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# Application of the theorem of minimum entropy production to growth of lamellar eutectics with an oscillating freezing rate

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## Abstract

The theorem of minimum entropy production is applied to steady and stationary periodic eutectic growth with an oscillating freezing rate. When the volume fractions of the two phases are significantly different, a finite lead distance makes the eutectic spacing  $\lambda$  larger than for a planar interface. Freezing rate oscillations reduce  $\lambda$ . If the interface is modulated on a length scale larger than  $\lambda$ , there can be regions with both smaller and larger  $\lambda$ . © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Background

Unsteady eutectic solidification is of practical importance, because solidification rarely occurs at steady state. The usual cause of a fluctuating freezing rate is a fluctuating temperature field in the melt ahead of the interface. We assume here that the fluctuations of temperature and freezing rate can be described by one harmonic of sinusoidal oscillations, and the interfacial composition by a phase-shifted sine function as revealed in Ref. [1].

An important theorem applicable to steady-state solutions in dissipative systems was stated in Ref. [2]: the principle of minimum entropy production, which can be represented using the variational principle

$$\delta \int \Theta \, d^3r = 0, \quad (1.1)$$

where  $\Theta$  is the entropy production, which will be defined in Eq. (2.6). It was noted in Ref. [3] that for time-dependent processes the principle of minimum entropy production might be preserved by forming

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a double variation integral

$$\delta^2 \iint \Theta \, d^3r \, dt = 0. \quad (1.2)$$

The beauty of stationary periodic systems<sup>1</sup> lies in the possibility of describing their evolution over one period. Entropy is conserved over one period, and all of the morphological changes that may take place are reversible. Then a stationary periodic system can be described by Eq. (1.1), where  $\Theta$  is the entropy production time averaged over one period of oscillations.

The objective of this paper is to describe steady state and stationary periodic eutectic growth, and find the optimal spacing  $\lambda$  using the principle of minimum entropy production. We heuristically assume here that  $\lambda$  is constant. That is, any periodic changes in melt composition and temperature have already changed  $\lambda$  so that the growth proceeds in a quasi-stationary way, with no further change in  $\lambda$ .

## 2. Entropy production for a binary eutectic system

Consider cooperative growth of two phases from a binary alloy melt at the eutectic composition. We assume that the growth takes place close to thermodynamic equilibrium. The specific free energy can be written for both solid and liquid phases as

$$f = C_V T - C_V T \ln T + \frac{R}{v_m} T (c \ln c + (1 - c) \ln(1 - c)) + \frac{\Omega}{v_m} T c(1 - c), \quad (2.1)$$

where  $C_V$  is the specific heat,  $\Omega$  is the excess entropy of mixing, and  $v_{mi}$  is the molar volume of component  $i$ , assumed to be the same for the two components ( $v_{m1} = v_{m2}$ ) and the same for solid and liquid phases. The composition  $c$  represents the atom fraction of component 1. We consider further an ideal solution so that  $\Omega = 0$ . From Eq. (2.1), the specific entropy becomes

$$s = C_V \ln T - \frac{R}{v_m} (c \ln c + (1 - c) \ln(1 - c)). \quad (2.2)$$

Differentiation of Eq. (2.2) gives

$$\frac{ds}{dt} = C_V \frac{1}{T} \frac{dT}{dt} - \frac{\bar{\mu}}{T} \frac{dc}{dt}. \quad (2.3)$$

Due to the periodic nature of the eutectic structure, we confine the calculation to a domain with dimension  $\lambda/2$  in the direction of the eutectic periodicity, where the integration limits  $x = 0$  and  $\lambda/2$  correspond to the centers of  $\alpha$  and  $\beta$  neighboring lamellae, respectively. In the direction of growth the integration is carried out from  $-w_S$  to  $+w_M$  ( $w_M$  from the freezing interface into the melt, and  $w_S$  from the freezing interface into the solid), which were taken to be equal  $w_S = w_M = w$ . The value of  $w$  must be large enough that the composition there is constant. We integrated to  $+\infty$  to obtain the contribution to the entropy production from chemical diffusion in the melt. The contribution from solid-state diffusion was neglected due to the very low diffusivity in solids. Thus, the calculation was carried out from  $z_0(x)$  to  $+\infty$ , where  $z_0(x)$  is the interface position.

<sup>1</sup> All physical parameters in the system averaged over one period of oscillations exhibit a steady-state behavior, i.e. they do not vary from one period to the next.

Assuming that there is no convection, and  $V$  is the translation rate of the interface (freezing rate), the expression for the entropy change can be represented as

$$\frac{\partial S}{\partial t} = \frac{1}{w\lambda} \int_{-w}^w dz \int_0^{\lambda/2} dx \left\{ \frac{1}{T} (\nabla(VT) + \nabla K \nabla T + \mathfrak{I}(\mathbf{Vn})\delta(z - z_0)) + \frac{\bar{\mu}}{T} \left( \nabla \left( \frac{D}{R} c(1 - c) \nabla \left( \frac{\bar{\mu}}{T} \right) \right) + \nabla(Vc) \right) \right\}, \tag{2.4}$$

where  $K$  is the thermal conductivity (assumed to be constant throughout the domain),  $\mathfrak{I}$  is the specific latent heat of the phase transformation, and  $n$  is the normal vector to the interface. It is possible to separate the rate of change of entropy into the entropy flux  $J_S$  and the entropy source  $\Theta$ :

$$\frac{\partial S}{\partial t} = -\nabla J_S + \Theta, \tag{2.5}$$

where these are given by

$$J_S = \frac{1}{w\lambda} \int_{-w}^w dz \int_0^{\lambda/2} dx \left\{ -\frac{K}{T} \nabla T + \frac{D}{Rv_m} c(1 - c) \frac{\bar{\mu}}{T} \nabla \left( \frac{\bar{\mu}}{T} \right) + sV \right\},$$

$$\Theta = \Theta_T + \Theta_C = \frac{1}{w\lambda} \int_{-w}^w dz \int_0^{\lambda/2} dx \left\{ \frac{K}{T^2} |\nabla T|^2 + \frac{D}{Rv_m} c(1 - c) \left| \nabla \left( \frac{\bar{\mu}}{T} \right) \right|^2 \right\}. \tag{2.6}$$

We are interested in the excess quantities  $\delta\Theta_T$  and  $\delta\Theta_C$  that describe the nonequilibrium part of the total entropy production, i.e. the difference between the entropy production for the stationary (steady-state or stationary periodic) solutions of temperature and composition fields and that for equilibrium<sup>2</sup> of those fields.

### 3. Entropy production due to diffusion in the melt

Integrating the second term in Eq. (2.6), the entropy production per unit volume is

$$\Theta_C = \frac{2}{w\lambda} \frac{DR}{v_m} \int_{x=0}^{\lambda/2} \int_{z=z_0(x)}^{\infty} \frac{(Vc)^2}{c(1 - c)} dz dx. \tag{3.1}$$

Now, we let  $c = c_E + \delta c$ , where  $\delta c$  is a small deviation of composition from  $c_E$  anywhere in the liquid. A similar representation of the entropy production due to diffusion in the liquid was used by Lesoult [4,5] and Wolzynski [6–8]. We limit the analysis to a eutectic composition  $c_E$  not near 0 or 1, i.e. where the variation of the chemical potential is small for small variations in composition. For values of  $\delta c$  not to exceed  $10^{-3}$ , a range of  $c_E$  from 0.01 to 0.99 is suitable. Then,

$$\begin{aligned} \delta\Theta_C &= \frac{2}{w\lambda} \frac{DR}{v_m c_E (1 - c_E)} \int_{x=0}^{\lambda/2} \int_{z=z_0(x)}^{\infty} (V\delta c)^2 dz dx \\ &\quad - \frac{2}{w\lambda} \frac{DR}{v_m} \frac{1 - 2c_E}{(c_E(1 - c_E))^2} \int_{x=0}^{\lambda/2} \int_{z=z_0(x)}^{\infty} \delta c (V\delta c)^2 dz dx \\ &\quad + \frac{2}{w\lambda} \frac{DR}{v_m (c_E(1 - c_E))^2} \int_{x=0}^{\lambda/2} \int_{z=z_0(x)}^{\infty} (\delta c)^2 (V\delta c)^2 dz dx. \end{aligned} \tag{3.2}$$

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<sup>2</sup>Equilibrium refers to the eutectic temperature  $T_E$  at the interface, eutectic composition  $c_E$  in the liquid, and terminal solid compositions  $c_\alpha$  and  $c_\beta$  in the two solid phases. Volume fractions are equal to those from the phase diagram at the eutectic composition.

Following Lesoult and Turpin [5], let us consider the first term, which requires the calculation of  $\int_{x=0}^{\lambda/2} \int_{z=z_0(x)}^{\infty} (\nabla \delta c)^2 dz dx$  over the melt region with appropriate boundary conditions. This integral can be integrated by parts to give

$$\begin{aligned} \int_{x=0}^{\lambda/2} \int_{z=z_0(x)}^{\infty} (\nabla \delta c)^2 dz dx &= \int_{x=0}^{\lambda/2} \int_{z=z_0(x)}^{\infty} \left\{ \left( \frac{\partial \delta c}{\partial x} \right)^2 + \left( \frac{\partial \delta c}{\partial z} \right)^2 \right\} dz dx \\ &= \int_{z=z_0(x)}^{\infty} \delta c \frac{\partial \delta c}{\partial x} \Big|_{x=0}^{x=\lambda/2} dz + \int_{x=0}^{\lambda/2} \delta c \frac{\partial \delta c}{\partial z} \Big|_{z=z_0(x)}^{z=\infty} dx \\ &\quad - \int_{x=0}^{\lambda/2} \int_{z=z_0(x)}^{\infty} \delta c \left\{ \left( \frac{\partial^2 \delta c}{\partial x^2} \right) + \left( \frac{\partial^2 \delta c}{\partial z^2} \right) \right\} dz dx. \end{aligned} \quad (3.3)$$

The first term on the r.h.s. of Eq. (3.3) is zero since  $\partial \delta c / \partial x = 0$  at the integration limits. The higher-order corrections in Eq. (3.2) can be evaluated similar to Eq. (3.3). We assume the nonequilibrium composition field is in a form similar to the Jackson–Hunt [9] solution of the diffusion field with a planar interface and constant freezing rate  $V$ :

$$\delta c = B_0 \left( \exp \left( -\frac{V}{D} z \right) - 1 \right) + \sum_{n=1}^{\infty} B_n \cos(K_n x) \exp(-M_n z), \quad (3.4)$$

where

$$K_n = \frac{2\pi n}{\lambda}, \quad M_n = \frac{V}{2D} + \sqrt{\left( \frac{V}{2D} \right)^2 + K_n^2}, \quad B_n = \frac{V}{D} c_0 \lambda \frac{1}{(\pi n)^2} \sin^2(\pi n \zeta). \quad (3.5)$$

Here, the coefficients  $B_n$  are given in the form appropriate for small values of  $\lambda V/D$ . By assuming that the diffusion length  $D/V$  is much larger than the interlamellar spacing  $\lambda$ , i.e.,  $D/V \gg \lambda/2\pi$ , we can make the following approximation for the wave number  $M_n$ :

$$M_n \cong K_n \left( 1 + \frac{V}{2DK_n} \right) \quad (3.6)$$

as used by Bolze et al. [10] in their steady-state analysis.

### 3.1. Contribution from diffusion in the melt for a flat interface

Now, using Eqs. (3.4) and (3.5), the contribution to entropy production from diffusion is calculated assuming that  $z_0(x) = 0$ , i.e. a flat interface. We assume that the segregation coefficient is constant for each phase, so that

$$\begin{aligned} \frac{\partial \delta c}{\partial z} &= -\frac{V}{D} (1 - k_\alpha) c = -\frac{V}{D} \left( 1 - \frac{c_\alpha^{(E)}}{c_E} \right) c \quad \text{for } 0 \leq x \leq \frac{\zeta \lambda}{2}, \\ \frac{\partial \delta c}{\partial z} &= -\frac{V}{D} (1 - k_\beta) c = -\frac{V}{D} \left( 1 - \frac{c_\beta^{(E)}}{c_E} \right) c \quad \text{for } \frac{\zeta \lambda}{2} \leq x \leq \frac{\lambda}{2}. \end{aligned} \quad (3.7)$$

The overall contribution from integral (3.3) is

$$\frac{1}{4} \frac{V}{D} \lambda B_0^2 + \frac{1}{2} \frac{V^2}{D^2} \lambda^2 c_0^2 P(\zeta) + \frac{1}{8} \frac{V^3}{D^3} \lambda^3 c_0^2 Q(\zeta) \left( 2 \frac{B_0}{c_E} - 1 \right) + \frac{1}{64} \frac{V^4}{D^4} \lambda^4 c_0^2 U(\zeta) + \frac{1}{256} \frac{V^5}{D^5} \lambda^5 c_0^2 W(\zeta) \quad (3.8)$$

with

$$\begin{aligned}
 P(\zeta) &= \sum_{n=1}^{\infty} \frac{1}{(\pi n)^3} \sin^2(\pi n \zeta), & Q(\zeta) &= \sum_{n=1}^{\infty} \frac{1}{(\pi n)^4} \sin^2(\pi n \zeta), \\
 U(\zeta) &= \sum_{n=1}^{\infty} \frac{1}{(\pi n)^5} \sin^2(\pi n \zeta), & W(\zeta) &= \sum_{n=1}^{\infty} \frac{1}{(\pi n)^6} \sin^2(\pi n \zeta).
 \end{aligned}
 \tag{3.9}$$

The second and third terms in Eq. (3.8) appear in the analysis of Lesoult and Turpin [5]. The first term arises when the bulk composition is off-eutectic, and does not appear in Ref. [5]. The last two terms are higher-order terms in the expansion for small  $(\lambda V/D)$  using Eq. (3.6) (in Ref. [5]  $M_n = K_n$  was used instead).

We also obtain corrections to the entropy production arising from the Taylor expansion of Eq. (3.2). Up to order  $\lambda^2$  the entropy production due to diffusion is

$$\delta\Theta_C = \frac{2R}{wv_m c_E(1 - c_E)} \left\{ \begin{aligned} &V \left( \frac{1}{4} B_0^2 + \frac{1}{12} \frac{1 - 2c_E}{c_E(1 - c_E)} B_0^3 + \frac{1}{24} \frac{1}{c_E(1 - c_E)} B_0^4 \right) \\ &+ \frac{V^2}{D} \lambda \left( \frac{1}{2} c_0^2 P(\zeta) \right) \\ &+ \frac{V^3}{D^2} \lambda^2 \left( \frac{1}{8} c_0^2 Q(\zeta) \left( \frac{B_0}{c_E(1 - c_E)} - 1 \right) \right) \end{aligned} \right\}.
 \tag{3.10}$$

The first term in Eq. (3.10) is independent of  $\lambda$ , and the only one that is applicable to single-phase alloy solidification. The correction to the result of Lesoult and Turpin in the  $\lambda^2$  term appears due to use of condition (3.6). This correction is shown in Fig. 1. Note that it is symmetric with respect to A and B. These corrections are significant only when the eutectic composition  $c_E$  is close to 0 or 1. When the volume fraction  $\zeta$  is far away from 0.5, then  $Q(\zeta)$  is small. Thus, the higher-order corrections in  $\lambda$  to Eq. (3.2) are insignificant for a melt at the eutectic composition. For solidification of symmetric systems from a eutectic melt, only the second term in Eq. (3.10) gives a significant contribution to the entropy production, and this contribution

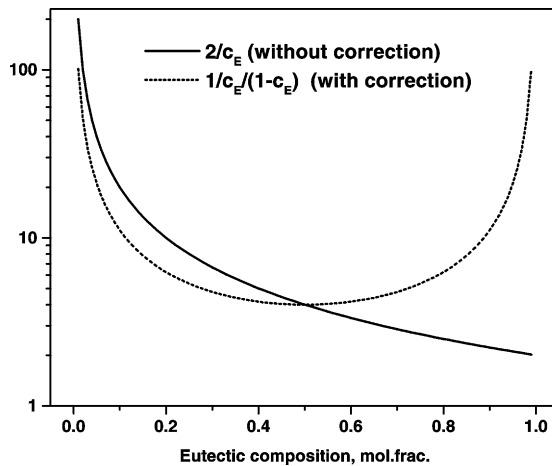


Fig. 1. Correction to the entropy production term  $\sim \lambda^2$  due to inclusion of higher-order terms from Eq. (3.2) in the expansion of  $1/c/(1 - c)$ .

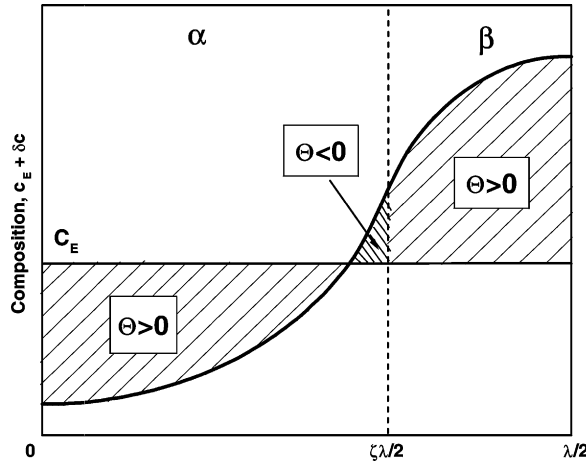


Fig. 2. The positive and negative contributions to the entropy production  $\Theta_C$  from the nonequilibrium composition field at the freezing interface. Second term in Eq. (3.10).

comes from the nonequilibrium interfacial composition (shown schematically in Fig. 2). The shaded areas show the positive and negative parts of entropy production  $\delta\Theta_C$  along the freezing interface.

### 3.2. Effect of interface nonplanarity on the melt composition

The freezing interface of each lamella is assumed to be of parabolic shape described by a second-order polynomial. Thus, for phase  $\alpha$ :

$$z_0^\alpha(x) = -\frac{\tan(\theta_\alpha)}{\zeta\lambda}x^2 + \frac{\zeta\lambda}{4}\tan(\theta_\alpha). \tag{3.11}$$

A similar expression can be written for the shape of the  $\beta$ /liquid interface. The lead distance is given by the last term of Eq. (3.11). The correction to the composition due to interface curvature is used only for the boundary term in Eq. (3.3). Lesoult and Turpin [5] used the correction  $\delta\tilde{c} = \delta c + a_i\kappa$ , where  $\kappa$  is the interface curvature,  $\delta\tilde{c}$  is the surface composition along the curved interface and  $a_i$  is a constant ( $i = \alpha, \beta$ ). Nash [11] claimed that this correction depends on the composition field, and can be either positive or negative, depending on volume fraction. However, this claim does not match the assumption made in Ref. [5] that the coefficient  $a$  is always positive. Here, we assume that the correction has the form

$$\delta\tilde{c} = c_\kappa \text{sign}(c_E - c_{(\alpha,\beta)}) + \delta c(1 + a_i\kappa), \tag{3.12}$$

where  $c_\kappa$  is the average deviation of the composition at the interface from the eutectic composition. The appearance of  $c_\kappa$  in correction (3.12) has nothing to do with interface curvature; it appears when one phase leads the other due to condition

$$\bar{d}_\alpha = \frac{2}{3}\left(\frac{\zeta\lambda}{4}\tan(\theta_\alpha)\right) > \bar{d}_\beta = \frac{2}{3}\left(\frac{(1-\zeta)\lambda}{4}\tan(\theta_\beta)\right), \tag{3.13}$$

using Eq. (3.11). According to Nash, if correction  $\delta c$  is written in the form (3.12), then coefficient  $a_i$  should be negative.

Using Eq. (3.11), it can be shown that  $a_i$  should be proportional to  $\lambda$ . For a parabolic approximation to the interface shape, the interface curvature  $\kappa$  and the average lead distance are related. To a first approximation, the correction to composition at the curved interface of  $\alpha$  is given by

$$\delta\tilde{c}_\alpha - \delta c_\alpha = \frac{V}{D} c_0 \lambda \left\{ \sum_{n=1}^{\infty} \frac{1}{(\pi n)^3} \sin^2(\pi n \zeta) \exp\left(-\frac{\pi n \zeta}{3} \tan(\theta_\alpha)\right) - P(\zeta) \right\}. \quad (3.14)$$

The assumption of small ( $< \pi/6$ )  $\theta_\alpha$  and  $\theta_\beta$  was made in order to simplify the evaluation integral (3.3) with the integrand  $\delta c$  given by Eq. (3.14). Using Eq. (3.12) with  $c_\kappa = 0$ , a very good approximation to  $a_\alpha$  in correction (3.14) is given by

$$a_\alpha = -\frac{\pi \zeta^2 \lambda}{6}. \quad (3.15)$$

### 3.3. Effect of interface curvature on the solid composition

The change of chemical potential at the interface due to interface curvature can be expressed in terms of solid and liquid composition using the Gibbs–Duhem relation and the differential van der Waals equation [5]

$$\delta c^{(\alpha,\beta)} = k_{(\alpha,\beta)} \delta c + N_{(\alpha,\beta)} \frac{k_{(\alpha,\beta)}}{m_{(\alpha,\beta)}} (\sigma \kappa), \quad (3.16)$$

where

$$N_{(\alpha,\beta)} = \left( \frac{1}{\Delta S_L} - \frac{1}{\Delta S_{(\alpha,\beta)}} \right),$$

$$\Delta S_L = (S_1^L - S_1^{(\alpha,\beta)})(1 - c^L) + (S_2^L - S_2^{(\alpha,\beta)})c^L,$$

$$\Delta S_{(\alpha,\beta)} = (S_1^L - S_1^{(\alpha,\beta)})(1 - c^{(\alpha,\beta)}) + (S_2^L - S_2^{(\alpha,\beta)})c^{(\alpha,\beta)} \quad (3.17)$$

and  $m_{(\alpha,\beta)}$  are the liquidus slopes in the  $(T, c)$  phase diagram. Note, that since  $c_\alpha < c_E$  and  $c_\beta > c_E$ ,  $m_\alpha$  is negative and  $m_\beta$  is positive. At the eutectic temperature,  $c^L = c_E$ ,  $c^\alpha = c_\alpha$  (terminal  $\alpha$ -phase composition), and  $c^\beta = c_\beta$  (terminal  $\beta$ -phase composition). Note that  $N_{(\alpha,\beta)}$  depends on the entropy of the pure components, and the compositions of the solids and the eutectic. For positive curvature  $\kappa$  of the solid/liquid interface and positive  $N_\alpha$  and  $N_\beta$ ,  $\delta c^\alpha < k_\alpha \delta c$  and  $\delta c^\beta > k_\beta \delta c$ . That is, there is more segregation than with a planar interface, yielding a positive contribution to entropy production.

### 3.4. Total contribution to entropy production from interface nonplanarity

The contribution to entropy production from interface nonplanarity was obtained by substituting corrections (3.16) and (3.12) into the first integral on the r.h.s. of Eq. (3.3), with the integration limits from  $z = z_0$  to  $z = \infty$ . Note that  $c_\kappa$  consists of two parts with different length scales:  $c_\kappa = c_\kappa^{(\lambda)} + c_\kappa^{(\omega)}$ . The first part  $c_\kappa^{(\lambda)}$  appears due to different leading conditions of  $\alpha$  and  $\beta$  on the scale of  $\lambda$ . If  $\bar{d}_\alpha = \bar{d}_\beta$  (lead distance  $d = \bar{d}_\alpha - \bar{d}_\beta = 0$ ), then  $c_\kappa^{(\lambda)} = 0$ . The second part,  $c_\kappa^{(\omega)}$ , is responsible for the deviation of composition at the interface from the eutectic due to long-wavelength<sup>3</sup> perturbations of the freezing interface shape. These

<sup>3</sup> Compared to  $\lambda$ .

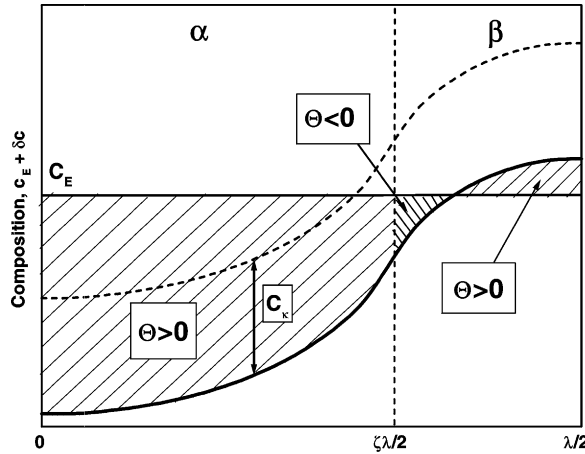


Fig. 3. The positive and negative contributions to the entropy production  $\Theta_c$  from the nonequilibrium composition field at the freezing interface when one phase leads. Here  $c_k$  is the offset of the average interfacial composition from the steady-state composition corresponding to the planar interface (dashed line) due to leading conditions.

perturbations are associated with spatial oscillations of temperature along the interface due to interface instability. We consider that part in Section 7.

Based on a Fourier series representation of the steady-state solution (Eqs. (3.4) and (3.5)), it is reasonable to assume that  $c_k^{(\lambda)} = V\lambda/Dc_k^{(0)}$ , i.e. proportional to  $\lambda$ , although it is not a linear function of the lead distance  $d = \bar{d}_\alpha - \bar{d}_\beta$ . Our numerical results for a planar interface [1] show that for small  $d$ ,  $|c_k^{(\lambda)}|$  drastically increases with increasing  $d$ . As  $d$  increases further, the dependence becomes less steep, and for high  $d$  Eq. (3.12) ceases to be valid.

The correction arising from interface nonplanarity possesses the following negative term that is proportional to  $\lambda$ :

$$-\frac{2R}{wv_m c_E(1 - c_E)} \lambda \frac{\pi}{6} \frac{V^2}{D} c_0 P(\zeta) \{ (c_E - c_\alpha) \zeta \tan(\theta_\alpha) - (c_E - c_\beta) (1 - \zeta) \tan(\theta_\beta) \}. \tag{3.18}$$

The following term is proportional to  $\lambda^2$ :

$$\frac{2R}{wv_m c_E(1 - c_E)} \lambda^2 \frac{V^2}{D} c_0^2 \frac{c_k^{(0)}}{c_E(1 - c_E)} P(\zeta) [1 - 2\zeta]. \tag{3.19}$$

For  $\bar{d}_\alpha = \bar{d}_\beta$ ,  $c_k^{(0)} = 0$  and the contribution from Eq. (3.19) is zero. For  $c_k^{(0)} \neq 0$ , the sign of Eq. (3.19) is determined by the sign of  $c_k^{(0)}$  and by the volume fraction  $\zeta$ . The constant  $c_k^{(0)}$  gives a contribution to entropy production that is of opposite sign for  $\alpha$  and  $\beta$  phases, as shown in Fig. 3. There is also a term that is proportional to  $1/\lambda$  for  $c_k = c_k^{(\omega)}$ :

$$-\frac{2R}{wv_m c_E(1 - c_E)} \frac{1}{\lambda} \left\{ V \sigma c_k^{(\omega)} \left( N_\alpha \frac{k_\alpha}{m_\alpha} \sin(\theta_\alpha) - N_\beta \frac{k_\beta}{m_\beta} \sin(\theta_\beta) \right) \right\}. \tag{3.20}$$

This contribution works on a larger length scale, and becomes important for long wavelength perturbations of the interface.

#### 4. Entropy production due to heat transfer

The entropy production due to heat transfer can be written as

$$\Theta_T = \frac{1}{w\lambda} \int_{x=0}^{\lambda/2} \int_{z=-w}^w \frac{K}{T^2} (\nabla T)^2 dz dx + \frac{1}{w\lambda} \mathfrak{S}V \int_{x=0}^{\lambda/2} \int_{z=-w}^w \frac{\delta(z - z_0(x))}{T} dz dx, \tag{4.1}$$

where  $K$  is the thermal conductivity, which can be different for solids and melt, and  $\mathfrak{S}$  is the latent heat. The first integral can be evaluated by parts to give

$$\begin{aligned} \int_{x=0}^{\lambda/2} \int_{z=-w}^w \frac{K}{T^2} (\nabla T)^2 dz dx &= K \int_{x=0}^{\lambda/2} \int_{z=-w}^w \frac{1}{T^2} \left\{ \left( \frac{\partial T}{\partial x} \right)^2 + \left( \frac{\partial T}{\partial z} \right)^2 \right\} dz dx \\ &= -K \int_{z=-w}^w \frac{1}{T} \frac{\partial T}{\partial x} \Big|_{x=0}^{x=\lambda/2} dz - K \int_{x=0}^{\lambda/2} \frac{1}{T} \frac{\partial T}{\partial z} \Big|_{z=-w}^{z=w} dx + K \int_{x=0}^{\lambda/2} \int_{z=-w}^w \frac{1}{T} \left\{ \left( \frac{\partial^2 T}{\partial x^2} \right) + \left( \frac{\partial^2 T}{\partial z^2} \right) \right\} dz dx. \end{aligned} \tag{4.2}$$

We consider a fully developed temperature profile with time-independent far-field boundary conditions (far from the interface into the solid and into the liquid). Under this assumption, we can neglect the last term on the r.h.s. of Eq. (4.2). The same considerations as for mass transfer set the first term on the r.h.s. of Eq. (4.2) equal to zero. Assuming the temperature gradient is constant for each phase,

$$-K \int_{x=0}^{\lambda/2} \frac{1}{T} \frac{\partial T}{\partial z} \Big|_{z=-w}^{z=w} dx = \frac{\lambda}{2} \left( \frac{K_S G_S}{T_S} - \frac{K_L G_L}{T_L} \right), \tag{4.3}$$

where  $T_S$  and  $T_L$  are the temperatures at  $z = -w$  and  $w$ , respectively.

The second integral in Eq. (4.1) is

$$\mathfrak{S}V \int_{x=0}^{\lambda/2} \int_{z=-w}^w \frac{\delta(z - z_0(x))}{T} dz dx = V \left\{ \mathfrak{S}_\alpha \int_{x=0}^{\zeta\lambda/2} \frac{1}{T_\alpha(z_0)} dx + \mathfrak{S}_\beta \int_{x=\zeta\lambda/2}^{\lambda/2} \frac{1}{T_\beta(z_0)} dx \right\}. \tag{4.4}$$

The difference between the interface temperature of  $\alpha$  and the eutectic temperature is given by the following equation:

$$\delta T_\alpha = T_\alpha(z_0) - T_E = \left( m_\alpha \delta c - \frac{\sigma_\alpha}{\Delta S_\alpha} \kappa_\alpha - \frac{1}{\beta_\alpha} V \right) \tag{4.5}$$

with a similar expression for  $\beta$ 's interface temperature. Since that temperature difference is less than the eutectic temperature  $T_E$ , the terms  $1/T_\alpha(z_0)$  and  $1/T_\beta(z_0)$  in Eq. (4.4) can be expanded into Taylor series and then integrated. The excess entropy production was calculated thereby to be

$$\begin{aligned} \delta \Theta_T &= \frac{V^2}{2wT_E^2} \frac{1}{\beta} (\mathfrak{S}_\alpha \zeta + \mathfrak{S}_\beta (1 - \zeta)) - \frac{V^2}{2wDT_E^2} \lambda c_0 P(\zeta) \{ \mathfrak{S}_\alpha m_\alpha - \mathfrak{S}_\beta m_\beta \} \\ &+ \frac{V}{wT_E^2} \frac{1}{\lambda} \left\{ \mathfrak{S}_\alpha \frac{\sigma_\alpha}{\Delta S_\alpha} \sin(\theta_\alpha) + \mathfrak{S}_\beta \frac{\sigma_\beta}{\Delta S_\beta} \sin(\theta_\beta) \right\}. \end{aligned} \tag{4.6}$$

All three terms in Eq. (4.6) are positive, since  $\sin(\theta_\alpha)$  and  $\sin(\theta_\beta)$  are both positive,  $m_\alpha < 0$ , and  $m_\beta > 0$ . So, the excess entropy production associated with a nonequilibrium interface temperature is positive.

## 5. Analysis of steady-state eutectic growth

Adding together the contributions for heat and mass transfer, the excess entropy production incorporates the following terms proportional to spacing  $\lambda$ :

$$\delta\Theta(\lambda) = \frac{V^2}{2wD} c_0 \lambda P(\zeta) \left\{ \begin{array}{l} \frac{2R}{v_m c_E (1 - c_E)} \left( \frac{1}{2} c_0 \right) \\ + \frac{1}{T_E} \{ -\Delta S_\alpha m_\alpha + \Delta S_\beta m_\beta \} \\ - \frac{2R}{v_m c_E (1 - c_E)} \frac{\pi}{6} \{ (c_E - c_\alpha) \zeta \tan(\theta_\alpha) - (c_E - c_\beta) (1 - \zeta) \tan(\theta_\beta) \} \end{array} \right\}. \quad (5.1)$$

The following terms are proportional to the inverse of the spacing ( $1/\lambda$ ):

$$\delta\Theta\left(\frac{1}{\lambda}\right) = \frac{V}{w\lambda} \left\{ \begin{array}{l} \frac{1}{T_E} \{ \Delta S_\alpha \Gamma_\alpha \sin(\theta_\alpha) + \Delta S_\beta \Gamma_\beta \sin(\theta_\beta) \} \\ - \frac{2R}{v_m c_E (1 - c_E)} \left\{ \sigma c_\kappa^{(\omega)} \left( N_\alpha \frac{k_\alpha}{m_\alpha} \sin(\theta_\alpha) - N_\beta \frac{k_\beta}{m_\beta} \sin(\theta_\beta) \right) \right\} \end{array} \right\}, \quad (5.2)$$

where  $\Gamma_i = \sigma_i/\Delta S_i$  is the Gibbs–Thomson coefficient for phase  $i$  ( $i = \alpha, \beta$ ). The term proportional to  $\lambda^2$  is

$$\delta\Theta(\lambda^2) = \frac{2R}{wv_m c_E (1 - c_E)} \lambda^2 \frac{V^2}{D} c_0 \frac{c_\kappa^{(0)}}{c_E (1 - c_E)} P(\zeta) \{ c_0 [1 - 2\zeta] \}. \quad (5.3)$$

### 5.1. Steady-state symmetric and asymmetric eutectics

We estimated the contributions to entropy production from Eqs. (5.1) and (5.2). First, we took  $c_\kappa^{(\omega)} = 0$ , thereby assuming that there is no long-wavelength modulation of the interface. We consider two lamellar eutectic structures: symmetric and asymmetric. The following physical properties are taken for both symmetric and asymmetric eutectics:  $c_0 = 0.9$ ;  $\Gamma_i = 10^{-5}$  cm K;  $v_m = 20$  cm<sup>3</sup>/mol;  $\Delta S_i = 4$  J/cm<sup>3</sup>/K;  $\theta_i = \pi/6$ ;  $|m_i| = 100$  K/at.frac;  $T_E = 5 \times 10^2$  K;  $V = 10^{-4}$  cm/s;  $D = 10^{-5}$  cm<sup>2</sup>/s,  $w = 1$  cm. The values of the resulting terms in Eqs. (5.1) and (5.2) are summarized in Table 1.

The contribution to entropy production from a nonequilibrium temperature (second term in Table 1) is proportional to  $\Delta S/T_E$ , which is large for semiconductors and small for metals. For semiconductors this contribution is comparable to that for mass transfer (first term in Table 1). The third term gives a negative contribution due to the effect of interface nonplanarity on the composition field at the interface. According to the theorem of minimum entropy production, the lamellar spacing  $\lambda$  can be found from minimization of all contributions with respect to  $\lambda$ . For a symmetric eutectic with the above properties, this minimization yields  $\lambda \cong 4.5 \times 10^{-4}$  cm.

Neglecting the effect of the interface nonplanarity on the melt composition near the interface, the eutectic spacing  $\lambda$  for minimum entropy production and can be expressed as

$$\lambda = \sqrt{\frac{2D \{ \Delta S_\alpha \Gamma_\alpha \sin(\theta_\alpha) + \Delta S_\beta \Gamma_\beta \sin(\theta_\beta) \}}{V c_0 P(\zeta) \left\{ \frac{RT_E c_0}{v_m c_E (1 - c_E)} + (-\Delta S_\alpha m_\alpha + \Delta S_\beta m_\beta) \right\}}}. \quad (5.4)$$

Table 1  
Contributions to entropy production for symmetric and asymmetric eutectics

	Symmetric eutectic: $c_E = 0.5; \zeta = 0.5; k_\alpha = 0.1; k_\beta = 1.9$	Asymmetric eutectic: $c_E = 0.8; \zeta = 0.167; k_\alpha = 0.063; k_\beta = 1.188$
Diffusion with planar interface $\frac{V^2}{D} c_0 \lambda P(\zeta) \frac{2R}{v_m c_E (1 - c_E)} \left( \frac{1}{2} c_0 \right)$	$4.5 \times 10^{-5} \lambda \frac{\text{J}}{\text{cm}^4 \text{K s}}$	$2.7 \times 10^{-5} \lambda \frac{\text{J}}{\text{cm}^4 \text{K s}}$
Compositional undercooling $\frac{V^2}{D} c_0 \lambda P(\zeta) \left( \frac{1}{T_E} \{ -\Delta S_\alpha m_\alpha + \Delta S_\beta m_\beta \} \right)$	$4.8 \times 10^{-5} \lambda \frac{\text{J}}{\text{cm}^4 \text{K s}}$	$1.9 \times 10^{-5} \lambda \frac{\text{J}}{\text{cm}^4 \text{K s}}$
Diffusion: effect on interface nonplanarity $-\frac{V^2}{6D} c_0 \lambda P(\zeta) \frac{\pi R}{v_m c_E (1 - c_E)} \times \{ (c_E - c_\alpha) \zeta \tan(\theta_\alpha) - (c_E - c_\beta) (1 - \zeta) \tan(\theta_\beta) \}$	$-0.67 \times 10^{-5} \lambda \frac{\text{J}}{\text{cm}^4 \text{K s}}$	$-0.18 \times 10^{-5} \lambda \frac{\text{J}}{\text{cm}^4 \text{K s}}$
Curvature undercooling $\frac{V}{\lambda} \frac{2}{T_E} \{ \Delta S_\alpha \Gamma_\alpha \sin(\theta_\alpha) + \Delta S_\beta \Gamma_\beta \sin(\theta_\beta) \}$	$1.6 \times 10^{-11} \frac{1}{\lambda} \frac{\text{J}}{\text{cm}^2 \text{K s}}$	$1.6 \times 10^{-11} \frac{1}{\lambda} \frac{\text{J}}{\text{cm}^2 \text{K s}}$

For a symmetric eutectic, the two terms in the denominator of Eq. (5.4) are approximately equal. To prove the validity of the order of magnitude analysis, we substitute the denominator of Eq. (5.4) by  $2 \times$  the second term. Eq. (5.4) for the eutectic spacing simplifies to

$$\lambda = \sqrt{\frac{D\bar{\sigma}}{V c_0 P(\zeta) \Delta \bar{S} \bar{m}}}, \quad (5.5)$$

where the entropy change, surface energy, and liquidus slope are averaged over the two phases. Eq. (5.5) is equivalent to the result obtained in Ref. [9] when appropriate substitutions are made.

The entropy production due to mass transfer and nonequilibrium temperature decreases as the asymmetry increases ( $\zeta \rightarrow 0$  or  $1$ ). As a result, for minimum entropy production,  $\lambda$  is larger for an asymmetric eutectic than for a symmetric eutectic.

## 5.2. Effect of lead distance

As shown in our numerical calculations [1], if one phase leads the other, the average interfacial composition deviates from the eutectic composition, even if the bulk of the melt is eutectic. This deviation contributes to nonequilibrium entropy production, as calculated in Section 3.4, and consists of two parts. The first part incorporates the effect of the nonequilibrium chemical potential difference on  $\lambda$ . This part is given by Eq. (5.3), and is proportional to  $\lambda^2$ . Its effect is considerable only for strongly asymmetric eutectics (see Fig. 4 and Table 2). Thus, the effect of a leading condition is to increase  $\lambda$ .

## 5.3. Conclusions from the steady-state analysis

As a result of the application of the theorem of minimum entropy production to steady-state eutectic growth, all of the following were predicted to increase the spacing  $\lambda$ :

- Increasing the difference in volume fractions of the two solid phases.
- Decreasing  $\Delta S/T_E$ .

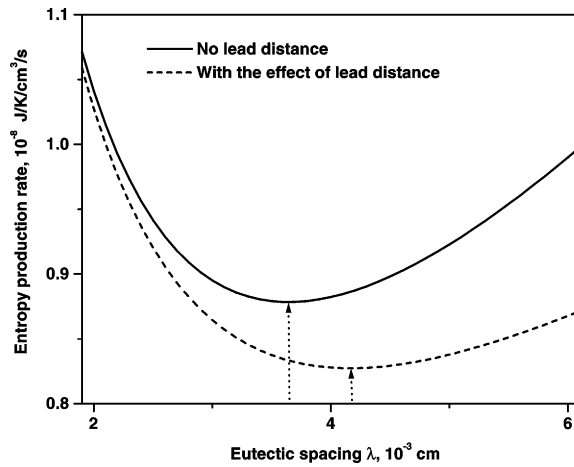


Fig. 4. The contribution from the lead distance to entropy production increases  $\lambda$ . The effect is significant only for asymmetric eutectics with a large difference in volume fractions. The plot corresponds to  $c_{\kappa} = 0.1$  and volume fraction of one phase  $\zeta = 0.02$ .

Table 2

Effect of the lead distance (represented by nonequilibrium composition  $c_{\kappa}^{(0)}$ ) and volume fraction on steady-state  $\lambda$

Eutectic composition $c_E$ atom frac.	Volume fraction $\zeta$	$\lambda$ , $10^{-4}$ cm				
		$c_{\kappa}^{(0)} = 0$	$c_{\kappa}^{(0)} = 0.01$	$c_{\kappa}^{(0)} = 0.03$	$c_{\kappa}^{(0)} = 0.05$	$c_{\kappa}^{(0)} = 0.1$
0.5	0.500	4.117	4.117	4.117	4.117	4.117
0.2	0.833	5.910	5.913	5.917	5.920	5.929
0.06	0.989	36.40	36.85	37.68	38.61	$\sim 169$

(c) Increasing the interfacial energy  $\sigma$ .

(d) Increasing the lead distance  $d$  for asymmetric eutectics with a large difference in volume fractions.

## 6. Excess entropy production due to an oscillating freezing rate

Here, we use the results of the analytical solution obtained in Ref. [1], where we specified the freezing rate as a periodic function with one harmonic

$$V(t) = V_0(1 + \varepsilon \sin(\omega t)). \quad (6.1)$$

The compositions in the melt and solid satisfy

$$\begin{aligned} \delta\tilde{c} &= \delta c(1 + \varepsilon \sin(\omega t - \varphi)), & i &= \alpha, \beta, \\ \delta\tilde{c}_i &= k_i \delta\tilde{c}, & i &= \alpha, \beta, \end{aligned} \quad (6.2)$$

where  $\omega$  is the frequency of oscillations, and  $\varphi$  is the phase lag between the oscillations of the composition at the interface and the freezing rate. The phase lag depends on an interplay between the forced oscillations (of frequency  $\omega$ ) and diffusion in the lateral direction. It is also a function of distance  $z$  from the freezing interface,

becoming larger for increasing  $z$ . Here, we consider that  $\varphi$  is constant and equals that at the freezing interface. The reason for this assumption is that the overwhelming part of the contribution to the entropy production comes from the nonequilibrium temperature and composition fields at the interface.

We want to find the contribution to the entropy production by an oscillating composition field and freezing rate, averaged over one period  $2\pi/\omega$  of freezing rate oscillations. In solving the interface composition in the form (6.2), the time-dependent part can be separated from the spatially dependent part. Therefore, the time averaging can be done independently of the evaluation of the integrals calculated in Section 3.4. The contribution to entropy production is for steady state multiplied by a result obtained from time averaging.

### 6.1. Time-averaged contribution from mass transfer, nonequilibrium temperature and finite lead distance

Substituting Eqs. (6.1) and (6.2) into Eqs. (3.2) and (4.1), the contribution from an oscillating freezing rate to the terms in Eq. (5.1) can be expressed as Eq. (5.1) multiplied by  $(\varepsilon^2/2) \cos(\varphi)$ . The same is true for Eq. (5.3), which represents the contribution from the effect of lead distance.

### 6.2. Contribution from interface curvature

In the sharp interface model, changes in morphology cause difficulties in rebuilding the domain used in the numerical calculations. A self-consistent solution for the interface shape in the oscillating regime is not possible since the operating point condition is not known. The minimum entropy production criterion may still be used for cooperative solidification with an oscillating shape of the freezing interface. We do not give here an explicit solution for the evolution of the interface shape. Nevertheless, the conclusions given in this paragraph are believed to be valid since, though they are based on a simplified treatment of the problem, they coincide with the results from our phase-field model of oscillatory eutectic solidification [12].

Following Ref. [13], we choose the  $\alpha$ /liquid and  $\beta$ /liquid interfaces to possess a shape that can be described by a cubic polynomial. Unlike a quadratic polynomial interface, Eq. (3.11), the cubic form contains four parameters that allow us to satisfy four boundary conditions:

- (a) tension force balance at the tri-junction ( $dz/dx = -\tan(\theta)$ );
- (b) zero slope at the center of each lamella ( $dz/dx = 0$ );
- (c)  $z = 0$  at the tri-junction;

(d) a specified lead distance at the center of the lamella with respect to the tri-junction ( $z = d_C$ ). We assume that  $d_C$  is a function of time, and, if the freezing rate oscillates, it evolves according to Fig. 5. This figure shows the shape of  $\alpha$  and the tri-junction region at different times during one period of oscillation.

The angle  $\theta_i$  ( $i = \alpha, \beta$ ) remains unchanged in time, since the tension forces are time independent. In this way, cubic representation for  $\alpha$ /liquid interface shape is

$$z = a'x^3 + b'x^2 + c'x + d', \quad (6.3)$$

where the constants are given by

$$a' = \frac{16d_C - 4 \tan(\theta_\alpha)\zeta\lambda}{\zeta^3\lambda^3}, \quad b' = \frac{-12d_C + 2 \tan(\theta_\alpha)\zeta\lambda}{\zeta^2\lambda^2}, \quad c' = 0, \quad d' = d_C. \quad (6.4)$$

A similar solution can be given for the  $\beta$ /liquid interface shape. The local curvature of the interface is

$$\kappa = -\frac{d^2z/dx^2}{(1 + (dz/dx)^2)^{3/2}}, \quad (6.5)$$

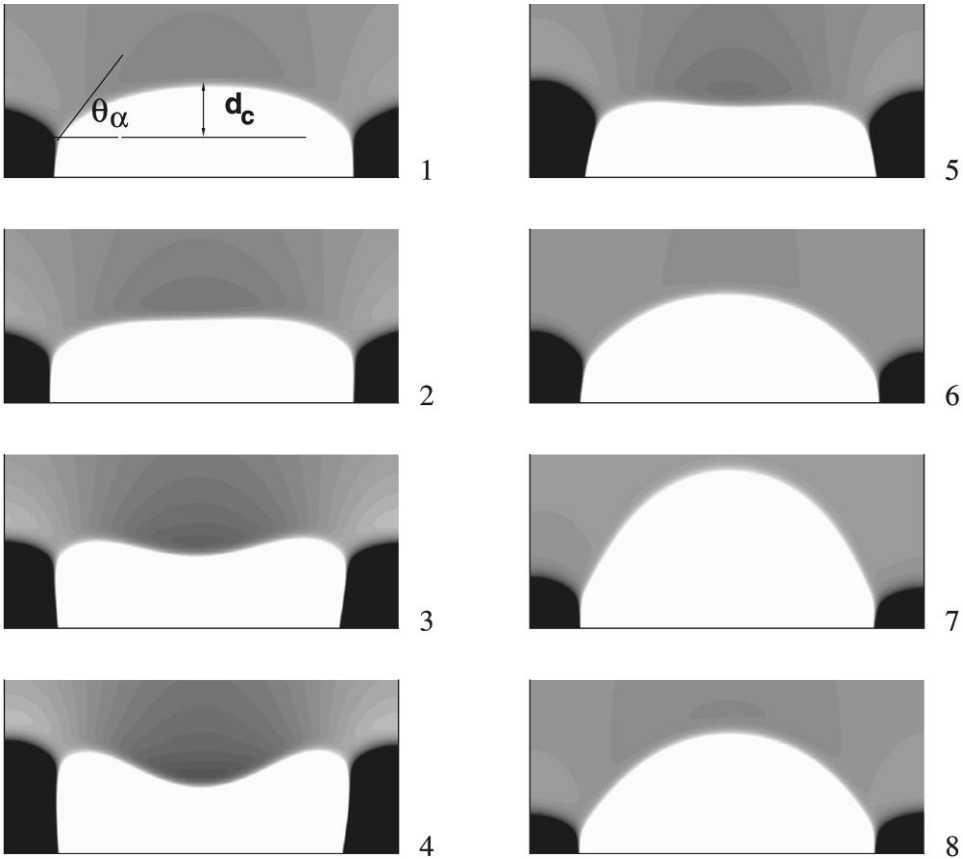


Fig. 5. Evolution of the interface shape when the freezing rate oscillates. The angles at which the phases meet at the tri-junction remain constant during oscillation. The result was obtained using a phase-field approach to oscillatory eutectic solidification [12]. The gray shading ahead of the freezing interface represents the nonequilibrium composition field. Note that the volume fraction changes during oscillations, but this change is not significant with respect to the change in the interface shape. The deep groove in the picture corresponds to the maximum freezing rate, whereas the largest protrusion distance of the white phase in the melt corresponds to the minimum freezing rate.

where a convex interface is assumed to have positive curvature. The average curvature along the  $\alpha$ /liquid interface can be obtained by integrating Eq. (6.5) over the half-width of  $\alpha$  (from  $x = 0$  to  $\zeta\lambda/2$ ):

$$\bar{\kappa} = \sin(\theta_\alpha). \tag{6.6}$$

Note that this is independent of  $d_c$ . This result suggests that, even though the interface shape oscillates, the average interface curvature is time independent. Therefore, an oscillating freezing rate does not change contribution (5.2) to entropy production that is proportional to  $1/\lambda$ , i.e.  $\Delta\delta\tilde{\Theta}(1/\lambda) = 0$ .

### 6.3. Total effect of oscillating freezing rate on entropy production

Consider the steady-state solution for spacing  $\lambda$  given by Eq. (5.4). As shown in Section 6.2, the numerator under the square root is time independent, and, therefore, does not have any dependence on the freezing rate oscillation amplitude  $\varepsilon$  or phase lag  $\varphi$ . The denominator is proportional to  $1 + (\varepsilon^2/2) \cos(\varphi)$ . The stationary

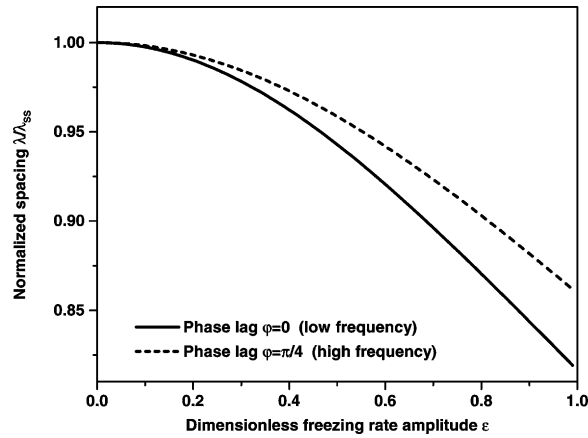


Fig. 6. The decrease in  $\lambda$  as a result of an oscillating freezing rate with dimensionless amplitude  $\varepsilon$ .

periodic solution for  $\lambda$  obtained using the principle of minimum entropy production is

$$\lambda = \lambda_{ss} \frac{\sqrt{2}}{\sqrt{2 + \varepsilon^2 \cos(\varphi)}}, \quad (6.7)$$

where  $\lambda_{ss}$  is the steady-state spacing given by Eq. (5.4). The decrease in spacing  $\lambda$  as a result of an oscillating freezing rate with dimensionless amplitude  $\varepsilon$  is shown in Fig. 6. The two curves are for different phase lags between freezing rate and compositional oscillations. The general trend is to decrease spacing  $\lambda$  by 13–18% for a 100% freezing rate oscillation ( $\varepsilon = 1$ ). Note that backmelting ( $\varepsilon > 1$ ) is not considered here.

## 7. Excess entropy production due to long-wavelength modulation of the freezing interface

The freezing interface becomes unstable if the temperature fluctuations exceed some critical value [14]. The solid then grows into the liquid with an interface modulated on a length scale larger than  $\lambda$ . Such interface instabilities also were obtained in our numerical simulation of unsteady eutectic growth using the phase-field model [12].

Here, we assume the eutectic structure grows with a modulated freezing interface. For eutectic melt solidification, the interfacial material balance requires that at the center of the protruding part of the interface the average composition changes by  $c_k^{(\omega)}$ , whereas at the center of the depressed part of the interface the average composition changes by  $-c_k^{(\omega)}$  (Fig. 7). When the amplitude of freezing rate oscillations increases, the amplitude of the composition oscillations at the protruding parts of the interface increases, whereas it decreases at the depressed parts. The second term in Eq. (5.2) is responsible for excess entropy production due to interface modulation. Though the signs of  $N_\alpha$  and  $N_\beta$  are not known (i.e. they are material dependent), it would give contributions to entropy production with opposite signs for those parts of the interface protruding in the melt and those that are depressed. It is instructive to estimate the value of that term in order to see its effect on the spacing  $\lambda$ . Taking the values from Section 5.1,  $\delta\Theta_k^{(\omega)} \approx 5 \times 10^{-10} c_k^{(\omega)}/\lambda$ , new  $\lambda$  can be found using the values for the other terms from Table 1 for a symmetric eutectic, using Eq. (5.4):

$$\lambda = \sqrt{\frac{1.6 \times 10^{-11} (1/\lambda) (\text{J}/\text{cm}^2 \text{ K s}) \pm 5 \times 10^{-10} (c_k^{(\omega)}/\lambda) (\text{J}/\text{cm}^2 \text{ K s})}{4.5 \times 10^{-5} \lambda (\text{J}/\text{cm}^4 \text{ K s}) + 4.8 \times 10^{-5} \lambda (\text{J}/\text{cm}^4 \text{ K s})}}. \quad (7.1)$$

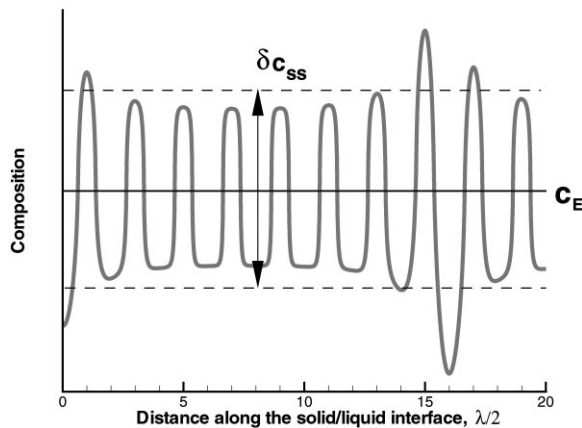


Fig. 7. Composition profile along the modulated freezing interface for a domain  $10\lambda$  in width. The maximum oscillation amplitude corresponds to the parts of the interface protruded into the melt.

Table 3

Effect of the amplitude of the interface modulation (represented by nonequilibrium composition  $c_{\kappa}^{(\omega)}$ ) on the value of steady state  $\lambda$

	$\lambda, 10^{-4} \text{ cm}$			
	$c_{\kappa}^{(\omega)} = 0$ Planar interface	$c_{\kappa}^{(\omega)} = 0.002$	$c_{\kappa}^{(\omega)} = 0.005$	$c_{\kappa}^{(\omega)} = 0.01$
$\lambda_{\max}$	4.15	4.28	4.46	4.75
$\lambda_{\min}$	4.15	4.02	3.81	3.44

Therefore, one predicts different  $\lambda$  for protruded and depressed parts of the interface. The maximum and minimum values of  $\lambda$  for different values of  $c_{\kappa}^{(\omega)}$  are shown in Table 3. Note that if the amplitude of the interface modulation is large, then  $c_{\kappa}^{(\omega)}$  is large and the difference in  $\lambda$  can be significant. This result may explain the experimental results on MnBi–Bi eutectics obtained in Ref. [15], wherein the freezing interface was perturbed by electric current pulses, causing in some places a reduction in  $\lambda$ , in others a breakdown in structure with coarsening.

## 8. Conclusions

Implementation of the principle of minimum entropy production for symmetric eutectics at steady state gave the Jackson–Hunt solution. When one phase leads the other, the deviation of the average interface composition from the equilibrium eutectic composition contributes to the entropy production in a way that increases  $\lambda$ . The larger the difference in volume fractions of the two phases (larger asymmetry), the larger the increase in  $\lambda$ . This result may explain why for faceted/nonfaceted growth when the growth is partially coupled, and large lead distances are observed, cooperative solidification takes place far from the minimum undercooling condition.

Freezing rate oscillations contribute to entropy production via terms proportional to  $\lambda$  and  $\lambda^2$ . The term responsible for the curvature undercooling at the interface, and possessing  $1/\lambda$  proportionality, is time independent, since the average curvature of the interface is time independent. It is predicted that the spacing

$\lambda$  should decrease when freezing rate oscillations are applied in the absence of convection. However, the amount of this decrease in spacing is not significant — only 13–18% for 100% freezing rate oscillations.

Analysis of the contributions to entropy production showed that a modulated eutectic interface shape can also change  $\lambda$ , making it smaller at some parts of the interface, and larger at others.

## Acknowledgements

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