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Residence times in diffusion processes

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We generalize the notion of "mean survival time" in diffusion processes, which characterizes the disappearance of probability density from the whole coordinate space into boundaries or sinks, by introducing "mean residence time," characterizing the time spent in a portion of the coordinate space. In particular, the time integral of the transition probability (Green's function) is the average residence time density at a point. It is a function of both initial and final variables and fulfills two differential equations, one for each variable. We demonstrate the solution of these equations and compare it to the time integral of the direct solution of the diffusion equation. We present the general solution for spherically symmetric diffusion, and compare it to results in the literature.

I. INTRODUCTION

In the theory of the diffusion equation (DE)[1–3] for reactive processes,[4] reaction may be described by appropriate boundary conditions (BC's), or else by coordinate dependent rate constants. In this theory one often encounters the notion of "mean first passage time," [5–8] which can be interpreted as the inverse steady-state rate constant. For diffusion in a coordinate space confined by absorbing or partly absorbing boundaries (or "sinks") the mean first passage time gives the average time for disappearance of the probability density in these sinks. The same quantity evidently gives also the average time that a diffusing particle spends in the diffusion space (prior to ultimate absorption) and can therefore be termed "average survival time."

When one wishes to focus attention on a portion of the coordinate (diffusion) space, these two facets of "passage" (or "absorbance") and "survival" times are no longer equivalent. Absorbance is into the sinks and hence involves the whole diffusion space, whereas survival can be considered for any region (or even for any point) in space. We therefore wish to define a quantity which we call "mean residence time" (MRT), since it represents the average time that a diffusing particle resides in a given region prior to its absorption. The MRT for the whole coordinate space is, of course, just the mean passage time.

The notion of MRT has already been used[9] for free (zero potential) diffusion. For an initial source at the origin, the MRT for an appropriate sphere around the origin has been interpreted[9] as the continuous analog for the mean number of returns to the origin in a random walk process on regular lattices.

In the above example "coordinate" is understood as a spatial coordinate for Brownian motion. Alternatively, it can be interpreted[10] as an internal degree of freedom of a macromolecule. For example, when this is a vibrational coordinate,[11] the MRT describes the lifetime of a given subset of vibrational states. The theory then becomes a certain kind of "state selected" rate theory.

The most fundamental MRT is for a given point and an initial delta-function density. We are therefore interested in a theory for the time integral[12] of the transition probability, whereas conventional mean passage time theories[5–8] deal with its time and space integral. First (Sec. II) we review these theories, present the MRT theory (Sec. III), demonstrate (Sec. IV) its calculation in two different ways, and finally (Sec. V) give the general solution for a spherically symmetric system.

II. MEAN PASSAGE TIME

We briefly review the mean passage time theory[5–8] for the DE:

$$\partial p(x, t)/\partial t = -\mathscr{L}(p). \tag{1}$$

Here $p(x, t)$ is the probability density for a given initial distribution $p(x,0) = p^0(x)$. The solution for an initial δ function, $p^0(x) = \delta(x - x_0)$ is known as a (finite-time) transition probability, or a Green's function, and would be denoted $p(x, t \mid x_0)$. Any other solution is obtained by averaging over the initial distribution. t is time multiplied by the diffusion constant D, and $\mathscr{L}$ is the diffusion operator which for spherical symmetric problems in d dimensions is defined by

$$-\mathscr{L} = x^{1-d}\frac{\partial}{\partial x}x^{d-1}e^{-\beta V(x)}\frac{\partial}{\partial x}e^{\beta V(x)}. \tag{2}$$

$V(x)$ is a coordinate dependent potential function, $\beta^{-1} = k_B T$, k_B is Boltzmann's constant, and T the absolute temperature.

The dependence of $p(x, t \mid x_0)$ on the initial variable x_0 is given by the adjoint (or "backward") equation

$$\partial p(x, t \mid x_0)/\partial t = -\mathscr{L}^\dagger_{x_0}(p), \tag{3}$$

where we have added a subscript to the adjoint operator $\mathscr{L}^\dagger$ to stress the independent variable. For a spherical symmetric problem in d dimensions,

$$-\mathscr{L}^\dagger_x = x^{1-d}e^{\beta V(x)}\frac{\partial}{\partial x}x^{d-1}e^{-\beta V(x)}\frac{\partial}{\partial x}. \tag{4}$$

Conventionally, one defines a survival probability (e.g., for an initial delta-function distribution)

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

$$Q(t \mid x_0) = \int_a^b x^{d-1} p(x, t \mid x_0)\, dx, \tag{5}$$

where $a<x<b$; a and b are the boundaries of the coordinate space (they may also be at infinity). We assume that at least one of the boundaries is absorbing, or partially absorbing, or at infinity, so that Q decreases monotonically to zero with increasing time. (Note that we have absorbed in p the geometric factors 2π, 4π, etc.).

To define the mean passage time, one notes that the fraction $-\partial Q/\partial t$ is absorbed between t and $t+dt$, i.e., lives up to time t. Therefore, $-\partial Q/\partial t$ is the probability density of the passage time. Its first moment is the mean passage time

$$\tau(x_0) = -\int_0^\infty t \frac{\partial Q(t \mid x_0)}{\partial t}\, dt = \int_0^\infty Q(t \mid x_0)\, dt. \tag{6}$$

Alternatively, Eq. (6) can be reasoned as follows. A diffusing particle occupies the diffusion space for time interval dt between t and $t+dt$, with a probability $Q(t \mid x_0)$. Hence the average time spent in the diffusion space is the weighted sum of the infinitisimal residence times, as in the right-hand side of Eq. (6).

The essence of the conventional theory[5-8] is to integrate the backward equation (3) over x and t, using the fact that $Q(0 \mid x_0) = 1$ and $Q(t \mid x_0) \underset{t\to\infty}{\longrightarrow} 0$. This gives an ordinary differential equation for $\tau(x_0)$:

$$\mathscr{L}^\dagger_{x_0}(\tau) = 1, \tag{7}$$

which can be solved explicitly for spherical symmetry. The BC's for Eq. (7) are deduced directly from those of $p(x, t \mid x_0)$.

III. MEAN RESIDENCE TIME

We would like to replace the integral over all space in the definition (5) of the survival probability by an integral over a portion of the coordinate space. We therefore perform the time integral first[12] and define the MRT density as the time integral of the fundamental solution (i.e., the Green's function)

$$\tau(x \mid x_0) \equiv \int_0^\infty p(x, t \mid x_0)\, dt. \tag{8}$$

We interpret this as follows: at time t, there is a probability $p(x, t \mid x_0)$ of residing at x an additional time dt. The MRT is just the weighted sum of the infinitesimal residence times. It describes the average time that a diffusing particle originating from x_0 spends at x. In contrast to the interpretation of Eq. (6), $-\partial p(x, t \mid x_0)/\partial t$ is not a probability density for absorbance in the boundary. It can even be negative due to momentary increase of $p(x, t \mid x_0)$ through flow from neighboring points.

Carrying the time integration of Eqs. (1) and (3), we conclude that $\tau(x \mid x_0)$ obeys two equations

$$\mathscr{L}_x(\tau) = \delta(x - x_0), \tag{9a}$$

$$\mathscr{L}^\dagger_{x_0}(\tau) = \delta(x - x_0). \tag{9b}$$

For each equation one has two BC's, derived from those of $p(x, t \mid x_0)$.

A possible approach is to solve for $x \neq x_0$:

$$\mathscr{L}_x(\tau) = 0, \tag{10a}$$

$$\mathscr{L}^\dagger_{x_0}(\tau) = 0. \tag{10b}$$

These equations have to be solved separately for $x < x_0$ and $x > x_0$. This would be demonstrated below.

The MRT for any subspace $\{x\}$ and initial distribution $p^0(x_0)$ is obtainable by integrating $\tau(x \mid x_0)$ over the subspace and averaging over the initial distribution

$$\tau(\{x\}) = \int_a^b \left[\int_{\{x\}} \tau(x \mid x_0)\, x^{d-1}\, dx \right] p^0(x_0)\, x_0^{d-1}\, dx_0, \tag{11}$$

while the mean first passage time [the solution of Eq. (7)] is given by

$$\tau(x_0) \equiv \int_a^b x^{d-1} \tau(x \mid x_0)\, dx. \tag{12}$$

IV. EXAMPLE: DIFFUSION IN A CONSTANT FORCE FIELD

We choose an example with a nonvanishing potential function $V(x)$ so that the diffusion operator and its adjoint are not identical, but which is solvable analytically in terms of $p(x, t \mid x_0)$. This can be compared with the solution of Eq. (10). The example chosen is one-dimensional diffusion in a constant force field directed towards the origin (i.e., a linear potential $\beta V(x) = cx$, $c > 0$) with an absorbing boundary at $x = 0$. This may represent diffusion of charged particles in an electric field with ultimate absorption at an electrode carrying the opposite charge.

The DE now reads

$$\partial p/\partial t = \frac{\partial}{\partial x} e^{-cx} \frac{\partial}{\partial x} e^{cx} p, \quad x \geqslant 0, \tag{13}$$

with BC's:

$$p(0, t \mid x_0) = p(\infty, t \mid x_0) = 0, \tag{14}$$

and an initial condition

$$p(x, 0 \mid x_0) = \delta(x - x_0), \quad x_0 > 0.$$

This can be solved exactly by introducing the transformation[3]

$$q(x, t \mid x_0) = p(x, t \mid x_0) \exp\left[\frac{c}{2}\left(x - x_0 + \frac{c}{2} t\right)\right], \tag{15}$$

which reduces it to a free diffusion problem $\partial q/\partial t = \partial^2 q/\partial x^2$ with the same BC's. This is now readily solved (e.g., by the method of images[2,3]) to give

$$\begin{aligned} p(x, t \mid x_0) = {} & (4\pi t)^{-1/2} \{\exp[-(x - x_0)^2/4t] \\ & - \exp[-(x + x_0)^2/4t]\} \\ & \times \exp\left[-\frac{c}{2}\left(x - x_0 + \frac{c}{2} t\right)\right]. \end{aligned} \tag{16}$$

The time integral is obtained by noticing that for positive constants α and s:

$$\int_0^\infty t^{-1/2} e^{-\alpha^2/4t} e^{-s^2 t}\, dt = \sqrt{\pi}\, e^{-\alpha s}/s. \tag{17}$$

Hence,

$$\begin{aligned} \tau(x \mid x_0) \equiv \int_0^\infty p(x, t \mid x_0)\, dt = {} & c^{-1}\left[\exp\left(-\frac{c}{2}|x - x_0|\right)\right. \\ & \left. - \exp\left(-\frac{c}{2}|x + x_0|\right)\right] \exp\left[-\frac{c}{2}(x - x_0)\right]. \end{aligned} \tag{18}$$

Instead of using absolute values we can divide the solution to the regions $x > x_0$ and $x < x_0$:

$$c\tau(x|\,x_0) = \begin{cases} 1 - e^{-cx}, & x < x_0 \\ e^{-cx}(e^{cx_0} - 1), & x > x_0. \end{cases} \tag{18'}$$

This solution is demonstrated in Fig. 1. Note that it is independent of x_0 for $x < x_0$. The physical reason for this is that all the density initially at $x_0 > x$, must reach x prior to absorption. From there, the mean time to absorption only depends on the value of x.

In particular, one may be interested in the MRT at $x < x_0$ vs that at $x > x_0$:

$$c^2\tau(\{x < x_0\}|\,x_0) = cx_0 + e^{-cx_0} - 1, \tag{19a}$$

$$c^2\tau(\{x > x_0\}|\,x_0) = 1 - e^{-cx_0}. \tag{19b}$$

This solution is shown in Fig. 2. The sum of these gives

$$\tau(x_0) = \tau(\{x < x_0\}|\,x_0) + \tau(\{x > x_0\}|\,x_0) = x_0/c, \tag{20}$$

which is indeed the solution of Eq. (7).

We now turn to the direct solution of Eq. (10).The integration of Eq. (10a) gives

$$\tau(x|\,x_0) = A(x_0)\,e^{-cx} + B(x_0). \tag{21}$$

For $x > x_0$, $\tau(\infty|\,x_0) = 0$ leads to $B = 0$. For $x < x_0$, $\tau(0|\,x_0) = 0$ leads to $B = -A$. Therefore,

$$\tau(x|\,x_0) = \begin{cases} A(x_0)(1 - e^{-cx}), & x < x_0 \\ A(x_0)\,e^{-cx}, & x > x_0. \end{cases} \tag{22}$$

Applying Eq. (10b), we consider the solution of $\mathscr{L}^{\dagger}_{x_0}(A) = 0$, which is of the general form $A(x_0) = \alpha_1 e^{cx_0} + \alpha_2$. Using the BC $A(0) = 0$, and the continuity of $\tau(x|\,x_0)$ at $x = x_0$, gives

$$A(x_0) = \begin{cases} \alpha, & x < x_0 \\ \alpha(e^{cx_0} - 1), & x > x_0. \end{cases} \tag{23}$$

Finally, in order that $\tau(x_0)$ [Eq. (12)] obeys Eq. (7), $\alpha = c^{-1}$. Hence one regains Eq. (18').

V. GENERAL SOLUTION FOR REACTIVE DIFFUSION

Following the discussion in the literature,[7,8] we now give the general solution for spherically symmetric reactive

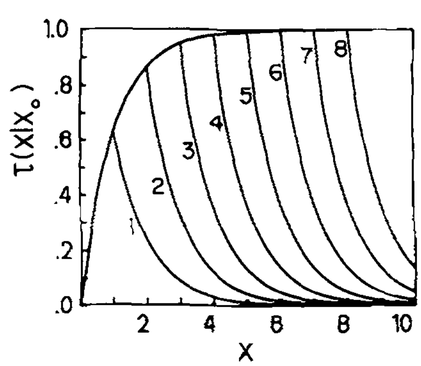

FIG. 1. Mean residence time densities for a linear potential [Eq. (18')] with $c = 1$ and different values for x_0 (indicated). The residence time is maximal at the initial point x_0, and decreases more slowly towards the absorbing boundary at the origin.

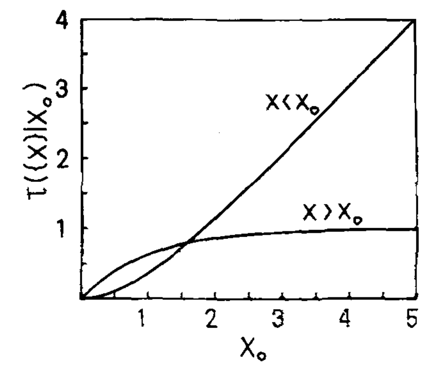

FIG. 2. Mean residence times for a linear potential out of the states with $x < x_0$ and $x > x_0$ [Eq. (19)] with $c = 1$, as a function of the initial coordinate x_0.

diffusion between two spheres or radii a and b, $a < b$. Reaction at $x = a$ is described by a "radiation" BC[3,4]:

$$j(a, t) = -\kappa p(a, t) \tag{24a}$$

(absorption is the limit $\kappa \to \infty$). The absence of reaction at $x = b$ is described by reflection ($\kappa = 0$):

$$j(b, t) = 0. \tag{24b}$$

The flux $j(x, t)$ for a spherically symmetric system is given by

$$-j(x, t) = e^{-\beta V(x)} \frac{\partial}{\partial x} e^{\beta V(x)} p(x, t), \tag{25}$$

so that the DE can be written as flux conservation

$$x^{d-1} \frac{\partial p(x, t)}{\partial t} + \frac{\partial}{\partial x} x^{d-1} j(x, t) = 0. \tag{26}$$

In particular, the above equations apply to $p(x, t\,|\,x_0)$. The BC's (24) for the DE then imply[7] that the BC's for the backward equation (3) are

$$\partial p(x, t\,|\,x_0)/\partial x_0|_{x_0 = a} = \kappa p(x, t\,|a), \tag{27a}$$

$$\partial p(x, t\,|\,x_0)/\partial x_0|_{x_0 = b} = 0. \tag{27b}$$

Taking the time integral of BC's (24) and (27) results in $p(x, t\,|\,x_0)$ being replaced by $\tau(x|\,x_0)$, which therefore fulfills the same BC's.

The solution of Eq. (10) subject ot BC's (24) and (27) is found in an analogous way to the solution for the example in the previous section. This gives

$$e^{\beta V(x)}\,\tau(x|\,x_0) = \int_a^{x_m} y^{1-d}\,e^{\beta V(y)}\,dy + \kappa^{-1} a^{1-d} e^{\beta V(a)}, \tag{28}$$

where $x_m \equiv \min(x, x_0)$. This is a central result in this section. Note that it is completely independent of x_0 for $x < x_0$, and independent of the upper bound b for all x. This is intuitively clear since all population located at some finite time at a value of the coordinate larger than x must eventually pass through x on its way to absorption at a. The values of x_0 and b determine the waiting time for the abovementioned event, but not its eventual occurrence.

The MRD density, Eq. (28) can now be integrated over the final value x or averaged over the initial value x_0 (or both). Let us first integrate over x. For $x < x_0$ one finds, by changing the order of integration in the double integral, that

$$\tau(\{x<x_0\}\,|\,x_0)\equiv \int_a^{x_0} x^{d-1}\,\tau(x|\,x_0)\,dx$$
$$= \int_a^{x_0} x^{1-d}\,e^{\beta V(x)} \int_x^{x_0} y^{d-1}\,e^{-\beta V(y)}\,dy\,dx$$
$$+\kappa^{-1}\,a^{1-d}\,e^{\beta V(a)} \int_a^{x_0} x^{d-1}\,e^{-\beta V(x)}\,dx. \tag{29a}$$

For $x>x_0$, integration gives

$$\tau(\{x>x_0\}\,|\,x_0)\equiv \int_{x_0}^{b} x^{d-1}\,\tau(x|\,x_0)\,dx$$
$$= \int_a^{x_0} x^{1-d}\,e^{\beta V(x)}\,dx \int_{x_0}^{b} y^{d-1}\,e^{-\beta V(y)}\,dy$$
$$+\kappa^{-1}\,a^{1-d}\,e^{\beta V(a)} \int_{x_0}^{b} x^{d-1}\,e^{-\beta V(x)}\,dx. \tag{29b}$$

The total mean passage time out of x_0 [Eq. (12)] is the sum of these two quantities:

$$\tau(x_0) = \int_a^{x_0} x^{1-d}\,e^{\beta V(x)} \int_x^{b} y^{d-1}\,e^{-\beta V(y)}\,dy\,dx$$
$$+\kappa^{-1}\,a^{1-d} Z\,e^{\beta V(a)}, \tag{30}$$

where Z is the partition function

$$Z\equiv \int_a^{b} x^{d-1}\,e^{-\beta V(x)}\,dx. \tag{31}$$

Equation (30) is the solution of Eq. (7), as given in the literature.[7,8]

If, instead, we average $\tau(x|\,x_0)$ over an initial equilibrium distribution we find

$$Z\tau(x)\equiv \int_a^{b} x_0^{d-1}\,e^{-\beta V(x_0)}\,\tau(x|\,x_0)\,dx_0$$
$$= e^{-\beta V(x)} \int_a^{x} x_0^{1-d}\,e^{\beta V(x_0)} \int_{x_0}^{b} y^{d-1}\,e^{-\beta V(y)}\,dy\,dx_0$$
$$+\kappa^{-1}\,a^{1-d}\,z e^{-\beta[V(x)-V(a)]}. \tag{32}$$

Integration of Eq. (32) over x or averaging of Eq. (30) over x_0 gives, of course, the same result, as cited in the literature.[7,8]

Returning to the fundamental solution [Eq. (28)] we see that Eq. (18′) is a special result obtained when $d=1$, $\kappa=\infty$, $a=0$, and $\beta V(x)=cx$. Another simple case of Eq. (28) is free diffusion [$V(x)=0$], which gives

$$\tau(x|\,x_0) = (2-d)^{-1}(x_m^{2-d}-a^{2-d})+\kappa^{-1}\,a^{1-d}, \quad d\neq 2, \tag{33a}$$

$$\tau(x|\,x_0) = \ln(x_m/a)+(\kappa a)^{-1}, \quad d=2, \tag{33b}$$

where, as before, $x_m=\min(x, x_0)$. Hence the MRT density, $\tau(x|\,x_0)$, is constant for $x>x_0$.

One could have alternatively solved the problem for reflection at the inner sphere ($x=a$) and partial absorption ("radiation") at the outer sphere. The result would then be

$$e^{\beta V(x)}\,\tau(x|\,x_0) = \int_{x_m}^{b} y^{1-d}\,e^{\beta V(y)}\,dy - \kappa^{-1}\,b^{1-d}\,e^{\beta V(b)}, \tag{28′}$$

where x_m is the maximum (rather than the minimum) of (x, x_0). In the simple case of free diffusion this reduces to

$$\tau(x|\,x_0) = (2-d)^{-1}(b^{2-d}-x_m^{2-d})-\kappa^{-1}\,b^{1-d} \tag{33a′}$$

for $d\neq 2$ and to

$$\tau(x|\,x_0) = \ln(b/x_m)-(\kappa b)^{-1} \tag{33b′}$$

for $d=2$.

These results, for $d=3$, $\kappa=\infty$ (pure absorption at $x=b$) and $x_m=x$ (i.e., $x_0=a=0$) have been used[9] to evaluate the MRT at a sphere around the origin. For a sphere of the appropriate radius this MRT has been interpreted[9] as the number of returns to the origin, of an excitation initially produced there.

VI. CONCLUSION

We have discussed the theory for mean residence time in an arbitrary portion of coordinate space. The mean passage time is a special case when the whole coordinate space is involved. The fundamental quantity is $\tau(x|\,x_0)$, which is the time integral of the transition probability density $p(x, t\,|\,x_0)$. It obeys a regular differential equation [Eq. (10)] in x and its adjoint equation in x_0.

We have demonstrated the solution of the abovementioned equations for a linear potential, and compared it with the full solution for the DE. We have also presented the general solution for $\tau(x|\,x_0)$ for spherically symmetric diffusion with an arbitrary potential, between two spheres. As boundary conditions we have assumed reflection from one sphere and radiation from the other. These results were compared with those in the literature.

The residence time density $\tau(x|\,x_0)$ can be integrated over x for any portion of coordinate space, averaged over x_0 or both. It can therefore be considered as a very suitable starting point for any theory of mean residence or passage times.

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