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Analysis of nonequilibrium hcp precipitate growth in fcc matrices: Application to Al–Ag

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1. Introduction

As but one example of many, high-aspect ratio γ-precipitates form rapidly in Al-rich, face-centered cubic (fcc) Al–Ag alloys [1], within seconds for Ag concentrations near maximum solubility. This has relevance both to age-hardening experiments [2] and to the current understanding of solid–solid phase transformations [3]. The Al–Ag system has served as a prototype solid–solution starting with the first observations of GP zones [4] and, more recently, precipitation in real time [1]. To a first approximation, the rapid growth of plate-like precipitates in a solid–solution is an example of the equilibrium–type Wulff construction [5], whereby, given the interface energies associated with the facets of a precipitate, one can determine the equilibrium shape by minimizing the precipitate’s surface free energy. However, when other details of precipitation are considered, such as solute-concentration, nucleation kinetics or crystallography, the models must be altered dramatically, as for Jones–Trivedi (JT) ledge mechanisms [6,7]. Numerical modeling is also often necessary to address all of the effects that determine shapes and growth rates for precipitates [8–10]. The models and mechanisms that affect precipitate growth have led to some controversy [11,12], and they pose many difficulties for comparing experimental data and theory.

Recently, via density-functional theory (DFT) for Al-rich Al–Ag alloys, we explained the thermodynamic driving force for high-aspect ratios of γ-plate precipitates observed in annealed solid-solutions [13]. It arises from a Suzuki effect [14,15] of asymmetric formation energy versus concentration, common in Al-based solid-solutions. Our interface energies calculated for equilibrium growth predict a higher aspect ratio than any previous estimates, however, we still fall an order of magnitude short from observed values [1]. To address this, we contrast here the nucleation and growth of both equilibrium (static shape) and nonequilibrium (time-varying shape) γ-precipitates.

As there is no model for nonequilibrium growth of γ-precipitates in fcc alloys relating the interphase energies and calculated bulk driving force, we derive a model within standard approximations [5], that accurately describes an increasing aspect-ratio versus time while still being consistent with the accepted mechanisms and observations on precipitate growth of γ-plates, in particular, for those in the Al–Ag prototype. In addition, we include the energetics of “offshoot” trapezoidal dendrites that describe a key observation during γ-precipitation, namely, the highly irregular, nonequilibrium plate shapes [16], as shown in Fig. 1. Wulff construction, as
an equilibrium-based theory, cannot account for these effects; and yet, we show that they are predictable from the energetics, and they can be included analytically within the nucleation and growth equations by comparing some possible growth patterns. Thus, we are able to include both ledge and secondary nuclei growth, and we emphasize the importance of energetics in our growth model.

Our paper is organized as follows. In Section 2 we describe the equilibrium shape and aspect ratio of γ-plate precipitates and discuss how nonequilibrium nucleation events could increase the aspect ratio. In Section 3, we reanalyze the nucleation energetics of a 1-d growth model for infinite plates and include the effect of inhibited transformation of fcc [1 1 1] to hcp [0 0 0 1]; the result differs from standard textbook treatments by including a kinetic model for the nucleation rate. The result does not include finite-size effects, as in a Ham, Horvay and Cahn type approach [17–19], but it could be easily modified to do so. We then derive, using a modified JT thickening model [6–9], a parabolic ledge-thickening rate and an incoherent ledge-growth rate consistent with allowed hexagonal-close-packed (hcp) crystallographic growth patterns. Our modified JT model yields the 1-d result when no energy barriers exist to ledge nucleation and otherwise includes the competing mechanisms of diffusion-limited growth of secondary nuclei and ledges to account for the difference in growth rates of coherent versus incoherent interfaces. We find that the slow growth of coherent interfaces compared to incoherent interfaces can give rise to a rapid increase in aspect ratio. While an edge-like structure can only grow linearly with time t, we find that an inhibited interface can grow between t and t1/2, depending on the t-dependence of ledge-spacing. We also report the nucleation rates and limits on energy barriers, required for these mechanisms. This nonequilibrium model is general to hcp precipitates in fcc solid-solution matrix, and it addresses the differing growth of precipitate facets based on kinetics. It gives a t-dependent approximation for the plate aspect ratio, depending on the ledge nucleation rate, and we find general agreement with observation [1]. We conclude in Section 4.

2. Equilibrium precipitate geometry

Using free energy arguments, we begin by motivating the mechanisms and derived quantities relevant to solid–solid transformations. For precipitates, the free energy per unit volume $\Delta G_V$ gives the bulk driving force to create a volume $V$ of precipitate. Also important are the $\gamma_{111}$ face and $\gamma_{211}$ rim interface energies. Given these and the geometry in Fig. 2, the surface free energy $s$ is

$$s = \sqrt{3}L^2\gamma_{111} + 2\sqrt{3}LW\gamma_{211}.$$  

(1)

with $L$ and $W$ the plate length and thickness, respectively. The equilibrium aspect ratio $A_{eq}$ is found by minimizing Eq. (1) at fixed volume (i.e., $L^2W/\sqrt{3}$),

$$A_{eq} \equiv \left( \frac{L}{W} \right)_{\text{min}} = \frac{\gamma_{211}}{\gamma_{111}}.$$  

(2)

$A_{eq}$ is independent of $\Delta G_V$ or plate composition, as expected, and it is constant in time. As is well-known, this is not the actual shape of precipitates in experiment, and we will contrast this case with nonequilibrium shapes, as in Fig. 1, where proportion, shape and time-dependence vary dramatically from the static, equilibrium picture.

3. Nonequilibrium precipitate geometry

A shortcoming of the static, equilibrium picture is that it fails to account for secondary nucleation events that can alter the plate aspect ratio. One example is the JT ledge-growth mechanism for plate thickening [6,7]. This model treats ledges or steps that nucleate on the face and allow mechanically inhibited interfaces to grow. However, there are dramatic examples of nonequilibrium lateral growth, as seen in experiment [16,20] and Fig. 1. Motivated by the importance of including secondary nucleation kinetics in our model, we will compare the effect of secondary nuclei (laterally and on the plate face) and derive their affect on the aspect ratio. The thickening kinetics will be derived from a standard JT treatment, however, we will include the nucleation rate of new ledges that gives a time-dependent ledge-spacing. These results are then used in the following to calculate nonequilibrium lateral growth rates, from which we obtain time-dependent aspect ratios.

3.1. Nonequilibrium dendritic offshoots

First, we calculate energetic properties of “offshoot” trapezoidal dendrites on a seed hexagon, as shown in Figs. 2 and 3. The word “dendrite” is used here to indicate a sequential nucleation pattern. The plate edge is assumed to grow by addition of successive trapezoidal offshoots, i.e., via geometry shown in Fig. 2, with length $\delta h$.
base \(L/\sqrt{3}\), thickness \(W\), and change \(\delta h\) in free energy,
\[
\delta G = \left(\frac{2}{\sqrt{3}}\gamma_{111}L + \frac{2}{\sqrt{3}}\gamma_{211}W - \frac{\Delta G}{\sqrt{3}} LW\right)\delta h
+ \frac{1}{\sqrt{3}}\Delta G LV - \frac{2}{\sqrt{3}}\gamma_{111}\delta h^2.
\]  
By rescaling Eq. (3) (tilde indicates scaling to critical values), we find:
\[
W^* = 4\gamma_{111}/\Delta G_V,
L^* = 4\gamma_{211}/\Delta G_V = \delta h^*,
\Delta G^* = 16\gamma_{211}^{3/2}\gamma_{111}^{1/2}/\Delta G_V.
\]
\[
\delta G = \frac{2}{3}[L + W - 2\tilde{W}\delta h + (2\tilde{W} - 1)\delta h^2].
\]
To establish whether trapezoid growth is favored, we analyze the energy surface of Eq. (5). The first term inside the brackets (linear in \(\delta h\)) is symmetric in \(L\) and \(W\) and exhibits a classic “saddle” shape. The minimal free energy on the saddle follows \(\tilde{h}\) for lath growth. Our model, while similar, predicts the coefficients of \(i\), applies more generally and gives a \(t^{1/2}\) 1-d interface growth rate in the limit \(\tilde{h} \to 0\).

The 1-d analytic solution is for an infinite plate and ignores finite-size effects but compares favorably to the more sophisticated 3-d diffusion-limited growth model of Ham, Horvay and Cahn [17–19] that must be solved numerically (see Appendix A). Notably, this approach, which includes finite-size effects in the linear growth, would not give any finite-size effects for the time-dependent aspect ratio because the effects are the same in width and length and would cancel in the ratio. Importantly also, the experimental evidence [1] supports that a \(t^{1/2}\) plate thickening can occur even if the underlying mechanism for growth is not simply diffusion-limited.

The next step is to relate ledge-spacing and nucleation rate to thickness. This is essentially the JT model, but here we derive the ledge-spacing analytically. The result (Appendix B) is a half-plate thickness that increases as
\[
x(t) = \sqrt{\frac{h^2 + f(T)\Omega^2D(t - t^*)}{kh}} - h/2,
\]
and the lengthening of the ledge is well described by linear growth,
\[
y(t) = A_{eq} + \frac{\Omega D(t - t^*)}{kh},
\]
where, at time \(t^*\), the half-plate thickness is \(h/2\) and the half-plate-length is \(A_{eq}h/2\), which is a critical nucleus. The geometric factor \(k(\Omega)\) is of order 10, (Appendix B). These equations yield a \(t^{1/2}\), 1-d result in some limits (e.g., no barrier to ledge nucleation) and linear \(t\) growth in others (e.g., initial). The mechanism is controlled by only a few ledges at early times, and becomes like an incoherent interface later, when there are many ledges. The thermal rate \(f(T) < 1\) is kept as a reminder that there are energy barriers to nucleation.

### 3.3. Geometric sequence for lateral growth

The nucleation patterns shown in Fig. 4 provide a picture of how a precipitate might assemble in an energetically favorable way. For each of these three cases, we can show the range of impact on relative interface growth rates, which will give the aspect ratio. Fig. 4(a) is simple 1-d growth. Fig. 4(b) is a Perrin sequence, and Fig. 4(c) produces triangular precipitates. Fig. 4(b) is the most complex, as it can...
give oblong, distorted hexagons, as seen in experiment [16,20] and in Fig. 1, but Fig. 4(c) is also interesting as it is the most symmetric shape, consistent with close-packed crystal structure. Importantly, the initial seed shape does not affect the final shape after a few steps.

First we compare the triangle heights in Fig. 4(b), which, in units of the original hexagon length are: 1/2, 1, 3/2, 2, ..., \( L(N−2) + L(N−3) \). The last term in the series is a recursion formula of the Perrin sequence. This recursion holds after five iterations and, within 30 iterations, the ratio of subsequent triangle sizes converges to the “plastic number” \( p = 1.324718 \), which is a root of \( p^3 = p + 1 \). The observed aspect ratio would only be affected every third iteration, because there is a step-rotation of 30°.

Integrating up the lateral growth, we get \( L_N = L_0 \sum_{i=3}^{N+1} p^i \), which increases every third step. The time to grow all of the triangles, from Eq. (A.1), is \( t_N = L_0(\lambda/\Omega D)^N p^N \). Note that \( (\Omega D/\lambda)t_{N+2} = (1 + p + p^2)Np = p^2(1 + p)Np \) (from definition of the plastic number), and since \( t_{N+2} \propto p^2 t_N \) for large \( N \), the (direction-averaged) lateral growth equation is

\[
L(t) \approx \Omega Dt \frac{(1 + p)kh}{(1 + p)k},
\]

which is a factor of “1 + \( p \)”-times slower than Eq. (11).

### 3.4. Time-dependent aspect ratio

Our shape considerations above showed that various lateral growth patterns could easily be described within a single equation, namely, Eq. (11) with the growth rate divided by a factor of \( g \) for any specific growth pattern. The narrow range of \( g \) values that we found (0.5–2.325) allow us to make some general determinations about the lateral growth rate, compared to the thickening rate. By dividing the lateral dimension of a given pattern by the ledge-based thickening formula Eq. (10), we obtain, as shown in Appendix B, a general expression for the time-dependent aspect ratio,

\[
A(t) = \left( \frac{1 + \tilde{t}}{2 \sqrt{1 + \frac{\tilde{t}}{\xi} - 1} \right) A_{eq}.
\]

We work in dimensionless time \( \tilde{t} = t/t^* \), with \( t^* \) defined in Appendix B, and our expression depends implicitly on experimentally determined parameters, \( D, \Omega h, and \) also on the derived geometric quantities, \( A_{eq}, g \) and \( k/\Omega \). The parameter \( \xi \) simplifies our expressions, as a dimensionless measure of the nucleation rate, and it is proportional to the thermal rate \( t/f \).

For the actual form of \( \xi \), we assume that the energy barrier \( \Delta G^b(T) \) for ledge nucleation is the primary inhibitor of plate thickening, from which we derive the \( T \)-dependence of \( \xi \) in Eq. (B.7). The exponential in \( \xi \) is maximized at a temperature of \( T_{opt} = T_e/T_m/(2T_m - T_e) \), with \( T_e \) and \( T_m \), the equilibrium solvus and melting temperatures, respectively. Near \( T_{opt} \), and for \( \Omega \ll 1 \),

\[
\xi \sim \frac{\xi_{eq} \sqrt{3\Omega}}{2} e^{-4\Delta G^b/[0(T_m - T_e)/(\bar{g}_k k T_e T_m)]}.
\]

For conservative estimates, we allow that \( 0 < \xi < 1 \), which gives an aspect ratio development in time \( \tilde{t} \) as shown in Fig. 5. The function gives a plateau of aspect ratio after an initial steep growth rate, as expected.

To further explore the development of aspect ratio, we can also make a connection to our model for inhibited ledge nucleation (Appendix A). We provide an argument that the rate of ledge nucleation is parabolic in nucleation number, i.e., that the time \( t_e \) of the \( i \)-th nucleation event goes as \( t_e = \frac{i}{\lambda} \). This type of nucleation rate has been applied by Spanos et al., in their numerical models of lath growth [9,10], where the thermal rate \( f \) was, effectively, fit to experiment. Our connection of time to the number of nucleations allows us to avoid knowing \( f \) or \( \xi \), directly, by re-expressing \( t_e \) as \( i^2/\xi \), giving

\[
A = \frac{\tilde{t}^2 - 1 + \xi}{2(2i - 1)\xi} A_{eq},
\]

which, by definition of \( t_e \) and \( k \), varies in time as

\[
\tilde{A} = \frac{\Omega D}{n^2 g} \left[ \sqrt{\frac{3}{2} + \left( \frac{3}{2} \right)^2 - \frac{1}{2}} \right]^{-1} \left( \tilde{t}^2 - i + 1 - \frac{\xi}{(2i - 1)^2} \right).
\]

This function is effectively independent of \( \xi (\ll 1) \), and the other factors in front separate into experimentally determined terms.

We find that the time rate of change of aspect ratio, as shown in Fig. 6, varies most rapidly in the early stages of growth, when only a few nuclei have formed. Also the supersaturation \( \Omega \) drives the rapid lateral growth, with large \( \Omega \) favoring higher aspect ratios. For an estimate of timescales, \( D \) for metals is \( 10^{-15} - 10^{-14} \text{m}^2/\text{s} \). The ledge height \( h \) can be taken as a (111) lattice-spacing, typically \( \sim 5 \text{Å} \), corresponding to stacking-fault-like ribbons becoming ledges, and, since \( g \) is of order unity, \( D/\Omega h^2 g \sim 10^5 \text{ s}^{-1} \). From Eq. (16), we can estimate that the initial aspect ratio will double within a time \( \sim 10 \text{Å} \), corresponding to stacking-fault-like ribbons becoming ledges, and, since \( g \) is of order unity, \( D/\Omega h^2 g \sim 10^5 \text{ s}^{-1} \). From Eq. (16), we can estimate that the initial aspect ratio will double within a time \( \sim 10 \text{Å} \), corresponding to stacking-fault-like ribbons becoming ledges, and, since \( g \) is of order unity, \( D/\Omega h^2 g \sim 10^5 \text{ s}^{-1} \). From Eq. (16), we can estimate that the initial aspect ratio will double within a time \( \sim 10 \text{Å} \), corresponding to stacking-fault-like ribbons becoming ledges, and, since \( g \) is of order unity, \( D/\Omega h^2 g \sim 10^5 \text{ s}^{-1} \). From Eq. (16), we can estimate that the initial aspect ratio will double within a time \( \sim 10 \text{Å} \), corresponding to stacking-fault-like ribbons becoming ledges, and, since \( g \) is of order unity, \( D/\Omega h^2 g \sim 10^5 \text{ s}^{-1} \). From Eq. (16), we can estimate that the initial aspect ratio will double within a time \( \sim 10 \text{Å} \), corresponding to stacking-fault-like ribbons becoming ledges, and, since \( g \) is of order unity, \( D/\Omega h^2 g \sim 10^5 \text{ s}^{-1} \). From Eq. (16), we can estimate that the initial aspect ratio will double within a time \( \sim 10 \text{Å} \), corresponding to stacking-fault-like ribbons becoming ledges, and, since \( g \) is of order unity, \( D/\Omega h^2 g \sim 10^5 \text{ s}^{-1} \).
ters, along with the supersaturation values, must be estimated from experiment or from first-principles-calculated values. This can be difficult, but in the long-time limit, many of these parameters have a diminished impact. To show this, we re-write our aspect-ratio model in its explicit form,

$$A_{eq}(t) \approx \frac{A_{eq} + (\Omega/ghk^2)DT}{2\sqrt{1 + (\Omega^2/\text{D}^2)T} - 1} \quad \text{for} \quad t < A_{eq},$$

$$A_{eq}(t) = \frac{1}{2gkh} \sqrt{\frac{D}{f}} \quad \text{for} \quad t \rightarrow \infty$$.

$A_{eq}(t)$ is a function of time $t$, dimensionless supersaturation $\Omega$ (often $\Omega \ll 1$), diffusion constant $D$, critical ledge height $h$, and thermal rate $f \leq 1$ that accounts for the inhibition of structural transformation. The factor $\Omega$ is of order ten. The dependence on interface energies, as in Eq. (2), is irrelevant here because, as we found for seed shape, it becomes rapidly negligible.

Using the recent TEM microscopy results by Moore and Howe [1], we can compare this result directly to in situ observations of high-aspect ratio, or length-to-width, of precipitate plates, as a function of time. Solute is depleted by $\sim 0.01$ adjacent to the precipitate in the experiment, and a plate composition of 50% bulk composition from 4% Ag solid-solution gives $\Omega \sim 0.02$. We estimate the critical nucleation timescale $t^* \sim 0.1$ s, using $D \sim 5 \times 10^{-15}$ m$^2$/s at 579 K [17], and $gk \sim 10$. This last estimate, on the orders of $g$ and $k$, takes a geometrical mean of the three lateral-growth sequences examined in Section 3.3, and in Fig. 4, and $k \sim 10$ for cylindrical solute-depletion at the edge. The initial thickness $h$ must be very small to have a low nucleation energy barrier, which suggests a physically minimal nucleus thickness, e.g., the close-packed (111) planar spacing in Al–Ag, $a_{111}/\sqrt{3} = 2.30$ Å, or the hcp c-axis repeat unit, $2a_{111}/\sqrt{3} = 4.60$ Å. The smaller value corresponds to stacking fault offshoots, while the larger accounts, e.g., for a complete unit of hcp AlAg. A comparison of the aspect ratios in differing approximations is plotted in Fig. 7. The equilibrium estimates of interface energies from DFT [21] will be detailed elsewhere; here we are interested only in the long-time limit of growth, where, as is apparent from Eq. (17), $A_{eq}$ does not matter. No equilibrium estimates, neither ours nor any other previous interface-energy estimates, come within an order of magnitude of the experimental values, and so the nonequilibrium kinetics model is apparently more important than the energetics for modeling Al–Ag precipitates. Compared with experimental data [1], this model is a better fit to experiment and gives a correct time-dependence for aspect ratio and, as a consequence, gives some support to a time-varying picture of shape and aspect ratio. Notably, we assume no significant energy barrier to ledge nucleation ($f = 1$), because a small thermal rate $f \leq 1$ would indicate an inhibited thickening and would make the aspect ratio grow much faster than observed. Thus our model suggests a low energy barrier to structural transformations and ledge nucleation on coherent interfaces, which, compared with DFT results [21], is consistent with a low $\gamma_{111}$ interface energy.

4. Conclusions

(1) Based on theoretical modeling of secondary nucleation on plate-like precipitates, we derived a generic, nonequilibrium description of hcp-precipitation from an fcc alloy solid-solution matrix phase. Our model is based on ledge motion with an estimated ledge nucleation rate.

(2) The model gives the observed time-dependence of the aspect ratio of hcp precipitates in fcc matrix but also produces the irregular-shaped, nonequilibrium $\gamma$-precipitate structures observed in experiment.

(3) Free energy arguments find that it is favorable to nucleate trapezoidal offshoots on the edges of hexagonal plate precipitates, more so for longer trapezoidal base lengths, which is consistent with the hexagonal crystal structure and observation.

(4) For plate thickening, the time-dependent ledge-spacing minimally needs knowledge of the nucleation kinetics of new ledges. The solute-depletion in the vicinity of a broad plate facet, along with a parabolic nucleation rate, can in general give $t$ or $t^{1/2}$ thickening, in the various limits, accounting for the low growth of coherent interfaces compared to incoherent interfaces. This is consistent with the parabolic nucleation rate proposed by Spanos et al. [9,10].

(5) While both nucleation theory and diffusion-limited growth both of secondary nuclei and ledges are included, the long-time behavior is like 1-d growth in the limit that ledges become widely spaced.

(6) The plate aspect ratio exhibits a rapid, initial increase from the equilibrium followed by a slow approach to steady-state. The time required to double the aspect ratio of an initial nucleus was found to be less than one second, given reasonable estimates of parameters for metals at annealing temperatures, which is consistent with recent in situ observations [1].

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Appendix A. Zener growth and nucleation rates in 1-d

We begin with a 1-d diffusion model to describe the growth of an infinite plate precipitate [5], as originally proposed by Zener to describe spherical precipitates [22]. We assume a linearized concentration profile as in Porter et al., Section 5.3.1 [5]. The concentration profile $X(x)$ can be related to the interface growth parameter $x$, for an infinite precipitate, using Fick’s Law and con-

![Fig. 7. Calculated aspect ratio, compared to experiment for Al–Ag (squares) [1]. Dashed lines are for $A_{eq}$ from Eq. (2) with estimated interface energies from DFT [21]. Solid lines are from Eq. (17) with $f = 1, g = 1, k = 10$.](image-url)
servation of solute. Within the linearized-gradient approximation (LGA) [23,24], the interface growth rate \( \dot{x} \) depends on the (linearized) depletion zone thickness \( \lambda \), as well as the dimensionless supersaturation \( \Omega \), as

\[
\dot{x}(t) = \frac{\Omega D}{\lambda} x(t) \tag{A.1}
\]

For dilute solid-solutions, within the LGA, conservation of solute gives \( \lambda x(t) \approx 2x(t)/\lambda \), which allows us to solve Eq. (A.1) for the 1-d growth rate,

\[
\dot{x}(t) \approx \Omega \sqrt{D/4\pi} \tag{A.2}
\]

Eq. (A.2) is for the half-thickness of the plate, without any consideration of interface-mobility restrictions and/or finite-size effects. It follows that \( \Delta t = \Delta(x^*/\Omega^2 D) \), and the time interval \( t \), between subsequent solute-accumulations up to a height \( h \), is

\[
\tau(t) = \frac{h^2}{2\Omega D} \left( 1 + 2x(t)/h \right). \tag{A.3}
\]

Solute accumulates up to a height \( h \) in a time \( \tau \), but it does not necessarily transform into a precipitate, mainly due to issues of interface-mobility. Athermal rate \( f(T) \) shall be introduced then to rescale the ledge nucleation rate \( \tau^{-1} \). If we integrate from zero to \( t_i \), we obtain the number of ledge nucleations \( i \). However, we must provide an estimate for the interface position \( x(t) \). In the next Appendix, we shall prove that \( x(t) = \sqrt{h^2 + f(T)Dt} - h/2 \), which gives \( t_i = (i^2-1)h^2/(\Omega^2 D) \), Eq. (8) in the text, and provides a physical basis for empirical forms used to fit experimental data.

Improvements to the 1-d growth model can be made, in particular to address finite-size effects. The approach of Ham, Horvay and Cahn [17–19] was to take ellipsoidal plate half-thickness and half-length as \( x(t) \) and \( y(t) = A_{eq} x(t) \). Both parameters grow as ideal 1-d interfaces, however, finite-size effects effectively increase the diffusive constant as \( D \rightarrow (2\sqrt{\Omega}/\Omega^2 D) \), where \( \beta \) satisfies

\[
\Omega = e^\beta[\beta^{1/2}A_{eq} \int_{ \beta }^{\infty} 1/[(A_{eq} - 1)^2/4])e^{-\beta/\sqrt{\pi}]d\beta}. \tag{A.4}
\]

This growth model succeeds in giving plate thickening rates that compare well with experiment [1], but since the rescaling is often nearly unity, as shown for a few plates in Table A.1, we choose not to consider finite-size effects here.

### Appendix B. Jones–Trivedi model for aspect ratio

For a sharp-edged dendrite, with a spherical tip [23,24], the solute-depletion zone length in Eq. (A.1) can be shown to be

\[
\lambda = k(\Omega)r, \tag{B.1}
\]

where \( r \) is the radius of curvature of the solute-depleted field, and \( k(\Omega) \) is a geometrical factor of order unity. For a sphere, \( k(\Omega) \) has been approximated [23] as \( (2\Omega^{-1} - 1)^{1/3} \). The exact solution [24] is given by the real root of \( k^3 + 4k^2 + 6k + 4 = 0 \), which is as much as 25% larger than in Ref. [23]. In spherical geometry \( k(\Omega) \) gives the maximal radial influx of solute, overestimating the growth rate. Moreover, it lacks a simple form. For hcp, then, we consider cylindrical symmetry in Fig. 3, giving

\[
k(\Omega) = \sqrt{\frac{3\Omega}{\Pi} + \frac{3\Omega^2}{2} - \frac{3\Omega^2}{2}}. \tag{B.2}
\]

Often factors of \( r \) can be replaced by the height (or thickness) \( h \) of edges, or ledges in JT models [6,7], in which case the lengthening rate \( y \) is a constant,

\[
y = \frac{\Omega D}{k(\Omega)h}. \tag{B.3}
\]

This expression is simple, and it relates even to coherent interfaces that are inhibited, structurally, from direct growth; rather, JT interfaces advance via ledge motion. Since ledges lengthen at a rate of Eq. (B.3), we can apply our knowledge of the ledge nucleation rate to obtain a time-dependent ledge-spacing, \( \lambda(t) \). From Fig. 4(a), we derive the JT thickening rate,

\[
\dot{x}(t) = \frac{\Omega D}{k(\Omega)\lambda(t)}. \tag{B.4}
\]

Clearly, different \( \lambda(t) \) will give different thickening rates. To estimate the actual ledge-spacing, we need to know the rate of ledge nucleation. If the maximal nucleation rate on a site is limited, as in Eq. (A.3), by diffusion, then the true nucleation rate will be reduced by a thermal rate of \( f(T) \). We assume that the nucleation rate and the velocity of ledges will give a rough estimate of the ledge-spacing. This assumption will be valid at early times when only a few ledges have nucleated, as well as at later times when distantly-spaced nuclei do not interact or overlap. Chen et al. used this approximation, \( \dot{A}(t) = y(t)/f(T) \), in their models of lath morphology in Ni–Cr [10]. We will use a similar approximation, \( \dot{A}(t) = y(t)/f(T) \), which gives a ledge-spacing of \( 2x(t) + h \). Using the derived ledge-spacing, we solve Eq. (B.4) as

\[
x(t) = \sqrt{\left[h^2 + f(T)D^2(t + \tau^*) \right] - h/2}. \tag{B.5}
\]

which supposes that, at time \( \tau^* \), the half-plate thickness is \( h/2 \). This form reproduces the 1-d result in some limits and linear growth in others, and it gives directly the \( x(t) \) profile used to obtain \( t_i \) in Appendix A.

So far we have not addressed the form of \( f(T) \), the thermal rate introduced by Ferrante and Doherty [25]. It rescales the ledge nucleation rate and takes into account the energetic barriers involved. Here we assume \( f(T) \) takes a form \( \exp[-\Delta G_n(T)/k_BT] \) [26], with a barrier

\[
\Delta G_n(T) = 2\sqrt{3h^2}y_{211}^2 \left( \frac{T_m - T}{T_m} \right)^2 \left( \frac{T_e}{T_e - T} \right). \tag{B.6}
\]

We have required that \( \gamma_{211} \) and \( \Delta G_n \) vanish linearly as \( T \to T_m \) and \( T_e \), the equilibrium melting and solvus temperatures, respectively. The requirement that \( \gamma_{211} \) vanish at the melting temperature accounts for the limiting case of a liquid layer forming preferentially at an incompatible interface. We ignore strain in general, since Al and Ag have very similar cubic lattice constants [21]. However, if strain–energy effects are negligible, the equations derived here give estimates of temperatures where precipitation is likely to occur. In the following, we will simplify our results dramatically by concatenating the parameters \( A_{eq}f(T)g(k(\Omega)/\Omega^2) \) into one term, \( \xi \), using Eqs. (2), (B.2) and (B.6):

\[
\xi = g_{\gamma_{211}} y_{211} \sqrt{3\Omega + \left( \frac{3\Omega^2}{2} \right) - \frac{3\Omega}{2}} \left( \frac{T_m - T}{T_m} \right)^2 \left( \frac{T_e}{T_e - T} \right)
\]

\[
e^{-2\sqrt{T_m}y_{211}^2(1-T/T_m)}/(k_BTm\Delta G_n(1-T/T_m)). \tag{B.7}
\]
For lengthening we solve Eq. (B.3) as
\[ y(t) = A_{eq} \frac{h}{2} + \frac{\Omega D(t - t^*)}{h k(\Omega^2)}, \] (B.8)
requiring at \( t^* \) that the half-plate-length is \( A_{eq} h/2 \), i.e., a critical nucleus. This form is for an incoherent interface, and so it does not depend on \( f(T) \).

Our equations now allow us to predict the aspect ratio. The total, relative length \( L/L^* \) is given by \( \tilde{L} = 1 + \tilde{t} \), with \( \tilde{t} \equiv (t - t^*)/t^* \). \( L^* \equiv A_{eq} h \) and \( t^* \equiv ghk(\Omega^2) L^*/(\Omega D) \). This comes from Eq. (B.8), representing JT lateral growth, but the rate is divided by the geometrical factor \( g \), as discussed in the text. The initial size is chosen to match a critical nucleus. The total, relative thickness \( W/W^* \) is just \( 2x/h \), from Eq. (B.5), with \( W^* = h \). However, we can express this in terms of \( \xi \), from Eq. (B.7), and in terms of \( \tilde{L} \) (or \( \tilde{t} \)) as \( W = 2\sqrt{1 + \xi(\tilde{L} - 1) - 1} \) or \( 2\sqrt{1 + \xi \tilde{t} - 1} \). The relative aspect ratio is given as a function of \( \tilde{L} \) (or \( \tilde{t} \)) by dividing \( \tilde{L} \) by \( \tilde{W} \):
\[ \tilde{A}(\tilde{L}) = \frac{\tilde{L}}{2\sqrt{1 + \xi(\tilde{L} - 1) - 1}}, \] (B.9)
or \[ \tilde{A}(\tilde{t}) = (1 + \tilde{t})/(2\sqrt{1 + \xi \tilde{t} - 1}). \] To summarize, our assumptions were:

1. The nucleation time of the \( i \)th ledge is parabolic.
2. A factor \( f(T) \) inhibits thickening and interface-mobility.
3. Ledges may proliferate to mimic an incoherent interface.
4. Ledges do not interact (no finite-size).
5. Strain and mismatch were neglected.
6. A geometric factor \( g \) accounts for crystallography.