A novel hybrid model combining continuum local nonequilibrium and discrete variables methods for solute trapping during rapid alloy solidification

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ABSTRACT

A novel hybrid model, which combines the advantages of micro-scale discrete approach and continuum local nonequilibrium diffusion model (LNDM), has been developed to describe solute trapping and solute drag during rapid alloy solidification with non-sharp interface. The model treats the solid-liquid interface as a region with well-defined borders, which consists of n interatomic (discrete) layers. The continuum LNDM, which is presented in Acta Mater. 93 (2015) 256–263, as well as in earlier publications, describes local nonequilibrium solute diffusion in a much wider bulk liquid region. The solute partition coefficient and the solute drag energy are studied as functions of the interface velocity, the interface width and other parameters. The model predicts that the abrupt transition to partitionless and dragless solidification occurs independently of the interface width and the equilibrium partition coefficient $K_E$ at a finite interface velocity $V_D$. The complete solute trapping velocity $V_D$ is a purely diffusion parameter, whereas the mid-transition velocity between $K_E$ and the complete solute trapping $K = 1$ depends on the interface width and $K_E$.

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1. Introduction

Substantial progress has been realized over the past decade in the modeling of alloy solidification under near-equilibrium conditions when a near-equilibrium system evolves toward its equilibrium state [1–8]. The near-equilibrium processes are usually described on the basis of the local equilibrium assumption, which implies that the local and instantaneous relations between the thermal and mechanical properties of a physical system are the same as for a uniform system at equilibrium [9–11]. The formalism based on the local equilibrium hypothesis is usually referred to as classical irreversible thermodynamics (CIT). In the context of the rapid alloy solidification, the local equilibrium assumption is valid at a relatively low interface velocity $V << V_D$, where $V_D – 1 – 20$ m/s is the characteristic diffusion velocity in the bulk liquid [12–20]. Thus, the near-equilibrium solidification with $V << V_D$ occurs under local equilibrium conditions and can be studied within the framework of CIT. At high interface velocity $V – V_D$ the deviation from equilibrium is significant and the local equilibrium hypothesis breaks down, which implies that such a process occurs under local nonequilibrium conditions [10–20]. Predictive models for rapid alloy solidification with $V – V_D$ remain less developed due to the need for a local nonequilibrium formalism, which should be used instead of CIT. Extended irreversible thermodynamics (EIT) goes beyond the local equilibrium hypothesis incorporating dissipative fluxes into the set of basic variables [9], EIT, as well as some other local nonequilibrium approaches [10,11], leads to a hyperbolic diffusion equation (HDE) as the simplest version of a transfer equation for local nonequilibrium processes. In comparison with the classical diffusion equation of parabolic type (PDE) [12,9], the HDE contains a second order time derivative $\tau_D \partial^2 \partial t^2$, where $\tau$ is the relaxation time to local equilibrium. This implies that such a process can be treated as a nonlocal in time, which reflects that mass transfer under local nonequilibrium condition has not only dissipative but also ballistic (wave) properties [9–11]. The work of Sobolev [10] was the first to introduce the second time derivative $\tau_D \partial^2 \partial t^2$ into the reaction-diffusion equation to study ultrafast moving phase interfaces. In this case the propagation velocity of the reaction-diffusion front $V$ has an upper limit $V_D = (D \tau_D)^{1/2}$, i.e. $V$ is always less than $V_D$ independently of the kinetics of reactions [10,21]. Note that the parabolic reaction–diffusion equation does not have such a limit. The approach developed in Ref. [10] has been...
used by the local nonequilibrium diffusion model (LNDM) [12–15] to study rapid alloy solidification with sharp planar interface. Nowadays, the local nonequilibrium approach is an integral part of understanding the underlying physics that is associated with all aspects of rapid alloy solidification [16–38]. In particular, the phase-filed-crystal (PFC) [27–30], cellular automata (CA) [36], and phase-filed (PF) [37,38] models take into account the local nonequilibrium effects by incorporating the second time derivative \( \tau_d \partial^2/\partial t^2 \) into the dynamic equations.

The most obvious manifestation of the deviation from equilibrium during rapid alloy solidification is solute trapping, which reduces the solute segregation at the solid-liquid interface [1–6,12–20,22–26,28–46]. 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. A complete understanding of the trapping phenomenon requires the dependence \( K(V) \) on the kinetic and thermodynamic properties of the alloy. Continuous growth model (CGM) of solute trapping proposed by Brice [2] and developed by Aziz et al. [3], as well as more recent theory of Jackson et al. [4], are based on the local equilibrium assumption and are valid only for a relatively low interface velocity \( V < V_c \). The LNDM extends the CGM and the Jackson et al. model of solute trapping to the local nonequilibrium case and predicts a sharp transition to partitionless solidification \( K = 1 \) at a finite interface velocity \( V = V_c \) [12–20]. However, the LNDM, the CGM and the Jackson et al. models are based on the sharp interface assumption, which provides in many cases a good description of solute trapping phenomena. However, a transition zone or interfacial layer, perhaps only a few atoms or molecules width, always exists [16,73,41,42]. The PFC [27–30], the PF [37–39] and the diffusive interface [33] models do not use the sharp interface assumption and might give new insight in the mechanisms of the phase transformations, but they are difficult to be implemented for practical experimental conditions as they are mathematically complicated and computationally expensive.

The LNDM, as well as the PF and the PFC models, is a continuum approach, which assumes that space and time are continuous variables. Alternative approaches, such as cellular automata (CA) [36] or discrete variables (DV) [10,11,23,47,48], are an algorithm that describes the discrete spatial and temporal evolution of complex systems by applying local interaction rules to the cells on a regular (or non-regular) lattice. The discrete approaches may operate on micro space-time scales and provide heat-mass transfer equations directly in the discrete form, which is convenient for numerical calculations [47,48]. In the continuum limit, when the micro space-time scales tend to zero, the DV model leads to a hierarchy of partial differential equations including both PDE and HDE, as well as partial differential equations of higher order [10,11,23,47,48]. This implies that the DV approach may serve as a bridge between the macro and micro-scale modeling of ultrafast phase transformations.

In recent years particular interest has centered on the hybrid models [36,49,50], which combine the advantages of micro-scale and continuum methods. The micro-scale methods can be used in the phase interface region, where active processes of phase transformations take place, whereas the continuum approaches are more efficient in a much wider region affected by the heat-mass transfer in the system. For example, Roth et al. [49] introduced a hybrid model, which combines molecular dynamics (MD) with the hyperbolic two-temperature model [10,11,48], to study the ultrafast laser melting and ablation in metals. A three-dimensional CA model of Zhao et al. [36] has been used in combination with the LNDM [13–15] for simulating dendrite growth during non-equilibrium alloy solidification.

In this paper we introduce a hybrid model, which combines the advantages of the LNDM and the DV approaches. The LNDM is used to describe solute concentration in the bulk liquid, whereas the DV approach is used inside the solid-liquid interface.

2. Discrete interface model for solute trapping

2.1. General formulation

MD simulations indicate that the solid-liquid interface may not be atomically sharp and that there is an interfacial region a few atomic layers wide in which the phase transformation takes place [41–43]. The dynamic density functional theory of Tegze et al. [6] and the PFC model of Tang et al. [7] predict a dynamic broadening (also termed as kinetic roughening) of the interface region with increasing interface velocity \( V \). This phenomenon has been observed recently for colloidal systems where the interface broadens from 8 to 9 particle diameters close to equilibrium to 15 particle diameters away from equilibrium [31]. This indicates that an ability of cope with a non-sharp interface becomes especially important for modeling far from equilibrium solidification at high interface velocity. Let us consider a non-sharp interface, which consists of \( n \) discrete interatomic layers between the pure solid and pure liquid phases (\( n \) is the number of the boarders between the discrete layers) [21,51]. In this case the interface width \( h \) is expressed as \( h = \lambda(n - 1) \), where \( \lambda \) is the interatomic spacing. Note that \( n = 1 \) corresponds to the sharp interface limit. Fig. 1 shows a planar discrete solid—liquid interface consisting of two interatomic layers (\( n = 3 \)). Solute concentrations in the liquid near the interface, in the solid, in the first interface layer, and in the second interface layer are denoted as \( C_i, C_{i1} \) and \( C_{i2} \), respectively. The total solute trapping coefficient is \( K_3 = C_{i3}/C_i \), whereas the solute partition coefficients for the discrete interface layers are \( K_{13} = C_{i1}/C_{i1} \), \( K_{23} = C_{i2}/C_i \), and \( K_{33} = C_{i3}/C_{i2} \), respectively, where the discrete interface layers are numbered as 1 and 2, respectively. Note that \( K_3 = K_{13}K_{12}K_{23} \).

The balance equations at the boundaries between the interface discrete layers, the solid and the liquid phases can be written as:

\[
\begin{align*}
(V/\Omega)(C_i - C_l) &= C_iR_{l1} - C_lR_{i1} \\
(V/\Omega)(C_{i1} - C_{l1}) &= C_{i1}R_{l1} - C_{l1}R_{i1} \\
(V/\Omega)(C_{i2} - C_{l2}) &= C_{i2}R_{l2} - C_{l2}R_{i2} \quad (1)
\end{align*}
\]

where \( V \) is interface velocity, \( R_{ij} \) are reaction rates, \( \Omega \) is atomic
volume. After some algebra, Eq. (1) give the solute partition coefficient in the form

$$K_3 = \frac{(V + \Omega R_{25})(V + \Omega R_{11})(V + \Omega R_{12})}{(V + \Omega R_{25})(V + \Omega R_{12})(V + \Omega R_{21})}$$

(2)

Taking into account that $K_{E1} = R_{11}/R_{12}$, $K_{E2} = R_{25}/R_{21}$, and $K_{E3} = R_{12}/R_{21}$, Eq. (2) can be rearranged as

$$K_3 = \frac{(K_{E1} + V/V_{12})(K_{E2} + V/V_{12})(K_{E3} + V/V_{12})}{(1 + V/V_{12})(1 + V/V_{25})(1 + V/V_{21})}$$

(3)

where $V_{12} = \Omega R_{12}$, $V_{12} = \Omega R_{12}$, and $V_{25} = \Omega R_{25}$ are the solute trapping characteristic velocities. Following [51], we can assume that $V_{12} = V_{25} = V_{25}$ and $K_{E1} = K_{E2} = K_{E3}$. In such a case Eq. (3) reduces to

$$K_3 = \frac{(K_{E1}^{1/3} + V/V_0)^3}{(1 + V/V_0)^3}$$

(4)

where $V_0$ is the characteristic solute trapping velocity, and $K_0 = C_s^0/C_i^0$ is equilibrium partition coefficient. Eq. (2) can be generalized for an arbitrary number of $n$ as follows

$$K_n = \prod_{k=0}^{n-1} \frac{V + \Omega R_{k+1}}{V + \Omega R_{k+1}}$$

(5)

The generalized versions of Eqs. (3) and (4) are

$$K_n = \prod_{k=0}^{n-1} \frac{K_{E1}^{1/n} + V/V_{k+1}}{1 + V/V_{k+1}}$$

(6)

$$K_n = \frac{(K_{E1}^{1/n} + V/V_0)^n}{(1 + V/V_0)^n}$$

(7)

Note that when $V_0 \to 0$, the complete solute trapping $K = 1$ is reached independently of $n$.

2.2. Characteristic solute trapping velocities under local equilibrium conditions

The physical sense of the characteristic solute trapping velocity $V_0$ needs to be discussed in more details. The Brice model [2] assumes that the rate at which solute atoms can join the solid is proportional to the so-called atomic diffusion speed in the bulk liquid $V_D^b = D/\lambda$, where $D$ is the solute diffusion coefficient in the bulk liquid, and $\lambda$ is the interatomic spacing. Using this assumption, one can obtain from the balance equations that $V_0 = V_D^b f/K_C$, where $f$ is a fraction of solute atoms which reach the solid surface and join the solid phase, i.e. a fraction of active surface growth sites [4]. The LNDM [10–20] introduces the bulk liquid diffusion velocity $V_{D}^{LNDM} = (D/\tau)^{1/2}$, where $\tau$ is the relaxation time of solute diffusion flux to local equilibrium, which is the velocity at which concentration disturbances propagate in the bulk liquid. Taking into account that $D = \lambda^2/\tau$, we obtain that $V_{D}^{LNDM} = D/\lambda$, which implies that the speed of diffusion disturbances $V_{D}^{LNDM}$ in the LNDM corresponds to the atomic diffusion speed $V_D^b$ in the bulk liquid, i.e. $V_{D}^{LNDM} = V_D^b = V_0$. Thus, the characteristic solute trapping velocity can be expressed as

$$V_0 = V_D^b f/K_C$$

(8)

The CGM of Aziz et al. [3,46,51] treats the characteristic solute trapping velocity as the interface diffusive velocity $V_i = D_1/\lambda$, where $D_1$ is the coefficient for interdiffusion across the interface. The interface diffusive velocity $V_i$ is also estimated by assuming that the interface diffusivity $D_1$ can be approximated by the solute diffusivity $D$ in the bulk liquid, and $\lambda$ can be replaced with the interface width $h$ [51]. MD simulation [42] suggests that the diffusive velocity is correctly defined as the diffusivity at the interface divided by the effective jump length $S_{eff} = (\lambda^2 + h^2/2)^{1/2}$, which is the distance needed to escape the influence of the growing solid. Thus, $V_0$ and $V_D$ have different physical meanings — $V_0$ is the bulk liquid diffusion velocity, which does not depend on the solute segregation kinetics, whereas $V_0$ is the characteristic solute trapping velocity, which depends on the solute segregation kinetics.

2.3. Characteristic solute trapping velocities under local nonequilibrium conditions

When the interface velocity $V$ is relatively high ($V \approx V_0$), the LNDM predicts that the local nonequilibrium diffusion effects depress solute diffusion ahead of the interface, which can be described by the effective diffusion coefficient $D_{LNDM}^{LNDM}$ [12–15]:

$$D_{LNDM}^{LNDM}(V)/D = \begin{cases} 1 - V^2/V_D^2; & V < V_D \\ 0; & V > V_D \end{cases}$$

(9)

where $D$ is the bulk liquid diffusion coefficient. The effective diffusion coefficient $D_{LNDM}^{LNDM}$, Eq. (9), decreases with increasing interface velocity and abruptly comes to zero at $V = V_0$, resulting in the sharp transition to diffusionless solidification $D_{LNDM}^{LNDM}(V) = 0$ at $V > V_0$ [10,12–20]. The velocity-dependence of the effective diffusion coefficient, Eq. (9), corresponds to the space and time dependence of the effective diffusion coefficients in anomalous diffusion theory [52,53], which treats physical processes far from local equilibrium in terms of “aging”.

Taking into account that $V_0$ in Eq. (8) is proportional to $D$, the characteristic solute trapping velocity $V_0^{LNDM}$ with allowance for the local nonequilibrium diffusion effects can be written as

$$V_0^{LNDM} = V_D^b \left(1 - V^2/V_D^2\right)/K_E$$

(10)

The characteristic solute trapping velocity $V_0^{LNDM}$, Eq. (10), depends not only on the kinetic parameters, such as $K_C$ and $f$, but also on the interface velocity $V$ and on the bulk liquid diffusion velocity $V_0$ due to the local nonequilibrium diffusion effects. $V_0^{LNDM}$ decreases with increasing $V$ and finally comes zero at $V > V_0$ leading to complete solute trapping $K = 1$ (see Eq. (7)).

2.4. Effective partition coefficient

Introducing Eqs. (10) into (7), we obtain the effective partition coefficient with allowance for the local nonequilibrium diffusion effects as

$$K_n^{LNDM} = \begin{cases} K_n^{LNDM}(1 - V^2/V_D^2 - V/V_0)^n; & V < V_D \\ 1; & V > V_D \end{cases}$$

(11)

where $T = K_0 f$ is the solute trapping parameter. Fig. 2 shows the effective partition coefficient $K_n^{LNDM}$, Eq. (11), as a function of the nondimensional interface velocity $V/V_0$ for different $n$. The local equilibrium partition coefficient, obtained from Eq. (11) in the limit $V << V_D$ with $n = 1$ and $n = 5$ (solid and dashed lines 2, respectively).
is also shown for comparison. The local nonequilibrium diffusion effects lead to the sharp transition to complete solute trapping $K_n^{\text{LNDM}} = 1$, which occurs independently of $n$ and $K_E$ when the interface velocity $V$ passes through the critical point $V = V_0$ (see Eq. (11) and Fig. 2). The local equilibrium partition coefficient (solid and dashed lines 2 in Fig. 2) demonstrates complete solute trapping $K = 1$ only asymptotically at $V \to \infty$. Horizontal dashed line in Fig. 2 shows the mid-transition partition coefficient $K_{\text{mid}}$ between $K_0$ and complete solute trapping $K = 1$, i.e. $K_{\text{mid}} = (K_0 + 1)/2$. The abscesses of the intersection points between $K_n^{\text{LNDM}}(V)$ and $K_{\text{mid}}$ represent the mid-transition velocities $V_n^{\text{mid}}$, which slightly increases with increasing $n$ (see Fig. 2). The difference between the local nonequilibrium and local equilibrium mid-transition velocities increases with increasing interface width $n$. Fig. 2 shows that, for fixed $V$, $K_n^{\text{LNDM}}$ decreases with increasing $n$, i.e. the increase of the interface width decreases solute trapping. However, the interface width in colloidal systems increases with increasing interface velocity $V$ [6,7,31]. The disagreement is connected with the CGM assumption that the solute trapping parameter $\gamma$ (or the interface diffusive velocity $V_d$) is independent of the interface width $n$ [3,46,51]. However, the interface broadening does not play an important role during the transition to diffusionless and partitionless solidification because it occurs at $V \to V_0$ independently of $n$ and $\gamma$ (see Eq. (12) and Fig. 2).

Note that the mid-transition velocity $V_n^{\text{mid}}$ coincides with the characteristic solute trapping velocity $V_0^{\text{LNDM}}$ only at $n = 1$, whereas at $n > 1$ the solute partition coefficient $K_n(V_0) = ([K_0^n + 1]/2)^n$ is not the mid-transition between $K_0$ and $K = 1$. Fig. 3 displays the effective partition coefficients $K_n^{\text{LNDM}}$ vs nondimensional interface velocity $V/V_0$ for different $K_E$. The corresponding local equilibrium partition coefficient is represented as a dashed curve and the mid-transition point $K_{\text{mid}}$ is represented as a horizontal dash-dotted line. As shown in Fig. 3, the mid-transition velocity, marked by vertical dashed lines, decreases with increasing $K_E$, which corresponds to the inverse correlation between the mid-transition velocity and $K_E$ found experimentally for several dilute aluminum alloys [51] and confirmed theoretically (see Refs. [29,30] and references therein). For $K_E = 0.1$ the mid-transition velocity in the local nonequilibrium case is distinctly smaller than in the local equilibrium limit (compare the abscissas of intersection points between the horizontal line 1 and curves 1), whereas at $K_E = 0.8$ the difference is negligible. At a relatively low equilibrium partition coefficient $K_E = 0.1$, the difference between $K_n^{\text{LNDM}}$ (solid curve 1 in Fig. 3) and its local equilibrium limit (dashed curve 1 in Fig. 3) is significant, whereas at $K_E = 0.8$ the corresponding difference is negligible (curves 4 in Fig. 3).

2.5. Solute drag

Solute drag is known to play an important role in a wide variety of phase transformations, but in rapid alloy solidification its importance is still under discussion [3,29,33,35,37–39,43,54]. According to its definition, solute drag arises due to solute diffusion around the interface (so-called trans-interface diffusion), which implies that the absence of solute diffusion means the absence of solute drag. In other words, a sharp transition to diffusionless solidification at $V \geq V_d$ predicted by the LNDM [10,12–20], is accompanied by a sharp disappearance of solute drag. It can be easily illustrated for ideal solution where the free energy dissipation due to the drag effects has the form [3].

$$\Delta G_{\text{drag}}/RT = -C_S(1-K)/\ln K/K_E$$

(12)

Substituting the effective partition coefficient, Eq. (11), in Eq. (12), we obtain the local nonequilibrium free energy dissipation due to drag effects $\Delta G_{\text{drag}}^{\text{LNDM}}$ as a function of the nondimensional interface velocity $V/V_0$. This is presented in Fig. 4 for different $n$. The local equilibrium solute drag free energy is also shown for comparison. The solute drag free energy first increases proportionally to the interface velocity. However, at higher velocities the solute diffusion and solute segregation at the interface decrease, which implies that the previous increase of the solute drag slows down. The solute drag $\Delta G_{\text{drag}}^{\text{LNDM}}$ thus reaches a maximum and then decreases and finally comes to zero at $V > V_d$ when complete solute trapping $K_n^{\text{LNDM}} = 1$ is reached (see Fig. 4). The sharp transitions to

![Fig. 2](image1.png)

**Fig. 2.** Effective partition coefficient $K_n^{\text{LNDM}}$ vs nondimensional interface velocity $V/V_0$. Eq. (11), with $K_0 = 0.01$ and variable $n$: $n = 1$ — solid line 1, $n = 2$ — dash-dotted line, $n = 3$ — dotted line, $n = 5$ — dashed line 1. Solid and dashed lines 2 are the local equilibrium limit with $n = 1$ and $n = 5$, respectively. Horizontal dash line is the mid-transition partition coefficient $K_{\text{mid}} = (K_0 + 1)/2$, while corresponding intersection points with $K(V)$ represent the mid-transition interface velocities (vertical dash lines).

![Fig. 3](image2.png)

**Fig. 3.** Effective partition coefficient $K_n^{\text{LNDM}}$ vs nondimensional interface velocity $V/V_0$. Eq. (11), with $n = 2$ and variable $K_E$: $K_E = 0.1$ — solid line 1, $K_E = 0.3$ — solid line 2, $K_E = 0.5$ — solid line 3, $K_E = 0.8$ — solid line 4. Corresponding dashed lines represent the local equilibrium limit, horizontal dash-dotted lines — the mid-transition partition coefficient $K_{\text{mid}}$, vertical dashed lines — the mid-transition interface velocities.
dragless solidification $\Delta G^{\text{LNDM}} = 0$ at $V \geq V_D$ arises due to the sharp transition to diffusionless and partitionless solidification, predicted by the LNDM due to the local nonequilibrium diffusion effects in the bulk liquid [10,12–20]. The local equilibrium $\Delta G_{\text{drag}}$ vanishes only asymptotically at $V \to \infty$ (dashed curves in Fig. 4). Interface velocity, at which the maximum of $\Delta G^{\text{LNDM}}_{\text{drag}}$ as a function of $V$ is reached, increases with increasing $n$, but still it significantly smaller than the complete solute trapping velocity $V_D$. In such a case the local nonequilibrium diffusion effects do not practically influence the maximum solute drag $\Delta G^{\text{max}}_{\text{drag}}$. It implies that $\Delta G^{\text{max}}_{\text{drag}}$ does not depend on the complete solute trapping velocity but it correlates with the mid-transition velocity $V_{n \text{mid}}$, because both $\Delta G^{\text{max}}_{\text{drag}}$ and $V_{n \text{mid}}$ depend on $K_E$. However, as the interface velocity increases ($V > V_D$), the local nonequilibrium effects depress solute diffusion leading to a sharp disappearance of solute drag at a finite value of the interface velocity $V = V_D$ for any $n$. Fig. 5 shows the solute drag free energy $\Delta G^{\text{LNDM}}_{\text{drag}}$ as a function of the nondimensional interface velocity $V/V_D$ with a fixed $n = 2$ and different $K_E$. Corresponding local equilibrium $\Delta G_{\text{drag}}$ are placed for comparison. The maximum solute drag free energy significantly decreases with increasing $K_E$, whereas the value of interface velocity at which the maximum is reached, decreases very weakly (see insert in Fig. 5). The local nonequilibrium effects are more pronounced at low values of $K_E$, whereas at higher $K_E$ the difference between $\Delta G^{\text{LNDM}}_{\text{drag}}$ and $\Delta G_{\text{drag}}$ is small (see Fig. 5). However, a sharp transition to diffusionless solidification with $\Delta G^{\text{LNDM}}_{\text{drag}} = 0$ occurs at a finite value of the interface velocity $V = V_D$ independently of $K_E$ (solid lines in Fig. 5) due to the local nonequilibrium diffusion effects. Thus, the solute drag energy plays an essential role only at a relatively low interface velocity $V < V_D$, whereas at $V \geq V_D$ it abruptly comes to zero due to local nonequilibrium effects.

3. Discussion and comparison with experiment

The present model predicts a sharp transition from a relatively slow ($V < V_D$) “diffusion controlled” solidification to relatively fast ($V > V_D$) “diffusionless” solidification $D^{\text{LNDM}} = 0$ with complete solute trapping $K^{\text{LNDM}} = 1$, which occurs independently of $n$ and $K_E$. The Jackson et al. model [4] describes a diffusionless growth in terms of a transition from the independent crystallization of each component near equilibrium, which is governed by the differences in the individual chemical potentials between the two phases, to a cooperative growth mode far from equilibrium, which depends on the difference in free energy between the two phases of the alloy. A dynamic density functional theory of Tegze et al. [6] predicts a transition from “slow” or “diffusive” crystal growth mode at low driving force to a ‘fast’ diffusionless mode with density trapping at high driving force during crystallization of a colloidal ‘soft’ material. But the Jackson et al. and the Tegze et al. models describe the transition only asymptotically at $V \to \infty$. The solute trapping models of Brice-Aziz [2,3] and Danilov and Nestler [5] also predict $K \to 1$ only at $V \to \infty$. Early molecular dynamics (MD) works by Cook and Clancy [41] showed partitionless crystal growth in a Leonard-Jones system at a finite interface velocity ($4 \text{ m/s}$). Cook and Clancy stressed that the local equilibrium theories of solute trapping cannot predict this result. Recently, Yang et al. [43] also observed that complete solute trapping does occur at finite velocity. The authors simulated the Leonard-Jones and the Cu-Ni systems and demonstrated that the LNDM was a better fit to their MD data, while the Brice-Aziz model [2,3] underestimated the high velocity cases when $K \to 1$. It is remarkable that the Yang et al. [43] and the Cook and Clancy [41] results confirmed complete solute trapping at a finite interface velocity on the basis of MD atomistic simulations, which fundamentally justifies the need for the hyperbolic dynamic equations with the second time derivative in the continuum description suggested by the LNDM [10,12–20] and used by the PF [37,38] and PFC [27–30] simulations. In addition to the MD justification, the LNDM shows a better fit for the experimental data on Si-As alloys by Kittl et al. [46] (see Refs. [5,14–16,19]) and on Ti-Ni alloys by Walder [44] (see Ref. [17]). More recently, splet cooling experiments of Al-Mg alloy also confirmed the LNDM prediction showing a change from a eutectic to supersaturated solid solution at a finite velocity [45]. Fig. 6 demonstrates the effective partition coefficient $K^{\text{LNDM}}_n$ predicted by Eq. (11) in comparison with the experimental data on Si-As alloy solidification [46]. The present model fits the experimental data well in the whole range of the measured interface velocity $0.2—2 \text{ m/s}$ with $n$ between 2 and 6. The sharp transition to partitionless solidification $K^{\text{LNDM}}_n = 1$ occurs

Fig. 4. Solute drag free energy $\Delta G^{\text{LNDM}}_{\text{drag}}$, scaled with $-1/RTC_0$, vs nondimensional interface velocity $V/V_D$ with $K_0 = 0.1$ and variable $n$: $n = 1$ — solid curve 1; $n = 3$ — solid curve 2; $n = 5$ — solid curve 3. Corresponding dashed curves are the local equilibrium limits.

Fig. 5. Solute drag free energy $\Delta G^{\text{LNDM}}_{\text{drag}}$, scaled with $-1/RTC_0$, vs nondimensional interface velocity $V/V_D$ with $n = 2$ and variable $K_0$: $K_0 = 0.1$— curves 1; $K_0 = 0.15$— curves 2; $K_0 = 0.2$— curves 3; $K_0 = 0.5$— curves 4. Dashed curves are the corresponding local equilibrium limits. The insert shows the difference between the interface velocities at which the maximum of $\Delta G^{\text{LNDM}}_{\text{drag}}$ is reached.
independently of $n$ at $V_D = 2.23$ m/s (see Fig. 6). The value of the interface width corresponds to MD simulations [41,42], which demonstrate that the solid-liquid interface is not sharp and extends approximately three atomic planes at the beginning of growth to five atomic planes during steady-state growth, and as high as eight atomic planes at the final stage of growth. A dynamic density functional theory of Tegze et al. [6] demonstrates that during crystallization of a colloidal ‘soft’ material the interface thickness extends to several particle layers with increasing driving force at $V \rightarrow \infty$.

The PFC microscopic simulations of Humadi et al. [29] predict that the complete trapping velocity is inversely proportional to the square root of the inertial dynamics parameter, which is an analogue of the relaxation time $\tau$ in our model. The result exactly corresponds to the complete solute trapping velocity $V_D = (D/\tau)^{1/2}$ in the present model. However, Humadi et al. also predict that the complete solute trapping velocity decrease with increasing $K_E$ [29]. In the present model the mid-transition velocity $V_{\text{mid}}$ decreases with increasing $K_E$ (see Fig. 3 and comments above), but the complete solute trapping velocity $V_D$ being a purely diffusion parameter, does not depend on $K_E$. The point is that Humadi et al. used $K_E = 0.97$ for the PFC simulation [28,29], which implies that the calculated $K(V)$-curve lies very close to the complete solute trapping line $K = 1$. In this case it is difficult to distinguish between the corresponding complete solute trapping and mid-transition velocities. The contradiction between the prediction of Humadi et al. and the present model may be clarified by the PFC simulations with smaller value of $K_E$.

The PFC microscopic formalism of Humadi et al. [29] introduces an effective solute diffusion coefficient, which decreases to zero as the interface velocity increases at the non-zero inertial dynamics parameter, whereas at the zero inertial dynamics parameter it does not change the classical diffusive nature of the concentration profile. Our effective diffusion coefficient $D^{\text{NDM}}(V)$, Eq. (9), is consistent with this PFC simulation.

Recent MD simulations [43] demonstrated that solute drag is significant only at the slower growth rates where there is appreciable solute partitioning at the interface, whereas the highest velocity points (where solidification is essentially partitionless) solute drag is negligible. This result is consistent with the present model, which predicts a sharp transition to dragless solidification $\Delta G_{\text{NDM}}^{\text{drag}} = 0$ at $V = V_D$ (see solid lines in Figs. 4 and 5), which is a consequence of the sharp transition to diffusionless and partitionless solidification due to the local nonequilibrium effects. Note that in the local equilibrium limit $\Delta G_{\text{drag}} \rightarrow 0$ only asymptotically at $V \rightarrow \infty$ (see dashed lines in Figs. 4 and 5). The analogous behavior of the solute drag energy has been observed in the PFC model of Humadi et al. [29], which also predicts that solute drag energy decreases as $K_E$ increases, suggesting that the materials with larger $K_E$ exhibit lower complete trapping velocities because less driving force is required to reach complete trapping for a decreasing concentration solute jump at the interface. The present model shows that $\Delta G_{\text{nd}}^{\text{drag}}$ decreases with increasing $K_E$ (see Fig. 5) due to the decreasing mid-transition velocity $V_{\text{mid}}$ (see Fig. 3), whereas the complete solute trapping velocity $V_D$ does not depend on $K_E$. As it has been discussed above, the contradiction may arise due to the nearly partitionless regimes with $K_E = 0.97$ used in the PFC simulations [28,29], which leads to some uncertainties about how to distinguish between the complete solute trapping velocity and the mid-transition velocity.

Thus, the sharp transition to diffusionless, partitionless and dragless solidification is a purely diffusion phenomena, which occurs independently of the interface kinetics as soon as the interface velocity passes through the critical point $V = V_D$. It implies that the transition may be adequately described within the framework of the LNDM with a sharp interface, whereas the non-sharp interface models, may be important for understanding the underlying physics that is associated with the phase transformation within the interface region and the microstructure formation at a relatively low interface $V < V_D$.

4. Conclusion

A novel hybrid model has been developed to describe solute trapping and solute drag during local nonequilibrium alloy solidification with non-sharp interface. The hybrid model combines the advantages of the micro–scale discrete approach and the continuum LNDM. The discrete approach is used in the relatively narrow interface region, where active processes of phase transformation takes place, whereas the LNDM is more efficient in a much wider bulk liquid region for description of solute diffusion under local nonequilibrium conditions. The model predicts that the effective solute partition coefficient $K_E^{\text{NDM}}$ and the solute drag energy $\Delta G_{\text{NDM}}^{\text{drag}}$ depend on the interface width and the equilibrium partition coefficient $K_E$ at intermediate values of the interface velocity $0 < V < V_D$. However, when $V \rightarrow V_D$, $K_E^{\text{NDM}} \rightarrow 1$ and $\Delta G_{\text{NDM}}^{\text{drag}} \rightarrow 0$ independently of the interface width and $K_E$ due to the sharp transition to diffusionless solidification $D^{\text{NDM}} = 0$, which is a consequence of the local nonequilibrium diffusion effects. When $V \rightarrow 0$, $K_E^{\text{NDM}} \rightarrow K_E$ and $\Delta G_{\text{NDM}}^{\text{drag}} \rightarrow 0$ also independently of the interface width. It implies that the complete solute trapping velocity $V_D = (D/\tau)^{1/2}$ is a purely diffusion parameter, while the mid-transition velocity $V_{\text{mid}}$ depends on both the interface width and $K_E$. The hybrid model is presented in terms of solidification from the melt, but it also can be applied to solid-state transformations [12], colloidal solidifications [6,12,55,56], and cryobiology [57].

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References
