Dendritic growth during liquid to solid phase transitions

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Some of the current controversial interpretations of dendritic growth data, including the recent space shuttle experimental data, have been reviewed here. Theoretical estimates of the tip temperatures of high purity succinonitrile dendrites, based on the space shuttle growth data, suggest a heretofore unsuspected influence of dendritic sidebranching effects on the tip itself. This has been neglected in all of the current theoretical analyses of dendritic growth. A simple method of investigating dendritic sidebranching effects is also described here. [S1063-651X(98)10102-2]

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I. INTRODUCTION AND BACKGROUND

In many natural and commercially important solidification processes, the solid phase that grows into the liquid develops a very complex, highly branched, treelike morphology, called a dendrite [1–8]. This structure often has a paraboloidal tip, which advances at a fixed rate R into the liquid. Ivantsov's famous solution to the heat diffusion limited growth of a branchless paraboloid of revolution [1], and/or various modifications of this solution, have therefore been used, quite extensively, over the last 50 years, as a useful starting point to interpret the growth kinetics of the dendritic structure [2–16]. All of these models essentially assume that the diffusion fields surrounding the tips of the rather complex, irregularly shaped, dendritic structures can be characterized by the Ivantsov diffusion fields.

The validity of this rather widely held viewpoint has been questioned in two recent papers by Laxmanan [17,18]. Also, it should be noted that the space shuttle experiments of Glicksman and co-workers [19], and the earth-based experiments of Bisang and Bilgram [20], have now clearly established that the dendrite tip region is far from being a perfect paraboloid of revolution. Indeed, in directional solidification experiments, the dendrite tip shape deviates from the perfect paraboloidal shape, within a very short distance behind the tip, as shown by Esaka [6]. Furthermore, other recent experiments [21] indicate that the concentration field surrounding the dendrite tip does not resemble the diffusion field around an isolated Ivantsovian paraboloid. Hence, a more general approach to the dendrite problem is needed, as also emphasized in Ref. [17].

Unfortunately, rather than challenge the basic premise of dendrite≡paraboloid, the popular view is that any deviations from the theoretical predictions, based on Ivantsov's solution, or simple modifications of this solution, signify the dominance of gravitational convective effects [2–4]. This view continues to be held even after the space shuttle experiments with succinonitrile. Indeed, efforts are now under way to reexamine the effect of the ''residual'' natural convection in the space environment [22], and also include other vanishingly small effects such as flows due to liquid-solid shrinkage [23] and ''wall'' effects [24,25]. These analyses are again aimed at modifying the Ivantsov solution, and so continue to neglect the importance of dendritic sidebranching effects. The heat and matter liberated by the dendritic sidebranches must surely diffuse through the liquid, and affect the tip regions of the dendrite.

This tip diffusion problem is admittedly very difficult to solve, rigorously, and has naturally been overlooked in favor of other, more mathematically tractable, analyses of the dendritic growth data. The potential importance of including sidebranching effects in the theoretical analysis [2,26–30], in a systematic manner, was also recognized by Glicksman and co-workers, and Langer and Müller-Krumbhaar (LM-K). Nevertheless, the theoretical focus during most of the 1980s and the 1990s has been on developing a detailed understanding of the influence of anisotropies in the surface energy and interfacial kinetic attachment effects, with attempts being made to calculate the interface shape as a part of the solution. These led to the development of the microscopic solvability theories [4,7,8,30,31], and the phase-field models [32,33]. However, as noted by Glicksman and Marsh (see [4], pp. 1107 and 1111), these theoretical approaches have not been very successful in explaining the large body of dendritic growth data that has been accumulated over the last two decades.

II. THE TIP TEMPERATURE OF A FREELY GROWING DENDRITE

New insights into any problem, such as the dendrite problem on hand, can only be obtained by analyzing the experimental data thoroughly, and considering *all of the implications* of the theory, especially when critical, and carefully planned, experiments appear to disagree with a well-established theoretical model; see, for example, the discussion by Hoffmann [34]. Hence, as a first step, we will reanalyze the space shuttle dendritic growth data of Glicksman and co-workers, within the context of the Ivantsov paraboloidal approximation for a dendrite. The calculations presented here illustrate the fundamental importance of including dendritic sidebranching effects, in a systematic manner, in the theoretical analysis.

Elementary physical considerations suggest that the dendrite tip temperature (T_t) must always be less than the equilibrium melting point (MP) of the liquid in which it is growing. However, it is not immediately obvious what T_t should be. This depends on both the growth rate (R) and the tip radius (r_t), and is given by Eq. (1) or (3) below. Other physical considerations, embodied in Eq. (2), also enter into the calculation of the tip temperature. Unfortunately, this important dendritic state variable has, thus far, been completely overlooked [2,3,26,27,35].

For example, the early efforts of Glicksman, Schaefer, and Ayers [2,26] were focused on an understanding of the growth-rate–supercooling behavior. However, a replotting of their 1976 raw data on a R-r_t diagram reveals the now well-known LM-K finding of $Rr_t^2 \cong \text{const}$ [27,28]. The complete R-r_t plot, for a fixed supercooling, see Refs. [27,35], also provides some new insights into the (R,r_t) selection mechanism in a given experiment. On such a plot, the experimental point lies in the region where the R-r_t curves predicted by most theories, based on the branchless paraboloidal approximation, begin to merge (see Fig. 1 of LM-K or the various plots provided by Doherty, Cantor, and Fairs, Ref. [35]). Hence, it is generally believed that dendritic sidebranching effects can be neglected, at least as a first approximation, in favor of a more rigorous attempt at estimating the dimensionless parameter σ^*. This parameter (i.e., $\sigma^* = 2\alpha_L d_0/Rr_t^2$) was identified in the stability analysis of LM-K. The above also provides some insights into the fundamental motivation for including the anisotropies in the surface energy and interfacial attachment kinetics. As noted by Glicksman and Marsh ([4], p. 1102), the modern attempts to determine σ^*, rigorously, represent the single largest collective theoretical effort expended to date to understand dendritic crystallization. (Here d_0 is the capillary length scale and α_L is the thermal diffusivity of the liquid.)

However, while addressing the tip selection problem, it was not recognized, until very recently [17], that each one of the *fictitious* dendrites, among the infinite manifold of (R,r_t) values predicted by heat flow theories [26,30,36–39], will have a different tip temperature. The (hypothetical) maximum velocity (MV) dendrite, with a sharp tip radius, also has a very low tip temperature, or equivalently a high ''tip undercooling.'' This MV dendrite, or ''highly undercooled'' dendrite, is not observed experimentally. The experimental dendrite has a large tip radius, and a much lower growth rate, and so also has a much lower tip undercooling [3]. The ''tip undercooling'' is the depression in T_t below the equilibrium MP of the material.

With the availability of the space shuttle dendritic growth data, it is now possible to obtain some very reliable estimates of T_t. It would appear that purely diffusive conditions, such as visualized in deriving Ivantsov's solution, should prevail in these truly remarkable experiments. Thus one can estimate T_t (see Fig. 3), *without invoking any ad hoc assumptions* regarding the growth mechanism, directly from Eq. (1).

$$T_t = T_\infty + (L_v/C_{pl}) I(p_t). \tag{1}$$

Here T_∞ is the far-field temperature of the supercooled bath, $p_t = Rr_t/2\alpha_L$ is the thermal Péclet number, and the function $\phi_t = p_t \exp(p_t) E_1(p_t)$ is now called the Ivantsov function. L_v, C_{pl}, and α_L are, respectively, the latent heat of fusion, specific heat, and thermal diffusivity of the liquid. $E_1(p_t)$ is the exponential integral function. The tip temperature determined from Eq. (1), which is obtained from heat flow considerations, must also be consistent with the tip temperature obtained by invoking ''local'' thermodynamic equilibrium at the tip, and then allowing for the kinetic effect. This leads to the tip temperature given by Eq. (2).

$$T_t = T_M + m_L C_t - 2\Gamma T_M/r_t - R/\mu. \tag{2}$$

Here T_M is the equilibrium melting point of the pure material, m_L is the slope of the equilibrium liquidus line on the phase diagram (considering a binary alloy, for simplicity), and C_t is the liquid composition in equilibrium with the tip. $\Gamma = \gamma/L_v$ is the capillary length, γ being the surface energy of the solid-liquid interface, and μ is the interfacial kinetic attachment coefficient. The intersection point of the graphs of Eqs. (1) and (2) gives the desired solution to the ''free'' dendritic growth problem in a pure or alloy melt. Ivantsov circumvents any discussion of the unknown tip temperature by assuming $T_t = T_M$. In other words, Ivantsov assumes that growth occurs in a supercooled pure melt, with zero impurities ($C_t \to C_0 \to 0$), with a zero surface energy effect ($\Gamma \to 0$ or $r_t \gg \Gamma$), and with infinitely rapid interfacial mobilities ($\mu \to \infty$).

In the space shuttle experiments, as well as in the control experiments on the ground, Glicksman and co-workers determined R, r_t (from direct photographic observations of the growth process), and T_∞, very accurately. These data are now available on the Isothermal Dendrite Growth Experiment (IDGE) Home Page [40], along with estimates of the measurement errors. There is no uncertainty regarding the material properties, at least for high purity succinonitrile [2–4,26]. Also, the equilibrium MP has been determined with a great deal of precision [41,42]. Hence, if the Ivantsov diffusion model truly describes the dendritic structure, Eq. (1) should yield ''reasonable'' values for T_t, as in a directional solidification experiment [6–8,43]. Specifically, one would expect the T_t values to be *less than* the equilibrium MP, and to decrease with increasing R, or supercoolings. The now widely accepted value for the equilibrium MP of high purity succinonitrile is 331.24 K [3,5,6,41,42,44].

III. THE TIP TEMPERATURE FOR DENDRITES GROWING IN MICROGRAVITY

Figures 1 and 2 illustrate the $T_t - r_t$ behavior for two microgravity (μ-g) experiments, and the corresponding earth-based (1-g) experiment. These represent the highest and lowest supercoolings, for which both R and r_t data are available, with the supercooling being nearly the same in 1-g and μ-g. In Fig. 1 we consider an experiment with a relatively large supercooling, 0.783 K, and the 1-g experiment with a supercooling of 0.775 K. In Fig. 2, we consider a space experiment with a relatively low supercooling, 0.103 K. The supercooling in the corresponding 1-g experiment was 0.102 K. The growth rate R was assumed to be equal to the experimental value in preparing these plots. The heat flow result in Eq. (1) indicates that the tip temperature will increase as the tip radius increases, for a fixed value of R. Hence, for a very large tip radius, the tip temperature can, theoretically speaking, exceed the equilibrium MP. The theoretical maximum tip temperature will be equal to $T_\infty + (L_v/C_{pl})$, corresponding to the limit of $r_t \to \infty$ for which $\phi_t \to 1$.

However, physical considerations dictate that T_t be less

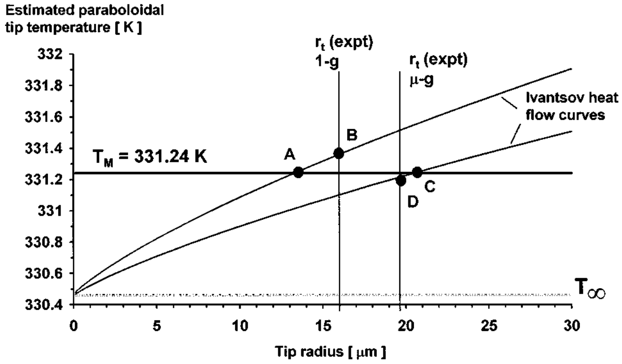

FIG. 1. Analysis of the tip temperature behavior for one of the microgravity experiments with high purity succinonitrile, and the corresponding ground-based experiment. The intersection of the heat flow curves with the horizontal line, representing the equilibrium MP, represents the maximum value of the tip radius, in the Ivantsov limit of zero impurities and infinitely rapid interfacial mobilities. The significance of points A, B, C, and D is discussed in the text.

than T_M, or in the limit be exactly equal to T_M. This Ivantsov limit is indicated by points A and C, which denote the intersection point of Eqs. (1) and (2) for the 1-g and μ-g experiments. The horizontal line is the equilibrium MP of high purity succinonitrile, i.e., the graph of Eq. (2) in the Ivantsov limit. For the 1-g experiment, the tip radius (point A) is significantly less than the experimental tip radius. An exact match with both R and r_t is obtained at point B, but the tip temperature at B is greater than the equilibrium MP. For the space experiment, the tip radius at point D (Fig. 1) is quite close to the experimental value, with the tip temperature being slightly less than the equilibrium melting point. However, for the space experiment at the lower supercooling (Fig. 2), the tip temperatures predicted at point D, where the tip radius is equal to the experimental value, is higher than the equilibrium melting point.

Figure 3 summarizes the T_t values estimated in this fashion for the space dendrites, in the regime of low supercoolings, where other discrepancies between theory and experiment have already been noted by Glicksman *et al.* *[36,37]*. Also indicated here is the MP determined during the USMP-3 flight. This higher MP is not consistent with the lower purity levels (99.999%) reported by LaCombe *et al.* [19], compared to the purity levels (99.99995%) reported earlier by Huang and Glicksman [3]. The reason for the higher MP is not clear, and will be overlooked, for the moment.

A more detailed discussion of the tip temperature behavior in the space, and the corresponding terrestrial, experiments may be found in Refs. [45–47]. Various modifications of the Ivantsov solution, and their effect on the tip temperatures, have also been considered here.

While the anticipated trends in T_t are observed in Fig. 3 (in spite of the large scatter, the tip temperature seems to decrease with increasing supercooling, or R), the absolute value of T_t exceeds the equilibrium MP at low supercoolings. It is tempting to follow conventional arguments, and attribute this discrepancy to ''residual'' gravity effects (even at $\sim 10^{-6} g_e$), or other secondary phenomena such as the wall proximity effect, liquid-solid density change, or the de-

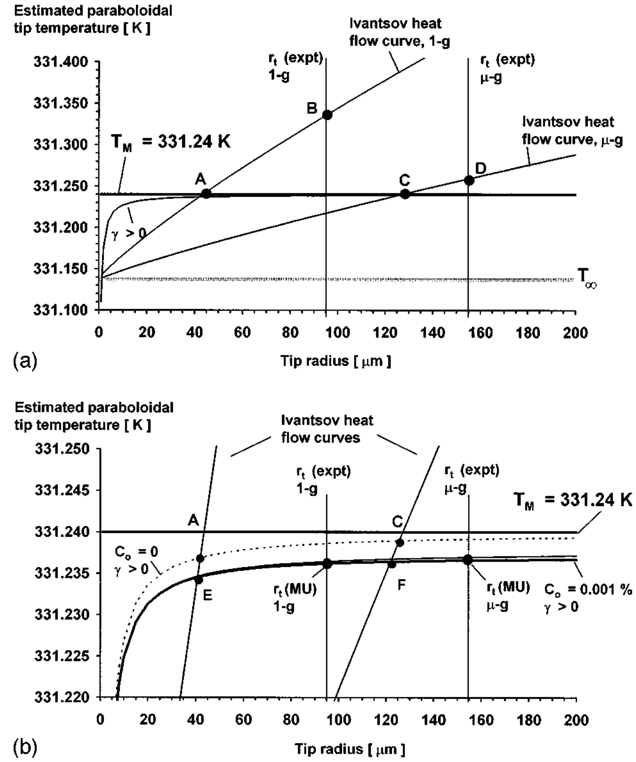

FIG. 2. (a) Analysis of the tip temperature behavior for a microgravity experiment, with a supercooling of 0.103 K, and a 1-g experiment with a supercooling of 0.102 K. The growth rate is assumed to be equal to the experimental value in preparing these plots. $R = 1.16\,\mu$m/sec for the space experiment and $R = 3.41\,\mu$m/sec for the 1-g experiment. The significance of points A, B, C, and D has been discussed in the text. (b) An expanded tip temperature scale for the experiments in (a). The effect of a finite surface energy and a finite impurity, $C_0 = 0.001\%$, is considered here. This produces a slightly sharper tip (points E and F, versus points A and C). The experimental tip radius in both 1-g and μ-g falls in the flat region of the tip undercooling curve, after accounting for the surface energy and the impurity effect, and has a ''minimum'' undercooling.

tails of the surface energy and interfacial kinetic attachment effect [22–25,30–32,36,37]. Instead, it is suggested that we carefully explore other tacit assumptions that have been made in deriving Ivantsov's result in Eq. (1).

The assumption that needs to be reexamined, immediately, is the assumption that the diffusion field surrounding the tip of a real dendrite is identical to the diffusion field surrounding an isolated, branchless, paraboloid. Ivantsov himself speculates about this in a 1956 paper [1], and suggests a verification of his solution by determining the surface temperature of a paraboloidal shaped crystal. Almost 40 years after this suggestion was made, and even after the elegant space shuttle experiments, no serious attempts have yet been made to determine the tip temperature, or the surface temperature, of a *freely growing dendrite.* Of course, within a short distance behind the tip, dendritic sidebranching changes the diffusion field from that calculated by Ivantsov. This has been confirmed by Emsellem and Tabeling [21]. Using a direct and noninvasive technique, they have shown that the isoconcentrates surrounding the tip of an ammonium bromide dendrite, growing in a viscous gel (thus minimizing

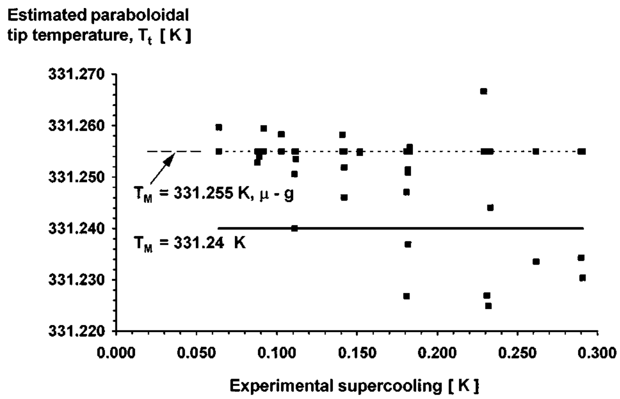

FIG. 3. The tip temperature behavior for the microgravity experiments (USMP-2, STS 62), based on the Ivantsov heat flow solution. The estimated tip temperatures exceed the currently accepted equilibrium MP of high purity succinonitrile, 331.24 K, in a large majority of these experiments. This discrepancy can be resolved if the equilibrium MP has the higher value of 331.255 K, as determined in the second flight (USMP-3). However, this higher MP would also imply a higher tip undercooling in the space experiment, and is also inconsistent with the lower purity level reported by LaCombe *et al.* for the material used in the space experiments.

convection), are not perfectly confocal paraboloids. The isoconcentrates are distorted because of the mass flux generated by the sidebranches. Likewise, Ananth and Gill [22], based on their analysis of the space shuttle dendritic growth data, have also concluded that the sidebranch structure must affect the heat transfer from the tip itself. The dendrite shape deviates from the paraboloidal shape within a short distance behind the tips, and theoretical relations, derived on the basis of the paraboloidal approximation for the dendrite shape, must clearly be at the root of the currently observed discrepancies between theory and experiment.
However, rather surprisingly, in all of the references cited here, no attempts have been made to include the tip temperature in the analysis. Even Pines, Chait, and Zlatkowski [48], who present a very general scaling analysis, based on the Buckingham Pi theorem (from the science of fluid mechanics), overlook T_t. This should be included as an important state variable in such an analysis.

IV. THE HEAT FLUX GENERATED BY THE DENDRITIC SIDEBRANCHES

Discrepancies in the estimated T_t values, similar to that revealed in Fig. 3, are also observed with the earth-based growth data of Huang and Glicksman (all 16 experimental points yield a tip temperature that is too high), the IDGE ground-based data (at *all* supercoolings), and the growth data in other materials such as xenon, pivalic acid, and binary succinonitrile-acetone solutions. In each case, the T_t values calculated on the basis of Eq. (1) exceed the equilibrium MP, *especially at low supercoolings*. The T_t estimates for xenon are almost 30 K to 50 K higher than the equilibrium MP, based on the current best estimates of the thermophysical properties of this substance.

From Figs. 1 and 2, it is clear that the space shuttle dendritic growth data can be rationalized on the basis of the ''minimum undercooling'' principle [17,18], i.e., the dendrite tip temperature rises to its maximum permissible value, consistent with the requirements of heat (and mass) diffusion, surface energy, and interfacial kinetic attachment effects. Note that when impurity effects are included, as in Fig. 2(b) the graph of Eq. (2) reveals a mathematical maximum point. The intersection of Eq. (1) with the graph of Eq. (2), around this maximum point, represents a ''minimum undercooled'' state. Even the high purity succinonitrile of Glicksman *et al.* can be treated as an extremely dilute alloy, as discussed in Refs. [49, 50]. The material used in the space shuttle experiment had an impurity content of $C_0 = 0.001\%$, see LaCombe *et al.* [19], whereas the ultrahigh purity material used in the Huang and Glicksman experiments had an impurity content of $C_0 = 5\times10^{-5}$ mole %.

Thus it appears that the dendrite problem can be solved, as discussed in Ref. [17], by circumventing the difficult task of finding solutions to the complicated partial differential equations that describe the transport processes around the paraboloidal shaped tip. It is also clear that a unique tip radius is obtained, even in the limit of zero surface tension and infinitely rapid interfacial attachment kinetics (points *A* and *C* of Fig. 1), if one properly accounts for the tip temperature of the ''freely'' growing dendrite or paraboloid. In this sense, the current analysis is in agreement with the recent analyses by Spencer and Huppert [51,52] which also reveal a unique tip radius in the zero surface tension limit. Spencer and Huppert have, however, considered the growth an array, rather than an isolated dendrite. The ''effective'' tip undercooling for an individual dendrite tip in the array is lower than that for the isolated Ivantsov paraboloid. Hence the predicted tip temperatures would be higher than that for the isolated dendrite. In the limit as the spacings in the array become very large, the Spencer-Huppert analysis yields the results obtained for the Ivantsov paraboloid. Hence it is likely that the Spencer-Huppert analysis, if tested critically with the space shuttle growth data, would also reveal the difficulties noted in Figs. 1–3 here.

The simple model proposed almost a decade ago by Laxmanan [17,39], which includes a side-branching (adjustable) parameter λ_t, can be shown to yield a satisfactory prediction of R, r_t, and T_t, in both the 1-g and the space experiments [48]. Sidebranching effects can also be treated, within the context of the paraboloidal approximation, by considering growth of the paraboloid within a second confocal paraboloid, as was done by Pines, Chait, and Zlatkowski and Sekerka, Coriell, and McFadden [24,25]. This second paraboloid may also be interpreted as an ''envelope'' which contains many dendritic side-branches. The heat flux generated by the sidebranches is contained within this ''envelope,'' and raises the temperature in the immediate vicinity of the tips. This is exactly the scenario visualized by LM-K to explain the systematic deviations between their predictions, based on the marginal stability hypothesis, and the classical 1976 dendritic growth data of Glicksman, Schaefer, and Ayers [2]. The interactions, or ''merging,'' of the long-range diffusion field from the sidebranches, suggest the notion of an ''effective tip radius'' that should enter into the energy balance calculations. Alternatively, one may assume that the heat flux generated by the sidebranches affects the thermal gradient at the tip and hence the tip temperature and the heat flux (q) dissipated from the tip, as follows:

$$T_t = T_\infty + (L_v / C_{pl})(1-\chi_t)\phi_t \quad (3)$$

and

$$G_{L(\text{tip})} = -(T_t - T_\infty)/(1-\chi_t)\phi_t, \quad (4)$$

where

$$\chi_t = E_1(p_t \alpha_B^2)/E_1(p_t), \quad (5)$$

giving

$$\lambda_t = (1-\chi_t)\phi_t / 2p_t \quad (6)$$

and

$$q = -k_L G_{L(\text{tip})} = k_L(T_t - T_\infty)/(1-\chi_t)\phi_t \quad (7)$$

$$\text{Nu} = hr_t / k_L = 1/\lambda_t . \quad (8)$$

Equations (3)–(5) can be deduced from the results given by Cantor and Vogel [53], Pines, Chait, and Zlatkowski [24], and Sekerka, Coriell, and McFadden [25]. Nu is the ''local'' value of the heat transfer Nusselt number at the tip [22]. The adjustable parameters of Pines, Chait, and Zlatkowski ($\alpha_B^2 = \Omega$) and Sekerka, Coriell, and McFadden, $\delta = (r_t/2)(\alpha_B^2 - 1)$ are clearly related to χ_t, and hence the sidebranching parameter λ_t. The thermal boundary layer δ_t as defined by Laxmanan is the same as δ' of Eckert and Drake [54]. Thus $\delta_t < \delta$. Also, unlike δ, the diffusion length scale δ_t, or δ', can be determined unambiguously, by solving the relevant transport equations and determining the gradient at the interface. Hence we can generalize the result in Eqs. (7) and (8) to the more complex dendritic case, by simply treating λ_t as an adjustable parameter, rather than using the values obtained by solving the relevant differential equations around some simple geometric shape, such as a paraboloid (or a sphere, ellipsoid, hyperboloid, sinusoid, Saffman-Taylor viscous finger, etc.).

The heat flux generated by sidebranching could also be modeled within the context of the phase-field theories by reinterpreting the significance of the ''diffuse interface'' in such models. This ''diffuse,'' or ''mushy region'' (see Wheeler in [33], p. 698), is analogous to the boundary layer in the analyses of Cantor and Vogel, Pines, Chait, and Zlatkowski and Sekerka, Coriell and McFadden. Within this ''mushy'' interface the enthalpy (or the free energy) can be varied continuously from the value for a pure liquid to that for a liquid plus solid mixture (i.e., sidebranches), and finally to the full solid. A unique solution that is also consistent with global conservation laws should thus be obtained. Invoking the global energy constraint (and, likewise, the mass balance), should remove the only remaining uncertainty in the problem, with regard to the exact value of λ_t.

In this context, a review of the discussions by Hoffmann [34], Aharoni [55], Jefferys and Berger [56], and Horgan [57] is also highly recommended. Each one of these authors has shed some light on the larger issues surrounding the subject at hand. How do we analyze this difficult problem in the simplest possible terms? What is the underlying mechanism governing the growth of this complex structure? Are there new fundamental secrets that the ubiquitous dendrite or snowflake is trying to reveal to us, from up above the sky so high, in the microgravity environment aboard the space shuttle? It appears that beneath all of this complexity also lies a new, and thus far unrecognized, natural constant of the dendritic growth process, the chemical version of the sidebranching parameter, denoted by the symbol λ [18,58,59]. To rephrase a quip from the final paragraph of Horgan's essay, with the recognition of the fundamental importance of the tip temperature, and sidebranching effects, the dendrite problem may be moving ''from perplexity to simplicity.'' Only time will tell, if there are any heads nodding today at this suggestion.

V. SUMMARY AND CONCLUSIONS

(1) The heat (and mass) flux generated by the dendritic sidebranches has been neglected in all of the current theories for dendritic growth, starting with the well-known Ivantsov solution for an isolated paraboloid of revolution. The Ivantsov model thus leads to a fundamentally erroneous estimate for the dendrite tip temperature. The dendritic growth data from the space shuttle experiments indicate that, at low supercoolings, the theoretically estimated tip temperatures are greater than the equilibrium MP of high purity succinonitrile.

(2) The simple model proposed earlier by Laxmanan is shown here to account for the heat flux generated by the dendritic sidebranches. This model is also compared to the stagnant boundary layer model of Cantor and Vogel, Pines, Chait, and Zlatkowski, and Sekerka, Coriell, and McFadden, as well as the phase-field models that have generated a lot of interest in recent years. Such a comparison also suggests a simple method of investigating sidebranching effects in greater detail within the context of the phase-field models.

(3) Global conservation laws must be incorporated into the phase-field, or boundary layer models, to obtain an accurate prediction of the growth kinetics. It is suggested that introducing this global constraint will also eliminate the need for any *ad hoc* assumptions in the theory, i.e., adjustable parameters such as those invoked by Laxmanan, Pines, Chait, and Zlatkowski, and Sekerka, Coriell, and McFadden.

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