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1993 J. Phys. A: Math. Gen. 26 5661

(http://iopscience.iop.org/0305-4470/26/21/008)

J. Phys. A: Math. Gen. 26 (1993) 5661–5673. Printed in the UK

Effective diffusion constant for inhomogeneous diffusion

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Received 26 January 1993, in final form 26 April 1993

Abstract. We consider the problem of determining analytically the effective diffusion constant D_{eff} for diffusion in an inhomogeneous medium, described by the diffusion equation $\partial_t P = \partial_x [D(x)\partial_x P]$ with a position-dependent diffusion coefficient $D(x)$. As there is no translational invariance, two different natural definitions are possible: From the *long-time* behaviour of the variance, $D_{\mathrm{eff}} = \mathfrak{D} = \lim \langle (\Delta x)^2 \rangle / 2t$. From the *large-distance* behaviour of the mean first passage time $T(\pm x|0)$ to reach exit points at $\pm x$ starting from the origin, $D_{\mathrm{eff}} = \mathbb{D} = \lim_{x\to\infty} x^2/2T(\pm x|0)$. In general, $\mathfrak{D} \neq \mathbb{D}$. We find an exact formula for $\mathbb{D}$ and examine a number of interesting special cases. If $D(x)$ tends to finite limits $D_\pm$ as $x \to \pm\infty$, *then $\mathbb{D}$ is simply the arithmetic mean $(D_+ + D_-)/2$. In the important case of a periodic* $D(x)$, we find that $\mathbb{D}$ is the *harmonic* mean of $D(x)$ in a period. We also give an argument suggesting that $\mathbb{D} = \mathfrak{D}$ in this case. If $D(x)$ is piecewise constant in an arbitrary fashion, with a finite number of discontinuities, and tends to $D_\pm$ and $x \to \pm\infty$, then $\mathbb{D} = (D_+ + D_-)/2$ as before, but $\mathfrak{D} = (D_+ D_-)^{1/2} + (1 - 2/\pi)(D_+^{1/2} - D_-^{1/2})^2 \leqslant \mathbb{D}$ (the equality obtaining only if $D_+ = D_-$). Thus $\mathfrak{D}$ is the *geometric* mean of D_+ and D_- plus a 'correction' term. We also illustrate the significant role of inhomogeneities in determining D_{eff} with the help of a simple example involving a discrete-time random walk on a chain.

1. Introduction

Diffusion in an inomogeneous medium is of interest in a variety of physical contexts. The corresponding diffusion equation obeyed by the probability density is, for an isotropic medium,

$$\partial_t P = \nabla \cdot [D(\mathbf{r}) \nabla P(\mathbf{r}, t)] \tag{1.1}$$

where $D(\mathbf{r})$ is a positive definite function. Analytical solutions of (1.1) are possible in only a few special cases; in general, one has to resort to numerical solutions [1].

In a homogeneous medium (i.e. when $D(\mathbf{r}) = D$, a constant), of course, the variance of the displacement scales as t. Likewise, the mean time to escape from a region of linear dimension r scales as r^2. The constant of proportionality in each case is essentially D (apart from a known numerical factor), so that the diffusion constant may be defined in either of two equivalent ways from the above-mentioned scaling relations. However, when $D(\mathbf{r})$ is position-dependent the translational invariance of (1.1) is lost, and so is the *exact* scaling of the variance with t, or that of the mean escape time with r^2. These quantities yield valuable information about the diffusion process. We would like to examine the conditions under which they scale *asymptotically* as t and r^2, respectively; and when they do, to find the actual constants of proportionality in each case. Each of these constants may quite justifiably be called the *effective diffusion constant* D_{eff} associated with the diffusion process. Our investigation (of the asymptotic behaviour of the variance and the mean escape time) may then be paraphrased as the determination of D_{eff}.

In order to find D_{eff} *analytically* in various cases, we assume the inhomogeneity to occur along a single direction and consider inhomogeneous diffusion in one dimension. The diffusion (or forward Kolmogorov) equation for the probability density $P(x,t)$ is

$$\partial_t P = \partial_x [D(x)\partial_x P] \tag{1.2}$$

subject to an initial condition $P(x,0)=\delta(x-y)$ where $-\infty<x,y<\infty$, and $D(x)$ is a deterministic but otherwise arbitrary positive definite function of x. (We do not address here the more complicated problem of a *random* position-dependent $D(x)$.) The Laplace transform of P with respect to t therefore satisfies

$$\partial_x [D(x)\partial_x \tilde{P}(x,s)] - s\tilde{P}(x,s) = -\delta(x-y). \tag{1.3}$$

This is a classic Sturm–Liouville problem [2]. In *principle*, therefore, we have complete information on the existence of the eigenvalues and eigenfunctions of the differential operator on the left, the formal expansion of the Green function $\tilde{P}$ in terms of the eigenfunctions, etc. Our interest, however, is in obtaining an *explicit* expression for D_{eff} in the case of a general function $D(x)$.

Heuristically, the obvious candidate for the effective diffusion constant would appear to be the 'average' diffusion constant defined by

$$\langle D(x)\rangle = \int_{-\infty}^{\infty} D(x)P_{st}(x)\,dx$$

but the density $P(x,t)$ does not tend (as $t\to\infty$) to any non-trivial stationary distribution $P_{st}(x)$. To overcome this difficulty, consider first the *steady-state* diffusion of particles across a *homogeneous* finite line segment with a source and sink, respectively, at the end points $x=-a$ and $x=a$, and let D be the diffusion constant of the particles. The steady-state current density is given by $j=D(d\rho/dx)$ where ρ is the local particle density. Integrating both sides, we find $2aj/[\rho(a)-\rho(-a)]=D$. Now consider the same physical situation when the diffusion coefficient is a function of position, $D(x)$. The steady-state current density is now $j=D(x)(d\rho/dx)$, whence

$$2aj/[\rho(a)-\rho(-a)] = 2a\left[\int_{-a}^{a} dx/D(x)\right]^{-1}.$$

It therefore seems plausible, by direct analogy with the previous case, to simply define the effective diffusion constant as

$$D_{eff} = \lim_{a\to\infty} 2a\left[\int_{-a}^{a} dx/D(x)\right]^{-1}. \tag{1.4}$$

While this expression certainly has the right physical dimensions, it is entirely phenomenological in nature, and its derivation does not anywhere refer to the microscopic dynamics of the underlying diffusion process. On the other hand, we are interested in precisely the latter aspect, as characterized by the probability density $P(x,t)$—or, in the absence of the exact knowledge of P, by the variance $\langle(\Delta x)^2\rangle$ of the displacement and by the mean time $T(\pm x|0)$ to start from the origin and cross the point $+x$ or the point $-x$ (where $x>0$) for the first time. For the conventional diffusion process on a line, the diffusion constant is a measure of the spread of the diffusion profile (a Gaussian) as quantified by $\langle(\Delta x)^2\rangle$. In contrast, for a position-dependent $D(x)$ the distribution is no longer Gaussian even if the process remains diffusive (i.e. the variance increases asymptotically as t). However, $\langle(\Delta x)^2\rangle$ continues in this case to be a measure of the spread of the diffusion profile, justifying its use in the definition of D_{eff}. On the other hand, the definition of D_{eff} in terms of the mean first passage time $T(\pm x|0)$ is equally justifiable, and indeed more meaningful in certain respects, as it probes the distribution P itself and not just its first and second moments. It is also the basic definition of D_{eff} on scale-invariant structures such as fractals [3], and so there is good reason to accept this as the more generally applicable prescription for the effective diffusion constant. In order to distinguish between the two alternatives for D_{eff} (they will in general be distinct), we shall henceforth denote them by different symbols $\mathfrak{D}$ and $\mathbb{D}$. Their precise definitions are, respectively

$$\mathfrak{D} = \lim_{t\to\infty} \langle(\Delta x)^2\rangle/2t \tag{1.5}$$

and

$$\mathbb{D} = \lim_{x\to\infty} x^2/2T(\pm x|0). \tag{1.6}$$

We reiterate that the constants $\mathfrak{D}$ and $\mathbb{D}$ characterize rather *different* properties of the diffusion process, and that there is really no unique quantity that represents an 'effective diffusion constant' in the problem under consideration. $\mathfrak{D}$ and $\mathbb{D}$ are merely the most *natural* objects that qualify for this label, for the reasons described above. When 'global' inhomogeneities are present, it is clear that both $\mathbb{D}$ and $\mathfrak{D}$ will depend on the details of the variation of $D(x)$ (which we may call the 'macroscopic geometry' of the medium). We shall compare and contrast these quantities in various representative cases. A number of interesting conclusions emerge.

An outline of the rest of the paper and a summary of the results are as follows. In section 2 we obtain an expression for $\mathbb{D}$ for a general $D(x)$, with the help of the backward Kolmogorov equation corresponding to (1.2). We use this to deduce conditions under which the x-dependence of $D(x)$ can lead to superdiffusive or subdiffusive behaviour. It is shown, too, that if $D(x)$ tends to *different* limiting values D_+ and D_- as $x\to\infty$ and $-\infty$, respectively, then $\mathbb{D}$ is simply the arithmetic mean $(D_+ + D_-)/2$. In section 3, we consider the important case of a periodic diffusion coefficient $D(x)$, i.e. $D(x) = D(x+\lambda)$. We show in a straightforward manner that $\mathbb{D}$ is, in this instance, simply the harmonic mean of $D(x)$ in a fundamental interval. The counterpart of this result for a discrete-time random walk on a chain with transition probabilities that depend in a periodic manner on the site index is already implicit in earlier work [4]: the effective diffusion constant obtained from the long-time behaviour of the variance indeed turns out to be given by the harmonic mean. We indicate how this may be shown to be identical to the effective diffusion constant obtained from the mean first passage time. We have also given simple physical arguments to support the harmonic-mean expression.

When $D(x)$ is neither constant everywhere nor a periodic function of x, there is no length-scale in the problem beyond which spatial homogeneity obtains. $\mathfrak{D}$ and $\mathbb{D}$ are in general different in this truly inhomogeneous situation. It is therefore of interest to investigate a case in which both these quantities can be computed exactly, and compared with each other. For this purpose, and also to include in our treatment the possible effects of finite discontinuities in $D(x)$, we consider in section 4 a $D(x)$ that is piecewise constant with a finite but arbitrary number of points of discontinuity. Hence $D(x)$ tends to well-defined, but possibly distinct, limiting values $D_\pm$ and $x \to \pm\infty$. We show rigorously that (i) $\mathfrak{D}$ and $\mathbb{D}$ are distinct in this case, (ii) each of them is equal to the corresponding value that obtains when $D(x)$ has a *single* discontinuity, e.g. $D(x) = D_+\theta(x) + D_-\theta(-x)$, and (iii) while $\mathbb{D} = (D_+ + D_-)/2$ (in conformity with what has been said earlier), we have

$$\mathfrak{D} = (D_+D_-)^{1/2} + (1 - 2/\pi)(D_+^{1/2} - D_-^{1/2})^2. \tag{1.7}$$

Thus $\mathfrak{D}$ is not simply the geometric mean of D_+ and D_-. Moreover $\mathfrak{D} < \mathbb{D}$ unless $D_+ = D_-$.

We conclude the paper with a simple illustration of the sensitive dependence of the effective diffusion constant on inhomogeneities, in a discrete-time random walk.

2. $\mathbb{D}$ from the mean first passage time

Let $F(x, t|y)$ denote the probability that the diffusing particle, having started from $y \in I = [-x, x]$ at $t = 0$, continues to be in the interval I at time t without having crossed $\pm x$. Then F obeys the backward Kolmogorov equation [5, 6] corresponding to (1.2), namely

$$\partial_t F = \partial_y[D(y)\partial_y F]. \tag{2.1}$$

It follows from this that the mean first passage time $T(\pm x|y)$ to reach either one of the exit points $+x$ and $-x$, starting at $y \in I$, is given by the solution of [7, 8]

$$\partial_y[D(y)\partial_y T(\pm x|y)] = -1 \tag{2.2}$$

with the boundary conditions

$$T(\pm x|-x) = T(\pm x|x) = 0. \tag{2.3}$$

Defining the functions

$$\phi(u, v) = \int_u^v \mathrm{d}z/D(z) \qquad \text{and} \qquad \psi(u, v) = \int_u^v z\,\mathrm{d}z/D(z) \tag{2.4}$$

we find that the solution to (2.2) satisfying the boundary conditions (2.3) is

$$T(\pm x|y) = [\phi(-x, y)\psi(-x, x) - \phi(-x, x)\psi(-x, y)]/\phi(-x, x). \tag{2.5}$$

The effective diffusion constant is therefore, from Eq. (1.6),

$$\mathbb{D} = \lim_{x\to\infty} x^2\phi(-x, x)/2[\phi(-x, 0)\psi(-x, x) - \phi(-x, x)\psi(-x, 0)]. \tag{2.6}$$

A number of special cases can be deduced from this general result. To begin with, we note that if the positive definite function $D(x)$ tends to the *same* constant D as x tends to $+\infty$ as well as $-\infty$, then $\mathbb{D} = D$ as one would expect. On the other hand, if $D(x)$ tends to *different* constants $D_\pm$ as $x \to \pm\infty$, it is easily shown from (2.6) that $\mathbb{D}$ is just the arithmetic mean

$$\mathbb{D} = (D_+ + D_-)/2. \tag{2.7}$$

If $D(x) \to 0$ as $|x| \to \infty$, $\mathbb{D}$ vanishes, indicating that the process is *subdiffusive*: that is, the variance of x does not increase as rapidly as t^1 asymptotically. For instance, if

$D(x) \sim O(|x|^{-\alpha})$ $(\alpha>0)$ as $|x| \to \infty$, then $\langle(\Delta x)^2\rangle \sim t^{2/(2+\alpha)}$. Similarly, if $D(x)$ becomes unbounded as $|x| \to \infty$, $\mathbb{D}$ diverges, indicating that the process is in fact *superdiffusive*. Thus if $D(x) \sim O(|x|^{\alpha})(\alpha>0)$ as $|x| \to \infty$, then $\langle(\Delta x)^2\rangle \sim t^{2/(2-\alpha)}$. This conclusion holds good for $\alpha<2$. The limiting case is $\alpha=2$, for which $\langle(\Delta x)^2\rangle$ increases *exponentially* with t: If $D(x) \sim O(x^2)$ as $|x| \to \infty$, $T(\pm x|0) \sim \ln x$. For $\alpha>2$ the variance grows even more rapidly in time than $\exp(t)$; for instance, if $D(x) \sim O(x^4)$ as $|x| \to \infty$ then $T(\pm\infty|0)$ is actually *finite*, i.e. the mean time for the particle to reach exit points at $\pm\infty$ is finite.

If $D(x)$ is symmetric in x, equation (2.6) simplifies considerably. Since $\psi(-x, x)= 0$ in this case, equation (2.5) reduces to $T(\pm x|y) = -\psi(-x, y) = \psi(|y|, x)$, using the symmetry of $D(x)$. As a result (2.6) simplifies to

$$\mathbb{D} = \lim_{x\to\infty} x^2/2\psi(0,x) = \lim_{x\to\infty} x^2/2\left(\int_0^x z\,\mathrm{d}z/D(z)\right). \tag{2.8}$$

3. $\mathbb{D}$ when $D(x)$ is a periodic function

It is interesting to see what the effective diffusion constant $\mathbb{D}$ becomes in the case of a periodic diffusion coefficient: $D(x)=D(x+\lambda)$. Thus $D(x)$ does not tend to a definite limit as $|x| \to \infty$. To apply (2.6) in this case, let $x=r\lambda+\xi$ where r is a positive integer and $0<\xi<\lambda$. Evaluating each of the four functions in (2.6) we find, using the periodicity property of $D(x)$, the following leading asymptotic behaviours for large r:

$$\begin{aligned}&\phi(-x,0) \simeq r\phi(0,\lambda) \qquad \phi(-x,x) \simeq 2r\phi(0,\lambda)\\ &\psi(-x,0) \simeq -\tfrac{1}{2}\lambda r^2\phi(-\lambda,0) \qquad \psi(-x,x) \simeq r[2\psi(0,\lambda)-\lambda\phi(-\xi,\xi)].\end{aligned} \tag{3.1}$$

Therefore, passing to the limit $r\to\infty$, equation (2.6) yields

$$\mathbb{D} = \lambda/\phi(-\lambda,0) = \lambda/\phi(0,\lambda) = \lambda/\left(\int_0^\lambda \mathrm{d}x/D(x)\right). \tag{3.2}$$

Hence when the diffusion coefficient $D(x)$ is a periodic function, the effective diffusion constant $\mathbb{D}$ is just the harmonic mean of $D(x)$ over a full period of $D(x)$.

A simple illustration is provided by

$$D(x) = D_0 + D_1\cos(2\pi x/\lambda) \qquad (0<D_1<D_0) \tag{3.3}$$

for which we get

$$\mathbb{D} = (D_0^2 - D_1^2)^{1/2}. \tag{3.4}$$

Similarly, for the sawtooth shape defined in the fundamental interval by

$$D(x) = \begin{cases} D_0 + 2(D_1-D_0)x/\lambda & (0 \leqslant x \leqslant \lambda/2) \\ D_0 + 2(D_1-D_0)(1-x/\lambda) & (\lambda/2 \leqslant x \leqslant \lambda) \end{cases} \tag{3.5}$$

we find

$$\mathbb{D} = (D_1 - D_0)/\ln(D_1/D_0). \tag{3.6}$$

We note that even isolated zeros of $D(x)$, if they occur on both sides of the starting point, $x=0$, suffice to cause $\mathbb{D}$ to vanish (as may be seen by letting $D_1 \to D_0$ in (3.4) or $D_0 \to 0$ in (3.6)). Again, even if $D(x)$ becomes unbounded at isolated points, the process remains diffusive with a finite value of $\mathbb{D}$. [Example: $D(x) = (\text{constant})/(\lambda^2 - 4x^2)$]. In making these statements, we assume that $D(x)$ is such that the singular points of the diffusion equation are regular.

If $D(x)$ is periodic and also *piecewise constant*, equation (3.2) leads to a very simple expression for $\mathbb{D}$. Suppose the fundamental interval of $D(x)$ comprises N segments of length l_i in which $D(x) = D_i$, $i = 1, \ldots, N$. Then

$$\mathbb{D}^{-1} = \sum_{i=1}^{N} l_i D_i^{-1} \Big/ \sum_{i=1}^{N} l_i. \tag{3.7}$$

(Equation (3.2) may be regarded as a limiting case of the above, when $N \to \infty$ and $l_i \to 0$.) This result is corroborated by a known result for its discrete analogue [4]. Consider a random walk in discrete time n on a linear chain $\{j\}$, $j \in \mathbb{Z}$. Let the probability of a jump from any site to either of its neighbours be α $(0 < \alpha \leqslant 1/2)$, so that the stay probability (after each time step) at each site is $(1 - 2\alpha)$. The diffusion constant K for the random walk is defined by

$$K = \lim_{n \to \infty} \langle j^2(n) \rangle / n$$

where $j(n)$ is the displacement in n steps. It is easily shown that $K = 2\alpha$. Now suppose the jump rates are site dependent in a periodic manner, such that each fundamental interval consists of n_1 sites with jump rates α_1, n_2 sites with jump rates $\alpha_2, \ldots, n_N$ sites with jump rates α_N. It can then be shown that

$$K^{-1} = \sum_{i=1}^{N} n_i K_i^{-1} \Big/ \sum_{i=1}^{N} n_i \tag{3.8}$$

where $K_i = 2\alpha_i$. (In fact, this result remains valid irrespective of the order in which the $n_1 + \cdots + n_N$ sites are arranged, as long as the entire sequence is repeated periodically.) We can go further; we can show that the same expression for K is obtained both from the asymptotic behaviour of the variance $\langle j^2(n) \rangle$ for large n, and from that of the mean first passage time $T(\pm j|0)$ for large j, where j is the site label. In Appendix 1, we have indicated how this may be done in the simplest such instance: a linear chain with two alternating types of sites, with jump rates α_1 and α_2, respectively. The effective diffusion constant is then the harmonic mean of $K_1 = 2\alpha_1$ and $K_2 = 2\alpha_2$. More complicated periodicities may be handled similarly, by a suitable decimation technique [9, 10]. Moreover, it can be shown that a smooth continuum limit of the random walk problem with periodic jump probabilities exists: starting from the recursion relations for the probability distribution for the random walk, one can rigorously establish [10] the diffusion equation (1.2) for the probability density in the limit of continuous space and time, with a diffusion coefficient satisfying $D(x) = D(x + \lambda)$. As the two effective diffusion coefficients are equal for the discrete random walk, and as a smooth continuum limit of this process exists, we may conclude that $\mathbb{D} = \mathfrak{D}$ in the case of a spatially period $D(x)$. (In passing, we mention that an elaborate coarse-graining procedure has been developed in the literature [11] to handle this case, leading to the conclusion that $\mathfrak{D}$ is simply the mean value

$$(1/\lambda) \int_0^\lambda D(x)\, \mathrm{d}x.$$

This conclusion is not justified.)

We remark that a harmonic mean result like (3.2) or (3.7) is physically quite plausible. That the effective diffusion constant cannot possibly be any other kind of mean value can be seen on simple grounds. If any of the $D_i \to 0$, then $\mathbb{D}$ must vanish because long-range diffusion would be cut off. This rules out any kind of (weighted) arithmetic mean. Similarly, if any $D_i \to \infty$, the diffusion is controlled by the rest of the set, and the process is still diffusive ($\mathbb{D}$ remains finite). This rules out any kind of geometric mean. The harmonic mean yields the expected answer in both these limiting cases as well. Again, we may anticipate this result by an analogy with the rule for the addition of conductances placed in series.

4. $\mathbb{D}$ for piecewise constant $D(x)$

Finally, let us consider a situation in which $D(x)$ is neither continuous nor periodic in x. For simplicity, we look at the case of a piecewise constant $D(x)$. Thus $D(x)$ takes on arbitrary positive values $\{D_i\}$ on segments of arbitrary lengths $\{l_i\}$ of the x-axis; moreover, we assume that there exist finite points x_- and x_+ such that $D(x)=D_-$ for $x<x_-$ and $D(x)=D_+$ for $x<x_+$, so that $D(x)$ has well-defined limits as $x \to \pm\infty$. Our aim is to calculate the effective diffusion constants as defined by the variance and by the mean first passage time, respectively. As the case at hand is truly inomogeneous, the two answers differ from each other, and we would like to compare them.

It turns out (and we shall establish this subsequently) that the result in each of the two approaches is the same as the corresponding one in the case when $D(x)$ has a *single* discontinuity (which we may take to occur at $x=0$)—in other words, for the case

$$D(x)=D_-\theta(-x)+D_+\theta(x). \tag{4.1}$$

Accordingly, we solve the problem for this form of $D(x)$ first. In order to appreciate the manner in which the dependence of the various quantities concerned on the initial position y disappears asymptotically, we consider an artibrary initial position: $P(x,0)=\delta(x-y)$. Taking up the first passage time method first, the backward Kolmogorov equation can be integrated out as in section 2 to yield the following result: the mean first passage time to reach exit points at $\pm x$, where $0 \leqslant |y| \leqslant x$, is found to be

$$T(\pm x|y)=\begin{cases} \dfrac{(x-y)[2D_+x+(D_++D_-)y]}{2D_-(D_++D_-)} & (-x\leqslant y\leqslant 0) \\[2ex] \dfrac{(x+y)[2D_-x-(D_++D_-)y]}{2D_-(D_++D_-)} & (0\leqslant y\leqslant x). \end{cases} \tag{4.2}$$

We note that T is continuous at $y=0$ (as a function of y). As $x\to\infty$, $T(\pm x|y)$ clearly tends to $x^2/(D_++D_-)$, which is the same as $T(\pm x|0)$. Hence

$$\mathbb{D}=\lim_{x\to\infty} x^2/2T(\pm x|y)=(D_++D_-)/2 \tag{4.3}$$

as we have already found in (2.7): $\mathbb{D}$ is just the arithmetic mean of the asymptotic values D_+ and D_-.

Now consider the forward Kolmogorov (or diffusion) equation $\partial_t P = \partial_x[D(x)\partial_x P]$ for the conditional density $P(x, t|y)$, with $D(x)$ as given by (4.1). An explicit solution can be found for $P(x, t|y)$, but we do not write it down here in the interests of brevity. However, it is instructive to look at the structure of the solution in the special case $y=0$: we find

$$P(x, t|0) = (\pi t)^{-1/2}(D_+^{1/2} + D_-^{1/2})^{-1}[\exp(-x^2/4D_+t)\theta(x) + \exp(-x^2/4D_-t)\theta(-x)] \tag{4.4}$$

with $\theta(0) = \frac{1}{2}$. The profile is thus two 'half-Gaussians' patched together at $x=0$. The mode remains at $x=0$ at all times, as does the median. However, since $D_+ \neq D_-$, the mean value is non-zero even though there is no bias. It grows as $t^{1/2}$, being given by

$$\langle x(t)\rangle = 2(t/\pi)^{1/2}(D_+^{1/2} - D_-^{1/2}). \tag{4.5}$$

The mean squared displacement is given by

$$\langle x^2(t)\rangle = 2t[D_+ + D_- - (D_+D_-)^{1/2}] = 2t[(D_+D_-)^{1/2} + (D_+^{1/2} - D_-^{1/2})^2]. \tag{4.6}$$

For an arbitrary starting point y (<0, say), we find

$$\langle x(t)\rangle = y + (D_+^{1/2} - D_-^{1/2})[yD_-^{-1/2}\,\mathrm{Erfc}(-y/(4D_-t)^{1/2}) + 2(t/\pi)^{1/2}\exp(-y^2/4D_-t)] \tag{4.7}$$

and

$$\langle x^2(t)\rangle = y^2 + 2D_-t + 2D_+^{1/2}(D_+^{1/2} - D_-^{1/2})t\exp(-y^2/4D_-t)$$
$$\times\left[{}_1F_1\left(\frac{3}{2};\frac{1}{2};\frac{y^2}{4D_-t}\right) + 2y(\pi D_-t)^{-1/2}{}_1F_1\left(2;\frac{3}{2};\frac{y^2}{4D_-t}\right)\right]. \tag{4.8}$$

As $t\to\infty$ (more precisely, as $y^2/D_-t\to 0$), $\langle x(t)\rangle$ and $\langle x^2(t)\rangle$ tend to the expressions given in (4.5) and (4.6), respectively. The variance of x therefore has the large-t behaviour $\langle x^2(t)\rangle - \langle x(t)\rangle^2 \to 2\mathfrak{D}t$, where

$$\mathfrak{D} = (D_+D_-)^{1/2} + (1 - 2/\pi)(D_+^{1/2} - D_-^{1/2})^2. \tag{4.9}$$

Equation (4.9) shows explicitly how the effective diffusion constant, as defined by the behaviour of the variance, differs from the geometric mean $(D_+D_-)^{1/2}$ that one might expect at first sight. Moreover, $\mathfrak{D}$ is always less than the value $\mathbb{D} = (D_+ + D_-)/2$ obtained earlier from the mean first passage time. The ratio $\mathfrak{D}/\mathbb{D}$ drops from unity (in the homogeneous case $D_+ = D_-$) to the minimum value $(2 - 4/\pi) \simeq 0.727$ in the extreme inhomogeneous limit when either D_+ or D_- tends to zero. We note, too, that if D_- is zero, for instance, then the result $\mathfrak{D} = (1 - 2/\pi)D_+$ is precisely the value of the diffusion constant as defined by the variance for diffusion on the semi-infinite line $0 \leqslant x < \infty$ in the presence of a reflecting boundary at $x=0$.

It remains to show that the foregoing conclusions remain valid when $D(x)$ is piecewise constant in an arbitrary fashion, as long as $D(x) = D_-$ to the left of some finite value x_-, and $D(x) = D_+$ to the right of some finite value x_+. As far as $\mathbb{D}$ is concerned, the argument is straightforward because the general result of section 2 (obtained by integrating the backward Kolmogorov equation) continues to hold good, as long as $D(x)$ has only finite discontinuities. Hence $\mathbb{D} = (D_+ + D_-)/2$, as in (4.3). On the other hand, we need a more elaborate argument to find the leading behaviour of the variance of x in the general case. This is given in Appendix 2. We find that $\mathfrak{D}$ continues to be given by (4.9), corroborating our earlier statement.

Finally, it is worth noting that, significant as the effects of a spatially varying $D(x)$ are upon the effective diffusion constant, the effects of such inhomogeneities can be even more pronounced in the discrete counterpart of the diffusion process. We illustrate this with a simple example, involving a discrete-time random walk on a linear chain. Let the jump probability from any negative site $-j$ (where $j=1,2,\ldots$) to either of its neighbours be β, and that from any positive site $j(j=1,2,\ldots)$ to either of its neighbours be α. At the origin, suppose the jump probability from 0 to $+1$ is p, while that from 0 to -1 is q. The mean first passage time $T(\pm j|0)$ from 0 to exit points at $-j$ and $+j$ is then found to be

$$T(\pm j|0)=j[1+(j-1)(p/2\alpha+q/2\beta)]/(p+q). \tag{4.10}$$

Hence the effective diffusion constant is

$$K=\lim_{j\to\infty} j^2/T(\pm j|0)=(p+q)/[p(2\alpha)^{-1}+q(2\beta)^{-1}]. \tag{4.11}$$

If all the transition probabilities had been α (respectively, β), the diffusion constant would have been $K_+=2\alpha$ (respectively, $K_-=2\beta$). In the inhomogeneous situation at hand, however, K is given by a weighted average of K_+ and K_-—namely

$$K^{-1}=(pK_+^{-1}+qK_-^{-1})/(p+q). \tag{4.12}$$

We note how the effect of the extra inhomogeneity at the origin (the starting point of the walk) persists in K, i.e. in controlling the coefficient of the leading asymptotic behaviour of the walk. If $p=q$, K is simply the harmonic mean of K_+ and K_-. On the other hand, if $p=\alpha$ and $q=\beta$, K switches to the arithmetic mean of K_+ and K_-. Of course, if the inhomogeneity is localized in a finite region—in the present example, this means it is restricted to the single site $j=0$ by setting $\alpha=\beta$—then K reduces to the value 2α independent of p and q, as expected.

Acknowledgments

We are very grateful to Dr D Dhar and Dr M Barma for their helpful comments on the manuscript.

Appendix 1. Diffusion constant for a random walk on a chain of period 2

Consider a random walk in discrete time n on a linear chain with two alternating types of sites. The jump probability from a type-1 (say even) site $2j$ to the adjacent type-2 site $(2j-1)$ or $(2j+1)$ is α_1, while that from a type-2 site $(2j+1)$ to site $2j$ or $(2j+2)$ is α_2. Here $0\leqslant\alpha_{1,2}\leqslant\frac{1}{2}$. Let $T(\pm 2|0)$ be the mean time to start from an arbitrary even site (which we may label as site 0) and reach the next site of the *same* type (i.e. site ± 2) for the first time. Using the Markov-chain property of the random walk, as well as the fact that $T(\pm 2|+1)=T(\pm 2|-1)$ by an obvious symmetry property, we have

$$\begin{aligned} T(\pm 2|0)&=1+(1-2\alpha_1)T(\pm 2|0)+2\alpha_1 T(\pm 2|+1) \\ T(\pm 2|+1)&=1+(1-2\alpha_2)T(\pm 2|+1)+\alpha_2 T(\pm 2|0). \end{aligned} \tag{A1.1}$$

Therefore the mean time to cover a distance of two lattice constants (on either side of the starting point) is

$$T(\pm 2|0)=(\alpha_1+\alpha_2)/\alpha_1\alpha_2. \tag{A1.2}$$

Similarly, we can show that the mean first passage time to cover a distance of $2j$ lattice constants to reach sites of the same type as the starting point on either side of it is

$$T(\pm 2j|0) = j^2(\alpha_1+\alpha_2)/\alpha_1\alpha_2 = j^2 T(\pm 2|0). \tag{A1.3}$$

The scaling of T (as a function of j) on this periodic structure is thus exact, and the effective diffusion constant defined via the mean first passage time is

$$K = (2j)^2/T(\pm 2j|0) = 4\alpha_1\alpha_2/(\alpha_1+\alpha_2). \tag{A1.4}$$

This is just the harmonic mean of the values $2\alpha_1$ and $2\alpha_2$ that would obtain on lattices with a single type of site and nearest-neighbour jump probabilities α_1 and α_2, respectively.

Now let us consider the effective diffusion constant as defined by the behaviour of the variance of the displacement of the random walker. The random walk problem on the chain is solved quite easily. Let $P_n(j)$ be the probability that the displacement of the walker in the n time steps is equal to j. Define the transform (with respect to j and n)

$$R(k,\xi) = \sum_{n=0}^{\infty}\sum_{j=-\infty}^{\infty} P_n(j)\xi^n \exp(\mathrm{i}jk). \tag{A1.5}$$

Then, averaging over both types of initial positions of the walker, we obtain the solution

$$R(k,\xi) = \frac{1+\xi[(\alpha_1+\alpha_2)(1-\cos k)-1]}{1+2\xi(\alpha_1+\alpha_2-1)+\xi^2(1-2\alpha_1-2\alpha_2+4\alpha_1\alpha_2\sin^2 k)}. \tag{A1.6}$$

The mean displacement $\langle j(n)\rangle$ is evidently zero. The variance $\langle j^2(n)\rangle$ is the inverse ξ-transform of

$$\langle j^2(\xi)\rangle = -(\partial^2 R/\partial k^2)_{k=0}. \tag{A1.7}$$

We find the exact result

$$\langle j^2(n)\rangle = \left(\frac{4\alpha_1\alpha_2}{\alpha_1+\alpha_2}\right) n + \frac{1}{2}\left(\frac{\alpha_1-\alpha_2}{\alpha_1+\alpha_2}\right)^2 [1-(1-2\alpha_1-2\alpha_2)^n] \tag{A1.8}$$

valid for all $n(=0,1,\ldots)$. We note in passing that it is only asymptotically that the process is purely diffusive ($\langle j^2\rangle/n=$ constant). The diffusion constant, defined as

$$\lim_{n\to\infty}\langle j^2(n)\rangle/n$$

is therefore $4\alpha_1\alpha_2/(\alpha_1+\alpha_2)$. This is exactly the same answer as that obtained in (A1.4) by the mean first passage time method.

Appendix 2. Asymptotic behaviour of $\langle(\Delta x)^2\rangle$ for a piecewise constant $D(x)$

We want to find the leading behaviour of the variance of x when $D(x)$ is a piecewise-constant function of the form

$$D(x) = D_-\theta(x_- - x) + \sum_{i=1}^{\nu} D_i[\theta(x_i - x) - \theta(x - x_{i-1})] + D_+\theta(x - x_+), \tag{A2.1}$$

with $x_0 \equiv x_-$ and $x_\nu \equiv x_+$, ν being any finite positive integer. The initial position is some arbitrary point, y say, in the interval $[x_{j-1}, x_j]$. As the initial density $P(x,0)=\delta(x-y)$ is normalized to unity, and the diffusion equation $\partial_t P = \partial_x[D(x)\partial_x P]$ is an equation of continuity, the density $P(x,t)$ is guaranteed to remain normalized for all t. With the notation $\alpha_\pm = (s/D_\pm)^{1/2}$, $\alpha_i = (s/D_i)^{1/2}$, the Laplace transform $\tilde{P}(x,s)$ is given by the following solution:

$$\tilde{P}(x,s) = \begin{cases} A_- \exp(\alpha_- x) & (-\infty < x \leqslant x_-) \\ A_i \exp(\alpha_i x) + B_i \exp(-\alpha_i x) & (x_{i-1} \leqslant x \leqslant x_i) \\ B_+ \exp(-\alpha_+ x) & (x_+ \leqslant x < \infty). \end{cases} \tag{A2.2}$$

The coefficients A_-, A_i, B_i and B_+ are functions of s and y. In the interval $[x_{j-1}, x_j]$ the solution is given by

$$\tilde{P}(x,s) = \begin{cases} A_j \exp(\alpha_j x) + B_j \exp(-\alpha_j x) & x_{j-1} \leqslant x \leqslant y \\ A'_j \exp(\alpha_j x) + B'_j \exp(-\alpha_j x) & y \leqslant x \leqslant x_j. \end{cases} \tag{A2.3}$$

The coefficients $\{A\}$ and $\{B\}$ are found by using the continuity of $\tilde{P}$ and $D(x)\partial_x\tilde{P}$ at the points $x = x_-, x_1, \ldots, x_{\nu-1}, x_+$; the continuity of $\tilde{P}$ at $x = y$; and the discontinuity of $\partial_x \tilde{P}$ at $x = y$, namely

$$\partial_x \tilde{P}(y+0,s) - \partial_x \tilde{P}(y-0,s) = -1/D_j. \tag{A2.4}$$

This last condition makes the set of equations for the coefficients $\{A\}$ and $\{B\}$ inhomogeneous. Moreover, since it yields the relation

$$A'_j \exp(\alpha_j y) + B'_j \exp(-\alpha_j y) = A_j \exp(\alpha_j y) + B_j \exp(-\alpha_j y) + (sD_j)^{-1/2} \tag{A2.5}$$

it is not difficult to see that all the coefficients $\{A\}$ and $\{B\}$ have a leading small-s behaviour $\sim s^{-1/2}$. This observation is crucial in the argument that follows.

Now consider the mean displacement $\langle x(t)\rangle$, whose transform is

$$\langle \tilde{x}(s)\rangle = \left(\int_{-\infty}^{x_-} + \sum_{i=1}^{\nu} \int_{x_{i-1}}^{x_i} + \int_{x_+}^{\infty}\right) x\tilde{P}\, \mathrm{d}x. \tag{A2.6}$$

The leading asymptotic behaviour ($\sim t^{1/2}$) of $\langle x(t)\rangle$ arises from the leading ($\sim s^{-3/2}$) singular part of $\langle \tilde{x}(s)\rangle$. Inserting in (A2.6) the form of the solution for $\tilde{P}$ given above, we find that the leading part of $\langle \tilde{x}(s)\rangle$ comes from the first and last of the integrals on the right—specifically, from the terms

$$-(A_-/\alpha_-^2)\exp(\alpha_- x_-) + (B_+/\alpha_+^2)\exp(-\alpha_+ x_+) \tag{A2.7}$$

obtained after integrating over x. In arriving at this conclusion, we have used the fact that a term like

$$(A_i/\alpha_i^2)(\exp(\alpha_i x_i) - \exp(\alpha_i x_{i-1}))$$

or

$$(B_i/\alpha_i^2)(\exp(-\alpha_i x_i) - \exp(-\alpha_i x_{i-1})) \tag{A2.8}$$

has a leading behaviour that is only $\sim s^{-1}$, and not $\sim s^{-3/2}$, because the leading term of the exponential (unity) cancels out in the difference of exponentials. Denoting the coefficient of $s^{-1/2}$ in A_- by a_-, and that of B_+ by b_+, we have

$$A_- = a_- s^{-1/2} + \cdots \qquad B_+ = b_+ s^{-1/2} + \cdots \tag{A2.9}$$

where the dots denote regular functions of $s^{1/2}$ (we shall determine a_- and b_+ shortly). It then follows from (A2.7) that the leading asymptotic behaviour of $\langle x(t)\rangle$ is the inverse transform of $(b_+D_+ - a_-D_-)s^{-3/2}$, namely,

$$\langle x(t)\rangle \sim 2(t/\pi)^{1/2}(b_+D_+ - a_-D_-). \tag{A2.10}$$

A similar argument for the mean squared displacement shows that its leading ($\sim t$) asymptotic behaviour arises from the leading ($\sim s^{-2}$) singular part of $\langle x^2(s)\rangle$, given by

$$(2A_-/\alpha_-^3)\exp(\alpha_- x_-) + (2B_+/\alpha_+^3)\exp(-\alpha_+ x_+). \tag{A2.11}$$

(All other contributions are $O(s^{-3/2})$ or less singular.) Therefore the leading behaviour of $\langle x^2(t)\rangle$ is given by the inverse transform of $2(a_-D_-^{3/2} + b_+D_+^{3/2})\, s^{-2}$, i.e.

$$\langle x^2(t)\rangle \sim 2t(a_-D_-^{3/2} + b_+D_+^{3/2}). \tag{A2.12}$$

It remains to find a_- and b_+. To do this, we note that a typical matching condition (at x_i, say) reads

$$\begin{pmatrix} \exp(\alpha_i x_i) & \exp(-\alpha_i x_i) \\ D_i^{-1/2}\exp(\alpha_i x_i) & -D_i^{-1/2}\exp(-\alpha_i x_i) \end{pmatrix} \begin{pmatrix} A_i \\ B_i \end{pmatrix} = \begin{pmatrix} \exp(\alpha_{i+1} x_i) & \exp(-\alpha_{i+1} x_i) \\ D_{i+1}^{-1/2}\exp(\alpha_{i+1} x_i) & -D_{i+1}^{1/2}\exp(-\alpha_{i+1} x_i) \end{pmatrix} \begin{pmatrix} A_{i+1} \\ B_{i+1} \end{pmatrix}. \tag{A2.13}$$

Retaining just the leading (or $O(s^{-1/2})$) singular part of $\{A_i\}$ and $\{B_i\}$, by writing $A_i = a_i s^{-1/2}$ + regular function of $s^{1/2}$, $B_i = b_i s^{-1/2}$ + regular function of $s^{1/2}$, we see that the coefficients $\{a_i\}$ and $\{b_i\}$ obey the following matching conditions:

$$\begin{pmatrix} 1 & 0 \\ (sD_-)^{1/2} & 0 \end{pmatrix} \begin{pmatrix} a_- \\ 0 \end{pmatrix} = \begin{pmatrix} 1 & 1 \\ (sD_1)^{1/2} & -(sD_1)^{1/2} \end{pmatrix} \begin{pmatrix} a_1 \\ b_1 \end{pmatrix} = \cdots$$

$$= \cdots = \begin{pmatrix} 1 & 1 \\ (sD_j)^{1/2} & -(sD_j)^{1/2} \end{pmatrix} \begin{pmatrix} a_j \\ b_j \end{pmatrix}$$

$$\begin{pmatrix} 1 & 1 \\ (sD_j)^{1/2} & -(sD_j)^{1/2} \end{pmatrix} \begin{pmatrix} a_j' - a_j \\ b_j' - b_j \end{pmatrix} = s^{1/2} \begin{pmatrix} 0 \\ -1 \end{pmatrix}$$

and

$$\begin{pmatrix} 1 & 1 \\ (sD_j)^{1/2} & -(sD_j)^{1/2} \end{pmatrix} \begin{pmatrix} a_j' \\ b_j' \end{pmatrix} = \begin{pmatrix} 1 & 1 \\ (sD_{j+1})^{1/2} & -(sD_{j+1})^{1/2} \end{pmatrix} \begin{pmatrix} a_{j+1} \\ b_{j+1} \end{pmatrix} = \cdots$$

$$= \cdots = \begin{pmatrix} 0 & 1 \\ 0 & -(sD_+)^{1/2} \end{pmatrix} \begin{pmatrix} 0 \\ b_+ \end{pmatrix}. \tag{A2.14}$$

This yields at once

$$\begin{pmatrix} 1 & 0 \\ (sD_-)^{1/2} & 0 \end{pmatrix} \begin{pmatrix} a_- \\ 0 \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ 0 & -(sD_+)^{1/2} \end{pmatrix} \begin{pmatrix} 0 \\ b_+ \end{pmatrix} + \begin{pmatrix} 0 \\ s^{1/2} \end{pmatrix} \tag{A2.15}$$

which is solved trivially to yield

$$a_- = b_+ = 1/(D_-^{1/2} + D_+^{1/2}) \tag{A2.16}$$

Substituting these solutions in (A2.10) and (A2.12) we obtain, finally, the leading asymptotic behaviours

$$\langle x(t)\rangle = 2(t/\pi)^{1/2}(D_+^{1/2} - D_-^{1/2}) \tag{A2.17}$$

$$\langle x^2(t)\rangle = 2t[D_+ + D_- - (D_+D_-)^{1/2}]. \tag{A2.18}$$

But these are precisely the expressions (cf (4.5) and (4.6)) obtained in the case of a single point of discontinuity in $D(x)$, i.e. in the case when all the x_i $(i=0,\ldots,\nu)$ collapse to a single point, which may be taken to be the origin—so that $D(x)=D_-\theta(-x)+D_+\theta(x)$. This completes the proof of the assertion made in section 4 to this effect.

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