Viscosity expansions in reactive diffusion processes

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Viscosity expansions in reactive diffusion processes

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Properties of chemical reactions in systems undergoing diffusional motion depend on the ratio of chemical to diffusional rates. The present work deals with perturbation expansions in this quantity. For bounded diffusion, the Laplace transformed survival probability, mean lifetime, eigenvalues, and eigenfunctions are expanded in this ratio. The theory is developed mainly in the fast diffusion limit. In this limit, the survival probability for an initial equilibrium state is shown to be exponential up to *linear* order. For unbounded diffusion, expansions are derived for the steady-state concentration profile and rate coefficient. By inverting the series one obtains Padé-like approximations for rate coefficients with much improved convergence. Several examples are worked out in detail. These include the "radiation" boundary condition, barrierless isomerization, steady-state binding, and Förster quenching.

I. INTRODUCTION

Diffusion influenced reactions[1] are often described by a diffusion equation in a potential field and with a reaction term (Smoluchowski's equation[2]). The simplest reaction terms are boundary conditions. For example, in treating recombination of neutral or charged particles[1-5] or "contact" quenching processes,[6] one introduces an absorbing[2] or partly absorbing ("radiation")[3] boundary condition which mimics the recombination or quenching process of two particles at contact.

A partially absorbing boundary is equivalent to a finite strength, delta function sink located at the boundary.[7] More generally, the sink need not coincide with the boundary.[8] For example, the photophysics of barrierless isomerization in solution has been described by a delta function ("pin hole") sink located at the minimum of a parabolic potential.[9] In the presence of a potential barrier, the isomerization rate is determined by the height of the barrier separating the two wells.[10] The predicted viscosity dependence of the reaction rate has been extensively investigated.[11]

The most general reaction term involves a coordinate-dependent rate coefficient, $k(x)$.[1,7,9,12-19] Indeed, several diffusion-influenced reactions have distance-dependent reactivities. Some examples are Förster quenching,[1,6,18,19] excitation transfer in polymers,[12] electron transfer in proteins[13(a)] or in solution[14] and ligand binding to heme proteins.[13(b)]

In most cases, the relevant diffusion equation cannot be solved analytically. Simple solutions can sometimes be obtained in the limit of reaction which is much faster or much slower compared to diffusion.[7,12-17] These can be expressed in terms of κ/D, where κ and D are proportional to the rate and diffusion coefficients, respectively. For a strictly coordinate-dependent reaction term, an expansion in terms of the slowness of reaction[16] is not identical to an expansion in $\eta \equiv 1/D$, though the two are related. The present paper in-

vestigates the dependence of the solutions on the "viscosity" η. This is closer to actual experimental situations.[11 (a)]

Consider the probability density $\langle p(x,t) \rangle$ for observing a value x of the coordinate at time t, the initial distribution being $p^0(x)$.[7,13] When $D = 0$, the x motion is frozen and each x reacts independently with a rate coefficient $k(x)$

$$\langle p(x,t) \rangle = p^0(x)\exp[-k(x)t]. \tag{1.1a}$$

In the opposite extreme, $D = \infty$, for a "bounded" system (which admits an equilibrium solution), the initial distribution relaxes infinitely fast to the equilibrium distribution, $p^{eq}(x)$, as do any "holes" created in this distribution by $k(x)$. The solution becomes[7]

$$\langle p(x,t) \rangle = p^{eq}(x)\exp[-\langle k \rangle_{eq} t] \tag{1.1b}$$

independently of p^0. Averages with respect to $p^0(x)$ and $p^{eq}(x)$ are denoted by $\langle \cdots \rangle$ and $\langle \cdots \rangle_{eq}$, respectively. The alternate procedure of expanding in the reaction rate gives $\langle p(x,t) \rangle = 0$ or $p^0(x)$ for infinitely fast or slow reactivity.

The survival probability, $\langle Q(t) \rangle$, which is the probability that the system is unreacted by time t, is obtained as the spatial integral of $\langle p(x,t) \rangle$. It follows that $\langle Q(t) \rangle$ is multiexponential when diffusion is comparatively slow and exponential in the limit of fast diffusion. In the latter case the exponent, which is the lowest eigenvalue (λ_0) of the diffusion operator, is equal to the averaged rate, $\langle k \rangle_{eq}$. The mean lifetime $\langle \tau \rangle$ namely, the temporal integral of the survival probability,[20] is given in the same two limits by

$$\langle \tau \rangle = \langle k^{-1} \rangle \quad \text{for } D = 0, \tag{1.2a}$$

$$\langle \tau \rangle = \langle k \rangle_{eq}^{-1} \quad \text{for } D = \infty. \tag{1.2b}$$

Interpolating between the limits of zero and infinite diffusivity is difficult.[13] The goal of obtaining complete asymptotic expansions (hereby termed "viscosity expansions"), rather than just a leading term, is usually simpler for small η. The small D limit leads in many cases to a singular perturbation problem which is difficult to treat.

The present work suggests a simple perturbation method for obtaining the small η expansions in a systematic way. It is shown below that in this limit Eqs. (1.1b) and (1.2b)

are valid even for the next term in the expansion, provided that the initial distribution is the equilibrium distribution. For bounded diffusion, expansions are derived for the eigenvalues, eigenfunctions, Laplace-transformed survival probability and average lifetime. For processes admitting only a steady-state solution, viscosity expansions are useful in evaluating the steady-state concentration profile and rate constant. Even these one-sided expansions give rise to Padé approximations with extended convergence range. The above is demonstrated for some interesting physical systems such as barrierless isomerization, recombination and Förster quenching.

II. GENERAL DEFINITIONS

Consider, for simplicity, the spherical-symmetric Smoluchowski equation[2] for diffusion in a potential field $V(x)$, with a coordinate dependent rate coefficient $k(x)$ in d dimensions.

$$\frac{\partial p(y,t\,|x)}{\partial t} = D\mathscr{L}p - k(y)p$$

$$= Dy^{1-d}\frac{\partial}{\partial y}y^{d-1}e^{-V(y)}\frac{\partial}{\partial y}e^{V(y)}p(y,t\,|x)$$

$$\qquad - k(y)p(y,t\,|x), \qquad (2.1a)$$

$$\frac{\partial p(y,t\,|x)}{\partial t} = D\mathscr{L}^\dagger p - k(x)p$$

$$= Dx^{1-d}e^{V(x)}\frac{\partial}{\partial x}x^{d-1}e^{-V(x)}\frac{\partial p(y,t\,|x)}{\partial x}$$

$$\qquad - k(x)p(y,t\,|x). \qquad (2.1b)$$

It describes the time (t) evolution of the probability density (p) for transitions from x to y. The diffusion operator $\mathscr{L}$ in the "forward" equation (2.1a) involves the final variable y, while its adjoint, $\mathscr{L}^\dagger$, in the "backward" equation (2.1b) operates on functions of the initial variable x. The potential $V(x)$ is in units of $k_B T$, where k_B is Boltzmann's constant and T the absolute temperature. The diffusion coefficient D may be coordinate dependent, in which case D is a scaling factor. The infinitesimal volume element in d dimensions is $\gamma x^{d-1}\,dx$, with $\gamma = 1, 2\pi$ or 4π for $d = 1, 2$, or 3, respectively.

The radial distances x and y can vary between a and b. In one dimension a may equal $-\infty$. In higher dimensions $a > 0$. In all dimensions $a < b \leqslant \infty$. At the boundaries, reflecting boundary conditions are imposed

$$\partial\,[e^{V(y)}p(y,t\,|x)]/\partial y|_{a,b} = \partial\,[p(y,t\,|x)]/\partial x|_{a,b} = 0,$$
$$\qquad (2.2)$$

because reaction is depicted by the sink term $k(x)$. A partially absorbing boundary[3] is a special case where $k(x) = \kappa\delta(x - a)$. For $y \neq a$, Eq. (2.2) may be written conveniently as

$$\int_a^b (\mathscr{L}^\dagger p)\exp[-V(x)]\,x^{d-1}\,dx = 0. \qquad (2.3)$$

In a bounded system, where $\exp(-V)$ is integrable, and in the absence of reaction ($k = 0$), any initial density evolves towards an equilibrium distribution

$$p^{\mathrm{eq}}(x) \equiv \exp[-V(x)]/Z,$$

$$\langle 1\rangle_{\mathrm{eq}} \equiv \gamma\int_a^b p^{\mathrm{eq}}(x)x^{d-1}\,dx = 1. \qquad (2.4)$$

Z is a normalization constant and $\langle \cdots \rangle_{\mathrm{eq}}$ denotes an average with respect to p^{eq}. Hence one may rewrite Eq. (2.3) as

$$\langle \mathscr{L}^\dagger p\rangle_{\mathrm{eq}} = 0. \qquad (2.3')$$

The probability density for arriving at y after time t is obtained as an average of $p(y,t\,|x)$ with respect to the initial distribution

$$\langle p(y,t)\rangle = \gamma\int_a^b p(y,t\,|x)p^0(x)x^{d-1}\,dx. \qquad (2.5)$$

Of major importance is the survival probability

$$Q(t\,|x) \equiv \gamma\int_a^b p(y,t\,|x)y^{d-1}\,dy \qquad (2.6)$$

which obeys the backward equation (2.1b). For a positive $k(x)$ the averaged survival probability $\langle Q\rangle$ decreases monotonically as a function of time from unity to zero. The Laplace transform of the survival probability

$$\widetilde{Q}(s|x) \equiv \int_0^\infty Q(t\,|x)\exp(-st)dt \qquad (2.7)$$

is often more accessible mathematically. Its value for $s = 0$ is the lifetime of the diffusing system for an initial location x

$$\tau(x) \equiv \int_0^\infty t\frac{\partial Q}{\partial t}\,dt = \widetilde{Q}(0|x). \qquad (2.8)$$

The mean lifetime is subsequently denoted by $\langle\tau\rangle$.

III. BOUNDED DIFFUSION

This section treats bounded diffusion which in the absence of reaction admits an equilibrium solution. Expansions are derived for eigenfunctions, eigenvalues, survival probability, and mean lifetime in the limit $\eta \to 0$. An interesting result on the exponentiality of the survival probability follows.

A. Eigenfunctions and eigenvalues

The long-time exponential decay of the survival probability is determined by the lowest eigenvalue. The separation of the first two eigenvalues is a measure for the exponentiality of the survival probability. The lowest eigenfunction is related to the lifetime for a given initial condition. The eigenvalues are determined together with the eigenfunctions by the procedure outlined below.

The two adjoint operators in Eqs. (2.1a) and (2.1b) have the same eigenvalues, λ_n, $n = 0,1,\dots$. Denoting the eigenfunctions of $k - D\mathscr{L}^\dagger$ by $h_n(x)$, one has

$$\mathscr{L}^\dagger h_n(x) = \eta\,[k(x) - \lambda_n]h_n(x), \quad n = 0,1,\cdots. \qquad (3.1)$$

The eigenfunctions of the forward equation (2.1a) are $p^{\mathrm{eq}}(x)h_n(x)$. For $k(x) > 0$, all λ_n are positive. $h_n(x)$ obeys the boundary conditions of Eq. (2.3), hence

$$\lambda_n\langle h_n\rangle_{\mathrm{eq}} = \langle kh_n\rangle_{\mathrm{eq}}. \qquad (3.2)$$

In addition, the eigenfunctions are orthogonal

$$\langle h_l h_n \rangle_{\text{eq}} = 0, \quad \text{for } l \neq n. \tag{3.3}$$

The lowest eigenfunction is normalized as a probability function

$$\langle h_0 \rangle_{\text{eq}} = 1. \tag{3.4}$$

From Eq. (3.2) it then follows that $\lambda_0 = \langle k h_0 \rangle_{\text{eq}}$.

First, consider the lowest eigenvalue and eigenfunction. Assume they admit the following "viscosity expansions," which are like perturbation expansions around the infinite diffusivity limit

$$h_0(x) = h_0^{(0)} + \eta h_0^{(1)}(x) \cdots \tag{3.5a}$$

$$\lambda_0 = \lambda_0^{(0)} + \eta \lambda_0^{(1)} + \cdots. \tag{3.5b}$$

In the sequel, a superscript in parenthesis denotes the corresponding power of η. Inserting in Eq. (3.1) and comparing powers of η, one obtains a hierarchy of equations

$$\mathcal{L}^\dagger h_0^{(0)} = 0,$$

$$\mathcal{L}^\dagger h_0^{(1)} = [k(x) - \lambda_0^{(0)}] h_0^{(0)},$$

$$\mathcal{L}^\dagger h_0^{(m)} = k(x) h_0^{(m-1)} - \sum_{j=0}^{m-1} \lambda_0^{(j)} h_0^{(m-j-1)}, \tag{3.6}$$

to be solved sequentially in the order m. First $h_0^{(m)}(x)$ is determined from the mth equation then $\lambda_0^{(m)}$ is obtained from

$$\lambda_0^{(m)} = \langle k h_0^{(m)} \rangle_{\text{eq}}. \tag{3.7}$$

The leading term in the expansion is derived from Eqs. (3.6), (3.4), and (3.2)

$$h_0^{(0)} = 1, \quad \lambda_0^{(0)} = \langle k \rangle_{\text{eq}}. \tag{3.8}$$

It agrees with what we already know. For the higher terms one finds

$$\langle h_0^{(m)} \rangle_{\text{eq}} = 0, \quad \text{for } m \geq 1. \tag{3.9}$$

This is consistent, since by inserting expansion (3.5) into Eq. (3.2) and using Eqs. (3.8) and (3.9) one gets Eq. (3.7).

The first correction term is obtained by direct integration in Eq. (3.6). Together with condition (3.9) one gets

$$h_0^{(1)}(x) = \langle I \rangle_{\text{eq}} - I(x), \tag{3.10}$$

where $I(x)$ is the double integral

$$I(x) \equiv \int_x^b dy\, y^{1-d} p^{\text{eq}}(y)^{-1} \int_a^y dz\, z^{d-1} p^{\text{eq}}(z)$$

$$\times [k(z) - \langle k \rangle_{\text{eq}}]. \tag{3.11}$$

The reflecting boundary conditions are satisfied because the integral over z vanishes when y equals either a or b. Using Eq. (3.7) and changing the order of integration in the double integral, one subsequently finds

$$\lambda_0^{(1)} = \langle k h_0^{(1)} \rangle_{\text{eq}} = \langle k \rangle_{\text{eq}} \langle I \rangle_{\text{eq}} - \langle k I \rangle_{\text{eq}}$$

$$= -\gamma \int_a^b dx\, x^{1-d} p^{\text{eq}}(x)^{-1}$$

$$\times \left\{ \int_a^x dy\, y^{d-1} p^{\text{eq}}(y) [k(y) - \langle k \rangle_{\text{eq}}] \right\}^2, \tag{3.12}$$

where γ is the geometrical factor defined in Sec. II. $\lambda_0^{(1)} \leq 0$ with equality if and only if k is constant. Continuing in this

fashion one may obtain higher order corrections by direct integration, but the expressions become exceedingly complicated. The same result can be obtained by applying conventional quantum-mechanical perturbation theory.

For the higher eigenvalues Eq. (3.5b) should be replaced by

$$\lambda_n = \eta^{-1} \lambda_n^{(-1)} + \lambda_n^{(0)} + \eta \lambda_n^{(1)} + \cdots, \quad n \geq 1 \tag{3.13}$$

with an additional term $\lambda_n^{(-1)}$ which is multiplied by D. As $\eta \to 0$, the higher eigenvalues become infinite, hence the exponential decay in Eq. (1.1b). The higher eigenfunctions are still given by Eq. (3.5a) above.

The following set of equations is obtained from Eq. (3.1) for $n \geq 1$

$$\mathcal{L}^\dagger h_n^{(0)} = -\lambda_n^{(-1)} h_n^{(0)}(x),$$

$$\mathcal{L}^\dagger h_n^{(1)} = [k(x) - \lambda_n^{(0)}] h_n^{(0)}(x) - \lambda_n^{(-1)} h_n^{(1)}(x),$$

$$\mathcal{L}^\dagger h_n^{(m)} = k(x) h_n^{(m-1)}(x)$$

$$- \sum_{j=-1}^{m-1} \lambda_n^{(j)} h_n^{(m-j-1)}(x). \tag{3.14}$$

This reduces to Eq. (3.6) when $\lambda_0^{(-1)} = 0$. The functions $h_n^{(0)}(x)$ are always the zero-reaction eigenfunctions. Since $\lambda_n^{(-1)} > 0$ for $n \geq 1$, it follows from Eq. (2.3') that $\langle h_n^{(0)} \rangle_{\text{eq}} = 0$, in agreement with the orthogonality condition, Eq. (3.3), applied to $h_n^{(0)}$ and $h_0^{(0)} = 1$. For the same reason, obtaining corrections for the higher eigenvalues from Eq. (3.14) becomes quite difficult.

B. Survival probability and mean lifetime

From Eqs. (2.1), (2.6), and (2.7) it follows that the Laplace transform of the survival probability obeys

$$\mathcal{L}^\dagger \tilde{Q}(s|x) = \eta \{ [s + k(x)] \tilde{Q}(s|x) - 1 \}. \tag{3.15}$$

A viscosity expansion is assumed

$$\tilde{Q}(s|x) = \tilde{Q}^{(0)}(s|x) + \eta \tilde{Q}^{(1)}(s|x) + \cdots \tag{3.16}$$

and a hierarchy of equations derived by comparing powers of η

$$\mathcal{L}^\dagger \tilde{Q}^{(0)}(s|x) = 0,$$

$$\mathcal{L}^\dagger \tilde{Q}^{(1)}(s|x) = [s + k(x)] \tilde{Q}^{(0)}(s|x) - 1,$$

$$\mathcal{L}^\dagger \tilde{Q}^{(m)}(s|x) = [s + k(x)] \tilde{Q}^{(m-1)}(s|x), \quad m \geq 2. \tag{3.17}$$

These are supplemented by the boundary conditions in the form of Eq. (2.3), namely

$$\langle [s + k(x)] \tilde{Q} \rangle_{\text{eq}} = 1. \tag{3.18}$$

Since this holds for arbitrary η, the terms in the expansion (3.16) obey

$$\langle (s + k) \tilde{Q}^{(0)} \rangle_{\text{eq}} = 1,$$

$$\langle (s + k) \tilde{Q}^{(m)} \rangle_{\text{eq}} = 0, \quad m \geq 1. \tag{3.19}$$

This is similar to the condition $\langle h_0^{(m)} \rangle$, Eqs. (3.8) and (3.9).

Equations (3.17) are solved sequentially. The zero-reaction solution is independent of x and therefore given by

$$\tilde{Q}^{(0)}(s|x) = \langle \tilde{Q}^{(0)} \rangle = [s + \langle k \rangle_{\text{eq}}]^{-1}. \tag{3.20}$$

The first correction is obtained by direct integration

$$(s + \langle k \rangle_{eq}) \widetilde{Q}^{(1)}(s|x)$$
$$= \langle (s + k) I \rangle_{eq} / (s + \langle k \rangle_{eq}) - I(x), \qquad (3.21)$$

where $I(x)$ is the double integral defined in Eq. (3.11). Its average over an arbitrary initial distribution p^0 is

$$(s + \langle k \rangle_{eq})^2 \langle \widetilde{Q}^{(1)}(s) \rangle$$
$$= s(\langle I \rangle_{eq} - \langle I \rangle) + \langle kI \rangle_{eq} - \langle k \rangle_{eq} \langle I \rangle \qquad (3.22)$$

which, for $s = 0$, agrees with Eq. (56) of Ref. 17. When $p^0 = p^{eq}$ it becomes

$$(s + \langle k \rangle_{eq})^2 \langle \widetilde{Q}^{(1)}(s) \rangle_{eq}$$
$$= \langle kI \rangle_{eq} - \langle k \rangle_{eq} \langle I \rangle_{eq} = - \lambda_0^{(1)} \qquad (3.23)$$

with $\lambda_0^{(1)}$ from Eq. (3.12). Note the relation with the first correction to the lowest eigenfunction [cf. Eq. (3.10)]

$$h_0^{(1)}(x) = \langle k \rangle_{eq} [\widetilde{Q}^{(1)}(0|x) - \langle \widetilde{Q}^{(1)}(0) \rangle_{eq}]. \qquad (3.24)$$

The time dependence of the survival probability may be obtained by inverting the Laplace transform. Hence Eq. (3.20) gives

$$Q^{(0)}(t) = \langle Q^{(0)}(t) \rangle = \exp(- \langle k \rangle_{eq} t) \qquad (3.25)$$

in agreement with the known Eq. (1.1b). Summing the first two terms for an initial equilibrium distribution

$$\langle \widetilde{Q}^{(0+1)} \rangle_{eq}$$
$$\equiv \langle \widetilde{Q}^{(0)} \rangle_{eq} + \eta \langle \widetilde{Q}^{(1)} \rangle_{eq}$$
$$= \frac{1}{s + \langle k \rangle_{eq}} - \frac{\eta \lambda_0^{(1)}}{(s + \langle k \rangle_{eq})^2}$$
$$\approx [s + \lambda_0^{(0)} + \eta \lambda_0^{(1)}]^{-1} \equiv [s + \lambda_0^{(0+1)}]^{-1} \qquad (3.26)$$

implies that

$$\langle Q^{(0+1)}(t) \rangle_{eq} = \exp(- \lambda_0^{(0+1)} t), \qquad (3.27)$$

where a superscript $(0 + 1)$ denotes the sum of the first two terms in the expansion. Hence, the temporal decay of the survival probability for bounded diffusion with an initial equilibrium distribution is exponential up to the *linear* term in an asymptotic $\eta \equiv 1/D$ expansion. This extends the known result,[7] Eq. (1.1b), that the above holds true for the leading term, $\langle Q^{(0)} \rangle$, for *any* initial distribution. This conclusion is not generally true for higher orders of η or other initial distributions. Neither does it indicate whether the approximation obtained by retaining a finite number of terms is useful at short times.

The average lifetime defined in Eq. (2.8) obeys

$$\mathcal{L}^{\dagger} \tau(x) = \eta [k(x) \tau(x) - 1] \qquad (3.28)$$

which is the $s = 0$ limit of Eq. (3.15). Assuming an expansion as in Eq. (3.16) one obtains a hierarchy of equations

$$\mathcal{L}^{\dagger} \tau^{(0)}(x) = 0,$$
$$\mathcal{L}^{\dagger} \tau^{(1)}(x) = k(x) \tau^{(0)} - 1,$$
$$\mathcal{L}^{\dagger} \tau^{(m)}(x) = k(x) \tau^{(m-1)}(x), \quad m \geq 2 \qquad (3.29)$$

which is a special case of Eq. (3.17) for $s = 0$. The solution

$$\tau(x) \sim \frac{1}{\langle k \rangle_{eq}} \left\{ 1 + \left[\frac{\langle kI \rangle_{eq}}{\langle k \rangle_{eq}} - I(x) \right] \eta + \cdots \right\} \qquad (3.30)$$

can be obtained by setting $s = 0$ in Eqs. (3.20) and (3.21).

(The $\sim$ sign indicates an asymptotic expansion.)

Denoting the sum of the first two terms by $\tau^{(0+1)}(x)$ and averaging gives

$$\langle \tau^{(0+1)} \rangle_{eq} = (\lambda_0^{(0)} - \eta \lambda_0^{(1)})(\lambda_0^{(0)})^{-2} \approx 1/\lambda_0^{(0+1)}, \qquad (3.31)$$

$$\langle k \rangle_{eq} [\tau^{(0+1)}(x) - \langle \tau^{(0+1)} \rangle_{eq}] = h_0^{(0+1)}(x) - 1. \qquad (3.32)$$

Hence for an initial equilibrium distribution the average lifetime is the reciprocal of the lowest eigenvalue up to the *linear* term in the expansion. This extends Eq. (1.2b), which says that for an *arbitrary* initial distribution $\langle \tau \rangle \approx \lambda_0^{-1}$ only to zeroth order namely, when $\eta = 0$. In addition, when $p^0 = p^{eq}$ the deviation of the lifetime from its mean equilibrium value is proportional to the deviation of the lowest eigenfunction from its mean equilibrium value.

The relation between the lowest eigenvalue and the mean lifetime can be used for approximating λ_0: The two sides of Eq. (3.31) agree up to linear order but one of them may be better at finite η values. It turns out that the series for $\langle \tau \rangle_{eq}$ is a better approximation for λ_0. More generally, by inverting expansion (3.5b) one obtains

$$\lambda_0 \approx (\lambda_0^{(0)})^2 \{ \lambda_0^{(0)} - \eta \lambda_0^{(1)}$$
$$+ \eta^2 [(\lambda_0^{(1)})^2 - \lambda_0^{(0)} \lambda_0^{(2)}] + \cdots \}^{-1}. \qquad (3.33)$$

Typically, using only the first two or three coefficients in Eq. (3.33) results in a much improved approximation.

IV. EXAMPLES

As a demonstration of the results of Sec. III, two one-dimensional examples with delta function reaction rates are presented.

A. "Radiation" boundary condition

This partly absorbing boundary condition[3]

$$D \, \partial p(y,t \, |x) / \partial x |_{x=b} = - \kappa p(y,t \, |b) \qquad (4.1)$$

as written for the backward equation, is equivalent[7] to a delta function sink

$$k(x) = \kappa \delta(x - b) \qquad (4.2)$$

located at the right boundary $x = b$. In one dimension this boundary condition mimics the effect of a potential barrier[21] in a one-dimensional barrier-crossing problem,[10] which is of great experimental interest.[11]

Equations derived[20(b)] for the mean first passage time from an initial location x can be obtained as a special case of the present formalism. By setting $k(x) = 0$ in Eq. (3.28) one obtains the well known result[20]

$$D \mathcal{L}^{\dagger} \tau(x) = - 1, \quad a \leqslant x < b. \qquad (4.3a)$$

The hierarchy of equations in this special case is like Eq. (3.29) with zero $k(x)$

$$\mathcal{L}^{\dagger} \tau^{(m)}(x) = 0, \quad m \neq 1,$$
$$\mathcal{L}^{\dagger} \tau^{(1)}(x) = - 1 \qquad (4.3b)$$

and supplemented by boundary conditions obtained by inserting the viscosity expansion into Eq. (4.1)

$$\left.\frac{\partial \tau^{(m)}(x)}{\partial x}\right|_{x=b} = -\kappa\tau^{(m-1)}(b), \quad \tau^{(-1)} \equiv 0. \quad (4.1')$$

The sum of the first two equations in the hierarchy (4.3b) already coincides with Eq. (4.3a), hence the linearized viscosity expansion for the mean lifetime is exact[16]

$$\tau^{(0+1)}(x) = \tau(x). \quad (4.4)$$

The solution to Eq. (4.3a) can be obtained from Eq. (4.3b) or the general theory, by setting $\langle kI \rangle_{eq} = 0$ and $\langle k \rangle_{eq} = \kappa b^{d-1} p^{eq}(b)$ in Eq. (3.30).

$$\tau(x) = [\kappa b^{d-1} p^{eq}(b)]^{-1}$$
$$+ \eta \int_x^b dy\, y^{1-d} p^{eq}(y)^{-1} \int_a^y dz\, z^{d-1} p^{eq}(z). \quad (4.5)$$

This agrees with Eq. (2.15) of Ref. 20(b).

As a specific example, consider one dimensional free diffusion $V(x) = 0$. A zero potential with the two boundary conditions mimics the Kramers problem[10,11] for a square well.[21] For simplicity, set $a = 0$ so that $p^{eq} = 1/b$, and intro-

duce the dimensionless parameters $\chi \equiv x/b$, $\theta \equiv \kappa\tau/b$, $\mu_n \equiv \eta\lambda_n b^2$ and $\zeta \equiv \eta\kappa b$. From Eq. (4.5) one finds that

$$\theta(\chi) \equiv \kappa\tau(x)/b = 1 + \tfrac{1}{2}\zeta(1 - \chi^2), \quad (4.6)$$
$$\langle \theta \rangle_{eq} = 1 + \zeta/3. \quad (4.7)$$

The eigenfunctions are

$$Nh_n(\chi) = \cos(\sqrt{\mu_n}\chi), \quad n = 0,1,2,..., \quad (4.8)$$

where N is a normalization constant. By inserting $h_n(x)$ into Eq. (4.1) the eigenvalues are found[22] to obey the transcendental equation

$$\sqrt{\mu_n} \tan\sqrt{\mu_n} = \zeta \quad (4.9a)$$
$$n\pi \leqslant \sqrt{\mu_n} \leqslant (n + \tfrac{1}{2})\pi. \quad (4.9b)$$

The eigenvalue expansion for the survival probability for an initial equilibrium distribution is given by

$$\langle Q(t) \rangle_{eq} = 2\zeta^2 \sum_{n=0}^{\infty} [\zeta + \zeta^2 + \mu_n]^{-1} \mu_n^{-1} \exp(-\lambda_n t). \quad (4.10)$$

The Laplace transform, $\Sigma(\sigma|\chi) \equiv \kappa\tilde{Q}(s|x)/b$, of $Q(t|x)$ is

$$\Sigma(\sigma|\chi) = \frac{1}{\sigma}\left\{ 1 - \frac{\exp(\sqrt{\zeta\sigma}\chi) + \exp(-\sqrt{\zeta\sigma}\chi)}{(1 + \sqrt{\sigma/\zeta})\exp(\sqrt{\zeta\sigma}) + (1 - \sqrt{\sigma/\zeta})\exp(-\sqrt{\zeta\sigma})} \right\}, \quad (4.11)$$

where $\sigma \equiv bs/\kappa$ is the Laplace variable adjoint to the dimensionless time $\kappa t/b$.

The above closed-form expressions may be used to demonstrate the results of Sec. III. Inserting $\tan(z) = z + z^3/3 + 2z^5/15 + 17z^7/135 + 62z^9/2835 + \cdots$ into Eq. (4.9) and comparing orders of ζ yields a small ζ expansion for the lowest eigenvalue

$$\mu_0 \sim \zeta - \zeta^2/3 + 4\zeta^2/45 - 16\zeta^4/945$$
$$+ 16\zeta^5/14,175 - \cdots. \quad (4.12)$$

Indeed, up to the linear term in η, but not beyond, λ_0 is the inverse of $\langle\tau\rangle_{eq}$, Eq. (4.7), in accord with Eq. (3.31). It is independent of viscosity only in the limit of infinitely fast diffusion.

For the higher eigenvalues, another expansion is obtainable by a similar procedure

$$\mu_n \sim (n\pi)^2 + 2\zeta - \zeta^2(n\pi)^{-2}$$
$$+ 2\zeta^3[1 - (n\pi)^2/3](n\pi)^{-4} - \cdots, \quad n \geqslant 1. \quad (4.13)$$

In the limit $\eta = 0$ one finds $\mu_n = (n\pi)^2$, in agreement with Eq. (4.9b). From the equations above it follows that the relative separation between the two lowest eigenvalues, $(\lambda_1 - \lambda_0)/\lambda_0$, goes as $\pi^2 D/\kappa b + 1 + \pi^2/3 + 0(1/D)$. This separation is large, so that the survival probability is nearly exponential in time, not only in the limit of infinite diffusivity but also for moderate values of D/κ.

Only a few terms need be calculated in the above expansions. These can then be used in Padé-like approximations to improve convergence. For example, from Eq. (3.33) the lowest eigenvalue expansion can be written as[23]

$$\mu_0 \approx \zeta[1 + \zeta/3 + \zeta^2/45]^{-1}. \quad (4.14)$$

This describes the behavior at finite ζ much better than Eq. (4.12).

For the present problem, though not in general, it is possible to obtain an analogous expansion in the limit of slow diffusion. Writing Eq. (4.9a) as

$$\sqrt{\mu_n} = \arctan(\zeta/\sqrt{\mu_n})$$
$$= (n + \tfrac{1}{2})\pi - \sqrt{\mu_n}/\zeta + \tfrac{1}{3}(\sqrt{\mu_n}/\zeta)^3 - \cdots \quad (4.15)$$

and comparing orders of ζ gives

$$\mu_n = (n + \tfrac{1}{2})^2\pi^2\{1 - 2/\zeta + 3/\zeta^2$$
$$- 2[2 - (n + \tfrac{1}{2})^2\pi^2/3]/\zeta^3$$
$$+ [19 - 4(n + \tfrac{1}{2})^2/3]/\zeta^4 - \cdots\} \quad (4.16)$$

for all values of $n \geqslant 0$.

The quality of the expansions for the lowest and first excited eigenvalues is shown in Figs. 1 and 2. Figures 1(a) and 2 show both fast, Eqs. (4.12) and (4.13), and slow, Eq. (4.16), diffusion limits. By taking a few terms from each expansion it is possible to represent the viscosity dependence over the whole range. The utility of approximation (4.14) is demonstrated in Fig. 1(b). Even when just a few terms in the $\eta \to 0$ expansion are derived, they can be used to improve the convergence over a wide viscosity range.

The lowest eigenfunction, given in Eq. (4.8), can be expanded around $\eta = 0$ by using $\cos(z) = 1 - z^2/2 + z^4/24 - ...$, expansion (4.12) and the normalization condition, Eq. (3.4). This yields
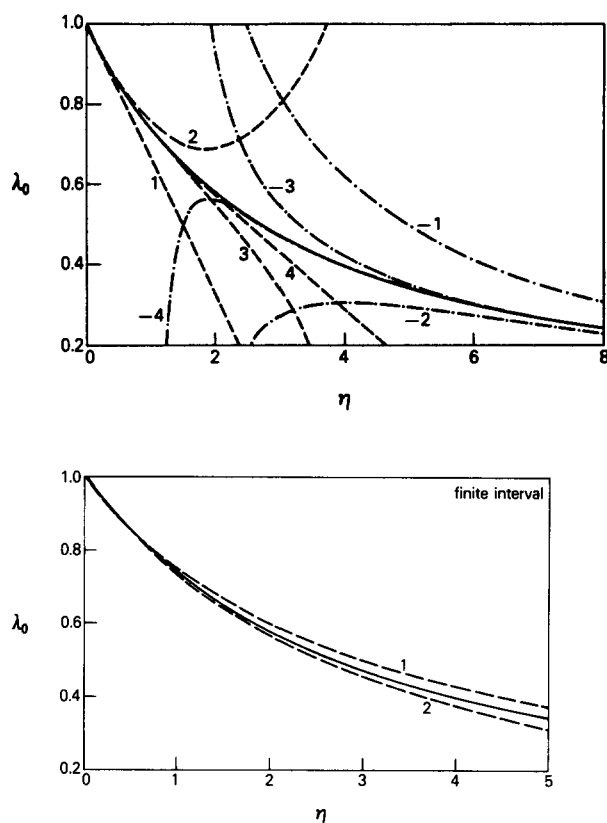
FIG. 1. (a) Viscosity ($\eta \equiv D^{-1}$) dependence of the lowest eigenvalue for one dimensional free diffusion in the unit interval ($b = 1$) with a "radiation" boundary condition (setting $\kappa = 1$) at $x = 1$. Full curve is the exact result, obtained from a numerical solution of the transcendental equation (4.9a). Dashed curves are partial sums in the small η expansion (4.12) up to the power of η labeling the curves. The large-η expansion (4.16) is similarly demonstrated by the dash–dotted curves. (b) Same as Fig. 1(a), but with the exact result compared with the approximation of Eq. (4.14).

$$h_0(x) \sim \frac{1 - (1/2)\zeta\chi^2 + (\zeta\chi)^2[1 + \chi^2/4]/6 - \cdots}{1 - \zeta/6 + 23\zeta^2/360 - \cdots}$$

$$\approx 1 - \tfrac{1}{2}\zeta\left[\chi^2 - \tfrac{1}{3}\right] + \tfrac{1}{12}\zeta^2\left[\tfrac{1}{2}\chi^4 + \chi^2 - \tfrac{13}{30}\right]$$

$$- \tfrac{1}{720}\zeta^3\left[\chi^6 + 15\chi^4 - \chi^2 - \tfrac{59}{21}\right] + \cdots, \qquad (4.17)$$

where, as above, $\zeta \equiv \eta\kappa b$ and $\chi \equiv x/b$. The equilibrium average (namely, the integral over χ from 0 to 1) of each term except the first is indeed zero, in agreement with Eq. (3.9). This result is demonstrated in Fig. 3.

To obtain the expansion for $h_0(x)$ from the theory of Sec. III one first evaluates the integral $I(x)$ of Eq. (3.11) by setting $k(y) = 0$ for $y < b$ and $\langle k \rangle_{eq} = \kappa/b$. This gives $I(x) = \kappa(x^2 - b^2)/(2b)$ and $\langle I \rangle_{eq} = -\kappa b/3$. Inserting into Eq. (3.10) reproduces the linear term in Eq. (4.17). To obtain the second order correction, $h_0^{(2)}(x)$, one needs to solve [cf. Eq. (3.6)]

$$\frac{d^2 h_0^{(2)}(x)}{dx^2} = (\kappa/b)^2(3x^2 + b^2)/6. \qquad (4.18)$$

Integrating twice and using condition (3.9) gives the coefficient of η^2 as in Eq. (4.17). The first correction term to λ_0 is obtained by inverting Eq. (4.6). The second correction term is found by inserting $h_0^{(2)}(x)$ into Eq. (3.7). Hence

$$\lambda_0^{(2)} = \langle k h_0^{(2)} \rangle_{eq} = \kappa h_0^{(2)}(b)/b = 4\kappa^3 b/45 \qquad (4.19)$$

in agreement with the coefficient of η^2 in Eq. (4.12). Higher order terms are derived in a similar fashion.

Finally, let us consider the survival probability. The fast diffusion expansion for its Laplace transform, $\Sigma(\sigma|\chi) \equiv \kappa \tilde{Q}(s|x)/b$, can be found from the general formalism of Sec. III by solving Eq. (3.17) or by directly expanding the numerator and denominator of the known solution (4.11) and dividing polynomials. Both routes lead to

$$\Sigma(\sigma|\chi) \sim (1 + \sigma)^{-1}\left\{ 1 - \frac{\zeta}{2}\left(\chi^2 - \frac{1 + \sigma/3}{1 + \sigma}\right)\right.$$

$$+ \frac{\sigma\zeta^2}{4(1 + \sigma)}\left[\frac{\chi^4}{6} - \frac{1 + \sigma/3}{1 + \sigma}(\chi^2 + \tfrac{2}{3})\right.$$

$$\left.\left. + \frac{2}{15}\right] + \cdots \right\}. \qquad (4.20)$$

Indeed, when $\sigma = 0$ the coefficients of ζ^n vanish for $n \geqslant 2$ and Eq. (4.20) reduces to Eq. (4.6). Integrating over χ from 0 to 1 gives

FIG. 2. Same as Fig. 1(a) for the first excited eigenvalue. Dashed curves are now from Eq. (4.13).
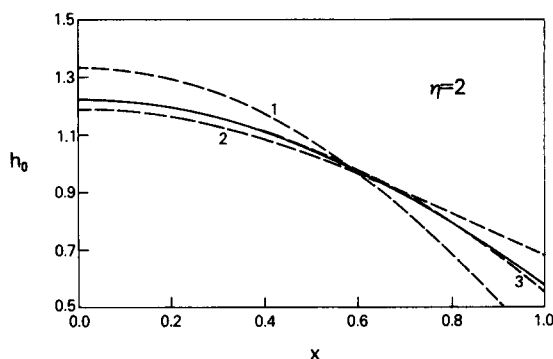

FIG. 3. The lowest eigenfunction under the conditions of Fig. 1(a). Full curve is the exact result, Eq. (4.8), with the lowest eigenvalue evaluated numerically from Eq. (4.9a). Dashed curves are partial sums in expansion (4.17), up to the power of η indicated.

$$\langle \Sigma \, (\sigma) \rangle_{eq} \sim (1 + \sigma)^{-1} \left[1 + \frac{\zeta}{3(1 + \sigma)} \right.$$

$$\left. - \frac{\sigma \zeta^2}{24} \frac{5 + \sigma}{(1 + \sigma)^2} + \cdots \right]. \qquad (4.21)$$

The expansion up to the linear term agrees with Eq. (3.26) and with $\lambda_0^{(1)}$ of Eq. (3.12). This implies, as in Eq. (3.27), that up to linear order the survival probability for an initial uniform distribution decays exponentially.

$$\langle Q(t) \rangle_{eq} \approx \exp[- (1 - \eta \kappa b /3) \kappa t /b]$$

$$\approx \exp[- \kappa t /(1 + \eta \kappa b /3) b]. \qquad (4.22)$$

The same can be seen from the eigenvalue expansion, Eq. (4.10): For $n \geqslant 1$ Eq. (4.13) implies that the leading terms are $\zeta^2 (n\pi)^{-4} \exp(- \lambda_n t)$ namely, of order η^2. Therefore, in a linear expansion of Eq. (4.10) all coefficients for $n \geqslant 1$ vanish and that of $n = 0$ is unity, hence the decay is exponential.

As demonstrated in Fig. 4, the survival probability in the present case decays almost exponentially with time even for slow diffusion. One may ask which is the best exponent in Eq. (4.22) for representing the exact survival probability.[20(b)] At very long times it is the lowest eigenvalue, so that the full Padé approximation (4.14) should be used. At intermediate times it is better to truncate this expansion at the linear term, as in the right-hand side of Eq. (4.22), leading to a mean first passage time approximation.[20(b)] The general rule may therefore require using more and more terms in expansion (4.14) with increasing time.

In the present case it is possible to obtain expansions of the survival probability also in the $D \to 0$ limit. Starting from the exact solution (4.11) and taking the limit of large ζ one obtains

$$\Sigma \, (\sigma | \chi) \approx \sigma^{-1} \{ 1 - \exp[\sqrt{\zeta \sigma} (\chi - 1)] \}. \qquad (4.23)$$

This can be inverted to give

$$Q(t | x) \approx \mathrm{erf}[(b - x)/2\sqrt{Dt}] \qquad (4.24)$$

which is just the solution for an absorbing boundary ($\kappa = \infty$) at $x = b$. More elaborate small D approximations can be obtained by retaining more terms in Eq. (4.11) prior to inversion.

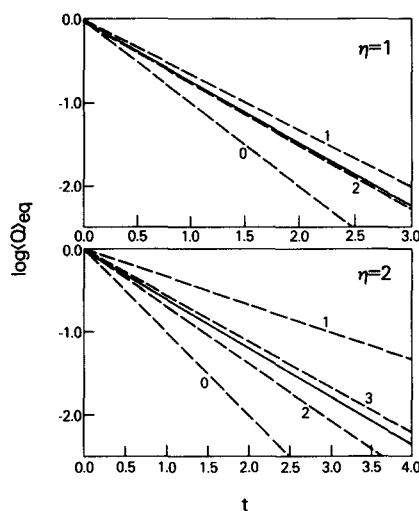A generalization to a linear potential is given in Appendix A.

FIG. 4. The equilibrium average of the survival probability for the problem of Fig. 1(a) for two values of the viscosity η in a (natural) logarithmic scale. Full curves are the exact result, evaluated from the sum (4.10) with eigenvalues calculated numerically from Eq. (4.9a). Dashed lines assume an exponential survival probability with an exponent equal to the lowest eigenvalue from the series (4.12), summed up to the power of η which labels each line. The slope of the full curves is very close to λ_0 or $\langle \tau \rangle_{eq}^{-1}$ in this viscosity range.

B. Harmonic potential with a delta sink

This one dimensional model may describe barrierless excited-state isomerization in solution,[9] with a sink term representing decay to the ground state. Specifically, one assumes

$$V(x) = \tfrac{1}{2} x^2, \quad k(x) = \kappa \delta(x) \qquad (4.25)$$

with boundaries at $\pm \infty$ ("natural" boundary conditions). The equilibrium solution in the absence of reaction is

$$p^{eq}(x) = \sqrt{2/\pi} \exp(- x^2/2). \qquad (4.26)$$

The equilibrium average of the rate coefficient is therefore

$$\langle k \rangle_{eq} = \sqrt{2/\pi} \, \kappa. \qquad (4.27)$$

For an initial equilibrium distribution, an analytic expression for the Laplace transformed survival probability has been obtained [Eq. (2.32) of Ref. 8]

$$\langle \tilde{Q}(s) \rangle_{eq} = \frac{1}{s} \left\{ 1 - \frac{\langle k \rangle_{eq}/s}{1 + (1/2)\eta \langle k \rangle_{eq} \sqrt{\pi} \, \Gamma(\eta s/2)/\Gamma[(\eta s + 1)/2]} \right\}. \qquad (4.28)$$

Using the small z limit of the gamma function [Eq. (2.33) of Ref. 8]

$$\Gamma(z/2)/\Gamma[(z + 1)/2] \approx 2(z^{-1} + \ln 2)/\sqrt{\pi} \qquad (4.29)$$

gives for small η

$$\langle \tilde{Q}(s) \rangle_{eq} \sim \frac{1 + \eta \langle k \rangle_{eq} \ln 2}{\langle k \rangle_{eq} + s(1 + \eta \langle k \rangle_{eq} \ln 2)}$$

$$\approx \frac{1}{s + \langle k \rangle_{eq}} + \frac{\eta \langle k \rangle_{eq}^2 \ln 2}{(s + \langle k \rangle_{eq})^2}. \qquad (4.30)$$

This is in the form of Eq. (3.26) when

$$\lambda_0^{(1)} = - \langle k \rangle_{eq}^2 \ln 2. \qquad (4.31)$$

Since the correction to the lowest eigenvalue is given by Eq. (3.12), one finds that

$$\int_0^\infty \exp(x^2) [erfc(x)]^2 \, dx = \ln 2/\sqrt{\pi} \qquad (4.32)$$

an integral that is hard to find in standard tables.[24]

The survival probability is exponential in a linearized η expansion [cf. Eq. (3.27)]

$$\langle Q^{(0+1)}(t) \rangle_{eq} = \exp[- \langle k \rangle_{eq} (1 - \eta \langle k \rangle_{eq} \ln 2)t] \qquad (4.33)$$

in agreement with the result of Sec. III. As before, a better representation is obtained by inverting the series [see Eq. (3.33)]. This gives

$$\langle Q(t) \rangle_{eq} \approx \exp[- \sqrt{2/\pi} \, \kappa Dt /(D + \sqrt{2/\pi} \ln 2 \, \kappa)]. \qquad (4.34)$$

Figure 5 shows that the representation for the lowest eigenvalue in the exponent of Eq. (4.34) is indeed much better than that of Eq. (4.33). The exact λ_0 in Fig. 5 was obtained by discretizing (spacing Δx), setting the transition probability from the minimum of the parabola to the "sink" to[5] $2\kappa/\Delta x$ and using the numerical method of Ref. 13.

The viscosity dependence of barrierless isomerization rate coefficients has been discussed in the context of the above model.[3] When experimental fluorescence traces[11(a)] show single exponential decay one may assume that the time scale and (the rotational) diffusion coefficient D are large enough for Eq. (4.34) to hold. The model in this case predicts a viscosity dependence of approximately the form $(1 + const.\eta)^{-1}$ rather than (the experimentally observed[11]) $\eta^{-\alpha}$, with $0 < \alpha < 1$.

V. UNBOUNDED DIFFUSION

This section treats unbounded diffusion, which propagates in an infinite spatial regime so that an equilibrium distribution does not exist. Some physical examples are bimolecular binding[1–5] and quenching[6,18,19] reactions in solution. For such processes steady state prevails when a source term

is provided, and one may obtain asymptotic expansions for the steady-state concentration profile and reaction rate. As seen below, these can be gotten from the bounded diffusion results by setting $\langle \cdots \rangle_{eq} = 0$.

Assume that particles of one type (e.g., an excited molecule) is at the origin, and that particles of another type (e.g., quenchers) are distributed around it, and let the coordinate r be the radial molecule-quencher separation. The distance of closest approach is a, but the molecule can be quenched at a distance with a rate coefficient $k(r)$.

To find the steady-state concentration of the quenchers around the excited molecule, $c(r) \equiv p^{ss}(r)$, one sets the time derivative to zero in Eq. (2.1a). Hence $c(r)$ obeys

$$\mathscr{L}c(r) = \eta k(r)c(r) \qquad (5.1)$$

which is an ordinary differential equation. Typically, $V(r)$ and $k(r) > 0$ tend to zero as $r \to \infty$, fast enough so that $k(r)$ is integrable in $[a, \infty]$. The boundary at the contact distance is assumed to be reflective

$$\frac{d}{dr} e^{V(r)}c(r) = 0, \quad at \ r = a \qquad (5.2)$$

since reaction is described by $k(r)$. A constant homogeneous concentration of reactants exists at large distances

$$c(r) \underset{r \to \infty}{\to} e^{-V(r)}. \qquad (5.3)$$

When the derivative of $V(r)$ vanishes at infinity, Eq. (5.3) becomes a special type of a reflecting boundary condition. Since for an infinite system $\lambda_0 = \langle k \rangle_{eq} = 0$, Eq. (5.1) is like the adjoint of Eq. (3.1). Hence $c(r)$ can be equated with $e^{-V}h_0$ and obtained from the expressions in Sec. III by setting all equilibrium averages to zero.

The steady-state rate constant in d dimensions can be defined in three different ways. First, it is the averaged $k(r)$

$$\langle k \rangle_{ss} \equiv \gamma \int_a^\infty k(r)c(r)r^{d-1} \, dr, \qquad (5.4a)$$

where $\langle \cdots \rangle_{ss}$ is analogous to $\langle \cdots \rangle_{eq}$ in Sec. III and γ is the appropriate geometric factor in the d dimensional volume element, $\gamma r^{d-1} \, dr$. Second, because for bounded diffusion $\lambda_0 = \langle kh_0 \rangle_{eq}$, it follows that $\langle k \rangle_{ss}$ can be calculated by confining the system to $r < R$, then taking the limit

$$\langle k \rangle_{ss} = \lim_{R \to \infty} \lambda_0(R)Z(R), \quad Z(R) \equiv \gamma \int_a^R e^{-V}r^{d-1} \, dr. \qquad (5.4b)$$

Finally, $\langle k \rangle_{ss}$ equals the flux eminating from infinity

$$\langle k \rangle_{ss} = \gamma D \lim_{r \to \infty} [r^{d-1} \, dc(r)/dr]. \qquad (5.4c)$$

Equations (5.4a) and (5.4b) determine $\langle k^{(m)} \rangle_{ss}$ from $c^{(m)}(r)$, while Eq. (5.4c) from $c^{(m-1)}(r)$.

The steady-state solution is expanded in a series

$$c(r) = e^{-V(r)} + \eta c^{(1)}(r) + \eta^2 c^{(2)}(r) + \cdots \qquad (5.5)$$

whose lowest order term is $c^{(0)}(r) = e^{-V(r)}$. The infinite diffusion limit of the steady-state rate constant is therefore [e.g., Eq. (5.4a)]

$$\langle k^{(0)} \rangle_{ss} = \gamma \int_a^\infty e^{-V(r)}k(r)r^{d-1} \, dr \qquad (5.6)$$
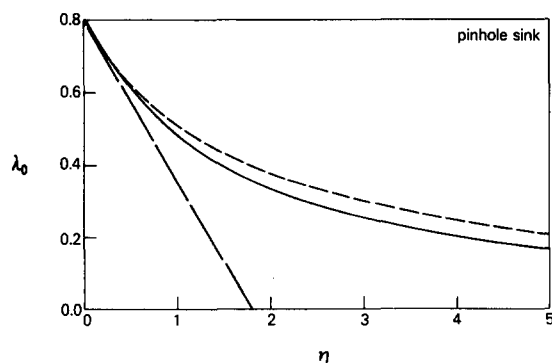

FIG. 5. The lowest eigenvalue for diffusion in a harmonic potential with a delta function reaction term at the parabola's minimum. The long dashed curve is the sum up to the linear term as in the exponent of Eq. (4.33). The short dashed curve is $\langle \tau \rangle_{eq}^{-1}$, as in the exponent of Eq. (4.34).

in analogy to $\langle k \rangle_{eq}$. From Eq. (5.1) one obtains the series of equations

$$\mathscr{L} c^{(m)}(r) = k(r)c^{(m-1)}(r), \quad m \geqslant 1 \tag{5.7}$$

with the boundary condition at infinity

$$c^{(m)}(\infty) = 0, \quad m \geqslant 1. \tag{5.8}$$

This is indeed like setting $\lambda_0^{(m)} = 0$ in Eq. (3.6).

The first order correction to the steady-state concentration is found by direct integration
$c^{(1)}(r)$

$$= - e^{-V(r)} \int_r^\infty dy\, y^{1-d} e^{V(y)} \int_a^y dx\, x^{d-1} e^{-V(x)} k(x). \tag{5.9}$$

Substituting $\langle \cdots \rangle_{eq} = 0$ in Eqs. (3.10) and (3.11) indeed gives, in the limit of an infinite system, $e^V c^{(1)}(r) = - I(r) = h_0^{(1)}(r)$. Clearly, $c^{(1)}(r)$ obeys the desired boundary conditions at a and ∞. It is negative, as expected for $k(r) > 0$ which depletes the concentration profile at small distances.

Differentiating Eq. (5.9) and taking the limit of Eq. (5.4c) gives $\langle k^{(0)} \rangle_{ss}$ as in Eq. (5.6). The first order correction to the steady-state rate constant is determined from Eq. (5.4a) to be

$$\langle k^{(1)} \rangle_{ss} \equiv \gamma \int_a^\infty k(r)c^{(1)}(r)r^{d-1}\, dr$$

$$= - \gamma \int_a^\infty dr\, r^{1-d} e^{V(r)}$$

$$\times \left[\int_a^r dx\, x^{d-1} e^{-V(x)} k(x) \right]^2. \tag{5.10}$$

It is smaller than for $\eta = 0$ due to the depletion of particles near contact. Again note that this result is related to Eq. (3.12) through Eq. (5.4b). The steady-state concentration profile and rate coefficient are analogous to the lowest eigenfunction and eigenvalue of bounded diffusion.

VI. EXAMPLES

This section demonstrates the theory of Sec. V for two cases of unbounded free diffusion in three dimensions. In both examples the spherically symmetric equation to be solved is

$$\frac{d}{dr} r^2 \frac{d}{dr} c(r) = \eta r^2 k(r)c(r), \quad r \geqslant a \tag{6.1}$$

with a source at infinity

$$c(\infty) = 1 \tag{6.2}$$

but with different reaction terms.

A. Radiation boundary condition

To represent a bimolecular binding reaction,[1-5] where reaction occurs only at contact, one may assume[7] $k(r) = \kappa \delta(r - a)$. Alternately,[3] one may set the right-hand side of Eq. (6.1) to zero and replace the reflective boundary condition at contact by

$$\left. \frac{dc(r)}{dr} \right|_{r=a} = \eta \kappa c(a). \tag{6.3}$$

Defining the dimensionless parameters $\rho \equiv r/a$ and $\zeta \equiv \eta \kappa a$, the solution to Eq. (6.1) is[1]

$$c(\rho) = 1 - \zeta [(1 + \zeta)\rho]^{-1}. \tag{6.4}$$

From definition (5.4), the steady-state rate coefficient is

$$\langle k \rangle_{ss} = 4\pi a^2 \kappa c(\rho = 1) = 4\pi a^2 \kappa / (1 + \zeta). \tag{6.5}$$

In the special case of a fully diffusion controlled reaction ($\kappa = \infty$), Eq. (6.5) reduces to the well known[1] result that $\langle k \rangle_{ss} = 4\pi Da$.

The expressions above can be expanded in ζ as

$$c(\rho) \sim 1 - \zeta(1 - \zeta + \zeta^2 - \cdots)/\rho, \tag{6.6}$$

$$\langle k \rangle_{ss} \sim 4\pi a^2 \kappa(1 - \zeta + \zeta^2 - \zeta^3 + \cdots). \tag{6.7}$$

By inserting $k(r) = \kappa \delta(r - a)$ into Eq. (5.9) one finds that the first correction to the concentration profile is $-\zeta/\rho$, in agreement with Eq. (6.6). Subsequently, $\langle k^{(1)} \rangle_{ss}/4\pi a^2 = \kappa c^{(1)}(\rho = 1) = -\kappa \zeta$ in agreement with Eq. (6.7). In this particular case the approximation (3.33) applied to $\langle k \rangle_{ss}$ is exact since the result is identical to Eq. (6.5).

B. Förster quenching

For a dipole–dipole excitation quenching the distance-dependent quenching rate is given by[1]

$$k(r) = \alpha/r^6, \quad r \geqslant a. \tag{6.8}$$

Some workers[6] assume instantaneous quenching at contact, leading to an absorbing boundary at $r = a$. However, in order to investigate the dependence on the ratio of reaction to diffusion rate, $\alpha\eta$, one needs to impose a reflecting boundary condition at contact. This might well be the proper physical description in certain quenching experiments.

Following Ref. 6, introduce the dimensionless variable $z \equiv \frac{1}{2}(\eta\alpha)^{1/2} r^{-2}$. Then for $v \equiv cr^{-1/2}$ Eq. (6.1) is converted into a modified Bessel equation

$$z^2 \frac{d^2 v}{dz^2} + z \frac{dv}{dz} - (z^2 + 4^{-2})v = 0 \tag{6.9}$$

whose solution is a linear combination of the modified Bessel functions $K_{1/4}(z)$ and $I_{1/4}(z)$. Taking into account the boundary conditions, $c(z = 0) = 1$ and $dc/dz = 0$ at $z_0 \equiv \frac{1}{2}(\eta\alpha)^{1/2} a^{-2}$, one obtains

$$c(z) = \frac{z^{1/4}}{\Gamma(1/4)} \left\{ 2^{3/4} K_{1/4}(z) \right.$$

$$\left. - 2^{1/4}\pi \left[\frac{I_{3/4}(z_0)}{I_{-3/4}(z_0)} - 1 \right] I_{1/4}(z) \right\}, \tag{6.10}$$

where $\Gamma(1/4) = 3.6256$. To verify the boundary condition at z_0, one can use the identities[25] $K_{1/4}(z) = \pi[I_{-1/4}(z) - I_{1/4}(z)]/\sqrt{2}$, $d[z^{1/4} I_{1/4}(z)]/dz = z^{1/4} I_{-3/4}(z)$, and $d[z^{1/4} I_{-1/4}(z)]/dz = z^{1/4} I_{3/4}(z)$. These are also used for differentiating Eq. (6.10) and inserting in Eq. (5.4c) to get

$$\langle k \rangle_{ss} = \frac{8\sqrt{2}\pi^2 \alpha^{1/4}}{\eta^{3/4} \Gamma(1/4)^2} \frac{I_{3/4}(z_0)}{I_{-3/4}(z_0)}. \tag{6.11}$$

The desired small η expansions are obtained from either Eqs. (6.10) and (6.11) or from an iterative solution of Eq. (5.7) which involves only integrals of r^{-m}. One finds
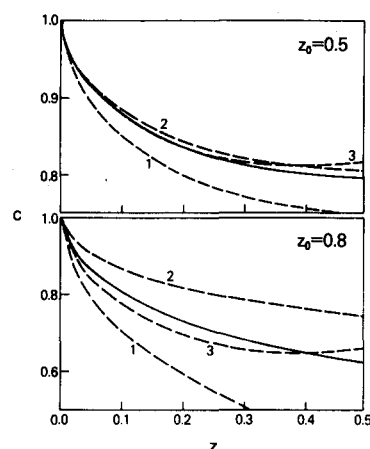
FIG. 6. The steady-state concentration profile as a function of $z \equiv \frac{1}{2}(\eta\alpha)^{1/2}r^{-2}$ for a diffusing quencher-particle pair in three dimensions, with a reflecting boundary condition at the contact distance a and Förster-type quenching, αr^{-6}, at larger separations. Results are shown for two values of $z_0 \equiv \frac{1}{2}(\eta\alpha)^{1/2}a^{-2}$. Full curves are the exact solution, (6.10). Dashed curves are partial sums in expansion (6.12). The curves are labeled by the appropriate power of η.

$$c(z) \sim 1 + \frac{1}{3} z^{1/2}\{ - (4z_0^{3/2} - z^{3/2})$$
$$+ (\tfrac{24}{7} z_0^{7/2} - \tfrac{4}{5} z_0^{3/2}z^2 + \tfrac{1}{14} z^{7/2})$$
$$- (\tfrac{168}{55} z_0^{11/2} - \tfrac{24}{5} z_0^{7/2}z^2 + \tfrac{2}{43}z_0^{3/2}z^4$$
$$- \tfrac{1}{462}z^{11/2}) + \cdots \}. \qquad (6.12)$$

From the definitions of z and z_0, this is clearly a power series in η. In Fig. 6 it is compared with the exact result, Eq. (6.10), for two values of z_0.

The (asymptotic) expansion for the steady-state rate is obtained from Eqs. (6.12) and (5.4)

$$\langle k \rangle_{ss} \sim 4\pi a a^{-3}\left[\tfrac{1}{3} - \tfrac{2}{7}z_0^2 + \tfrac{14}{55}z_0^4 - \tfrac{92}{403}z_0^6 + \cdots \right]. \qquad (6.13)$$

This result is derived elsewhere[18,19] in a more tedious route. A recursive solution of "viscosity expansions" like Eq. (5.7) seems to be the most direct way. As before, an improved approximation for finite z_0 is obtained[23] by inverting the series (6.13).
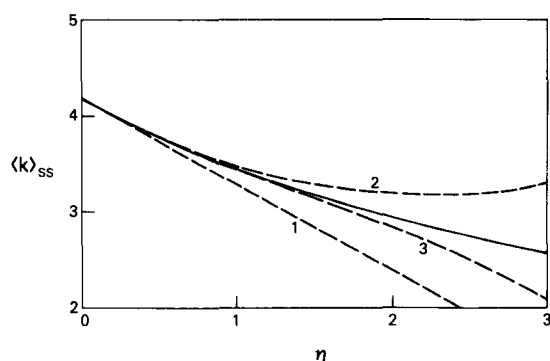

FIG. 7. The steady-state rate coefficient for the quenching problem of Fig. 6 as a function of the viscosity for $a = 1$ and $\alpha = 1$. Full curve is the exact result, Eq. (6.11). Dashed curves are the appropriate partial sums in the expansion (6.13).
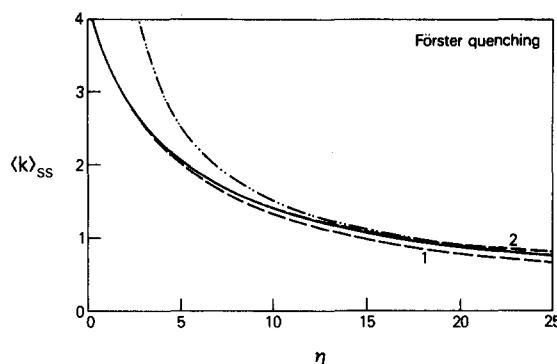

FIG. 8. Same as Fig. 7, on an extended viscosity scale and in comparison with approximation (6.14) shown as (the two) dashed curves. The dash-dotted curve is the slow diffusion limit, Eq. (6.15).

$$\langle k \rangle_{ss} \approx \tfrac{4}{3} \pi a a^{-3}\left[1 + \tfrac{6}{7}z_0^2 - \tfrac{78}{2695}z_0^4 + \cdots \right]^{-1}. \qquad (6.14)$$

This is similar to the lowest eigenvalue expansion for bounded systems, Eq. (3.33).

Figure 7 compares expansion (6.13) with the exact result, Eq. (6.11). It is seen that the convergence is only asymptotic. The inverted expansion, Eq. (6.14), provides a drastic improvement, as can be seen from Fig. 8 (note the change in scale). It describes the viscosity dependence all the way to the small D limit

$$\langle k \rangle_{ss} \sim \frac{8\sqrt{2}\pi^2\alpha^{1/4}}{\eta^{3/4}\Gamma(1/4)^2}, \quad D\to 0 \qquad (6.15)$$

which is gotten from Eq. (6.11) by noting[25] that the asymptotic behavior of $I_\nu(z)$ for large z depends only on ν^2.

VII. CONCLUSION

Viscosity expansions involve expanding the probability density and derived quantities in powers of the diffusion coefficient or its inverse, the viscosity, for systems with a finite, possibly coordinate dependent, reaction sink term. The present work dealt particularly with the limit of small viscosity where it is straightforward to show that such expansions exist. These were obtained for the survival probability and eigenvalues for bounded diffusion and the concentration profile and steady-state rate coefficient for unbounded diffusion. Comparison with exact analytic solutions showed that they indeed provide a useful approximation.

Although determination of higher order terms may become exceedingly difficult, the first few terms in an asymptotic expansion often suffice for constructing approximations with more uniform convergence properties. Specifically, it was demonstrated how the inverted series provided a much improved description for the lowest eigenvalue and the steady-state rate coefficient. In cases where no analytic solutions exist, one may still obtain analytic approximations using this method. Such results can be quite helpful in fitting experimental data.

ACKNOWLEDGMENTS

APPENDIX A

In this Appendix viscosity expansions are obtained for one-dimensional diffusion in the interval $[0,b]$, with reflection at $x = 0$ and a radiation boundary condition, Eq. (4.1), at $x = b$ and under the influence of a linear potential

$$V(x) = cx. \tag{A1}$$

This may represent unimolecular dissociation of an isolated molecule, the coordinate x being the vibrational state, and can be solved semianalytically.[22]

The normalized equilibrium distribution is

$$p^{eq}(x) = c \exp(-cx)/[1 - \exp(-cb)]. \tag{A2}$$

The lifetime for an initial delta-function distribution is given by [cf. Eq. (4.5)]

$$\tau(x) = [\kappa p^{eq}(b)]^{-1}$$
$$+ \eta c^{-2}[\exp(cb) - \exp(cx) - c(b - x)]. \tag{A3}$$

Its equilibrium average is

$$\langle \tau \rangle_{eq} = [\kappa p^{eq}(b)]^{-1}$$
$$+ \eta c^{-2}\{1 + \exp(cb) - 2cb/[1 - \exp(-cb)]\}. \tag{A4}$$

When η is small, the lowest eigenfunction is

$$Nh_0(x) = [(c + \xi)\exp(-\xi x/2)$$
$$- (c - \xi)\exp(\xi x/2)]\exp(cx/2), \tag{A5}$$

where $\xi^2 \equiv c^2 - 4\eta\lambda_0$ and N is a normalization constant, so that $\langle h_0 \rangle_{eq} = 1$. The lowest eigenvalue λ_0 obeys the following transcendental equation

$$(\xi + c)(\xi - c - 2\eta\lambda_0)\exp(-\xi b)$$
$$= (\xi - c)(\xi + c + 2\eta\lambda_0). \tag{A6}$$

One can expand the above results in powers of η and compare with the theory of Sec. III. Writing $\xi = c - 2\eta\lambda_0/c + \cdots$ and $\exp(-\xi b) = \exp(-cb)[1 + 2\eta\lambda_0 b/c - \cdots]$ converts Eq. (A6) to

$$\lambda_0 = \kappa p^{eq}(b) - \eta\lambda_0[\kappa p^{eq}(b)]c^{-2}\{1 + \exp(cb)$$
$$- 2cb[1 + \lambda_0/(\kappa c)]\} + \cdots. \tag{A7}$$

The last equation can be solved iteratively. Setting $\eta = 0$ gives $\lambda_0^{(0)} = \kappa p^{eq}(b)$. Inserting this in the right-hand side of Eq. (A7) yields

$$\lambda_0^{(0+1)} = \kappa p^{eq}(b) + \eta[\kappa p^{eq}(b)]^2 c^{-2}\{1 + \exp(cb)$$
$$- 2cb/[1 - \exp(-cb)]\} \tag{A8}$$

which is indeed the inverse of $\langle \tau \rangle_{eq}$, Eq. (A4), in agreement with the results of Sec. III. As for the other examples studied, one expects $\langle \tau \rangle_{eq}^{-1}$, Eq. (A4), to agree with the viscosity

dependence of the lowest eigenvalue over a larger range than Eq. (A8).

Expanding the lowest eigenfunction in Eq. (A5) up to first order in η gives

$$Nh_0^{(0+1)}(x) = 1 - \eta[\kappa p^{eq}(b)]c^{-2}[1 - cx + \exp(cx)]. \tag{A9}$$

Normalizing, and collecting terms up to η, one finds that

$$h_0^{(1)}(x) = -\kappa p^{eq}(b)c^{-2}$$
$$\times [1 - cx + \exp(cx) - cb \coth(cb/2)]$$
$$= \kappa p^{eq}(b)[\tau(x) - \langle \tau \rangle_{eq}] \tag{A10}$$

in agreement with Eq. (3.29).

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