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Relaxation times in diffusion processes

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Relaxation time for diffusion between reflecting boundaries is defined and the theory for its evaluation using the backward-equation approach is presented. A few simple examples are given and comparison with other results in the literature is made. We expect that relaxation time for nonreactive processes might assume the role of mean first passage times in reactive processes.

I. INTRODUCTION

The notion of mean first passage (or survival) time is an important subject in stochastic processes[1] in general and diffusion processes in particular.[2,3] This is the case of an absorbing (or partially absorbing) boundary, and one asks how long, on the average, does the total population $\int p(\mathbf{x},t\,|\mathbf{x}_0)d\mathbf{x}$ survive before its ultimate absorption. In particular, for initial population located at some $\mathbf{x}_0$, the mean survival time is defined as the spacial and temporal integral of the transition probability

$$\tau(\mathbf{x}_0)\equiv\int_0^\infty\int p(\mathbf{x},t\,|\mathbf{x}_0)d\mathbf{x}\,dt. \tag{1}$$

An extension of this notion is the mean residence time[4] density at a given point $\mathbf{x}$ in the coordinate space, which is defined as the temporal integral alone

$$\tau(\mathbf{x}|\mathbf{x}_0)\equiv\int_0^\infty p(\mathbf{x},t\,|\mathbf{x}_0)dt. \tag{2}$$

For both quantities it is possible to derive[3,4] ordinary differential equations in terms of the diffusion operator and its adjoint.

In contrast to the absorption problem mentioned above, there is no general theory for the case of reflecting boundaries. Under these conditions, probability density does not disappear, it just relaxes to equilibrium. Can one define, in analogy to the absorbing case, a quantity that would describe some characteristic time for this relaxation process? A generalization of a quantity used by Northrup and Hynes[5] in their theory for diffusional barrier crossing seems appropriate

$$\tau_r(\mathbf{x}|\mathbf{x}_0)\equiv p^e(\mathbf{x})^{-1}\int_0^\infty [\,p(\mathbf{x},t\,|\mathbf{x}_0)-p^e(\mathbf{x})]\,dt. \tag{3}$$

Here $p^e(\mathbf{x})\equiv\lim_{t\to\infty}p(\mathbf{x},t\,|\mathbf{x}_0)$ is the equilibrium distribution function. The relaxation time is then defined as $\tau_r(\mathbf{x}|\mathbf{x})$, since for $\mathbf{x}=\mathbf{x}_0$ $p(\mathbf{x},t\,|\mathbf{x})$ decreases monotonically to its equilibrium value and the defined quantity is positive. It measures the weighted time of deviation from equilibrium at the initial point. In Ref. 5, $\tau_r(\mathbf{x}|\mathbf{x})^{-1}$ at the reflecting boundary was used as the rate constant for relaxation from the barrier region into the reactants' (or products') well.

The purpose of this work is to derive an equation for the relaxation time in terms of the adjoint diffusion operator and solve it for spherical symmetric diffusion in d dimensions. We then give the explicit solutions for a few simple one-dimensional systems.

II. GENERAL BACKGROUND

We consider the evolution of a distribution density function $p(x,t)$ as governed by the diffusion equation[1]

$$\partial p/\partial t=-\mathscr{L}_x(p). \tag{4}$$

For a spherically symmetric system in d dimensions, the diffusion operator can be written as

$$\mathscr{L}_x=-x^{1-d}\,\frac{\partial}{\partial x}\,x^{d-1}D(x)\;e^{-\beta V(x)}\frac{\partial}{\partial x}\,e^{\beta V(x)}. \tag{5}$$

In Eq. (5) $D(x)$ is the (possibly coordinate dependent) diffusion coefficient, $V(x)$ is a potential function (its negative derivative is the "drag force"), $\beta=1/k_BT$ where k_B is Boltzmann's constant, and T the absolute temperature. Note that the vector notation has been dropped. Equation (4) can be also written as a continuity equation

$$x^{d-1}\partial p/\partial t=-\partial(x^{d-1}j)/\partial x, \tag{6}$$

where the definition of the flux $j(x,t)$ is evident from Eq. (5).

We restrict the stochastic motion to the region in between two concentric spheres of radii a and b, $a<b$, $a\leqslant x\leqslant b$. At the boundaries we impose reflecting boundary conditions

$$j(a,t)=j(b,t)=0. \tag{7}$$

The finite-time transition probability (Green's function) $p(x,t\,|x_0)$ is the solution of Eq. (4) for a distribution initially concentrated at x_0:

$$x^{d-1}\,p(x,0|x_0)=\delta(x-x_0). \tag{8}$$

The solution for any other initial distribution is obtained by averaging the Green's function over this initial distribution. It is normalized so that $\int_a^b x^{d-1}\,p(x,t)dx=1$. (The geometric factors 2π, 4π, etc. are included for convenience in p).

For any initial condition (any x_0) the reflecting boundary conditions ensure that the distribution function would eventually reach its equilibrium form

$$p^e(x)=Z^{-1}\;e^{-\beta V(x)},$$
$$Z\equiv\int_a^b x^{d-1}\;e^{-\beta V(x)}\;dx. \tag{9}$$

In the theory we shall also make use of the adjoint (backward) equation

$$\partial p/\partial t=-\mathscr{L}^\dagger_{x_0}(p), \tag{10}$$

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which describes evolution in the initial variable x_0. For spherically symmetric diffusion in d dimensions the adjoint operator is given by

$$\mathscr{L}_x^\dagger = -x^{1-d}e^{\beta V(x)}\frac{\partial}{\partial x}x^{d-1}D(x)e^{-\beta V(x)}\frac{\partial}{\partial x}. \quad (11)$$

The reflecting boundary conditions (zero flux) of the forward equation now become[3]

$$\partial p/\partial x_0|_{x_0=a} = \partial p/\partial x_0|_{x_0=b} = 0. \quad (12)$$

If $p(x,t)$ is a solution of the forward (diffusion) equation (4), then $p(x,t)/p^e(x)$ is a solution of the backward equation (in x).

For the boundary value problem described above, a solution in terms of eigenvalues λ_n of the diffusion operator or its adjoint (they have the same spectrum) is always possible[6]:

$$p(x,t\,|x_0) = \sum_{n=0}^{\infty} h_n(x_0)g_n(x)e^{-\lambda_n t}, \quad (13)$$

where $g_n(x)$ are the eigenfunctions of $\mathscr{L}$ and $h_n(x)$ are the eigenfunctions of $\mathscr{L}^\dagger$. These two families are biorthogonal $\int_a^b g_n(x)h_m(x)x^{d-1}dx = \delta_{nm}$, and $g_n = p^e h_n$. $\lambda_0 = 0$ and all other $\lambda_n > 0$. $g_0(x) = p^e(x)$ and $h_0(x) = 1$ (g_n and h_n obey the "nodal theorem"). Hence the solution in terms of Green's functions is

$$p(x,t\,|x_0) = p^e(x) + \sum_{n=1}^{\infty} h_n(x_0)h_n(x)p^e(x)e^{-\lambda_n t}. \quad (13')$$

III. THEORY

We now consider the relaxation time $\tau_r(x|x_0)$ as defined in Eq. (3). Operating $\mathscr{L}_x$ on this equation we find that

$$\mathscr{L}_x(\tau_r p^e) = -\int_0^\infty \frac{\partial p}{\partial t}dt = x^{1-d}\delta(x-x_0) - p^e(x). \quad (14)$$

Dividing by $p^e(x)$ gives

$$\mathscr{L}_x^\dagger(\tau_r) = x^{1-d}p^e(x)^{-1}\delta(x-x_0) - 1. \quad (15a)$$

Similarly, by operating with $\mathscr{L}_{x_0}^\dagger$ on Eq. (3) we find that

$$\mathscr{L}_{x_0}^\dagger(\tau_r) = x^{1-d}p^e(x)^{-1}\delta(x-x_0) - 1. \quad (15b)$$

For $x \neq x_0$ we write Eq. (15) as

$$\mathscr{L}_x^\dagger(\tau_r) = -1, \quad (16a)$$

$$\mathscr{L}_{x_0}^\dagger(\tau_r) = -1. \quad (16b)$$

$\tau_r(x|x_0)$ obeys the same equation in both variables. This immediately implies that $\tau_r(x|x_0) = \tau_r(x_0|x)$. Note that Eq. (16b) differs from the analogous result[3] for the mean survival time $\tau(x_0)$ by a minus sign. Equations (16) are to be solved subject to the boundary conditions [derived from Eq. (12)]

$$\partial\tau_r(x|x_0)/\partial x|_{x=a} = \partial\tau_r(x|x_0)/\partial x|_{x=b} = 0, \quad (17a)$$

$$\partial\tau_r(x|x_0)/\partial x_0|_{x_0=a} = \partial\tau_r(x|x_0)/\partial x_0|_{x_0=b} = 0, \quad (17b)$$

and the normalization condition [derived from Eq. (3) using the normalization of the probability density and changing the integration order]

$$\int_a^b x^{d-1}p^e(x)\tau_r(x|x_0)dx = 0. \quad (18)$$

Alternatively, one can use the symmetry relation $\tau_r(x|x_0) = \tau_r(x_0|x)$ to write

$$\int_a^b x_0^{d-1}p^e(x_0)\tau_r(x|x_0)dx_0 = 0. \quad (18')$$

This last equation states that the relaxation time of the equilibrium distribution is zero.

Using the expression (11) for the adjoint operator, one solves Eq. (16) separately for $x < x_0$ and $x_0 < x$. This gives

$$\begin{aligned}\tau_r(x|x_0) = \tau_r(a|b) &+ \int_a^{x_m}[D(y)p^e(y)y^{d-1}]^{-1}dy\int_a^y p^e(z)z^{d-1}dz \\ &+ \int_{x_M}^b [D(y)p^e(y)y^{d-1}]^{-1}dy\int_y^b p^e(z)z^{d-1}dz, \quad (19)\end{aligned}$$

where $x_m = \min(x,x_0)$ and $x_M = \max(x,x_0)$. The boundary to boundary relaxation time is obtained from condition (18):

$$\begin{aligned}\tau_r(a|b) &= \tau_r(b|a) \\ &= -\int_a^b p^e(x)x^{d-1}dx \\ &\quad\times\int_a^x [D(y)p^e(y)y^{d-1}]^{-1}dy\int_a^y p^e(z)z^{d-1}dz \\ &= -\int_a^b p^e(x)x^{d-1}dx\int_x^b [D(y)p^e(y)y^{d-1}]^{-1}dy \\ &\quad\times\int_y^b p^e(z)z^{d-1}dz \quad (20)\end{aligned}$$

and is always negative, since $p(a,t\,|b) < p^e(a)$ or $p(b,t\,|a) < p^e(b)$. When $V(x)\to\infty$ as $x\to\infty$ ($x\to-\infty$), we can consider the case where $b\to\infty$ ($a\to-\infty$). Then both $\tau_r(a|b)$ and the other terms in Eq. (19) may diverge: the first to $-\infty$ and the other to ∞. Under such conditions $\tau_r(a|b)$ serves as a "renormalization factor," ensuring that $\tau_r(x|x_0)$ stays finite.

The physically interesting case is $x = x_0$. Then

$$\begin{aligned}\tau_r(x|x) = \tau_r(a|b) &+ \int_a^x [D(y)p^e(y)y^{d-1}]^{-1}dy\int_a^y p^e(z)z^{d-1}dz \\ &+ \int_x^b [D(y)p^e(y)y^{d-1}]^{-1}dy\int_y^b p^e(z)z^{d-1}dz. \quad (19')\end{aligned}$$

The analogous result in Ref. 5 is for $\tau_r(b|b)$ with $a = -\infty$ [or $\tau_r(a|a)$ with $b = \infty$]. However, $\tau_r(a|b)$ is missing there. Note that $\tau_r(x|x)$ does not obey Eq. (18), since both initial and final coordinates are changed here simultaneously, while Eq. (18) requires that $x_0 = \text{const}$. Instead, one has

$$\int_a^b x^{d-1}p^e(x)\tau_r(x|x)dx = -\tau_r(a|b) \quad (18'')$$

with $\tau_r(a|b)$ given by Eq. (20).

In cases where the full solution of the diffusion equation $p(x,t\,|x_0)$ is obtainable in terms of eigenfunctions, Eq. (19) can be compared to [cf. Eq. (13')]

$$\tau_r(x|x_0) = \sum_{n=1}^{\infty} h_n(x_0)h_n(x)/\lambda_n. \quad (21)$$

In particular, this provides a direct proof that $\tau_r(x|x) > 0$.

It is interesting to note the connection between the relaxation time $\tau_r(x|x)$ and the mean first passage (absorption) times at the boundaries a or b, which we denote by $\tau_a(x)$ and $\tau_b(x)$, respectively. $\tau_a(x)$ is calculated for absorption at a and reflection at b. The converse holds for $\tau_b(x)$. These are given by[3]

$$\tau_a(x) = \int_a^x [D(y)p^e(y)y^{d-1}]^{-1}dy \int_y^b p^e(z)z^{d-1}dz, \quad (22a)$$

$$\tau_b(x) = \int_x^b [D(y)p^e(y)y^{d-1}]^{-1}dy \int_a^y p^e(z)z^{d-1}dz. \quad (22b)$$

Using these notations one can write Eq. (19′) as

$$\tau_r(x|x) = \tau_r(a|b) - \tau_a(x) - \tau_b(x) + \int_a^b [D(x)p^e(x)x^{d-1}]^{-1}dx. \quad (23)$$

Suppose the potential is one-dimensional and monotonically increasing from a to b. Then we observe that the integral in the right-hand side of Eq. (23) is twice the reciprocal of Kramers' approximation for the rate constant[7,8], k_K, for escape from the well at $x = a$ across the barrier at $x = b$. (The factor 2 implies a symmetric potential for reflection at b.) Averaging Eq. (23) over the equilibrium distribution we find that

$$k_K^{-1} = \tfrac{1}{2}(\tau_a^e + \tau_b^e) - \tau_r(a|b). \quad (24)$$

Here we have used Eq. (18″) and denoted the equilibrium average of $\tau_a(x)$ and $\tau_b(x)$ by τ_a^e and τ_b^e, respectively. Note that $\tau_r(a|b)$ is negative and symmetric, so that it equals $\frac{1}{2}[\tau_r(a|b) + \tau_r(b|a)]$. Equation (24) decomposes Kramers' rate constant into two contributions: for reaction (absorption) and relaxation.

IV. EXAMPLES

We give a few one-dimensional, constant D examples, demonstrating the results of the previous section. In what follows, $a = 0$ and $b = L$.

A. Free diffusion, $V(x) = 0$

In this case, we find [cf. Eq. (20)] $\tau_r(0|L) = -L^2/6$ and [cf. Eq. (19)]

$$D\tau_r(x|x_0) = L^2/3 + \tfrac{1}{2}(x^2 + x_0^2) - Lx_M, \quad (25)$$

where, as before, $x_M = \max(x,x_0)$. For the physically interesting case $x = x_0$ we have

$$D\tau_r(x|x) = L^2/3 - x(L - x). \quad (25')$$

These results are demonstrated in Fig. 1. Obviously, $\tau_r(x|x)$ is maximal at the boundaries and minimal for $x = L/2$, from which relaxation proceeds with equal effectiveness to both directions.

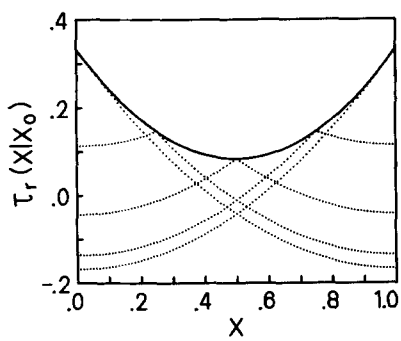

FIG. 1. Relaxation times for free diffusion ($V = 0$) in the interval [0,1]. Dotted lines show $\tau_r(x|x_0)$ [Eq. (25)] for $x_0 = 0$, 0.25, 0.5, 0.75, and 1. (The value of x_0 is evident from the cusp in these curves.) $\tau_r(x|x)$ [Eq. (25′)] is shown as a bold line. $D = L = 1$.

It is easy to solve for $p(x,t|x_0)$ directly. The eigenfunctions are $h_n(x) = \sqrt{2}\cos(n\pi/L)x$ and the eigenvalues $\lambda_n = (n\pi/L)^2D$. This gives [cf. Eq. (21)]

$$D\tau_r(x|x_0) = \frac{2L^2}{\pi^2}\sum_{n=1}^{\infty} n^{-2}\cos\left(\frac{n\pi}{L}x_0\right)\cos\left(\frac{n\pi}{L}x\right). \quad (26)$$

This series for $x = x_0$ is easily identified as the Fourier expansion of Eq. (25′). The eigenvalue which governs the long-time relaxation of $p(x,t|x_0)$ is λ_1. One can see from our results that $\tau_r(x|x_0)$ may be both smaller or larger than $\lambda_1^{-1} = L^2/D\pi^2$.

B. Linear potential

Diffusion in a linear potential $\beta V(x) = cx$ can describe sedimentation[8] or motion of charged particles in an electric field. In these cases the coordinate x is a simple physical distance. Another possibility is that x is energy (e.g., a vibrational quantum number). The solution for $c > 0$ can then represent[9-11] relaxation of the vibrational states of an oscillator through an interaction with a heat bath (which may be the other degrees of freedom in a polyatomic molecule[10] or a colliding gas[9,11]). The ground state is at $x = 0$ and the highest state is at $x = L$ (which may also be taken as infinity, for a nontruncated harmonic oscillator). Unlike a well known model for unimolecular dissociation,[12] which imposes an absorbing boundary condition at $x = L$, we now want to ignore this possibility by assuming a reflecting boundary there.

Inserting $p^e(x) = ce^{-cx}/(1 - e^{-cL})$ in Eqs. (19′) and (20) we find that

$$c^2D\tau_r(0|L) = 2 - cL\coth(cL/2), \quad (27)$$

$$c^2D\tau_r(x|x) = (1 + e^{-cL})\,e^{cx} - 2c[L/(e^{cL} - 1) + x], \quad (28)$$

$\tau_r(x,x)$ remains finite even when $L \to \infty$. Then

$$c^2D\tau_r(x|x) = e^{cx} - 2cx. \quad (28')$$

This relaxation time first decreases with increasing x. If L or c are large enough it reaches a minimum and then increases with further increase in x. Hence, depending on the parameters, the relaxation time can show either weak or strong x dependence. This behavior is shown in Fig. 2.

For comparison, the problem can be easily solved by eigenfunctions (this is a special case of the problem solved in Ref. 10). The eigenvalues are still $\lambda_n = (n\pi/L)^2D$ and the

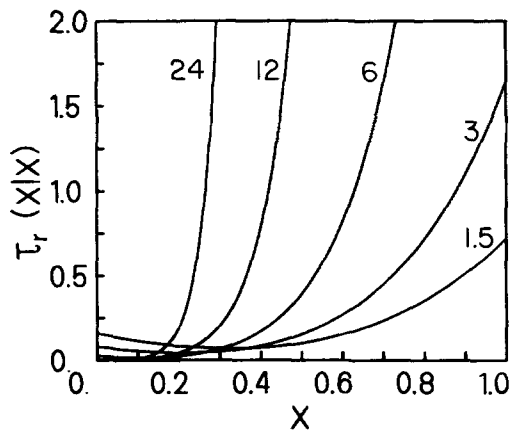

FIG. 2. Relaxation times for diffusion in a linear potential $\beta V(x) = cx$ [Eq. (28)]. The five different values of c are marked in the figure. $D = L = 1$.

eigenfunctions of $\mathcal{L}^\dagger$ for $n = 1, 2, \ldots$ are

$$h_n(x) = \left[\cos\left(\frac{n\pi}{L}x\right) - \frac{Lc}{2n\pi}\sin\left(\frac{n\pi}{L}x\right)\right]e^{cx/2}. \quad (29)$$

Insertion into Eq. (21) gives $\tau_r(x|x_0)$ in a form that looks complicated in comparison to Eq. (28).

The probability density for $L = \infty$ has a closed form solution.[8] This gives

$$p(x,t\,|x) - p^e(x) = (4\pi Dt)^{-1/2}\left[1 + \exp\left(-\frac{x^2}{Dt}\right)\right] \times \exp\left(-\frac{c^2}{4}Dt\right) - \frac{1}{2}p^e(x)\ \mathrm{erfc}\left[\frac{Dct - 2x}{(4Dt)^{1/2}}\right] \quad (30)$$

($c > 0$ and $x \geqslant 0$), where erfc is the complementary error function, and the equilibrium distribution is

$$p^e(x) = ce^{-cx}. \quad (31)$$

We can now perform the time integral directly [cf. Eq. (3)] and compare with Eq. (28'). The integral of the first term in the right-hand side of Eq. (30) is a known Laplace transform[13]

$$c\int_0^\infty (4\pi t)^{-1/2}[1 + \exp(-x^2/t)]\exp(-c^2t/4)dt = 1 + \exp(-cx). \quad (32)$$

We have not found the integral of the second term in the standard tables.[13] This integral

$$\int_0^\infty \mathrm{erfc}(a\sqrt{t} - b/\sqrt{t})\ dt = 2\int_0^\infty \mathrm{erfc}(az - b/z)\ zdz = (\tfrac{1}{2} + 2ab)/a^2 \quad a > 0, \quad b \geqslant 0 \quad (33)$$

is a special case of the result given in Ref. 14. Hence agreement with Eq. (28') is obtained.

V. CONCLUSION

We have presented a theory for mean relaxation times in diffusion processes with reflecting boundary conditions. The backward equation approach enabled us to obtain explicit solutions. The physically interesting case is when one observes the relaxation at the point of initial excitation, since the distribution there decays monotonically to equilibrium. [Our solution for this case differs from the one presently in the literature of diffusive barrier crossing[5] by the term $\tau_r(a|b)$.] One can envision other possible applications of relaxation times. This quantity for nonreactive diffusion processes may acquire the same central role that mean survival (first passage) times have in reactive diffusion processes.

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