CHAPTER 11

APPLICATIONS TO DIFFUSION PROBLEMS

Our aim in this chapter is to expose the interesting role played by differintegrals (specifically, semiderivatives and semiintegrals) in solving certain diffusion problems. Along with the wave equation and Laplace's equation, the diffusion equation is one of the three fundamental partial differential equations of mathematical physics. The books of Crank (1956), Barrer (1941), and Jost (1952), as well as any treatise on partial differential equations, provide ample background reading about this important equation which plays such a paramount role in the theories of heat conduction (Carslaw and Jaeger, 1947), diffusion (Babbitt, 1950; Crank, 1956) viscous flow (Moore, 1964), neutron migration (Davison, 1957), flow through porous media (Muskat, 1937), electrical transmission lines (Johnson, 1950), and in other instances of transport theory.

We shall not discuss conventional solutions of the diffusion equation at all. These range from closed form solutions for very simple model problems to computer methods for approximating the concentration of the diffusing substance on a network of points. Such solutions are described extensively in the literature. Our purpose, rather, is to expose a technique for partially solving a family of diffusion problems, a technique that leads to a compact equation which is first order spatially and half order temporally. We shall show that, for semiinfinite systems initially at equilibrium, our semidifferential equation leads to a relationship between the intensive variable and the flux at the boundary. Use of this relationship then obviates the need to solve the original diffusion equation in those problems for which this behavior at the boundary is of primary importance.

Each section of this chapter will first discuss some theoretical aspect of the link between transport processes and the fractional calculus, and then apply this theory to a problem of practical importance. Each problem is drawn from a different area of application to illustrate the diversity of situations amenable to our technique.

As is inevitable when results proved generally are put to practice, some of the restrictions that were found to be useful in establishing the theory may be difficult, even impossible, to verify in practice. No good scientist, however, would let this prevent him from applying the theory. Indeed, applications of the theory are frequently made without such verification, and the results obtained often point the way to extensions and improvements of the previous theoretical foundations. We shall, therefore, not apologize for our inability to show that every function we shall ever want to differintegrate is a differintegrable series according to the definition given in Section 3.1. Nor will we apologize for our present inability to extend to a broader class of functions general results proved earlier in the book. We shall, in fact, freely make use of the general properties established for differintegral operators as if all our functions were differintegrable.

11.1 TRANSPORT IN A SEMIINFINITE MEDIUM

We begin our study of transport processes by considering the diffusion equation

$$\frac{\partial}{\partial t} F(\xi, \eta, \zeta, t) = \kappa \nabla^2 F(\xi, \eta, \zeta, t) \tag{11.1.1}$$

in which F is some intensive scalar quantity (temperature, concentration, vorticity, electrical potential, or the like) that varies with time and from point to point in a three dimensional homogeneous medium, while κ is a constant appropriate to the medium and the type of transport. In equation (11.1.1), $\partial/\partial t$ effects partial differentiation with respect to time and ∇^2 is the Laplacian operator with respect to the spatial coordinates ξ, η, and ζ. When equation (11.1.1) is augmented by an initial condition and appropriate boundary conditions, its solution F is uniquely specified as a function of time and space.

Three commonly encountered boundary geometries allow a reduction from three to one in the number of spatial coordinates needed to describe transport through the medium. We shall use three different values of a geometric factor g to characterize these simplifying geometries, namely:

the convex sphere, $g = 1$;
the convex cylinder, $g = \frac{1}{2}$; and
the plane, $g = 0$.

The significance of the adjective "convex" will be clarified by glancing at item I of Fig. 11.1.1 and noting that the boundary appears convex as viewed from the diffusion medium. The term "semiinfinite" is commonly applied

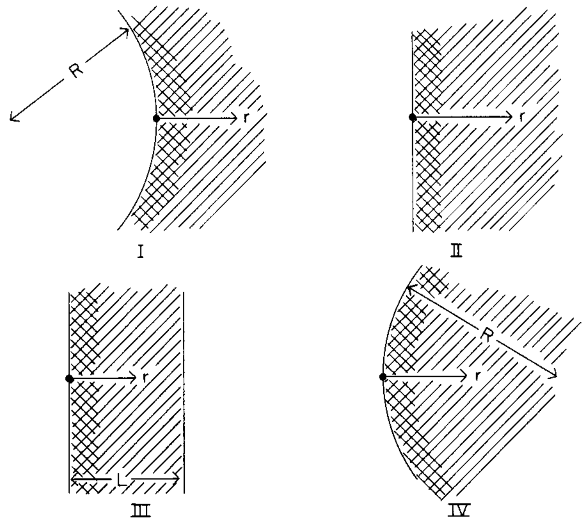

FIG. 11.1.1. This diagram illustrates, by means of cross sections, those geometries for which a single distance coordinate r suffices. Diagram I illustrates the convex spherical and cylindrical cases, $g = 1$ and $\frac{1}{2}$, it being, of course, impossible to distinguish between a sphere and a cylinder in cross section. Diagram II shows the planar, $g = 0$, case. Whereas the I and II geometries are truly semiinfinite, those diagrammed as III and IV are finite, though they behave as if they were semiinfinite at short enough times. In all four illustrations, the shaded areas represent the medium within which transport is proceeding, while the cross-hatched areas depict the zone adjacent to each boundary in which a significant perturbation occurs during the time domain $0 < t < \tau$ of interest. It is because this zone is narrow compared with L or R that these geometries behave semiinfinitely. The concave cylindrical and spherical, $g = -\frac{1}{2}$ and -1, cases are illustrated as IV.

to the three cases diagrammed as I and II; by this is meant that the diffusion medium extends indefinitely in one direction from the boundary. In these geometries the Laplacian operator simplifies so that equation (11.1.1) becomes

$$\frac{\partial}{\partial t} F(r, t) - \kappa \frac{\partial^2}{\partial r^2} F(r, t) - \frac{2g\kappa}{r \pm R} \frac{\partial}{\partial r} F(r, t) = 0, \tag{11.1.2}$$

encompassing the three values of g. Here r is the spatial coordinate directed normal to the boundary and having its origin at the boundary surface. In the cases of spherical and cylindrical geometries, the R in equation (11.1.2) represents the radius of curvature of the surface; R is without significance in the planar case.

The motive in restricting consideration to semiinfinite geometries is that thereby the diffusion medium has only one boundary of concern, the other being "at infinity." The same situation may be achieved with media that are less than infinite in extent, such as III in Fig. 11.1.1, provided that the time domain is sufficiently restricted. As long as any perturbation which starts at the $r = 0$ boundary at time zero does not approach any other boundary of the medium within times of interest,[1] the medium behaves as if it were semiinfinite. With the proviso that we shall only ever be concerned with times short enough to ensure that a large reservoir of virtually unperturbed medium always exists, we may admit two other geometries, illustrated as IV in Fig. 11.1.1, namely,

the concave cylinder, $g = -\frac{1}{2}$; and
the concave sphere, $g = -1$,

to the class we may represent using a single distance coordinate. These two geometries are decidedly not semiinfinite, but they nevertheless behave as if they were, subject to our stated proviso. Equation (11.1.2) now applies to all five geometries, the sign to be selected in the $r \pm R$ term being that of g. Many important physical systems approximate closely to one or another of these cases.

The situations we shall treat are those in which the system is initially at equilibrium, so that

$$F(r, t) = F_0, \quad \text{a constant}; \qquad t < 0, \quad r \geqq 0. \tag{11.1.3}$$

At $t = 0$ a perturbation of the system commences by some unspecified process occurring at the boundary. During times of interest, this perturbation does not affect regions remote from the $r = 0$ boundary, so that the relationship

$$F(r, t) = F_0, \qquad t \leqq \tau, \qquad r = \begin{cases} \infty, & g = 0, \frac{1}{2}, 1, \\ R, & g = -\frac{1}{2}, -1, \end{cases} \tag{11.1.4}$$

applies.

Thus our problem is described by the partial differential equation (11.1.2), initial condition (11.1.3) and the asymptotic condition (11.1.4). It may be shown (Oldham and Spanier, 1972; Oldham, 1973b) that the single equation

$$\frac{\partial}{\partial r} F(r, t) + \frac{1}{\sqrt{\kappa}} \frac{\partial^{\frac{1}{2}}}{\partial t^{\frac{1}{2}}} [F(r, t) - F_0] + \frac{g}{r + R} [F(r, t) - F_0] = 0 \tag{11.1.5}$$

describes the problem equally well. Equation (11.1.5) is exact in the $g = 1$ or 0 cases, and represents a short time approximation for $g = \frac{1}{2}, -\frac{1}{2}$, or -1. The derivation of equation (11.1.5) is given in the next section for the planar $g = 0$ case.

[1] Quantitatively, the requirement is that L, the dimension of the quasi-semiinfinite medium, must be related to the maximum time τ of interest by the inequality $\tau \ll L^2/\kappa$.

11.2 PLANAR GEOMETRY

In this section we will demonstrate that the relationship

$$\frac{\partial}{\partial r} F(r, t) = -\frac{1}{\sqrt{\kappa}} \frac{\partial^{\frac{1}{2}}}{\partial t^{\frac{1}{2}}} F(r, t) + \frac{F_0}{\sqrt{\pi \kappa t}} \tag{11.2.1}$$

is a direct consequence of equations (11.1.2)–(11.1.4) in the planar $g = 0$ case, and will show how this relationship proves useful in studying heat transfer. We notice that, whereas the diffusion equation (11.1.2) is second order in space and first order in time, equation (11.2.1) [or the more general equation (11.1.5)] is first order in space and half order in time. This reduction in order has come about by incorporating the initial and asymptotic boundary conditions so that equation (11.2.1) represents the entire boundary value problem save only the boundary condition imposed at the $r = 0$ surface. This partial reduction of the complexity of the original problem will lead to important savings in a variety of situations.

The key to the derivation of equation (11.2.1) will be an understanding of the relationship between the Laplace transform of semiderivatives and semiintegrals and the Laplace transform of the undifferintegrated function. More precisely [see equation (8.1.3)], the equations[2]

$$\int_0^\infty \exp(-st) \frac{d^{\pm\frac{1}{2}}}{dt^{\pm\frac{1}{2}}} f(t)\, dt = s^{\pm\frac{1}{2}} \int_0^\infty \exp(-st) f(t)\, dt \tag{11.2.2}$$

will play a vital role in this derivation.

First we change variables to $u = r/\sqrt{\kappa}$ and $V(u, t) = F(r, t) - F_0$, obtaining the following equations in the new variables in the planar $g = 0$ case:

$$\frac{\partial^2}{\partial u^2} V(u, t) = \frac{\partial}{\partial t} V(u, t), \tag{11.2.3}$$

$$V(u, 0) = 0, \tag{11.2.4}$$

$$V(\infty, t) = 0. \tag{11.2.5}$$

[2] Equation (8.1.3) for $q = \frac{1}{2}$ actually is

$$\int_0^\infty \exp(-st) \frac{d^{\frac{1}{2}}}{dt^{\frac{1}{2}}} f(t)\, dt = \sqrt{s} \int_0^\infty \exp(-st) f(t)\, dt - \frac{d^{-\frac{1}{2}} f}{dt^{-\frac{1}{2}}}(0).$$

However, the semiintegral on the right will vanish at zero provided f is differintegrable and bounded (an even milder assumption will do). We cheerfully make such an assumption here inasmuch as the physically defined functions we shall encounter throughout this chapter are necessarily finite everywhere.

Upon Laplace transformation of equations (11.2.3) and (11.2.5), the relationships

$$\frac{\partial^2}{\partial u^2}\bar{V}(u,s) = s\bar{V}(u,s) - V(u,0) \tag{11.2.6}$$

and

$$\bar{V}(\infty,s) = 0 \tag{11.2.7}$$

are obtained, where $\bar{V}(u,s)$ is the transform of $V(u,t)$. Utilizing (11.2.4) and temporarily treating the dummy variable s as a constant, we obtain

$$\frac{d^2}{du^2}\bar{V}(u,s) - s\bar{V}(u,s) = 0$$

from equation (11.2.6). Standard methods for solving ordinary differential equations [for example, see Murphy (1960)] may be invoked to give

$$\bar{V}(u,s) = P_1(s)\exp(u\sqrt{s}\,) + P(s)\exp(-u\sqrt{s}\,),$$

where P_1 and P are arbitrary functions of s. The boundary condition (11.2.7) shows that $P_1(s) = 0$ so that

$$\bar{V}(u,s) = P(s)\exp(-u\sqrt{s}), \tag{11.2.8}$$

where $P(s)$ remains unspecified.

The unknown function $P(s)$ depends, of course, upon the boundary condition at $r = 0$. Leaving this unspecified for now, we may eliminate $P(s)$ between (11.2.8) and the expression

$$\frac{\partial}{\partial u}\bar{V}(u,s) = -\sqrt{s}\,P(s)\exp(-u\sqrt{s}),$$

which results upon differentiating (11.2.8). The resulting equation in transform space,

$$\frac{\partial}{\partial u}\bar{V}(u,s) = -\sqrt{s}\,\bar{V}(u,s),$$

may be inverted, utilizing equation (11.2.2) to give

$$\frac{\partial}{\partial u}V(u,t) = -\frac{\partial^{\frac{1}{2}}}{\partial t^{\frac{1}{2}}}V(u,t).$$

Restoration of the original variables produces (11.2.1).

The exploitation of equation (11.2.1) will be illustrated with an example drawn from the theory of heat conduction. Specifically, consider the problem of determining the heat flux at the surface of a heat conductor from measurements of the surface temperature. This need arises in studies of heat transfer in wind tunnels (Meyer, 1960; Allegre, 1970) and other engineering applications.

The equation of one-dimensional heat conduction in a semiinfinite planar medium is

$$\text{(11.2.9)} \qquad \frac{\partial}{\partial t} T(r, t) = \frac{K}{\rho\sigma} \frac{\partial^2}{\partial r^2} T(r, t), \qquad 0 \leqq r \leqq \infty, \quad 0 \leqq t \leqq \infty,$$

where K, ρ, and σ are respectively the conductivity, density, and specific heat of the conducting material, T is the difference between the local and the ambient temperature, t the time, and r the distance from the surface of interest. Upon identification of T with F and κ with $K/\rho\sigma$, equations (11.2.9) and (11.1.2) are seen to be identical in the planar $g = 0$ case. Appropriate boundary conditions for this problem, analogous to equations (11.1.3) and (11.1.4), are

$$T(r, 0) = 0 \qquad \text{and} \qquad T(\infty, t) = 0.$$

The sought surface heat flux is

$$J(t) \equiv -K \frac{\partial}{\partial r} T(0, t),$$

which Meyer (1960) showed to be obtainable in the form

$$\text{(11.2.10)} \qquad J(t) = \sqrt{\frac{K\rho\sigma}{4\pi}} \left[\frac{2T(0, t)}{\sqrt{t}} + \int_0^t \frac{T(0, t) - T(0, \tau)}{[t - \tau]^{\frac{3}{2}}} d\tau \right].$$

Our approach to this problem proceeds directly from equation (11.2.1) (replacing F by T, κ by $K/\rho\sigma$, specializing to $r = 0$, and remembering that T_0 is zero) as follows:

$$\sqrt{\frac{\rho\sigma}{K}} \frac{\partial^{\frac{1}{2}}}{\partial t^{\frac{1}{2}}} T(0, t) = -\frac{\partial}{\partial r} T(0, t) = \frac{J(t)}{K}.$$

Thus,

$$J(t) = \sqrt{K\rho\sigma} \frac{d^{\frac{1}{2}}}{dt^{\frac{1}{2}}} T(0, t),$$

the desired heat flux being obtainable from the surface temperature by simple semidifferentiation. Reference to the table in Section 7.1 shows that our result and Meyer's equation (11.2.10) are equivalent.

11.3 SPHERICAL GEOMETRY

The derivation in the $g = 1$ case of equation (11.1.5),

$$\frac{\partial}{\partial r} F(r, t) = \frac{-1}{\sqrt{\kappa}} \frac{\partial^{\frac{1}{2}}}{\partial t^{\frac{1}{2}}} [F(r, t) - F_0] - \frac{F(r, t) - F_0}{r + R}, \tag{11.3.1}$$

follows a course so similar to that employed in the previous section that we shall omit it, referring the interested reader to Oldham and Spanier (1972) and Oldham (1973b). We shall demonstrate the utility of equation (11.3.1) with an example drawn from electrochemistry.

Electroanalytical chemists frequently employ a hanging mercury sphere (radius R) as an electrode immersed in an aqueous solution. By negatively polarizing the electrode it is possible to cause the surface electroreduction of any reducible species (e.g., metal ions, dissolved oxygen) that might be present in the solution at low concentrations, and thereby effect a chemical analysis. One such method, semiintegral electroanalysis (Grenness and Oldham, 1972, and Oldham, 1973a) utilizes equation (11.3.1).

Imagine that initially the electroreducible species is present throughout the solution at a uniform concentration C_0 and that its transport through the solution is solely by diffusion with a diffusion coefficient D. The electrode is then given progressively more negative electrical potential, leading to a monotonic diminution of the surface concentration $C(0, t)$ of the electroreducible species. This, in turn, leads to the diffusion of the species towards the electrode in accordance with Fick's first law,

$$-J(0, t) = D \frac{d}{dr} C(0, t). \tag{11.3.2}$$

Moreover, Faraday's electrochemical law asserts the proportionality

$$i(t) = -4\pi R^2 n F_y J(0, t) \tag{11.3.3}$$

between the surface flux[3] $J(0, t)$ and the electric current $i(t)$ that flows from the electrode to the external circuit. The constants in equation (11.3.3) are the electrode area $4\pi R^2$, the number n of electrons needed to reduce each molecule of diffusant, and Faraday's constant F_y ($= 96{,}500$ coulomb/equivalent). When equation (11.3.1) is specialized to $r = 0$ and its symbols replaced by those appropriate to the present problem,

$$\frac{d}{dr} C(0, t) = \frac{-1}{\sqrt{D}} \frac{d^{\frac{1}{2}}}{dt^{\frac{1}{2}}} \{C(0, t) - C_0\} - \frac{C(0, t) - C_0}{R}$$

[3] Sign conventions demand that the flux be negative when transport occurs *toward* the coordinate origin from positive values of r.

emerges. Combination with equations (11.3.2) and (11.3.3) now leads to the expression

$$(11.3.4)\quad i(t) = -4\pi R^2 nF_y\sqrt{D}\left[\frac{d^{\frac{1}{2}}}{dt^{\frac{1}{2}}}\{C(0,t) - C_0\} + \frac{\sqrt{D}}{R}[C(0,t) - C_0]\right],$$

relating the time-dependent current to the surface concentration $C(0, t)$. Semiintegration of equation (11.3.4) and application of the composition rule, valid for bounded $C(0, t)$ (see footnote 2), yields

$$(11.3.5)\quad \frac{d^{-\frac{1}{2}}}{dt^{-\frac{1}{2}}}i(t) = KC_0\left[\left\{1 - \frac{C(0,t)}{C_0}\right\} + \frac{\sqrt{D}}{R}\frac{d^{-\frac{1}{2}}}{dt^{-\frac{1}{2}}}\left\{\frac{C_0 - C(0,t)}{C_0}\right\}\right]$$

after rearrangement and after adoption of K as a convenient abbreviation for the constant $4\pi R^2 nF_y\sqrt{D}$.

If the electrode polarization becomes progressively greater, a time $t = \tau$ will be reached after which $C(0, t)$ is virtually zero. Equation (11.3.5) then becomes

$$(11.3.6)\quad \frac{d^{-\frac{1}{2}}}{dt^{-\frac{1}{2}}}i(t \geqq \tau) = KC_0\left\{1 + \frac{\sqrt{D}}{R}\left[\frac{d^{-\frac{1}{2}}}{dt^{-\frac{1}{2}}}\left\{\frac{C_0 - C(0,t)}{C_0}\right\}\right]_{t\geqq\tau}\right\}.$$

Were it not for the curvature correction term

$$\frac{\sqrt{D}}{R}\left[\frac{d^{-\frac{1}{2}}}{dt^{-\frac{1}{2}}}\left\{\frac{C_0 - C(0,t)}{C_0}\right\}\right]_{t\geqq\tau},$$

equation (11.3.6) would be a simple result asserting that the semiintegral of the current becomes a constant for $t \geqq \tau$, which constant is proportional to the initial concentration C_0. Hence measuring $[d^{-\frac{1}{2}}i/dt^{-\frac{1}{2}}]_{t\geqq\tau}$ would permit quantitative chemical analysis of the reducible species, were it not for the curvature correction term.

For a typical electrochemical experiment ($R \approx 10^{-3}$ m, $\tau \approx 1$ sec, $D \approx 10^{-9}$ m^2/sec), the curvature correction term, necessarily less[4] than $[2/R]\sqrt{D\tau/\pi}$ at $t = \tau$, is small compared with unity and is frequently ignored. Alternatively, the following approximation scheme may be adopted (see Fig. 11.3.1 for clarification):

$$\frac{\sqrt{D}}{R}\left[\frac{d^{-\frac{1}{2}}}{dt^{-\frac{1}{2}}}\left\{\frac{C_0 - C(0,t)}{C_0}\right\}\right]_{t\geqq\tau} \approx \frac{\sqrt{D}}{R}\left[\frac{d^{-\frac{1}{2}}}{dt^{-\frac{1}{2}}}H(t - t_{\frac{1}{2}})\right]_{t\geqq\tau}$$

$$= \left[\frac{2}{R}\sqrt{\frac{D[t - t_{\frac{1}{2}}]}{\pi}}\right]_{t\geqq\tau},$$

[4] That this is so may be seen by replacing $[C_0 - C(0, t)]/C_0$ by its upper bound, unity, in equation (11.3.6).

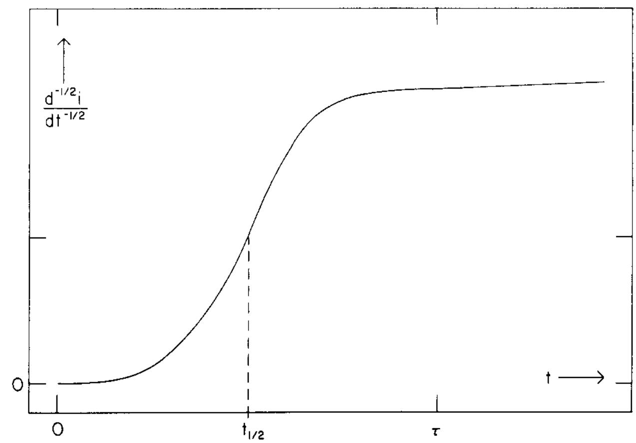

FIG. 11.3.1. The curve shows how the semiintegral of the faradaic current increases sigmoidally with time to become almost constant after $t = \tau$. The slight inconstancy is caused by electrode curvature. In an approximate procedure for correcting for this effect, the sigmoid curve is replaced by a Heaviside step function at $t = t_{\frac{1}{2}}$, the time at which the semiintegral reaches half its $t = \tau$ value.

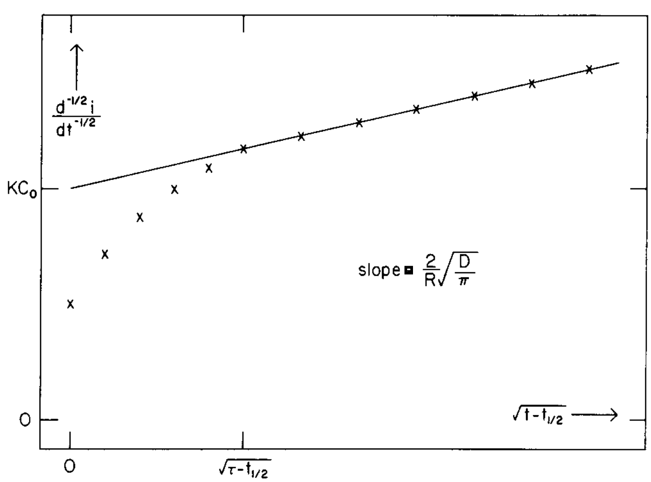

FIG. 11.3.2. To correct for the curvature effect, the semiintegral of the current is plotted versus $\sqrt{t - t_{\frac{1}{2}}}$ and extrapolated to find KC_0. The points are linear only for times exceeding τ, corresponding to the semintegral's having attained its limiting value.

where H is the Heaviside unit function and $t_{\frac{1}{2}}$ is the time at which $C(0, t) \approx \frac{1}{2}C_0$. The graphical procedure indicated in Fig. 11.3.2 then permits a correction to be made for the small curvature effect.

11.4 INCORPORATION OF SOURCES AND SINKS

Equation (11.1.2) describes the diffusion of an entity in the absence of sources and sinks; that is, where there is no creation or annihilation of the diffusing substance within the medium. Many practical problems, however, require the inclusion of volume sources or sinks. We now turn our attention to this subject.

The equation

$$\frac{\partial}{\partial t} F(r, t) - \kappa \frac{\partial^2}{\partial r^2} F(r, t) = S - kF(r, t) \tag{11.4.1}$$

replaces the $g = 0$ instance of equation (11.1.2) when the transport is accompanied by a constant source S and a first-order removal process, embodied in the $kF(r, t)$ term. We shall assume that the uniform steady-state condition

$$F(r, t) = S/k, \qquad t \leqq 0, \tag{11.4.2}$$

is in effect prior to the time $t = 0$. We shall sketch a derivation of the relationship

$$F(0, t) = \frac{S}{k} - \sqrt{\kappa} \exp(-kt) \frac{d^{-\frac{1}{2}}}{dt^{-\frac{1}{2}}} \left[\exp(kt) \frac{d}{dr} F(0, t)\right] \tag{11.4.3}$$

between the boundary value $F(0, t)$ of the intensive variable and the boundary value of the flux, which is proportional to the term $-dF(0, t)/dr$.

Upon Laplace transformation of equation (11.4.1), we obtain the equation

$$s\bar{F}(r, s) - F(r, 0) - \kappa \frac{\partial^2}{\partial r^2} \bar{F}(r, s) = \frac{S}{s} - k\bar{F}(r, s).$$

Use of our initial condition (11.4.2) leads to the ordinary differential equation

$$\frac{d^2}{dr^2} \bar{F}(r, s) - \frac{s + k}{\kappa} \bar{F}(r, s) + \frac{S}{\kappa} \left[\frac{s + k}{sk}\right] = 0 \tag{11.4.4}$$

in the transform of F. The most general solution of equation (11.4.4) is

$$\bar{F}(r, s) - \frac{S}{sk} = P(s) \exp\left(-r\sqrt{\frac{s + k}{\kappa}}\right) + P_1(s) \exp\left(r\sqrt{\frac{s + k}{\kappa}}\right), \tag{11.4.5}$$

where $P(s)$ and $P_1(s)$ are arbitrary functions of s. If the geometry is semi-infinite, which we now assume, the physical requirement that F remain bounded as r tends to infinity demands that $P_1(s) \equiv 0$. Eliminating the function $P(s)$ between equation (11.4.5) and the equation obtained from it upon differentiation with respect to r, we find

$$\bar{F}(r, s) = \frac{S}{sk} - \sqrt{\frac{\kappa}{s+k}} \frac{d}{dr} \bar{F}(r, s).$$

It now requires only Laplace inversion (see Section 8.1) and specialization to $r = 0$ to obtain equation (11.4.3).

An interesting application of the preceding theory arises in modeling diffusion of atmospheric pollutants. We now describe such a model problem.

Consider a vertical column of unstirred air into the base of which a pollutant commences to be injected at time $t = 0$. Prior to $t = 0$ the air is unpolluted, so that

$$C(r, 0) = 0,$$

where $C(r, t)$ denotes the pollutant concentration at height r at time t. After $t = 0$ the rate of pollutant injection is some unspecified function $J(t)$ of time. The pollutant reacts with air by some chemical reaction that is first order (or pseudo-first order) with a rate constant k. The pollutant diffuses through air with a diffusion coefficient D that is assumed independent of height and of concentration. There are no volume sources of pollutants. We seek to relate the ground-level pollutant concentration

$$C(t) \equiv C(0, t)$$

to the input flux $J(t)$.

Identifying $C(0, t)$ with $F(0, t)$ and D with κ in equation (11.4.3), and setting $S = 0$ and $J(0, t) = -D\, dC(0, t)/dr$, we discover that

$$C(t) = \frac{\exp(-kt)}{\sqrt{D}} \frac{d^{-\frac{1}{2}}}{dt^{-\frac{1}{2}}} \{\exp(kt)J(t)\}. \tag{11.4.6}$$

The generality of equation (11.4.6) is worth emphasizing. It enables the ground concentration of pollutant to be predicted from the rate of pollutant generation for *any* time dependent $J(t)$. Similarly, the inverse of equation (11.4.6),

$$J(t) = \sqrt{D} \exp(-kt) \frac{d^{\frac{1}{2}}}{dt^{\frac{1}{2}}} \{\exp(kt)C(t)\}, \tag{11.4.7}$$

permits the generation rate to be reconstructed from a record of the time variation of ground pollution levels.

As a trivially simple application of equation (11.4.6), consider the case where the generation rate $J(t)$, zero prior to $t = 0$, is a constant J thereafter. Then

$$C(t) = \frac{\exp(kt)}{\sqrt{D}} \frac{d^{-\frac{1}{2}}}{dt^{-\frac{1}{2}}} \{J \exp(kt)\} = \frac{J \operatorname{erf}(\sqrt{kt})}{\sqrt{Dk}},$$

which shows that the pollutant concentration will rise to reach a final constant level of $J/\sqrt{Dk}$ and that the time to reach one-half of this final level is $0.23/k$.

As a more realistic example, consider the pollution generation rate to be sinusoidal with a mean value J and a minimum value of zero:

(11.4.8)
$$J(t) = J + J \sin(at).$$

With a equal to $\pi/[12 \text{ hours}]$ and $t = 0$ corresponding to 9.00 A.M., this could represent a diurnal variation in pollution generation, typified by automobile traffic. Introduction of equation (11.4.8) into (11.4.6) followed by the indicated semiintegration leads eventually to the result

(11.4.9)
$$C(t) = \frac{J \operatorname{erf}(\sqrt{kt})}{\sqrt{Dk}} - \frac{J \exp(-kt)}{\sqrt{D[k^2 + a^2]}} \{\beta \operatorname{Rew}([\beta + i\alpha]\sqrt{t}) + \alpha \operatorname{Imw}([\beta + i\alpha]\sqrt{t})\}$$
$$+ \frac{J}{\sqrt{D[k^2 + a^2]}} \{\beta \cos(at) - \alpha \sin(at)\},$$

where α and β are positive quantities defined by

$$2\alpha^2 = \sqrt{k^2 + a^2} + k, \qquad 2\beta^2 = \sqrt{k^2 + a^2} - k,$$

and Rew( ) and Imw( ) are the real and imaginary parts of the complex error function of Faddeeva and Terent'ev (1961).

As t becomes large, the transient terms within equation (11.4.9) vanish and leave

$$C(t \to \infty) = \frac{J}{\sqrt{D}} \left[\frac{1}{\sqrt{k}} + \frac{1}{[k^2 + a^2]^{\frac{1}{4}}} \sin\left(at - \arctan\left(\frac{\beta}{\alpha}\right)\right) \right].$$

This relationship gives

$$\frac{J}{\sqrt{D}} \left[\frac{1}{\sqrt{k}} \pm \frac{1}{[k^2 + a^2]^{\frac{1}{4}}} \right]$$

as the extreme pollutant concentrations, with the peak level occurring at some time between 3.00 and 6.00 P.M.

11.5 TRANSPORT IN FINITE MEDIA

Our equation (11.2.1) was derived on the basis that the transport medium was semiinfinite in extent, $0 \leq r < \infty$. The modification engendered when r has a finite upper bound L is the subject of the present section. Three cases of the boundary will be treated: first as a perfect sink

$$F(L, t) = 0,$$

second as a boundary of zero flux

$$\frac{d}{dr} F(L, t) = 0,$$

and third as a plane in which the proportionality

$$\frac{d}{dr} F(L, t) \propto F(L, t)$$

is enforced. As we shall see, the finiteness of L destroys the simplicity of the formulation in terms of the fractional calculus. Our interest will concentrate on the short-time approximation to the finite problem; that is, we shall study the breakdown of equation (11.2.1) as L becomes discernibly less than infinity.

The physical setting will be that of electrical conduction along a transmission line,[5] and we first establish that equation (11.2.1) does, in fact, hold for an infinite line.

A two-conductor transmission line, exemplified by a coaxial cable, generally has a number of impedances associated with it, including inductance along and between the conductors and leakage conductance between them (Johnson, 1950). Here, however, we restrict consideration to an idealized transmission line in which resistance along one conductor and capacitance between the two conductors are the only significant elements. Such a line is symbolized in Fig. 11.5.1. By ρ and γ we denote the resistance and capacitance per unit length of the line.

The potential and current at the end of the resistive–capacitative line will be represented by $e(0, t)$ and $i(0, t)$. Similarly, $e(r, t)$ and $i(r, t)$ will be used to represent the interconductor potential and intraconductor currents at a distance r from the end of the line at time t. These definitions will be clarified by reference to Fig. 11.5.1.

[5] A very similar circumstance, though with added complexity arising from source terms, is to be found in models of the propagation of nerve impulses.

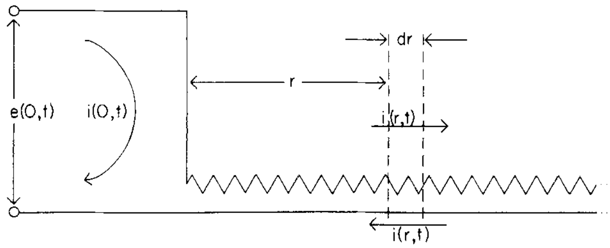

FIG. 11.5.1. Diagram displaying the symbolism adopted in the discussion of resistive–capacitative transmission lines. The interconductor potential is $e(r, t)$ at distance r.

The line is initially at rest, the potential and current being everywhere zero at $t = 0$. Subsequently a signal is applied to the end of the line, as a result of which a perturbation is transmitted down the line. The equations governing the transmission may be deduced by applying Ohm's law (the voltage difference developed by the passage of a current i through a resistor equals the product iR of the current and the resistance R of the resistor)

$$e(r + dr, t) = e(r, t) - [\rho\, dr]i(r, t)$$

to a section of line of length dr, and relating the interconductor reactance current, by means of Coulomb's law (the current flowing through a capacitor equals the product $C\, dE/dt$ of the capacitance C of the capacitor and the time derivative of the potential E across it)

$$i(r, t) - i(r + dr, t) = [\gamma\, dr] \frac{\partial}{\partial t} e(r, t),$$

to the time derivative of the interconductor potential. These two equations may be rewritten as

$$\frac{\partial}{\partial r} e(r, t) + \rho i(r, t) = 0 \tag{11.5.1}$$

and

$$\frac{\partial}{\partial r} i(r, t) + \gamma \frac{\partial}{\partial t} e(r, t) = 0,$$

and combined into the single partial differential equation

$$\frac{\partial^2}{\partial r^2} e(r, t) = \rho\gamma \frac{\partial}{\partial t} e(r, t) \tag{11.5.2}$$

by elimination of the current.

Comparison with equation (11.1.2) shows (11.5.2) to be a typical one-dimensional diffusion equation in which $1/\rho\gamma$ plays the role of κ. The procedures of Section 11.2 may be employed to convert equation (11.5.1) to

$$\frac{\partial}{\partial r} e(r, t) = -\sqrt{\rho\gamma}\,\frac{\partial^{\frac{1}{2}}}{\partial t^{\frac{1}{2}}} e(r, t) \tag{11.5.3}$$

by incorporation of the initial condition

$$e(r, t) = 0, \qquad \text{all } r, \quad t \leqq 0, \tag{11.5.4}$$

and the semiinfiniteness condition

$$e(\infty, t) = 0, \qquad \text{all } t < \infty.$$

We may now use equation (11.5.1) and specialize to $r = 0$ to obtain

$$i(0, t) = -\frac{1}{\rho}\frac{d}{dr} e(0, t) = \sqrt{\frac{\gamma}{\rho}}\,\frac{d^{\frac{1}{2}}}{dt^{\frac{1}{2}}} e(0, t). \tag{11.5.5}$$

In words, equation (11.5.5) demonstrates that the current drawn by a resistive–capacitative transmission line of infinite length is proportional to the time-semiderivative of the applied voltage signal.

We now return to equation (11.5.2) to consider its solution when the transmission line is of finite length L. On Laplace transformation, equation (11.5.2) becomes the ordinary differential equation

$$\frac{d^2}{dr^2}\bar{e}(r, s) = \rho\gamma[s\bar{e}(r, s) - e(r, 0)],$$

of which the general solution, after incorporation of the initial condition (11.5.4), is

$$\bar{e}(r, s) = P(s)\exp(-r\sqrt{\rho\gamma s}) + P_1(s)\exp(r\sqrt{\rho\gamma s}). \tag{11.5.6}$$

As before, $P(s)$ and $P_1(s)$ are arbitrary functions of the dummy variable s. Unlike our Section 11.2 procedure, however, we do not now find that $P_1(s)$ vanishes.

If the $r = L$ end of the transmission line is short circuited, $e(L, t)$ is necessarily zero, so that

$$0 = \bar{e}(L, s) = P(s)\exp(-L\sqrt{\rho\gamma s}) + P_1(s)\exp(L\sqrt{\rho\gamma s}).$$

This equation now provides an interrelationship between $P(s)$ and $P_1(s)$ which can be used to eliminate the latter from equation (11.5.6). Following this procedure, the result

$$\bar{e}(r, s) = P(s)[\exp(-r\sqrt{\rho\gamma s}) - \exp([r - 2L]\sqrt{\rho\gamma s})] \tag{11.5.7}$$

emerges. The remaining arbitrary function $P(s)$ is eliminated at this stage, as in Section 11.2, between equation (11.5.7) and its r derivative. This leads to

$$\frac{\partial}{\partial r}\bar{e}(r, s) = -\sqrt{\rho\gamma s}\,\bar{e}(r, s)\coth([L - r]\sqrt{\rho\gamma s})$$

after some algebra, and to

$$\frac{d}{dr}\bar{e}(0, s) = -\sqrt{\rho\gamma s}\,\bar{e}(0, s)\coth(L\sqrt{\rho\gamma s}) \tag{11.5.8}$$

on specialization to $r = 0$.

For large enough L, the hyperbolic cotangent term in equation (11.5.8) approximates to unity for all but the smallest values of s (corresponding to large values of t). This cotangent term lies within 1 % of unity provided

$$L\sqrt{\rho\gamma s} \geqq 2.6. \tag{11.5.9}$$

Now, $L\rho$ and $L\gamma$ are, respectively, the total resistance R and total capacitance C of the finite line, so that inequality (11.5.9) may be rewritten

$$\frac{1}{s^2} \leqq \frac{RC}{7.1s},$$

which gives

$$t \leqq 0.14RC \tag{11.5.10}$$

on inversion.[6] Hence, a short-circuited finite line reproduces the properties of an infinite line to within 1 %, for times up to about 14 % of the RC time constant of the finite line.

The above discussion referred to a finite line the distant end of which was short circuited, as shown in I in Fig. 11.5.2. For an open-circuited termination, diagrammed as II, the analog of equation (11.5.8) is found to be

$$\frac{d}{dr}\bar{e}(0, s) = -\sqrt{\rho\gamma s}\,\bar{e}(0, s)\tanh(L\sqrt{\rho\gamma s}). \tag{11.5.11}$$

[6] Strictly, one may not invert an inequality in this way. However, if one examines the departures of the exact Laplace inverse of equation (11.5.8), namely,

$$\frac{d}{dr}e(0, t) = -2\sqrt{\rho\gamma}\sum_{j=0}^{\infty}\int_0^t [t - \tau]^{-\frac{3}{2}}\exp\left(\frac{-j^2RC}{t - \tau}\right)\frac{d^{\frac{1}{2}}}{d\tau^{\frac{1}{2}}}e(0, \tau)\,d\tau,$$

from result (11.5.5), one finds that these are very close to 1 % for t values of $0.14RC$ for a variety of simple $e(0, t)$ signals.

Since this result is strictly complementary to (11.5.8), the same time restriction, namely, inequality (11.5.10), governs the range over which the open-circuited finite line adequately (that is to within 1 %) simulates a transmission line of infinite length.

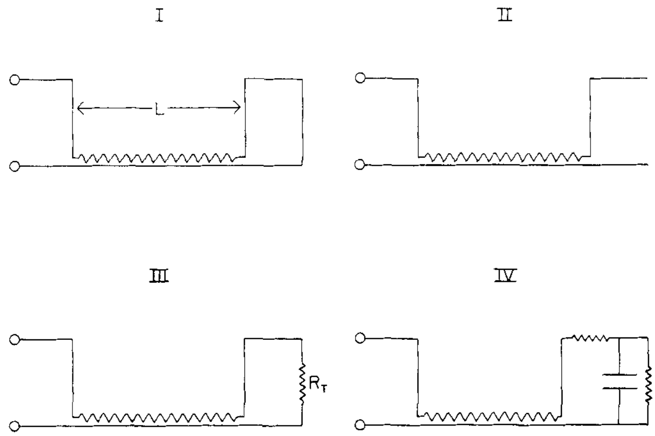

FIG. 11.5.2. Four terminations of a finite resistive–capacitative transmission line. Diagrams I and II show, respectively, a short-circuited and an open-circuited termination. In III a single resistor R_T provides a terminal impedance, while three components fill this role in diagram IV.

Judicious termination of a finite resistive–capacitative line, as for instance by a well-chosen terminating resistor R_T shown in Fig. 11.5.2 as III, will greatly increase the time range over which the transmission line behaves adequately as a semidifferentiator. To investigate the optimum value of this resistor, we need to carry out the following, rather lengthy, analysis. We first note that the Ohm's law requirement

$$e(L, t) = R_T\, i(L, t) = -\frac{R_T}{\rho}\frac{d}{dr}\, e(L, t)$$

at the $r = L$ boundary transforms to

$$\bar{e}(L, s) = -\frac{R_T}{\rho}\frac{d}{dr}\,\bar{e}(L, s),$$

which may be combined with equation (11.5.6) to provide the relationship

$$P_1(s) = P(s)\,\frac{R_T\sqrt{\gamma s} - \sqrt{\rho}}{R_T\sqrt{\gamma s} + \sqrt{\rho}}\exp\!\left(-2L\sqrt{\rho\gamma s}\right)$$

between the arbitrary functions $P_1(s)$ and $P(s)$. We now introduce this relationship into (11.5.6) to eliminate $P_1(s)$ and provide an expression for $\bar{e}(r, s)$ in terms of $P(s)$. This expression is next differentiated with respect to r and $P(s)$ is in turn eliminated between the expression and its derivative. This results in

(11.5.12)

$$\frac{d}{dr}\bar{e}(0, s) = -\sqrt{\rho\gamma s}\,\bar{e}(0, s)\frac{[R_T\sqrt{\gamma s}+\sqrt{\rho}]\exp(2L\sqrt{\rho\gamma s}) - R_T\sqrt{\gamma s}+\sqrt{\rho}}{[R_T\sqrt{\gamma s}+\sqrt{\rho}]\exp(2L\sqrt{\rho\gamma s}) + R_T\sqrt{\gamma s}-\sqrt{\rho}},$$

which, as a consideration of Fig. 11.5.2 would lead one to expect, reduces to (11.5.8) on setting $R_T = 0$ and to (11.5.11) on letting $R_T \to \infty$. In equation (11.5.12) the quotient term, which may be rewritten as

$$\text{(11.5.13)}\qquad \frac{R_T\sqrt{Cs}\sinh(\sqrt{RCs}) + \sqrt{R}\cosh(\sqrt{RCs})}{R_T\sqrt{Cs}\cosh(\sqrt{RCs}) + \sqrt{R}\sinh(\sqrt{RCs})} \equiv 1 + \Delta,$$

defines a relative error Δ that expresses the extent to which there is a departure from the infinite length case. When s^{-1} is small, corresponding to short times, Δ is negligible; but as s^{-1} increases, Δ becomes negative, passes through a minimum at some critical value s_c of s, crosses zero, and eventually acquires

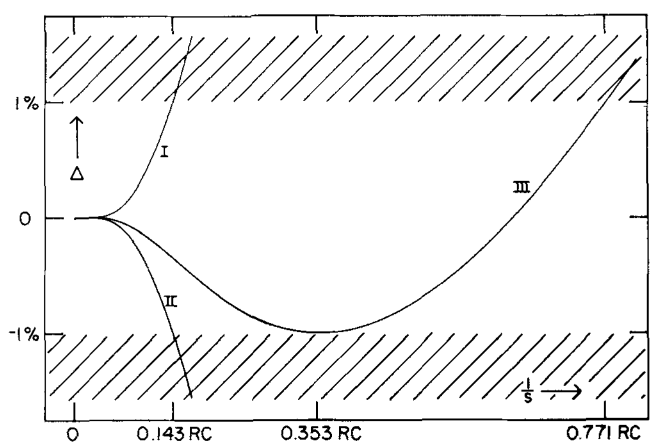

FIG. 11.5.3. Departures from perfection in semidifferentiating arising from the finiteness of a resistive–capacitative transmission line. The notations I, II, and III refer to the terminations shown in Fig. 11.5.2, the terminating resistor R_T in III having been optimally chosen for a 1 % semidifferentiating error. The times $0.143RC$ and $0.771RC$ mark the limits of valid semidifferentiation for the I and II cases and for III, respectively.

ever-increasing positive values, as illustrated in Fig. 11.5.3. By differentiating Δ with respect to s and setting $d\Delta/ds$ to zero, it can be shown that the critical value of s is given by

$$\frac{1}{s_c} = \frac{R_T{}^2 C}{R + R_T}.$$

By substituting this expression back into equation (11.5.13), one can solve for values of the parameter R_T/R that cause the minimum Δ value to correspond to any chosen percentage. For a $-1\%\,\Delta$, for example, an R_T/R ratio of 0.797 is needed. The effect of this terminating resistor in prolonging the time interval during which the action of the finite transmission line closely approximates that of an infinite line is best brought out in Fig. 11.5.3, wherein the performances of the I, II, and III configurations of Fig. 11.5.2 are compared. Note that the time limit for III has been extended over five-fold from that given by inequality (11.5.10) for I and II to

$$t \leqq 0.77RC$$

for the optimally terminated configuration III.

Still greater improvements are possible by refining the termination through addition of a capacitor, for example, or the network shown as IV in Fig. 11.5.2, but we shall not consider such circuits further. These matters are of some practical importance in designing circuitry to effect semidifferentiation since, of course, an infinite transmission line is an abstraction. The reader will recall from Section 8.3 that discrete resistors and capacitors may be used, not only as terminating elements, but to simulate the entire transmission line in a practical semidifferentiating (or semiintegrating) network.

11.6 DIFFUSION ON A CURVED SURFACE

Whereas most diffusion problems are representable by a partial differential equation of the second order, the situation we consider in this section requires a fourth-order equation for its description. The fractional calculus may be used to solve these problems and introduces differintegrals other than those of one-half order.

Where the flat surface of a homogeneous metal is intersected by a grain boundary normal to the surface, a groove slowly develops as a result of the higher chemical potential of the metal atoms in the grain boundary plane. The metal removed in the groove formation appears as ridges parallel to the groove as depicted in profile in Fig. 11.6.1. It may be shown (Mullins, 1957) that, on the assumption that the metal atoms move by surface diffusion under a driving force provided by the variation of surface curvature, the equation

$$\frac{\partial}{\partial t} z(x, t) = -b^2 \frac{\partial^4}{\partial x^4} z(x, t)$$

applies for small values of the angle β (see Fig. 11.6.1). Here x represents distance measured from the grain boundary parallel to the original surface. The constant b^2 is proportional to the surface diffusion coefficient of the metal. The initial condition

$$z(x, t) = 0$$

and the boundary conditions

$$z(\pm\infty, t) = \frac{\partial^2}{\partial x^2} z(\pm\infty, t) = 0,$$

specifying the semiinfiniteness of the problem, generally apply.

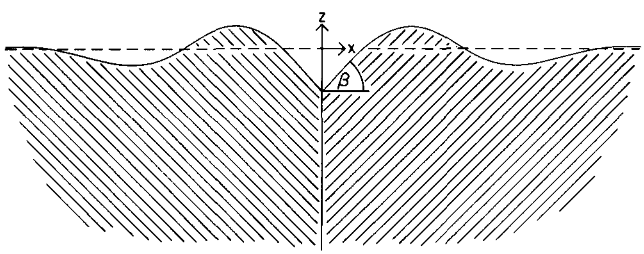

FIG. 11.6.1. An intergranular groove depicted in cross section. The dashed line denotes the original metal surface.

Robertson (1971) solved the above system of equations by employing a technique similar to that used in Section 11.2. His solution,

$$\frac{\partial}{\partial x} z(x, t) = b \frac{\partial^{-\frac{1}{2}}}{\partial t^{-\frac{1}{2}}} \left\{ \frac{\partial^3}{\partial x^3} z(x, t) \right\} - \sqrt{\frac{2}{b}} \frac{\partial^{\frac{1}{4}}}{\partial t^{\frac{1}{4}}} z(x, t),$$

relates the slope of the surface to the semiintegral of $\partial^3 z/\partial x^3$ and to the quarter-order temporal differintegral of the surface height. However, $\partial^3 z/\partial x^3$ is proportional to the local flux of metal atoms along the surface, which symmetry demands be zero at $x = 0$. By applying this boundary condition and the $d^{-\frac{1}{4}}/dt^{-\frac{1}{4}}$ operator, Robertson then obtained

$$z(0, t) = -\sqrt{\frac{b}{2}} \frac{d^{-\frac{1}{4}}}{dt^{-\frac{1}{4}}} \left\{ \frac{d}{dx} z(0, t) \right\}$$

as the equation dictating the groove depth as a function of time. If the angle β is treated as a constant, we find

$$z(0, t) = -\sqrt{\frac{b}{2}}\,\frac{t^{\frac{1}{4}}}{\Gamma(\frac{5}{4})}\tan(\beta),$$

a result originally derived by Mullins (1963) using conventional techniques.