

Solute trapping and diffusionless solidification in a binary system

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Numerous experimental data on the rapid solidification of binary systems exhibit the formation of metastable solid phases with initial (nominal) chemical composition. This fact is explained by complete solute trapping leading to diffusionless (chemically partitionless) solidification at a finite growth velocity of crystals. Special attention is paid to developing a model of rapid solidification which describes a transition from chemically partitioned to diffusionless growth of crystals. Analytical treatments lead to the condition for complete solute trapping which directly follows from the analysis of the solute diffusion around the solid-liquid interface and atomic attachment and detachment at the interface. The resulting equations for the flux balance at the interface take into account two kinetic parameters: diffusion speed V_{DI} on the interface and diffusion speed V_D in bulk phases. The model describes experimental data on nonequilibrium solute partitioning in solidification of Si-As alloys for the whole range of solidification velocity investigated.

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I. INTRODUCTION

The concept of “solute trapping” has been introduced to define the processes of solute redistribution at the interface which are accompanied by (i) the increasing of the chemical potential [1] 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) [2].

In experimental investigations of rapid solidification, a complete solute trapping leading to diffusionless (chemically partitionless) solidification was first observed by Olsen and Hultgren and Duwez *et al.* in experiments on rapid solidification [3]. They showed that rapidly solidifying alloy systems lead to the originating of supersaturated solid solution with the initial (nominal) chemical composition of the alloy. Later on, crystal microstructures with the initial chemical composition were found by Biloni and Chalmers in rapidly solidified pre-dendritic and dendritic patterns [4].

Backer and Cahn [1] have shown that with a finite solidification velocity in a Cd-Zn system the coefficient of the Cd distribution becomes equal to the unit that characterizes diffusionless solidification. This fact has been confirmed in many binary systems by Miroshnichenko [5]. He investigated dendritic crystal microstructure after quenching from the liquid state by splat-quenching and melt-spinning methods. The results of Miroshnichenko’s microstructural analysis show that at a cooling rate greater than some critical value (depending on an alloy and experimental method this value is in the range 10^5 – 10^6 K/s) a core of main stems of dendrites has initial (nominal) chemical composition of the alloy. A critical value for undercooling in the transition to purely thermally controlled growth with a homogeneous distribution of chemical composition in Ni-B solidifying samples processed by an electromagnetic levitation facility has been obtained by Eckler *et al.* [6]. Finally, it is necessary to note that many eutectic systems undergo chemically par-

tionless solidification with an initial composition [5] that can be explained by the transition to diffusionless solidification [7].

As a consequence, experimental investigations [1,3–6] show that with increasing driving force of solidification solute traps are much more pronounced by solidifying microstructure. At a finite value of the critical governing parameters (undercooling, cooling rate or temperature gradient) complete solute trapping occurs. Because the finite value of the governing parameter defines the concrete solidification velocity, complete solute trapping and diffusionless solidification begin to proceed with a fixed critical growth velocity of crystals.

The main purpose of the present paper is to describe a model for solute trapping and the transition from chemically partitioned to diffusionless solidification in a binary system. Using the local nonequilibrium approach to rapid solidification, an analysis of diffusion mass transport in bulk phases together with conditions of atomic attachment and detachment on the solid-liquid interface is given.

The paper is organized as follows. In Sec. II, previous investigations of solute trapping are shortly reviewed. In Sec. III, an analysis of solute diffusion leading to pronounced solute trapping and complete solute trapping is given. The nonequilibrium solute partitioning function for atoms on the interface is derived in Sec. IV. A comparison with previous models and experimental data on solidification of binary systems is presented in Sec. V. Finally, in Sec. VI conclusions of the work are summarized.

II. PREVIOUS INVESTIGATIONS

For the simplest case of an atomic system, let us consider an isobaric and isothermal binary system (the pressure P and temperature T are constant) with concentration X_A and X_B of atoms A and B , respectively. In this article, we denote X as the concentration of the atoms of B sort. For a brief overview, we summarize the equilibrium and nonequilibrium solute distribution on the solid-liquid interface.

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A. Equilibrium

In equilibrium, the concentration of atoms X at the phase interface is not equal from both sides of the interface due to the different solubility of atoms in phases. During the equilibrium coexistence of phases (gas-solid, liquid-solid, gas-liquid) the atoms are distributed along the interface in consistency with the diagram of a phase state. A difference in atomic concentration in phases at the interface can be characterized by the equilibrium coefficient k_e of the atomic distribution between phases. For equilibrium coexistence of phases (e.g., between crystal and melt, vapor and crystal, crystal and liquid), the coefficient k_e can be expressed in the general form [8]

$$k_e(X_L, X_S, T) = \frac{X_S^e}{X_L^e} \equiv \exp\left(-\frac{\Delta\mu'}{RT}\right). \quad (1)$$

In Eq. (1), X_L^e and X_S^e are the mole fractions of the B component in the liquid phase (L) or crystal (S), respectively, R is the gas constant, and $\Delta\mu'$ is the difference in chemical potentials described by

$$\Delta\mu' = \Delta\mu'_B - \Delta\mu'_A, \quad (2)$$

with

$$\Delta\mu'_B = \mu'_{BS} - \mu'_{BL}, \quad \Delta\mu'_A = \mu'_{AS} - \mu'_{AL}, \quad (3)$$

where $\Delta\mu'_A$ and $\Delta\mu'_B$ are the driving forces for redistribution of atoms A and B , respectively, which are defined by redistribution potentials μ'_A and μ'_B for phases L and S . The differences $\Delta\mu'_A$ and $\Delta\mu'_B$, Eq. (3), define the sign of $\Delta\mu'$ in Eq. (2). For instance, if $\Delta\mu'$ is negative ($\Delta\mu'_A > \Delta\mu'_B$), one has $k_e < 1$ —the case of smaller solubility of atoms B in the phase S in comparison with their solubility in the phase L .

As a general characteristic of phase equilibria in binary systems, expression (1), together with Eqs. (2) and (3), is usually considered as a measure of the driving force for atomic redistribution at the phase interface. It can also be considered as one of the main parameters for the construction of the diagrams of a phase state.

B. Nonequilibrium

Expressions (1)–(3) assume local equilibrium at the interface, which is a useful approximation for many systems transforming at small interface velocities. At a large driving force for the interface advancing and with increasing of the interface velocity, the local equilibrium is not maintained [1]. Therefore, the condition for local interfacial equilibrium was relaxed by taking into account a kinetic interface undercooling and deviations from chemical equilibrium at the alloy solidification front [8,10].

A number of models [2,9–13] have been proposed to account for solute trapping and related phenomena observed during rapid phase transformations. One of the well-established boundary conditions for solute redistribution can be taken from the continuous growth model (CGM) applied to solute trapping by Aziz and Kaplan [2,13,14]. The CGM assumes alloy solidification at a “rough interface;” i.e., all interface sites are potential sites for crystallization events.

With a high solidification rate, the atom can be trapped on a high-energy site of the crystal lattice. This leads to a local nonequilibrium on the interface and to the formation of metastable solids (see examples in Ref. [15]). As a result, the solute partitioning function at the solid-liquid interface is described by [2,13]

$$k(V) = \frac{k_e + V/V_{DI}}{1 + V/V_{DI}}, \quad (4)$$

where V_{DI} is the speed of diffusion at the interface and k_e is the value of the equilibrium partition coefficient given by Eq. (1)—i.e., with the negligible interface motion $V \rightarrow 0$. Equation (4) evaluates the ratio X_S/X_L at the interface for dilute solutions of B (“solute”) in A (“solvent”).

The interfacial diffusion speed V_{DI} is the kinetic parameter describing the deviation from chemical equilibrium at the interface. It has been defined as the ratio between the diffusion coefficient D_I at the interface and the characteristic distance λ for the diffusion jump [2,13]: $V_{DI} = D_I/\lambda$. The distance λ is assumed to be equal to the width of the solid-liquid interface (few interatomic distances), and the diffusion jumps are taken along the direction of growth. Therefore, this definition for V_{DI} is corrected by results of molecular dynamic simulations [16]. They include diffusion in all spatial directions; i.e., the diffusion speed is $V_{DI} = 6D_I/\lambda$, where the factor of 6 accounts for the possibility of jumps along the six $(\pm x, y, z)$ Cartesian axes.

Outcomes following from the solute partitioning function (4) were compared in the modeling of solute trapping using numerical computations based on the phase-field theory of alloy’s solidification. Wheeler *et al.* [17] naturally included an energy penalty for high composition gradients in the liquid that suppresses the partitioning of solute at a rapidly moving interface and leads to solute trapping. They also showed that the construction of common tangents to the curves of free energy (in the spirit of Baker and Cahn [18]) has to be defined for nonequilibrium concentrations which already depend on the solidification velocity. In order to eliminate or reduce the solute trapping effect by the diffuse interface at small growth velocity, Karma and co-workers proposed an *ad hoc* suitable antitrapping condition to the diffusion flux [19]. These works [17,19] showed that when the solute trapping effect comes to modeling alloy solidification with both phase and concentration fields, a crucial issue arises concerning the relative magnitudes of the gradients of the two fields within the solidification front as well as the relative thickness of the concentration jump interface. Additionally, Conti [20] investigated the usual one-dimensional (1D) formulation of the phase-field model without the concentration gradient corrections of Wheeler *et al.* [17]. He resolved the governing equations numerically for the interface temperature and the solute concentration field as a function of the growth velocity. The partition coefficient $k(V)$ is monotonically increasing towards unity at large growth rates following the predictions of the continuous growth model (4). However, in contrast to the results of natural experiments [1,3–6], numeric predictions [17,20] were not able to reach complete chemically

partitionless (diffusionless) solidification at a finite solidification velocity.

One of the deficiencies of the function (4) is the difficulty to describe complete solute trapping at the finite solidification velocity: Equation (4) predicts $k \rightarrow 1$ only with $V \rightarrow \infty$. Contrary to this prediction, a transition to partitionless solidification occurs at a finite solidification velocity as has been shown in numerous experiments [1,3–6]. Molecular dynamic simulations also show that the transition to complete solute trapping is observed at a finite interface velocity in rapid solidification of a binary system [16]. Therefore, as an extension of Eq. (4), a generalized function for solute partitioning in the case of local nonequilibrium solute diffusion within the approximation of a dilute system has been introduced by Sobolev [21]. This yields

$$k(V) = \frac{(1 - V^2/V_D^2)k_e + V/V_{DI}}{1 - V^2/V_D^2 + V/V_{DI}}, \quad V < V_D, \quad (5)$$

$$k(V) = 1, \quad V \geq V_D.$$

The diffusion speed V_D introduced in Eq. (5) is the characteristic bulk speed. It is defined as a maximum speed for solute diffusion propagation or as a speed for the front of the solute diffusion profile. In particular the speed V_D is obtained by the speed of propagation of the plane harmonic wave away from the solid-liquid interface (see the Appendix in Ref. [22]). As the velocity V of the interface is comparable by magnitude to the speed V_D , the high-frequency limit takes place: $\omega\tau_D \gg 1$, where ω is the real cyclic frequency of the plane harmonic wave and τ_D is the time for relaxation of the diffusion flux to its steady state. In this case, V_D has to be considered finite and it is defined as $V_D = (D/\tau_D)^{1/2}$, where D is the diffusion coefficient in bulk liquid.

In the local equilibrium limit—i.e., when the bulk diffusive speed is infinite, $V_D \rightarrow \infty$ —expression (5) reduces to the function $k(V)$, which takes into account the deviation from local equilibrium at the interface only as described by Eq. (4). The function (5) includes the deviation from local equilibrium at the interface (introducing interfacial diffusion speed V_{DI}) and in the bulk liquid (introducing diffusive speed V_D in the bulk liquid). As Eq. (5) shows, complete solute trapping $k(V)=1$ proceeds at $V=V_D$. This result has been introduced by Sobolev from a postulation about the zero value for the diffusion coefficient at $V \geq V_D$. The next section further details that the condition for complete solute trapping follows directly from the analysis of solute diffusion flux.

III. DIFFUSION MASS TRANSPORT AND SOLUTE TRAPPING

In 1D solidification along the z axis, the mass balance is given by

$$\frac{\partial X}{\partial t} = -\frac{\partial J}{\partial z}, \quad (6)$$

where t is the time and J is the diffusion flux. To consider solute trapping in 1D local nonequilibrium solidification, we take one of the results from a model of rapid phase transi-

tions [23]. Using this model, the evolution equation for diffusion flux J along the z axis is described by

$$J = M \left[\frac{\partial}{\partial z} \left(\frac{\partial s}{\partial X} + \varepsilon_x^2 \frac{\partial^2 X}{\partial z^2} \right) - \alpha_j \frac{\partial J}{\partial t} \right], \quad (7)$$

where s is the entropy density, ε_x the factor proportional to the correlation length, and M is the diffusion mobility of atoms. The latter is defined by

$$M = T\bar{D}, \quad \bar{D} = D[\partial(\Delta\mu)/\partial X]^{-1}, \quad (8)$$

where D is the diffusion coefficient and $\Delta\mu$ is the difference of chemical potentials between solvent and solute. From known thermodynamic expressions [24] one can accept that

$$\frac{\partial s}{\partial X} = -\frac{\Delta\mu}{T}, \quad \alpha_j = \frac{\tau_D}{TD} \frac{\partial(\Delta\mu)}{\partial X} = \frac{\tau_D}{T\bar{D}}, \quad (9)$$

where τ_D is the time for diffusion flux relaxation to its steady state. Then, omitting the term responsible for atomic correlation—i.e., assuming that $\varepsilon_x=0$ —one can get from Eq. (7) the expression

$$J = M \left[\frac{1}{T} \frac{\partial(\Delta\mu)}{\partial z} - \frac{\tau_D}{T\bar{D}} \frac{\partial J}{\partial t} \right]. \quad (10)$$

Using Eq. (8), the evolution equation (10) results as follows:

$$J = -\bar{D} \frac{\partial(\Delta\mu)}{\partial z} - \tau_D \frac{\partial J}{\partial t}. \quad (11)$$

We find the solution for the diffusion flux J which has significance in the analysis of solute trapping. Using the expression for the diffusion speed, $V_D = (D/\tau_D)^{1/2}$, from Eqs. (6) and (11) one gets

$$\tau_D \frac{\partial^2 J}{\partial t^2} + \frac{\partial J}{\partial t} = D \frac{\partial^2 J}{\partial z^2}. \quad (12)$$

Equation (12) is a partial differential equation of hyperbolic type. It describes the flux J in the so-called “hyperbolic evolution,” which proceeds with a sharp front of the profile for the solute transport. It occurs due to both the diffusive and propagative nature of the transport in the high-frequency limit $\omega\tau_D \gg 1$ with $V \sim V_D$.

For a steady-state regime of interfacial motion Eq. (12) takes the form

$$D \left(1 - \frac{V^2}{V_D^2} \right) \frac{d^2 J}{dz^2} + V \frac{dJ}{dz} = 0, \quad (13)$$

which is true in a reference frame moving at constant velocity V with the interface $z=0$. A general solution of Eq. (13) is

$$J(z) = c_1 + c_2 \exp\left(-\frac{Vz}{D(1 - V^2/V_D^2)}\right). \quad (14)$$

To define a particular solution one can assume the following boundary conditions: the balance on the interface is $J(z=0) = V(X_L^* - X_S^*)$, and the flux is limited by the expression $J(z \rightarrow \infty) = 0$ far from the interface with $z \rightarrow \infty$. The latter condition gives $c_1 = 0$ for any velocity V , and one gets $c_2 = 0$ for

$V \geq V_D$. Also, from the interfacial balance with $z=0$ one gets $c_2 = V(X_L^* - X_S^*)$ for $V < V_D$. As a result, solution (14) transforms into the particular solution

$$J(z) = V(X_L^* - X_S^*) \exp\left(-\frac{Vz}{D(1 - V^2/V_D^2)}\right), \quad V < V_D, \quad (15)$$

$$J(z) = 0, \quad V \geq V_D,$$

where X_L^* and X_S^* are the liquid concentration and solid concentration, respectively, on the interface.

Solution (15) gives the condition for complete solute trapping with finite velocity $V \geq V_D$. This is expressed by the expression for the solute partitioning function:

$$k(V) = X_S^*/X_L^* \neq 1, \quad V < V_D, \quad (16)$$

$$k(V) = 1, \quad X_S^* = X_L^*, \quad V \geq V_D.$$

The latter condition in Eq. (16) defines the equality of the concentrations in the phases and leads to complete solute trapping.

To obtain an explicit form for the solute partitioning function (16), we analyze the balance of diffusion fluxes on the interface. Taking again the steady-state regime of solidification constant velocity V , from the system (6) and (11) one can obtain the equations

$$\frac{dJ}{dz} = V \frac{dX}{dz}, \quad J = -\bar{D} \frac{d(\Delta\mu)}{dz} + \tau_D V \frac{dJ}{dz}, \quad (17)$$

from which we get the single equation for the diffusion flux J . This yields

$$J = -D \left(\frac{\partial(\Delta\mu)}{\partial X} \right)^{-1} \frac{d(\Delta\mu)}{dz} + D \frac{V^2}{V_D^2} \frac{dX}{dz}. \quad (18)$$

The above-defined above thermodynamic parameter \bar{D} and the diffusion speed V_D in bulk have been taken into account. Defining the gradient of the difference of the chemical potentials as $d(\Delta\mu)/dz = [\partial(\Delta\mu)/\partial X] dX/dz$, Eq. (18) gives

$$J = -D \left(\frac{\partial(\Delta\mu)}{\partial X} \right)^{-1} \left[1 - \frac{V^2}{V_D^2} \right] \frac{d(\Delta\mu)}{dz}. \quad (19)$$

This equation is a general expression for the steady diffusion flux into the liquid from the interface. Within the local equilibrium limit $V_D \rightarrow \infty$ one can obtain the known Fickian approximation, which has been used previously for analysis of solute trapping [25,26].

Analytical solutions [27] for solidification under local nonequilibrium diffusion show that the concentration in both phases becomes equal to the initial (nominal) concentration and the diffusion flux is absent for $V \geq V_D$. It is also given by Eq. (15). Therefore, in addition to Eq. (19), one can finally obtain

$$J = -D \left(\frac{\partial(\Delta\mu)}{\partial X} \right)^{-1} \left[1 - \frac{V^2}{V_D^2} \right] \frac{d(\Delta\mu)}{dz}, \quad V < V_D, \quad (20)$$

$$J = 0, \quad V \geq V_D.$$

At the phase interface one assumes in Eq. (20), first, that the term $D[(\partial\Delta\mu)/\partial X]^{-1}$ is proportional to concentration such that

$$D \left(\frac{\partial(\Delta\mu)}{\partial X} \right)^{-1} = \frac{D_L X_L^*}{RT}. \quad (21)$$

Second, the chemical inhomogeneity (solutal segregation) exists due to the jump of the chemical potential $\Delta\mu$ which has the interfacial gradient $-d(\Delta\mu)/dz \cong \Delta\mu/W_0$ at a small distance W_0 of the order of a few interatomic distances. Third, in an approximation of ideal (or even real) solutions, one can assume for the interfacial difference of chemical potentials

$$\Delta\mu = \Delta\mu^L(X) - \Delta\mu^S(X) \cong RT(\ln X_L^e - \ln X_L^*) - RT(\ln X_S^e - \ln X_S^*) = RT \ln(X_S^*/X_L^*) - RT \ln(X_S^e/X_L^e) = RT[\ln k(V) - \ln k_e],$$

where X_L^e and X_S^e are equilibrium concentrations on the interface from the liquid phase and solid phase, respectively, and $k(V)$ is the ratio of concentrations on the interface defined by Eq. (16). Taking into account these last evaluations, one can get for the chemical potential gradient the expression

$$-\frac{d(\Delta\mu)}{dz} \cong \frac{RT}{W_0} \ln \frac{k(V)}{k_e}. \quad (22)$$

Integration of the balance (17) on the interface gives the flux

$$J = V(X_L^* - X_S^*). \quad (23)$$

Substituting Eqs. (21) and (22) into the expression for diffusion flux, Eq. (20), with using the balance (23) gives the following expression for the solute partitioning function:

$$\left[1 - \frac{V^2}{V_D^2} \right] \ln \frac{k(V)}{k_e} = \frac{V}{V_{DI}} [1 - k(V)], \quad V < V_D,$$

$$k(V) \equiv X_S^*/X_L^* = 1, \quad V \geq V_D, \quad (24)$$

where $V_{DI} = D_I/W_0$ is the speed for solute diffusion on the interface.

Equation (24) gives the evaluation of solute trapping effect through the solute partitioning function $k(V)$ derived initially from the analysis of the evolution equation (7) for the diffusion flux J . This equation takes into account finite diffusion speeds on the interface and in bulk liquid. The introduction of these two speeds is a consequence of the local nonequilibrium both on the interface and in bulk liquid. As Eq. (24) shows, the complete solute trapping $k(V)=1$ proceeds at $V=V_D$. Equation (24) transforms into a previously known expression for the function $k(V)$ derived in Refs. [25,26] with relaxing local equilibrium on the interface and using local equilibrium in bulk liquid ($V_D \rightarrow \infty$) for the diluted binary system ($X_L^* \ll 1$).

IV. SOLUTE PARTITIONING FUNCTION

We use a model of diffusion in which particles move by diffusion jumps in random time between two phases (states). This model was called the “two-level model of diffusion,” and it was introduced in the context of various applications—e.g., in chromatography [28] or for a longitudinal solute dispersion in a tube with flowing water (Taylor’s dispersion) [29].

Let $P_i(t, z)$ be the probability density of a particle position in the phase $i=L$ or in the phase $i=S$ at the moment t . Then local conservation of the probability density in a point with coordinate z belonging to the phase i is defined by

$$\frac{\partial P_i}{\partial t} = -\frac{\partial J_i}{\partial z}. \quad (25)$$

If the interface moves with a velocity comparable to the solute diffusion speed V_D in bulk phases, then the flux $J_i(t, z)$ of the density probability depends on the prehistory of the diffusion process. The flux, therefore, is defined by

$$J_i(t, z) = -\int_{-\infty}^t D_i(t-t^*) \frac{\partial P_i(t^*, z)}{\partial z} dt^*. \quad (26)$$

The relaxation function $D_i(t-t^*)$ can be chosen in the form $D_i(t-t^*)=D_i(0)\exp[-(t-t^*)/\tau_D]$ of exponential decay. In such a case, Eq. (26) is reduced to the Maxwell-Kattaneo equation

$$\tau_D \frac{\partial J_i}{\partial t} + J_i + D_i(0) \frac{\partial P_i}{\partial z} = 0. \quad (27)$$

It is accepted in Eq. (27) that $D_i(0)$ is the diffusion coefficient at the final moment of relaxation prehistory so that $D_i(0)=D$. System (25) and (27) gives a single equation of a hyperbolic type for the density of probability,

$$\tau_D \frac{\partial^2 P_i}{\partial t^2} + \frac{\partial P_i}{\partial t} = D_i \frac{\partial^2 P_i}{\partial z^2}, \quad (28)$$

or for the flux,

$$\tau_D \frac{\partial^2 J_i}{\partial t^2} + \frac{\partial J_i}{\partial t} = D_i \frac{\partial^2 J_i}{\partial z^2}. \quad (29)$$

As was shown in Ref. [30], the density of probability described by Eq. (28) gives a positive entropy production for the particle exchange between two levels (between two sub-systems or phases).

Integration of Eq. (28) by an infinitesimal layer including an interface leads to the balance

$$\left[D_i \frac{\partial P_i}{\partial z} + \tau_D \frac{\partial(VP_i)}{\partial t} + J_i \right] \Big|_S^L = 0. \quad (30)$$

In the steady-state regime one can get the following equation for the i th phase:

$$\begin{aligned} D_i \frac{\partial P_i}{\partial z} + \tau_D \frac{\partial(VP_i)}{\partial t} + J_i \\ = D_i \frac{dP_i}{dz} - \tau_D V^2 \frac{dP_i}{dz} + J_i = D_i \left(1 - \frac{V^2}{V_{Di}^2} \right) \frac{dP_i}{dz} + J_i, \end{aligned} \quad (31)$$

which is true in a reference frame moving with constant velocity V and placed on the interface where the balance (25) is described as $dJ_i/dz=VdP_i/dz$. Using Eq. (31), the balance (30) is

$$J_L - J_S = - \left[D_L \left(1 - \frac{V^2}{V_{DL}^2} \right) \frac{dP_L}{dz} - D_S \left(1 - \frac{V^2}{V_{DS}^2} \right) \frac{dP_S}{dz} \right]. \quad (32)$$

In Eq. (32) we introduce the speeds V_{DL} and V_{DS} of interfacial solute diffusion from the liquid and solid phases, respectively. They are defined by

$$V_{DL} = D_L/l_D = \nu_L l_D, \quad V_{DS} = D_S/l_D = \nu_S l_D, \quad (33)$$

where D_L and D_S are the diffusion coefficients in the phases, l_D scales for diffusion within which the diffusion jumps occur in phases (or on the interface), and ν_L and ν_S are the frequencies of diffusion jumps in phases (or on the interface). From the theory of the transitive state [31] one can define the frequencies of atomic jumps as

$$\nu_L = \nu_0 \exp\left(-\frac{Q_D}{RT}\right),$$

$$\nu_S = \nu_0 \exp\left(-\frac{Q_D + \Delta\mu'}{RT}\right), \quad (34)$$

where ν_0 is the attempt frequency of atomic jumps of the order of the vibrational frequency [8,32], Q_D the activation barrier for atomic diffusion through the interface, and $\Delta\mu'$ is the difference of chemical potentials defined by Eqs. (2) and (3). Obviously, interfacial equilibrium exists for

$$\nu_S/\nu_L = \exp[-\Delta\mu'/(RT)] \equiv k_e. \quad (35)$$

From the interfacial balance (32) there follows

$$J_L - J_S = - \left(1 - \frac{V^2}{V_{DL}^2} \right) \frac{d}{dz} [D_L P_L - D_S(V) P_S], \quad (36)$$

where $D_S(V)$ is the function of the interfacial velocity V defined by

$$D_S(V) = D_S \frac{1 - V^2/V_{DS}^2}{1 - V^2/V_{DL}^2} = \begin{cases} 0, & V_{DS} \ll V_{DL}, \\ D_S, & V_{DS} \approx V_{DL}, \\ D_S(1 - V^2/V_{DL}^2)^{-1}, & V_{DS} \rightarrow \infty. \end{cases} \quad (37)$$

The function (37) describes the following cases: (a) $V_{DS} \rightarrow 0$, negligible diffusion in solid ($D_S=0$) in comparison with the diffusion in liquid; (b) $V_{DS} \approx V_{DL}$, approximate equality for diffusion speeds in the liquid and solid around the inter-

face; and (c) $V_{DS} \rightarrow \infty$, condition of local equilibrium in the diffusion field of the solid (that occurs with high frequency jumps of atoms in solid).

From now on, the above case (b) for approximate equality of diffusion speeds in phases around the interface is taken. First, we use the finite difference $-dx=l_D$ in the balance (32). Second, we take into account that the factor $(1 - V^2/V_{DL}^2)$ is related to the bulk diffusion. Finally, using the definition (33), the balance (32) is described by

$$J_L - J_S = \left(1 - \frac{V^2}{V_D^2}\right) [V_{DL}P_L - V_{DS}P_S], \quad (38)$$

where V_D is the solute diffusion speed in bulk liquid around the interface. Using Eqs. (33)–(35), this balance can be rewritten as

$$J_L - J_S = V_{DL} \left(1 - \frac{V^2}{V_D^2}\right) [P_L - k_e P_S]. \quad (39)$$

For the concentrated binary system the probabilities P_L and P_S in Eq. (39) are directly proportional to the atomic concentrations in phases. This leads to

$$P_L = X_S(1 - X_L)/\Omega, \quad P_S = X_L(1 - X_S)/\Omega, \quad (40)$$

where Ω is the atomic volume. Therefore, Eq. (39) can be rewritten as

$$J_L - J_S = \left(1 - \frac{V^2}{V_D^2}\right) [X_S(1 - X_L) - k_e X_L(1 - X_S)] \frac{V_{DL}}{\Omega}. \quad (41)$$

We further use the already obtained result (20) according to which the diffusion flux is absent at $V \geq V_D$. Then, the difference (41) of fluxes on the interface takes the form

$$J_L - J_S = \left(1 - \frac{V^2}{V_D^2}\right) [X_S(1 - X_L) - k_e X_L(1 - X_S)] \frac{V_{DL}}{\Omega}, \quad (42)$$

$$V < V_D,$$

$$J_L = J_S, \quad V \geq V_D.$$

The net flux (42) must be equal to the diffusion flux

$$J_D = (X_L - X_S) \frac{V}{\Omega}. \quad (43)$$

From the equality of Eqs. (42) and (43) one gets

$$(X_L - X_S) \frac{V}{V_{DI}} = \left(1 - \frac{V^2}{V_D^2}\right) [X_S(1 - X_L) - k_e X_L(1 - X_S)], \quad (44)$$

$$V < V_D,$$

$$X_L = X_S, \quad V \geq V_D,$$

in which $V_{DI} = V_{DL}$ is the diffusion speed on the interface from the liquid phase. Equation (44) can be easily resolved regarding the function $k(V) = X_S/X_L$ of nonequilibrium solute partitioning. This yields

$$k(V, X_L^*) = \frac{(1 - V^2/V_D^2)k_e + V/V_{DI}}{(1 - V^2/V_D^2)[1 - (1 - k_e)X_L^*] + V/V_{DI}}, \quad V < V_D,$$

$$k(V, X_L^* = X_0) = 1, \quad V \geq V_D, \quad (45)$$

where X_L^* is the solute concentration in the liquid at the interface.

V. DISCUSSION AND COMPARISON WITH EXPERIMENTAL DATA

Expression (45) gives the general functional dependence of solute partitioning at the phase interface for concentrated binary systems, and with application to rapid solidification, it exhibits the two known limits. In the first limit, when solidification proceeds with local nonequilibrium at the interface only—i.e., with $V_D \rightarrow \infty$ —Eq. (45) leads to the solute partitioning function of Aziz and Kaplan [2]. In the second limit, as the concentration X_L^* of the second dissolved component becomes small—i.e., the term $(1 - k_e)X_L^*$ might be negligible in comparison with unity—Eq. (45) transforms into Eq. (5) as suggested by Sobolev [21].

From the analytical solution of the problem of rapid solidification under the steady-state regime [27], the concentration at the planar interface is given by

$$X_L^* = \frac{X_0}{k(V)}, \quad V < V_D,$$

$$X_L^* = X_0, \quad V \geq V_D, \quad (46)$$

where X_0 is the nominal (initial) concentration of the solute in the system. In accordance with the solutions obtained in Refs. [27], a source of concentration perturbations—i.e., the solid-liquid interface—moving at a 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 for the interface, one obtains in Eq. (46) that $X_L = X_S = X_0$ with $V \geq V_D$. Then the substitution of Eq. (46) into Eq. (45) leads to the following expression for nonequilibrium solute partitioning function:

$$k(V, X_0) = \frac{(1 - V^2/V_D^2)[k_e + (1 - k_e)X_0] + V/V_{DI}}{1 - V^2/V_D^2 + V/V_{DI}}, \quad V < V_D,$$

$$k(V, X_0) = 1, \quad V \geq V_D. \quad (47)$$

Figure 1 demonstrates the behavior of solute partitioning, Eq. (47), as a function of the interface velocity at various nominal solute concentrations. As the system deviates from a diluted one, the trapping of a solute becomes much more pronounced. Also, Eq. (47) shows that, independently from the solute concentration within the system, the complete solute trapping $k(V, X_0) = 1$ proceeds when the interface velocity becomes equal to or greater than the diffusion speed—i.e., with $V \geq V_D$. The condition of equality of concentrations in the liquid and solid [see Eqs. (44) and (45)] means that the lines of the nonequilibrium kinetic liquidus and solidus in the kinetic phase diagram are merging. It can also be considered

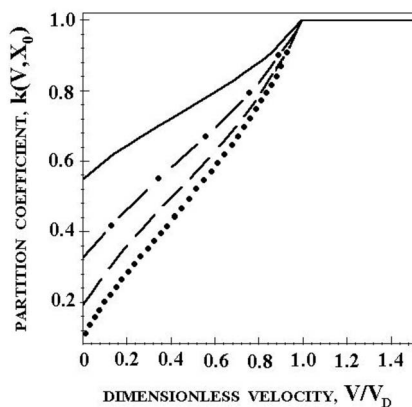


FIG. 1. Predictions of the model given by Eq. (47). Constants of the binary system are equilibrium partition coefficient $k_e=0.1$, bulk diffusion speed $V_D=25$ (m/s), and interface diffusion speed $V_{DI}=20$ (m/s). The curves present: diluted system, $(1-k_e)X_0 < 1$ (dotted line); slightly concentrated system, $X_0=0.10$ (dashed line); concentrated system, $X_0=0.25$ (dash-dotted line); and equiconcentrated system, $X_0=0.50$ (solid line).

as the characteristics of diffusionless processes.

As a general outcome, Eq. (47) includes the following important cases for nonequilibrium phase transformations: (i) the dilute limit described by Aziz’s model [13], Eq. (4),

$$(1 - k_e)X_0 \ll 1 \quad \text{and} \quad V_D \rightarrow \infty,$$

(ii) dilute limit described by Sobolev’s solute partitioning function, Eq. (5),

$$(1 - k_e)X_0 \ll 1 \quad \text{and with the finite } V_D,$$

(iii) the concentrated system described by Aziz and Kaplan’s model, Ref. [2],

$$V_D \rightarrow \infty \quad \text{for arbitrary concentration } X_0.$$

In comparison with the present model’s prediction described by Eq. (47) these limits are plotted in Fig. 2.

Figure 3 exhibits theoretical predictions for solute partitioning in comparison with experimental data on the solidification of Si-As alloys. Introducing the deviation from equilibrium at both the interface and bulk liquid allows one to describe the whole set of experimental data. Particularly, the complete solute trapping is predicted by Eq. (47) for Si-4.5 at. % As with $V_D=2.5$ m/s and for Si-9.0 at. % As with $V_D=2.1$ m/s (Table I). This provides a much better agreement with experiments than that shown by the Aziz-Kaplan model.

As can be seen in Fig. 3, predictions of the model of Aziz and Kaplan [Eq. (47) with $V_D \rightarrow \infty$] disagree with experimental data in the region $1.7 < V$ (m/s) < 2.2 of solidification velocities. One may note that at the same solidification velocity—i.e., below about $V=2$ (m/s)—the “interface-temperature-velocity” relationship also exhibits a clear deviation from experimental data (see Fig. 11 in Ref. [34]). One may also attribute this deviation to the increasing influence of local nonequilibrium solute diffusion around the interface and intensive solute trapping. Thermodynamic analy-

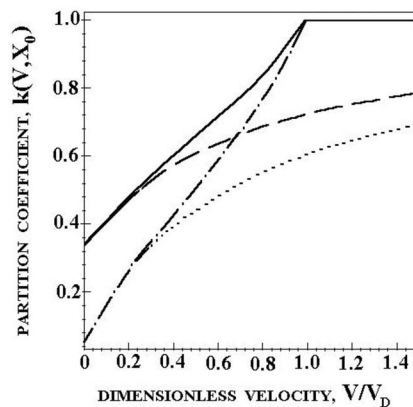


FIG. 2. Nonequilibrium solute partitioning function $k(V, X_0)$ given by the various models. Constants of the binary system are nominal concentration of a solute $X_0=0.05$ mole fraction, equilibrium partition coefficient $k_e=0.22$, bulk diffusion speed $V_D=19$ (m/s), and interface diffusion speed $V_{DI}=16$ (m/s). The dotted line is given by the model of Aziz [13] for the diluted system $(1-k_e)X_0 < 1$, the dashed line is given by the model of Aziz and Kaplan [2], the dash-dotted line is given by the model of Sobolev [21] for diluted system, and the solid line is predicted by the present model given by Eq. (47).

sis and numeric evaluations confirm the idea about the pronounced influence of local equilibrium in bulk liquid on solute trapping and interface-temperature-velocity relationship at high solidification velocity [22,35]. This example confirms that local nonequilibrium in the solute diffusion field is responsible for nonequilibrium effects appearing in rapid solidification (such as solute trapping and solute drag) and essential influence on the interface response functions

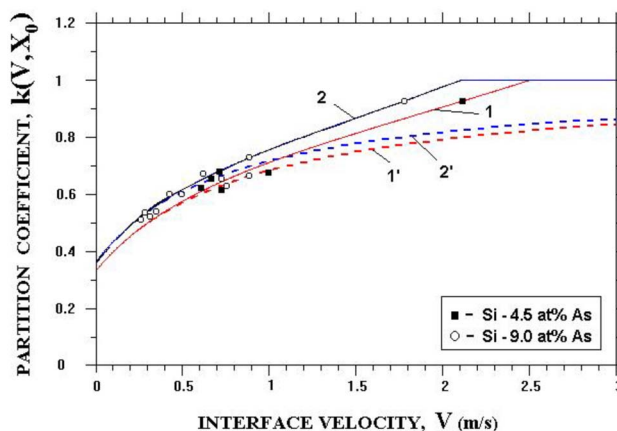


FIG. 3. (Color online) Solute partitioning versus interface velocity for experimental data [33,34] on the solidification of Si-As alloys. Curves 1’ and 2’ are given by Eq. (47) with $V_D \rightarrow \infty$ for 4.5 at. % and 9.0 at. % of As in Si, respectively (which gives the model of Aziz and Kaplan [2]). They describe experiments at small and moderate solidification velocities. Curves 1 and 2 are given by Eq. (47) with finite speed V_D for 4.5 at. % and 9.0 at. % of As in Si, respectively. These show the ability to describe experiments in a whole region of investigated solidification velocities for both alloys. Data for calculations are given in Table I.

TABLE I. Interface diffusion speed V_{DI} and bulk diffusion speed V_D for binary systems used in the calculations of the partitioning function $k(V, X_0)$ at the solid-liquid planar interface. Equilibrium partition coefficient is taken as $k_e=0.3$ from Refs. [33,34].

Model	Binary system	V_{DI} (m/s)	V_D (m/s)	Reference
Aziz and Kaplan's model [2]	Si-4.5 at. % As	0.46		[33]
		0.37		[34]
Aziz and Kaplan's model [2]	Si-9 at. % As	0.46		[33]
		0.37		[34]
Sobolev's solute partitioning function, Eq. (5)	Si-4.5 at. % As and Si-9 at. % As	0.75	2.7	[21]
Present model, Eq. (47)	Si-4.5 at. % As	0.8	2.5	Current data
	Si-9 at. % As	0.8	2.1	[22]

(temperature, concentration, velocity) [35]. Thus, the agreement between Eq. (47) and experimental data demonstrates the pronounced effect of deviation from local equilibrium in bulk liquid on solute trapping at higher solidification velocity.

Summarizing the behavior for solute partitioning shown in Figs. 1–3, one can conclude that during rapid solidification the consequences of deviations from local chemical equilibrium are threefold. First, the partition coefficient becomes dependent on the growth velocity. Second, the liquidus and solidus lines approach each other. For these two cases it can be enough to introduce into the theory deviation from local equilibrium at the interface only. Third, in the extreme case (if the solidification velocity is equal to or greater than the atomic diffusive speed in bulk liquid) the partition coefficient $k(V)$ becomes unity and the liquidus and solidus lines coincide. This leads to a solid being far from chemical equilibrium upon diffusionless solidification. Such three conditions are of special importance in the preparation of metastable supersaturated solutions [15].

VI. CONCLUSIONS

Solute trapping in rapid solidification of a binary alloy's system has been considered. It has been shown that the condition for complete solute trapping leading to diffusionless solidification follows directly from the solution for the diffusion task. This task assumes both the low-frequency regime (purely diffusion) and high-frequency regime (diffusion and propagative regime) of atomic motion in a phenomenological statement.

The two-level model has been used to define the solute partitioning function. This model has been used previously (e.g., in chromatography and for investigation of longitudinal solute dispersion), and it has been formally reduced to expressions for an extended version of the continuous growth

model. The extended version adopts two kinetic parameters: solute diffusion speed V_{DI} on the interface and solute diffusion speed V_D in bulk liquid.

A condition of complete solute trapping at the finite solidification velocity equal to the diffusion speed, $V=V_D$, has been found. This fact is expressed by the general expression (16) for the solute partitioning function. This condition defines the equality of the concentration in the phases and describes complete solute trapping. Analysis leads to concrete forms for the solute partitioning function. The first function is given by Eq. (24), and the second function for solute partitioning is described by Eq. (45). Both these functions predict a sharp finishing of solute trapping and the onset of diffusionless crystal growth at the solidification velocity V equal to the solute diffusion speed V_D in bulk liquid. A concrete expression for the liquid concentration X_L^* at the interface allows us to give predictions comparable with experimental data.

The model predicts the complete behavior for the solute partitioning function dependent on the solidification velocity and alloy concentration. In comparison with the experimental data of Aziz *et al.* [33,34] on solidification of Si-As alloys, the model well predicts deviation of the solute partitioning from equilibrium and complete solute trapping (Fig. 3). The transition from chemically partition growth to diffusionless growth at $V=V_D$ occurs sharply. As has been shown for dendritic growth [36] such a sharp transition leads to an abrupt exchange of growth kinetics in consistency with experimental data.

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