Dissipation-theory treatment of the transition from diffusion-controlled to diffusionless solidification

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The steady-state velocity of a planar liquid-solid interface is predicted by calculating the free energy dissipated by irreversible processes at the interface and equating it to the available driving free energy. A solute drag term and an intrinsic interfacial mobility term are included in the dissipation calculations for a binary alloy. The solute drag calculation employs a solute trapping model, which has been extended to concentrated alloys. The result is presented in terms of a single unknown parameter, the interfacial diffusivity \( D_t \). A transition from diffusion-controlled to diffusionless solidification occurs over approximately an order of magnitude in growth velocity, as the interface speed surpasses the maximum speed with which solute atoms can diffuse across the interface to remain ahead of the growing crystal.

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Experiments on splat quenching \(^1\) of molten metallic alloys and on pulsed laser annealing \(^2\) of doped Si have shown that the chemical potential of the minor component of a binary alloy often increases during rapid solidification. The discovery of this phenomenon, termed "solute trapping," rendered invalid the assumptions of local equilibrium and independence of atomic species. In this letter a simple theory is developed which predicts solute trapping and diffusionless solidification as the interface speed becomes faster than the diffusive speed of solute across the interface.

Conventional modeling of interface kinetics \(^3\) uses the same atomic motions to describe crystallization as those to describe interdiffusion in the liquid. In such a case, the growth speed \( u \) can never exceed the maximum diffusive speed, which is typically on the order of 10 meters per second, given by \( u_0 = D_0/\lambda \), where \( D_0 \) is the coefficient for interdiffusion across (not along) the interface and \( \lambda \) is the interatomic distance. However, the collision-limited growth model developed by Turnbull and coworkers \(^4\) \(-\)\(^1\) recently confirmed by the molecular dynamics work of Broughton et al. \(^11\) indicates that for metallic and other simple molecular systems such a scaling is invalid and that \( u_\lambda \), the speed of sound, should be the only limit to the crystal growth rate. Consequently, the growth speed can very much exceed the diffusive speed, and when it does so in alloys we expect suppressed segregation and a diffusionless transformation.

Atoms in the interface region tend to interdiffuse in order to establish equilibrium compositions on either side of the interface. As the interface passes, solute-solvent redistribution only occurs for a limited time. Before the interface arrives, the driving force for partitioning is zero; afterwards, atomic mobilities are too low to permit significant interdiffusion. When \( u < u_0 \), there is plenty of time for the atoms at the interface to equilibrate. As the growth speed becomes greater, solute and solvent atoms have less time while they are in the interface region to interdiffuse and maintain local equilibrium. When \( u > u_0 \), the atoms have no time to interdiffuse; the interface passes and locks the liquid composition into the bulk of the solid.

Given an interface velocity, solute trapping models predict the segregation coefficient. They require knowledge of the velocity as a function of composition and undercooling. In many cases the local equilibrium assumption of no interfacial undercooling is a useful one, but even for systems with the highest mobilities the assumption can hardly be valid at high speeds and solute concentrations. The problem then is to predict the interface velocity in terms of the local conditions at the interface. Some 20 years ago, Cahn \(^10\) developed a dissipation-theory approach for grain boundary migration. The basic idea is to evaluate the drag forces on the interface due to dissipative processes and, by equating their sum to the driving force, predict a steady-state velocity. Linear force-flux laws are assumed. Coupling between different force-flux pairs is neglected. This approach has met with considerable \(^15\) but not unlimited \(^16\) success for grain boundaries. When applied to the kinetics of motion of other solid phase boundaries, \(^17\) \(^18\) it has met with mixed success.

Hillert and Sundman \(^19\) made the first attempt to apply these ideas to alloy solidification. The present work differs from theirs in several respects. First, the interface is planar. Second, the analysis is limited to the interface alone. Third, the force-flux laws are nonlinear at large driving forces, as experience indicates. Fourth, and most important, are a finite interface mobility and free-energy dissipation due to the crystallization reaction, which make major qualitative changes in the results.

Solute trapping model. A derivation and discussion of the dilute-solution solute trapping model have been published elsewhere. \(^20\) The assumptions used are summarized as follows:

Stepwise growth model. The interface is assumed to be planar and to be executing instantaneous jumps of length \( \lambda \) separated by a time interval \( \tau = \lambda / u \). The jump of the interface is assumed to incorporate one liquid monolayer, including all solute atoms, into the crystal lattice. The assumption is made that there is no excess adsorption or desorption of solute at the interface in equilibrium. Solute atoms diffuse back into the liquid during the interval \( \tau \); diffusive rate equations give the composition in the solid monolayer at the interface as a function of time. Solute atoms remaining in the
solid monolayer at $t = \tau$ are permanently buried in the bulk of the solid, where diffusion is negligible, by the advance of the interface across the next monolayer. A transition from equilibrium segregation to complete solute trapping is found, centered at $u = u_0$.

The stepwise growth model should apply whenever the chemical potential of the solute atom is raised from its liquid value to its solid value during a time interval that is very short compared to $\tau$.

Continuous growth model. If continuous solidification occurs, the impurity atom is being dragged toward its lattice site during a time period of order $\tau$. In the limit of strict steady-state fluxes on a microscopic scale, the fluxes and concentrations become time independent and the same diffusive rate equations used before yield here a transition with the same qualitative features as in stepwise growth.

Concentrated solutions. When the activity coefficients are not constant and the mole fraction of solute is not negligible, corrections to the dilute solution results must be made. This can easily be done for the continuous growth model. Continuous, steady-state growth will be assumed in the rest of this work because the solute drag does not vanish at slow growth speeds (as it should) in stepwise growth.

As in Ref. 20, the diffusive flux of species $B$ out of the crystal is written $J_{B_{\text{out}}} = f \nu \lambda \frac{X_B}{V_m} (1 - X_B) \exp \left( - \frac{Q}{RT} \right)$, where $\lambda$ is the fraction of interfacial sites where a diffusive jump can occur, $\nu$ is the attempt frequency, which is on the order of an atomic vibrational frequency, $X_B$ is the mole fraction of $B$ in the solid, $X_B$ is the mole fraction of $B$ in the liquid at the interface, $V_m$ is the molar volume, $Q$ is the activation barrier for interdiffusion, and $T$ is the temperature of the undercooled interface. The difference with Eq. (1) of Ref. 20 is that for $\lambda = X_B$ has been included to account for the exchange of like atoms contributing nothing to interdiffusion. Similarly, the diffusive flux in the reverse direction is $J_{B_{\text{in}}} = f \nu \lambda \frac{X_B}{V_m} (1 - X_B) \exp \left[ \Delta \left( \frac{\mu_B - \mu_B^\text{m}}{RT} \right) \right]$, where $\Delta$ means solid minus liquid at interface and $\mu_B^\text{m}$ is the chemical potential minus the contribution from the ideal mixing entropy. That is,

$$\mu(B, T) = \mu(B, T) - RT \ln X_B = \mu(B, T) + RT \ln \gamma(B, T).$$

The activity coefficient $\gamma$ is included in $\mu_B$ and therefore does not appear explicitly in the rate equations. Subtracting the fluxes, we get the net diffusive flux:

$$J_D = \left( \frac{f \nu \lambda}{V_m} \right) \exp \left( - \frac{Q}{RT} \right) \times \left[ X_B (1 - X_B) - X_B (1 - X_B) \exp \left( \frac{\Delta \left( \mu_B - \mu_B^\text{m} \right)}{RT} \right) \right].$$

Defining the interface diffusivity $D_I = f \nu \lambda \exp \left( Q / RT \right)$ and the segregation parameter

$$\lambda \Delta \mu_B X_B, T = 1$$

we arrive at

$$J_D = \left( - \frac{D_I}{\lambda V_m} \right) \times \left[ X_B (1 - X_B) - X_B (1 - X_B) \lambda \Delta \mu_B \right].$$

Note that $\lambda \Delta \mu_B$ becomes the equilibrium segregation coefficient $k_e(T)$ for dilute solutions. Invoking the steady state, where we must have

$$J_D = \left( X_B - X_B \right) \frac{d u}{d t},$$

we have

$$(X_B - X_B \frac{d u}{d t}) = X_B (1 - X_B) - X_B (1 - X_B) \lambda \Delta \mu_B.$$

Solving for the segregation coefficient $k_e = X_B / X_B$, the result is

$$k_e = \frac{(X_B - X_B) \frac{d u}{d t}}{(X_B - X_B) \frac{d u}{d t} + \lambda \Delta \mu_B}.$$

which reduces to the previous result [Eq. (6) of Ref. 20] for a dilute solution of $B$ in $A$. Note that in practice, $D_I$ may be temperature and composition dependent.

Growth velocity. Assuming that transport of heat and solute through the bulk of the two phases proceeds in the conventional manner, a complete theory for planar crystal growth in a binary alloy requires the simultaneous solution of two "interface response functions". Equations like (3) for solute trapping must be accompanied by an expression relating the growth velocity to the local conditions at the interface (temperature, pressure, composition, etc.).

For pure systems, the process is easily understood. In equilibrium, the rates at which atoms join and leave the crystal are equal. When there is a finite driving force for crystallization, the former exceeds the latter by a Boltzmann factor $\exp(\Delta\mu / RT)$; the growth velocity is given by their difference. The kinetics are manifested by an intrinsic growth-velocity limit, which is the speed of the forward reaction alone, $u_0(T)$. This is the speed with which the interface would propagate at infinite driving force (i.e., when the back reaction disappears). The growth velocity is then written as $u = u_0(T) + [1 - \exp(\Delta\mu / RT)]$. This expression becomes the familiar $u = MA \tilde{G}$ at small driving forces. Inverting the above expression, we have $\Delta\mu = RT \ln(1 - u / u_0)$. The left-hand side is the driving free energy; the right-hand side can be thought of as the free energy dissipated by the irreversible crystallization reaction at the interface. Thus the velocity-driving force relation can be written $\Delta G_D = \Delta G_p$, where $\Delta G_D$ is the driving energy, expressed as free energy per mole, and $\Delta G_p$, the "interface friction energy" due to a finite interfacial mobility, is the free energy dissipated per mole of material solidified. The available driving force is dissipated by the irreversible processes at the interface.

For alloys, we can write $\Delta G_D = \Sigma \Delta G_{\text{Diss}}$, where the $\Delta G_{\text{Diss}}$ are the losses due to all of the simultaneous dissipative processes. In the steady state, the system does no work on the surroundings and so the driving free energy must be entirely dissipated by irreversible processes during the transformation. If we can calculate the dissipation and the driving force as functions of velocity, we have an equation that predicts the growth velocity. Ignoring heat conduction, the two dissipative processes at the interface are the crystallization and redistribution reactions. The dissipative terms associated with them are, respectively, the "interface friction energy" $\Delta G_p$ and the "solute drag energy" $\Delta G_\nu$. By assuming interface friction to be the same for all alloys as for pure systems, we can calculate these terms and predict the growth velocity. As in pure systems, we will have

$$\Delta G_p = RT \ln(1 - u / u_0)$$

for the interface friction energy. The solute drag energy can be evaluated as follows.

In the formalism of irreversible thermodynamics, the
rate of entropy production, or of free energy dissipation, per unit volume is given by the product of the irreversible flux and its conjugate driving force.\textsuperscript{2,3} For the solute-solvent redistribution reaction at the solid-liquid interface, \( J_D \) is the interdiffusive flux, \( \Delta (\mu_B - \mu_A) \) is the conjugate driving force, and thus the rate of free energy dissipation at the interface, per unit area, is \( J_D \Delta (\mu_B - \mu_A) \). The continuous growth model is steady state and therefore the fluxes and driving forces are time independent; the solute drag energy is then 
\[ \Delta G_D = \left( V_m / u \right) J_D \Delta (\mu_B - \mu_A), \]
per mole of material solidified. Using the steady-state requirement that \( J_D = (X_B - X_0) \mu / V_m \), we have 
\[ \Delta G_D = (X_B - X_0) \times \Delta (\mu_B - \mu_A). \]
Using Eqs. (1) and (2), this can be written as
\[ \Delta G_D = X_0 \left[ \left( 1 - k_B / k_B \right) / \left( 1 - X_0 \right) \right] RT \ln \left( k_B / k_B \right), \]
where \( k_B = (1 - X_b) / (1 - X_c) \). The solute drag energy becomes
\[ \Delta G_D = X_0 \left[ \left( 1 - k_B / k_B \right) / \left( 1 - X_0 \right) \right] R T \ln \left( k_B / k_B \right) \]
for a dilute solution. The growth velocity equation is thus
\[ \Delta G_D \mu = \Delta G_D \mu + \Delta G_D \mu, \]
where the driving free energy \textsuperscript{1,19,20} is
\[ \Delta G_D \mu = X_0 \Delta \mu_B + (1 - X_0) \Delta \mu_A, \] and the dissipative terms are given by Eqs. (4) and (5). Note that Eq. (6) is applied across the interface only; no dissipation or driving force in the bulk enters into consideration.

The dissipation at the interface due to heat conduction can safely be ignored. The product of the heat flux and its conjugate driving force is always at least an order of magnitude smaller than \( \Delta G \), and the solidification problem has therefore been treated as an isothermal one.

The complete theory for binary alloy plane-front solidification is contained in Eqs. (3)-(6). The application of the theory to the systems Ag(Cu) and Si(Bi), using the thermodynamic modeling of Murray,\textsuperscript{24} and a numerical solution of the equations, will be presented in a later publication.\textsuperscript{25} The most striking result is that the inclusion of interface friction eliminates the singularities predicted by Hillert and Sundman,\textsuperscript{19} resulting in a more gradual transition from diffusion controlled to diffusionless solidification. It also predicts a concentration-dependent \( k_B \) in some regimes. An important result is that the heat-flow calculations of the interface speed for laser anneling of doped Si, invariably made by assuming no interfacial undercooling,\textsuperscript{26}-\textsuperscript{28} may be seriously in error in certain ranges of velocity and composition. In order to make a reliable comparison between theory and experiment for alloy solidification, direct velocity measurements\textsuperscript{25} may be necessary during segregation experiments.

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