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EXPANSIONS IN TIME FOR THE SOLUTION OF ONE-DIMENSIONAL STEFAN PROBLEMS OF CRYSTAL GROWTH*

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Abstract – A new method is presented for the solution of mass transport Stefan problems in one dimension and in semi-infinite regions. It relies on expansions of the concentration distribution and growth rate in powers of $t^{1/2}$. Field conditions at the moving boundary are not necessarily constant; they can be arbitrary. Such conditions often lead to non-similar solutions. Although these problems are nonlinear, the expansion coefficients satisfy linear recurrence relations. These coefficients result from simple algebraic manipulations of functions closely related to the iterated error functions. The method is applied to several examples of crystal growth from supersaturated solutions. The first two examples assume isothermal conditions; they illustrate the difference between surface equilibrium and finite surface kinetics. The third example demonstrates effects due to homogeneous cooling.

NOMENCLATURE

b,	cooling rate;
C,	molar concentration;
D,	diffusion coefficient;
f,	growth rate (surface velocity);
g_n,	inhomogeneous term of equation (2.12);
G_n,	Green's function, equation (2.24);
$h(t)$,	$= \int_0^t dt' f(t')$, surface position;
K,	reaction constant;
m,	liquidus slope;
t,	time;
$u(\xi, \eta)$,	normalized concentration (2.6);
U,	generalized iterated error functions, equations (2.19) and (A.9);
v,	$\equiv u(\xi, 0)$, normalized surface concentration;
W,	wronskian;
$x(z, t)$,	mole fraction;
x_0,	initial value of $x_e(t)$;
y,	$\equiv \eta + \lambda_0$, argument of general solution (2.23);
z,	distance from moving surface.

Greek symbols

η,	similarity variable (2.5);
$\lambda(\xi)$,	function (2.6) that describes growth rate;
μ,	strength of cooling (5.5);
ξ,	proportional to $t^{1/2}$;
σ,	supersaturation ratio $(x_\infty - x_e)/(x_s - x_e)$;
τ,	relaxation time for cooling;
φ,	$\equiv -\partial u(\xi, 0)/\partial \eta$, surface gradient.

Subscripts

e,	equilibrium value;
k, m, n,	integer indices;
s,	value for the solid;
μ, ν,	arbitrary indices;
∞,	far field value.

1. INTRODUCTION

THE GROWTH of defect-free single crystals of carefully controlled composition is a prerequisite for successful device fabrication. Indeed, it is the backbone of the semiconductor industry. Its applications include all of planar silicon device technology, magnetic garnet bubble memories, high efficiency GaAs solar cells, and III–V compound heterostructure lasers, to name a few.

Calculations of crystal growth kinetics require, by their very nature, the solution of transport equations together with the motion of the phase front, i.e. the crystal–fluid surface. Thus, they are Stefan problems akin to those that arise, for example, during freezing, ablation, casting, and geophysical processes. The literature pertaining to such questions is truly immense. A recent survey [1] lists more than 3000 references, and several books and reviews [2–5] deal with the theory and applications of Stefan problems. Although recent efforts have emphasized numerical techniques, particularly for multidimensional problems [6–8], much practical information may be gleaned from analytic procedures. Among these are expansions for small [9–10] and large [11] values of time.

Problems of crystal growth, and more generally of mass transport, differ from typical thermal problems in the boundary conditions at the moving surface and in its equation of motion. Thus, while temperature is continuous across this surface and is anchored there at the melting point, the concentration distribution is discontinuous and its values there may be given or, *a*

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priori, unknown functions of time. In addition, mass conservation requires that one multiply the surface velocity by the concentration jump; for thermal problems, only the latent heat is a multiplicative factor of this velocity. The differences between these two classes of problems is clearly seen if one compares the methodology and examples in Tao's excellent recent paper [12] with the results of this work. Although Tao allows for arbitrary initial conditions and arbitrary boundary conditions at the *fixed* boundaries, he assumes constancy of the temperature field at the moving surface. Here, in keeping with the complex chemical physics of growth and dissolution, the conditions at the *moving* surface are arbitrary.

This paper deals with small time expansions for Stefan problems of mass transport in semi-infinite regions that admit planar moving phase fronts. The method differs from earlier cited efforts that take advantage of transform techniques or of the reduction to integral equations. It more closely resembles Müller-Krumbhaar's technique [13], a perturbation series in inverse powers of the solid's concentration. However, many problems of crystal growth, such as the question of impurity redistribution, do not fit this scheme because there is no standard constant concentration that can serve as an expansion parameter. It also resembles the remarkable recent results of Boley [14], although this author dealt mainly with a simplified model of impurity redistribution caused by a thermal driving force. The origin of the present method rests on provocative remarks by Hartree [15], Crank [16], and Cohen [17], although a large portion of this paper was complete before the author became acquainted with their contents. One first derives a hierarchy of coupled ordinary differential equations in a similarity variable. Each can then be solved in *closed* form so that the solution is analytically representable, in principle, to all orders. Expansions of this type are sometimes accurate representations of a practical process, such as in liquid phase epitaxy, when the time constant of the system is larger than the processing time. Such expansions always allow one to step away from ubiquitous initial singularities, and are thus starting solutions for finite difference schemes. The next section derives the general formalism and the following ones deal with particular examples of interest for the theory and practice of crystal growth.

2. TRANSPORT EQUATIONS AND THEIR SOLUTION

Let $h(t)$ be the position of the planar phase front in a laboratory frame (z'). The nutrient phase* occupies the half-space $z' > h$, the growing or dissolving solid occupies the half-space $z' < h$. Thus, one deals with one-dimensional transport and motion; these models approximately describe many methods of crystal growth such as liquid phase epitaxy, and the Czochralski and float zone techniques. Again, one limits consideration to binary diffusion in the fluid, no diffusion in the solid or on the surface, no reactions in either bulk phase, and the assumption of constant total molar concentrations C and C_s in the fluid and solid, respectively. It is easy to lift some of these restrictions, such as in recent calculations [18] that consider multicomponent diffusion in both bulk phases.

Under the foregoing assumptions one derives the transport equation for the mole fractions $x(z, t)$ and x_s of either species in the fluid and solid, respectively:

$$\frac{\partial x}{\partial t} = D\frac{\partial^2 x}{\partial z^2} + (fC_s/C)\frac{\partial x}{\partial z}, \quad (z, t) > 0, \tag{2.1}$$

$$x_s = \text{const.}, \; z < 0, t > 0. \tag{2.2}$$

Here, following many authors, one has transformed to a frame $z = z' - h$ that moves with the surface; $f \equiv \dot{h}$ is its velocity (the growth rate), and D is the diffusion coefficient in the fluid. In addition, the surface's equation of motion is

$$(fC_s/C)(x_s - x) = D\,\partial x/\partial z, \quad z = 0, \tag{2.3}$$

and the initial and far field conditions are assumed uniform:

$$x(z,0) = x(\infty, t) = x_\infty. \tag{2.4}$$

The factor C_s/C in equations (2.1) and (2.3) stems from unequal fluid and solid densities (cf. [18] [19] pp. 290–291). The system of equations (2.1–4) for the unknown functions $x(z, t)$ and $f(t)$ is as yet incomplete, for one has expressed nothing but mass conservation. Each specific problem will depend on an additional boundary condition that expresses the chemical physics of molecular exchanges at the moving surface. The formalism that follows is independent of such a condition.

First, transform equations (2.1–4) through the introduction of new independent variables

$$\xi = t^{1/2}, \quad \eta = z/2(Dt)^{1/2}, \tag{2.5}$$

and of new unknown functions

$$u(\xi, \eta) = \frac{x_\infty - x(z, t)}{x_s - x_\infty},$$

$$\lambda(\xi) = [f(t)C_s/C](t/D)^{1/2}, \tag{2.6}$$

to get:

$$2\xi\frac{\partial u}{\partial \xi} = \frac{\partial^2 u}{\partial \eta^2} + 2(\eta + \lambda)\frac{\partial u}{\partial \eta}, \quad (\xi, \eta) > 0, \tag{2.7}$$

$$u(\xi, \infty) = 0, \quad \xi > 0 \tag{2.8}$$

$$-\frac{\partial u}{\partial \eta} = 2\lambda(1 + u), \quad \eta = 0. \tag{2.9}$$

Then, note that equation (2.7) is homogeneous in ξ, i.e. it is invariant under arbitrary choices of the time scale, and that its form suggests an expansion in powers of ξ[10, 12, 14–17]. Accordingly, assume the following expansions

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* This phase can be liquid, gaseous, or solid; to be definite it will be called a fluid.

$$u(\xi,\eta) = \sum_{n=0}^{\infty} u_n(\eta)\xi^n, \quad \lambda(\xi) = \sum_{n=0}^{\infty} \lambda_n \xi^n, \tag{2.10}$$

and insert these into equations (2.7–9) to get

$$u_0'' + 2(\eta + \lambda_0)u_0' = 0, \tag{2.11}$$

$$u_n'' + 2(\eta + \lambda_0)u_n' - 2nu_n = -2\sum_{k=0}^{n-1} \lambda_{n-k}u_k', \quad n \geq 1, \tag{2.12}$$

$$u_n(\infty) = 0, \quad \forall n, \tag{2.13}$$

$$\varphi_0 = 2\lambda_0(1 + v_0), \tag{2.14}$$

$$\varphi_n = 2\lambda_n + 2\lambda_0 v_n + 2\sum_{k=0}^{n-1} \lambda_{n-k}v_k, \quad n \geq 1, \tag{2.15}$$

in which the convenient abbreviations

$$v_n \equiv u^n(0), \quad \varphi_n \equiv -u_n'(0) \tag{2.16}$$

stand for the surface values and gradients of the coefficients u_n.

Proceeding to the solution of this coupled system (2.11–16), one notes first that the zeroth order corresponds exactly to Neumann's solution (cf. chapter XI of [19]). Indeed the solution of equations (2.11) and (2.13) is

$$u_0(\eta) = v_0 \frac{\operatorname{erfc}(\eta + \lambda_0)}{\operatorname{erfc}(\lambda_0)}, \tag{2.17}$$

which inserted into equation (2.14) yields

$$v_0/(1 + v_0) = \sqrt{\pi}\,\lambda_0 \exp(\lambda_0^2)\operatorname{erfc}(\lambda_0), \tag{2.18}$$

i.e. a condition for the determination of the constant λ_0 should one know v_0. Equation (2.18) has a unique real solution for any value of the supersaturation ratio $\sigma \equiv v_0/(1 + v_0)$ less than unity. This imposes the physical restriction $v_0 > -1$.

General solutions of the higher order equations are easily obtained, for the iterated error functions satisfy the left hand side of equations (2.12). Appendix A lists some properties of these and related functions. In addition, one notes that all solutions must depend only on the argument $y \equiv \eta + \lambda_0$. For example, one can choose* the basis functions

$$U_n(\pm y) \equiv i^n \operatorname{erfc}(\pm y). \tag{2.19}$$

By standard techniques (cf. Appendix B) one shows that their wronskian has the form

$$W\{U_n(y),\ U_n(-y)\} = W_n \exp(-y^2), \tag{2.20}$$

where W_n, its value at $y = 0$, is given by

$$W_n = (\sqrt{\pi}\,2^{n-2}n!)^{-1}, \tag{2.21}$$

and thus the functions (2.19) are linearly independent. If one assumes that the gradient φ_n and (minus) the right hand side of equation (2.12), i.e.

$$g_n \equiv 2\sum_{k=0}^{n-1} \lambda_{n-k}u_k', \quad n \geq 1, \tag{2.22}$$

are known, then one easily derives the representation

$$u_n(y) = \varphi_n \frac{U_n(y)}{U_{n-1}(\lambda_0)} + \int_{\lambda_0}^{\infty} \mathrm{d}s g_n(s)\exp(s^2)G_n(y|s) \tag{2.23}$$

valid for $n \geq 1$. Here the Green's function

$$G_n(y|s) = W_n^{-1}\begin{cases} U_n(y)[U_n(-s) + \\ \dfrac{U_{n-1}(-\lambda_0)}{U_{n-1}(\lambda_0)}U_n(s)], & \lambda_0 \leq s < y, \\ U_n(s)[U_n(-y) + \\ \dfrac{U_{n-1}(-\lambda_0)}{U_{n-1}(\lambda_0)}U_n(y)], & s > y \geq \lambda_0, \end{cases} \tag{2.24}$$

is expressed in terms of the basis functions (2.19) and the reduced argument $y = \eta + \lambda_0$. Using equation (2.20) one evaluates G_n at the surface ($y = \lambda_0$); this leads to a representation of the surface value

$$v_n = [U_{n-1}(\lambda_0)]^{-1}[\varphi_n U_n(\lambda_0) + \exp(-\lambda_0^2)\int_{\lambda_0}^{\infty} \mathrm{d}s g_n(s)\exp(s^2)U_n(s)]. \tag{2.25}$$

In view of equation (2.22), formulas (2.23) and (2.25) constitute recursion sequences whose zeroth term is simply Neumann's solution (2.17–18). Once the coefficients λ_n have been computed, the surface's schedule $h(t)$ follows by integrating equation (2.6) with equation (2.10). These formulas are applied to specific examples in the next three sections.

3. CONSTANT SURFACE CONCENTRATION

Assume that the mole fraction x is pinned to its equilibrium value x_e at the surface for all values of time. This is the mass transport analog of melting and freezing problems. Then

$$v_0 = (x_\infty - x_e)/(x_s - x_\infty) \equiv u_e, \tag{3.1}$$

$$v_n = 0, \quad n \geq 1. \tag{3.2}$$

One must now prove that the expansions (2.10) are consistent with known results, namely that all u_n and λ_n vanish identically except the zeroth terms, equations (2.17–18), that correspond to Neumann's solution.

To begin, examine the first order. Using equation (2.17) one gets the inhomogeneous term (2.22)

$$g_1(y) = 2\lambda_1 u_0' = -4u_e\lambda_1\pi^{-1/2}\exp(-y^2)/U_0(\lambda_0). \tag{3.3}$$

If one inserts this expression into equation (2.25), then formula (A.1) allows evaluation of the integral, and the condition $v_1 = 0$ leads to

$$\varphi_1 - \frac{2u_e\exp(-\lambda_0^2)U_2(\lambda_0)}{\sqrt{\pi}\,U_0(\lambda_0)U_1(\lambda_0)}2\lambda_1 = 0. \tag{3.4}$$

Application of the formula (2.15) for $n = 1$ then yields

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* By suitable transformations other basis functions (parabolic cylindrical, Hermite, or confluent hypergeometrical) are equally acceptable. However, the iterated error functions are more familiar in diffusion theory [19].

$$\varphi_1 - (1 + u_e)2\lambda_1 = 0. \tag{3.5}$$

Therefore, equations (3.4–5) form a linear homogeneous system in $(\varphi_1, 2\lambda_1)$. A general argument for the regularity of this system follows shortly. Thus $\varphi_1 = \lambda_1 = 0$, and, according to equation (2.23), $u_1 \equiv 0$ since it is a linear combination of these quantities.

Now one proceeds by induction. Assume $u_1 = u_2 = \cdots = u_{n-1} \equiv 0$ (therefore the related quantities v and φ also vanish), and $\lambda_1 = \lambda_2 = \cdots \lambda_{n-1} = 0$. Then, as in the case $n = 1$, one readily gets

$$\varphi_n - \frac{2u_e \exp(-\lambda_0^2)U_{n+1}(\lambda_0)}{\sqrt{\pi}\, U_0(\lambda_0)U_n(\lambda_0)} 2\lambda_n = 0. \tag{3.6}$$

$$\varphi_n - (1 + u_e)2\lambda_n = 0, \tag{3.7}$$

a homogeneous system for $(\varphi_n, 2\lambda_n)$ whose determinant is

$$\Delta_n = -(1 + u_e)[2(n + 2)U_{n+2}(\lambda_0)/U_n(\lambda_0)]. \tag{3.8}$$

Here, one has used the condition (2.18) that λ_0 must satisfy and the recurrence relation (A.3). The first factor of equation (3.8) cannot vanish since $u_e > -1$ is necessary and sufficient for obtaining physical solutions of equation (2.18). Neither does the second factor ever vanish since the iterated error functions are analytic and have no zero on the finite real axis. Therefore, $\varphi_n = \lambda_n = 0$, and, as before, $u_n \equiv 0$. Finally, the determinant Δ_1 of the system (3.4–5) also never vanishes because it too has the form (3.8), and the proof is complete.

In summary, the expansions (2.10) reduce to Neumann's solution when the surface concentration is constant. The same holds true for multicomponent diffusion including thermal effects due to latent heat, as long as the surface concentrations are at equilibrium and are given by the appropriate phase diagram. In particular, Neumann's solution is valid for impurity redistribution as long as the system can be considered unbounded and is not subject to time dependent external driving forces such as cooling or electrical stressing programs.

4. THE EFFECT OF SURFACE KINETICS

There exist problems of mass transport where the surface concentration deviates from its equilibrium value x_e. This arises because growth and dissolution involve surface processes such as nucleation, adsorption, surface diffusion and kink incorporation [20, 21]. The same holds true for electrode processes [22]. Then, one cannot expect constancy of the surface concentration. The simplest model for surface rate limitations can be expressed through

$$D(\partial x/\partial z) = K(x - x_e), \quad z = 0, \tag{4.1}$$

a boundary condition that mimics Newton's Law of Cooling. In words, the flux at the surface must balance exactly a first order heterogeneous reaction, the coefficient K being a reaction constant. For example, such a model accurately predicts the growth of garnets by liquid phase epitaxy [23, 24]. Here, the surface concentration is unknown, *a priori*. Returning to a remark that followed equation (2.9), one notes that D/K^2 can serve as a unit of time. Since $\eta = z/2(Dt)^{1/2}$ is dimensionless, D/K must then be the distance unit. Thus, one writes

$$\xi = (tK^2/D)^{1/2}, \quad \lambda(\xi) = (C_s f/CK)\xi, \tag{4.2}$$

and the additional boundary condition (4.1) becomes

$$-\partial u/\partial\eta = 2\xi(u_e - u), \quad \eta = 0 \tag{4.3}$$

in the reduced variables (ξ, η, u); equation (3.1) defines u_e. When expressed in terms of the expansion (2.10) and the auxiliary quantities (2.16), equation (4.3) then yields the relations

$$\varphi_0 = 0, \tag{4.4}$$

$$\varphi_1 = 2(u_e - v_0), \tag{4.5}$$

$$\varphi_n = -2v_{n-1}, \quad n \geq 2. \tag{4.6}$$

Proceeding to the computation of the coefficients of expansions (2.10), one first remarks that relation (4.4), when combined with equation (2.14), yields $\lambda_0 = 0$ because $v_0 > -1$ as has been noted before. Then, equations (2.18) and (2.17) give $v_0 = 0$ and $u_0 \equiv 0$, respectively. Thus, the zeroth order vanishes identically. In particular, $\lambda_0 = 0$ implies that the growth rate (4.2) is non-singular at the origin; this is precisely the effect of surface rate limitations.

The first order is equally simple. Equations (4.5) and (2.15) immediately yield $\varphi_1 = 2u_e$ and $\lambda_1 = u_e$. Furthermore, since the inhomogeneous term g_1 vanishes identically, the representation (2.23) reduces to $u_1(\eta) = 2u_e U_1(\eta)$, and the use of equation (A.13) implies $v_1 = 2\pi^{-1/2}u_e$.

This computational pattern $(\varphi_n, \lambda_n, u_n, v_n)$ is conserved for the higher order terms because φ_n and λ_n do not depend on v_n. Therefore, equation (2.25) is superfluous. To illustrate again with the next order, equation (4.6) yields immediately $\varphi_2 = -4\pi^{-1/2}u_e$, and equation (2.15) can then be solved for λ_2 to give $\lambda_2 = -2\pi^{-1/2}u_e(1 + u_e)$. Now $g_2 = 2\lambda_1 u_1'$ is non-zero, and use of equation (A.10) and the above results permit its evaluation, namely $g_2(\eta) = -(2u_e)^2 U_0(\eta)$. Then, equation (B.4) applied to the case $m = 0$, $n = 2$, together with formulas (A.13), allow one to reckon the terms of equation (2.23) to get $u_2(\eta) = -u_e\{4U_2(\eta) + u_e[U_0(\eta) - 2U_2(\eta)]\}$, hence the surface value $v_2 = -u_e(1 + u_e/2)$. One notes that terms of order higher than two involve U-functions of negative index, as is clear from the derivative of u_2 that enters the inhomogeneous term g_3. Thus, in general, the nth coefficient $u_n(\eta)$ is a linear combination of U-functions of positive index not greater than n (iterated error functions) and of negative index greater than $-n + 1$ (exponentials that multiply Hermite polynomials). Similar rules apply to each specific problem depending on the order of the first non-zero coefficients (u_n, λ_n). Collecting the above terms one can express the expansions (2.10) in the form

$$u(\xi,\eta)/2\xi u_e = U_1(\eta) - \{2U_2(\eta) + u_e[\eta U_1(\eta) + U_2(\eta)]\}\xi + \cdots, \quad (4.7)$$

$$C_s f(\xi)/CKu_e = 1 - 2\pi^{-1/2}(1 + u_e)\xi + \cdots. \quad (4.8)$$

It is interesting to compare these expressions with approximate ones used for the analysis of crystal growth kinetics. There, one often makes the following two assumptions: (1) The surface moves slowly with respect to the concentration profiles; (2) The concentration at the surface is much less than x_s, the solid's concentration. In the present case one finds [23]

$$u(\xi,\eta)/u_e = \operatorname{erfc}(\eta) - \exp(-\eta^2)\exp(\eta + \xi)^2 \operatorname{erfc}(\eta + \xi), \quad (4.9)$$

$$C_s f(\xi)/CK = [(x_\infty - x_e)/x_s]\exp(\xi^2)\operatorname{erfc}(\xi). \quad (4.10)$$

If one expands these formulas in powers of ξ, then one gets

$$u(\xi,\eta)/2\xi u_e = U_1(\eta) - 2\xi U_2(\eta) + \cdots, \quad (4.11)$$

$$C_s f(\xi)/CK = [x_\infty - x_e)/x_s][1 - 2\pi^{-1/2}\xi + \cdots]. \quad (4.12)$$

Indeed, equations (4.7) and (4.11) are comparable when the concentration ratio $u_e = (x_\infty - x_e)/(x_s - x_\infty)$ is much less than unity. The same holds true for equations (4.8) and (4.12), with the additional proviso $x_s \gg x_\infty$ that stems from the second assumption preceding equation (4.9).

5. THE EFFECT OF COOLING RATE

In addition to the effect of supersaturation, the action of external forces can also cause crystal growth. Among these, homogeneous cooling of the entire system is widely used to promote accretion of matter on nucleation sites. If surface processes are fast, then the surface concentration $x(0,t)$ must be close to equilibrium. But x_e, the equilibrium value, depends on temperature, which in turn depends on the cooling program. Thus, contrary to the last example, the surface concentration is a *known* function of time. One can easily show [25, 26] that the surface concentration obeys

$$x(0,t) = x_0(1 - t/\tau), \quad (5.1)$$

where the relaxation time $\tau = mx_0/b$ is related to the liquidus slope m and to the cooling rate b. For example, this model accurately predicts the liquid phase epitaxial growth kinetics of III–V compounds. Equation (5.1) holds for relatively small values of time; it can be generalized [27]. In addition to this surface supersaturation induced by cooling, fluid mixtures are prepared, by chance or by design, with an initial uniform concentration x_∞ that may be different from the initial value x_0 of x_e. Dimensionless variables result from the obvious time scale τ, distance scale $(D\tau)^{1/2}$, and the definitions (2.6). Thus,

$$\xi = (t/\tau)^{1/2}, \quad \lambda(\xi) = [C_s f/C](\tau/D)^{1/2}\xi \quad (5.2)$$

$$v(\xi) = u_e + \mu\xi^2. \quad (5.3)$$

Here, the normalized surface concentration v results from two distinct driving forces, the initial supersaturation

$$u_e \equiv (x_\infty - x_0)/(x_s - x_\infty), \quad (5.4)$$

in accordance with definition (3.1), and cooling $\mu t/\tau$ whose "strength" is

$$\mu \equiv x_0/(x_s - x_\infty). \quad (5.5)$$

From equations (5.3) it follows that $v_0 = u_e, v_1 = 0, v_2 = \mu$, and $v_n = 0$ for $n > 2$. Although the driving forces appear additively in the boundary condition (5.3), this example illustrates interferences in their effects, as the final part of this section will show.

Computations are now carried out to second order; higher order estimates are meaningless unless equation (5.1) remains an accurate description of surface behavior for large values of time. Since $v_0 = u_e$ and $v_1 = 0$, the zeroth and first order coefficients duplicate those in Section 3, namely

$$u_0(\eta) = u_e U_0(\eta + \lambda_0)/U_0(\lambda_0), \quad (5.6)$$

$$u_e/(1 + u_e) = \sqrt{\pi}\,\lambda_0 \exp(\lambda_0^2)U_0(\lambda_0), \quad (5.7)$$

$$\lambda_1 = u_1(\eta) \equiv 0. \quad (5.8)$$

These terms are independent of the cooling rate. The second order, and possible higher ones, set the following computational pattern: Solve a linear system for φ_n and λ_n, then obtain u_n. Explicitly, equation (2.15) yields

$$\varphi_2 - 2\lambda_2(1 + u_e) = 2\lambda_0\mu, \quad (5.9)$$

and insertion of the inhomogeneous term $g_2 = 2\lambda_2 u_0'$ into equation (2.25) implies

$$\varphi_2 U_2(\lambda_0) - 2\lambda_2(1 + u_e)2\lambda_0 U_3(\lambda_0) = \mu U_1(\lambda_0). \quad (5.10)$$

Solving the system (5.9–10) and using the recurrence (A.11), one gets

$$\lambda_2 = [3\mu/8(1 + u_e)]U_3(\lambda_0)/U_4(\lambda_0), \quad (5.11)$$

$$\varphi_2 = \mu[2\lambda_0 + 3U_3(\lambda_0)/4U_4(\lambda_0)]. \quad (5.12)$$

One then inserts these expressions, together with the previously computed value of g_2, into the representation (2.23). With the aid of formula (B.4), one finally obtains

$$\begin{aligned} u_2(\eta + \lambda_0) = \mu[2\lambda_0 &+ (1 + 2\lambda_0^2/3)3U_3(\lambda_0)/\\ &4U_4(\lambda_0)]U_2(\eta + \lambda_0)/U_1(\lambda_0)\\ &- \mu\lambda_0 \exp(\lambda_0^2)[U_3(\lambda_0)/\\ &4U_4(\lambda_0)]\exp[-(\eta + \lambda_0)^2)], \quad (5.13) \end{aligned}$$

i.e. a linear combination of U_2 and U_{-1}. Collecting the above results, one can write to second order the expansions (2.10) for the concentration and growth rate

$$u(\xi,\eta) = u_0(\eta + \lambda_0) + u_2(\eta + \lambda_0)\xi^2, \quad (5.14)$$

$$C_s f(\xi)(\tau/D)^{1/2}/C = \lambda_0\xi^{-1} + \lambda_2\xi. \qquad (5.15)$$

The coefficients u_0, u_2, λ_0, and λ_2 are given explicitly by equations (5.6–7), (5.11) and (5.13). One notes that the zeroth order depends only on the initial supersaturation, i.e. λ_0 is a function of the supersaturation ratio

$$\sigma \equiv u_e/(1 + u_e) = (x_\infty - x_0)/(x_s - x_0). \qquad (5.16)$$

However, the second order clearly shows nonlinear terms in the products of the driving forces $\sigma(\lambda_0)$ and μ.

Here again, it is instructive to compare these results with approximate calculations. Under the same assumptions as those stated at the end of Section 4, one finds [26] for the concentration and growth rate

$$u(\xi,\eta) = u_e U_0(\eta) + 4\mu\xi^2 U_2(\eta) \qquad (5.17)$$

$$C_s f(\xi)(\tau/D)^{1/2}/C$$
$$= [(x_\infty - x_0)/x_s\pi^{1/2}]\xi^{-1} + (2x_0/\pi^{1/2}x_s)\xi. \qquad (5.18)$$

In this case, the effect of the two driving forces is clearly additive. It is also the limiting case $\sigma \to 0$ under the additional proviso $x_s \gg x_\infty$, as the following calculations show. One need only expand to first order in λ_0. Thus for small supersaturation, equation (5.7) yields

$$\lambda_0 \cong \sigma/\pi^{1/2} \cong u_e/\pi^{1/2} \qquad (5.19)$$

and equations (5.6–7) then become comparable to the first terms of equations (5.17–18). Likewise, using equations (A.10) and (A.13) for the expansions of U_ν, one gets for the second order coefficients (5.11) and (5.13)

$$\lambda_2 \cong \frac{2\mu}{\sqrt{\pi}(1 + u_e)}\left[1 - \frac{3\sigma}{2} + \frac{16\sigma}{3\pi}\right], \qquad (5.20)$$

$$u_2(\eta + \lambda_0) \cong 4\mu U_2(\eta) + \frac{2}{\sqrt{\pi}}\mu\sigma\left[\left(1 - \sqrt{\pi}\right.\right.$$
$$\left.\left. + \frac{32}{3\sqrt{\pi}}\right)U_2(\eta) - 2U_1(\eta) - \frac{1}{3}U_{-1}(\eta)\right], \qquad (5.21)$$

so that the second order terms of (5.14) and (5.15) are comparable to those of (5.17) and (5.18) when $\lambda_0 \to 0$, i.e. when the supersaturation σ is low.

6. SUMMARY

This paper has dealt with one-dimensional moving boundary problems that occur during mass transport processes, and in particular during crystal growth. These problems require special attention because the boundary conditions at the moving surface are often not Dirichlet conditions, and because the surface's equation of motion itself contains the unknown concentrations. One can obtain series solutions in powers of the square root of time; these are *not* similarity solutions. The zeroth term, if it exists, is always Neumann's classical solution; it constitutes the only nonlinearity. All higher order terms are solutions of linear differential equations that have exact solutions. Formal recursive solutions are obtained in terms of mild generalizations of the iterated error functions. These expansions are heuristic and no attempt to investigate their convergence has been made. However, the formulas are easy to apply, for the problem has been reduced to simple *algebraic* manipulations that could easily be programmed in a language such as SCRATCHPAD [28]. Similar methods have been applied to the boundary layer equations of hydrodynamics to give the series solutions of Blasius, Howarth, Görtler, Goldstein, and others [29]. However, in that area one must compute the various terms numerically.

The present method was applied to three specific examples of interest for crystal growth. The first assumes that the surface concentration always be at equilibrium. Then the expansions reduce to their zeroth terms, regardless of the number of diffusing species. Such problems are mere extensions of Neumann's solution for melting and freezing. The second example allows for deviations from equilibrium. At the surface one then has a radiation boundary condition, so that the surface concentration is, *a priori*, unknown. The expansion coefficients are particularly easy to compute because the two main recursions are independent of one another. The third example demonstrates the effect of external driving forces that constrain the surface concentration's schedule. Here, calculations are somewhat more arduous because the external forces can interact with internal ones such as supersaturation. In both the second and third example it was shown how approximate results that essentially neglect the boundary's motion can be considered the limit of low supersaturation. This is in accordance with similar observations concerning known Stefan problems that admit analytic solutions.

Uniform initial conditions were assumed throughout this paper. If $x(z,0)$ is not constant, $x_0(z)$ say, then $u = x_0 - x$ satisfies the conditions of Section 2 as long as x_0 is analytic in the variables (2.5). Then one expects generalizations of equations (2.12) and (2.15) in which the right hand sides will contain additional inhomogeneities due to x_0. However, in all cases, the general solution (2.23) ought still apply, and Neumann's solution should still constitute the zeroth order. Again, the reader may consult Tao's work [12] for advances in this direction. Finally, only one-dimensional problems in semi-infinite regions were considered. It is conceivable that, with ingenuity, similar methods might be devised for slab geometries, and for cylinders, spheres, and other quadratic surfaces.

REFERENCES

1. C. W. Cryer, A bibliography of free boundary problems, Technical Report No. 1793, Mathematics Research Center, University of Wisconsin (1977).
2. S. G. Bankoff, Heat conduction or diffusion with change of phase, in *Advances in Chemical Engineering*, edited by T. B. Drew, J. W. Hooper, Jr., T. Vermeulen and G. R. Cokelet, Vol. 5, pp. 75–150. Academic Press, New York (1964).
3. L. Rubinstein, The Stefan problem, *Transl. Math. Monog.* 27. American Mathematical Society, Providence (1971).

4. J. R. Ockendon and W. R. Hodgkins, editors, *Moving Boundary Problems in Heat Flow and Diffusion.* Clarendon Press, Oxford (1975).
5. D. G. Wilson, A. D. Solomon and P. T. Boggs, editors, *Moving Boundary Problems.* Academic Press, New York (1978).
6. G. H. Meyer, Multidimensional Stefan problems, *SIAM J. Num. Anal.* **10,** 522–538 (1973).
7. G. H. Meyer, An alternating direction method for multidimensional parabolic free surface problems, *Int. J. Num. Meth. Engng* **11,** 741–752 (1977).
8. A. B. Crowley, Numerical solution of Stefan Problems, *Int J. Heat Mass Transfer* **21,** 215–219 (1978).
9. G. W. Evans II, E. Isaacson and J. K. L. MacDonald, Stefan-like problems, *Q. Appl. Math.* **8,** 312–319 (1950).
10. B. A. Boley, A method of heat conduction analysis of melting and solidification problems, *J. Math. Phys.* **40,** 300–313 (1961).
11. H. Katz, A large time expansion for the Stefan Problem, *SIAM J. Appl. Math* **32,** 1–20 (1977).
12. L. N. Tao, The Stefan problem with arbitrary initial and boundary conditions, *Q. Appl. Math.* **36,** 223–233 (1978).
13. H. Müller-Krumbhaar, Diffusion theory for crystal growth at arbitrary solute concentration, *J. Chem. Phys.* **63,** 5131–5138 (1975).
14. B. A. Boley, Time dependent solidification of binary mixtures, *Int. J. Heat Mass Transfer* **21,** 821–824 (1978).
15. D. R. Hartree, Some properties and applications of the repeated integrals of the error function, *Mem. Proc. Manchester Lit. Phil. Soc.* **80,** 85–102 (1935).
16. J. Crank, Two methods for the numerical solution of moving boundary problems in diffusion and heat flow, *Q. J. Mech. Appl. Math.* **10,** 220–231 (1957).
17. H. Cohen, Nonlinear diffusion problems, in *Studies in Applied Mathematics,* Vol. 7, pp. 27–64. Mathematical Association of America (1971).
18. M. B. Small and R. Ghez, Growth and dissolution kinetics of III–V heterostructures formed by LPE, *J. Appl. Phys.* **50,** 5322–5330 (1979).
19. H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids,* 2nd. edn. Clarendon Press, Oxford (1959).
20. W. K. Burton, N. Cabrera and F. C. Frank, The growth of crystals and the equilibrium structure of their surfaces, *Phil. Trans. R. Soc.* **A243,** 299–358 (1951).
21. R. Ghez, Correlation of the interface reaction constant with elementary surface processes, *J. Crystal Growth* **43,** 618–620 (1978).
22. V. G. Levich, *Physicochemical Hydrodynamics.* Prentice Hall, New Jersey (1962).
23. R. Ghez and E. A. Giess, Liquid phase epitaxial growth kinetics of magnetic garnet films grown by isothermal dipping with axial rotation, *Mater. Res. Bull.* **8,** 31–42 (1973).
24. R. Ghez and E. A. Giess, The temperature dependence of garnet liquid phase epitaxial growth kinetics, *J. Crystal Growth* **27,** 221–226 (1974).
25. W. A. Tiller and C. Kang, On the growth rate of crystals from solution, *J. Crystal Growth* **2,** 345–355 (1968).
26. M. B. Small and J. F. Barnes, The distribution of solvent in an unstirred melt under the conditions of crystal growth by liquid phase epitaxy and its effect on the rate of growth, *J. Crystal Growth* **5,** 9–12 (1969).
27. M. B. Small and R. Ghez, Conditions for constant growth rate by LPE from a cooling static solution, *J. Crystal Growth* **43,** 512–514 (1978).
28. J. H. Griesmer and R. D. Jenks, Experience with an online symbolic mathematics system, in *Proceedings of the ONLINE72 Conference,* Brunel University, Uxbridge, Middlesex, England, 4–7 September 1972. (Also available as IBM Research Report RC 3925, entitled *The SCRATCHPAD System*).
29. L. Rosenhead, editor, *Laminar Boundary Layers,* chapter VI. Clarendon Press, Oxford (1963).
30. M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions.* Dover, New York (1965).
31. N. N. Lebedev, *Special Functions and their Applications.* Dover, New York (1972).

APPENDIX A

Some Properties of the Iterated Error Functions and Related Functions

The recursion

$$i^n \operatorname{erfc}(z) = \int_z^\infty \mathrm{d}s\, i^{n-1} \operatorname{erfc}(s), \tag{A.1}$$

with $i^{-1} \operatorname{erfc}(z) = 2\pi^{-1/2} \exp(-z^2)$, defines the nth iterated error function. Therefore, $i^0 \operatorname{erfc}(z)$ coincides with the complementary error function, and one has the integral representation

$$i^n \operatorname{erfc}(z) = \frac{2}{\sqrt{\pi}} \int_z^\infty \mathrm{d}s \frac{(s-z)^n}{n!} \exp(-s^2). \tag{A.2}$$

Integration by parts and differentiation of equation (A.2) show that the iterated error functions satisfy the recurrence relation

$$2(n+1) i^{n+1} \operatorname{erfc}(z) = -2z i^n \operatorname{erfc}(z) + i^{n-1} \operatorname{erfc}(z), \tag{A.3}$$

and the differential equation

$$u'' + 2zu' - 2nu = 0. \tag{A.4}$$

Relations (A.1–4) hold for all non-negative integer values of n. Other useful properties of the iterated error functions may be found in [15] and [30].

However, their relation to Hermite functions $H_\nu(z)$ is generally not recognized. When ν is a non-negative integer the latter reduce to Hermite polynomials; when ν is a non-positive integer one has the relation

$$i^n \operatorname{erfc}(z) = 2\pi^{-1/2} \exp(-z^2) H_{-n-1}(z), \tag{A.5}$$

valid for $n \geq -1$. Hermite functions satisfy the same differential equation, recurrences, and differential relations as do the Hermite polynomials. Reference [31] develops the theory of these functions. In particular, one has the power series representation

$$H_\nu(z) = \frac{1}{2\Gamma(-\nu)} \sum_{k=0}^\infty \frac{(-1)^k \Gamma[(k-\nu)/2]}{k!} (2z)^k, \tag{A.6}$$

and the asymptotic representations

$$H_\nu(z) \sim (2z)^\nu \sum_{k=0}^\infty \frac{(-1)^k (-\nu)_{2k}}{k!(2z)^{2k}}, \quad |\arg(z)| < 3\pi/4 \tag{A.7}$$

and

$$H_\nu(z) \sim -\frac{\sqrt{\pi}\, \mathrm{e}^{\nu i\pi + z^2}}{\Gamma(-\nu) z^{\nu+1}} \sum_{k=0}^\infty \frac{(\nu+1)_{2k}}{k!(2z)^{2k}}, \quad |\arg(-z)| < \pi/4. \tag{A.8}$$

It is convenient to define the functions

$$U_\nu(z) = 2\pi^{-1/2} \exp(-z^2) H_{-\nu-1}(z) \tag{A.9}$$

for arbitrary index ν. For integer values of $\nu > -1$, they coincide with the iterated error functions; for negative integer values $\nu \leq -1$ they can be expressed in terms of Hermite polynomials. Finally, one easily shows that

$$U_\nu'(z) = -U_{\nu-1}(z), \tag{A.10}$$

$$2\nu U_\nu(z) = -2zU_{\nu-1}(z) + U_{\nu-2}(z), \tag{A.11}$$

$$U_\nu'' + 2zU_\nu' - 2\nu U_\nu = 0, \tag{A.12}$$

$$U_\nu(0) = [2^\nu \Gamma(1+\nu/2)]^{-1}, \tag{A.13}$$

i.e. relations that duplicate those obeyed by the iterated error functions.

APPENDIX B

Some Reduction Formulas

Here one derives formulas that allow expansions to be carried out to any degree of accuracy. To this end, one requires evaluation of the integrals that appear in equations (2.23) and (2.25). Since the inhomogeneous term g_n will be seen to be a linear combination of U_m functions where m is a signed integer less than n, it follows that one must first evaluate the integrals

$$\int_0^y \mathrm{d}s U_\mu(s) U_\nu(\pm s) \exp(s^2). \tag{B.1}$$

Both $U_\nu(s)$ and $U_\nu(-s)$ satisfy equations (A.12), so that the wronskian $W\{U_\mu(s), U_\nu(\pm s)\}$ satisfies $W' + 2sW - 2(\nu - \mu)U_\mu U_\nu = 0$. This differential equation is easily integrated to give

$$W\{U_\mu(y),\ U_\nu(\pm y)\}\exp(y^2) = \text{const.}$$
$$+ 2(\nu - \mu)\int_0^y \mathrm{d}s U_\mu(s) U_\nu(\pm s)\exp(s^2), \tag{B.2}$$

where the constant is just the wronskian's value at $y = 0$. In particular, with equations (A.10), (A.13), and the duplication formula for gamma functions, one gets

$$W\{U_\nu(y),\ U_\nu(-y)\}_{y=0} = [\sqrt{\pi}\, 2^{\nu-2}\Gamma(1+\nu)]^{-1}, \tag{B.3}$$

which reduces to equation (2.21) when ν is a non-negative integer.

Finally, one applies equation (B.2) to the various definite integrals that appear in equation (2.23). Elementary manipulations, together with the use of equation (2.20) and the cognizance of the asymptotic behaviour (A.7) then leads to the remarkably simple formula

$$\int_{\lambda_0}^{y} \mathrm{d}s U_m(s)\exp(s^2) G_n(y|s)$$
$$= \frac{1}{2(n-m)}\left[U_m(y) - \frac{U_{m-1}(\lambda_0)}{U_{n-1}(\lambda_0)} U_n(y)\right]. \tag{B.4}$$

This relation is valid for any signed integer values of $m \neq n$; it expresses the integral as a linear combination of U-functions of the positive argument y. Since the first non-vanishing coefficient u_k must be proportional to such a function, as is its derivative, it follows from equations (2.23) and (B.4) that all its successors must be a linear combination of U-functions.

DEVELOPPEMENTS DANS LE TEMPS POUR LA SOLUTION DES PROBLEMES DE STEFAN MONODIMENSIONNELS DE CROISSANCE D'UN CRISTAL

Résumé — On présente une nouvelle méthode de résolution des problèmes de transfert massique selon Stefan, dans une dimension et dans des régions semi-infinies. Elle repose sur des développements de la distribution de la concentration et la croissance en puissances de $t^{1/2}$. Les conditions à la frontière mobile ne sont pas nécessairement constantes ; elles peuvent être arbitraires. De telles conditions conduisent souvent à des solutions non similaires. Bien que ces problèmes ne soient pas linéaires, les coefficients du développement satisfont les relations linéaires de récurrence. Ces coefficients résultent de manipulations algébriques simples de fonctions étroitement reliées à des fonctions erreurs itérées, la méthode est appliquée à plusieurs exemples de croissance cristalline à partir de solutions sursaturées. Les deux premiers exemples supposent des conditions isothermes ; ils illustrent la différence entre l'équilibre de surface et la cinétique de surface finie. Le troisième exemple montre des effets dus au refroidissement homogène.

LÖSUNG VON EINDIMENSIONALEN STEFAN-PROBLEMEN DER KRISTALLBILDUNG DURCH REIHENENTWICKLUNG NACH DER ZEIT

Zusammenfassung Es wird eine neue Methode für die Lösung von Stefan-Stoffübertragungsproblemen in einer Dimension und für halbunendliche Bereiche angegeben. Sie beruht auf Reihenentwicklungen der Konzentrationsverteilung und der Wachstumsrate nach Potenzen von $t^{1/2}$. Die Feldbedingungen an dem fortschreitenden Rand sind nicht unbedingt konstant, sie können willkürlich sein. Solche Bedingungen führen öfter zu nicht-ähnlichen Lösungen. Obwohl diese Probleme nicht-linear sind, erfüllen die Koeffizienten der Reihen lineare Rekursionsbeziehungen. Diese Koeffizienten ergeben sich aus einfachen algebraischen Umformungen von Funktionen, die in engem Zusammenhang zu den iterierten Fehlerfunktionen stehen. Die Methode wird für verschiedene Beispiele von Kristallbildung in übersättigten Lösungen angewendet. Für die beiden ersten Beispiele werden isotherme Bedingungen angenommen: sie veranschaulichen den Unterschied zwischen Oberflächengleichgewicht und endlicher Oberflächenkinetik. Das dritte Beispiel zeigt die Einflüsse homogener Abkühlung.

РЕШЕНИЯ РАЗЛОЖЕНИЕМ ПО ВРЕМЕНИ ОДНОМЕРНЫХ СТЕФАНОВСКИХ ЗАДАЧ РОСТА КРИСТАЛЛОВ

Аннотация — Предложен новый метод решения стефановских задач, связанных с массопереносом в одномерных и полубесконечных областях, основанный на разложении распределения концентрации и скорости роста кристалла по степеням $t^{1/2}$. Условия на перемещающейся границе не обязательно должны быть постоянными; они могут быть произвольными, что часто приводит к неавтомодельным решениям. Несмотря на то, что такие задачи являются нелинейными, коэффициенты разложения удовлетворяют линейным рекуррентным соотношениям. Эти коэффициенты определяются с помощью простых алгебраических преобразований функций, родственных функциям ошибок. Метод проверен на нескольких примерах роста кристаллов из перенасыщенных растворов. В первых двух примерах предполагается наличие изотермических условий; иллюстрируется различие между равновесием на поверхности и конечной поверхностной кинетикой. Третий пример иллюстрирует эффекты, вызванные однородным охлаждением.