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# The thermodynamics of non-equilibrium interfaces during phase transformations in concentrated multicomponent alloys

Christopher A. Hareland<sup>a,\*</sup>, Gildas Guillemot<sup>b</sup>, Charles-André Gandin<sup>b</sup>, Peter W. Voorhees<sup>a</sup>

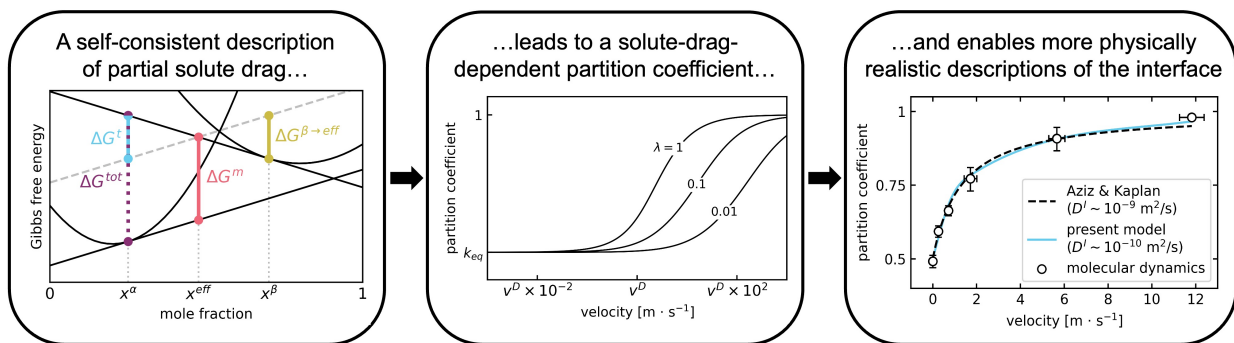
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## Abstract

A unified thermodynamic description of moving non-equilibrium interfaces is developed for both solid/solid and solid/liquid transformations. The theory is applicable to concentrated multicomponent alloys where diffusion is possible in both phases or in just the parent phase, and where energy is dissipated due to solute drag. To be consistent with energy dissipation, we find that solute drag affects both the velocity of the interface and distribution coefficients for the compositions of the two phases at the interface. In the limit of binary alloy solidification, the theory predicts significant changes in the interfacial compositions from that given by the phase diagram at velocities commonly found during additive manufacturing. Since the distribution coefficient is affected by solute drag, the solute-trapping behavior observed in molecular dynamics simulations implies that the interfacial diffusivity lies between the diffusivity of the bulk solid and liquid. A comparison to past work on non-equilibrium interfaces during solid/solid and solid/liquid phase transformations is also given.

## Graphical Abstract



**Keywords:** phase transformations, multicomponent alloys, modeling, thermodynamics, kinetics

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## 1. Introduction

Additive manufacturing (AM) has been increasing in popularity due to the exceptional control it offers over macroscopic part geometry. The final properties of components made via AM are controlled by the solidification microstructures that form during processing. Because the solidification velocities in powder-bed fusion AM processes can easily approach  $\sim 1 \text{ m} \cdot \text{s}^{-1}$  [1, 2, 3], quantitative predictions of the microstructures formed during AM require models of rapid solidification that incorporate the effects of an interface that departs from local equilibrium [4, 5]. This is further supported by observations of non-equilibrium effects such as solute trapping via experiment [6, 7], molecular dynamics simulations [8, 9], phase-field simulations [10, 11], and phase-field-crystal simulations [12].

A central assumption of many models of the conditions at interfaces during rapid solidification is negligible mass diffusion in the solid. The literature on non-equilibrium solid/solid transformations has evolved somewhat independently from that for solidification. Solid-state transformations are primarily concerned with transformations for which the rate is controlled by diffusion in both the parent ( $\beta$ ) and growing ( $\alpha$ ) phases [13, 14, 15], while rapid solidification is able to safely neglect diffusion in the growing (solid) phase and focuses on effects such as solute trapping [16, 17, 18, 19].

Additionally, during both rapid solidification and solid/solid phase transformations, the phenomenon known as “solute drag” consumes part of the total driving force for transformation to desorb solute from the interface, which reduces the driving force available to drive the motion of the interface. Since Hillert and Sundman [20] first introduced a unified treatment of solute drag at grain boundaries and solid/liquid interfaces, the effects of solute drag have been shown to be significant through both molecular dynamics [8, 9] and phase-field simulations [10, 11, 21, 22], as well as analytical modeling of experimental results [23, 24, 25, 26, 27].

A wide variety of sharp-interface models have been developed to describe the effects of solute drag during phase transformations. *Full-drag models* — the most famous of which is the Continuous Growth Model (CGM) of Aziz [16, 17, 18] — assume that material adsorbs to the interface at the interfacial composition of the parent phase,  $x^\beta$ . Before the material is incorporated into the growing phase at  $x^\alpha$ , an amount of solute equal to  $x^\beta - x^\alpha$  must be desorbed from the interface back into the parent phase, which is exactly the solute-drag effect described above. In *partial-drag models*, which arose from the rapid solidification community [19], the degree of solute drag can be varied with the “solute-drag parameter”,  $\lambda$ , which weights the interfacial compositions of the growing and the parent phases to give an “effective concentration” of the material adsorbing to the interface:

$$x^{eff} = \lambda x^\beta + (1 - \lambda)x^\alpha \quad (1)$$

In these treatments of solidification,  $\lambda$  is typically assumed to vary between zero (“zero drag”) and unity (“full drag”) [19, 25], but this domain will be more rigorously defined in Section 2.2. Higher values of  $\lambda$  indicate increasingly favorable adsorption of solute to the interface from the growing phase and a correspondingly larger reduction in the driving force available for interface motion due to the need to desorb this extra solute. Alternatively, *partial-drag models from bulk diffusion* describe solid/solid transformations by defining the interfacial concentration,  $x^{tr}$ , in terms of the bulk fluxes in each phase [13, 14] instead of a solute-drag parameter. However, these models assume that material always adsorbs to the interface with a composition

58  $x^\beta$ , implying that the interfacial velocity is always described by the case of complete solute drag. Thus,  
 59 this *partial-drag from bulk diffusion* approach cannot treat partial solute drag during rapid solidification,  
 60 which subsequent molecular dynamics simulations [8, 9] found to be important. A detailed comparison and  
 61 discussion of these three approaches (*full-drag*, *partial-drag* and *partial-drag from bulk diffusion*) is found in  
 62 Section 4. Regardless, assigning a representative concentration to a sharp interface enables more detailed  
 63 and physically realistic sharp-interface models.

64 Additionally, many of the models for non-equilibrium interfaces are limited to binary alloys. Since  
 65 most alloys used commercially contain appreciable amounts of several solutes, a model that allows for  
 66 many components and non-dilute solutions is needed. Sharp-interface models have been developed for  
 67 multicomponent systems by, for example, Ludwig [28] for solidification under the no-drag case of the CGM  
 68 [18], Sobolev et al. [29] for solute partitioning considering local non-equilibrium diffusion in the liquid, Kuang  
 69 et al. [30] for a two-step drag model under the thermodynamic extremal principle, Wang et al. [31] for full-  
 70 drag models under local non-equilibrium diffusion and the thermodynamic extremal principle, and Du et al.  
 71 for the CGM with drag during rapid solidification [32] and solid-state transformations [33]. Additionally, Du  
 72 et al. [32] formulated a model for multicomponent alloys that can be coupled with CALPHAD methodology.  
 73 However, a complete model including partial solute drag and diffusion in both phases for multicomponent  
 74 alloys is not available. Herein, we develop a model for multicomponent alloys incorporating both bulk  
 75 diffusion and partial solute drag at interfaces, employing the general approach to non-equilibrium migrating  
 76 interfaces developed for binary alloys by Gurtin and Voorhees [34].

77 Due to the various definitions of the interfacial concentration, sharp-interface models differ in their  
 78 selection and development of the kinetic equations describing two energy-dissipating processes: interface  
 79 migration and trans-interface diffusion [35]. The relationships between the driving forces, which are functions  
 80 of the jumps across the interface in both the grand potential and the diffusion potentials, and the interfacial  
 81 fluxes for each process are described by kinetic equations known as “interfacial response functions”. There are  
 82 two types of interfacial response function; the velocity response function (VRF) gives the interface velocity  
 83 in the direction normal to the interface,  $v$  ( $\text{m} \cdot \text{s}^{-1}$ ), and the concentration response functions (CRFs) can  
 84 be used to determine the ratio of the concentrations of each component  $i$  in each phase at the interface, i.e.,  
 85 the velocity-dependent distribution coefficient, which is defined as  $k_v^i = x_i^\alpha / x_i^\beta$  for the growth of  $\alpha$  from  $\beta$ .  
 86 Note that a binary alloy will have one VRF and one CRF, while an  $N$ -component alloy will have one VRF  
 87 and  $N - 1$  CRFs (one for each independent chemical species,  $i \in \{2, \dots, N\}$ ). For binary alloys, the fluxes  
 88 for these processes can be obtained from an interdiffusion approach and the driving forces can be obtained  
 89 from graphical constructions [15, 35]. These graphical constructions are described in Section 4 to illustrate  
 90 various interpretations of these fluxes and driving forces. For multicomponent alloys, a dissipation relation  
 91 [36, 37, 38] combined with an interfacial mass balance is a convenient method of obtaining the fluxes and  
 92 driving forces in a self-consistent way.

93 To predict the interface response functions during both rapid solidification and solid-state transfor-  
 94 mations, a model for phase transformations in concentrated multicomponent alloys under general non-  
 95 equilibrium conditions at the interface is required. Here, we unify the approaches developed for non-  
 96 equilibrium interfaces in the solidification and solid-state communities by allowing diffusion in the growing  
 97 phase, but retaining the effective concentration defined in Eq. (1) to incorporate partial solute drag at the

98 velocities relevant to additive manufacturing. The effects of solid-state diffusion and partial solute drag  
 99 are incorporated self-consistently into the interfacial response functions for multicomponent alloys using an  
 100 energy dissipation approach [34], which also allows for additional effects, such as interfacial energy, to be  
 101 incorporated if desired.

## 102 2. Non-equilibrium Thermodynamics of Interface Migration

### 103 2.1. Interfacial mass balance

104 For an  $N$ -component system with a curved interface, Gurtin and Voorhees [34] give a mass balance for  
 105 component  $i$  in phase  $\phi$  with respect to a control volume attached to an interface moving with velocity  
 106  $\mathbf{v}$  ( $\text{m} \cdot \text{s}^{-1}$ ). Throughout this work, it is assumed that the partial molar volumes,  $V_i^\phi$  ( $\text{m}^3 \cdot \text{mol}^{-1}$ ), of all  $i$   
 107 components in each phase are equal to the molar volume of the alloy,  $V_m = \sum_{i=1}^N V_i^\phi x_i^\phi$  ( $\text{m}^3 \cdot \text{mol}^{-1}$ ), where  
 108  $x_i^\phi$  ( $\text{mol} \cdot \text{mol}^{-1}$ ) is the mole fraction of component  $i$  in phase  $\phi$ . Because  $\sum_{i=1}^N x_i^\phi = 1$ , this is equivalent  
 109 to a constant number density,  $\rho_i^\phi = 1/V_i^\phi$  ( $\text{mol} \cdot \text{m}^{-3}$ ), for all  $i$  components in each phase, i.e.,  $\rho_i^\phi = \rho_0$ .  
 110 Additionally, atoms are assumed to diffuse by a direct exchange mechanism—neglecting sources, sinks, and  
 111 diffusion of vacancies—so there are  $N - 1$  independent fluxes in an  $N$ -component system, denoted by the  
 112 subscript  $i \in \{2, \dots, N\}$ . In the absence of surface diffusion, the mass balance for component  $i$  at the interface  
 113 in phase  $\phi$  is given by

$$j_i^\phi + \rho_0 x_i^{eff} \mathbf{v} \cdot \hat{\mathbf{n}}^\phi = -\mathbf{J}_i^\phi \cdot \hat{\mathbf{n}}^\phi + \rho_0 x_i^\phi \mathbf{v} \cdot \hat{\mathbf{n}}^\phi \quad (2)$$

114 where  $j_i^\phi$  ( $\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ ) is the diffusion flux entering phase  $\phi$  through the interface,  $\rho_0 x_i^\phi$  ( $\text{mol} \cdot \text{m}^{-3}$ ) is  
 115 the volumetric concentration of component  $i$  in phase  $\phi$  at the interface,  $\rho_0 x_i^{eff}$  ( $\text{mol} \cdot \text{m}^{-3}$ ) is the effective  
 116 volumetric concentration of component  $i$  within the interface as defined by Eq. (1), and  $\mathbf{J}_i^\phi$  ( $\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ )  
 117 and  $\hat{\mathbf{n}}^\phi$  are the bulk flux of component  $i$  in phase  $\phi$  and the outward normal vector of phase  $\phi$ , respectively.

118 To describe the growth of  $\alpha$  from  $\beta$ , we assume that the growing and parent phases remain in continuous  
 119 contact (i.e.,  $\hat{\mathbf{n}}^\alpha = -\hat{\mathbf{n}}^\beta$  and  $\mathbf{v} \cdot \hat{\mathbf{n}}^\alpha = -\mathbf{v} \cdot \hat{\mathbf{n}}^\beta = v$ ) and define the bulk flux in each phase at the interface as  
 120  $J_i^\phi = \mathbf{J}_i^\phi \cdot \hat{\mathbf{n}}^\alpha$ . Under these assumptions, Eq. (2) gives two expressions for the trans-interface diffusive flux  
 121 of component  $i$ ,  $J_i^t$ , where  $J_i^t = j_i^\beta = -j_i^\alpha$ :

$$J_i^t = \rho_0 v (x_i^{eff} - x_i^\alpha) + J_i^\alpha \quad (3)$$

$$J_i^t = \rho_0 v (x_i^{eff} - x_i^\beta) + J_i^\beta \quad (4)$$

122 The terms comprising Eqs. (3) and (4) are shown in Figure 1, where a closed system is schematized by a  
 123 domain  $\Omega$  comprised of  $N$  components in two bulk phases,  $\alpha$  and  $\beta$ , which occupy the regions  $\Omega^\alpha$  and  $\Omega^\beta$ ,  
 124 respectively. The system is surrounded by an inert medium, which enforces zero-flux boundary conditions  
 125 everywhere except at the surface  $\partial\Omega$ , which is the interface between  $\Omega^\alpha$  and  $\Omega^\beta$ .  $J_i^t$  is the flux of component  
 126  $i$  rejected from the interface back into the parent phase, which is the flux giving rise to the solute-drag effect.  
 127 The first terms on the right-hand sides of Eqs. (3) and (4) result solely from the motion of the interface, and  
 128 the second terms on the right-hand sides are the bulk diffusion fluxes evaluated at the interface. Equating  
 129 Eqs. (3) and (4) gives the standard interfacial mass balance:

$$[[J_i]] = \rho_0 v [[x_i]] \quad (5)$$

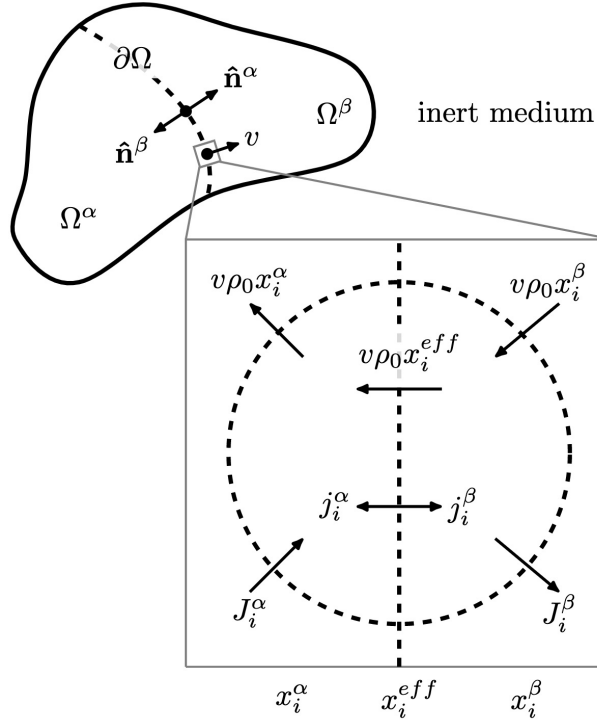


Figure 1: Schematic of a system with a sharp interface comprised of the growing ( $\alpha$ ) and parent ( $\beta$ ) phase surrounded by an inert medium. The inset shows an interfacial control volume in each phase. The terms comprising the fluxes defined in Eqs. (2) – (4) are marked, and the inset illustrated is sufficiently small for each flux component to be normal to the interface.

130 where the notation  $[[\Phi]] = \Phi^\beta - \Phi^\alpha$  denotes the jump across the interface in a quantity  $\Phi$ . Recovering  
 131 the standard mass-balance condition indicates that the net mass transfer for the phase transformation is  
 132 independent of the interfacial concentration and the effects of partial solute drag.

### 133 2.2. Energy dissipation

134 The thermodynamics of interfaces in this non-equilibrium case must be consistent with the first and  
 135 second laws of thermodynamics. In general, evolution equations are obtained from the rate of entropy  
 136 production; however, if the system is assumed to be at constant temperature and volume, this is equivalent  
 137 to the rate of Helmholtz energy dissipation. Because the phenomenological equations for multicomponent  
 138 systems can require many kinetic coefficients, the thermodynamic extremal principle has been widely used  
 139 to formulate the evolution equations of multicomponent systems [30, 31, 39]. Here, we instead use the  
 140 classical dissipation approach [36, 37, 38], which requires that the Helmholtz free energy decreases, but not  
 141 necessarily at the maximum possible rate. Using the principle that the energy must decrease, it is possible  
 142 to identify constitutive laws for non-equilibrium interfaces [34, 40, 41, 42].

143 The dissipation rate of Helmholtz free energy  $\dot{F}$  ( $\text{J} \cdot \text{s}^{-1}$ ) for this system with a planar interface is

$$\dot{F} = \int_{\Omega^\alpha} \frac{\partial f_v^\alpha}{\partial t} dV + \int_{\Omega^\beta} \frac{\partial f_v^\beta}{\partial t} dV - \int_{\partial\Omega} [[f_v]] v dA \quad (6)$$

144 where  $f_v^\phi = \rho_0 \sum_{i=1}^N \mu_i^\phi x_i^\phi$  ( $\text{J} \cdot \text{m}^{-3}$ ) is the volumetric Helmholtz free energy in phase  $\phi$  at constant temper-  
 145 ature and volume. Each volume integral describes the energy dissipation rate in a bulk phase, while the  
 146 surface integral describes the energy dissipation rate due to creation of  $\alpha$  lattice sites at the expense of  $\beta$   
 147 lattice sites resulting from the motion of the interface. For a closed, isothermal, stress-free system, we have

$$\frac{\partial f_v^\phi}{\partial t} = \rho_0 \sum_{i=2}^N \tilde{\mu}_i^\phi \frac{\partial x_i^\phi}{\partial t} \quad (7)$$

148 where  $\rho_0 \tilde{\mu}_i^\phi = \rho_0(\mu_i^\phi - \mu_1^\phi) = \partial f_v^\phi / \partial x_i$  ( $\text{J} \cdot \text{m}^{-3}$ ) is the diffusion potential of component  $i$  with respect to the  
 149  $i = 1$  component. Additionally, the standard continuity equation without sources or sinks of mass is given  
 150 by

$$\rho_0 \frac{\partial x_i^\phi}{\partial t} = -\nabla \cdot \mathbf{J}_i^\phi \quad (8)$$

151 By substituting Eqs. (7) and (8) into Eq. (6) and then using the product rule for divergences followed by  
 152 the divergence theorem, the fluxes and driving forces comprising  $\dot{F}$  can be split into terms describing the  
 153 dissipation by diffusion in the bulk,  $\dot{F}_\Omega$ , and by processes occurring at the interface,  $\dot{F}_{\partial\Omega}$ :

$$\dot{F}_\Omega = \int_{\Omega^\alpha} \sum_{i=2}^N \nabla \tilde{\mu}_i^\alpha \cdot \mathbf{J}_i^\alpha dV + \int_{\Omega^\beta} \sum_{i=2}^N \nabla \tilde{\mu}_i^\beta \cdot \mathbf{J}_i^\beta dV \quad (9)$$

$$\dot{F}_{\partial\Omega} = - \int_{\partial\Omega} \left\{ \sum_{i=2}^N \tilde{\mu}_i^\alpha \mathbf{J}_i^\alpha \cdot \hat{\mathbf{n}}^\alpha + \sum_{i=2}^N \tilde{\mu}_i^\beta \mathbf{J}_i^\beta \cdot \hat{\mathbf{n}}^\beta + \llbracket f_v \rrbracket v \right\} dA \quad (10)$$

154 The total free energy dissipation,  $\dot{F} = \dot{F}_\Omega + \dot{F}_{\partial\Omega}$ , is equivalent to Eq. (8) of Ref. [31] if the assumption of  
 155 local equilibrium holds for mass transfer in the bulk phases. Inserting the mass-balances, Eqs. (3) and (4),  
 156 into Eq. (10) and rearranging gives

$$\dot{F}_{\partial\Omega} = \int_{\partial\Omega} \left\{ - \left( \llbracket \Omega_v \rrbracket + \rho_0 \sum_{k=2}^N x_k^{eff} \llbracket \tilde{\mu}_k \rrbracket \right) v + \sum_{i=2}^N \llbracket \tilde{\mu}_i \rrbracket J_i^t \right\} dA \quad (11)$$

157 where  $\Omega_v^\phi$  ( $\text{J} \cdot \text{m}^{-3}$ ) is the volumetric grand potential in phase  $\phi$ :

$$\Omega_v^\phi = f_v^\phi(x_2^\phi, \dots, x_N^\phi) - \rho_0 \sum_{i=2}^N \tilde{\mu}_i^\phi x_i^\phi \quad (12)$$

158 Using the Helmholtz free energy as defined previously in the case of constant temperature and volume, the  
 159 molar grand potential reduces to the chemical potential of the dependent component, i.e.,  $\rho_0^{-1} \Omega_v^\phi = \mu_1^\phi$ , as  
 160 noted by Chatterjee and Moelans [43]. The first term of Eq. (11) describes the dissipation due to the motion  
 161 of the interface that involves the adsorption of components at their respective effective concentrations,  $x_i^{eff}$ ,  
 162 while the second term describes the dissipation due to solute drag that requires the desorption of excess  
 163 solute, i.e., the concentration above that of the growing phase  $x_i^\alpha$ , from the interface back into the parent  
 164 phase.

165 For  $\dot{F}$  to be strictly negative for any process, we require that both  $\dot{F}_\Omega$  and  $\dot{F}_{\partial\Omega}$  be negative. Requiring  
 166  $\dot{F}_\Omega < 0$  can lead to the usual relationship between the mass flux and the gradient in diffusion potential,

167 which is discussed further in Section 2.4. To guarantee that  $\dot{F}_{\partial\Omega} < 0$  in the most general case, each term in  
 168 Eq. (11) must be negative. This gives two dissipation inequalities:

$$v \left( \llbracket \Omega_v \rrbracket + \rho_0 \sum_{k=2}^N x_k^{eff} \llbracket \tilde{\mu}_k \rrbracket \right) > 0 \quad (13)$$

$$\sum_{i=2}^N \llbracket \tilde{\mu}_i \rrbracket J_i^t < 0 \quad (14)$$

169 Because the solute-drag parameter,  $\lambda$ , appears in both Eqs. (13) and (14) through  $x^{eff}$ , these dissipation  
 170 inequalities provide upper and lower bounds on the solute-drag parameter for the  $\beta \rightarrow \alpha$  transformation  
 171 considered here. The lower bound of  $\lambda$  is set by Eq. (14) which, because  $\llbracket \tilde{\mu}_i \rrbracket$  is independent of  $x_i^{eff}$ , entirely  
 172 depends on the trans-interface diffusion flux that gives rise to solute drag,  $J_i^t$ , defined in Eqs. (3) and (4).  
 173 Physically, for the product  $\llbracket \tilde{\mu}_i \rrbracket J_i^t$  to be negative, the effective concentration must be sufficiently high such  
 174 that the magnitude of the flux due to the motion of the interface,  $\rho_0 v (x_i^{eff} - x_i^\alpha)$ , exceeds the magnitude  
 175 of the flux due to bulk diffusion,  $J_i^\alpha$ . For example, if  $J_i^\alpha = 0$ , as is typically assumed in rapid solidification  
 176 ( $\alpha = s, \beta = l$ ), we must have  $x_i^{eff} > x_i^s$ , i.e.,  $\lambda > 0$  (assuming  $\llbracket \tilde{\mu}_i \rrbracket < 0$  and  $x_i^l > x_i^s$ ). The upper bound of  
 177  $\lambda$  is set by Eq. (13), as the  $\beta \rightarrow \alpha$  transformation requires  $v > 0$  by definition. While the upper bound was  
 178 assumed to be unity in the solidification models in which  $\lambda$  was first introduced [18, 19], the upper bound  
 179 from Eq. (13) can be greater than one, and corresponds to a system for which the term in the parenthesis  
 180 is zero, which occurs when the effects of solute drag are sufficiently large to completely halt the motion of  
 181 the interface.

182 Additionally, we note that there is only a single value of  $\lambda$  in the current formulation, even for multi-  
 183 component systems. From the definition of  $x_i^{eff}$  in Eq. (1), it can be shown that the value of  $\lambda$  must be  
 184 the same for all  $i \in \{1, \dots, N\}$  components in order for  $\sum_{i=1}^N x_i^{eff} = 1$ . As such,  $\lambda$  represents the response  
 185 of the interface to the collective effect of solute drag from all components. However, if one species interacts  
 186 much more strongly with the interface than the others,  $\lambda$  could become a function of  $x_i^{eff}$ .

### 187 2.3. Interfacial response functions

188 Assuming that the two types of dissipative processes obey linear kinetics gives the interfacial response  
 189 functions from Eqs. (13) and (14), a VRF and  $N - 1$  CRFs, respectively:

$$v = M^m \rho_0^{-1} \left( \llbracket \Omega_v \rrbracket + \rho_0 \sum_{k=2}^N x_k^{eff} \llbracket \tilde{\mu}_k \rrbracket \right) - \sum_{j=2}^N m_j^m \llbracket \tilde{\mu}_j \rrbracket \quad (15)$$

$$J_i^t = m_i^t \left( \llbracket \Omega_v \rrbracket + \rho_0 \sum_{k=2}^N x_k^{eff} \llbracket \tilde{\mu}_k \rrbracket \right) - \rho_0 \sum_{j=2}^N M_{ij}^t \llbracket \tilde{\mu}_j \rrbracket \quad (16)$$

190 where  $M^m$ ,  $m_j^m$ ,  $m_i^t$ , and  $M_{ij}^t$  ( $\text{mol} \cdot \text{m} \cdot \text{J}^{-1} \cdot \text{s}^{-1}$ ) are the kinetic coefficients. The processes of interface  
 191 migration and trans-interface diffusion are denoted with superscript  $m$  and  $t$ , respectively. The coefficients  
 192  $M^m$  and  $M_{ij}^t$  represent the mobility of the interface and the mobility of component  $i$  across the interface,  
 193 respectively, and the coefficients  $m_j^m$  and  $m_i^t$  represent the cross-coupling between the processes of interface



194 migration and trans-interface diffusion. These constitutive equations at the interface can be written in  
 195 matrix-vector form as:

$$\begin{bmatrix} \rho_0 v \\ J_2^t \\ \vdots \\ J_N^t \end{bmatrix} = \rho_0 \begin{bmatrix} M^m & m_2^m & \cdots & m_N^m \\ m_2^t & M_{22}^t & \cdots & M_{2N}^t \\ \vdots & \vdots & \ddots & \vdots \\ m_N^t & M_{N2}^t & \cdots & M_{NN}^t \end{bmatrix} \begin{bmatrix} \rho_0^{-1} \left( [\Omega_v] + \rho_0 \sum_{k=2}^N x_k^{eff} [\tilde{\mu}_k] \right) \\ -[\tilde{\mu}_2] \\ \vdots \\ -[\tilde{\mu}_N] \end{bmatrix} \quad (17)$$

196 where the matrix of kinetic coefficients must be positive-definite. Note that when moving from Eq. (15) to  
 197 Eq. (17), a factor of  $\rho_0$  was multiplied into Eq. (15) in order to write the left-hand side of the VRF as a  
 198 flux. This result only assumes that energy must decrease during isothermal processes, and no assumption  
 199 has been made regarding the rate of energy dissipation. Thus, it is not surprising that Eq. (17) differs from  
 200 the result obtained by maximizing the energy dissipation [31].

201 Hereafter, we neglect cross-coupling between the fluxes and driving forces for the two types of interfacial  
 202 processes by letting  $m_i^m = m_i^t = 0$ , which reduces Eqs. (15) and (16) to:

$$v = M^m \rho_0^{-1} \left( [\Omega_v] + \rho_0 \sum_{k=2}^N x_k^{eff} [\tilde{\mu}_k] \right) \quad (18)$$

$$J_i^t = -\rho_0 \sum_{j=2}^N M_{ij}^t [\tilde{\mu}_j] \quad (19)$$

#### 203 2.4. Kinetic coefficients

204 The  $M^m$  kinetic coefficient describes the mobility of the interface, and is typically given by

$$M^m = \frac{v_0}{RT} \quad (20)$$

205 where  $v_0$  ( $\text{m} \cdot \text{s}^{-1}$ ) is a constitutive parameter representing the maximum possible transformation velocity  
 206 and  $T$  (K) is the interfacial temperature [18, 31, 33]. The value of  $v_0$  for a specific material system must be  
 207 determined experimentally. For solidification processes,  $v_0$  is typically found to be on the order of, but less  
 208 than, the velocity of sound in the liquid,  $\sim 10^3 \text{ m} \cdot \text{s}^{-1}$ . With this kinetic coefficient, the VRF in Eq. (18)  
 209 contains two constitutive parameters:  $v_0$  and  $\lambda$ .

210 From Eq. (9), assuming linear kinetics between the mass flux and gradient in diffusion potential yields  
 211 the usual relationship between the mass flux and the gradient in diffusion potential for a multicomponent  
 212 alloy:

$$\mathbf{J}_i^\phi = -\rho_0 \sum_{j=2}^N M_{ij}^\phi \nabla \tilde{\mu}_j^\phi \quad (21)$$

213 where the kinetic coefficients  $M_{ij}^\phi$  ( $\text{mol} \cdot \text{m}^2 \cdot \text{J}^{-1} \cdot \text{s}^{-1}$ ) describe diffusion in the bulk phase  $\phi$ . Following  
 214 Andersson and Ågren [44] under the assumption of constant molar volumes, the  $M_{ij}^\phi$  coefficients are given  
 215 by:

$$M_{ij}^\phi = \sum_{k=1}^N (\delta_{ik} - x_i) (\delta_{jk} - x_j) x_k \frac{D_k^*}{RT} \quad (22)$$

216 where  $D_k^*$  is the tracer diffusivity of component  $k$ . To convert from the bulk  $M_{ij}^\phi$  kinetic coefficients, which  
 217 link fluxes to gradients in diffusion potential, to the  $M_{ij}^t$  coefficients of the present sharp-interface model,  
 218 which link fluxes to jumps in diffusion potentials, we write

$$M_{ij}^t = M_{ij}^\phi / \delta \quad (23)$$

219 where  $\delta$  is approximately the width of the interface. Additionally, because the  $M_{ij}^t$  coefficients describe the  
 220 motion of solute across the interface, we take the concentrations as the effective concentrations. Finally, we  
 221 assume that  $D_k^* = D_i^I$ , where  $D_i^I$  is the diffusivity of component  $i$  within the interface. These assumptions  
 222 yield the following  $M_{ij}^t$  kinetic coefficients:

$$M_{ij}^t = -x_i^{eff} x_j^{eff} \frac{v_i^D}{RT}, \quad i \neq j \quad (24)$$

$$M_{ii}^t = x_i^{eff} (1 - x_i^{eff}) \frac{v_i^D}{RT}, \quad i = j \quad (25)$$

223 where we have introduced the trans-interface diffusive speed,  $v_i^D = D_i^I / \delta$ , which describes the velocity at  
 224 which an atom of component  $i$  traverses the interface. As both  $D_i^I$  and  $\delta$  are typically unknown,  $v_i^D$  is  
 225 often used alongside  $v_0$  to apply the interfacial response functions to experimental or simulation data. With  
 226 these kinetic coefficients, each CRF in Eq. (19) (i.e., one for the trans-interface diffusion of each component  
 227  $i \in \{2, \dots, N\}$ ) contains two constitutive parameters:  $\lambda$  and  $v_i^D$ . Notably, the solute-drag parameter,  $\lambda$ ,  
 228 appears in both interfacial response functions, self-consistently incorporating the effects of partial solute  
 229 drag as an additional degree of freedom available to describe the transformation.

230 These kinetic coefficients can be modified accordingly by following Refs. [45, 44], if, for example, vacancy  
 231 diffusion cannot be neglected, the assumption of constant molar volumes for all components is poor, or  
 232 interstitial species are to be considered.

### 233 2.5. Incorporating additional effects

234 The effects of interfacial energy can be incorporated into the dissipation relation (see, for example,  
 235 Ramanathan and Voorhees [42]) via an additional term in Eq. (10):

$$\dot{E}_\kappa = \int_{\partial\Omega} \gamma \kappa v \, dA \quad (26)$$

236 where  $\gamma$  ( $\text{J} \cdot \text{m}^{-2}$ ) is the interfacial energy and  $\kappa = \nabla \cdot \hat{\mathbf{n}}^\alpha$  ( $\text{m}^{-1}$ ) is the interfacial mean curvature of the  
 237 growing phase. Eq. (26) assumes a constant, isotropic surface energy, but anisotropy can be added if desired.  
 238 Carrying this extra term through the dissipation relation, the CRF in Eq. (19) is unchanged, but the VRF  
 239 in Eq. (18) becomes

$$v = M^m \rho_0^{-1} \left( \llbracket \Omega_v \rrbracket + \rho_0 \sum_{k=2}^N x_k^{eff} \llbracket \tilde{\mu}_k \rrbracket - \gamma \kappa \right) \quad (27)$$

240 assuming  $\gamma \kappa$  is sufficiently small such that the driving force does not change sign. The presence of an  
 241 interfacial energy reduces the driving force for interfacial motion, but does not change the driving force for  
 242 diffusion through the interface.

243 Additionally, due to the use of the dissipation relation, it is straightforward to include additional terms  
 244 describing the energy dissipation due to, for example, local non-equilibrium diffusion [27, 31], elastic stress  
 245 [40, 41], or convection in the melt (as proposed by [46]), and the interfacial response functions will follow  
 246 naturally.

### 247 2.6. The case of a stationary interface

248 Thus far, the analysis has not made any assumptions about diffusion in the growing phase. Inserting  
 249 Eq. (3) into Eq. (19) gives the following CRF:

$$\rho_0 v \left( x_i^{eff} - x_i^\alpha \right) + J_i^\alpha = -\rho_0 \sum_{j=2}^N M_{ij}^t \llbracket \tilde{\mu}_j \rrbracket \quad (28)$$

250 In the  $v = 0$  limit, which could be relevant in certain solid/solid transformations where the mobility of  
 251 the interface,  $M^m$ , is exceptionally low, only  $J_i^\alpha$  remains on the left-hand side of Eq. (28). Because it is  
 252 assumed that  $\alpha$  and  $\beta$  are in continuous contact and no surface diffusion is occurring, the  $v = 0$  limit also  
 253 gives  $J_i^\alpha = J_i^\beta$  from Eq. (5), reducing Eq. (28) to

$$J_i^\alpha = J_i^\beta = -\rho_0 \sum_{j=2}^N M_{ij}^t \llbracket \tilde{\mu}_j \rrbracket \quad (29)$$

254 which states that there can still be fluxes across a stationary interface if the diffusion potentials across the  
 255 interface are unequal, and that the fluxes at the interface will be equal in both phases. Thus, even in the  
 256 absence of interfacial motion, the interfacial compositions are functions of the fluxes flowing through the  
 257 interface. Eq. (29) can be viewed as the mass-transfer analog of the thermal boundary resistance [47] —  
 258 also known as the Kapitza resistance, where the magnitude of the thermal flux,  $J_Q$ , across an interface is  
 259 given by  $J_Q = M_Q \llbracket T \rrbracket$  — and has been observed in the sharp-interface limit of diffuse-interface theories for  
 260 diffusion couples [48].

## 261 3. Solidification of binary alloys

262 To illustrate the physics described by this model and the effect of the solute-drag parameter, Eqs. (18)  
 263 and (19) are applied to the solidification ( $\alpha = s$ ,  $\beta = l$ ) of a binary alloy (components  $a$  and  $b$ ) with a  
 264 planar interface and zero diffusion in the solid. Because the diffusive speed in the liquid is several orders of  
 265 magnitude larger than that in the solid, this is a reasonable assumption during rapid solidification. Thus,  
 266 we set  $J_b^s = 0$  in Eq. (3). Under these assumptions and with the kinetic coefficients in Eqs. (20) and (25),  
 267 the interfacial response functions in Eqs. (18) and (19) become

$$v = \frac{v_0}{RT} \left( x_b^{eff} \llbracket \mu_b \rrbracket + \left( 1 - x_b^{eff} \right) \llbracket \mu_a \rrbracket \right) \quad (30)$$

$$\left( x_b^{eff} - x_b^s \right) v = \left( 1 - x_b^{eff} \right) x_b^{eff} \frac{v^D}{RT} \left( \llbracket \mu_a \rrbracket - \llbracket \mu_b \rrbracket \right) \quad (31)$$

268 The full derivation of Eqs. (30) and (31) from Eqs. (18) and (19), respectively, is provided in Appendix A.  
 269 Note that, because of the assumption of diffusion via a direct exchange mechanism, a binary alloy only has  
 270 one unique diffusive speed.

271 Notably, Eqs. (30) and (31) are both dependent on the degree of solute drag in the system through  
 272  $x_b^{eff}$ . Thus,  $\lambda$  is critical in setting both the velocity of the interface and the distribution coefficient, which  
 273 follows from Eq. (31). To illustrate the effects of solute drag on the distribution coefficient, we examine a  
 274 dilute-ideal solution, in which the chemical potential of component  $i$  is given by  $\mu_i = \mu_i^o + RT \ln x_i$ , so the  
 275 driving force in Eq. (31) is

$$[[\mu_a]] - [[\mu_b]] = \mu_a^{o,l} - \mu_a^{o,s} - \mu_b^{o,l} + \mu_b^{o,s} + RT \ln \left\{ \frac{(1 - x_b^l)x_b^s}{(1 - x_b^s)x_b^l} \right\} \quad (32)$$

276 From the equilibrium condition, i.e.,  $\mu_i^l = \mu_i^s$ , we have

$$\mu_i^{o,l} - \mu_i^{o,s} = RT \ln \left\{ \frac{x_i^{s,eq}}{x_i^{l,eq}} \right\} \quad (33)$$

277 Using the definition of  $x_b^{eff}$  and the dilute-solution approximation, i.e.,  $x_a^s \approx 1$  and  $x_a^l \approx 1$ , Eq. (31) becomes

$$(1 - k_v)\lambda v = v^D [\lambda + (1 - \lambda)k_v] \ln \left\{ \frac{k_v}{k_{eq}} \right\} \quad (34)$$

278 Fixing  $k_{eq} = 0.25$ , we solve Eq. (34) for  $k_v$ , which is plotted as a function of velocity for various values of  
 279 (Figure 2a)  $v^D$  and (Figure 2b)  $\lambda$ . Figure 2b also provides a comparison to the CGM, shown as the dotted  
 280 line. In the dilute-solution limit, the expression for the distribution coefficient from the CGM is

$$k_v = \frac{k_{eq} + v/v^D}{1 + v/v^D} \quad (35)$$

281 An analogous analytic expression can be obtained from the present model. Assuming an expression for  
 282  $k_v$  of a similar form to the CGM, substituting it into Eq. (34), and performing a Taylor expansion in the  
 283 limit of  $v \ll v^D$  yields

$$k_v = \frac{k_{eq} + \alpha v/v^D}{1 + \alpha v/v^D} \quad \text{where} \quad \alpha = \frac{k_{eq} \lambda}{k_{eq}(1 - \lambda) + \lambda} \quad (36)$$

284 As shown by the dotted lines in Figure 2, this expression gives a reasonable approximation to the numerical  
 285 solution for  $k_v$  using Eq. (34), especially for  $v < v^D$ .

286 We employ numerical solutions to the non-linear equations in the subsequent analyses (Sections 3.1 and  
 287 3.2) and use the CRF given in Eq. (31). Note that the derivation of Eq. (35) does not incorporate  $\lambda$  in  
 288 the solute-drag flux [18], which results in an expression for  $k_v$  that is independent of  $\lambda$ . The effects of this  
 289 assumption on the full expression for  $k_v$  will be discussed in Section 3.2. Here,  $\lambda$  is present in Eq. (3),  
 290 leading to a solute-drag-dependent distribution coefficient.

291 Because of the assumed linearity between the fluxes and gradients in diffusion potentials, the  $k_v$  curve  
 292 obtained here resembles that of the CGM; it is a sigmoidal curve with the asymptotic behavior  $k_v \rightarrow k_{eq}$   
 293 as  $v \rightarrow 0$  and  $k_v \rightarrow 1$  (i.e., “complete solute trapping”) as  $v \rightarrow \infty$ . However, the model does not include  
 294 potentially important effects that occur in the very high velocity regime; see, for example, Sobolev [49, 50],  
 295 Li et al. [25], and Wang et al. [27, 31, 51]. These models show a sharp transition to complete solute  
 296 trapping when  $v$  reaches the bulk diffusion speed in the liquid, which is typically  $\approx 10 \text{ m} \cdot \text{s}^{-1}$ . Thus, our  
 297 model only gives approximate values of the velocities in this range, and is most relevant to velocities at which  
 298 only the interface departs from local equilibrium, such as those encountered in additive manufacturing. As

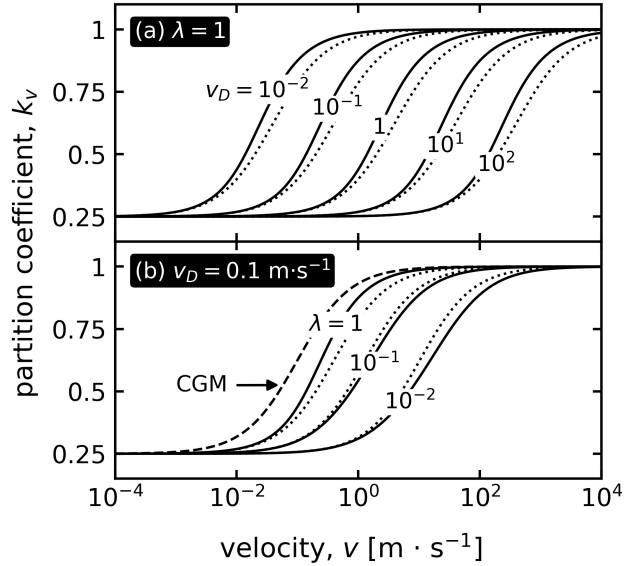


Figure 2: The velocity-dependent distribution coefficient,  $k_v = x_b^s/x_b^l$ , for different values of (a) the diffusive speed,  $v^D$ , and (b) the solute-drag parameter,  $\lambda$ . The solid curves are the numerical solution to Eq. (34), and the dotted curves are the analytical approximation in Eq. (36). Figure (b) includes (dashed line) the Aziz CGM. Increasing  $v^D$  simply translates the sigmoidal  $k_v$  curve to higher  $v$ , while decreasing  $\lambda$  both translates it to higher  $v$  and slightly flattens it.

299 can be seen from Figure 2a, increasing  $v^D$  increases the velocity at which solute trapping begins by simply  
 300 translating the  $k_v$  curve along the  $v$ -axis. This is expected, as the speed at which the interface must move  
 301 to trap the atom in the growing phase increases as the speed at which the atom can cross the interface,  
 302  $v^D$ , increases. Figure 2b shows that decreasing the amount of solute drag (i.e., decreasing  $\lambda$ ) also translates  
 303 the  $k_v$  curve to higher velocities. This occurs because smaller values of  $\lambda$  indicate that material adsorbs to  
 304 the interface at a composition closer to  $x_b^s$ . Thus, less trans-interface diffusion is required to adjust  $x_b^{eff}$   
 305 to  $x_b^s$ , so  $x_b^s$  can be maintained to higher velocities than if the material adsorbs to the interface with a  
 306 composition closer to  $x_b^l$ . If experimental or simulation data are available, it is possible to determine the  
 307 materials parameters  $v_0$  and  $\lambda$  that appear in the VRF, as shown in Section 3.1 and 3.2.

### 308 3.1. Estimation of the trans-interface diffusion coefficient

309 The effects of partial solute drag on the velocity of the interface can be investigated using molecular  
 310 dynamics following the methodology of Yang et al. [8]. Using the tabulated velocities and Gibbs free  
 311 energy differences from Table IV of the supplementary information of Ref. [8], the value of  $\lambda$  is determined  
 312 by varying  $\lambda$  until the best linear-least-squares fit is obtained between the MD data and the VRF. The  
 313 results are shown in Figure 3 alongside the zero-drag case. In agreement with Yang et al. [8] we find that  
 314 partial solute drag is necessary to obtain a linear relationship between the measurements of the velocity  
 315 and the driving force for interface motion, and that the effects of solute drag are most significant at low  
 316 velocities where appreciable solute partitioning occurs and least significant at high velocities where the  
 317 system approaches complete solute trapping.

318 From the above analysis, we obtain  $v_0 = 890 \text{ m} \cdot \text{s}^{-1}$  and  $\lambda = 0.29$  for the  $\{100\}$  interface and  $v_0 =$

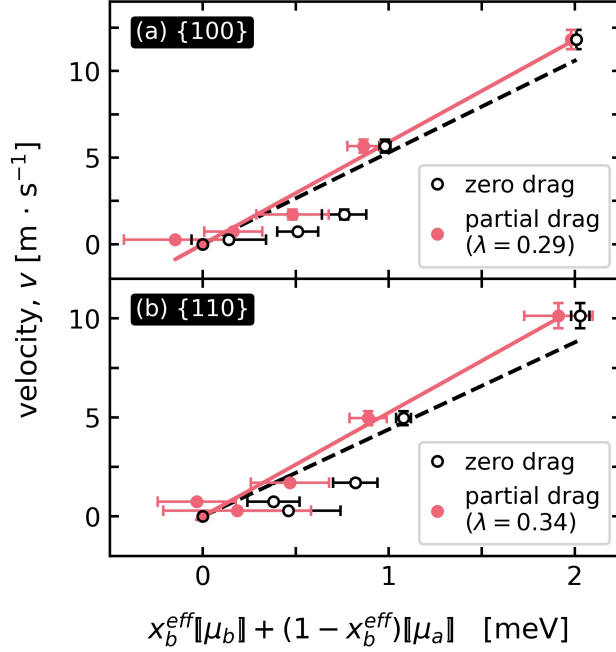


Figure 3: Fitting the driving force for interface migration to the velocity response function, Eq. (30), for (a)  $\{100\}$  and (b)  $\{110\}$  interfaces. Open circles are the results from the molecular dynamics simulations of Ni-Cu by Yang et al. [8].

319  $790 \text{ m} \cdot \text{s}^{-1}$  and  $\lambda = 0.34$  for the  $\{110\}$  interface. These values of  $\lambda$  agree with the values permitted by the  
 320 dissipation relation in Section 2.2, within the uncertainties in the measurements of the free energy changes  
 321 from molecular dynamics. The value of  $T$  is assumed to remain constant at 1750 K. As the sound velocity  
 322 in liquid Ni at 1750 K and atmospheric pressure is approximately  $4000 \text{ m} \cdot \text{s}^{-1}$  [52], these values of  $v_0$  are  
 323 a factor of 5 smaller than the sound velocity.

324 The supplementary information of Ref. [8] also reports  $x_b^s$  and  $x_b^l$  at the various solidification velocities,  
 325 allowing  $k_v$  to be calculated. While Yang et al. describe the  $k_v$  measurements with the CGM, i.e., Eq. (35),  
 326 we use the present CRF with the reported  $x_b^l$  in Eq. (31), solving for  $x_b^s$  while determining the optimal value  
 327 of  $v^D$ . Because the value of  $\lambda$  is already known from analyzing the velocity/driving force measurements,  $v^D$   
 328 is the only as-yet-unknown constitutive parameter in both models. Figure 4 shows the descriptions of the  
 329  $k_v$  data with both the present CRF and the CGM. Note that the current model is not able to be evaluated  
 330 between the provided data points because free energies are only available at the measured velocities, so a  
 331 spline was used to obtain continuous curves in both Figures 4a and 4b. The CRF gives diffusive speeds of  
 332  $v^D = 0.32 \text{ m} \cdot \text{s}^{-1}$  for the  $\{100\}$  interface and  $v^D = 0.46 \text{ m} \cdot \text{s}^{-1}$  for the  $\{110\}$  interface. The values obtained  
 333 here are an order of magnitude lower than the values obtained from the CGM and the local non-equilibrium  
 334 model of Galenko and Sobolev [53] reported by Yang et al., which fall between  $1.3 - 1.6 \text{ m} \cdot \text{s}^{-1}$  [8].

335 Using the values of  $v^D$  and the definition  $v^D = D^I/\delta$ , the magnitude of the trans-interface diffusion  
 336 coefficient can be estimated. While the exact values of  $\delta$  for Ni-Cu interfaces are not reported in Ref. [8],  
 337 Monte-Carlo simulations by Ramalingam et al. [54] report equilibrium “10-90” interface widths of  $7.2 \pm 0.9 \text{ \AA}$   
 338 for  $\{100\}$  and  $\{111\}$  orientations in Ni-Cu. Here, we assume that the interface width is independent of

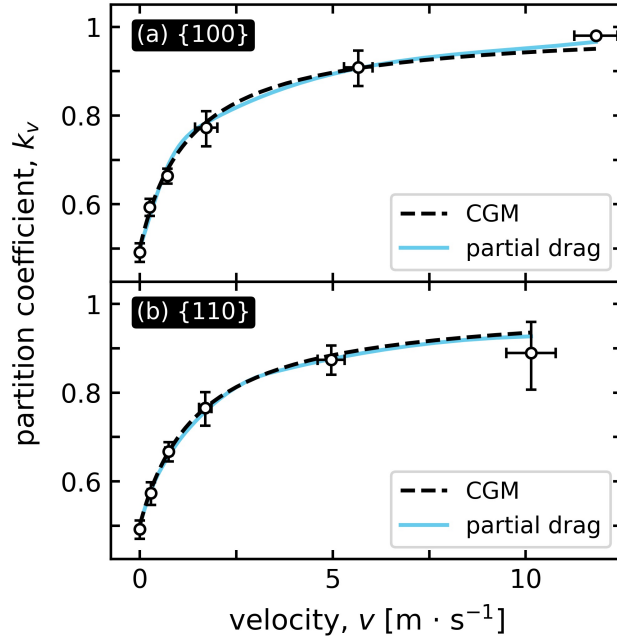


Figure 4: Fitting the distribution coefficient to the concentration response function, Eq. (31), for (a)  $\{100\}$  and (b)  $\{110\}$  interfaces, with comparison to the CGM. Open circles are the results from the molecular dynamics simulations of Ni-Cu by Yang et al. [8].

339 velocity, which is reasonable for the velocity range analyzed here, but perhaps not so for  $v$  approaching  
 340 the diffusive speed in the bulk liquid [26]. Using the values of  $v^D$  obtained from the CGM and the local  
 341 non-equilibrium model gives  $D^I = 0.94 - 1.15 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ , which are equivalent to typical diffusive  
 342 speeds in a metallic melt,  $D^I \sim 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ . In contrast, the values of  $v^D$  from the present model give  
 343 values of  $D^I = 2.3 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$  for the  $\{100\}$  interface and  $D^I = 3.3 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$  for the  $\{110\}$   
 344 interface. These values are between the typical diffusivities in bulk solids and metallic melts, which agrees  
 345 with the behavior intuitively expected for a solid/liquid interface. A more in-depth study on the nature of  
 346 diffusion through the interface will be reported elsewhere [55]. The reason for this improved prediction is  
 347 evident from Figure 2 — to predict a given amount of solute trapping,  $v^D$  must decrease if  $\lambda$  decreases.

### 348 3.2. Calculation of non-equilibrium phase boundaries

349 The interfacial response functions can also provide the temperature of the interface. However, the  
 350 standard expression for the interfacial temperature [56, 57, 58, 59] and its partial-drag extension [19] is  
 351 obtained by linearizing Eq. (30) in the concentration, i.e., by assuming a dilute-ideal solution. Here, to  
 352 illustrate the effects of partial solute drag in a non-ideal, non-dilute alloy, the non-equilibrium solidus and  
 353 liquidus curves for the Ag-Cu system are calculated by solving the full interfacial response functions for  $x_b^s$   
 354 and  $x_b^l$  at various values of  $T$  and  $\lambda$ .

355 To apply the present model to this binary alloy, we again use Eqs. (30) and (31). We also examine the  
 356 widely used CGM of Aziz and Kaplan [18], which uses reaction rate theory to derive the interfacial response

357 functions for a binary alloy, which can be written as:

$$x_b^{eff} \llbracket \mu_b \rrbracket + (1 - x_b^{eff}) \llbracket \mu_a \rrbracket = -RT \ln \left\{ 1 - \frac{v}{v_0} \right\} \quad (37)$$

$$\llbracket \mu_a \rrbracket - \llbracket \mu_b \rrbracket = -RT \ln \left\{ 1 - \frac{x_b^l - x_b^s}{x_b^s(1 - x_b^l)} \cdot \frac{v}{v^D} \right\} \quad (38)$$

358 Using the free energies for Ag-Cu from Murray [60] in Thermo-Calc software [61, 62] to evaluate the  
 359 chemical potentials, the systems of Eqs. (30)–(31) for the present model and (37)–(38) for the Aziz and  
 360 Kaplan model [18] are solved at various values of temperature,  $T$ , and solute-drag parameter,  $\lambda$ , to obtain  
 361  $x_{Cu}^s$  and  $x_{Cu}^l$ . We fix  $v = 0.1 \text{ m} \cdot \text{s}^{-1}$  and, as a first approximation, use kinetic parameters on the order  
 362 of the results found in Section 3.1:  $v^D = 0.4 \text{ m} \cdot \text{s}^{-1}$  and  $v_0 = 850 \text{ m} \cdot \text{s}^{-1}$ . A simplex method [63] is  
 363 implemented to solve these non-linear systems, yielding the kinetic phase diagrams in Figure 5, where 5(a)  
 364 and 5(b) correspond to the present model and 5(c) and 5(d) correspond to the Aziz and Kaplan model.

365 The present model is symmetric with respect to the  $a$  and  $b$  species, meaning that one can either decide  
 366 to consider  $a$  to be Cu and  $b$  to be Ag or vice-versa without modifying the equations and their solutions.  
 367 This behavior is inherent to the mathematical formulation of Eqs. (30)–(31), and is also consistent with  
 368 the expectation that the  $\text{Ag}_{(x_a=x)}\text{Cu}_{(x_b=1-x)}$  alloy gives the same solution as the  $\text{Cu}_{(x_a=1-x)}\text{Ag}_{(x_b=x)}$  alloy.  
 369 Consequently, the results displayed in Fig. 5a and 5b combine calculations using both Cu and Ag as  
 370 component  $b$ , and are able to fully capture the retrograde solidus behavior observed in this system at local  
 371 equilibrium.

372 The Aziz and Kaplan model is asymmetric with respect to the choice of component  $a$  and  $b$  due to the  
 373 use of reaction-rate theory in the development of their CRF, which describes the exchange of a  $b$  atom in  
 374 the solid with an  $a$  atom in the liquid under exponential kinetics. Upon replacing all values of  $x_b$  in Eqs.  
 375 (37)–(38) with  $x_a$  and vice-versa, Eq. (37) remains the same, while the right-hand side of (38) becomes  
 376  $RT \ln\{1 + \dots\}$ . While the relationship  $\ln(1 - \epsilon) \approx -\epsilon$  can be used to linearize Eq. (38) in the limit of  $v \ll v^D$ ,  
 377 the asymmetry remains due to the use of  $x_b^s x_a^l$  to describe the trans-interface mobility. Thus, the choice  
 378 of species corresponding to components  $a$  and  $b$  will affect the resulting diagram, so one must decide on a  
 379 methodology to draw the phase boundaries. Here, we have reproduced the kinetic phase diagrams published  
 380 in Ref. [18] and reapplied the original methodology. For the Ag-rich domain shown in Fig. 5c, we solve  
 381 Eqs. (37)–(38) with  $a \simeq \text{Ag}$  and  $b \simeq \text{Cu}$ , only keeping solutions with  $x_{Cu}^s \leq 0.5$ . The Cu-rich domain shown  
 382 in Figure 5d is solved with an analogous procedure, where  $a \simeq \text{Cu}$  and  $b \simeq \text{Ag}$  and only the solutions with  
 383  $x_{Ag}^s \leq 0.5$  are retained. The results are further filtered to discard solutions where  $x^s$  falls inside the region  
 384 of spinodal decomposition of the solid phase. The boundary of this region, shown by the dotted lines drawn  
 385 in Figures 5c and 5d, is defined by the inflection points of the Gibbs free energy of the solid phase. This  
 386 information is provided in Thermo-Calc software using the QF (*phase stability*) function [64].

387 The results of the present model and the Aziz and Kaplan model agree qualitatively in that increasing the  
 388 amount of solute drag will depress the interfacial temperature for a given concentration and that the effect  
 389 of this “solute-drag undercooling” becomes more significant as the concentration increases. However, the  
 390 shapes of the calculated phase boundaries are remarkably different between the two models. Most notably,  
 391 the Aziz and Kaplan model lacks any sort of retrograde solidus behavior, causing the solid compositions to



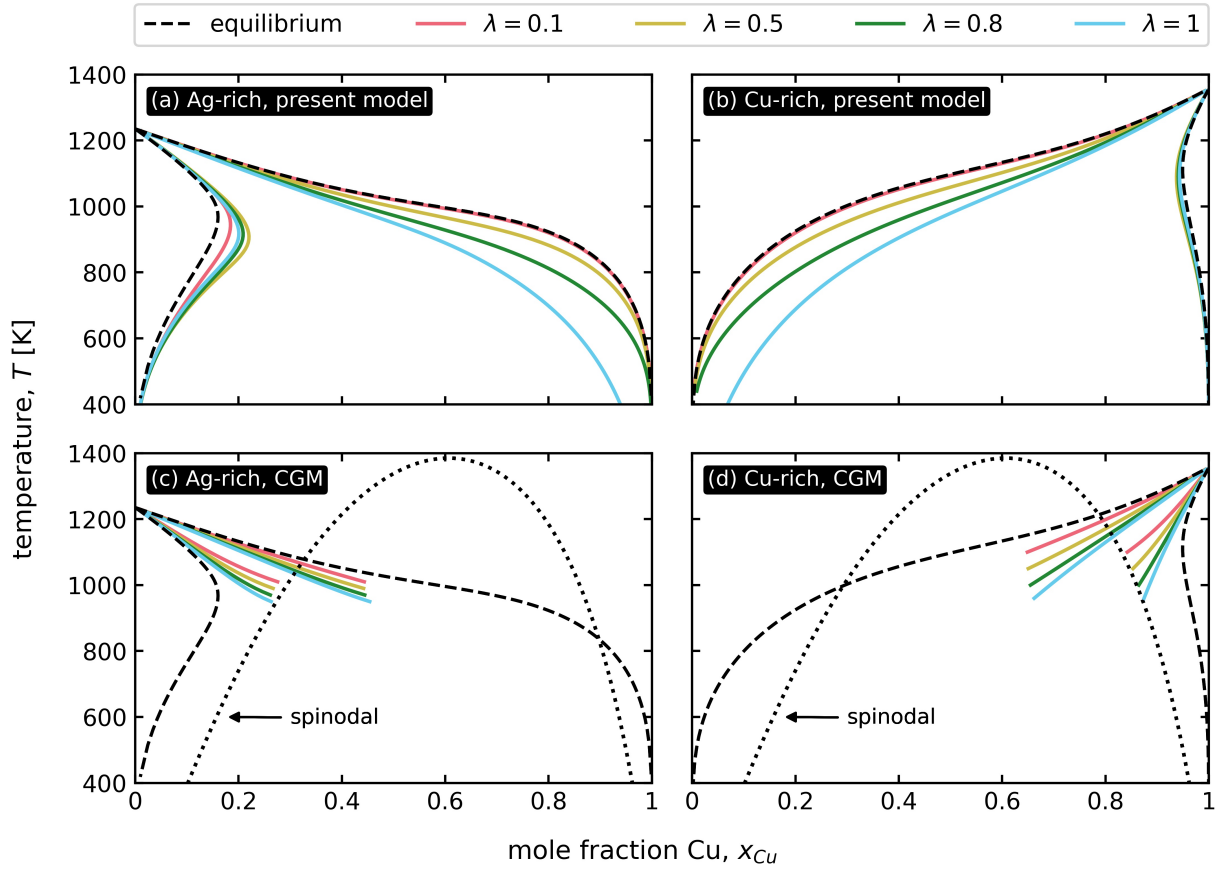


Figure 5: Kinetic phase boundaries for the Ag-Cu system as a function of the solute-drag parameter for  $v = 0.1 \text{ m} \cdot \text{s}^{-1}$ ,  $v^D = 0.4 \text{ m} \cdot \text{s}^{-1}$ , and  $v_0 = 850 \text{ m} \cdot \text{s}^{-1}$ . The results of the present model, i.e., Eqs. (30) and (31), are shown in (a) and (b), and those of the CGM [18], i.e., Eqs. (37) and (38), are shown in (c) and (d). Only the boundaries where the compositions are stable, i.e., outside the spinodal of the solid phase (dotted lines), are shown. The equilibrium liquidus and solidus lines and their metastable extensions are shown with dashed lines.

392 quickly enter the spinodal, while the present model is able to capture the retrograde solidus behavior, so  
 393 the phase boundaries never enter the region of spinodal decomposition at any values of  $\lambda$  examined here.

394 As  $\lambda \rightarrow 0$ , the factor of  $\lambda$  in the solute-drag flux of the present model (i.e., the left-hand side of Eq. (31))  
 395 becomes significant. While Aziz and Kaplan allow partial-solute drag to modify the driving force of each  
 396 response function, they do not account for its effect on the solute-drag flux (i.e., the numerator of the log  
 397 term in Eq. (38)), using  $x_b^l - x_b^s$  for both the full- and zero-drag cases discussed in their analysis. This causes  
 398 the kinetic phase boundaries to deviate significantly from the equilibrium phase boundaries, even for small  
 399 amounts of solute drag. However, the presence of  $\lambda$  in the present model scales the solute-drag flux with  
 400 the available driving force, and the concentrations approach their equilibrium values as  $\lambda \rightarrow 0$  (although, as  
 401 before, we must have  $\lambda > 0$  to obey the dissipation inequality).

402 While the solute-drag fluxes of Eqs. (31) and (38) are equal when  $\lambda = 1$ , the choice of trans-interface  
 403 mobility remains a differentiating factor between the two models. The Aziz model uses reaction-rate theory,  
 404 leading to a concentration dependence given by  $x_b^s x_a^l$ , while the present model accounts for the effective  
 405 concentration of the interface, as discussed in Section 2.3, leading to  $x_b^l x_a^l$  when  $\lambda = 1$ . Notably, because  
 406 the product  $x_b^s x_a^l$  is asymmetric with respect to the choice of components  $a$  and  $b$ , the CGM is unable to  
 407 capture the retrograde solidus behavior.

#### 408 4. Discussion: Interpretations of solute drag in the context of binary alloys

409 To compare the current model with the other sharp-interface models available in the literature, it is  
 410 instructive to take the constitutive laws derived using energy dissipation and re-interpret them with the  
 411 classical approach using Gibbs free energy changes. To make the comparison as simple as possible, we  
 412 use the expressions for a binary alloy and neglect cross-coupling, as given by Eqs. (18) and (19) in the  
 413 binary limit. Using the dissipation inequality, is possible to directly identify the driving forces ( $\text{J} \cdot \text{mol}^{-1}$ )  
 414 for interface motion,  $D^m = (M^m)^{-1}v$ , and trans-interface diffusion,  $D^t = (\rho_0 M_{bb}^t)^{-1} J_b^t$ , in the binary limit.  
 415 Although the driving forces in this limit are identical to those in Eqs. (30) and (31), there can be diffusion  
 416 in both phases, i.e., a non-zero  $J_b^\alpha$  term in Eq. (31). These driving forces can then be related to the Gibbs  
 417 free energy changes for those processes as given by Hillert [35]:

$$\Delta G^p = D^p \Delta \xi^p \quad (39)$$

418 where  $\Delta \xi^p$  is the “extent of the process” in moles per mole of material transformed and the superscript  
 419  $p = \{m, t, tot\}$  denotes the relevant process. Thus, the free energy changes can vary with the model for the  
 420 conditions at the interface.

421 These free energy changes are illustrated for the full-drag (subscript “*full*”), partial-drag (subscript  
 422 “*eff*”), and partial drag from bulk diffusion (subscript “*tr*”) models in Figure 6a, 6b, and 6c, respectively.  
 423 Various graphical constructions are used to calculate the Gibbs free energy changes for interface migration,  
 424  $\Delta G^m$  (marked in red), and trans-interface diffusion,  $\Delta G^t$  (marked in blue), for each model. The sum of  
 425 these values of the total Gibbs free energy change for the  $\beta \rightarrow \alpha$  transformation,  $\Delta G^{tot} = \Delta G^m + \Delta G^t$   
 426 (marked in purple). We only show these constructions for the growing phase in order to emphasize the  
 427  $\beta \rightarrow \alpha$  transformation.

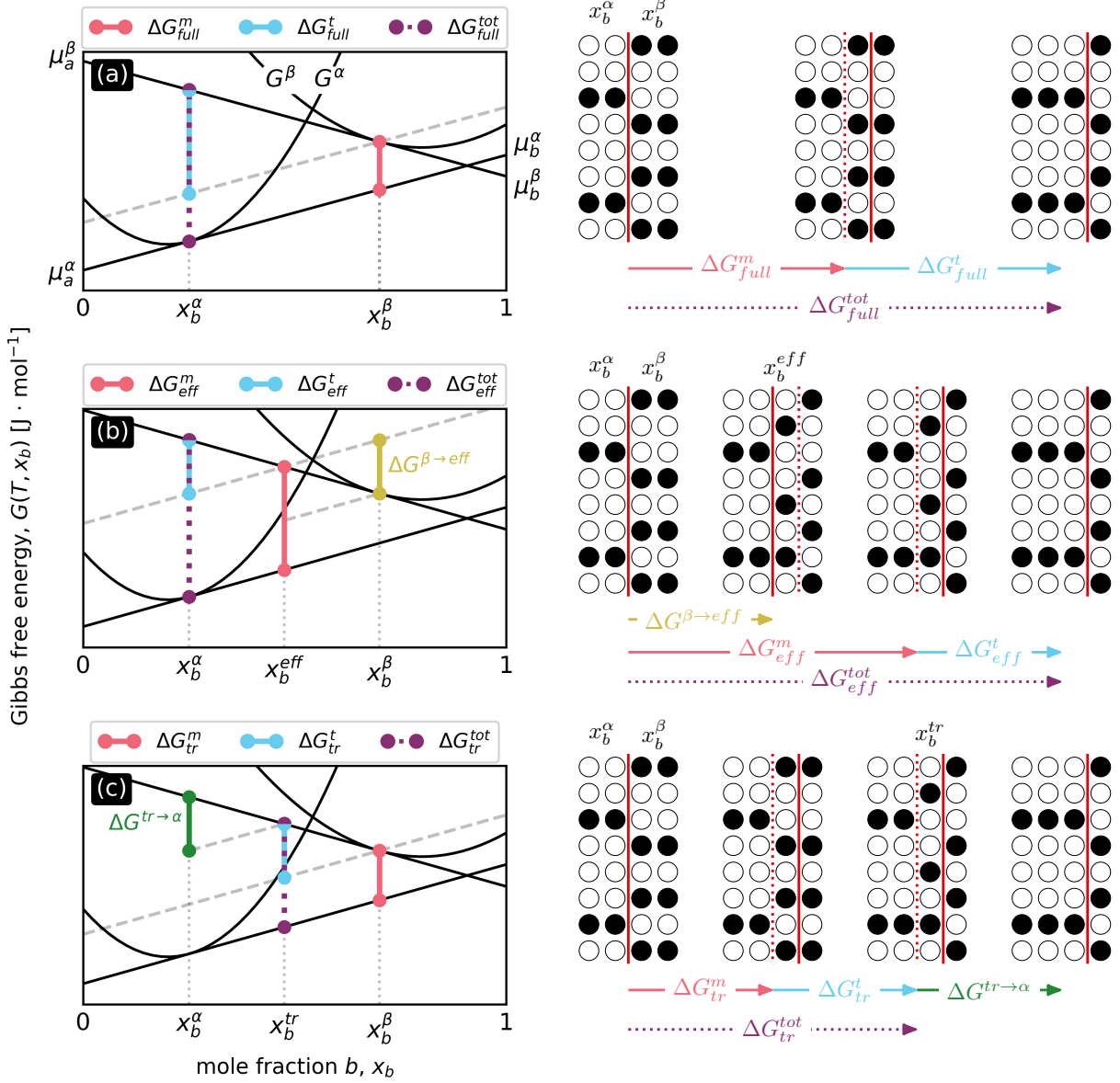


Figure 6: Graphical constructions and schematics for binary alloys showing the dissipative processes in the three classes of sharp-interface models incorporating solute drag: (a) the full-drag model in which material is adsorbed to the interface at  $x_b^\beta$  and transferred to the growing phase at  $x_b^\alpha$ , (b) a partial-drag model in which the interface can adsorb material at  $x_b^{eff} \neq x_b^\beta$ , and (c) a partial-drag model in which material can be transferred to the growing phase at  $x_b^{tr} \neq x_b^\alpha$ . Similarly, the first and last columns of the schematics are the same, corresponding to the initial and final distribution of (white dots)  $a$  and (black dots)  $b$  species in the (left)  $\alpha$  growing and (right)  $\beta$  parent phases. Here, we set  $x_b^{eff} = x_b^{tr}$  to facilitate comparison between the three approaches. In the graphical constructions, red vertical lines indicate  $\Delta G^m$ , blue vertical lines indicate  $\Delta G^t$ , and purple vertical lines indicate  $\Delta G^{tot}$  for each class of model. In the schematics, solid red vertical lines denote the location of the sharp interface, and the dotted red line is used in conjunction with the solid red line to denote a transition state for which the process of concentration adjustment has yet to occur.

428 4.1. “Full-drag” models

429 With  $\lambda = 1$  in the present model, we recover a class of sharp-interface models known as “full-drag  
 430 models”. From Eq. (1), this sets  $x_b^{eff} = x_b^\beta$ , indicating that the motion of the interface dissipates  $\Delta G_{full}^m$   
 431 by adsorbing  $\Delta \xi_{full}^m = 1$  mole of material at composition  $x_b^\beta$  and that solute drag dissipates  $\Delta G_{full}^t$  by  
 432 desorbing  $\Delta \xi_{full}^t = x_b^\beta - x_b^\alpha$  moles of  $b$  from the interface back to the parent phase. The overall  $\beta \rightarrow \alpha$  phase  
 433 transformation dissipates  $\Delta G_{full}^{tot}$  and represents the growth of  $\alpha$  at composition  $x_b^\alpha$  from  $\beta$  at composition  
 434  $x_b^\beta$ . From the graphical construction in Figure 6a, these Gibbs free energy changes are

$$\Delta G_{full}^m = x_b^\beta \llbracket \mu_b \rrbracket + (1 - x_b^\beta) \llbracket \mu_a \rrbracket \quad (40)$$

$$\Delta G_{full}^t = (x_b^\beta - x_b^\alpha) (\llbracket \mu_a \rrbracket - \llbracket \mu_b \rrbracket) \quad (41)$$

$$\Delta G_{full}^{tot} = x_b^\alpha \llbracket \mu_b \rrbracket + (1 - x_b^\alpha) \llbracket \mu_a \rrbracket \quad (42)$$

435 and from Eq. (39), the corresponding driving forces for the two interfacial processes are

$$D_{full}^m = x_b^\beta \llbracket \mu_b \rrbracket + (1 - x_b^\beta) \llbracket \mu_a \rrbracket \quad (43)$$

$$D_{full}^t = \llbracket \mu_a \rrbracket - \llbracket \mu_b \rrbracket \quad (44)$$

436 Full-drag models were initially developed for binary alloys by Aziz and Kaplan [18] (the “with-drag” case  
 437 of the CGM) and subsequently discussed by Hillert [35] and used by Rettenmayr and coworkers [65, 66].  
 438 Additionally, the full-drag flux is used by Galenko and Sobolev [49, 50, 53, 67, 68] in the framework of  
 439 extended irreversible thermodynamics to discuss solute trapping in binary alloys with non-equilibrium dif-  
 440 fusion in the liquid ( $\beta$  in the current notation). Galenko also performs analyses with extended irreversible  
 441 thermodynamics using the full-drag driving forces [69, 70].

442 4.2. Partial-drag models motivated by rapid solidification (using  $x^{eff}$ )

443 The present model allows  $\lambda$  in Eq. (1) to take any value permitted by the dissipation inequalities in Eqs.  
 444 (13) and (14). In this case, the motion of the interface dissipates  $\Delta G_{eff}^m$  by adsorbing  $\Delta \xi_{eff}^m = 1$  mole of  
 445 material at composition  $x_b^{eff}$  and that solute drag dissipates  $\Delta G_{eff}^t$  by desorbing  $\Delta \xi_{eff}^t = x_b^{eff} - x_b^\alpha$  moles  
 446 of  $b$  from the interface back to the parent phase. The overall  $\beta \rightarrow \alpha$  transformation dissipates  $\Delta G_{eff}^{tot}$  and  
 447 represents the growth of  $\alpha$  at composition  $x_b^\alpha$  from  $\beta$  at composition  $x_b^\beta$ . From the graphical construction  
 448 in Figure 6b, these Gibbs free energy changes are

$$\Delta G_{eff}^m = x_b^{eff} \llbracket \mu_b \rrbracket + (1 - x_b^{eff}) \llbracket \mu_a \rrbracket \quad (45)$$

$$\Delta G_{eff}^t = (x_b^{eff} - x_b^\alpha) (\llbracket \mu_a \rrbracket - \llbracket \mu_b \rrbracket) \quad (46)$$

$$\Delta G_{eff}^{tot} = x_b^\alpha \llbracket \mu_b \rrbracket + (1 - x_b^\alpha) \llbracket \mu_a \rrbracket \quad (47)$$

449 and from Eq. (39), the corresponding driving forces for the two interfacial processes are identical to those  
 450 of the present model in the case of a binary alloy with a planar interface, i.e., those in Eqs. (30) and (31):

$$D_{eff}^m = x_b^{eff} \llbracket \mu_b \rrbracket + (1 - x_b^{eff}) \llbracket \mu_a \rrbracket \quad (48)$$

$$D_{eff}^t = \llbracket \mu_a \rrbracket - \llbracket \mu_b \rrbracket \quad (49)$$

451 These driving forces can also be obtained directly from the energy dissipation approach, as shown in Ap-  
 452 pendix A. Comparing Figures 6a and 6b, it is evident that  $\Delta G_{eff}^m$  is greater than  $\Delta G_{full}^m$  and that  $\Delta G_{eff}^t$   
 453 is less than  $\Delta G_{full}^t$  by the same amount. Eq. (45) can be rewritten as

$$\Delta G_{eff}^m = x_b^\beta \llbracket \mu_b \rrbracket + (1 - x_b^\beta) \llbracket \mu_a \rrbracket + (x_b^\beta - x_b^{eff}) (\llbracket \mu_a \rrbracket - \llbracket \mu_b \rrbracket) \quad (50)$$

454 This difference in energy,  $\Delta G^{\beta \rightarrow eff}$ , is marked in yellow on Figure 6b and given by

$$\Delta G^{\beta \rightarrow eff} = (x_b^\beta - x_b^{eff}) (\llbracket \mu_a \rrbracket - \llbracket \mu_b \rrbracket) \quad (51)$$

455 and is the energy required to adjust the concentration ahead of the interface so the interface can adsorb  
 456 material at  $x_b^{eff}$  instead of  $x_b^\beta$ . From Eq. (50), we can see that adsorbing one mole of material to the  
 457 interface at  $x_b^{eff}$  dissipates an amount of energy equivalent to that dissipated by both adsorbing one mole  
 458 of material at  $x_b^\beta$  and displacing  $\Delta \xi^{\beta \rightarrow eff} = x_b^\beta - x_b^{eff}$  moles in the liquid ahead of the advancing interface.  
 459 This clearly makes the process of interface motion more difficult, but because  $\Delta \xi^{\beta \rightarrow eff}$  must no longer be  
 460 desorbed from the interface, less energy is required by the solute-drag process. Physically, the expressions  
 461 for  $\Delta G_{eff}^t$  and  $\Delta G_{eff}^m$  are obtained by simply transferring the energy  $\Delta G^{\beta \rightarrow eff}$  from  $\Delta G_{full}^t$  to  $\Delta G_{full}^m$ .  
 462 This has no effect on the total energy dissipated by the net transformation, as Eq. (47) is identical to Eq.  
 463 (42), and remains conceptually consistent with Eq. (5), where the net mass transfer is independent of  $x_b^{eff}$ .

464 The first use of the variable solute-drag parameter as defined in Eq. (1) is due to the rapid solidification  
 465 model of Aziz and Boettinger [19], who extended the full-drag case of the CGM to partial drag by multiplying  
 466  $\Delta G^t$  by the solute-drag parameter,  $\lambda$ , which was assumed to lie between  $0 \leq \lambda \leq 1$  (i.e.,  $x_b^\alpha \leq x_b^{eff} \leq x_b^\beta$ ).  
 467 However, they did not incorporate  $\lambda$  in the flux of their CRF; hence, the expression for  $k_v$  in the widely  
 468 used CGM is independent of the solute-drag parameter, as discussed in Sections 3.1 and 3.2. Another  
 469 sharp-interface model incorporating a solute-drag parameter was developed by Li et al. [25] by extending  
 470 Galenko's full-drag model [69] to the case of partial solute drag and concentrated solutions, although their  
 471 analysis is limited to binary alloys without diffusion in the growing phase, while the present model can treat  
 472 multicomponent alloys with diffusion in both phases.

#### 473 4.3. Partial-drag models motivated by solid-state transformations (using $x^{tr}$ )

474 As in the present model, other sharp-interface models allow for bulk diffusion on both sides of the inter-  
 475 face, which is essential for modeling solid-state phase transformations. The approach of Hillert, Rettenmayr,  
 476 and coworkers [13, 14, 71, 72, 73] differs from those previously described in that a composition  $x_b^{tr}$  ( $x^i$  or  
 477  $x^{trans}$  in their notation) is used to represent “the composition of material actually transferred across the  
 478 interface” [13]. We refer to models using this interpretation as *partial-drag models from bulk diffusion*, as this  
 479 composition is not defined with a solute-drag parameter, as in Eq. (1), but by the bulk fluxes of component  
 480  $b$  near the interface in each phase,  $J_b^\phi$ , as [13, 14]:

$$x_b^{tr} = \frac{x_b^\alpha J_b^\beta - x_b^\beta J_b^\alpha}{J_b^\beta - J_b^\alpha} \quad (52)$$

481 One limitation of this approach arises immediately from the definition of  $x_b^{tr}$ ; if diffusion does not occur  
 482 in the growing phase (i.e.,  $J_b^\alpha = 0$ ), Eq. (52) gives  $x_b^{tr} = x_b^\alpha$ . Thus, when solid-state diffusion can be

483 reasonably neglected, as in rapid solidification, this model reduces to the full-drag case described in Section  
 484 4.1. While this may have initially seemed a reasonable assumption, the inability to treat partial solute drag  
 485 during solidification implies that the model cannot be used to describe relatively recent molecular dynamics  
 486 simulations of rapid solidification [8, 9], and thus does not recover the predictions of the partial-drag models  
 487 described above.

488 In general, the interpretation of the interfacial processes differs from that of the present model. In  
 489 partial-drag models from bulk diffusion, the motion of the interface dissipates  $\Delta G_{tr}^m$  by adsorbing  $\Delta \xi_{tr}^m = 1$   
 490 mole of material at composition  $x_b^\beta$  and that solute drag dissipates  $\Delta G_{tr}^t$  by desorbing  $\Delta \xi_{tr}^t = x_b^\beta - x_b^{tr}$   
 491 moles of  $b$  from the interface back to the parent phase. The overall  $\beta \rightarrow \alpha$  transformation dissipates  $\Delta G_{tr}^{tot}$ ,  
 492 but unlike the previous models, does not necessarily represent the growth of  $\alpha$  at composition  $x_b^\alpha$  from  $\beta$  at  
 493 composition  $x_b^\beta$ . From the graphical construction in Figure 6c, these Gibbs free energy changes are

$$\Delta G_{tr}^m = x_b^\beta \llbracket \mu_b \rrbracket + (1 - x_b^\beta) \llbracket \mu_a \rrbracket \quad (53)$$

$$\Delta G_{tr}^t = (x_b^\beta - x_b^{tr}) (\llbracket \mu_a \rrbracket - \llbracket \mu_b \rrbracket) \quad (54)$$

$$\Delta G_{tr}^{tot} = x_b^{tr} \llbracket \mu_b \rrbracket + (1 - x_b^{tr}) \llbracket \mu_a \rrbracket \quad (55)$$

494 and from Eq. (39), the corresponding driving forces for the two interfacial processes are

$$D_{tr}^m = x_b^\beta \llbracket \mu_b \rrbracket + (1 - x_b^\beta) \llbracket \mu_a \rrbracket \quad (56)$$

$$D_{tr}^t = \llbracket \mu_a \rrbracket - \llbracket \mu_b \rrbracket \quad (57)$$

495 Comparing Eqs. (42), (47), and (55), it is evident that  $\Delta G_{tr}^{tot}$  is less than both  $\Delta G_{full}^{tot}$  and  $\Delta G_{eff}^{tot}$  by the  
 496 same amount:

$$\Delta G^{tr \rightarrow \alpha} = (x_b^{tr} - x_b^\alpha) (\llbracket \mu_a \rrbracket - \llbracket \mu_b \rrbracket) \quad (58)$$

497 which is also marked in green on Figure 6c. Although  $x_b^{tr}$  is described as the composition of the material  
 498 transferred across the interface, it is not the interfacial composition of the solid (unless  $x_b^{tr} = x_b^\alpha$ ), as the  
 499 solid tangent in Figure 6c is drawn from  $x_b^\alpha$  regardless of the value of  $x_b^{tr}$ . Evidently, the material at  $x_b^{tr}$  is  
 500 still in the interface, yet the redistribution of  $\Delta \xi^{tr \rightarrow \alpha}$  is not considered to dissipate energy at the interface,  
 501 as it is clear from both Eq. (55) and Figure 6c that the total driving force only considers the transformation  
 502 to the composition  $x_b^{tr}$ . In the present model, the flux between the interfacial control volume and the bulk  
 503 growing phase is incorporated in the dissipation by solute drag via the  $J^\alpha$  term in the CRF.

504 These differences between the partial-drag models and partial-drag models from bulk diffusion are due  
 505 to different interpretations of solute drag. Note that  $\Delta G^{tr \rightarrow \alpha}$  is exactly  $\Delta G_{eff}^t$  (with  $x_b^{eff}$  replacing  $x_b^{tr}$ ),  
 506 and that  $\Delta G^{\beta \rightarrow eff}$  is exactly  $\Delta G_{tr}^t$ . The partial-drag models assume that material can be adsorbed at  
 507  $x_b^{eff} < x_b^\beta$ , and that solute drag adjusts the adsorbed concentration to the interfacial concentration of  
 508 the growing phase. The partial-drag models further assume that the redistribution  $\Delta \xi^{\beta \rightarrow eff}$  ahead of the  
 509 advancing interface is not solute drag, but necessary for the motion of the interface. Contrarily, the partial-  
 510 drag models from bulk diffusion assume that material must be adsorbed at  $x_b^\beta$ , and that solute drag adjusts  
 511 this adsorbed material to the composition that is incorporated into the growing phase at some composition  
 512  $x_b^{tr}$ , which is not necessarily equal to  $x_b^\alpha$ . However, the energy dissipated by the adjusting  $x_b^{tr}$  to  $x_b^\alpha$ ,  $\Delta G^{tr \rightarrow \alpha}$ ,

513 is not considered to be solute drag or contribute to the total energy dissipated at the interface, except in  
 514 the two-step solute-drag process described by Kuang et al. [30]; even then,  $\Delta G^m$  is modified such that the  
 515 total driving force for the phase transformation is still given by Eq. (55).

516 The partial-drag models from bulk diffusion have been extended to describe highly non-equilibrium  
 517 solidification by Wang and coworkers [27, 31, 74, 46, 51], which apply the maximal entropy production  
 518 principle and consider non-equilibrium bulk diffusion in both the solid and the liquid. In the present model,  
 519 we simply require that the response functions ensure that the energy decreases with interfacial motion, i.e.,  
 520 they are consistent with the dissipation inequalities, Eqs. (13) and (14). In contrast, the maximal entropy  
 521 production approach assumes that the process dissipates the free energy at the fastest possible rate. The  
 522 present model is unable to recover the results of these analyses, as they report that partial solute drag is  
 523 inconsistent with the maximal entropy production principle [27]. However, a partial-solute drag model is  
 524 briefly proposed in Ref. [27] as a “simplified treatment for the diffuse interface” with the following driving  
 525 forces:

$$D^m = x_b^{eff} \llbracket \mu_b \rrbracket + (1 - x_b^{eff}) \llbracket \mu_a \rrbracket \quad (59)$$

$$D^t = \gamma (\llbracket \mu_a \rrbracket - \llbracket \mu_b \rrbracket) \quad (60)$$

526 where  $\gamma$  is analogous to  $\lambda$ , ranging from  $0 < \gamma \leq 1$  to weight  $x_b^{eff}$  from  $x_b^{tr}$  to  $x_b^\beta$ . The driving force  $D^m$   
 527 is the same as the present model, i.e., Eq. (48), but the driving force  $D^t$  differs from that of the present  
 528 model, i.e., Eq. (49).

#### 529 4.4. Comparison to diffuse-interface approaches

530 We now show how the various sharp-interface models can be recovered from the classical diffuse-interface  
 531 models. From Hillert’s reformulation [71] of the classical Cahn result [75], the dissipation due to interfacial  
 532 motion can be written as

$$\Delta G_{diff}^m = \int_0^\delta \sum_{i=1}^N x_i \frac{d(\mu_i - \mu_i^\alpha)}{d\eta} d\eta \quad (61)$$

533 where both  $x_i$  and  $\mu_i$  are functions of position within the diffuse interface,  $\eta$ , where  $\eta < 0$  is the bulk  $\alpha$  phase  
 534 and  $\eta > \delta$  is the bulk  $\beta$  phase. From Hillert [71], the classical Hillert and Sundman result [20], representing  
 535 the dissipation due to solute drag, can be generalized to

$$\Delta G_{diff}^t = - \int_0^\delta \sum_{i=1}^N (x_i - x_i^\alpha) \frac{d\mu_i}{d\eta} d\eta \quad (62)$$

536 As in the sharp-interface models from the previous sections, Eqs. (61) and (62) must sum to the total free  
 537 energy change for the  $\beta \rightarrow \alpha$  transformation:

$$\Delta G_{diff}^{tot} = \int_0^\delta \sum_{i=1}^N x_i \frac{d(\mu_i - \mu_i^\alpha)}{d\eta} d\eta - \int_0^\delta \sum_{i=1}^N (x_i - x_i^\alpha) \frac{d\mu_i}{d\eta} d\eta \quad (63)$$

538 Using the Gibbs-Duhem relation,  $\sum_{i=1}^N x_i d\mu_i^\alpha = 0$ , gives

$$\Delta G_{diff}^{tot} = \int_0^\delta \sum_{i=1}^N x_i \frac{d\mu_i}{d\eta} d\eta - \int_0^\delta \sum_{i=1}^N (x_i - x_i^\alpha) \frac{d\mu_i}{d\eta} d\eta \quad (64)$$

$$= \int_0^\delta \sum_{i=1}^N x_i^\alpha \frac{d\mu_i}{d\eta} d\eta \quad (65)$$

539 Because  $x_i^\alpha$  is constant in the sharp interface limit, i.e.,  $\delta \rightarrow 0$ , Eq. (65) becomes

$$\Delta G_{diff}^{tot} = \sum_{i=1}^N x_i^\alpha [\mu_i] \quad (66)$$

540 which is identical to the total Gibbs free energy change of the present model, i.e., the multicomponent  
 541 extension of Eq. (47), and also that of the full-drag model, Eq. (42). The partial-drag models from bulk  
 542 diffusion opt to use  $x_i^{tr}$  instead of  $x_i^\alpha$  in Eq. (62), leading to a different total driving force when diffusion  
 543 can occur in the growing phase.

544 The original formulation of Cahn's result [75] has also been extended for grain growth by Alkayyali and  
 545 Abdeljawad [76], who add an additional term that results from considering asymmetric solute segregation at  
 546 grain boundaries by incorporating a regular solution model. Furthermore, Li et al. [26] extend the Hillert-  
 547 Sundman result [20] to include local non-equilibrium liquid diffusion by following Galenko's treatment [67]. Li  
 548 et al. also incorporate partial solute drag and find it necessary to reproduce the experimental measurements  
 549 of Si-9As by Kittl et al. [77]. While diffuse-interface models are inherently more detailed, sharp-interface  
 550 models avoid the uncertainty of interpolating properties through the interface. The present model provides  
 551 a convenient way to add detail to a sharp-interface model through the solute-drag parameter with only a  
 552 small increase in complexity. Work on solid-state transformations in steels [78, 79] has shown that interface  
 553 kinetics depend heavily on the choice of potential well for solutes at the interface, inviting a comparison to  
 554 the solute-drag parameter,  $\lambda$ , in the present sharp-interface model. This parameter could be derived from a  
 555 diffuse-interface model simply by evaluating Eq. (61) or Eq. (62) and comparing to Eq. (45) or Eq. (46),  
 556 respectively. Because the total free energy change for the transformation is independent of the degree of  
 557 solute drag, the parameters  $\lambda$ ,  $x_i(\eta)$ , and  $\mu_i(\eta)$  must be specified such that  $\Delta G_{diff}^m + \Delta G_{diff}^t = \Delta G_{diff}^{tot} =$   
 558  $\Delta G_{eff}^{tot}$  in order to draw a comparison between a diffuse-interface model and the present sharp-interface  
 559 model.

## 560 5. Conclusion

561 A dissipation relation for the free energy is used to drive thermodynamically consistent interfacial re-  
 562 sponse functions for the interfacial compositions and velocity during phase transformations in concentrated  
 563 multicomponent alloys. The theory accounts for solute drag at the interface and diffusion in both phases, and  
 564 is applicable to both solid/solid and solid/liquid transformations. The potential for cross-coupling between  
 565 the dissipative processes at the interface is presented. Even when cross-coupling is neglected, the driving  
 566 force for the motion of the interface is a function of both the grand potential and the diffusion potentials



567 for each independent component. Both the interfacial velocity and compositions (e.g., the distribution co-  
568 efficient) depend on the degree of solute drag. In the current formulation, the cumulative effect of solute  
569 drag on a multicomponent system is described by a single value of the solute drag parameter, which can be  
570 determined by fitting the interfacial response functions to experimental or simulation data. However, the  
571 solute drag parameter could also be a function of composition, and the limits to this parameter that are  
572 consistent with energy dissipation are given. Additionally, effects such interfacial energy, interfacial energy  
573 anisotropy, elastic stress, and non-equilibrium bulk diffusion can be incorporated via additional terms in the  
574 dissipation relation, which naturally yields interface response functions for these various cases.

575 The interfacial response functions are simplified to the case of the rapid solidification of a binary alloy  
576 with the goal of describing the conditions at solid/liquid interfaces during additive manufacturing. Due to the  
577 dependence of the distribution coefficient on the degree of solute drag, we find that the present partial-drag  
578 model yields more reasonable estimates of trans-interface diffusivities than do full-drag models. Additionally,  
579 the response functions are used to calculate non-equilibrium phase boundaries in Ag-Cu, in which increasing  
580 the amount of solute drag increases the amount of kinetic undercooling for a given concentration. The phase  
581 boundaries calculated with the present model significantly deviate from the predictions of other widely used  
582 models, and the present model is able to capture the retrograde solidus curves at all values of the solute-drag  
583 parameter examined here. These findings indicate that the effects of partial solute drag are important at  
584 solidification velocities relevant to additive manufacturing.

#### 585 **Declaration of competing interest**

586 The authors declare that they have no known competing financial interests or personal relationships that  
587 could have appeared to influence the work reported in this paper.

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# Appendices

## A. The interfacial response functions for a rapidly solidifying binary alloy

### A.1. Velocity response function

Neglecting cross-coupling, the VRF for a multicomponent alloy is given by Eq. (18) in the main text:

$$v = M^m \rho_0^{-1} \left( \llbracket \Omega_v \rrbracket + \rho_0 \sum_{k=2}^N x_k^{eff} \llbracket \tilde{\mu}_k \rrbracket \right) \quad (18)$$

For a binary alloy ( $a = 1, b = 2$ ), this becomes

$$v = M^m \left( \rho_0^{-1} \llbracket \Omega_v \rrbracket + x_b^{eff} \llbracket \mu_b - \mu_a \rrbracket \right) \quad (A.1)$$

Using Eq. (12) to expand the grand potential yields

$$v = M^m \left( \llbracket \rho_0^{-1} f_v - (\mu_b - \mu_a) x_b \rrbracket + x_b^{eff} \llbracket \mu_b - \mu_a \rrbracket \right) \quad (A.2)$$

Expanding the jumps yields

$$v = M^m \left( \rho_0^{-1} f_v^l - (\mu_b^l - \mu_a^l) x_b^l - \rho_0^{-1} f_v^s + (\mu_b^s - \mu_a^s) x_b^s + x_b^{eff} [\mu_b^l - \mu_a^l - \mu_b^s + \mu_a^s] \right) \quad (A.3)$$

For a system at constant temperature and volume, the bulk Helmholtz free energies are given by:

$$\rho_0^{-1} f_v^\phi = \mu_a^\phi x_a^\phi + \mu_b^\phi x_b^\phi \quad (A.4)$$

which gives

$$v = M^m \left( \mu_a^l - \mu_a^s + x_b^{eff} [\mu_b^l - \mu_a^l - \mu_b^s + \mu_a^s] \right) \quad (A.5)$$

$$= M^m \left( x_b^{eff} \llbracket \mu_b \rrbracket + (1 - x_b^{eff}) \llbracket \mu_a \rrbracket \right) \quad (A.6)$$

Using  $M^m$  from Eq. (20) yields the VRF for the rapid solidification of a binary alloy in Eq. (30).

### A.2. Concentration response function

Neglecting cross-coupling, the CRF for a multicomponent alloy is given by Eq. (19) in the main text:

$$J_i^t = -\rho_0 \sum_{j=2}^N M_{ij}^t \llbracket \tilde{\mu}_j \rrbracket \quad (19)$$

For a binary alloy ( $a = 1, b = 2$ ), the solute-drag flux of component  $b$  is given by

$$J_b^t = -\rho_0 M_{bb}^t \llbracket \mu_b - \mu_a \rrbracket \quad (A.7)$$

Expanding the jump yields

$$J_b^t = -\rho_0 M_{bb}^t (\mu_b^l - \mu_a^l - \mu_b^s + \mu_a^s) \quad (A.8)$$

$$= \rho_0 M_{bb}^t (\llbracket \mu_a \rrbracket - \llbracket \mu_b \rrbracket) \quad (A.9)$$

Using Eq. (3) with  $J_b^\alpha = 0$  yields

$$v(x_b^{eff} - x_b^s) = M_{bb}^t (\llbracket \mu_a \rrbracket - \llbracket \mu_b \rrbracket) \quad (A.10)$$

Using  $M_{bb}^t$  from Eq. (25) yields the CRF for the rapid solidification of a binary alloy in Eq. (31).

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