Direct energy transfer in the diffusion case, numerically treated by the use of Green functions

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The energy decay function for an excited donor molecule surrounded by acceptors in diffusional motion is computed for a finite-size donor and arbitrary characteristics of the boundary. We evaluate the donor-acceptor—pair diffusion function via a Green-function approach for the Feynman-Kac equation in Laplace space. Quick and stable numerical solutions for the acceptor-averaged pair diffusion function, and thereby the energy decay functions, can be obtained, thus allowing model parametrization from time-resolved fluorescence measurements.

I. INTRODUCTION

Energy transfer between donors and acceptors (be they mobile or not) has been studied intensely in recent years, though more from the theoretical[1–14] than the experimental point of view.[4,15–17] The elementary processes leading to the deactivation of an electronically excited molecule (donor) via radiationless energy transfer to an acceptor molecule are, in principle, well known by now.[18] Measurements of delayed fluorescence should bear out the interplay between donor-acceptor motion and energy-transfer processes, but have been relatively scarce thus far as they require very precise knowledge of the functional form of the donor's decay function. The challenge for the theory therefore is to compute donor decay laws in terms of model parameters (transfer rates, diffusion coefficients, etc.) with such accuracy that they can be matched to very precise time-resolved fluorescence measurements, e.g., by time-correlated photon counting.

In previous theoretical work decay functions could only be calculated for point molecules and, to our knowledge, corrections for finite extension of the donors and acceptors have not been taken into account within the framework of a rigorous treatment. Owing to the power laws for energy transfer, however, molecular size effects must influence the decay function significantly. The same is true for dimensionality, not only because low-dimensional systems will play a role in experimentation, but because lower, and possibly fractional, dimensions may be a way to describe nonisotropic interactions. These effects cannot be dealt with by seeking analytical solutions. We found that a Green-function approach was possible which allowed us to compute numerical solutions over the entire range of interest of the transport and interaction parameters (dimension, acceptor density, diffusion constant, donor-acceptor interaction, cutoff parameter, and boundary characteristics). By employing the Green functions for the spherically symmetric Laplace-type diffusion operator we could transform the transport equation of the entire problem, the Feynman-Kac equation, into an integral equation. This integral equation deserves some interest in its own right. It was treated in a simplified case before[19] and derived in a different physical context (energy migration by an average T-matrix approximation in three dimensions) in Ref. 9. This author approached a special case by numerical methods similar to ours.

We will first (Sec. II) describe our physical model which allows to reduce the energy decay function via an integral formula to a donor-acceptor—pair decay function fulfilling a diffusion equation with a loss term (the Feynman-Kac equation). The latter can be converted by a complete Laplace transformation to an integral equation with symmetrical kernel, allowing us to incorporate the boundary of the donor in general form (Sec. III). The reflecting-boundary case is discussed explicitly (Sec. IV). For both absorbing- and reflecting-boundary conditions we can then evaluate the time-dependent transfer rate in Laplace space (Sec. V); explicit expressions can be given for long times (Sec. VI) and the ergodic limit (Sec. VII); (cf. Refs. 20 and 21). The numerical treatment of the Feynman-Kac equation requires the introduction of dimensionless quantities (Sec. VIII). The concrete numerical algorithm is developed in Sec. IX, based on a Laguerre integration scheme. The results are discussed in Sec. X and an assessment of the numerical accuracy and computational stability is made. Mathematical details and useful listings are found in Appendices A and B.

II. ENERGY TRANSFER TO DIFFUSING ACCEPTORS

We want to find the numerical solution for a general model of direct, incoherent energy transfer between molecules in viscous fluids. Our model assumptions are as follows.

Electronically excited donors present in a viscous fluid transfer their excitation energy radiationlessly to acceptors (examples: delayed fluorescence[17] and transfer of the excitation from the antenna pigment to the reaction center in photosynthesis and similar processes[22,23]). The concentration of donors should be small compared to that of acceptors to allow for neglect of donor-donor interactions. Thus one donor can be studied in a viscous fluid surrounded by randomly distributed acceptors. In this case the internal conversion determining the lifetime of the excitation becomes independent of the energy-transfer pro-

cesses such that the time development of donor excitation splits into a trivial intramolecular part and the more complicated energy-transfer part.

The stochastic properties of the system are characterized in the usual way as follows.

A liquid molecule has a probability p to be an acceptor and probability $1-p$ for being inert (i.e., a nonparticipant in energy-transfer processes). The incoherent isotropic energy transfer can then be described by a transfer rate $w(R)$, the probability per unit of time that a donor transfers its energy to an acceptor over a distance R. Two distinctive forms of w are in use,

$$w(R)=\alpha R^{-s} \tag{1}$$

for multipole interactions, and

$$w(R)=\alpha\exp(-\gamma R) \tag{2}$$

for exchange interactions. In both cases, α is the strength of the interaction.

If d is the nearest-neighbor distance and τ the corresponding average transfer time, then $\alpha=d^s/\tau$ in the multipole and $\alpha=e^{\gamma d}/\tau$ in the exchange case. We have $s=6$ for dipole-dipole, $s=8$ for dipole-quadrupole, and $s=10$ for quadrupole-quadrupole interactions. Characteristic values of γd range from 3 to 10. As we use numerical methods, the analytic form of $w(R)$ is not of a major concern to us.

We further assume Brownian motion for the donor and acceptor molecules. The direct, incoherent, and isotropic energy transfer from donor to the acceptors in Brownian movement is then described by the probability $\Phi(t)$ for the donor excited at time $t=0$ to be still excited at time $t>0$. Under the above assumptions the following expression was derived in Ref. 20 for the macroscopic energy decay function Φ:

$$\Phi(t)=\exp\left[-\Delta V_\Delta p\rho\int_b^\infty [1-E(t,R)]R^{\Delta-1}dR\right] . \tag{3}$$

This expression for Φ is valid at low concentrations and without back transfer.[20] $\Delta=1,2,3$ is the dimensionality of the problem. Two- and one-dimensional systems are of interest as orientational dependence [represented by $w(\vec{R})$] in higher dimensions can often be simulated in terms of orientational independence in lower dimensions. $V_\Delta=\pi^{\Delta/2}/\Gamma(\Delta/2+1)$ is the volume of the Δ-dimensional unit sphere, ρ is the number density, and p is the probability of a molecule to be an acceptor. Equation (3) reduces the determination of Φ to that of the energy decay function $E(t,R)$ of a donor-acceptor pair separated by R at $t=0$. The model for $E(t,R)$ is defined by the combined molecular diffusion and transfer rate equations

$$\frac{\partial}{\partial t}E(t,R)=[D\vec{\nabla}^2_{\vec{R}}-w(R)]E(t,R) \quad \text{with } E(0,R)=1 . \tag{4}$$

In the case of reflecting boundary conditions this equation describes a model where $E(t,R)$ is an average over all Brownian motion pathways $t\mapsto\vec{R}(t)$, namely

$$E(t,R)=\left\langle\exp\left[-\int_0^t w(\boldsymbol{R}(t'))dt'\right]\right\rangle_{\{\vec{R}(t')\}} .$$

The equivalence of Eq. (4) and this equation is the statement of the Feynman-Kac theorem.[24] We therefore call Eq. (4) the Feynman-Kac equation. In the following we will be concerned with the computational aspects of Eq. (4). It will be shown that transformation into Laplace space is the method of choice. With respect to the time t, the Laplace transform of (4) yields an integral equation, the kernel of which can be given explicitly. The lower limit b of the integral in (3) is a cutoff parameter of the order nearest-neighbor distance d defining a lower boundary. Thus the Laplace transform of (4) will also depend on this lower boundary condition, allowing for numerical integration of the Feynman-Kac differential equation in Laplace space simultaneously with (3) under arbitrary, but fixed, boundary conditions.

III. THE FEYNMAN-KAC EQUATION IN INTEGRAL EQUATION FORM

Applying the Laplace transform $\mathscr{L}_s$ in the time variable t to the Feynman-Kac equation (4), we obtain

$$D\vec{\nabla}^2_{\vec{R}}E(s,R)-w(R)E(s,R)=sE(s,R)-1 . \tag{5}$$

The initial condition $E(0,R)=1$ is incorporated into this equation.

For the spherically symmetric function $E(s,r)$ we only need the radial part of the Laplace operator. Defining, as is usually done,

$$\kappa\equiv\sqrt{s/D} \tag{6}$$

and

$$z\equiv\kappa R, \quad E(s,R)\equiv z^{-\lambda}v(z), \quad \lambda\equiv\frac{\Delta-2}{2} , \tag{7}$$

we rewrite (5) as

$$\left[\frac{d}{dz}\left[z\frac{d}{dz}\right]-\left[z+\frac{\lambda^2}{z}\right]\right]v(z) = -\left[\frac{z^{1+\lambda}}{s}-\frac{w(z/\kappa)}{s}zv(z)\right] . \tag{8}$$

The self-adjoint differential operator on the left-hand side (lhs) has the symmetric bounded Green function (see Appendix A)

$$G_\Delta(z,z')=I_{|\lambda|}(z_<)K_\lambda(z_>)+AK_\lambda(z)K_\lambda(z') , \tag{9}$$

where $z_<$ and $z_>$ are the minimum and maximum of z and z', respectively. We will subsequently drop the index Δ in most cases; G_1 and G_3 will turn out to be equal. The free parameter A has to be fitted to the boundary conditions at b. The important properties of this Green function are listed in Appendix A.

By the definition of G, Eq. (8) corresponds to the integral equation[25]

$$v(z)=\frac{z^\lambda}{s}-\frac{1}{s}[I_\mu(z_b)-AK_{1+\lambda}(z_b)]z_b^{1+\lambda}K_\lambda(z) -\frac{1}{s}\int_{z_b}^\infty w(z'/\kappa)v(z')G(z,z')z'dz' , \tag{10}$$

where Eq. (A3) has been used, and

$$\mu \equiv \begin{cases} \lambda = -\frac{1}{2} & \text{for } \Delta = 1, \\ 1+\lambda & \text{for } \Delta \geq 2. \end{cases}$$

Again, we have

$$z_b \equiv z(R=b) = \kappa b \ . \tag{11}$$

As to the Green function $D^{-1}(RR')^{-\lambda}G(\kappa R, \kappa R')$, which occurs in the corresponding integral equation for $E(s,R)$, compare Eq. (A7) and find (A4).

The integral equation for v and E depends on the boundary conditions implicitly via the parameter A. A "trick" allows us to eliminate A and construct integral equations with explicit boundary conditions: The quantity

$$y(z) \equiv v(z) - \frac{z^\lambda}{s} + \frac{K_\lambda(z)}{K_\lambda(z_b)} \left[\frac{z_b^\lambda}{s} - v(z_b) \right]$$

fulfills the differential equation (8) without its first term on the right-hand side (rhs), and with the *homogeneous* boundary condition

$$y(z_b) = 0 \ .$$

Therefore the $y(z)$ equals the last term on the rhs of (10), yielding

$$v(z) = \frac{z^\lambda}{s} - \frac{K_\lambda(z)}{K_\lambda(z_b)} \left[\frac{z_b^\lambda}{s} - v(z_b) \right] - \frac{1}{s} \int_{z_b}^{\infty} w(z'/\kappa) v(z') G(z,z') z' dz' \ , \tag{12}$$

where A from Eq. (9) is to be determined such that G fulfills the same homogeneous boundary condition as y,

$$A = -I_{|\lambda|}(z_b)/K_\lambda(z_b) \ . \tag{13}$$

A is the same for dimensions $\Delta = 1$ and 3. According to (A5), by this choice of A, i.e., $A = A_{\mathrm{Sm}}$, G characterizes a diffusion with an absorbing boundary in b: G fulfills the Smoluchowski boundary condition. We therefore denote the Green function in the case $A = A_{\mathrm{Sm}}$ as $G_{\Delta,\mathrm{Sm}}$. Note that also $G = G_{\Delta,\mathrm{Sm}}$. $v(z_b)$ vanishes in Eq. (12) in the "Smoluchowski case" $E(t,b) \equiv 0$, and we therefore use Eq. (12) accordingly.

In previous literature the size of the donor was often neglected (i.e., $b = 0$). We therefore derive the behavior of the general Eq. (12) for $z_b \to 0$. In the case $\Delta \geq 2$ the asymptotic behavior of $z_b^{-\lambda} K_\lambda(z_b)$ in the limit $z_b \to 0$ makes Eq. (12), for $b = 0$, independent of boundary conditions altogether: The term in Eq. (12) containing z_b vanishes and $A \equiv 0$ in G_Δ, Eq. (9). This behavior can be rationalized by the notion that for $\Delta > 1$ the probability of a point acceptor molecule to hit a point boundary is zero. In Ref. 26 it was demonstrated that for the evaluation of $\Phi(t)$ for long times b could be taken to zero. However, in the case $\Delta = 1$, the assumption $b = 0$ turns (12) into an equation which depends essentially on $E(s,0)$.

IV. REFLECTING BOUNDARY CONDITION

We now turn to the case where the derivative of E is given at the boundary. We multiply (12) by $z^{-\lambda}$ [cf. (7)] and differentiate it with respect to z, then substitute the result at the boundary $z = z_b$ back into Eq. (12). This procedure yields an integral equation for v which contains explicitly the derivative of E according to (7):

$$v(z) = \frac{z^\lambda}{s} - \frac{z_b^\lambda K_\lambda(z)}{K_{1+\lambda}(z_b)} \frac{d}{dz}(z^{-\lambda} v(z)) \Big|_{z=z_b} - \frac{1}{s} \int_{z_b}^{\infty} w(z'/\kappa) v(z') G_{\Delta,\mathrm{re}}(z,z') z' dz' \ . \tag{14}$$

$G_{\Delta,\mathrm{re}}$ is defined by (A11) with $A = A_{\mathrm{re}}$. It is the Green function for diffusion of acceptors with a reflecting boundary in b,

$$G_{\Delta,\mathrm{re}} = G_\Delta \quad \text{for } A = A_{\mathrm{re}} = I_\mu(z_b)/K_{1+\lambda}(z_b) \ , \tag{15}$$

where μ is defined as in (10).

Moroever, for reflecting boundary conditions,

$$\frac{d}{dR} E(t,R) \,|_{R=b} = 0 \ ,$$

and the second term in Eq. (14) vanishes. Evidently, Eq. (12) with absorbing boundary and Eq. (14) with reflecting boundary are the same in the case $b = 0$.

V. THE ENERGY DECAY LAW Φ IN LAPLACE SPACE

Equations for the time-dependent rate $k(t)$ of the energy decay can be worked out. $k(t)$ can be measured directly (e.g., Ref. 12). It is

$$k(t) \equiv -\frac{\dot{\Phi}(t)}{\Phi(t)} = \frac{d}{dt}[\ln \Phi(t)] \ . \tag{16}$$

In Laplace space we define

$$k(s) \equiv \mathcal{L}_s(k(t)) = s\mathcal{L}_s(-\ln \Phi(t)) \ , \tag{17}$$

and the derivative in Eq. (16) turns into a multiplication by s. It is then sufficient to determine the rate $k(s)$ numerically. From Eq. (3), by Eq. (7), we obtain

$$k(s) = \Delta V_\Delta p \rho \kappa^{-\Delta} s \int_{\kappa b}^{\infty} (z^\lambda/s - v(z)) z^{1+\lambda} dz \ , \tag{18}$$

which we now evaluate in the Smoluchowski and the reflecting-boundary case.

A. Smoluchowski case

If v is given for z_b we can use Eqs. (12) and (A6), arriving at

$$k(s) = \Delta V_\Delta p \rho \kappa^{-\Delta} \left[\frac{K_{1+\lambda}(\kappa b)}{K_\lambda(\kappa b)} (\kappa b)^{\Delta-1} s \mathcal{L}_s(1 - E(t,b)) + \int_{\kappa b}^{\infty} w(z/\kappa) v(z) \left[1 - \frac{z^{-\lambda} K_\lambda(z)}{(\kappa b)^{-\lambda} K_\lambda(\kappa b)} \right] z^{1+\lambda} dz \right] . \tag{19}$$

We will show later, by numerical computations, that for $b\neq 0$ in the Smoluchowski case [$E(t,b)\equiv 0$], the interaction w does not play a role. k is simply determined by the probability at which one of the diffusing acceptors reaches the boundary to the donor. For $w\equiv 0$, Eq. (19) becomes

$$k_{w\equiv 0}(s)=k_{w\equiv 0,\mathrm{Sm}}(s)s\mathscr{L}_s(1-E(t,b)) . \tag{20}$$

The index Sm stands for $E(t,b)\equiv 0$. Explicitly, we obtain, for $\Delta=1,2,3$ (Appendix A),

$$k_{w\equiv 0,\mathrm{Sm}}(s)=\begin{cases} 2p\rho\sqrt{D}/\sqrt{s} & \text{for } \Delta=1, \\ 2\pi bp\rho K_1(\kappa b)/[\kappa K_0(\kappa b)] & \text{for } \Delta=2, \\ 4\pi b^2 p\rho[\sqrt{D}/\sqrt{s}+D/(bs)] & \text{for } \Delta=3. \end{cases} \tag{21}$$

For one and three dimensions one can readily give the Laplace inverse for this purely diffusive case. In the $\Delta=2$ case the inverse of (21) is now known analytically.[27]

B. Reflecting boundary

We assume now that at the boundary z_b the derivative of v is given. With (14) and (A10) we obtain for the rate $k(s)$

$$k(s)=\Delta V_\Delta p\rho\kappa^{-\Delta}\left[(\kappa b)^{\Delta-1}\kappa^{-1}s\mathscr{L}_s\left[\frac{d}{dR}E(t,R)\bigg|_{R=b}\right]+\int_{\kappa b}^{\infty} w(z/\kappa)v(z)z^{1+\lambda}dz\right] . \tag{22}$$

Equations (19) and (22) for the Laplace-transformed rates are completely equivalent. Nevertheless, there is an advantage in using these more specialized forms in either case.

In the purely diffusive case ($w\equiv 0$), Eq. (22) yields

$$k_{w\equiv 0}(t)=\Delta V_\Delta p\rho b^{\Delta-1}D\frac{d}{dR}E(t,R)\bigg|_{R=b} . \tag{23}$$

Consequently, because of (16), the reflecting boundary

$$\frac{d}{dR}E(t,R)\bigg|_{R=b}=0$$

is equivalent to the condition $\Phi_{w\equiv 0}(t)=1$. Other boundary conditions will, even when $w\equiv 0$, induce decay of the donor's excitation energy, and thus give rise to an w-independent contribution to the decay rate.

VI. LONG-TIME RATES

Rate expressions for long times are particularly useful for the experimental determination of the parameters occurring in our model. We first remark that in the case $\Delta>2$, $k(t)$ has a time-independent limit for $t\to\infty$, denoted by k. Considerations regarding the existence of long-time rates are given in Appendix B. The exact and numerical computation of k will be discussed subsequently.

Let $\Delta>2$, i.e., $\lambda>0$, and then

$$\begin{aligned} g_{\mathrm{Sm}}(R,R')&\equiv\lim_{\kappa\to 0}[(RR')^{-\lambda}G_{\Delta,\mathrm{Sm}}(\kappa R,\kappa R')] \\ &=(\Delta-2)^{-1}(RR')^{-(\Delta-2)}(R_<^{\Delta-2}-b^{\Delta-2}) . \end{aligned} \tag{24}$$

g_{Sm} is the Green function of the self-adjoint differential operator

$$\frac{d}{dR}\left[R^{\Delta-1}\frac{d}{dR}\right] .$$

The limiting processes in (24) were carried out by using formulas (9.6.7) and (9.6.9) of Ref. 28.

Equation (12) yields for $u(R)$, given by

$$u(R)\equiv\lim_{s\to 0}sE(s,R)=D\lim_{\kappa\to 0}\kappa^2(\kappa R)^{-\lambda}v(\kappa R) , \tag{25}$$

the integral equation

$$u(R)=1-(R/b)^{-(\Delta-2)}[1-u(b)]-D^{-1}\int_b^{\infty} w(R')u(R')g_{\mathrm{sm}}(R,R')R'^{\Delta-1}dR' . \tag{26}$$

Remembering that g_{Sm} is the Green function of the above-mentioned differential operator, we are lead to the differential equation

$$[D\vec{\nabla}^2_{\vec{R}} - w(R)]u(R) = 0 \ . \tag{27}$$

Looking back to Eq. (4) we recognize that $u(R)$ solving (27) is the stationary solution $E_{st}(R)$ of the Feynman-Kac differential equation,

$$u = E_{st}(R) \ . \tag{28}$$

By definition (25), it is evident that u must fulfill the same boundary conditions as E. For a given $u(b)$, Eq. (26) allows for the numerical computation of $u(R)$.

We now rewrite the integral Eq. (26) for the case where the derivative of u is given at the boundary b. Differentiation of (26) at $R = b$ and substitution back into (26) gives us an integral equation for u with its explicit derivative at the boundary b,

$$u(R) = 1 - \frac{b}{\Delta - 2}\left[\frac{d}{dR}U(R)\bigg|_{R=b}\right](R/b)^{-\Delta-2} - D^{-1}\int_b^\infty w(R')u(R')g_{re}(R,R')R'^{\Delta-1}dR' \ , \tag{29}$$

where the Green function g_{re} with reflecting boundary is given by

$$g_{re}(R,R') \equiv \frac{1}{\Delta - 2}R_>^{-(\Delta-2)} \ . \tag{30}$$

The long-time rate k can be calculated by a theorem by Tauber (see, e.g., Ref. 19).

We can start from

$$k \equiv \lim_{t\to\infty} k(t) = \lim_{s\to 0} sk(s) \ , \tag{31}$$

provided the limits do exist. Equations (19) and (22), respectively, allow for the $t \to \infty$ limit by introducing the stationary function u,[29]

$$\begin{aligned} k &= (\Delta-2)\Delta V_\Delta p\rho b^{\Delta-2}D(1-u(b)) + \Delta V_\Delta p\rho \int_b^\infty w(R)u(R)(R^{\Delta-2} - b^{\Delta-2})R\,dR \\ &= \Delta V_\Delta p\rho b^{\Delta-1}D\frac{d}{dR}u(R)\bigg|_{R=b} + \Delta V_\Delta p\rho \int_b^\infty w(R)u(R)R^{\Delta-1}dR \ . \end{aligned} \tag{32}$$

The limits of (19) are obtained by using Eq. (9.6.9) of Ref. 28. The two equations (32) are written in sequence to demonstrate their equivalence.

The differential equation (27) for u substituted into (32) leads to

$$k = \Delta V_\Delta p\rho D \lim_{R\to\infty} R^{\Delta-1}\frac{d}{dR}u(R) \ . \tag{33}$$

This is a well-known equation by now.[30–32] In Ref. 32, for example, Eqs. (27) and (33) were effectively used in the evaluation of long-time rates. Ghosh *et al.*[9] compared exact long-time rates with numerical solutions of the integral equation (26) and found excellent agreement in the $b = 0$ case. In Appendix B, a rationale for the derivation of Eq. (33) in time space can be found.

VII. ERGODIC LIMIT

The case where molecular motion is fast on the timescale of energy transfer merits special consideration. In Refs. 20 and 21 the time-independent rate

$$k = \Delta V_\Delta p\rho \int_b^\infty w(R)R^{\Delta-1}dR \tag{34}$$

was derived. We will show in this section how this result can be derived from our more general theory and which correction terms depending on time and diffusion coefficients must be added.

Aiming for a suitable asymptotic expansion we will iterate our integral equations for the decay rates. We substitute Eq. (14) for the reflecting boundary into (22) and replace $v(z')$ [definition (7)] in the first approximation by the integral free part of Eq. (14),

$$v(z') \approx z'^{\lambda}/s \ . \tag{35}$$

Applying the transformation $z = \kappa R$, $z' = \kappa R'$ [according to (7)] in the reflecting-boundary case, we arrive at

$$k(s) \approx \Delta V_\Delta p\rho \left[s^{-1}\int_b^\infty w(R)R^{\Delta-1}dR - s^{-1}\int_b^\infty dR\int_b^\infty dR'w(R)w(R')[D^{-1}(RR')^{-\lambda}G_{\Delta,re}(\kappa R,\kappa R')](RR')^{\Delta-1}\right] \ . \tag{36}$$

A similar procedure is possible in the absorbing case, leading to a more lengthy expression for $k(s)$.

The Green functions $D^{-1}(RR')^{-\lambda}G_{\Delta,\mathrm{re}}$ in the reflecting-boundary case, and, respectively, $D^{-1}(RR')^{-\lambda}G_{\Delta,\mathrm{Sm}}$ in the absorbing-boundary case, can be Laplace-inverted by Eqs. (A19), and, respectively, (A17), (A20), and (A18). For a reflecting boundary, Eq. (36) yields the $k(t)$ expression

$$k(t)\approx\Delta V_\Delta p\rho\left[\int_b^\infty w(R)R^{\Delta-1}dR-\int_b^\infty dR\,R^{\Delta-1}\int_b^\infty dR'R'^{\Delta-1}w(R)w(R')\int_0^t dt'\mathcal{L}_s^{-1}[D^{-1}(RR')^{-\lambda}G_{\Delta,\mathrm{re}}(\kappa R,\kappa R')\right]. \tag{37}$$

Let us now look into the functional form of the asymptotic behavior of $k(t)$. We can do the Laplace inversion explicitly for $b=0$ and will therefore confine ourselves to this case in the subsequent discussion. As shown in Sec. III, $b=0$ implies, for $\Delta\geq 2$, that the absorbing- and reflecting-boundary conditions are all the same. Moreover, the numerical solutions presented in Sec. X suggest that the role of the cutoff parameter b is diminished with increasing times as the $\Phi(t)$ curves for different b approach each other asymptotically (cf. Ref. 26).

The time-dependent part of (37) takes the following form for $b=0$ [cf. arguments to Eq. (A23)]:

$$\int_0^t dt'\mathcal{L}_s^{-1}(D^{-1}(RR')^{-\lambda}G_{\Delta,\mathrm{re}}(\kappa R,\kappa R'))$$
$$=(\Delta-1)V_{\Delta-1}\pi^{-\Delta/2}(4D)^{-1}\int_0^\pi\Gamma\left[\Delta/2-1,\frac{|\vec{\mathrm{R}}-\vec{\mathrm{R}}'|^2}{4Dt}\right]|\vec{\mathrm{R}}-\vec{\mathrm{R}}'|^{2-\Delta}\sin^{\Delta-2}\theta\,d\theta\,, \tag{38}$$

where Eq. (A23) was incorporated and θ denotes the angle between $\vec{\mathrm{R}}$ and $\vec{\mathrm{R}}'$.

In particular, for $\Delta=3$ one can use, according to Ref. 28, the asymptotic relationship

$$\Gamma\left[\frac{1}{2},\frac{|\vec{\mathrm{R}}-\vec{\mathrm{R}}'|^2}{4Dt}\right]=\sqrt{\pi}\,\mathrm{erfc}\left[\frac{|\vec{\mathrm{R}}-\vec{\mathrm{R}}'|}{\sqrt{4Dt}}\right]\sim\sqrt{\pi}\left[1-\frac{2}{\sqrt{\pi}}\frac{|\vec{\mathrm{R}}-\vec{\mathrm{R}}'|}{\sqrt{4Dt}}\right], \tag{39}$$

and by integration, again in the $t\to\infty$ limit,

$$\int_0^t dt'\mathcal{L}_s^{-1}(D^{-1}(RR')^{-\lambda}G_{\Delta,\mathrm{re}}(\kappa R,\kappa R'))=\frac{1}{DR_>}-\frac{1}{D}\frac{1}{\sqrt{\pi Dt}}$$
$$=D^{-1}[g_{\mathrm{re}}(R,R')-(\pi Dt)^{-1/2}] \tag{40}$$

[for the definition of g_{re}, see Eq. (30)]. Finally, $k(t)$ takes the form

$$k(t)\sim 4\pi p\rho\left[\int_0^\infty w(R)R^2dR-\frac{1}{D}\int_0^\infty\int_0^\infty w(R)w(R')\frac{R^2R'^2}{R_>}dR\,dR'+D^{-1}(\pi Dt)^{-1/2}\left[\int_0^\infty w(R)R^2dR\right]^2\right]$$
$$\approx 4\pi p\rho DI_3(1+I_3/\sqrt{\pi Dt})\ \text{ as } t\to\infty\,, \tag{41}$$

with

$$I_3\equiv D^{-1}\int_b^\infty w(R)R^2dR\,. \tag{42}$$

The t-independent part of (41) (first term on the rhs) is just the ergodic rate of Eq. (34). Comparing it with the exact form of $k(\infty)$ from Ref. 32, we realize that the $1/D$ expansion given here is indeed asymptotic. The exact limit of $k(t)$, however, is not analytic in D.

For $\Delta=2$ we would like to remark that the above procedure, valid for $\Delta=3$, would not lead to a sensible expansion in this case.

VIII. DIMENSIONLESS QUANTITIES

To make the equations numerically tractable proper dimensionless quantities have to be defined. Obviously, the natural unit of distance is the nearest-neighbor distance d, and that of time is the transfer rate $\tau=w^{-1}(d)$ to the nearest neighbor,

$$\tilde{R}\equiv R/d,\quad T\equiv t/\tau\,. \tag{43}$$

For the Laplace transform we use

$$S\equiv\tau s\,. \tag{44}$$

This defines the rest of the dimensionless quantities

$$\begin{aligned}&\beta=b/d\ \text{ (cutoff parameter)},\\ &\tilde{D}\equiv D\tau/d^2\ \text{ (diffusion constant)},\\ &\tilde{\kappa}\equiv(S/\tilde{D})^{1/2}=\kappa d\,.\end{aligned} \tag{45}$$

Note that $z_b=\kappa b=\beta\tilde{\kappa}$.

Furthermore, we define the following functions:

$$\begin{aligned}&\tilde{w}(\tilde{R})\equiv\tau w((\tilde{R}+\beta)d)=\tau w(R+b)\,,\\ &\tilde{G}(z,z')\equiv G(\beta\tilde{\kappa}+z,\beta\tilde{\kappa}+z')=G(z_b+z,z_b+z')\,,\\ &\tilde{v}(z)\equiv\tau^{-1}v(\beta\tilde{\kappa}+z)=\tau^{-1}v(z_b+z)\,,\\ &\tilde{\Phi}(T)\equiv\Phi(\tau T)=\Phi(t)\,,\\ &\tilde{k}(T)\equiv\tau k(\tau T)=\tau k(t)\,,\end{aligned} \tag{46}$$

In particular, we have

$$\tilde{k}(S)=k(S/\tau)=k(s)\,.$$

Then we define the quantity

$$\Omega \equiv V_\Delta \rho d^\Delta . \tag{47}$$

ρ is just the density of atoms in a solid of corresponding lattice constant,[26] a linear chain for $\Delta=1$, a square lattice for $\Delta=2$, and a fcc lattice for $\Delta=3$.

The long-time rates (for $\Delta>2$) can be expressed in terms of the natural unit k_0 given by

$$k_0 \equiv \tau^{-1}\Delta\Omega p = \Delta V_\Delta p \rho d^\Delta/\tau . \tag{48}$$

At last we define the function

$$\tilde{u}(\tilde{R}) \equiv u((\tilde{R}+\beta)d) = u(R+b) . \tag{49}$$

The fundamental equations (12) and (14) can then be converted into dimensionless equations for $v(z)$, and then the Laplace-transformed rates $\tilde{k}(S)$ can be expressed by the functions $\tilde{v}(z)$ via Eqs. (19) and (22).

In the Smoluchowski case, one obtains

$$\tilde{k}(S) = \Delta\Omega p \tilde{\kappa}^{-\Delta}\left[\frac{K_{1+\lambda}(\beta\tilde{\kappa})}{K_\lambda(\beta\tilde{\kappa})}(\beta\tilde{\kappa})^{\Delta-1} + \int_0^\infty \tilde{w}(z/\tilde{\kappa})\tilde{v}(z)\left[1-\frac{(\beta\tilde{\kappa}+z)^{-\lambda}K_\lambda(\beta\tilde{\kappa}+z)}{(\beta\tilde{\kappa})^{-\lambda}K_\lambda(\beta\tilde{\kappa})}\right](\beta\tilde{\kappa}+z)^{1+\lambda}dz\right] , \tag{50}$$

where $\tilde{v}$ fulfills the integral equation

$$\tilde{v}(z) = \frac{(\beta\tilde{\kappa}+z)^\lambda}{S} - \frac{1}{S}\frac{K_\lambda(\beta\tilde{\kappa}+z)}{(\beta\tilde{\kappa})^{-\lambda}K_\lambda(\beta\tilde{\kappa})} - S^{-1}\int_0^\infty \tilde{w}(z'/\tilde{\kappa})\tilde{v}(z')\tilde{G}_{\Delta,\mathrm{Sm}}(z,z')(\beta\tilde{\kappa}+z')dz' . \tag{51}$$

In Appendix A, simple expressions for the Bessel functions K are given for odd dimensions.

On the other hand, we find, with reflecting-boundary conditions,

$$\tilde{k}(S) = \Delta\Omega p \tilde{\kappa}^{-\Delta}\int_0^\infty \tilde{w}(z/\tilde{\kappa})\tilde{v}(z)(\beta\tilde{\kappa}+z)^{1+\lambda}dz , \tag{52}$$

and the integral equation for $\tilde{v}$ reads

$$\tilde{v}(z) = S^{-1}(\beta\tilde{\kappa}+z)^\lambda - S^{-1}\int_0^\infty \tilde{w}(z'/\tilde{\kappa})\tilde{v}(z')\tilde{G}_{\Delta,\mathrm{re}}(z,z')(\beta\tilde{\kappa}+z')dz' . \tag{53}$$

Equations (50) and (51), and, respectively, (52) and (53), will be the basis for our numerical solution of the energy-transfer problem in the next section.

In the case $\Delta>2$, we obtain, from (32) and (33), for the long-time rate in units of k_0,

$$\begin{aligned} k/k_0 &= (\Delta-2)\beta^{\Delta-2}\tilde{D}(1-\tilde{u}(0)) + \int_0^\infty \tilde{w}(\tilde{R})\tilde{u}(\tilde{R})[(\tilde{R}+\beta)^{\Delta-2}-\beta^{\Delta-2}](\tilde{R}+\beta)d\tilde{R} \\ &= \beta^{\Delta-1}\tilde{D}\frac{d}{d\tilde{R}}\tilde{u}(\tilde{R})\Big|_{\tilde{R}=0} + \int_0^\infty \tilde{w}(\tilde{R})\tilde{u}(\tilde{R})(\tilde{R}+\beta)^{\Delta-1}d\tilde{R} \\ &= \tilde{D}\lim_{\tilde{R}\to 0}\left[(\tilde{R}+\beta)^{\Delta-1}\frac{d}{d\tilde{R}}\tilde{u}(\tilde{R})\right] , \end{aligned} \tag{54}$$

where $\tilde{u}$, according to (26) and (30), fulfills a time-independent integral equation.

Equation (54) allows the numerical computation of k/k_0 for arbitrary interactions w and boundary conditions. In addition, by virtue of (27), $\tilde{u}$ satisfies the differential equation

$$\tilde{D}\left[\frac{d^2}{d\tilde{R}^2}+\frac{\Delta-1}{\tilde{R}+\beta}\frac{d}{d\tilde{R}}\right]\tilde{u}(\tilde{R}) - \tilde{w}(\tilde{R})\tilde{u}(\tilde{R}) = 0 . \tag{55}$$

We note that Eq. (55) can be solved analytically by means of modified Bessel functions for multipole interactions, and in the $\Delta=3$ case as well for exchange interactions (see Ref. 32). In the next section we will therefore concentrate on the numerical treatment of the time-dependent problem.

IX. NUMERICAL INTEGRATION OF THE FEYNMAN-KAC EQUATION

In this section we give a brief description of the numerical procedures used.

A. Laguerre integration

Laguerre integration is suitable for the evaluation of the definite integrals between the limits 0 and ∞, with integrands giving large contributions near the origin [cf. Ref. 28, Eq. (25.4.45)].

Let x_j be the jth zero of the Laguerre polynomial $L_n(x)$, and let g_j be the weight factors of the Laguerre integration such that

$$\int_0^\infty f(x)dx \approx \sum_{j=1}^n g_j f(x_j) . \tag{56}$$

The x_j and g_j can be found tabulated in Table (25.9) of Ref. 28.

B. Smoluchowski case

Discretization according to (56) turns the integral equation (51) in the absorbing-boundary case into

$$S\tilde{v}(x)\approx(\beta\tilde{\kappa}+x)^{\lambda}-\frac{K_{\lambda}(\beta\tilde{\kappa}+x)}{(\beta\tilde{\kappa})^{-\lambda}K_{\lambda}(\beta\tilde{\kappa})}$$
$$-\sum_{j=1}^{n}g_j\tilde{w}(x_j/\tilde{\kappa})\tilde{v}(x_j)\tilde{G}_{\Delta,\mathrm{Sm}}(x,x_j)(\beta\tilde{\kappa}+x_j)\ , \tag{57}$$

which under substitution of $x=x_1,x_2,\ldots$ shapes up to a system of linear equations of the general form

$$\underline{A}\,\underline{v}=\underline{b}\ . \tag{58}$$

The matrix $\underline{A}$ is given by

$$A_{i,j}\equiv S^{-1}g_j\tilde{w}(x_j/\tilde{\kappa})(y_iy_j)^{-\lambda}\tilde{G}_{\Delta,\mathrm{Sm}}(x_i,x_j)y_j^{\Delta-1}+\delta_{i,j}\ ,$$

and the vectors $\underline{v}$ and $\underline{b}$ are defined as

$$v_i\equiv Sy_i^{-\lambda}\tilde{v}(x_i)\ ,$$

$$b_i\equiv\begin{cases}1-e^{-x_i} & \text{for } \Delta=1,\\ 1-K_0(y_i)/K_0(\beta\tilde{\kappa}) & \text{for } \Delta=2,\\ 1-\beta\tilde{\kappa}e^{-x_i}/y_i & \text{for } \Delta=3,\end{cases}$$

with the abbreviation

$$y_i=\beta\tilde{\kappa}+x_i\ .$$

$\underline{A}$ is constructed so that the diagonal elements are of the order 1 and nondiagonal elements tend to be much smaller.

With $\underline{v}$ calculated, we can turn to evaluating the rate $\tilde{k}(S)$ by Laguerre-integrating Eq. (50). It takes the form

$$\frac{1}{p}S\tilde{k}(S)\approx\Delta\Omega\kappa^{-\Delta}\left[Sb_0+\sum_{i=1}^{n}g_i\tilde{w}(x_i/\tilde{\kappa})v_iy_i^{\Delta-1}b_i\right]\ , \tag{59}$$

where

$$b_0\equiv\begin{cases}1 & \text{for } \Delta=1.\\ \beta\tilde{\kappa}K_1(\beta\tilde{\kappa})/K_0(\beta\tilde{\kappa}) & \text{for } \Delta=2,\\ \beta\tilde{\kappa}(\beta\tilde{\kappa}+1) & \text{for } \Delta=3.\end{cases}$$

Except for b_0, all of the parameters occurring in (59) have been used in (58) already. We found that the algorithm for the computation of k based on (58) and (59) is quite satisfactory with respect to computer time and core requirements.

C. Reflecting-boundary conditions

As in the preceding subsection we first have to evaluate a numerical representation of $\tilde{v}(z)$ via a system of linear equations. Equation (53) takes, by Laguerre integration, the form

$$\underline{A}\,\underline{v}=\underline{\mathbb{1}}\ , \tag{60}$$

with

$$A_{i,j}\equiv S^{-1}g_j\tilde{w}(x_j/\tilde{\kappa})(y_iy_j)^{-\lambda}\tilde{G}_{\Delta,\mathrm{re}}(x_i,x_j)y_i^{\Delta-1}+\delta_{i,j}\ ,$$
$$v_i\equiv Sy_i^{-\lambda}\tilde{v}(x_i)\ ,$$

and

$$y_i=\beta\tilde{\kappa}+x_i\ .$$

Then, Eq. (52) has to be written in Laguerre-integration fashion,

$$p^{-1}S\tilde{k}(S)\approx\Delta\Omega\tilde{\kappa}^{-\Delta}\sum_{i=1}^{n}g_i\tilde{w}(x_i/\tilde{\kappa})v_iy_i^{\Delta-1}\ . \tag{61}$$

The strict analogy between Eqs. (58), with (59) on one hand, and (60), with (61) on the other, allows for considerable computational and programming economy.

X. NUMERICAL RESULTS AND CONCLUSIONS

We now discuss the numerical evaluation of Eqs. (58) and (60) in the cases of special interest.

A. Numerical procedures and stability

The systems of linear equations (58) and (60) for the Smoluchowski and reflecting cases, respectively, represented their original integral equations quite well, although such linear systems are said to be sometimes ill conditioned.[33] Our solutions yielded rather accurate results for a relatively small number of linear equations; with 16 equations [$n=16$ in (56) and the simple Gauss-Jordan procedure] we obtained "drawing-board" precision, which is partly due to the favorable choice of matrix elements A_{ij}. Figure 1 demonstrates how the choice of 6, 8, and 16 discrete points in the Laguerre integration influences the precision of the decay functions Φ in the case of reflecting-boundary conditions. The numerical accuracy could easily be increased if necessary. It is thus conceivable to employ more equations of the form (57) and, respectively, (60), than the number of x values to compute the rates. The ensuing overdetermined system of equations could be solved by the method of least squares.

For the Laplace inversion (confined in our problem to the real axis in Laplace space) the short algorithm given by Stehfest[34] was sufficient. In general, the Laplace inver-

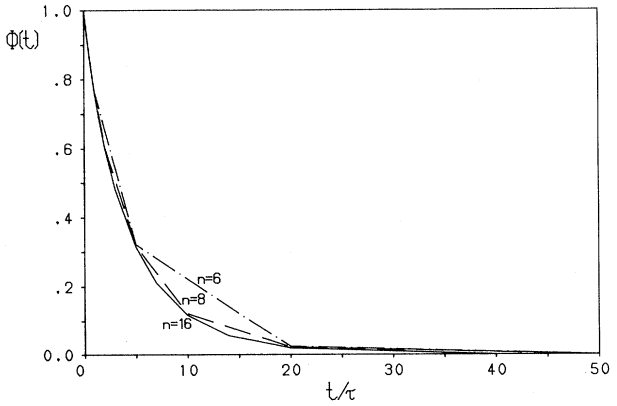

FIG. 1. Demonstration of numerical stability in the reflecting-boundary case for dimension $\Delta=3$; numerical evaluation of the decay function $\Phi(t)$, Eqs. (60) and (61) for dipole-dipole interactions between the donor and the acceptors. We chose the diffusion constant $\tilde{D}=0.2$, the probability of a molecule to be an acceptor $p=0.05$, and the cutoff parameter $\beta=1$.

sion of a function given only on the real axis is, numerically speaking, an ill-posed problem. However, the strict monotonous and continuous properties of $k(t)$ work in our favor as the Laplace inversion does not need to bring out any rough features of the original function.

B. Smoluchowski case with cutoff $\beta \neq 0$

Figure 2 shows Φ for an exchange interaction w and $\Delta = 1,2,3$. We chose a small acceptor density $p\rho$, and $\tilde{D}$ characterizes a moderately viscous fluid. Plots for other exchange [Eq. (2)] and multipole [Eq. (1)] interactions indicate that for $\beta \neq 0$ in all three dimensions the energy decay is nearly independent of any reasonable choice for the interaction w. This is a consequence of the absorbing barrier, which simulates the assumption that the donor loses its energy to an acceptor as soon as their distance falls below b. Thus $\Phi(t)$ is just 1 minus the probability for an acceptor to reach the boundary. This Φ is given exactly by (21). The independence of w allows to exploit all the classical results for heat transfer with respect to the pure diffusion equation (e.g., long-time expansions[27,35]). As can be expected, in one dimension Φ does not even depend on the cutoff β.

In the two- and three-dimensional cases, Φ does depend on β. As shown in Fig. 3, a smaller β implies a slowdown in energy transfer as the probability of the boundary being hit by an acceptor is decreased (in the reflecting-boundary case, we will find the opposite behavior of Φ).

The dimension dependence of energy transfer (Fig. 2) is largely determined by the number of reactive trajectories. The larger the Δ, the faster the decay of $\Phi(t)$.

The variation with $\tilde{D}$ shows that $\tilde{D}$ enhances the energy-decay process as more acceptors hit the boundary.

C. Reflecting-boundary conditions

Reflecting-boundary conditions characterize the other limiting case where $w(R)$ is the only interaction causing energy transfer. The donor boundary just reflects the acceptor and this process has no further consequences. In Fig. 4, a comparison is made for decay laws due to different forms of the interaction. Generally speaking, the stronger the interaction the faster the energy decay. Interactions of a given type are more efficient if they are of larger range, as borne out in Fig. 4.

The reflecting-boundary condition is less effective for energy decay than the absorbing-boundary one. This is understandable in the light of remarks made (see Sec. X B). The variation of Φ with the diffusion constant (Fig. 5) is less obvious. The decay is enhanced by a larger diffusion constant, and one may wonder how faster diffusion can "shove" more acceptors within energy-transfer range

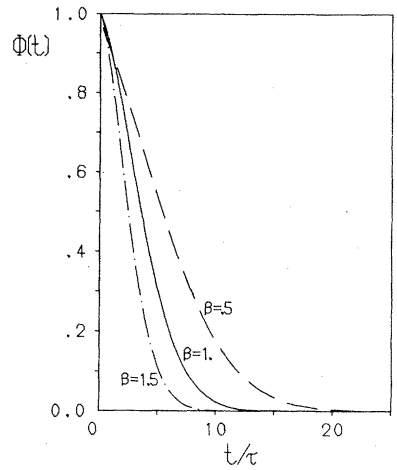

FIG. 3. Decay function $\Phi(t)$ in dependence of the cutoff parameters $\beta = 0.5$, 1.0, and 1.5, in the absorbing-boundary case for dipole-dipole interactions between the donor and the acceptors. We chose the dimension $\Delta = 3$, the diffusion constant $\tilde{D} = 0.2$, and the probability of a molecule to be an acceptor $p = 0.01$.

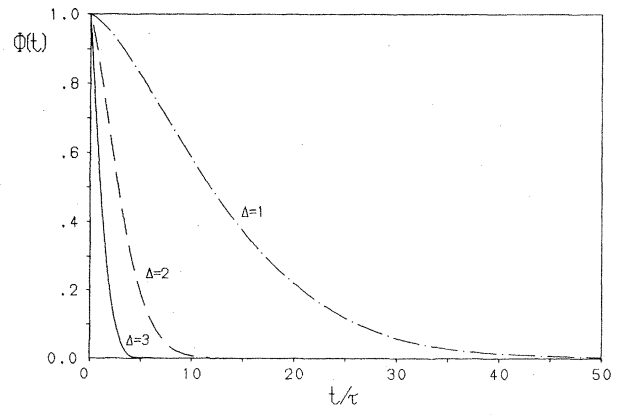

FIG. 2. Dimension dependence $\Delta = 1,2,3$ of the decay function $\Phi(t)$ in the absorbing-boundary case for exchange interactions between the donor and the acceptors, Eq. (2), with $\gamma d = 3$. We chose the diffusion constant, $\tilde{D} = 0.2$, the probability of a molecule to be an acceptor $p = 0.05$, and the cutoff parameter $\beta = 1$.

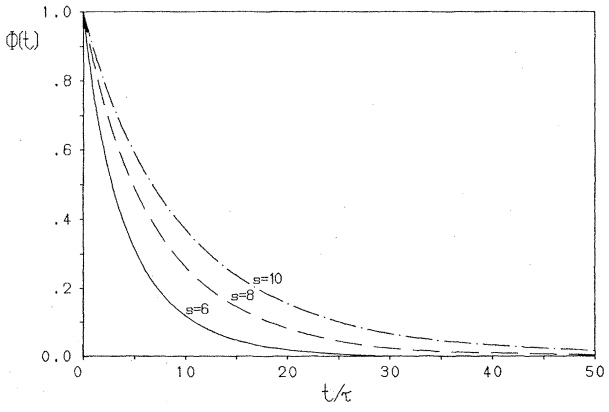

FIG. 4. Decay function $\Phi(t)$ in the reflecting-boundary case for the most important multipolar interactions w, Eq. (1): dipole-dipole interactions, $s = 6$; dipole-quadrupole interactions, $s = 8$; quadrupole-quadrupole interactions, $s = 10$. We chose the dimension $\Delta = 3$, the diffusion constant $\tilde{D} = 0.2$. the probability of a molecule to be an acceptor $p = 0.05$, and the cutoff parameter $\beta = 1$.

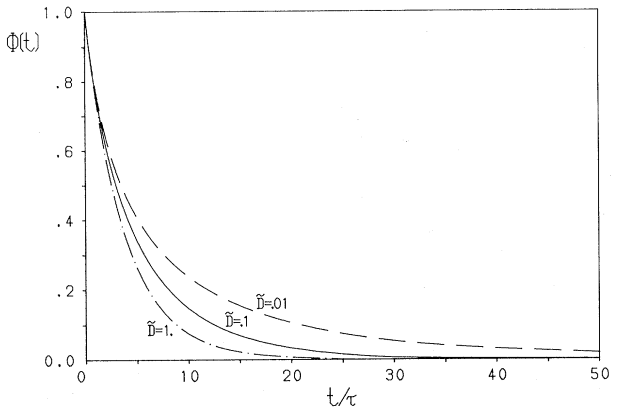

FIG. 5. Diffusion dependence $\tilde{D}=0.01$, 0.1, and 1.0, in the reflecting-boundary case for dipole-dipole interactions between the donor and the acceptors. We chose the dimension $\Delta=3$, the probability of a molecule to be an acceptor $p=0.05$, and the cutoff parameter $\beta=1$.

of the donor. The reason, of course, lies in the reflection suffered by the acceptor molecules which hit the boundary, and are thus close to the donor on the coming-and-going branch of their trajectory, while the number of reflections grows with $\tilde{D}$. The dependence of Φ on the dimensionality is similar as in the absorbing case. In higher dimensions, energy transfer is increased.

The dependence on the cutoff, however, is just the opposite of that in the Smoluchowski case. A decrease of β enhances the energy transfer (Fig. 6). This is due to the strong falloff in $w(R)$ with R so that acceptors at shorter distances are most effective.

Referring to the discussion subsequent to Eq. (12) concerning the identity of the two cases for $\beta=0$ and $\Delta=2,3$, we add here that in one dimension there is still a finite probability for an acceptor to hit a point boundary. This again makes the Smoluchowski boundary much more effective than the reflecting one.

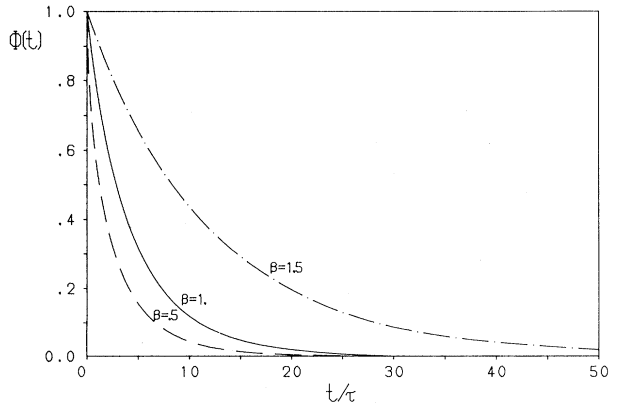

FIG. 6. Decay function $\Phi(t)$ in dependence of the cutoff parameters $\beta=0.5$, 1.0, and 1.5, in the reflecting-boundary case for dipole-dipole interactions between the donor and the acceptors. We chose the dimension $\Delta=3$, the diffusion constant $\tilde{D}=0.2$, and the probability of a molecule to be an acceptor $p=0.05$.

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APPENDIX A: THE GREEN FUNCTION G_Δ

The relevant properties of the G_Δ are subsequently collected.

1. Definitions and solutions of the differential equation

$$\mathscr{D}y(z)=0 \quad \text{with} \quad \mathscr{D}\equiv\frac{d}{dz}\left[z\frac{d}{dz}\right]-\left[z+\frac{\lambda^2}{z}\right] \tag{A1}$$

are the modified Bessel functions $K_\lambda(z)$ and $I_{|\lambda|}(z)$ [cf. Ref. 28, Eq. (9.6.1)]. Thus the following Green function G (symmetrical and limited in the infinite) belongs to the self-adjoint differential operator $\mathscr{D}$,

$$G(z,z')=I_{|\lambda|}(z_<)K_\lambda(z_>)+AK_\lambda(z)K_\lambda(z')\,, \tag{A2}$$

where $z_<$ and $z_>$ are defined in the text following (9). [See also Ref. 36, and Ref. 27, Eq. (14.8.2).] Equation (A2) is identical to Eq. (9) of Sec. III.

The parameter A can be chosen freely and thus allows to adjust G to different boundary conditions. For λ, the values $-\frac{1}{2},0,\frac{1}{2},1,\frac{3}{2},\ldots$ are to be considered. We first evaluate the integral over G which is needed,

$$\int_{z_0}^{\infty}G(z,z')z^{1+\lambda}dz = z'^{\lambda}-[I_\mu(z_0)-AK_{1+\lambda}(z_0)]z_0^{1+\lambda}K_\lambda(z')\,, \tag{A3}$$

where z_0 is arbitrary and μ is defined as in Eq. (10),

$$\mu\equiv\begin{cases}\lambda=-\frac{1}{2} & \text{for } \lambda=-\frac{1}{2},\\ 1+\lambda & \text{otherwise.}\end{cases}$$

To this end we use the derivation rules [Ref. 28, Eq. (9.6.28)] and Wronskians [Ref. 28, Eq. (9.6.15)] for Bessel functions.

The first boundary condition we consider is the absorbing one in z_0 (Smoluchowski case),

$$K_\lambda(z)[I_{|\lambda|}(z_0)+AK_\lambda(z_0)]=G(z,z_0)=0 \text{ for all } z>z_0\,, \tag{A4}$$

and, consequently,

$$A_{\mathrm{Sm}}=-I_{|\lambda|}(z_0)/K_\lambda(z_0)\,. \tag{A5}$$

In this case we obtain

$$\int_{z_0}^{\infty}G_{\mathrm{Sm}}(z,z')z^{1+\lambda}dz=z'^{\lambda}-\frac{K_\lambda(z')}{z_0^{-\lambda}K_\lambda(z_0)}\,, \tag{A6}$$

where we have used the Wronskian of the Bessel function again. As G is the Green function to $\mathscr{D}$,

$$\left[\frac{d}{dz'}\left[z'^{1+2\lambda}\frac{d}{dz'}\right]-z'^{1+2\lambda}\right](zz')^{-\lambda}G(z,z')$$
$$=(z'/z)^{\lambda}\mathscr{D}G(z,z')=-\delta(z-z')\ . \quad \text{(A7)}$$

Integration over z' yields

$$\frac{d}{dz'}[(zz')^{-\lambda}G(z,z')]\,|_{z'=z_0}$$
$$=z_0^{2\lambda+1}\left[1-z^{-\lambda}\int_{z_0}^{\infty}G(z,z')z'^{1+\lambda}dz'\right]$$
$$=z^{-\lambda}K_{\lambda}(z)z_0^{-\lambda}[I_{\mu}(z_0)-AK_{1+\lambda}(z_0)]\ . \quad \text{(A8)}$$

Thus the reflecting-boundary condition, i.e.,

$$\frac{d}{dz'}[(zz')^{-\lambda}G(z,z')]\,|_{z'=z_0}=0 \text{ for all } z>z_0\ , \quad \text{(A9)}$$

simply means that the integral expression

$$\int_{z_0}^{\infty}G_{\rm re}(z,z')z^{1+\lambda}dz=z'^{\lambda} \quad \text{(A10)}$$

is fulfilled, and, simultaneously,

$$A_{\rm re}=\frac{I_{\mu}(z_0)}{K_{1+\lambda}(z_0)} \quad \text{(A11)}$$

holds.

2. $\lambda=n+\frac{1}{2}$

We now consider the special case

$$\lambda=n+\tfrac{1}{2},\quad n=-1,0,1,2,\ldots \quad \text{(A12)}$$

corresponding to odd dimensions $\Delta=2n+3=1,3,5,\ldots$ [cf. Eq. (7)]. In this case $I_{|\lambda|}$ and K_{λ} are so-called "spherical" Bessel functions which can be expressed by means of exponential functions and polynomials.

As in Ref. 28, Eq. (10.2.11), we define

$$R(\nu+\tfrac{1}{2},z)\equiv\sum_{k=0}^{\nu}\frac{(\nu+k)!}{k!(\nu-k)!}(2z)^{-k} \text{ for } \nu=0,1,\ldots . \quad \text{(A13)}$$

According to Ref. 28, Eq. (10.2.9/10/15), we find for G, with $n\geq 0$,

$$(zz')^{1/2}G(z,z')=\tfrac{1}{2}R(\lambda,z_>)R(\lambda,-z_<)e^{-|z-z'|}$$
$$+\tfrac{1}{2}[\pi A-(-1)^n]R(\lambda,z)R(\lambda,z')e^{-(z+z')}\ . \quad \text{(A14)}$$

For $n=-1$ one has $G_{n=-1}=G_{n=0}$. The Green functions needed for the two boundary conditions are all compiled in Table I.

3. $G_{\rm Sm}$ and $G_{\rm re}$ extremal properties

We now want to show that $G_{\rm Sm}$ and $G_{\rm re}$ are defined by extremum conditions: For $A_{\rm Sm}\leq A\leq A_{\rm re}$, i.e., $G_{\rm Sm}\leq G\leq G_{\rm re}$, we have

$$0\leq\int_{z_0}^{\infty}(zz')^{-\lambda}G(z,z')z^{1+2\lambda}dz\leq 1 \text{ for all } z'\geq z_0\ ,$$

and *vice versa*. Thus $G_{\rm Sm}$ is minimal and $G_{\rm re}$ maximal, so that a probability is defined by the above integral expression: To prove this we first consider the lhs of the above inequality. By using (A3), this positiveness is equivalent to

$$[I_{\mu}(z_0)-AK_{1+\lambda}(z_0)]z_0^{1+\lambda}K_{\lambda}(z')\leq z'^{\lambda} \text{ for all } z'\ .$$

Taking into account

$$\min\{1/[z'^{-\lambda}K_{\lambda}(z')]\}=1/[z_0^{-\lambda}K_{\lambda}(z_0)]\ ,$$

and the equation following from the Wronskian, namely

$$z_0I_{\mu}(z_0)K_{\lambda}(z_0)=1-z_0I_{|\lambda|}(z_0)K_{1+\lambda}(z_0)\ ,$$

we recognize the equivalence to

$$1-z_0K_{1+\lambda}(z_0)[I_{|\lambda|}(z_0)+AK_{\lambda}(z_0)]\leq 1\ .$$

which means

$$A\geq-\frac{I_{|\lambda|}(z_0)}{K_{\lambda}(z_0)}=A_{\rm Sm}\ .$$

Furthermore, the equivalent of the positiveness of G is given by

$$I_{|\lambda|}(z_<)K_{\lambda}(z_>)+AK_{\lambda}(z)K_{\lambda}(z')=G(z,z')\geq 0\ ,$$
$$\Leftrightarrow A\geq-\frac{I_{|\lambda|}(z_<)K_{\lambda}(z_>)}{K_{\lambda}(z)K_{\lambda}(z')}=-\frac{I_{|\lambda|}(z_<)}{K_{\lambda}(z_<)} \text{ for all } z,z'\ ,$$
$$\Leftrightarrow A\geq-\min\{I_{|\lambda|}(z)/K_{\lambda}(z)\,|\,z\geq z_0\}=-I_{|\lambda|}(z_0)/K_{\lambda}(z_0)=A_{\rm Sm}\ .$$

TABLE I. Green function $(zz')^{-\lambda}G(z,z')$, Eq. (A2), in the cases of absorbing and reflecting boundaries at z_0 for $\Delta=1,2,3,4$.

Δ	λ	$(zz')^{-\lambda}G_{\rm Sm}(z,z')$	$(zz')^{-\lambda}G_{\rm re}(z,z')$
1	$-\frac{1}{2}$	$\dfrac{e^{-\lvert z-z'\rvert}-e^{-[(z-z_0)+(z'-z_0)]}}{2}$	$\dfrac{e^{-\lvert z-z'\rvert}+e^{-[(z-z_0)+(z'-z_0)]}}{2}$
2	0	$I_0(z_<)K_0(z_>)-\dfrac{I_0(z_0)}{K_0(z_0)}K_0(z)K_0(z')$	$I_0(z_<)K_0(z_>)+\dfrac{I_1(z_0)}{K_1(z_0)}K_0(z)K_0(z')$
3	$\frac{1}{2}$	$\dfrac{e^{-\lvert z-z'\rvert}-e^{-[(z-z_0)+(z'-z_0)]}}{2zz'}$	$\dfrac{e^{-\lvert z-z'\rvert}+[(z_0-1)/(z_0+1)]e^{-[(z-z_0)+(z'-z_0)]}}{2zz'}$
4	1	$\dfrac{1}{zz'}\left[I_1(z_<)K_1(z_>)-\dfrac{I_1(z_0)}{K_1(z_0)}K_1(z)K_1(z')\right]$	$\dfrac{1}{zz'}\left[I_1(z_<)K_1(z_>)+\dfrac{z_0I_0(z_0)-2I_1(z_0)}{z_0K_0(z_0)+2K_1(z_0)}K_1(z)K_1(z')\right]$

In conclusion, one obtains, in a condensed form,

$$G_{\mathrm{Sm}}=\min\left\{G\,\middle|\,\int_{z_0}^{\infty}(zz')^{-\lambda}G(z,z')z^{1+2\lambda}dz\geq 0 \text{ for all } z'\right\}$$
$$=\min\{G\mid G(z,z')\geq 0 \text{ for all } z,z'\}\ . \tag{A15}$$

We now consider the condition

$$\int_{z_0}^{\infty}(zz')^{-\lambda}G(z,z')z^{1+2\lambda}dz\leq 1 \text{ for all } z'\geq z_0\ ,$$

which according to (A3) is equivalent to

$$[I_\mu(z_0)-AK_{1+\lambda}(z_0)]z_0^{1+\lambda}K_\lambda(z')\geq 0 \text{ for all } z'\ ,$$

yielding

$$A\leq\frac{I_\mu(z_0)}{K_{1+\lambda}(z_0)}=A_{\mathrm{re}}\ .$$

Thus it holds that

$$G_{\mathrm{re}}=\max\left\{G\,\middle|\,\int_{z_0}^{\infty}(zz')^{-\lambda}G(z,z')z^{1+2\lambda}dz\leq 1 \text{ for all } z'\right\}\ . \tag{A16}$$

4. Laplace inversion of G

In order to show the relationships with the corresponding formulas in time space found in the literature,[12,27] we will Laplace-invert the Green function

$$H\equiv D^{-1}(RR')^{-\lambda}G(\kappa R,\kappa R')\ ,$$

which determines $E(S,R)$ through an integral equation, where $\kappa=\sqrt{s/D}$ and $R_0\equiv b$.

For the case $\Delta=1$, according to the table of Green functions and Ref. 28, Eq. (29.3.84),

$$\mathcal{L}_s^{-1}(H_{\mathrm{Sm/re}})=(4\pi Dt)^{-1/2}\{e^{-(R-R')^2/(4Dt)}\mp e^{-[(R-b)+(R'-b)]^2/(4Dt)}\}\ . \tag{A17}$$

For the case $\Delta=3$,

$$\mathcal{L}_s^{-1}(H_{\mathrm{Sm}})=(4\pi Dt)^{-1/2}\{e^{-(R-R')^2/(4Dt)}-e^{-[(R-b)+(R'-b)]^2/(4Dt)}\}/(RR')\ , \tag{A18}$$

and with Ref. 28, Eq. (29.3.88),

$$\mathcal{L}_s^{-1}(H_{\mathrm{re}})=(4\pi Dt)^{-1/2}\{e^{-(R-R')^2/(4Dt)}+e^{-[(R-b)+(R'-b)]^2/(4Dt)}\}/(RR')$$
$$-(e^2b)^{-1}e^{Dt/b^2}e^{(R+R')/b}\mathrm{erfc}\left[\frac{\sqrt{Dt}}{b}+\frac{(R-b)+(R'-b)}{2\sqrt{Dt}}\right]\Big/(RR') \tag{A19}$$

[cf. Ref. 27, Eq. (14.7.16)].

Turning to the dimension $\Delta=2$, we examine the Green function in the general case: For $R\neq R'$ we have, according to Ref. 37, p. 284, Eq. (5.16.56), and p. 285, Eq. (5.16.64),

$$\mathcal{L}_s^{-1}(H)=(RR')^{-\lambda}\{(2Dt)^{-1}e^{-(R^2+R'^2)/(4Dt)}I_{|\lambda|}[RR'/(2Dt)]$$
$$+\int_0^t A(t-u)(2Du)^{-1}e^{-(R^2+R'^2)/(4Du)}K_\lambda[RR'/(2Du)]du\}\ , \tag{A20}$$

with $A(t)\equiv\mathcal{L}_s^{-1}(A(s))$.

We now see that for $\Delta=1$ the first term on the rhs is the Smoluchowski part for $b=0$ by virtue of (A17),

$$(RR')^{1/2}(2Dt)^{-1}e^{-(R^2+R'^2)/(4Dt)}I_{1/2}[RR'/(2Dt)]=\mathcal{L}_s^{-1}(D^{-1}(RR')^{1/2}G_{\mathrm{Sm}}(\kappa R,\kappa R'))\,|_{\,b=0}\ . \tag{A21}$$

However, for $\Delta\geq 2$ the first terms on the rhs of (A20) is the Green function ϵ of free diffusion,

$$\epsilon(t,\vec{R},\vec{R}')\equiv(4\pi Dt)^{-\Delta/2}e^{-|\vec{R}-\vec{R}'|^2/(4Dt)}\ , \tag{A22}$$

which is summed over angles θ between the Δ-dimensional vectors $\vec{R}$ and $\vec{R}'$. Because of Ref. 28, Eq. (9.6.18), we have

$$(\Delta-1)V_{\Delta-1}\int_0^\pi\epsilon(t,\vec{R},\vec{R}')\sin^{\Delta-2}\theta\,d\theta=(RR')(2Dt)^{-1}e^{-(R^2+R'^2)/(4Dt)}I_{|\lambda|}\left[\frac{RR'}{2Dt}\right] \tag{A23}$$

[cf. Ref. 27, Eq. (10.3.5)] which represents the $b=0$ part of the Green function. In the $\Delta=2$ case, $A(t)$ can be evaluated along the lines of Ref. 27, Sec. 13.5I.

APPENDIX B: DERIVATION OF THE RATE EQUATION (33) IN TIME SPACE

1. Integration of E

According to the integral representation of the decay function Φ, Eq. (3), the term

$$[1-E(t,R)]R^{\Delta-1}$$

is integrable for physically realistic transfer probability laws, thus decaying more strongly than $1/R$ for sufficiently larger R.

As $\partial E/\partial R$ is positive throughout, we have

$$R^{\Delta-1}\frac{\partial}{\partial R}E(t,R)\leq R^{\Delta-1}\int_R^\infty \frac{\partial E(t,R')}{\partial R'}dR' = R^{\Delta-1}[1-E(t,R)] , \tag{B1}$$

implying that

$$R^{\Delta-1}\frac{\partial}{\partial R}E(t,R)$$

also decays more rapidly than $1/R$ in the region of sufficiently large R. Then the following limit exists:

$$\lim_{R\to\infty} R^{\Delta-1}\frac{\partial}{\partial R}E(t,R)=0 . \tag{B2}$$

2. Definition of k

By definition of the time-dependent rate k [Eqs. (16) and (18)]

$$k(t)=\frac{\partial}{\partial t}[-\ln\Phi(t)]=-\Delta V_\Delta p\rho\int_b^\infty R^{\Delta-1}\frac{\partial E(t,R)}{\partial t}dR , \tag{B3}$$

and E fulfills the Feynman-Kac equation [Eq. (4)]. As a consequence, we see that

$$R^{\Delta-1}\frac{\partial E(t,R)}{\partial t}=D\frac{\partial}{\partial R}\left[R^{\Delta-1}\frac{\partial}{\partial R}E(t,R)\right] - R^{\Delta-1}w(R)E(t,R) . \tag{B4}$$

Substituting into the expression for $k(t)$ [Eq. (B3)], we obtain, after employing (B2),

$$k(t)=\Delta V_\Delta p\rho D\lim_{R\to b} R^{\Delta-1}\frac{\partial}{\partial R}E(t,R) + \Delta V_\Delta p\rho\int_b^\infty w(R)E(t,R)R^{\Delta-1}dR . \tag{B5}$$

The first term on the rhs is just $k(t)$ for $w\equiv 0$ [cf. Eq. (23)].

3. Decay of $w(R)$

In reality, $w(R)$ will decay with R at least as strongly as a dipole-dipole term, and thus for $B>b$ large, it is

$$k(t)\approx\Delta V_\Delta p\rho D\lim_{R\to b} R^{\Delta-1}\frac{\partial}{\partial R}E(t,R) + \Delta V_\Delta p\rho\int_b^B w(R)E(t,R)R^{\Delta-1}dR . \tag{B6}$$

Let $B>b$ be fixed.

We now assume that there exists a nontrivial, normalizable solution $E_{st}(R)$ [cf. Eq. (28)] within the range $[b,B]$ of the stationary problem, Eq. (27). Thus an $E_{st}(R)$ exists with the properties $E_{st}(R)\not\equiv 0$, and its limit for $R\to B$ exists.

As the differential equation (27) is linear we can assume the normalization $\lim_{R\to B}E_{st}(R)=1$ without loss of generality. We list the following relevant properties:

(i) $E(t,R)\geq E_{st}(R)$,

(ii) $E(t,R)\to E_{st}(R)$ for $t\to\infty$, $R\leq B$,

(iii) $\lim_{t\to\infty}\left[\lim_{R\to b}\frac{\partial}{\partial R}E(t,R)\right]=\lim_{R\to b}\frac{d}{dR}E_{st}(R)$.

For long times t, then,

$$w(R)E(t,R)R^{\Delta-1}\sim w(R)E_{st}(R)R^{\Delta-1}$$

holds uniformly in R for $R\leq B$.

Then the integral part of (B6) becomes

$$\Delta V_\Delta p\rho\int_b^B w(R)E(t,R)R^{\Delta-1}dR \sim\Delta V_\Delta p\rho D\left[R^{\Delta-1}\frac{d}{dR}E_{st}(R)\right]_{R=b}^{R=B} . \tag{B7}$$

Finally, because of (iii) we have, for large t,

$$k(t)\sim\Delta V_\Delta p\rho D\left[R^{\Delta-1}\frac{d}{dR}E_{st}(R)\right]\Bigg|_{R=B} \quad (t\to\infty) . \tag{B8}$$

4. Solution of $E_{st}(R)$

Should there exist a nontrivial normalizable solution $E_{st}(R)$ of the stationary problem (27) within $[b,\infty]$, i.e., for $B\to\infty$, then, of course, Eq. (33) is valid.

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