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Diffusion with back reaction

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The diffusion equation for a constant and a linear potential is solved with boundary conditions which account for back-reaction (desorption). The solution is given in terms of Green's function, from which expressions for the survival probability are derived. Inclusion of back reaction generally results in an ultimate survival probability of unity.

I. INTRODUCTION

In the discussion of diffusion controlled reactions,[1–9] one often seeks the solution of the diffusion (Smoluchowski[3]) equation (DE) with a boundary condition (BC) that may mimic a chemical reaction. The one-dimensional DE is given by

$$\frac{\partial p}{\partial \tau} = \frac{\partial^2 p}{\partial x^2} + \beta \frac{\partial}{\partial x}\left(p \frac{\partial V}{\partial x}\right), \quad x > 0, \tag{1}$$

where $p(x, t)$ is a probability distribution function $\tau = Dt$, D a diffusion constant, t is time, $V(x)$ a potential function, and $\beta = 1/k_B T$, where k_B is Boltzmann's constant and T the absolute temperature. The flux through any point $x \geqslant 0$ is given by

$$-j = \frac{\partial p}{\partial x} + \beta \frac{\partial V}{\partial x} p. \tag{2}$$

Equation (1) can be written as the conservation condition

$$\partial p/\partial \tau = -\partial j/\partial x. \tag{3}$$

The total population is known as the "survival probability"

$$Q(\tau) \equiv \int_0^\infty p(x,\tau)dx = 1 + \int_0^\tau j(0,\tau')d\tau' \tag{4}$$

and would be smaller than unity if there is loss of population by absorption [by normalization $Q(0) = 1$]. The second equality follows from integration of Eq. (3) for $j \to 0$ at infinity. Some customary BC's at $x = 0$ are[10]:

(i) a reflecting boundary $j(0, t) = 0$ (no reaction);

(ii) an absorbing boundary, $p(0, t) = 0$ (maximal reaction rate at the boundary);

(iii) "radiation" boundary condition[1,5]

$$j(0, t) + \kappa p(0, t) = 0 \tag{5}$$

(reaction with an "intrinsic" rate constant κD). This is a partly reflecting, partly absorbing boundary. The above limits are realized when $\kappa = 0$ or $\kappa = \infty$, respectively.

Both absorption and radiation BC's neglect the back reaction (i.e., desorption or return of population into $x = 0$). Recently Weaver[8(a),8(b)] has suggested to include this effect by generalizing the above BC's.

This is a rediscovery of an earlier work by Goodrich.[8(c)] Other discussions of back-reaction BC's have appeared in the literature[8(d),8(e)], but we limit our exposition to the Goodrich–Weaver BC's. The central assumption is that the rate of desorption is proportional to the total absorbed population $1 - Q$. Hence we have

(iv) "absorption desorption" as a generalization of an absorbing boundary

$$p(0, t) = \kappa[1 - Q(t)]; \tag{6}$$

(v) "radiation desorption" as a generalization of the radiation BC:

$$j(0, t) + \kappa\{p(0, t) - \lambda[1 - Q(t)]\} = 0, \tag{7}$$

κD and $\kappa\lambda D$ are forward and reverse rate constants for transitions between $x = 0$ and the "product's sink." The BC suggested by Schurr[8(d)] is a special case of Eq. (7) when $Q(t) \ll 1$, while Eq. (6) is obtained when $j \ll \kappa$ (relaxation slower than reaction). $1 - Q$ is given by Eqs. (2) and (4).

We will solve the DE for these two newly suggested BC's and an initial distribution concentrated at $x_0 > 0$:

$$p(x,0) = \delta(x - x_0). \tag{8}$$

At infinity we demand that $p(x, t) \underset{x \to \infty}{\longrightarrow} 0$. The solution $p(x, t\,|x_0)$ is known as Green's function. The solution for any other initial distribution $p^0(x)$ is given by its integral

$$p(x, t\,|p^0) = \int_0^\infty p(x, t\,|x_0)p^0(x_0)dx_0. \tag{9}$$

The DE with BC's (6) and (7) has been solved[8(a),8(c)] only for free diffusion with a uniform initial distribution. We will give the general solution (in terms of Green's functions) of five problems: Free diffusion ($V = 0$) with BC's (6) and (7), diffusion in a constant field (linear potential) with BC's (5) and (6), and spherical symmetric free diffusion in three dimensions for BC (6).

II. GENERAL

The general solution in one dimension for $V = 0$ starts with the observation that for $\kappa = 0$ in Eqs. (6) and (7), we have a pure absorbing or reflecting barrier for which the answer is known.[1,2] This solution we denote by $f(x, t\,|x_0)$. For $\kappa > 0$ we try the general form

$$p(x, t\,|x_0) = f(x, t\,|x_0) + \kappa g(x, t). \tag{10}$$

Since f accounts for the whole initial population $g(x,0) = 0$. This makes the application of the Laplace transform method[1,2] convenient

$$\tilde{g}(x, s) = \int_0^\infty g(x,\tau)e^{-s\tau}\, d\tau, \quad s > 0, \tag{11}$$

[a)] Bat-Sheva de Rothschild Fellow for 1983.

$\bar{g}(x, s)$ obeys the DE which is transformed to

$$s\bar{g} = \partial^2\bar{g}/\partial x^2. \tag{12}$$

Its solution is

$$\bar{g}(x, s) = A(s)\exp(-x\sqrt{s}). \tag{13}$$

The negative sign was chosen to insure that $\bar{g}(x, s) \to 0$ as $x \to \infty$. $A(s)$ is now determined from the BC at $x = 0$. The more complicated cases would be first reduced to a one-dimensional free diffusion problem.

III. FREE DIFFUSION $V(x) = 0$

(i) Absorption desorption BC (6). The limit $\kappa = 0$ is an absorbing barrier for which[1–4]

$$f(x,\tau|x_0) = (4\pi\tau)^{-1/2}\{\exp[-(x-x_0)^2/4\tau] - \exp[-(x+x_0)^2/4\tau]\}, \tag{14}$$

$$\left.\frac{\partial f}{\partial x}\right|_{x=0} = x_0(4\pi\tau^3)^{-1/2}\exp(-x_0^2/4\tau). \tag{15}$$

Since $f(0,\tau) = 0$, Eq. (6) is transformed to

$$A(s) = \bar{g}(0, s) = s^{-1}\left.\left\{\overline{\frac{\partial f}{\partial x}} + \kappa\frac{\partial \bar{g}}{\partial x}\right\}\right|_{x=0} = s^{-1}[\exp(-x_0\sqrt{s}) - \kappa\sqrt{s}A(s)]. \tag{16}$$

Hence

$$\bar{g}(x, s) = \exp[-(x+x_0)\sqrt{s}]/[\sqrt{s}(\sqrt{s}+\kappa)] \tag{17}$$

which gives by the inverse transform[11]

$$g(x,\tau) = \exp[\kappa(x + x_0 + \kappa\tau)]\operatorname{erfc}[(x + x_0 + 2\kappa\tau)/2\sqrt{\tau}], \tag{18}$$

$$\operatorname{erfc}(y) = 2\pi^{-1/2}\int_y^\infty e^{-x^2}\,dx = 1 - \operatorname{erf}(y) \tag{19}$$

is the complementary error function.

The survival probability $Q(\tau|x_0)$ can be deduced directly from Eq. (6):

$$Q(\tau|x_0) = 1 - g(0,\tau) = 1 - \exp[\kappa(x_0 + \kappa\tau)]\operatorname{erfc}[(x_0 + 2\kappa\tau)/2\sqrt{\tau}] \tag{20}$$

as can be also verified by direct integration of $p(x,\tau|x_0)$.[12]

Since the DE for $V(x) = 0$ is self-adjoint, its solutions are symmetric in x and x_0, so that Eq. (20) with x_0 replaced by x is also the solution $p(x,\tau)$ for a uniform initial distribution, as obtained by Weaver.[8(a)] [Note, though, that a uniform distribution contradicts the BC (6) at $t = 0$, resulting in a nonphysical solution for short times.[8(a)]]

The limit $\kappa = 0$ in Eq. (20) gives the known[1–4] expression for the survival probability for a pure absorbing boundary

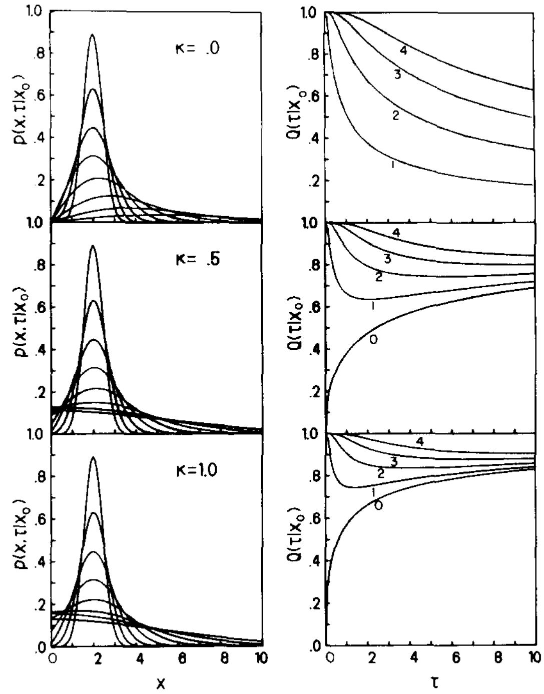

FIG. 1. Free diffusion with an absorption–desorption boundary condition [Eq. (6)] for (top to bottom) increasing amounts of desorption (κ). Left panels show the time development of the probability distribution [Eqs. (10), (14), and (18)] for $x_0 = 2$ and (in the order of decreasing peaks) $\tau = 0.1, 0.2, 0.4, 0.8, 1.6, 3.2, 6.4$, and 12.8. Right panels show the time dependence of the survival probability [Eq. (20)] for various values of x_0 (each curve is marked by the appropriate value). For the upper panel $Q(\tau|0) = 0$.

$$Q(\tau|x_0) = \operatorname{erf}(x_0/2\sqrt{\tau}). \tag{21}$$

This is so in spite of the fact that the function $g(x,\tau)$ in Eq. (20) does not appear at all in the solution for an absorbing barrier [$\kappa = 0$ in Eq. (10)].

The solution is demonstrated in Fig. 1. When $\kappa = 0$ the population decays to zero, $Q \to 0$ as $\tau \to \infty$ [cf. Eq. (21)]. When $\kappa > 0$ however, after some initial decay the absorbed population returns from the "sink" and builds up again. In this case [cf. Eq. (20)] $Q \to 1$ as $\tau \to \infty$.[13]

(ii) Radiation desorption [Eq. (7)]. The limit $\kappa = 0$ is a reflecting boundary, for which[1–4]

$$f(x,\tau|x_0) = (4\pi\tau)^{-1/2}\{\exp[-(x-x_0)^2/4\tau] + \exp[-(x+x_0)^2/4\tau]\} \tag{22}$$

since $\partial f/\partial x = 0$ at $x = 0$, Eq. (7) is transformed to

$$\left(1 + \frac{\kappa\lambda}{s}\right)\left.\frac{\partial\bar{g}}{\partial x}\right|_{x=0} = s^{-1/2}\exp(-x_0\sqrt{s}) + \kappa\bar{g}(0, s). \tag{23}$$

We can present Eq. (23) as known Laplace transforms when $s + \kappa\sqrt{s} + \kappa\lambda$ has real roots. Then

$$A(s)[\sqrt{s} + (\kappa - \Delta)/2][\sqrt{s} + (\kappa + \Delta)/2] = -\exp(-x_0\sqrt{s}), \tag{24}$$

where $\Delta^2 \equiv \kappa^2 - 4\kappa\lambda$. Hence[11] for Δ real and positive

$$\bar{g}(x, s) = \Delta^{-1}\exp[-(x+x_0)\sqrt{s}]\{[\sqrt{s} + (\kappa+\Delta)/2]^{-1} - [\sqrt{s} + (\kappa-\Delta)/2]^{-1}\}, \tag{25}$$

$$g(x,\tau) = -\frac{\kappa+\Delta}{2\Delta}\exp\left[\frac{\kappa+\Delta}{2}\left(x+x_0+\frac{\kappa+\Delta}{2}\tau\right)\right]\operatorname{erfc}\left[\frac{x+x_0+(\kappa+\Delta)\tau}{2\sqrt{\tau}}\right] + \frac{\kappa-\Delta}{2\Delta}\exp\left[\frac{\kappa-\Delta}{2}\left(x+x_0+\frac{\kappa-\Delta}{2}\tau\right)\right]\operatorname{erfc}\left[\frac{x+x_0+(\kappa-\Delta)\tau}{2\sqrt{\tau}}\right]. \tag{26}$$

In the special case that $\lambda = 0$, $\Delta = \kappa$, and Eq. (26) reduces to the solution with the radiation BC[1,5]

$$g(x,\tau) = -\exp[\kappa(x+x_0+\kappa\tau)]\operatorname{erfc}\left(\frac{x+x_0+2\kappa\tau}{2\sqrt{\tau}}\right). \tag{27}$$

For $\kappa = 4\lambda$ Eq. (26) is inadequate. We therefore proceed[11] directly from Eq. (24):

$$g(x,\tau) = \kappa\left(\frac{\tau}{\pi}\right)^{1/2}\exp\left[-\frac{(x+x_0)^2}{4\tau}\right] - \tfrac{1}{2}[2+\kappa(x+x_0)+\kappa^2\tau]\exp\left[\frac{\kappa}{2}\left(x+x_0+\frac{\kappa}{2}\tau\right)\right]\operatorname{erfc}\left(\frac{x+x_0+\kappa\tau}{2\sqrt{\tau}}\right). \tag{26'}$$

Unfortunately, we do not know how to write the solution for $\kappa < 4\lambda$.

To calculate the survival probability one can use Eqs. (7) and (26) to derive (for $\Delta > 0$):

$$\begin{aligned}Q(\tau|x_0) &= 1 + \lambda^{-1}\left[\left.\frac{\partial g}{\partial x}\right|_{x=0} - f(0,\tau|x_0) - \kappa g(0,\tau)\right]\\ &= 1 + \frac{\kappa}{\Delta}\left\{\exp\left[\frac{\kappa+\Delta}{2}\left(x_0+\frac{\kappa+\Delta}{2}\tau\right)\right]\operatorname{erfc}\left[\frac{x_0+(\kappa+\Delta)\tau}{2\sqrt{\tau}}\right] - \exp\left[\frac{\kappa-\Delta}{2}\left(x_0+\frac{\kappa-\Delta}{2}\tau\right)\right]\operatorname{erfc}\left[\frac{x_0+(\kappa-\Delta)\tau}{2\sqrt{\tau}}\right]\right\}\end{aligned} \tag{28}$$

which can be verified by direct integration.[12] For $\Delta = \kappa$ it reduces again to the known[1,5] result for a radiation BC:

$$Q(\tau|x_0) = \operatorname{erf}\left(\frac{x_0}{2\sqrt{\tau}}\right) + \exp[\kappa(x_0+\kappa\tau)]\operatorname{erfc}\left(\frac{x_0+2\kappa\tau}{2\sqrt{\tau}}\right). \tag{29}$$

Replacement of x_0 by x in Eq. (28) gives the solution $p(x,\tau)$ for a uniform initial distribution, as obtained by Goodrich[8(c)]. For the special case $\kappa = 4\lambda$ we have [cf. Eq. (26')]:

$$Q(\tau|x_0) = 1 - 2\kappa\left(\frac{\tau}{\pi}\right)^{1/2}\exp\left(\frac{-x_0^2}{4\tau}\right) + \kappa(x_0+\kappa\tau)\exp\left[\frac{\kappa}{2}\left(x_0+\frac{\kappa}{2}\tau\right)\right]\operatorname{erfc}\left(\frac{x_0+\kappa\tau}{2\sqrt{\tau}}\right). \tag{28'}$$

The solution is demonstrated in Fig. 2. Again, $Q \xrightarrow[\tau\to\infty]{} 0$ for $\lambda = 0$ and $Q \xrightarrow[\tau\to\infty]{} 1$ for $\lambda > 0$.

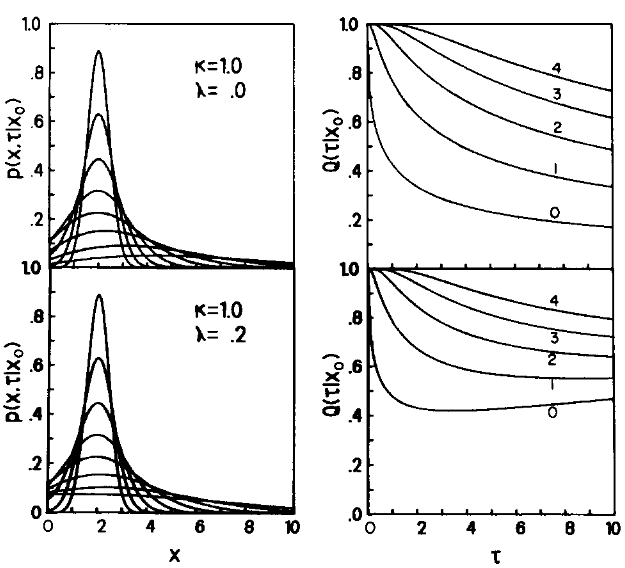

FIG. 2. Free diffusion with a radiation–desorption boundary condition [Eq. (7)] for (top to bottom) increasing desorption (λ). Left panels show the time development of the probability distribution [Eqs. (10), (22), and (26)]. Right panels show the survival probability [Eq. (28)]. Other details are the same as in Fig. 1.

IV. DIFFUSION IN A CONSTANT FIELD

We solve the one-dimensional DE for a linear potential

$$\frac{\partial p}{\partial \tau} = \frac{\partial^2 p}{\partial x^2} + 2c\frac{\partial p}{\partial x}, \quad x > 0, \tag{30}$$

$$p \to 0 \text{ as } x \to \infty, \quad p = \delta(x-x_0) \text{ at } \tau = 0, \quad x_0 > 0 \tag{31}$$

with the above BC's at $x = 0$. This may describe adsorption of particles moving under the influence of a gravitational field[4] or the motion of electrons in amorphous insulators under the influence of an electric field and ultimate recombination with holes at the electrode.[7]

We first note[4] that the function q defined by

$$q(x,\tau|x_0) = p(x,\tau|x_0)\exp[c(x-x_0+c\tau)] \tag{32}$$

obeys the zero field $[V(x) = 0]$ DE with the properly transformed BC's discussed below.

(i) Absorption desorption. Since $-j = \partial p/\partial x + 2cp$, Eq. (6) becomes

$$qe^{-c^2\tau} = \kappa\int_0^\tau (\partial q/\partial x + cq)e^{-c^2\tau'}d\tau', \quad \text{at } x = 0. \tag{33}$$

The BC for the Laplace transform is therefore

$$\bar{q} = \frac{\kappa}{s - c^2}\left(\frac{\partial \bar{q}}{\partial x} + c\bar{q}\right), \quad \text{at } x = 0. \tag{34}$$

We set, as in Eq. (10),

$$q = f + \kappa g \tag{35}$$

with f given by Eq. (14), $f(0,\tau) = 0$. Hence we have for $A(s)$ [cf. Eq. (13)]:

$$A(s)(\sqrt{s} - c)(\sqrt{s} + \kappa + c) = \exp(-x_0\sqrt{s}). \tag{36}$$

This is in the same form as Eq. (24), so the solution for g resembles Eq. (26):

$$(\kappa + 2c)\, g(x,\tau) = (\kappa + c)\exp[(\kappa + c)(x + x_0) + (\kappa + c)^2\tau] \times \operatorname{erfc}\left[\frac{x + x_0 + 2(\kappa + c)\tau}{2\sqrt{\tau}}\right] + c\exp[-c(x + x_0) + c^2\tau]\operatorname{erfc}\left(\frac{x + x_0 - 2c\tau}{2\sqrt{\tau}}\right). \tag{37}$$

The solution (37) is well defined even when $\kappa = -2c$, since then g is minus that of Eq. (26′). For $c = 0$ (and $c = -\kappa$), Eq. (37) reduces to the previously derived result [Eq. (18)]. For $\kappa = 0$ we get the solution for an absorbing BC, $p = f\exp[-c(x - x_0 + c\tau)]$.

Again, we can deduce the survival probability from Eqs. (6) and (37):

$$Q(\tau|x_0) = 1 - g(0,\tau)\exp(cx_0 - c^2\tau)$$
$$= 1 - \frac{\kappa + c}{\kappa + 2c}\exp[(\kappa + 2c)(x_0 + \kappa\tau)]\operatorname{erfc}\left[\frac{x_0 + 2(\kappa + c)\tau}{2\sqrt{\tau}}\right] - \frac{c}{\kappa + 2c}\operatorname{erfc}\left(\frac{x_0 - 2c\tau}{2\sqrt{\tau}}\right). \tag{38}$$

In the special case that $c = -\kappa/2$ one has instead of Eq. (38),

$$Q(\tau|x_0) = 1 - \kappa\left(\frac{\tau}{\pi}\right)^{1/2}\exp\left[-\left(\frac{x_0 - \kappa\tau}{2\sqrt{\tau}}\right)^2\right] + \tfrac{1}{2}(2 + \kappa x_0 + \kappa^2\tau)\exp(\kappa x_0)\operatorname{erfc}\left(\frac{x_0 + \kappa\tau}{2\sqrt{\tau}}\right). \tag{39}$$

For $\kappa = 0$ (absorbing BC) Eq. (38) reduces to

$$Q(\tau|x_0) = \frac{1}{2}\left[\operatorname{erfc}\left(\frac{-x_0 + 2c\tau}{2\sqrt{\tau}}\right) - \exp(2cx_0)\operatorname{erfc}\left(\frac{x_0 + 2c\tau}{2\sqrt{\tau}}\right)\right]. \tag{40}$$

Therefore, for $\kappa = 0$, $Q \underset{\tau\to\infty}{\longrightarrow} 0$ for $c \geqslant 0$, and $Q \to 1 - \exp(2cx_0)$ for $c < 0$ (motion *away* from the absorbing boundary).

This situation changes when $\kappa > 0$. For $\kappa > 0$ and $c \leqslant 0$, $Q \to 1$ as $\tau \to \infty$ and all the population ultimately escapes to infinity. However, for $c > 0$ (motion *towards* the origin) there is a steady-state distribution

$$p^{\mathrm{ss}}(x) \equiv \lim_{\tau\to\infty} p(x,\tau|x_0) = \frac{2\kappa c}{\kappa + 2c}\exp(-2cx) \tag{41}$$

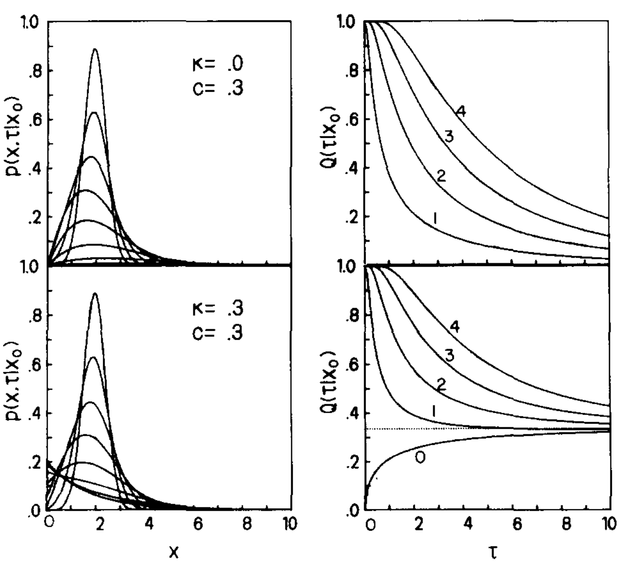

FIG. 3. Diffusion in a constant force field (directed towards the origin) [Eq. (30)] with an absorption–desorption boundary condition [Eq. (6)]. Left panels demonstrate Eqs. (32), (35), (14), and (37). Right panels demonstrate Eq. (38). In the upper panel $Q(\tau|0) = 0$. In the lower panel the dotted lines are the steady state solutions (41) and (42). Other details are the same as in Fig. 1.

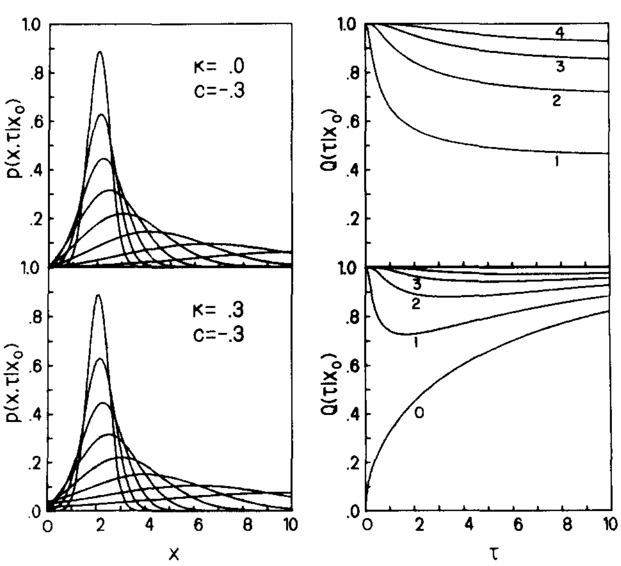

FIG. 4. Diffusion in a constant force field (directed away from the origin $c < 0$) [Eq. (30)] with an absorption–desorption boundary condition [Eq. (6)]. Other details are the same as in Figs. 1 and 3 (except that there is no steady-state solution).

and an ultimate survival probability

$$Q(\infty|x_0)=\int_0^\infty p^{ss}(x)dx=\kappa/(\kappa+2c). \tag{42}$$

The solutions for positive and negative values of c are demonstrated in Figs. 3 and 4, respectively.

(ii) Radiation–desorption. Equation (7) becomes

$$\left[\frac{\partial q}{\partial x}+(c-\kappa)q\right]e^{-c^2\tau}=-\kappa\lambda\int_0^\tau\left(\frac{\partial q}{\partial x}+cq\right)e^{-c^2\tau'}d\tau',$$

at $x=0$. (43)

The BC for the Laplace transform is therefore

$$[(c-\kappa)(s-c^2)+c\kappa\lambda]\bar{q}=-(s-c^2+\kappa\lambda)\partial\bar{q}/\partial x,$$

at $x=0$ (44)

when we try for q a solution of the type (35), with f given by Eq. (22), $\partial f/\partial x=0$ at $x=0$, we find for $A(s)$:

$$\kappa[(c-\kappa)(s-c^2)+c\kappa\lambda-(s-c^2+\kappa\lambda)\sqrt{s}]\sqrt{s}A(s)$$

$$=-[(c-\kappa)(s-c^2)+c\kappa\lambda]\exp(-x_0\sqrt{s}). \tag{45}$$

Equation (45) is too complicated to invert and find $g(x,\tau)$ analytically.

(iii) Although not related to the topic of "back reaction," the present methods can be used for the simpler, "radiation" BC ($\lambda=0$), where one has

$$\partial q/\partial x=(\kappa-c)q,\quad \text{at } x=0. \tag{46}$$

Hence for

$$q=f+(\kappa-c)g \tag{47}$$

with f of Eq. (22) one has [cf. Eq. (27)]

$$g(x,\tau)=-\exp[(\kappa-c)(x+x_0)+(\kappa-c)^2\tau]\times\operatorname{erfc}\left[\frac{x+x_0+2(\kappa-c)\tau}{2\sqrt{\tau}}\right]. \tag{48}$$

For $\kappa=0$ this reduces to the known solution[4] for a reflecting barrier (and p tends to an equilibrium distribution as $\tau\to\infty$). For $\kappa>0$, $c=0$, it becomes the solution (27) for a radiation BC. By direct integration[12]

$$Q(\tau|x_0)=\int_0^\infty q(x,\tau|x_0)\exp[-c(x-x_0+c\tau)]dx$$
$$=\frac{\kappa-c}{\kappa-2c}\exp[\kappa x_0+\kappa(\kappa-2c)\tau]\operatorname{erfc}\left[\frac{x_0+2(\kappa-c)\tau}{2\sqrt{\tau}}\right]$$
$$+\frac{1}{2}\left[\operatorname{erfc}\left(\frac{-x_0+2c\tau}{2\sqrt{\tau}}\right)-\frac{\kappa}{\kappa-2c}\exp(2cx_0)\operatorname{erfc}\left(\frac{x_0+2c\tau}{2\sqrt{\tau}}\right)\right]. \tag{49}$$

This solution is well defined even for $\kappa=2c$, when

$$Q(\tau|x_0)=\frac{1}{2}\left[\operatorname{erfc}\left(\frac{-x_0+\kappa\tau}{2\sqrt{\tau}}\right)+(1+\kappa x_0+\kappa^2\tau)\exp(\kappa x_0)\operatorname{erfc}\left(\frac{x_0+\kappa\tau}{2\sqrt{\tau}}\right)\right]-\kappa\left(\frac{\tau}{\pi}\right)^{1/2}\exp\left[-\left(\frac{x_0-\kappa\tau}{2\sqrt{\tau}}\right)^2\right]. \tag{50}$$

For $\kappa=0$, $Q=1$ as should be for a purely reflecting boundary. For $\kappa>0$ and $c\geqslant0$, $Q\to0$ as $\tau\to\infty$. For $\kappa>0$ and $c<0$ (motion *away* from the partially absorbing origin) there is an ultimate survival probability

$$Q(\infty|x_0)=1-\frac{\kappa}{\kappa-2c}\exp(2cx_0). \tag{51}$$

These solutions are demonstrated in Fig. 5.

V. FREE DIFFUSION IN THREE DIMENSIONS

We solve the DE for a three dimensional system with spherical symmetry[10]

$$\frac{\partial p}{\partial\tau}=\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial p}{\partial r}\right),\quad r>R \tag{52}$$

for a spherical source initial condition

$$4\pi r_0^2\,p(r,0)=\delta(r-r_0),\quad r_0>R \tag{53}$$

and an absorption–desorption BC

$$4\pi R^2p(R,\tau|r_0)=\kappa(1-Q)=4\pi R^2\kappa\int_0^\tau\left.\frac{\partial p}{\partial r}\right|_{r=R}d\tau'. \tag{54}$$

This may correspond to geminate recombination of an isolated radical pair in solution.[9] Here the survival probability is defined by

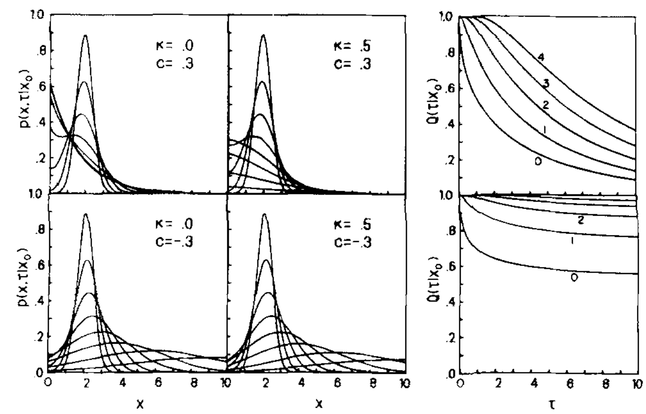

FIG. 5. Diffusion in a constant force field [Eq. (30)] with a radiation–desorption boundary condition [Eq. (7)]. In the upper panels the force field is directed *towards* and in the lower panel *away* from the origin (positive and negative values of c, respectively). For $\kappa=0$ (left panels) we have a reflecting boundary at $x=0$; so that $Q=1$. For $\kappa=0.5$, the central and right panels demonstrate the solutions for the probability distribution [Eqs. (32), (35), (22), and (48)] and the survival probability [Eq. (49)], respectively. Other details are the same as in Fig. 1.

$$Q(\tau|r_0) = 4\pi \int_R^\infty r^2 p(r,\tau|r_0) dr \qquad (55)$$

and $p(r,\tau|r_0) \to 0$ faster than r^2 for $r \to \infty$. Defining[1,2]

$$w(r,\tau|r_0) \equiv 4\pi r_0\, r p(r,\tau|r_0) \qquad (56)$$

reduces Eq. (52) to a one dimensional DE

$$\partial w/\partial \tau = \partial^2 w/\partial r^2, \quad r > R,$$

$$w(r,0) = \delta(r - r_0), \quad w(r,\tau|r_0) \underset{r\to\infty}{\to} 0 \qquad (57)$$

with the BC at R,

$$w = \kappa \int_0^\tau (\partial w/\partial r - w/R) d\tau', \quad \text{at } r = R. \qquad (58)$$

As before, we try a solution of the type

$$w = f + \kappa g. \qquad (59)$$

Setting $x \equiv r - R$ and $x_0 \equiv r_0 - R$, we find that f and its derivative are given by Eqs. (14) and (15), and $\bar{g}$ by Eq. (13) with

$$A(s)[\sqrt{s} + (\kappa - \Delta)/2][\sqrt{s} + (\kappa + \Delta)/2] = \exp[-(r_0 - 2R)\sqrt{s}], \qquad (60)$$

$$\Delta^2 \equiv \kappa(\kappa - 4/R). \qquad (61)$$

This again limits this solution to $\kappa = 0$ or $\kappa \geqslant 4/R$. The solution for g is [cf. Eq. (26)] given in terms of $y \equiv x + x_0 = r + r_0 - 2R$:

$$g(r,\tau) = (2\Delta)^{-1}\left\{(\kappa+\Delta)\exp\left[\frac{\kappa+\Delta}{2}\left(y + \frac{\kappa+\Delta}{2}\tau\right)\right]\operatorname{erfc}\left[\frac{y + (\kappa+\Delta)\tau}{2\sqrt{\tau}}\right] - (\kappa-\Delta)\exp\left[\frac{\kappa-\Delta}{2}\left(y + \frac{\kappa-\Delta}{2}\tau\right)\right]\operatorname{erfc}\left[\frac{y + (\kappa-\Delta)\tau}{2\sqrt{\tau}}\right]\right\}. \qquad (62)$$

For the special case $\kappa = 4/R$ we have [cf. Eq. (26')]

$$g(r,\tau) = -\kappa\left(\frac{\tau}{\pi}\right)^{1/2}\exp\left(\frac{-y^2}{4\tau}\right) + \tfrac{1}{2}(2 + \kappa y + \kappa^2\tau)\exp\left[\frac{\kappa}{2}\left(y + \frac{\kappa}{2}\tau\right)\right]\operatorname{erfc}\left(\frac{y + \kappa\tau}{2\sqrt{\tau}}\right). \qquad (62')$$

From Eq. (54) we find for the survival probability

$$Q(\tau|r_0) = 1 - \frac{R}{r_0} g(R,\tau) \qquad (63)$$

which, in the special case $\kappa = 0$, reduces to the known result[1–4] for an absorbing boundary

$$Q(\tau|r_0) = 1 - \frac{R}{r_0}\operatorname{erfc}\left(\frac{r_0 - R}{2\sqrt{\tau}}\right). \qquad (64)$$

By symmetry in r_0 and r, Eq. (63) with r_0 replaced by r gives the distribution function for a uniform initial distribution.

As in the one-dimensional case, the inclusion of back reaction alters the ultimate survival probability. In this case for $\kappa = 0$, $Q(\infty|r_0) = 1 - R/r_0$, whereas for $\kappa \geqslant 4/R > 0$, $Q(\infty|r_0) = 1$. The solution is demonstrated in Fig. 6.

VI. DISCUSSION

The boundary conditions suggested[8] for representing back reactions [Eqs. (6) and (7)] seem at first quite complicated. Therefore, a full solution in terms of Green's functions, which give the solution for arbitrary initial conditions, has not been previously attempted. We have demonstrated in this work that, using the Laplace transform technique, an analytic solution can be obtained for simple potentials (zero or linear) for "open" systems (space available for diffusion not restricted by an additional boundary condition). Even in these simple examples, the mathematics becomes quite tedious and the solution obtained is in two cases restricted to a certain range of the parameters [real Δ in Eqs. (26) and (62)].

The physical interpretation of our mathematical results may seem, at first, puzzling. Having introduced back reaction, one expects that any reactive diffusional process would tend to equilibrium between forward and backward reactions. What we notice is that, for free diffusion in the absence of back reaction, an initial delta-function distribution results

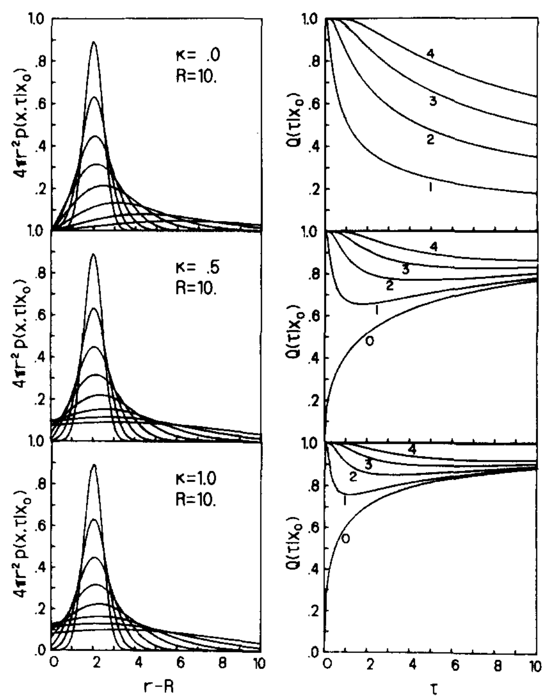

FIG. 6. Spherical symmetric free diffusion in three dimensions [Eq. (52)] with an absorption–desorption boundary condition [Eq. (54)] for (top to bottom) increasing desorption (κ). Left panels demonstrate Eqs. (56), (59), (14), and (62). Right panels demonstrate Eqs. (63) and (62). Other details are the same as in Fig. 1.

in an ultimate survival probability which is smaller than unity. When back reaction is introduced, the survival probability always ultimately tends to unity. The population returns eventually from the sink and escapes to infinity.

This result is physically perfectly sound. Consider, e.g., geminate recombination of radicals.[9] If we deal with an ensemble of isolated pairs in an infinite diffusion space, the two particles would eventually separate forever. This fate could be different if the space is made finite or the geminate pair not completely isolated. If one adds a reflective boundary condition or the potential tends to infinity with increasing x, we expect a steady state situation to prevail at long times [e.g., Eq. (41)]. If the geminate pair is immersed in a solution of identical radicals, homogeneous recombination[9] would eventually replace geminate recombination. In this case, back reaction simply ensures that, after a long time, no molecule is bound to its original geminate partner. Therefore, the isolated pair limit (which we have dealt with) is applicable for small concentrations or short times.

Our results can also be used to describe the equilibrium situation which pertains in homogeneous recombination.[9] In this case one solves the steady-state (time independent) DE for a distribution function which tends to its zero-reaction equilibrium value at infinity. For free diffusion, such a solution equals the infinite time limit of the solution we have obtained with an initial uniform distribution.

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[10] In one dimension we can take the left boundary at $x=0$ without loss of generality. Replacing zero by some $a \neq 0$ is equivalent to replacement of x by $x-a$, and x_0 by x_0-a. This is no longer true for spherical symmetric problems in higher dimensions, since it corresponds to a reduction in the dimensionality of the reactive sphere.
[11] For a table of relevant Laplace transforms, see, for example, Appendix V in Ref. 1.
[12] Use $\int_{y_0}^{\infty} \exp(ay)\,\mathrm{erfc}\,(y)\,dy = a^{-1}\{-\exp(ay_0)\,\mathrm{erfc}\,(y_0) + \exp(a^2/4)\,\mathrm{erfc}\,[y_0-(a/2)]\}$.
[13] $\exp(y)\,\mathrm{erfc}\,(\sqrt{y}) \to 0$ as $y \to \infty$.