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Abstract

In previous work, we found approximate solutions for paraboloids having perturbations with four-fold axial symmetry in order to model dendritic growth in cubic materials. These solutions provide self-consistent corrections through second order in a shape parameter ϵ to the Peclet number – supercooling relation of the Ivantsov solution. The parameter ϵ is proportional to the amplitude of the four-fold correction to the dendrite shape, as measured from the Ivantsov paraboloid of revolution. We calculate ϵ by comparing the dendrite tip shape to the portion of the equilibrium shape near the growth direction, [001], for anisotropic surface free energy of the form $\gamma = \gamma_0[1 + 4\epsilon_4(n_x^4 + n_y^4 + n_z^4)]$, where the n_i are components of the unit normal of the crystal surface. This comparison results in $\epsilon = -2\epsilon_4$, independent of the Peclet number. From the experimental value of ϵ_4, we find $\epsilon \approx -0.011$, in good agreement with the measured value $\epsilon \approx -0.008$ of LaCombe et al.

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1 Introduction

In a previous paper [1] we calculated the correction to the relationship between the Peclet number P and the dimensionless supercooling, S, for a non-axisymmetric isothermal dendrite growing from a pure supercooled melt. For four-fold axial symmetry, the dendrite shape in cylindrical coordinates (r, ϕ, z) is of the form

$$\frac{z}{\rho} = \frac{1}{2} - \frac{1}{2}\left(\frac{r}{\rho}\right)^2 - \frac{\epsilon}{2}\cos 4\phi\left(\frac{r}{\rho}\right)^4 + \frac{\epsilon^2}{2}\left[\alpha(P)\left(\frac{r}{\rho}\right)^4 + \beta(P)\left(\frac{r}{\rho}\right)^6\right] + O(\epsilon^3), \tag{1}$$

where the shape parameter ϵ represents the amplitude of the four-fold perturbation to the axisymmetric paraboloid, and ρ is the radius of curvature of the dendrite tip. Specifically, $P = V\rho/2\kappa$ and $S = c_V(T_M - T_\infty)/L_V$, where V is the dendrite growth speed, κ is the thermal diffusivity of the melt, c_V is heat capacity per unit volume, L_V is the latent heat per unit volume, T_M is the melting point, and T_∞ is the far-field temperature of the supercooled melt. The corresponding correction to the P–S relation is found to have the form

$$S = Pe^P E_1(P) + \frac{\epsilon^2}{2} S^{(2)}(P) + O(\epsilon^3), \tag{2}$$

The specific dependence of the coefficients α and β, and the correction $S^{(2)}$, on Peclet number are worked out in detail in Ref. [1]. Here, the function E_1 is the exponential integral [2]. For $\epsilon = 0$ this yields the well-known result of Ivantsov [3]. Other researchers have also noted that the first-order term proportional to $r^4 \cos 4\phi$ is consistent with an isothermal solution that has been employed in microscopic solvability theory [4–7].

Based on the experimental measurements of LaCombe et al [8], for succinonitrile (SCN) at $P \approx 0.004$, we estimated a value of $\epsilon \approx -0.008$, with the convention that $\phi = 0$ corresponds to the [100] direction. The corresponding correction to S was about a 9% increase, in general agreement with the experimental results [8–10].

In this paper, we estimate the shape parameter ϵ theoretically on the basis of a simple idea, namely, that the shape of the isothermal but anisotropic dendrite tip is approximately the same as a portion of the equilibrium shape of an isothermal body with slightly anisotropic surface free energy. For a cubic crystal, such as SCN, we assume a surface free energy $\gamma(\hat{\mathbf{n}})$

of the form

$$\gamma = \gamma_0[1 + 4\epsilon_4(n_x^4 + n_y^4 + n_z^4)], \tag{3}$$

where γ_0 and ϵ_4 are constants, and $\hat{\mathbf{n}} = (n_x, n_y, n_z)$ is the unit normal of the crystal surface. This corresponds to the leading order expansion of γ in spherical harmonics compatible with cubic symmetry; the next non-vanishing term is of sixth degree in $\hat{\mathbf{n}}$. In the subsequent analysis, we will assume $|\epsilon_4| \ll 1$ and neglect all higher order contributions of ϵ_4 [11,12]. We note that the equilibrium shape is a closed convex body in a strictly isothermal environment, whereas our dendrite model [1] corresponds to a semi-infinite body with an isothermal surface that is growing from a non-isothermal melt. For small supercoolings, however, we expect the dendrite tip shape to be similar to the *portion* of the equilibrium shape near the growth direction, which is [001] for SCN.

2 Analysis

It is well-known that for small anisotropy, the equilibrium shape is geometrically similar to a polar plot of the surface free energy [12–15]. Thus the equilibrium shape can be written in the form

$$\frac{r_s}{R} = 1 + 4\epsilon_4\left[\cos^4\Theta + \sin^4\Theta\left(\frac{3}{4} + \frac{1}{4}\cos 4\Phi\right)\right] + O(|\epsilon_4|^2), \tag{4}$$

where $\mathbf{r_s}$ is the position vector of the equilibrium shape, $r_s = |\mathbf{r_s}|$, R is a constant scale factor, and Θ and Φ are the spherical angles of the unit normal, so that $\hat{\mathbf{n}} = (\sin\Theta\cos\Phi, \sin\Theta\sin\Phi, \cos\Theta)$. Furthermore, to first order in the anisotropic term, Θ and Φ can be replaced by the angles θ and ϕ that specify the orientation of the vector $\mathbf{r_s}$. Thus a polar plot of the equilibrium shape has the form

$$\frac{r_s(\theta, \phi)}{R} = 1 + 4\epsilon_4\left[\cos^4\theta + \sin^4\theta\left(\frac{3}{4} + \frac{1}{4}\cos 4\phi\right)\right] + O(|\epsilon_4|^2). \tag{5}$$

We proceed to write this expression in terms of cylindrical coordinates to compare with

Eq. (1). Using $r_s = \sqrt{r^2+z^2}$, $\cos\theta = z/\sqrt{r^2+z^2}$ and $\sin\theta = r/\sqrt{r^2+z^2}$, we have

$$\frac{\sqrt{r^2+z^2}}{R} = 1 + \frac{4\epsilon_4}{(r^2+z^2)^2}\left[z^4 + r^4\left(\frac{3}{4}+\frac{1}{4}\cos 4\phi\right)\right] + O(|\epsilon_4|^2). \tag{6}$$

Near the [001] direction, $|r/z| \ll 1$, so we can expand Eq. (6) to obtain

$$\frac{z}{R} = 1 + 4\epsilon_4 - \frac{1}{2}\frac{r^2}{R^2}(1+12\epsilon_4) - \frac{1}{8}\frac{r^4}{R^4}(1-36\epsilon_4) + \epsilon_4\frac{r^4}{R^4}\cos 4\phi + O(|\epsilon_4|^2, (r/R)^6) \tag{7}$$

In order to compare Eqs. (1) and (7), we first recognize that the origin of z is arbitrary, so that the constant terms may be ignored. Multiplication of Eq. (7) by R/ρ and comparison of the term in r^2 with the corresponding term in Eq. (1) shows that $R = \rho(1+12\epsilon_4) + O(|\epsilon_4|^2)$. Then comparison of the terms in $\cos 4\phi$ yields our central result,

$$\epsilon = -2\epsilon_4 + O(|\epsilon_4|^2). \tag{8}$$

We note that the the axisymmetric term proportional to r^4 in Eq. (7) has no counterpart in Eq. (1). This arises because the equilibrium shape is a closed convex body, whereas the dendrite is a semi-infinite body. The closure of this equilibrium shape is described properly by Eqs. (4)–(6), but is lost once one resorts to the expansion in Eq. (7).

3 Discussion

The anisotropy of the surface free energy for SCN has been measured by Glicksman and Singh [11] and Muschol et al. [12], resulting in $\epsilon_4 = 0.0055 \pm 0.0015$, which from Eq. (8) yields $\epsilon = -0.011 \pm 0.003$. This compares favorably with the direct measurements of LaCombe et al. [8] which result in $\epsilon \approx -0.008$. Note, however, that the experimental determination of ϵ is based on measurements of the dendrite shape for distances of up to ten tip radii from the tip, whereas our comparison to the equilibrium shape is only valid within a fraction of a tip radius from the tip. Another theoretical estimate of ϵ has been made by Brener et al. [6, 7] based on microscopic solvability theory, and, in our notation, results in $|\epsilon| = 1/48 \approx 0.02$, which is about a factor of two larger than the experimental value. Their result is independent of ϵ_4.

By means of numerical computations based on a phase-field model, Karma and Rappel [16] calculated a shape anisotropy for $S = 0.45$ and an effective surface free energy anisotropy of 0.0066, resulting in $|\epsilon| = 0.019$, close to the value of Brener et al. Karma and Rappel find that $|\epsilon|$ increases for larger values of the effective anisotropy.

A value of $\epsilon_4 = 0.025$ has been measured for pivalic acid [12]. This anisotropy is about five times larger than that of SCN. No measurements of the actual shape anisotropy are yet available, but we caution that this value of ϵ_4 might be too large for our expansion to be valid. One could, however, extend the equilibrium shape to higher order in ϵ_4, which would also delineate the range of validity of the linear expansion.

Note that the value of ϵ given by Eq. (8) is independent of the Peclet number P. This is supported by preliminary measurements by LaCombe [17] over a limited range of supercoolings. Accordingly, in Fig. 1 we plot the value of S from Eq. (2) for $\epsilon = -0.008$. For the smaller values of P in the figure, our corrections to S are too large for our expansion in ϵ to be valid, resulting in a nearly vertical curve near $P = 0.001$. In the range $0.004 < P < 0.01$, our results resemble the experimental values measured by Koss et al., which also lie slightly below the Ivantsov curve (see Fig. 6 of Ref. [9]). For P much below 0.004, the experimental data actually lie above the Ivantsov curve, possibly due to the effects of finite container size and/or convection [18, 19]. Thus, the effects of non-axisymmetry versus those due to finite container sizes and/or convection tend to affect S in an opposing manner.

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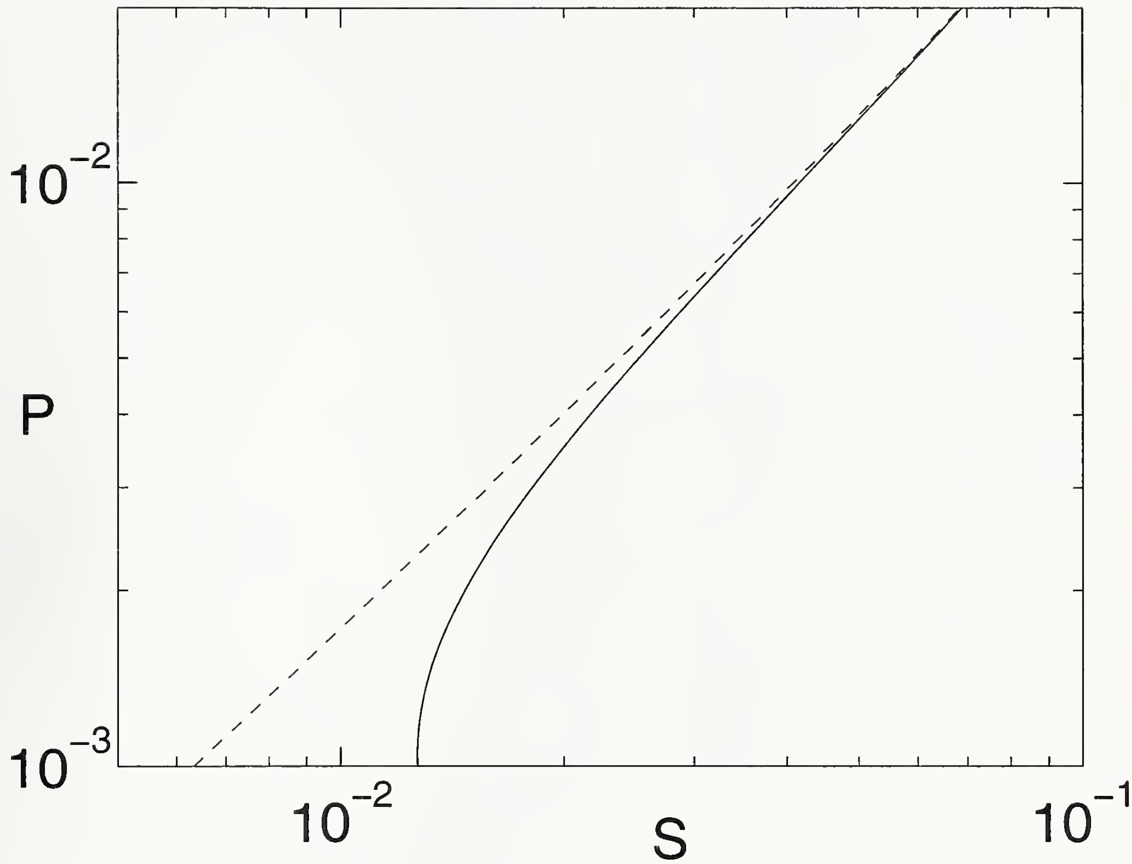

Figure 1: The Peclet number P as a function of dimensionless supercooling S for shape parameter $\epsilon = -0.008$ (solid curve) and $\epsilon = 0$ (dashed curve); the dashed curve corresponds to the Ivantsov solution.