AIP | The Journal of Chemical Physics

Conditional lifetimes in geminate recombination

Noam Agmon

Citation: The Journal of Chemical Physics **82**, 2056 (1985); doi: 10.1063/1.448340
View online: http://dx.doi.org/10.1063/1.448340
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/82/4?ver=pdfcov
Published by the AIP Publishing

Conditional lifetimes in geminate recombination

Noam Agmon[a)]
Department of Physical Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

(Received 15 February 1984; accepted 14 September 1984)

In addition to overall mean lifetimes, with which one is well acquainted in the theory of reactive diffusion processes, mean conditional lifetimes for absorption in a given sink also have physical significance. In the theory of geminate recombination of nonisolated pairs, when one imposes an additional outer absorbing sphere, the conditional lifetime for absorption in the inner sphere is the risetime for the recombination products. In the theory of geminate recombination in an homogeneous scavenger concentration, both overall and conditional lifetimes are physically significant. The first describes reactants' decay, the second products' formation. We derive, in the backward equation formalism, equations governing the initial variable dependence of these lifetimes. We give the explicit solution for geminate recombination of neutrals (free diffusion). Experimental measurements of recombination lifetimes would supply new data, independent of the yields typically measured in such experiments.

I. INTRODUCTION

In the theory of stochastic processes[1,2] and reactive diffusion processes[3–5] in particular, one often deals with mean first passage (or "survival") times.[6–10] Most attention has been directed[7–10] to the "overall" survival time of the diffusing species prior to absorption. However, in the case of several different sinks, one can also consider the conditional survival time[6] of the fraction of the population that is ultimately absorbed in a particular sink. This is the characteristic time for populating that particular sink. Not enough attention was given to the physical significance of conditional survival times, as we demonstrate below for two problems in the theory of geminate recombination.[11–20]

The first problem[20] is recombination of nonisolated geminate pairs. Here, in addition to an inner absorbing (or partially absorbing) sphere which represents the recombination reaction, one introduces an outer absorbing sphere, which represents assimilation into the homogeneous process of those pairs whose separation has exceeded a given distance. Since experimentally one is able to follow the appearance of the recombination products (not the change in separation of the pairs), it is the conditional passage time into the inner sphere (not the overall passage time into both spheres) that is physically relevant.

The second problem[18] is recombination of isolated pairs in the presence of an homogeneous scavenger concentration (no outer boundary condition is imposed). When no scavengers are present, the mean lifetime of the diffusing geminate pairs is infinite, due to the unbounded diffusion space. In the presence of scavengers, escape is no longer possible. All pairs are ultimately either recombined or scavenged. As a result, lifetimes become finite. The overall mean lifetime of the diffusing pairs is then a weighted average of the conditional mean lifetimes for recombination and scavenging.

The aim of this paper is to derive expressions for the conditional lifetimes in the above mentioned processes since, as we have argued above, these have a clear experimental significance.

II. GENERAL DEFINITIONS

We restrict attention to cases where the evolution of a probability distribution $p(x,t)$ is governed by a spherically symmetric diffusion equation in d dimensions

$$\frac{\partial p}{\partial t} = -x^{1-d}\frac{\partial}{\partial x}x^{d-1}j$$

$$= x^{1-d}\frac{\partial}{\partial x}De^{-\beta V}x^{d-1}\frac{\partial}{\partial x}e^{\beta V}p = -\mathscr{L}p, \qquad (1)$$

where $D(x)$ is a (possibly coordinate dependent) diffusion coefficient, $V(x)$ is a potential function (its negative derivative is the "drag force"), $\beta = 1/k_B T$, where k_B is Boltzmann's constant and T the absolute temperature. Equation (1) also defines the flux, $j(x,t)$, and the diffusion operator $\mathscr{L}$.

We will consider solutions for a δ-function initial condition

$$x^{d-1}p(x,0) = \delta(x - x_0) \qquad (2)$$

known as "fundamental solutions," "Green functions," or "finite-time transition probabilities." We denote such solutions by $p(x,t\,|x_0)$. Any other solution is obtainable by averaging these over an initial distribution. Note that we have absorbed the geometric factors (2π, 4π, etc.) in p.

The dependence of the transition probabilities on the initial variable x_0 is governed by the adjoint (or "backward") equation

$$\frac{\partial p(x,t\,|x_0)}{\partial t} = -\mathscr{L}^{\dagger}_{x_0}p$$

$$= e^{\beta V(x_0)}x_0^{1-d}\frac{\partial}{\partial x_0}D(x_0)$$

$$\times e^{-\beta V(x_0)}x_0^{d-1}\frac{\partial}{\partial x_0}p(x,t\,|x_0). \qquad (3)$$

Equation (3) serves also as a definition of the adjoint operator $\mathscr{L}^{\dagger}$. The backward equation is a starting point for some first passage time discussions.[6,7,9]

[a)] Bat-Sheva de Rothschild Fellow for 1984.

III. GEMINATE RECOMBINATION OF NONISOLATED PAIRS

As discussed in the introduction, we consider[20] the case of diffusion between two concentric spheres of radii a and b, $a<b$. At the inner sphere we impose a radiation boundary condition[4]

$$j(a,t\,|x_0) = -\kappa p(a,t\,|x_0) \tag{4}$$

describing recombination with an "intrinsic" rate constant κ. At the outer sphere the absorbing boundary condition

$$p(b,t\,|x_0) = 0 \tag{5}$$

eliminates all the pairs whose separation reaches the critical value b (which can be taken as the average distance in the homogeneous solution). By assumption, such pairs are no longer considered "geminate."

Denote by

$$\phi_a(t\,|x_0) = -a^{d-1}\int_0^t j(a,s|x_0)\,ds \tag{6}$$

the fraction of recombined pairs up to time t. An analogous quantity $\phi_b(t\,|x_0)$ can be defined for the boundary $x=b$. Evidently [e.g., by integrating Eq. (1) over x and t] probability conservation implies that

$$\phi_a(t\,|x_0) + \int_a^b p(x,t\,|x_0)x^{d-1}dx + \phi_b(t\,|x_0) = 1. \tag{7}$$

The ultimate recombination probability (or reaction yield) is

$$\eta(x_0) = \lim_{t\to\infty} \phi_a(t\,|x_0). \tag{8}$$

In these notations the overall survival time for a process starting at x_0, $\tau(x_0)$ is defined by

$$\begin{aligned}\tau(x_0) &= \int_0^\infty t\,[b^{d-1}j(b,t\,|x_0) - a^{d-1}j(a,t\,|x_0)]\,dt\\ &= \int_0^\infty [1-\phi_a(t\,|x_0) - \phi_b(t\,|x_0)]\,dt.\end{aligned} \tag{9}$$

(The difference in sign for the fluxes at a and b is due to j being inwardly directed at a and outwards at b.) The conditional lifetime for the fraction $\eta(x_0)$ that ultimately recombines $\sigma(x_0)$ is defined by

$$\begin{aligned}\sigma(x_0) &= -\eta(x_0)^{-1}\int_0^\infty t a^{d-1}j(a,t\,|x_0)\,dt\\ &= \int_0^\infty [1-\phi_a(t\,|x_0)/\eta(x_0)]\,dt.\end{aligned} \tag{10}$$

This is the quantity related to the rise time in the experimental signal of the recombination products. (If absorption at the outer boundary $x=b$ had also been experimentally significant, we would have defined η_a and σ_a as above for absorption at $x=a$ and also, in an analogous way, η_b and σ_b. It is then clear from the definitions that $\tau = \eta_a\sigma_a + \eta_b\sigma_b$.)

Instead of solving the complete diffusion equation for $p(x,t\,|x_0)$ and hence $j(x,t\,|x_0)$, one can use the backward equation approach to derive[2,7,9] the following ordinary differential equations for the abovementioned quantities:

$$\mathscr{L}^\dagger\tau = 1 \tag{11a}$$

with the boundary conditions

$$D\tau'(a) = \kappa\tau(a), \quad \tau(b) = 0 \tag{11b}$$

(a prime denotes differentiation),

$$\mathscr{L}^\dagger\eta = 0 \tag{12a}$$

with boundary conditions

$$-D\eta'(a) = \kappa[1-\eta(a)], \quad \eta(b) = 0, \tag{12b}$$

and[6]

$$\mathscr{L}^\dagger\eta\sigma = \eta \tag{13a}$$

with boundary conditions

$$\begin{aligned}&D(\eta\sigma)' = \kappa\eta\sigma, \quad \text{at} \quad x=a\\ &\eta\sigma = 0, \quad \text{at} \quad x=b.\end{aligned} \tag{13b}$$

The last equation can also be written as

$$\mathscr{L}^\dagger\sigma - 2D\eta'\sigma'/\eta = 1 \tag{13a'}$$

with boundary conditions (see Appendix A)

$$D\sigma'(a) = \kappa\sigma(a)/\eta(a), \quad \sigma'(b) = 0. \tag{13b'}$$

Hence the conditional survival time for the fraction η absorbed at a, obeys a reflecting boundary condition at the other absorbing boundary.

The solutions of the above equations for three dimensional free diffusion (this zero potential case can represent recombination of noncharged particles, e.g., radicals) is given below

$$\begin{aligned}6xD\tau(x) &= -x^3 + \frac{1}{L}[a^3(b-x) + b^3(x-a)]\\ &\quad + \frac{aLD(b+2a)}{\kappa aL + bD}(b-x),\end{aligned} \tag{14}$$

$$x\eta(x) = \frac{\kappa a^2}{\kappa aL + bD}(b-x), \tag{15}$$

where $L \equiv b-a$. These results were obtained by a different method in Ref. 20 [see Eqs. (13) and (14) there]. However, $\tau(x)$ measures the depletion of the unrecombined reactants due to both reaction and assimilation. It is not an observable quantity. The physically interesting function is the conditional lifetime, which is a solution of [cf. Eqs. (13')]

$$D\,[x^{-2}(x^2\sigma')' - 2b\sigma'/x(b-x)] = -1 \tag{16a}$$

with boundary conditions

$$aLD\sigma'(a) = (\kappa aL + bD)\sigma(a), \quad \sigma'(b) = 0. \tag{16b}$$

This gives

$$\begin{aligned}6D\sigma(x) &= x(2b-x) - a(2b-a)\\ &\quad + 2aL^2D/(\kappa aL + bD).\end{aligned} \tag{17}$$

The special case of an absorbing boundary at $x=a$ is gotten by taking the limit $\kappa\to\infty$. These solutions are demonstrated in Fig. 1. For future reference, we give in Appendix B solutions for the case of radiation boundary conditions at both a and b.

IV. SCAVENGING OF GEMINATE RECOMBINATION

We now consider the case of geminate recombination of isolated pairs (no outer absorbing sphere imposed) in a media with a homogeneous concentration c_s of scavenger mole-

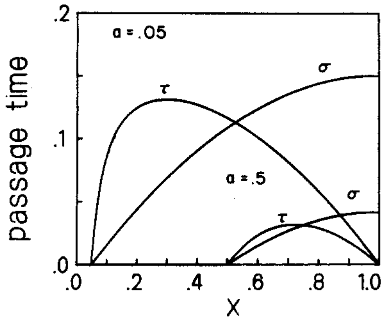

FIG. 1. Conditional mean recombination time σ compared with the overall mean lifetime τ for two radii a of the reaction sphere, for spherically symmetric three dimensional free diffusion between two absorbing spheres [Eqs. (17) and (14) for $\kappa = \infty$]. D and b are unity.

cules whose scavenging rate constant is κ_s. The reactive diffusion process now obeys

$$\partial p/\partial t = -\mathscr{L}\, p - \kappa_s c_s\, p, \quad x \geqslant a, \tag{18}$$

where $\mathscr{L}$ is the same operator as in Eq. (1) and recombination described, as above, by a radiation boundary condition at $x = a$ with an intrinsic rate constant κ.

In the presence of scavengers escape is no longer possible. There is either recombination with probability η_r or scavenging, with probability η_s. Recombination takes place only from the boundary $x = a$, whereas scavenging occurs from every point with the same rate constant $\kappa_s c_s$. The probabilities for these two reactions are given, as before, by the time integral of the appropriate fluxes. Hence

$$\eta_r(x_0) = \kappa a^{d-1} \int_0^\infty p(a,t\,|x_0)\, dt, \tag{19a}$$

$$\eta_s(x_0) = \kappa_s c_s \int_0^\infty \int_a^\infty p(x,t\,|x_0)\, x^{d-1}\, dx\, dt, \tag{19b}$$

where [by integrating Eq. (18) over x and t]

$$\eta_r(x) + \eta_s(x) = 1. \tag{20}$$

The backward equation formulation for the recombination probability is well known.[18(b)] One solves

$$\mathscr{L}^\dagger\, \eta_r + \kappa_s c_s \eta_r = 0, \tag{21a}$$

with boundary conditions [cf. Eq. (12b)]

$$-D\eta_r'(a) = \kappa[1 - \eta_r(a)], \quad \eta_r(\infty) = 0. \tag{21b}$$

The solution for free diffusion in three dimensions is[18(b)]

$$x\eta_r(x) = A \exp\left[-\sqrt{\kappa_s c_s/D}\,(x-a)\right] \tag{22}$$

where $A \equiv \kappa a/(\kappa + \sqrt{\kappa_s c_s D} + D/a)$.

Not discussed in the literature[18] are the survival times. When no scavengers are present, the overall and conditional lifetimes coincide: They diverge due to the infinite diffusion space. This is no longer when $\kappa_s c_s > 0$, since there is then scavenging from any x. Now both overall survival time τ and the conditional lifetimes for recombination and scavenging (which we denote by σ_r and σ_s, respectively) are finite and physically meaningful. The first is the time constant for depletion of the reactants, while the conditional lifetimes describe the appearance of the recombination and scavenging products. These are defined by [cf. Eqs. (9) and (10)]

$$\eta_r(x_0)\, \sigma_r(x_0) = \kappa \int_0^\infty t a^{d-1}\, p(a,t\,|x_0)\, dt, \tag{23a}$$

$$\eta_s(x_0)\, \sigma_s(x_0) = \kappa_s c_s \int_0^\infty t \left[\int_a^\infty p(x,t\,|x_0)\, x^{d-1} dx\right] dt, \tag{23b}$$

while the overall lifetime is defined as usual[7-10] by

$$\tau(x_0) = \int_0^\infty \int_a^\infty p(x,t\,|x_0)\, x^{d-1}\, dx\, dt. \tag{24}$$

In the notations of Eq. (7),

$$\partial\phi_r(t\,|x_0)/\partial t = \kappa a^{d-1} p(a,t\,|x_0), \tag{25a}$$

$$\partial\phi_s(t\,|x_0)/\partial t = \kappa_s c_s \int_a^\infty p(x,t\,|x_0)\, x^{d-1}\, dx. \tag{25b}$$

Therefore [cf. Eq. (7)] the overall lifetime is just the weighted average of the conditional lifetimes

$$\tau = \eta_r \sigma_r + \eta_s \sigma_s\,. \tag{26}$$

Another simple relation is obtained from Eq. (19b):

$$\tau(x) = \eta_s(x)/\kappa_s c_s\,. \tag{27}$$

Hence, of the five quantities η_r, η_s, σ_r, σ_s, and τ, one needs to calculate only two. The other three are determined from Eqs. (20), (26), and (27).

In the backward equation formalism one can supplement the solution for η_r by solving for the overall lifetime

$$\mathscr{L}^\dagger \tau + \kappa_s c_s \tau = 1 \tag{28a}$$

with the boundary conditions

$$D\tau'(a) = \kappa\tau(a), \quad \tau(\infty) = 1/\kappa_s c_s \tag{28b}$$

and for both conditional lifetimes

$$\mathscr{L}^\dagger \eta\sigma + \kappa_s c_s \eta\sigma = \eta \tag{29a}$$

with the same boundary conditions at $x = a$:

$$D\,(\eta\sigma)'(a) = \kappa\eta(a)\sigma(a), \tag{29b}$$

but different boundary conditions at infinity

$$\eta_r(\infty)\sigma_r(\infty) = 0, \quad \sigma_s(\infty) = 1/\kappa_s c_s \tag{29c}$$

To complete the solution for free diffusion in three dimensions we solve the equation for $\sigma_r(x)$, which can also be written in the form (13a') but with $\sigma_r(\infty) = \infty$ in Eq. (13b'). This is easily solved to give

$$2\sqrt{\kappa_s c_s D}\;\sigma_r(x) = x - A\,(1 + \sqrt{\kappa_s c_s D}/\kappa), \tag{30}$$

where A is the same as in Eq. (22).

In the special case of an absorbing boundary $\kappa = \infty$, the results simplify to

$$x\eta_r(x) = a \exp\left[-\sqrt{\kappa_s c_s/D}\,(x-a)\right], \tag{31a}$$

$$2\sqrt{\kappa_s c_s D}\;\sigma_r(x) = x - a. \tag{31b}$$

These results show that there is a large difference between the mean lifetime of the reactants $\tau(x) = [1 - \eta_r(x)]/\kappa_s c_s$ and the mean recombination time $\sigma_r(x)$. The first increases to $1/\kappa_s c_s$ with increasing x, where the scavenging process becomes dominant. The second quantity diverges with increasing x, when for the decreasing fraction of the population that recombines it takes longer to reach $x = a$.

V. CONCLUSION

We have demonstrated the significance of conditional mean survival times in two types of geminate recombination processes—geminate recombination of nonisolated pairs and geminate recombination in the presence of a homogeneous scavenger concentration. We have given explicit solutions for neutrals (radicals), where the interparticle potential is taken as zero. The solution for ions (Coulomb potential) requires some numerical integration. An experimental verification of the theory requires temporal monitoring of the recombination products. Such experiments are desirable since they would supply data which is independent of that obtained from the traditional yield (recombination probability) measurements.

ACKNOWLEDGMENT

Work supported in part by the Bat-Sheva de Rothschild Foundation.

APPENDIX A

We show that an absorbing boundary condition for $\eta\sigma$ at $x = b$ [Eq. (13b)] implies a reflecting boundary condition for σ there [Eq. (13b')]. Denote $\theta \equiv \eta\sigma$. Then

$$\sigma' = (\eta\theta' - \theta\eta')/\eta^2. \tag{A1}$$

As $x \to b$ both η and θ tend to zero, hence the limit is of the form 0/0. By L'Hopital's rule we should differentiate numerator and denominator. If we multiply both by $x^{d-1}e^{-\beta V(x)}$, differentiate, and then multiply by $-Dx^{1-d}e^{\beta V(x)}$, we find

$$\lim_{x\to b} \sigma'(x) = \lim_{x\to b} \frac{\eta\mathscr{L}^\dagger\theta - \theta\mathscr{L}^\dagger\eta}{\eta[\eta\mathscr{L}^\dagger x - 2D]}$$

$$= \lim_{x\to b} \eta/(\eta\mathscr{L}^\dagger x - 2D) = 0, \tag{A2}$$

where for the second equality we have used Eqs. (12a) and (13a).

APPENDIX B

We give solutions for absorption probabilities η_a and η_b and conditional mean lifetimes σ_a and σ_b for spherical symmetric diffusion in d dimensions with radiation boundary conditions at both a and b (intrinsic rate constants κ_a and κ_b), $a < x < b$.

For the absorption probabilities the boundary conditions are

$$-D\eta_a'(a) = \kappa_a[1-\eta_a(a)], \quad -D\eta_a'(b) = \kappa_b\eta_a(b), \tag{B1a}$$

$$D\eta_b'(a) = \kappa_a\eta_b(a), \quad D\eta_b'(b) = \kappa_b[1-\eta_b(b)]. \tag{B1b}$$

The solution of Eq. (12a) for $d \neq 2$ now reads

$$\eta_a(x) = \kappa_a(g_b - \kappa_b x^{2-d})/f, \tag{B2a}$$

$$\eta_b(x) = \kappa_b(g_a + \kappa_a x^{2-d})/f, \tag{B2b}$$

where

$$g_a = D(2-d)a^{1-d} - \kappa_a a^{2-d}, \tag{B3a}$$

$$g_b = D(2-d)b^{1-d} + \kappa_b b^{2-d}, \tag{B3b}$$

$$f = \kappa_a g_b + \kappa_b g_a. \tag{B3c}$$

For $d = 3$ *and* $k_b \to \infty$ Eq. (B2a) reduces to Eq. (15). In two dimensions the solution is

$$\eta_a(x) = \kappa_a(g_b - \kappa_b \ln x)/f, \tag{B4a}$$

$$\eta_b(x) = \kappa_b(g_a + \kappa_a \ln x)/f, \tag{B4b}$$

where f given by Eq. (B3c) but

$$g_a = D/a - \kappa_a \ln a, \tag{B5a}$$

$$g_b = D/b + \kappa_b \ln b. \tag{B5b}$$

For the conditional lifetimes the boundary conditions are

$$D\theta_a'(a) = \kappa_a\theta_a(a), \quad -D\theta_a'(b) = \kappa_b\theta_a(b), \tag{B6a}$$

$$D\theta_b'(a) = \kappa_a\theta_b(a), \quad -D\theta_b'(b) = \kappa_b\theta_b(b), \tag{B6b}$$

where $\theta = \eta\sigma$. We solve Eq. (13a) only for the one dimensional case, with $a = 0$ and $b = L$:

$$Df\theta_0(x)/\kappa_0 = h_0(D/\kappa_0 + x) - \tfrac{1}{2}(D + L\kappa_L)x^2 + \tfrac{1}{6}\kappa_L x^3, \tag{B7a}$$

$$Df\theta_L(x)/\kappa_L = h_L(D/\kappa_0 + x) - \tfrac{1}{2}Dx^2 - \tfrac{1}{6}\kappa_0 x^3, \tag{B7b}$$

where the constants h_0, h_L, and f are given by

$$h_0 = L\kappa_0(D^2 + DL\kappa_L + \tfrac{1}{3}L^2\kappa_L^2)/f, \tag{B8a}$$

$$h_L = L\kappa_0[D^2 + \tfrac{1}{2}DL(\kappa_0 + \kappa_L) + \tfrac{1}{6}L^2\kappa_0\kappa_L]/f, \tag{B8b}$$

$$f = D(\kappa_0 + \kappa_L) + L\kappa_0\kappa_L. \tag{B8c}$$

Both σ_0 and σ_L tend to the same limit at the other boundary

$$\sigma_0(L) = \sigma_L(0)$$

$$= L[D + \tfrac{1}{2}L(\kappa_0 + \kappa_L) + \tfrac{1}{6}L^2\kappa_0\kappa_L/D]/f. \tag{B9}$$

The solution for the overall survival time [Eq. (11a)] is given by

$$D\tau(x) = h(1/\kappa_0 + x) - x^2/2, \tag{B10}$$

where

$$h = L\kappa_0(1 + \tfrac{1}{2}L\kappa_L)/(\kappa_0 + \kappa_L + L\kappa_0\kappa_L).$$

When both κ's tend to infinity we have the solution for two absorbing boundaries

$$\eta_0(x) = (L-x)/L, \tag{B11a}$$

$$\eta_L(x) = x/L, \tag{B11b}$$

$$6D\sigma_0(x) = x(2L - x), \tag{B12a}$$

$$6D\sigma_L(x) = L^2 - x^2, \tag{B12b}$$

$$2D\tau(x) = x(L-x). \tag{B13}$$

These relations are also small D approximations for finite κ's. The solutions for σ and τ are compared in Fig. 2.

When D is very large one obtains

$$\eta_0 = \kappa_0/(\kappa_0 + \kappa_L), \quad \eta_L = \kappa_L/(\kappa_0 + \kappa_L), \tag{B14}$$

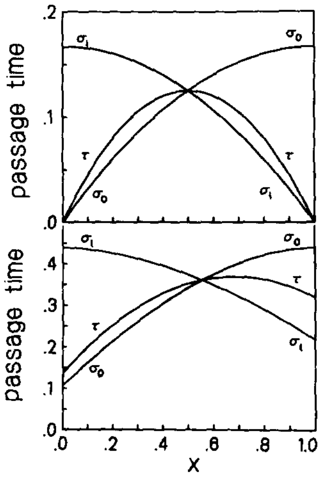

FIG. 2. Conditional mean waiting time for absorption at $x = 0$ and $x = 1$ (σ_0 and σ_1) compared with overall mean lifetime τ for one dimensional free diffusion on the unit interval. Top panel is for two absorption boundary conditions, demonstrating Eqs. (B12) and (B13). Bottom panel is for two radiation boundary conditions (with $\kappa_0 = 5$ and $\kappa_1 = 1$), demonstrating Eqs. (B7) and (B10). $D = 1$.

$$\sigma_0 = \sigma_L = L/(\kappa_0 + \kappa_L). \tag{B15}$$

These are the same as the results obtainable from a simple kinetic model where an initial state is transformed to two possible final states, with rate constants κ_0/L and κ_L/L.

[1]N.G.Van Kampen, *Stochastic Processes in Physics and Chemistry* (North–Holland, Amsterdam, 1981).
[2]C. W. Gardiner, *Handbook of Stochastic Methods for Physics, Chemistry and the Natural Sciences* (Springer, Berlin, 1983).
[3]M. von Smoluchowski, Ann. Phys. **48**, 1103 (1915); Z. Phys. Chem. **92**, 129 (1917).
[4]F. C. Collins and G. E. Kimball, J. Colloid. Sci. **4**, 425 (1949).
[5]G. Wilemski and M. Fixman, J. Chem. Phys. **58**, 4009 (1973).
[6]Sections 5.2.8 and 5.4.2 in Ref. 2.
[7]L. Pontryagin, A. Andronow, and A. Witt, Zh. Eksp. Theor. Fiz. **3**, 172 (1933).
[8](a) G. H. Weiss, Adv. Chem. Phys. **13**, 1 (1967); (b) J. Stat. Phys. **24**, 587 (1981).
[9]A. Szabo, K. Schulten, and Z.Schulten, J. Chem. Phys. **72**, 4350 (1980).
[10]J. M. Deutch, J. Chem. Phys. **73**, 4700 (1980).
[11]L. Onsager, Phys. Rev. **54**, 554 (1938).
[12]L. Monchick, J. Chem. Phys. **24**, 381 (1956).
[13](a) A. Mozumder, Adv. Radiat. Chem. **1**, 1 (1969); (b) G.C.Abell and A. Mozumder, J. Chem. Phys. **56**, 4079 (1972); (c) G.C.Abell, A. Mozumder, and J. L. Magee, *ibid.* **56**, 5422 (1972).
[14]P. K. Ludwig, J. Chem. Phys. **50**, 1787 (1969).
[15]Z. Schulten and K. Schulten, J. Chem. Phys. **66**, 4616 (1977).
[16]S. A. Rice, P. R. Butler, M. J. Pilling, and J. K. Baird, J. Chem. Phys. **70**, 4001 (1979).
[17]K. M. Hong and J. Noolandi, J. Chem. Phys. **68**, 5163 (1978).
[18](a) M. Tachiya, J. Chem. Phys. **69**, 2375 (1978); **70**, 238 (1979); (b) H. Sano and M. Tachiya, *ibid.* **71**, 1276 (1979).
[19]Yu. A. Berlin, P. Cordier, and J. A. Delaire, J. Chem. Phys. **73**, 4619 (1980).
[20]A. Mozumder, J. Chem. Phys. **76**, 5107 (1982).