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Diffusion with Random Traps: Transient One-Dimensional Kinetics in a Linear Potential

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The problem of one-dimensional diffusion with random traps is solved without and with a constant field of force. Using an eigenvalue expansion for long times and the method of images for short times we give an exact, straightforward solution for the time dependence of the mean survival probability and the mean probability density for returning to the origin. Using the backward equation approach, we determine the mean survival time and the mean residence time density at the origin. We comment on the relation between these solutions and those for one-dimensional diffusion with random reflectors.

KEY WORDS: Diffusion; random traps; random reflectors; survival probability; mean survival, residence and relaxation times; method of images.

1. INTRODUCTION

There has recently been considerable interest in the temporal properties of a random walk or a diffusion process among a random distribution of stationary sinks.[1-20] The main properties investigated were[1-17] (a) the survival probability, (b) the probability density for returning to the origin, (c) the mean absorption time,[18-20] and (d) the mean square deviation.[3,12] The experimental significance of these properties, especially for kinetic processes in random materials, is discussed in the literature.[1-20]

The problem of determining the survival probability over the whole time regime can be tackled analytically only for the one-dimensional problem.[11-13] The solutions given in the literature are not always the most straightforward or complete and tend to put most emphasis on the asymptotic long-time behavior. In particular, the fact that for short times

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the "method of images"[21] is the most natural route to the solution has not been appreciated. We show (Sec. 2) that only a few terms from the ensuing function series are needed to smoothly connect the solution with the first few terms from the eigenfunction expansion, which converges rapidly for long times.

The case of biased random walk (or diffusion in an external potential) has been treated asymptotically[7b,15c] to show that bias restores exponentially in the temporal decay. Reference 11(c) obtained the full one-dimensional solution for the survival probability in a very tedious way, by inverting the Laplace transform. We generalize (Sec. 3) in a straightforward manner the free diffusion case to that of a constant field of force (linear potential) in one dimension to obtain both short- and long-time solutions. We also determine, by the backward equation approach, the mean survival time and the mean residence time at the origin.

Finally (Sec. 4) we discuss the relaxation process for diffusion with random reflectors. The mean return (to the origin) probability density and relaxation time are simply related to corresponding properties of diffusion with random traps.

The results below are for the continuous diffusion model, which serves as a good approximation to the discrete random walk problem for low trap concentration. (Of course, it is exact for all concentrations in the continuous case). For high trap concentration the discrete problem would have to be solved analogously or by other methods.

2. FREE DIFFUSION

The diffusion equation to be solved is

$$\partial p/\partial t = \partial^2 p/\partial x^2 \tag{1}$$

where x is a one-dimensional coordinate, t is time multiplied by a diffusion constant D, and p is the probability density. For infinitely deep traps no density can cross from one side of a trapping point to the other. Hence, the line is divided to intervals of length l, which is a randomly distributed parameter. The problem is reduced to obtaining the appropriate average of the solution for diffusion in an interval with two absorbing boundaries

$$p(0, t) = p(l, t) = 0 \tag{2}$$

As an initial condition we take a point source at x_0

$$p(x, 0) = \delta(x - x_0) \tag{3}$$

and denote the solution obtained under these conditions by $p(x, t \mid x_0)$. It is the transition probability density for transitions from x_0 to x in a time interval t/D.

Given the one-dimensional solution with two absorbing boundaries, $p(x, t \mid x_0)$, one can (i) sum over x and average uniformly over x_0 to obtain the survival probability $Q(t)$

$$Q(t) = l^{-1} \int_0^l dx_0 \int_0^l dx\, p(x, t \mid x_0) \tag{4}$$

or (ii) set $x = x_0$ and average to obtain the probability density $P(t)$ for returning to the origin

$$P(t) = l^{-1} \int_0^l p(x, t \mid x)\, dx \tag{5}$$

The desired result for random traps is reached by averaging these solutions with respect to the weight $w(l)$ for an interval of length l

$$\langle Q \rangle = \int_0^\infty Q(t)\, w(l)\, dl \tag{6a}$$

$$\langle P \rangle = \int_0^\infty P(t)\, w(l)\, dl \tag{6b}$$

The probability of finding an interval of length l, formed by a random distribution of points on the line, is just the one-dimensional nearest-neighbor distribution ce^{-cl}, where c is the trap concentration (number of point traps per unit length). Since the uniform distribution of starting points weighs each interval by its length l, we multiply the nearest-neighbor distribution by l and normalize to obtain[12]

$$w(l) = c^2 l e^{-cl} \tag{7}$$

The solution of (1) under conditions (2) and (3) is an infinite sum which can be written in two ways. The first is an eigenfunction expansion, isomorphic to that of a "particle in a box" in quantum mechanics

$$p(x, t \mid x_0) = \frac{2}{l} \sum_{j=1}^{\infty} \sin\left(\frac{j\pi x}{l}\right) \sin\left(\frac{j\pi x_0}{l}\right) \exp\left(-\frac{j^2\pi^2 t}{l^2}\right) \tag{8}$$

This solution converges rapidly for large t. As $t \to \infty$ only the lowest eigenvalue, $j = 1$, contributes. For shorter times additional terms are needed.

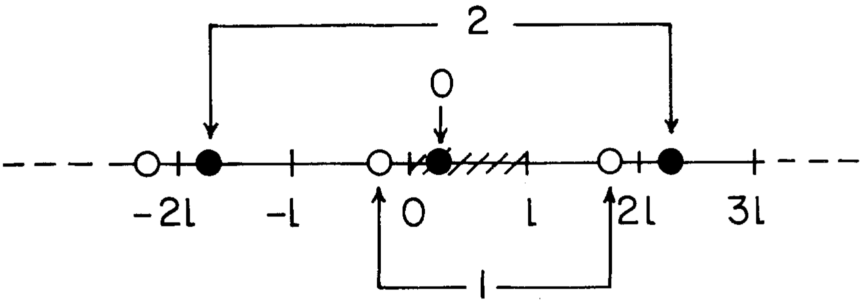


Fig. 1. The point sources on the line for the solution by the method of images, (9), for free diffusion in the interval $(0, l)$ and an initial delta function at x_0. Full circles: positive sources [first term in (9)]; open circles: negative sources (second term). The contributions from these sources are collected in the order 0, 1, 2,... shown, according to their proximity to the initial excitation.

The second solution is obtained by the "method of images,"[21] with which one is well-acquainted in electrostatics

$$p(x, t \mid x_0) = \frac{1}{2\sqrt{\pi t}} \sum_{j=-\infty}^{\infty} \left\{ \exp\left[-\frac{(x - x_0 + 2jl)^2}{4t} \right] - \exp\left[-\frac{(x + x_0 + 2jl)^2}{4t} \right] \right\} \tag{9}$$

(The initial density is concentrated at the points shown in Fig. 1). This solution converges rapidly for small t. Equations (8) and (9) are connected by the "Poisson summation formula."[21]

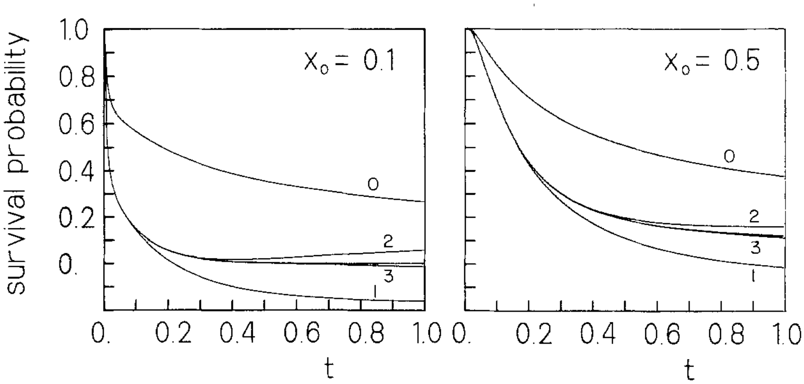


Fig. 2. Convergence of the serial solution (16) for two different initial conditions x_0. The first five partial sums are shown.

When $t \sim 0$ the effect of the boundaries is not felt yet, so the initial delta function at x_0 widens just as if it were free diffusion. This is the term $j=0$ in the first exponential. As time advances and probability density reaches the boundaries, it is nullified there by the two negative point sources located initially at $-x_0$ and $2l-x_0$ (see Fig. 1). These are the terms $j=0$ and $j=-1$ in the second exponential. Later these densities reach the further boundaries and are nullified there by the positive sources located initially at $\pm 2l + x_0$, which are the terms $j=\pm 1$ in the first exponential, and so on. This is the order in which we will collect the terms in the short time expansions.

Following this preliminary background, we now give the relevant solutions for free diffusion.

Survival Probability

For long times we find, by inserting (8) in (4), that

$$Q(t) = \frac{8}{\pi^2} \sum_{j=0}^{\infty} (2j+1)^{-2} \exp\left(- \frac{(2j+1)^2 \pi^2}{l^2} t \right) \tag{10}$$

Note that the even terms in (8) have disappeared (the integral of a sine over a multiple of 2π is zero). Subsequently, using (7) one has

$$\langle Q \rangle = \frac{8c^2}{\pi^2} \sum_{j=0}^{\infty} (2j+1)^{-2} \int_0^{\infty} \exp\left(- \frac{(2j+1)^2 \pi^2 t}{l^2} - cl \right) l\, dl \tag{11}$$

It is possible[1,11c] to perform the summation analytically as in (52b) or, defining $v_j \equiv [(2j+1)^2 \pi^2 t/c]^{-1/3}\, l$ and $\alpha_j \equiv [c^2 (2j+1)^2 \pi^2 t]^{1/3}$ to rewrite (11) as

$$\langle Q \rangle = 8(c^2 t/\pi)^{2/3} \sum_{j=0}^{\infty} (2j+1)^{-2/3} \int_0^{\infty} \exp[-\alpha_j (v_j + v_j^{-2})]\, v_j\, dv_j \tag{12}$$

The complete asymptotic expansion of the integral (for the dominant $j=0$ term) is obtained in Ref. 13b

$$\langle Q \rangle \sim 16c(t/3\pi)^{1/2} \exp\left(-\frac{3}{2} z \right) \left[1 + \sum_{k=1}^{\infty} a_k z^{-k} \right] \tag{13}$$

with $z \equiv (2\pi^2 c^2 t)^{1/3}$. The first term in the expansion is the steepest descent approximation, as given in Ref. 11, (the erratum to) Ref. 9(a), and Eq. (13) of Ref. 12 [after correcting the printing errors therein. In the discrete case discussed there c is replaced by $-\ln(1-c)$]. The first few coefficients in the expansion are $a_1 = 17/18$, $a_2 = 205/648$, $a_3 = -3115/34992$, and $a_4 = 137305/2519424$. This agrees with the asymptotic expansion for the survival probability obtained in Ref. 13(a) by a different route.

Considering next the short time solution, by integral (A1) of Appendix A and (9), one gets

$$Q(t \mid x_0) \equiv \int_0^l p(x, t \mid x_0)\, dx$$
$$= \frac{1}{2} \sum_{j=-\infty}^{\infty} \left[2 \operatorname{erf}\left(\frac{x_0 + 2jl}{2\sqrt{t}}\right) - \operatorname{erf}\left(\frac{x_0 + (2j-1)l}{2\sqrt{t}}\right) - \operatorname{erf}\left(\frac{x_0 + (2j+1)l}{2\sqrt{t}}\right)\right] \tag{14}$$

where $\operatorname{erf}(x)$ is the error function. As discussed following (9), we collect the terms in the formal series (14) according to their importance for short-time convergence. This leads to the following finite-sum approximation

$$Q_0(t \mid x_0) = \frac{1}{2} \left[\operatorname{erf}(\tfrac{1}{2} x_0 t^{-1/2}) + \operatorname{erf}(\tfrac{1}{2} x_1 t^{-1/2})\right] \tag{15}$$

$$Q_n(t \mid x_0) = Q_{n-1}(t \mid x_0) - \frac{1}{2}(-1)^n \left[\operatorname{erf}\left(\frac{(n-1)l + x_0}{2\sqrt{t}}\right) + \operatorname{erf}\left(\frac{(n-1)l + x_1}{2\sqrt{t}}\right) - \operatorname{erf}\left(\frac{nl + x_0}{2\sqrt{t}}\right) - \operatorname{erf}\left(\frac{nl + x_1}{2\sqrt{t}}\right)\right] \tag{16}$$

where Q is the limit of Q_n as $n \to \infty$. Notice that this solution is invariant for interchanging x_0 and $x_1 \equiv l - x_0$, as it should be. This solution is demonstrated in Fig. 2 for $n = 0$ to 4.

We now calculate

$$\langle Q_n \rangle \equiv c^2 \int_0^\infty dl\, e^{-cl} \int_0^l dx_0\, Q_n(t \mid x_0) \tag{17}$$

Using the integral (A3) of Appendix A we find that

$$\langle Q_0 \rangle = f_1(c) \equiv e^{c^2 t} \operatorname{erfc}(c\sqrt{t}) \tag{18a}$$

$$\langle Q_1 \rangle = \langle Q_0 \rangle + 2f_1(c) - f_2(c) \tag{18b}$$

$$\langle Q_n \rangle = \langle Q_{n-1} \rangle + (-1)^n [f_{n+1}(c) - 2f_n(c) + f_{n-1}(c)] \tag{18c}$$

where $\langle Q \rangle = \lim_{n \to \infty} \langle Q_n \rangle$,

$$f_j(x) \equiv j \exp(x^2 t/j^2) \operatorname{erfc}(x\sqrt{t}/j) \tag{19}$$

and $\operatorname{erfc}(x) \equiv 1 - \operatorname{erf}(x)$ is the complementary error function.

Equation (18c) is the general solution for all $n = 0, 1, \ldots$ when we define $f_{-1}(x) \equiv f_0(x) = 0$ and $\langle Q_{-1} \rangle \equiv 0$. The necessary criterion for convergence, that the term $f_{n+1} - 2f_n + f_{n-1}$ decreases with n, holds because $f_n(x) \to n$ as $n \to \infty$. This term also vanishes for $t \to 0$, since $f_n(0) = n$, and the main contribution is from $\langle Q_0 \rangle$. Equation (18c) can also be written as

$$\langle Q_n \rangle = -4 \sum_{j=1}^{n-1} (-1)^j f_j(c) + (-1)^n [f_{n+1}(c) - 3f_n(c)] \tag{20}$$

The zero-order approximation, (18a), is just a nearest-neighbor approximation. The survival probability due to a nearest-neighbor static trap at distance x_0 (we ignore the other traps) is easily obtainable by the method of images[21]

$$Q^{nn}(t \mid x_0) = \mathrm{erf}(\tfrac{1}{2} x_0 t^{-1/2}) \tag{21}$$

Averaging over the nearest-neighbor distribution, we find for $t \to 0$

$$\langle Q \rangle \approx c \int_0^\infty Q^{nn}(t \mid x_0)\, e^{-cx_0}\, dx_0 = e^{c^2 t}\, \mathrm{erfc}(c \sqrt{t}) \tag{22}$$

The nearest-neighbor approximation is the asymptotic solution for $t \to 0$, and a strict upper bound in any dimensionality, a fact not appreciated in the literature.

The solution of the one-dimensional problem via (11) and (18) is demonstrated in Fig. 3. The criterion for convergence is that the two solutions connect smoothly at intermediate times. We see from the left panel of Fig. 3(a) that when we take $\langle Q_2 \rangle$ from (18) and the first two eigenvalues in (11) the connection is almost perfect (with one additional term the curves already overlap). It is seen that, for these short times the steepest-descent approximation [the zeroth term in (13)] grossly underestimates the exact integral (11). Hence the importance of the complete asymptotic expansion (13).

The left panel of Fig. 3(a) also shows (line with circles) the short-time approximation[1] for the discrete random walk model[12,14]

$$\langle Q \rangle \approx \exp\left[-c \left(\frac{\ln(1/c) t}{\pi(1-c)} \right)^{1/2} \right] \tag{23}$$

We see that (23) is somewhat better than our zero-order approximation $\langle Q_0 \rangle$, but still a rather poor approximation for the exact result in this time regime. The right panel of Fig. 3(a) shows the decay of the survival probability for longer times. Fig. 3(b) shows it in a logarithmic scale.

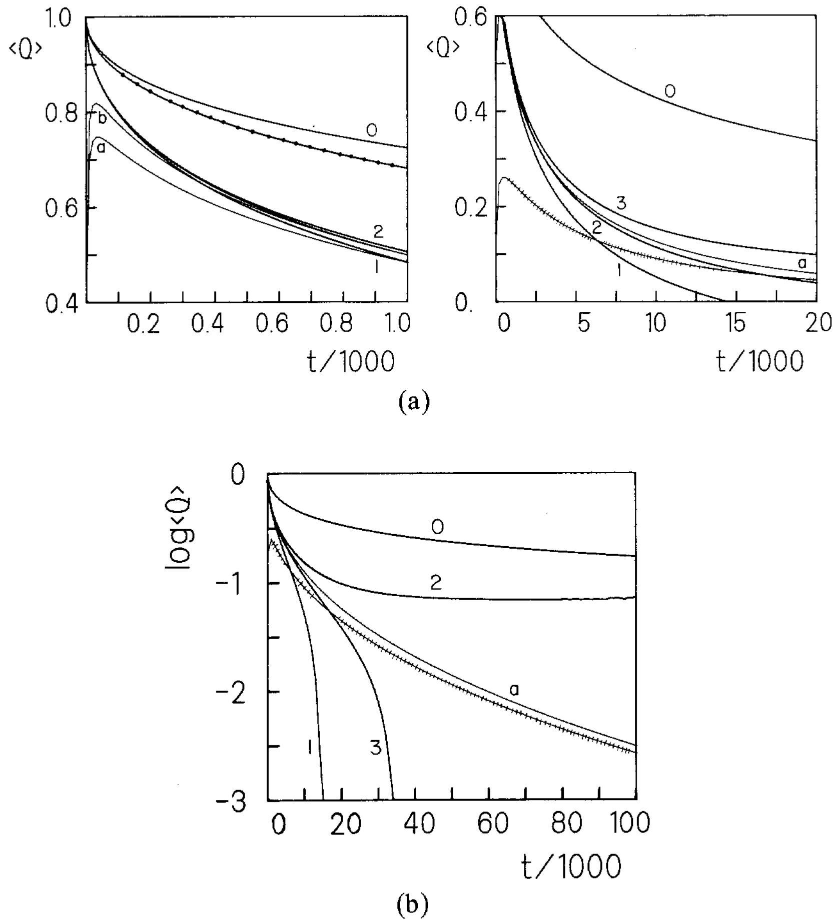


Fig. 3. (a) Temporal decay of the survival probability for one-dimensional free diffusion with random traps at a concentration $c = 0.01$. Curves denoted by 0, 1, 2 are the short-time solutions $\langle Q_0 \rangle$, $\langle Q_1 \rangle$, and $\langle Q_2 \rangle$; (18). Curves, denoted by a, b, etc., are the eigenvalue expansions, (11) with 1, 2,... eigenvalues. The line with circles is the short-time approximation, (23), that with tick marks is the steepest-descent approximation. Inclusion of three to four terms in the expansion (13), gives[13b] an adequate representation of the exact integral (line a) for $t > 200$. Short- and medium-time regimes are shown in the two panels. In the short-time regime numerical integration in (12) was performed using 750 points for $v = 0.05$ to 17. For long times 500 points were used for $v = 0.1$ to 10. (b) Same as (a) in a logarithmic (base 10) scale.

The Return Probability Density

For long times we set $x = x_0$ in (8) to give

$$p(x, t \mid x) = \frac{2}{l} \sum_{j=1}^{\infty} \sin^2\left(\frac{j\pi x}{l}\right) \exp\left(-\frac{j^2\pi^2}{l^2} t\right) \tag{24}$$

Inserting in (5) and subsequently in (6b) one finds

$$P(t) = l^{-1} \sum_{j=1}^{\infty} \exp(-j^2\pi^2 t/l^2) \tag{25}$$

$$\langle P \rangle = c \sum_{j=1}^{\infty} \alpha_j \int_0^{\infty} \exp[-\alpha_j(v_j + v_j^{-2})]\, dv_j \tag{26}$$

where α_j and v_j are defined as in (12). The complete asymptotic expansion (for $j = 1$) yields[13b]

$$\langle P \rangle \sim c \left(\frac{2\pi z}{3}\right)^{1/2} \exp\left(-\frac{3}{2} z\right)\left[1 + \sum_{k=1}^{\infty} b_k z^{-k}\right] \tag{27}$$

with $z \equiv (2c^2\pi^2 t)^{1/3}$. The zeroth term is the steepest descent approximation, as given in the literature.[7a,11] The additional three coefficients are[13b] $b_1 = 5/18$, $b_2 = -35/648$, and $b_3 = 665/34992$.

For short times we set $x = x_0$ in (9) to give

$$p(x, t \mid x) = \frac{1}{2\sqrt{\pi t}} \left\{1 + 2 \sum_{j=1}^{\infty} \exp(-j^2 l^2/t) - \sum_{j=-\infty}^{\infty} \exp[-(x + jl)^2/t]\right\} \tag{28}$$

For averaging over x as in (5) we use integral (A1) of appendix A. The term in the curly brackets there, when summed over all j from $-\infty$ to ∞, gives $2\,\mathrm{erf}(\infty) = 2$. Therefore

$$P(t) = \tfrac{1}{2}[(\pi t)^{-1/2} - l^{-1}] + (\pi t)^{-1/2} \sum_{j=1}^{\infty} \exp(-j^2 l^2/t) \tag{29}$$

Finally, inserting into (6b) one finds (the Laplace transform of the Gaussian terms is determined by completing to squares)

$$2\langle P \rangle = (\pi t)^{-1/2} - c + c^2 t \sum_{j=1}^{\infty} j^{-2}[(\pi t)^{-1/2} - c(2j)^{-2} f_{2j}(c)] \tag{30}$$

where $f_j(x)$ is given by (19).

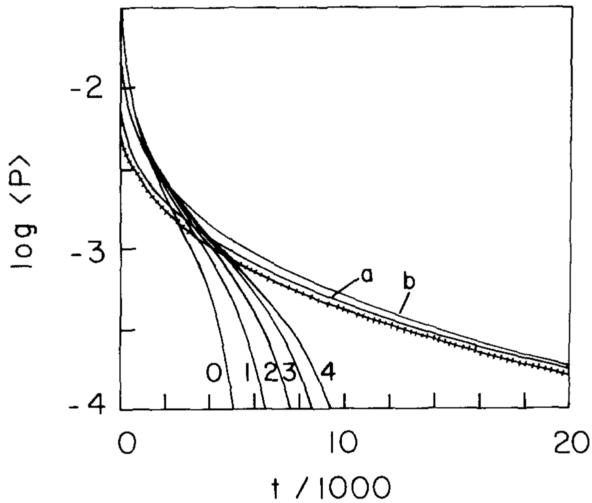


Fig. 4. Temporal decay of the mean return-to-the-origin probability density, $\langle P \rangle$, for one-dimensional free diffusion with random traps at a concentration $c = 0.01$. Logarithmic scale (base 10). Curves denoted by 1, 2,... are partial sums in (30). Curves denoted by a and b are for 1 and 2 eigenvalues in (26), integrated numerically (400 grid points for $v = 0.1$ to 10). The line with tick marks is the steepest-descent approximation. Inclusion of just one term in the expansion (27), gives[13b] an adequate approximation to the exact integral (line a).

The convergence of the solutions in (26) and (30) is shown in Fig. 4, as well as the zeroth term in (27). This graph should be compared to Fig. 6 of Ref. 11(b). Note however, that as a probability density $\langle P \rangle \to \infty$ (not to 1) as $t \to 0$.

First Passage Times

The average survival time for free diffusion in an interval of length l with two absorbing boundaries

$$\tau = \int_0^\infty Q(t)\, dt \tag{31}$$

(the survival probability $Q(t)$ is defined in (4)) can determined from a direct integration of (10)

$$\tau = \frac{8l^2}{\pi^4} \sum_{j=0}^{\infty} (2j+1)^{-4} = \frac{l^2}{12} \tag{32}$$

or, in the backward equation, approach[22] by solving

$$d^2\tau(x_0)/dx_0^2 = -1 \tag{33}$$

for

$$\tau(x_0) \equiv \int_0^\infty dt \int_0^l dx\, p(x, t \mid x_0) \tag{34}$$

with absorbing boundary conditions at $x_0 = 0$ and l. The result is

$$\tau(x_0) = \tfrac{1}{2} x_0 (l - x_0) \tag{35}$$

Averaging over x_0

$$\tau = l^{-1} \int_0^l \tau(x_0)\, dx_0 = \frac{l^2}{12} \tag{36}$$

gives the same result as (32). The final stage is averaging with respect to the distribution $w(l)$ of (7)

$$\langle \tau \rangle = \int_0^\infty \tau\, w(l)\, dl = \tfrac{1}{2} c^{-2} \tag{37}$$

In the discrete case, the average number of steps to trapping, $\langle N \rangle$, is given by[19]

$$\langle N \rangle = (1 - c)/c^2 \tag{38}$$

After identifying $\tau = N/2$ we see that (37) is indeed a small concentration approximation to (38).

It may be interesting to evaluate the mean residence time density at the origin, $\langle T \rangle$. This quantity relates to the return probability density $\langle P \rangle$ just as $\langle \tau \rangle$ relates to the survival probability $\langle Q \rangle$

$$\langle \tau \rangle = \int_0^\infty \langle Q \rangle\, dt \tag{39a}$$

$$\langle T \rangle = \int_0^\infty \langle P \rangle\, dt \tag{39b}$$

First we evaluate the mean residence time density[22b]

$$\tau(x \mid x_0) = \int_0^\infty p(x, t \mid x_0)\, dt \tag{40}$$

for a segment of length l. It obeys[22b]

$$\partial^2 \tau(x \mid x_0)/\partial x^2 = \partial^2 \tau(x \mid x_0)/\partial x_0^2 = 0 \tag{41}$$

with the appropriate absorbing boundary conditions. The solution

$$l\,\tau(x\,|\,x_0)=\begin{cases}x(l-x_0), & x<x_0\\ x_0(l-x), & x>x_0\end{cases} \tag{42}$$

evaluated at $x=x_0$, is averaged over a uniform distribution in x_0

$$T\equiv l^{-1}\int_0^l \tau(x\,|\,x)\,dx=\frac{l}{6} \tag{43}$$

and finally over the random trap distribution to obtain

$$\langle T\rangle=c^2\int_0^\infty T\,e^{-cl}\,l\,dl=(3c)^{-1} \tag{44}$$

The same result is obtained from the time integral of (26).

Roughly speaking, if ε is an infinitely small interval around the origin (so small that the probability $ce^{-c\varepsilon}$ of finding a trap in it is negligible) then $\varepsilon\langle T\rangle$ would be the average time spent in this interval. In the discrete case, if ε is the distance between adjacent sites, $2\varepsilon\langle T\rangle$ estimates the average number of returns to the origin, which is therefore inversely proportional to c.

Mean Square Deviation

An asymptotic evaluation for large t is given at the end of Ref. 12.

3. LINEAR POTENTIAL

The diffusion equation to be solved is now

$$\frac{\partial p}{\partial t}=\frac{\partial^2 p}{\partial x^2}+2a\frac{\partial p}{\partial x}=\frac{\partial}{\partial x}e^{-2ax}\frac{\partial}{\partial x}e^{2ax}p \tag{45}$$

with the same boundary and initial conditions as in (2) and (3). In the discrete case, this is a biased random walk with jump probabilities $W_\pm$ for transitions $n\to n\pm 1$ given by

$$W_\pm=\tfrac{1}{2}e^{\pm a}\approx\tfrac{1}{2}(1\pm a) \tag{46}$$

It is well-known that the transformation

$$q(x,t\,|\,x_0)=\exp[a(x-x_0+at)]\,p(x,t\,|\,x_0) \tag{47}$$

reduces (45) to the free diffusion case, $\partial q/\partial t = \partial^2 q/\partial x^2$ with the same boundary and initial conditions. Therefore, the long- and short-time expansions of (8) and (9) should simply be multiplied by $\exp[-a(x-x_0+at)]$.

As a result, the average return probability density, $\langle P\rangle$ in (26), (27), and (30), should simply be multiplied by e^{-a^2t}. Asymptotically at large t, t wins over $t^{1/3}$ and the decay becomes exponential, irrespective of the value of a. For any $x \neq x_0$, the free diffusion solution is multiplied also by $\exp[-a(x-x_0)]$. Hence the result for $\langle Q\rangle$ is not simply[(7b)] that of free diffusion multiplied by e^{-a^2t}. We shall now carry out the necessary integrations for evaluating the survival probability.

Survival Probability, Long Times

Our starting point is (8). Using the result

$$\int_0^l e^{ax} \sin\left(\frac{j\pi x}{l}\right) dx = \frac{j\pi l[1-(-1)^j e^{al}]}{a^2 l^2 + j^2\pi^2} \tag{48}$$

we find [cf. (4)]

$$\begin{aligned} Q(t) = 2\pi^2 e^{-a^2 t} \sum_{j=1}^{\infty} & j^2[1-(-1)^j e^{al}][1-(-1)^j e^{-al}] \\ & \times (a^2 l^2 + j^2\pi^2)^{-2} \exp[-j^2\pi^2 t/l^2] \end{aligned} \tag{49}$$

This result is invariant for replacement of a by $-a$. For $a=0$ it reduces to (10). For $z \equiv al$ the normalization condition, $Q(0)=1$, yields the following identity

$$1 = 2\pi^2 \sum_{j=1}^{\infty} [1-(-1)^j e^z][1-(-1)^j e^{-z}] j^2/(z^2+j^2\pi^2)^2 \tag{50}$$

valid for any real z. The special case $z=0$ is a well-known sum (0.234.2 in Ref. 23(b)). The more general (50) is also derived in Appendix B by methods of complex analysis. The convergence of the series (49) and (50) deteriorates rapidly with increasing z.

Inserting (49) in (6a) we finally get

$$\begin{aligned} \langle Q\rangle = 4\pi^2 c^2 e^{-a^2 t} \int_0^{\infty} \sum_{j=1}^{\infty} & [1-(-1)^j \cosh(al)] \\ & \times [j/(a^2 l^2 + j^2\pi^2)]^2 \exp(-j^2\pi^2 t/l^2 - cl) l\, dl \end{aligned} \tag{51}$$

This result reduces for $a=0$ to (11). It has been obtained in Ref. 11(c) by a more tedious route. By substituting $x = l/j$ it is possible to transfer the summation variable j to the second exponent. Summation of the resulting geometrical series gives[11c] for $|a| < c$

$$\langle Q \rangle = 2\pi^2 c^2 e^{-a^2 t} \int_0^\infty \left[\frac{e^{ax}}{e^{cx} + e^{ax}} + \frac{2}{e^{cx} - 1} + \frac{e^{-ax}}{e^{cx} + e^{-ax}} \right]$$

$$\times \frac{x}{(a^2 x^2 + \pi^2)^2} \exp(-\pi^2 t / x^2)\, dx \tag{52}$$

Note that (52) is invariant for replacement of a by $-a$, as it should be, and its asymptotic behavior for large t is $e^{-a^2 t}$.

When $|a| \geqslant c$: (i) it is not permissible to change the order of summation and integration in (51), (ii) the geometric series does not converge, and (iii) analytic continuation of (52) in the complex a-plane is probably not possible. The asymptotic behavior in this case is worked out in Ref. 11c.

Survival Probability, Short Times

We shall first integrate $p(x, t \mid x_0)$ over x to get $Q(t \mid x_0)$ then average over x_0 and l. In the first step, use of Eq. (7.4.32) in Ref. 23(a) gives

$$Q(t \mid x_0) \equiv e^{-a^2 t} \int_0^\infty e^{-a(x - x_0)} p^f(x, t \mid x_0)\, dx$$

$$= \tfrac{1}{2} \sum_{j=-\infty}^{\infty} e^{2ajl} \{ \operatorname{erf}[(\tfrac{1}{2}x_0 - at - jl)/\sqrt{t}\,] + \operatorname{erf}[(\tfrac{1}{2}x_1 + at + jl)/\sqrt{t}\,]$$

$$+ e^{2ax_0} \operatorname{erf}[(\tfrac{1}{2}x_0 + at + jl)/\sqrt{t}\,]$$

$$- e^{2ax_0} \operatorname{erf}[(\tfrac{1}{2}x_0 + \tfrac{1}{2}l + at + jl)/\sqrt{t}\,] \} \tag{53}$$

$p^f(x, t \mid x_0)$ is the solution for free diffusion, as given in (9), and $x_1 \equiv l - x_0$. To recall the order in which the terms in (53) should be collected [see discussion following (9)], we rewrite it as finite sum approximations

$$Q_0(t \mid x_0) = \tfrac{1}{2}[\operatorname{erf}(\tfrac{1}{2}x_0/\sqrt{t} - a\sqrt{t}) + \operatorname{erf}(\tfrac{1}{2}x_1/\sqrt{t} + a\sqrt{t})] \tag{54a}$$

$$Q_1(t \mid x_0) = Q_0(t \mid x_0)$$

$$+ \tfrac{1}{2} e^{2ax_0} \{ \operatorname{erf}(\tfrac{1}{2}x_0/\sqrt{t} + a\sqrt{t}) + e^{-2al} \operatorname{erf}(\tfrac{1}{2}x_1/\sqrt{t} - a\sqrt{t})$$

$$- \operatorname{erf}[\tfrac{1}{2}(l + x_0)/\sqrt{t} + a\sqrt{t}\,]$$

$$- e^{-2al} \operatorname{erf}[\tfrac{1}{2}(l + x_1)/\sqrt{t} - a\sqrt{t}\,] \} \tag{54b}$$

$$
\begin{aligned}
Q_2(t \mid x_0) = Q_1(t \mid x_0) & \\
& - \tfrac{1}{2}\{e^{-2al}\operatorname{erf}[\tfrac{1}{2}(l+x_0)/\sqrt{t} - a\sqrt{t}] \\
& + e^{2al}\operatorname{erf}[\tfrac{1}{2}(l+x_1)/\sqrt{t} + a\sqrt{t}] \\
& - e^{-2al}\operatorname{erf}[\tfrac{1}{2}(2l+x_0)/\sqrt{t} - a\sqrt{t}] \\
& - e^{2al}\operatorname{erf}[\tfrac{1}{2}(2l+x_1)/\sqrt{t} + a\sqrt{t}]\}
\end{aligned} \tag{54c}
$$

In the second step we wish to evaluate

$$
\langle Q_n \rangle = c^2 \int_0^\infty dl\, e^{-cl} \int_0^l dx_0\, Q_n(t \mid x_0) \tag{55}
$$

Using the integrals of Appendix A we find

$$
\langle Q_0 \rangle = \tfrac{1}{2} e^{-a^2 t} [f_1(c+a) + f_1(c-a)] \tag{56a}
$$

$$
\begin{aligned}
[\langle Q_1 \rangle - \langle Q_0 \rangle]\, e^{a^2 t} = {} & \frac{c}{c+2a} f_1(c+a) + \frac{c}{c-2a} f_1(c-a) \\
& - \frac{c^2}{c^2 - 4a^2} f_2(c)
\end{aligned} \tag{56b}
$$

$$
\begin{aligned}
2[\langle Q_2 \rangle - \langle Q_1 \rangle]\, e^{a^2 t} = {} & \left(\frac{c}{c+2a}\right)^2 f_1(c+a) + \left(\frac{c}{c-2a}\right)^2 f_1(c-a) \\
& - 2\left[\left(\frac{c}{c+2a}\right)^2 + \left(\frac{c}{c-2a}\right)^2\right] f_2(c) \\
& + \left(\frac{c}{c+2a}\right)^2 f_3(c-a) + \left(\frac{c}{c-2a}\right)^2 f_3(c+a)
\end{aligned} \tag{56c}
$$

where $f_j(x)$ is defined in (19).

The general solution can be written as follows: For odd n

$$
\begin{aligned}
[\langle Q_n \rangle - \langle Q_{n-1} \rangle]\, c^{-2} e^{a^2 t} = {} & -[c^2 - (n-1)^2 a^2]^{-1} f_{n-1}(c) \\
& + [c + (n+1)a]^{-1} [c - (n-1)a]^{-1} f_n(c+a) \\
& + [c - (n+1)a]^{-1} [c + (n-1)a]^{-1} f_n(c-a) \\
& - [c^2 - (n+1)^2 a^2]^{-1} f_{n+1}(c)
\end{aligned} \tag{57a}
$$

and for even n

$$\begin{aligned}
&2[\langle Q_n\rangle - \langle Q_{n-1}\rangle]\, c^{-2} e^{a^2 t} \\
&\quad = (c+na)^{-2} f_{n-1}(c+a) + (c-na)^{-2} f_{n-1}(c-a) \\
&\qquad - 2[(c+na)^{-2} + (c-na)^{-2}] f_n(c) \\
&\qquad + (c-na)^{-2} f_{n+1}(c+a) + (c+na)^{-2} f_{n+1}(c-a) \qquad (57\text{b})
\end{aligned}$$

Several remarks are appropriate: (a) (57) can be made valid for all $n=0, 1,...$ by defining $f_{-1}(x) \equiv 0$ and $\langle Q_{-1}\rangle \equiv 0$. (b) It is invariant for replacement of a by $-a$, as it should be. (c) It reduces to (18c) for $a=0$. (d) It is evidently not valid for $c = \pm 2na$, but since it is valid in any proximity of these points, we will not give the special form valid at these exact values.

The solution by (51) and (57) is shown in Fig. 5. It converges nicely with just a few terms. We notice that for larger bias, as determined by the parameter a (compare with Fig. 3): (a) the decay becomes faster, due to the larger drift term and (b) the solution by the method of images converges faster, while the eigenvalue expansion, (51), converges much slower. The reason is physically clear: The larger the drift term, a, the faster an initial delta function moves downhill to its fatal destiny at the absorbing boundary, and the less it widens by diffusion, almost retaining its initial shape. Such a function is, of course, very poorly described by a Fourier expansion, and very nicely as a Gaussian.

First Passage Times

Let us use the methods of Ref. 22. $\tau(x_0)$ of (34) obeys[22a] (instead of (33))

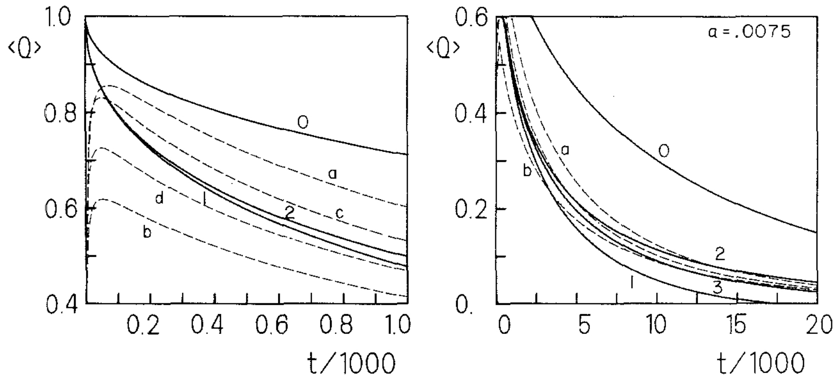
$$e^{2ax_0} \frac{\partial}{\partial x_0} e^{-2ax_0} \frac{\partial \tau(x_0)}{\partial x_0} = -1 \qquad (58)$$

with absorbing boundary conditions $\tau(0) = \tau(l) = 0$. The solution is

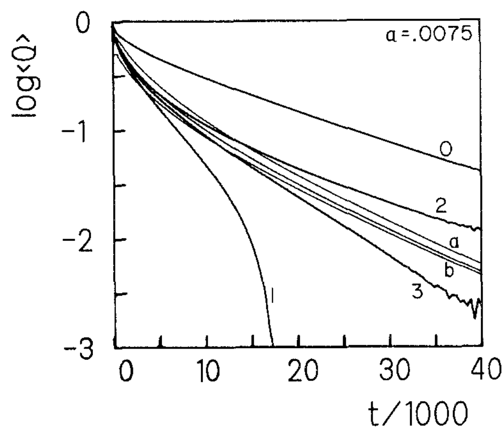
$$2a(e^{2al} - 1)\, \tau(x_0) = x_0(e^{2al} - 1) - l(e^{2ax_0} - 1) \qquad (59)$$

Averaging over x_0 gives

$$2al\, \tau = l(l - a^{-1})/2 + l^2/(e^{2al} - 1) \qquad (60)$$



(a)



(b)

Fig. 5. (a) Same as in Fig. 3a, but in a constant field of force with $a = 7.5 \cdot 10^{-3}$. Thick curves, denoted by 0, 1, 2,..., are the short-time solution $\langle Q_0 \rangle$, $\langle Q_1 \rangle$,..., of (56). Thin dashed curves, denoted by a, b,..., are the long-time solution (51) with 1, 2,..., eigenvalues. [When a new variable v is defined as in (12), the range of the numerical integration is similar to Fig. 3]. (b) Same as (a) in a logarithmic (base 10) scale. Numerical instabilities at long time are due to single-precision evaluation of error functions. (Double-precision arithmetic is needed for longer times).

These reduce to (35) and (36) by expanding the exponential terms up to second order for (59) and up to third order in (60). Finally one has

$$2a\langle \tau \rangle = c^{-1} - (2a)^{-1} + c^2 \int_0^\infty e^{-cl}(e^{2al} - 1)^{-1}\, l^2\, dl \qquad (61)$$

The same result has been obtained in Eq. (7) of Ref. 11(c) by a different route. It is demonstrated in Fig. 6 together with the $a = 0$ limit, (37). Note that the time integral of (52) leads to a more complicated-looking integral.

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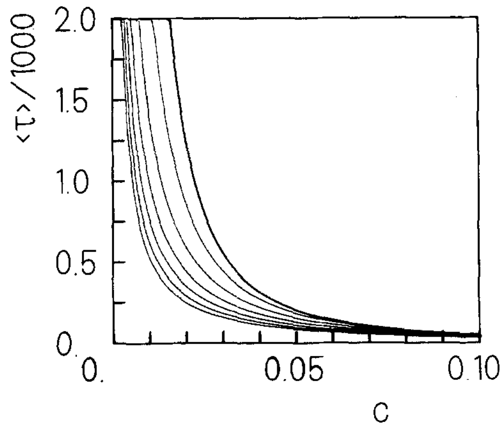

Fig. 6. Mean survival time for one-dimensional diffusion with random traps at a concentration $c = 0.01$. Thick upper line = free diffusion (37). Thin lines below are for $a = 1.5 \cdot 10^{-2}m$, $m = 1-6$ (top to bottom), in (61). Numerical integration in (61) was performed using 600 grid points for $0.1 \leq l \leq 120$.

$\tau(x \mid x_0)$ of (40) obeys[22b] [instead of (41)]

$$\frac{\partial}{\partial x} e^{-2ax} \frac{\partial}{\partial x} e^{2ax} \tau(x \mid x_0) = 0 \tag{62a}$$

$$\frac{\partial}{\partial x_0} e^{-2ax_0} \frac{\partial}{\partial x_0} \tau(x \mid x_0) = 0 \tag{62b}$$

again, with absorbing boundary conditions

$$\tau(0 \mid x_0) = \tau(l \mid x_0) = \tau(x \mid 0) = \tau(x \mid l) = 0 \tag{63}$$

The solution is

$$2a(e^{2al} - 1)\, \tau(x \mid x_0) = \begin{cases} (e^{2al} - e^{2ax_0})(1 - e^{-2ax}), & x < x_0 \\ (e^{2ax_0} - 1)(e^{2a(l-x)} - 1), & x > x_0 \end{cases} \tag{64}$$

where the factor $2a(e^{2al} - 1)$ has been determined from the condition that $\int_0^l \tau(x \mid x_0)\, dx$ coincides with $\tau(x_0)$ of (59), which in turn is a consequence of the normalization of $p(x, t \mid x_0)$.

From (64) we get [cf. (43) and (44)]

$$2aT = \coth(al) - (al)^{-1} \tag{65}$$

$$2a\langle T \rangle = \int_0^\infty e^{-y} \coth(ay/c)\, y\, dy - c/a \tag{66}$$

The integrals in (61) and (66) can also be written as ζ functions.[23] When $c = a$ the integral in (66) can be performed analytically, to yield $\pi^2/4 - 1$. The solution (66) is shown in Fig. 7 together with the $a = 0$ limit (44).

At first, the qualitative difference between the two solutions may look striking: (66) tends to 1 as $c \to 0$ and exhibits a maximum at larger c, while (44) smoothly increases from zero to infinity with decreasing concentration. This difference can be traced to the qualitative difference in the asymptotic behavior. When $a = 0$, the solution at the origin decays as $\exp[-\frac{3}{2}(2c^2\pi^2 t)^{1/3}]$, which becomes slower with decreasing c. Hence, in the $c \to 0$ limit its temporal integral diverges. In contrast, when $a \neq 0$, the asymptotic decay is $\exp[-a^2 t]$, which is independent of concentration and has a finite temporal integral.

More physically, when $a = 0$, $p(x, t \mid x_0)$ is centered around x_0 for all $t \geqslant 0$; hence, the number of times a stochastic trajectory returns to the origin x_0 increases with t until it terminates at a trap. In contrast, when $a \neq 0$, the drift force carries $p(x, t \mid x_0)$ away from the origin, only the boundaries preventing it from escaping to infinity. When the distance between these boundaries (traps) increases above a certain value, this effect becomes dominant (over the diminishing trapping), and the number of returns to the origin decreases with decreasing concentration.

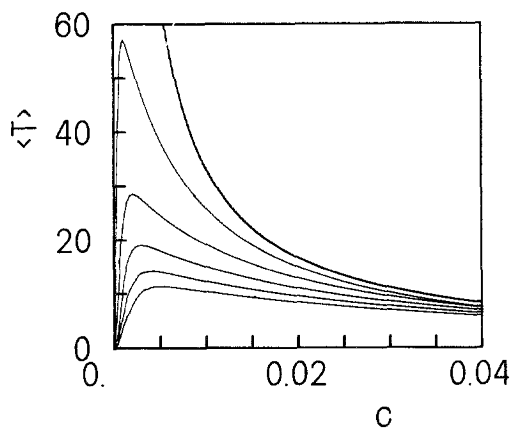

Fig. 7. Mean residence time at the origin for one-dimensional diffusion with random traps at a concentration $c = 0.01$. Thick uper curve = free diffusion (44). Thin lines below are for $a = 7.5 \cdot 10^{-3} m$, $m = 1 - 5$ (top to bottom), in (66). Numerical integration in (66) was performed using 600 grid points for $0.1 \leqslant y \leqslant 120$.

4. DIFFUSION WITH RANDOM REFLECTORS

A dual problem to that of diffusion with random traps is diffusion with random reflectors, where we simply replace the previously imposed absorbing boundary conditions by reflecting boundary conditions. This may represent, for example, energy transfer in a lattice with random defects. The initial excitation does not decay but relaxes to equilibrium. The survival probability is unity throughout, but we can still ask about $\langle P \rangle$. Similarly, the survival time is infinite, but the mean relaxation time is meaningful.[24] We solve this problem below for free diffusion, denoting all quantities by a superscript r (for "relaxation") and all previously calculated quantities (for random traps, Sec. 2) by a superscript t.

The solution for free diffusion (1) in an interval $(0, l)$ with reflecting boundary conditions

$$\left.\frac{\partial p(x,t)}{\partial x}\right|_{x=0} = \left.\frac{\partial p(x,t)}{\partial x}\right|_{x=l} = 0 \tag{67}$$

[instead of (2)], and the initial conditions of (3), is given [analogously to (8) and (9)] by

$$l\, p^r(x, t \mid x_0) = 1 + 2 \sum_{j=1}^{\infty} \cos(j\pi x/l) \cos(j\pi x_0/l) \exp[-(j\pi/l)^2\, t] \tag{68}$$

$$\begin{aligned} &2\sqrt{\pi t}\; p^r(x, t \mid x_0) \\ &\quad = \sum_{j=-\infty}^{\infty} \{\exp[-(x - x_0 + 2jl)^2/4t] + \exp[-(x + x_0 + 2jl)^2/4t]\} \end{aligned} \tag{69}$$

From which it is immediately evident that

$$P^r = l^{-1} + P^t \tag{70}$$

where l^{-1} is the equilibrium probability density. Finally

$$\langle P^r \rangle = c + \langle P^t \rangle \tag{71}$$

where $\langle P^t \rangle$ is given by (26) and (30). After a transient decay period, the system reaches an equilibrium situation where the average return probability density is determined by the concentration.

The relaxation time in the segment $(0, l)$ is defined by[24]

$$\tau^r(x) \equiv l \int_0^{\infty} [p^r(x, t \mid x) - l^{-1}]\, dt \tag{72}$$

From which it immediately follows that

$$\langle T^r \rangle = \langle T^t \rangle = (3c)^{-1} \tag{73}$$

This is clear, since the transient behavior in both cases is the same; only the final equilibrium situation is different.

The solution for a linear potential is not derived simply from the above results for free diffusion via the transformation (47): The reflecting boundary conditions (zero flux) now become "radiation" boundary conditions. One has to solve first for free diffusion with radiation boundary conditions at $x = 0$ and l.

5. CONCLUSION

We have given an exact solution for one-dimensional diffusion with random traps and reflectors. We believe several points in our exposition to be novel: (a) the use of the method of images for these problems as a short-time solution; (b) the observation that with just a few terms the short-time solution connects smoothly with the long-time solution obtained by an eigenvalue expansion, when the integrals are evaluated numerically or by their complete asymptotic expansion (rather than by the saddle-point approximation alone). This conclusion should be checked on systems with higher dimensionality; (c) the full solution for the case of a constant field of force (linear potential) for $\langle Q \rangle$, $\langle P \rangle$, $\langle \tau \rangle$, and $\langle T \rangle$ (as compared with Ref. 11(c), the long-time solution is derived in a simpler, more direct way); (d) the introduction of the mean residence time density at the origin, $\langle T \rangle$, in this context; (e) the discussion of diffusion with random reflectors. We believe this last model to have experimental significance, especially for relaxation processes in random media.

APPENDIX A

We evalute some integrals needed in the sequel; $f_j(x)$ is defined in (19).

$$\int_0^l \exp[-(x+jl)^2/t]\,dx = \tfrac{1}{2}\sqrt{\pi t}\,\{\operatorname{erf}[(j+1)l/\sqrt{t}] - \operatorname{erf}(jl/\sqrt{t})\} \tag{A1}$$

$$c\int_0^\infty e^{-cl}\operatorname{erf}(\tfrac{1}{2}jl/\sqrt{t} + a\sqrt{t})\,dl = \operatorname{erf}(a\sqrt{t}) + j^{-1}e^{-a^2 t} f_j(c+ja) \tag{A2}$$

$$\begin{aligned} &c^2\int_0^\infty dl\, e^{-cl}\int_0^l dx\,\operatorname{erf}[\tfrac{1}{2}(x+jl)/\sqrt{t} + a\sqrt{t}] \\ &\quad = \operatorname{erf}(a\sqrt{t}) + e^{-a^2 t}\{f_{j+1}[c+(j+1)a] - f_j(c+ja)\} \end{aligned} \tag{A3}$$

$$(c+2aj)\int_0^\infty dl\, e^{-cl}\int_0^l dx\, e^{2ax}\,\mathrm{erf}[\tfrac{1}{2}(x+jl)/\sqrt{t}+a\sqrt{t}]$$

$$=\frac{j+1}{c-2a}\{\mathrm{erf}(a\sqrt{t})+j^{-1}e^{-a^2t}f_j[c+(j-2)a]\}$$

$$-c^{-1}\{j\,\mathrm{erf}(a\sqrt{t})+e^{-a^2t}f_j(c+ja)\} \tag{A4}$$

APPENDIX B

Identity (50) can be derived from partial-fraction expansions of trigonometric and hyperbolic functions, as obtained from the residuum theorem of complex analysis. These expansions are listed in Sec. 1.42 of Ref. 23(b). From these we obtain

$$S_1 \equiv 8\sum_{k=1}^{\infty}\frac{(2k-1)^2\pi^2}{[(2k-1)^2\pi^2+z^2]^2}=\frac{1}{2}\cosh^{-2}\left(\frac{z}{2}\right)+z^{-1}\tanh\left(\frac{z}{2}\right) \tag{B1}$$

$$S_2 \equiv 8\sum_{k=1}^{\infty}\frac{(2k)^2\pi^2}{[(2k)^2\pi^2+z^2]^2}=-\frac{1}{2}\sinh^{-2}\left(\frac{z}{2}\right)+z^{-1}\coth\left(\frac{z}{2}\right) \tag{B2}$$

Equation (50) reads

$$S_1\cosh^2\left(\frac{z}{2}\right)-S_2\sinh^2\left(\frac{z}{2}\right)=1 \tag{B3}$$

The identity is easily established by inserting (B1) and (B2) in (B3).

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