Green's Functions for the Graetz Problem and Interfacial Concentrations

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Green's functions for various Graetz problems are identified. Multiple forms of Duhamel's formula with improved convergence were obtained, using particular solutions to unit flux, linear prescribed flux, and similar problems. The method makes it possible to quickly calculate interfacial concentrations from a knowledge of outlet concentrations at several flow rates. The analysis is illustrated with experimental combustion data from a tubular reactor.

The problem of heat or mass transfer in a channel in fully developed laminar or turbulent flow with negligible axial diffusion is usually known as the "Graetz problem" (*1* to *4*). Eigenfunction solutions to this problem have been obtained for laminar flow between parallel plates (*2, 3, 5* to *11*), in circular tubes (*1, 2, 3, 5, 6, 12* to *14*), and in concentric annuli (*5, 15* to *17*) for the Sturm-Liouville boundary conditions of the first, second, and third kind. For fully developed turbulent flow the eigenfunction method has also been used (*4, 18* to *21*). Variable surface temperature, flux, or ambient temperature has generally been handled by superposition using Duhamel's formula (*5, 14, 15, 22, 23*). In this manner integral equations were set up for arbitrary reaction at the wall (*17, 21*) or for the fourth power radiation law (*24*). No paper known to the author has, however, approached this subject from the more general point of view through the use of Green's functions.

The Green's function approach not only yields all the results obtained by Duhamel's principle and sheds light on convergence difficulties often encountered in the literature, but it also gives solutions to the nonhomogeneous convective diffusion equations in terms of available eigenfunctions. For concentration or temperature dependent sources and sinks, the Green's function approach immediately yields integral equations. These are useful in numerical work and in the study of the existence, uniqueness, and bounds using the contraction-mapping principle.

Green's functions for the diffusion, Laplace's, and the wave equation are, of course, well known and frequently used for the solution of practical problems (*25* to *27*) Numerous applications to the diffusion equation are given in Carslaw and Jaeger (*27*). Friedman (*28*) extends some of the theory to the general parabolic equations. In this paper integral relations are derived for the convective diffusion equations with Graetz's assumptions, which give solutions to the completely nonhomogeneous problems in terms of Green's functions. The Green's functions, that is, solutions to the unit pulse problems, are identified. The convective problems with nonhomogeneous or nonlinear boundary conditions are expressed in terms of multiple integrals of pulses: step, linear, quadratic, and higher order inputs. This method permits quick calculations of interfacial concentrations from a knowledge of outlet concentrations at several flow rates.

CONVECTIVE DIFFUSION IN A TUBE

Consider laminar diffusion in a round tube with an inlet distribution $f(r)$, a prescribed flux at the inside surface $\phi(x)$, and with generation in the fluid $\psi(x,r)$.

$$(1-r^2)\frac{\partial C}{\partial x}=\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right)+\psi \tag{1}$$

$$C(0,r)=f(r) \tag{2}$$

$$\frac{\partial C(x,1)}{\partial r}=\phi(x) \tag{3}$$

$$\frac{\partial C(x,0)}{\partial r}=0 \tag{4}$$

The adjoint partial differential equation in source coordinates is

$$-(1-r'^2)\frac{\partial G}{\partial x'}=\frac{1}{r'}\frac{\partial}{\partial r'}\left(r'\frac{\partial G}{\partial r'}\right) \tag{5}$$

Expressing Equation (1) in source coordinates, multiplying it through by $r'G$, and Equation (5) by $r'C(x',r')$, subtracting and integrating, taking care to exclude the singularity, one obtains

$$\int_0^{x-\epsilon}dx'\int_0^1 r'(1-r'^2)\frac{\partial(GC)}{\partial x'}dr'=$$
$$=\int_0^{x-\epsilon}dx'\int_0^1\frac{\partial}{\partial r'}\left(Gr'\frac{\partial C}{\partial r'}-Cr'\frac{\partial G}{\partial r'}\right)dr'$$
$$+\int_0^{x-\epsilon}dx'\int_0^1 r'\psi G\,dr' \tag{6}$$

Define a unit source at $x'=x$, $r'=r$ so that

$$\lim_{\epsilon\to 0}\int_0^1 r'(1-r'^2)G(x,r;x-\epsilon,r')\,C(x-\epsilon,r')dr'=C(x,r) \tag{7}$$

Take the limit as $\epsilon\to 0$ of both sides of Equation (6). Use the relation (7) and the initial condition in source coordinates to evaluate the left-hand side of (6). The right-hand side is evaluated using condition (3) in source coordinates and the homogeneous Neumann condition for

G. The solution to this completely nonhomogeneous problem becomes

$$C(x,r) = \int_0^1 r'(1-r'^2)\,f(r')G(x,r;0,r')dr' + \int_0^x \phi(x')G(x,r;x',1)dx' + \int_0^x\int_0^1 r'\psi(x',r')G(x,r;x',r')dx'dr' \quad (8)$$

The Green's function $G(x,r;x',r')$ can be considered defined by the equation

$$C(x,r) = \int_0^1 r'(1-r'^2)f(r')G(x,r;0,r')dr' \quad (9)$$

with $C(x,r)$ as the solution to the homogeneous problem defined by Equations (1) to (4) with ϕ and ψ zero. Such a problem is always solved when one finds eigenfunction solutions to the Graetz problem for the tube or annulus. Thus Green's functions are available for these geometries. From Hsu's (*14*) article, the Green's function for the problem defined by Equations (1) to (4) is

$$G(x,r;x',r') = 4 + \sum_{n=1}^{\infty} \frac{1}{N_n} R_n(r)R_n(r')e^{-\beta_n^2(x-x')} \quad (10)$$

where

$$N_n = \int_0^1 r'(1-r'^2)R_n^2(r')dr' \quad (11)$$

Here x is used in place of $x/r_0N_{Re}N_{Pr}$ in Hsu's notation. The "4" in Equation (10) removes the arbitrariness in the Neumann problem. By use of the well-known relation [given by Hsu's Equation (11)] $N_n = -R_n(1)/\beta_n^2C_n$, the Green's function can be written as

$$G(x-x',r;r') = 4 - \sum_{n=1}^{\infty} \frac{\beta_n^2 C_n}{R_n(1)} R_n(r)R_n(r')e^{-\beta_n^2(x-x')} \quad (12)$$

MULTIPLE FORMS OF DUHAMEL'S FORMULA

The solution to the unit-prescribed flux problem, with zero inlet concentration $f = 0$ and no generation in the fluid $\psi = 0$, is given by the second integral in Equation (8) with $\phi(x) = 1$. This is the kernel $G^{(1)}$ needed to solve the prescribed flux problem; recall that (x, x') occurs only as $x - x'$. Then

$$G^{(1)}(x,r) = \int_0^x G(x-x',r;1)dx' \quad (13)$$

can be written as an integral with respect to λ by letting $\lambda = x - x'$. Substitution of $x - x'$ for x in the resulting equation and differentiation by Leibnitz rule shows that

$$\frac{\partial G^{(1)}(x-x',r)}{\partial x} = G(x-x',r;1) \quad (14)$$

The relation given by Equation (14) when substituted into Equation (8) yields the well-known form of Duhamel's formula

$$C(x,r) = \int_0^x \phi(x')\frac{\partial G^{(1)}(x-x',r)}{\partial x}dx' = -\int_0^x \phi(x')\frac{\partial G^{(1)}(x-x',r)}{\partial x'}dx' \quad (15)$$

Also well known is that these formulas hold for boundary conditions of the Dirichlet and convection type. The numerical difficulty with their use, however has not been fully recognized. For example, the application of Duhamel's theorem to diffusion in a finite slab problem in Carslaw and Jaeger (*27*) is given by Equation (3.5-2). It yields zero at both boundaries, $x = 0$ and $x = 1$, rather than the given values of the prescribed temperature. The utility of such a solution is highly questionable, especially near the boundaries where it is often needed. The solution satisfied the homogeneous conditions at the boundaries because the eigenfunctions corresponding to $R_n(r)$ in this paper all passed through zero at the boundaries. No matter how many zeros are added, one still obtains zero. The extended form of Duhamel's formula does not have this difficulty. This fact and its derivation by integration by parts suggest that a continued application of the process should yield even more rapidly converging solutions.

Integrating the second form of Equation (15) by parts yields the well-known alternate form of Duhamel's theorem

$$C(x,r) = \phi(0)\cdot G^{(1)}(x,r) + \int_0^x \frac{d\phi(x-x')}{dx'}G^{(1)}(x',r)\,dx' \quad (16)$$

The convergence is better because the singularity in the Green's function has been smoothed out by integration. This form does not satisfy the homogeneous conditions because $G^{(1)}(x,r)$ does not by construction. Continued integration by parts, assuming ϕ to be differentiable, yields multiple forms of Duhamel's formula

$$C(x,r) = \sum_{n=1}^{N} \frac{d\phi^{n-1}(0)}{dx^{n-1}}\cdot G^{(n)}(x,r) + \int_0^x \frac{d^N\phi(x-x')}{dx'^N}\cdot G^{(N)}(x',r)dx' \quad (17)$$

where

$$G^{(n)}(x,r) = \int_0^x G^{(n-1)}(x',r)dx', \quad n \geqq 2 \quad (18)$$

In case ϕ is an infinite series itself, successive differentiation may be limited as in the problem solved by Lyczkowski, Gidaspow, and Solbrig (*23*). This extended form offers no advantages. However, frequently ϕ is a function that may be differentiated any number of times, such as the sine function (*5*). Such a representation yields very rapidly converging series because every time the Green's function of form given by Equation (10) is integrated with respect to x', a division by β_n^2 takes place. The utility of this multiple representation requires also that $G^{(n)}(x,r)$ be a quickly converging series. Thus $G^{(n)}(x,r)$ should be obtained by superposition of general and particular solutions rather than from integration of the lower order expressions. This approach will be illustrated in the next section.

Construction of $G^{(n)}$

The solution $G^{(1)}$ to the unit-prescribed flux problem is given as the integral of (12) from zero to x evaluated at r' of one

$$G^{(1)}(x,r) = 4x + \sum_{n=1}^{\infty} C_nR_n(r)e^{-\beta_n^2x} - \sum_{n=1}^{\infty} C_nR_n(r) \quad (19)$$

A comparison of this unique solution to Hsu's well-known Equation (7) shows that

$$\sum_{n=1}^{\infty} C_n R_n(r) = -\left(r^2 - \frac{1}{4}r^4 - \frac{7}{24}\right) \qquad (19a)$$

The difficulty with $G^{(1)}$ as given by Equation (19) is of course the convergence of the series given by Equation (19*a*). Summation of similar series will be necessary for higher order $G^{(n)}$ and can be accomplished by constructing particular solutions. For example, $G^{(2)}$ is obtained first from integration of $G^{(1)}$

$$G^{(2)}(x, r) = 2x^2 + x\left(r^2 - \frac{1}{4}r^4 - \frac{7}{24}\right)$$

$$- \sum_{n=1}^{\infty} \frac{1}{\beta_n^2} C_n R_n\, e^{-\beta_n^2 x} + \sum_{n=1}^{\infty} \frac{1}{\beta_n^2} C_n R_n \qquad (20)$$

But $G^{(2)}$ is simply the solution to the homogeneous convective diffusion equation with zero inlet concentration and with the flux proportional to x. In Equation (3), $\phi(x) = x$. The fact that $G^{(2)}$ is the solution to this problem follows formally from Equation (17). $C(x, r)$ becomes $G^{(2)}(x, r)$ when $\phi(x) = x$. The solution for $G^{(2)}$ is obtained by superposition—by letting $G^{(2)} = C_p + u$ where C_p is a particular solution that makes u satisfy the homogeneous partial differential equation and the homogeneous Neumann conditions. The particular solution is the expression in x and r before the sums in Equation (20) plus an arbitrary function of r, $h(r)$ which satisfies the convective diffusion equation and the homogeneous boundary conditions. In this manner, $G^{(2)}$ becomes the expression given by Equation (20) with the sum of Graetz functions

$$\sum_{n=1}^{\infty} \frac{1}{\beta_n^2} C_n R_n(r) =$$

$$-\frac{7}{96}r^2 + \frac{31}{384}r^4 - \frac{5}{144}r^6 + \frac{1}{256}r^8 + \frac{9}{640} \qquad (21)$$

In the construction the function $h(r)$ was the polynomial in r in Equation (21), excluding the constant. The constant was obtained from the evaluation of u using $-h(r)$ as the initial condition in this homogeneous problem.

Interfacial Concentrations

In addition to solution of prescribed flux problems, the higher order kernels $G^{(n)}$ are expected to be useful in reaction rate data analysis. According to the suggestion of Katz (29), rates of surface reactions may be determined from measurements of outlet mixing-cup concentrations as a function of contact time, x for a given inlet concentration. Let the dimensionless rate of consumption of the reactant be R, which is a function of concentrations of the species present, and scale the concentration using the inlet as the scale factor so that $C(0, r) = 1$. In other words, let $f = 1$ and $\phi = -R$ in our boundary value problem. Then integration of Equation (1) over r from zero to one, with no internal sources $\psi = 0$, yields

$$\frac{1}{4}\frac{dC_m}{dx} = -R = -\text{(rate)}\left(\frac{r_0}{C_0 D}\right) \qquad (22)$$

where the mixing-cup concentration is

$$\frac{1}{4} C_m = \int_0^1 r(1 - r^2) C(x, r)\, dr \qquad (23)$$

Thus, measurement of C_m as a function of x clearly yields R simply as its derivative. The difficulty arises with the evaluation of the wall concentration corresponding to the point rate. The concentration is given by Equation (8)

$$C(x, r) = 1 - \int_0^x R(x') G(x, r; x', 1)\, dx' \qquad (24)$$

Evaluation of $C(x, r)$ at $r = 1$ yields the formal solution to the wall concentration. As already pointed out, however, this solution behaves very poorly because the derivative at the wall is not the rate prescribed but zero. This difficulty may be the reason that nobody since the suggestion of Katz in 1958 has applied this method to rate data analysis, except in a degenerate case where the Leveque assumption is valid (*30*). It should be noted that, in most kinetic measurements in flow systems (*31*), the rate of flow is varied at a constant inlet composition. As is now clear, the convergence problem can be overcome by use of higher order kernels. For example, the wall concentration can be evaluated in terms of three kernels as

$$C(x, 1) = 1 - R(0) \cdot G^{(1)}(x, 1) - \frac{dR(0)}{dx} \cdot G^{(2)}(x, 1)$$

$$- \frac{d^2R(0)}{dx^2} \cdot G^{(3)}(x, 1) - \int_0^x \frac{d^3R(x - x')}{dx'^3} G^{(3)}(x', 1)\, dx' \qquad (25)$$

One merely needs to evaluate $G^{(1)}$, $G^{(2)}$, $G^{(3)}$ at the wall once and for all, for a given geometry and flow. Suppose C_m is fitted by least squares to a polynomial in x

$$C_m = 1 - A_1 x - A_2 x^2 - A_3 x^3 \qquad (26)$$

where A_i are the empirical constants determined. Then the wall concentration in the range of x experimentally measured can be obtained by hand calculation from

$$C(x, 1) = 1 - \frac{1}{4} A_1 G^{(1)}(x, 1) - \frac{1}{2} A_2 G^{(2)}(x, 1)$$

$$- \frac{3}{2} A_3 G^{(3)}(x, 1) \qquad (27)$$

This analysis holds for laminar flow between parallel plates and in the annulus. For turbulent flow in a tube and Neumann boundary conditions, the Green's function can be obtained from Equation (14) in the article by Sparrow, Hallman, and Siegel (*4*). It is simply the derivative of that expression with the same properties.

Because, however, the Green's function depends upon the Reynolds number as an additional parameter, data collection for such an analysis is more complicated in turbulent flow. Length of reactor may have to be varied at constant flow.

REACTION RATE DATA ANALYSIS

A. S. Predvoditelev (32) presents experimental data for the reaction of carbon dioxide with carbon and gases flowing at approximately constant temperature in a tube in laminar flow. He solved the Graetz problem with first-order reaction at the wall and calculated the first-order rate constants. (The present analysis does not need an assumption of a first-order reaction.) Concentrations were given at four different flow rates at very near 1050°C. Interpolated outlet mixing-cup concentrations for carbon dioxide at 1050°C. were fitted by least squares to the parabola

$$C_m = 1.0 - 0.4721\, x + 0.07345\, x^2 \qquad (28)$$

$$0.15 < x < 1.6$$

An additional data point $x = 0$, $c = 1$ was included in the fit. The dimensionless reaction rate R becomes

$$R = -\frac{1}{4}\frac{dC_m}{dx} = 0.11805 - 0.036705\, x \qquad (29)$$

$$0.15 < x < 1.6$$

In the flow rate range common to convective diffusion in gases the expressions for $G^{(1)}$ and $G^{(2)}$ assume simple forms, their convergence being so rapid that no more than one term in the series is necessary. In this case, x is greater than one tenth. Thus to three significant figures we can write

$$G^{(1)}(x,1) = \frac{11}{24} + 4x - 0.198\, e^{-25.68\,x} \quad \text{for} \quad x > 0.1 \tag{30}$$

$$G^{(2)}(x,1) = -\,8.94 \times 10^{-3} + \frac{11}{24}x + 2x^2 \quad \text{for} \quad x > 0.1 \tag{31}$$

Substitution of the coefficients obtained from the least square fit into Equation (27), and the simplified expressions for $G^{(1)}$ and $G^{(2)}$ yield the concentration of carbon dioxide at the wall C_w:

$$C_w = 0.9456 - 0.4552\, x + 0.07345\, x^2 + 0.0234\, e^{-25.68\,x}$$

$$0.15 < x < 1.6 \tag{32}$$

The results are summarized in the accompanying table.

A plot of reaction rate R vs. the dimensionless wall concentration C_w shows that Predvoditelev's assumption that the reaction was first order was not bad. The order of the reaction determined is about 0.9. It is clear that inlet compositions other than the given inlet of 96.5% carbon dioxide are needed for a more precise kinetic determination. It should be noted also that the reactor was not operated as a differential reactor because the highest conversion was over 50%. Obviously, such an operation is not necessary. Wall concentrations at the exit turned out to be close to the outlet mixing-cup concentrations because of an only 1:10 ratio of diffusional to reaction resistance at this temperature. This example illustrates how a Graetz-type analysis can be used to obtain reaction rate vs. wall concentration data from an integral reactor and how the Green's functions can be utilized in this area.

LAMINAR DIFFUSION BETWEEN PARALLEL PLATES

The analysis is equally applicable to convective diffusion between parallel plates. Consider the nonhomogeneous boundary condition of the third type. It degenerates into the first type for infinite coefficient h and into the second type for zero h. For reaction at one wall only, the solution to the boundary value problem

$$(1-y^2)\frac{\partial C}{\partial x} = \frac{\partial^2 C}{\partial y^2} + \psi(x,y) \tag{33}$$

$$C(0,y) = f(y) \tag{34}$$

$$\frac{\partial C(x,-1)}{\partial y} = h[C(x,-1) - \phi(x)] \tag{35}$$

$$\frac{\partial C(x,1)}{\partial y} = 0 \tag{36}$$

in terms of the Green's function G is

$$\begin{aligned} C(x,y) &= \int_{-1}^{1} (1-y'^2) G(x,y;0,y')\, f(y')\, dy' \\ &\quad + h \int_0^x \phi(x')\, G(x,y;x',-1)\, dx' \\ &\quad + \int_0^x \int_{-1}^{1} \psi(x',y')\, G(x,y;x',y')\, dx'\, dy' \end{aligned} \tag{37}$$

Graetz Analysis of Predvoditelev's* Data

x	C_m	R rate $(r_0/C_0\, D)$	C_w
1.568	0.44	0.0605	0.412
0.511	0.782	0.0993	0.732
0.317	0.85	0.1064	0.809
0.1526	0.933	0.1125	0.878

* See reference 32.

The Green's function can be obtained from a solution of the homogeneous problem $\phi = 0$ and $\psi = 0$. For a unit inlet distribution $f(y) = 1$, the solution can be easily obtained by separation of variables in terms of the eigenfunctions Y_n and eigenvalues β_n:

$$C(x,y) = \sum_{n=1}^{\infty} A_n\, e^{-\beta_n^2 x}\, Y_n(y) \tag{38}$$

The coefficients A_n are given by

$$A_n = \frac{1}{N_n} \int_{-1}^{1} (1-y'^2)\, Y_n(y')\, dy' \tag{39}$$

$$N_n = \int_{-1}^{1} (1-y'^2)\, Y_n^2\, dy' \tag{40}$$

By reversing the integration and summation processes in Equation (38), the unique solution can be written in the form given by Equation (37) to give the Green's function below, noting that (x, x') enters as $(x - x')$

$$G(x,y;x',y') = \sum_{n=1}^{\infty} \frac{1}{N_n} Y_n(y)\, Y_n(y')\, e^{-\beta_n^2 (x-x')} \tag{41}$$

These eigenvalues and eigenfunctions have been computed for a few values by Schenk (*10*) and more completely by Solbrig and Gidaspow (*11*). Equation (37) with $\phi = 0$ and $\psi = 0$ can also serve as the definition of the Green's function. Friedman (*28*) introduces the Green's function for the first initial boundary value problem in this manner, but without the weight function used here.

For Dirichlet-type boundary conditions, $C(x, -1) = \phi(x)$, the boundary integral two in Equation (37) becomes

$$\int_0^x \phi(x')\, \frac{\partial G(x,y;x',-1)}{\partial y'}\, dx' \tag{42}$$

The Green's function is that given by Equation (41) for infinite h. For the Neumann boundary conditions,

$$\frac{\partial C(x,-1)}{\partial y} = -\,\phi(x) \tag{43}$$

The second integral in Equation (37) is replaced by the integral

$$\int_0^x \phi(x')\, G(x,y;x',-1)\, dx' \tag{44}$$

The Green's function for the Neumann condition is in terms of present definitions

$$G_N(x,y;x',y') = \frac{3}{4} + \sum_{n=2}^{\infty} \frac{1}{N_n} Y_n(y) Y_n(y') e^{-\beta_n^2 (x-x')} \tag{45}$$

$G^{(1)}$ for the Neumann problem is defined the same as for the tube; for the Dirichlet problem it is equal to the integral given by Equation (42) with $\phi(x')$ equal to one; and for the convection boundary condition problem it is the second integral in Equation (37), with $\phi(x')$ again equal to unity.

The symmetrical problem of laminar convective diffusion is also completely solved. The Green's function can be obtained from Equations (24) and (27) in the paper by Sideman, Luss, and Peck (3) for the boundary conditions of the third type. It is of the form given here by Equation (41) with only a change in notation and interval.

MULTICOMPONENT DIFFUSION

Another application of the Green's function method is in the case of a ternary mixture. The linearized multicomponent diffusion equations given by Toor (33), for example, for a fluid flowing in fully developed laminar flow between parallel plates with Graetz's assumption may be written as

$$(1-y^2)\frac{\partial C_1}{\partial z} = D_{11}\frac{\partial^2 C_1}{\partial y^2} + D_{12}\frac{\partial^2 C_2}{\partial y^2} + \psi_1 \quad (46)$$

$$(1-y^2)\frac{\partial C_2}{\partial z} = D_{21}\frac{\partial^2 C_1}{\partial y^2} + D_{22}\frac{\partial^2 C_2}{\partial y^2} + \psi_2 \quad (47)$$

To apply the method of Green's functions, an integral expression over the space of z and y is formed to give the solution to the nonhomogeneous problem in terms of the Green's functions. That is, the expression $(LU)^*G - U^*$ $(\mathbf{L}G)$ becomes a divergence of a row vector.

This procedure gives

$$\begin{aligned}(LU)^*G - U^*(\mathbf{L}G) &= \psi_1 G_{1i} + \psi_2 G_{2i}\\
&= (1-y'^2)\frac{\partial(C_1G_{1i})}{\partial z'} - D_{11}\frac{\partial}{\partial y'}\left(G_{1i}\frac{\partial C_1}{\partial y'} - C_1\frac{\partial G_{1i}}{\partial y'}\right)\\
&\quad - D_{12}\frac{\partial}{\partial y'}\left(G_{1i}\frac{\partial C_2}{\partial y'} - C_2\frac{\partial G_{1i}}{\partial y'}\right)\\
&\quad - D_{21}\frac{\partial}{\partial y'}\left(G_{2i}\frac{\partial C_1}{\partial y'} - C_1\frac{\partial G_{2i}}{\partial y'}\right)\\
&\quad + (1-y'^2)\frac{\partial(C_2G_{2i})}{\partial z'} - D_{22}\frac{\partial}{\partial y'}\left(G_{2i}\frac{\partial C_2}{\partial y'} - C_2\frac{\partial G_{2i}}{\partial y'}\right),\\
&\qquad i = 1, 2 \quad (48)\end{aligned}$$

Let the range of y be between minus one and plus one. Integrate both sides of Equation (48) with respect to z' between $z' = 0$ and $z' = z - \epsilon$ and with respect to y' between $y' = -1$ and $y' = 1$. Choose the initial distributions of C_1 and C_2 to be

$$C_1(0, y) = f_1(y) \quad \text{and} \quad C_2(0, y) = f_2(y) \quad (49)$$

Take the limit as ϵ approaches zero and define unit sources for C_1 and C_2 so that

$$\lim_{\epsilon\to 0}\int_{-1}^{1}(1-y'^2)G_{ij}(y; y', \epsilon)C_i(z-\epsilon, y')dy' = \begin{matrix} C_i(z, y) & i = j \\ 0 & i \neq j \end{matrix} \quad (50)$$

The solution to the problem with completely homogeneous Sturm-Liouville boundary conditions and zero ψ_i, $i = 1, 2$ then becomes

$$C_{1h}(z, y) = \int_{-1}^{1} f_1(y')(1-y'^2)G_{11}(y; y', z)dy' + \int_{-1}^{1} f_2(y')(1-y'^2)G_{21}(y; y', z)\,dy' \quad (51)$$

and

$$C_{2h}(z, y) = \int_{-1}^{1} f_1(y')(1-y'^2)G_{12}(y; y', z)dy' + \int_{-1}^{1} f_2(y')(1-y'^2)G_{22}(y; y', z)\,dy' \quad (52)$$

Once the homogeneous coupled problem with initial distribution f_1 and f_2 is solved, the four components of the Green's matrix can be picked out by comparison to Equations (51) and (52). For Dirichlet and Neumann conditions, the problem can be decoupled using the Henry-Toor method. Thus, in these two cases the Green's matrix is known.

For all three Sturm-Liouville boundary conditions, the solution to the completely nonhomogeneous problem using Equation (48) becomes

$$\begin{aligned}C_i(z, y) &= C_{ih}(z, y) + \sum_{j=1}^{2}\int_0^z dz'\int_{-1}^{1}\psi_j G_{ji}\,dy'\\
&\quad + D_{11}\int_0^z\left[G_{1i}\frac{\partial C_1}{\partial y'} - C_1\frac{\partial G_{1i}}{\partial y'}\right]_{-1}^{1}dz'\\
&\quad + D_{12}\int_0^z\left[G_{1i}\frac{\partial C_2}{\partial y'} - C_2\frac{\partial G_{1i}}{\partial y'}\right]_{-1}^{1}dz'\\
&\quad + D_{21}\int_0^z\left[G_{2i}\frac{\partial C_1}{\partial y'} - C_1\frac{\partial G_{2i}}{\partial y'}\right]_{-1}^{1}dz'\\
&\quad + D_{22}\int_0^z\left[G_{2i}\frac{\partial C_2}{\partial y'} - C_2\frac{\partial G_{2i}}{\partial y'}\right]_{-1}^{1}dz'\\
&\qquad i = 1, 2 \quad (53)\end{aligned}$$

When ψ_1, ψ_2 or the boundary conditions are functions of concentration, Equation (53) becomes an integral equation. This is particularly useful for the Neumann boundary conditions for which the components of the Green's matrix are obtained by use of the Henry-Toor decoupling method.

From Toor's (33) article and from Equation (45) the Green's matrix for the Neumann boundary conditions becomes

$$G = \frac{1}{1 - s_{12}s_{21}}\begin{pmatrix} g_1 & -s_{12}g_1 \\ -s_{21}g_2 & g_2 \end{pmatrix} \quad (54)$$

where s_{12} and s_{21} are given by Toor's Equation (23) as

$$s_{21} = \frac{D_1 - D_{11}}{D_{21}}, \quad s_{12} = \frac{D_2 - D_{22}}{D_{12}} \quad (55)$$

The diffusivities of the decoupled convective diffusion Equations D_1 and D_2 are given by Toor's Equation (21) as

$$2D_{1,2} = D_{11} + D_{22} \pm \sqrt{(D_{11} - D_{22})^2 + 4D_{12}D_{21}} \quad (56)$$

The Green's functions g_1 and g_2 for the decoupled equations are

$$g_j = \frac{3}{4} + \sum_{n=2}^{\infty}\frac{1}{N_n}Y_n(y)\,Y_n(y')\,e^{-\beta_n^2 D_j(z-z')} \quad j = 1, 2 \quad (57)$$

from which it is clear that the new axial dimensionless coordinate is now D_jz. As D_{12} approaches zero, s_{21} and thus G_{21} approach zero.

Equation (53) then shows that C_1 is not affected by C_2, as is demanded by the physics of the problem. Similarly, C_2 will not be affected by C_1 unless the effect of C_1 comes in via C_2 through its boundary condition or source ψ_2.

The form of the integral representation, Equation (53), and the Green's matrix show that all the properties, such as multiple forms of Duhamel's theorem and application to rate data analysis, remain true for the simultaneous partial differential equations considered. An extension to other velocity profiles and geometries involves essentially only a change of interval of integration and the replacement of the weight function $(1 - y^2)$ by the appropriate function for the situation considered. For boundary conditions of the first and second type, the decoupling technique yields the Green's matrix. For boundary conditions of the third type, the Green's matrix must be found by simultaneous solution of the coupled equations.

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NOTATION

A_n = coefficient in the series expansion for parallel plates
a = one half the distance between parallel plates
C = concentration, dimensionless
C_i = concentration of the i^{th} component, Equations (46) and (47)
C_m = mixing-cup concentration, Equation (23)
C_n = coefficient in the series expansion for the tube
C_0 = inlet concentration, lb.$_A$/cu.ft.
D = molecular diffusivity, sq.ft./sec.
D_j = combine diffusion coefficient, Equation (56)
D_{ij} = multicomponent practical diffusivity
f = inlet distribution
G = Green's function or matrix with components G_{ij}
G_{ij} = i^{th} row, j^{th} column component in Green's matrix
$G^{(1)}$ = kernel in Duhamel's formula
$G^{(n)}$ = integrals of Green's function defined by Equation (18)
g_j = Green's function for Neumann conditions for a combine
h = convection constant in the boundary condition of the third type, Equation (35)
L = differential operator matrix for Equations (46) and (47)
N_n = normalizing integral for the n^{th} eigenfunction
N_{Pr} = Prandtl number
R = dimensionless reaction rate at the surface, rate $(r_0/C_0\, D)$
N_{Re} = Reynolds number
N_{Sc} = Schmidt number
R_n = n^{th} eigenfunction for the tube
r = dimensionless radial coordinate, actual divided by the tube radius
rate = rate of consumption of species A per unit surface area, lb.$_A$/sec.-sq.ft.
r_i = rate of production of species i in the fluid
r_0 = tube radius, ft.
$s_{12,21}$ = decoupling parameters in Toor's analysis
U = unknown column vector (C_1, C_2)
u = average velocity
x = axial dimensionless coordinate, $\dfrac{8}{3}\, x_A/(a\, N_{Re}\, N_{Sc})$ for parallel plates; $x_A/(r_0\, N_{Re}\, N_{Pr})$ or $x_A/(r_0\, N_{Re}\, N_{Sc})$ for the sube
x_A = axial distance from channel entrance
y = lateral dimensionless coordinate, y_A/a
y_A = actual lateral distance
z = axial coordinate, $2x_A/3ua^2$

Greek Letters

β_n^2 = n^{th} eigenvalue
ϕ = prescribed source at the boundary or given ambient distribution
ψ = source in the fluid
ψ_i = source in multicomponent problem, $r_i a^2$

Operators

= source coordinates
L = adjoint differential operator
$*$ = transpose of a matrix

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