Coupling of Translational and Reactive Dynamics for a Simple Lattice Model

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The problem of the coupling of translational and reactive dynamics is investigated in terms of a simple lattice model. A master equation description including repulsive and reactive interactions is analyzed in terms of a boundary layer region and reduced to source term equations at the diffusion level. Comparison is made at this level with boundary condition approaches.

1. INTRODUCTION

Interest in the theoretical description of chemical reactions in condensed phases has recently been stimulated by a number of developments. Picosecond spectroscopy[1] and CIDNP experiments[2] promise the ability to resolve fast reactive events at a more detailed level than previously accessible. Computer experiments[3,4] for modeled reactive systems are beginning to provide even more detailed information on motional and reactive processes. Finally, the emergence of tractable statistical mechanical descriptions of motion in fluids (see, e.g., Ref. 5) allows the beginning of investigation of these complex processes.

Adequate descriptions of such reactions will involve the coupling of translational (and internal) motion to reactive dynamics. One possible starting point involves the complete microscopic equations of motion for the many-body system.[6] We choose, however, to approach the problem from the other direction by examining a sequence of increasingly more realistic models. In

this paper, we consider a simple lattice model for coupled translational and reactive dynamics. In a subsequent paper, we will consider a more detailed description involving a Fokker–Planck[7,8] level translational description coupled with a Kramers-type barrier crossing treatment.[9] The rationale for this direction of approach is twofold. First, even for the simple lattice model, a number of subtle questions arise regarding, e.g., location of boundaries and relevant time scales. Second, it is well known[10] that chemical rate equations and constants themselves involve a number of subtleties. We believe that these aspects are, at least initially, most clearly exposed and handled at a level of description other than the fully microscopic level.

In this first paper, we restrict ourselves to obtaining a final description at the diffusion level only. We focus on the important questions that arise even in reaching this level. (For simplicity we work in one dimension, but generalization to three dimensions is immediate.) The diffusion level description of reactions is, of course, well known.[11] In the standard formulation, homogeneous diffusion equations are supplemented by (often inhomogeneous) boundary conditions imposed on intuitive grounds. Two examples of the latter are (a) the "radiative" boundary condition (BC) introduced by Collins and Kimball,[12] which equates diffusive and reactive fluxes at a "reactive surface," and (b) the Smoluchowski[13] condition that the distribution of particles vanish at such a surface. An alternate formulation, recently espoused by Wilemski and Fixman at the diffusion level,[14] is the source term approach. In our derivation, an equation of motion for reactive species is constructed to be valid in a region extended to include a "boundary layer" in which homogeneous equations break down due to the effects of short-range forces. In this way the effects of such forces appear explicitly in the dynamical equation as a source term [cf. Eq. (24) below]. Our construction of source terms involves a much more detailed analysis of short-range dynamics (within the context of the model) than the intuitive imposition of a BC. Indeed, we find that, even at the diffusion level of description, some intuitive BCs assumed in the past are not correct or must be qualified (cf. Section 5).

Some advantages of a source term formulation itself are (i) it lends itself naturally to powerful formal methods of analysis closely related to those employed in the absence of boundaries[15]; (ii) for realistic descriptions of reactive–translational dynamics, a simple BC can be inadequate. For example, as pointed out by Wilemski and Fixman,[14] the coupling can be nonlocal in space. A source term approach can easily accommodate such generalizations; (iii) this approach may also be applied to more detailed descriptions, for example, at the Fokker–Planck level.[16]

In this paper, we examine the derivation of source term equations for a simple one-dimensional model which includes short-range repulsion effects and reaction. The master equation governing various transitions is derived

and transformed, in appropriate limits, to a continuous equation of the diffusion form with reactive sources. In using a discrete lattice model we do not claim to provide an adequate description of either translational or reactive dynamics. Our intention here is rather to derive the basic structure of a source term equation and elucidate its validity conditions. This study of the lattice model in fact serves as an extremely useful guide for the derivation of source terms for more realistic, and thus more complex, dynamical descriptions.[16]

In Section 2 we present a derivation of the source term equation for diffusion for the case of two particles interacting via purely repulsive short-range forces. It is found that a source term appears even in the absence of chemical reaction. We also introduce here the basic ideas and techniques required in Section 3 for the case where chemical reaction can occur. In Section 4, Green's function techniques are utilized to transform the basic result into more convenient forms. Comparison with other treatments is given in Section 5.

2. REFLECTING WALL SOURCE TERM

Here we consider the relative motion of two particles interacting through purely short-range repulsive forces and thus incapable of reacting. We utilize a one-dimensional lattice model in which the dynamics are described by a discrete master equation (ME). This model (Fig. 1) consists of a discrete one-dimensional space of points $n = 0, 1, 2,..., \infty$, which specify *relative*
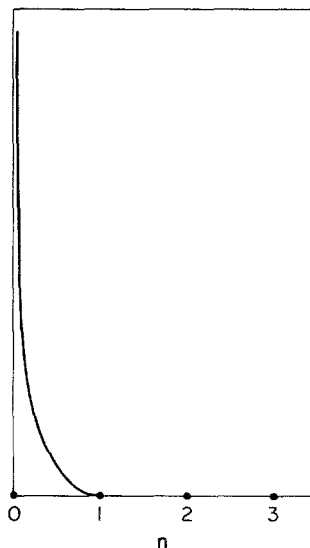
Fig. 1. Lattice model and associated repulsive potential (solid line).

positions of a particle pair. The probability of finding the pair at relative position n at time t is $p_n(t)$. Transitions are allowed only between adjacent lattice points. In this relative coordinate system, we can speak in terms of one fixed particle and one moving particle. Some aspects of boundary conditions have been investigated on a related model by van Kampen and Oppenheim.[17]

We identify certain lattice points with certain regions of interaction. The state $n = 0$ corresponds to a highly repulsive state of interaction; states $n \geqslant 1$ are noninteractive.

We begin by writing the ME for the probability p_n as

$$dp_n/dt = rp_{n+1} + rp_{n-1} - 2rp_n; \qquad n > 1 \tag{1}$$

Here r is the probability per unit time of a transition between adjacent lattice points (excluding transitions $0 \leftrightarrow 1$). Equation (1) is restricted to points $n > 1$; the presence of the interaction region modifies the transition frequencies into and out of state $n = 1$. Due to repulsive forces, lattice points $n = 0, 1$ have the unique equations of motion

$$dp_1/dt = rp_2 + drp_0 - (1 + c)rp_1 \tag{2}$$

$$dp_0/dt = crp_1 - drp_0 \tag{3}$$

Here cr and dr are modified transition frequencies into and out of state $n = 0$, respectively.

The ME for ordinary points on the lattice breaks down at $n = 1$. We refer to this point as a boundary layer because its occupation dynamics are affected by short-range forces (even though no forces exist there). We are thus led to consider where the BC is actually applied in any continuous model. It should be clear that the boundary point in Eq. (1) is not a point where forces are strongly repulsive. It is, rather, a point at the surface of a boundary layer and outside the force region.

We now wish to construct an equation valid not only for $n > 1$, but which also includes the boundary layer point $n = 1$. With the introduction of the Kronecker delta, Eqs. (1) and (2) can be combined to give

$$dp_n/dt = rp_{n+1} + rp_{n-1} - rp_n + \delta_{n,1}(rp_1 - rp_0 - crp_1 + drp_0);$$
$$n > 0 \tag{4}$$

Equation (4) contains the usual ME terms as in Eq. (1) with an additional corrective source term contributing solely at $n = 1$. Equation (4) requires specification of an appropriate BC at the new boundary point $n = 0$; by solving Eq. (3), we obtain this as

$$p_0(t) = p_0(0)e^{-drt} + \int_0^t dt' \, e^{-drt'} crp_1(t - t') \tag{5}$$

Equation (4) is exactly the type of equation sought. We are, however, ultimately concerned with continuous systems. We thus transform the discrete space variable n to a continuous variable $x = n\epsilon$, where ϵ is an infinitesimal scaling length; it may be interpreted as the characteristic length previously represented by a lattice point. The probability $p_n(t)$ transforms to a probability density $P(x, t)$ as $p_n(t) = \epsilon P(x, t)$ and the Kronecker delta transforms to a delta function $\delta_{n,1} = \epsilon \delta(x - \epsilon)$. With these definitions Eq. (4) is converted to the continuous equation

$$\partial P(x, t)/\partial t = rP(x + \epsilon) + rP(x - \epsilon) - 2rP(x)$$
$$+ \epsilon\delta(x - \epsilon)[rP(\epsilon) - rP(0) - crP(\epsilon) + drP(0)]; \qquad x > 0 \quad (6)$$

Taylor expansion for small ϵ then yields

$$\frac{\partial P(x, t)}{\partial t} = \epsilon^2 r \frac{\partial^2 P}{\partial x^2} + \frac{\epsilon^4 r}{12} \frac{\partial^4 P}{\partial x^4} + \cdots$$

$$+ \delta(x - \epsilon)\left[\epsilon^2 r \left(\frac{\partial P}{\partial x}\right)_{\epsilon -} + O(\epsilon^3) + \cdots - cr\epsilon P(\epsilon)\right.$$

$$\left. + dr\epsilon P(0)\right]; \qquad x > 0 \tag{7a}$$

which can be rewritten more compactly as

$$\partial P(x, t)/\partial t = L_d(\epsilon)P(x, t) + \mathscr{S}(x, t; \epsilon) \tag{7b}$$

The leading term in $L_d(\epsilon)P$, the expansion of ordinary transition terms, has the Fick's law diffusion form, where the (relative) diffusion constant $D = \epsilon^2 r$. The gradient term $\epsilon^2 r(\partial P/\partial x)_{\epsilon -}$ in the source is evaluated in the interval $(0, \epsilon)$, as indicated by the notation $\epsilon -$. In the limit of small ϵ, a discontinuity will exist in the gradient at $x = \epsilon$, and it becomes imperative to specify this evaluation point carefully (see Fig. 2). This will be discussed subsequently in greater detail.

The c and d terms in $\mathscr{S}$ are respectively transition rates into and out of the repulsive force region. Together they represent the net flux $J(t)$ between the boundary layer and the repulsive region defined as

$$J(t) = cr\epsilon P(\epsilon, t) - dr\epsilon P(0, t) = J_f - J_r \tag{8}$$

Although these forward and reverse fluxes separately may be large, the net flux into a small repulsive region should vanish under conditions where repulsive encounters take place rapidly on the diffusion time scale. To see how this might come about, we first examine the magnitudes of the individual fluxes and then determine the behavior of the net flux $J(t)$ in the appropriate limit.

The quantity cr is the transition frequency for the unidirectional transi-
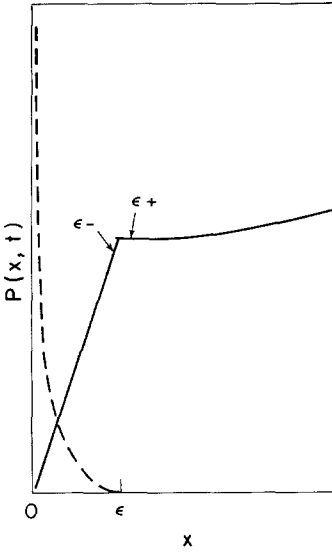
Fig. 2. Distribution behavior in the interaction region. Dashed line denotes the repulsive potential.

tion from the boundary layer into the repulsive interaction region. This frequency should not differ too greatly from ordinary transition frequencies r in the medium, as a particle at $x = \epsilon$ has no direct knowledge of the repulsive forces. For this reason, we expect c to be $O(1)$. However, once the particle has encountered the repulsive forces, it will respond extremely rapidly. Thus, the exit transition frequency $dr \gg r$. Just how much larger dr is than r will depend upon the details of the interaction region. Since the repulsive forces are localized in a length of $O(\epsilon)$, their magnitude tends to infinity as ϵ tends to zero. Therefore, the factor d is appropriately scaled by the reciprocal of ϵ as $d = \Delta/\epsilon$.

To demonstrate how $J(t)$ vanishes for small ϵ, we require a closed form for $J(t)$ in terms of $P(\epsilon, t)$. Equation (5) transforms as

$$P(0, t) = P(0, 0)e^{-r\Delta t/\epsilon} + cr \int_0^t dt'\, P(\epsilon, t')e^{-(r\Delta/\epsilon)(t - t')} \tag{9}$$

so that, with the $P(0, 0) = 0$ initial condition imposed, we obtain

$$J(t) = J_f(t) - \int_0^t dt'\, k(t - t')J_f(t') \tag{10}$$

Here the transition kernel

$$k(t - t') = (r\Delta/\epsilon)\exp[-(r\Delta/\epsilon)(t - t')] \tag{11}$$

gives the contribution to the flux $J_r(t)$ out of the interaction region arising from particles entering at a previous time t'. For small ϵ, $k(t - t')$ is a rapidly decaying function of the time $t - t'$ a particle spends in the interaction region. Indeed, to lowest order in ϵ, $k(t)$ is a delta function in time. This confirms our expectations that a particle entering the interaction region returns to the boundary layer virtually instantaneously (on the diffusion time scale) when the extent of the interaction region is $O(\epsilon)$. Thus, to lowest order in ϵ, the reverse flux $J_r(t) = \int_0^t dt' \, \delta(t - t') J_f(t')$ cancels the forward flux $J_f(t)$ to give a vanishing net flux $J(t)$. Then, Eq. (7) may be written as

$$\frac{\partial P}{\partial t} = \epsilon^2 r \frac{\partial^2 P}{\partial x^2} + \cdots + \delta(x - \epsilon)\left[\epsilon^2 r \left(\frac{\partial P}{\partial x}\right)_{\epsilon_-} + \cdots\right]; \qquad x > 0 \qquad (12)$$

Finally, to maintain consistency we write $P(x, t)$ as a power series in the small parameter so that

$$P(x, t) = P^{(0)}(x, t) + \epsilon P^{(1)}(x, t) + \cdots \qquad (13)$$

Defining a new time variable $\tau = \epsilon^2 r t$ characteristic of the diffusion time scale, and using the expansion Eq. (13), we then obtain the following zeroth-order equation:

$$\frac{\partial P^{(0)}}{\partial \tau} = \frac{\partial^2 P^{(0)}}{\partial x^2} + \delta(x - \epsilon)\left(\frac{\partial P^{(0)}}{\partial x}\right)_{\epsilon_-}; \qquad x > 0 \qquad (14)$$

The retention of the delta function in an unexpanded form, while not totally consistent, signifies that the source term contributes in an ϵ neighborhood to the right of the end point ($x = 0$) of the domain.

Equation (14) is the desired inhomogeneous equation of motion. It must be provided with a consistent boundary value applied at the point $x = 0$. Since the repulsive interaction region contains this point, the probability of being found there should be essentially zero (at least on the diffusion time scale). We can explicitly establish the BC for Eq. (14) by transforming Eq. (9) for $P(0, t)$ to time variable τ to obtain [with $P(0, 0) = 0$]

$$P(0, \tau) = (c/\epsilon^2) \int_0^\tau d\tau' \, P(\epsilon, \tau') \exp[-(\Delta/\epsilon^3)(\tau - \tau')] \qquad (15)$$

If we introduce the Laplace transform of Eq. (15), then

$$\hat{P}(0, s) \equiv \int_0^\infty d\tau \, e^{-s\tau} P(0, \tau) = \epsilon c \hat{P}(\epsilon, s)/(\Delta + \epsilon^3 s)$$
$$= \epsilon(c/\Delta)\hat{P}(\epsilon, s) + O(\epsilon^4) \qquad (15')$$

where we have used the convolution theorem and expanded in ϵ. The distribution $P(0, \tau)$ in time then has the power series representation

$$P(0, \tau) = \epsilon(c/\Delta)P(\epsilon, \tau) + O(\epsilon^4) + \cdots \qquad (16)$$

Expansion of the distribution according to Eq. (13) gives the zeroth-order BC for Eq. (14) as the expected result

$$P^{(0)}(0, \tau) = 0 \qquad (17)$$

After suppression of the superscripts for convenience and conversion back to time t, the final result of the ME treatment of the repulsive wall case can be written as

$$\frac{\partial P}{\partial t} = D \frac{\partial^2 P}{\partial x^2} + \delta(x - \epsilon)D\left(\frac{\partial P}{\partial x}\right)_{\epsilon-}, \quad x > 0; \quad P(0, t) = 0 \qquad (18)$$

It can be shown via integration that the *reflecting wall source term* $\delta(x - \epsilon)D(\partial P/\partial x)_{\epsilon-}$ conserves probability in the domain of the equation. This term appears even in the absence of reaction, and arises *solely* from repulsive forces.

It may seem paradoxical to obtain what appears to be the same BC used by Smoluchowski[13] to treat reactions which proceed with virtual certainty when reactive particles encounter. This treatment invoked a vanishing BC on a particular reaction surface to absorb particles from the system. However, this surface was taken to be in what we consider the boundary layer and thus implies a reactive loss rapid on the diffusion time scale (cf. Section 4). The vanishing BC on Eq. (18), on the other hand, is invoked at a point deep within the repulsive force region, where we can reasonably expect the probability density to always vanish.

Although both BCs discussed above have fundamentally different interpretations, upon implementation they both absorb particles from the system on their respective surfaces. The BC on Eq. (18) generates a flux out of the system, whose magnitude is given by the reflecting wall source term. Probability conservation is maintained, however, since the source term instantaneously injects these particles back into the boundary layer. Thus it is crucial to evaluate the gradient in the source term in the interval $(0, \epsilon)$ as previously noted, and hold its contribution point at $x = \epsilon$.

Equation (18) is a formulation equivalent[18,19] to the following homogeneous equation with "reflecting wall" BC:

$$\frac{\partial P}{\partial t} = D \frac{\partial^2 P}{\partial x^2}, \quad x > \epsilon; \quad D\left(\frac{\partial P}{\partial x}\right)_{\epsilon+} = 0 \qquad (19)$$

It is important to note that the gradient in the BC of Eq. (19) is evaluated to the *right* of the discontinuity at $x = \epsilon$, in contrast to the reflecting wall source term (see Fig. 2). This ensures zero net flux through the point $x = \epsilon$ in the limit of fast events within the repulsive region. The boundary point in Eq. (19) is outside the repulsive region. This is consistent with our previous discussion of the general features of boundary value formulations.

Finally, we note that, although repulsive forces lead to a source term, the transition frequencies *cr* and *dr* characteristic of these forces do not appear explicitly in this term.

3. INCLUSION OF REACTIVE TERMS

We now allow for a reversible reaction, again through short-range interactions. A particle at $n = 1$ making a transition to the left now has two possible fates: (i) it may proceed to form a stable reacted state (with a lifetime nonnegligible on the diffusion time scale); (ii) it may encounter conditions unfavorable for reaction and quickly return to the boundary layer, as anticipated in Section 2 (there, all particles were on unreactive trajectories). Figure 3 gives a schematic illustration.

The inclusion of reaction requires a reinterpretation of the discrete lattice state $n = 0$, which, in the absence of reaction, was unambiguously interpreted as an extremely short-lived, high-energy repulsive state. Here we consider the state $n = 0$ to be one of interactive encounter on unreactive trajectories. Thus, p_0 is the (conditional) probability of finding the particles interacting *given* that they will ultimately (but rapidly) fall apart rather than attain a stable configuration on that particular encounter. For example, a particle encountering a potential barrier without sufficient energy to cross will return to the boundary layer as rapidly as if the barrier had no maximum. Therefore, with this change in interpretation, we may treat lattice state $n = 0$ exactly as in the purely repulsive case.
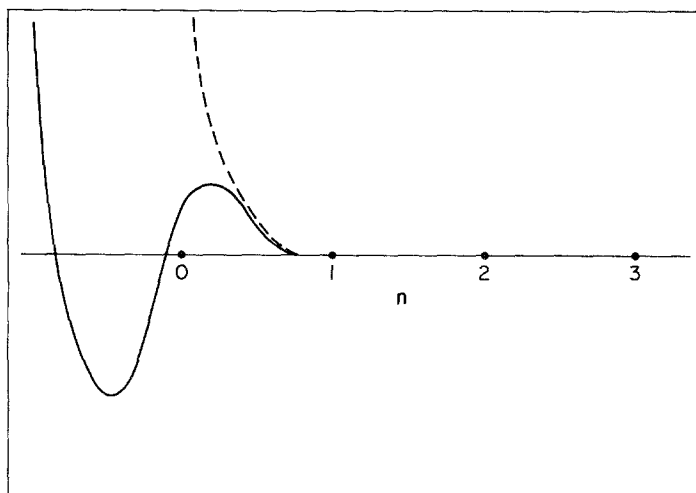

Fig. 3. Model for reversible reaction case. (—) Potential energy; (---) effective potential for nonreacting particles. The point $n = 0$ is associated with this potential (see text).

The quantity p_n is now the probability of finding the system *unreacted* in state n. We further define P_{rx} as the probability of finding the system in a reacted state accessible only via transitions from $n = 1$. With these definitions, we may write the following ME for p_1 (the only modified equation) to replace Eq. (2):

$$dp_1/dt = rp_2 - rp_1 - crp_1 + drp_0 - arp_1 + brP_{rx} \qquad (20)$$

The new terms with frequency factors a and b represent, respectively, the forward and reverse unidirectional fluxes between stable separated ($n = 1$) and stable reacted states. The quantities ar and br then have the nature of conditional phenomenological rate constants, i.e., frequencies for particles leaving one stable state and attaining another stable state on a reactive trajectory when a steady-state condition exists over the intermediate states.

The source term ME valid in the boundary layer and at ordinary lattice points is

$$dp_n/dt = rp_{n+1} + rp_{n-1} - 2rp_n + \delta_{n,1}(rp_2 - rp_1 - crp_1 + drp_0 \\ - arp_1 + brP_{rx}); \qquad n > 0 \qquad (21)$$

Equation (21) is transformed to a continuous equation in a fashion analogous to Eq. (4), with one exception. The reacted state remains as a discrete state outside the unreacted domain. The continuous equation for the reactive case is thus

$$\partial P/\partial t = L_d(\epsilon)P + \delta(x - \epsilon)[\epsilon^2 r(\partial P/\partial x)_{\epsilon_-} + \cdots - J(t) \\ - ar\epsilon P(\epsilon) + brP_{rx}]; \qquad x > 0 \qquad (22)$$

where $J(t)$ is the net unreactive particle flux given by Eq. (8).

We note that the reactive terms in Eq. (22) appear to be intrinsically orders of magnitude larger than the leading terms in the diffusion operator and the reflecting wall source term. Indeed, unless the frequency factors a and b are small, the net reactive flux $J_{rx} = ar\epsilon P(\epsilon) - brP_{rx}$ will have much the same characteristics as $J(t)$. There would be an instantaneous local equilibrium between the boundary layer and the reacted state which would cause J_{rx} to vanish on the diffusion time scale. This might correspond to the case where the potential well has a depth $O(k_B T)$ (e.g., Ar–Ar), but the reacted state would certainly not conform to the chemical idea of a stable state. For the reactive terms to survive, the frequency factors must necessarily be small. We first examine this feature for the forward reaction.

The quantity a will be $O(1)$ when reactive transitions are nearly as frequent as encounters. As noted above, however, the probability of reaction upon encounter must be small in order for reactive events to enter the dynamics explicitly on the diffusion time scale. We therefore scale the frequency factor for the forward reaction by a small dimensionless parameter

κ as $a = \alpha\kappa$. We require that $\kappa = O(\epsilon)$ for the forward reactive flux to be of the same intrinsic magnitude as other leading terms in Eq. (22). There are a number of important situations where (reaction frequency/encounter frequency) $\ll 1$. (i) An activation barrier between separated and combined molecular fragments will selectively repel low-energy particles. (ii) Due to improper angular orientation, reactions between rotationally asymmetric fragments may not always proceed.

For the reverse reaction, b must also be intrinsically small so that this reaction is sufficiently slow to enter the dynamics on the diffusion time scale. (This might correspond to the case in which the depth of the potential well is $\gg k_B T$.) However, Eq. (22) shows that dissociation rate reduction by a single order of magnitude will be insufficient for this purpose. That b must be scaled by the frequency parameter κ is clear, but, in fact, another order of magnitude is intrinsic in b. In the discrete model, br is a transition frequency from the reacted state to $n = 1$. After transformation to a continuous system, br is the transition frequency to an infinitesimal *region* of width ϵ; the frequency factor b is approximately a linear function of the region width ϵ. We introduce both scale factors for b in one definition as $b = \beta\kappa\epsilon$. The continuum-limit inhomogeneous equation is then obtained to lowest order in ϵ as

$$\frac{\partial P^{(0)}}{\partial \tau} = \frac{\partial^2 P^{(0)}}{\partial x^2} + \delta(x - \epsilon)\left[\left(\frac{\partial P^{(0)}}{\partial x}\right)_{\epsilon-} - \alpha\left(\frac{\kappa}{\epsilon}\right)P^{(0)}(\epsilon) + \beta\left(\frac{\kappa}{\epsilon}\right)P_{rx}^{(0)}\right], \quad x > 0;$$

$$P^{(0)}(0, \tau) = 0 \tag{23}$$

Naturally, the inclusion of a reaction has no effect on the BC.

Transforming Eq. (23) back to time variable t and dropping superscripts for convenience, we obtain the desired result

$$\frac{\partial P}{\partial t} = D\frac{\partial^2 P}{\partial x^2} + \delta(x - \epsilon)\left[\left(\frac{\partial P}{\partial x}\right)_{\epsilon-} - k_f P(\epsilon, t) + k_r P_{rx}(t)\right], \quad x > 0;$$

$$P(0, t) = 0 \tag{24}$$

Here the forward and reverse rate constants are $k_f = (\alpha\kappa)r\epsilon$ and $k_r = (\beta\kappa\epsilon)r$. Equation (24) may also be written solely in terms of P by eliminating P_{rx} in terms of $P(\epsilon, t)$. With the initial condition $P_{rx}(0) = 0$, the reactive flux $J_{rx}(t)$ in the source can be rewritten as

$$J_{rx}(t) = k_f P(\epsilon, t) - k_f k_r \int_0^t dt' \, P(\epsilon, t - t')e^{-k_r t'} \tag{25}$$

Our result can be readily generalized to include internal states of the reacted species. Its basic structure remains unchanged as long as time scale consistency is maintained.

4. ALTERNATE REPRESENTATIONS VIA GREEN'S FUNCTIONS

Equation (24) contains, as a consequence of short-range repulsive forces, a gradient of the probability in the source term. This particular formulation proves to be inconvenient (see below). Therefore, we consider here alternative representations.

We first introduce the Green's function G_a defined by

$$\frac{\partial G_a(x, x', t)}{\partial t} = D \frac{\partial^2 G_a}{\partial x^2} + \delta(x - x')\, \delta(t); \qquad G_a(0, x', t) = 0 \qquad (26)$$

and whose explicit form is

$$G_a(x, x', t) = (4\pi Dt)^{-1/2}[\exp(-|x - x'|^2/4Dt) - \exp(-|x + x'|^2/4Dt)] \quad (27)$$

With this function the formal solution to Eq. (24) can be written as[18,19]

$$P(x, t) = \int_0^\infty dx'\, G_a(x, x', t)P(x', 0)$$

$$+ \int_0^t dt'\, G_a(x, \epsilon, t - t')[D\, (\partial P/\partial x')_{\epsilon-} - J_{rx}](t') \qquad (28)$$

The term arising from the reflecting wall source is

$$T = \int_0^t dt'\, G_a(x, \epsilon, t - t')D(\partial P/\partial x')_{\epsilon-}(t')$$

Its presence requires evaluation of a *gradient* within the source term, rather than simple evaluation of P at a point. In addition, one would like, if possible, to have only the reactive flux as a source. This may be accomplished by eliminating T from Eq. (28) by rearranging to give a construction in terms of a new Green's function G_{rf}. (Details are given elsewhere[19]; the evaluation of the reflecting wall source term in the appropriate interval $(0, \epsilon)$ is crucial in obtaining the desired form.) Equation (28) then reduces to the basic result

$$P(x, t) = \int_0^\infty dx'\, G_{rf}(x, x', t)P(x', 0)$$

$$+ \int_0^t dt'\, G_{rf}(x, \epsilon, t - t')[-J_{rx}(t')] \qquad (29)$$

The new Green's function G_{rf} satisfies the reflecting wall BC at $x = 0$ in the limit as $\epsilon \to 0$. The effect of hard-core repulsion is now contained in G_{rf}, which describes the diffusive motion of two impenetrable particles. Equation

(29) is identically[18,19] the formal solution to the alternate inhomogeneous equation

$$\partial P(x, t)/\partial t = L_d P - \delta(x - \epsilon)J_{rx}(t), \quad x > \epsilon-; \qquad D(\partial P/\partial x)_{\epsilon-} = 0 \quad (30)$$

solved with the reflecting wall Green's function G_{rf}.[3] At a more formal level, Eq. (29) can be regarded as the solution of

$$\partial P(x, t)/\partial t = L_{r,d} P - \delta(x - \epsilon)J_{rx}(t) \tag{31}$$

with *no* imposed BC, where $L_{r,d}$ is the dynamical operator for diffusion *with short-range repulsion*. This last form is, in fact, the most convenient for analysis. For example, we show elsewhere[16] from Eq. (31) and projection operator techniques that the "closure approximation" of Wilemski and Fixman[14] is, in fact, exact for local reactive sources. Finally, we note that the solution to the equivalent Eqs. (24), (30), and (31) reduces, in the limit of reaction fast compared to diffusion, to the Smoluchowski absorbing BC solution.[13]

5. COMPARISON WITH OTHER RESULTS

While there is no treatment in the literature at the level of our derivations, we can compare some of our resulting equations with those of others. These comparisons serve to illustrate the usefulness of detailed examination of repulsive force effects, boundary layers, and time scale considerations.

Wilemski and Fixman[14] have written (without derivation) a reactive source equation of the general form

$$\partial P/\partial t = L_d P + S_{rx} \tag{32}$$

where L_d is a generalized diffusion operator and the reactive source S_{rx} vanishes in the absence of reaction. As we have seen, such an equation is acceptable (cf. Sections 2 and 4) only if L_d is understood to include a term which prevents particles from diffusing through each other.[4]

If there is no reverse reaction, our result Eq. (24) is equivalent[18,19] to the formulation utilizing the ordinary diffusion equation with the radiative BC (here in one dimension)

$$D(\partial P/\partial x)_{\epsilon+} = k_f P(\epsilon, t) \tag{33}$$

For this case (as well as for reversible reactions), we have established the location of this boundary, elucidated the time scale requirements for repulsive force effects, and emphasized the slow reaction requirement for its validity.

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[3] G_{rf} is given by Eq. (27) with plus replacing minus between the exponentials.

[4] Wilemski and Fixman do not appear to make reference to the existence of such a term, but it is accounted for in later work.[20]

In this latter connection, we note that some aspects of this requirement have been discussed by Collins and Kimball[12] and Goodrich.[21]

For the reversible reaction case, Eq. (24) is equivalent[18,19] to the problem in which the BC

$$D(\partial P/\partial x)_{\epsilon+} = k_f P(\epsilon, t) - k_r P_{rx}(t) \tag{34}$$

is imposed on the ordinary diffusion equation. A similar BC is quoted by Goodrich[21] without derivation. Equation (34) differs from the BC quoted by Schurr,[22] in which no time dependence appears in the reverse reaction term.

Monchick[23] has presented an interesting version of a radiative BC to account for the delay time in return of particles from the interaction region on unreactive trajectories. The flux across reactive surface S is written (in our notation and in one dimension) as

$$D(\partial P/\partial x)_S = \text{const} \times [P(S, t) - \kappa P(S, t - \tau)] \tag{35}$$

where κ is the fraction of particles crossing S at time $t - \tau$ which return at time t. This is similar in spirit to our treatment in the sense that it accounts for the fate of all particles entering the interaction region from points outside. An important consequence of a single finite delay time is, however, the prediction of *oscillatory* behavior in the reactive flux $J_{rx}(t)$. We disagree with this conclusion and with two features of Monchick's analysis.

First, the characteristic delay time of unreactive particles is taken to be finite on the diffusion time scale. This lifetime, however, will not be finite under ordinary circumstances, and thus should not appear in the radiative BC or corresponding source term. A second difficulty is the absence of any restriction (which we previously considered) on the magnitude of the reaction probability per encounter.

One might think that the time delay could correspond to the finite lifetime associated with a stable state in a reversible reaction. However, Eq. (35) does not have the convolution form [Eq. (25)] we have found; the true loss rate for the stable state population is of the form $k_r P_{rx}(t)$ rather than of the form $\kappa P(s, t - \tau)$ associated with a single lifetime.

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