A Green's Function Method for the Solution of Diffusion-Reaction Problems

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There has been considerable interest in the chemical engineering literature in relating concentration profiles of systems with first-order homogeneous reactions to the concentration profiles for nonreacting systems. At least two different methods have been used to establish relationships of this type. The first method was suggested by Danckwerts (1951), who showed that the solution of an unsteady diffusion-reaction problem can be obtained from the solution of the corresponding problem with no reaction if the appropriate formula connecting the solutions is available. The Danckwerts approach has been extended and discussed (Crank, 1956; Carslaw and Jaeger, 1959; Bird et al., 1960; Lightfoot, 1964; Slattery, 1972), and a generalized version of the Danckwerts method has been presented recently (Vrentas and Vrentas, 1987). In the latter study, an appropriate formula connecting solutions was presented for a wider class of problems than had been considered in the other above studies. A second method of solving problems of this type has been suggested by Stewart (1968, 1969). He used what he called a superposition method to analyze unsteady diffusion and first-order reaction in a flowing fluid. Stewart essentially used a Green's function approach although he did not identify his method as such.

The objective of both techniques is to develop a solution for a certain class of diffusion-reaction problems in terms of a solution to a simpler problem, where the solution to the simpler problem is already available or can be derived rather easily. In both methods, therefore, it is necessary to derive an equation relating the solution of the problem of interest to a simpler or basic solution. There are, however, important differences in the two methods. First, the basic solutions used in the two methods are very different. In the Danckwerts method, the basic solution is the solution of a comparable problem with no reaction and time-independent boundary conditions (Vrentas and Vrentas, 1987). In the Green's function approach, the basic solution consists of one or more Green's functions formulated for the problem in the absence of the reaction term. Consequently, the forms of the equations relating solutions are different. A second difference, which is noted below, is that the Green's function approach can be used to solve a somewhat wider class of problems. For example, it is possible to solve problems with time-dependent velocity fields. The choice of which method should be used to solve a particular diffusion-reaction problem will depend on the type of problem being considered and on the availability of the simpler or basic solution.

One important disadvantage of the Green's function method presented by Stewart is that the solutions of two Green's function problems must be used to derive the desired solution to the diffusion-reaction problem. The purpose of this note is to use the theory of Green's functions to show that a solution to the diffusion-reaction problem can be formulated using only one Green's function. Hence, only one Green's function problem for the no-reaction case, rather than two, needs to be solved to determine the basic solution.

Problem Formulation

We consider the same absorption, diffusion, and reaction problem described previously (Vrentas and Vrentas, 1987) with three generalizations that are discussed below. This is essentially the problem treated by Stewart (1968).

$$\frac{\partial c_A}{\partial t} + v \cdot \nabla c_A = D\nabla^2 c_A - kc_A + Q(\xi, t) \tag{1}$$

$$c_A(\xi, 0) = q(\xi) \quad \xi \in V \tag{2}$$

$$c_A(\xi, t) = h_1(\xi, t) \quad \xi \in \partial V_D \tag{3}$$

$$\frac{\partial c_A}{\partial n} + Kc_A = h_2(\xi, t) \quad \xi \in \partial V_R \tag{4}$$

$$v = v(\xi, t) \tag{5}$$

$$K = K(\xi, t) \tag{6}$$

$$\nabla \cdot v = 0 \tag{7}$$

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The volume V is bounded by two types of surfaces, ∂V_D and ∂V_R; Dirichlet boundary conditions are imposed on ∂V_D and Robin boundary conditions on ∂V_R. For the Green's function method, v and K are permitted to be functions of time as well as of spatial position, whereas it appears that v and K must be independent of time for the Danckwerts method. A third generalization is the inclusion of a source term, $Q(\xi, t)$, in the diffusion equation.

The causal Green's function, $g(\xi, t \mid \xi_0, t_0)$, for the above problem is given by the following set of equations:

$$\frac{\partial g}{\partial t} + v \cdot \nabla g = D\nabla^2 g - kg + \delta(\xi - \xi_0)\delta(t - t_0) \tag{8}$$

$$g(\xi, t \mid \xi_0, t_0) = 0 \quad t < t_0 \tag{9}$$

$$g = 0 \quad \xi \in \partial V_D \tag{10}$$

$$\frac{\partial g}{\partial n} + Kg = 0 \quad \xi \in \partial V_R \tag{11}$$

In addition, the adjoint Green's function, $g^*(\xi, t \mid \xi_0, t_0)$, for the problem is described by the following equations:

$$-\frac{\partial g^*}{\partial t} - v \cdot \nabla g^* = D\nabla^2 g^* - kg^* + \delta(\xi - \xi_0)\delta(t - t_0) \tag{12}$$

$$g^*(\xi, t \mid \xi_0, t_0) = 0 \quad t > t_0 \tag{13}$$

$$g^* = 0 \quad \xi \in \partial V_D \tag{14}$$

$$D\frac{\partial g^*}{\partial n} + DKg^* + v \cdot \boldsymbol{n} g^* = 0 \quad \xi \in \partial V_R \tag{15}$$

Finally, the Green's function for the problem without chemical reaction, $G(\xi, t \mid \xi_0, t_0)$, is given by the following equation set:

$$\frac{\partial G}{\partial t} + v \cdot \nabla G = D\nabla^2 G + \delta(\xi - \xi_0)\delta(t - t_0) \tag{16}$$

$$G(\xi, t \mid \xi_0, t_0) = 0 \quad t < t_0 \tag{17}$$

$$G = 0 \quad \xi \in \partial V_D \tag{18}$$

$$\frac{\partial G}{\partial n} + KG = 0 \quad \xi \in \partial V_R \tag{19}$$

The objective here is to obtain a relationship between c_A, the solution to the reaction-diffusion problem, and G, the solution of the Green's function problem with no reaction.

Problem Solution

The key to obtaining relationships between solutions of the above four problems is the utilization of the following integral identity written for two general functions, u and w:

$$\begin{aligned} &\int_0^\tau \int_V \left[w\left(D\nabla^2 u - \frac{\partial u}{\partial t}\right) - u\left(D\nabla^2 w + \frac{\partial w}{\partial t}\right)\right] dV\,dt \\ &= \int_0^\tau \int_{\partial V_D} D\left(w\frac{\partial u}{\partial n} - u\frac{\partial w}{\partial n}\right) dS\,dt \\ &+ \int_0^\tau \int_{\partial V_R} D\left(w\frac{\partial u}{\partial n} - u\frac{\partial w}{\partial n}\right) dS\,dt \\ &+ \int_V [(uw)_{t=0} - (uw)_{t=\tau}]\,dV \end{aligned} \tag{20}$$

Introduction of Eqs. 8–11 and Eqs. 12–15 into Eq. 20 yields the following relationship between g and g^*:

$$g(\xi, t \mid \xi_0, t_0) = g^*(\xi_0, t_0 \mid \xi, t) \tag{21}$$

Also, utilization of Eqs. 12–15 and Eqs. 16–19 in Eq. 20 and introduction of Eq. 21 produces the following result after appropriate manipulation:

$$g(\xi, t \mid \xi_0, t_0) = e^{-k(t-t_0)}G(\xi, t \mid \xi_0, t_0) \tag{22}$$

Equation 22 was derived by Stewart (1968) using Laplace transforms. Finally, introduction of Eqs. 1–4 and Eqs. 12–15 into Eq. 20 and utilization of Eqs. 21 and 22 leads to a solution form for $c_A(\xi, t)$:

$$\begin{aligned} c_A(\xi, t) &= \int_0^t \int_V Q(\xi_0, t_0)e^{-k(t-t_0)}G(\xi, t \mid \xi_0, t_0)\,dV_0\,dt_0 \\ &- \int_0^t \int_{\partial V_D} Dh_1(\xi_0, t_0)e^{-k(t-t_0)}\frac{\partial G}{\partial n_0}(\xi, t \mid \xi_0, t_0)\,dS_0\,dt_0 \\ &+ \int_0^t \int_{\partial V_R} Dh_2(\xi_0, t_0)e^{-k(t-t_0)}G(\xi, t \mid \xi_0, t_0)\,dS_0\,dt_0 \\ &+ \int_V q(\xi_0)e^{-kt}G(\xi, t \mid \xi_0, 0)\,dV_0 \end{aligned} \tag{23}$$

Equation 23 is the desired equation connecting $c_A(\xi, t)$ to $G(\xi, t \mid \xi_0, t_0)$, the solution to the Green's function problem with no chemical reaction. This equation is clearly a more desirable solution form than the one presented by Stewart since the solution to only one Green's function problem is required for its utilization. The solution form presented by Stewart has two Green's functions.

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Notation

c_A = molar density of component A
D = mutual diffusion coefficient
g = causal Green's function, Eqs. 8–11
g^* = adjoint Green's function, Eqs. 12–15
G = Green's function for no-reaction problem, Eqs. 16–19
h_1 = function in surface boundary condition, Eq. 3
h_2 = function in surface boundary condition, Eq. 4
k = first-order reaction rate constant
K = function in surface boundary condition, Eqs. 4, 6
n = outward normal direction for volume of phase
$\boldsymbol{n}$ = outward unit normal vector to surface of V
q = initial concentration distribution of component A, Eq. 2

Q = source term in diffusion equation
t = time
v = velocity vector of fluid
V = volume of phase
δ = Dirac delta function
ξ = point in space characterized by three independent distance variables

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Errata

In the paper titled "Low Flow Limits of Coatability on a Slide Coater" by E.B. Gutoff and C.E. Kendrick (33(1), p. 141, Jan. 1987), the following corrections are made:

1. In Eq. 1, the exponent on G in the denominator was omitted. It should be 0.25. The corrected equation is

$$t > \frac{2.19\sigma^{0.25}\,\mu V^{0.5}}{\rho^{0.25}\,\Delta P G^{0.25}} \qquad \frac{\Delta P}{\rho V^2} \leq 3.32 \tag{1}$$

2. In Table 3, p. 145, column b at low ΔP should read 0.5, instead of 0.7, and column c at high ΔP should read 0.7, instead of 0.5.