IMA Journal of Applied Mathematics (1987) **39**, 1–15

Existence and Stability for Spherical Crystals Growing in a Supersaturated Solution

J. CHADAM

Indiana University, Bloomington, Indiana, USA and *McMaster University, Hamilton, Ontario, Canada*

S. D. HOWISON

Mathematical Institute, 24–29 *St Giles, Oxford* OX1 3LB

AND

P. ORTOLEVA

Indiana University, Bloomington, Indiana, USA

[Received 28 July 1986]

We consider the growth of a spherical crystal in a supersaturated solution. In the first part, existence and uniqueness results for radially symmetric growth are obtained, provided that the supersaturation is not too large; conversely, when the far-field supersaturation exceeds a critical value, it is shown that the radially symmetric solution ceases to exist in finite time. In the second part, we examine the linear stability of a radially symmetric similarity solution (in which the radius grows as $t^{\frac{1}{2}}$) to shape perturbations. The results are compared with previous quasi-static analyses, and, in particular, the critical radius at which the crystal becomes unstable is found to be larger for small supersaturations, but smaller for large supersaturations, than those predicted by the quasi-static analysis.

1. Introduction

IN THIS paper, we study the growth of an amorphous solid from a diffusing growth material which surrounds it (for example, a precipitate particle growing from a supersaturated solute). Our mathematical model is similar to the classic Mullins–Sekerka model [1, 2] (cf., in addition, the excellent review article of Langer [3] and the references therein), but does not impose the quasi-steady-state assumption whereby the diffusion equation is replaced by Laplace's equation. Specifically, if c is the concentration of the solute and the solid–solute interface is $S(\boldsymbol{x}, t) = 0$, then the problem is to find these two quantities subject to

$$c_t = D\Delta c \quad \text{in } \{S(\boldsymbol{x}, t) > 0\}, \tag{1.1a}$$

$$c = c_{\text{eq}}[1 + \gamma\kappa(S)] \quad \text{on } \{S(\boldsymbol{x}, t) = 0\}, \tag{1.1b}$$

$$D\frac{\partial c}{\partial n} = (\rho - c)V_n \quad \text{on } \{S(\boldsymbol{x}, t) = 0\}, \tag{1.1c}$$

$$c \to c_\infty \quad \text{as } |\boldsymbol{x}| \to \infty, \tag{1.1d}$$

$$c(\boldsymbol{x}, 0) = c_0(\boldsymbol{x}) \quad \text{in } \{S(\boldsymbol{x}, 0) = S_0(\boldsymbol{x}) > 0\}, \tag{1.1e}$$

for given initial functions $c_0(\boldsymbol{x})$ and $S_0(\boldsymbol{x})$. Here, ρ is the density of the solid, c_{eq} is the equilibrium concentration on a planar interface, c_∞ is the ambient concentration far from the solid, and $\boldsymbol{n}$ is the normal to $S(\boldsymbol{x}, t) = 0$. The function $\kappa(S)$ is the mean curvature of the surface $S = 0$, and $\gamma \geq 0$ is a measure of the interfacial energy. That is, the equilibrium concentration on $S = 0$ is given by the Gibbs–Thompson relation. Lastly, we shall take $D = 1$ by rescaling distance with a typical length L and time with L^2/D.

Problem (1.1) is a generalization of the classical one-phase Stefan problem [4–7] in that it includes the nonlinear function $\kappa(S)$ in (1.1b) and that $\rho - c$ in (1.1c) is not constant (which would result from assuming $\rho \gg c$). The most important difference, however, is that we will study growing solutions of problem (1.1) rather than the shrinking ones associated with melting problems. This is the basis for the instabilities which we will later analyse. In Section 2, we shall study spherically symmetric versions of problem (1.1) along the same lines as previous treatments of the planar version [8, 9]. In particular, we shall examine the existence and uniqueness questions of global (in time) solutions. If the ratio $(c_\infty - c_{eq})(\rho - c_{eq})^{-1}$ (a measure of the supersaturation) is positive (corresponding to growing solutions) and sufficiently small, we prove an existence and uniqueness result and establish $\sqrt{t}$ growth bounds on the radius of the expanding solid. An explicit similarity solution (in the variable $r/2\sqrt{t}$, where $r = |\boldsymbol{x}|$) is given which has the same growth bounds and is unique for each $0 \leq (c_\infty - c_{eq})(\rho - c_{eq})^{-1} < 1$. Section 2 is concluded by showing that these restrictions on the size of $(c_\infty - c_{eq})(\rho - c_{eq})^{-1}$ were not merely an inadequacy of the methods. We show that if the ratio is larger than one, then the solution for growing spheres will blow up in finite time.

In Section 3 we study the shape stability of spherical solutions to small harmonic perturbations. We postulate that the $r/2\sqrt{t}$ similarity solution is marginally stable among all spherical solutions with a given value of $(c_\infty - c_{eq})(\rho - c_{eq})^{-1}$. (A similar result was proved in the planar case [7].) As expected from physical principles, and demonstrated by Mullins and Sekerka [1, 2] in the quasi-steady-state diffusion model, we show that all spherical harmonics (Y_{lm}-modes, for $l \geq 2$) are always linearly unstable if surface tension is not included (i.e. $\gamma = 0$). Further, the quasi-steady-state diffusion growth rate $t^{\frac{1}{2}(l-1)}$ of the perturbations is obtained in the present case. In the quasi-steady-state model, the inclusion of surface tension (i.e. $\gamma > 0$) reduces this growth rate, and indeed stabilizes the spherical growth while the radius is sufficiently small, although all perturbations eventually grow again when the radius is sufficiently large. The radius at which any Y_{lm}-mode stops decaying and starts growing is termed the *critical radius* for that mode; it increases with l.

In the full diffusion model, we have more freedom in that we must prescribe $c_0(\boldsymbol{x})$ (equation (1.1e)) as well as $S_0(\boldsymbol{x})$. We find a class of similarity solutions to the linearly perturbed problem which have 'sensible' initial data and which are comparable to those used by Mullins & Sekerka in the quasi-steady-state limit. These solutions also have a critical radius for each Y_{lm}-mode, which is found to be *smaller* than the corresponding quasi-steady-state value, for all l, when the crystal is growing very fast (c_∞ is nearly equal to ρ) and, for a slowly growing crystal, when $l = 2$ (the most unstable mode); conversely, the present critical radius is *larger* than the Mullins–Sekerka radius for the slowly growing crystal for all $l > 2$.

2. Spherical solutions: existence and uniqueness

With $S(\boldsymbol{x}, t) = r - R(t)$, the spherical version of equations (1.1) with $D = 1$ is

$$c_t = r^{-2}(r^2 c_r)_r \qquad (r > R(t)), \tag{2.1a}$$

$$c = c_{eq}[1 + 2\gamma/R(t)] \qquad (r = R(t)), \tag{2.1b}$$

$$c_r = (\rho - c)\dot{R}(t) \qquad (r = R(t)), \tag{2.1c}$$

$$c \to c_\infty \qquad (r \to \infty), \tag{2.1d}$$

$$c_0(r, 0) = c_0(r) \qquad (r \geq R(0) = R_0). \tag{2.1e}$$

We begin by noting that a similarity solution in the variable $\xi = r/2\sqrt{t}$ can be computed explicitly, using standard methods [4: p. 23; 10: pp. 50–51; 11, 12]. Indeed, denoting this special solution with an overbar,

$$\bar{R}(t) = \beta t^{\frac{1}{2}}, \tag{2.2}$$

$$\bar{c}(r, t) = A\zeta_0(\xi) + B\bar{\zeta}_0(\xi) + t^{-\frac{1}{2}}[C\zeta_{-1}(\xi) + D\bar{\zeta}_{-1}(\xi)], \tag{2.3}$$

where ζ_p and $\bar{\zeta}_p$ are linearly independent solutions of

$$\zeta'' + 2(\xi^{-1} + \xi)\zeta' - 2p\zeta = 0.$$

One finds [10: pp. 50–51] that it is convenient to write

$$\zeta_0(\xi) = \xi^{-1}\int_\xi^\infty \operatorname{erfc}\tau \, d\tau, \qquad \zeta_{-1}(\xi) = \xi^{-1}\operatorname{erfc}\xi, \tag{2.4a,b}$$

$$\bar{\zeta}_0(\xi) = \zeta_0(-\xi), \qquad \bar{\zeta}_{-1}(\xi) = \zeta_{-1}(-\xi), \tag{2.4c,d}$$

so that the constants A, B, C, D, β can be computed explicitly from the interface and asymptotic conditions (2.1b–d). Since the explicit form of $\bar{c}(r, t)$ is never required in what follows, we only write down the equation which determines β:

$$f(\beta) := \frac{\beta^2}{2}\left(1 - \beta e^{\beta^2/4}\int_{\beta/2}^\infty e^{-\tau^2}\, d\tau\right) = \frac{c_\infty - c_{eq}}{\rho - c_{eq}}. \tag{2.5}$$

Thus β depends on the single parameter

$$\alpha = (c_\infty - c_{eq})/(\rho - c_{eq}); \tag{2.6}$$

in a metallurgical context, α would be the dimensionless undercooling [1], while, for crystal growth, α represents the supersaturation.

The function f defined in (2.5) is monotonically increasing on $[0, \infty]$, with $f(0) = 0$ and $f(\infty) = 1$ (this can be proved using the continued fraction expansion [13: 7.1.14, p. 298] for $e^{y^2}\int_y^\infty e^{-\tau^2}\, d\tau$). Thus, for positive values of the ratio

$(c_\infty - c_{eq})(\rho - c_{eq})^{-1}$, we obtain a solution, growing like $\beta t^{\frac{1}{2}}$, with β the unique solution of (2.5), provided that

$$0 \leq \alpha < 1. \tag{2.7}$$

While (as we mentioned) the precise form of $c(r, t)$ is not required, it is interesting to note that it arises from the physically most simple initial condition

$$\bar{c}(r, 0) = c_\infty + \text{const} \cdot c_{eq}\gamma/r;$$

i.e., when $\gamma = 0$, c is initially constant and equal to the ambient concentration.*

Having observed that the above special solution restricts the size of α, it is not surprising that similar, more restrictive conditions will be necessary to prove existence for all time of solutions to problem (2.1) for arbitrary data $c_0(r)$ and $R(0) = R_0$.

The method to be used is an extension of the integral equation technique used by Rubinstein [4] and later by Friedman [14–16]. Indeed, since the problem defined by equations (2.1) has so many features in common with the two problems studied in [15, 16], and, since the proof of existence and uniqueness here is a straightforward combination of the proofs there, we shall omit all the details and content ourselves with an outline of the proof. The result is contained in the following theorem.

THEOREM 2.1 *Let $c(r, t)$ satisfy equations* (2.1) *with the additional assumptions*

(a) $c_\infty > c_{eq}(1 + 2\gamma/R_0)$; (b) $\rho > c_{eq}(1 + 2\gamma/R_0)$;
(c) $c(r, 0) = c_0(r)$ *must be such that* $r^2[c_\infty - c_0(r)] \in L^1(R_0, \infty) \cap L^\infty(R_0, \infty)$ *and* $c_{eq}(1 + 2\gamma/R_0) = c_0(R_0) \leq c_0(r) \leq c_\infty$;
(d) $\alpha \geq 0$.

Then there is a number $\alpha_0 > 0$ such that the solution to equations (2.1) *exists for all t provided that $0 \leq \alpha < \alpha_0$. Moreover, there exists a positive constant A such that, for sufficiently large t, $[2\alpha/(1-\alpha)]^{\frac{1}{2}}[t^{\frac{1}{2}} + o(t^{\frac{1}{2}})] \leq R(t) < At^{\frac{1}{2}}$.*

Outline of proof. We introduce a new variable $u(r, t) = r[c_\infty - c(r, t)]/(c_\infty - c_{eq})$. Then u satisfies

$$u_t = u_{rr} \qquad (R(t) < r < \infty), \tag{2.8a}$$

$$u = R(t) - \bar{\gamma} \qquad (r = R(t)), \tag{2.8b}$$

$$\alpha u_r = \alpha - R\dot{R} + \alpha\bar{\gamma}(\dot{R} - 1/R) \quad (r = R(t)), \tag{2.8c}$$

with $u(r, 0) = u_0(r) \geq 0$, where $u_0(r) \to 0$ as $r \to \infty$, and where

$$u_0(R_0) = R_0 - \bar{\gamma}, \qquad \bar{\gamma} = \frac{2\gamma c_{eq}}{c_\infty - c_{eq}}, \qquad \dot{R} = \frac{dR}{dt}.$$

The first stage is to reformulate the problem for $u(r, t)$ as an integral equation for

* See note added in proof.

$\bar{v}(t) = t^{\frac{1}{2}}u_r(R(t), t)$. This is achieved by introducing the kernel

$$K(r, t; \xi, \tau) = \frac{1}{2\pi^{\frac{1}{2}}(t-\tau)^{\frac{1}{2}}} \exp\left(\frac{-(r-\xi)^2}{4(t-\tau)}\right)$$

and integrating the relation

$$\frac{\partial}{\partial \xi}(Ku_\xi - uK_\xi) - \frac{\partial}{\partial \tau}(Ku) = 0$$

over the region $\{0 < \tau < t, R(\tau) < \xi < \infty\}$, to give

$$u(r, t) = \int_0^t \{K(r, t; R(\tau), \tau)[u(R(\tau), \tau)\dot{R}(\tau) + u_r(R(\tau), \tau)] - u(R(\tau), \tau)K_\xi(r, t; R(\tau), \tau)\} \, d\tau + \int_{R_0}^\infty K(r, t; \xi, 0)u_0(\xi) \, d\xi. \quad (2.9)$$

Letting $r \to R(\tau)$, and after some manipulation (including a correct treatment of the singularity at $t = \tau$, details of which are given in [14]), we obtain the equation

$$\begin{aligned}\bar{v}(t) = &-2(R_0 - \bar{\gamma})t^{\frac{1}{2}}K(R(t), t; R_0, 0) \\ &+ 2\int_{R_0}^\infty t^{\frac{1}{2}}K_r(R(t); t; \xi, 0)u_0(\xi) \, d\xi \\ &- 2\alpha\int_0^t t^{\frac{1}{2}}K(R(t), t; R(\tau), \tau)\frac{d\tau}{R(\tau) - \alpha\bar{\gamma}} \\ &+ 2\alpha\int_0^t t^{\frac{1}{2}}K(R(t), t; R(\tau), \tau)\frac{\bar{v}(\tau)\, d\tau}{\tau^{\frac{1}{2}}[R(\tau) - \alpha\bar{\gamma}]} \\ &- 2\int_0^t t^{\frac{1}{2}}K_r(R(t), t; R(\tau), \tau)\frac{\bar{v}(\tau)\, d\tau}{\tau^{\frac{1}{2}}} \\ &+ 2\alpha\bar{\gamma}\int_0^t t^{\frac{1}{2}}K(R(t), t; R(\tau), \tau)\frac{d\tau}{R(\tau)[R(\tau) - \alpha\bar{\gamma}]},\end{aligned} \quad (2.10)$$

where, from (2.8c), $\dot{R}(t) = [-\alpha\bar{v}t^{-\frac{1}{2}} - \alpha\bar{\gamma}/R(t) + \alpha]/[R(t) - \alpha\bar{\gamma}]$. The right-hand side of (2.10) can be thought of as a transformation of $\bar{v}$ denoted by $\bar{T}\bar{v}$. Clearly from (2.9) knowledge of $\bar{v}(t)$ and $R(t)$ gives us $u(r, t)$.

Let $C_{\sigma,m}$ be the space of functions $t \mapsto \bar{v}(t)$ that are continuous for $0 \leq t \leq \sigma$, with norm $\|\bar{v}\| = \sup_{0 \leq t \leq \sigma}|\bar{v}(t)| \leq m$. The first stage of the proof establishes existence for small times by showing that T defined by equation (2.10) maps $C_{\sigma,m}$ into itself and is a contraction for some positive m and sufficiently small α and $\sigma > 0$. This is achieved by proving a series of lemmas (analogous to the results of [15: §§ 3.1, 3.2] and [16: §3]) which establish bounds on the terms for the r.h.s. of (2.10), and for $R(t)$, with the result that there exist α_0, σ_0, and M such that, if $0 \leq \alpha < \alpha_0$ and $0 \leq \sigma \leq \sigma_0$, then $\|\bar{T}\bar{v}\| < \|\bar{v}\|$. The operator $\bar{T}$ is thus a contraction, and its unique fixed point in $C_{\sigma,m}$ is the solution of (2.10).

The global existence result now follows by a continuation argument, provided that we can show that $R(t)$ is bounded for $t>0$; in order to do this, we must show that $\dot{R}\geqslant 0$ in the interval of existence.

LEMMA 2.1 *Under the conditions of Theorem* (2.1), $\dot{R}(t)\geqslant 0$.

Proof. Letting $w=c-c_{eq}\,(1+2\gamma/R_0)$, one finds that

$$w_t=\Delta w \qquad (r>R(t)), \tag{2.11a}$$

$$w=2\gamma c_{eq}[1/R(t)-1/R_0] \qquad (r=R(t)), \tag{2.11b}$$

$$w_r=[\rho-c_{eq}-2\gamma c_{eq}/R(t)]\dot{R} \qquad (r=R(t)), \tag{2.11c}$$

$$w\to c_\infty-c_{eq}(1+2\gamma/R_0) \qquad (r\to\infty). \tag{2.11d}$$

Because $c_0(r)\geqslant c_0(R_0)$ (by assumption), we have that

$$w_r(R_0)=(\rho-c_{eq}-2\gamma c_{eq}/R_0)\dot{R}(0)>0.$$

Since $\rho>c_{eq}(1+2\gamma/R_0)$, then $\rho-c_{eq}-2\gamma c_{eq}/R_0>0$, giving that $\dot{R}(0)>0$. But $\dot{R}(t)$ is continuous so that $\dot{R}(t)>0$ in some interval $0\leqslant t\leqslant\lambda$. We now show that this interval can be enlarged by means of an argument which is independent of λ. Thus the procedure can be repeated to fill the interval of existence. Letting $\xi=r-R(t)$ and $\tau=t$ one obtains

$$w_\tau=\Delta w+\dot{R}(\tau)w_\xi \qquad (\xi>0) \tag{2.12a}$$

$$w=2\gamma c_{eq}[1/R(\tau)-1/R_0] \qquad (\xi=0) \tag{2.12b}$$

$$w_\xi=[\rho-c_{eq}-2\gamma c_{eq}/R(\tau)]\dot{R}(\tau) \qquad (\xi=0) \tag{2.12c}$$

$$w\to c_\infty-c_{eq}[1+2\gamma/R(\tau)] \qquad (\xi\to\infty) \tag{2.12d}$$

The problem has been transformed to one with fixed boundaries, at the expense of a term $\dot{R}(\tau)w_\xi$ in (2.12a) that does not affect the maximum principle. In particular, since $0=w(0,0)<w(y,0)$, the strong maximum principle implies that $w(0,\tau)<w(\xi,\tau)$ for $\xi>0$ and $0\leqslant\tau\leqslant\lambda$. Thus, $w(0,\lambda)<w(\xi,\lambda)$ for all $\xi>0$, which gives

$$0<w_\xi(0,\lambda)=[\rho-c_{eq}-2c_{eq}\gamma/R(\lambda)]\dot{R}(\lambda).$$

But $R(\lambda)>R_0$ ensures that $[\rho-c_{eq}-2c_{eq}\gamma/R(\lambda)]>(\rho-c_{eq}-2\gamma c_{eq}/R_0)>0$, so that $\dot{R}(\lambda)>0$. Again, continuity of $\dot{R}$ allows the enlargement of the interval where $\dot{R}>0$ and the proof is complete.

Boundedness of R is now achieved by integrating the equation $u_{\xi\xi}=u_\tau$ over the region $\{0<\tau<t,\ R(t)<\xi<K\}$ (where $K>R_0$) to obtain

$$t-[R^2(t)-R_0^2](1-\alpha)/2\alpha$$
$$=\int_{R_0}^{K}u_0(\xi)\,d\xi+\int_0^t u_r(K,\tau)\,d\tau+\int_0^t\bar{\gamma}\frac{d\tau}{R(\tau)}-\int_{R(t)}^{K}u(\xi,t)\,d\xi. \tag{2.13}$$

We now use (2.10) to estimate $I=\int_{R(t)+H}^{K}|u(\xi,t)|\,d\xi$ where $H=H_0t^{\frac{1}{4}}$ and H_0 is a constant at our disposal. We will then write $\int_R^K$ as $\int_R^{R+H}+\int_{R+H}^K$ in the last term of (2.13) and let $K\to\infty$ in order to obtain an inequality showing that $R(t)$ is bounded for finite t. This procedure is analogous to that of [15: §5] and [16: §6]. After some manipulation we obtain the result that, as $K\to\infty$,

$$I \leq c_0 + c_1 t^{\frac{1}{2}}[R(t)-\bar{\gamma}] + c_2 t(1+\bar{\gamma}/R_0) + c_3 R^2(t)/\alpha,$$

where c_1, c_2, and c_3 tend to zero as $H_0\to\infty$. Noting also that, by the maximum principle, $|u(\xi,t)| \leq \max\{\|u_0\|, R(t)-\bar{\gamma}\}$ and so

$$\int_{R(t)}^{R(t)+H} |u(r,t)|\,dr \leq H_0 t^{\frac{1}{2}}[\|u_0\| + R(t)-\bar{\gamma}],$$

we finally obtain

$$|t-\tfrac{1}{2}(\alpha^{-1}-1)[R^2(t)-R_0^2]| \leq c_0 + t^{\frac{1}{2}}\{c_1[R(t)-\bar{\gamma}] + H_0[\|u_0\|+R(t)-\bar{\gamma}]\} + c_2 t\left(1+\frac{\bar{\gamma}}{R_0}\right) + \bar{\gamma}\int_0^t \frac{d\tau}{R(\tau)} + c_3\frac{R^2(t)}{\alpha},$$

which establishes the boundedness of $R(t)$. The bound $R(t) < At^{\frac{1}{2}}$ (for all sufficiently large t) also follows from this equation by choosing H_0 sufficiently large.

Lastly, we show that $R^2(t) > [2\alpha/(1-\alpha)][t+o(t)]$ as $t\to\infty$. Observe that, since $u(r,t)\geq 0$ by the maximum principle, then the right-hand side of (2.13) is less than $\int_{R_0}^{\infty} u_0(r)\,dr$. Noting also that

$$\int_0^t \frac{\bar{\gamma}\,d\tau}{R(\tau)} < \frac{\bar{\gamma}t}{R_0}$$

(since $R(t) > R_0$), we obtain from (2.13) (as $K\to\infty$)

$$R^2(t) - R_0^2 \geq \frac{2\alpha}{1-\alpha}\left[t\left(1-\frac{\bar{\gamma}}{R_0}\right) - \int_{R_0}^{\infty} u_0(r)\,dr\right], \tag{2.14}$$

and the existence of $A_1 \geq 0$ with $R(t) > A_1 t^{\frac{1}{2}}$ for large t follows immediately. This, in turn, means that

$$\int_0^t \frac{\bar{\gamma}\,d\tau}{R(\tau)} \leq 2\bar{\gamma}t^{\frac{1}{2}}A_1 + o(t^{\frac{1}{2}})$$

as $t\to\infty$, and returning to (2.13) we have $R^2(t) \geq [2a/(1-\alpha)][t+o(t)]$ as $t\to\infty$. (Note that, for small α, equation (2.5) also gives $R^2(t) = \beta^2 t \sim 2\alpha t$.)

We have thus shown that if α is small and positive, the solution for a growing crystal exists for all time.

The methods outlined here can also be used to treat the case of a shrinking crystal with $\rho > c_{eq}(1+2\gamma/R_0)$ still but now $c_{eq}(1+2\gamma/R_0) \geq c_0(r) \geq c_\infty$; some modifications must be made to the final stage, to take account of the possibility that $R(t)\to 0$ in finite time, and we shall not pursue this question here. We now show that for larger positive values of α, specifically, for $\alpha > 1$, the solution blows up after finite time. Thus the restrictions on α in Theorem 2.1 and especially in the special solution (2.2, 3) are not merely deficiencies of the methods.

THEOREM 2.2 *With the assumptions of Theorem* 2.1 *and, in addition,* $c_\infty > \rho$ (*i.e.* $\alpha = (c_\infty - c_{eq})(\rho - c_{eq})^{-1} > 1$), *the solution of equations* (2.1) *exists for only a finite time.*

Proof. Integrating (2.8a) over the region $\{R(\tau) < \xi < \infty : 0 < \tau < t\}$ and using (2.8b,c) one has

$$\int_{R_0}^{\infty} u_0(\xi)\,d\xi + \int_{\infty}^{R(t)} u(\xi, t)\,d\xi - \int_0^t \left(1 - \frac{\bar{\gamma}}{R} - \alpha^{-1}R\dot{R} + \bar{\gamma}\dot{R}\right) d\tau + \int_0^t (R - \bar{\gamma})\dot{R}\,d\tau = 0$$

which can be reduced to

$$\tfrac{1}{2}(1 - \alpha^{-1})[R^2(t) - R_0^2] = \int_{R_0}^{\infty} u_0(\xi)\,d\xi - \int_{R(t)}^{\infty} u(\xi, t)\,d\xi + \int_0^t \left(\frac{\bar{\gamma}}{R} - 1\right) d\tau. \quad (2.15)$$

Because of the assumed rate of convergence of $c_0(r) - c_\infty$ as $r \to \infty$, the first term on the right of (2.15) (denoted by A) is finite while the second is negative. Moreover, $R(t) \geq R_0$, so that

$$\int_0^t \left(\frac{\bar{\gamma}}{R} - 1\right) d\tau \leq \left(\frac{\bar{\gamma}}{R_0} - 1\right) t.$$

Thus $\tfrac{1}{2}(1 - \alpha^{-1})[R^2(t) - R_0^2] \leq A + (\bar{\gamma}/R_0^{-1})t$ and, because $1 - \alpha^{-1} \geq 0$, we have

$$R(t)^2 < R_0^2 + 2(1 - \alpha^{-1})^{-1}[A + (\bar{\gamma}/R_0 - 1)t]. \quad (2.16)$$

But $\gamma/R_0 - 1 < 0$ by assumption (a) of Theorem 2.1, and hence we have a contradiction after a finite time t^*. It follows that the solution cannot exist for $t > t^*$ (indeed it may even blow up for some $t < t^*$). A similar result for a one-dimensional Stefan problem in a finite region and without surface energy was established by Sherman [17].

3. Linearized stability of spherical solutions

We assume that a global spherical solution with arbitrary data (as discussed in Theorem 2.1) asymptotically is bounded close to the special solution with the same value of α. More precisely, if $r = R(t)$ is the position of the interface of the solution, there exist constants $a_1, a_2 \geq 0$ such that, as $t \to \infty$,

$$a_1 < R(t) - \beta t^{\frac{1}{2}} < a_2,$$

where β is given by (2.5). The growth estimates proved in Theorem 2.1 suggest this but do not give the precise values of β. We do not obtain these more precise bounds here, as we have done in the planar case [8], but rather assume them to be true in order to carry out the stability analysis which is more in the mainstream of our purpose.

With this ansatz in order to study the shape stability of any global spherical solution with arbitrary data, it suffices to study the stability of the limiting special solution (2.2), (2.3), (2.5) with the same value of α.

In spherical polar coordinates (r, θ, ϕ) we write

$$c_\varepsilon(r, \theta, \phi, t) = \bar{c}(r, t) + \varepsilon c(r, \theta, \phi, t) + O(\varepsilon^2), \tag{3.1a}$$

$$R_\varepsilon(\theta, \phi, t) = \bar{R}(t) + \varepsilon R(\theta, \phi, t) + O(\varepsilon^2); \tag{3.1b}$$

with ε small, the linearized (first variational) equations for $c(r, \theta, \phi, t)$, $R(\theta, \phi, t)$ are

$$c_t = \Delta c \qquad (r > \bar{R}(t)), \tag{3.2a}$$

$$c = -\left(\rho - c_{eq} - 2\frac{c_{eq}\gamma}{\bar{R}}\right)\dot{\bar{R}}R + c_{eq}\gamma\kappa_1 \qquad (r = \bar{R}(t)), \tag{3.2b}$$

$$c_r = -R\frac{\partial^2\bar{c}}{\partial r^2} + \left[\rho - c_{eq}\left(1 + \frac{2\gamma}{\bar{R}}\right)\right]\dot{R} - c_{eq}\gamma\dot{\bar{R}}\kappa_1 \qquad (r = \bar{R}(t)), \tag{3.2c}$$

in which $2/\bar{R} + \varepsilon\kappa_1 + O(\varepsilon^2)$ is the curvature of the surface $r = R_\varepsilon(\theta, \phi, t)$; also

$$c \to 0 \qquad (r \to \infty) \tag{3.2d}$$

$$c(r, \theta, \phi, t_0) = c_0(r, \theta, \phi) \qquad (r > \bar{R}(t_0)) \tag{3.2e}$$

where the initial data $c_0(r, \theta, \phi)$ and $R(\theta, \phi, t_0) = R_0(\theta, \phi)$ are given.

We now seek solutions to these linear equations of the form

$$c(r, \theta, \phi, t) = c_l(r, t)\mathrm{Y}_{lm}(\theta, \phi) \tag{3.3a}$$

$$R(\theta, \phi, t) = \delta_l(t)\mathrm{Y}_{lm}(\theta, \phi) \tag{3.3b}$$

where, as usual, the amplitudes do not depend on m, and equations (3.2) become

$$\frac{\partial c_l}{\partial t} = \frac{\partial^2 c_l}{\partial r^2} + \frac{2}{r}\frac{\partial c_l}{\partial r} - \frac{l(l+1)c}{r^2} \qquad (r > \beta t^{\frac{1}{2}}), \tag{3.4a}$$

$$c_l = \left(-\frac{\rho - c_{eq}}{2}\beta t^{-\frac{1}{2}} + \frac{c_{eq}\gamma}{\beta^2}[(l+2)(l-1) + \beta^2]t^{-1}\right)\delta_l(t) \qquad (r = \beta t^{\frac{1}{2}}), \tag{3.4b}$$

$$\frac{\partial c_l}{\partial r} = \left[\frac{\rho - c_{eq}}{2}\left(\frac{\beta^2}{2} + 2\right)t^{-1} - \frac{c_{eq}\gamma}{2\beta}[\beta^2 + (l+2)(l-1) + 2]t^{-\frac{3}{2}}\right]\delta_l(t)$$
$$+ \left((\rho - c_{eq}) - \frac{2c_{eq}\gamma}{\beta}t^{-\frac{1}{2}}\right)\dot{\delta}_l(t) \qquad (r = \beta t^{\frac{1}{2}}) \tag{3.4c}$$

along with the asymptotic and initial conditions.

At this stage we could follow Wey *et al.* [18] and consider the local stability analysis of (3.4) in which all the coefficients are frozen temporally; by considering initial data $c(r, \theta, \phi, t_0) = Ar^{-(l+1)}\mathrm{Y}_{lm}(\theta, \phi)$ related to the corresponding quasi-steady-state analysis, results similar to those of Mullins & Sekerka [1, 2] can be obtained. Instead we present a class of similarity solutions to the linearized solutions to the problem (3.4) which, being intrinsically diffusive in nature, cannot necessarily be expected to reduce precisely to the Mullins & Sekerka results (which can be obtained by first letting $D \to \infty$ in (1.1)). This reflects the fact that initial data for c must be specified for our parabolic problem, whereas such data are implicit in the elliptic quasi-steady-state case once the perturbed free boundary is prescribed. We thereby seek to generalize the results of Mullins & Sekerka to the case when diffusive effects are included; our initial data has been chosen so that diffusive length scales are necessarily important.

We begin by noticing that equation (3.4a) has solutions of the form

$$c_l(r, t) = t^{p/2}\zeta_{l,p}(r/2t^{\frac{1}{2}}) \tag{3.5}$$

where $\zeta_{l,p}(\xi)$ satisfies

$$\zeta'' + 2(\xi^{-1} + \xi)\zeta' - \left[2p + \frac{l(l+1)}{\xi^2}\right]\zeta = 0. \tag{3.6}$$

The linearly independent solutions of (3.6) can be expressed in terms of Whittaker functions [19: §16.12, p. 339]:

$$\zeta_{l,p}(\xi) = e^{-\frac{1}{2}\xi^2}\xi^{-\frac{3}{2}}W_{-\frac{1}{2}p-\frac{3}{4},\frac{1}{2}l+\frac{1}{4}}(\xi^2), \tag{3.7a}$$

$$\xi_{l,p}(\xi) = e^{-\frac{1}{2}\xi^2}\xi^{-\frac{3}{2}}W_{-\frac{1}{2}p-\frac{3}{4},\frac{1}{2}l+\frac{1}{4}}(-\xi^2), \tag{3.7b}$$

but it is sufficient for our purposes to note that the first has an integral representation

$$\zeta_{l,p}(\xi) = e^{-\xi^2}\xi^{-(p+3)}\int_0^\infty t^{\frac{1}{2}(l+p+1)}(1+\xi^{-2}t)^{\frac{1}{2}(l-p-2)}e^{-t}\,dt, \tag{3.8}$$

which follows from that in reference [19: p. 340]. For $p \leqslant l-2$, it is clear from (3.8) that

$$\zeta_{l,p}(\xi) \sim O(\xi^{-(l+1)}) \quad \text{as } \xi \to 0, \tag{3.9a}$$

$$\zeta_{l,p}(\xi) \sim O(e^{-\xi^2}\xi^{-(p+3)}) \quad \text{as } \xi \to \infty, \tag{3.9b}$$

and from the asymptotic behaviour of the Whittaker functions [19: §§16.3–16.4, pp. 342–3] that

$$\xi_{l,p}(\xi) \sim O(\xi^p) \quad \text{as } \xi \to \infty. \tag{3.10}$$

Motivated by the special solution (2.2)–(2.3) to the spherical equation, we first look for solutions of the form

$$\delta_l(t) = dt^{(p+1)/2}, \tag{3.11a}$$

$$\begin{aligned} c_l(r, t) = {} & t^{p/2}[A\zeta_{l,p}(r/2t^{\frac{1}{2}}) + B\xi_{l,p}(r/2t^{\frac{1}{2}})] \\ & + t^{(p-1)/2}[C\zeta_{l,p-1}(r/2t^{\frac{1}{2}}) + D\xi_{l,p-1}(r/2t^{\frac{1}{2}})]. \end{aligned} \tag{3.11b}$$

The interface conditions (3.4b,c) then impose the following conditions on the coefficients A, B, C, D:

$$A\zeta_{l,p} + B\xi_{l,p} = -\tfrac{1}{2}(\rho - c_{eq})\beta d, \tag{3.12a}$$

$$A\zeta'_{l,p} + B\xi'_{l,p} = \tfrac{1}{2}(\rho - c_{eq})[\beta^2 + 2(p+3)]d, \tag{3.12b}$$

$$C\zeta_{l,p-1} + D\xi_{l,p-1} = \frac{c_{eq}\gamma}{\beta^2}[\beta^2 + (l+2)(l-1)]d, \tag{3.12c}$$

$$C\zeta'_{l,p-1} + D\xi'_{l,p-1} = -\frac{c_{eq}\gamma}{\beta}[\beta^2 + (l+2)(l-1) + 2(p+2)]d, \tag{3.12d}$$

where $\zeta_{l,p} = \zeta_{l,p}(\beta/2)$ etc. Clearly, when $\gamma = 0$ one has $C = D = 0$. In order to obtain the (presumably maximum) Mullins–Sekerka expansion rate for solutions without surface tension, $t^{(l-1)/2}$, we must take $p = l-2$ in (3.11a). But from (3.8) we find that

$$\zeta_{l,l-2}(\xi) = \text{const} \cdot e^{-\xi^2}\xi^{-(l+1)} \tag{3.13}$$

which implies in (3.12a,b) that $B = 0$. In summary, we have shown the following result.

PROPOSITION 3.1 *For $\gamma = 0$ (no surface energy) there are solutions of the linearized equations* (3.4) *of the form*

$$\delta_l(t) = dt^{(l-1)/2}, \tag{3.14a}$$

$$c_l(r, t) = At^{(l-2)/2}\zeta_{l,l-2}(r/2t^{\frac{1}{2}}) \tag{3.14b}$$

where $A = A(\beta, d)$ and $\zeta_{l,l-2}$ is given by (3.13).

It was fortuitous that $B = 0$, because, setting $p = l-2$, $\xi_{l,l-2}(\xi) \sim O(\xi^{(l-2)})$ as $\xi \to \infty$, which is never of finite mass (that is, $\int_R^\infty \xi^2 \xi_{l,l-2}(\xi)\, d\xi = \infty$), and hence would have to be excluded on physical grounds. On the other hand, when $\gamma \neq 0$, then also $D \neq 0$, because

$$\frac{\zeta'_{l,l-3}(\xi)}{\zeta_{l,l-3}(\xi)} \neq -2\xi\frac{4\xi^2 + (l+2)(l-1) + 2l}{4\xi^2 + (l+2)(l-1)},$$

which is straightforward to verify. Thus, to see how the solution (3.14) is modified by the inclusion of surface tension, we are forced to look for solutions of the form

$$\begin{aligned} c_l(r, t) = {} & t^{(l-2)/2}A_1\zeta_{l,l-2}(r/2t^{\frac{1}{2}}) + t^{(l-3)/2}A_2\zeta_{l,l-3}(r/2t^{\frac{1}{2}}) \\ & + t^{(l-4)/2}A_3\zeta_{l,l-4}(r/2t^{\frac{1}{2}}) + \cdots \\ & + t^{-4/2}[A_{l+5}\zeta_{l,-4}(r/2t^{\frac{1}{2}}) + B\xi_{l,-4}(r/2t^{\frac{1}{2}})], \end{aligned} \tag{3.15a}$$

where the sum ends with $\xi_{l,-4}(r/2t^{\frac{1}{2}})$, because it is the first tilded solution which has finite mass. To balance (3.15a) in the interface condition, we must choose

$$\delta_l(t) = d_0t^{(l-1)/2} + d_1t^{(l-2)/2} + \cdots + d_{l+1}t^{-2/2}, \tag{3.15b}$$

and we find the following recursion formula for the coefficients of $\delta_l(t)$ (those in $c_l(r, t)$ can also be found, but are unnecessary for what follows). For $i = 1, \ldots, l+1$,

$$d_i = \frac{2c_{eq}\gamma}{\beta^2(\rho - c_{eq})}\frac{\beta(\beta^2 + l^2 + 3l - 2i)\zeta_{l,l-2-i} + [\beta^2 + (l-1)(l+2)]\zeta'_{l,l-2-i}}{[\beta^2 + 2(l+1-i)]\zeta_{l,l-2-i} + \beta\zeta'_{l,l-2-i}}d_{i-1}. \tag{3.16}$$

In summary, we have the following result.

PROPOSITION 3.2 *For $\gamma \neq 0$, there exists a solution of equations* (3.4) *of the form* (3.15), *where the coefficients in the amplitude $\delta_l(t)$ of the perturbation are given by* (3.16).

The coefficients d_i are too complicated to compute explicitly for all β. Instead, we examine them in the limits $\beta \to 0$ and $\beta \to \infty$. In the former, using (3.9a), we find that

$$d_i = \left(2\frac{c_{eq}\gamma}{\rho - c_{eq}}\frac{(l+2)(l+1)(l-1)}{\beta^3}\right)^i \frac{d_0}{i} \quad (i = 1, \ldots l+1). \tag{3.17}$$

Thus, if K_l is the quantity in large parentheses in (3.17) we have

$$\delta_l(t) = d_0\left(t^{(l-1)/2} + K_l t^{(l-2)/2} + K_l^2 \frac{t^{(l-3)/2}}{2} + \cdots + K_l^{l+1}\frac{t^{-2/2}}{l+1}\right). \tag{3.18}$$

If the amplitude in (3.18) with $\gamma \neq 0$ is initially the same as that with $\gamma = 0$ (i.e. 3.11a), then, at subsequent times, $\delta_{l,\gamma\neq 0}(t) \leq \delta_{l,\gamma=0}(t)$; i.e. the surface energy slows down the growth rate, as one expects on physical grounds. The question then arises, whether this solution with $\gamma \neq 0$ predicts a critical radius and, if so, how it compares with that from the quasi-steady-state model. Letting $\tau = K_l^{-1}t^{\frac{1}{2}}$, (3.18) can be written as

$$\delta_l = d_0 K_l^{l-1}\left(\tau^{(l-1)/2} + \tau^{(l-2)/2} + \frac{\tau^{(l-3)/2}}{2} + \cdots + \frac{\tau^{-2}}{l+1}\right).$$

Because $d\tau/dt \geq 0$, the sign of the derivative of δ_l is the same as that of $D_l'(\tau)$, where

$$D_l(\tau) = \left(\tau^{(l-1)} + \tau^{(l-2)} + \cdots + \frac{1}{l-1} + \frac{\tau^{-1}}{l} + \frac{\tau^{-2}}{l+1}\right). \tag{3.19}$$

Clearly,

$$D_l'(\tau) = \left((l-1)\tau^{(l-2)} + \cdots - \frac{\tau^{-2}}{l} - \frac{2\tau^{-3}}{l+1}\right),$$

$$D_l''(\tau) = \left((l-1)(l-2)\tau^{(l-3)} + \cdots + \frac{2\tau^{-3}}{l} + \frac{6\tau^{-4}}{l+1}\right),$$

which shows that D_l' is a monotonically increasing function on $(0, \infty)$, going from $-\infty$ to $+\infty$. Thus the Y_{lm}-mode is stable for $0 < \tau < \tau_l$, where τ_l denotes the zero of D', or (equivalently) for

$$\frac{\beta^2(\rho - c_{eq})}{2c_{eq}\gamma(l+2)(l+1)(l-1)}\bar{R}(t) < \tau_l. \tag{3.20}$$

For $\beta \to 0$, one has from (2.5) that $\beta^2 \sim 2(c_\infty - c_{eq})(\rho - c_{eq})^{-1}$, so that the critical radius is

$$\bar{R}_c = \tau_l \frac{(l+2)(l+1)(l-1)c_{eq}\gamma}{c_\infty - c_{eq}} \tag{3.21}$$

$$= \tfrac{1}{2}\tau_l(l+2)(l+1)(l-1)R^*, \tag{3.22}$$

where, in Mullins & Sekerka's notation, $R^* = 2c_{eq}\gamma(c_\infty - c_{eq})^{-1}$ is the so-called critical nucleation radius. Thus the behaviour is qualitatively (if not quantitatively) similar to the quasi-steady-state diffusion model.

In order to compare our results quantitatively with the Mullins–Sekerka critical radius $R^*[1+\frac{1}{2}(l+1)(l+2)]$, we investigate the dependence of τ_l upon l.

Firstly we write

$$D_l'(\tau)=p_l(\tau)-q_l(\tau),$$

where p_l and q_l are positive increasing functions of τ. We can then show that, for $l>2$:

(a) τ_l is less than the root of

$$2\tau/(l-2)+1/(l-1)-1/l\tau^2-2/(l+1)\tau^3=0,$$

which, in turn, is less than the root of

$$2\tau+(l-2)/(l-1)-1/\tau^2-2/\tau^3=0,$$

whose zero is between 1 and 2; thus $\tau_l<2$.

(b) $\tau_l>1/(l+1)$; in fact, $l\tau_l\to\infty$ as $l\to\infty$, so $\tau_l\gg O(1/l)$.

The first two roots are $\tau_2\simeq 1.06$ and $\tau_3\simeq 0.68$, giving critical radii of $6.4R^*$ and $13.6R^*$, compared to $7R^*$ and $11R^*$ from the Mullins–Sekerka analysis. The $l=2$ mode thus becomes unstable at a slightly smaller radius than that predicted by the quasi-steady-state theory, but the critical radius for the modes with $l\geq 3$ is larger, and indeed the ratio of the two critical radii tends to ∞ as $l\to\infty$.

For $\beta\to\infty$ (i.e. $c_\infty\simeq\rho$) one requires more precise behaviour of $\zeta_{l,p}$ because of cancellations in (3.17). In particular, using

$$\zeta_{l,p}(\xi)\cong e^{-\xi^2}(\xi^{-(p+3)}+A\xi^{-(p+5)}+B\xi^{-(p+7)}+\cdots) \tag{3.23}$$

where $A=\frac{1}{4}[l(l+1)-(p+2)(p+3)]$ and $B=\frac{1}{8}[l(l+1)-(p+4)(p+5)]A$, one finds, for $i=1,\ldots,l+1$, that

$$d_i=\frac{2c_{eq}\gamma}{\beta(\rho-c_{eq})}\left(1+\frac{(l-1)(l+2)(l+1-i)}{2i(2l+1-i)}\right)d_{l-1}. \tag{3.24}$$

For $l=2$, we obtain

$$\delta_2(t)=d_0(t^{\frac{1}{2}}+2L+\tfrac{8}{3}L^2t^{-\frac{1}{2}}+\tfrac{8}{3}L^3t^{-1}), \tag{3.25}$$

where $L=2[c_{eq}\gamma/(\rho-c_{eq})\beta]$. Thus, if $\eta=L^{-1}t^{\frac{1}{2}}$, then

$$\delta_2=d_0L(\eta+2+\tfrac{8}{3}\eta^{-1}+\tfrac{8}{3}\eta^{-2}). \tag{3.26}$$

The same argument gives that, for $l=2$,

$$\bar{R}_c=2\frac{c_{eq}\gamma}{\rho-c_{eq}}\eta_2,$$

where $\eta_2\simeq 2.25$ is the zero of $d\delta_2/d\eta$; since $\rho\simeq c_\infty$, we have

$$\bar{R}_c=\eta_l R^* \tag{3.27}$$

when $l=2$. The more general case $l>2$ is harder to treat because of the more complicated form of the recurrence relation (3.24), but we can obtain an upper bound on η_l, the zero of $d\delta_l/d\eta$, by approximating δ_l by its last four terms (this argument is the same as that used previously). We find that $\eta_l < \eta^*$, the root of

$$\frac{d}{d\eta}\left\{\eta + 2\left[1 + \frac{3l^2 + 3l - 2}{2l(l+1)}\left(\frac{1}{\eta} + \frac{1}{\eta^2}\right)\right]\right\} = 0,$$

which, in turn, is less than the root obtained by replacing the term involving l by $\frac{3}{2}$; the net result is $\eta_l < 2.36$. We thus conclude, from (3.27)—which holds for all l—that the critical radius for large β is *always* less than $2.36R^*$; this is a considerable quantitative difference from the Mullins–Sekerka formula $R_c = R^*[1 + \frac{1}{2}(l+1)(l+2)]$, especially for large l. The diffusion model predicts much earlier instabilities, which must be due to the high velocity of the moving front (the Mullins–Sekerka formula is independent of β).

4. Conclusion

The inclusion of the time-derivative term, then, enlarges the class of solutions; those we have written down explicitly are reasonable ones to consider, in that they agree with the $t^{(l-1)/2}$ growth rate of Mullins & Sekerka when $\gamma = 0$, and they have well-behaved initial data. Moreover, the critical radii for these solutions for large β are smaller than those for the quasi-steady state model, and we conclude that the diffusion is a destabilizing influence here; indeed, our results on blow-up and instability for large supersaturation highlight the shortcomings of the model, e.g. the assumption of local thermodynamic equilibrium on the solidification front (see [20] for discussion of this point). When β is small, our results agree broadly with the quasi-steady-state analysis of Mullins & Sekerka [1, 2], although the inclusion of diffusive effects results in some difference of detail, in particular the slightly smaller critical radius for the $l = 2$ mode.

Acknowledgements

The authors were supported, in part, by grants from the National Science Foundation (USA) (J.C., P.O.), Natural Science and Engineering Research Council (Canada) (J.C.), the Science and Engineering Research Council (UK) (S.D.H), the United States Office of Naval Research (S.D.H.), and a travel grant from NATO (J.C., S.D.H.).

References

1. Mullins, W. W., & Sekerka, R. F. 1963 *J. appl. Phys.* **34**, 323–329.
2. Mullins, W. W., & Sekerka, R. F. 1964 *J. appl. Phys.* **35**, 444–451.
3. Langer, J. S. 1980 *Rev. mod. Phys.* **52**, 1–28.
4. Rubenstein, L. I. 1971 *The Stefan Problem*. Translations of Mathematical Monographs **27**. American Mathematical Society, Providence.
5. Friedman, A. 1964 *Partial Differential Equations of Parabolic Type*. Prentice Hall, Englewood Cliffs.

6. FRIEDMAN, A. 1982 *Variational Principles and Free Boundary Problems*. Wiley, New York.
7. ELLIOTT, C. M., & OCKENDON, J. R. 1982 *Weak and Variational Methods for Moving Boundary Problems*. Pitman, London.
8. CHADAM, J., BAILLON, J-C., BERTSCH, M., ORTOLEVA, P., & PELETIER, L. A. 1985 *College de France Seminar* Vol. VI (Brezis, H., & Lions, J.L., Eds). Research Notes in Mathematics 109. Pitman, London.
9. CHADAM, J. & ORTOLEVA, P. 1983 *J.I.M.A.* **30**, 57–66.
10. CARSLAW, H. S., & JAEGER, J. C. 1959 *Conduction of Heat in Solids*. Clarendon, Oxford.
11. CHADAM, J., & ORTOLEVA, P. 1980 *Proceedings of the Conference on Mathematical Biology, Carbondale, Illinois*. Pergamon Press, Oxford.
12. KRUKOWSKI, S., & TURSKI, L. A. 1982 *J. Crystal Growth* **58**, 631–635.
13. ABRAMOWITZ, M., & STEGUN, I. A. 1964 *Handbook of Mathematical Functions*. U.S. Government Printing Office, Washington, D.C.
14. FRIEDMAN, A. 1959 *J. Math. and Mech.* **8**, 499–516.
15. FRIEDMAN, A. 1960 *J. Math. and Mech.* **9**, 19–66.
16. FRIEDMAN, A. 1960 *J. Math. and Mech.* **9**, 327–345.
17. SHERMAN, B. 1971 *Quart. appl. Math.* **28**, 377–382.
18. WEY, J. S., GAUTESEN, A. K., & ESTRIN, J. 1973 *J. Crystal Growth* **19**, 169–176.
19. WHITTAKER, E. T., & WATSON, G. N. 1927 *A Course of Modern Analysis*. University Press, Cambridge.
20. GLICKMAN, M. E., & SCHAEFFER, R. J. 1967 *J. Crystal Growth* **1**, 297–310.
21. SEKERKA, R. F., VOORHEES, P. W., CORIELL, S. R., & MCFADDEN, G. B. 1987 Initial conditions implied by $t^{\frac{1}{2}}$ solidification of a sphere with capillarity and interfacial kinetics. Preprint.

Note added in proof

The applicability of this similarity solution in the 'near nucleation' range ($\bar{R}(t) \sim R^* = 2\gamma c_{eq}/(c_\infty - c_{eq})$, the critical nucleation radius) has recently been called into question by Sekerka *et al.* [21]. They argue that, when β is small and $\bar{R} \leqslant 2R^*$, the concentration profile (2.3) exceeds c_∞ and is hence physically unrealistic. On the other hand, the concentration is a monotonically increasing function of r for all $\bar{R} \geqslant 2R^*$, and in this respect the similarity solution is physically reasonable in this 'post-nucleation' regime. In any event, all the stability results in Section 3 for small β involve values of $\bar{R}$ several times bigger than $2R^*$. For larger values of β, this question remains to be investigated.

We are grateful to Professor Sekerka who drew this point to our attention.