

# Concentration effects on the Mullins–Sekerka instability

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(Received 6 October 1986; accepted 3 March 1987)

The Mullins–Sekerka linear stability analysis of a perturbation on a growing interface is extended to take into account concentration effects. The concentration dependence is included by considering the surrounding particles as an effective medium in the form of a sink term  $[x - \kappa^2 c]$  in the diffusion equation. This problem is analyzed without the effects of surface tension for  $d = 2$  and  $d = 3$  and with surface tension for  $d = 3$ . The stability analysis is also applied to two particles in isolation as well as  $N$  particles arranged in a regular planar polygon to study directly the competition for the diffusing species between the  $N$  growing spheres. We conclude that the Mullins–Sekerka criterion for growth or decay of an instability is only valid for an isolated particle and that in the presence of an effective medium, the surrounding particles have the effect of increasing an otherwise negative growth rate to a positive value.

## I. INTRODUCTION

Many examples of spontaneous pattern formation in nature are found in directional solidification or crystal growth. There are two main approaches to studying dendritic growth, the type of tree-like branching observed in the growth of alloy crystals and snowflakes.

Computer simulations of the type performed by Meakin<sup>1</sup> and Witten and Sander<sup>2</sup> create aggregates with a complex random dendritic structure called fractals.<sup>3</sup> Although surface tension and heat of aggregation are known to be important in understanding solidification, the computer simulations do not take these effects into account. For example, in diffusion limited aggregation,<sup>1,2</sup> a seed particle is placed at a lattice site, a random walk is released isotropically from a long distance, and when it reaches a nearest neighbor site, it becomes part of the growing cluster. Once the particle sticks to the cluster, it cannot rearrange in any way.

Another approach to studying pattern formation is to consider an advancing unafaceted solidification front and examine its stability properties. The systems studied are those in which the particle grows by a diffusion controlled process. Convective effects are ignored. Langer,<sup>4</sup> who recently modeled dendritic solidification including interfacial kinetics, crystalline anisotropy, and a local approximation for the dynamics of the thermal diffusion field, has reviewed this subject at length.<sup>5</sup>

Mullins and Sekerka<sup>6</sup> (MS) were the first to show that the competition between heat flow or diffusion and the surface tension is the underlying mechanism which leads to instability in the growth of the interface. They employed a linear stability analysis to determine the conditions of growth or decay of a spherical harmonic perturbation on the surface of a spherical particle undergoing diffusion controlled growth. They assumed local equilibrium at the interface and steady state, so that the concentration field obeyed Laplace's equation. Their results show that for all spherical

harmonics greater than ( $l = 1$ ) there is a certain critical radius  $R_c$ : for  $R > R_c$ , the spherical particle grows, and for  $R < R_c$ , the spherical particle shrinks.

Goldstein<sup>7</sup> has studied interparticle interference effects in diffusion controlled growth with and without surface tension. He derives a criterion for the mean number density of precipitating particles which assumes that morphological instability with respect to a harmonic perturbation of degree  $l$  or higher will never be attained in the course of a precipitation process. He obtains an expression for the rate of growth of the  $l$ th harmonic of a spherical perturbation in the presence of a nearest neighbor. This implies that the initiation of a harmonic perturbation does not require an adventitious fluctuation to start it off. Goldstein's equations are strictly deterministic compared to the MS treatment, where the equations are deterministic, but there is an assumed random event to produce the initial shape distortion (in the form of a spherical harmonic).

The purpose of this work is to investigate the concentration dependence of the Mullins–Sekerka (MS) linear stability analysis of a perturbation on a growing interface. This is accomplished by replacing Laplace's equation with a phenomenological steady state transport equation<sup>8</sup> that has a sink term which depends on the density  $\rho$  of the surrounding particles qualitatively treated as an effective medium.

In the following section, we review the Mullins–Sekerka result without surface tension for both two and three dimensions. We derive a steady state growth law for the “bumps” or perturbations on the growing spherical surface taking into account concentration effects in the form of a sink term in the diffusion equation. We also present our result for the growth law including surface tension for three dimensions and compare it to the MS result. In Sec. III, we derive a growth law for the perturbations on a sphere, without surface tension, using a microscopic approach instead of an effective medium approach: We consider two particles in isolation as well as  $n$  particles arranged in a regular planar polygon to study directly the competition for the diffusing species between the  $n$  growing spheres. In the last section, we discuss the results.

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## II. PHENOMENOLOGICAL APPROACH

### A. MS result without surface tension in two and three dimensions

In three dimensions, Mullins and Sekerka<sup>6</sup> obtained a growth law as follows. They considered an equation for the distorted sphere of initial radius  $R$ :

$$r(\theta, \phi) = R + \delta_l Y_{lm}(\theta, \phi), \quad (2.1)$$

where the  $Y_{lm}$ 's are the spherical harmonics of order  $l, m$  and  $\delta$  is small; powers higher than the first will be neglected.

The concentration field  $c(r, \theta, \phi)$  obeys Laplace's equation:

$$\nabla^2 c(r, \theta, \phi) = 0 \quad (2.2)$$

and in general has the form

$$c(r, \theta, \phi) = c_\infty + \frac{A}{r} + \sum_l \frac{B_l \delta_l Y_{lm}}{r^{l+1}} \quad (2.3)$$

when subject to the boundary condition

$$c(r, \theta, \phi)|_{r=\infty} = c_\infty. \quad (2.4)$$

At the surface of the now "bumpy" sphere, Eq. (2.4) becomes

$$c(r, \theta, \phi)|_{r=R+\delta_l Y_{lm}} = c_s = c_\infty + \frac{A}{R + \delta_l Y_{lm}} + \frac{B \delta_l Y_{lm}}{(R + \delta_l Y_{lm})^{l+1}}, \quad (2.5)$$

where  $c_s$  = equilibrium value of  $c$  at the interface with the precipitate. Equation (2.5) is expanded to first order in  $\delta_l$ . Since the expansion in harmonics is unique,  $A$  and  $B$  are easily determined by equating coefficients of like harmonics so that the concentration becomes

$$c(r, \theta, \phi) = (c_\infty - c_s) \left( \frac{c_\infty}{c_\infty - c_s} - \frac{R}{r} - \frac{R^{l+1}}{r^{l+1}} \delta_l Y_{lm} \right). \quad (2.6)$$

The velocity  $v$  describes the diffusion controlled growth of the interface

$$v = \frac{D}{(C - c_s)} \left( \frac{\partial c}{\partial n} \right) \Big|_{r=R+\delta_l Y_{lm}} = \frac{D}{C - c_s} (c_\infty - c_s) \left[ \frac{1}{R} + (l-1) \frac{\delta_l Y_{lm}}{R^2} \right]. \quad (2.7)$$

Here,  $D$  = diffusion coefficient of solute,  $C$  = fixed concentration of solute in the precipitate, and  $\partial c / \partial n$  = normal derivative of solute concentration. Since the tangent plane of the precipitate particle deviates only slightly from the tangent plane of the original sphere, the velocity can also be obtained by taking the radial derivative

$$v = \frac{dR}{dt} + Y_{lm} \frac{d\delta_l}{dt}. \quad (2.8)$$

Continuity requires Eqs. (2.7) and (2.8) to be identical and we obtain expressions for the diffusion controlled growth law  $\dot{R}$  and for  $\dot{\delta}_l$ , the rate of growth of the amplitude of the spherical harmonic,

$$\dot{R} = \frac{D(c_\infty - c_s)}{(C - c_s)R}, \quad (2.9)$$

$$\dot{\delta}_l = \frac{D(c_\infty - c_s)(l-1)\delta_l}{(C - c_s)R^2}. \quad (2.10)$$

Thus, when the bulk concentration is higher than the concentration at the interface, both the sphere and the bump grow; otherwise, both the sphere and the bump will dissolve. This is the simplest possible expression for  $\dot{\delta}_l / \delta_l$  since surface tension is not included; it guarantees the growth of bumps on the sphere for  $l > 1$ .

We can follow a similar procedure to derive expressions for  $\dot{R}$  and  $\dot{\delta}_l$  in two dimensions. However, since the general solution of the steady state diffusion equation in a cylindrically symmetric two-dimensional system is

$$c(r) = A + B \ln r, \quad (2.11)$$

the boundary condition  $c(r, \theta)|_{r=\infty} = c_\infty$  cannot be satisfied. We introduce a cutoff distance  $R_1$  which serves as an outer limit at which the boundary condition is satisfied. Using this approach,<sup>9</sup> which will be justified later, we find

$$\dot{R} = \frac{D(c_\infty - c_s)}{(C - c_s)R \ln(R_1/R)} \quad (2.12)$$

and

$$\dot{\delta}_l = \frac{D(c_\infty - c_s)\delta_l}{(C - c_s)R^2 \ln(R_1/R)} \times \left[ -1 + l \frac{(R_1/R)^l + (R/R_1)^l}{(R_1/R)^l - (R/R_1)^l} \right]. \quad (2.13)$$

### B. Concentration effects on the MS instability without surface tension in two and three dimensions

Concentration effects on one particle growth are included by considering the surrounding particles as an effective medium. A phenomenological steady state transport equation of the form

$$D\nabla^2 c - kc = 0 \quad (2.14)$$

is adopted. A heuristic argument for the sink term follows.

Consider a single particle undergoing diffusion controlled growth. The concentration field obeys Laplace's equation (2.2) and has the form

$$c(r) = c_\infty [1 - R/r] \quad (2.15)$$

with the absorbing boundary condition at the surface of the particle  $c(R) = 0$  and the usual boundary condition at infinity  $c(\infty) = c_\infty$ . Then the total flux into the particle is

$$J_T = 4\pi R^2 D \nabla c|_{r=R} = 4\pi R D c_\infty. \quad (2.16)$$

If instead of one absorbing particle, there were many such sinks with an average number density  $\rho$ , then the bulk concentration  $c_\infty$  would obey the equation

$$\frac{dc_\infty}{dt} = -kc_\infty, \quad (2.17)$$

where  $k = 4\pi R D \rho$ . Therefore, a sink term of the form  $-kc$  (where  $c$  is a local concentration) would act as an "effective medium" in the steady state one particle diffusion equation. A more detailed microscopic justification for a mean field

reaction–diffusion equation of this form has been presented by many authors including Felderhof and Deutch.<sup>10</sup>

We define a new parameter, the screening length  $\kappa^{-1}$ , as follows:

$$\kappa^2 = k/D. \tag{2.18}$$

At low density, the screening length  $\kappa^{-1}$  is large and at high density,  $\kappa^{-1}$  is small. The steady state transport equation (2.14) becomes

$$\nabla^2 c - \kappa^2 c = 0. \tag{2.19}$$

In three dimensions, a general solution for the above Helmholtz equation, assuming the surface of the bumpy sphere is perfectly absorbing, i.e.,  $c_s = 0$ , is

$$c(z, \theta, \phi) = c_\infty + \sqrt{\pi/2z} \left\{ AK_{1/2}(z) + BI_{1/2}(z) + \sum_{l>1} Y_{lm}(\theta, \phi) [C_l K_{l+1/2}(z) + D_l I_{l+1/2}(z)] \right\}, \tag{2.20}$$

where  $z = kr$  and the  $K_{l+1/2}$ ,  $I_{l+1/2}(z)$  are the modified spherical Bessel functions of the third kind and of fractional order.<sup>11</sup> Since the outer boundary condition requires  $c \rightarrow c_\infty$  as  $r \rightarrow \infty$ , the  $I_{l+1/2}(z)$  solutions are discarded. The inner boundary condition requires  $c = 0$  at  $z = \kappa R + \kappa \delta_L Y_{LM}$ , the surface of the sphere. To first order in  $\delta_L$  one finds

$$A = \frac{-2c_\infty \kappa R}{\pi}$$

and

$$C_L = -\frac{c_\infty \delta_L (1/R + \kappa)}{\sqrt{\pi/(2\kappa R)} K_{L+1/2}(\kappa R)}. \tag{2.21}$$

The other  $C_l$ 's are all zero and

$$K_{1/2}(z) = \sqrt{\pi/(2z)} \exp(-z).$$

Since the velocity  $v$  obeys

$$v = \frac{D}{C} \kappa \frac{\partial c}{\partial z} \tag{2.22}$$

as well as Eq. (2.8), we find

$$\dot{R} = \frac{Dc_\infty}{CR} \{1 + \kappa R\}, \tag{2.23}$$

$$\dot{\delta}_L = \frac{Dc_\infty \delta_L}{CR^2} \left\{ -2\kappa R - 2 - \kappa^2 R^2 + (\kappa R + \kappa^2 R^2) \times \frac{[LK_{L-1/2}(\kappa R) + (L+1)K_{L+3/2}(\kappa R)]}{(2L+1)K_{L+1/2}(\kappa R)} \right\}. \tag{2.24}$$

In two dimensions, a general solution to Eq. (2.19), assuming  $c_s = 0$ , is

$$c(z, \theta) = A_0 \left[ \frac{K_0(z)}{K_0(\kappa R_1)} - \frac{I_0(z)}{I_0(\kappa R_1)} \right] + c_\infty + \sum_{m>1} B_m \left[ \frac{K_m(z)}{K_m(\kappa R_1)} - \frac{I_m(z)}{I_m(\kappa R_1)} \right] e^{i\theta m}, \tag{2.25}$$

where  $z = \kappa R$  and the  $K_m(z)$ ,  $I_m(z)$  are the modified Bessel

functions of integer order.<sup>11</sup> In order to satisfy steady state conditions in two dimensions, the solution (2.25) was required to approach the bulk concentration  $c_\infty$  at the cutoff distance  $R_1$ . The inner boundary condition requires  $c = 0$  at  $r = \kappa R + \kappa \delta_L e^{iL\theta}$ , the surface of the absorbing sink. Therefore, to first order in  $\delta_L$ , the coefficients are

$$A_0 = \frac{-c_\infty}{\frac{K_0(\kappa R)}{K_0(\kappa R_1)} - \frac{I_0(\kappa R)}{I_0(\kappa R_1)}},$$

$$B_L = \frac{A_0 \kappa \delta_L \left[ \frac{K_1(\kappa R)}{K_0(\kappa R_1)} - \frac{I_1(\kappa R)}{I_0(\kappa R_1)} \right]}{\frac{K_l(\kappa R)}{K_l(\kappa R_1)} - \frac{I_l(\kappa R)}{I_l(\kappa R_1)}}. \tag{2.26}$$

All other  $B_m$ 's are zero.

The rates of growth of the sphere and the instability  $\delta_L$  are derived in the usual manner

$$\dot{R} = \frac{Dc_\infty \kappa R}{CR} \frac{\frac{I_1(\kappa R)}{I_0(\kappa R_1)} + \frac{K_1(\kappa R)}{K_0(\kappa R_1)}}{\frac{K_0(\kappa R)}{K_0(\kappa R_1)} - \frac{I_0(\kappa R)}{I_0(\kappa R_1)}}, \tag{2.27}$$

$$\dot{\delta}_L = \frac{D\kappa \delta_L}{2C} \left\{ A_0 \kappa \left[ \frac{K_0(\kappa R) + K_2(\kappa R)}{K_0(\kappa R_1)} - \frac{I_0(\kappa R) + I_2(\kappa R)}{I_0(\kappa R_1)} \right] - \frac{B_L}{\delta_L} \left[ \frac{K_{L-1}(\kappa R) + K_{L+1}(\kappa R)}{K_L(\kappa R_1)} + \frac{I_{L-1}(\kappa R) + I_{L+1}(\kappa R)}{I_L(\kappa R_1)} \right] \right\}. \tag{2.28}$$

Since  $R_1$  is the radius for which  $c \rightarrow c_\infty$ ,  $\kappa R_1$  is large and the ratios  $x = [K_0(\kappa R_1)]/[I_0(\kappa R_1)]$  and  $y = [K_L(\kappa R_1)]/[I_L(\kappa R_1)]$  are very small. Equations (2.27) and (2.28) can be rewritten in terms of  $x$  and  $y$  and these terms can be neglected such that

$$\dot{R} = \frac{Dc_\infty \kappa R}{CR} \frac{K_1(\kappa R)}{K_0(\kappa R)}, \tag{2.29a}$$

$$\dot{\delta}_L = \frac{D\kappa^2 R^2 c_\infty \delta_L}{2CR^2} \times \left[ -1 - \frac{K_2(\kappa R)}{K_0(\kappa R)} + \frac{K_1(\kappa R)}{K_0(\kappa R)} \right] \times \frac{K_{L-1}(\kappa R) + K_{L+1}(\kappa R)}{K_L(\kappa R)}. \tag{2.29b}$$

It is clear from Eq. (2.23) that the rate of growth  $\dot{R}$  of the sphere in three dimensions is linear with  $\kappa R$ . For two dimensions  $\dot{R}$  is also linear with  $\kappa R$ . This result is, not surprisingly, in agreement with the simple case of concentration effects on a smooth growing sphere: The growth rate of a smooth growing sphere can easily be derived and is identical to Eq. (2.27) for  $d = 2$  and to Eq. (2.23) for  $d = 3$ . Therefore, the overall rate of growth of the sphere remains the same whether the sphere is bumpy or smooth. In Figs. 1 and 2,  $F(\delta_L) = \dot{\delta}_L / [\delta_L Dc_\infty / (CR^2)]$  is plotted as a function

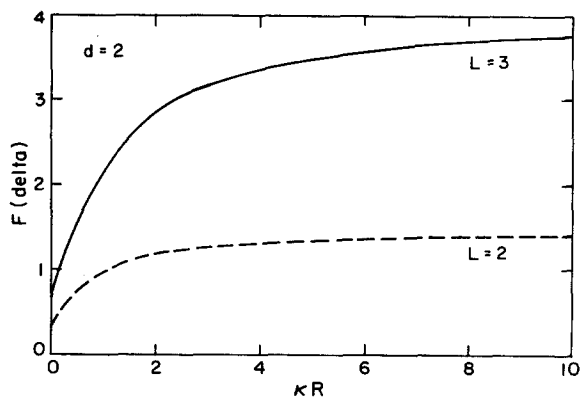


FIG. 1.  $F(\delta) = \dot{\delta}_L / [\delta_L D c_\infty / (CR^2)]$  [Eq. (2.29b)] is plotted vs the dimensionless variable  $\kappa R$  for  $L = 2, 3$  ( $d = 2$ ).

of  $\kappa R$  for different values of  $L$  and  $d = 2$  and  $3$ , respectively. The function  $F(\delta)$  increases linearly at first but then quickly reaches a plateau which is different for different  $L$ .

In the limit of very large  $\kappa R$  in three dimensions, we find that  $F(\delta) \sim -\kappa R$  for  $L = 2$ ; this implies that as the number density  $\rho$  in the square of the inverse screening length  $\kappa^2 = 4\pi R\rho$  increases, there is more competition between the sinks, and the bumps not only stop growing but actually shrink. However, in this same limit of large  $\kappa R$ , the overall growth rate  $\dot{R}$  is proportional to  $\kappa R$  and the sphere grows with  $\rho$ . For moderate screening  $0 < \kappa R < 6$ , both the sphere and its bumps grow with the screening parameter  $\kappa R$ . The effect of concentration on the rate coefficient was investigated previously<sup>10,12</sup>: This local rate coefficient was found to increase with sink number density. In a system of static sinks reacting with diffusing molecules, one would expect the competition for molecules between the sinks to lead to a decrease in the total rate of reaction relative to independent sinks.

When Figs. 1 and 2 are compared, it is evident that  $F(\delta)$  behaves very similarly in two and three dimensions; for example, the  $L = 2$  curve in three dimensions is the same as the  $L = 2$  curve in two dimensions shifted by a constant equal to 0.6. The cutoff distance  $R_1$  in the two-dimensional case is not significant.

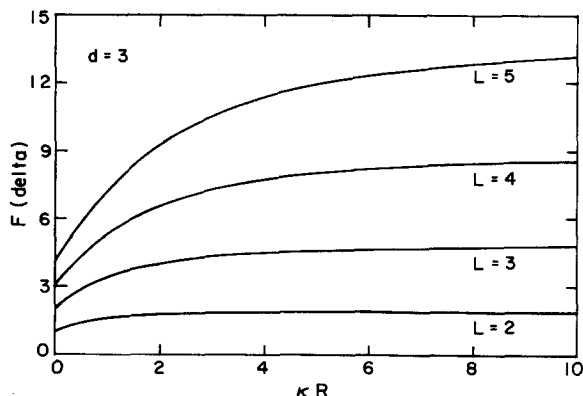


FIG. 2.  $F(\delta) = \dot{\delta}_L / [\delta_L D c_\infty / (CR^2)]$  [Eq. (2.24)] is plotted vs the dimensionless variable  $\kappa R$  for  $L = 2, 3, 4, 5$  ( $d = 3$ ).

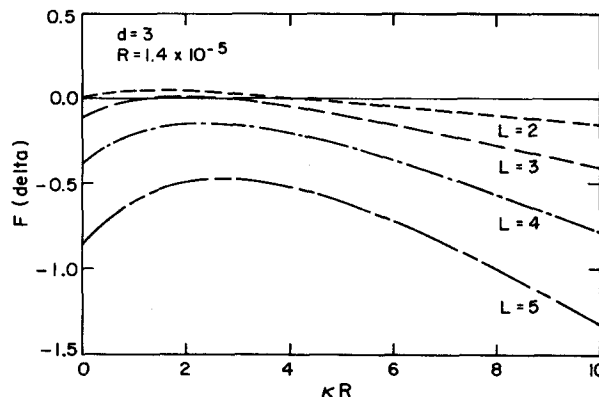


FIG. 3.  $F(\delta) = \dot{\delta}_L / [\delta_L D c_0 / (CR^2)]$  with surface tension effects ( $d = 3$ ) [Eq. (2.30)] is plotted vs  $\kappa R$  for  $L = 2, 3, 4, 5$  and  $R = 1.4 \times 10^{-5}$  cm.

The limit of large  $R_1/R$  can be taken in Eqs. (2.27) and (2.28) to obtain expressions for  $\dot{R}$  and  $F(\delta)$  which are independent of  $R_1$  [see Eqs. (2.29a) and (2.29b)]. One finds that  $\dot{R}$  and  $F(\delta)$  behave qualitatively the same for both  $d = 2$  and  $d = 3$ ,

### C. Concentration effects on MS instability with surface tension in 3D

The effects of surface tension are included in the  $d = 3$  case of the previous section according to the MS approach.<sup>6</sup> The Helmholtz equation (2.19) now obeys the following boundary conditions:

$$c(z = \infty) = 0,$$

$$c[z = \kappa R + \kappa \delta_L Y_{LM}(\theta, \phi)] = c_s = c_0 + c_0 \Gamma_D G,$$

where  $c_0$  = equilibrium value of  $c$  at a flat interface.

$G$  = mean curvature.

$\Gamma_D = \gamma \Omega / RT$  = the capillarity constant (typically  $\Gamma_D = 10^{-7}$  cm) in which  $\gamma$  is the interfacial free energy,  $\Omega$  the increment of precipitate volume per mole of added solute,  $R$  the gas constant, and  $T$  the absolute temperature.

The result of this calculation is simply

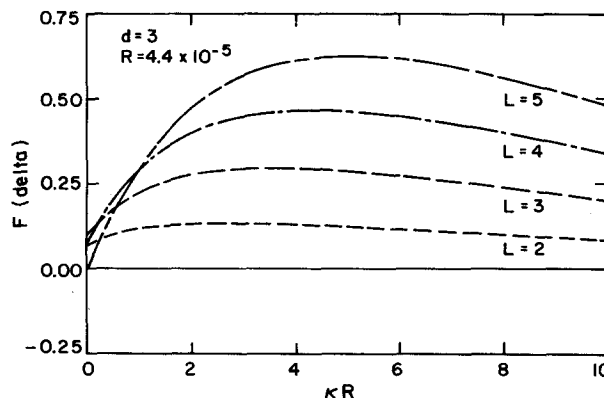


FIG. 4.  $F(\delta) = \dot{\delta}_L / [\delta_L D c_0 / (CR^2)]$  with surface tension effects ( $d = 3$ ), Eq. (2.30), is plotted vs  $\kappa R$  for  $L = 2, 3, 4, 5$  and  $R = 4.4 \times 10^{-5}$  cm.

$$\frac{\delta_L}{\delta_L} = \frac{Dc_0\delta_L}{R^2(C - c_R)} \left\{ \left( 1 + \frac{2\Gamma_D}{R} - \frac{c_\infty}{c_0} \right) (2\kappa R + \kappa^2 R^2 + 2) - \left[ \Gamma_D \frac{\kappa R}{R} (L + 2)(L - 1) + \left( 1 + \frac{2\Gamma_D}{R} - \frac{c_\infty}{c_0} \right) \times (\kappa R + \kappa^2 R^2) \right] \times \frac{LK_{L-1/2}(\kappa R) + (L + 1)K_{L+3/2}(\kappa R)}{(2L + 1)K_{L+1/2}(\kappa R)} \right\}, \quad (2.30)$$

$$\dot{R} = \frac{D(c_\infty - c_R)}{(C - c_R)} \left( \kappa + \frac{1}{R} \right), \quad (2.31)$$

where

$c_R = c_0 \left[ 1 + \frac{2\Gamma_D}{R} \right]$  = concentration on the undistorted sphere.

It is easy to show, for each  $L$ , that as  $\kappa \rightarrow 0$ , Eq. (2.30) becomes the MS result<sup>6</sup>:

$$\frac{\delta_L}{\delta_L} = \frac{Dc_0(L - 1)}{(C - c_R)R^2} \left\{ \frac{c_\infty - c_0}{c_0} - \frac{\Gamma_D}{R} [(L + 1)(L + 2) + 2] \right\}. \quad (2.32)$$

For  $L = 1$ ,  $\delta_L/\delta_L$  is zero. There is a critical radius  $R_c$  for which Eq. (2.32) is zero:

$$R_c = \frac{[(L + 1)(L + 2) + 2]\Gamma_D}{(c_\infty/c_0) - 1}. \quad (2.33)$$

For  $R > R_c$ ,  $\delta_L/\delta_L$  is positive and the perturbations grow; for  $R < R_c$ ,  $\delta_L/\delta_L$  is negative and the perturbations decay in the zero  $\kappa R$  limit. In Figs. 3 and 4,  $F(\delta) = \delta_L/\{\delta_L Dc_0/[R^2(C - c_R)]\}$  is plotted vs the dimensionless variable  $\kappa R$  which is a measure of the screening effect for different values of  $L$  ( $L = 2, 3, 4, 5$ ).  $R$  has been chosen to equal  $R_c$  ( $L = 2$ ) which is  $14\Gamma_D/(c_\infty/c_0 - 1) \sim 1.4 \times 10^{-5}$  cm in Fig. 3 and  $R_c$  ( $L = 5$ ) =  $4.4 \times 10^{-5}$  cm in Fig. 4.

Thus, for  $R = 1.4 \times 10^{-5}$  cm, the  $L = 2$  curve is zero at  $\kappa R = 0$  and the curves for higher  $L$ 's are all negative at  $\kappa R = 0$  in agreement with the results of Mullins and Sekerka.<sup>6</sup> However, as the parameter  $\kappa R$  increases, some of the growth curves  $\delta_L/\{\delta_L Dc_0/[R^2(C - c_R)]\}$  change sign. As  $R$  is increased to  $R_c$  ( $L = 5$ ) =  $4.4 \times 10^{-5}$  cm, all four curves are positive. For small values of  $R$  ( $\sim 1.4 \times 10^{-5}$  cm) the effect of including the surface tension is to change the growth rate of the bumps from the simpler case of concentration effects in  $d = 3$  (see Fig. 2). The growth rate of some harmonics will be positive at first, then as  $\kappa R$  increases further, it will become negative. Other harmonics will have negative growth rates for small  $\kappa R$ , positive growth rates for intermediate  $\kappa R$ , and then again negative growth rates for very large  $\kappa R$ . Without the effect of surface tension, the gradient effect dominates and the bumps grow; however, for very large  $\kappa R$  ( $> 10$ ), the concentration effect kicks in and the bumps shrink. In this section, we have seen that introducing surface tension rescales this behavior into a narrower regime of  $\kappa R$  values:  $\delta_L/\delta_L$  reaches a maximum at smaller  $\kappa R$  ( $\sim 2$ ) and has a negative slope at  $\kappa R = 10$ . This occurs because, for small  $\kappa R$ , the gradient effect dominates and the

bumps grow while, for large values of  $\kappa R$  ( $\sim 10$ ) the capillary effect kicks in and the bumps start to shrink. However, the growth rate of the sphere  $\dot{R}$  is not affected much by the surface tension [cf. Eqs. (2.23) and (2.31)] and increases linearly with  $\kappa R$ .

### III. MICROSCOPIC APPROACH

#### A. Two particles

The concentration dependence of this diffusion controlled process, which in the previous sections is included phenomenologically through the  $-\kappa^2 c$  term, physically arises from the competition of the diffusing species among many growing spheres: The many surrounding particles absorb some of the diffusing species before it reaches the central particle.

In this section and the next, we examine the growth of not one but two or more particles. The net effect of this model of competition is the same: reduction of the effective rate coefficient below the value obtained from  $N$  independent sinks. For two particles, the competition between the growing spheres of radius  $R$  separated by a distance  $a$  must have the form<sup>11,13</sup>

$$c(\mathbf{r}) = c_\infty + A \left[ \frac{1}{|\mathbf{r} - \mathbf{r}_1|} + \frac{1}{|\mathbf{r} - \mathbf{r}_2|} \right] + \sum_{l=1}^{\infty} A_l P_l \left[ \frac{1}{|\mathbf{r} - \mathbf{r}_1|^{l+1}} + \frac{1}{|\mathbf{r} - \mathbf{r}_2|^{l+1}} \right] \quad (3.1)$$

which satisfies Laplace's equation (2.2). For convenience, we choose  $\mathbf{r} = 0$  and  $\mathbf{r}_2 = (a, \theta, \phi = 0)$ .

Expression (3.1) satisfies the outer boundary condition,  $c \rightarrow c_\infty$  as  $r \rightarrow \infty$ . The inner boundary condition  $c(R + \delta_L P_L) = 0$  determines the coefficients  $A$  and  $A_L$ . To first order in  $\delta_L$ ,

$$A = -\frac{c_\infty R}{1 + R/a}, \quad A_L = \frac{-c_\infty \delta_L}{R [1 + R/a] [1/R^{L+1} + 1/a^{L+1}]}. \quad (3.2)$$

All other  $A_l$ 's are zero. In determining the coefficients  $A$  and  $A_L$ , we assume  $R \ll a$ , otherwise the spheres will overlap.

The flux  $\partial c/\partial r$  evaluated at  $r = R + \delta_L P_L$  to first order in  $\delta_L$  and for  $R \ll a$  is

$$\left. \frac{\partial c}{\partial r} \right|_{r=R+\delta_L P_L} = c_\infty \left\{ \frac{1}{R [1 + (R/a)]} \left( 1 - \frac{2\delta_L P_L}{R} \right) + \frac{\delta_L P_L (L + 1)}{R^2 [1 + (R/a)] [1 + (R/a)^{L+1}]} \right\}. \quad (3.3)$$

Therefore, the overall rate of growth of the sphere and the rate of growth of the perturbation obey

$$\frac{\delta_L}{\delta_L} = \frac{Dc_\infty}{R^2 C (1 + R/a)} \left\{ -2 + \frac{L + 1}{1 + (R/a)^{L+1}} \right\}, \quad (3.4)$$

$$\dot{R} = \frac{Dc_\infty}{RC} [1 + R/a]^{-1}. \quad (3.5)$$

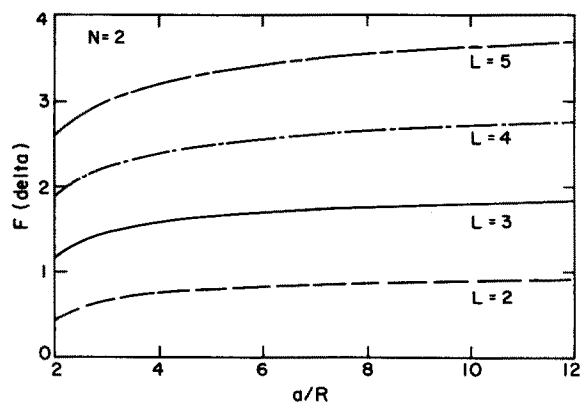


FIG. 5.  $F(\delta) = \delta_L / [\delta_L D c_\infty / CR^2]$  [Eq. (3.4)] is plotted vs  $a/R$  for  $L = 2, 3, 4, 5$ .

For large separation of the two spheres, i.e.,  $R/a \rightarrow 0$ , Eq. (3.4) reduces to

$$\frac{\delta_L}{\delta_L} = \frac{Dc_\infty}{CR^2} (L-1) \quad (3.6)$$

which is the result for the single particle perturbation growth rate, Eq. (2.10) (for  $c_s = 0$ ). In Fig. 5,  $F(\delta) = \delta_L / [\delta_L D c_\infty / (CR^2)]$  is plotted vs  $a/R$  for different values of  $L$  ( $L = 2, 3, 4, 5$ ). For large  $a/R$ ,  $F(\delta)$  correctly approaches the single sphere  $F(\delta)$  in Fig. 2 for  $\kappa R = 0$ . It is unfortunate that this two sink problem could not be solved

$$\frac{\delta_L}{\delta_L} = -\frac{DA}{CR^3} \left\{ \frac{L+1}{1 + (R/a)^{L+1} [\sin(\pi/N)]^{L+1} \sum_{n=1}^{N-1} [\sin(\pi n/N)]^{-L-1}} - 2 \right\}. \quad (3.10)$$

In Figs. 6 and 7,  $F(\delta) = \delta_L / (\delta_L c_\infty D / CR^2)$  is plotted vs  $a/R$  for  $N = 3$  and  $N = 20$ , respectively. As expected,  $\delta_L / \delta_L$  increases as a function of the separation ratio  $a/R$ . However, the rate of growth of the perturbation decreases as the number of sinks is increased; this happens because the competition for molecules between sinks leads to a decrease in the total rate of reaction as the number of sinks is increased.

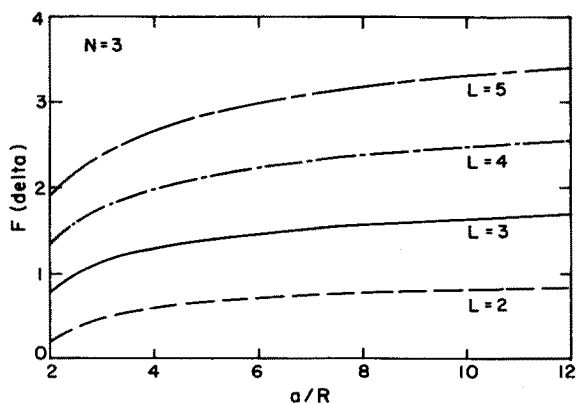


FIG. 6.  $F(\delta) = \delta_L / [\delta_L c_\infty D / (CR^2)]$  [Eq. (3.10)] is plotted vs  $a/R$  for  $N = 3$ .

exactly since it is the small  $a/R$  domain that is of most interest. The overall rate of growth of the sphere  $\dot{R}$  is not linear with  $a/R$  and the quantity  $\dot{R}RC / (Dc_\infty)$  approaches unity at large separation.

## B. Polygon

Another case of a many sink problem which can easily be analyzed is that of  $N$  spheres of equal radius  $R$  arranged in a regular planar polygon<sup>11</sup> with sides of length  $a$ .

The concentration field must satisfy Laplace's equation (2.2) and has the form

$$c(r) = c_\infty + A \sum_{n=1}^N \frac{1}{|r - r_n|} + A_L P_L \sum_{n=1}^N \frac{1}{|r - r_n|^{L+1}}, \quad (3.7)$$

where the coefficients are determined as in the previous section:

$$A = -c_\infty \left\{ \frac{1}{R} + \frac{\sin(\pi/N)}{a} \sum_{n=1}^{N-1} [\sin(\pi n/N)]^{-1} \right\}^{-1}, \quad (3.8)$$

$$A_L = (A\delta_L/R^2) \left\{ R^{-L-1} + \frac{[\sin(\pi/N)]^{L+1}}{a^{L+1}} \times \sum_{n=1}^{N-1} [\sin(\pi n/N)]^{-L-1} \right\}^{-1}. \quad (3.9)$$

The flux  $\partial c / \partial r$  evaluated at  $r = R + \delta_L P_L$  and Eq. (2.8) give the following expression for the rate of growth of the perturbation:

## IV. CONCLUDING REMARKS

We have extended the Mullins–Sekerka linear stability analysis to include concentration effects. This concentration dependence is included by considering the surrounding particles as an effective medium. The dimensionless parameter  $\kappa R$  is a measure of the density of the surrounding particles which constitute the effective medium: Small values of  $\kappa R$

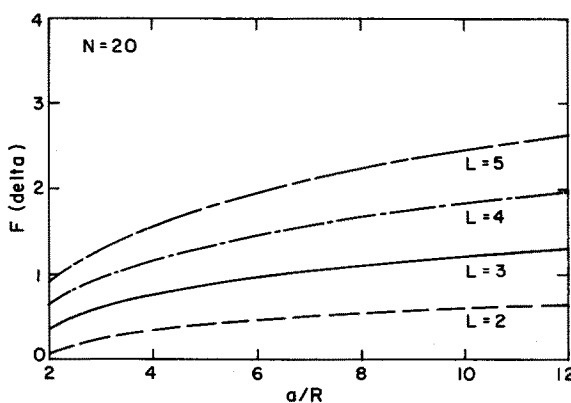


FIG. 7.  $F(\delta) = \delta_L / (\delta_L c_\infty D / CR^2)$  [Eq. (3.10)] is plotted vs  $a/R$  for  $N = 20$ .

correspond to a low density of surrounding particles while large values of  $\kappa R$  correspond to a thick entourage of particles.

Mullins and Sekerka showed that the competition between diffusion and surface tension is the underlying mechanism which leads to instability in the growth of the interface. They determined conditions of growth or decay. For all harmonics greater than  $l = 1$  there is a certain critical radius  $R_c$ : for  $R > R_c$  the bumps grow, for  $R < R_c$  the bumps shrink.

We have identified another variable  $\kappa R$ , which is a measure of the concentration dependence and which plays a role similar to the surface tension in that it attenuates the growth of the instabilities. When both decay mechanisms (surface tension and concentration effect) are included, the surface tension effectively rescales the rise and decay of the growth rate ( $\delta_L/\delta_L$ ) to a narrower regime of  $\kappa R$  values. The critical radius  $R_c$  of Mullins and Sekerka is no longer the only critical factor which determines the growth or decay of the bumps. This  $R_c$  is the starting value to  $\delta_L/\delta_L$  which increases with  $\kappa R$ , levels out at some intermediate value of  $\kappa R$ , and finally decreases again for large  $\kappa R$ . It is possible for a given spherical harmonic perturbation to begin at  $\kappa R = 0$  with a negative  $\delta_L/\delta_L$  but to reach a positive  $\delta_L/\delta_L$  for some intermediate  $\kappa R$ . However, for two same particles of radius  $R_c$ , it is also certain that for a large enough value of the spherical harmonic order  $L$ , the rate of growth of the bumps will never be positive.

We have observed that, in the absence of surface tension, for  $L > 1$ , the higher the harmonic the greater the maximum growth rate because as the order of the spherical harmonic  $L$  is increased, the  $Y_{LM}$ 's oscillate more rapidly and thus form sharper bumps more quickly (Figs. 1 and 2). The behavior is similar in  $d = 2$  and  $d = 3$ . Finally, in Sec. III of this paper

we take a microscopic approach and we derive a growth law for the perturbations on a sphere, without surface tension by directly including the one or more competing particle sinks. As expected, the growth law for each particle's bumps increases as the competing particles are moved further away (by increasing  $a/R$ , see Figs. 5, 6, and 7). Similarly, the growth rate of the bumps decreases overall as the number of competing particles is increased.

In our next paper, we will address the microscopic problem of  $N$  particles arranged randomly in space in order to determine how the reaction rate depends on the density of these sinks.

## ACKNOWLEDGMENTS

This work was supported in part by the Defense Advanced Research Projects Agency. One of us, A.A.R., would like to thank Raymond Lim and Daniel F. Calef for helpful discussion, and J. A. Marqusee for sending a preprint of Ref. 9.

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