continuous growth model¹⁰(CGM) provides the boundary condition for solute diffusive transport. The CGM gives a way to evaluate the solute trapping effect which can be expressed in terms of the solute partitioning function (32). Considering only dilute solutions, this function is described by^{10,33}

$$k(V) = \frac{k_e + V/V_{DI}}{1 + V/V_{DI}}, \quad (39)$$

where V_{DI} is the speed of diffusion at the interface.

One of the deficiencies of the function (39) is the difficulty of the description of complete solute trapping at finite solidification velocity, i.e., it predicts $k \rightarrow 1$ only with $V \rightarrow \infty$. However, as has been detected in a final crystalline structure of rapidly solidified binary alloys,³⁴ a transition to partitionless solidification occurs at a finite solidification ve-

locity. Also, molecular dynamic simulation has shown³⁵ that the transition to complete solute trapping is observed at finite crystal growth velocity.

The extended version of the CGM which takes into account local nonequilibrium solute diffusion eliminates this inconsistency. Particularly for solute partitioning function (32), Sobolev²⁶ suggested a generalized function for solute partitioning in the case of local nonequilibrium solute diffusion within the approximation of a dilute alloy. This yields

$$k(V) = \frac{k_e(1 - V^2/V_D^2) + V/V_{DI}}{1 - V^2/V_D^2 + V/V_{DI}}, \quad V < V_D, \\ k(V) = 1, \quad V \geq V_D, \quad (40)$$

where V_{DI} is the interfacial diffusion speed with $V_{DI} \leq V_D$.^{26,27} In the local equilibrium limit, i.e., when the bulk diffusive speed is infinite, $V_D \rightarrow \infty$, expression (40) reduces to the function $k(V)$, which takes into account the deviation from local equilibrium at the interface only, Eq. (39). In addition to previous model,^{10,33} the function $k(V)$ described by Eq. (40) includes the deviation from local equilibrium not only at the interface (introducing interfacial diffusion speed V_{DI}) but also in the bulk liquid (introducing diffusive speed V_D in the bulk liquid). As Eq. (40) shows, complete solute trapping, $k(V) = 1$, proceeds at $V = V_D$.

Thermodynamic analysis based on the hypothesis of local equilibrium in solidification of a binary system⁴ provided an approach for the two models of solute trapping with or without solute drag.^{8–10} These models have taken a shift from local equilibrium at the interface which can be expressed in unified form for the slope $m(V)$ of the kinetic liquidus by the following equation:

$$m(V) = \frac{m_e}{1-k_e} \left\{ 1 - k + [k + (1-k)\delta_0] \ln\left(\frac{k}{k_e}\right) \right\}. \quad (41)$$

Here $\delta_0 = 0$ is for the model of solute trapping without solute drag and $\delta_0 = 1$ is for the model of solute trapping with solute drag. Introducing Eq. (39) into Eq. (41) one obtains the constant liquidus slope m (independent from V) only with infinite solidification velocity, $V \rightarrow \infty$.

Using the results of the present analysis, from Eq. (38) one can get the slope of the liquidus line in the following form:

$$m(V) = \frac{m_e}{1-k_e} \left\{ 1 - k + \ln\left(\frac{k}{k_e}\right) + (1-k)^2 \frac{V}{V_D} \right\}, \quad V < V_D, \\ m = \frac{m_e \ln k_e}{k_e - 1}, \quad V \geq V_D. \quad (42)$$

With $V < V_D$, such a form of the function $m(V)$ includes the function $m(V)$ described by Eq. (41) for solute trapping with solute drag ($\delta_0 = 1$) and an additional term $(1-k)^2 V/V_D$ which arises from analysis of the Gibbs free energy by taking into account local nonequilibrium solute diffusion around the interface (see Sec. III). Also note that the function $m(V)$ described by Eq. (42) plays a crucial role for self-consistency of the theory of local nonequilibrium solidification. This

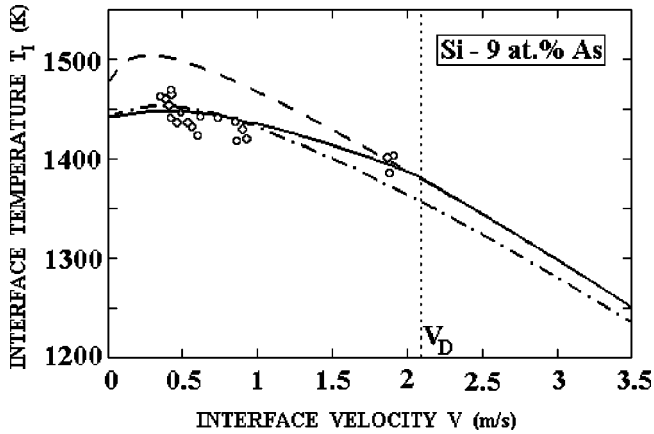


FIG. 1. Function “interface temperature versus solidification velocity” obtained for the Si–9 at. % As system. Curves are given by solution of Eq. (37). In addition to this, the dashed curve is given by Eq. (39) and Eq. (41) with the absence of the solute-drag effect, $\delta_0=0$; the dashed-dotted curve is given by Eq. (39) and Eq. (41) with including solute-drag effect, $\delta_0=1$; the solid curve is given by Eqs. (40) and (42). Data points are from Refs. 37 and 38.

form of the $m(V)$ function has been used in a self-consistent model for rapid dendritic growth and gave quantitative agreement with experimental data on the kinetics of alloy solidification.²⁷ In particular, the self-consistent dendritic growth model obtained by inclusion of Eq. (42) predicts a breakpoint at $V=V_D$, providing good agreement with data on a number of investigated alloys.²⁷

In order to verify the predictions of the present model we calculate the temperature-velocity relationship at the planar solid-liquid interface, Eq. (37), for rapid solidification of a binary alloy. As a well-tested binary system we chose a Si-As alloy which has been investigated in detail by Aziz and co-workers,^{36,37} particularly for obtaining material parameters when undergoing rapid solidification. Experimental measurements in liquid and resolidifying layers of the Si-As alloys by pulsed-laser melting have provided data on the temperature-velocity relationship and solute trapping with the guarantee of planar solid-liquid front motion.³⁷ The main result of the investigations of these authors is the absence of the solute-drag effect in solidification and a good description of the obtained experimental data by means of the CGM.¹⁰ A complete available experimental test of previously suggested

models confirms this conclusion.³⁸ However, the predictions of the CGM for solute trapping deviate significantly from their experimental data at high growth velocities of solidification, namely, below about 2 (m/s) (see, e.g., Fig. 9 in Ref. 38). The solute partitioning function described by Eq. (40) eliminates this inconsistency, and experimental data on solute trapping in the Si-As alloys^{37,38} can be satisfactorily described in all regions of the solidification velocities investigated (see Fig. 1 in Ref. 26).

At the same solidification velocity, i.e., below about $V=2$ (m/s), the interface temperature versus velocity also exhibit a clear deviation from experimental data (see Fig. 11 in Ref. 38). We attribute this deviation to the increasing influence of the local nonequilibrium solute diffusion around the interface at high solidification velocity. Therefore we make an attempt to describe the whole set of experimental data by means of the present outcome of the extended thermodynamic analysis.

Using material parameters presented in Table I, we have calculated the temperature response function (37) substituting the solute partitioning function (40) and slope for kinetic liquidus (42) which take into account deviations from local equilibrium both at the interface and bulk liquid due to local nonequilibrium diffusion. In comparison with the two previous models based on the CGM, the curve calculated using Eqs. (37), (40), and (42) is shown in Fig. 1. As can be seen, remarkably, in comparison with the CGM model which adopts the deviation from local equilibrium at the interface only (and with or without solute drag in solidification), the present model is able to describe experimental data in the whole region of the solidification velocity investigated. It should be noted especially for the present calculations, Fig. 1, that we have used the dilute alloy approximation, Eqs. (37), (40), and (42), which, strictly speaking, does not apply to the Si–9 at. % As alloy. Due to the satisfactory description of experimental data in the whole region of velocity, we believe that this result confirms the correctness of the local nonequilibrium approach to rapid solidification. An extension of the local nonequilibrium theory for the case of concentrated binary alloys can be made in detail on the basis of the analysis presented in this paper.

V. CONCLUSIONS

Rapid solidification of a binary alloy has been considered for conditions of strongly nonequilibrium transformation

TABLE I. Material parameters of the Si–9 at. % As alloy used in the calculations of the temperature response function at the solid-liquid planar interface.

Parameter	Denotation	Dimension	Value
Initial concentration	x_0	at. %	9
Solidification temperature of Si	T_e	K	1673
Liquidus slope	m_e	K/at. %	–7.9
Partition coefficient	k_e	—	0.3
Diffusion speed in bulk liquid	V_D	m/s	2.1
Interface diffusion speed	V_{DI}	m/s	0.8
Limiting speed for interface advancing	V_0	m/s	1500
Fraction of sites for growth	f	—	1×10^{-2}

from the liquid to solid crystal phase. Following the assumption of the absence of local equilibrium both at the solid-liquid interface and in the solute diffusion field around the interface, we have developed a phenomenological model for the response functions at the interface (the temperature, chemical composition, and solidification velocity) which is based on the formalism of extended irreversible thermodynamics. Taking into account the finite speed for solute diffusion propagation in bulk liquid we obtained equations for (i) the diffusion and crystallization fluxes and their driving forces, Eqs. (15)–(18); (ii) the total driving free energy which includes the sum of energy for phase transformation and kinetics of interface advancing, Eqs. (25), (34), and (35); and (iii) the equation for the slope of the nonequilibrium liquidus line in the kinetic phase diagram, Eqs. (38) and (42).

Starting from the generalized Gibbs equation (1), we found that the present results differ from the results of the previous thermodynamic formalism^{8–10,32} by an additional term proportional to the derivative of the diffusion flux with respect to time, dJ_B/dt , arising in equations for the driving force for diffusion, Eq. (17), driving free energies for the diffusion and phase transformation, Eqs. (29) and (31), respectively. As dJ_B/dt tends to zero for local equilibrium solidification, these equations are reduced to those obtained by using classical irreversible thermodynamics.

The resulting interface response function “temperature versus solute concentration and velocity,” Eq. (37), has been tested with available experimental data on a binary alloy’s solidification with planar interface. Using the dilute alloy approximation and model’s functions for solute trapping, Eq. (40), and nonequilibrium liquidus line slope, Eq. (42), we compared the model predictions with the experimental data for the Si–9 at. % As alloy.^{37,38} As is shown in Fig. 1, the temperature velocity relationship predicted by the present model describes satisfactorily the set of experimental data in the whole range of the velocity investigated.

ACKNOWLEDGMENTS

The author is grateful to Dieter M. Herlach for the valuable discussions as well as Michael J. Aziz for his constructive criticism of this work. The helpful comments of David Jou on the manuscript are kindly acknowledged with great thanks. This work was performed with support from the Alexander von Humboldt Foundation through research program No. IV RUS 1068584.

APPENDIX A: ASSUMPTIONS UNDERLYING EXTENDED IRREVERSIBLE THERMODYNAMICS FOR THE PROBLEM OF SOLUTE DIFFUSION

Here we shall give the basic ideas of the modern thermodynamical formalism applicable for local nonequilibrium solute diffusion. This formalism is based on extended irreversible thermodynamics which is a suitable theoretical framework for the description of non-Fickian aspects of solute diffusion.³⁹ In addition to classical irreversible thermodynamics, EIT goes beyond the hypothesis of local equilibrium and avoids the paradox of propagation of disturbances with

an infinite speed.^{15,21} Due to the high interest of researchers in systems far from equilibrium, today EIT has a theoretical foundation originating from the kinetic approach and at the mesoscopic level of description. On this subject, original monographs have been published^{23,40} and a wide spectrum of applications were considered.^{21,41} To clarify a phenomenological approach to the problem of non-Fickian diffusion, we shall enlarge the space of independent variables and formulate the evolution equation for solute diffusion flux. Readers can also refer to Ref. 42 where the influence of the inclusion of dissipative fluxes on a set of thermodynamic variables is discussed in more formal detail.

1. Choice of the independent variables

For the isothermal and isobaric system (the temperature T and pressure P are constants), classical irreversible thermodynamics⁷ adopts the set $\{C\}_{T,P}$ consisting of the only independent variable, the concentration X . This fact can be expressed formally as follows:

$$\{C\}_{T,P} = X. \quad (\text{A1})$$

The concentration X satisfies the balance law equation of the general form:

$$\frac{\partial X}{\partial t} = -\nabla \cdot \vec{J}^C + \sigma^C, \quad (\text{A2})$$

where \vec{J}^C is the flux corresponding to the quantity X from the set $\{C\}_{T,P}$, σ^C is the source term.

Besides the classical variables, EIT enlarges the set of independent variables by including the dissipative fluxes.^{23,42} For the case of isothermal non-Fickian diffusion, the extended space of independent variables V_N is formed by the union of the classical set $\{C\}_{T,P}$ and the space consisting of the vector of the diffusion flux \vec{J} . This yields

$$V_N = \{C\}_{T,P} \cup \vec{J}. \quad (\text{A3})$$

The variables from the set $\{C\}_{T,P}$ are characterized as the set consisting of the conserved and slow variables, as their behavior is governed by the conservation law and as they decay slowly in time. Contrary to this, the independent variable \vec{J} is nonconserved and its rate of decay has a relatively high value. It is of the order of magnitude of the time for the relaxation of the diffusion flux to its steady-state value or the time for smoothing of the concentrational inhomogeneity by diffusion in a local bulk of the system, or the time for diffusion jumps of atoms or molecules. Consequently, the rate of decay of \vec{J} can be estimated by the time $\tau_D = D/V_D^2$, where D is the diffusion constant and V_D is the finite speed for diffusion (see Appendix B). For instance, at the usual or higher temperatures in a binary alloy’s system or inorganic solution, this time changes within a wide interval: $10^{-7} \text{ s} < \tau_D < 10^{-11} \text{ s}$. For time intervals much larger than τ_D , the rate of variation of \vec{J} can be ignored.

2. Evolution equation for the diffusion flux

By analogy with Eq. (A2) which describes changing of the classic variable X , one can assume that the \vec{J} variable satisfies the following evolution equation:

$$\frac{\partial \vec{J}}{\partial t} = -\nabla \vec{J}^F + \vec{\sigma}^F, \quad (\text{A4})$$

where \vec{J}^F and $\vec{\sigma}^F$ denote the corresponding flux and source terms respectively, and the upper index F is related to the fast variable of the diffusion flux \vec{J} . The functions \vec{J}^F and $\vec{\sigma}^F$ include the variables from the whole set V_N , Eq. (A3), and for the lowest order of approximation they can be derived from the relevant constitutive equations

$$\vec{J}^F(X, \vec{J}) = a_1(X) \vec{U}, \quad \vec{\sigma}^F(X, \vec{J}) = a_2(X) \vec{J}, \quad (\text{A5})$$

where \vec{U} is the identity tensor, and a_1 and a_2 are undetermined functions of concentration X . Substituting Eq. (A5) for Eq. (A4), one can get the evolution equation for the solute diffusion flux. This yields

$$\frac{\partial \vec{J}}{\partial t} = -\frac{\partial a_1}{\partial X} \nabla X + a_2 \vec{J}. \quad (\text{A6})$$

Defining $\partial a_1 / \partial X = D / \tau_D$ and $a_2 = \tau_D^{-1}$, one obtains from Eq. (A6) the evolution equation

$$\tau_D \frac{\partial \vec{J}}{\partial t} + \vec{J} + D \nabla X = 0. \quad (\text{A7})$$

Equation (A7) can be treated as the simplest generalization of the classical Fick's first law $\vec{J} + D \nabla X = 0$, which is recovered when $\tau_D = 0$ or in stationary situations in which $\partial \vec{J} / \partial t = 0$. The evolution equation (A7) takes into account the relaxation to local equilibrium of the diffusion flux and is known as the Maxwell-Cattaneo equation in the context of heat transport.¹⁵ As follows from Eq. (A7), the concentration gradient ∇X at a point of a system defines the vector \vec{J} of the solute flux, not at time t as in the local equilibrium approximation, but with a delay equal to the relaxation time τ_D .

The mass transfer in a system is governed by the balance law

$$\frac{\partial X}{\partial t} + \nabla \cdot \vec{J} = 0. \quad (\text{A8})$$

In contrast with Fick's first law, which leads to the diffusion equation of parabolic type, Eqs. (A7) and (A8) give rise to the hyperbolic equation for the mass concentration:

$$\frac{\partial X}{\partial t} + \tau_D \frac{\partial^2 X}{\partial t^2} = D \nabla^2 X. \quad (\text{A9})$$

Equation (A9) is the simplest mathematical model combining the diffusive (dissipative) mode and the propagative (wave) mode of mass transport under local nonequilibrium conditions. In such a case, Eq. (A9) describes mass transport processes under non-Fickian diffusion.

APPENDIX B: A FINITE SPEED OF SOLUTE DIFFUSION PROPAGATION

Let us obtain a substance propagation law that follows from analysis of the one-dimensional version of hyperbolic equation (A9). For this purpose, we shall examine the plane harmonic wave as the simplest solution of Eq. (A9).

We examine a wave moving along the x direction. Using a complex amplitude method, one can write

$$X(x, t) = X_0 \exp[i(k_\omega x - \omega_c t)], \quad (\text{B1})$$

where X_0 is an initial amplitude of the concentrational wave, k_ω is the complex wave number, i.e., the component of the wave vector in the x direction, ω_c is the real cyclic frequency, and $(k_\omega x - \omega_c t)$ is the phase of the concentrational wave.

Substituting Eq. (B1) for Eq. (A9), we get a dispersion equation

$$D k_\omega^2 = \tau_D \omega_c + i \omega_c^2 T(\omega_c), \quad (\text{B2})$$

where

$$T(\omega_c) = \tau_D + i \omega_c^{-1} \quad (\text{B3})$$

is the complex time. Equation (B2) defines the concentrational wave propagation versus the frequency ω_c . The elimination of the amplitude X_0 from Eq. (B1) takes into account the fact that the initial amplitude X_0 may be defined if the source of the concentrational wave is known.

For further analysis, the wave number can be taken of the form $k_\omega = \rho \exp(i\lambda)$. Substituting this expression for Eq. (B2), one can get the following system of equations: $\rho^2 \cos(2\lambda) = \omega_c^2 \tau_D / D$, $\rho^2 \sin(2\lambda) = \omega_c / D$. A solution of this system relative to ρ and λ allows one to obtain the wave number. This yields

$$\begin{aligned} k_\omega &= \text{Re}(k_\omega) + i \text{Im}(k_\omega) \\ &= \omega_c \left(\frac{\tau_D + |T(\omega_c)|}{2D} \right)^{1/2} + i \omega_c \left(\frac{|T(\omega_c)| - \tau_D}{2D} \right)^{1/2}, \end{aligned} \quad (\text{B4})$$

where $\text{Re}(k_\omega)$ and $\text{Im}(k_\omega)$ are the real and imaginary parts of the wave number, respectively, and

$$|T(\omega_c)| = (\tau_D^2 + \omega_c^{-2})^{1/2} \quad (\text{B5})$$

is the modulus of the complex time, Eq. (B3).

The plane harmonic wave which propagates away from the source of concentrational disturbances has a phase speed v_p and characteristic distance l_a of attenuation. From the expressions (B4) and (B5) one can find v_p and l_a . They are

$$\begin{aligned} v_p &= \frac{\omega_c}{\text{Re}(k_\omega)} = \left(\frac{2D}{\tau_D + |T(\omega_c)|} \right)^{1/2}, \\ l_a &= \frac{1}{\text{Im}(k_\omega)} = \omega_c^{-1} \left(\frac{2D}{|T(\omega_c)| - \tau_D} \right)^{1/2}. \end{aligned} \quad (\text{B6})$$

From Eqs. (B6) we have for slow frequencies, $\omega_c \ll \tau_D^{-1}$, that $|T(\omega_c)| = \omega_c^{-1}$ and, then, from Eqs. (B6) one gets

$$v_p = (2D\omega_c)^{1/2}, \quad l_a = (2D/\omega_c)^{1/2}. \quad (\text{B7})$$

Expressions for v_p and l_a , Eqs. (B7), can also be obtained from the classical Fick's theory of mass transfer.

In order to obtain the phase speed and the attenuation distance in the high-frequency limit $\omega_c \gg \tau_D^{-1}$, we expand the time $|T(\omega_c)|$ in Eq. (B5) by $(\omega_c \tau_D)$ to first order. This yields $|T(\omega_c)| = \tau_D [1 + (\omega_c \tau_D)^{-2}]^{1/2} \cong \tau_D (1 + \omega_c \tau_D / 2)$. Then, we obtain from Eqs. (B6) that the phase speed and the attenuation distance tend to the following finite limits:

$$v_p = (D/\tau_D)^{1/2} = V_D, \quad l_a = 2(D\tau_D)^{1/2}. \quad (\text{B8})$$

As follows from Eqs. (B8), in the high-frequency limit, $\omega_c \gg \tau_D^{-1}$, the phase speed of the wave is equal to the diffusive speed or, in other words, to the speed of propagation for diffusion signals.²³

Thus, in the regions $\omega_c \ll \tau_D^{-1}$ and $\omega_c \sim \tau_D^{-1}$ the speed and attenuation of the concentrational wave will depend on the frequency ω_c [see Eqs. (B6) and (B7)]. Such a dependence on the frequency is directly connected to the phenomenon of dispersion. In addition to this result in the high-frequency limit, $\omega_c \gg \tau_D^{-1}$, the speed and attenuation of the concentrational wave will not depend on the frequency ω_c [see Eqs. (B8)]. In such a case, the concentrational wave moves without dissipation and its phase speed v_p is equal to the diffusive speed V_D .

*Electronic address: Peter.Galenko@dir.de

¹*Advances in Research and Applications*, Vol. 3. of *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1956); *Science and Technology of the Undercooled Melt*, edited by P.R. Sahn, H. Jones, and C.M. Adam (Martinus Nijhoff, Dordrecht, 1986); *Science and Technology of Crystal Growth*, edited by J.P. van der Eerden and O.S.L. Bruinsma (Kluwer Academic, Dordrecht, 1995); *Phase Transformations and Systems Driven Far From Equilibrium*, MRS Symposia Proceedings No. 481, edited by E. Ma, M. Atzmon, P. Bellon, and R. Trivedi (Materials Research Society, Warrendale, PA, 1998).

²V.T. Borisov, Dokl. Akad. Nauk SSSR **142**, 69 (1962) [Sov. Phys. Dokl. **7**, 50 (1962)].

³I.L. Aptekar and D.S. Kamenetskaya, Fiz. Met. Metalloved. **14**, 358 (1962).

⁴J.C. Baker and J.W. Cahn, in *Solidification*, edited by T.J. Hughel and G.F. Bolling (American Society of Metals, Metals Park, OH, 1971), p. 23.

⁵M. Hillert and B. Sundman, Acta Metall. **24**, 731 (1976); *ibid.* **25**, 11 (1977); C.V. Thompson and F. Spaepen, *ibid.* **27**, 1855 (1979); D.E. Temkin, Kristallografiya **32**, 1331 (1987); M.J. Aziz and W.J. Boettinger, Acta Metall. Mater. **42**, 527 (1994).

⁶M. Hillert, Acta Mater. **47**, 4481 (1999).

⁷I. Prigogine, *Introduction to Thermodynamics of Irreversible Processes* (Interscience, New York, 1961); S. De Groot and P. Mazur, *Non-equilibrium Thermodynamics* (North-Holland, Amsterdam, 1962); P. Glansdorff and I. Prigogine, *Thermodynamical Theory of Structure, Stability and Fluctuations* (Wiley, New York, 1971).

⁸W.J. Boettinger and S. R. Coriell, in *Science and Technology of the Undercooled Melt*, edited by P.R. Sahn, H. Jones, and C. M. Adam (Martinus Nijhoff, Dordrecht, 1986), p. 81.

⁹W.J. Boettinger, S.R. Coriell, and R. Trivedi, in *Rapid Solidification Processing: Principles and Technologies IV*, edited by R. Mehrabian and P.A. Parrish (Claitor's, Baton Rouge, 1988), p. 13.

¹⁰M.J. Aziz and T. Kaplan, Acta Metall. **36**, 2335 (1988).

¹¹I. Prigogine, Physica (Amsterdam) **15**, 272 (1949).

¹²P.K. Galenko, Kristallografiya **38** (6), 238 (1993) [Crystallogr. Rep. **38**, 836 (1993)]; Dokl. Akad. Nauk **334**, 707 (1994) [Phys. Dokl. **39**, 111 (1994)]; Phys. Lett. A **190**, 292 (1994); J. Tech. Phys. **65** (11), 110 (1995).

¹³D.M. Herlach, Mater. Sci. Eng., R. **12**, 177 (1994).

¹⁴P. Galenko and S. Sobolev, Phys. Rev. E **55**, 343 (1997).

¹⁵D. Jou, J. Casas-Vazquez, and G. Lebon, Rep. Prog. Phys. **51**, 1005 (1988).

¹⁶As soon as the interface velocity is of the order of the diffusive speed in bulk liquid we take into account the motion of the front of the solute profile which moves with the diffusive speed V_D . Therefore, under the "wave mechanism" of solute propagation we imply the propagation of the solute profile ahead of the moving interface.

¹⁷On some occasions [see, e.g., W. Dreyer and H. Struchtrup, Continuum Mech. Thermodyn. **5**, 3 (1993); T. Dedeurwaerdere, J. Casas-Vazquez, D. Jou, and G. Lebon, Phys. Rev. E **53**, 498 (1996)] the "wave" mechanism of solute propagation can also be considered as "ballistic" propagation. The study of the ballistic regime is directly connected with the transition from the collision-dominated diffusive regime to the collisionless ballistic regime. In this case, one would expect to describe the transition from short-relaxation time (collision-dominated behavior) to long-relaxation time (ballistic behavior) for solute propagation.

¹⁸P.K. Galenko and D.A. Danilov, J. Cryst. Growth **216**, 512 (2000); Phys. Lett. A **272**, 207 (2000).

¹⁹The term "solute trapping" has been introduced to define the processes of solute redistribution at the interface which are accompanied by (i) the increasing of chemical potential (Ref. 4), and (ii) the deviation of the partition coefficient for solute distribution towards unity from its equilibrium value (independently of the sign of the chemical potential) (Ref. 10). The exact analytical solutions for planar and nonplanar configurations of the interface show that complete solute trapping, i. e., partitionless solidification with the initial chemical composition, proceeds in a solidifying system if the steady-state interface velocity is equal to or greater than the diffusive speed (Ref. 18). These solutions do not depend on the form of a function for solute partitioning vs velocity, and such a phenomenon can be also related to "solute trapping" by terminology.

²⁰D. Josef and L. Preziosi, Rev. Mod. Phys. **61**, 41 (1989); *ibid.* **62**, 375 (1990).

²¹D. Jou, J. Casas-Vazquez, and G. Lebon, Rep. Prog. Phys. **62**, 1035 (1999).

²²C. Truesdell, *Rational Thermodynamics* (McGraw-Hill, New York, 1969).

- ²³D. Jou, J. Casas-Vazquez, and G. Lebon, *Extended Irreversible Thermodynamics*, 2nd ed. (Springer, Berlin, 1996).
- ²⁴G.A. Maugin, *The Thermodynamics of Nonlinear Irreversible Behaviors* (World Scientific, Singapore, 1999).
- ²⁵A.A. Chernov, in *Modern Crystallography*, Vol. III, edited by M. Cardona, P. Fulde, and H.-J. Queisser, *Springer Series in Solid-State Science*, Vol. 36 (Springer, Berlin, 1984), Chap. 3.
- ²⁶S.L. Sobolev, *Phys. Status Solidi A* **156**, 293 (1996).
- ²⁷P.K. Galenko and D.A. Danilov, *Phys. Lett. A* **235**, 271 (1997); *J. Cryst. Growth* **197**, 992 (1999).
- ²⁸D.E. Temkin, in *Rost Kristallov*, edited by E.I. Givargizov (Nauka, Moscow, 1980), Vol. 13, p. 134. [English translation: *Growth of Crystals* (Consultants Bureau, New York, 1984)].
- ²⁹D. Turnbull, *J. Phys. Chem.* **66**, 609 (1962).
- ³⁰S.R. Coriell and D. Turnbull, *Acta Metall.* **30**, 2135 (1982).
- ³¹Note that the crystal growth of many metals and metallic systems give evidence for a collision-limited mechanism of kinetics (Ref. 13). On the other hand, growth of a superlattice structure in intermetallic systems is expected to be governed by short-range atomic diffusion [see, e.g., M. Barth, B. Wei, and D. Herlach, *Phys. Rev. B* **51**, 3422 (1995)]. In such a case, the atomic attachment kinetics are controlled by diffusion processes, and the prefactor V_0 in Eq. (24) is given by the atomic diffusion speed defined by the activation energy for atomic diffusion at the interface. If the growth velocity V can be of the order of the upper limit V_0 of interface advance for the growth limited by the short-range atomic diffusion, then the analysis presented in Sec. III might need to be revised.
- ³²W. Kurz and D.J. Fisher, *Fundamentals of Solidification*, 3rd ed. (Trans Tech Publications, Aedermannsdorf, 1992).
- ³³M.J. Aziz, *J. Appl. Phys.* **53**, 1158 (1982).
- ³⁴I.S. Miroshnichenko, *Quenching From the Liquid State* (Metallurgia, Moscow, 1982); K. Eckler, R.F. Cochrane, D.M. Herlach, B. Feuerbacher, and M. Jurisch, *Phys. Rev. B* **45**, 5019 (1992).
- ³⁵S.J. Cook and P. Clancy, *J. Chem. Phys.* **99**, 2175 (1993).
- ³⁶J.A. Kittl, R. Reitano, M.J. Aziz, D.P. Brunco, and M.O. Thompson, *J. Appl. Phys.* **73**, 3725 (1993).
- ³⁷J.A. Kittl, M.J. Aziz, D.P. Brunco, and M.O. Thompson, *Appl. Phys. Lett.* **64**, 2359 (1994); *J. Cryst. Growth* **148**, 172 (1995); M.J. Aziz, *Metall. Mater. Trans. A* **27**, 671 (1996).
- ³⁸J.A. Kittl, P.G. Sanders, M.J. Aziz, D.P. Brunco, and M.O. Thompson, *Acta Mater.* **48**, 4797 (2000).
- ³⁹D. Jou, J. Camacho, and M. Grmela, *Macromolecules* **24**, 3597 (1991).
- ⁴⁰B.C. Eu, *Kinetic Theory and Irreversible Thermodynamics* (Wiley, New York, 1992); in *Extended Thermodynamic Systems*, edited by S. Sieniutycz and P. Salamon (Taylor & Francis, New York, 1992); I. Müller and T. Ruggery, *Rational Extended Thermodynamics* (Springer, New York, 1999); D. Jou, J. Casas-Vazquez, and M. Criado-Sancho, *Thermodynamics of Fluids Under Flow* (Springer, Berlin, 2000).
- ⁴¹R.E. Nettleton and S.L. Sobolev, *J. Non-Equilib. Thermodyn.* **20**, 205 (1995); *ibid.* **21**, 1 (1996); D. Y. Tzou, *Macroscale to Microscale Heat Transport: The Lagging Behavior* (Taylor & Francis, New York, 1997).
- ⁴²R. Luzzi, A.R. Vasconcellos, J. Casas-Vazquez, and D. Jou, *Physica A* **248**, 111 (1998).