

Electron transfer reaction dynamics in non-Debye solvents

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The dynamics of electron transfer in a non-Debye solvent is described by multidimensional Markovian reaction-diffusion equation. To highlight differences with existing approaches in the simplest possible context, the irreversible outer-sphere reaction in a solvent with a biexponential energy-gap autocorrelation function, $\Delta(t)$, is studied in detail. In a Debye solvent, $\Delta(t) = \exp(-t/\tau_L)$ and the rate can be rigorously expressed as an explicit functional of $\exp(-t/\tau_L)$. It has been suggested that the exact rate in a non-Debye solvent can be found by replacing $\exp(-t/\tau_L)$ with the appropriate (nonexponential) $\Delta(t)$. For a “biexponential” solvent, our approach is based on an anisotropic diffusion equation for motion on a harmonic surface in the presence of a two-dimensional delta function sink. Three approximations, which reduce the solution of this equation to effective one-dimensional ones, are considered and compared with exact Brownian dynamics simulation results. The crudest approximation replaces the non-Debye solvent with an effective Debye one with $\tau_{\text{eff}}^{-1} = (-d\Delta/dt)_{t=0}$. The second is obtained by invoking the Wilemski–Fixman-type closure approximation for the equivalent two-dimensional integral equation. This approximation turns out to be identical to the above mentioned “substitution” procedure. When the relaxation times of the two exponentials are sufficiently different, it is shown how the two-dimensional problem can be reduced to a one-dimensional one with a nonlocal sink function. This anisotropic relaxation time approximation is in excellent agreement with simulations when the relaxation times differ by at least a factor of three and the activation energy is greater than $k_B T$. Finally, it is indicated how the influence of intramolecular vibrational modes (i.e., nonlocal sink functions) can be treated within the framework of this formalism. © 1998 American Institute of Physics. [S0021-9606(98)50930-0]

I. INTRODUCTION

Outer-sphere electron transfer can occur only when the solvent configuration is such that the reactant and product energies are equal.^{1,2} When the fluctuations of the solvent are sufficiently fast, the rate of electron transfer is determined by the equilibrium probability of such configurations around the reactants. In general, the rate is influenced by the time scale of solvent fluctuations.^{3–14} The relevant time scale is determined by the decay of the energy gap autocorrelation function,¹⁵ $\Delta(t)$. The energy gap¹⁶ is the instantaneous change in the solvation energy upon moving an electron from the donor to the acceptor. For a Debye solvent, $\Delta(t) = \exp(-t/\tau_L)$, where τ_L is the longitudinal dielectric relaxation time. For most solvents, the decay of $\Delta(t)$ is more complex but can often be well described (except at very short times) by the sum of two exponentials.

This paper deals with the theory of solvent-controlled adiabatic electron transfer in such non-Debye solvents. With some notable exceptions,^{4,13} previous theoretical attempts^{9–12,14} to treat the effect of non-Debye solvents boil down to generalizing Zusman’s treatment³ of a Debye solvent in the following way. For a Debye solvent, the Green’s function that describes the time evolution of the probability of solvent fluctuations has a Gaussian functional form and

depends explicitly on $\exp(-t/\tau_L)$. In the absence of intramolecular vibrational modes, the electron transfer rate can be rigorously expressed as a certain integral of this function. When the solvent fluctuations can be described by the non-Markovian Gaussian process, the Green’s function has the identical form but with $\exp(-t/\tau_L)$ being replaced by the appropriate (nonexponential) $\Delta(t)$. The rate of electron transfer is then obtained by substituting this exact non-Markovian Green’s function into the expression that was rigorously derived for a Debye solvent. This “substitution” procedure seems plausible and in fact has been claimed to be exact.¹¹

In this paper we generalize Zusman’s treatment to non-Debye solvents by representing the solvent coordinate (the energy gap) by an appropriate linear combination of Markovian variables. For the sake of simplicity, we explicitly consider a solvent for which $\Delta(t)$ is a sum of two exponentials with positive amplitudes. In this case, our formalism is based on a two-dimensional reaction-diffusion equation or equivalently, on a two-dimensional integral equation that relates the Green’s functions in the absence and presence of reaction. We show that the above mentioned “substitution” procedure can be obtained from this integral equation only by invoking a Wilemski–Fixman-type closure approximation.¹⁷ Based on comparison with Brownian dynamics simulations, we found that in the solvent-controlled adiabatic regime, the “substitution” approximation is not

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accurate when the two relaxation times in $\Delta(t)$ differ by more than about a factor of 3. When the solvent relaxation is highly anisotropic, we reduce the two-dimensional reaction-diffusion equation to a one-dimensional one containing an effective sink term. The combination of this "anisotropic relaxation time" approximation and the "substitution" approximation reproduced the simulation results over the whole range of relaxation anisotropy when the activation energy was greater than the thermal energy.

The outline of the paper is as follows. In Sec. II the theory of nonadiabatic outer-sphere electron transfer in a Debye solvent is reviewed. In Sec. III, we show how to describe the dynamics of electron transfer in a "biexponential" solvent by means of a two-dimensional reaction-diffusion equation. Section IV considers three approximate solutions of this equation: (1) the effective Debye solvent, (2) Wilemski-Fixman or "substitution," and (3) anisotropic relaxation time approximations. These are compared with simulation results in Sec. V. Section VI contains a brief summary and discusses how to handle intramolecular vibrational modes within the framework of our formalism. Appendix A describes a finite-difference algorithm for solving a one-dimensional Smoluchowski equation in the presence of a nonlocal sink function, and Appendix B describes the Brownian dynamics algorithm used for the simulations.

II. OUTER-SPHERE ELECTRON TRANSFER IN DEBYE SOLVENTS

To introduce notation, we consider outer-sphere nonadiabatic electron transfer between a donor and acceptor. Let ΔV be the energy gap defined as the instantaneous change in the solvation energy upon moving an electron from the donor to the acceptor. ΔV depends on the configuration of the solvent and hence fluctuates. Let $p_{\text{eq}}(z)$ be the normalized probability density that the energy gap has value z when the solvent is in equilibrium with the reactant state. Electron transfer occurs only when the solvent configuration is such that the total energy of the reactants and the products is the same. Let ΔV^\ddagger denote the value of the energy gap for such solvent configurations. When the solvent dynamics is fast, the rate of electron transfer from reactants to products is given by the transition-state-like expression

$$k_{na} = \kappa p_{\text{eq}}(\Delta V^\ddagger), \quad (2.1)$$

with $\kappa = 2\pi |H_{RP}|^2 / \hbar$, where H_{RP} is the electronic coupling matrix element between reactant and product states. This relation is the classical limit of the Golden-Rule expression¹⁸ for the nonadiabatic rate constant.

When the solvent responds linearly to changes in the charge distributions, k_{na} is given by the Marcus result

$$k_{na} = \kappa \left(\frac{\beta}{4\pi\lambda} \right)^{1/2} \exp\{-\beta\Delta G^\ddagger\} \\ = \frac{\kappa}{[4\pi\lambda k_B T]^{1/2}} \exp\left\{-\frac{(\lambda + \Delta G)^2}{4\lambda k_B T}\right\}, \quad (2.2)$$

where $\beta = (k_B T)^{-1}$, λ is the solvent reorganizational energy, and ΔG is the total free energy change of the reaction. Equations (2.1) and (2.2) can then be rewritten as,

$$k_{na} = \kappa p_{\text{eq}}(z^\ddagger) = \kappa \int_{-\infty}^{\infty} \delta(z - z^\ddagger) p_{\text{eq}}(z) dz, \quad (2.3)$$

where

$$p_{\text{eq}}(z) = \frac{1}{[2\pi\langle z^2 \rangle]^{1/2}} \exp\left\{-\frac{z^2}{2\langle z^2 \rangle}\right\}, \quad (2.4)$$

with $\langle z^2 \rangle = 2\lambda k_B T$ and $z^\ddagger = \lambda + \Delta G$. For future reference, note that $\beta\Delta G^\ddagger = z^\ddagger^2 / 2\langle z^2 \rangle$. The reaction coordinate z is related to the energy gap ΔV as $z = \langle \Delta V \rangle - \Delta V$, where $\langle \Delta V \rangle$ is the average value of the energy gap in the reactant state.

The time scale of the solvent fluctuations is characterized by the normalized energy gap correlation function

$$\Delta(t) = \frac{\langle z(t)z(0) \rangle}{\langle z^2 \rangle}. \quad (2.5)$$

For a Debye solvent, $\Delta(t)$ is a single exponential

$$\Delta(t) = e^{-t/\tau_L}, \quad (2.6)$$

where τ_L is the longitudinal relaxation time. Equation (2.1) is valid in the limit $\tau_L \rightarrow 0$.

The time evolution of the probability density, $p(z, t)$, of a random variable with equilibrium distribution given in Eq. (2.4) and correlation function given in Eq. (2.6), satisfies the differential equation

$$\frac{\partial p}{\partial t} = D \frac{\partial}{\partial z} e^{-\beta V(z)} \frac{\partial}{\partial z} (e^{\beta V(z)} p); \beta V(z) = \frac{z^2}{2\langle z^2 \rangle}, \quad (2.7)$$

with $D = \langle z^2 \rangle / \tau_L$. This is just the diffusion equation in a harmonic potential. The corresponding Green's function, $G_0(z, t | z_0)$ (i.e., the conditional probability that the system is at z at time t given that it was at z_0 initially), is

$$G_0(z, t | z_0) = \frac{1}{[2\pi\langle z^2 \rangle(1 - \Delta^2)]^{1/2}} \\ \times \exp\left\{-\frac{(z - z_0\Delta)^2}{2\langle z^2 \rangle(1 - \Delta^2)}\right\}, \quad (2.8)$$

where $\Delta(t)$ is given in Eq. (2.6).

An expression for the rate of electron transfer when $\tau_L \neq 0$ can be obtained as follows. For the sake of simplicity we consider an irreversible reaction. The generalization to reversible reactions is straightforward. The simplest way to treat the reaction is to incorporate a sink term into the evolution Eq. (2.7)

$$\frac{\partial P}{\partial t} = D \frac{\partial}{\partial z} e^{-\beta V(z)} \frac{\partial}{\partial z} (e^{\beta V(z)} P(z, t)) - k(z) P(z, t). \quad (2.9)$$

This term must be chosen in such a way that in the limit $D \rightarrow \infty$ [or $\tau_L \rightarrow 0$], the rate expression given in Eq. (2.3) is recovered. The appropriate choice is

$$k(z) = \kappa \delta(z - z^\ddagger). \quad (2.10)$$

Equations (2.9) and (2.10) were first proposed by Zusman.³ The survival probability of the reactant state, given that the initial distribution of the reaction coordinate is the equilibrium distribution in the absence of the sink [i.e., $p_{\text{eq}}(z)$], is

$$S(t) = \int_{-\infty}^{\infty} dz_0 \int_{-\infty}^{\infty} dz P(z, t | z_0) p_{\text{eq}}(z_0), \quad (2.11)$$

where $P(z, t | z_0)$ is the reactive Green's function. The rate of electron transfer is then defined as the reciprocal of the mean lifetime of the system

$$\frac{1}{k_{\text{et}}} = \int_0^{\infty} S(t) dt. \quad (2.12)$$

For a delta function sink, exact analytic expression for k_{et} can be obtained using several approaches. Using the theory of the first passage times, it can be shown that¹⁹

$$\frac{1}{k_{\text{et}}} = \frac{1}{k_{\text{na}}} + \frac{1}{k_d(z^{\ddagger})}, \quad (2.13)$$

where $k_{\text{na}} = \langle k(z) \rangle$ is given in Eq. (2.3) [the equilibrium average being defined as $\langle (\dots) \rangle = \int_{-\infty}^{\infty} (\dots) p_{\text{eq}}(z) dz$], and the diffusive part of the rate is given by

$$\frac{1}{k_d(z^{\ddagger})} = \frac{\tau_L}{\langle z^2 \rangle} \left\{ \int_{-\infty}^{z^{\ddagger}} \frac{dx}{p_{\text{eq}}(x)} \left[\int_{-\infty}^x p_{\text{eq}}(y) dy \right]^2 + \int_{z^{\ddagger}}^{\infty} \frac{dx}{p_{\text{eq}}(x)} \left[\int_x^{\infty} p_{\text{eq}}(y) dy \right]^2 \right\}, \quad (2.14)$$

where p_{eq} is given by Eq. (2.4). We note that this result is valid even when p_{eq} is not Gaussian (i.e., for diffusion on an arbitrary one-dimensional surface).

An alternative procedure,^{3,5,6,19,20} which at first sight appears to be able to handle non-Debye solvents, is based on the Dyson-type equation

$$P(z, t | z_0) = G_0(z, t | z_0) - \int_0^t dt' \int_{-\infty}^{\infty} dz' \times G_0(z, t - t' | z') k(z') P(z', t' | z_0) \quad (2.15a)$$

$$= G_0(z, t | z_0) - \kappa \int_0^t dt' \times G_0(z, t - t' | z^{\ddagger}) P(z^{\ddagger}, t' | z_0), \quad (2.15b)$$

which relates the Green's functions in the absence (G_0) and presence (P) of the reaction. The above integral equation is equivalent to Eq. (2.9).

Laplace transforming Eq. (2.15b) we have

$$\hat{P}(z, s | z_0) = \hat{G}_0(z, s | z_0) - \kappa \hat{G}_0(z, s | z^{\ddagger}) \hat{P}(z^{\ddagger}, s | z_0), \quad (2.16)$$

where $\hat{g}(s) = \int_0^{\infty} e^{-st} g(t) dt$. Setting $z = z^{\ddagger}$, solving the resulting equation for $\hat{P}(z^{\ddagger}, s | z_0)$ and using this in Eq. (2.16) one obtains

$$\hat{P}(z, s | z_0) = \hat{G}_0(z, s | z_0) - \frac{\kappa \hat{G}_0(z, s | z^{\ddagger}) \hat{G}_0(z^{\ddagger}, s | z_0)}{1 + \kappa \hat{G}_0(z^{\ddagger}, s | z^{\ddagger})}. \quad (2.17)$$

Using this in Eq. (2.11), the Laplace transform of the survival probability becomes

$$\hat{S}(s) = \frac{1}{s} - \frac{\kappa p_{\text{eq}}(z^{\ddagger})}{s^2 [1 + \kappa \hat{G}_0(z^{\ddagger}, s | z^{\ddagger})]}. \quad (2.18)$$

When $p_{\text{eq}}(z)$ is given by Eq. (2.4) and $\Delta G^{\ddagger} = z^{\ddagger} = 0$, $\hat{S}(s)$ is given by²⁰

$$\hat{S}(s) = \frac{1}{s} - \frac{2\kappa\Gamma[(1+s\tau_L)/2]}{\pi^{1/2}s^2[\kappa\tau_L\Gamma(s\tau_L/2) + \sqrt{8\langle z^2 \rangle}\Gamma[(1+s\tau_L)/2]]}, \quad (2.19)$$

where $\Gamma(x)$ is the gamma function. When $\kappa \rightarrow \infty$ this can be inverted and we recover the well known result^{7,20,21}

$$S(t) = \frac{2}{\pi} \arcsin(e^{-t/\tau_L}). \quad (2.20)$$

From Eq. (2.12) it follows that $k_{\text{et}}^{-1} = \hat{S}(0)$. Taking the $s \rightarrow 0$ limit of Eq. (2.18), and using the small s expansion

$$\lim_{s \rightarrow 0} \hat{G}_0(z, s | z_0) = \frac{p_{\text{eq}}(z)}{s} + \int_0^{\infty} dt [G_0(z, t | z_0) - p_{\text{eq}}(z)], \quad (2.21)$$

one finds that k_{et}^{-1} is given by Eq. (2.13) with

$$\frac{1}{k_d(z^{\ddagger})} = \int_0^{\infty} dt \left\{ \frac{G_0(z^{\ddagger}, t | z^{\ddagger})}{p_{\text{eq}}(z^{\ddagger})} - 1 \right\}. \quad (2.22)$$

For one-dimensional diffusion in an arbitrary potential $V(z)$, Eqs. (2.22) and (2.14) are completely equivalent.

For motion on a harmonic surface, using Eqs. (2.8) and (2.6), we have

$$\frac{1}{k_d(z^{\ddagger})\tau_L} = \int_0^{\infty} dt' \left\{ \frac{\exp\left\{\left(\frac{2e^{-t'}}{1+e^{-t'}}\right)\beta\Delta G^{\ddagger}\right\}}{(1-e^{-2t'})^{1/2}} - 1 \right\}, \quad (2.23)$$

where we have used $\beta\Delta G^{\ddagger} = z^{\ddagger 2}/2\langle z^2 \rangle$. When $\Delta G^{\ddagger} = 0$, this integral can be done analytically. When $\beta\Delta G^{\ddagger} \gg 1$, the main contribution to the integral comes from the short time behavior of the integrand and thus

$$k_d\tau_L = \frac{1}{\ln(2)}; \quad \beta\Delta G^{\ddagger} = 0 \quad (2.24a)$$

$$= \left(\frac{\beta\Delta G^{\ddagger}}{\pi} \right)^{1/2} e^{-\beta\Delta G^{\ddagger}} = |z^{\ddagger}| p_{\text{eq}}(z^{\ddagger}); \quad \beta\Delta G^{\ddagger} \gg 1, \quad (2.24b)$$

as found by Zusman.³

We end this section by pointing out that the exact expression for the survival probability in Eq. (2.18) can be rewritten in terms of the Laplace transform of the equilibrium sink-sink correlation as

$$s\hat{S}(s) = 1 - \frac{\langle k \rangle}{s} \left[1 + \frac{\langle \widehat{k(s)k(0)} \rangle}{\langle k \rangle} \right]^{-1}, \quad (2.25)$$

where $\langle \widehat{k(s)k(0)} \rangle$ is the Laplace transform of the equilibrium sink-sink correlation function, and

$$\langle A(t)B(0) \rangle = \int_{-\infty}^{\infty} dx_0 \int_{-\infty}^{\infty} dx A(x) G_0(x, t | x_0) \times B(x_0) p_{\text{eq}}(x_0). \quad (2.26)$$

Similarly, the exact expression for k_{et} given in Eqs. (2.13) and (2.22) can also be rewritten as a time integral of an equilibrium sink-sink correlation.¹⁹ Defining $\delta k(z) = k(z) - \langle k \rangle$, these equations become

$$\frac{1}{k_{et}} = \frac{1}{\langle k \rangle} + \int_0^\infty dt \frac{\langle \delta k(t) \delta k(0) \rangle}{\langle k \rangle^2}, \quad (2.27)$$

for $k(z) = \kappa \delta(z - z^\ddagger)$.

These equations were first obtained by Wilemski and Fixman using a “closure approximation” for arbitrary multidimensional sink terms. However, they are exact only when $k(z)$ is a one-dimensional delta function. As we shall show later, several existing treatments of the rate of irreversible electron transfer reaction in non-Debye solvents are in fact equivalent to using Eqs. (2.25) and (2.27) for a multidimensional problem, where they are not exact.

III. OUTER-SPHERE ELECTRON TRANSFER IN NON-DEBYE SOLVENTS

In non-Debye solvents, the energy gap correlation function, $\Delta(t)$, is not a single exponential. When the dynamics of the reaction coordinate can be described as a non-Markovian Gaussian process, the Green’s function, $G(z, t|z_0)$, has the same functional form as the Markovian Green’s function G_0 given in Eq. (2.8)

$$G(z, t|z_0) = \frac{1}{[2\pi\langle z^2 \rangle(1 - \Delta^2)]^{1/2}} \exp\left\{-\frac{(z - z_0\Delta)^2}{2\langle z^2 \rangle(1 - \Delta^2)}\right\}, \quad (3.1)$$

but with $\Delta(t)$ being an arbitrary function of time that vanishes as $t \rightarrow \infty$. The equilibrium distribution, $p_{eq}(z) = \lim_{t \rightarrow \infty} G(z, t|z_0)$, is given by Eq. (2.4). This is an exact result. As can be shown by direct differentiation, this Green’s function satisfies the non-Markovian Smoluchowski equation

$$\frac{\partial G}{\partial t} = D(t) \frac{\partial}{\partial z} e^{-z^2/2\langle z^2 \rangle} \frac{\partial}{\partial z} (e^{z^2/2\langle z^2 \rangle} G); \quad (3.2)$$

$$G(z, t=0|z_0) = \delta(z - z_0),$$

where the time-dependent diffusion coefficient is given by

$$D(t) = -\langle z^2 \rangle \frac{d}{dt} (\ln[\Delta(t)]). \quad (3.3)$$

This is also an exact result.

A number of approaches to calculate the rate of electron transfer in non-Debye solvents^{9–12} are equivalent to simply replacing $G_0(z, t|z_0)$ in the exact one-dimensional expression given in Eq. (2.22) with the exact non-Markovian $G(z, t|z_0)$ given in Eq. (3.1). This seems reasonable and at first sight may even appear to be exact. However, this is not the case, because in the non-Markovian case, the reactive Green’s function does not satisfy the integral Eq. (2.15a) with G_0 being replaced with G . The simplest way to see this is to consider a Langevin oscillator [diffusion in phase space $(z, \dot{z} \equiv v)$ on a harmonic potential]. In coordinate space the dynamics of such an oscillator is non-Markovian and the reduced Green’s function has the form given by Eq. (3.1).²²

In the presence of a position dependent sink, the reactive Green’s function in *phase space* does satisfy a two-dimensional Dyson-like equation analogous to Eq. (2.15a). However, it is not possible to integrate out the velocity and obtain an Eq. (2.15a) with G_0 replaced by the reduced coordinate space Green’s function (i.e., G), without invoking approximations. In the context of a “biexponential” solvent, this will be made explicit in Sec. IV B.

In this paper we exploit the equivalence between a non-Markovian process and the suitable projection of an underlying multidimensional Markovian process. Our theory is based on the appropriate multidimensional generalization of the reaction-diffusion Eq. (2.9) and the equivalent multidimensional integral equation that relates the Green’s functions in the absence and the presence of the reaction. We shall show that the aforementioned “substitution” approximation (i.e., replacing G_0 with G) can be derived from our multidimensional Markovian formalism by invoking a Wilemski-Fixman-like “closure” approximation.

To illustrate this approach, we consider in detail the problem in which $\Delta(t)$ is biexponential. For reasons that will become evident shortly, we choose the following notation for $\Delta(t)$:

$$\Delta(t) = \frac{\langle z(t)z(0) \rangle}{\langle z^2 \rangle} = \frac{\langle x^2 \rangle}{\langle x^2 \rangle + \langle y^2 \rangle} e^{-D_x t / \langle x^2 \rangle} + \frac{\langle y^2 \rangle}{\langle x^2 \rangle + \langle y^2 \rangle} e^{-D_y t / \langle y^2 \rangle}. \quad (3.4)$$

This suggests that we represent the *observable* coordinate z as the sum of two *independent* diffusive oscillator variables x and y that are described by diffusion coefficients D_x and D_y , have zero means, and satisfy $\langle z^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle$. Since the time correlation functions of such variables satisfy

$$\Delta_x(t) = \frac{\langle x(t)x(0) \rangle}{\langle x^2 \rangle} = e^{-D_x t / \langle x^2 \rangle} = e^{-t/\tau_x}, \quad (3.5a)$$

$$\Delta_y(t) = \frac{\langle y(t)y(0) \rangle}{\langle y^2 \rangle} = e^{-D_y t / \langle y^2 \rangle} = e^{-t/\tau_y}, \quad (3.5b)$$

and since $\langle xy \rangle = 0$, it immediately follows that Eq. (3.4) holds when $z = x + y$. We can further show that the reduced Green’s function $G(z, t|z_0)$ is given by Eq. (3.1) with $\Delta(t)$ given by Eq. (3.4). This reduced Green’s function is defined as

$$G(z, t|z_0) p_{eq}(z_0) = \int_{-\infty}^{\infty} dx_0 \int_{-\infty}^{\infty} dy_0 \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \times \delta(x + y - z) \times G_0(x, y, t|x_0, y_0) \times \delta(x_0 + y_0 - z_0) p_{eq}(x_0, y_0), \quad (3.6)$$

where $p_{eq}(z_0)$ is given by

$$p_{eq}(z) = \frac{e^{-\beta V(z)}}{\int_{-\infty}^{\infty} e^{-\beta V(z)} dz} = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \times \delta(x + y - z) p_{eq}(x, y). \quad (3.7)$$

Since x and y are independent, $G_0(x, y, t|x_0, y_0)$ is just the product of the one-dimensional Green’s function for x and y .

Each of these has the same functional form as Eq. (2.8) with $\Delta_x(t)$ or $\Delta_y(t)$ given in Eqs. (3.5a) and (3.5b). Similarly, $p_{\text{eq}}(x,y) = p_{\text{eq}}(x)p_{\text{eq}}(y)$ where, for example, $p_{\text{eq}}(x) = (2\pi\langle x^2 \rangle)^{-1/2} \exp\{-x^2/2\langle x^2 \rangle\}$. Using these results in Eqs. (3.6) and (3.7) and evaluating the Gaussian integrals, it follows that $G(z,t|z_0)$ is indeed given by Eq. (3.1) with $\Delta(t)$ given by Eq. (3.4), and $p_{\text{eq}}(z_0)$ is given by Eq. (2.4).

We are now in a position to find the generalization of the reaction-diffusion Eq. (2.9) that describes electron transfer in a solvent with biexponential dynamics. Since x and y are independent, their dynamics can be described as diffusion on a potential surface

$$\beta V(x,y) = \frac{x^2}{2\langle x^2 \rangle} + \frac{y^2}{2\langle y^2 \rangle}, \quad (3.8)$$

with diffusion coefficients D_x and D_y . Thus the generalization of Eq. (2.9) is

$$\begin{aligned} \frac{\partial P(x,y,t)}{\partial t} = & \left[D_x \frac{\partial}{\partial x} e^{-\beta V(x,y)} \frac{\partial}{\partial x} e^{\beta V(x,y)} \right. \\ & \left. + D_y \frac{\partial}{\partial y} e^{-\beta V(x,y)} \frac{\partial}{\partial y} e^{\beta V(x,y)} - k(x+y) \right] \\ & \times P(x,y,t), \end{aligned} \quad (3.9)$$

with

$$k(x+y) = \kappa \delta(x+y-z^\ddagger). \quad (3.10)$$

The survival probability, $S(t)$, is given by the two-dimensional analog of Eq. (2.11) and the rate by Eq. (2.12).

In spite of the apparent simplicity of the above two-dimensional reaction-diffusion equation, it is not possible to solve it analytically to get a close form expression for k_{et} . A variety of approximations of increasing sophistication are considered in the next section.

IV. APPROXIMATE TREATMENTS OF ELECTRON TRANSFER IN A "BIEXPONENTIAL" NON-DEBYE SOLVENT

A. Effective Debye solvent

The simplest conceivable approximation is to replace the two-dimensional reaction-diffusion Eq. (3.9) with a one-dimensional equation of the same structure of Eq. (2.9) but with an *effective* diffusion coefficient D_{eff} ,

$$\frac{\partial P(z,t)}{\partial t} = D_{\text{eff}} \frac{\partial}{\partial z} e^{-\beta V(z)} \frac{\partial}{\partial z} e^{\beta V(z)} P(z,t) - k(z) P(z,t), \quad (4.1)$$

with $\beta V(z) = z^2/2\langle z^2 \rangle$ and $k(z) = \kappa \delta(z-z^\ddagger)$. From Eqs. (3.7) and (3.8) it follows that $V(z)$ is just the potential of mean force along z . The dynamics of the effective Debye solvent is described by

$$\Delta_{\text{eff}}(t) = \exp\left\{-\frac{D_{\text{eff}} t}{\langle z^2 \rangle}\right\} = \exp\left\{-\frac{t}{\tau_{\text{eff}}}\right\}. \quad (4.2)$$

How should τ_{eff} be chosen? The biexponential correlation in Eq. (3.4) can be characterized by two correlation times. The short time or high-frequency correlation time τ_∞ defined as

$$\frac{1}{\tau_\infty} = -\left.\frac{d\Delta(t)}{dt}\right|_{t=0} = \frac{D_x + D_y}{\langle z^2 \rangle}, \quad (4.3)$$

and the low-frequency correlation time τ_0 defined as

$$\tau_0 = \int_0^\infty \Delta(t) dt = \frac{\langle x^2 \rangle D_y + \langle y^2 \rangle D_x}{\langle z^2 \rangle D_x D_y}. \quad (4.4)$$

From the discussion below Eq. (2.23), it follows that for high barriers, the diffusive part of the rate constant corresponding to Eq. (4.1) is determined by the short time behavior of $\Delta_{\text{eff}}(t)$. This suggests that one determines τ_{eff} by requiring that

$$\left.\frac{d\Delta_{\text{eff}}(t)}{dt}\right|_{t=0} = \left.\frac{d\Delta(t)}{dt}\right|_{t=0}. \quad (4.5)$$

Thus, $\tau_{\text{eff}} = \tau_\infty$, or equivalently, $D_{\text{eff}} = D_x + D_y$. In the present context, the relevance of τ_∞ (rather than τ_0) was first recognized by Hynes.⁹ The resulting expression, for the survival probability $S_{\text{eff}}^\infty(t)$ is then given by Eq. (2.18), and for k_{et} is given by Eq. (2.13) with $k_{d,\text{eff}}^\infty$ given by Eq. (2.23) with τ_L replaced by τ_∞ , i.e.,

$$k_{d,\text{eff}}^\infty(z^\ddagger) = \frac{1}{\ln(2)\tau_\infty}; \quad \beta\Delta G^\ddagger = 0 \quad (4.6a)$$

$$= \frac{1}{\tau_\infty} \left(\frac{\beta\Delta G^\ddagger}{\pi}\right)^{1/2} e^{-\beta\Delta G^\ddagger}; \quad \beta\Delta G^\ddagger \gg 1. \quad (4.6b)$$

We expect Eq. (4.6b) to be exact in the limit $\Delta G^\ddagger \rightarrow \infty$.

B. The Wilemski-Fixman and the "substitution" approximations

The solution of the two-dimensional Eq. (3.9) is equivalent to solving the Dyson-type integral equation which relates the Green's function in the absence (G_0) and presence (P) of reaction

$$\begin{aligned} P(x,y,t|x_0,y_0) = & G_0(x,y,t|x_0,y_0) - \int_0^t dt' \int_{-\infty}^\infty dx' \int_{-\infty}^\infty dy' \\ & \times G_0(x,y,t-t'|x',y') \\ & \times k(x'+y') P(x',y',t'|x_0,y_0), \end{aligned} \quad (4.7)$$

where, for the moment, $k(x+y)$ is an arbitrary sink function. Unlike its one-dimensional analog [Eq. (2.15a)], it does not appear to be possible to analytically solve this equation and express the Laplace transform of P in terms of the Laplace transform of G_0 even if $k(x+y)$ is a delta function. This integral equation can be reduced to a one-dimensional one involving z only if we employ a Wilemski-Fixman-like closure approximation. We make the following "local equilibrium" approximation²³ for $P(x',y',t'|x_0,y_0)$ in Eq. (4.7),

$$P(x', y', t' | x_0, y_0) = p_{\text{eq}}(x', y') \frac{\int_{-\infty}^{\infty} dx'' \int_{-\infty}^{\infty} dy'' \delta[x'' + y'' - (x' + y')] P(x'', y'', t' | x_0, y_0)}{\int_{-\infty}^{\infty} dx'' \int_{-\infty}^{\infty} dy'' \delta[x'' + y'' - (x' + y')] p_{\text{eq}}(x'', y'')} \quad (4.8)$$

Substituting this into Eq. (4.7), using the relation $k(x' + y') = \int_{-\infty}^{\infty} dz' k(z') \delta(x' + y' - z')$, multiplying both sides by $\delta(x + y - z) \delta(x_0 + y_0 - z_0) p_{\text{eq}}(x_0, y_0)$, integrating over (x_0, y_0) and (x, y) from $-\infty$ to ∞ , and using Eqs. (3.6) and (3.7), we find

$$P(z, t | z_0) = G(z, t | z_0) - \int_0^t dt' G(z, t - t' | z') \times k(z') P(z', t' | z_0) \quad (4.9a)$$

$$= G(z, t | z_0) - \kappa \int_0^t dt' G(z, t - t' | z^{\ddagger}) \times P(z^{\ddagger}, t' | z_0), \quad (4.9b)$$

where on going from Eq. (4.9a) to Eq. (4.9b) we specialized to $k(z) = \kappa \delta(z - z^{\ddagger})$. These approximate integral equations are identical to Eqs. (2.15a) and (2.15b) with G_0 being replaced by the non-Markovian $G(z, t | z_0)$ given in Eq. (3.1) with $\Delta(t)$ being a biexponential.

For the sake of completeness, we note that the conventional Wilemski-Fixman closure approximation as applied to Eq. (4.9a) is

$$P(z', t' | z_0) = p_{\text{eq}}(z') \frac{\int_{-\infty}^{\infty} dz'' k(z'') P(z'', t' | z_0)}{\int_{-\infty}^{\infty} dz'' k(z'') p_{\text{eq}}(z'')} \quad (4.10)$$

This approximation leads to the rate expression given in Eq. (2.27).

Given Eq. (4.9b), it immediately follows from Sec. II that within this approximation, the Laplace transform of the survival probability is

$$\hat{S}_{\text{wf}}(s) = \frac{1}{s} - \frac{\kappa p_{\text{eq}}(z^{\ddagger})}{s^2 [1 + \kappa \hat{G}(z^{\ddagger}, s | z^{\ddagger})]}. \quad (4.11)$$

The rate of electron transfer is given by Eq. (2.13) with

$$\frac{1}{k_{d,\text{wf}}(z^{\ddagger})} = \int_0^{\infty} dt \left\{ \frac{\exp \left\{ \left(\frac{2\Delta}{1+\Delta} \right) \beta \Delta G^{\ddagger} \right\}}{(1-\Delta^2)^{1/2}} - 1 \right\}, \quad (4.12)$$

where $\Delta(t)$ is given in Eq. (3.4). We have thus shown that this “substitution” approximation is equivalent to the Wilemski-Fixman closure approximation in Eq. (4.8). It is interesting to note that this expression for the rate can also be obtained from the Wilemski-Fixman sink-sink correlation function expression Eq. (2.27) for the two-dimensional delta function sink, $k(x + y) = \kappa \delta(x + y - z^{\ddagger})$. In the high barrier limit, the main contribution to the integral in Eq. (4.12) occurs at short times. Since as $t \rightarrow 0$, $\Delta(t) \simeq 1 - (t/\tau_{\infty}) + \dots$, it follows that when $\beta \Delta G^{\ddagger}$ is sufficiently large:

$$k_{d,\text{wf}}(z^{\ddagger}) = \frac{1}{\tau_{\infty}} \left(\frac{\beta \Delta G^{\ddagger}}{\pi} \right)^{1/2} e^{-\beta \Delta G^{\ddagger}}, \quad (4.13)$$

which is the same as in Eq. (4.6b). Thus as $\beta \Delta G^{\ddagger} \rightarrow \infty$, $k_{d,\text{wf}} = k_{d,\text{eff}}^{\infty}$ (i.e., the rate constant for an effective Debye solvent with $\tau_{\text{eff}} = \tau_{\infty}$).

C. Anisotropic relaxation time [$\tau_x > \tau_y$]: The effective sink approximation

We consider the situation when the two relaxation times, τ_x and τ_y , that describe the biexponential energy gap correlation function in Eq. (3.4), are very different. Without loss of generality we take $\tau_x > \tau_y$ so that it is the dynamics along y that is relatively fast. We shall show that in the case when $\beta \Delta G^{\ddagger}$ is moderately large, the two-dimensional reaction-diffusion Eq. (3.9) can be reduced to a one-dimensional one involving the slow x coordinate with an effective sink function, $k_{\text{eff}}(x)$. The adiabatic elimination procedure we adopt here is similar to that used by Berezhkovskii and Zitserman²⁴ in their analysis of the multidimensional Kramers problem for large frictional anisotropy and by Spirina and Cukier²⁵ in their analysis of bond breaking electron transfer reactions.

This procedure begins by freezing all motions along the slow x coordinate. The probability distribution along y decays because of reaction. If this decay is close to exponential, the second and third terms in Eq. (3.9) can be approximated as

$$D_y \frac{\partial}{\partial y} e^{-y^2/2(y^2)} \frac{\partial}{\partial y} e^{y^2/2(y^2)} P(x, y, t) - \kappa \delta(x + y - z^{\ddagger}) P(x, y, t) \simeq -k_{\text{eff}}(x) P(x, y, t), \quad (4.14)$$

where $k_{\text{eff}}(x)$ is the reaction rate resulting from motions along y for fixed x . The system moving along y encounters a sink of the form $\kappa \delta(y - z_{\text{eff}}^{\ddagger}(x))$, where $z_{\text{eff}}^{\ddagger}(x) = z^{\ddagger} - x$. Since the initial distribution along y is the equilibrium one, $k_{\text{eff}}(x)$ is just the rate of electron transfer obtained in Sec. II with $z^{\ddagger} \rightarrow z_{\text{eff}}^{\ddagger}(x)$, $\langle z^2 \rangle \rightarrow \langle y^2 \rangle$, and $D \rightarrow D_y$, or equivalently, $\tau_L \rightarrow \tau_y = \langle y^2 \rangle / D_y$. Thus, from Eqs. (2.3) and (2.23) we have

$$\frac{1}{k_{\text{eff}}(x)} = \frac{\sqrt{2\pi\langle y^2 \rangle}}{\kappa} e^{\xi^2/2} + \tau_y \int_0^{\infty} dt' \left\{ \frac{\exp \left[\left(\frac{e^{-t'}}{1 + e^{-t'}} \right) \xi^2 \right]}{\sqrt{1 - e^{-2t'}}} - 1 \right\}, \quad (4.15a)$$

$$\xi = \frac{z^{\ddagger} - x}{\sqrt{\langle y^2 \rangle}},$$

or, using the quadrature expression in Eq. (2.14), one has

$$\frac{1}{k_{\text{eff}}(x)} = \frac{\sqrt{2\pi\langle y^2 \rangle}}{\kappa} e^{\xi^2/2} + \left(\frac{\pi}{2}\right)^{1/2} \frac{\tau_y}{2} \left\{ \int_{-\infty}^{\xi} dy e^{y^2/2} \left(\text{erfc} \left[-\frac{y}{\sqrt{2}} \right] \right)^2 + \int_{\xi}^{\infty} dy e^{y^2/2} \left(\text{erfc} \left[\frac{y}{\sqrt{2}} \right] \right)^2 \right\}. \quad (4.15b)$$

Finally, using the approximation

$$P(x, y, t) = (2\pi\langle y^2 \rangle)^{-1/2} e^{-y^2/2\langle y^2 \rangle} P(x, t) \quad (4.16)$$

in Eqs. (3.9) and (4.14), and integrating over y from $-\infty$ to $+\infty$, we have

$$\frac{\partial P(x, t)}{\partial t} = \left[D_x \frac{\partial}{\partial x} e^{-x^2/2\langle x^2 \rangle} \frac{\partial}{\partial x} e^{x^2/2\langle x^2 \rangle} - k_{\text{eff}}(x) \right] P(x, t). \quad (4.17)$$

The survival probability within the framework of this approximation is calculated from

$$S_{\text{AR}}(t) = \int_{-\infty}^{\infty} dx_0 \int_{-\infty}^{\infty} dx P(x, t | x_0) p_{\text{eq}}(x_0), \quad (4.18)$$

where $P(x, t | x_0)$ is the Green's function of Eq. (4.17). The rate of electron transfer is then defined as the reciprocal of the relaxation time of this survival probability as in Eq. (2.11). For the problem under consideration in this paper, Eq. (4.17) must be solved numerically (see Appendix A). The rate given by the Wilemski–Fixman sink–sink correlation function expression in Eq. (2.27), as applied to the above one-dimensional nonlocal $k_{\text{eff}}(x)$, turns out to be a poor approximation for low barriers. However, for very high activation energy, this works quite well and the rate is given by the leading first term of Eq. (2.27). One can thus show that, when $\kappa \rightarrow \infty$, the above “anisotropic relaxation” (AR) time approximation predicts that

$$k_{d,\text{AR}}(z^{\ddagger}) = \frac{1}{\tau_y} \frac{\langle y^2 \rangle}{\langle z^2 \rangle} \left(\frac{\beta \Delta G^{\ddagger}}{\pi} \right)^{1/2} e^{-\beta \Delta G^{\ddagger}}, \quad (4.19)$$

which is to be compared with the corresponding results obtained in the effective Debye solvent [Eq. (4.6b)] and multi-dimensional Wilemski–Fixman approximation [Eq. (4.13)]. Both these theories involve τ_{∞} rather than τ_y . To insure the AR time approximation gives the exact rate as $\beta \Delta G^{\ddagger} \rightarrow \infty$, we shall replace τ_y by $\tau_{\infty} \langle y^2 \rangle / \langle z^2 \rangle = \langle y^2 \rangle / (D_x + D_y)$ in Eqs. (4.15a) and (4.15b). When $D_y \gg D_x$ this has a negligible effect. However, we have found that this “renormalization” does extend the range of utility of the AR time approximation.

Up to this point, x and y were both harmonic solvent coordinates. However, if one identifies x with a Debye solvent coordinate and y with a diffusive vibrational coordinate, then Eq. (3.9) describes electron transfer in the presence of an intramolecular vibrational mode. In the limit when the vibrational motion is fast compared to the solvent dynamics, we have shown that this system is described by Eq. (4.17). This is just the Sumi–Marcus equation.⁷ The Sumi–Marcus sink function is given by the first term in Eqs. (4.15a) and

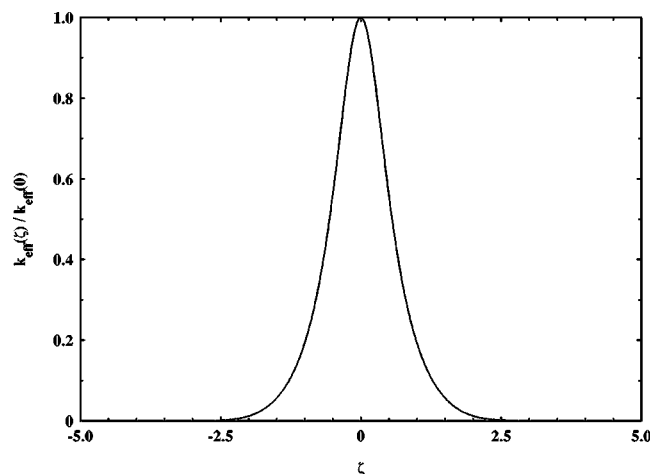


FIG. 1. Effective Gaussian sink function as given in Eq. (5.1) vs ζ , with $[k_{\text{eff}}(0)]^{-1} = (\ln 2)(D_x + D_y)/\langle y^2 \rangle$.

(4.15b) since they assumed $\tau_y = 0$. Thus Eq. (4.15a) [or, Eq. (4.15b)] is a generalization of the Sumi–Marcus sink function when the vibrational mode is diffusive with a finite relaxation time that is faster than the longitudinal solvent relaxation time.

V. COMPARISON BETWEEN THEORY AND SIMULATIONS

We consider the case when the reaction rate is determined by the solvent relaxation [i.e., $\kappa \rightarrow \infty$, solvent-controlled adiabatic electron transfer). In this case, the sink term in Eq. (3.9) is replaced by an absorbing line along $x + y = z^{\ddagger}$, and the effective sink in Eq. (4.17) becomes

$$k_{\text{eff}}(x) = \frac{(D_x + D_y)}{\langle y^2 \rangle} \times \left[\int_0^{\infty} dt' \left\{ \frac{\exp \left[\left(\frac{e^{-t'}}{1 + e^{-t'}} \right) \zeta^2 \right]}{\sqrt{1 - e^{-2t'}}} - 1 \right\} \right]^{-1}; \quad (5.1)$$

$$\zeta = \frac{x - z^{\ddagger}}{\sqrt{\langle y^2 \rangle}}.$$

This sink function exhibits a Gaussian-like form as displayed in Fig. 1.

In order to compare the approximate theories developed in the previous section with exact results, we have performed Brownian dynamics simulations to compute both the exact survival probability and rate for electron transfer reaction for a biexponential non-Debye solvent. As discussed in Sec. III, we simulate the motion of a particle diffusing on a two-dimensional harmonic potential surface in the presence of an absorbing line, $x + y = z^{\ddagger}$. The simulation algorithm used is described in Appendix B.

The ratio of the two relaxation times of a “biexponential” non-Debye solvent is

$$\eta = \frac{\tau_x}{\tau_y} = \frac{\langle x^2 \rangle D_y}{\langle y^2 \rangle D_x}. \quad (5.2)$$

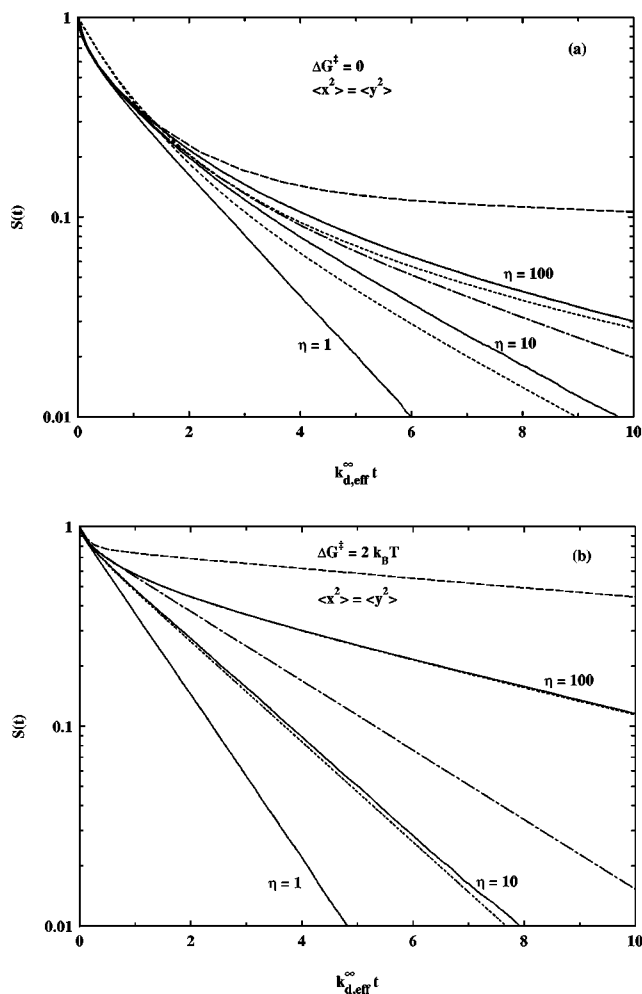


FIG. 2. Survival probability $S(t)$ as a function of reduced time $k_{d,\text{eff}}^\infty t$, where $k_{d,\text{eff}}^\infty$ is the rate for electron transfer in an effective Debye solvent with $\tau_L = \tau_\infty$ [see Sec. IV A]. Solid lines correspond to Brownian dynamics results, the dash-dotted [$\eta=10$] and long-dashed [$\eta=100$] lines to the Wilemski-Fixman or “substitution” approximation, $S_{\text{wf}}(t)$, and dashed lines to anisotropic relaxation time approximation, $S_{\text{AR}}(t)$ [numerical solution of Eq. (4.17)]. Both (a) and (b) refer to the case when $\langle x^2 \rangle = \langle y^2 \rangle$ and $\eta = D_y/D_x$.

Clearly, $\eta=1$ for a Debye solvent. Deviations from Debye behavior ($\eta>1$) can arise in two extreme ways: (i), $\langle x^2 \rangle = \langle y^2 \rangle$ but $D_y > D_x$ and (ii), $D_x = D_y$ but $\langle x^2 \rangle > \langle y^2 \rangle$. Below we consider these two cases in turn. Our results for the rate, k_d , will be presented relative to $k_{d,\text{eff}}^\infty$ (see Sec. IV A) which is the rate constant for solvent-controlled adiabatic electron transfer in an effective Debye solvent with $\tau_L = \tau_\infty$ [i.e., $D_{\text{eff}} = D_x + D_y$].

A. $\langle x^2 \rangle = \langle y^2 \rangle$ and $\eta = D_y/D_x$

In this case the frequencies of the two independent harmonic wells along the slow x and fast y coordinates are identical [i.e., the amplitudes of the two exponentials in $\Delta(t)$ are the same]. The non-Debye behavior originates exclusively from the anisotropy in diffusion coefficients.

Figures 2(a)–2(b) display the survival probability, $S(t)$, versus reduced time $k_{d,\text{eff}}^\infty t$ for selected values of η and activation energy. Solid lines are simulation results, the dash-

dotted and long-dashed lines correspond to the Wilemski-Fixman approximation, $S_{\text{wf}}(t)$, and dashed lines to anisotropic relaxation time approximation, $S_{\text{AR}}(t)$. $S_{\text{eff}}^\infty(t)$ and $S_{\text{wf}}(t)$ were obtained from the numerical inversion of Eq. (2.18) (with $\tau_L = \tau_\infty$) and Eq. (4.11), respectively, using the Stehfest algorithm with $n=10$ terms, and $S_{\text{AR}}(t)$ is computed from the numerical solution of the effective reaction-diffusion equation in Eq. (4.17). The curve for $\eta=1$ (i.e., the Debye case) corresponds to $S_{\text{eff}}^\infty(t)$. For all η , $S(t)$ in a non-Debye solvent is quite different from $S_{\text{eff}}^\infty(t)$.

Zero activation energy: All curves of survival probability are nonexponential. At short times [$k_{d,\text{eff}}^\infty t \leq 1$] $S(t)$, $S_{\text{eff}}^\infty(t)$, and $S_{\text{wf}}(t)$ are identical for all η , while $S_{\text{AR}}(t)$ underestimates $S(t)$ in this time range. The difference between these curves becomes more pronounced at long time. It appears that both $S_{\text{eff}}^\infty(t)$ and $S_{\text{wf}}(t)$ become very poor approximations to $S(t)$ when η gets larger. $S_{\text{eff}}^\infty(t)$ underestimates while $S_{\text{wf}}(t)$ overestimates $S(t)$ by almost the same percentage. Considering that $S_{\text{AR}}(t)$ was obtained assuming that ΔG^\ddagger is moderately large (i.e., the kinetics for fixed y is nearly single exponential) it works surprisingly well even when $\Delta G^\ddagger = 0$. However, none of the approximations is really very good in this case.

$\Delta G^\ddagger > k_B T$: A part from the initial nonexponential decay, all survival probabilities are essentially exponential for all η examined, i.e. $S_i(t) \approx \exp(-\alpha t)$, where α is equal to k_d , $k_{d,\text{eff}}^\infty$, $k_{d,\text{wf}}$, and $k_{d,\text{AR}}$ for $S(t)$, $S_{\text{eff}}^\infty(t)$, $S_{\text{wf}}(t)$, and $S_{\text{AR}}(t)$, respectively. $S_{\text{eff}}^\infty(t)$ and $S_{\text{wf}}(t)$ are poor approximations. However, even when $\Delta G^\ddagger = 2k_B T$, $S_{\text{AR}}(t)$ is an excellent approximation to $S(t)$ and is virtually exact for $\eta=100$. For larger ΔG^\ddagger 's, it works even better.

The rate constants are presented in Figs. 3(a)–3(c), where the ratio $k_{d,\text{eff}}^\infty/k_d$ is plotted against η for various values of the activation energy, $\beta\Delta G^\ddagger$, ranging from 0 to 4.5. The data (closed circles) represent k_d obtained from Brownian dynamics simulations, the long-dashed straight line $k_{d,\text{eff}}^\infty$, the solid line $k_{d,\text{wf}}$, and the dashed line $k_{d,\text{AR}}$. If one is content with an estimate of the rate that is good to an order of magnitude, using an effective Debye solvent with $\tau_L \equiv \tau_\infty$ [i.e., $k_{d,\text{eff}}^\infty$] suffices. The more sophisticated, $k_{d,\text{wf}}$ is better than $k_{d,\text{eff}}^\infty$ for small η , but it underestimates the rate by about the same percentage that $k_{d,\text{eff}}^\infty$ overestimates it for η greater than about 3.

However, we find an excellent agreement between $k_{d,\text{AR}}$ and simulation results over almost the whole range of η even for small activation energies. However, the agreement for small barriers, $\beta\Delta G^\ddagger \leq 1$, is accidental as can be seen from the survival probabilities in Fig. 2(a). The time area between $S_{\text{AR}}(t)$ and $S(t)$ at short times $k_{d,\text{eff}}^\infty t \leq 1$ is almost canceled by the (negative) area at long times, leading to the correct value of the rate. The combination of the Wilemski-Fixman approximation (for $\eta < 3$) and anisotropic relaxation approximation lead to accurate results for the rate for all η and all activation energies.

In Fig. 4 the ratio $k_{d,\text{eff}}^\infty/k_d$ is plotted as a function of activation energy for $\eta=10$ and $\eta=100$. k_d (closed circles) represent the simulation data, the long-dashed lines $k_{d,\text{wf}}$,

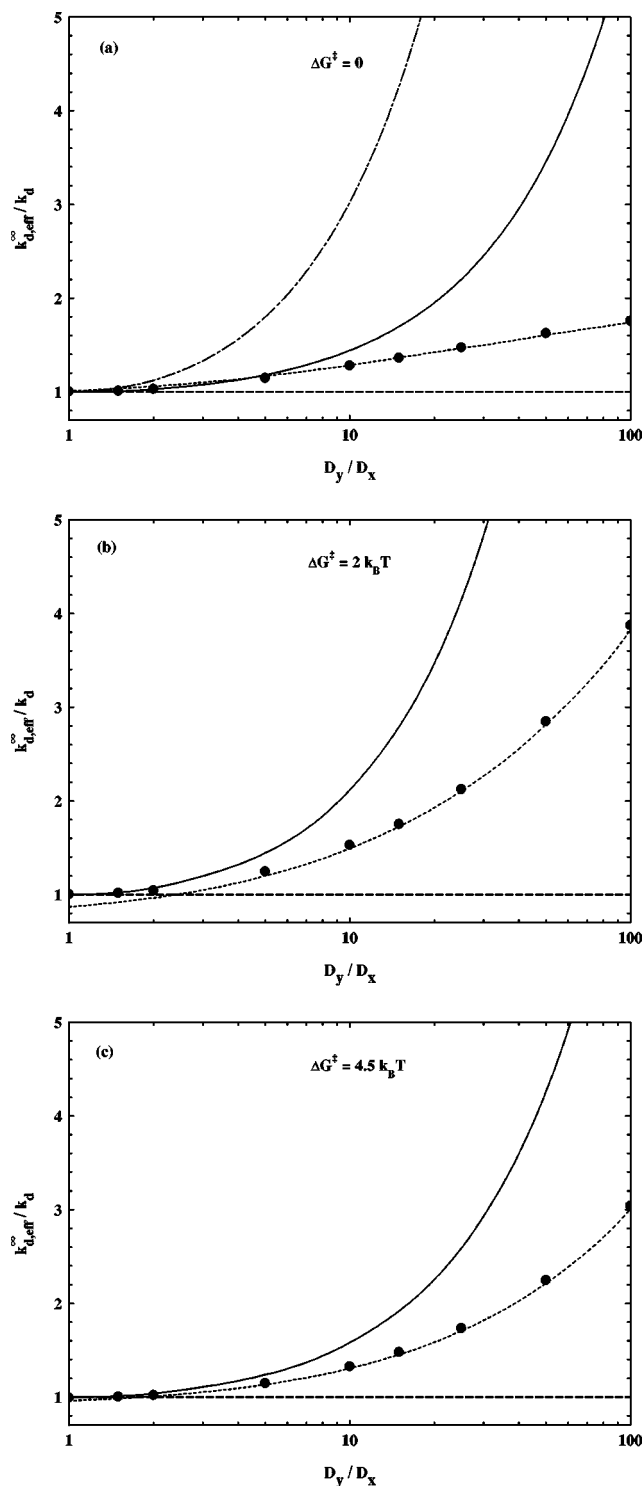


FIG. 3. Reduced rate, $k_{d,\text{eff}}^\infty/k_d$, as a function of the ratio D_y/D_x for $\langle x^2 \rangle = \langle y^2 \rangle = 1/2$, and various values of activation energy. (See Fig. 2 for the definition of $k_{d,\text{eff}}^\infty$.) (a) $k_{d,\text{eff}}^\infty \tau_\infty = 1.443$, (b) $k_{d,\text{eff}}^\infty \tau_\infty = 0.103$, and (c) $k_{d,\text{eff}}^\infty \tau_\infty = 0.012$. The data (closed circles) are obtained from Brownian dynamics simulations, the long-dashed straight line corresponds to the effective Debye solvent theory with $\tau_L = \tau_\infty$, the solid line to the two-dimensional Wilemski-Fixman approximation, and the dashed line to the anisotropic relaxation time approximation [numerical solution of Eq. (4.17)].

and the solid lines, $k_{d,\text{AR}}$. As one can see, the difference between k_d and $k_{d,\text{eff}}^\infty$ is maximum when ΔG^\ddagger is a few $k_B T$ and for very high activation energies all rate constants asymptotically tend to $k_{d,\text{eff}}^\infty$.

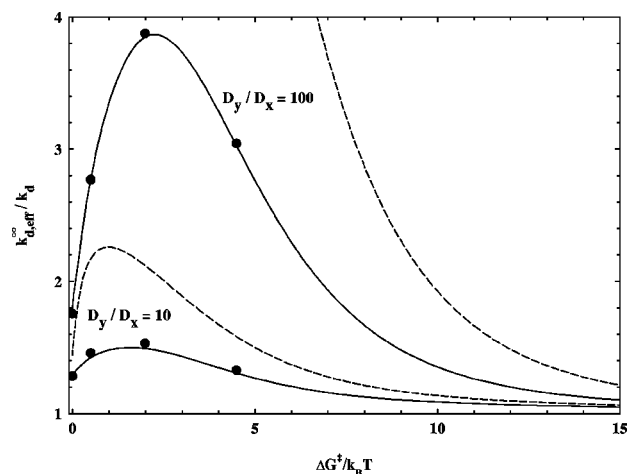


FIG. 4. Reduced rate, $k_{d,\text{eff}}^\infty/k_d$, as a function of activation energy $\beta \Delta G^\ddagger$ for $\langle x^2 \rangle = \langle y^2 \rangle = 1/2$. (See Fig. 2 for the definition of $k_{d,\text{eff}}^\infty$.) The data (closed circles) are obtained from Brownian dynamics simulations, the dashed curves represent the two-dimensional Wilemski-Fixman approximation, and the lines through the data to the anisotropic relaxation time approximation [numerical solution of Eq. (4.17)].

B. $D_x = D_y$ and $\eta = \langle x^2 \rangle / \langle y^2 \rangle$

In this limiting case, diffusion is isotropic but frequencies of the two independent harmonic wells are different [i.e., the relaxation times are proportional to the amplitudes in $\Delta(t)$].

Figures 5(a) and 5(b) display $S(t)$ versus reduced time $k_{d,\text{eff}}^\infty t$ for some selected values of η and activation energy. Solid lines are simulation results, the dash-dotted and long-dashed lines correspond to the Wilemski-Fixman approximation, $S_{\text{wf}}(t)$, and the dashed lines to the anisotropic relaxation time approximation, $S_{\text{AR}}(t)$. The curves for $\eta=1$ (i.e., the Debye case) correspond to $S_{\text{eff}}^\infty(t)$. We see that values of $S(t)$ in a non-Debye solvent [$\eta > 1$] differ from those of $S_{\text{eff}}^\infty(t)$. The survival probabilities are nonexponential only for very small activation energies, $\Delta G^\ddagger \ll k_B T$. For larger activation energies, except at very short time, the survival probabilities are essentially single exponential, i.e., $S(t) \approx \exp(-k_d t)$, $S_{\text{wf}}(t) \approx \exp(-k_{d,\text{wf}} t)$, and $S_{\text{AR}}(t) \approx \exp(-k_{d,\text{AR}} t)$. Both the Wilemski-Fixman and the anisotropic relaxation time approximations are in reasonable agreement with simulation results.

Figures 6(a)–6(c) show $k_{d,\text{eff}}^\infty/k_d$ as a function of η for various values of the activation energy, $\beta \Delta G^\ddagger$, ranging from 0 to 4.5. The data (closed squares) represent k_d obtained from Brownian dynamics simulations, the long-dashed straight line $k_{d,\text{eff}}^\infty$, the solid line $k_{d,\text{wf}}$, and the dashed line $k_{d,\text{AR}}$. While $k_{d,\text{eff}}^\infty$ (effective Debye solvent with $\tau_L = \tau_\infty$) remains a useful zeroth order estimate, in this case both the Wilemski-Fixman and the anisotropic relaxation time approximations are clearly better.

VI. CONCLUDING REMARKS

Our treatment of nonadiabatic outer-sphere electron transfer in a “biexponential” non-Debye solvent was based on the two-dimensional reaction-diffusion Eq. (3.9). We considered three approximations of increasing sophistication and

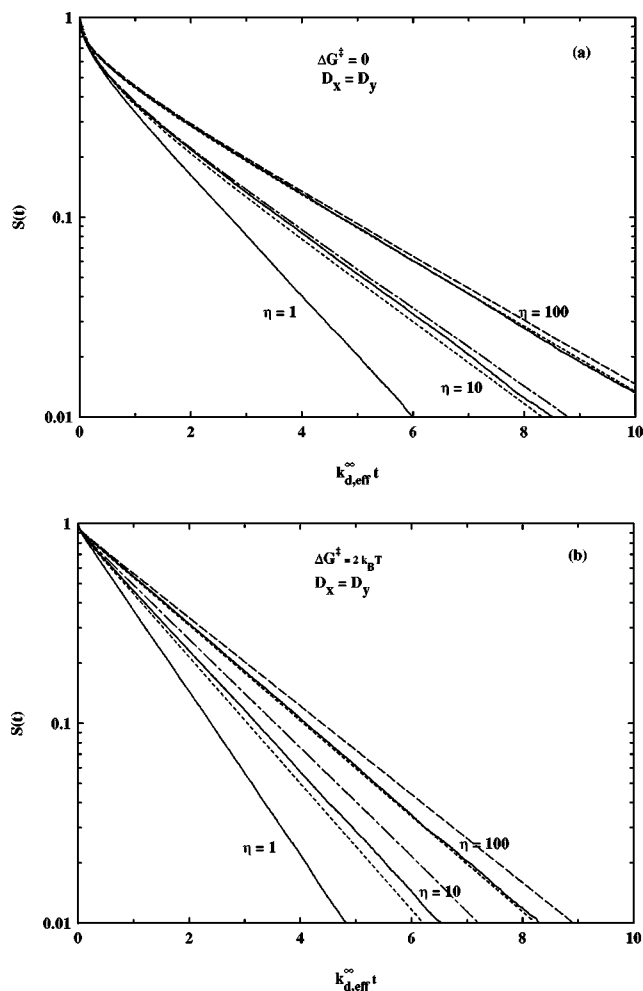


FIG. 5. Survival probability $S(t)$ as a function of reduced time $k_{d,\text{eff}}^{\infty} t$ (see Fig. 2 for the definition of $k_{d,\text{eff}}^{\infty}$). Solid lines correspond to Brownian dynamics results, the dash-dotted [$\eta=10$] and long-dashed [$\eta=100$] lines to the Wilemski-Fixman or “substitution” approximation, $S_{\text{WF}}(t)$, and dashed lines to anisotropic relaxation time approximation, $S_{\text{AR}}(t)$ [numerical solution of Eq. (4.17)]. Both (a) and (b) refer to the case when $D_x = D_y$ and $\eta = \langle x^2 \rangle / \langle y^2 \rangle$.

compared their predictions with the solution of this equation obtained using Brownian dynamics simulations. The effective Debye solvent approximation was based on Eq. (4.1). When D_{eff} is equated to $D_x + D_y$ (or equivalently, the effective relaxation time is chosen as the high frequency correlation time τ_{∞}), this turns out to be a reasonable zeroth order approximation.

By invoking a Wilemski-Fixman-like “closure” approximation, the multidimensional integral equation that relates the Green’s functions in the absence and presence of reaction is transformed into a one-dimensional integral equation involving the non-Markovian unreactive Green’s function. The “substitution” procedure [i.e., formally replacing $\exp(-t/\tau_L)$ by $\Delta(t)$ in the expressions for the survival probability and the reaction rate in a Debye solvent] is implicitly based on this one-dimensional equation and hence is an approximation. We found that in the solvent-controlled adiabatic regime, when the amplitudes of the two exponentials in $\Delta(t)$ are the same, this is a useful approximation only when two relaxation times differ by less than a factor of 3.

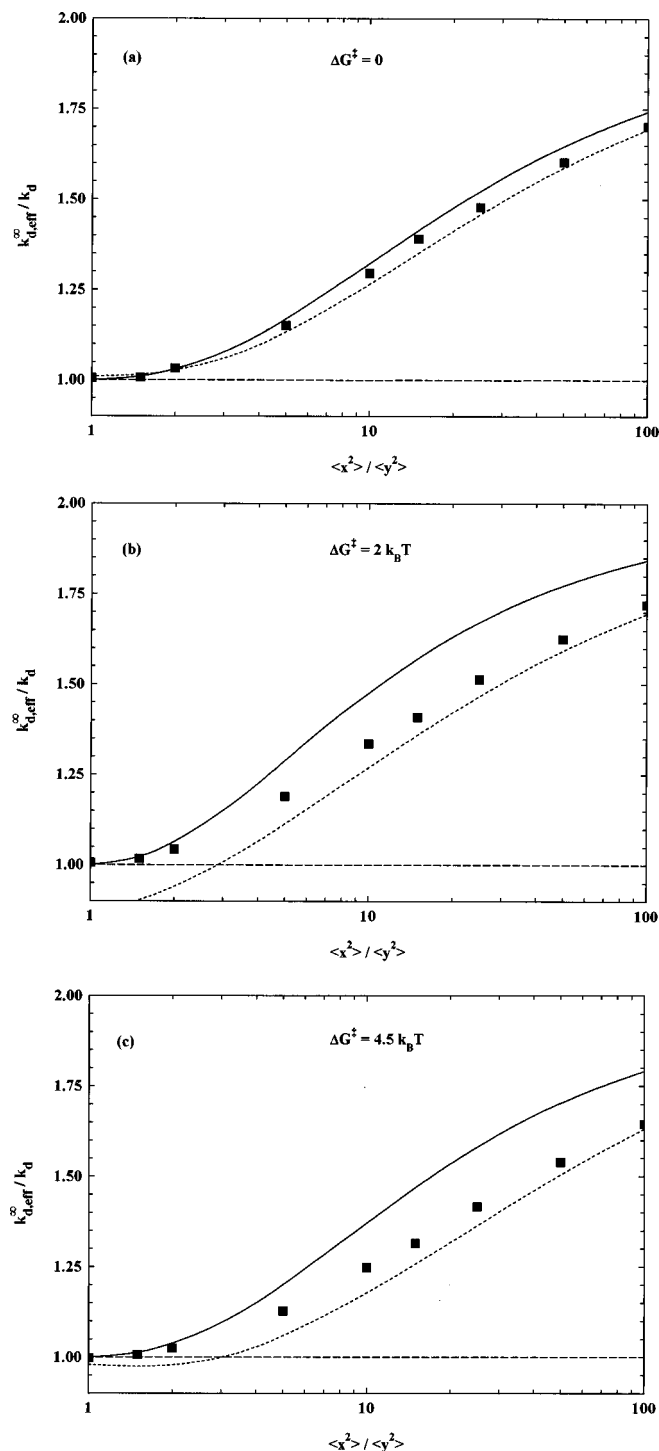


FIG. 6. Reduced rate, $k_{d,\text{eff}}^{\infty} / k_d$, as a function of the ratio $\langle x^2 \rangle / \langle y^2 \rangle$ for $D_x = D_y = 1$, and various values of activation energy. (See Fig. 2 for the definition of $k_{d,\text{eff}}^{\infty}$.) (a) $k_{d,\text{eff}}^{\infty} \tau_{\infty} = 1.443$, (b) $k_{d,\text{eff}}^{\infty} \tau_{\infty} = 0.103$, and (c) $k_{d,\text{eff}}^{\infty} \tau_{\infty} = 0.012$. The data (closed squares) are obtained from Brownian dynamics simulations, the long-dashed straight line corresponds to the effective Debye solvent theory with $\tau_L = \tau_{\infty}$, and the solid line to the two-dimensional Wilemski-Fixman approximation, and the dashed line to the anisotropic relaxation time approximation [numerical solution of Eq. (4.17)].

When the difference is greater, we have shown that the two-dimensional reaction-diffusion equation can be reduced to a one-dimensional one involving the slow coordinate with an effective nonlocal sink function. This sink function is equal to the rate of electron transfer due to motion along the

fast coordinate for each fixed value of the slow one. The combination of this and the “substitution” approximation reproduces simulation results over the entire range of relaxation anisotropies when the activation energy is greater than $k_B T$.

This work can readily be extended in a number of directions. Perhaps the most important is to take into account the contribution of intramolecular vibrational modes (i.e., a classical low frequency mode as in the Sumi–Marcus treatment,⁷ a quantum high frequency mode as in the Jortner–Bixon model,²⁶ or a combination of both as proposed by Barbara and co-workers²⁷). When the dynamics of these modes is fast, their effect can be incorporated into our formalism by simply using a nonlocal sink function [i.e., $k(x+y)$ instead of $\kappa\delta(x+y-z^\ddagger)$] for a “biexponential” solvent, see Eq. (3.9). In the effective Debye solvent approximation one must solve Eq. (4.1) with $D_{\text{eff}}=D_x+D_y$ using, for example, the algorithm given in Appendix A. The Wilemski–Fixman-like approximation leads to Eq. (4.9a) in which G is the non-Markovian Green’s function given in Eq. (3.1) with $\Delta(t)$ given in Eq. (3.4). When $k(z)$ is nonlocal this must be solved numerically. This is basically what Gayathri and Bagchi¹² did and consequently their treatment of “biexponential” solvent dynamics is not exact. One can further approximate the solution of Eq. (4.9a) by using the conventional Wilemski–Fixman closure approximation [see Eq. (4.10)]. For the rate, this leads to Eq. (2.27), where the sink–sink correlation function is evaluated using the non-Markovian Green’s function in Eq. (3.1). For an irreversible reaction, this appears to be equivalent to the Zhu–Rasaiah¹¹ treatment of nonlocal sinks.

The anisotropic relaxation time approximation for nonlocal sinks is still based on Eq. (4.17) but with $k_{\text{eff}}(x)$ being identified with the rate of electron transfer at fixed x , obtained by solving

$$\frac{\partial P}{\partial t} = (D_x + D_y) \frac{\partial}{\partial y} e^{-y^2/2\langle y^2 \rangle} \frac{\partial}{\partial y} e^{y^2/2\langle y^2 \rangle} P - k(x+y)P, \quad (6.1)$$

numerically.

These approximations should be compared with the numerical solution of Eq. (3.9) obtained using finite-difference or Brownian dynamics simulation techniques. For nonlocal sinks, the survival probability can readily be calculated from the expression

$$S(t) = \langle e^{-\int_0^t k[z(t')] dt'} \rangle, \quad (6.2)$$

where the average is taken over nonreactive trajectories starting from an equilibrium initial distribution. For a “biexponential” solvent these can be generated using the algorithm in Appendix B. When the integral in Eq. (6.2) is approximated by trapezoidal rule, $S(t)$ can be calculated by accumulating $\frac{1}{2}[k(z_i) + k(z_{i+1})](t_{i+1} - t_i)$ along a trajectory, exponentiating the sum and averaging over many trajectories starting out from an equilibrium distribution. When $\Delta(t)$ cannot adequately be described as a sum of a few exponentials, the unreactive trajectories can be generated by simulating a generalized (diffusive) Langevin equation either in real time²⁸ or in Fourier space.¹³

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APPENDIX A: NUMERICAL SOLUTION OF THE SINK–SMOLUCHOWSKI EQUATION

We consider the one-dimensional reaction-diffusion equation in the presence of an arbitrary nondelta sink term

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial x} D(x) e^{-\beta V(x)} \frac{\partial}{\partial x} (e^{\beta V(x)} P) - k(x)P, \quad (A1)$$

with initial condition $P(x, t=0|x_0) = \delta(x-x_0)$. In order to compute both the survival probability and the mean first passage time, we discretize the space in such a way that the continuous variable x takes discrete values on a grid of size $(N+1)d$ with mesh size d such that: $x \equiv x_n = nd$ with $d = x_{n+1} - x_n$. For N even, the number n runs from $n = -N/2$ to $n = N/2$. The first derivatives are successively approximated as

$$\left(\frac{\partial f}{\partial x} \right)_{x_n} = \frac{f(n+\frac{1}{2}) - f(n-\frac{1}{2})}{d}; \quad f(n) \equiv f(x_n), \quad (A2)$$

and then

$$f\left(n \pm \frac{1}{2}\right) = \frac{f(n) + f(n \pm 1)}{2} \quad (A3)$$

is used. In this way, Eq. (A1) leads to the master equation of the form

$$\begin{aligned} \frac{\partial P(n, t)}{\partial t} = & \varpi(n|n+1)P(n+1, t) + \varpi(n|n-1) \\ & \times P(n-1, t) - [\varpi(n+1|n) + \varpi(n-1|n)] \\ & \times P(n, t) - k(n)P(n, t), \end{aligned} \quad (A4)$$

where the transition frequencies from n to m are given by

$$\begin{aligned} \varpi(m \leftarrow n) = & \varpi(m|n) \\ = & \frac{[D(n) + D(m)]}{2d^2} \\ & \times \exp\left\{-\frac{\beta[V(m) - V(n)]}{2}\right\}. \end{aligned} \quad (A5)$$

The ends are treated as reflecting so that for $n = \pm N/2$,

$$\varpi(-(N/2+1)|-N/2) = \varpi(-N/2|-(N/2+1)) = 0, \quad (A6a)$$

$$\varpi(N/2+1|N/2) = \varpi(N/2|N/2+1) = 0. \quad (A6b)$$

These rate constants satisfy the detailed balance relation

$$\varpi(m|n)p_{\text{eq}}(n) = \varpi(n|m)p_{\text{eq}}(m), \quad (A7)$$

where the equilibrium distribution, $p_{\text{eq}}(n)$, is defined as

$$p_{\text{eq}}(n) = \frac{e^{-\beta V(n)}}{Z}; \quad Z = \sum_{n=-N/2}^{N/2} e^{-\beta V(n)}. \quad (A8)$$

It is convenient to symmetrize the problem by making the transformation,

$$Q(n,t) = \frac{P(n,t)}{\sqrt{p_{\text{eq}}(n)}}. \quad (\text{A9})$$

The master Eq. (A4) then becomes,

$$\frac{\partial Q}{\partial t} = M Q, \quad (\text{A10})$$

in which $Q \equiv (\dots, Q(n,t), \dots)^T$ is a column vector and the $(N+1) \times (N+1)$ symmetric matrix M is

$$\begin{cases} M_{n,n} = -\varpi(n+1|n) - \varpi(n-1|n), \\ M_{n,n\pm 1} = M_{n\pm 1,n} = \sqrt{\varpi(n\pm 1|n)\varpi(n|n\pm 1)}. \end{cases} \quad (\text{A11})$$

We denote by λ_α and ψ_α the eigenvalues and associated eigenvectors of M ,

$$M\psi_\alpha = -\lambda_\alpha \psi_\alpha \quad (\alpha=0, \dots, N), \quad (\text{A12})$$

where $\psi_\alpha \equiv (\psi_\alpha(-N/2), \dots, \psi_\alpha(0), \dots, \psi_\alpha(N/2))^T$ is the normalized column vector. Once the eigenvalues and eigenvectors are determined, the Green's function for the original master Eq. (A4) is

$$G(m,t|n) = \exp\left\{-\frac{\beta[V(m)-V(n)]}{2}\right\} \times \sum_{\alpha=0}^N \psi_\alpha(n)\psi_\alpha(m)e^{-\lambda_\alpha t}. \quad (\text{A13})$$

The survival probability is therefore obtained as

$$S(t) = \sum_{n,m=-N/2}^{N/2} G(m,t|n)p_{\text{eq}}(n) = \sum_{\alpha=0}^N \left(\sum_{n=-N/2}^{N/2} \psi_\alpha(n)\sqrt{p_{\text{eq}}(n)} \right)^2 e^{-\lambda_\alpha t}, \quad (\text{A14})$$

and the reaction rate, k , calculated as the reciprocal of the relaxation time of $S(t)$, is subsequently given by

$$\frac{1}{k} = \sum_{\alpha=0}^N \frac{1}{\lambda_\alpha} \left(\sum_{n=-N/2}^{N/2} \psi_\alpha(n)\sqrt{p_{\text{eq}}(n)} \right)^2. \quad (\text{A15})$$

The algorithms described above were applied to Eq. (4.17) in order to calculate both the survival probability and the rate. It is convenient to transform Eq. (4.17) by rescaling the time and the x coordinate as, $t \leftrightarrow t/\tau_x$ and $x \leftrightarrow x/\sqrt{\langle x^2 \rangle}$,

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial x} e^{-x^2/2} \frac{\partial}{\partial x} (e^{x^2/2} P) - k_{\text{eff}}(x)P, \quad (\text{A16})$$

where the sink function, in the $\kappa \rightarrow \infty$ limit, is now

$$k_{\text{eff}}(x) = \frac{D_x + D_y \langle x^2 \rangle}{D_x \langle y^2 \rangle} \times \left[\int_0^\infty dt' \left\{ \frac{\exp\left[\left(\frac{e^{-t'}}{1+e^{-t'}}\right)\zeta^2\right]}{\sqrt{1-e^{-2t'}}} - 1 \right\} \right]^{-1};$$

$$\zeta = \frac{z^\pm - x\sqrt{\langle x^2 \rangle}}{\sqrt{\langle y^2 \rangle}}, \quad (\text{A17})$$

and the potential of mean force, the transition frequencies in Eq. (A5) are

$$\beta V(n) = \frac{n^2 d^2}{2}, \quad (\text{A18})$$

$$\varpi(m|n) = \frac{1}{d^2} \exp\left\{-\frac{[m^2 - n^2]d^2}{4}\right\} \quad \text{for } -N/2 \leq n, m \leq N/2. \quad (\text{A19})$$

Calculations for two types of parameter sets were performed. When $\langle x^2 \rangle = \langle y^2 \rangle = 1/2$ [$\langle z^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle = 1$], then the control parameter [see Eq. (5.2)] is just $\eta = D_y/D_x$ and the sink function becomes

$$k_{\text{eff}}(x) = (1 + \eta) \left[\int_0^\infty dt' \left\{ \frac{\exp\left[\left(\frac{e^{-t'}}{1+e^{-t'}}\right)\zeta^2\right]}{\sqrt{1-e^{-2t'}}} - 1 \right\} \right]^{-1};$$

$$\zeta = \sqrt{2}z^\pm - nd. \quad (\text{A20})$$

This is a Gaussian sink function with the strength linearly increasing with η . For the second type of calculations, we set $D_x = D_y = 1$ and used $\eta = \langle x^2 \rangle / \langle y^2 \rangle$ such that $\langle x^2 \rangle = \eta/(1 + \eta)$ and $\langle y^2 \rangle = 1/(1 + \eta)$ since $\langle x^2 \rangle + \langle y^2 \rangle = 1$. The sink function in this case writes as

$$k_{\text{eff}}(x) = 2\eta \left[\int_0^\infty dt' \left\{ \frac{\exp\left[\left(\frac{e^{-t'}}{1+e^{-t'}}\right)\zeta^2\right]}{\sqrt{1-e^{-2t'}}} - 1 \right\} \right]^{-1};$$

$$\zeta = z^\pm \sqrt{\eta+1} - nd\sqrt{\eta}. \quad (\text{A21})$$

In addition to the linear increase of the strength with η , the position of the maximum and the width of the Gaussian sink also changes with η .

In both cases the rate constant is measured in units of τ_x . All calculations were carried out for $0 \leq z^\pm \leq 3$, $1 \leq \eta \leq 100$, with parameters for the grid chosen as $N=300$ and $d=0.04$, and giving $-6 \leq x_n \leq 6$. [A mesh size of $d=0.06$, i.e., $-9 \leq x_n \leq 9$, was used only for Fig. 4 where the largest value of z^\pm is $z^\pm \approx 6$.] The QL implicit algorithm²⁹ was used to compute eigenvalues and eigenvectors of the 301×301 symmetric matrix M .

APPENDIX B: BROWNIAN DYNAMICS ALGORITHM

In this Appendix an algorithm is presented simulating the diffusive motion of a particle diffusing on a two-

dimensional harmonic potential surface in the presence of an absorbing line located at $x+y=z^\ddagger$ or $z=z^\ddagger$. In the absence of reaction, this algorithm is valid for arbitrary step sizes. The Green's function for the diffusion on two independent harmonic potential surfaces is

$$G_0(x, y, t | x_0, y_0) = G_0(x, t | x_0) G_0(y, t | y_0), \quad (\text{B1a})$$

$$G_0(x, t | x_0) = [2\pi\langle x^2 \rangle (1 - e^{-2t/\tau_x})]^{-1/2} \times \exp\left\{-\frac{(x - x_0 e^{-t/\tau_x})^2}{2\langle x^2 \rangle (1 - e^{-2t/\tau_x})}\right\}, \quad (\text{B1b})$$

$$G_0(y, t | y_0) = [2\pi\langle y^2 \rangle (1 - e^{-2t/\tau_y})]^{-1/2} \times \exp\left\{-\frac{(y - y_0 e^{-t/\tau_y})^2}{2\langle y^2 \rangle (1 - e^{-2t/\tau_y})}\right\}. \quad (\text{B1c})$$

The corresponding Brownian trajectories can be generated using the following algorithm

$$\begin{cases} x_{n+1} = x_n e^{-\epsilon_{n+1}} + \sqrt{\langle x^2 \rangle [1 - e^{-2\epsilon_{n+1}}]} X_{n+1} \\ y_{n+1} = y_n e^{-\eta_{n+1}} + \sqrt{\langle y^2 \rangle [1 - e^{-2\eta_{n+1}}]} Y_{n+1} \end{cases}, \quad (\text{B2})$$

where (x_n, y_n) and (x_{n+1}, y_{n+1}) are, respectively, the coordinates of the particle at successive time steps t_n and t_{n+1} . The time interval $\delta t_{n+1} = t_{n+1} - t_n$ is not necessarily uniform and $\epsilon_{n+1} = \delta t_{n+1} / \tau_x$, with $\eta = \tau_x / \tau_y$. At each step, n , X_n , and Y_n are independent Gaussian random numbers such that

$$\begin{aligned} \langle X_n \rangle = \langle Y_n \rangle = 0; \quad \langle X_n X_m \rangle = \langle Y_n Y_m \rangle = \delta_{nm}; \\ \langle X_n Y_m \rangle = 0. \end{aligned} \quad (\text{B3})$$

It is convenient to measure the time in unit of τ_x and the length in unit of $\langle z^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle = 1$, so that Eq. (B2) becomes

$$\begin{cases} x_{n+1} = a_{n+1} x_n + \sqrt{\langle x^2 \rangle [1 - a_{n+1}^2]} X_{n+1} \\ y_{n+1} = b_{n+1} y_n + \sqrt{\langle y^2 \rangle [1 - b_{n+1}^2]} Y_{n+1} \end{cases}; \quad n \geq 0 \quad (\text{B4})$$

where

$$a_n = e^{-\epsilon_n} \quad \text{and} \quad b_n = e^{-\eta \epsilon_n}. \quad (\text{B5})$$

Setting $z_n = x_n + y_n$, and combining x_n and y_n in Eq. (B4), we end up with the algorithm

$$z_1 = a_1 x_0 + b_1 y_0 + Z_1 \quad (\text{B6a})$$

$$z_{n+1} = \left[\frac{a_{n+1} a_n - b_{n+1} b_n}{a_n - b_n} \right] z_n - \left[\frac{a_n b_n (a_{n+1} - b_{n+1})}{a_n - b_n} \right] z_{n-1} + Z_{n+1}; \quad n \geq 1, \quad (\text{B6b})$$

where the random number Z_{n+1} is

$$\begin{aligned} Z_{n+1} = & \sqrt{\langle x^2 \rangle [1 - a_{n+1}^2]} X_{n+1} - \alpha_{n+1} b_n \sqrt{\langle x^2 \rangle [1 - a_n^2]} X_n \\ & + \sqrt{\langle y^2 \rangle [1 - b_{n+1}^2]} Y_{n+1} \\ & - \alpha_{n+1} a_n \sqrt{\langle y^2 \rangle [1 - b_n^2]} Y_n; \quad n \geq 0, \end{aligned} \quad (\text{B7})$$

with

$$\alpha_{n+1} = \frac{a_{n+1} - b_{n+1}}{a_n - b_n}; \quad \alpha_1 = 0. \quad (\text{B8})$$

For each trajectory, i , starting at $t_0=0$, the initial particle position $z_0 = x_0 + y_0$ is generated from the equilibrium distribution

$$p_{\text{eq}}(x_0, y_0) = \frac{1}{[4\pi^2\langle x^2 \rangle \langle y^2 \rangle]^{1/2}} \exp\left\{-\frac{x_0^2}{2\langle x^2 \rangle} - \frac{y_0^2}{2\langle y^2 \rangle}\right\}. \quad (\text{B9})$$

To simulate the diffusion in the presence of an absorbing line at $z=z^\ddagger$, each trajectory is terminated at the time $t_{n^*(i)}$ when either the condition $z_{n^*(i)} \leq z^\ddagger$ if $z_0 > z^\ddagger$, or $z_{n^*(i)} \geq z^\ddagger$ if $z_0 < z^\ddagger$ is satisfied for the first time. The first passage time (or lifetime) $t_{n^*(i)}$ and the survival probability $S_i(t)$ for this given trajectory are recorded, with

$$\begin{cases} S_i(t) = 1 & \text{for all } t < t_{n^*(i)} \\ S_i(t) = 0 & \text{for all } t \geq t_{n^*(i)}. \end{cases} \quad (\text{B10})$$

The survival probability, $S(t)$, and the reaction rate, k_d , are then obtained by averaging over a large number M of trajectories

$$S(t) = \frac{1}{M} \sum_{i=1}^M S_i(t), \quad (\text{B11})$$

$$k_d^{-1} = \frac{1}{M} \sum_{i=1}^M t_{n^*(i)}. \quad (\text{B12})$$

Two types of calculations have been performed. The first is when $\langle x^2 \rangle = \langle y^2 \rangle = 1/2$ and the control parameter is simply $\eta = D_y/D_x$. In the second type of calculation, we set $D_x = D_y = 1$ and $\eta = \langle x^2 \rangle / \langle y^2 \rangle$ so that $\langle x^2 \rangle = \eta / (1 + \eta)$ and $\langle y^2 \rangle = 1 / (1 + \eta)$ since $\langle x^2 \rangle + \langle y^2 \rangle = 1$. When the particle is near the absorbing line, very small time steps must be used.²³ But when the particle is far away from this line, we can use fairly large time steps because our algorithm does not have a time-step error. For all simulations reported in this paper, we used

$$\epsilon_{n+1} = \epsilon_{\text{low}} + \frac{\epsilon_{\text{high}}}{\eta} (z_n - z^\ddagger)^2; \quad 1 \leq \eta \leq 100, \quad (\text{B13})$$

with $\epsilon_{\text{low}} = 10^{-7}$ and $\epsilon_{\text{high}} = 1/50$. A total of $M = 10^5$ trajectories was used to perform the averages. All calculations were carried out on a Silicon Graphics XS24/4000 workstation.

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