

## An analytical model for local-nonequilibrium solute trapping during rapid solidification

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**Abstract:** Updated version of local non-equilibrium diffusion model (LNDM) for rapid solidification of binary alloys was considered. The LNDM takes into account deviation from local equilibrium of solute concentration and solute flux fields in bulk liquid. The exact solutions for solute concentration and flux in bulk liquid were obtained using hyperbolic diffusion equations. The results show the transition from diffusion-limited to purely thermally controlled solidification with effective diffusion coefficient  $D_b^{LNDM} \rightarrow 0$  and complete solute trapping  $K^{LNDM}(v) \rightarrow 1$  at  $v \rightarrow v_{Db}$  for any kind of solid-liquid interface kinetics. Critical parameter for diffusionless solidification and complete solute trapping is the diffusion speed in bulk liquid  $v_{Db}$ . Different models for solute trapping at the interface with different interface kinetic approaches were considered.

**Key words:** binary alloys; solute trapping; rapid solidification; local-nonequilibrium diffusion; hyperbolic diffusion equation; solute concentration; solute flux fields

### 1 Introduction

Rapid solidification phenomena occur under conditions that are far from equilibrium [1–22]. The most obvious manifestations of the deviations from local equilibrium is solute trapping which increases the solute concentration in solid phase and reduces the segregations in the liquid side of interface. The degree of solute trapping is usually quantified by the partition coefficient  $K$ , defined as a ratio of the concentration of solute in the solid to that in the liquid at the interface. This process is useful to obtain very fine structure with uniform properties. Examples of rapid solidification products accompanied by solute trapping are powders, wires and foils which can be used in powder metallurgy or in producing higher performance composite materials. As an emerging rapid solidification technology, direct strip casting is a continuous casting process for producing as cast metallic sheet of carbon and stainless steels, aluminum, magnesium, titanium and other alloys without any further thermo-mechanical processing. Therefore, the development of capability in predicting solute trapping phenomena is an important task in designing new materials and new processes.

The effect of solute trapping has been investigated

theoretically using analytical models [1,2,8–13,16–18, 21,22], phase-field models [14], molecular dynamics simulations [15, 23], Monte Carlo computer simulations [19] as well as experimental investigations [1 – 7,9]. The most outstanding question in all these studies is transition to complete solute trapping  $K(v)=1$ , where  $v$  is the interface velocity. The continuous growth model (CGM) [8], the stepwise growth model (SGM) [9], the aperiodic stepwise growth model (ASGM) [9], and the JACKSON et al model [18,19] predict complete solute trapping  $K(v)=1$  only at  $v \rightarrow \infty$ . By contrast, the local nonequilibrium diffusion model (LNDM) [10–13], based on the assumption of absence of local-equilibrium during solute diffusion in bulk liquid, leads to diffusionless solidification with complete solute trapping  $K(v)=1$  at a finite interface velocity  $v=v_{Db}$ , where  $v_{Db}$  is the diffusive velocity in the bulk liquid, i.e. the speed of atomic diffusion in liquid phase. The complete solute trapping was also observed in the experiment [3–7, 9], phase-field models [14], and molecular dynamics simulations [15].

The classical theoretical treatments of rapid solidification [1,8,9,18,19] take into account only the deviation from equilibrium at the interface introducing the velocity dependent partition coefficient  $K(v)$ . Such a modeling is valid only for relatively low interface velocities  $v \ll v_{Db}$ . With increasing undercooling, and

correspondingly increasing driving force for crystallization, the growth rates increase and may reach rates of the order of 100 m/s, while the diffusive speed is of the order of 1–30 m/s. In these cases, i.e. when  $v \sim v_{Db}$ , the diffusion field in the liquid is far from local equilibrium and the solute concentration and solute flux differ significantly from those predicted by the classical local-equilibrium theory [10–13,25].

## 2 Local nonequilibrium diffusion model (LNDM)

According to extended irreversible thermodynamics (EIT) [24] and some other local-nonequilibrium approaches [25–28], the simplest generalization of the classical Fick law for mass transport, which includes the relaxation to local equilibrium of the diffusion field, is given as

$$J + \tau \partial J / \partial t = -D_b \nabla C \quad (1)$$

where  $J$  is the solute flux,  $C$  is the solute concentration,  $D_b$  is the diffusion coefficient in bulk liquid,  $\tau$  is the relaxation time of  $J$ . In contrast to the Fick law, which is based on local-equilibrium approach, the evolutional Eq. (1) takes into account deviation of diffusion field from local equilibrium. Thus, local nonequilibrium diffusion model (LNDM) for solute concentration during rapid solidification takes the form [10–13, 25]:

$$\begin{cases} \frac{\partial C}{\partial t} + \frac{D_b}{v_{Db}^2} \frac{\partial^2 C}{\partial t^2} = D_b \nabla^2 C \\ \frac{\partial J}{\partial t} + \frac{D_b}{v_{Db}^2} \frac{\partial^2 J}{\partial t^2} = D_b \nabla(\nabla J) \end{cases} \quad (2)$$

The hyperbolic Eq. (2) predict the finite speed of the diffusive wave, i.e. maximum speed with which the diffusional perturbations can propagate in the liquid [10–13,24–28]:

$$v_{Db} = (D_b / \tau)^{1/2} \quad (3)$$

It should be noted that  $v_{Db}$  limits only the speed of diffusive perturbations (diffusive signal), but the interface velocity  $v$  can be greater than  $v_{Db}$ . To derive the interface condition, we integrate the balance law over an infinitesimal zone that includes the interface between liquid and solid phases. The interface condition is

$$v(C - C_S) = J - J_S \quad (4)$$

where  $C_S$  and  $J_S$  are the solute concentration and solute flux in the solid at the interface. Assuming  $J_S=0$  and using Eq. (1), we can rewrite the interface condition as

$$(v + \tau v')(C - C_S) + \tau v \left( \frac{\partial C}{\partial t} - \frac{\partial C_S}{\partial t} \right) = -D_b \nabla C \quad (5)$$

where the superscript dot implies differentiation with respect to time. Note that condition Eq. (5) includes not only the interface velocity, but also the interface acceleration.

Now let us consider the solute concentration field ahead of the interface moving with constant velocity  $v = \text{const}$ . Following the usual steady-state approach, we view the solidification from a reference frame attached to a planar liquid-solid interface. In such a case, a one-dimensional version of Eqs. (2) and (4) takes the form:

$$D_b \left(1 - \frac{v^2}{v_{Db}^2}\right) \frac{d^2 C}{dX^2} + v \frac{dC}{dX} = 0 \quad (6)$$

$$D_b \left(1 - \frac{v^2}{v_{Db}^2}\right) \frac{dJ}{dX} + vJ = 0 \quad (7)$$

$$v(C - C_S) = -D_b \left(1 - \frac{v^2}{v_{Db}^2}\right) \frac{dC}{dX} \quad (8)$$

Equations (5) and (6) result in the solute concentration and solute flux distributions in the liquid  $X > 0$  (the origin of the reference frame is fixed on the beginning of interface  $X=0$ ) [10–13,25]:

$$C^{\text{LNDM}}(X) = \begin{cases} (C_i - C_0) \exp[-vX / D_b (1 - v^2 / v_{Db}^2)] + C_0; & v < v_{Db} \\ C_0; & v > v_{Db} \end{cases} \quad (9)$$

$$J^{\text{LNDM}}(X) = \begin{cases} J_i \exp[-vX / D_b (1 - v^2 / v_{Db}^2)]; & v < v_{Db} \\ 0; & v > v_{Db} \end{cases} \quad (10)$$

where  $C_0$  and  $C_i$  are the solute concentration in the liquid far from ( $X \rightarrow \infty$ ) and at the interface ( $X=0$ ), respectively.

The results of LNDM Eqs. (9) and (10) clearly demonstrate that the diffusion speed  $v_{Db}$  decisively affects the diffusion field in the bulk liquid. When  $v < v_{Db}$ , the diffusion process affects the solute concentration field in the liquid and the solidification is essentially controlled by the solute flux. It is noted that as the interface velocity approaches zero, the relaxation model approaches the classical formulation. However, as the velocity increases, the solute boundary layer shrinks more rapidly than expected from the classical mass transport theory, and its thickness  $d$  defined as (see Eqs. (9) and (10))

$$d^{\text{LNDM}}(v/v_{Db}) = \begin{cases} D_b (1 - v^2 / v_{Db}^2) / v; & v < v_{Db} \\ 0; & v > v_{Db} \end{cases} \quad (11)$$

approaches zero at  $v = v_{Db}$ .

When  $v > v_{Db}$ , LNDM Eqs. (9) and (10) imply that  $C(X) = C_0$ ,  $J(X) = 0$ , and  $d(v) = 0$ . This means that the solute

concentration field ahead of the interface is undisturbed. The result has a clear physical meaning: a source of perturbations (i.e. the interface) moving with a velocity greater than the maximum speed of perturbations cannot disturb the medium ahead of itself [24,25]. In this case, the solute atoms do not have enough velocity to escape the solid-liquid interface. Thus, there is no diffusion of solute in the liquid at  $v > v_{Db}$  and, consequently, the solidification cannot be controlled by diffusion. Hence, the solidification mechanism changes qualitatively when the interface velocity  $v$  passes through the critical point  $v = v_{Db}$ . In this point, a sharp transition from diffusion controlled to purely thermally controlled growth occurs.

Now, let us compare the solute concentration and solute flux distributions according to LNDM, Eqs. (9)–(11), with classical local equilibrium ones:

$$C(X) = (C_i - C_0) \exp(-vX/D_b) + C_0 \quad (9a)$$

$$J(X) = J_i \exp(-vX/D_b) \quad (10a)$$

$$d(v) = D_b / v \quad (11a)$$

Equations (9a)–(11a) are the solutions to the solute concentration and solute flux fields obtained from local equilibrium diffusion equation of parabolic type. Thus, the comparison of exact solutions to LNDM, Eqs. (9)–(11), with classical solute concentration and solute flux fields, Eqs. (9a)–(11a), allows us to introduce the effective diffusion coefficient in bulk liquid  $D_b^{LNDM}$  [10–13] as

$$D_b^{LNDM}(v/v_{Db}) = \begin{cases} D_b(1 - v^2/v_{Db}^2); & v < v_{Db} \\ 0, & v > v_{Db} \end{cases} \quad (12)$$

If  $v \ll v_{Db}$ , the effective diffusion coefficient  $D_b^{LNDM}$  reduces to the classical diffusion coefficient  $D_b$  for the local-equilibrium conditions. But when  $v$  is of the order of  $v_{Db}$ ,  $D_b^{LNDM}$  predicts less solute flux  $J = -D_b^{LNDM} \nabla C$  than expected from the classical Fick law  $J = -D_b \nabla C$ . If  $v \geq v_{Db}$ , then  $D_b^{LNDM} = 0$  that differs qualitatively from the prediction of the classical approach. It implies the absence of solute diffusion ahead of the interface. The effective diffusion coefficient Eq. (12) can be used to modify some results of classical rapid solidification theory based on Fick law by substituting  $D_b^{LNDM}$  for  $D_b$  at least for steady-state regimes. WALDER [5] took into account the effective diffusion coefficient Eq. (12) to modify the dendritic growth theory of TRIVEDI, LIPTON and KURZ and obtained better agreement with experiment.

### 3 Models for solute partitioning

The partition coefficient  $K(v)$  (ratio of solid to liquid concentration of solute at the interface) plays an important part in rapid solidification phenomena. The

results of LNDM Eqs. (9) and (10) clearly demonstrate that when  $v \geq v_{Db}$  there is no any diffusion of solute at the interface and therefore the partition coefficient  $K^{LNDM}$  does not depend on  $v$  and  $K^{LNDM} = 1$ . It should be stressed that the result of LNDM,  $K^{LNDM} = 1$  at  $v \geq v_{Db}$ , does not depend on kinetic effects at the solid-liquid interface. It is purely diffusive effects [9–12]. It means that for any interface kinetic model the limit  $K^{LNDM}(v) \rightarrow 1$  at  $v \rightarrow v_{Db}$  must be achieved as long as no other mass transport process apart from diffusion (for example, convective solute flow or something like that) comes into play. The fact will be illustrated here below.

#### 3.1 Continuous growth model (CGM)—Dilute limit

The continuous growth model (CGM) of AZIZ and KAPLAN [6,8,9] treats the case when the interface is atomically rough enough that growth and redistribution occur simultaneously as strictly steady-state processes, even on the microscopic scale of the crystal lattice. It predicts a velocity dependence of the partition coefficient given by

$$K(v) = [K_E + v/v_{Di}] / [1 + v/v_{Di}] \quad (13)$$

where  $K_E$  is the equilibrium partition coefficient,  $v_{Di}$  is the interface diffusion speed. At  $v = v_{Di}$ , Eq. (13) describes mid-transition between  $K_E$  and unity and predicts complete solute trapping  $K_E = 1$  only at  $v \rightarrow \infty$ .

The diffusive speed in LNDM,  $v_{Db}$ , and the interface diffusion speed,  $v_{Di}$ , in Eq. (13) require further discussion. The CGM defines the  $v_{Di}$  as the ratio of solute diffusivity through the interface  $D_i$  to the atomic jump distance at the interface  $\lambda_i$ . In other words,  $v_{Di}$  is the average diffusive speed over the interface region and it has been called as the interface diffusive speed  $v_{Di}$ . The interface diffusive speed is a kinetic rate parameter for solute redistribution at the interface for relatively low interface velocity  $v < v_{Db}$ . The LNDM, Eqs. (1)–(10), define the diffusive speed  $v_{Db}$  as the speed of propagation of diffusive wave in the bulk liquid [10–13,25]. The diffusive speed  $v_{Db}$  is a diffusive parameter for solute diffusion in bulk liquid under local-nonequilibrium conditions and it does not depend on interface kinetics of solidification. Taking into account that the relaxation time  $\tau$  in LNDM can be rewritten as  $\tau = \lambda_b/v_{Db}$ , where  $\lambda_b$  is the atomic jump distance in the bulk liquid, the diffusive speed in the LNDM takes the form  $v_{Db} = D_b/\lambda_b$ , where  $D_b$  is the solute diffusion coefficient in the bulk liquid. Assuming that  $D_i \approx D_b$  and  $\lambda_i \approx \lambda$ , one is led to  $v_{Di} \approx v_{Db}$ . This assumption was considered in Refs. [10,13]. In a general case these two velocities can be different and the partitioning of solute depends on both  $v_{Db}$  and  $v_{Di}$  [11,12]. The interface region can be treated as a two phase zone consisting of both solid and liquid phases. This implies

that the interface diffusive coefficient  $D_i$  attains a value between  $D_b$ , the bulk liquid diffusion coefficient, and,  $D_s$ , the bulk solid diffusion coefficient. This holds true for the interface diffusive speed, too, i.e.  $v_{Db} > v_{Di} > v_{Ds} \approx 0$ , where  $v_{Ds}$  is the diffusive speed in the solid [11,12]. The interface diffusive speed governs the partitioning at a relatively low interface velocity  $v \sim v_{Di} < v_{Db}$ , when the diffusion through the solid-liquid interface is a limiting stage of solute redistribution. At high interface velocity  $v \sim v_{Db}$ , the limiting stage of solute redistribution is the solute diffusion in the bulk liquid with  $v_{Db}$  being the characteristic parameter.

Thus, introduction of  $D_b^{LNDM}(v)$ , Eq. (12), into the expression for  $K(v)$ , Eq. (13), leads to the generalized partition coefficient  $K^{LNDM}(v)$ , which takes into account both interfacial kinetic effects according to CGM (the interface redistribution parameter  $v_{Di}$ ) and local-nonequilibrium diffusion effects according to LNDM (the bulk liquid diffusion speed  $v_{Db}$ ) [11,12]:

$$K^{LNDM}(v) = \begin{cases} \frac{K_E(1 - v^2/v_{Db}^2) + v/v_{Di}}{(1 - v^2/v_{Db}^2) + v/v_{Di}}, & v < v_{Db} \\ 1; & v > v_{Db} \end{cases} \quad (14)$$

Expression (14) clearly demonstrates that the transition to complete solute trapping  $K^{LNDM}(v)=1$  occurs at a finite interface velocity  $v=v_{Db}$ , while the CGM, Eq. (13) predicts the complete solute trapping only at  $v \rightarrow \infty$ . The result of LNDM, Eq. (14), is in good agreement with the phase-field simulation [14], molecular dynamic simulation [15], and experimental data [6,7] (see also Refs. [11,12] and references therein).

### 3.2 Continuous growth model (CGM)—Non-dilute limit

According to CGM the partition coefficient in non-dilute limit takes the form:

$$K(v, C_0) = [k_E + (1 - k_E)C_0 + v/v_{Di}] / [1 + v/v_{Di}] \quad (15)$$

where  $k_E$  is the equilibrium partition coefficient for the solute divided by the equilibrium partition coefficient for the solvent [7,8]. This equation can be modified to local nonequilibrium diffusion case by using concept of the effective diffusion coefficient  $D_b^{LNDM}(v)$ , Eq.(12). After some algebra we have

$$K^{LNDM}(v, C_0) = \begin{cases} \frac{[(1 - v^2/v_{Db}^2)(k_E + (1 - k_E)C_0) + v/v_{Di}]}{[1 - v^2/v_{Db}^2 + v/v_{Di}]}, & v < v_{Db} \\ 1; & v > v_{Db} \end{cases} \quad (16)$$

The partition coefficient  $K^{LNDM}(v, C)$  takes into account both interfacial kinetic effects in non-dilute limit, according to CGM [7,8], and local nonequilibrium

diffusion effects according to LNDM, Eqs. (6)–(12). As it was predicted earlier, the partition coefficient  $K^{LNDM}(v, C_0) \rightarrow 1$  when  $v \rightarrow v_{Db}$  due to local nonequilibrium diffusion effects.

### 3.3 Stepwise growth model (SGM)

The SGM [9] treats the case in which an atomically smooth, sharp interface advances by the periodic lateral passage of monolayer, including any solute atoms in the layer. Solute diffuses back into the liquid during the period before the passage of the next step, at which point any remaining solute is assumed to be permanently trapped into the solid. The predicted velocity-dependence of  $K$  for this mechanism is

$$K(v) = K_E + (1 - K_E) \exp(-v_{Di}/v) \quad (17)$$

Note that in the SGM dependence  $K$  from  $v$ , Eq. (17), yields complete solute trapping  $K=1$  only at  $v \rightarrow \infty$ . Taking into account local-nonequilibrium diffusion effects in bulk liquid according to LNDM approach, Eq. (17) can be rewritten as

$$K^{LNDM}(v) = \begin{cases} K_E + (1 - K_E) \exp[-(1 - v^2/v_{Db}^2)v_{Di}/v]; & v < v_{Db} \\ 1; & v > v_{Db} \end{cases} \quad (18)$$

The expression for  $K^{LNDM}(v)$ , Eq. (18), takes into account both departure from local equilibrium of diffusion process in bulk liquid according to LNDM and interface kinetic conditions assumed by SGM. It leads to complete solute trapping  $K^{LNDM}(v)=1$  at  $v \geq v_{Db}$ .

### 3.4 Aperiodic stepwise growth model (ASGM)

The ASGM [6,9] treats the same case as the SGM, except that the passage of steps is assumed to occur randomly, rather than periodically, in time. It predicts variation of  $K$  with interface orientation. The ASGM assumes that at any orientation the interface is broken into (111) terraces of single double-layer height and random width and that solidification proceeds by the lateral passage of these steps at random intervals. Some (not all, as in SGM) of the solute atoms in the monolayer of liquid adjacent to the interface are trapped as a step passes. The ASGM expression for  $K(v, \theta)$  is given by

$$K(v, \theta) = \frac{K_E + \beta_T [(K_E + \beta_L)/(1 + \beta_L)]}{1 + \beta_T} \quad (19)$$

where  $\beta_T = v/(v_D^T \cos \theta)$ ,  $\beta_L = v/(v_D^L \cos \theta)$ ,  $v_D^L$  is diffusive speed at the ledge,  $v_D^T$  is diffusive speed at the terrace, and  $\theta$  is the angle of inclination from (111). Using the effective diffusion coefficient Eq. (12) LNDM leads to

$$K^{\text{LNDM}}(v, \theta) = \begin{cases} \{(1-v^2/v_{\text{Db}}^2)K_{\text{E}} + \beta_{\text{T}}[(1-v^2/v_{\text{Db}}^2)K_{\text{E}} + \beta_{\text{L}}]/(1-v^2/v_{\text{Db}}^2 + \beta_{\text{L}})\} / \\ (1-v^2/v_{\text{Db}}^2 + \beta_{\text{T}}); v < v_{\text{Db}} \\ 1; v > v_{\text{Db}} \end{cases} \quad (20)$$

Equation (20) generalizes Equation (19) for local nonequilibrium case and predicts complete solute trapping at  $v \geq v_{\text{Db}}$  in contrast to Eq. (19) which gives  $K(v, \theta) \rightarrow 1$  only at  $v \rightarrow \infty$ .

### 3.5 JACKSON et al model

Another theory for solute trapping due to JACKSON et al [18,19] is derived using reaction rate theory to describe the rate of atom attachments to the active sites of a sharp solid-liquid interface. The model is based on the standard quasi-equilibrium model for crystallization, which has been extended to include the non-equilibrium effects found in the Monte Carlo simulations of alloy solidification. The parameter in the model,  $\beta$ , is clearly identified as the important parameter for solute trapping. This parameter embodies the relationship between the growth and diffusion parameters found in the Monte Carlo simulations. This parameter is interpreted as the ratio of the distance that the interface advances to the distance that an atom can move by diffusion during the time in which it is at the interface. If  $\tau$  is the average time it takes for an atom to join the crystal, the distance that the interface advances during this time is  $v\tau$ . The distance that an atom can move by diffusion during this time is  $(D_{\text{b}}\tau)^{1/2}$ , where  $D_{\text{b}}$  is the diffusion coefficient of B atoms in the liquid. The ratio of these two distances is the dimensionless parameter  $\beta$  [18,19]:

$$\beta = \frac{V\tau}{(D_{\text{b}}\tau)^{1/2}} \quad (21)$$

Taking into account Eq. (3) for diffusive velocity in bulk liquid and the fact that the relaxation time in LNDM corresponds to the average time it takes for an atom to join the crystal in JACKSON et al model, the parameter  $\beta$ , Eq. (21), transforms to the ratio  $\beta = v/v_{\text{Db}}$ . The parameter  $v/v_{\text{Db}}$  is also the critical parameter in LNDM, Eqs. (1)–(12), and in some other models [25], but in LNDM  $v/v_{\text{Db}}$  governs solute diffusion in bulk liquid, and hence, solute partitioning at  $v \rightarrow v_{\text{Db}}$ , and in JACKSON et al model parameter  $\beta$  governs non-equilibrium segregation at the solid-liquid interface. Solute partitioning is governed by both solute segregation process at the interface with governing parameter  $\beta$  and local nonequilibrium diffusion effects with governing parameter  $v/v_{\text{Db}}$ . But the parameter  $\beta$  in JACKSON et al model [18,19] plays an important role at moderate

interface velocity  $v < v_{\text{Db}}$  and parameter  $v/v_{\text{Db}}$  in LNDM comes into play when  $v \rightarrow v_{\text{Db}}$  and local nonequilibrium diffusion effects are mostly decisive. Note that in our opinion parameter  $\beta$ , Eq. (21), depends on  $D_{\text{i}}$  (interface diffusion coefficient) rather than  $D_{\text{b}}$  (bulk liquid diffusion coefficient), because B atom is considered one jump to the interface and, hence, the close presence of interface affects the distance that an atom can move by its last jump. Parameter  $(D_{\text{b}}\tau)^{1/2}$  is the distance that an atom can move by diffusion during time  $\tau$  in bulk liquid far from interface when the interface does not influence the diffusion process in liquid. But in some case assumption  $D_{\text{i}} = D_{\text{b}}$  is a reasonable approximation.

Thus, for rough interfaces and small concentration of solute, the theory of JACKSON et al yields [18,19]

$$K(v) \approx K_{\text{E}}^{1/(1+A'v)} \quad (22)$$

where  $A'$  depends on the square root of the diffusion coefficient, namely,  $A' = A''/(D_{\text{b}})^{1/2}$ . From Eqs. (12) and (22) one can calculate

$$K^{\text{LNDM}}(v) = \begin{cases} K_{\text{E}}^{\sqrt{D(1-v^2/v_{\text{Db}}^2)}/(\sqrt{D(1-v^2/v_{\text{Db}}^2)} + A'v)}; v < v_{\text{Db}} \\ 1; v > v_{\text{Db}} \end{cases} \quad (23)$$

The partition coefficient Eq. (23) incorporates both interface kinetic model of JACKSON et al [17,18] and local nonequilibrium diffusion field according to LNDM. As it was expected one can observe partitionless solidification  $K^{\text{LNDM}}(v) \rightarrow 1$  when  $v \rightarrow v_{\text{Db}}$  in contrast to Eq. (22) that leads to complete solute trapping only at  $v \rightarrow \infty$ .

## 4 Hierarchy of deviation from local equilibrium

Solidification of undercooled melts occurs at wide range of velocities up to hundreds m/s and includes various physical phenomena such as solute diffusion, heat conduction, interface kinetics of solidification. Each of these processes has its own characteristic time and length scales (in a steady-state – characteristic velocities). It implies that while interface velocity increases, the solute diffusion, interface kinetics, and heat conduction deviate from equilibrium at different values of interface velocity. This allows us to introduce a hierarchy of deviations from equilibrium which is followed by increasing solidification velocity [2,11,12]:

1)  $v=0$ . Full equilibrium. No chemical potential gradient (composition of phases are uniform), no temperature gradients,  $K=K_{\text{E}}$ .

2)  $v \ll v_{\text{Db}}$ . Local equilibrium. There are concentration and temperature gradients near the interface, i.e.

there is no full equilibrium, but there is local equilibrium both in the bulk liquid and at the interface. The partition coefficient is equal to its equilibrium value  $K_E$ . Diffusion and temperature fields are described by local-equilibrium transfer equation of parabolic type.

3)  $v < v_{Db}$ . Non-equilibrium interface kinetics. There is no local equilibrium at the interface and the partition coefficient depends on the interface velocity  $v$ . In this case (as well as in case 2), the solute concentration and temperature fields are governed by the classical (local equilibrium) transport equation of parabolic type.

4)  $v \leq v_{Db}$ . Non-equilibrium diffusion field. In this case, there is no local equilibrium in the bulk liquid. Hence, according to LNDM, solute concentration and solute flux fields in bulk liquid are governed by the mass transport equations of hyperbolic type (1)–(2) [10–13]. The temperature field is still at local equilibrium due to  $v \sim v_{Db} \ll v_T$  and it can still be described by the classical heat conduction equation of parabolic type. Partition coefficients  $K^{LNDM}(v)$  are given by Eqs. (14), (16), (18), (20), and (23) for different types of interface kinetic model. The choice of the model depends on the characteristics of a particular rapid solidification process at the interface. In this case, solute partitioning is governed by both interface kinetics and solute diffusion in bulk liquid. But when the interface velocity increases, the dependence of  $K$  from interface kinetics parameters is weaker and solidification mainly depends on  $v_{Db}$  demonstrating transition to diffusionless regime ( $D_b^{LNDM}(v) \rightarrow 0$ ) with complete solute trapping ( $K^{LNDM}(v) \rightarrow 1$  at  $v \rightarrow v_{Db}$  for all interface kinetic models (see Eqs. (14), (16), (18), (20), and (23)).

5)  $v \geq v_{Db}$ . Diffusionless solidification. According to LNDM, at this interface velocity  $K^{LNDM}(v) \equiv 1$  and  $D_b^{LNDM}(v) \equiv 0$ . This implies thermally controlled diffusionless solidification with complete solute trapping. Ahead of the interface  $C(X) = C_0$  and  $J(X) = 0$ . The result does not depend on the interface kinetics and is a consequence of deviation from local equilibrium in bulk liquid with  $v_{Db}$  being the critical parameter [10–13].

6)  $v \sim v_T$ . Local-nonequilibrium temperature field. At such high velocities heat transport occurs far from local equilibrium. The temperature field is governed by hyperbolic transport equations [20–23]. If solid-liquid interface propagates only due to undercooling effects, the interface velocity  $v$  is limited by  $v_T$ —the speed of heat wave [25].

## 5 Conclusions

LNDM clearly demonstrates that a sharp transition from diffusion-controlled to purely thermally controlled solidification occurs due to local nonequilibrium solute

diffusion in the bulk liquid. The critical parameter for the transition is  $v_{Db}$  (the diffusive velocity in the bulk liquid), i.e. the speed of atomic diffusion in liquid phase. When  $v < v_{Db}$ , solidification is governed mostly by the diffusion processes in bulk liquid, whereas at  $v > v_{Db}$ , diffusion flux ahead of the interface  $J^{LNDM}(X) = 0$ , and  $C^{LNDM}(X) = C_0$ . This implies that solidification occurs in diffusionless regime without solute segregation at the interface (complete solute trapping). The transition from diffusion-controlled to thermally controlled partitionless solidification was observed in experiments.

Local nonequilibrium diffusion effects lead to the effective (velocity dependent) diffusion coefficient in bulk liquid  $D_b^{LNDM}(v)$ . The effective diffusion coefficient has been used to modify a number of existing solute partitioning models. Due to local nonequilibrium diffusion effects all the models predict the transition to diffusionless solidification with complete solute trapping  $K^{LNDM}(v) = 1$  when the interface velocity  $v$  passes through the critical point  $v = v_{Db}$ . Thus, at high interface velocity  $v \rightarrow v_{Db}$ , the solute partitioning at the solid-liquid interface is mainly governed by solute diffusion in bulk liquid rather than by interface kinetics of solidification.

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## 快速凝固中局部非平衡溶质截留的分析模型

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**摘要:** 对二元合金快速凝固过程中的局部非平衡扩散模型(LNDM)进行改进。改进的模型考虑了熔体中溶质浓度和溶质通量流场与局部平衡的偏差。采用双曲函数扩散方程求得了熔体中溶质浓度和通量的准确解。结果表明, 对任何固-液界面的动力学, 当有效扩散系数  $D_b^{\text{LNDM}} \rightarrow 0$  和在  $v \rightarrow v_{\text{Db}}$  发生完全溶质截留  $K^{\text{LNDM}}(v) \rightarrow 1$  时, 凝固过程将由扩散控制转变为完全的热控制。非扩散凝固和完全溶质截留的临界参数为在溶体中的扩散速度  $v_{\text{Db}}$ , 考察了不同界面动力学途径的溶质截留模型。

**关键词:** 二元合金; 溶质截留; 快速凝固; 局部非平衡扩散; 双曲扩散方程; 溶质浓度; 溶质通量流场

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