Int. J. Heat Mass Transfer. Vol. 17, pp. 945–953. Pergamon Press 1974. Printed in Great Britain

ON THE INTEGRAL TECHNIQUE FOR SPHERICAL GROWTH PROBLEMS

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(*Received* 2 *October* 1973)

Abstract—The diffusion problems with moving boundary are formulated into a general integral form. Fundamental Green's function is used to derive a transcendental equation that gives readily the interface advancement, the concentration profile, and the boundary concentration of a growing sphere.

Examples dealing with the diffusion-controlled spherical growth in finite and infinite regions are calculated and compared to the results available in the literature.

Potential applications of this technique are briefly discussed.

NOMENCLATURE

C,	solute concentration;
C_0, C_s,	initial and interface concentration;
C_I,	solute concentration of the particle;
C_s^0,	interface concentration at infinite radius;
C^∞, C_s^∞,	reference concentrations;
D,	diffusivity;
σ,	surface energy;
V,	molar volume of the particle;
Rg,	gas constant;
T,	temperature;
r,	radial coordinate;
t,	time;
$R(t)$,	radius of the particle;
R_0,	initial radius of the particle;
R_s,	radial outer boundary;
Q,	dimensionless concentration of the particle;
u,	transform quantity $rC(r, t)$;
G_1, G_2,	Green's functions for instantaneous plane source;
G,	Green's function for instantaneous spherical surface source;
ξ,	position of instantaneous source;
τ,	time of occurrence of instantaneous source;
k, K, n, N,	integers;
p_k,	partition point of the original diffusion zone;
t_n,	corresponding time steps;
λ,	proportional constant for parabolic growth;
S_n,	approximated growing rate;
Rn,	corresponding position of the interface.

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INTRODUCTION

THE GROWTH of a spherical second phase from a mother phase containing more than one chemical constituent is of considerable fundamental and practical interest. Problems such as crystallization, melting, solidification, and precipitation hardening of metals are only a few practical examples frequently encountered in science and engineering.

Theoretically, these problems belong to the class of diffusion or conduction processes known as moving boundary problems. Numerous investigations have been made in this field as seen in several review articles and books [1–4]. In general, closed-form solutions exist only for relatively simple cases and most of the solution processes involve approximate procedure and numerical treatment.

In applying these methods to diffusion or conduction in a multi-component system, difficulties arise owing to the fact that the concentration or temperature at the phase boundary is depending upon the interface advancement and is thus a function of time [5, 6]. This extra degree of non-linearity would make the use of numerical approach inevitable, which, additional to its stability and convergence problems, requires considerable amount of computations in most of the problems.

For these reasons, quasi-stationary approximations are frequently used in practical applications to describe the diffusion growth [7–9]. However, these approximations are restricted to the case of a slow growing sphere and their range of validity remain to be determined. In view of this, it should be of basic interest to develop a new technique that can solve this type of problem in a general way.

It seems that the application of the integral technique could circumvent the mathematical difficulties to a large extent by introducing appropriate fundamental Green's function to reformulate the differential system into an integral form. Thus the melting and solidification of slab and cylindrical rod in a binary liquid metal could readily be calculated by solving a transcendental equation derived from the integral formula [10, 11]. The superiority of this technique in comparison with finite-difference method was further demonstrated by its readiness and accuracy in calculating the solute enrichment during the solidification of alloy [12].

Another advantage of the integral technique is its rather unified approach to the diffusion problems in either finite or infinite region. While it is true that diffusion in a finite domain can be subjected to various successful treatments [13–16], integral technique might be indispensable in solving diffusion processes in an infinite medium. As far as the formulation is concerned, there is virtually no difference in adopting the Green's technique to problems with various domain of interest.

In this paper, the integral formulation of the spherical growth will firstly be derived in a sufficiently general way so that a wide range of diffusion processes would be included. Decomposition of the integral form will then be made to facilitate the numerical calculations which are then illustrated by actual computation on several examples. To estimate the accuracy, the analytical solution of particle growth from zero radius in an infinite medium will be used for comparison.

The influences of initial particle size, surface tension, and the diffusion range on the particle growth rate will be examined in the subsequent examples.

INTEGRAL FORMULATION

To apply Green's function to the moving boundary problems in a general way, a diffusion model sketched in Fig. 1 will be appropriate. A particle with solute concentration C_I grows under the control of solute diffusing toward the interface. The surrounding is imagined to be a region of spherical shell with radius R_s centered at $r = 0$. This is the model used by Ham [7] for the study of particle precipitation from a supersaturated solution. The governing equations for this system are the following:

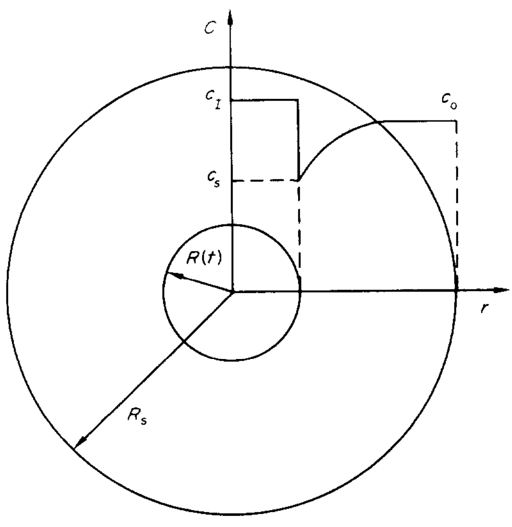

FIG. 1. Diffusion model.

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right), \quad R(t) < r < R_s \tag{1}$$

$$C = C_0, \quad t = 0 \tag{1a}$$

$$C = C_s, \quad r = R(t) \tag{1b}$$

$$\frac{\partial C}{\partial r} = 0, \quad r = R_s \tag{1c}$$

$$R(t) = R_0, \quad t = 0 \tag{1d}$$

$$D\left.\frac{\partial C}{\partial r}\right|_{r=R(t)} = (C_I - C_s)\frac{\mathrm{d}R}{\mathrm{d}t}, \quad r = R(t). \tag{1e}$$

Equation (1) is the diffusion equation with constant diffusivity and equations (1a)–(1d) are the corresponding initial and boundary conditions. The material balance of the solute at the interface is described in equation (1e). Various symbols are to be referred to the notation compiled at the end of the paper.

It is to be noted that the quantities C_0 and C_s might not assume constant values. In fact, the interface concentration is related to the particle size by the Gibbs–Thomson equation

$$C_s = C_s^0\, \mathrm{e}^{(2\sigma V/R_g T)[1/R(t)]} \tag{1f}$$

which is a relationship that could be of importance at the early stage of the growth.

Equations (1)–(1e) can be transformed into dimensionless forms by defining

$$r^* = \frac{r}{R_\infty}, \quad t^* = \frac{Dt}{R_\infty^2}, \quad R^*(t^*) = \frac{R(t)}{R_\infty},$$

$$R_s^* = \frac{R_s}{R_\infty}, \quad R_0^* = \frac{R_0}{R_\infty},$$

$$C^*(r^*, t^*) = \frac{C(r,t) - C_s^\infty}{C^\infty - C_s^\infty}, \quad C_0^*(r^*) = \frac{C_0(r) - C_s^\infty}{C^\infty - C_s^\infty},$$

$$C_s^* = \frac{C_s - C_s^\infty}{C^\infty - C_s^\infty}, \quad Q^* = \frac{C_I - C_s^\infty}{C^\infty - C_s^\infty},$$

so that the resulting equations become

$$\frac{\partial C^*}{\partial t^*} = \frac{\partial^2 C^*}{\partial r^{*2}} + \frac{2}{r^*}\frac{\partial C^*}{\partial r^*}, \quad R^*(t^*) < r^* < R_s^* \tag{1g}$$

$$C^* = C_0^*, \quad t^* = 0 \tag{1h}$$

$$C^* = C_s^*, \quad r^* = R^*(t^*) \tag{1i}$$

$$\frac{\partial C^*}{\partial r^*} = 0, \quad r^* = R_s^* \tag{1j}$$

$$R^* = R_0^*, \quad t^* = 0 \tag{1k}$$

$$\left.\frac{\partial C^*}{\partial r^*}\right|_{r^*=R^*} = (Q^* - C_s^*)\frac{\mathrm{d}R^*}{\mathrm{d}t^*}, \quad r^* = R^*(t^*). \tag{1l}$$

For the simplicity of operations, all the stars (*) will be dropped from the subsequent development, with the understanding that dimensionless quantities are being referred to.

To derive the integral equation for this system, the transformation $u(r,t) = rC(r,t)$ is made to convert equation (1g)–(1l) into the following forms:

$$\frac{\partial u}{\partial t}-\frac{\partial^2 u}{\partial r^2}=0, \quad R(t)<r<R_s \tag{2}$$

$$u = rC_0, \quad t=0 \tag{2a}$$

$$u = rC_s, \quad r=R(t) \tag{2b}$$

$$\frac{\partial u/r}{\partial r}=0, \quad r=R_s \tag{2c}$$

$$R(t)=R_0, \quad t=0 \tag{2d}$$

$$\left.\frac{\partial u/r}{\partial r}\right|_{r=R(t)}=\left(Q-\frac{u}{R}\right)\frac{\mathrm{d}R}{\mathrm{d}t}, \quad r=R(t). \tag{2e}$$

One can introduce a Green's function $G_1 = G_1(r, t/\xi, \tau)$ satisfying the diffusion equation with an instantaneous plane source of unit strength at $r=\xi$ and $t=\tau$, namely:

$$\frac{\partial^2 G_1}{\partial r^2}-\frac{\partial G_1}{\partial t}=-\delta(r-\xi)\delta(t-\tau). \tag{3}$$

The Green's function also satisfies its adjoint equation in the source coordinates (ξ,τ), which, after a small positive value ε is added to the time t to avoid the singularity, can be written as

$$\frac{\partial^2 G_2}{\partial \xi^2}+\frac{\partial G_2}{\partial \tau}=-\delta(r-\xi)\delta(t+\varepsilon-\tau). \tag{4}$$

Here the symbol $G_2 = G_1(r, t+\varepsilon/\xi, \tau)$ is used to distinguish from G_1 appearing in equation (3). Similarly, equation (2) can also be written into an expression in the source coordinates to become

$$\frac{\partial^2 u}{\partial \xi^2}-\frac{\partial u}{\partial \tau}=0, \quad R(\tau)<\xi<R_s. \tag{5}$$

Multiplying equation (4) by u and equation (5) by G_2, subtracting from each other, and then integrating with respect to ξ and τ over the region surrounded by the contour designated in Fig. 2, one obtains the double integral equation

$$\iint\left[G_2\frac{\partial^2 u}{\partial \xi^2}-u\frac{\partial^2 G_2}{\partial \xi^2}\right]\mathrm{d}\xi\,\mathrm{d}\tau-\iint\frac{\partial uG_2}{\partial \tau}\mathrm{d}\xi\,\mathrm{d}\tau=0. \tag{6}$$

Making use of Green's theorem to convert area to line integral, equation (6) is simplified to the following:

$$\oint\left[G_2\frac{\partial u}{\partial \xi}-u\frac{\partial G_2}{\partial \xi}\right]\mathrm{d}\tau+\oint uG_2\,\mathrm{d}\xi=0. \tag{7}$$

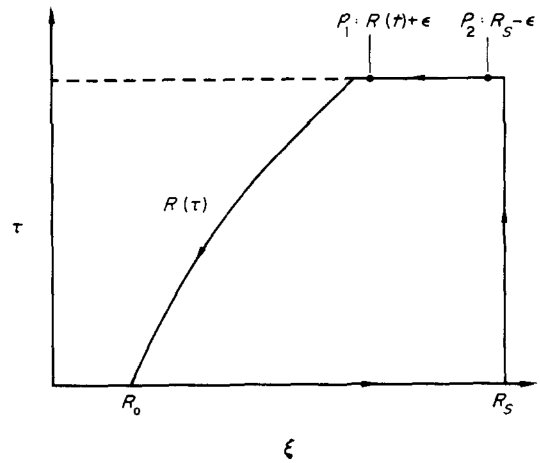

FIG. 2. Integration contour.

By taking $\varepsilon \to 0$ as the limit, it ends up with the integral equation

$$u(r,t)=\int_{R_0}^{R_s}\left.uG_1\right|_{\tau=0}\mathrm{d}\xi+\int_{R(t)}^{R_0}\left.uG_1\right|_{R(\tau)}\mathrm{d}\xi+\int_0^t\left[G_1\frac{\partial u}{\partial \xi}-u\frac{\partial G_1}{\partial \xi}\right]_{R_s}\mathrm{d}\tau-\int_0^t\left[G_1\frac{\partial u}{\partial \xi}-u\frac{\partial G_1}{\partial \xi}\right]_{R(\tau)}\mathrm{d}\tau \tag{8}$$

which in terms of variable $C(r,t)$ takes the final form:

$$C(r,t)=\int_{R_0}^{R_s}C_0.4\pi\xi^2\left.G\right|_{\tau=0}\mathrm{d}\xi+\int_{R(t)}^{R_0}C.4\pi\xi^2\left.G\right|_{R(\tau)}\mathrm{d}\xi+\int_0^t 4\pi\xi^2\left[G\frac{\partial C}{\partial \xi}-C\frac{\partial G}{\partial \xi}\right]_{R_s}\mathrm{d}\tau-\int_0^t 4\pi\xi^2\left[G\frac{\partial C}{\partial \xi}-C\frac{\partial G}{\partial \xi}\right]_{R(\tau)}\mathrm{d}\tau \tag{9}$$

where G is the Green's function for an instantaneous spherical surface source of unit strength, which is related to the plane source Green's function G_1 by the relation

$$G = G_1/4\pi r\xi. \tag{10}$$

Detailed derivations of equation (8) are given in references [12, 17, 19].

Equation (9) expresses the concentration distribution at any arbitrary r and t in terms of the concentration and its gradients at the boundaries. Obviously, this is the main advantage of this technique since the original problem is reduced from one involving a domain of interest to one involving only its interfaces. However, equation (9) still contains unknown quantities $R(t)$ and $C(R_s, t)$ that remain to be determined. Furthermore, the singularity of G as $r\to\xi$ and $t\to\tau$ would cause considerable difficulties during the numerical evaluation of integrals. These problems will be solved by the method developed in the next section.

APPROXIMATE SOLUTION

The Green's function selected for equation (9) is as follows:

$$G(r, t/\xi, \tau) = \frac{1}{8\pi r\xi\sqrt{\pi(t-\tau)}} \left[e^{-[(r-\xi)^2/4(t-\tau)]} - e^{-[(r+\xi)^2/4(t-\tau)]}\right] \quad (11)$$

which has zero gradient at $r = 0$ and vanishes as $r \to \infty$.

The integration of this function over the half space $r > 0$ gives unit value corresponding to the strength of the instantaneous source.

As mentioned in the previous section, equation (9) contains two unknown quantities that are the prerequisite to the computation of the concentration profile.

This would require two integral equations that have to be solved simultaneously to produce the interface $R(t)$ and the concentration at the outer boundary $C(R_s, t)$. These equations are to be provided by the Green's boundary formula obtained by letting r approach respectively to the two boundaries in equation (9). Consequently, we obtain

$$\int_{R_0}^{R_s} C_0 . 4\pi\xi^2 G\Big|_{\tau=0} d\xi + \int_{R(t)}^{R_0} C . 4\pi\xi^2 G\Big|_{R(\tau)} d\xi + \int_0^t 4\pi\xi^2\left[G\frac{\partial C}{\partial\xi} - C\frac{\partial G}{\partial\xi}\right]_{R_s} d\tau - \int_0^t 4\pi\xi^2\left[G\frac{\partial C}{\partial\xi} - C\frac{\partial G}{\partial\xi}\right]_{R(\tau)} d\tau = \begin{cases}\frac{1}{2}C_s, & r = R(t) \\ \frac{1}{2}C(R_s, t), & r = R_s.\end{cases} \quad (12, 13)$$

It is to be noted that a factor of 1/2 appears in the above formula as a result of the discontinuity of $\partial G/\partial\xi$ across the boundary. Equation (12) and (13) are usually considered as the real analogy of Plemelj formula in complex plane and its proof will be referred to the literature [18, 19].

Equation (12) and (13) include the integration up to the singular points at the boundaries, which could cause enormous error if straightforward numerical integration is used. An alternative would be to replace these equation by directly applying equation (9) to two positions infinitesimally close to but inside the boundaries designated as P_1 and P_2 in Fig. 2. At such a point, the concentration can be set to the exact boundary concentration without introducing significant error and, most important of all, the integration over the singularity can be avoided.

Equation (9) can further be simplified by the substitution of conditions (1j) and (11) and by combining common terms to yield the following:

$$C(r, t) = \int_{R_0}^{R_s} C_0 . 4\pi\xi^2 G\Big|_{\tau=0} d\xi - \int_0^t C . 4\pi\xi^2\frac{\partial G}{\partial\xi}\Big|_{R_s} d\tau - Q . \int_0^t \frac{dR}{d\tau} . 4\pi\xi^2 G\Big|_{R(\tau)} d\tau + \int_0^t C . 4\pi\xi^2\frac{\partial G}{\partial\xi}\Big|_{R(\tau)} d\tau. \quad (14)$$

The integral can be written as the summation of integrals over certain sub-intervals, which, according to the mean value theorem for Reimann–Stieltjes integral, are decomposed into quadratures as follows:

$$C(r, t) = \sum_{k=1}^{k=K} C_0(p_m)\int_{p_k}^{p_{k+1}} 4\pi\xi^2 G\Big|_{\tau=0} d\xi - \sum_{n=1}^{n=N} C(R_s, t_m)\int_{t_n}^{t_{n+1}} 4\pi\xi^2\frac{\partial G}{\partial\xi}\Big|_{R_s} d\tau - \sum_{n=1}^{n=N} Q . \frac{dR(t_m)}{dt}\int_{t_n}^{t_{n+1}} 4\pi\xi^2 G\Big|_{R(\tau)} d\tau + \sum_{n=1}^{n=N} C[R(t_m), t_m]\int_{t_n}^{t_{n+1}} 4\pi\xi^2\frac{\partial G}{\partial\xi}\Big|_{R(\tau)} d\tau \quad (15)$$

with

$$p_1 = R_0$$
$$p_{k+1} = R_s$$
$$t_1 = 0$$
$$t_{N+1} = t$$
$$p_k \leqslant p_m \leqslant p_{k+1}$$
$$t_n \leqslant t_m \leqslant t_{n+1}.$$

While the exact values of p_m and t_m can not be predetermined, a feasible choice would be the middle of the interval. For sufficiently small interval, linear interpolation can be used to evaluate the concentrations at p_m and t_m.

The remaining task will be the evaluation of those integrals over sub-intervals. It is noticed that, if the intervals are sufficiently small, the integration over the free boundary could be approximated by a series of linear chords with slope s_n as shown in Fig. 3. This enables us to integrate equation (15) analytically to obtain a transcendental equation containing $R(t_n)$ and $C(R_s, t_n)$ as unknown variables. This procedure is decisive in an effort to cut down the computational work while retaining enough accuracy at the same time.

The results of this integration are given here for the convenience of future application:

$$\int 4\pi\xi^2 G\bigg|_{\tau=0} \mathrm{d}\xi = \frac{1}{2}\left[E\left(\frac{r+\xi}{\sqrt{4t}}\right) - E\left(\frac{r-\xi}{\sqrt{4t}}\right)\right] + \frac{1}{r}\sqrt{\frac{t}{\pi}}\left[\mathrm{e}^{-[(r+\xi)^2/4t]} - \mathrm{e}^{-[(r-\xi)^2/4t]}\right] + \text{const.} \quad (15a)$$

$$\int 4\pi\xi^2 \frac{\partial G}{\partial \xi}\bigg|_{R_s} \mathrm{d}\tau = \frac{1}{2}\left\{E\left(\frac{r-R_s}{y}\right) - E\left(\frac{r+R_s}{y}\right) + \frac{y}{r\sqrt{\pi}} \cdot \left[\mathrm{e}^{-[(R_s-r)^2/y^2]} - \mathrm{e}^{-[(R_s+r)^2/y^2]}\right]\right\} + \text{const.} \quad (15b)$$

$$\int 4\pi\xi^2 G\bigg|_{R(\tau)} \mathrm{d}\tau = \frac{H^2}{8r}\left\{E(z_1)\left(\frac{1}{2}-\frac{r}{H}\right) + E(z_2)\,\mathrm{e}^{-(4A/H)} \cdot \left(\frac{1}{2}-\frac{r}{H}+\frac{2A}{H}\right) - E(z_3)\left(\frac{1}{2}+\frac{r}{H}\right) - E(z_4)\,\mathrm{e}^{-(4B/H)}\left(\frac{1}{2}+\frac{r}{H}+\frac{2B}{H}\right) - \frac{2y}{H\sqrt{\pi}} \cdot (\mathrm{e}^{-z_1^2} - \mathrm{e}^{-z_3^2})\right\} + \text{const.} \quad (15c)$$

$$\int 4\pi\xi^2 \frac{\partial G}{\partial \xi}\bigg|_{R(\tau)} \mathrm{d}\tau = \frac{H}{2r}\left\{\frac{1}{2}E(z_1) + E(z_2)\,\mathrm{e}^{-(4A/H)} \cdot \left(\frac{1}{2}-\frac{r}{H}+\frac{2A}{H}\right) - \frac{1}{2}E(z_3) - E(z_4) \cdot \mathrm{e}^{-(4B/H)}\left(\frac{1}{2}+\frac{r}{H}+\frac{2B}{H}\right) - \frac{y}{H\sqrt{\pi}} \cdot (\mathrm{e}^{-z_1^2} - \mathrm{e}^{-z_3^2})\right\} + \text{const.} \quad (15d)$$

where

$$S_n = \frac{R_{n+1}-R_n}{t_{n+1}-t_n}$$
$$H = 4/S_n$$
$$A = -S_n(t-t_n) - R_n + r$$
$$B = -S_n(t-t_n) - R_n - r$$
$$y = \sqrt{[4(t-\tau)]}$$
$$z_1 = y/H + A/y$$
$$z_2 = y/H - A/y$$
$$z_3 = y/H + B/y$$
$$z_4 = y/H - B/y$$
$$E(x) = \mathrm{erf}(x).$$

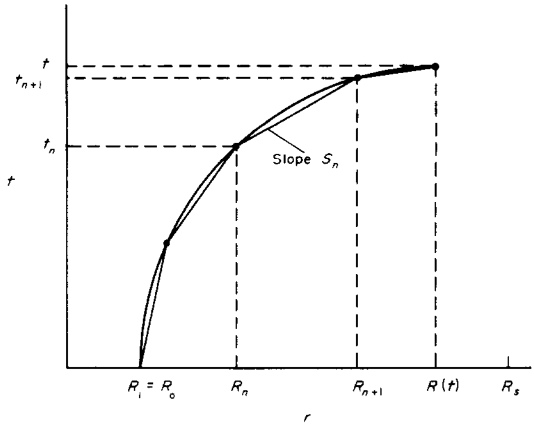

FIG. 3. Interface advancement.

Equations (15a)–(15d) contain only simple functions that can be readily calculated with the aid of a digital computer. Thus starting from the initial point at $t = t_1$, one solves for $R(t)$ and $C(R_s, t)$ at $t = t_2$ by requiring that equation (15) be satisfied at point P_1 and P_2. This may then proceed to subsequent points in a similar manner.

In the following section, equation (15) will be used to solve several diffusion problems, including one that has an analytical solution for comparison. Since equation (15) is derived in a general way, application to heat conduction problems follows automatically and thus will not be elaborated here.

EXAMPLES

Consider the growth of a particle from zero radius in an infinite medium with initially uniform concentration C_0. If the surface concentration C_s is assumed to be constant throughout the process, this system then possesses an analytical solution [20] describing a parabolic law of growth as shown by straight lines in Fig. 4.

If we take $C^\infty = C_0$ and $C_s^\infty = C_s$ as the reference concentrations in equations (1g)–(1l), and let the outer boundary R_s approach to infinity at the same time, the resulting integral equation is immediately deduced from equation (14) as follows:

$$C(r, t) = 1 - Q\int_0^t \frac{\mathrm{d}R}{\mathrm{d}\tau} \cdot 4\pi\xi^2 G\bigg|_{R(\tau)} \mathrm{d}\tau. \quad (16)$$

The unit value for the first term of the r.h.s. of equation (16) is the result of the selection of the special type of Green's function in equation (11). The corresponding transcendental equation in equation (15) is then used to calculate the particle growth. The results are plotted as discrete points in Fig. 4, which shows

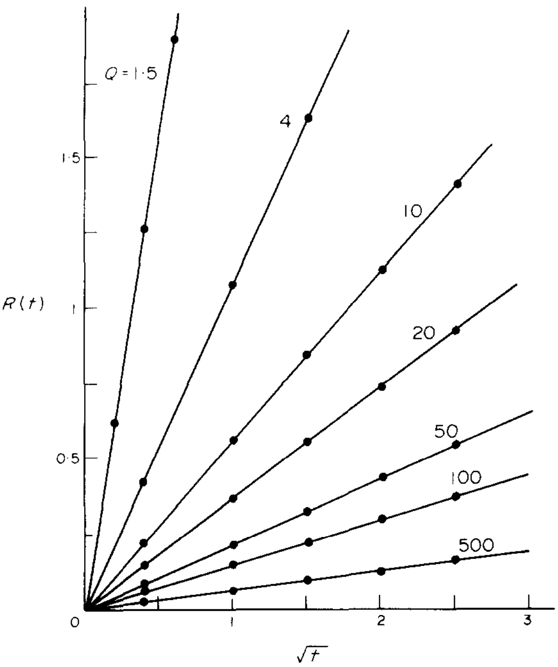

FIG. 4. Parabolic growth of a particle from $R(0) = 0$.

good agreements over a wide range of the growing rate with the analytical solution.

It is also of interest to know that equation (16) can be integrated analytically if the similarity relation $R(t) = 2\lambda\sqrt{t}$ is assumed. The result of integration is just the Frank's solution [20] in dimensionless form:

$$C(r,t) = 1 + 4Q\lambda^3 e^{\lambda^2} \times \left[\frac{\sqrt{\pi}}{2}\operatorname{erfc}\left(\frac{r}{2\sqrt{t}}\right) - \frac{\sqrt{t}}{r} e^{-(r^2/4t)}\right]. \quad (17)$$

Regarding the computation, the required time steps are quickly established by reducing the intervals until little improvement of the results is observed. The computation was performed on a small PDP-10 machine that requires user's supply of error function as a program subroutine, which demands a substantial amount of computer time. As a comparison, about 4 min is needed for the calculation up to $t = 2$ at $Q = 4$ when the approximate formula of the error function given in reference [21] is used. The maximum error of the computation is found to be about 0·85 per cent for $Q = 500$ at $t = 3$. For still higher value of Q, the double precision would be required in the computation in order to retain adequate accuracy.

A slight modification of the problem is that, instead of zero size, an initial particle radius of $R_0 > 0$ is assumed while all other conditions remain unchanged. By choosing the reference concentrations and the length to be $C_s^\infty = C_s$, $C^\infty = C_0$, and $R_\infty = R_0$ in equations (1g)–(11), the corresponding integral equation is readily obtained from equation (14) as follows:

$$C(r,t) = \frac{1}{r}\sqrt{\frac{t}{\pi}}\left[e^{-[(r-1)^2/4t]} - e^{-[(r+1)^2/4t]}\right] + \frac{1}{2}\left[2 + \operatorname{erf}\left(\frac{r-1}{\sqrt{4t}}\right) - \operatorname{erf}\left(\frac{r+1}{\sqrt{4t}}\right)\right] - Q\int_0^t \frac{dR}{d\tau}.4\pi\xi^2 G\bigg|_{R(\tau)} d\tau \quad (18)$$

which differs from equation (16) by merely the initial term. The computational procedure is essentially the same as in the previous example and the results are plotted as light solid lines in Fig. 5.

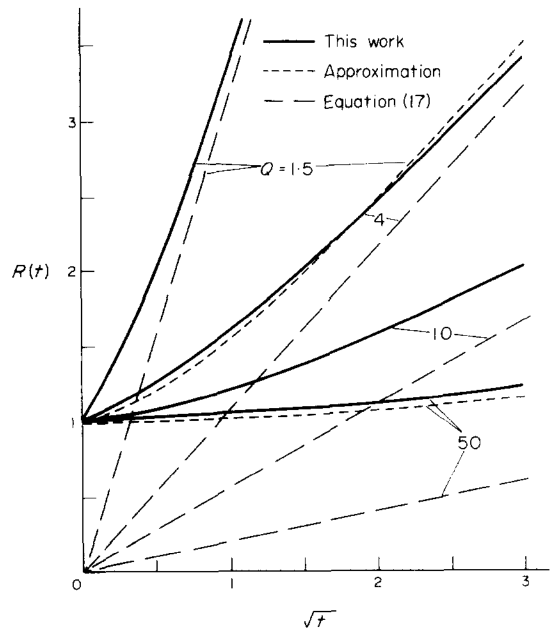

FIG. 5. Growth from $R(0) = 1$.

As physically expected, the growth at large time should approach asymptotically to the exact solution (17) that are superimposed as broken lines on the same diagram. On the other hand, the growth rate at $t = 0$ should match that of the planar growth given by

$$\left.\frac{dR}{d\sqrt{t}}\right|_{t=0} = \frac{2\lambda}{Q} \quad (19)$$

where λ is the solution of

$$\lambda e^{\lambda^2}\operatorname{erfc}(\lambda) = \frac{1}{Q\sqrt{\pi}}. \quad (20)$$

It can be proved from equation (18) that equation (19) and (20) are exactly the initial growth rate of the sphere. Since this would require rather lengthy derivations, including the use of a different type of Green's function, the details will not be given here.

Figure 5 also shows the range of the validity of the quasi-steady state approximations extensively used in the literature [8, 9] as designated by dotted lines for two extreme cases. Conceivably, the approximation agrees reasonably well with current calculations in the region of higher Q value. In the opposite, attempt to use the simplified solution at lower Q may raise the error to an intolerable extent and one must therefore be very cautious in such a practice.

The effect of the surface tension on the individual growth of the particle can be illustrated by incorporating equation (1f) into equation (15) for the calculations. The results are plotted in Fig. 6 for the particular situation of the growth under surface tension in an infinite medium. The curve corresponding to zero surface tension ($W = 0$) is given for comparison. These curves show that the growth is considerably suppressed at the earlier stage. It must be pointed out that the particle-particle interaction is not taken into account here so that the completely opposite phenomena of enhanced growth of certain particle under surface tension due to the Ostwald–Ripening [8, 9] has to be excluded.

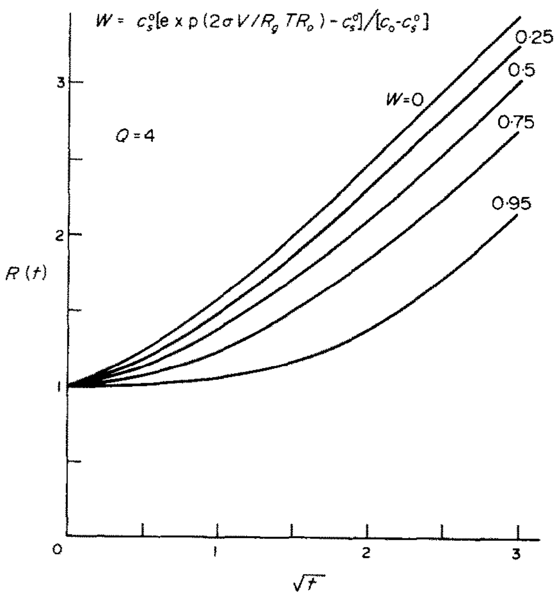

FIG. 6. Growth under surface tension.

Final example involves the diffusion within limited space as shown previously in Fig. 1. This is an idealized model used to describe the precipitation from a supersaturated solution under the condition that particles of a uniform size and of zero surface tension are evenly distributed throughout the medium [7]. Following the computational procedures outlined in the previous section, the computed results are plotted as solid lines in Fig. 7 for an arbitrarily selected diffusion domain of $R_s/R_0 = 10$. It is noted that the growth in the early stage resembles that in Fig. 5 since the conditions on the outer boundary has relatively little influence on the diffusion in the vicinity of the interface. This effect becomes pronounced only after a certain period of time when the solute is gradually depleted, which is observed by the reducing growth rate of the particle. The diagram shows clearly the range of the validity of the approximate solution developed by Ham [7].

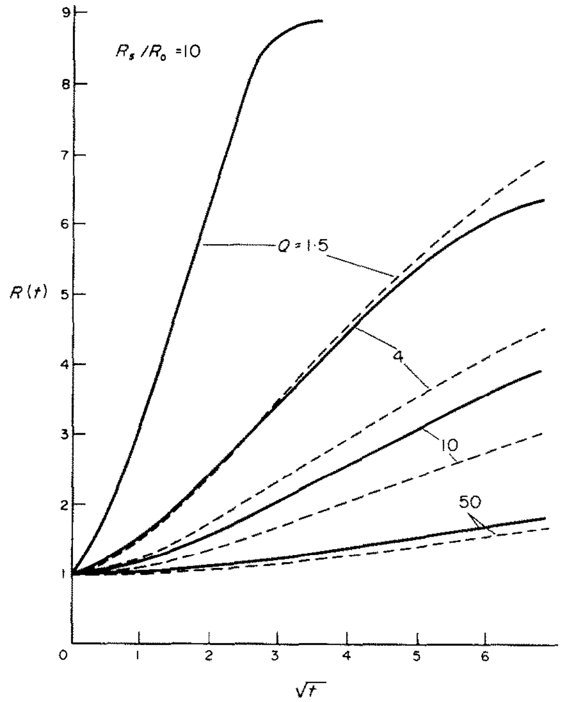

FIG. 7. Diffusion in finite domain.

CONCLUSIONS

The unified approach of the integral technique to the moving boundary problem in spherical coordinates has been demonstrated by solving a variety of diffusion problems. The general equations (14) and (15) were derived for immediate applications to a wide range of diffusion and conduction problems.

The essential features of this technique are the decomposition procedure and the subsequent approximation of the interface advancement by a set of linear relationships. These approximations, together with the special way of avoiding the singularity, are jointly responsible for the success of this technique.

An outstanding characteristic of this approach is that it is rather immaterial to the complexity of the boundary and initial conditions, which enables us to treat a problem with highly non-linear boundary conditions as usual.

The valid range of various approximate solutions are reexamined by testing with the computer results. It is found that those approximations are strictly valid for lower growth rate only. In case of fast growing, they underpredict the growth rate substantially and thus should be used with caution.

From experience, the potential applications of this technique are likely to be in those fields where rather complicated situations are involved. Problems such as the coring and surrounding of alloys, microsegregation of elements in metals, phase transformation with more than one moving boundaries, and the diffusion with surface reactions are only a few examples to be mentioned.

Acknowledgement—The authors wish to thank the Max-Planck-Gesellschaft of West Germany for financial support of this investigation through a fellowship to one of them (O.E.).

REFERENCES

1. S. G. Bankoff, Heat conduction or diffusion with change of phase, *Adv. Chem. Engng* **5**, 75–150 (1964).
2. J. C. Muehlbauer and J. E. Sunderland, Heat conduction with freezing or melting, *Appl. Mech. Rev.* **18**(12), 951–959 (1965).
3. L. I. Rubinshtein, *Problema Stefana*. Izdatelstvo Zvaigzne, Riga (1967).
4. H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, Chapter 11. Oxford University Press, Oxford (1959).
5. I. P. Gorkusha and B. Ya. Lyubov, Effect of surface tension on the diffusion-controlled growth of new phase centers, *Fiz. Metal. Metalloved.* **17**(3), 335–342 (1964).
6. J. Szekely, Y. K. Chuang and J. W. Hlinka, The melting and dissolution of low-carbon steels in iron–carbon melts, *Met. Transc.* **3**, 2825–2833 (1972).
7. F. S. Ham, Theory of diffusion-limited precipitation, *J. Phys. Chem. Solids* **6**, 335–351 (1958).
8. C. Wagner, Theorie der Alterung von Niederschlägen durch Umlösen, *Z. Electrochem.* **65**(7/8), 581–591 (1961).
9. I. M. Lifshitz and V. V. Slyozov, The kinetics of precipitation from supersaturated solid solutions, *J. Phys. Chem. Solids* **19**(1/2), 35–50 (1961).
10. Y. K. Chuang and J. Szekely, On the use of Green's functions for solving melting or solidification problems, *Int. J. Heat Mass Transfer* **14**, 1285–1294 (1971).
11. Y. K. Chuang and J. Szekely, The use of Green's function for solving melting or solidification problems in the cylindrical coordinate system, *Int. J. Heat Mass Transfer* **15**, 1171–1174 (1972).
12. Y. K. Chuang, W. Wepner and K. Schwerdtfeger, Berechnung der interdendritischen Anreicherung von Kohlenstoff und Sauerstoff bei der Erstarrung von Stahl, *Arch. Eisenhütt Wes.* **44**(4), 243–250 (1973).
13. T. R. Goodman, Application of integral methods to transient nonlinear heat transfer, in *Advances in Heat Transfer*, edited by T. F. Irvine and J. P. Hartnett, Vol. 1, p. 52. Academic Press, New York (1964).
14. M. Sami Selim and R. C. Seagrave, Solution of moving boundary transport problems in finite media by integral transform—II. Problems with a cylindrical or spherical moving boundary, *I/EC Fundamentals* **12**(1), 9–13 (1973).
15. P. B. Grimado and B. A. Boley, A numerical solution for the symmetric melting of spheres, *Int. J. Num. Meth. Engng* **2**, 175–188 (1970).
16. L. C. Tao, Generalized numerical solutions of freezing a saturated liquid in cylinders and spheres, *A.I.Ch.E. Jl* **13**(1), 165–169 (1967).
17. P. M. Morse and H. Feshbach, *Methods of Theoretical Physics*, Vol. 1, p. 857. McGraw-Hill, New York (1953).
18. A. Friedman, Free boundary problems for parabolic equations—II. Evaporation or condensation of a liquid drop, *J. Math. Mech.* **9**(1), 19–66 (1960).
19. A. N. Tikhonov and A. A. Samarshii, *Equations of Mathematical Physics*, p. 521. Macmillan, New York (1963).
20. F. C. Frank, Radially symmetric phase growth controlled by diffusion, *Proc. R. Soc.* **A201**, 586–599 (1950).
21. M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions*, p. 299. National Bureau of Standards, Washington, D.C. (1964).

SUR LA TECHNIQUE INTEGRALE POUR LES PROBLEMES DE CROISSANCE SPHERIQUE

Résumé—Les problèmes de diffusion avec des frontières mobiles sont formulées sous une forme intégrale générale. On utilise la fonction fondamentale de Green pour traiter une équation transcendante qui donne rapidement l'avancement de l'interface, le profil de concentration et la concentration à la frontière de la sphère en croissance.

Des exemples de croissance sphérique controlée par la diffusion, dans des domaines finis ou infinis, sont calculés et comparés aux résultats disponibles dans la documentation.

On discute brièvement des applications potentielles de cette technique.

ÜBER DIE ANWENDUNG DER INTEGRALTECHNIK AUF SPHÄRISCHE WACHSTUMSPROBLEME

Zusammenfassung—Das Diffusionsproblem mit einer beweglichen Grenzfläche wird in allgemeiner Integralform formuliert. Ausgehend von der Greenschen Funktion wird eine transzendente Gleichung abgeleitet, aus der sich die Grenzflächenbewegung, das Konzentrationsprofil und die Grenzflächenkonzentration für den Fall einer wachsenden Kugel ergibt.

Es werden Beispiele für das diffusions-kontrollierte sphärische Wachstum im begrenzten und unbegrenzten Raum berechnet und mit vorhandenen Literaturangaben verglichen. Anwendungsmöglichkeiten des Verfahrens werden kurz diskutiert.

ОБ ИНТЕГРАЛЬНОМ МЕТОДЕ РЕШЕНИЯ ЗАДАЧ ОБРАЗОВАНИЯ СФЕРИЧЕСКИХ ЧАСТИЦ

Аннотация — Задачи диффузии с подвижными границами приводятся в общей интегральной формулировке. Фундаментальная функция Грина используется для вывода трансцендентного уравнения, которое описывает перемещение движущейся границы, профиль концентрации и концентрацию на границе растущей сферической частицы. Результаты расчета влияния диффузии на регулируемый рост сферических частиц в ограниченных и бесконечных областях сравниваются с имеющимися данными.

Кратко рассматривается возможное применение данного метода.