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Weakly nonlinear morphological instability of a spherical crystal growing from a pure undercooled melt

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We develop a weakly nonlinear morphological stability analysis for a sphere growing from its pure undercooled melt. For a sphere perturbed by a specific planform (a single spherical harmonic) we perform an expansion in the planform amplitude, A, to calculate the nonlinear critical radius (above which the chosen planform will be unstable for finite A), to lowest order in A, by setting the normal velocity corresponding to the fundamental perturbing mode to zero. We study the nonlinear critical radius as a function of the amplitude to identify the various bifurcations, which are transcritical (requiring an expansion to second order in A) for planforms generating physically distinct shapes for positive and negative amplitudes, and subcritical or supercritical (requiring an expansion to third order in A) for planforms for which the positive and negative amplitude shapes are related by rotation or translation. Bifurcations that are not transcritical are subcritical, except for a few harmonics of lower order or extreme ratios of the thermal conductivity in the solid to that in the liquid. We also treat the anomalous case of a perturbation by a first-order spherical harmonic (which is neutrally stable according to the linear theory, corresponding to a translation without any shape change) and observe that the second harmonic becomes unstable before the perturbing mode itself.

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I. INTRODUCTION

In this paper we consider the free growth of an initially spherical crystal from its pure undercooled melt, subject to the quasistationary approximation. The process of crystallization from the melt is a first-order phase transformation from a liquid to a solid. Such a phase transformation is always associated with the release of latent heat, which is conducted away into both the solid and the liquid as crystallization continues. For simplicity, we assume isotropy of all crystalline properties including surface tension. A mathematical description of this problem involves solving the Fourier equation for the thermal fields in the solid and the liquid phases, subject to the boundary conditions of heat conservation, continuity of temperature, and the Gibbs-Thomson equation at the solid-liquid interface. The stability of the interface is investigated analytically by perturbation theory.

The linear stability analysis of a growing spherical crystal from its pure undercooled melt was performed by Mullins and Sekerka [1], in which they established a criterion for the onset of instability for an arbitrary perturbation. A similar analysis was applied by Mullins and Sekerka to investigate the stability of a planar interface during directional solidification of a dilute binary alloy [2]. A weakly nonlinear analysis was developed for hydrodynamic stability [3] and applied by Wollkind and Segel [4] to the morphological stability of a planar interface. Since then, some excellent review articles [5–16] and a large number of research papers have been published on this subject. The weakly nonlinear analysis of a two-dimensional circular geometry was performed by Brush, Sekerka, and McFadden [17], who carried out an expansion to third order in the perturbing amplitude. They found that, in most cases, the system has small amplitude stable solutions (subcritical bifurcations).

In our work, we extend the work of Brush, Sekerka, and McFadden [17] to three-dimensional shapes to bring both principal radii of curvature into play. The three-dimensional problem shows some important features that are absent in the two-dimensional case.

II. UNDERLYING PHYSICS AND MODEL

We consider the thermal problem of a sphere growing from its pure undercooled melt. In the quasistationary approximation [1,15], the nondimensional governing equation and boundary conditions for thermal diffusion in the solid phase and the liquid phase may be written in the form

$$\nabla^2 U_L = 0 \ , \tag{2.1}$$

$$\nabla^2 U_s = 0 \tag{2.2}$$

in the bulk solid and the liquid, respectively. At the solid-liquid interface

$$V_N = \nabla U \cdot \hat{\mathbf{n}} \ , \tag{2.3}$$

$$U_L = U_S = 1 - K/2 \ , \tag{2.4}$$

where $U = -U_L + \beta U_S$, β is the ratio of thermal conductivity in the solid phase to that in the liquid phase, and

$$U_L \to 0 \quad \text{as } r \to \infty \; . \tag{2.5}$$

The choice of dimensionless variables is similar to that of previous work [18,17] where lengths are scaled by the nucleation radius $R^* = 2T_M \gamma / L_0(T_M - T_\infty)$ and time by $\tau = (R^*)^2/\alpha_L S$, where γ is the surface tension, T_M is the melting temperature, T_∞ is the far field temperature, L_0 is the latent heat, and α_L is the thermal diffusivity in the liquid phase. The dimensionless undercooling $S = \rho_L C_L (T_M - T_\infty)/L_0$ and we also use the dimensionless temperature fields $U_{S,L} = (T_{S,L} - T_\infty)/(T_M - T_\infty)$, where ρ_L and C_L are the density and the heat capacity of the liquid phase, respectively, and $T_{S,L}$ are the respective temperature fields in the solid and the liquid.

III. PERTURBATION EXPANSION

We examine the behavior of a perturbed spherical crystal to the third order in a small parameter ϵ, to be defined later. Thus, at a particular instant of time, we consider a perturbed interface of the form

$$r(\theta,\phi) = R + AH_{l,m}(\theta,\phi) \; , \tag{3.1}$$

where

$$R = R_0 + \epsilon R_1 + \epsilon^2 R_2 + \epsilon^3 R_3 \; , \tag{3.2}$$

$$A = \epsilon A_1 + \epsilon^2 A_2 + \epsilon^3 A_3 \; , \tag{3.3}$$

and

$$H_{l,m}(\theta,\phi) = \begin{cases} Y_{l,0}(\theta) & \text{for } m = 0 \\ \dfrac{1}{\sqrt{2}}[Y_{l,m}(\theta,\phi) + Y^*_{l,m}(\theta,\phi)] & \text{for } m \neq 0 \; , \end{cases} \tag{3.4}$$

where the $Y_{l,m}$ are the familiar spherical harmonics of quantum mechanics [19]. We can choose a definite phase for $H_{l,m}$ because any other phase would amount to a different choice of origin for ϕ, which is physically insignificant. For later convenience, we also write Eq. (3.1) in the form

$$r(\theta,\phi) = R_0 + \epsilon Z_1 + \epsilon^2 Z_2 + \epsilon^3 Z_3 \; , \tag{3.5}$$

where

$$Z_i(\theta,\phi) = R_i + A_i H_{l,m}(\theta,\phi) \quad \text{for } i = 1,2,3 \; . \tag{3.6}$$

Similarly we expand the temperature fields

$$U_L = U_{L0} + \epsilon U_{L1} + \epsilon^2 U_{L2} + \epsilon^3 U_{L3} \; , \tag{3.7}$$

$$U_S = U_{S0} + \epsilon U_{S1} + \epsilon^2 U_{S2} + \epsilon^3 U_{S3} \; , \tag{3.8}$$

the curvature,

$$K = K_0 + \epsilon K_1 + \epsilon^2 K_2 + \epsilon^3 K_3 \; , \tag{3.9}$$

and the radial growth speed

$$V_N = V_{N0} + \epsilon V_{N1} + \epsilon^2 V_{N2} + \epsilon^3 V_{N3} \; . \tag{3.10}$$

Explicit values of the K_i in the curvature expansion are given in Appendix A. The differential equations and the interfacial boundary conditions at each order of ϵ then appear as follows.

Order ϵ^0. The differential equations are

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2 \frac{\partial U_{L0}}{\partial r} \right] = 0 \; , \tag{3.11}$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2 \frac{\partial U_{S0}}{\partial r} \right] = 0 \tag{3.12}$$

and the interface boundary conditions are

$$U_{L0} = 1 - \frac{1}{R_0} \; , \tag{3.13}$$

$$U_{S0} = 1 - \frac{1}{R_0} \; , \tag{3.14}$$

$$\frac{\partial U_0}{\partial r} = V_{N0} \; . \tag{3.15}$$

Order ϵ^n, $n = 1,2,3$. The differential equations are

$$\nabla^2 U_{Ln} = 0 \; , \tag{3.16}$$

$$\nabla^2 U_{Sn} = 0 \tag{3.17}$$

and the boundary conditions are

$$U_{Ln} + \frac{\partial U_{L0}}{\partial r} Z_n - \frac{Z_n}{R_0^2} - \frac{\Omega^2 Z_n}{2R_0^2} = I_{Ln} \; , \tag{3.18}$$

$$U_{Sn} + \frac{\partial U_{S0}}{\partial r} Z_n - \frac{Z_n}{R_0^2} - \frac{\Omega^2 Z_n}{2R_0^2} = I_{Sn} \; , \tag{3.19}$$

$$\frac{\partial U_n}{\partial r} + \frac{\partial^2 U_0}{\partial r^2} Z_n - V_{Nn} = I_{Un} \; , \tag{3.20}$$

where the I's on the right-hand sides denote inhomogeneous terms that are zero for $n = 1$, but otherwise complicated functions of the solutions at lower order. The inhomogeneous terms that contribute to our results are given in Appendix A.

There appear to be several ways to choose the expansion parameter ϵ because it was only introduced in a formal way. Thus, in Eq. (3.3), only the products of ϵ or its powers with expansion coefficients can have physical significance, so a certain degree of arbitrariness exists. A very convenient choice is to set $\epsilon = A$, the perturbation amplitude [which amounts to setting $A_1 = 1$ and $A_2 = A_3 = 0$ in Eq. (3.3)]. This is a perfectly general choice and does not restrict the calculation in any way [20].

IV. PERTURBATION BY $Y_{2l,0}(\theta)$ (AXIALLY SYMMETRIC HARMONICS OF EVEN ORDER)

A. Zeroth-order solution

The solutions to Eqs. (3.11) and (3.12) subject to the boundary conditions Eqs. (3.13)–(3.15) are radially symmetric and readily found to be

$$U_{L0}(r) = \frac{R_0 - 1}{r} \; , \tag{4.1}$$

$$U_{S0}=\frac{R_0-1}{R_0}\ , \tag{4.2}$$

$$V_{N0}=\frac{R_0-1}{R_0^2}\ . \tag{4.3}$$

B. First-order solution

Trial solutions to Eqs. (3.16) and (3.17), subject to the boundary conditions Eqs. (3.18)–(3.20), can be written in the form

$$U_{L1}(r,\theta,\phi)=\frac{\alpha_{L1}^{(0)}}{r}+\frac{\alpha_{L1}^{(1)}}{r^{2l+1}}Y_{2l,0}(\theta)\ , \tag{4.4}$$

$$U_{S1}(r,\theta,\phi)=\alpha_{S1}^{(0)}+\alpha_{S1}^{(1)}r^{2l}Y_{2l,0}(\theta)\ , \tag{4.5}$$

$$V_{N1}(\theta,\phi)=V_{N1}^{(0)}+V_{N1}^{(1)}Y_{2l,0}(\theta)\ , \tag{4.6}$$

$$Z_1(\theta,\phi)=R_1+Y_{2l,0}(\theta)\ , \tag{4.7}$$

where $\alpha_{L1}^{(0)},\alpha_{L1}^{(1)},\alpha_{S1}^{(0)},\alpha_{S1}^{(1)},V_{N1}^{(0)},V_{N1}^{(1)}$, and R_1 are yet undetermined coefficients. To find them, we substitute the trial solutions into Eqs. (3.18)–(3.20). The resulting set of six equations can be split into two sets of three equations each, one set being proportional to $Y_{2l,0}(\theta)$ and the other set independent of it. The equations independent of $Y_{2l,0}(\theta)$ give

$$\alpha_{L1}^{(0)}=R_1\ , \tag{4.8}$$

$$\alpha_{S1}^{(0)}=\frac{R_1}{R_0^2}\ , \tag{4.9}$$

$$V_{N1}^{(0)}=\frac{R_1(2-R_0)}{R_0^3}\ . \tag{4.10}$$

Note that $V_{N1}^{(0)}$ is just R_1 times $\partial V_{N0}/\partial R_0$, as expected. The other set of equations, after elimination of the common factor $Y_{2l,0}(\theta)$, can be written in matrix form:

$$\begin{bmatrix} R_0^{-(2l+1)} & 0 & \dfrac{l(2l+1)-R_0}{R_0^2} \\ 0 & R_0^{2l} & \dfrac{l(2l+1)-1}{R_0^2} \\ \dfrac{2l+1}{R_0^{2l+2}} & \beta 2lR_0^{2l-1} & \dfrac{-2(R_0-1)}{R_0^3} \end{bmatrix} \times \begin{bmatrix} \alpha_{L1}^{(1)} \\ \alpha_{S1}^{(1)} \\ 1 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ V_{N1}^{(1)} \end{bmatrix}\ . \tag{4.11}$$

At the onset of instability, the component of normal velocity proportional to the fundamental mode of perturbation is zero to all orders. Thus, for the first-order solution, the velocity component proportional to $Y_{2l,0}(\theta)$ must vanish and so we set

$$V_{N1}^{(1)}=0 \tag{4.12}$$

in Eq. (4.11), which now represents three homogeneous equations in two unknowns $\alpha_{L1}^{(1)}$ and $\alpha_{S1}^{(1)}$. Therefore, nontrivial solutions for $\alpha_{L1}^{(1)}$ and $\alpha_{S1}^{(1)}$ exist only if the determinant of the above matrix vanishes, a condition which upon simplification yields the well known results of Mullins and Sekerka [1] for the radius R_0 in terms of β and l:

$$R_0(\beta,2l)=1+(l+1)(2l+2\beta l+1)\ . \tag{4.13}$$

This is called the critical radius since any sphere with radius greater than R_0 will be unstable according to the linear theory.

Therefore, the complete first-order solution is

$$U_{L1}(r,\theta,\phi)=\frac{R_1}{r}+\frac{R_0-l(2l+1)}{R_0^{-2l+1}r^{2l+1}}Y_{2l,0}(\theta)\ , \tag{4.14}$$

$$U_{S1}(r,\theta,\phi)=\frac{R_1}{R_0^2}+\frac{1-l(2l+1)}{R_0^{2l+2}}r^{2l}Y_{2l,0}(\theta)\ , \tag{4.15}$$

$$V_{N1}=\frac{R_1(2-R_0)}{R_0^3}\ , \tag{4.16}$$

$$Z_1(\theta,\phi)=R_1+Y_{2l,0}(\theta)\ , \tag{4.17}$$

and of the seven unknown coefficients we started out with, R_1 still remains undetermined.

C. Second-order solution

The interface boundary conditions are inhomogeneous and involve spherical harmonics and their squares, which, owing to the completeness of the harmonic functions, can be expanded in terms of them. Such an expansion, in general, would be an infinite series, but group theoretical considerations reduce it to a finite series, as is well known in quantum mechanics. Therefore,

$$Y_{2l,0}(\theta)Y_{2l,0}(\theta)=\sum_{i=0}^{2l}C_{2i}Y_{2i,0}(\theta,\phi)\ , \tag{4.18}$$

where the C_{2i} are related to the Clebsch-Gordan coefficients [19] and are given in Appendix B.

For our purposes, it is convenient to write the inhomogeneous terms in Eqs. (3.18)–(3.20) in the form

$$I=I^{(0)}+\sum_{i=1}^{2l}I^{(2i)}Y_{2i,0}(\theta,\phi)\ , \tag{4.19}$$

where the coefficients I are given in Appendix B, and take the trial solutions to Eqs. (3.16) and (3.17) as follows:

$$U_{L2}(r,\theta,\phi)=\frac{\alpha_{L2}^{(0)}}{r}+\sum_{i=1}^{2l}\frac{\alpha_{L2}^{(2i)}}{r^{2i+1}}Y_{2i,0}(\theta,\phi)\ , \tag{4.20}$$

$$U_{S2}(r,\theta,\phi)=\alpha_{S2}^{(0)}+\sum_{i=1}^{2l}\alpha_{S2}^{(2i)}r^{2i}Y_{2i,0}(\theta,\phi)\ , \tag{4.21}$$

$$V_{N2}(\theta,\phi)=V_{N2}^{(0)}+\sum_{i=1}^{2l}V_{N2}^{(2i)}Y_{2i,0}(\theta,\phi)\ , \tag{4.22}$$

$$Z_2=R_2\ . \tag{4.23}$$

As before, the trial solutions are substituted into the boundary condition Eqs. (3.18)–(3.20) and coefficients of the same spherical harmonic on opposite sides of each equation are equated to give

$$\alpha_{L2}^{(0)}=I_{L2}^{(0)}R_0+R_2\ ,$$

$$\alpha_{S2}^{(0)}=I_{S2}^{(0)}+\frac{R_2}{R_0^2}\ ,$$

$$V_{N2}^{(0)}=\frac{I_{L2}^{(0)}}{R_0}-I_{U2}^{(0)}+\frac{R_2(2-R_0)}{R_0^3}$$

and

$$\alpha_{L2}^{(2i)}=I_{L2}^{(2i)}R_0^{2i+1}\ , \tag{4.24}$$

$$\alpha_{S2}^{(2i)}=\frac{I_{S2}^{(2i)}}{R_0^{2i}}\ , \tag{4.25}$$

$$V_{N2}^{(2i)}=\frac{(2i+1)}{R_0}I_{L2}^{(2i)}+\frac{\beta 2i}{R_0}I_{S2}^{(2i)}-I_{U2}^{(2i)} \tag{4.26}$$

for i from 1 to $2l$. For $i\neq l$, all the $I^{(2i)}$ terms are completely known and Eqs. (4.24)–(4.26) uniquely determine the coefficients $\alpha_{L2}^{(2i)}$, $\alpha_{S2}^{(2i)}$, and $V_{N2}^{(2i)}$. For $i=l$ the marginal stability condition requires

$$V_{N2}^{(2l)}=0$$

and so Eq. (4.26) with l substituted for i provides us with the solvability condition

$$\frac{(2l+1)}{R_0}I_{L2}^{(2l)}+\frac{\beta 2l}{R_0}I_{S2}^{(2l)}-I_{U2}^{(2l)}=0\ . \tag{4.27}$$

The $I^{(2l)}$ terms in Eq. (4.27) contain the free parameter R_1, which may be solved to yield

$$R_1=[-\beta l\{l(2l+1)-1\}-\beta 2l(2l+1)\{2l(2l+1)-1\}+R_0 l(l+\tfrac{1}{2})-(l+\tfrac{1}{2})(l-2)]\frac{C_{2l}}{R_0(2l-1)} \tag{4.28}$$

with

$$C_{2l}=\left[\frac{(4l+1)^3}{4\pi}\right]^{1/2}\left[\frac{2l!}{l!l!}\right]^3\frac{3l!3l!}{(6l+1)!}\ .$$

Going back to Eq. (3.2) and recognizing that our choice of $A_1=1$, $A_2=A_3=0$ requires $\epsilon=A$, the amplitude of the perturbation, we have

$$R(\beta,l)=R_0(\beta,2l)+AR_1(\beta,l)\ . \tag{4.29}$$

A plot (Fig. 1) of R versus A will be a straight line passing through R_0 with slope equal to R_1. Such a bifurcation is said to be transcritical. If we analyze the expression for R_1, we find that for a given value of the parameter l, R_1 is positive if β is below a certain value β_l, zero if $\beta=\beta_l$, and negative otherwise (Fig. 2). The value of β_l can be readily found to be

$$\beta_l=\frac{(l+\frac{1}{2})(2l^3+3l^2+l+2)}{(2l+1)(7l^3+4l^2-2l)-1} \tag{4.30}$$

and a plot of β_l versus l appears in Fig. 3. For large values of l, β_l attains a limiting value

$$\beta^*=\lim_{l\to\infty}\beta_l=\tfrac{1}{7} \tag{4.31}$$

and any β less than $\frac{1}{7}$ will give positive R_1 for all values of l.

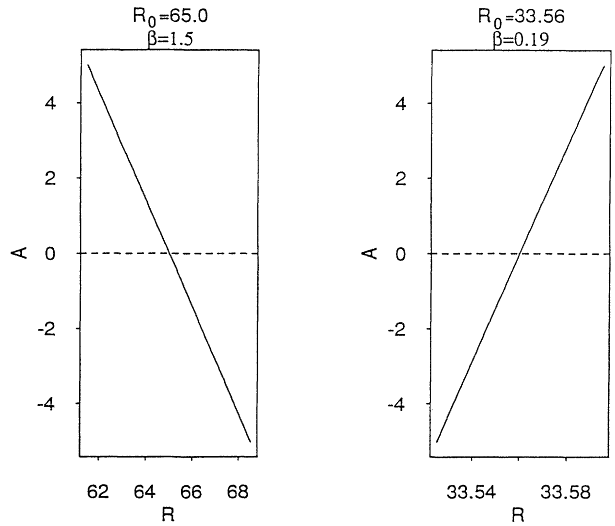

FIG. 1. Perturbation amplitude A as a function of radius R, for perturbation by $Y_{6,0}(\theta)$, for two different values of β. The straight line plot indicates that the bifurcation is transcritical. Since $\beta_6=0.1967$, the slope is positive for $\beta<\beta_6$ and negative for $\beta>\beta_6$.

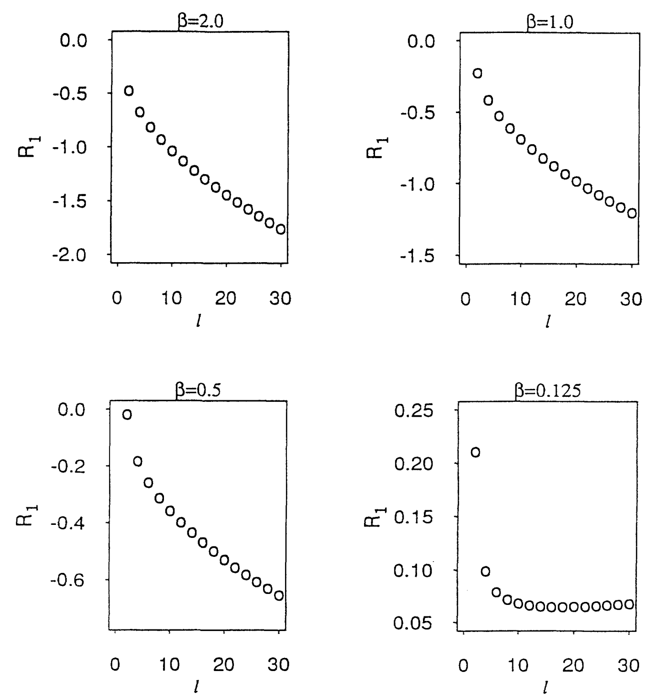

FIG. 2. R_1 as a function of the order l, for perturbation by an even axially symmetric spherical harmonic. For $\beta<\beta^*$ (the bottom right plot) R_1 is positive for all values of l as predicted by Eq. (4.31).

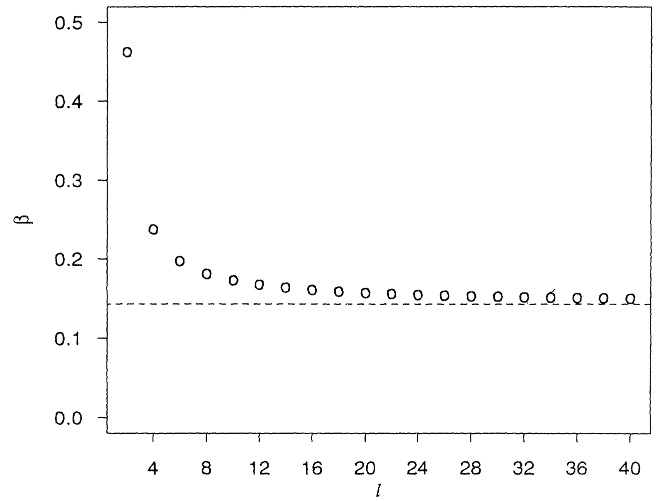

FIG. 3. Critical conductivity ratio β_l as a function of the order l for perturbation by an even axially symmetric spherical harmonic. The broken line represents the limiting value $\beta^* = \frac{1}{7}$ of β_l for very large l.

V. PERTURBATION BY $Y_{l,m}(\theta,\phi)$ $(l \neq 1)$

We now consider the case for general l and m. We want the perturbation to be real, so we use $H_{l,m}(\theta,\phi)$ introduced in Eq. (3.4). We shall treat the case $l=1$ in a subsequent section, since it has some unique features that will become evident as we proceed. We have already treated the case $m=0$ and l even in Sec. IV, so we will only briefly indicate how it is related to the general case.

A. Zeroth-order solution

The zeroth-order solution is the same as before and is given by Eqs. (4.1)–(4.3).

B. First-order solution

The first-order solution, found by the method of Sec. IV, is

$$U_{L1}(r,\theta,\phi) = \frac{R_1}{r} + \frac{\{R_0 - l/2(l+1)\}}{R_0^{-l+1}} \frac{H_{l,m}(\theta,\phi)}{r^{l+1}} , \tag{5.1}$$

$$U_{S1}(r,\theta,\phi) = \frac{R_1}{R_0^2} + \frac{\{1 - l/2(l+1)\}}{R_0^{l+2}} r^l H_{l,m}(\theta,\phi) , \tag{5.2}$$

$$V_{N1}(\theta,\phi) = \frac{R_1(2-R_0)}{R_0^3} , \tag{5.3}$$

$$Z_1(\theta,\phi) = R_1 + H_{l,m}(\theta,\phi) \tag{5.4}$$

and the critical radius condition is

$$(l-1)\left[R_0 - \left\{\frac{l(l+3)}{2} + \beta l(l/2+1) + 2\right\}\right] = 0 . \tag{5.5}$$

If $l=1$, then Eq. (5.5) does not give any critical radius; but for $l \neq 1$ it gives

$$R_0(\beta,l) = 1 + \tfrac{1}{2}(l+2)(l+\beta l+1) , \tag{5.6}$$

which is in agreement with Eq. (4.13). As before, the first-order solution is not complete, since R_1 is unknown, and we proceed to the second order to find it.

C. Second-order solution

The second-order interface boundary conditions are inhomogeneous. The inhomogeneous terms contain the spherical harmonics, their derivatives, and their products, which can be expanded in a finite series of the spherical harmonics themselves. Thus, for example,

$$H_{l,m}(\theta,\phi)^2 = \sum_{j=0}^{l} [C_{2j,2m} H_{2j,2m}(\theta,\phi) + (-1)^m \bar{C}_{2j,0} Y_{2j,0}(\theta)] .$$

Consequently the inhomogeneous terms can be written formally as

$$I = I^{(0)} + I^{(l)} R_1 H_{l,m} + \sum_{j=0}^{l} I^{2j} [C_{2j,2m} H_{2j,2m} + (-1)^m \bar{C}_{2j,0} Y_{2j,0}] ,$$

where $C_{2j,2m}$, $\bar{C}_{2j,0}$, $I^{(0)}$, $I^{(l)}$, and $I^{(2j)}$ are given in Appendix C. Therefore, the trial solutions are chosen to be

$$U_{L2}(r,\theta,\phi) = \frac{\alpha_{L2}^{(0)}}{r} + \sum_{j=0}^{l} \frac{\alpha_{L2}^{(2j)}}{r^{2j+1}} [C_{2j,2m} H_{2j,2m} + (-1)^m \bar{C}_{2j,0} Y_{2j,0}] + \frac{\alpha_{L2}^{(l)}}{r^{l+1}} H_{l,m} , \tag{5.7}$$

$$U_{S2}(r,\theta,\phi) = \alpha_{S2}^{(0)} + \sum_{j=0}^{l} \alpha_{S2}^{(2j)} r^{2j} [C_{2j,2m} H_{2j,2m} + (-1)^m \bar{C}_{2j,0} Y_{2j,0}] + \alpha_{S2}^{(l)} r^l H_{l,m} , \tag{5.8}$$

$$V_{N2}(\theta,\phi) = V_{N2}^{(0)} + \sum_{j=0}^{l} V_{N2}^{(2j)} [C_{2j,2m} H_{2j,2m} + (-1)^m \bar{C}_{2j,0} Y_{2j,0}] + V_{N2}^{(l)} H_{l,m} , \tag{5.9}$$

$$Z_2 = R_2 . \tag{5.10}$$

The coefficients are found by substituting these solutions in Eqs. (3.18)–(3.20) and equating coefficients of the same spherical harmonic on either side of the equation. For $m \neq 0$ and any l or for $m=0$ and odd l, the terms in the sum in Eq. (5.10) do not contain the fundamental mode, in which case the coefficients of $H_{l,m}(\theta,\phi)$ give

$$\alpha_{L2}^{(l)} = I_{L2}^{(l)} R_0^{l+1} R_1 ,$$

$$\alpha_{S2}^{(l)} = I_{S2}^{(l)} R_0^{-l} R_1 ,$$

and

$$I_{U2}^{(l)}R_1=\frac{(l+1)\alpha_{L2}^{(l)}}{R_0^{l+2}}+\beta\alpha_{S2}^{(l)}lR_0^{l-1}-V_{N2}^{(l)} . \qquad (5.11)$$

In Eq. (5.11) we set $V_{N2}^{(l)}=0$ (marginal stability for a perturbation of finite amplitude) and substitute for $I_{L2}^{(l)}$, $I_{S2}^{(l)}$, and $I_{U2}^{(l)}$ from Appendix B to get

$$(1-l)\tfrac{1}{2}R_1[\beta l(2l-1)(l+2)+l^2+3l+4]=0 . \qquad (5.12)$$

Since the expression in the square brackets in Eq. (5.12) is nonzero, we must have

$$R_1=0 \quad \text{for } l\neq 1 ,$$

forcing $\alpha_{L2}^{(l)}=\alpha_{S2}^{(l)}=0$. Moreover, if $m=0$ and l is even, the sum in Eq. (5.10) *does* contain the fundamental mode and Eq. (4.28) is recovered. The coefficients of $H_{0,0}$ give

$$\alpha_{L2}^{(0)}=R_2,\quad \alpha_{S2}^{(0)}=R_2/R_0^2,\quad V_{N2}^{(0)}=R_2(2-R_0)/R_0^3 .$$

The other coefficients are similarly found, leading to the second-order solution

$$U_{S2}(r,\theta,\phi)=\frac{R_2}{R_0^2}+\sum_{j=0}^{l}\frac{\left\{l^2\frac{(l+3)}{2}-1\right\}}{R_0^{2j+3}}\times r^{2j}[C_{2j,2m}H_{2j,2m}+(-1)^m\overline{C}_{2j,0}Y_{2j,0}] , \qquad (5.13)$$

$$U_{L2}(r,\theta,\phi)=\frac{R_2}{r}+\sum_{j=0}^{l}\frac{l\left\{R_0+\frac{(1-l)(1+l)}{2}\right\}}{R_0^{-2j+2}r^{2j+1}}\times[C_{2j,2m}H_{2j,2m}+(-1)^m\overline{C}_{2j,0}Y_{2j,0}] , \qquad (5.14)$$

$$V_{N2}(\theta,\phi)=R_2(2-R_0)/R_0^3+\sum_{j=0}^{l}V_{N2}^{(2j)}[C_{2j,2m}H_{2j,2m}+(-1)^m\overline{C}_{2j,0}Y_{2j,0}] , \qquad (5.15)$$

$$Z_2=R_2 . \qquad (5.16)$$

R_2 is still unknown, so we must go to the third order. If $l=1$, we get no information about R_1 from Eq. (5.12); we treat this case in Sec. VI.

D. Third-order solution

The third-order interface boundary conditions are also inhomogeneous, with the inhomogeneous terms containing derivatives and cubes of spherical harmonics. As in second order, they can also be expressed as a finite series of the harmonics themselves. Thus

$$H_{l,m}(\theta,\phi)^3=\sum_{j=0}^{l}(C_{2j,2m}^2+\overline{C}_{2j,0}^2)H_{l,m}(\theta,\phi)+(\text{other terms}) ,$$

where the other terms are not given explicitly because they will not be needed for evaluating R_2. We notice that in the expansion of $H_{l,m}(\theta,\phi)^3$ (with nonzero l and m), we have $H_{l,m}(\theta,\phi)$ as one of the terms, a situation not occurring in the expansion of $H_{l,m}(\theta,\phi)^2$, and this feature will enable us to find R_2.

We are now in a position to write the trial solutions for the third order and, once again, we will write only the relevant terms. Therefore,

$$U_{L3}(r,\theta,\phi)=\frac{\alpha_{L3}^{(l)}}{r^{l+1}}H_{l,m}(\theta,\phi)+(\text{other terms}) ,$$

$$U_{S3}(r,\theta,\phi)=\alpha_{S3}^{(l)}r^lH_{l,m}(\theta,\phi)+(\text{other terms}) ,$$

$$V_{N3}(\theta,\phi)=V_{N3}^{(l)}H_{l,m}(\theta,\phi)+(\text{other terms}) ,$$

$$Z_3=R_3$$

and substitution in the interface boundary conditions [Eqs. (3.18)–(3.20)] gives us, for terms proportional to $H_{l,m}(\theta,\phi)$,

$$\alpha_{L3}^{(l)}=I_{L3}^{(l)}R_0^{l+1},\quad \alpha_{S3}^{(l)}=I_{S3}^{(l)}R_0^{-l} ,$$

along with a third equation

$$\beta lR_0^{l-1}\alpha_{S3}^{(l)}+(l+1)\alpha_{L3}^{(l)}R_0^{-l-2}-V_{N3}^{(l)}=I_{U3}^{(l)} .$$

We set $V_{N3}^{(l)}=0$ (marginal stability for a perturbation of finite amplitude) and get the solvability condition

$$\beta lI_{S3}^{(l)}+(l+1)I_{L3}^{(l)}-R_0I_{U3}^{(l)}=0 , \qquad (5.17)$$

which on substituting for $I_{S3}^{(l)}$, $I_{L3}^{(l)}$, and $I_{U3}^{(l)}$ from Appendix C and simplification gives

$$R_2=\frac{R_0^2}{(l-1)}[R_0\overline{I}_{U3}^{(l)}-(l+1)\overline{I}_{L3}^{(l)}-\beta l\overline{I}_{S3}^{(l)}] , \qquad (5.18)$$

where $\overline{I}^{(l)}$ is the same as $I^{(l)}$, but with omission of the terms involving R_2, which has been solved for.

For $l\neq 1$, Eq. (5.18) gives R_2 as a function of β and l, and going back to Eqs. (3.2) and (3.3) we have

$$R(\beta,l,m)=R_0(\beta,l)+A^2R_2(\beta,l,m) . \qquad (5.19)$$

A plot of $R(\beta,l,m)$ versus A will be a parabola and the bifurcation will be subcritical if $R_2(\beta,l,m)$ is negative

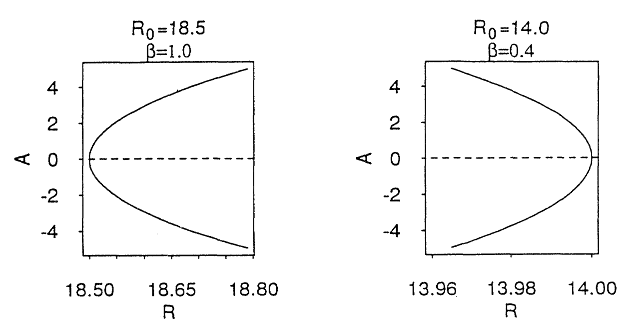

FIG. 4. Amplitude A as a function of the radius R, for perturbation by $Y_{3,0}(\theta)$, for values of β above and below $\beta_{3,0}=0.4397$. The bifurcation is supercritical in the left-hand plot and subcritical in the right-hand plot. The planar interface is stable for $R<R_0$.

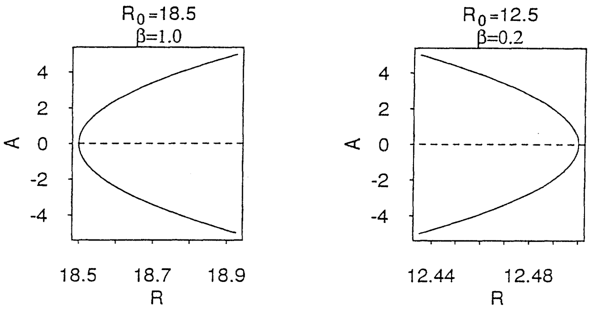

FIG. 5. Amplitude A as a function of the radius R, for perturbation by $Y_{3,2}(\theta,\phi)$, for values of β above and below $\beta_{3,2}=0.2526$. The bifurcation is supercritical in the left-hand plot and subcritical in the right-hand plot. The planar interface is stable for $R<R_0$.

and supercritical if $R_2(\beta,l,m)$ is positive. Examples are shown in Fig. 4 for $Y_{3,0}$ and in Fig. 5 for $Y_{3,2}$. If we set the right-hand side of Eq. (5.18) equal to zero, we can find a value of β denoted by β_{lm}, for a given l and m, for which R_2 will vanish. Thus, for a given value of l and m, R_2 will change sign as β goes through β_{lm}. Figure 6 shows β_{lm}, as a function of l and m. Plots of R_2 as a function of the order l appear in Fig. 7. We see that the bifurcations are subcritical, except for a few small values of l.

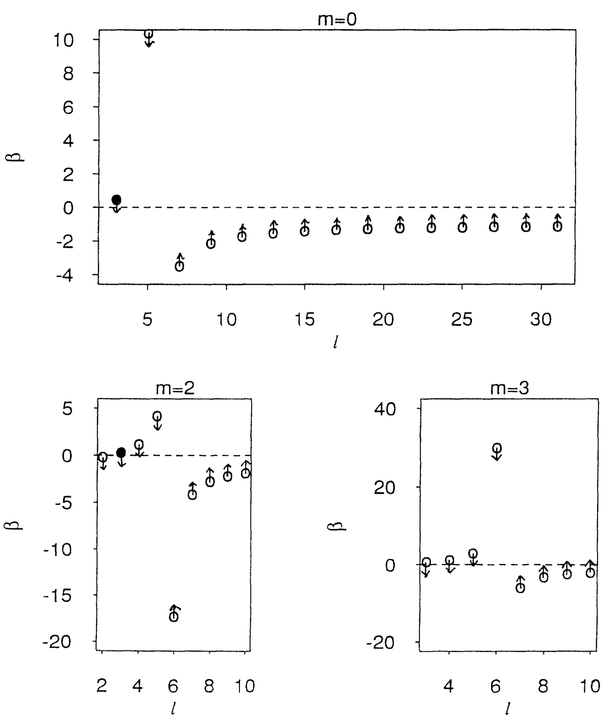

FIG. 6. β_{lm} as a function of the order l for three different values of m. R_2 is negative if β lies on the side of β_{lm} indicated by the arrows. The solid circles correspond to the values of $\beta_{l,m}$ used in Fig. 5.

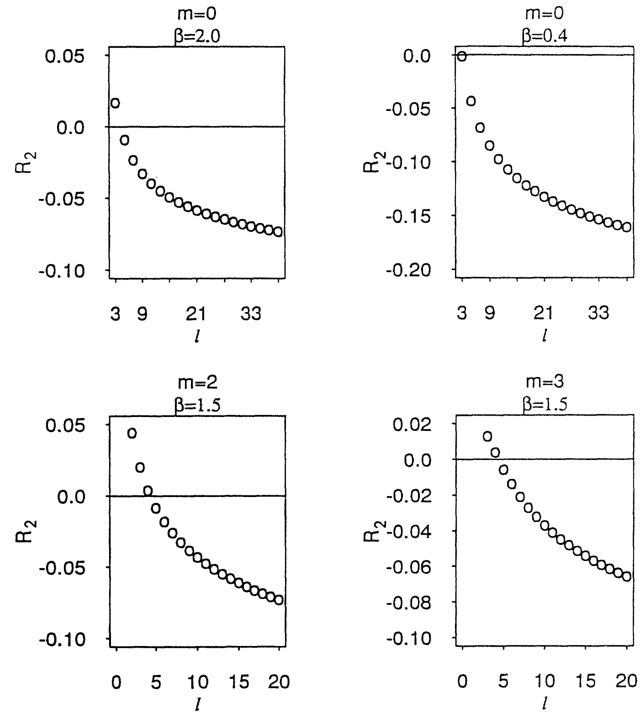

FIG. 7. R_2 as a function of the order l where l runs through all the *odd integral* values from 3 to 39 for $m=0$ and all the *integral* values from 2 to 19 for $m\neq0$. The sign of R_2 depends on the relationship of β to β_{lm} as shown in Fig. 6. From the plots we observe that the bifurcation is subcritical, except for small values of l.

VI. PERTURBATION BY $Y_{1,m}(\theta,\phi)$

As is evident from Eq. (5.12), the mode $l=1$ must be treated separately.

A. Zeroth-order solution

The zeroth-order solution is similar to the case of $l\neq1$ and is given by Eqs. (4.1)–(4.3), except we now substitute $\bar{R}_0$ for R_0 for reasons that will become clear after we examine the first-order solution.

B. First-order solution

The first-order solution is obtained easily by substituting $l=1$ in Eqs. (5.1)–(5.4) to give

$$U_{L1}(r,\theta,\phi)=\frac{R_1}{r}+\frac{(\bar{R}_0-1)}{r^2}H_{1,m}(\theta,\phi)\ , \tag{6.1}$$

$$U_{S1}==\frac{R_1}{\bar{R}_0^2}\ , \tag{6.2}$$

$$V_{N1}=\frac{R_1(2-\bar{R}_0)}{\bar{R}_0^3}\ , \tag{6.3}$$

$$Z_1(\theta,\phi)=R_1+H_{1,m}(\theta,\phi)\ . \tag{6.4}$$

The coefficient of $H_{1,m}(\theta,\phi)$ in the normal velocity V_{N1}

vanishes identically for $l=1$. This is unlike the case for $l\neq 1$, where this coefficient was set equal to zero to give an expression for the critical radius. We note that the coefficient of R_1 in V_{N1} is just the derivative of V_{N0} with respect to $\bar{R}_0$, as expected. The first-order solution in this case does *not* provide us with an expression for the critical radius $\bar{R}_0$. The $l=1$ mode is therefore a neutrally stable mode. This occurs because a perturbation of a sphere by $H_{1,m}(\theta,\phi)$ is equivalent to a translation, to first order, without any shape change. Thus, in the first-order solution we have two unknowns R_1 and $\bar{R}_0$ and the bar is used over R_0 to distinguish it from its $l\neq 1$ counterpart.

C. Second-order solution

The second-order solution is

$$U_{S2}(r,\theta,\phi)=U_{S2}^{(0)}+\frac{r^2}{\bar{R}_0^5}[C_{2,2m}H_{2,2m}(\theta,\phi)+(-1)^m\bar{C}_{0,0}Y_{2,0}(\theta)] , \quad (6.5)$$

$$U_{L2}(r,\theta,\phi)=\frac{U_{L2}^{(0)}}{r}+\frac{R_1}{r^2}H_{1,m}(\theta,\phi)+\frac{\bar{R}_0}{r^3}[C_{2,2m}H_{2,2m}(\theta,\phi)+(-1)^m\bar{C}_{2,0}Y_{2,0}(\theta)] , \quad (6.6)$$

$$V_{N2}(\theta,\phi)=V_{N2}^{(0)}+\frac{7+4\beta-\bar{R}_0}{2\bar{R}_0^4}[C_{2,2m}H_{2,2m}(\theta,\phi)+(-1)^m\bar{C}_{2,0}Y_{2,0}(\theta)] , \quad (6.7)$$

$$Z_2=R_2 , \quad (6.8)$$

where $U_{S2}^{(0)}$, $U_{L2}^{(0)}$, and $V_{N2}^{(0)}$ are functions of R_2, R_1, and $\bar{R}_0$ and are given in Appendix D. Once again, the coefficient of $H_{1,m}(\theta,\phi)$ in the normal velocity vanishes identically for $l=1$ and does not give us any information regarding R_1 or $\bar{R}_0$ [see Eq. (5.12)]. The second-order solution, however, provides us with an opportunity to find an expression for $\bar{R}_0$ by setting $V_{N2}^{(2)}$, the coefficient of $H_{2,2m}(\theta,\phi)$ in the normal velocity, equal to zero. This gives

$$\bar{R}_0=7+4\beta . \quad (6.9)$$

The important point here is that the *second harmonic* of the perturbing mode becomes unstable rather than the fundamental mode itself. This is contrary to the case for $l\neq 1$, where the perturbing mode would become unstable first. To find the critical radius for which the $l=1$ mode will become unstable, we will have to go to the third order. Therefore, at the end of the second order, we have found an expression for the critical radius and it is the same as that for the $l=2$ mode; i.e., the expression for the critical radius Eq. (6.9) is the same as that obtained from Eq. (5.6) for $l=2$. This is because a sphere perturbed by $l=1$ undergoes a shape change, at *second* order, that is proportional to that produced by $l=2$, at first order.

D. Third-order solution

The second-order solution leaves R_1 and R_2 undetermined. Therefore, we must go to third order to try to determine them. Furthermore, since the mode under consideration couples with itself at third order, we should be able to compute the radius above which the perturbing mode becomes unstable. We begin by writing down the trial solution for the third-order problem in the form

$$U_{L3}(r,\theta,\phi)=\frac{\alpha_{L3}}{r^2}H_{1,m}(\theta,\phi)+(\text{other terms}) , \quad (6.10)$$

$$U_{S3}(r,\theta,\phi)=\alpha_{S3}rH_{1,m}(\theta,\phi)+(\text{other terms}) , \quad (6.11)$$

$$V_{N3}(\theta,\phi)=V_{N3}^{(1)}H_{1,m}(\theta,\phi)+(\text{other terms}) , \quad (6.12)$$

$$Z_3=R_3 , \quad (6.13)$$

where we only indicate the relevant terms. The coefficients can be found by substituting the trial solutions in the boundary condition Eqs. (3.18)–(3.20). For $V_{N3}^{(1)}$ this gives

$$V_{N3}^{(1)}=\frac{1}{\bar{R}_0^5}\sum_{j=0}^{1}[\beta(j^4+j^3+j^2/4-6j-1)+\{2-j(2j+1)\}\{2-j(j+\tfrac{1}{2})\}-8](C_{2j,2m}^2+\bar{C}_{2j,0}^2)+\frac{1}{\bar{R}_0^4}\sum_{j=0}^{1}[4j^2+2j-2](C_{2j,2m}^2+\bar{C}_{2j,0}^2) , \quad (6.14)$$

where we notice that the terms involving R_1 and R_2 have canceled out. Therefore, even the expansion to third order does not determine R_1. We can, however, set $V_{N3}^{(1)}$ equal to zero in Eq. (6.14) to find the radius above which the perturbing mode will become unstable. This gives

$$R_c=9+4\beta . \quad (6.15)$$

The critical radius R_c thus found does not indicate when the system first becomes unstable, but merely gives the condition for which the *fundamental* perturbing mode will become unstable. The system is already unstable at this point because the second harmonic starts to grow for any radius greater than $\bar{R}_0=7+4\beta$, as given by Eq. (6.9).

A generalized phase plane analysis [20] for the coefficient of the second harmonic ($B_{2,2m}^{(2)}$) as a function of the unperturbed radius $\bar{R}_0$ yields Fig. 8. For our

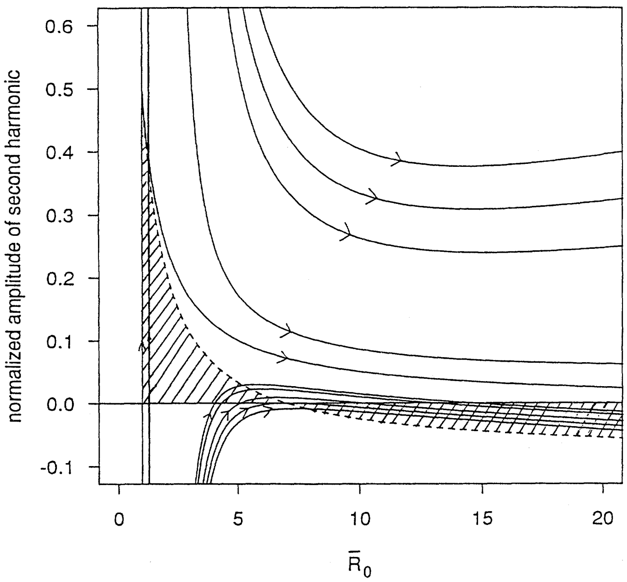

FIG. 8. Phase plane trajectories for the second harmonic ($l=2$ mode) that result from perturbation by $Y_{1,m}$. The ordinate is the ratio of $B^{(2)}_{2,2m}$ to the Clebsch-Gordan coefficient $C_{2,2m}$. The critical point is at $(1,\frac{1}{2})$ in these coordinates and the arrows show the direction of increasing time. β has been chosen to be 1.5. The broken line represents the neutral stability curve and cuts the $\bar{R}_0$ axis at $\bar{R}_0=4+2\beta=7$. Any trajectory starting beyond this value will result in evolution into the shaded unstable region.

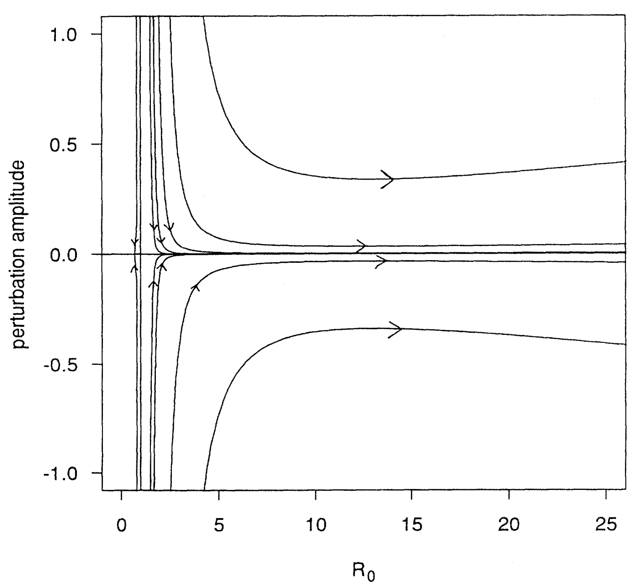

FIG. 9. Phase plane trajectories for the amplitude of the $l=2$ mode that result from perturbation by $Y_{2,m}$, shown for $\beta=1.5$. The critical point is at (1,0) and the neutral stability line is the R_0 axis. Beyond $R_0(1.5,2)=13$, the magnitude of the perturbation amplitude increases with R_0 and with time.

present purpose, however, the perturbation is by a single fundamental mode and so the initial value of $B^{(2)}_{2,2m}$ is zero. Thus, only the trajectories that start from the $\bar{R}_0$ axis are relevant. An analysis shows for $B^{(2)}_{2,2m}=0$ that $\dot{B}^{(2)}_{2,2m}$ changes sign from positive to negative at $\bar{R}_0=4+2\beta$. Therefore, any trajectory that starts from the $\bar{R}_0$ axis beyond that value will result in evolution into the shaded unstable region. Due to nonlinearity, however, the normal velocity corresponding to the perturbing mode contains $\dot{B}^{(2)}_{2,2m}$ as well as other terms. Consequently, the *normal* velocity vanishes at a larger value $\bar{R}_0=7+4\beta$. Thus, in Fig. 8, only the trajectories that start beyond $R_0=7+4\beta$ correspond to growth of the normal velocity of the $l=2$ mode. The shaded region of instability in Fig. 8 is a characteristic of the $l=1$ mode and is absent for any other mode. A typical phase plane diagram for the $l=2$ mode for perturbation by $Y_{2,m}$ is shown in Fig. 9.

VII. CONCLUSIONS

An expansion in the perturbation amplitude, A, is performed and the critical radius, to the lowest order in A, is found by setting the normal velocity corresponding to the fundamental perturbing mode equal to zero. Depending on the symmetries of the perturbing mode [21], the following results were obtained.

(i) $m=0, l$ even, and $l\neq 0$. The critical radius, given by

$$R_c(l,\beta,A)=R_0(l,\beta)+R_1(l,\beta)A ,$$

is found by carrying the perturbation expansion in A to second order. This is a transcritical bifurcation and a manifestation of the fact that for these perturbations, the shapes corresponding to positive and negative amplitudes are physically distinct. The governing equations can therefore depend on the sign of A.

(ii) $m=0$ and l odd, but $l\neq 1$. The critical radius, given by

$$R_c(l,\beta,A)=R_0(l,\beta)+R_2(l,\beta)A^2 ,$$

is found by carrying out the expansion in A to the third order. The bifurcation is supercritical if $R_2(l,\beta)>0$ and subcritical if $R_2(l,\beta)<0$. In this case the shapes generated by positive and negative amplitudes are related by simple rotation $(\theta\to\theta+\pi)$ and are not physically distinct. Therefore the governing equations are independent of the sign of A.

(iii) $m\neq 0$ and any l. The critical radius is given by

$$R_c(l,m,\beta,A)=R_0(l,\beta)+R_2(l,m,\beta)A^2 .$$

The situation is identical to the preceding case except that the shapes corresponding to the positive and negative amplitudes are related by the rotation $(\phi\to\phi+\pi/m)$.

(iv) The coefficients $R_1(l,\beta)$, $R_2(l,\beta)$, and $R_2(l,m,\beta)$ have been calculated. When R_2 is relevant, most bifurcations are subcritical, except for a few low values of l and extremely large β.

(v) The $l=1$ mode. This mode is unique since it is neutrally stable in the linear regime, corresponding to a translation of the sphere with no shape distortion. A nonlinear analysis showed that the fundamental mode generates the second harmonic, which becomes unstable at second order for $R>R_0=7+4\beta$, before the fundamental mode itself. In other words, a sphere perturbed by the $l=1$ mode is actually an ellipsoid, to second order. The fundamental mode itself becomes unstable at $R_c=9+4\beta$. To find the bifurcation parameter one would have to carry out the perturbation expansions to fourth or higher order in A.

In three dimensions, we conclude that the nature of the bifurcations depends on the symmetry of the specific planform, which has great variability for the perturbing spherical harmonics because there are two rotational degrees of freedom. In two dimensions [17], by contrast, there is only one degree of rotational freedom, so no transcritical bifurcations are found. We emphasize that our nonlinear results correspond to the instantaneous condition of no growth of a given planform and represent an attempt at applying the weakly nonlinear stability analysis to three-dimensional shapes with nonsteady unperturbed states. As in the two-dimensional case, we get mostly subcritical bifurcations. It has been suggested by Mullins [22] that the reason one gets supercritical bifurcations for small values of l and high values of the thermal conductivity ratio β is because of nonlinear effects associated with heat flow in the solid as opposed to the liquid. So far, we have not found a way to give a simple quantitative explanation along these lines.

Aside from theoretical interest, these results form a nontrivial test bed for the extension of numerical algorithms to the calculation in three dimensions of the shape evolutions beyond morphological instability. Moreover, the behavior of specific planforms would be expected to be influenced strongly by the anisotropy of surface tension and/or interface kinetics as in unidirectional solidification [23]. If it can be shown that the character of nonlinear evolution can be correlated with the nature of the bifurcation, it might be possible to predict certain aspects of pattern formation for free growth in three dimensions. It might also be possible to apply the methods developed herein to study a sphere perturbed by Kubic harmonics in an effort to understand the morphology of the dendrite tips observed during the growth of transparent cubic materials [24–28].

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APPENDIX A

We define the operator

$$\mathbf{\Omega}:=\hat{\theta}\frac{\partial}{\partial\theta}+\frac{\hat{\phi}}{\sin\theta}\frac{\partial}{\partial\phi} .$$

Then for the curvature expansion Eq. (3.9) we find

$$K_0=\frac{2}{R_0} ,$$

$$K_1=-\frac{2Z_1}{R_0^2}-\frac{\Omega^2 Z_1}{R_0^2} ,$$

$$K_2=-\frac{2Z_2}{R_0^2}-\frac{\Omega^2 Z_2}{R_0^2}+\frac{2Z_1^2}{R_0^3}+\frac{2Z_1\Omega^2 Z_1}{R_0^3} ,$$

$$K_3=-\frac{2Z_3}{R_0^2}-\frac{\Omega^2 Z_3}{R_0^2}+\frac{4Z_1Z_2}{R_0^3}+\frac{2Z_1\Omega^2 Z_2}{R_0^3}+\frac{2Z_2\Omega^2 Z_1}{R_0^3}-\frac{2Z_1^3}{R_0^4}-\frac{3Z_1^2\Omega^2 Z_1}{R_0^4}+\frac{\mathbf{\Omega}\cdot[|\mathbf{\Omega}Z_1|^2\mathbf{\Omega}Z_1]}{2R_0^4} .$$

The inhomogeneous terms for Sec. II are

$$I_{L2}=-\frac{\partial U_{L1}}{\partial r}Z_1-\frac{1}{2}\frac{\partial^2 U_{L0}}{\partial r^2}Z_1^2-\frac{Z_1^2}{R_0^3}-\frac{Z_1\Omega^2 Z_1}{R_0^3} ,$$

$$I_{S2}=-\frac{\partial U_{S1}}{\partial r}Z_1-\frac{1}{2}\frac{\partial^2 U_{S0}}{\partial r^2}Z_1^2-\frac{Z_1^2}{R_0^3}-\frac{Z_1\Omega^2 Z_1}{R_0^3} ,$$

$$I_{U2}=-\frac{\partial^2 U_1}{\partial r^2}Z_1-\frac{1}{2}\frac{\partial^3 U_0}{\partial r^3}Z_1^2+\frac{A_1}{R_0^2}\frac{\partial U_1}{\partial\theta}\frac{\partial H}{\partial\theta}+\frac{A_1}{R_0^2\sin^2\theta}\frac{\partial U_1}{\partial\phi}\frac{\partial H}{\partial\phi}+\frac{\partial U_0}{\partial r}\frac{|\mathbf{\Omega}H|^2A_1^2}{2R_0^2}$$

and

$$I_{L3}=-\frac{\partial U_{L2}}{\partial r}Z_1-\frac{1}{2}\frac{\partial^2 U_{L1}}{\partial r^2}Z_1^2-\frac{1}{6}\frac{\partial^3 U_{L0}}{\partial r^3}Z_1^3-\frac{\partial U_{L1}}{\partial r}Z_2-\frac{\partial^2 U_{L0}}{\partial r^2}Z_1Z_2-\frac{2Z_1Z_2}{R_0^3}$$
$$-\frac{Z_1\Omega^2 Z_2}{R_0^3}-\frac{Z_2\Omega^2 Z_1}{R_0^3}+\frac{Z_1^3}{R_0^4}+\frac{3Z_1^2\Omega^2 Z_1}{2R_0^4}-\frac{\mathbf{\Omega}\cdot[|\mathbf{\Omega}Z_1|^2\mathbf{\Omega}Z_1]}{4R_0^4},$$

$$I_{S3}=-\frac{\partial U_{S2}}{\partial r}Z_1-\frac{1}{2}\frac{\partial^2 U_{S1}}{\partial r^2}Z_1^2-\frac{1}{6}\frac{\partial^3 U_{S0}}{\partial r^3}Z_1^3-\frac{\partial U_{S1}}{\partial r}Z_2-\frac{\partial^2 U_{S0}}{\partial r^2}Z_1Z_2-\frac{2Z_1Z_2}{R_0^3}$$
$$-\frac{Z_1\Omega^2 Z_2}{R_0^3}-\frac{Z_2\Omega^2 Z_1}{R_0^3}+\frac{Z_1^3}{R_0^4}+\frac{3Z_1^2\Omega^2 Z_1}{2R_0^4}-\frac{\mathbf{\Omega}\cdot[|\mathbf{\Omega}Z_1|^2\mathbf{\Omega}Z_1]}{4R_0^4},$$

$$I_{U3}=-\frac{\partial^2 U_2}{\partial r^2}Z_1-\frac{1}{2}\frac{\partial^3 U_1}{\partial r^3}Z_1^2-\frac{1}{6}\frac{\partial^4 U_0}{\partial r^4}Z_1^3-\frac{\partial^2 U^1}{\partial r^2}Z_2-\frac{\partial^3 U_0}{\partial r^3}Z_1Z_2+\frac{A_2}{R_0^2}\frac{\partial U_1}{\partial\theta}\frac{\partial H_{l,m}}{\partial\theta}+\frac{A_2}{R_0^2\sin^2\theta}\frac{\partial U_1}{\partial\phi}\frac{\partial H_{l,m}}{\partial\phi}$$
$$+\frac{A_1}{R_0^2}\frac{\partial U_2}{\partial\theta}\frac{\partial H}{\partial\theta}+\frac{A_1}{R_0^2\sin^2\theta}\frac{\partial U_2}{\partial\phi}\frac{\partial H_{l,m}}{\partial\phi}+\frac{A_1Z_1}{R_0^2}\frac{\partial^2 U_1}{\partial r\partial\theta}\frac{\partial H_{l,m}}{\partial\theta}+\frac{A_1Z_1}{R_0^2\sin^2\theta}\frac{\partial^2 U_1}{\partial r\partial\phi}\frac{\partial H_{l,m}}{\partial\phi}-\frac{2A_1Z_1}{R_0^3}\frac{\partial U_1}{\partial\theta}\frac{\partial H_{l,m}}{\partial\theta}$$
$$-\frac{2A_1Z_1}{R_0^3\sin^2\theta}\frac{\partial U_1}{\partial\phi}\frac{\partial H_{l,m}}{\partial\phi}+\frac{|\mathbf{\Omega}H_{l,m}|^2A_1^2}{2R_0^2}\left[\frac{\partial^2 U_0}{\partial r^2}Z_1+\frac{\partial U_1}{\partial r}\right]+\frac{|\mathbf{\Omega}H_{l,m}|^2}{R_0^2}\frac{\partial U_0}{\partial r}\left[A_1A_2-\frac{A_1^2Z_1}{R_0}\right].$$

APPENDIX B

From Eq. (4.18)

$$Y_{2l,0}(\theta)Y_{2l,0}(\theta)=\sum_{j=0}^{2l}C_{2j}Y_{2j,0}(\theta,\phi),$$

where

$$C_{2j}=\left[\frac{(4l+1)(4l+1)(4j+1)}{4\pi}\right]^{1/2}\begin{bmatrix}2l & 2l & 2j\\ 0 & 0 & 0\end{bmatrix}\begin{bmatrix}2l & 2l & 2j\\ 0 & 0 & 0\end{bmatrix},$$

where we have used the Wigner $3j$ symbols [19]. The inhomogeneous terms for Sec. IV are

$$\tilde{I}_{L2}^{(0)}=\frac{1}{R_0^3\sqrt{4\pi}}C_0[2R_0l+l(2l+1)(1-2l)],$$

$$\tilde{I}_{L2}^{(2l)}=(R_1+C_{2l})\frac{1}{R_0^3}[2R_0l+l(2l+1)(1-2l)],$$

$$\tilde{I}_{L2}^{(2j)}=\frac{1}{R_0^3}C_{2j}[2R_0l+l(2l+1)(1-2l)],$$

$$\tilde{I}_{S2}^{(0)}=\frac{-R_1^2}{R_0^3}+\frac{1}{R_0^3\sqrt{4\pi}}C_0(2l+1)(2l^2+2l-1),$$

$$\tilde{I}_{S2}^{(2l)}=\frac{R_1}{R_0^3}(l+1)(4l^2+2l-2)+\frac{1}{R_0^3}C_{2l}(2l+1)(2l^2+2l-1),$$

$$\tilde{I}_{S2}^{(2j)}=\frac{1}{R_0^3}C_{2j}(2l+1)(2l^2+2l-1),$$

$$\tilde{I}_{U2}^{(0)}=\frac{R_1^2}{R_0^4}(3-R_0)+\frac{1}{R_0^4}C_0[R_0(2l^2+5l-1)+3-l(2l+1)(4l+3)-4\beta l(2l^2+l-1)],$$

$$\tilde{I}_{U2}^{(2l)}=\frac{R_1}{R_0^4}[R_0(4l^2+6l-1)+6-2l(2l+1)^2(l+1)+\beta 2l(2l-1)(2l^2+l-1)]$$
$$+\frac{1}{R_0^4}C_{2l}[R_0(2l^2+5l-1)+3-l(2l+1)(4l+3)-4\beta l(2l^2+l-1)],$$

$$\tilde{I}_{U2}^{(2j)}=\frac{1}{R_0^4}C_{2j}[-(2l+1)(2l+2)\{l(2l+1)-R_0\}+\beta 2l(2l-1)(2l^2+l-1)-3R_0+3$$
$$+\{2l(2l+1)-j(2j+1)\}\{l(2l+1)-R_0-\beta l(2l+1)+\beta+R_0/2-0.5\}].$$

APPENDIX C

The relevant terms for Sec. V are

$$C_{2j,2m}=\frac{1}{\sqrt{2}}\left[\frac{(2l+1)(2l+1)(4j+1)}{4\pi}\right]^{1/2}\begin{bmatrix} l & l & 2j \\ 0 & 0 & 0\end{bmatrix}\begin{bmatrix} l & l & 2j \\ m & m & -2m\end{bmatrix},$$

$$\bar{C}_{2j,0}=\left[\frac{(2l+1)(2l+1)(4j+1)}{4\pi}\right]^{1/2}\begin{bmatrix} l & l & 2j \\ 0 & 0 & 0\end{bmatrix}\begin{bmatrix} l & l & 2j \\ m & -m & 0\end{bmatrix},$$

$$I_{L1}^{(l)}=\left[R_0-\frac{l}{2}(l+1)\right],$$

$$I_{S1}^{(l)}=\left[1-\frac{l}{2}(l+1)\right],$$

$$I_{L2}^{(0)}=0,$$

$$I_{L2}^{(l)}=\frac{1}{R_0^3}[R_0 l-\tfrac{1}{2}l(l+1)(l-1)],$$

$$I_{L2}^{(2j)}=\frac{1}{R_0^3}[R_0 l-\tfrac{1}{2}l(l+1)(l-1)],$$

$$I_{S2}^{(0)}=-\frac{R_1^2}{R_0^3},$$

$$I_{S2}^{(l)}=\frac{1}{2R_0^3}(l+2)(l-1)(l+2),$$

$$I_{S2}^{(2j)}=\frac{1}{R_0^3}[\tfrac{1}{2}l^2(l+3)-1],$$

$$I_{U2}^{(0)}=\frac{R_1^2}{R_0^4}(3-R_0),$$

$$I_{U2}^{(l)}=\frac{1}{R_0^4}\left[R_0(l^2+3l-2)-\frac{l}{2}(l+1)^2(l+2)+6-\beta l(l-1)^2(l+2)\right],$$

$$I_{U2}^{(2j)}=\frac{1}{R_0^4}\left[-\beta I_{S1}^{(l)}l(l-1)+I_{L1}^{(l)}(l+1)(l+2)-3(R_0-1)\right.$$
$$\left.+\left[\beta I_{S1}^{(l)}-I_{L1}^{(l)}+\frac{R_0-1}{2}\right]\{l(l+1)-j(2j+1)\}\right],$$

$$I_{L3}^{(l)}=\frac{R_2}{R_0^3}\left[lR_0-\frac{l(l-1)(l+1)}{2}\right]+\frac{I_{L2}^{(2j)}}{R_0}\sum_{j=0}^{l}\{(2j+1)(C_{2j,2m}^2+\bar{C}_{2j,0}^2)\}$$
$$+\frac{1}{R_0^4}\left\{R_0-\frac{(l+1)}{2}[I_{L1}^{(l)}(l+2)+3l]\right\}\sum_{j=0}^{l}(C_{2j,2m}^2+\bar{C}_{2j,0}^2)$$
$$+\frac{1}{4R_0^4}\sum_{j=0}^{l}[l(l+1)-j(2j+1)]^2(C_{2j,2m}^2+\bar{C}_{2j,0}^2)+(\text{other terms}),$$

$$I_{S3}^{(l)}=\frac{R_2}{R_0^3}\left[\frac{l^2}{2}(l+3)-2\right]-\frac{I_{S2}^{(2j)}}{R_0}\sum_{j=0}^{l}\{2j(C_{2j,2m}^2+\bar{C}_{2j,0}^2)\}$$
$$+\frac{1}{R_0^4}\left[1-\frac{l}{2}[I_{S1}^{(l)}(l-1)+3(l+1)]\right]\sum_{j=0}^{l}(C_{2j,2m}^2+\bar{C}_{2j,0}^2)$$
$$+\frac{1}{4R_0^4}\sum_{j=0}^{l}[l(l+1)-j(2j+1)]^2(C_{2j,2m}^2+\bar{C}_{2j,0}^2)+(\text{other terms}),$$

$$
\begin{aligned}
I_{U3}^{(l)} = {} & \frac{R_2}{R_0^4}[-4R_0-\beta I_{S1}^{(l)} l(l-1)+I_{L1}^{(l)}(l+1)(l+2)+6] \\
& + \sum_{j=0}^{l}\left[\frac{I_{L2}^{(2j)}(2j+1)(2j+2)-\beta I_{S2}^{(2j)} 2j(2j-1)}{R_0^2}\right](C_{2j,2m}^2+\bar{C}_{2j,0}^2) \\
& + \frac{1}{R_0^5}\{4R_0-4-\tfrac{1}{2}\beta I_{S1}^{(l)} l(l-1)(l-2)-\tfrac{1}{2}I_{L1}^{(l)}(l+1)(l+2)(l+3)\}\sum_{j=0}^{l}(C_{2j,2m}^2+\bar{C}_{2j,0}^2) \\
& + \frac{1}{R_0^2}(\beta I_{S2}^{(2j)}-I_{L2}^{(2j)})\sum_{j=0}^{l} j(2j+1)(C_{2j,2m}^2+\bar{C}_{2j,0}^2) \\
& + \frac{1}{R_0^5}[I_{L1}^{(l)}(\tfrac{3}{2}l+\tfrac{7}{2})+\beta I_{S1}^{(l)}(\tfrac{3}{2}l-2)-2(R_0-1)]\sum_{j=0}^{l}[l(l+1)-j(2j+1)](C_{2j,2m}^2+\bar{C}_{2j,0}^2) \, .
\end{aligned}
$$

APPENDIX D

Terms corresponding to Sec. VI are

$$U_{S2}^{(0)} = \frac{1}{\bar{R}_0^3}[(R_2\bar{R}_0 - R_1^2)+(C_{0,2m}H_{0,2m}+(-1)^m\bar{C}_{0,0}Y_{0,0})] \, ,$$

$$U_{L2}^{(0)} = R_2 + \frac{1}{\bar{R}_0}[C_{0,2m}H_{0,2m}+(-1)^m\bar{C}_{0,0}Y_{0,0}] \, ,$$

$$V_{N2}^{(0)} = \frac{1}{\bar{R}_0^4}[R_2\bar{R}_0(2-\bar{R}_0)+R_1^2(3-\bar{R}_0)+(2-\bar{R}_0)\{C_{0,2m}H_{0,2m}+(-1)^m\bar{C}_{0,0}Y_{0,0}\}] \, .$$

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