

Boundary interface conditions and solute trapping near the transition to diffusionless solidification

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Abstract. The process of rapid solidification of a binary mixture is considered in the framework of local nonequilibrium model (LNM) based on the assumption that there is no local equilibrium in solute diffusion in the bulk liquid and at the solid-liquid interface. According to LNM the transition to complete solute trapping and diffusionless solidification occurs at a finite interface velocity $V = V_D$, where V_D is the diffusion speed in bulk liquid. In the present work, the boundary conditions at the phase interface moving with the velocity V close to V_D ($V \lesssim V_D$) have been derived to find the non-equilibrium solute partition coefficient. In the high-speed region, its comparison with the partition coefficient from the work [Phys. Rev. E 76 (2007) 031606] is given.

1 Introduction

In the present time the process of rapid solidification is a well established method for production of the metastable materials and, in particular, supersaturated solid solutions, which can form due to the decrease of solute segregation at the rapidly moving solid-liquid interface [1, 2, 3, 4, 5]. Quantitatively this effect can be characterized by the partition coefficient k defined as the ratio of solid and liquid concentrations of the solute at the phase interface. The phenomenon of "solute trapping" by the growing phase implies the deviation of chemical partition coefficient from its equilibrium value k_e with its increasing towards unity at large growth rates. This phenomenon has been attracting considerable attention over of several decades both from experimental and theoretical points of view [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29].

In experiments with rapid solidification, very high velocities of the phase interface can be reached such that the deviations from local equilibrium in bulk phases and at an interface become considerable [7, 8, 13, 14, 22, 25, 30]. For theoretical description of

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solute trapping and related phenomena observed during rapid solidification a number of models have been proposed [6,7,8,10,15,16] in which, in particular, the deviation from local (chemical) equilibrium at solid-liquid interface is described by the partition coefficient $k(V)$ depending on growth velocity V . These models predict that the complete solute trapping with $k = 1$ is possible only asymptotically at $V \rightarrow \infty$.

Meantime there are a number of the experimental works [13,14,17,31,32,33] in which it has been shown that the transition to complete solute trapping giving rise to diffusionless solidification occurs at substantially finite values of V . This circumstance is automatically taken into account within the scope of the local nonequilibrium model (LNM) developed in the works [5,22,23,24,25,26,29]. At high growth velocities the deviation from local equilibrium can be essential not only at the interface but in the bulk of the liquid phase as well. The partition coefficient taking into account these points has been introduced in [22,23] and for the concentrated melt in [29] and in the latter case it has the form

$$k(V) = \begin{cases} \frac{(1 - V^2/V_D^2)[k_e + (1 - k_e)c_0] + V/V_{DI}}{1 - V^2/V_D^2 + V/V_{DI}}, & V < V_D \\ 1, & V \geq V_D, \end{cases} \quad (1)$$

where c_0 is the initial concentration of the melt and V_{DI} is the atom diffusive speed at the interface. The expression (1) takes naturally into account the fact that when the growth velocity V exceeds the speed V_D of the concentration disturbances propagation in the liquid, the solute transfer in the liquid has no time to occur and the transition to the diffusionless solidification begins at the finite velocity $V = V_D$.

Despite the fact that the partition coefficient (1) is consistent with experimental data and MD modeling of rapid solidification of a number of binary systems [17,34,35,36,37,38,39], some theoretical questions still remain open. In particular, according to LNM the transition to complete solute trapping at $V = V_D$ is purely a diffusion effect independent on the details of interface kinetics (i.e., independently of the collision-limited or diffusion-limited growth mechanism exists at the atomically rough or atomically smooth faces of the crystal). This means that in the high-speed region, $V \lesssim V_D$, the nonequilibrium partition coefficient $k(V)$ is also likely not to experience such a dependence and to a greater extent should be determined from the macroscopic boundary conditions at the interface.

Bearing above, it is interesting to consider the process of rapid solidification near the transition to a complete solute trapping, $V \lesssim V_D$, when the state of the system out of local equilibrium and local nonequilibrium diffusion effects play a significant role. The purpose of this work is to derive the boundary conditions at the interface in this high-speed region to analyze the nonequilibrium partition coefficient.

2 Boundary conditions

Let us consider a solidifying binary mixture of two species A (solvent) and B (solute). The process of nonequilibrium solidification is accompanied by an increase in entropy. In the case of isothermal solidification and the absence of convection in the bulk phases the interface entropy production, σ , at the sharp interface has the form [40,41]

$$T\sigma = j_A\Delta\mu_A + j_B\Delta\mu_B, \quad (2)$$

where T is the interface temperature, $\Delta\mu_i = \mu_i^S - \mu_i^L$ and μ_i^{LS} are the chemical potentials per unit mass of species i ($i = A, B$) at the liquid (L) and solid (S) sides of the interface. Normal to the interface the component of the mass current of i -th species is defined by

$$j_i = \rho_i^{LS}(\mathbf{v}_i^{LS} - \mathbf{V}) \cdot \mathbf{n}, \quad (3)$$

where \mathbf{n} is the unit vector normal to the interface pointing into the liquid, \mathbf{V} is the interface velocity, \mathbf{v}_i^{LS} is the velocity of species i and ρ_i^{LS} its mass density in the L (S) phase. Due to mass conservation, each of the currents j_i 's is conserved across the interface.

Equality (2) defines the differences of chemical potentials $\Delta\mu_i$ as thermodynamic driving forces which cause mass currents of j_i -component¹. From a physical point of view, it is more convenient to use another system of independent currents, namely the total mass current

$$J = j_A + j_B, \quad (4)$$

and the diffusion solute current of in each phase

$$J_D^{LS} = \rho_B^{LS} \mathbf{v}_B^{LS} \cdot \mathbf{n} = (1 - C_{LS})j_B - C_{LS}j_A, \quad (5)$$

where $C_{LS} = \rho_B^{LS}/\rho$ is the mass concentration species B and the density of the medium at both sides of the interface is assumed to be equal to ρ .

Using (4) and (5) one can rewrite the production of entropy in the form (see also [41])

$$T\sigma = [(1 - C_L)\Delta\mu_A + C_L\Delta\mu_B]J + (\Delta\mu_B - \Delta\mu_A)J_D^L, \quad (6a)$$

$$= [(1 - C_S)\Delta\mu_A + C_S\Delta\mu_B]J + (\Delta\mu_B - \Delta\mu_A)J_D^S. \quad (6b)$$

The combination of the relations (6), together with the equality $J = j_A + j_B = -\rho V$, where $V = \mathbf{V} \cdot \mathbf{n}$, gives the well-known boundary condition for the diffusion currents

$$J_D^L - J_D^S = (C_S - C_L)J = (C_L - C_S)\rho V. \quad (7)$$

Taking into account that the diffusion current can be neglected in the solid phase, $J_D^S = 0$, further will be convenient for the production of entropy to proceed from the expression (6b):

$$T\sigma = -[(1 - C_S)\Delta\mu_A + C_S\Delta\mu_B]\rho V. \quad (8)$$

The Gibbs free energy change of the system for the formation of a unit mass of solid of composition C_S , $\Delta G_m = (1 - C_S)\Delta\mu_A + C_S\Delta\mu_B$, included in equality (8), is the thermodynamic driving force causing the mass current $J = -\rho V$. For small V the linear Onsager relation follows from (8)

$$\Delta G_m = -LV, \quad (9)$$

with the positive kinetic coefficient $L > 0$ providing the positive definiteness of σ and $\Delta G_m < 0$. At finite V , the linear approximation becomes unsuitable and the right hand side in (9) should be replaced by some nonlinear function of V , i.e.

$$\begin{aligned} \Delta G_m &= (1 - C_S)\Delta\mu_A + C_S\Delta\mu_B = -f(V) \\ f(V) &\geq 0. \end{aligned} \quad (10)$$

The form of function $f(V)$ can be set from the following considerations. It is known [42] that the velocity of the interface is related to the free energy change for solidification of one mole of substance $\Delta G = M\Delta G_m$, where M is the molar mass, by the kinetic equation

$$V = V_0(1 - e^{M\Delta G_m/RT}), \quad (11)$$

¹ The connection of equality (2) with the local nonequilibrium approach will be discussed below, after the formula (14).

where V_0 is the upper limit interface speed at $\Delta G \rightarrow \infty$ and R is the gas constant. Comparing this expression with (10), one obtains

$$f(V) = -\frac{RT}{M} \ln(1 - V/V_0). \quad (12)$$

Thus, the boundary conditions at the interface, moving at an arbitrary velocity, can be represented as

$$(1 - C_S)\Delta\mu_A + C_S\Delta\mu_B = \frac{RT}{M} \ln(1 - V/V_0) \quad (13)$$

$$J_D^L - J_D^S = (C_L - C_S)\rho V. \quad (14)$$

It should be noted that in the derivation of the thermodynamic equality (2) no assumptions about the nature of dissipative processes in the bulk of phases were made, so that (2) and (13) are valid also in the local nonequilibrium state, for which J_D^L satisfies the Maxwell-Cattaneo equation. Although formally, the equation (8) coincides with the known expression for entropy production (see, for example, [8]), however, in the local nonequilibrium state entropy S depends not only on classical variables, but also on dissipative currents, which, together with temperature and concentration, are considered as independent variables, in our case $S = S(C, T, J_D^L)$. It follows from the above that the chemical potentials $\mu^{LS} = -T\partial S/\partial C_{LS}$ included in (8) and (13) are functions of the same variables.

Now let the interface move stationary at a velocity V close to V_D ($V \lesssim V_D$) for which diffusionless solidification takes place with $J_D^L = 0$ and the solute concentration in both phases equal to the initial concentration in the melt c_0 . Taking into account the above, one can write down for the chemical potentials the following expansion

$$\mu_i^L(C_L, J_D^L) = \mu_{leq,i}^L(C_l) - \alpha_i \frac{RT}{\rho V_{DI} M} J_D^L + \dots \quad (15)$$

$$\mu_i^S(C_S, J_D^S = 0) = \mu_{leq,i}^L(C_S). \quad (16)$$

The terms in (15)-(16) independent of J_D^L represent the local equilibrium part of the chemical potential. As can be seen from (15), in the first approximation μ depends linearly on J_D^L . In contrast to the bulk liquid, where scalar functions can depend on the vector only through the scalar product $J_D^2 = \mathbf{J}_D \cdot \mathbf{J}_D$, at the interface a dependence on $J_D = \mathbf{n} \cdot \mathbf{J}_D$ is possible. The coefficient at J_D^L has been chosen such that α_i is a dimensionless parameter of the order of unity, the sign of which will be discussed later.

Using Eqs.(15)-(16), let us find the explicit form the Gibbs free energy change at the interface, ΔG_m . It should be noted that in the framework of LNM the expression for it, depending on J_D^2 only, has been earlier derived. (see, for example, Ref. [4]). In fact, such expression can be obtained from Eq. (15) if in this equation one retains second-order terms proportional to J_D^2 and neglects the linear terms of the current. A subsequent substitution of $\Delta\mu_i = \mu_i^S - \mu_i^L$ in ΔG leads to Eq. (2.14) from Ref. [4]). However, taking into account that at $J_D^L \rightarrow 0$ the main contribution to the chemical potential is just given by the linear terms in the current, further we will use Eq. (15) in the linear approximation.

For the local equilibrium part of the chemical potential at C close to c_0 in the linear approximation one can write

$$\mu_{leq}(C) = \mu_{leq}(c_0) + \frac{\partial \mu_{leq}(c_0)}{\partial c_0} (C - c_0) + \dots \quad (17)$$

Thus, in a state close to diffusionless solidification the chemical potentials at the interface can be represented as follows

$$\mu_i^L(C_L, J_D^L) = \mu_i^{*L} + \frac{\partial \mu_{eq,i}^L(c_0)}{\partial c_0} (C_L - c_0) - \alpha_i \frac{RT}{\rho V_{DI} M} J_D^L + \dots \quad (18)$$

$$\mu_i^S(C_S) = \mu_i^{*S} + \frac{\partial \mu_{eq,i}^S(c_0)}{\partial c_0} (C_S - c_0) + \dots, \quad (19)$$

where

$$\mu_i^{*LS} = \mu_{eq,i}^{LS}(c_0) = \mu_i^{LS}(C_{LS} = c_0, J_D^{LS} = 0)$$

are the chemical potentials for the state of diffusionless solidification.

In the case of dilute solution and using Henry's and Raoult's laws (per unit mass) we have

$$\mu_{eq,A}^{LS}(c_0) = \mu_{0A}^{LS} + \frac{RT}{M} \ln(1 - c_0) \quad (20)$$

$$\mu_{eq,B}^{LS}(c_0) = \mu_{0B}^{LS} + \frac{RT}{M} \ln c_0, \quad (21)$$

where μ_{0i}^{LS} is the standard chemical potential of species i . Calculating the derivatives of (20)-(21) and substituting them in (18)-(19), one obtains for thermodynamic forces

$$\Delta\mu_A = \mu_A^S - \mu_A^L = \Delta\mu_A^* + \frac{RT}{M} \frac{(C_L - C_S)}{(1 - c_0)} + \alpha_A \frac{RT}{\rho V_{DI} M} J_D^L \quad (22)$$

$$\Delta\mu_B = \mu_B^S - \mu_B^L = \Delta\mu_B^* - \frac{RT(C_L - C_S)}{c_0 M} + \alpha_B \frac{RT}{\rho V_{DI} M} J_D^L, \quad (23)$$

where

$$\Delta\mu_i^* = \mu_i^{*S} - \mu_i^{*L}$$

are the thermodynamic driving forces for the state of diffusionless solidification satisfying, by virtue of (13) at $C_{LS} = c_0$, $V = V_D$ and $J_D^L = 0$, the equation

$$(1 - c_0)\Delta\mu_A^* - c_0\Delta\mu_B^* = -f(V_D) = \frac{RT}{M} \ln(1 - V_D/V_0). \quad (24)$$

Now substituting Eqs.(22)-(23) in Eq.(13) and using the equality (24), we obtain

$$\begin{aligned} & (c_0 - C_S)(\Delta\mu_A^* - \Delta\mu_B^*) + (1 - C_S)(RT/M) \left(\frac{C_L - C_S}{1 - c_0} + \frac{\alpha_A J_D^L}{\rho V_{DI}} \right) \\ & - C_S(RT/M) \left(\frac{C_L - C_S}{c_0} - \frac{\alpha_B J_D^L}{\rho V_{DI}} \right) = (RT/M) \ln \frac{1 - V/V_0}{1 - V_D/V_0} \end{aligned} \quad (25)$$

Expression (25) together with Eq.(14) defines the required boundary conditions in the high-speed region, $V \lesssim V_D$.

3 The partition coefficient

In the absence of diffusion in the solid phase, $C_S \approx c_0$, and for a dilute solution, $1 - c_0 \approx 1$, Eq.(25) reduces to

$$(\alpha_A + \alpha_B c_0) J_D^L / \rho V_{DI} = \ln \frac{1 - V/V_0}{1 - V_D/V_0} > 0, \quad (26)$$

if $V < V_D$. At $C_L > C_S$ from (14) it follows that $J_D^L > 0$ and $\alpha_A + \alpha_B c_0 > 0$. The last inequality is automatically satisfied if $\alpha_A > 0$ and $\alpha_B > 0$.

For $C_S = c_0$, combination of Eq.(14) with Eq. (26) gives

$$C_L - c_0 = \frac{V_{DI}/V}{\alpha_A + \alpha_B c_0} \ln \frac{1 - V/V_0}{1 - V_D/V_0}. \quad (27)$$

From Eq. (27) we obtain the non-equilibrium solute partition coefficient $k(V)$ ($V \lesssim V_D$) in the form

$$k(V) = \frac{c_0}{C_L} = \frac{c_0(\alpha_A + \alpha_B c_0)V/V_{DI}}{c_0(\alpha_A + \alpha_B c_0)V/V_{DI} + \ln \frac{1 - V/V_0}{1 - V_D/V_0}} \quad (28)$$

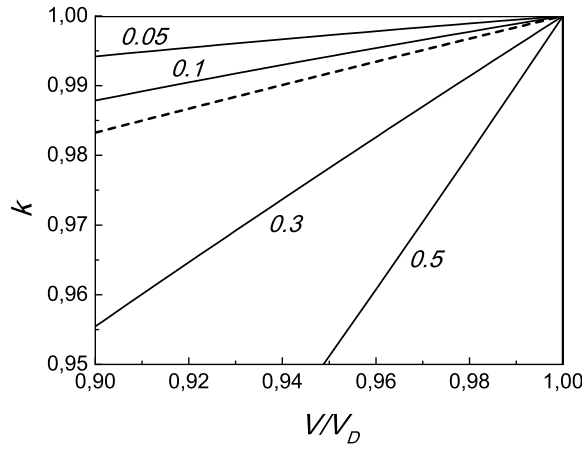


Fig. 1. The solute partition coefficients k_1 given by Eq.(28) is shown by solid curves and the solute partition coefficient k_2 given by Eq.(1) is shown by dotted curve both as functions of the ratio V/V_D . For the calculations we have chosen the following values $k_e = 0, 1$; $c_0 = 0, 1$; $V_D/V_{DI} = 1$; $\alpha_A = 1$, $\alpha_B = 0$, $V_D/V_0 = 0, 05; 0,1; 0,3; 0,5$ (values are given at curves).

Figures 1 and 2 show the behavior of the partition coefficients $k_1(V/V_D)$ and $k_2(V/V_D)$ calculated by (28) and (1) at some values of the parameters V_D/V_{DI} , k_e , α_A , α_B and different values of V_D/V_0 (indicated at curves). For a dilute solution, the term c_0^2 in denominator of Eq. (28) can be neglected ($\alpha_B = 0$). Parameter α_A (of the order of one) has been taken to be equal to one, $\alpha_A = 1$. As can be seen from Figs. 1 and 2, the partition coefficients are quite close at relatively small values of V_D/V_0 , remaining, perhaps, within the experimental errors. However as V_D/V_0 increases, the corresponding curves begin to differ markedly. At relatively large V_D/V_0 , the partition coefficient $k_1(V/V_D)$ changes rapidly enough close to $V/V_D = 1$ compared to the coefficient $k_2(V/V_D)$.

4 Conclusion

Unlike other models, LNM predicts the sharp transition to diffusionless solidification and the complete solute trapping at a finite interface velocity $V = V_D$. When the

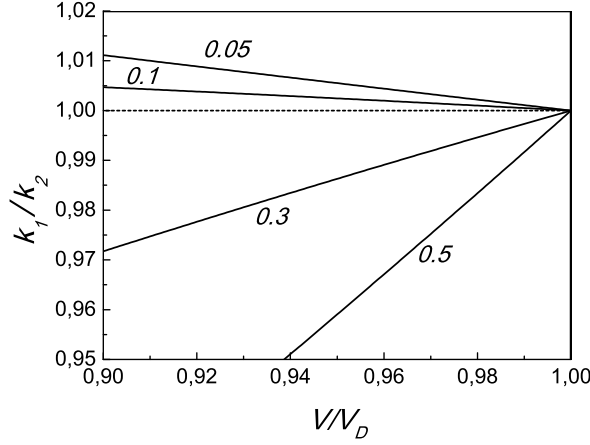


Fig. 2. The ratio of the solute partition coefficients k_1/k_2 versus V/V_D ; $k_e = 0, 1$; $c_0 = 0, 1$; $V_D/V_{DI} = 1$; $\alpha_A = 1$, $\alpha_B = 0$, $V_D/V_0 = 0, 05; 0,1; 0,3; 0,5$ (values are given at curves).

interface velocity equal to or greater than the diffusion speed in the liquid V_D the solute atoms do not have time to diffuse into the bulk of the liquid and are completely trapped by the interface with a concentration equal to the initial melt concentration regardless of the interfacial kinetics mechanism. This means that in the high-speed region, $V \lesssim V_D$, the non-equilibrium partition coefficient should mainly be dependent on the macroscopic boundary conditions at the interface.

Considering solidification of a binary mixture with a velocity $V = V_D$ as a "reference state" we have derived the boundary conditions at the interface moving with a velocity $V \lesssim V_D$ and determined the non-equilibrium partition coefficient (28). A comparison with the partition coefficient (1) shows, that at relatively small values of V_D/V_0 , where V_0 is the upper boundary of the interface velocity, both coefficients show similar behavior in the high-speed region. However with the increase of V_D/V_0 their behavior sufficiently differs.

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Author contribution statement

All authors contributed equally to the present research article.

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