Reprinted from JOURNAL OF APPLIED PHYSICS, Vol. 41, No. 11, 4404–4410, October 1970

Diffusion-Limited Phase Transformations: A Comparison and Critical Evaluation of the Mathematical Approximations

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(Received 6 April 1970)

Mathematical analyses previously made for diffusion-limited growth and dissolution of spherical and planar precipitates have been reviewed. The analyses include the invariant-field (Laplace), the invariant-size (stationary interface) and the linear-gradient approximations, and where possible, exact solutions of the differential time-dependent diffusion equation and of the independent flux balance. The kinetic parameters are calculated and the different solutions compared. For virtually all cases of practical interest it is shown that the stationary-interface approximation is the best one. By considering a reversed-growth analysis and showing that it is merely an approximation to the dissolution of a spherical precipitate, it is thereby shown that growth and dissolution cannot be generally considered as simply conjugate processes.

I. INTRODUCTION

Exact analytical solutions for the kinetics of a given diffusion-controlled phase transformation are often difficult if not impossible to obtain. And even when these exact solutions are obtainable, they are often too cumbersome to use conveniently. For these reasons, several approximate analyses have been proposed in the past to simplify the mathematics either by eliminating the rather complicated transcendental equation which governs the eigenvalues and/or by putting the field equation itself into a more manageable form. The approximations which we will discuss are the invariant-field (Laplace), the invariant-size (stationary interface), the linearized-gradients and the reversed-growth analyses. It is the purpose of this paper to compare and evaluate these approximate analyses for growing and dissolving spherical and planar precipitates. By considering all of the solutions simultaneously it is possible to determine the range of physical parameters over which a given approximation is useful and also to ascertain, in those ranges where more than one approximation is appropriate, which is best. We limit our discussion to spherical and planar precipitates only.

II. DISCUSSION OF THE APPROXIMATIONS

For growth or dissolution, in one or three dimensions, we are treating the diffusion-controlled transformation of an isolated precipitate in an infinite matrix and want to solve the field equation

$$D\nabla^2 C = \partial C/\partial t, \tag{1}$$

where D (assumed independent of composition) is the volume diffusion coefficient in the matrix and $C = C(r, t)$ is the concentration field in the matrix surrounding the precipitate, subject to the conditions

$$C(r=R, t) = C_I \qquad 0 < t \leq \infty \tag{2a}$$

and

$$C(r, t=0) = C_M \qquad r \geq R \tag{2b}$$

or

$$C(r=\infty, t) = C_M \qquad 0 \leq t \leq \infty, \tag{2c}$$

where $r = R$ at the precipitate–matrix interface, C_I is the concentration in the matrix at the precipitate–matrix interface, and C_M is the far-field composition of the alloy. It is also necessary to satisfy the independent flux balance

$$(C_P - C_I)(dR/dt) = D(\partial C/\partial r)\,|_{r=R}, \tag{3}$$

where C_P, the composition of the precipitate, is taken as a constant independent of r and t. R_0 will denote the value of R at $t=0$: $R_0 = 0$ for growth, $R_0 > 0$ for dissolution (Fig. 1).

The invariant field approximation is generally made in morphological stability calculations.[1–3] This is an attempt to simplify the field equation [Eq. (1)] by setting $\partial C/\partial t = 0$ and solving the simpler resulting Laplace equation $\nabla^2 C = 0$. Here if $(C_P - C_M) \gg (C_I - C_M)$ then the dissolution or growth problem may be approached, with reasonable accuracy, by considering R constant and solving the time-independent (Laplace) diffusion problem in the matrix. One obtains $C(r)$, and thus $\partial C/\partial r$, from the Laplace equation and then dR/dt from Eq. (3). The justification for this procedure is discussed in detail by Coriell and Parker.[2] The concentration inequality guarantees $R(t)$ to be a slowly varying function of time. We will show later that $\partial C/\partial r\,|_{r=R}$ obtained from the exact solution of the diffusion equation for the growth of a sphere becomes identical to that obtained from the Laplace equation in the limit when the concentration inequality is introduced.

The invariant size approximation used by Whelan[4] and a few others[5,6] in dissolution calculations, relaxes the invariant field constraint of the Laplace approximation but maintains the requirement of a stationary interface, $dR/dt \approx 0$. The stationary-interface approximation restricts the field to have no memory of the past motion of the interface. That is, the diffusion field around the precipitate is assumed to be the same as that which would exist if the precipitate–matrix interface had been fixed at R from the start and ignores the effect on the diffusion field of interface motion. The solution for $C(r, t)$ from Eq. (1) (for $dR/dt = 0$) which satisfies the conditions in Eqs. (2) is then used in Eq. (3) to obtain $R(t)$. This, like the Laplace approximation is based on the same concentration inequality, $(C_P-C_M)\gg(C_I-C_M)$ ensuring that $R(t)$ is a slowly varying function of time. We will see later that the stationary interface is a better approximation than the Laplace under all conditions.

Finally, the linearized gradients approximation, originally discussed by Zener[7] for the *sole* purpose of obtaining a convenient concentration parameter suitable for expressing his exact results, is an attempt to simplify the diffusion field by assuming that the concentration gradient immediately surrounding the precipitate is linear in the spatial variable (r). (In a sense this "approximation" cannot be justified being a heuristic argument in contrast with the other approximations.) The extent of the linear field, d, is determined by conservation of mass, subject to the constraints of Eqs. (2). Then, for $r\geq R+d$ (where R and d are both functions of time), $C(r,t)=C_M$. This simplified field set in Eq. (3) yields (in certain cases discussed by Zener[7] and expanded upon later) reasonable estimates for $R(t)$.

III. CALCULATIONS

A. Growth

1. *Spherical Precipitates*

Analysis of the growth of spherical precipitates affords us a special opportunity because the problem can be solved exactly and by all three approximate methods. This case will therefore be discussed first. For the sphere, Eq. (1) takes the form

$$D[(\partial^2C/\partial r^2)+(2/r)(\partial C/\partial r)]=\partial C/\partial t.$$

The exact solution to this equation, subject to the conditions of Eqs. (2) and (3) is[8]:

$$C(r,t)-C_M=\frac{2\lambda(C_I-C_M)}{\exp(-\lambda^2)-\lambda(\pi)^{1/2}\,\mathrm{erfc}\lambda}\times\left[\frac{(Dt)^{1/2}}{r}\exp\left(-\frac{r^2}{4Dt}\right)-\tfrac{1}{2}(\pi)^{1/2}\,\mathrm{erfc}\left(\frac{r}{2(Dt)^{1/2}}\right)\right],\quad(4)$$

where

$$R=\lambda_1(Dt)^{1/2},\quad(5)$$

$$\lambda_1=2\lambda,\quad(6)$$

and λ is given by

$$\lambda^2\exp(\lambda^2)[\exp(-\lambda^2)-\lambda(\pi)^{1/2}\,\mathrm{erfc}\lambda]=-k/4,\quad(7)$$

where

$$k\equiv2(C_I-C_M)/C_P-C_I).\quad(8)$$

There is only one positive value of λ which satisfies Eq. (7). For the Laplace approximation, the resultant field is simply (1, 2)

$$C(r,t)-C_M=(C_I-C_M)(R/r),\quad(9)$$

whence

$$R=\lambda_3(Dt)^{1/2},\quad(10)$$

where

$$\lambda_3=(-k)^{1/2}.\quad(11)$$

For the stationary-interface approximation the resultant field is given by (8)

$$C(r,t)-C_M=[(C_I-C_M)/r]R\,\mathrm{erfc}[(r-R)/2(Dt)^{1/2}],\quad(12)$$

and therefore

$$R=\lambda_2(Dt)^{1/2},\quad(13)$$

where

$$\lambda_2=\{-k/[2(\pi)^{1/2}]\}+[k^2/(4\pi)-k]^{1/2}.\quad(14)$$

For the linearized-gradients approximation, $\partial C/\partial r\rightarrow\Delta C/\Delta r=$ const. Conservation of mass requires that

$$\tfrac{4}{3}\pi R^3(C_P-C_M)=\tfrac{4}{3}\pi[(\Delta r+R)^3-R^3][(C_M-C_I)/2],\quad(15)$$

which can be reduced to

$$\Delta r=\gamma R,\quad(16)$$

where

$$\gamma=[1-f(k)]/f(k)\quad(17)$$

and

$$f(k)=[-4k/(1+4k)]^{1/3}.\quad(18)$$

Therefore

$$R=\lambda_4(Dt)^{1/2}\quad(19)$$

where

$$\lambda_4=(-k/\gamma)^{1/2}.\quad(20)$$

2. *Planar Precipitates*

Here Eq. (1) is the simple one-dimensional expression

$$D(\partial^2C/\partial x^2)=\partial C/\partial t$$

where $x=S$ at the precipitate–matrix interface. The exact solution under the above-stated boundary conditions is[9,7]

$$C(x,t)-C_M=(C_I-C_M)\frac{\mathrm{erfc}[x/2(Dt)^{1/2}]}{\mathrm{erfc}(\lambda)},\quad(21)$$

where

$$S=\lambda_1(Dt)^{1/2},\quad(22)$$

$$\lambda_1=2\lambda$$

and λ must satisfy

$$(\pi)^{1/2}\lambda\exp(\lambda^2)\,\mathrm{erfc}(\lambda)=-k/2.\quad(23)$$

For planar precipitate growth the Laplace solution does not exist since it is not possible to satisfy, simultaneously, $\partial^2C/\partial x^2=0$ and the boundary and initial conditions. Hence, λ_3 is undefined.

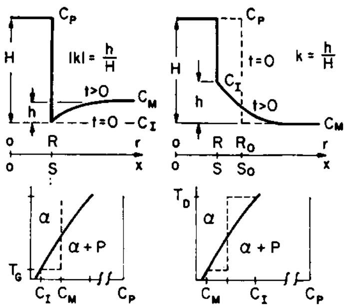

FIG. 1. Schematic of concentration fields for growth and dissolution and corresponding portions of the phase diagrams showing the single phase region α and the two-phase region $\alpha+p$.

For the stationary-interface approximation

$$C(r,t)-C_M=(C_I-C_M)\ \mathrm{erfc}[(x-S)/2(Dt)^{1/2}]. \quad (24)$$

Therefore, since $S(t=0)=0$,

$$S=\lambda_2(Dt)^{1/2}, \quad (25)$$

where

$$\lambda_2=-k/(\pi)^{1/2}. \quad (26)$$

And finally, the linearized-gradients approximation yields (7):

$$S=\lambda_4(Dt)^{1/2}, \quad (27)$$

where

$$\lambda_4=(C_M-C_I)/[(C_P-C_I)^{1/2}(C_P-C_M)^{1/2}] = k/[2(1+k/2)^{1/2}]. \quad (28)$$

B. Dissolution

1. *Spherical Precipitates*

Here we have the same boundary and initial conditions as for growth of spherical precipitates except that $R(t=0)=R_0>0$ as previously noted. For physical reasons considered briefly in the discussion it has not yet been possible to obtain an exact solution to the dissolving sphere problem. The linearized-gradient approximation has proved to be sufficiently involved to negate its usefulness,[10] and it therefore will not be discussed. Only the Laplace and stationary-interface analyses will be treated.

The solution of the Laplace equation is

$$C(r,t)-C_M=(C_I-C_M)(R/r).$$

This is the same as the result obtained for growth [Eq. (9)] except that $C_I>C_M$ whereas for growth $C_I<C_M$ (Fig. 1). On substitution into Eq. (3) and integrating

$$R^2=R_0^2-kDt. \quad (29)$$

[Note that k, as defined in Eq. (8), is positive for dissolution and negative for growth.]

The stationary-interface approximation leads to[4,8]

$$C(r,t)-C_M=\{[(C_I-C_M)R]/r\} \times \mathrm{erfc}[(r-R)/2(Dt)^{1/2}],$$

which again, is formally identical to Eq. (12) obtained for growth. For this field the boundary, initial, and flux conditions are satisfied by the implicit relation[4]

$$\ln[y+2p(\tau)^{1/2}y+\tau] = \frac{-2p}{(1-p^2)^{1/2}}\arctan\left(\frac{(1-p^2)^{1/2}}{[y/(\tau)^{1/2}]+p}\right), \quad (30)$$

where

$$y=R/R_0, \quad (31a)$$

$$\tau=a^2t/R_0^2, \quad (31b)$$

$$a^2=kD, \quad (31c)$$

$$p^2=k/4\pi. \quad (31d)$$

It is useful for subsequent discussion, to rewrite Eq. (29) using the reduced variables defined in Eqs. (31) to obtain

$$y^2=1-\tau. \quad (32)$$

2. *Planar Precipitates*

The exact solution for the field is

$$C(x,t)-C_M=(C_I-C_M)\frac{\mathrm{erfc}[(x-S_0)/2(Dt)^{1/2}]}{\mathrm{erfc}(-\lambda)}, \quad (33)$$

which yields

$$S=S_0-\lambda_1(Dt)^{1/2} \quad (34)$$

for

$$\lambda_1=\lambda/2 \quad (35)$$

and

$$(\pi)^{1/2}\lambda e^{\lambda^2}\,\mathrm{erfc}(-\lambda)=k/2. \quad (36)$$

Similarly for the stationary-interface approximation[8]

$$C(x,t)-C_M=(C_I-C_M)\ \mathrm{erfc}[(x-S)/2(Dt)^{1/2}]$$

which is formally identical to Eq. (24) and yields[4]

$$S=S_0-\lambda_2(Dt)^{1/2}, \quad (37)$$

where

$$\lambda_2=k/(\pi)^{1/2}. \quad (38)$$

On the linearized-gradients analysis[7,10]

$$S=S_0-\lambda_4(Dt)^{1/2}, \quad (39)$$

where

$$\lambda_4=\frac{k}{2[1+(k/2)]^{1/2}}$$

exactly as in the growth case [Eq. (28)]. As in previous analyses of planar precipitates, the Laplace approximation is undefined.

IV. RESULTS AND DISCUSSION

Tables I and II summarize the salient results giving the various solutions together with their limiting forms at small k. The parameter k [Eq. (8)] is central in defining the kinetics and is simply related to the supersaturation ratio. While it is not difficult to derive the inequalities (Tables I and II) analytically, it is more instructive, in the present context, to examine the

TABLE I. Precipitate growth.

	Sphere $R=\lambda_j(Dt)^{1/2}$	Plane $S=\lambda_j(Dt)^{1/2}$
Exact solution	$\lambda_1=2\lambda$ $\lambda^2\exp(\lambda^2)[\exp(-\lambda^2)-\lambda(\pi)^{1/2}\,\mathrm{erfc}\lambda]=-k/4$ $\lim_{k\to 0}\lambda_1=\lambda_2$ $\lim_{k\to 0}\lambda_1=\lambda_3$ $k<0: \lambda_1>\lambda_2>\lambda_3$ $\lim_{k\to 0}\lambda_1=\lambda_4;\ k\neq -2;\ \lambda_1>\lambda_4$	$\lambda_1=2\lambda$ $(\pi)^{1/2}\lambda\exp(\lambda^2)\,\mathrm{erfc}\lambda=-k/2$ $\lim_{k\to 0}\lambda_1=\lambda_2$ $k<0: \lambda_1>\lambda_2$ $\lvert k\rvert>1.98: \lambda_1<\lambda_4$
Invariant-size approximation	$\lambda_2=[-k/(2\pi^{1/2})]+[k^2/(4\pi)-k]^{1/2}$ $\lim_{k\to 0}\lambda_2=\lambda_3$	$\lambda_2=-k/(\pi)^{1/2}$
Invariant-field approximation	$\lambda_3=(-k)^{1/2}$	Not defined (cannot satisfy the far-field condition)
Linearized-gradients approximation	$f(k)=[-4k/(1+4k)]^{1/3}$ $\gamma=[1-f(k)]/f(k)$ $\lambda_4=(-k/\gamma)^{1/2}$	$\lambda_4=k/\{2[1+(k/2)]^{1/2}\}$ $\lim_{k\to 0}\lambda_4=-k/2$

question graphically. For growth (Figs. 2 and 3 and Table III) we see immediately that (a) the exact solution always has the largest λ; (b) for $\lvert k\rvert<0.7$, λ_2 is the best approximation; (c) for planar growth the linearized-gradient approximation is reasonable for all $\lvert k\rvert<1.98$, which covers almost the entire range of k ($0\leq\lvert k\rvert\leq 2$); and (d) for spherical growth the linearized-gradient approximation is the best one for $\lvert k\rvert\gtrsim 0.7$. Since the stationary-interface and the linearized-gradient approximations are convenient and tractable and

TABLE II. Precipitate dissolution.

	Sphere	Plane $S=S_0-\lambda_j(Dt)^{1/2}$
Exact solution	No exact solution available	$\lambda_1=2\lambda$ $(\pi)^{1/2}\lambda\exp(\lambda^2)\,\mathrm{erfc}(-\lambda)=k/2$ $\lim_{k\to 0}\lambda_1=\lambda_2>\lambda_4$ $k>0: \lambda_2>\lambda_1$ $0\leq k\lesssim 1.5: \lambda_2\geq\lambda_1>\lambda_4$
Invariant-size approximation	$\ln(y+2p(\tau)^{1/2}y+\tau)$ $=[-2p/(1-p^2)^{1/2}]\arctan\{(1-p^2)^{1/2}/[(y/\tau^{1/2})+p]\}$ where $y=R/R_0,\ \tau=a^2t/R_0^2$ $a^2=kD,\ p^2=k/4\pi$ and reduces to $y^2=1-\tau$ in the limit as p (or k) goes to zero.	$\lambda_2=k/(\pi)^{1/2}$
Invariant-field approximation	$R^2=R_0^2-kDt$ or $y^2=1-\tau$	Not defined
Linearized-gradients approximation	Sufficiently complex to negate its usefulness.	$\lambda_4=(C_I-C_M)/[(C_P-C_M)^{1/2}(C_P-C_I)^{1/2}]$ $=k/\{2[1+(k/2)]^{1/2}\}$ $\lim_{k\to 0}\lambda_4=k/2$

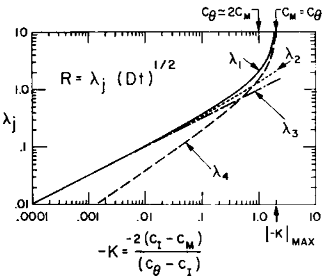

FIG. 2. Growth kinetics for spherical precipitates as a function of $|k|$—λ_1, exact solution: λ_2, invariant-size approximation: λ_3, invariant-field approximation: λ_4, linear-gradient approximation.

are better than the invariant-field approximation, the latter should not be used. Since for many alloy systems of interest $|k|<0.3$, the invariant-size approximation should probably be used exclusively for the analysis of precipitate growth.

For planar precipitate dissolution (unlike the case of growth just discussed) the stationary-interface approximation exceeds the exact solution at all k, whereas the linear-gradient approximation lies below the exact solution at small k and above at large k (Table IV). An explanation for this difference between growth and dissolution may be found in the diffusion fields [$C(r$ or $x, t)$] in the matrix. During growth the field has its minimum at the precipitate–matrix interface, its maximum at infinity, and is convex upwards. In dissolution the minimum is at infinity, the maximum at the interface, and the curve convex downwards. If one compares the approximate forms of $C(r$ or $x, t)$ with the exact, wherever $C(\text{approx})<C(\text{exact})$, or, more precisely $\nabla C(\text{approx})\geq\nabla C(\text{exact})$ then the corresponding $\lambda(\text{approx})>\lambda(\text{exact})$. From Table IV it is further seen that, for $k<0.314$, the stationary-interface approximation provides λ's in better agreement with the exact solution than does the linearized-gradient approximation. For higher values of k, the reverse is true. Since in a great number of alloy systems $k<0.3$, the invariant-size approximation is more widely applicable.

If we treat dissolution of spheres as essentially the reverse of growth it may be shown that

$$C(r,t)=C_M+A\left[\frac{[D(t_0-t)]^{1/2}}{r}\exp\left(\frac{-r^2}{4D(t_0-t)}\right)-\frac{(\pi)^{1/2}}{2}\operatorname{erfc}\left(\frac{r}{2[D(t_0-t)]^{1/2}}\right)\right], \quad (40)$$

where

$$A=\{2\lambda_R(C_I-C_M)/[\exp(-\lambda_R^2)-(\pi)^{1/2}\lambda_R\operatorname{erfc}(\lambda_R)]\} \quad (41)$$

and

$$R=2\lambda_R[D(t_0-t)]^{1/2} \quad (42a)$$

with

$$R_0=2\lambda_R(Dt_0)^{1/2} \quad (42b)$$

satisfies the flux equation [Eq. (3)] for the appropriate boundary conditions $C(\infty,t)=C_M$ and $C(R,t)=C_I$ for all λ's which satisfy

$$\lambda_R^2\exp(\lambda_R^2)[\exp(-\lambda_R^2)-(\pi)^{1/2}\lambda_R\operatorname{erfc}(\lambda_R)]=k/4. \quad (43)$$

As stated earlier [Eq. (7)], there is only one positive value of λ which satisfies Eq. (43). However, Eq. (40) does not satisfy Eq. (1) and at $t=0$, $C(r\geq R,0)\neq C_M$. Rather, there is a finite gradient surrounding the precipitate at zero time resulting from the fact that $R_0\neq0$. Contrary to the growth case, the Eqs. (42) and (43) form only an approximation. It is easy to show that Eqs. (42) reduce to the Laplace solution in the limit of small k.

TABLE III. Growth of planar and spherical precipitates.

$-k=2(C_I-C_M)/(C_P-C_I)$ $-k$	Spherical precipitate $R=\lambda_j(Dt)^{1/2}$ λ_1	Planar precipitate $S=\lambda_j(Dt)^{1/2}$ λ_1
7.186×10^{-10}	2.681×10^{-5}	4.054×10^{-10}
6.108×10^{-9}	7.816×10^{-5}	3.446×10^{-9}
6.180×10^{-8}	0.0002486	3.487×10^{-8}
6.173×10^{-7}	0.000786	3.483×10^{-7}
6.173×10^{-6}	0.002487	3.483×10^{-6}
6.173×10^{-5}	0.007884	3.483×10^{-5}
0.0003086	0.01771	
0.0006173	0.02512	0.0003483
0.003086		0.001743
0.006173	0.08143	0.003490
0.01235	0.1169	
0.01852	0.1449	
0.02469	0.1691	0.01404
0.06173	0.2801	0.03553
0.08642	0.3397	0.05014
0.1481		0.08777
0.2099		0.1270
0.2716	0.6911	0.1681
0.3333		0.2110
0.3951	0.9000	0.2561
0.4568		0.3034
0.5802	1.217	0.4058
0.8889	1.818	0.7221
1.198	2.626	1.181
1.383		1.589
1.506	3.953	1.965
1.568	4.361	
1.630	4.873	
1.691	5.609	2.868
1.722	6.313	
1.815		4.056
1.877		5.185
1.938		7.437
1.969		9.489
1.981		10.521
1.988		11.072
1.994		11.641
1.997		11.931
1.9999		12.218
2.0	∞	12.224

TABLE IV. Dissolution of planar and spherical precipitates.

k	λ_R[a]	$S=S_0-\lambda_j(Dt)^{1/2}$ λ_1	λ_2	λ_4
7.186×10^{-10}	1.340×10^{-5}	4.054×10^{-10}	4.054×10^{-10}	3.593×10^{-10}
6.180×10^{-8}	0.0001243	3.487×10^{-8}	3.487×10^{-8}	3.090×10^{-8}
6.173×10^{-6}	0.001244	3.483×10^{-6}	3.483×10^{-6}	3.086×10^{-6}
0.0006175	0.01256	0.0003483	0.0003484	0.0003087
0.0030912	0.02851	0.001742	0.001744	0.001544
0.006192	0.04078	0.003487	0.003493	0.003091
0.01242	0.05866	0.006981	0.007009	0.006192
0.01869	0.07283	0.01048	0.01055	0.009302
0.025	0.08512	0.01399	0.01410	0.01242
0.04416	0.1161	0.02457	0.02492	0.02184
0.06369	0.1426	0.03523	0.03594	0.03135
0.07692		0.04237	0.04340	0.03774
0.09032	0.1743	0.04954	0.05096	0.04417
0.1246	0.2108	0.06763	0.07029	0.06044
0.16	0.2456	0.08594	0.09027	0.07698
0.2345		0.1232	0.1323	0.1109
0.3143	0.3820	0.1615	0.1773	0.1461
0.4923	0.5323	0.2411	0.2778	0.2205
0.8174	0.8333	0.3695	0.4612	0.3443
1.24	1.383			
1.6	2.305	0.6147	0.9027	0.5963
1.703	2.903			
2.985		0.9188	1.684	0.9453
6.1		1.334	3.442	1.516
8.8		1.561	4.965	1.893
19.6		2.061	11.058	2.982
30.4		2.328	17.151	3.776
62.8		2.749	35.431	5.516
127.6		3.133	71.991	7.926
214.0		3.397	120.737	10.296

[a] λ_R applies to the reversed-growth approximation as defined in Eqs. (42) and (43).

We now compare the Laplace, stationary-interface and reverse-growth approximations for dissolving spherical precipitates. The easiest way to study the stationary-interface approximation [Eq. (30)] is to graph $(R/R_0)^2$ vs τ (Fig. 4) as has been done previously.[4,5] The Laplace approximation then, from Eq. (32), is merely the $p=0$ line in Fig. 4, independent of k.

Using the parameters in Eqs. (31) with Eqs. (42) in the reverse-growth approximation

$$y^2=1-(4\lambda_R^2/k)\tau \tag{44}$$

λ_R is tabulated as a function of k in Table IV. For small p (i.e., $\lesssim 0.04$) the linear relation from the reversed-growth approximation is in reasonable agreement with

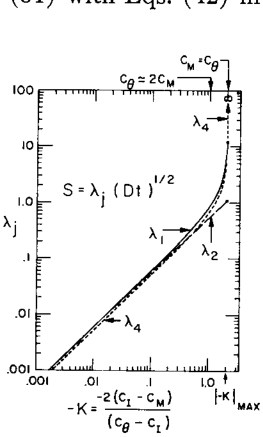

FIG. 3. Growth kinetics for planar precipitates as a function of $|k|$—λ_1, exact solution: λ_2, Invariant-size approximation: λ_4, Linear-gradient approximation.

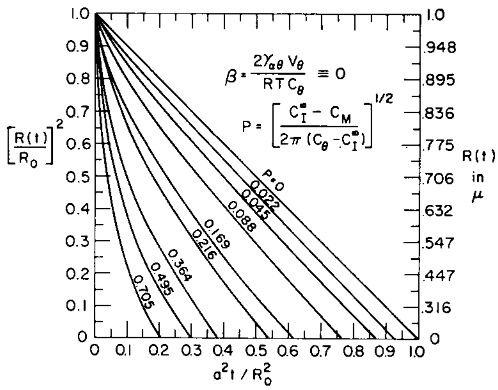

FIG. 4. Dissolution of spherical precipitates according to the invariant-field approximation ($p=0$) and the invariant-size approximation ($p\geq0$).[5]

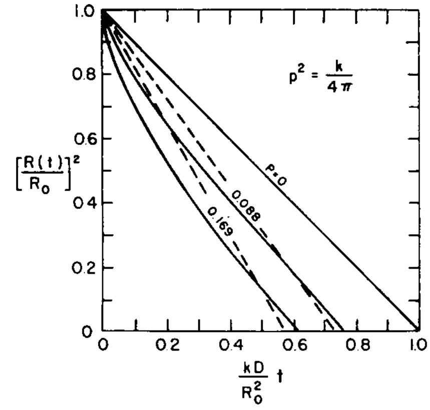

FIG. 5. Dissolution of spherical precipitates according to the invariant-size approximation (solid lines) and reversed-growth approximation (solid line at $p=0$, dashed lines at $p>0$).

the stationary-interface results. At progressively larger p's the difference between $\tau_{\max}(p)$, reversed growth and $\tau_{\max}(p)$, stationary interface becomes progressively greater (Fig. 5). While we cannot compare the stationary-interface and reversed-growth results with an exact solution it appears reasonable to conclude that the stationary interface is the better approximation since it alone properly satisfies the initial conditions. However, the relative simplicity of the reversed-growth solution makes it quite useful especially in the limit of small p. The reversed-growth solution also makes clear the inherent difference between growth and dissolution.

V. SUMMARY AND CONCLUSIONS

The salient feature of this investigation is that the stationary-interface approximation, for small values of $|k|$, is the best of the three approximations considered (Laplace, stationary interface and linearized gradients). It is in fact the only one valid for both growth and dissolution of spherical and planar precipitates. Furthermore, in the precipitate-growth analyses the equations obtained from the stationary-interface approximation are sufficiently simple as to render the use of less accurate approximations unnecessary.

For dissolution, where no exact solution is currently available, the stationary-interface analysis appears, for the reasons already stated, to be the most accurate approximation. Its form is rather complicated and the other analyses may therefore have greater practical utility. Among these, the one which must closely approaches the stationary-interface approximation is the reversed-growth approximation, which, though it requires the solution of a transcendental equation, is an explicit expression for $R(t)$. Solutions to the transcendental equation are given in Table IV thereby making its use particularly simple.

It is clear from this study that the relation between growth and dissolution is not independent of the shape of the precipitate. While for planar precipitates the kinetics of growth and dissolution are analogous in the sense that both are governed by a $t^{1/2}$ law, for spherical precipitates a similar statement can not be properly made except in certain limiting cases. It is important to note that, for dissolution, only the stationary-interface approximation satisfies all of the boundary conditions without further assumptions. The other approximations (Laplace and reversed growth) ignore the initial requirement that $C(r, t=0)=C_M$ for all $r\geq R$. This fact points out the inherent difference between growth and dissolution for spherical precipitates and has led us to state that the stationary-interface approximation is the most accurate approximation here as it is in all other cases investigated.

ACKNOWLEDGMENTS

The authors are pleased to thank Professor R. Sekerka and Dr. A. D. Brailsford whose help and encouragement were invaluable. We are also indebted to Dr. H. I. Aaronson, Dr. J. Gillis, and Dr. G. F. Bolling for their extremely useful comments and criticisms of the manuscript.

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