Diffusion in a Moving Medium with Time-dependent Boundaries

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The problem of diffusion in a moving medium with given motion of the boundaries is considered. The method presented yields the analytical solution to any desired degree of accuracy provided that solutions for certain associated problems of diffusion in a medium at rest with boundaries at rest are known. The method is applied to the analysis of partial and approximate solutions previously presented for the one-dimensional case of a spherical cavity in a liquid with radial boundary motion induced by evaporation.

In melting and freezing and frequently in the propagation of chemical reactions through some material an important group of problems arises in which one substance changes into another with emission or absorption of heat. One essential feature of such problems is the existence of a moving surface of separation between the two phases at which heat is being liberated or absorbed. In melting, freezing, and similar cases the change in specific volume caused by change of phase is negligible and the medium may be considered at rest. The problem in which the motion of the *free* (phase) *boundary* caused by diffusion in a medium *at rest* is to be found is well known as *Stefan's problem.** In cases of condensation and evaporation (bubbles in boiling and cavitation, rather than evaporation of droplets) an added difficulty arises, because these processes are accompanied by a marked change in specific volume whereby the medium in which the phase change is taking place is set in motion. Thus the problem becomes one of diffusion in a moving medium, which is, in the case of heat diffusion, the problem of heat transfer by simultaneous heat conduction and heat convection. On the other hand, the same circumstance also introduces, for condensation and evaporation, a simplification in Stefan's problem: owing to the large change of volume in evaporation the motion of the phase boundary is determined by the increase of volume of the vapor phase, and the influence of the decrease of volume of liquid by evaporation may, in comparison, be neglected.

*Some references to Stefan's problem may be found in reference *4*, p. 71.

In view of the foregoing discussion this paper presents a rather general method which yields, to any desired degree of accuracy, the solution of problems of combined heat conduction and heat convection with *given* motion of the boundaries. The general method will then be used to discuss, analyze, and compare partial and approximate solutions previously presented (*1*, *2*) for the special case of a spherical cavity with radial boundary motion induced by evaporation.

DIFFUSION IN A MOVING MEDIUM

In the problem of heat conduction in a moving, incompressible, inviscid fluid with given motion of the boundaries (*3*), $T(\mathbf{r}, t)$ is the temperature and $\mathbf{v}(\mathbf{r}, t)$ the local velocity of the medium, $\mathbf{r}$ being the radius vector (x, y, z); then the differential equation to be solved is

$$a \nabla^2 T - \mathbf{v}(\mathbf{r}, t) \cdot \text{grad}\, T - \frac{\partial T}{\partial t} = 0 \qquad (1)$$

The motion of the boundary may be given by $\mathbf{r} = \mathbf{r}_0(t)$ as a known function of time, and the boundary conditions which shall be considered in this paper are those of constant temperature or of vanishing heat flux on the moving boundary:

$$T = 0; \quad \text{or} \quad \frac{\partial T}{\partial n} = 0; \qquad \text{for:} \quad \mathbf{r} = \mathbf{r}_0(t) \qquad (2)$$

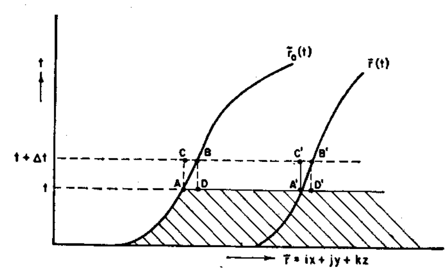

Fig. 1. Continuous and step-by-step boundary motion in the ($\bar{r}$, t) plane.

As indicated in Equation (1) the velocity $\mathbf{v}$ is in general a function of time and position and the equation thereby becomes one with variable coefficients to be solved for moving boundary conditions. No method for the solution of this general problem exists.

The problem is to find a solution to Equation (1) for boundary conditions given by Equation (2). In the $(\mathbf{r}, t)$ space, which is four dimensional but which may be shown diagrammatically in Figure 1, the domain of integration is a strip bounded by the $\mathbf{r}$ axis and by the curve $\mathbf{r}_0(t)$. The curves $\mathbf{r}_0(t)$ and $\mathbf{r}(t)$ in Figure 1 represent respectively the motion of a fluid particle at the boundary and the motion of a representative fluid particle anywhere in the fluid.

If the motion of the fluid starts at time t_0 with the boundary in position P_0 and proceeds until time t, when the boundary may be at position P_t (see Figure 2), at the intermediate times t_1, t_2, t_3 $\cdots$ the boundary moves through positions P_1, P_2, P_3 $\cdots$, with the liquid moving accordingly in some prescribed manner.

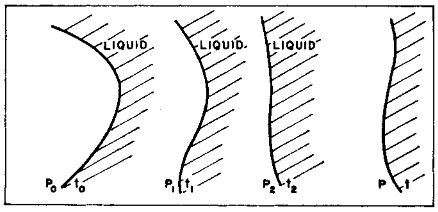

Fig. 2. Motion of the boundary from positions P_0 to P_t; intermediate positions P_1, P_2, etc., are shown.

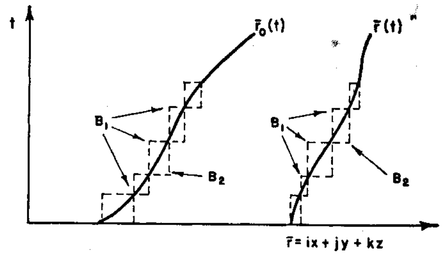

Fig. 3. Path of boundary and of fluid particles in the ($\bar{r}$, t) plane.

The motion of fluid and boundary is approximated as follows. The boundary remains at P_0 for time $(t_1 - t_0)$; at time t_1 it moves (instantly) to position P_1, where it remains for time $(t_2 - t_1)$; at time t_2 the boundary moves instantly to P_2, where it remains for time $(t_3 - t_2)$, and so on, until position P_t at time t is reached by the boundary, with all fluid particles occupying the position prescribed for them for time t.

It is quite clear that the solution of the heat conduction-convection problem for the step-by-step motion of the fluid particles will converge to the solution of the problem for the given motion of the fluid particles because the given fluid motion is the limiting case of the step-by-step motion for decreasing step size, and for an inviscid fluid the boundary conditions [Equation (2)] can be satisfied throughout the process. The *exact* solution of Equation (1) for the *approximated* fluid motion, however, can be reduced to solutions of the simpler conduction equation

$$a \nabla^2 T - \frac{\partial T}{\partial t} = 0 \qquad (3)$$

Solutions to Equation (3) are well known for most cases of practical interest.

In the diagram for the $(\mathbf{r}, t)$ space (Figure 3) the motion of the fluid boundary described above appears as either one of the boundaries B_1 or B_2 approximating $\mathbf{r}_0(t)$. The space-time path of the general fluid particle is then uniquely determined and approximates $\mathbf{r}(t)$ in a manner similar to the approximation of $\mathbf{r}_0(t)$ by B_1 or B_2. Consequently B_1 or B_2 as used here will include not only the boundary motion but also the motion of the entire fluid as caused by the motion of the boundary B_1 or B_2 respectively.

The details of the calculation may be explained by reference to Figure 1. Between times t and $(t + \Delta t)$ it is assumed that the solution is known for time t; that is, $T(\mathbf{r}, t)$ is known and the solution for time $(t + \Delta t)$, during which the boundary has moved from A to B, is desired. Instead of proceeding from A to B directly, one proceeds from A to C to B, and observes that during the integration from A to C, A' to C', etc., the velocity $\mathbf{v}(\mathbf{r}, t)$ is everywhere zero (because $\mathbf{r}$ remains constant) and Equation (1) goes over into Equation (3), for which the solution may be assumed known. Thus the exact temperature for time $(t + \Delta t)$ for fluid boundary at point C and fluid particles at point C' is obtained; each fluid particle is shifted (instantaneously) from C to B, from C' to B', whereby the redistribution of temperature due to heat convection is achieved, and each fluid particle attains the position it should occupy in accordance with the prescribed motion.

Mathematically these steps are most easily performed by the use of Green's function for Equation (3) (for the domain bounded by AC), which may be denoted by $G(\mathbf{r}, \mathbf{r}', t)$. The temperature $\theta[\mathbf{r}, (t + \Delta t)]$ at the representative point C' is then given in terms of the temperature $T(\mathbf{r}, t)$ by

$$\theta(\mathbf{r}, t + \Delta t) = \int_{\mathbf{r}_0(t)}^{\infty} T(\mathbf{r}') \, G(\mathbf{r}, \mathbf{r}', \Delta t) \, dr' \qquad (4)$$

where dr' is written symbolically for the volume element $(dx' \, dy' \, dz')$ at $\mathbf{r}'$.

The displacement $\Delta\mathbf{r}$ of the fluid particle situated at $\mathbf{r}$ is easily calculated, as the local velocity $\mathbf{v}(\mathbf{r}, t)$ of the fluid is given. Then, as each fluid particle is shifted by $\Delta\mathbf{r}$ (from the representative point C' to the representative point B') the temperature $T(\mathbf{r}, t + \Delta t)$ is given from Equation (4) by $\theta[(\mathbf{r} - \Delta\mathbf{r}), (t + \Delta t)]$ or, explicitly,

$$T(\mathbf{r}, t + \Delta t) = \int_{\mathbf{r}_0(t)}^{\infty} T(\mathbf{r}', t) \cdot G[(\mathbf{r} - \Delta\mathbf{r}), \mathbf{r}', \Delta t] \, dr' \qquad (5)$$

Equation (5) is the exact solution of Equation (1) for the approximating boundary motion A to C to B. Thus, given an initial temperature distribution $T(\mathbf{r}, 0)$, the time interval t may be subdivided into n subintervals and the *exact* solution of Equation (1) is obtained for the strip bounded by B_1 (see Figure 3) by repeated application of Equation (5) to the n subintervals.

For the fluid motion represented by B_2 a related formula may be derived by performing the operations given by Equation (4) and previous to Equation (5) in reverse order, i.e., taking the path (see Figure 1) from A to D to B and from A' to D' to B'.

$T_1^n(\mathbf{r}, t)$ then is the solution of Equation (1) for B_1 and $T_2^n(\mathbf{r}, t)$ that for B_2, both for time t in n intervals. This is not the place to treat questions of convergence mathematically, but the following can be concluded from physical considerations as n tends to infinity: Both T_1 and T_2 tend to the solution of Equation (1) for boundary motion $\mathbf{r}_0(t)$, since both B_1 and B_2 tend to $\mathbf{r}_0(t)$; the difference $(T_1 - T_2)$ tends to zero as n increases; considering that the path $\mathbf{r}(t)$ of every fluid particle is always intermediate between B_1 and B_2, one may assume that for a certain class of fluid motions the temperature of the fluid particle for the given motion is intermediate between T_1^n and T_2^n.

In the foregoing section the problem of diffusion in a moving medium with time-dependent boundaries was reduced to a series of quadratures of known functions, namely, the solutions of a diffusion problem in a medium at rest with boundaries at rest. The method does not involve numerical integrations or procedures; neither does it replace differential equations by difference equations; rather, it yields the final solution as a function of position and time. For instance, if Green's function for diffusion in a moving medium is to be obtained one merely has to insert the temperature distribution of a unit heat source for the initial temperature in Equation (5). Also, by use of Duhamel's theorem very general time dependence of the boundary conditions may be included.

HEAT TRANSFER INTO A SPHERICAL CAVITY WITH RADICAL MOTION

Qualitative Considerations and Application of the Preceding Theory

It is evident from the discussion above that the mathematical expressions for heat conduction-convection problems will in general be quite involved. Fortunately the physical conditions prevailing in vapor-liquid systems permit substantial simplifications in the general formulism. The system of a spherically symmetric vapor bubble in an infinite liquid will be considered in some detail because of its importance in boiling and in cavitation.

To begin with, it must be clearly understood what bearing the transport of liquid has upon the transport of heat toward the bubble wall. In Figure 4 the growing bubble is shown at two successive times, and the influence of liquid convection is seen to arise from two processes:

1. While the bubble grows, the surface area of the bubble increases; to the extent to which heat *conduction* depends on the bubble radius the increase in radius changes the amount of heat conducted to the wall.

2. While the bubble grows, its curva-

ture changes; owing to this change the *relative* position of fluid particles $(ABCD) \rightarrow (A'B'C'D')$ changes and this *relative change* constitutes the convective contribution to the transfer of heat to or from the bubble wall.

It is important to realize that the *absolute* change in position of fluid particles (liquid convection) does not entail the convection of *heat toward* the bubble wall: if the liquid-vapor boundary in Figure 4 is flat (a plane), the *relative* position of fluid particles is not changed by the motion of the boundary and then no convective heat transfer takes place within the liquid or toward the boundary despite considerable convective motion of the liquid. The same is true for the case of a radially moving *spherical* vapor-liquid boundary if the domain under consideration is small compared with the radius. This is evident from the fact that in a region so restricted the flow of liquid is the same as that caused by a moving plane, a circumstance which will prove important and which will be referred to later.

In reference *2* the preceding theory was applied to the present problem. The appropriate Green's function to be used in Equation (5) can be found in Carslaw and Jaeger (*4*). Vapor bubbles, even at slight superheats, grow so fast or, conversely, the time interval under consideration is so short that a *mean value between* $T_1{}^1$ and $T_2{}^1$ represents the temperature of the phase boundary with sufficient accuracy. This involves the

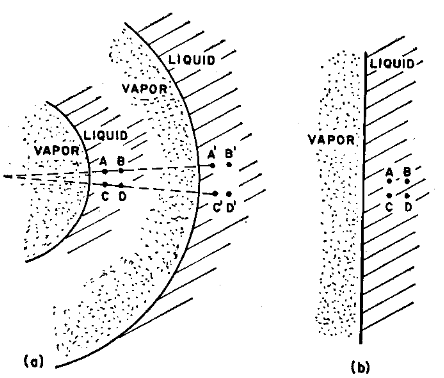

Fig. 4. Relative motion of fluid particles induced by (*a*) radial motion of spherical boundary, (*b*) motion of plane boundary.

calculation of a mean value for $R(\xi)$ for the following expression; it represents the temperature increment at the bubble wall of radius $R(t)$ at time t due to an amount of heat $dQ(x)$ liberated on the bubble of radius $R(x)$ at time x:

$$dT = \frac{dQ(x)}{4\pi\sqrt{\pi a}\,\sqrt{t-x}R^2(\xi)} \cdot \left[1 - \sqrt{\pi}\,\frac{\sqrt{a(t-x)}}{R(\xi)} \cdot \exp\left\{\frac{a(t-x)}{R^2(\xi)}\right\} \cdot \operatorname{erfc}\frac{\sqrt{a(t-x)}}{R(\xi)}\right] \tag{6}$$

where ξ ranges from time x to time t and $R(\xi)$ starts at $R(x)$ and grows to $R(t)$. An appropriate mean value for $R(\xi)$ is calculated in reference *2* to be $R(\xi) = \sqrt{R(x) \cdot R(t)}$, which is the geometric mean of the initial and final radii; Equation (6) then becomes

$$dT = \frac{dQ(x)}{4\pi\sqrt{\pi a}\,\sqrt{t-x}R(x)R(t)} \cdot \left[1 - \sqrt{\pi}\left(\frac{a(t-x)}{R(x)R(t)}\right)^{1/2} \cdot \exp\left\{\frac{a(t-x)}{R(x)R(t)}\right\} \cdot \operatorname{erfc}\left(\frac{a(t-x)}{R(x)R(t)}\right)^{1/2}\right] \tag{7}$$

If greater accuracy is desirable, the time interval must be further subdivided; on the other hand, if Equation (7) is to be used for the calculation of pressure in Rayleigh's equation of bubble dynamics the following circumstance is of importance. Since the time of the process starts at x (and lasts until t), $(t - x)$ starts at zero and therefore the second term in the bracket starts at zero while the factor in front starts at infinity; thus the second term is negligible in the vicinity of the singularity of Equation (7). As time increases, the second term grows, but for the case of a bubble growing by evaporation (even in a slightly superheated liquid) the radius $R(t)$ as well as $\sqrt{t-x}$ increases so fast that the factor in front decreases strongly while the second factor in the bracket increases to about ½. For a vapor bubble growing in water at 103°C., for example, by the time the second term in the bracket has increased to about ½, the radius $R(t)$ has increased by a factor of about 100 and the contribution dT is then less than 1% of its initial value. The second term in the bracket is small when the contribution (dT) is large and the contribution (dT) is small by the time the second term becomes important. For the sake of applications, where Equation (7), integrated, is used in Rayleigh's equation, it is advantageous to accept the small error involved and to neglect the second term in order to make the analysis and integration of Rayleigh's equation feasible without resort to numerical computations from which very little can be learned.

Integration of Equation (7) without the second term yields for the temperature of the bubble wall at time t (*2*) the approximation

$$T(t) = \frac{L\rho_v}{c_L\rho_L(\pi a)^{1/2}} \cdot \int_0^t \frac{R^2(x)\dot{R}(x)\,dx}{R(x)R(t)\sqrt{t-x}} \tag{8}$$

The integrand of Equation (8), it may be noted, is simply the amount of heat liberated (or absorbed) divided by the geometric mean squared of the radius, multiplied by $\sqrt{t-x}$.

Thin–thermal-boundary–layer Theory

A first attempt at the problem of combined heat conduction and convection with moving boundaries was published a few years ago by Plesset and Zwick (*1*), who considered the one-dimensional problem of a radially expanding sphere. They presented a partial solution in the sense that they included in their theory the effect of the surface-area increase of the moving boundary (cf. item 1 above) while inadvertently excluding the effect of heat convection (cf. item 2).

The crucial assumption in Plesset's theory is that the temperature throughout the liquid is constant except in a thin layer of liquid (adjacent to the bubble) which has small thickness compared with $r_0(t)$. Pinney (*5*) pointed out that this assumption implies significant restrictions on the solution but that this question was not discussed by Plesset and Zwick. Inasmuch as controversy arose on this and related matters on several occasions in the last two years (*6, 7*) it will here be analyzed in some detail.

From the point of view of the general theory which was developed in the present paper the implications of the "thin–thermal-boundary–layer" assumption become quite apparent. In Figure 1 this assumption amounts to a restriction of the domain of integration (which extends from $\mathbf{r}_0(t)$ to infinity) to a thin strip to the right of $\mathbf{r}_0(t)$ instead. In terms of the basic equation (5) the thin–thermal-layer assumption implies that the integral is extended from $r_0(t)$ to $(r_0 + h)$ with $h \ll r_0$ instead of from r_0 to infinity; the integral, then, instead of adding up the varying temperature contributions from the entire liquid surrounding the cavity takes in only the variations from the immediate vicinity of the cavity of radius $r_0(t)$. Thereby, of course, *all* effects of convection and conduction in the liquid contained between $(r_0 + h)$ and infinity are eliminated from calculation. In simple words, in a region of assumed constant temperature (i.e., everywhere except in the thin thermal-boundary layer) no effects of convection or conduction exist. In the calculation of the temperature in the boundary layer itself, conduction and convection are included *to the extent to which the latter exists within the thin layer.* However, it must be observed (compare Figure 5) that in consequence of the assumed thinness of the region, explicitly $h \ll r_0(t)$, the calculation is restricted to only those fluid particles which have negligible relative velocity with respect to the moving boundary ($r_0(t)$) as well as with respect to each other and which therefore do not contribute to heat convection; all other fluid particles which are at greater distance and which do have sizable relative velocities were eliminated previously by the assumption of constancy of temperature at any distance beyond ($r_0 + h$).

As long as h is considered small compared with $r_0(t)$, the region where convection is important is automatically excluded; on the other hand, Plesset's method of successive approximations cannot be extended to include a thickness of liquid equal to or larger than the radius $R(t)$ because, as will be shown, it then diverges.

The method in reference *1* depends critically on the development of

$$r^4 = R^4\left(1 + \frac{3h}{R^3}\right)^{4/3}$$

[stemming from Equation (2*a*), reference *1*] into a power series, in powers of the perturbation parameter (h/R^3),

$$r^4 = R^4\left[1 + 4\frac{h}{R^3} + 2\left(\frac{h}{R^3}\right)^2 + \cdots\right]$$

where the terms in the bracket enter successively the 0, 1, 2 ··· order approximation [cf. sequel to Equation (11) of reference *1*]. However, as is well known, the power series

$$(1 + x)^n = 1 + nx + \frac{n(n-1)}{2}x^2 + \cdots$$

for noninteger n and $x \geq 1$ is divergent. The method of successive approximations therefore cannot be extended to include the convective transport of heat to the bubble wall.

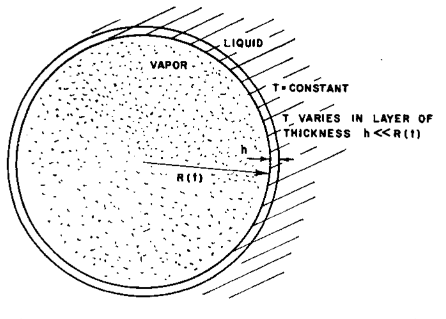

Fig. 5. Temperature conditions under the thin-thermal-boundary-layer assumption.

By means of the thin-boundary-layer theory Plesset and Zwick derive an approximate expression for the temperature at the boundary

$$T(t) = \frac{L\rho_v}{c_L\rho_L(\pi a)^{1/2}} \cdot \int_0^t \frac{R^2(x)\dot{R}(x)\,dx}{\left[\int_x^t R^4(y)\,dy\right]^{1/2}} \qquad (9)$$

which they use throughout their subsequent work. According to their method the differential equation is developed in powers of (h/R^3) and "to the first order h/R^3" [cf. reference *1*, Equation (11), Plesset and Zwick],

$$a\frac{\partial^2 u}{\partial h^2} - \frac{\partial u}{\partial \tau} = -\frac{4h}{R^3}\frac{\partial^2 u}{\partial h^2}$$

This equation, however, which is approximate to the first order in h, is not the one for which Equation (9) is a solution; rather, Equation (9) is the solution of the following equation [cf. reference *1*, Equation (12), Plesset and Zwicki]:

$$a\frac{\partial^2 u^0}{\partial h^2} - \frac{\partial u^0}{\partial \tau} = 0$$

which follows from the previous equation only if the thickness h of the boundary layer is no longer assumed small compared with the radius but is set equal to zero. Equation (9) then represents the "zero-order solution" for $h = 0$ and every effect of convection within the fluid has been completely eliminated previous to its calculation. This leaves the effect of surface-area increase due to boundary motion, as the only effect taken into consideration.

Comparison of the Results of the Two Theories

Both Equations (9) and (8) are obviously grossly simplified approximations to an otherwise complex problem. One is therefore led to suspect that the two expressions, despite their entirely different derivation and appearance, must be mathematically very similar, and indeed they are.

The numerator and coefficient of Equations (8) and (9) are identical; therefore one need compare only the denominator of Equation (8)

$$R(x)R(t)\sqrt{t-x} \qquad (10)$$

$$\equiv [\text{geometric mean of } R^2]\cdot\sqrt{t-x}$$

with the denominator in Plesset's Equation (9). Inasmuch as expression (10) was derived by calculating a mean value for R^2, the denominator in Plesset's formulations should also represent a mean value for R^2. If the definition of the root mean square (R.M.S.) of a function $f(y)$ for the interval $x \leq y \leq t$

$$[\text{R.M.S. of } f(y)] = \frac{1}{\sqrt{t-x}}\left[\int_x^t f^2(y)\,dy\right]^{1/2} \qquad (11)$$

is recalled, it is manifest that the denominator of Plesset's Equation (9) is in fact such a mean value, namely

$$\left[\int_x^t R^4(y)\,dy\right]^{1/2} = [\text{R.M.S. of } R^2]\cdot\sqrt{t-x} \qquad (12)$$

Equations (8) and (9) are thereby recognized to differ only in the way in which two closely related mean values are used for R^2 to represent approximately the influence of the continuous radial increase from $R^2(x)$ to $R^2(t)$. Moreover, in the neighborhood of the all-important singularity of the integrand at $x = t$ these mean values are identical. The greater usefulness of Equation (8) lies in its simplicity in application to bubble dynamics. The integral over the square root of another integral in Equation (9) renders Rayleigh's equation (in which either Equation (8) or (9) is to be used) difficult to analyze.

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NOTATION

- $\mathbf{r}$ = radius vector ($xi + yj + zk$)
- $\mathbf{r}_0 = \mathbf{r}_0(t)$ = radius vector to the boundary
- $r_0(t)$ = $R(t)$ = radius of spherical cavity
- $\mathbf{v}(\mathbf{r}, t)$ = velocity of a fluid particle
- a = thermal diffusivity
- L = latent heat of vaporization
- $\rho_{v,L}$ = density of vapor or liquid, respectively
- c_L = specific heat of liquid
- T, θ = temperature
- t = time
- x = a time between $t = 0$ and $t = t$ (except as used in $\mathbf{r}$)
- ξ = time integration variable $x \leq \xi \leq t$
- $Q(x)$ = heat liberated at time x
- h = thickness of thermal-boundary layer (cf. reference *1*)
- U, defined by $\partial U/\partial h = T - T_0$; T_0 is the temperature at infinity
- τ = $\int_0^t R^4(t)\,dt$ (cf. reference *1*)

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