Journal of Statistical Physics, Vol. 31, No. 2, 1983

Order Statistics for First Passage Times in Diffusion Processes

George H. Weiss,[1] Kurt E. Shuler,[2,3] and Katja Lindenberg[2]

Received October 14, 1982

We consider the problem of the first passage times for absorption (trapping) of the first j ($j = 1, 2, \ldots$) of k, $j < k$, identical and independent diffusing particles for the asymptotic case $k \gg 1$. Our results are a special case of the theory of order statistics. We show that in one dimension the mean time to absorption at a boundary for the first of k diffusing particles, $\mu_{1,k}$, goes as $(\ln k)^{-1}$ for the set of initial conditions in which none of the k particles is located at a boundary and goes as k^{-2} for the set of initial conditions in which some of the k particles may be located at the boundary. We demonstrate that in one dimension our asymptotic results ($k \gg 1$) are independent of the potential field in which the diffusion takes place for a wide class of potentials. We conjecture that our results are independent of dimension and produce some evidence supporting this conjecture. We conclude with a discussion of the possible import of these results on diffusion-controlled rate processes.

KEY WORDS: Diffusion; order statistics; mean first passage times; mean trapping times.

1. INTRODUCTION

Many problems in chemical physics that involve rates can be phrased in terms of the theory of first passage times.[1-6] Such applications go back at least to the early twentieth century.[7,8] The usual formulation of first passage times problems is in terms of the diffusion of a single particle until

[1] Division of Computer Research and Technology, National Institutes of Health, Bethesda, Maryland 20205.

[2] Department of Chemistry, University of California, San Diego, La Jolla, California 92093.

[3] Supported in part by grants from the Chevron Research Company and from Charles and Renée Taubman.

0022-4715/83/0500-0255$03.00/0

it encounters a trap or triggers some reaction. No explicit account is taken of the fact that there may be a finite number of diffusing particles. In an earlier paper[9] we analyzed the effect of the number of lattice random walkers on the mean time for the first l ($l = 1, 2, \ldots$) of k independent walkers to reach a designated point in an infinite lattice. We showed that, in one dimension (1-D), if the number of independent random walkers is at least equal to 3, the earliest one of them to reach a designated point will do so in a finite average time. In contrast, it is well known[10] that in 1-D a single random walker reaches a designated point with probability equal to 1 but the mean time to do so is infinite. These results prompted us to investigate the statistics of absorption or trapping times of a number of diffusing particles. In particular, we will focus on a simple version of the jth passage time ($j = 1, 2, \ldots, k$) problem for a system with k diffusing particles where by the jth passage time we mean the time for the jth walker of the k diffusing ones to reach a trap or designated point. The simplification arises from our assumption that the k diffusing particles do not interact. Our results can be regarded as a special case of the theory of order statistics[11] which has been of interest in statistics since the pioneering work of Fisher and Tippett.[12] We will deal with the case $k \gg 1$, deriving results for the moments of the jth passage time using asymptotic techniques appropriate to diffusion processes. These results will be shown, for simple diffusion described by Fick's law in 1-D, to be independent of many of the details of the initial conditions. What is perhaps more remarkable is the fact that the asymptotic results are independent of the potential field in which the diffusion takes place for a wide class of potentials. We conjecture that these results are independent of dimension and produce some evidence supporting the conjecture, although we have nothing like a proof.

Finally, we present a short discussion on the possible application of these results to chemical and physical rate processes.

2. PRELIMINARY DEFINITIONS

Let us start with a single diffusing particle in a medium with traps and assume one knows the probability $G(t)$ that absorption has not occurred in the time interval $(0, t)$. In all cases of practical interest, $G(t)$ is differentiable for $t > 0$. The probability density for the absorption time (the first passage time density) will be denoted by $g(t)$ and is given by $g(t) = -dG(t)/dt$. We will assume that eventual absorption occurs with certainty so that $G(\infty) = 0$. The probability density, $q_{j,k}(t)$, for the absorption time of the jth out of k indistinguishable and noninteracting particles is

$$q_{j,k}(t) = j\binom{k}{j} g(t)\left[1 - G(t)\right]^{j-1} G^{k-j}(t), \qquad j = 1, 2, \ldots, k \quad (2.1)$$

This is easily seen since if the jth passage time is t, $j-1$ absorptions took place in $(0, t)$ with probability

$$\binom{k}{j-1}[1 - G(t)]^{j-1}$$

and the jth particle to be absorbed is chosen from the remaining $k - j + 1$. Equation (2.1) follows by noting the identity

$$(k - j + 1)\binom{k}{j-1} = j\binom{k}{j} \tag{2.2}$$

It is convenient to consider all values of j simultaneously by introducing the generating function

$$Q_k(z;t) = \sum_{j=1}^{k} q_{j,k}(t) z^{j-1} = kg(t)\{G(t) + [1 - G(t)]z\}^{k-1} \tag{2.3}$$

Let us note that if k is also considered to be a random variable, we can simultaneously handle all values of k by introducing another generating function. Let the random number of diffusing particles be K and let $p_k = \Pr(K = k)$. If $P(s)$ is the generating function

$$P(s) = \sum_{k=1}^{\infty} p_k s^k \tag{2.4}$$

then the average of $Q_k(z; t)$ averaged over all values of k is

$$Q(z;t) = g(t)\left.\frac{dP(s)}{ds}\right|_{s = G + (1-G)z} \tag{2.5}$$

For example, if p_k is a Poisson distribution so that

$$p_k = \frac{1}{e^{\mu} - 1}\frac{\mu^k}{k!}, \qquad k = 1, 2, \ldots \tag{2.6}$$

then

$$Q(z;t) = \frac{\mu g(t)}{e^{\mu} - 1}\exp\{\mu[G(t)] + \mu[1 - G(t)]z\} \tag{2.7}$$

Since the function $G(t)$ has remained unspecified, the results enumerated so far are model independent. To establish a relation between Eqs. (2.1)–(2.7) and a specific model, let us suppose that a single particle moves by diffusion in some space Ω with absorbing points or boundaries. If the dynamics allow us to calculate a probability density for the location of the particle at time t, $p(\mathbf{r}, t)$, $\mathbf{r}$ being a D-dimensional vector, then

$$G(t) = \int_{\Omega} p(\mathbf{r}, t)\, d^D r \tag{2.8}$$

with an analogous formula with a sum in place of the integral when Ω is a lattice. When $p(\mathbf{r}, t)$ satisfies a Fokker–Planck equation in 1-D, or when the system can be described as a 1-D lattice random walk with steps to nearest neighbors only, one can write down directly an equation for moments of the first passage time for a single diffusing particle.[1] No comparable simplification occurs when $k > 1$, but in the limit of large k we will see that one does not need to know $G(t)$ in great detail to find the leading term in the expression for the moments.

3. DIFFUSION IN ONE DIMENSION

Our first example is that of simple diffusion on a line with absorbing points at either end. We will see later that certain of the qualitative features of this example are easily generalized and appear also in the case of diffusion in a nonuniform field. The 1-D diffusion equation is

$$\frac{\partial p}{\partial t} = D\frac{\partial^2 p}{\partial x^2} \tag{3.1}$$

If $x = 0$ and $x = L$ are absorbing points, this equation is to be solved subject to $p(0, t) = p(L, t) = 0$. The general solution to this equation can be written as

$$p(x,t) = \int_0^L p(y,0)K(x,y;t)\,dy \tag{3.2}$$

where[13]

$$K(x,y;t) = 2\sum_{n=0}^{\infty}\sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n\pi y}{L}\right)\exp\left(\frac{-n^2\pi^2 Dt}{L^2}\right) \tag{3.3}$$

Combining Eqs. (2.8), (3.2), and (3.3) we can derive the following expression for $G(t)$:

$$G(t) \equiv 1 - h(t) = \int_0^L p(y,0)H(y,t)\,dy \tag{3.4}$$

with

$$H(y,t) = \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{\sin[(2n+1)\pi y/L]}{2n+1}\exp\left[-\frac{(2n+1)^2\pi^2 Dt}{L^2}\right] \tag{3.5}$$

To see why one needs very little information about $G(t)$ to calculate moments of the jth passage time, consider the case $j = 1$. The mean passage time for the first of k particles to be absorbed is

$$\mu_{1,k} = \int_0^\infty t q_{1,k}(t)\,dt = \int_0^\infty G^k(t)\,dt = \int_0^\infty e^{k\ln[1-h(t)]}\,dt \tag{3.6}$$

Since $G(0) = 1$, and $G(t)$ decreases monotonically to zero with increasing t, it is evident that the major contribution to the integral comes from the neighborhood of $t = 0$ in the limit of large k. If we write $H(y,t) = 1 - h(y,t)$ in Eq. (3.5), then a Poisson transformation of the series for $H(y,t)$ leads to the expression

$$h(y,t) = 2\left[1 - \phi\left(\frac{y}{2Dt}\right)\right] + 2\sum_{l=1}^{\infty}(-1)^l\left[\phi\left(\frac{lL-y}{(2Dt)^{1/2}}\right) - \phi\left(\frac{lL+y}{(2Dt)^{1/2}}\right)\right] \tag{3.7}$$

where $\phi(x)$ is the error function

$$\phi(x) = \frac{1}{(2\pi)^{1/2}}\int_{-\infty}^{x} e^{-u^2/2}\,du \tag{3.8}$$

which has the asymptotic property

$$\phi(x) \sim 1 - \frac{1}{(2\pi)^{1/2}}\,\frac{e^{-x^2/2}}{x} \tag{3.9}$$

Thus, when $y \neq 0$, Eq. (3.7) can be written, for small $\tau = Dt/L^2$, as

$$h(y,t) \sim \left(\frac{4Dt}{\pi}\right)^{1/2}\left[\frac{1}{y}e^{-y^2/(4Dt)} + \frac{1}{L-y}e^{-(L-y)^2/(4Dt)}\right] \tag{3.10}$$

which is symmetric around $y = L/2$, as it should be, and which tends to 0 as $\tau \to 0$ provided that $y \neq 0$ or L. The expression for $\mu_{1,k}$ is, from Eq. (3.6)

$$\mu_{1,k} \sim \int_0^{\infty} e^{-kh(t)}\,dt \tag{3.11}$$

to leading order in $h(t)$. This expression is valid when $h(t) \ll 1$, but this regime is the only one of interest when $k \gg 1$. In the present case the expression for $h(t)$ is

$$h(t) \sim \left(\frac{4Dt}{\pi}\right)^{1/2}\int_0^L p(y,0)\left[\frac{1}{y}e^{-y^2/(4Dt)} + \frac{1}{L-y}e^{-(L-y)^2/4Dt}\right]dy \tag{3.12}$$

In the limit of large k, the major contribution to the integral defining $\mu_{1,k}$ will come from the values of t for which $h(t)$ is small. The asymptotics of $\mu_{1,k}$ will depend on how, in detail, $h(t)$ approaches 0. Since the term $\exp[-y^2/(4Dt)]$ goes to 0 as $t \to 0$ for $y > 0$, we may expect different qualitative behavior depending on whether or not $p(y,0)$ approaches a nonzero value as $y \to 0$ (a similar statement is valid in the neighborhood of $y = L$). If, for example, we assume the uniform distribution

$$p(y,0) = 1/L \qquad (0 \leqslant y \leqslant L) \tag{3.13}$$

as a prototype of the case in which $p(0,0)$ and $p(L,0) \neq 0$, then we must return to Eq. (3.7) to determine the behavior of $h(t)$ as $t \to 0$. We find, in that case, that asymptotically

$$h(t) \sim \frac{2}{L}\int_0^L \left[1-\phi\left(\frac{y}{(2Dt)^{1/2}}\right)\right]dy + \frac{2}{L}\int_0^L \left[1-\phi\left(\frac{L-y}{(2Dt)^{1/2}}\right)\right]dy$$

$$\sim \frac{4}{L}\left(\frac{Dt}{\pi}\right)^{1/2} \tag{3.14}$$

plus error terms that go to zero at least as fast as $\exp[-L^2/(4Dt)]$ as $Dt/L^2 \to 0$. Therefore, for the initial condition specified in Eq. (3.13), the formula in Eq. (3.11) implies that for large k

$$\mu_{1,k} \sim \frac{\pi L^2}{8D}\frac{1}{k^2} \tag{3.15}$$

This is to be compared with the exact result for $k = 1$,

$$\mu_{1,1} = \frac{L^2}{12D} \tag{3.16}$$

It will be noted that, as one would expect for the initial condition (3.13), the mean time, $\mu_{1,k}$, for the first of the k walkers (for $k \gg 1$) to be absorbed at $x = 0$, or $x = L$, is much less than the mean time, $\mu_{1,1}$, for only one random walker. One can show that whenever $p(y,0)$ is continuous at $y = 0$ (or $y = L$) and $p(0,0)$ or $p(L,0) = \text{const} \neq 0$, $\mu_{1,k}$ will go to 0 as k^{-2} whenever $k \gg 1$.

A different behavior results whenever the initial conditions preclude a random walker from being in the neighborhood of either absorbing point. Let us suppose that there is an open interval (y_1, y_2) satisfying $0 < y_1 < y_2 < L$, such that $p(y,0) = 0$ in $(0, y_1)$ and (y_2, L). Then, for all y in (y_1, y_2) it is true that $\lim_{t\to 0}\exp[-y^2/(4Dt)] = 0$. Therefore, we can expect that the integral appearing in the definition of $h(t)$, Eq. (3.14), tends to 0 as $t \to 0$. Furthermore, using techniques familiar in the asymptotic evaluation of integrals,[14] we can assert that the principal contributions to the value of the integral come from the neighborhood of the end points, y_1 and y_2, and depend on the behavior of $p(y,0)$ in those neighborhoods. Let us consider the contribution at y_1, assuming that $p(y,0)$ is continuous in a neighborhood of that point, and that

$$\lim_{y\to y_1} p(y,0) \equiv p_1 = \text{const} \tag{3.17}$$

Then

$$I(t) \equiv \int_{y_1}^{y_2} \frac{p(y,0)}{y}\exp\left(-\frac{y^2}{4Dt}\right)dy$$

$$= \exp\left(-\frac{y_1^2}{4Dt}\right)\int_0^{y_2-y_1}\frac{p(y_1+v,0)}{y_1+v}\exp\left[-\frac{v}{4Dt}(2y_1+v)\right]dv \tag{3.18}$$

It is evident that in the limit $Dt/y_1^2 \to 0$ the dominant contribution to the integral will come from small v. Therefore, we can neglect v^2 with respect to $y_1 v$ in the exponent and write

$$
\begin{aligned}
I(t) &\sim e^{-y_1^2/(4Dt)} \int_0^{y_2-y_1} \frac{p(y_1+v,0)}{y_1+v} e^{-y_1 v/2Dt}\, dv \\
&\sim \frac{p_1}{y_1} e^{-y_1^2/(4Dt)} \int_0^{y_2-y_1} e^{-y_1 v/(2Dt)}\, dv \\
&\sim \frac{2p_1 Dt}{y_1^2} e^{-y_1^2/(4Dt)}
\end{aligned}
\tag{3.19}
$$

A similar contribution can be derived for y_2 with the exponential term replaced by $\exp[-(L-y_2)^2/4Dt]$. If $L - y_2 > y_1$, the contribution from y_1 will be the dominant one; and when $y_1 > L - y_2$, the contribution from y_2 dominates. In either case we see that for $Dt/L^2 \to 0$,

$$
h(t) \sim C_1 t^{3/2} \exp(-t_0/t) \tag{3.20}
$$

where C_1 and t_0 are constants. The parameter t_0 has the dimensions of time and in the present case is given by

$$
t_0 = \frac{\min\left[y_1^2, (L-y_2)^2\right]}{4D} \tag{3.21}
$$

and $C_1 = 4p_1 D^{3/2}/(y_1^2 \pi^{1/2})$ has the dimensions of $(\text{time})^{-3/2}$. It should be emphasized that this is valid only when Eq. (3.17) is true. When $p(y,0)$ behaves like $(y-y_1)^\alpha$ near $y = y_1$, the exponent $3/2$ in Eq. (3.20) must be replaced by $\alpha + 3/2$.

The results obtained in the last paragraph allow us to write, as an approximation,

$$
\mu_{1,k} \sim \int_0^\infty \exp\left[-kC_1 t^{3/2} \exp(-t_0/t)\right] dt \tag{3.22}
$$

More generally, Eq. (2.3) enables us to write a generating function for the mean absorption time of the jth out of k random walkers:

$$
\begin{aligned}
U_k(z) &= \sum_{j=1}^{k} \mu_{j,k} z^{j-1} = \int_0^\infty t Q_k(z,t)\, dt \\
&= \frac{1}{(1-z)} \int_0^\infty \left(\left\{G(t) + [1-G(t)]z\right\}^k - z^k\right) dt
\end{aligned}
\tag{3.23}
$$

where the second representation is obtained from the first by an integration by parts. We will be interested in $j \ll k$, in which case we can write

$$U_k(z) \sim \frac{1}{(1-z)} \int_0^\infty \exp\{k \ln[1 - h(t)(1-z)]\}\, dt$$
$$\sim \frac{1}{(1-z)} \int_0^\infty \exp[-kh(t)(1-z)]\, dt$$
$$\sim \frac{1}{(1-z)} \int_0^\infty \exp[-kC_1 t^{3/2}(1-z)\exp(-t_0/t)]\, dt \quad (3.24)$$

Thus, we see that the evaluation of all of the average absorption times requires an asymptotic analysis of an integral of the form

$$f(\lambda) = t_0 \int_0^\infty \exp[-\lambda\tau^{3/2}\exp(-1/\tau)]\, d\tau \quad (3.25)$$

for large λ, i.e., large k. The relationship between Eq. (3.24) and this form for the integral is established by setting

$$\lambda = kC_1 t_0^{3/2}(1-z) = k\lambda_0(1-z) \quad (3.26)$$

where $\lambda_0 \equiv C_1 t_0^{3/2}$. Using results established in Appendix A, we can show that for large λ,

$$U_k(z) \sim \frac{t_0}{(1-z)}\left[\frac{1}{\ln\lambda} - \frac{(3/2 + C) + (3/2)\ln(\ln\lambda)}{(\ln\lambda)^2} + \cdots\right] \quad (3.27)$$

where $C = 0.5771 +$. This result will be used to find approximations to the $\mu_{j,k}$.

A first step in finding the coefficient of z^j in Eq. (3.27) [which depends on z through Eq. (3.26)] is to observe that if one is given a generating function $A(z)$ of a set of coefficients, $\{a_n\}$, then the coefficient of z^n in $A(z)/(1-z)$ is $a_0 + a_1 + \cdots + a_n$. The significance of this remark is that we can restrict ourselves to the analysis of the two terms in brackets in Eq. (3.27). Consider the contributions from the lowest-order term

$$\frac{1}{\ln\lambda} = \frac{1}{\ln\lambda_0 k + \ln(1-z)} \quad (3.28)$$

The coefficient $\mu_{1,k}$ is obtained from Eq. (3.27) by setting $z = 0$. Thus, we have

$$\mu_{1,k} \sim \frac{t_0}{\ln\lambda_0 k}\left[1 - \frac{(3/2 + C) + (3/2)\ln(\ln\lambda_0 k)}{\ln\lambda_0 k} + \cdots\right] \quad (3.29)$$

The dependence on k is contained in the term $\ln\lambda_0 k$.

To evaluate the order of magnitude of the terms in Eq. (3.29) as a function of k, it is necessary to determine the order of λ_0. Let us suppose for simplicity that the interval y_1 to y_2 is symmetrically located within the interval 0 to L. From (3.21) we then find $t_0 = y_1^2/4D$. Using the expression of C_1 below Eq. (3.21) we obtain

$$\lambda_0 \equiv C_1 t_0^{3/2} = \frac{p_1 y_1}{2\pi^{1/2}} \tag{3.30}$$

which is dimensionless, as it should be, since p_1 has dimension $(\text{length})^{-1}$. Since p_1 and y_1 are at our disposal, we can choose them so that λ_0 is of order 1.

If we now assume that k is of order 10^{23}, i.e., one mole of diffusing particles, then $\ln(\ln \lambda_0 k)$ is of order 1 and Eq. (3.29) reduces to

$$\mu_{1,k} \sim \frac{t_0}{\ln \lambda_0 k} \sim \min \frac{\left[y_1^2, (L-y_2)^2\right]}{4D} \frac{1}{\ln \lambda_0 k} \tag{3.31}$$

A comparison of this result with the $\mu_{1,k}$ of Eq. (3.15) where $\mu_{1,k} \sim 1/k^2$ indicates the importance of the initial distribution of the k random walkers with respect to the absorbing barriers on the k dependence of $\mu_{1,k}$.

The $\mu_{j,k}$ are obtained from the more complete expression in Eq. (3.27). A detailed development, outlined in Appendix B, leads to the result

$$\mu_{j,k} \sim \mu_{1,k} + \frac{t_0}{(\ln \lambda_0 k)^2}\left(1 + \frac{1}{2} + \frac{1}{3} + \cdots + \frac{1}{j-1}\right) \tag{3.32}$$

Equations (3.29) and (3.32) allow us to conclude that the first trapping event takes place on a time scale that is approximately of the order of $(\ln \lambda_0 k)^{-1}$. However, once that first event has occurred, successive events take place on a shorter time scale. This can be seen by calculating the difference between average trapping times of the $(j-1)$st and the jth random walkers,

$$\mu_{j,k} - \mu_{j-1,k} \sim \frac{t_0}{(j-1)} \cdot \frac{1}{(\ln \lambda_0 k)^2} \tag{3.33}$$

which is of the order of $(\ln \lambda_0 k)^{-2}$ in contrast to the behavior of $\mu_{1,k}$. In Fig. 1 we have plotted curves of $q_{j,20}(t)$, where $q_{j,k}(t)$ is the probability density for the passage time of the jth walker out of a total of k walkers [Eq. (2.1)], for $j = 1$–5, as a function of $t/t_{\max}$, where $t_{\max}$ is the time at which $q_{1,20}$ is maximized. Since the distributions are fairly symmetric, these maxima are close to the average trapping times, $\mu_{j,k}$. Although k is not very large, we can observe that the time intervals between successive maxima are less than $t_{\max}$, consistent with the conclusions from our asymptotic calculations.

Similar calculations can be made for higher moments. In particular, if $\mu_{j,k}(m)$ denotes the mth moment of the trapping time for the jth walker, then the variance is expressed as

$$\sigma_{j,k}^2 = \mu_{j,k}(2) - \mu_{j,k}^2(1) \tag{3.34}$$

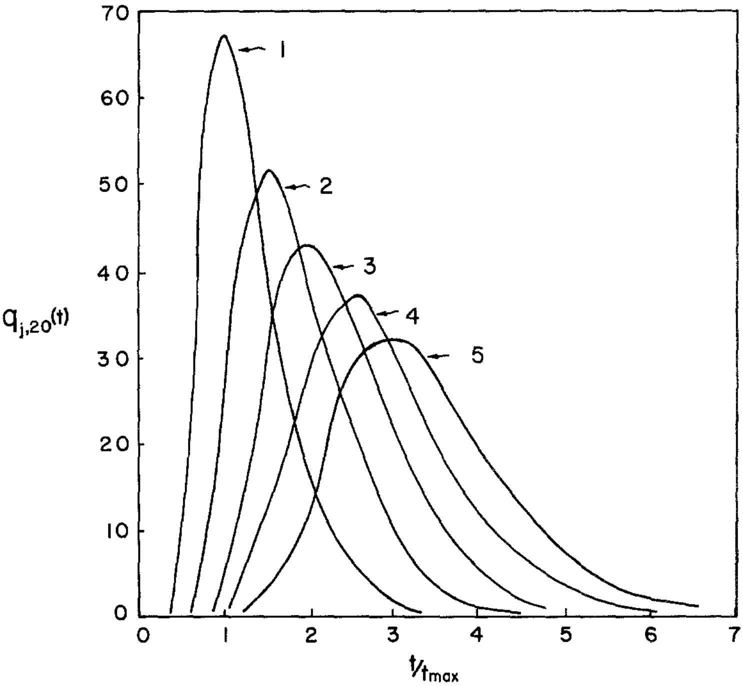

Fig. 1. Curves of $q_{j,20}(t)$, $j = 1$–5, plotted as a function of $t/t_{\max}$ where $t_{\max}$ is the value of t at which $q_{1,20}(t)$ is a maximum.

The coefficient of variation, $\sigma_{j,k}/\mu_{j,k}$, is, to lowest order in $1/\ln \lambda_0 k$

$$\sigma_{j,k}/\mu_{j,k} \sim (\ln \lambda_0 k)^{-1/2} \tag{3.35}$$

The interesting feature of this formula is that the coefficient of variation goes to 0 with k very slowly. Again, using $\lambda_0 k = 10^{23}$ to establish an order of magnitude, we find that $\sigma_{j,k}/\mu_{j,k} = 0.14$. From the law of large numbers, one might naively expect $\sigma_{j,k}/\mu_{j,k}$ to go to zero with k as $k^{-1/2}$, but our calculation shows the actual dependence on k to be much weaker.

So far we have dealt with the case of two absorbing points on a line. If we change one of the points to a reflecting point, say $x = 0$, then Eq. (3.12) remains valid except that

$$h(t) \sim \left(\frac{4Dt}{\pi}\right)^{1/2} \int_0^L \frac{p(y,0)}{L-y} \exp\left[-\frac{(L-y)^2}{4Dt}\right] dy \tag{3.36}$$

for small values of Dt/L^2. The asymptotic properties of this expression for $h(t)$ are identical with those found in the case of two absorbing points.

Consequently, the asymptotic dependence of $\mu_{j,k}(m)$ on k remains unchanged.

All of the results obtained so far are for $j \ll k$. A natural extension of these ideas lies in the examination of the case $j/k = \theta$ where $0 < \theta < 1$. The expected number of random walkers that remain in the system at time t is $kG(t)$. A crude argument to calculate the time t_θ at which the jth random walker is absorbed is to equate the expected number of random walkers remaining in the system to $k - j$, i.e., we define the time t_θ as the solution to

$$G(t_\theta) = 1 - \theta \tag{3.37}$$

To determine the utility of this approximation, we must determine whether the probability density $q_{j,k}(t)$ defined in Eq. (2.1) is in any sense sharply peaked, as a function of t, around t_θ. The ideas involved are straightforward and have been described in the context of the theory of order statistics.[11] Let us return to Eq. (2.1) and consider the factor

$$[1 - G(t)]^{j-1}G^{k-j}(t) = \{[1 - G(t)]^\theta G^{1-\theta}(t)\}^k/[1 - G(t)] \tag{3.38}$$

The term in curly brackets tends to zero exponentially in k and is peaked around the solution to Eq. (3.37). If $G(t)$ is expressed as $G(t) = G(t_\theta) + \Delta G$, then

$$\begin{aligned}\{[1 - G(t)]^\theta G^{1-\theta}(t)\}^k \\ &= \exp(k\{\theta \ln[1 - G(t)] + (1 - \theta)\ln G(t)\}) \\ &\sim \exp\left[k\{\theta \ln[1 - G(t_\theta)] + (1 - \theta)\ln G(t_\theta)\} - \frac{k(\Delta G)^2}{2\theta(1-\theta)}\right]\end{aligned} \tag{3.39}$$

where the expansion is to lowest order in ΔG. If $G(t)$ is differentiable at $t = t_\theta$, then we can write $\Delta G \sim -(t - t_\theta)g(t_\theta)$. Hence, when the binomial coefficient in Eq. (2.1) is replaced by the corresponding Stirling's approximation, one finds that $q_{j,k}(t)$, the probability density for the absorption time $t_{\theta k,k}$, of the jth random walker, is approximated by

$$q_{j,k}(t) \sim \left[\frac{k}{2\pi\theta(1-\theta)}\right]^{1/2} g(t_\theta)\exp\left[-\frac{k^2 g^2(t_\theta)(t - t_\theta)^2}{2\theta(1-\theta)}\right] \tag{3.40}$$

Owing to the form of $q_{j,k}(t)$ in (3.40), the absorption time t_θ has a Gaussian distribution with mean and variance, respectively, given by

$$\lim_{k\to\infty}\langle t_{\theta k,k}\rangle = t_\theta, \qquad \sigma^2_{\theta k,k} \sim \frac{\theta(1-\theta)}{kg(t_\theta)} \tag{3.41}$$

We see that the heuristic device of assuming that the absorption time t_θ is equal to the solution of Eq. (3.37) is justified by the preceding analysis since $\sigma^2_{\theta k,k}$ goes to 0 as $1/k$. It should also be pointed out that this analysis does not depend in any critical way on the form of $G(t)$, requiring only that $\Delta G \sim -(t - t_\theta)g(t_\theta)$ locally. The properties appropriate to the limit $j/k \to 1$ have been extensively investigated by statisticians and are of lesser interest in physical applications; they will therefore not be discussed here.

4. DIFFUSION IN AN INHOMOGENEOUS FIELD

Our results in the last section were shown to be valid in the limit of large k for diffusion in a force-free field. However, the only feature of this discussion that played a role in the analysis was the early time behavior of $G(t)$. This suggests the possibility that more general diffusion models might also give rise to the same dependence on k for moments of absorption times. This indeed is true and can be shown to be valid for a large class of diffusion processes in 1-D. The basic idea underlying the analysis is that the first few out of a large number of diffusing particles to be absorbed tend to move essentially without reversing direction and without sensing details of the structure of the field. This is analogous to the behavior of particles performing a random walk on a discrete lattice in discrete time, as discussed by Lindenberg *et al.*[9] Specifically, we assume that the diffusion process can be characterized in terms of a time homogeneous Fokker–Planck equation:

$$\frac{\partial p}{\partial t} = D\frac{\partial^2[a_2(x)p]}{\partial x^2} - v\frac{\partial}{\partial x}[a_1(x)p] \tag{4.1}$$

in which D has the dimensions of a diffusion constant, v has the dimensions of a velocity and the $a_i(x)$, $i = 1, 2$, are dimensionless functions of x. To avoid difficulties with boundary conditions, we will assume that $a_2(x)$ is bounded away from 0, i.e., there exists a positive constant M such that $a_2(x) > M > 0$. A further assumption is that $a_1(x)/a_2(x)$ is integrable over the entire interval $(0, L)$, allowing us to define the function

$$U(x) = \int_0^x \frac{a_1(\xi)}{a_2(\xi)}\, d\xi \tag{4.2}$$

for $0 \leqslant x \leqslant L$. The idea behind the calculation is that Eq. (4.1) can be formally solved by separating variables, and the result expressed in terms of an eigenfunction expansion. The behavior of the solution at very early times will be determined by asymptotic properties (for large index) of the eigenfunctions and eigenvalues. But these properties are known and lead to short-time behavior identical in form to that resulting from simple diffusion. Hence, the moments of trapping times have the same dependence on k as we have found in the last two sections.

As a first step it is convenient to transform Eq. (4.1) to dimensionless variables via

$$y = \frac{x}{L}, \qquad \tau = \frac{Dt}{L^2}, \qquad \epsilon = \frac{vL}{D} \tag{4.3}$$

to find that p satisfies

$$\frac{\partial p}{\partial \tau} = \frac{\partial^2}{\partial y^2}(a_2 p) - \epsilon \frac{\partial}{\partial y}(a_1 p) \tag{4.4}$$

The next step is to transform this equation to self-adjoint form by introducing the dependent variable $\rho(y,\tau)$ through

$$p(y,\tau) = \frac{1}{a_2(y)} \exp[\epsilon U(y)] \rho(y,\tau) \tag{4.5}$$

where $U(y)$ is defined in Eq. (4.2). When this transformation is made, $\rho(y,\tau)$ is found to satisfy

$$\frac{\partial \rho}{\partial \tau} = a_2(y) e^{-\epsilon U(y)} \frac{\partial}{\partial y}\left(e^{\epsilon U(y)} \frac{\partial \rho}{\partial y} \right) \tag{4.6}$$

which is the desired result. With the assumption that both end points are absorbing points, this equation is to be solved subject to the boundary conditions

$$\rho(0,\tau) = \rho(1,\tau) = 0 \tag{4.7}$$

Equation (4.6) can be solved by a separation of variables. Setting $\rho(y,\tau) = \phi(y)\exp(-\lambda\tau)$, we find that $\phi(y)$ satisfies the Sturm–Liouville equation:

$$\frac{d}{dy}\left[e^{\epsilon U(y)} \frac{d\phi}{dy} \right] + \frac{\lambda e^{\epsilon U(y)}}{a_2(y)} \phi = 0 \tag{4.8}$$

The formal solution to Eq. (4.4) can be written in terms of the eigenfunctions and eigenvalues of this last equation as

$$p(y,\tau) = \frac{\exp[\epsilon U(y)]}{a_2(y)} \int_0^1 a_2(\xi) e^{-\epsilon U(\xi)} p(\xi, 0) K(y, \xi; \tau)\, d\xi \tag{4.9}$$

where

$$K(y,\xi;\tau) = \sum_{j=0}^{\infty} \phi_j(y)\phi_j(\xi)\exp(-\lambda_j \tau) \tag{4.10}$$

As in the case of simple diffusion, we must investigate the small τ behavior of the function $h(\tau)$ derived from Eq. (4.10). It is shown in Appendix D that this behavior depends only on the asymptotic form of the

$\phi_j(y)$ and λ_j for large j. This behavior, however, is known,[14] and one can assert that $h(\tau)$ has the same behavior as was found for simple diffusion for $\tau \to 0$. It therefore follows that when $j = 0(1) \ll k$

$$\mu_{j,k} \sim C_1/\ln k, \qquad \sigma_{j,k}^2 \sim C_2/(\ln k)^3 \tag{4.11}$$

where C_1 and C_2 are constants, as is the case for simple diffusion.

5. FIRST PASSAGE PROBLEMS IN HIGHER DIMENSIONS

It is not difficult to show that the first passage time problem to a closed absorbing boundary for spherically symmetrical simple diffusion leads to exactly the same k dependence for the moments as does simple diffusion on a line.

Having shown that the lowest-order moments have the same dependence on k in a number of one-dimensional cases, including those with quite general force fields, we may speculate that the dependence on k of these moments holds in higher dimensions. This conjecture can be supported by an analysis that is heuristic rather than rigorous at the present time. If the first few random walkers, or diffusing particles, to be absorbed in D dimensions move essentially in a straight line, i.e., do not exhibit noticeable excursions in the other D-1 directions, then one would expect first passage times to be independent of dimension. Conversely, if the first passage times turn out to be independent of dimension, the motion of the first few of the k walkers to be absorbed will be essentially straight line motions. Let us consider the case where the entire boundary is absorbing. In the cases analyzed so far, we required for the proof of results in Eq. (4.11) that there be some finite interval in contact with the absorbing point such that the initial condition is strictly equal to zero within the interval. When this class of initial conditions is valid, one needs only to calculate the short-time form for the probability that a single particle is not absorbed. In higher dimensions absorption takes place on a hypersurface rather than at a point so that to draw an analogy with diffusion in a sphere we need to require that $p(r, 0)$ be zero in a shell of finite width in contact with the absorbing boundary. When this holds, at sufficiently short time, we will ignore the boundary altogether and calculate $p(r, t)$ in the infinite space. We then approximate $G(t)$ as the volume integral of $p(r, t)$ within the hypersurface. Strictly speaking, this procedure is not correct because it counts particles which have crossed the hypersurface and then returned. This contribution to $G(t)$ should, however, be small at short times. In the one-dimensional examples that we have studied, this procedure leads to the correct time-dependent behavior of $h(t)$ but with an incorrect multiplicative constant. Since only the correct time dependence of $h(t)$ is needed to derive Eq. (4.11), this heuristic treatment leads to the correct form of the answer.

Let us suppose that p satisfies a D-dimensional equation of the form

$$\frac{\partial p}{\partial \tau} = \mathscr{L} p \tag{5.1}$$

where $\mathscr{L}$ is a second-order differential operator which we write

$$\mathscr{L} = \sum_i \sum_j b_{ij} \frac{\partial^2}{\partial x_i \partial x_j} + \sum_i c_i \frac{\partial}{\partial x_i} \tag{5.2}$$

The coefficients b_{ij} and c_i are allowed to depend on the spatial coordinates but not on time and $\mathbf{B} = (b_{ij})$ is positive definite. Molchanov[15] has discussed the problem of deriving the solution to Eq. (5.1) with (5.2) valid at short times. If the metric in the space is

$$ds^2 = g_{ij} dx^i dx^j \tag{5.3}$$

where the matrix $\mathbf{g}$ [$= (g_{ij})$] is determined from $\mathbf{B}$ [$= (b_{ij})$] by $\mathbf{g} = \mathbf{B}^{-1}$, then for $p(\mathbf{r}, 0) = \delta(\mathbf{r} - \mathbf{r}_0)$ the small τ expansion of p has the form

$$p(\mathbf{r}, \tau \mid \mathbf{r}_0, 0) \sim \frac{H(\mathbf{r}, \mathbf{r}_0)}{\tau^{D/2}} \exp\left(- \frac{\|\mathbf{r} - \mathbf{r}_0\|^2}{2\tau} \right) \tag{5.4}$$

where $H(\mathbf{r}, \mathbf{r}_0)$ is a function that can be calculated and $\|\mathbf{r} - \mathbf{r}_0\|$ is the distance in the metric defined in Eq. (5.3). Therefore, for a general initial condition described by an arbitrary density $f(\mathbf{r}_0)$, one has

$$G(\tau) \sim \int \underset{\Omega}{\cdots} \int \frac{H(\mathbf{r}, \mathbf{r}_0)}{\tau^{D/2}} \exp\left\{ - \frac{\|\mathbf{r} - \mathbf{r}_0\|^2}{2\tau} \right\} f(\mathbf{r}_0) \, d^D\mathbf{r} \, d^D\mathbf{r}_0 \tag{5.5}$$

An analysis of this integral under quite general conditions leads to the asymptotic results in Eq. (4.11). We therefore expect that Eq. (4.11) is also valid for D-dimensional diffusion, although the constants may be quite difficult to calculate.

6. DISCUSSION

The result displayed in Eq. (3.13), i.e., $\mu_{1,k} \sim 1/\ln k$, is somewhat surprising in that the mean time to absorption of the first of k random walkers decreases so slowly with k. Thus, a change from 10^4 to 10^{23} random walkers, which is 19 orders of magnitude, leads to only a sixfold decrease of $\mu_{1,k}$. Since the first few of the k random walkers to be absorbed will move from their initial position to the absorbing boundary essentially in a straight line motion with a minimum of "reversals" as compared with the later arrivals, one might have expected a much larger effect in comparing $\mu_{1,k}$ with $\mu_{1,1}$. As we will show in a sequel to this paper, the effect is more pronounced for random walks on a discrete lattice where $\mu_{1,k} \sim 1/k^{\alpha}$, where α is a constant which depends upon the number of lattice sites N in the interval $(0, L)$. There, the first of k walkers also moves essentially in a unidirectional walk to the absorbing boundary but does so by jumping between lattice points spaced a finite distance apart. In diffusion, however, the motion of the particles involves, by definition, a sequence of infinitesimal changes in position. In the limit as $N \to \infty$ for fixed L, the lattice random walk approaches a diffusion process and $\mu_{1,k}$ tends to $1/\ln k$.

In considering possible applications of our results, it is more instructive to look at $(\mu_{1,k})^{-1}$, i.e., the mean *rate* to absorption (trapping) of the first of k random walkers. For the special cases of diffusion-controlled rate processes, where the absorption or reaction of the first (or first few) of the particles by the "absorber" can lead to a "trigger effect," an increase by a factor of about 23, for $k = 10^{23}$, in the rate of arrival at the absorber may not be negligible. As specific examples, we mention nucleation (precipitation) processes of various types, growth of colloid or aerosol particles, combustion of fuel droplets, and the onset of fluorescence in diffusive exciton trapping. Since calculations now in the literature for the mean rate to absorption in diffusion-controlled reactions are based on the diffusion of *one* particle, rather than the first of k particles, it would be of some interest to review the agreement between calculations and experimental data to see whether this factor of $(\ln k)^{-1}$ is in evidence.

APPENDIX A. ASYMPTOTIC EVALUATION OF THE INTEGRALS IN EQ. (3.25)

The integrals in question both have the general form

$$f(\lambda) = \int_0^\infty \exp\left[-\lambda\left(\frac{v}{t_0}\right)^{3/2}\exp\left(-\frac{t_0}{v}\right)\right]dv$$

$$= t_0\int_0^\infty \exp\left[-\lambda\tau^{3/2}\exp(-1/\tau)\right]d\tau \tag{A.1}$$

where we have inserted the parameter $t_0^{-3/2}$ into the exponent to express the integrand in terms of dimensionless variables. To develop the asymptotic form of Eq. (A.1) for large λ, set

$$\rho = \tau^{3/2}e^{-1/\tau} \tag{A.2}$$

so that

$$f(\lambda) = t_0\int_0^\infty e^{-\lambda\rho}\frac{d\rho}{(d\rho/d\tau)} = t_0\int_0^\infty \frac{e^{-\lambda\rho}}{\rho}\,\frac{\tau^2(\rho)}{1+(3/2)\tau(\rho)}\,d\rho \tag{A.3}$$

where $\tau(\rho)$ is the solution to Eq. (A.2) for τ in terms of ρ. Since $f(\lambda)$ is expressed as a Laplace transform, we expect that the behavior for large λ will depend on the behavior of the integrand near $\rho = 0$.

To determine this behavior, we take logarithms of Eq. (A.2),

$$\ln\frac{1}{\rho}=\frac{1}{\tau}+\frac{3}{2}\ln\left(\frac{1}{\tau}\right) \tag{A.4}$$

Since ρ is a monotonically increasing function of τ and $\rho(\tau=0)=0$, small values of τ will correspond to small ρ. Therefore, to a first approximation

$$\tau \sim \frac{1}{\ln(1/\rho)} \tag{A.5}$$

This suggests that the exact solution to Eq. (A.2) can be expressed as

$$\tau(\rho)=\frac{1}{\ln(1/\rho)+\xi(\rho)} \tag{A.6}$$

where

$$\lim_{\rho\to 0}\xi(\rho)/\ln\frac{1}{\rho}=0 \tag{A.7}$$

Although it is not possible to find an expression in closed form for $\xi(\rho)$, we can determine its behavior for $\rho \sim 0$ by substituting Eq. (A.6) into (A.4), taking advantage of Eq. (A.7) to write a perturbation series. In this way we find as a first approximation to $\xi(\rho)$:

$$\xi(\rho)\sim\frac{3}{2}\ln\left(\ln\frac{1}{\rho}\right) \tag{A.8}$$

and the next-order approximation is

$$\xi(\rho)\sim\frac{3}{2}\ln\left(\ln\frac{1}{\rho}\right)\left[1-\frac{3}{2\ln(1/\rho)}\right] \tag{A.9}$$

Succeeding correction terms go like $\ln[\ln(1/\rho)]$ multiplied by powers of $[\ln(1/\rho)]^{-1}$. For our present purposes, we shall need only the first approximation given in Eq. (A.9).

The range of integration in Eq. (A.3) will be divided into two pieces, $(0,\epsilon)$ and (ϵ,∞), where $\epsilon \ll 1$ and where $\lambda\epsilon \gg 1$. In the first of these integrals, we substitute the representation in Eq. (A.6) and expand to first order in $\xi(\rho)$. This yields

$$\int_0^{\epsilon}\frac{e^{-\lambda\rho}}{\rho}\,\frac{\tau^2(\rho)}{1+\frac{3}{2}\tau(\rho)}\,d\rho$$

$$\sim\int_0^{\epsilon}\frac{e^{-\lambda\rho}}{\rho}\left[\frac{1}{\ln\frac{1}{\rho}\left(\ln\frac{1}{\rho}+\frac{3}{2}\right)}-\frac{\xi(\rho)\left(2\ln\frac{1}{\rho}+\frac{3}{2}\right)}{\left(\ln\frac{1}{\rho}\right)^2\left(\ln\frac{1}{\rho}+\frac{3}{2}\right)}\right]d\rho \tag{A.10}$$

The asymptotic behavior of the integral will be determined by the singular behavior of the term in square brackets. These can be written in terms of $u = \ln(1/\rho)$ as

$$[\ ] = \frac{1}{u^2} - \frac{3\ln u + \frac{3}{2}}{u^3} + \cdots \tag{A.11}$$

Hence, we must determine asymptotic properties of two classes of integrals:

$$\begin{aligned} I_n &= \int_0^{\epsilon} \frac{e^{-\lambda\rho}}{\rho} \frac{1}{[\ln(1/\rho)]^n} d\rho \\ J_n &= \int_0^{\epsilon} \frac{e^{-\lambda\rho}}{\rho} \frac{\ln[\ln(1/\rho)]}{[\ln(1/\rho)]^n} d\rho \end{aligned} \tag{A.12}$$

To evaluate the asymptotic behavior of I_n, we start by integrating by parts, setting

$$U = e^{-\lambda\rho}, \qquad dV = \frac{1}{\rho} \frac{1}{[\ln(1/\rho)]^n} d\rho \tag{A.13}$$

so that

$$dU = -\lambda e^{-\lambda\rho} d\rho, \qquad V = \frac{1}{(n-1)[\ln(1/\rho)]^{n-1}} \tag{A.14}$$

The contribution from UV can be neglected at $\rho = \epsilon$ because $\exp(-\lambda\epsilon) \ll 1$, and at the lower limit because $\lim_{\rho\to 0} 1/[\ln(1/\rho)] = 0$. Hence, we can write

$$I_n \sim \frac{\lambda}{n-1} \int_0^{\epsilon} e^{-\lambda\rho} \frac{d\rho}{[\ln(1/\rho)]^{n-1}} = \frac{1}{(n-1)} \int_0^{\lambda\epsilon} \frac{e^{-u}\, du}{(\ln\lambda - \ln u)^{n-1}} \tag{A.15}$$

Using the identity

$$\frac{1}{s^{n-1}} = \frac{1}{(n-2)!} \int_0^{\infty} t^{n-2} e^{-st}\, dt \tag{A.16}$$

we can write the expression for I_n as

$$\begin{aligned} I_n &\sim \frac{1}{(n-1)!} \int_0^{\infty} t^{n-2} e^{-t\ln\lambda}\, dt \int_0^{\lambda\epsilon} e^{-u+t\ln u}\, du \\ &= \frac{1}{(n-1)!} \int_0^{\infty} t^{n-2} e^{-t\ln\lambda}\, dt \int_0^{\lambda\epsilon} e^{-u} \left[1 + t\ln u + \frac{t^2}{2} (\ln u)^2 + \cdots \right] du \end{aligned} \tag{A.17}$$

With negligible error for our purposes, we can extend the upper limit of the

u integral to ∞ [i.e., we neglect terms like $\exp(-\lambda\epsilon)$]. We therefore find

$$I_n \sim \frac{1}{(n-1)(\ln\lambda)^{n-1}} - \frac{C}{(\ln\lambda)^n} + \cdots \tag{A.18}$$

where

$$C = -\int_0^\infty \exp(-u)\ln u\, du = 0.5771 +$$

The J_n can be integrated by parts in similar fashion, leading to

$$\begin{aligned} J_n &\sim \frac{I_n}{n-1} + \frac{1}{(n-1)}\int_0^{\lambda\epsilon} e^{-u}\frac{\ln(\ln\lambda - \ln u)}{(\ln\lambda - \ln u)^{n-1}}\, du \\ &= \frac{I_n}{n-1} + \frac{1}{(n-1)!}\int_0^\infty t^{n-2}e^{-t\ln\lambda}\, dt \\ &\quad \times \int_0^{\lambda\epsilon} e^{-u}\ln(\ln\lambda - \ln u)\left[1 + t\ln u + \frac{t^2}{2}(\ln u)^2 + \cdots\right] du \end{aligned} \tag{A.19}$$

The lowest-order term will be given by

$$\frac{1}{(n-1)}\,\frac{1}{(\ln\lambda)^{n-1}}\int_0^{\lambda\epsilon} e^{-u}\ln(\ln\lambda - \ln u)\, du \tag{A.20}$$

and it is to the asymptotic properties of this last integral that we now turn our attention. The logarithmic term is infinite at $u = 0$, but otherwise the integrand is well behaved over the range of integration. Let us therefore dispose of the singular behavior at the origin by decomposing the range of integration into $(0, 1/\lambda) + (1/\lambda, \lambda\epsilon)$. In the first interval we have

$$\int_0^{1/\lambda} e^{-u}\ln\left(\ln\frac{\lambda}{u}\right) du \sim \int_0^{1/\lambda}\ln\left(\ln\frac{\lambda}{u}\right) du = \lambda\int_{\lambda^2}^\infty \ln(\ln v)\,\frac{dv}{v^2} \tag{A.21}$$

An integration by parts leads to

$$\lambda\int_{\lambda^2}^\infty \frac{\ln(\ln v)}{v^2}\, dv = \frac{\ln(2\ln\lambda)}{\lambda} + \lambda\int_{\lambda^2}^\infty \frac{dv}{v^2\ln v} \tag{A.22}$$

but

$$\lambda\int_{\lambda^2}^\infty \frac{dv}{v^2\ln v}\, dv < \frac{\lambda}{2\ln\lambda}\int_{\lambda^2}^\infty \frac{dv}{v^2} = \frac{1}{2\lambda\ln\lambda} \tag{A.23}$$

so that the contribution from the interval $(0, 1/\lambda)$ goes to 0 like $\ln(\ln\lambda)/\lambda$. Next, consider the integral over $(1/\lambda, \lambda\epsilon)$. The important point here is that the integrand in Eq. (A.20) is nowhere singular on this interval. We can therefore write

$$\int_{1/\lambda}^{\lambda\epsilon} e^{-u}\ln\left(\ln\frac{\lambda}{u}\right)du = \ln(\ln\lambda)\int_{1/\lambda}^{\lambda\epsilon} e^{-u}\,du + \int_{1/\lambda}^{\lambda\epsilon} e^{-u}\ln\left(1-\frac{\ln u}{\ln\lambda}\right)du \quad \text{(A.24)}$$

The first integral on the right-hand side is effectively equal to 1. The second integral can be written

$$-\int_{1/\lambda}^{\lambda\epsilon} e^{-u}\sum_{n=1}^{\infty}\frac{(\ln u)^n}{n(\ln\lambda)^n}\,du \sim -\sum_{n=1}^{\infty}\frac{1}{n(\ln\lambda)^n}\int_0^{\infty} e^{-u}(\ln u)^n\,du$$
$$\sim \frac{C}{\ln\lambda} + O\left(\frac{1}{\ln^2\lambda}\right) \quad \text{(A.25)}$$

Thus, we find that to lowest order

$$J_n \sim \frac{I_n}{n-1} + \frac{\ln(\ln\lambda)}{(n-1)(\ln\lambda)^{n-1}} \sim \frac{1}{(n-1)(\ln\lambda)^{n-1}}\left[\frac{1}{(n-1)} + \ln(\ln\lambda)\right] \quad \text{(A.26)}$$

We will not require any corrections to this formula for the text.

As a final step in the analysis, we must return to the integral in Eq. (A.3) and dispose of the contribution from ϵ to ∞. Since $\tau(\rho)$ is a monotonic function of ρ, we write

$$\int_{\epsilon}^{\infty}\frac{e^{-\lambda\rho}}{\rho}\,\frac{\tau^2(\rho)}{1+\frac{3}{2}\tau(\rho)}\,d\rho < \frac{2}{3}\int_{\epsilon}^{\infty}\frac{e^{-\lambda\rho}}{\rho}\,\tau(\rho)\,d\rho$$
$$= \frac{2}{3}\int_{\lambda\epsilon}^{\infty}\frac{e^{-\xi}}{\xi}\,\tau\left(\frac{\xi}{\lambda}\right)d\xi < \frac{2}{3}\int_{\lambda\epsilon}^{\infty}\frac{e^{-\xi}}{\xi}\,\tau(\xi)\,d\xi \quad \text{(A.27)}$$

By our assumption that $\lambda\epsilon \gg 1$, we can use the large ξ form [derived from Eq. (A.2)] for $\tau(\rho)$,

$$\tau(\rho) \sim \rho^{2/3} \quad \text{(A.28)}$$

which allows us to approximate the last integral on the right-hand side of Eq. (A.27) as

$$\frac{2}{3}\int_{\lambda\epsilon}^{\infty}\frac{e^{-\xi}\tau(\xi)}{\xi}\,d\xi \sim \frac{2}{3}\,\frac{e^{-\lambda\epsilon}}{(\lambda\epsilon)^{1/3}} \quad \text{(A.29)}$$

which tends to 0 as $\lambda\epsilon \to \infty$ at a faster rate than the terms retained from the integral over $(0, \epsilon)$.

APPENDIX B. EXPANSION OF EQ. (3.28) IN POWERS OF z

Let us first calculate the contribution to $\mu_{j,k}$ from the term $(\ln\lambda)^{-1}$, i.e., we will find the coefficient of z^{j-1}. Start by making the expansion

$$\frac{1}{\ln\lambda} = \frac{1}{\ln\lambda_0 + \ln(1-z)} = \sum_{n=0}^{\infty}(-1)^n \frac{\ln^n(1-z)}{(\ln\lambda_0)^{n+1}} \tag{B.1}$$

The powers of logarithms in this expression can be further expanded as[16]

$$\ln^n(1-z) = n! \sum_{j=n}^{\infty}(-1)^j S_j(n)\frac{z^j}{j!} \tag{B.2}$$

where $S_j(n)$ is a Stirling number of the first kind. Combining Eqs. (B.1) and (B.2), we find that the coefficient of z^{j-1} in $(\ln\lambda)^{-1}$ is

$$\frac{1}{(l-1)!}\sum_{n=1}^{\infty}(-1)^{n+l-1}\frac{n!}{(\ln\lambda_0)^{n+1}}S_{j-1}(n) \sim \frac{1}{(j-1)}\cdot\frac{1}{(\ln\lambda_0)^2}, \quad j>1 \tag{B.3}$$

where the last result is the lowest-order contribution in powers of $(\ln\lambda_0)^{-1}$. The next order term from $(\ln\lambda)^{-1}$ will be $O[(\ln\lambda_0)^{-3}]$. A second set of contributions will come from the term $1/(\ln\lambda)^2$. But

$$\frac{1}{(\ln\lambda)^2} = \sum_{n=1}^{\infty}(-1)^{n+1} n\frac{\ln^{n-1}(1-z)}{(\ln\lambda_0)^{n+1}} \tag{B.4}$$

so that the only correction that is $O[(\ln\lambda_0)^{-2}]$ will be that to $\mu_{1,k}$, the other corrections being at least $O[(\ln\lambda_0)^{-3}]$. The same conclusion follows from an analysis of the term $\ln(\ln\lambda)/(\ln\lambda)^2$. As a result, Eq. (3.29) gives the expression for $\mu_{1,k}$ correct to terms in $(\ln\lambda_0)^{-2}$.

APPENDIX C. ASYMPTOTIC EVALUATION OF HIGHER MOMENTS

The generating functions for higher moments are given by

$$\begin{aligned} U_{k,m}(z) &= \sum_{j=1}^{k}\mu_{j,k}(m)z^{j-1} = k\int_0^{\infty}t^{m-1}\left[1-h(t)(1-z)\right]^{k-1}\frac{dh}{dt}\,dt \\ &= \frac{m}{1-z}\int_0^{\infty}t^{m-1}\left\{\left[1-h(t)(1-z)\right]^k - z^k\right\}dt \\ &\sim \frac{m}{1-z}\int_0^{\infty}t^{m-1}e^{-k(1-z)h(t)}\,dt \end{aligned} \tag{C.1}$$

We transform to the dimensionless variable τ as in Eq. (A.1), allowing us to write

$$U_{k,m}(z) = \frac{mt_0^m}{1-z}\int_0^\infty \frac{\tau^{m+1}(\rho)}{1+\frac{3}{2}\tau(\rho)} e^{-\lambda\rho}\frac{d\rho}{\rho} = \frac{mt_0^m}{1-z} f_m(z) \tag{C.2}$$

where $f_m(z)$ is the integral by itself. The analog of Eq. (A.10) is found to be

$$f_m(z) \sim \int_0^\tau \frac{e^{-\lambda\rho}}{\rho}\left\{\frac{1}{\left(\ln\frac{1}{\rho}\right)^m\left(\ln\frac{1}{\rho}+\frac{3}{2}\right)} - \frac{\xi(\rho)\left[(m+1)\ln\frac{1}{\rho}+\frac{3m}{2}\right]}{\left(\ln\frac{1}{\rho}\right)^{m+1}\left(\ln\frac{1}{\rho}+\frac{3}{2}\right)^2}\right\} d\rho \tag{C.3}$$

Specifically, we will be interested in $f_2(z)$, which allows us to calculate the variance. For this case we can expand the terms in brackets in powers of $u = 1/[\ln(1/\rho)]$, finding

$$\{\ \} = \frac{1}{u^3} - \frac{3}{2u^4}(3\ln u + 1) + \cdots \tag{C.4}$$

so that when $m = 2$

$$f_2(z) \sim I_3 - \tfrac{3}{2}I_4 - \tfrac{9}{2}J_4 \tag{C.5}$$

where I's and J's are defined in Eq. (A.12). Using the estimates derived in Appendix A, we find that

$$f_2(z) \sim \frac{1}{2(\ln\lambda)^2} - \frac{\{C + 1 + \frac{3}{2}\ln[\ln(\lambda)]\}}{(\ln\lambda)^3} + \cdots \tag{C.6}$$

Expressions for the generating functions of higher moments are easily developed using the same techniques.

APPENDIX D. SMALL τ BEHAVIOR OF $h(\tau)$ FOR GENERAL FP EQUATIONS

Equation (4.9) has a formal expression for $p(y,\tau)$ which can be used to furnish the following formula for $h(\tau)$:

$$h(\tau) = \int_0^1 p(\xi,0)a_2(\xi)e^{-\epsilon U(\xi)}\,d\xi \int_0^1 \frac{e^{\epsilon U(y)}}{a_2(y)} \times \left\{\sum_{j=0}^\infty \phi_j(y)\phi_j(\xi)(1-e^{-\lambda_j\tau})\right\} dy \tag{D.1}$$

Thus, we need to investigate properties of the series

$$I(y,\xi;\tau) \equiv \sum_{j=0}^{\infty} \phi_j(y)\phi_j(\xi)(1 - e^{-\lambda_j\tau}) \tag{D.2}$$

for small τ. Since the part of this series containing the exponential terms is a Dirichlet's series,[17] its behavior as $\tau \to 0$ will be determined by the large j behavior of the $\phi_j(y)$ and λ_j. These properties were first investigated by Liouville and can be written in terms of the function

$$\beta(y) = \int_0^y \frac{d\xi}{[a_2(\xi)]^{1/2}}, \qquad \gamma(y) = \beta(y)/\beta(1) \tag{D.3}$$

For large j one finds[14]

$$\lambda_j \sim j^2\pi^2/\beta^2(1), \qquad \phi_j(y) \sim A_j\left[a_j(y)e^{-\epsilon U(y)/2}\right]^{1/4} \sin \pi j\gamma(y) \tag{D.4}$$

where A_j is the normalizing constant found from

$$\frac{1}{A_j^2} = \int_0^1 \left[a_2(y)e^{-\epsilon U(y)/2}\right]^{1/2} \sin^2 \pi j\gamma(y)\, dy \tag{D.5}$$

For large j we can invoke the Riemann–Lebesgue[18] lemma to infer that $A_j^2 \to A^2$ where

$$A^2 = 2\left\{\int_0^1 a^{1/2}(y)e^{-\epsilon U(y)/4}\, dy\right\}^{-1} \tag{D.6}$$

Hence, the small τ behavior of $I(y,\xi;\tau)$ is, to lowest order, that of

$$I(y,\xi;\tau) \sim A^2\left(a_2(y)a_2(\xi)\exp\left\{-\frac{\epsilon}{2}\left[U(y) + U(\xi)\right]\right\}\right)^{1/2} \times \sum_{j=0}^{\infty} \sin \pi j\gamma(y) \sin \pi j\gamma(\xi)\left\{1 - \exp\left[-\frac{j^2\pi^2\tau}{\beta^2(1)}\right]\right\} \tag{D.7}$$

But the last series can be regarded as the difference of two series, the first of which is proportional to $\delta[\gamma(y) - \gamma(\xi)]$ and the second of which has the same form as Eq. (3.3). Therefore, its asymptotic dependence on τ, to lowest order is the same as that derived from Eq. (3.3). We may infer from this that the dependence of the moments on k is the same as that for simple diffusion, at least to lowest order.

REFERENCES

1. G. H. Weiss, *Adv. Chem. Phys.* **13**:1 (1967).
2. I. Oppenheim, K. E. Shuler, and G. H. Weiss, *Physica* **88A**:191 (1977).
3. R. M. Levy, M. Karplus, and J. A. McCammon, *Chem. Phys. Lett.* **65**:4 (1979).

4. A. Szabo, K. Schulten, and Z. Schulten, *J. Chem. Phys.* **72**:4350 (1972).
5. V. Seshadri, B. J. West, and K. Lindenberg, *J. Chem. Phys.* **72**:1145 (1980).
6. K. Schulten, Z. Schulten, and A. Szabo, *J. Chem. Phys.* **74**:4426 (1981).
7. M. von Smoluchowski, *Ann. Phys. (Leipzig)* **21**:756 (1906).
8. E. Schrödinger, *Phys. Z.* **16**:289 (1915).
9. K. Lindenberg, V. Seshadri, K. E. Shuler, and G. H. Weiss. *J. Stat. Phys.* **23**:11 (1980).
10. W. Feller, *An Introduction to Probability Theory and Its Applications*, 2nd ed., Vol. I (John Wiley & Sons, New York, 1957).
11. E. J. Gumbel, *Statistics of Extremes* (Columbia University Press, New York, 1958).
12. R. A. Fisher and L. H. C. Tippett, *Proc. Camb. Phil. Soc.* **24**:180 (1928).
13. V. Seshadri and K. Lindenberg, *J. Stat. Phys.* **22**:69 (1980).
14. R. Courant and D. Hilbert, *Methods of Mathematical Physics*, Vol. I (Interscience Publishers, Inc., New York, 1953).
15. S. A. Molchanov, *Russ. Math. Surveys* **30**:1 (1975).
16. M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (U.S. Government Printing Office, Washington, D.C., 1964), p. 824.
17. G. H. Hardy, *Divergent Series* (Oxford University Press, London, 1949).
18. E. C. Titchmarsh, *The Theory of Functions*, 2nd ed., (Oxford University Press, London, 1939).