

ILLiad Request Printout

Transaction Number: 279353

Username: morozova Name: Alexandre Morozov

ISSN/ISBN:

NotWantedAfter:

Accept Non English: Yes

Accept Alternate Edition: No

Request Type: Article - Article

Loan Information

LoanAuthor:

LoanTitle:

LoanPublisher:

LoanPlace:

LoanDate:

LoanEdition:

NotWantedAfter:

Article Information

PhotoJournalTitle: Advances in chemical physics

PhotoJournalVolume: 13

PhotoJournalIssue:

Month:

Year: 1966

Pages: 1-18

Article Author:

Article Title: First Passage Time Problems in Chemical Physics

Citation Information

AL2B01/06

FIRST PASSAGE TIME PROBLEMS IN CHEMICAL PHYSICS*

GEORGE H. WEISS, *National Cancer Institute, National
Institutes of Health, Bethesda, Maryland, U.S.A.*

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I. INTRODUCTION

There are many processes in chemical physics that require the calculation of rates or rate constants. In several of these calculations one assumes that the underlying process can be described in terms of stochastic models, and more specifically in terms of the properties of random walks. Chandrasekhar¹ has given an excellent introduction to some of these topics. There is one class of problem, mentioned only briefly in his article, that has recently found increasing application in many fields of chemical physics, namely, first passage time problems. As an example, several authors²⁻⁴ have proposed models for the dissociation of diatomic molecules in which dissociation occurs when the molecules acquire a certain critical energy E_c through collisions. If the changes in energy can be described in probabilistic terms, then the time to reach E_c is known as the first passage time. Since the theory of first passage times plays an integral role in the formulation of many models in chemical physics, and since no general account of the theory is to be found in chemical literature, various techniques useful for solving such problems are collected below.

In order to define a first passage time problem we consider a space Ω that can be decomposed into two non-overlapping sub-

* This paper was presented at the La Jolla Summer School on Chemical Physics, August 1965, University of California, San Diego, California, U.S.A.

spaces V and \bar{V} . It will be assumed that initially the random variable of interest lies in the subspace V : the first passage time is defined to be the time elapsing before passage to \bar{V} for the first time. For example, in the dissociation model mentioned above Ω would consist of all energies, the space V would be all energies satisfying $E < E_c$, and \bar{V} would consist of all energies satisfying $E \geq E_c$. In more elaborate dissociation models several quantum numbers might be involved, in which cases Ω would be multidimensional.

There are many specific models involving first passage times to be found in the literature. The first of these appears to have been developed in connection with Brownian motion studies by Schrödinger⁵ and by Smoluchowski.⁶ A first passage time model is relevant in the discussion of the Ehrenfest urn model,⁷ in the theory of escape of stars from star clusters,⁸ in the theory of reaction rates,²⁻⁴ and in certain problems in the theory of polyelectrolytes.⁹ Although there is a considerable mathematical literature on first passage time problems,¹⁰ there have been few publications in the physical or chemical literature on the subject.

Although our principal concern in this article will be first passage problems for Markov processes it is well to point out that there are occasional applications which are non-Markovian in nature. As an example the recurrence of colloid counts in a fixed volume as in the experiments of Svedberg¹¹ and Westgren¹² analysed by Smoluchowski,¹³ is a fundamentally non-Markovian process. Although Smoluchowski's early analysis did not make use of any assumption of Markovian evolution Chandrasekhar's later account¹ erred in deriving the fundamental relations. This error was pointed out by Bartlett, who gave a more complete account of the general problem.¹⁴ Some related material is also to be found in a paper by Siegert.¹⁵ Most applications, however, fall under the heading of Markov processes, which will be the subject of our future developments.

The plan of the present article is as follows: Section II contains a general account of the calculation of first passage time moments for Markov processes in continuous time, together with the specialization to the case of a discrete set of states. Section III contains the specialization to systems where the transition probabilities satisfy a Fokker-Planck equation.

II. GENERAL FORMULAE FOR MOMENTS OF THE FIRST PASSAGE TIME

We shall label the random variable of interest $X(t)$, which can be a vector or a scalar. It will be assumed that the development of $X(t)$ in time can be described as a stationary Markov process. To describe the statistical properties of $X(t)$ we choose a probability density $p(x,t|y)$, defined so that $p(x,t|y)dx$ is the probability that $x < X(t) \leq x + dx$ given that $X(0) = y$, i.e., y is the initial position. When $X(t)$ takes on integer values only $p(n,t|m)$ will be the probability that $X(t) = n$, given that $X(0) = m$. In both cases the variables x or n can refer to multidimensional vectors unless otherwise noted. The function $p(x,t|y)$ in general satisfies a linear operator equation of the form:

$$\partial p / \partial t = -L_x p, \quad (1)$$

where L_x operates on x only, and where $p(x,0|y) = \delta(x - y)$ for X continuous, and $p(x,0|y) = \delta_{xy}$ for X discrete. To encompass both cases we introduce the symbol $\Delta(x - y)$ which will denote a delta function or a Kronecker delta depending on whether x and y are continuous or discrete. When X is continuous the most commonly used form for L_x is the Fokker-Planck operator which in one dimension is

$$-L_x = \frac{1}{2} \cdot \frac{\partial}{\partial x} \left(a_2 \frac{\partial}{\partial x} \right) - \frac{\partial}{\partial x} (a_1), \quad (2)$$

where a_1 and a_2 are the first and second moments of the infinitesimal transition rates.¹ When X is discrete, as is the case for many quantum problems, L_x is a difference operator. There appears to have been no study of the case of mixed discrete and continuum problems, although they do arise in the context of neutron thermalization.

The probability that $X(t)$ is still in V at time t given that it started at y in V will be denoted by $p_V(y,t)$ and is given by

$$p_V(y,t) = \int_V p(x,t|y) dx. \quad (3)$$

Let $\eta(y,t)$ be the probability density for the first passage time: that is, if T is the first time that $X(t)$ reaches \bar{V} , given that

$X(0) = y$, then $\eta(y,t)dt$ is the probability that $t < T \leq t + dt$ given that $X(0) = y$. An expression for $\eta(y,t)$ is obtained by noting that if $X(t)$ is in V at time t , then it either makes a first passage in $(t, t + dt)$ or it remains in V at $t + dt$. These two possibilities lead to

$$p_V(y,t) = \eta(y,t)dt + p_V(y,t + dt) \quad (4)$$

or

$$\eta(y,t) = -\partial p_V(y,t)/dt. \quad (5)$$

Moments of the first passage time are defined by

$$\langle t^n(y) \rangle = \int_0^\infty t^n \eta(y,t) dt = n \int_0^\infty t^{n-1} p_V(y,t) dt, \quad (6)$$

$$n = 1, 2, \dots$$

where the last form is obtained by an integration by parts.

We can obtain other, formal, expressions for the moments in terms of the operator L_x by starting from the formal solution to eq. (1):

$$p(x,t|y) = e^{-L_x t} \Delta(x - y). \quad (7)$$

Substituting this expression into eqs. (3) and (6) we find

$$\langle t^n(y) \rangle = n \int_0^\infty t^{n-1} dt \int_V e^{-L_x t} \Delta(x - y) dx \quad (8)$$

$$= n! \int_V L_x^{-n} \Delta(x - y) dx,$$

where we have freely interchanged orders of integration.

In order to use eq. (8) for computation we must introduce a more explicit representation of the quantities involved. When $X(t)$ ranges over the integers, the operator L_x can be represented as a matrix $L = (L_{mn})$, Eq. (3) becomes

$$p(n,t|m) = (e^{-L t})_{nr} \delta_{rm} = (e^{-L t})_{nm}, \quad (9)$$

and the r 'th moment of the first passage time conditional on $X(0) = m$ is

$$\langle t^r(m) \rangle = r! \sum_{n \in V} (L^{-r})_{nj} \delta_{jm} = r! \sum_{n \in V} (L^{-r})_{nm}. \quad (10)$$

Hence the r 'th moment is simply related to the r 'th power of the inverse of the rate matrix. When L_x is the Fokker-Planck operator, the operator L_x^{-1} can be identified with a Green's function and operators L_x^{-n} are iterates of the Green's function. To establish this fact we expand the Green's function associated with the operator L_x and the boundary conditions of the problem, in terms of the eigenfunctions of L_x . It will then be seen that the resulting expansion is that which arises in the evaluation of $\langle t(y) \rangle$.

The eigenfunctions of $L_x u_n(x)$, are defined by

$$L_x u_n(x) = \lambda_n u_n(x), \quad (11)$$

where it will be assumed that the λ_n are real, distinct, and positive. These conditions are fulfilled in most problems of physical interest, although the theory can be extended to deal with more complicated situations. Since L_x is not necessarily self-adjoint the $u_n(x)$ do not directly form an orthonormal set, but are orthogonal with respect to the eigenfunctions of the adjoint operator \tilde{L} which satisfy¹⁶

$$\tilde{L} v_n(x) = \lambda_n v_n(x). \quad (12)$$

The relation of orthogonality can be expressed as

$$\int_\Omega u_m(x) v_n(x) dx = \delta_{nm}. \quad (13)$$

One can easily verify by means of this property that the Dirac delta function $\delta(x - y)$ has the representation

$$\delta(x - y) = \sum_{n=0}^{\infty} u_n(x) v_n(y). \quad (14)$$

Since $L_x^{-1} u_n(x) = u_n(x)/\lambda_n$ by application of eq. (8), we have

$$\langle t(y) \rangle = \int L_x^{-1} \sum_n u_n(x) v_n(y) dx = \int \sum_n \frac{u_n(x) v_n(y) dx}{\lambda_n}; \quad (15)$$

and, by the same argument

$$\langle t^r(y) \rangle = r! \int \sum_n \frac{u_n(x) v_n(y) dx}{\lambda_n^r}. \quad (16)$$

One can now verify that the expression for $\langle t(y) \rangle$ is an integral over the Green's function, $G(x,y)$, associated with L_x , and that

$\langle t^r(y) \rangle$ can be written in terms of iterates of the Green's function. The Green's function, $G(x,y)$, associated with the operator L_x is the solution to

$$L_x G(x,y) = \delta(x-y), \quad (17)$$

i.e., it is the continuous analogue of the matrix inverse. If one expands $G(x,y)$ in a series of eigenfunctions associated with L_x :

$$G(x,y) = \sum_n g_n u_n(x), \quad (18)$$

and uses the representation of eq. (14) in eq. (17), it is found that $g_n = v_n(y)/\lambda_n$ or

$$G(x,y) = \sum_n \frac{u_n(x)v_n(y)}{\lambda_n}. \quad (19)$$

A comparison of eqs. (15) and (19) shows that

$$\langle t(y) \rangle = \int G(x,y) dx. \quad (20)$$

Iterates of $G(x,y)$ are defined by

$$G_{n+1}(x,y) = \int G_n(x,z)G(z,y)dz \quad (21)$$

$$G_1(x,y) = G(x,y).$$

The expansion in terms of eigenfunctions of L or $G_n(x,y)$ reads

$$G_n(x,y) = \sum_m \frac{u_m(x)v_m(y)}{\lambda_m^n}, \quad (22)$$

as may readily be confirmed from eqs. (19) and (21). Hence $\langle t^r(y) \rangle$ can also be written

$$\langle t^r(y) \rangle = r! \int G_r(x,y) dx. \quad (23)$$

The expansions of eqs. (10) and (22) are analogues because of the formal relation between the matrix inverse and Green's functions.

So far our results have taken the form of a reduction of a problem stated in probabilistic terms to a purely computational problem. In practice, the applications treated in the literature contain further restrictions on the form of the operator L_x , so that analytic results are possible. In the case of a master equation defined over a discrete set of states it is most often assumed that L represents a nearest-neighbor system, that is $L_{ij} = 0$ for $|i-j| > 1$. A

typical example of this is the Montroll-Shuler model of the dissociation of a diatomic molecule, in which the elements of L are

$$L_{j,j+1} = -\kappa(j+1)e^{-\Theta}, \quad L_{j,j-1} = -\kappa j,$$

and

$$L_{ii} = L_{j,j-1} + L_{j,j+1}, \quad (24)$$

where κ is a rate parameter, and $\Theta = h\nu/(kT)$ where ν is the characteristic oscillator frequency.² It is possible to derive formulae for the $\langle t^r(m) \rangle$ in closed form for these nearest-neighbor systems. Let us consider, as an example, a derivation of the formula for $\langle t(m) \rangle$ when states 0, 1, 2, . . . , N are non-reactant but state $N+1$ is a reactant state. We can first observe that we need only calculate $\langle t(0) \rangle$ since if $T_{0,j}$ is the random variable representing the time for the system to reach state j for the first time starting from state 0, it follows from the assumption of a nearest-neighbor system that

$$T_{0,N+1} = T_{0,m} + T_{m,N+1}. \quad (25)$$

That is to say, since every state must necessarily be traversed in passing from state 0 to state $N+1$, the total first passage time is made up of the time to reach state m for the first time plus the time to reach state $N+1$ for the first time starting from state m . If we let $\langle t_k \rangle$ denote the mean first passage time for getting from state 0 to state k , eq. (25) implies that

$$\langle t(m) \rangle = \langle t_{N+1} \rangle - \langle t_m \rangle, \quad (26)$$

so that we need only calculate a formula for $\langle t(0) \rangle$ with an arbitrary upper reaction level.

In order to calculate $\langle t(0) \rangle$ most expeditiously we will start, not from the general formulation of eq. (10), but rather from eq. (1) which in the present case can be written:

$$\begin{aligned} \dot{p}_0 &= L_{10}p_1 - L_{01}p_0 \\ \dot{p}_1 &= L_{01}p_0 - (L_{10} + L_{12})p_1 + L_{21}p_2 \\ \dot{p}_2 &= L_{12}p_1 - (L_{21} + L_{23})p_2 + L_{32}p_3 \\ &\vdots \\ \dot{p}_N &= L_{N-1,N}p_{N-1} - (L_{N,N-1} + L_{N,N+1})p_N, \end{aligned} \quad (27)$$

where it is to be understood that $p_j(0) = \delta_{j0}$.

Since $p_V(t) = p_0(t) + p_1(t) + \dots + p_N(t)$, eq. (6) indicates that

$$\langle t(0) \rangle = \int_0^\infty [p_0(t) + p_1(t) + \dots + p_N(t)] dt; \quad (28)$$

or, introducing the Laplace transforms $p_j^*(s) = \int_0^\infty e^{-st} p_j(t) dt$, we can also write

$$\langle t(0) \rangle = \sum_{j=0}^N p_j^*(0). \quad (29)$$

It is in this form that the calculation becomes most convenient. The Laplace transform of eq. (27) with $s = 0$ is

$$\begin{aligned} L_{01} p_0^*(0) &= L_{10} p_1^*(0) + 1 \\ (L_{10} + L_{12}) p_1^*(0) &= L_{01} p_0^*(0) + L_{21} p_2^*(0) \\ &\vdots \\ &\vdots \\ (L_{N,N-1} + L_{N,N+1}) p_N^*(0) &= L_{N-1,N} p_{N-1}^*(0). \end{aligned} \quad (30)$$

These may be solved recursively to yield

$$p_j^*(0) = \theta_j p_0^*(0) - \eta_j, \quad (31)$$

where

$$\begin{aligned} \theta_0 &= 1, \theta_j = \frac{L_{01} L_{12} L_{23} \dots L_{j-1,j}}{L_{10} L_{21} L_{32} \dots L_{j,j-1}} \\ \eta_0 &= 0, \eta_j = \frac{1}{L_{j,j-1}} \left[1 + \frac{L_{j-1,j}}{L_{j-1,j-2}} + \frac{L_{j-1,j} L_{j-2,j-1}}{L_{j-1,j-2} L_{j-2,j-3}} \right. \\ &\quad \left. + \dots + \frac{L_{j-1,j} L_{j-2,j-1} \dots L_{12}}{L_{j-1,j-2} L_{j-2,j-3} \dots L_{10}} \right]. \end{aligned} \quad (32)$$

Eq. (31) is derived from the first N lines of eq. (30): if we now substitute eq. (31) into the last line of eq. (30) we obtain an expression for $p_0^*(0)$:

$$p_0^*(0) = \eta_{N+1} / \theta_{N+1}. \quad (33)$$

Thus the mean first passage time is given by

$$\langle t(0) \rangle = \frac{\eta_{N+1}}{\theta_{N+1}} \sum_{j=0}^N \theta_j - \sum_{j=0}^N \eta_j. \quad (34)$$

In a similar fashion it can be shown that if states 0 and $N+1$ form absorbing barriers (that is, the reaction ends when either state is reached) the mean first passage time conditional on the initial state's being r is

$$\langle t(r) \rangle = \frac{\eta_{N+1}}{\theta_{N+1}} \sum_{j=0}^N \theta_j - \sum_{j=r+1}^N \eta_j. \quad (35)$$

For particular models which are appropriately described by the nearest-neighbor approximation the sums indicated in eqs. (32) and (34) may be rather simple to evaluate. For example, in the Montroll-Shuler treatment of dissociation characterized by the transition rates of eq. (24) it is easily verified that the parameters θ_j and η_j are, respectively:

$$\begin{aligned} \theta_j &= e^{-j\theta}, \\ \eta_j &= \frac{1}{k} \left(\frac{1}{j} + \frac{e^{-\theta}}{j-1} + \frac{e^{-2\theta}}{j-2} + \dots + \frac{e^{-(j-1)\theta}}{1} \right); \end{aligned} \quad (36)$$

so that the mean first passage time to reach state $N+1$ in the case of a single reactive state is

$$\begin{aligned} \langle t(0) \rangle &= \frac{1}{k} e^{(N+1)\theta} \left(\frac{1}{N+1} + \frac{e^{-\theta}}{N} + \frac{e^{-2\theta}}{N-1} + \dots + \frac{e^{-N\theta}}{1} \right) \\ &\quad \left(\frac{1 - e^{-(N+1)\theta}}{1 - e^{-\theta}} \right) \\ &= \frac{1}{k(1 - e^{-\theta})} \left[1 - e^{-N\theta} + \frac{1}{2} (1 - e^{-(N-1)\theta}) + \frac{1}{3} (1 - e^{-(N-2)\theta}) \right. \\ &\quad \left. + \dots + \frac{1}{N} (1 - e^{-\theta}) \right] \\ &= \frac{1}{k(1 - e^{-\theta})} \sum_{j=1}^{N+1} \frac{e^{j\theta} - 1}{j}. \end{aligned} \quad (37)$$

One can derive expressions for higher moments of the first passage time by following the same line of proof as above. A general treatment of the theory of equations of the form of eq. (27), i.e., with nearest-neighbor transitions only, has been developed by Ledermann and Reuter,¹⁷ and by Karlin and MacGregor.¹⁸ Their results include a general solution to eq. (27) in

terms of recursively defined orthogonal polynomials. In particular, Karlin and MacGregor are able to discuss the statistics of the first passage time problem in terms of the orthogonal polynomials appropriate to the particular set of equations. With their results it is possible to derive expressions for moments of the first passage time rather easily, but I have chosen to omit a discussion of the orthogonal polynomial technique from this article because the moments can be obtained directly. It would be of considerable interest to have results as simple as those of eqs. (34) and (35) for systems not restricted to the nearest-neighbor type, as there are indications¹⁹ that the nearest-neighbor theory does not give results of the right order of magnitude for dissociation times.¹

III. FIRST PASSAGE TIME AND THE FOKKER-PLANCK EQUATION

We have obtained a general formula for moments of the first passage time in terms of the Green's function of the Fokker-Planck operator. This formulation is useful for problems involving multidimensional geometries. The one-dimensional case can be solved in detail for moments of the first passage time. This is not surprising since the one-dimensional problem is the continuous analogue of the nearest-neighbor models just discussed. We shall present results for the one-dimensional case. These are due originally to Pontryagin, Andronow, and Witt,²⁰ although special cases were treated earlier by Schrödinger. Recent contributions to the mathematical theory have been made by Darling and Siegert.²¹ Jackson and his collaborators have made extensive use of this theory in certain polymer problems.^{9,22,23}

In what follows we use the mathematical terminology "absorbing" or "reflecting" barrier to describe the properties of a designated point or surface. A surface is said to be absorbing if it forms a boundary between V and \bar{V} , that is, if the process terminates when $X(t)$ reaches a point of the surface. A surface is called reflecting if, when $X(t)$ reaches a point of the surface, it is automatically transferred to a point in the interior of V . In the present article we consider only the case of infinitesimal reflection, i.e., when $X(t)$ is transferred to an infinitesimal neighborhood of the point of impingement.

We begin by considering the one-dimensional case in which $X(t)$ is constrained to lie between $x = 0$ and $x = A$. It will be assumed that $x = A$ is always an absorbing point and $x = 0$ is either reflecting or absorbing.

The probability density for the position of $X(t)$ satisfies eq. (1) with L_x given in eq. (2). Theoretically one can find statistical properties of the first passage time by solving the Fokker-Planck equation for $p(x,t)$ with appropriate boundary conditions. However, it proves considerably more convenient to derive an equation for a function $\phi(x,t)$ defined to be the probability that the first passage time is less than t , given that $X(0) = x$. If $W(y,dt|x)dy$ is the probability that $y \leq X(dt) \leq y + dy$, given that $X(0) = x$, then we may write the equation

$$\phi(x,t + dt) = \int_0^A W(y,dt|x)\phi(y,t)dt, \quad (38)$$

which expresses the fact that a transition $x \rightarrow (y, y + dy)$ took place in time dt , and the new position can be regarded as a starting point for the process. The next step is to expand $\phi(y,t)$ in a Taylor series around the point x and substitute into the last equation. This leads to

$$\begin{aligned} \phi(x,t + dt) = \phi(x,t) \int_0^A W(y,dt|x)dy \\ + \frac{\partial\phi(x,t)}{\partial x} \int_0^A (y - x)W(y,dt|x)dy \\ + \frac{1}{2} \cdot \frac{\partial^2\phi(x,t)}{\partial x^2} \int_0^A (y - x)^2W(y,dt|x)dy + \dots \quad (39) \end{aligned}$$

The Fokker-Planck equation is derived on the assumption that

$$\lim_{dt \rightarrow 0} \frac{1}{dt} \int_0^A (y - x)^n W(y,dt|x)dy = 0 \quad (40)$$

for $n \geq 3$. On this assumption, eq. (39) implies that $\phi(x,t)$ is the solution to

$$\frac{\partial\phi}{\partial t} = \frac{a_2(x)}{2} \frac{\partial^2\phi}{\partial x^2} + a_1(x) \frac{\partial\phi}{\partial x}, \quad (41)$$

where the $a_j(x)$ are infinitesimal transition moments

$$a_j(x) = \lim_{dt \rightarrow 0} \frac{1}{dt} \int_0^A (y-x)^j W(y, dt | x) dy. \quad (42)$$

The boundary conditions for eq. (41) are $\phi(A, t) = 1$ and $\phi(0, t) = 1$ for $x = 0$ an absorbing point, or $\frac{\partial \phi(0, t)}{\partial x} = 0$ for $x = 0$ a reflecting point. A comprehensive discussion of requirements on $a_2(x)$ to ensure a finite first passage time has been given by Feller.²⁴ For all problems of physical interest there is no difficulty with this point since $a_2(x)$ is strictly positive and bounded away from zero. In dimensions greater than one, it is possible to derive the equation

$$\frac{\partial \phi}{\partial t} = \sum_i a_i \frac{\partial \phi}{\partial x_i} + \frac{1}{2} \sum_i \sum_j b_{ij} \frac{\partial^2 \phi}{\partial x_i \partial x_j} \quad (43)$$

for the distribution of first passage time. In this equation the coefficients are defined, analogously to eq. (40), by

$$a_i(x) = \lim_{dt \rightarrow 0} \frac{1}{dt} \int_V (y_i - x_i) W(y, dt | x) d^n y \quad (44)$$

$$b_{ij}(x) = \lim_{dt \rightarrow 0} \frac{1}{dt} \int_V (y_i - x_i)(y_j - x_j) W(y, dt | x) d^n y;$$

and it is assumed that higher infinitesimal transition moments are zero. Equation (43) is to be solved under the initial condition $\phi(x, 0) = 0$ for x in V , and $\phi(x, t) = 0$ for x belonging to an absorbing portion of the boundary between V and \bar{V} , and $\partial \phi / \partial n = 0$ for x belonging to a reflecting part of the boundary, where $\partial / \partial n$ denotes a normal derivative.

Equation (41) together with the boundary conditions on $\phi(x, t)$ enables us to calculate moments fairly readily. The same argument as has led to eq. (6) implies that the j 'th moment of the first passage time starting from a point x is expressible as

$$\mu_j(x) = \int_0^\infty t^j \frac{\partial \phi(x, t)}{\partial t} dt. \quad (45)$$

If we differentiate eq. (41) with respect to t , multiply by t^j , and integrate over all t , we find that the $\mu_j(x)$ are the solution to the set of equations

$$\begin{aligned} \frac{1}{2} b_2 \frac{d^2 \mu_j}{dx^2} + b_1 \frac{d \mu_j}{dx} &= -j \mu_{j-1} \quad j = 2, 3, \dots \\ \frac{1}{2} b_2 \frac{d^2 \mu_1}{dx^2} + b_1 \frac{d \mu_1}{dx} &= -1 \end{aligned} \quad (46)$$

with boundary conditions $\mu_j(A) = 0$ for $x = A$ an absorbing point and $d \mu_j(A) / dx = 0$ for $x = A$ a reflecting point.

The equation for $\mu_1(x)$ can be solved in closed form. The general solution is

$$\mu_1(x) = -2 \int_0^x e^{-U(y)} dy \int_0^y \frac{e^{U(z)}}{b_2(z)} dz + C_1 \int_0^x e^{-U(y)} dy + C_2, \quad (47)$$

where $U(x)$ is defined by

$$U(x) = 2 \int_0^x [b_1(y) / b_2(y)] dy. \quad (48)$$

When both boundaries are absorbing,

$$C_1 = 2 \int_0^A e^{-U(y)} dy \int_0^y [e^{U(z)} / b_2(z)] dz / \int_0^A e^{-U(y)} dy \quad (49)$$

and $C_2 = 0$;

and when $x = A$ is absorbing and $x = 0$ reflecting we have

$$\begin{aligned} C_1 &= 0 \\ C_2 &= 2 \int_0^A e^{-U(x)} dx \int_0^x [e^{U(y)} / b_2(y)] dy. \end{aligned} \quad (50)$$

Formulae for higher moments can be derived recursively from eq. (46), with $\mu_1(x)$ given by eq. (47).

The simplest illustration of the use of these formulae is in terms of simple Brownian motion in one dimension for which $a_1(x) = 0$

and $a_2(x) = 2D$ with D the diffusion constant. The equation for the mean first passage time reduces to $\mu_1'' = -1/D$. If $x = 0$ and $x = A$ are both absorbing, then the expression for mean first passage time is

$$\mu_1(x) = \frac{1}{2D} x(A - x). \quad (51)$$

It is instructive to calculate the statistical properties of one dimensional Brownian motion in a constant force field. Let us consider the case of a semi-infinite interval $(0, \infty)$ with absorption at $x = 0$. The coefficients in eq. (41) are $a_1(x) = -v$ and $a_2(x) = 2D$, where v is assumed to be a constant. The expression for $\mu_1(x)$ is found to be

$$\mu_1(x) = x/v, \quad (52)$$

independent of diffusion effects. The diffusion constant D does, however, appear in the expression for $\mu_2(x)$. An equation for the distribution of absorption times can be written, following eq. (41), as

$$\frac{\partial \phi}{\partial t} = D \frac{\partial^2 \phi}{\partial x^2} - v \frac{\partial \phi}{\partial x}, \quad (53)$$

subject to $\phi(x, 0) = 0$ for $x > 0$ and $\phi(0, t) = 1$. The solution to this equation is

$$\phi(x, t) = \frac{x}{\sqrt{\pi D}} \int_0^t \frac{dt}{t^{3/2}} \exp \left[-\frac{1}{4Dt} (2x - vt)^2 \right], \quad (54)$$

as given by Schrödinger.⁵

First passage time problems in spaces of dimension greater than one require a simple geometry if useful information is to be obtained in closed form. Thus, solutions for the distribution function of first passage times and the moments are readily obtained for force-free Brownian motion in cylinders or spheres, and between parallel plates when these form the absorbing boundaries.^{25,26} More complicated geometries may require purely numerical techniques in the solution of associated first passage time problems.

An interesting example of the use of first passage time techniques in chemical physics is provided by Lifson and Jackson's attempt⁹ to explain long association times of sodium ions and

polymer macroions observed in transference experiments for polyelectrolytes. Their model is that of the Brownian motion of a counterion in the electrostatic field of a polyelectrolyte molecule. The simplest way to pose the problem in detail is to suppose that we have two bounding planes of $\pm X$. Within this region is a series of equidistant parallel charged planes at $x = 2jL$, $j = -n, -n + 1, \dots, n - 1, n$ where $X = 2nL$. Lifson and Jackson then go on to calculate the expected time for an ion initially at $x = 0$ to reach a boundary plane. The force on an ion of charge e will be written $\mathbf{F} = -e\nabla\Psi$. It is convenient to define a reduced potential $\phi = e\Psi/(kT)$. The equation for the mean first passage time for a particle performing Brownian motion in a force field derivable from a potential is

$$D\nabla^2\mu_1 + (1/\gamma)\mathbf{F} \cdot \nabla\mu_1 = -1, \quad (55)$$

where \mathbf{F} is the force and γ is the hydrodynamic friction constant. Substituting the expression for \mathbf{F} in terms of Ψ into this equation, and making use of the Einstein relation $D = kT/\gamma$, we find that eq. (55) can be rewritten

$$\nabla \cdot (e^\phi \nabla \mu_1) = -e^\phi/D \quad (56)$$

Since the system is homogeneous on a macroscopic scale, we might expect that the diffusion process is characterized by a diffusion constant D^* which depends on D and the local electrostatic field of the polyelectrolyte molecule. The object of Lifson and Jackson's analysis was to calculate D^* for a model system. One solves for D^* by calculating $\mu_1(0)$ and equating it to the expression

$$\mu_1(0) = X^2/(2D^*), \quad (57)$$

which is the expression relevant for the case of field-free Brownian motion. The average time $\mu_1(0)$ is given by

$$\mu_1(0) = \frac{1}{D} \int_0^X du e^{-\phi(u)} \int_0^u e^{\phi(v)} dv. \quad (58)$$

To obtain an expression for D^* we introduce the notation

$$\langle e^\phi \rangle = \frac{1}{2L} \int_0^{2L} e^{\phi(y)} dy. \quad (59)$$

Since $\phi(x)$ is periodic with period $2L$, far from the boundaries, eq. (58) can be rewritten

$$\begin{aligned}\mu_1(0) &= \frac{1}{D} \sum_{m=0}^{n-1} \int_{2mL}^{2(m+1)L} du e^{-\phi(u)} \int_0^u dv e^{\phi(v)} \\ &= \frac{1}{D} \sum_{m=0}^{n-1} \int_{2mL}^{2(m+1)L} du e^{-\phi(u)} \left[2mL \langle e^{\phi} \rangle + \int_{2mL}^u dv e^{\phi(v)} \right] \\ &= \frac{1}{2D} (2nL)^2 \langle e^{-\phi} \rangle \langle e^{\phi} \rangle = \frac{X^2}{2D} \langle e^{\phi} \rangle \langle e^{-\phi} \rangle\end{aligned}\quad (60)$$

A comparison between eqs. (57) and (60) yields the result

$$D^* = D / (\langle e^{\phi} \rangle \langle e^{-\phi} \rangle) \quad (61)$$

for the particular one-dimensional model under consideration. The Cauchy-Schwartz inequality can be used to show that $\langle e^{\phi} \rangle \langle e^{-\phi} \rangle \geq 1$, so that

$$D^* \leq D. \quad (62)$$

Jackson and Coriell²² have shown that this inequality holds in any number of dimensions. Lifson and Jackson concluded from their study that the retardation of drift of counterions in polyelectrolyte solutions might be accounted for by their entrapment in the electrostatic fields of the macroions.

Another problem related to the first passage time problem is that of calculating the probability of absorption by a particular one of a set of absorbing barriers. For example, in one dimension we can consider the probability of termination at $x = 0$, given that $x = 0$ and $x = A$ both offer the possibility of absorption. Such a mathematical problem finds application in elucidation of the theory of competitive rate processes. If the transfer of energy can be described in terms of a stochastic process, e.g., if the energy distribution obeys a Fokker-Planck equation, then the probability of one of a set of outcomes can be calculated by the technique to be described.

Let us first consider the one-dimensional case in which absorption can occur at either $x = 0$ or $x = A$. Let $\phi_0(x)$ be the probability of absorption at $x = 0$ given a starting point x . We define a function $\phi_0(x, t)$ to be the probability of absorption at

$x = 0$ before time t , given the starting point x . The desired probability $\phi_0(x)$ is then

$$\phi_0(x) = \lim_{t \rightarrow 0} \phi_0(x, t). \quad (63)$$

The function $\phi_0(x, t)$ is a solution to eq. (41), the derivation being the same as given above. However, the boundary conditions are now to be changed to

$$\phi_0(0, t) = 1, \phi_0(A, t) = 0. \quad (64)$$

Setting $\partial \phi_0 / \partial t = 0$ in eq. (41), we see that $\phi_0(x)$ is the solution to

$$\frac{1}{2} a_2(x) \frac{d^2 \phi_0}{dx^2} + a_1(x) \frac{d \phi_0}{dx} = 0 \quad (65)$$

with boundary conditions $\phi_0(0) = 1, \phi_0(A) = 0$. The solution to eq. (65) under these circumstances is

$$\phi_0(x) = \int_x^A e^{-U(y)} dy / \int_0^A e^{-U(y)} dy, \quad (66)$$

where $U(x)$ is defined in eq. (48). For Brownian motion in a constant force field $\phi_0(x)$ is found to be

$$\phi_0(x) = \frac{1 - e^{-(v/D)(A-x)}}{1 - e^{-(vA/D)}}. \quad (67)$$

In the limit $v \rightarrow 0$ this reduces to $\phi_0(x) = 1 - (x/A)$, as is to be expected. The theory for more complicated geometries is similar. If the boundary between V and \bar{V} is broken up into n segments S_1, S_2, \dots, S_n the probability of absorption by a particular segment S_j , $\phi_j(x)$, satisfies eq. (43) with $\partial \phi_j(x) / \partial t = 0$ and the boundary conditions $\phi_j(x) = 0$ for x in

$$S_1, S_2, \dots, S_{j-1}, S_{j+1}, \dots, S_n, \text{ and } \phi_j(x) = 1 \text{ for } x \text{ in } S_j.$$

There are many further applications of first passage time problems in chemical physics, particularly in the study of polymers.²⁷ Some of these involve first passages defined on Markov chains, a subject that has not been touched in the present article. However, the theory is similar to that developed here. The interested reader should refer to Kemeny and Snell's book²⁸ for a discussion of first passage time problems in discrete time.

Although it might appear at first glance that such problems would be completely unphysical, they have applications in polymer physics, where the analogue of time units are bond lengths of monomers.

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REACTION KINETICS IN HYPERSONIC FLOWS*

ALAN Q. ESCHENROEDER, *General Motors Corporation, Santa Barbara, California*

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SYMBOLS

A	Cross-sectional area in equations
A,B,C	Schematic chemical symbols in reactions
c_j	Mass concentration of j'th species
d	Sphere diameter
e	Internal energy
h	Enthalpy
J_j	Diffusion flux of j'th species
M	Mach number
m_j	Molecular weight of j'th species
p	Pressure
Q	Heat flux

* This paper follows lecture material presented at the La Jolla Summer Institute of Chemical Physics, August 1965, at the University of California, San Diego, California, U.S.A.