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SOME RECENT RESULTS FOR HEAT-DIFFUSION MOVING BOUNDARY PROBLEMS

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Integral formulations for the three classical single phase Stefan problems involving the infinite slab and inward solidifying cylinders and spheres are utilized to generate standard analytical approximations. These approximations include the pseudo steady state estimate, large Stefan number expansions, upper and lower bounds, approximations based on integral iteration and related results such as formal series solutions. In order to demonstrate the applicability and limitations of the integral formulations three generalizations of the classical Stefan problem are considered briefly. These problems are diffusion with two simultaneous chemical reactions, a Stefan problem with two moving boundaries and the genuine two phase Stefan problem.

1. Introduction

Heat-diffusion moving boundary problems have numerous applications in fields such as the freezing and thawing of foods, production of ice, thawing or formation of ice around pipes, solidification of steel and diffusion limited chemical reactions, where either a moving freezing,

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moving melting or moving reaction front is present. Mathematically these problems involve solving the heat-diffusion equation in an unknown region, which has to be determined as part of the problem. Exact solutions to moving boundary problems are limited in number and for heat-diffusion problems the only physically relevant exact solutions occur when the position of the moving boundary (or boundaries) varies as the square root of time (that is, similarity solutions). The mathematical difficulties associated with solving other moving boundary problems exactly are considerable and are of a fundamental character. The mathematical literature on the subject has developed in three main areas, namely, approximate analytical methods, numerical techniques and qualitative results such as existence and uniqueness theorems. In each of these areas the literature is extensive. This paper deals primarily with the first area for the classical phase change or Stefan problems, involving the semi-infinite slab and the inward solidifying cylinder or sphere. Approximate and semi-analytical estimates are important for at least two reasons. Firstly, an analytical result is generally more revealing (in terms of parameter dependence) than a numerical result. Secondly, short time analytical approximations are frequently necessary as starting solutions in a numerical scheme. The purpose of this paper is to demonstrate that a number of important approximate analytical estimates readily emerge from an integral formulation for such Stefan problems and the paper provides a survey of recent results described in Dewynne and Hill [2], [3], [4], [5] and Hill and Dewynne [8], [9] and further is a summary of the Ph.D. thesis of Dewynne [1].

We are primarily concerned with the classical single phase Stefan problem either for the infinite slab $(-\infty,1)$ or for inward solidifying cylinders or spheres. Such problems arise from the idealized isothermal freezing of a pure liquid, which does not change density upon freezing, and which is initially uniformly at its fusion temperature. In non-dimensional variables we may summarize these three problems in the general form by

$$\frac{\partial T}{\partial t} = \frac{\partial^2 T}{\partial r^2} + \frac{\lambda}{r}\frac{\partial T}{\partial r}, \qquad R(t) < r < 1, \tag{1.1}$$

$$T(1,t) + \beta\frac{\partial T}{\partial r}(1,t) = 1, \qquad T(R(t),t) = 0, \tag{1.2}$$

$$\frac{\partial T}{\partial r}(R(t),t) = -\alpha\frac{dR}{dt}, \qquad R(0) = 1, \tag{1.3}$$

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where $T(r,t)$, r, $R(t)$ and t denote the dimensionless temperature of the solid, (radial) position, moving boundary position and time, respectively. The parameter λ takes the values 0, 1 and 2 for the slab, cylinder and sphere, respectively. We note that $T(r,t)$ is non-dimensionalized so that it satisfies the inequalities

$$0 \le T(r,t) \le 1. \tag{1.4}$$

The constant α called the Stefan number, is the ratio of latent heat of fusion to sensible heat of the solid and is therefore strictly positive. The inverse Biot modulus, β, is a non-negative measure of thermal resistance at the surface $r = 1$. In Section 5 we establish a new formal integral for the boundary motion

$$t = \int_{R(t)}^{1} \xi^{\lambda}[K_{\lambda}(1,\xi) + \beta]\,[T(\xi,t) + \alpha]d\xi, \tag{1.5}$$

where the function $K_{\lambda}(x,y)$ is defined by

$$K_{\lambda}(x,y) = \int_{y}^{x} \xi^{-\lambda}d\xi. \tag{1.6}$$

Equation (1.5) represents the basic equation, deduced from the integral formulation (5.1), for the boundary motion. We emphasize that if $T(r,t)$ is the exact temperature occurring in (1.1)-(1.3) then (1.5) coincides with the boundary motion determined by the Stefan condition (1.3). However, if estimates only of the temperature are available, then in general (1.3) and (1.5) lead to distinct approximate boundary motions.

In the following section we give a brief description of a simple numerical enthalpy scheme and present temperature profiles and boundary motions produced by this scheme. In Section 3 we discuss the pseudo steady state approximation for the problem (1.1)-(1.3), and in Section 4 a large α approximation is given. In Section 5 we sketch two derivations of the integral formulation, one by direct integration and one using the symmetric Green's function associated with the spatial component in (1.1) (see equation (4.4)). The integral formulation is used in Section 6 to derive upper and lower bounds for the boundary motion and in Section 7 to produce an iterative integral technique which may be used to generate approximate solutions to (1.1)-(1.3). In Section 8 formal series solutions,

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in terms of r and $R(t)$, are derived from the integral formulation. In the final three sections we briefly discuss a number of more general moving boundary problems which admit analogous integral formulations. In Section 9 we consider a moving boundary problem involving two simultaneous chemical reactions. In Section 10 we consider a multiphase (multicomponent) Stefan problem, that is where more than one moving boundary is present and in Section 11 we treat the genuine two phase Stefan problem arising from the freezing of a material initially above its freezing temperature. Finally in this section, we refer the interested reader to the books by Ockendon and Hodgkins [10] and Wilson *et. al.* [12] for general background material and references concerning heat-diffusion moving boundary problems.

2. Numerical enthalpy scheme

The problem (1.1)-(1.3) can be reformulated as a fixed domain problem by introducing the enthalpy or total heat content H, defined by

$$T = \begin{cases} H - \alpha, & H > \alpha, \\ 0, & H \in [0, \alpha] . \end{cases} \tag{2.1}$$

We regard an enthalpy $H = 0$ as representing the liquid at the fusion point, whereas an enthalpy $H = \alpha$ represents the solid at the fusion point. Thus, there is a jump discontinuity in enthalpy H of magnitude α across the moving boundary $R(t)$. In terms of H and T we may reformulate (1.1)-(1.3) as

$$\frac{\partial H}{\partial t} = \frac{\partial^2 T}{\partial r^2} + \frac{\lambda}{r}\frac{\partial T}{\partial r}, \quad 0 < r < 1, \tag{2.2}$$

$$T(1,t) + \beta\frac{\partial T}{\partial r}(1,t) = 1, \quad T(0,t) = 0, \quad \frac{\partial T}{\partial r}(0,t) = 0, \quad H(r,0) = 0, \tag{2.3}$$

where the no flux and fixed temperature conditions at $r = 0$ actually apply at $r = -\infty$ for the slab and for the cylinder and sphere only remain valid while there is liquid present in the region (0,1). Since H is discontinuous across the phase change boundary, (2.2) holds only in a weak sense, but even so a simple and effective finite difference scheme results from discretizing (2.2) and applying conditions (2.1) and (2.3). To find the moving boundary $R(t)$, we need only locate the jump discontinuity in H, and this can be done in a numerical scheme using the method of Voller and Cross [11], which results in an accurate determination

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of $R(t)$.

An explicit discretization of (2.2) with a small mesh spacing leads to particularly accurate numerical solutions, albeit at the expense of a good deal of computing time due to stability restrictions. The figures shown in this paper are generated using such a scheme with a mesh spacing of $1/60$. Figures 1 and 2 show temperature profiles for the sphere with $\alpha = 0.1$ and $\alpha = 10.0$ and β zero, respectively, at four equally spaced positions of the moving boundary $R(t)$ which do not correspond to equal time intervals. Note the change in the concavity of the profiles with increasing α, and the growth of the thermal boundary layer as the boundary approaches the origin. This boundary layer becomes more pronounced with increasing α and β, that is, with decreasing boundary speeds. Figures 3, 4, 5 and 6 show boundary motions for slabs, cylinder and sphere with a variety of values of α and β. From $(1.2)_1$ and (1.3) we may show that the initial boundary velocity is $(\alpha\beta)^{-1}$, while the final velocity, as $R \to 0$, is theoretically infinite and these features are apparent from the numerical boundary motions shown in these figures.

3. Pseudo steady state approximation

The pseudo steady state solution of (1.1)-(1.3) arises from (1.1)-(1.3) by ignoring the time partial derivative in (1.1), that is, by replacing the heat equation by Laplace's equation. Using the boundary conditions (1.2) at $r = 1$ and $r = R$ we obtain an expression for the pseudo steady state temperature, which can be substituted into the Stefan condition (1.3) to obtain either an approximate boundary position as a function of the actual time or an approximate time as a function of the actual boundary position. For our purposes we adopt the latter point of view, and find that the pseudo steady state approximation is

$$T_{pss}(r,R) = K_\lambda(r,R)/[K_\lambda(1,R) + \beta] , \tag{3.1}$$

$$t_{pss}(R) = \alpha\int_R^1 \xi^\lambda[K_\lambda(1,\xi) + \beta]d\xi. \tag{3.2}$$

As we show in the following section, the pseudo steady state solution is asymptotically valid, as $\alpha \to \infty$, that is, as the boundary motion becomes

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very much slower than the heat conduction. As well, we demonstrate in Section 5 that the pseudo steady state temperature is an upper bound on the actual temperature, for a given position of the moving boundary R, while in Section 6 we show that the pseudo steady state boundary motion (3.2) provides a lower bound on the actual boundary motion. These results might be expected, considering the physical significance of replacing the heat equation by Laplace's equation. Finally we note that by putting $R = 0$ in (3.2) we have the approximation t_{pssc}

$$t_c \sim t_{pssc} = \frac{\alpha(1 + 2\beta)}{2(1 + \lambda)}, \tag{3.3}$$

for the time t_c taken for the liquid to freeze completely, that is for the boundary to reach the origin, $R(t_c) = 0$.

4. Large α approximation

If we introduce a new time variable $\tau = t/\alpha$ into (1.1)-(1.3) and expand

$$T(r,\tau) = T_0(r,\tau) + \alpha^{-1}T_1(r,\tau) + o(\alpha^{-1}), \tag{4.1}$$

we find that

$$T_0(r,\tau) = T_{pss}(r,R(t)), \tag{4.2}$$

$$T_1(r,\tau) = \int_{R(t)}^{1} G^*(r,\xi;R(\tau))\xi^{\lambda}\frac{\partial T_0}{\partial \tau}(\xi,\tau)\,d\xi\ , \tag{4.3}$$

where G^* is a symmetric Green's function given by

$$G^*(r,\xi;R) = \begin{cases} -[K_\lambda(1,r) + \beta]K_\lambda(\xi,R)/[K_\lambda(1,R) + \beta], & R \le \xi \le r, \\ -[K_\lambda(1,\xi) + \beta]K_\lambda(r,R)/[K_\lambda(1,R) + \beta], & r \le \xi \le 1. \end{cases} \tag{4.4}$$

For the cylinder and sphere $(\lambda = 1,2)$ the first order correction T_1 and higher terms become singular as $R \to 0$. Nevertheless, substituting (4.2) and (4.3) into the Stefan condition and reverting to the time scale t gives respectively the following approximations for t, namely

$$t_0(R) = t_{pss}(R)\ , \tag{4.5}$$

$$t_1(R) = t_{pss}(R) + \int_R^1 \xi^{\lambda}[K_\lambda(1,\xi) + \beta]T_{pss}(\xi,R)\,d\xi\ . \tag{4.6}$$

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In particular, the order one corrected approximation $t_1(R)$ remains finite as $R \to 0$. In fact, as we show in Section 6, $t_0(R)$ and $t_1(R)$ are lower and upper bounds, respectively, for the boundary motion.

5. Derivation of the integral formulation

On integrating the heat equation (1.1) from $R(t)$ to r twice, changing the order of integration and applying $(1.2)_2$ and (1.3) we have

$$T(r,t) = \frac{\partial}{\partial t}\int_{R(t)}^{r} \xi^{\lambda} K_{\lambda}(r,\xi)[\alpha + T(\xi,t)]d\xi \ , \tag{5.1}$$

which together with the surface condition $(1.2)_1$ yields

$$1 = \frac{d}{dt}\int_{R(t)}^{1} \xi^{\lambda}[K_{\lambda}(1,\xi) + \beta][\alpha + T(\xi,t)]d\xi \ , \tag{5.2}$$

and on integrating (5.2) with respect to time we obtain the formal integral for the boundary motion (1.5). Alternatively, if we form the difference

$$u(r,t) = T(r,t) - T_{pss}(r,R(t)), \tag{5.3}$$

and consider the homogeneous (moving) boundary value problem for $u(r,t)$ which results, we find that

$$T(r,t) = T_{pss}(r,R(t)) + \int_{R(t)}^{1} G^{*}(r,\xi;R(t))\xi^{\lambda}\frac{\partial T}{\partial t}(\xi,t)d\xi \ , \tag{5.4}$$

where G^* is given by (4.4). This, together with $(1.2)_1$ gives (5.2) and hence (1.5). As well, if use the physically apparent result that $\frac{\partial T}{\partial t} \geq 0$ and note that $G^* \leq 0$ then from (5.4) we can deduce that

$$T(r,t) \leq T_{pss}(r,R(t)). \tag{5.5}$$

We use this upper bound on $T(r,t)$ in the next section to obtain upper bounds for the boundary motion. Finally in this section we note that in terms of the enthalpy H, given by (2.1), we may write the integral formulation (5.1) and (5.2) as

$$T(r,t) = \frac{\partial}{\partial t}\int_{0}^{r} \xi^{\lambda} K_{\lambda}(r,\xi)H(\xi,t)d\xi \ , \tag{5.6}$$

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(5.7) $$1 = \frac{d}{dt}\int_0^1 \xi^\lambda[K_\lambda(1,\xi) + \beta]H(\xi,t)d\xi ,$$

since H is zero between the origin and the moving boundary $R(t)$, and these results may also be formally deduced from the enthalpy formulation (2.2)-(2.3).

6. Upper and lower bounds

Substituting the inequalities (1.4) into the integral (1.5) gives the results

(6.1) $$t_{pss}(R) \le t \le (1 + \frac{1}{\alpha})t_{pss}(R) ,$$

where $t_{pss}(R)$ is given by (3.2) and in particular, putting $R = 0$ gives the bounds

(6.2) $$\frac{\alpha(1 + 2\beta)}{2(1 + \lambda)} \le t_c \le \frac{(\alpha + 1)(1 + 2\beta)}{2(1 + \lambda)} ,$$

for the time t_c to complete freezing. Using the pseudo steady state upper bound for the temperature, (5.5), in the integral (1.5) gives the bound

(6.3) $$t \le t_{pss}(R) + \int_R^1 \xi^\lambda[K_\lambda(1,\xi) + \beta][\alpha + T_{pss}(\xi,R)]d\xi,$$

which is merely the order one corrected boundary motion and is an improvement on the upper bound in (6.1). For the cylinder and sphere $(\lambda = 1,2)$, putting $R = 0$ in (6.3) leads to the same upper bound (6.2) on t_c because for these geometries $T_{pss}(r,0) = 1$. However, for the slab $(\lambda = 0)$ putting $R = 0$ in (6.3) leads to the new upper bound for t_c

(6.4) $$t_c \le \frac{\alpha}{2}(1 + 2\beta) + \frac{(1 + 3\beta)}{6(1 + \beta)} ,$$

which is superior to that arising from (6.2).

To improve the pseudo steady state lower bound (6.1) for the boundary motion, we substitute the expression (5.1) for $T(r,t)$ into (1.5) and integrate. After using the inequalities $T(r,t) \ge 0$ and

(6.5) $$-\frac{dt}{dR} \ge \alpha R^\lambda[K_\lambda(1,R) + \beta] = -\frac{dt_{pss}}{dR} ,$$

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(which arises from (5.2) and the inequality $\frac{\partial T}{\partial t} \geq 0$), we find that

$$t^2 \geq t_{pss}^2(R) + 2\alpha \int_R^1 \int_R^\xi (\xi\eta)^\lambda [K_\lambda(1,\xi) + \beta] K_\lambda(\xi,\eta) d\eta d\xi. \tag{6.6}$$

Since the double integral occurring in this expression is a positive quantity, this result improves the lower bound given in (6.1). For the precise details of the derivation of (6.6) we refer the interested reader to [8]. Although it is possible to continue this process, using (5.1) to substitute for $T(r,t)$ and (6.5) to simplify the integral at each step, the results are generally inferior to (6.6), and we refer the reader to [8] for a discussion of this point. Figure 3 compares the upper and lower bounds (6.1), (6.3) and (6.6) for the slab with $\alpha = 1.0$ and β zero with the well known exact boundary motion (see for example [2]). Figure 4 compares the upper and lower bounds (6.1), (6.3) and (6.6) for the cylinder with $\alpha = 10.0$ and $\beta = 1.0$ with the numerical boundary motion.

For large values of the Stefan number α the bounds given by (6.3) and (6.6) are sufficiently tight for most practical purposes. For small values of α there is, however, scope for improvement. Obviously, improved bounds on $T(r,t)$ could be exploited directly, using (1.5). As well, a non-trivial lower bound on $T(r,t)$ could be used to replace the trivial bound $T(r,t) \geq 0$ in the derivation of (6.6), leading to a tighter lower bound than direct substitution in (1.5). If a non-trivial lower bound for the speed $-\frac{dR}{dt}$ were found, it could be used in conjunction with the pseudo steady state temperature to obtain tighter upper bounds, in a manner analogous to that in which (6.5) and the lower bound $T(r,t) \geq 0$ are used to deduce (6.6). As well, such a lower bound on $-\frac{dR}{dt}$ could be used in conjunction with the inequality

$$T(r,t) \geq -\alpha \frac{dR}{dt} R(t)^\lambda K_\lambda(r,R(t)), \tag{6.7}$$

(which comes from (5.1) and the inequality $\frac{\partial T}{\partial t} \geq 0$), to obtain a non-trivial lower bound on $T(r,t)$.

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7. Approximation by integral iteration

Using the notation $T^*(r,R)$ to denote the temperature as a function of r and boundary position $R(t)$, we use the integral formulation (5.1), (5.2) and (1.5) to deduce the iterative scheme

$$(7.1)\qquad T^*_{n+1}(r,R) = \frac{\frac{\partial}{\partial R}\int_R^r \xi^\lambda K_\lambda(r,\xi)[\alpha + T^*_n(\xi,R)]\,d\xi}{\frac{\partial}{\partial R}\int_R^1 \xi^\lambda[K_\lambda(1,\xi) + \beta][\alpha + T^*_n(\xi,R)]\,d\xi},$$

$$(7.2)\qquad t_{n+1}(R) = \int_R^1 \xi^\lambda[K_\lambda(1,\xi) + \beta][\alpha + T^*_n(\xi,R)]\,d\xi .$$

The initial estimate $T^*_{-1} \equiv 0$ gives T^*_0 and t_0 as T_{pss} and t_{pss} respectively, (see (3.1)-(3.2)), and the order one corrected boundary motion t_1 emerges from the next iteration, (see (4.6)). Thus, t_0 and t_1 respectively constitute lower and upper bounds for the actual boundary motion, and it can be shown that the next iteration t_2 lies within these bounds, for all three geometries with $\alpha > 0$ and $\beta \geq 0$. For the details we refer the reader to Dewynne [1].

For the slab with β zero it appears that the sequences resulting from (7.1) and (7.2) do indeed converge to the known similarity solution of (1.1)-(1.3) (see Dewynne [1]). However, for the cylinder and sphere $(\lambda = 1,2)$ we find that t_2 has the undesirable property of not being uniquely invertible. Specifically, when the boundary is 'near' the origin it is possible to find pairs R_1 and R_2 such that $t_2(R_1) = t_2(R_2)$, that is, for a given time t_2 (close to t_c, the time to complete freezing), there are two boundary positions. This situation is of course physically absurd, violates the assumption that $R(t)$ is invertable (on which (7.1) and (7.2) are based), and leads to an infinite boundary velocity 'before' the boundary reaches the origin. We use quotations here because, this infinite velocity occurs at time $t > t_2(0)$, that is after the approximate boundary reaches the origin! Since the denominator in (7.1) is $\frac{\partial t_{n+1}}{\partial R}$, one might expect that, for the sphere and

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cylinder, the iteration T_2 would be singular for some value of R, and an extensive calculation confirms this. Indeed it appears that this singularity is propagated throughout the higher order terms in both sequences. However, these problems only arise for large times, that is for times when the boundary is near the origin. For short times numerical and graphical results indicate that both T_1 and t_2 are excellent approximations to the actual temperature and boundary motion. Figures 5 and 6 compare t_0, t_1 and t_2 to the numerical boundary motion for the cylinder, with $\alpha = 2.0$ and β zero, and the sphere, with $\alpha = 5.0$ and $\beta = 1.0$ and the unphysical behaviour of t_2 in both cases is apparent.

8. Formal series solutions

On writing (5.1) as

$$(8.1)\quad T(r,t) = \alpha \frac{\partial}{\partial t} \int_{R(t)}^{r} \xi^{\lambda} K_{\lambda}(r,\xi)\, d\xi + \frac{\partial}{\partial t} \int_{R(t)}^{r} \xi^{\lambda} K_{\lambda}(r,\xi) T(\xi,t)\, d\xi,$$

and repeatedly substituting this expression for $T(r,t)$ into the right hand side of the equation to obtain

$$(8.2)\qquad T(r,t) = \alpha \sum_{n=1}^{\infty} \frac{\partial^n}{\partial t^n} C_n^{\lambda}(r,R(t)),$$

on assuming a remainder term tends to zero and where the functions C_n^{λ} satisfy

$$(8.3)\quad C_{n+1}^{\lambda}(r,R) = \int_{R}^{r} \xi^{\lambda} K_{\lambda}(r,\xi) C_n^{\lambda}(\xi,R)\, d\xi, \qquad n > 0, \qquad C_0^{\lambda}(r,R) = 1.$$

Explicit formulae for $C_n^{\lambda} (\lambda = 0,1,2)$ may be found in Dewynne [1]. For the slab and sphere $(\lambda = 0,2)$ these formulae are relatively simple, and their general form may be easily deduced, inductively, from (8.3). For the cylinder $(\lambda = 1)$ the general form of the functions C_n^1 is far more complicated, and the interested reader is referred to Hill and Dewynne [9].

The formal solution (8.2) is important for two reasons. Firstly by choosing some particular function $R(t)$ we can deduce the temperature and hence the boundary conditions necessary to produce the boundary motion $R(t)$. As such (8.2) represents the general solution of the

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'inverse Stefan problem' and is the only systematic means of generating exact solutions to Stefan problems, albeit artifical problems. Such solutions usually have little physical relevance but are useful for testing and evaluating numerical and approximate techniques. Secondly (8.2) may be used to suggest the functional form of approximate series solutions of such problems. In particular, by this process we may deduce suitable approximating expressions for the cylindrical Stefan problem. Unlike planar and spherical problems for which polynomial approximating expressions apply, there has been some speculation for cylindrical problems as to the precise dependence of approximating expressions on $\log r$ and $\log R(t)$. From (8.2), for $\lambda = 1$, we may deduce (see Hill and Dewynne [9]) the general structure for the temperature

$$T(r,t) = (r^2 - R^2)F(r^2,R^2) + G(r^2,R^2)\log(r/R), \tag{8.4}$$

where F and G denote complicated functions which are analytic and therefore may be approximated in the usual manner and in the first instance may be approximated simply by functions of time only. Finally, by substituting (8.2) into a given boundary condition, such as $(1.2)_1$, an infinite order differential equation for the boundary $R(t)$ results. Normally this differential equation cannot be solved, but it can be transformed into a non-linear integral equation for the inverse boundary motion and for details of this process we refer the reader to Hill [7].

9. Two simultaneous chemical reactions

In this section we describe the application of the integral formulation to a problem which arises from the oxydesulphurization of coal. Coal contains organic sulphur, which oxidizes slowly, and inorganic sulphur, which oxidizes rapidly. Thus, we consider a slab, cylinder or sphere consisting of an inert solid matrix in which two solid reactants are uniformly distributed. We assume that the solid is porous, allowing a fluid reactant to diffuse in and react instantaneously with one of the reactants giving rise to a moving reaction front. In the region between the reaction front and the surface of the solid the fluid is involved in a slower reaction with the other solid reactant, and we assume that the

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rate of this slow reaction depends only on the concentration of fluid. In non-dimensional variables we can write this problem as

$$\frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial r^2} + \frac{\lambda}{r}\frac{\partial c}{\partial r} - k^2 c, \quad R(t) < r < 1, \tag{9.1}$$

$$c(1,t) + \beta\frac{\partial c}{\partial r}(1,t) = 1, \quad c(R(t),t) = 0, \tag{9.2}$$

$$\frac{\partial c}{\partial r}(R(t),t) = -\alpha\frac{dR}{dt}, \quad R(0) = 1, \tag{9.3}$$

where $c(r,t)$, r, $R(t)$ and t denote non-dimensional concentration of the fluid, position, moving boundary position and time respectively. The constants $\alpha > 0$, $\beta \geq 0$ and k are given by

$$\alpha = \frac{\rho\omega}{c_0}, \quad \beta = \frac{1}{ah_D} \text{ or } 0, \quad k^2 = \frac{a^2 k_1}{D}, \tag{9.4}$$

where ρ is the density of the solid, ω a stoichiometric constant determined by the rapid reaction, c_0 the surface concentration of fluid, a is a characteristic length scale, h_D the surface mass transfer mass transfer coefficient, k_1 the rate constant for the slow reaction and D the fluid's diffusivity.

To obtain an integral formulation of the problem (9.1)-(9.3) we introduce the function $K_\lambda(r,\xi;k)$ which is a generalization of the function $K_\lambda(r,\xi)$ and is defined to be the solution of

$$\frac{\partial^2 K_\lambda}{\partial r^2}(r,\xi;k) + \frac{\lambda}{r}\frac{\partial K_\lambda}{\partial r}(r,\xi;k) = 0, \tag{9.5}$$

$$K_\lambda(r,r;k) = 0, \quad \lim_{r\to\xi} \xi^\lambda \frac{\partial K_\lambda}{\partial r}(r,\xi;k) = 1. \tag{9.6}$$

Using $K_\lambda(r,\xi;k)$ we can define a pseudo steady state approximation which arises from (9.1)-(9.3) by ignoring the time partial derivative in (9.1) and is given by

$$c_{pss}(r,R) = K_\lambda(r,R;k) \Big/ \left[K_\lambda(1,R;k) + \beta\frac{\partial K_\lambda}{\partial r}(1,R;k)\right], \tag{9.7}$$

$$t_{pss}(R) = \alpha\int_R^1 \xi^\lambda \left[K_\lambda(1,\xi;k) + \beta\frac{\partial K_\lambda}{\partial r}(1,\xi;k)\right] d\xi, \tag{9.8}$$

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and by taking the difference $c(r,t)-c_{pss}(r,R(t))$ and applying a Green's function we can deduce (as in Section 5) the integral formulation

$$c(r,t) = \frac{\partial}{\partial t}\int_{R(t)}^{r} \xi^{\lambda} K_{\lambda}(r,\xi;k)[\alpha + c(\xi,t)]d\xi, \tag{9.9}$$

$$t = \int_{R(t)}^{1} \xi^{\lambda}\left[K_{\lambda}(1,\xi;k) + \beta\frac{\partial K_{\lambda}}{\partial r}(1,\xi;k)\right][\alpha + c(\xi,t)]d\xi. \tag{9.10}$$

Proceeding as in Section 6 we can develop upper and lower bounds for the moving boundary using the inequalities $0 \le c(r,t) \le c_{pss}(r,R(t)) \le 1$ and $\frac{\partial c}{\partial t} \ge 0$. These bounds are particularly tight when either of α or k is large compared to unity. For full details, we refer the reader to Dewynne and Hill [3]. Using (9.9) and (9.10) we can set up an integral iteration scheme similar to that described in Section 7, and from (9.9) formal series solutions can also be developed. We refer the reader to Hill [7] for the details. Finally we remark that in Hill [6] it is shown that the integral formulation (9.9)-(9.10) is both distinct from and superior to the integral formulation which arises from (9.1)-(9.3) by direct integration.

10. A Stefan problem with two moving boundaries

Multiphase and multicomponent Stefan problems, with several moving boundaries separating several distinct phases or components, have been used to model many processes such as the melting or freezing of polymorphous materials or multicomponent systems such as alloys or food products. We consider the freezing of a material which has two solid phases and which is initially in liquid state, uniformly at its fusion temperature and subject to a subfreezing temperature at a surface. For planar, cylindrical and spherical geometries we can write the problem in non-dimensional form as

$$\frac{\partial T_1}{\partial t} = \frac{\partial^2 T_1}{\partial r^2} + \frac{\lambda}{r}\frac{\partial T_1}{\partial r}, \qquad R_1(t) < r < 1, \tag{10.1}$$

$$c\frac{\partial T_2}{\partial t} = \frac{\partial^2 T_2}{\partial r^2} + \frac{\lambda}{r}\frac{\partial T_2}{\partial r}, \qquad R_2(t) < r < R_1(t), \tag{10.2}$$

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(10.3) $$T_1(1,t) = 1, \quad T_1(R_1(t),t) = 0,$$

(10.4) $$T_2(R_1(t),t) = 0, \quad T_2(R_2(t),t) = V,$$

(10.5) $$-\alpha_1 \frac{dR_1}{dt} = \frac{\partial T_1}{\partial r}(R_1(t),t) - \frac{\partial T_2}{\partial r}(R_1(t),t), \quad R_1(0) = 1,$$

(10.6) $$-\alpha_2 \frac{dR_2}{dt} = \frac{\partial T_2}{\partial r}(R_2(t),t), \quad R_2(0) = 1,$$

where r and t denote non-dimensional position and time respectively and $T_i(r,t)$ and $R_i(t)$ denote the non-dimensional temperature in the ith phase and the non-dimensional position of the ith moving boundary. The constants α_i are the ratio of the latent heats of phase change to the sensible heat of the first phase. The non-dimensional initial temperature of the liquid is $V < 0$ and the constant c is given by $c = k_1c_2/k_2c_1$, where c_i and k_i are the heat capacity and thermal conductivity of the ith phase.

It is shown in Dewynne and Hill [5] that (10.1)-(10.6) admits an integral formulation similar to (5.6)-(5.7) although considerably more complicated. A simple integral relating the boundary motions arises from this integral formulation, and is given by

(10.7) $$\begin{aligned}(1 - V)t = &\int_{R_1(t)}^{1} \xi^{\lambda} K_{\lambda}(1,\xi)[\alpha_1 + \alpha_2 - cV + T_1(\xi,t)]d\xi, \\ &+ \int_{R_2(t)}^{R_1(t)} \xi^{\lambda} K_{\lambda}(1,\xi)[\alpha_2 - cV + T_2(\xi,t)]d\xi,\end{aligned}$$

where $K_{\lambda}(r,\xi)$ is given by (1.6). This integral can be generalized to accommodate the situation where $(10.3)_1$ is replaced by a Newton radiation surface condition. In [5] it is observed that (10.7) is equivalent to

(10.8) $$(1 - V)t = \int_0^1 \xi^{\lambda} K_{\lambda}(1,\xi) H(\xi,t)d\xi,$$

where $H(\xi,t)$ is the non-dimensional enthalpy for the problem (10.1)-(10.6). From this observation it is possible to find the general form of the integral relating the boundary motions for an n-phase problem. In the absence of further independent relations between the moving boundaries,

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however, it is not possible to exploit (10.7) or (10.8) to find non-trivial bounds for the moving boundaries. The integral (10.8) does lend itself to a simple and convenient check on the accuracy of a numerical enthalpy scheme. Finally in [5] it is shown that we can define a pseudo steady state solution of (10.1)-(10.2), and it is given by

$$T_{1pss}(r,t) = K_\lambda(r,R_1(t))/K_\lambda(1,R_1(t)), \quad R_1(t) < r < 1, \tag{10.9}$$

$$T_{2pss}(r,t)=VK_\lambda(r,R_2(t))/K_\lambda(R_1(t),R_2(t)), \quad R_2(t)< r < R_1(t), \tag{10.10}$$

but only for the slab $(\lambda = 0)$ is it possible to integrate the differential equations for the approximate boundary motions R_{1pss} and R_{2pss}.

11. A two phase Stefan problem

As a final example, we consider the genuine two phase Stefan problem describing the solidification of a slab or the inward solidification of a cylinder or sphere of liquid, initially above its freezing point. In non-dimensional variables we can write the problem as

$$\frac{\partial T_s}{\partial t} = \frac{\partial^2 T_s}{\partial r^2} + \frac{\lambda}{r}\frac{\partial T_s}{\partial r}, \quad R(t) < r < 1, \tag{11.1}$$

$$c\frac{\partial T_\ell}{\partial t} = \frac{\partial^2 T_\ell}{\partial r^2} + \frac{\lambda}{r}\frac{\partial T_\ell}{\partial r}, \quad 0 < r < R(t), \tag{11.2}$$

$$T_s(1,t) = 1, \quad \frac{\partial T_\ell}{\partial r}(0,t) = 0, \quad T_\ell(r,0) = \phi(r) \le 0, \tag{11.3}$$

$$T_s(R(t),t) = 0, \quad T_\ell(R(t),t) = 0, \tag{11.4}$$

$$-\alpha\frac{dR}{dt} = \frac{\partial T_s}{\partial r}(R(t),t) - \frac{\partial T_\ell}{\partial r}(R(t),t), \quad R(0) = 1, \tag{11.5}$$

where subscripts s and ℓ are used to distinguish between the properties of solid and liquid respectively. The constant α is the ratio of latent heat to the sensible heat of the solid, while the constant c is given in terms of the heat capacities and thermal conductivities of the two phases by $c = k_s c_\ell / k_\ell c_s$. The no flux condition at $r = 0$, $(11.3)_2$, is essential for the cylinder and sphere, physically because of symmetry and mathematically in order to obtain finite solutions, while

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for the slab it simply represents an insulated face at $r = 0$.

In Dewynne and Hill [4] we obtain an integral formulation for this problem, which we use to deduce the formal integral for the boundary motion,

$$t - \int_0^t T_\ell(0,\tau)d\tau = \int_{R(t)}^1 \xi^\lambda K_\lambda(1,\xi)[\alpha + T_s(\xi,t)]d\xi$$

(11.6)

$$+c\int_0^{R(t)} \xi^\lambda K_\lambda(1,\xi)T_\ell(\xi,t)d\xi - c\int_0^1 \xi^\lambda K_\lambda(1,\xi)\phi(\xi)d\xi,$$

where $\phi(r)$ denotes the initial temperature of the liquid (see (11.3)$_3$). Using (11.6) and the integral formulation given in [4] it is possible to find bounds for the boundary motion $R(t)$. However the presence of the time integral on the left hand side of (11.6) makes the analysis more complicated than it is for a single phase problem (see Section 6), and in particular, limits the lower bounds for the two phase problem to those given in Section 6 for the single phase problem. For a detailed discussion of this problem, we refer the reader to [4] . As in previous sections, it is possible to interpret (11.6) in terms of enthalpy H, namely

$$t - \int_0^t T_\ell(0,\tau)d\tau = \int_0^1 \xi^\lambda K_\lambda(1,\xi)[H(\xi,t) - H(\xi,0)]d\xi, \tag{11.7}$$

where, for the problem (11.1)-(11.5), the enthalpy is given by

$$T = \begin{cases} H - \alpha, & H > \alpha, \\ 0, & H \in [0,\alpha], \\ H/c, & H < 0. \end{cases} \tag{11.8}$$

Equation (11.7) can be used as a convenient check on the accuracy of a numerical enthalpy scheme. Finally we mention that similar integral formulations and integrals for the boundary motion are possible for two phase Stefan problems posed in concentric cylindrical and spherical regions with a variety of boundary conditions on the inner and outer surfaces, and for two phase problems posed in semi-infinite slabs and in the infinite regions surrounding cylinders and spheres and we refer the reader to [4] for these problems.

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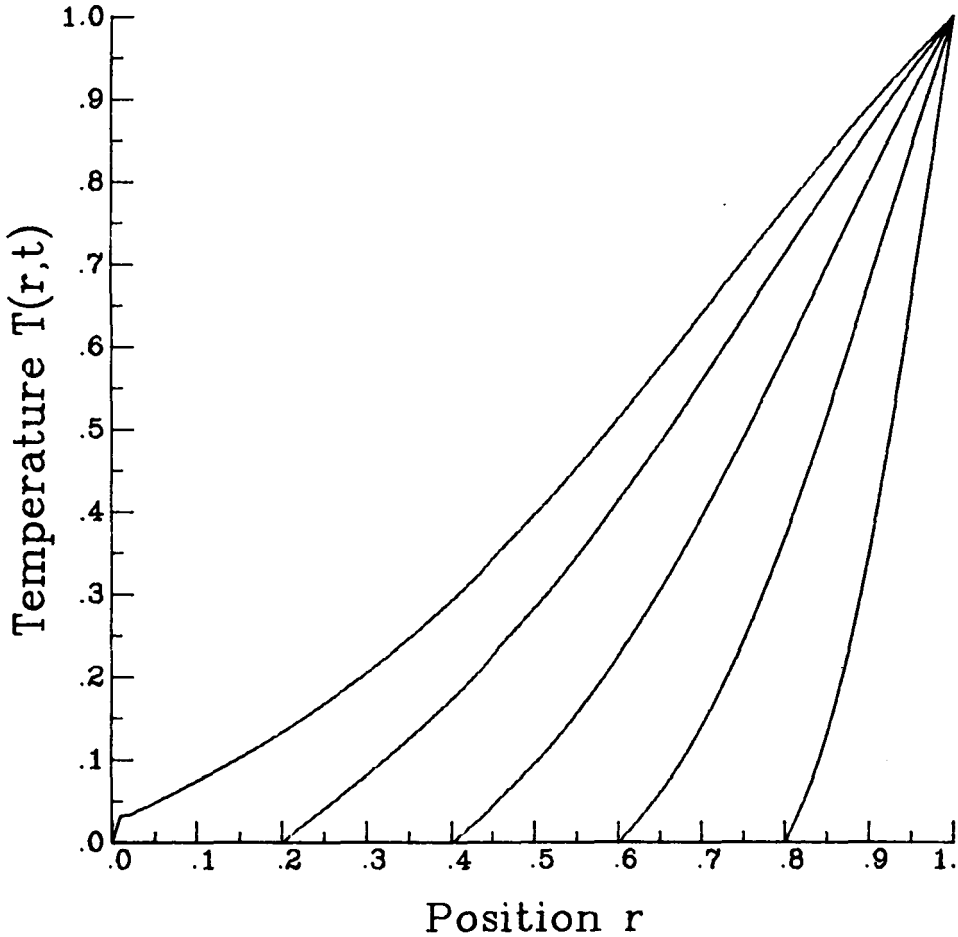

FIGURE 1

Numerical temperature profiles at four equally spaced positions of the moving boundary $R(t)$ for the sphere with $\alpha = 0.1$ and β zero.

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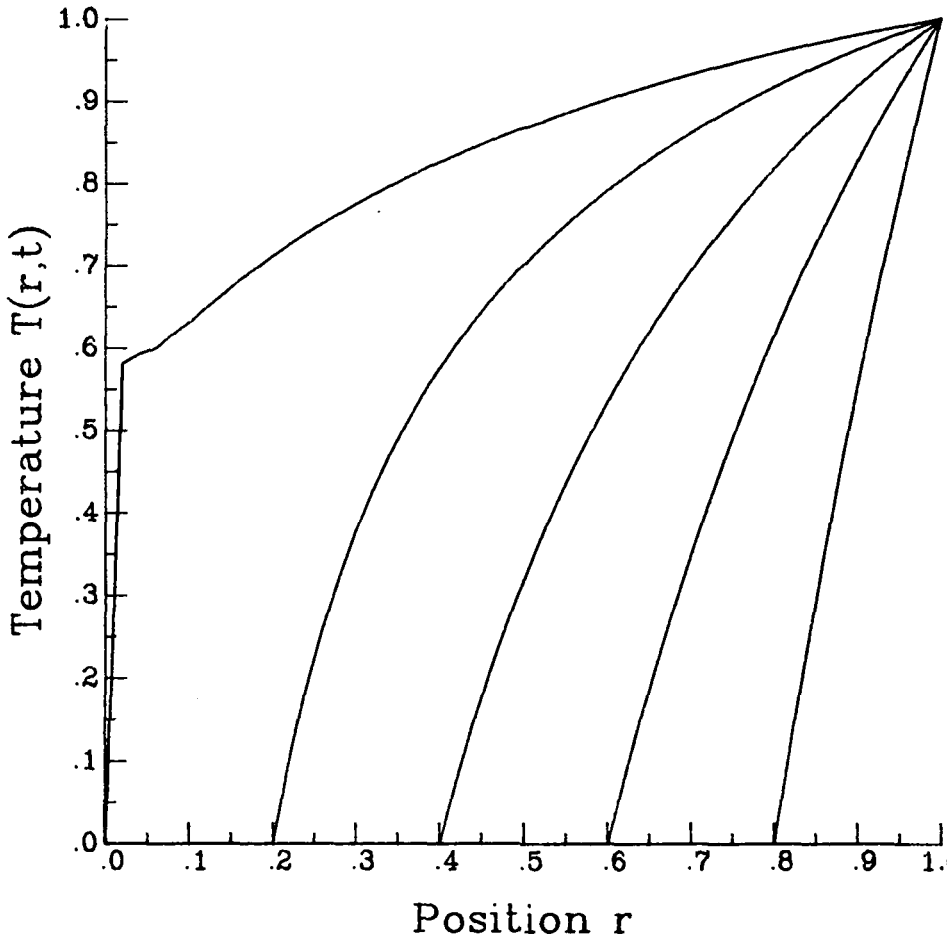

FIGURE 2

Numerical temperature profiles at four equally spaced positions of the moving boundary $R(t)$ for the sphere with $\alpha = 10.0$ and β zero.

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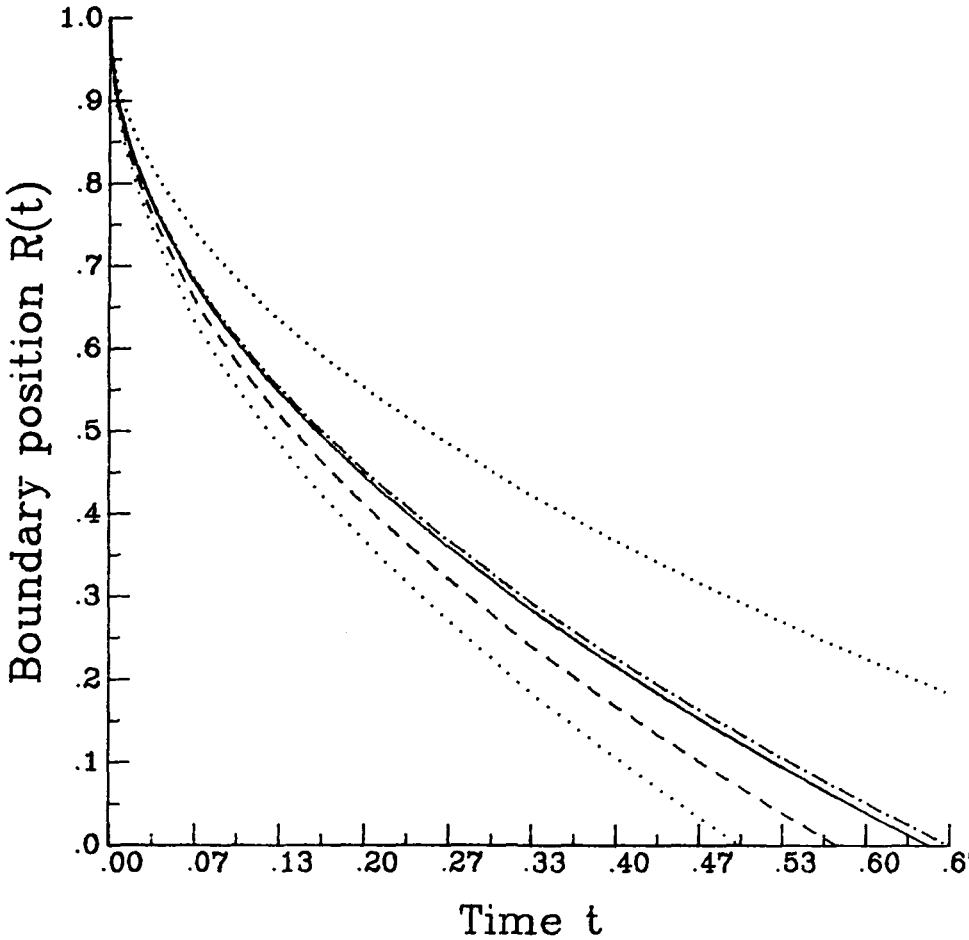

FIGURE 3

Comparison of the simple upper and lower bounds (6.1)(···), improved upper bound (6.3)(-·-) improved lower bound (6.6)(--) and exact boundary motion (—) for the slab with $\alpha = 1.0$ and β zero.

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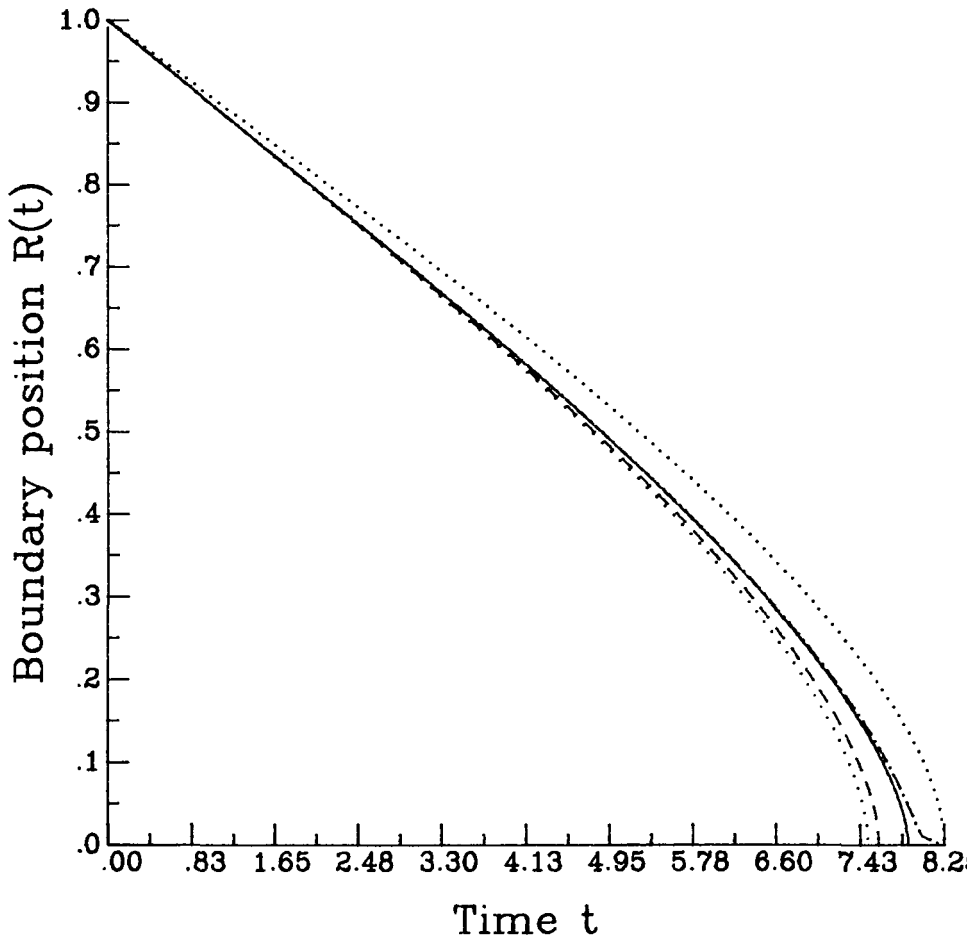

FIGURE 4

Comparison of the simple upper and lower bounds (6.1)(···), improved upper bound (6.3)(-·-) improved lower bound (6.6)(--) and numerical boundary motion (—) for the cylinder with $\alpha = 10.0$ and $\beta = 1.0$.

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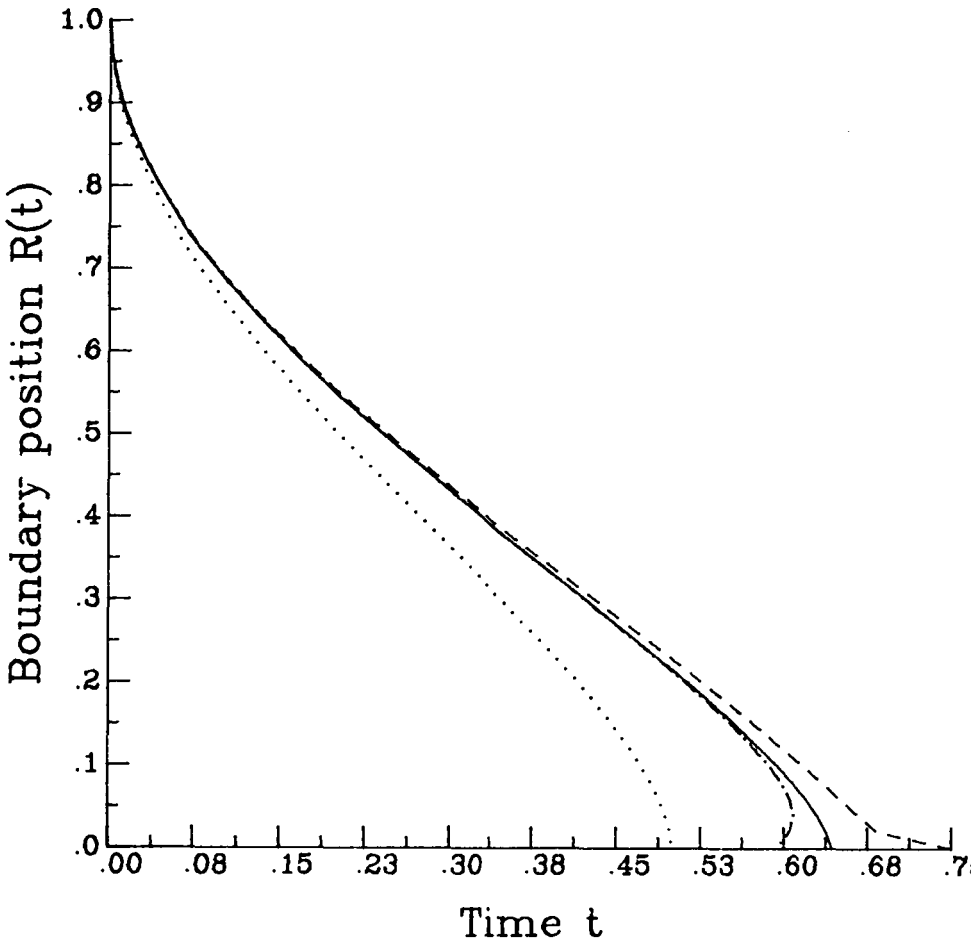

FIGURE 5

Comparison of the approximate boundary motions t_0 (···), t_1 (--) and t_2 (-·-) arising from (7.2) with the numerical boundary motion (—) for the cylinder with $\alpha = 2.0$ and β zero.

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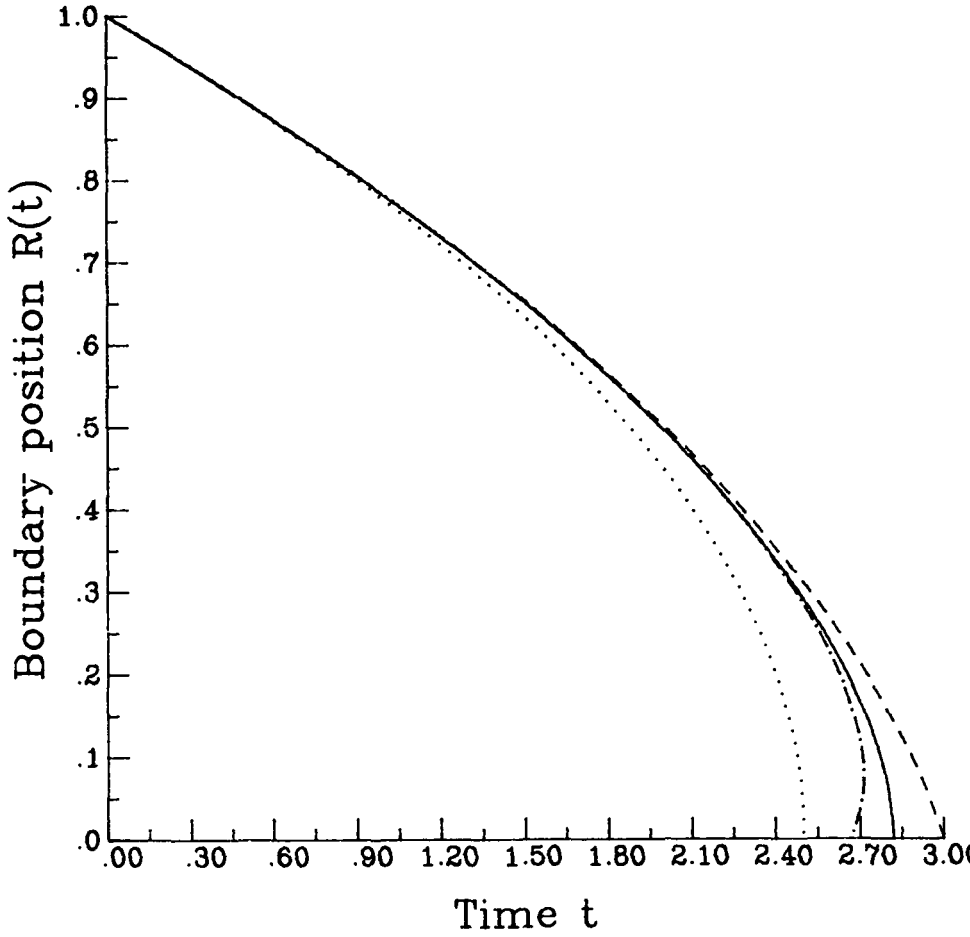

FIGURE 6

Comparison of the approximate boundary motions t_0 (···), t_1 (--) and t_2 (-·-) arising from (7.2) with the numerical boundary motion (—) for the sphere with $\alpha = 5.0$ and $\beta = 1.0$.

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