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# Two-state random walk model of lattice diffusion. 1. Self-correlation function

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**Abstract.** Diffusion with interruptions (arising from localized oscillations, or traps, or mixing between jump diffusion and fluid-like diffusion, etc.) is a very general phenomenon. Its manifestations range from superionic conductance to the behaviour of hydrogen in metals. Based on a continuous-time random walk approach, we present a comprehensive two-state random walk model for the diffusion of a particle on a lattice, incorporating arbitrary holding-time distributions for both localized residence at the sites and inter-site flights, and also the correct first-waiting-time distributions. A synthesis is thus achieved of the two extremes of jump diffusion (zero flight time) and fluid-like diffusion (zero residence time). Various earlier models emerge as special cases of our theory. Among the noteworthy results obtained are: closed-form solutions (in $d$ dimensions, and with arbitrary directional bias) for temporally uncorrelated jump diffusion and for the 'fluid diffusion' counterpart; a compact, general formula for the mean square displacement; the effects of a continuous spectrum of time scales in the holding-time distributions, etc. The dynamic mobility and the structure factor for 'oscillatory diffusion' are taken up in part 2.

**Keywords.** Diffusion; self-correlation function; continuous-time random walk theory; two-state random walk; renewal process.

## 1. Introduction

Diffusion in a periodic potential is of considerable current interest. It provides a description of the diffusion of an impurity atom in a crystal, including certain aspects of the complex phenomenon of the motion of hydrogen interstitials in metals. In addition, the general problem of Brownian motion in a periodic potential has a large number of applications, such as superionic conductance, orientational diffusion in molecular crystals, etc. A basic problem is to elucidate the consequences of the simultaneous occurrence of two features: random flights from site to site, and localized oscillations about each site. The non-trivial interference between these two aspects is manifested in physical quantities such as the frequency-dependent mobility $\mu(\omega)$ and the dynamic structure factor $S(\boldsymbol{k}, \omega)$.

There are two broad approaches to the problem. The first is a 'stochastic process' approach that deals with Brownian motion in a periodic potential. For technical reasons, explicit calculations are restricted to the one-dimensional case, *i.e.*, the position and the velocity of the diffusing particle are treated as scalar random processes. One may then write down the Langevin equation for a particle in a sinusoidal potential, and use a generalization of Mori's well-known continued-fraction method to obtain a representation for $\mu(\omega)$ (Fulde *et al* 1975; Schneider

1976). Alternatively, one can work with the Fokker-Planck equation for the conditional probability density $P(x, v, t \mid x_0, v_0)$ of the position and velocity of the particle in a periodic potential. A short-time expansion coupled with a perturbative technique may be employed (Dieterich *et al* 1977) to generate representations for $\mu(\omega)$ and $S(\boldsymbol{k}, \omega)$. An eigenfunction expansion method (Risken and Vollmer 1978) yields similar results.

The second approach is more directly concerned with diffusion in a three-dimensional lattice. Random walk analysis is combined with assumptions regarding uncorrelated jumps to develop what are essentially variants of a certain *jump diffusion* model. The diffusing particle is assumed to hop instantaneously (*i.e.*, with vanishing flight time) from site to site, while simultaneously executing localized oscillations whenever it is resident at a site. Starting with the simple model of Chudley and Elliott (1961), a considerable literature exists on various refinements of detail (Gissler and Rother 1970; Springer 1972 and references therein). Simultaneously, work has been carried out on two- and multi-state random walk models, one of the earliest being that of Singwi and Sjölander (1960) for diffusion in liquids. This permits the introduction of a *finite* mean flight time for the jumps. Now the mean residence and flight times can be quite comparable in many instances of diffusion in solids. It is therefore of great interest to examine such models in the framework of diffusion on a lattice (Gissler and Stump 1973; Wert 1978 and references therein; Kutner and Sosnowska 1979). Neutron scattering is the experimental probe primarily kept in mind in these analyses.

Concurrently with these developments, a picture has emerged of the relevance of continuous time random walk (CTRW) theory (Montroll and Weiss 1965; Weiss 1976) to generalized diffusion (see, in particular, Kehr and Haus 1978 and references therein). This technique offers a powerful approach to a wide variety of such problems, including that of diffusion in disordered media (Scher and Lax 1973). It is our purpose, in what follows, to present a general theory of the diffusion of a particle in a lattice based on the principles of CTRW. This will be done in two parts. In the first (the present paper), our primary objective is the evaluation of the conditional probability density for the *position* of the particle. In the classical limit (which is all that we consider), this quantity is equal to the van Hove self-correlation function, whose Fourier transform is measured by the differential cross-section for incoherent neutron scattering. We shall also be concerned with the mean square displacement. In paper 2 of this series, we shall consider the *velocity* of the diffusing particle. The velocity autocorrelation function (and thence the dynamic mobility and the effective diffusion constant) will be evaluated in a CTRW model in velocity space, allowing for localized oscillations at each lattice site as well as a distribution of flight times between sites.

To summarize: we shall calculate the self-correlation function for a particle diffusing by nearest-neighbour flights on a regular lattice. An arbitrary holding-time distribution for the state of residence at a site is allowed for; so is a distribution for the flight time between sites. Since these distributions are not restricted to exponential ones, cognizance must be taken of the first-waiting-time distribution in each case. A general, complete solution is obtained, in the sense that a closed expression is presented for the Laplace transform of the generating function of the random walk. There is no restriction to one-dimension, and the random walk may have an arbitrary directional bias.

The paper is organized as follows. In § 2, it is shown that all the quantities of interest are derivable from the generating function for the ' steps ' of the random walk. In § 3, this function is constructed using CTRW theory. In § 4, an explicit solution for the Laplace transform of the self-correlation function is presented for the case of the linear lattice. In § 5, the asymptotic (long-time) behaviour of the conditional density is deduced in the general case. Section 6 deals with the mean square displacement. A convenient closed expression is derived for this quantity, and its short-time and long-time behaviour discussed. Section 7 specializes the formalism to the case of jump diffusion. The Chudley-Elliott model is shown to be the simplest of this class of models, corresponding to an uncorrelated (Poisson) sequence of jump-triggering pulses. In § 8, a complementary class of models is studied; those in which the halt time at sites vanishes, the mean inter-site flight time being finite. Section 9 deals with the general case in which both the mean residence and flight times are finite. This enables one to see clearly the gradual transition, on taking limits appropriately, from jump diffusion to fluidlike diffusion. It is precisely this sort of behaviour that occurs in the diffusion of hydrogen in metals in a certain temperature regime (Kehr 1978), and is one of the motivating factors of the present study. Section 10 contains a capsule summary of the main results, together with some concluding remarks. It may be helpful to read this section once at this stage before returning to § 2.

## 2. The self-correlation function

Consider a classical particle executing a random walk in an empty lattice, with a randomly varying flight time between sites. It has halts of random duration at each site, when it executes oscillations localized about the lattice point labelling the site—*i.e.*, there is a ' local mode '. There are thus three characteristic times in the problem: the mean residence time at a site, the reciprocal of the local mode frequency, and the mean flight time between neighbouring sites. There are two characteristic lengths (the lattice is taken to be infinite in extent): the range of the potential well about each site, or the (related) mean amplitude of oscillation of the particle in the well, and the lattice spacing, which is supposed to be distinctly greater than the oscillation amplitude. The entire space can therefore be broken up into cells surrounding each lattice point, with bonds connecting the cells. If the instantaneous position of the particle is within a cell, it is overwhelmingly probable that the particle is in the oscillatory or localized ' state ', denoted by $L$. On a bond between cells, it may be considered to be in the diffusive or flight state, $F$. As the state at a given instant of time is markedly dependent on the position of the particle, one must carefully take into account all possible initial and final states of the particle by considering the self-correlation function $P(\mathbf{m}, t)$ defined as follows: given that, at $t=0$, the particle is oscillating about the site $\mathbf{0}$, *or* is on one of the bonds connecting this site to its nearest neighbours, $P(\mathbf{m}, t)$ is the probability of finding it in oscillation about the site $\mathbf{m}$ *or* on a bond connecting the latter to one of its neighbours, at time $t$. Our main objective in *this* paper is to understand the complications arising from the simultaneous occurrence of finite mean residence and flight times. We shall therefore neglect the details of the oscillatory motion henceforth.

It is natural to separate the dynamical aspect of the problem from the purely combinatorial one. Only nearest neighbour jumps are explicitly assumed*. Now the *number* of jumps increases in a random manner as time elapses. On the other hand, the actual *location* of the diffusing particle is determined by the solution of a certain enumeration problem on the lattice concerned, for each *given* number of steps. The latter problem has an answer (known in principle for all lattice graphs) that depends on the dimensionality and structure of the lattice. A complete ' step ' will be understood as a line joining two nearest neighbour cells. The combinatorial problem asks for the probability $p_n(\mathbf{m})$ of reaching the cell around the site $\mathbf{m}$ from that around $\mathbf{0}$ in $n$ steps. To be specific, let us henceforth consider a $d$-dimensional hypercubic lattice, with the lattice constant set equal to unity, for convenience. (Extension to other lattices, including non-Bravais ones, is tedious but straightforward). Then $\mathbf{m}$ is specified by $d$ integers $(m_1, \ldots, m_d)$. The generating function of $p_n(\mathbf{m})$, namely

$$G_n(z_1,\ldots,z_d) = \sum_{m_i=-\infty}^{\infty} p_n(\mathbf{m})\, z_1^{m_1}\, z_2^{m_2}, \ldots, z_d^{m_d}, \tag{1}$$

is then given by (see, for instance, Kasteleyn 1967)

$$G_n(z_1,\ldots,z_d) = [g(z)]^n, \tag{2}$$

where
$$g(z) = \sum_{i=1}^{d} (r_i z_i + l_i z_i^{-1}) \tag{3}$$

is the generating function of a single step on the lattice concerned. We have allowed for a possible asymmetrical environment at each site, *i.e.*, for a *biased* random walk, by taking $(r_i, l_i)$ to be the *a priori* probabilities of a jump in the $+i$ and $-i$ directions respectively: we have $0 < r_i, l_i < 1$, and

$$\sum_{i=1}^{d} (r_i + l_i) = 1. \tag{4}$$

Such a biased random walk will be relevant in many situations, such as diffusion in the presence of an applied field that makes the potential barriers around each site anisotropic. In the absence of bias, each $r_i = (2d)^{-1} = l_i$. The actual expression for $p_n(\mathbf{m})$ will automatically take care of the fact that one cannot reach $\mathbf{m}$ from $\mathbf{0}$ in less than $\sum_1^d |m_i|$ steps; and further, if $n$ has $n_i$ steps in the $i$-direction, then $n_i \geqslant |m_i|$, and $n_i = m_i \pmod 2$. The expression for $p_n(\mathbf{m})$ is rather cumbersome, and it is bypassed by working with the generating function (1).

Now consider the temporal aspect of the problem. The number $n$ of steps is a stationary, discrete random process for which a distribution must be deduced from first

**Jump* diffusion models incorporating nearest-neighbour as well as some multiple jumps (e.g., next-nearest-neighbour jumps) have been considered in the literature (see, e.g., Haus and Kehr 1979). For the hydrogen diffusion problem, this may be a more relevant generalization than the introduction of a finite flight time (Lottner *et al* 1979).

principles. Let $W(n, t)$ denote this distribution: it is the probability that the particle executes $n$ complete steps in a time interval $t$. Given this quantity, the fundamental probability we seek to compute is given by

$$P(\mathbf{m}, t) = \sum_{n=0}^{\infty} W(n, t)\, p_n(\mathbf{m}). \tag{5}$$

In practice, it is most convenient to re-express this connection in terms of the corresponding generating functions. Let $W(n, t)$ have the generating function

$$H(z, t) = \sum_{n=0}^{\infty} W(n, t)\, z^n. \tag{6}$$

Similarly, let

$$L(z_1, \ldots, z_d, t) = \sum_{m_i=-\infty}^{\infty} P(\mathbf{m}, t)\, z_1^{m_1} z_2^{m_2}, \ldots, z_d^{m_d}. \tag{7}$$

Then, using the fact that the generating function of $p_n(\mathbf{m})$ has the structure (2), it can be shown that

$$L(z_1, \ldots, z_d, t) = H(g(z), t), \tag{8}$$

where $g(z)$ is the single step generating function defined in (3). $P(\mathbf{m},t)$ may then be obtained in principle by the inversion

$$P(\mathbf{m}, t) = (1/2\,\pi i)^d \oint \prod_{i=1}^{d} (dz_i/z_i^{m_i+1})\, H(g(z), t). \tag{9}$$

The fundamental problem is therefore reduced now to the determination of the step-generating function $H(z, t)$. Conservation of probability requires that

$$\sum_{n=0}^{\infty} W(n, t) = H(1, t) = 1. \tag{10}$$

Of considerable importance in what follows is the first moment of $W(n, t)$, namely, the mean number of steps in the time interval $t$. This is given by

$$\nu(t) = \sum_{n=1}^{\infty} n\, W(n, t) = [\partial H(z, t)/\partial z]_{z=1}. \tag{11}$$

With the help of (8), it is easy to show that the mean displacement from the (arbitrarily chosen) origin is given by

$$\langle m_i(t) \rangle = (r_i - l_i)\, \nu(t). \tag{12}$$

This quantity vanishes, of course, for an unbiased random walk. The mean square displacement, a basic object in any diffusion process, is likewise given by

$$\langle \mathbf{m}^2(t)\rangle = \sum_{i=1}^{d} \langle m_i^2(t)\rangle = \nu(t) + \nu_2(t) \sum_{i=1}^{d} (r_i - l_i)^2, \tag{13}$$

where $$\nu_2(t) = \sum_{n=2}^{\infty} n(n-1)\, W(n, t) = (\partial^2 H/\partial z^2)_{z=1}. \tag{14}$$

We shall also be interested, at several junctures, in estimating the extent to which the solutions $P(\mathbf{m}, t)$ corresponding to various unbiased random walks depart from the normal distribution of conventional diffusion theory in an infinite continuum. As in well known, this is measured by the excess of kurtosis, denoted by $\gamma_2(t)$ and given by

$$\gamma_2(t) = (\langle \mathbf{m}^4(t)\rangle - 3\langle \mathbf{m}^2(t)\rangle^2)/\langle \mathbf{m}^2(t)\rangle^2. \tag{15}$$

After some algebra, we obtain the result

$$\gamma_2(t) = [(1 + 2/d)\,\nu_2(t) + \nu(t) - 3\,\nu^2(t)]/\nu^2(t), \tag{16}$$

which will be used in the sequel.

## 3. Evaluation of $W(n, t)$ and its generating function $H(z, t)$

We shall now derive expressions for $W(n, t)$ and $H(z, t)$ using a continuous-time random walk technique. In order to ensure the correctness of the enumeration procedure, it is necessary first to clarify what we mean by a ' complete step '.

The temporal development of the diffusion process is an alternating sequence of states of the particle, of the form..*LFLFLF*..... A basic assumption is that the $L$ and $F$ states are not correlated with each other. A *complete step* is then defined as an $F$ that is bracketed on either side by $L$, indicating that the flight between sites has been completed. Figure 1 shows the possible one-step processes, with the convention that earlier events stand to the right. The corresponding sequences are *LFL, FLFL, LFLF* and *FLFLF*. There are four such sequences for each $n \geqslant 1$. The CTRW theory leads to an analytical expression for the probability associated with each sequence in terms of two basic functions of time: the $L \rightleftharpoons F$ transition probabilities. The answer for $W(n, t)$ is then a certain weighted sum of these expressions. Note that there are *five* diagrams that contribute to the zero-step probability $W(0, t)$ in our method of book-keeping, arising from the event sequences *L, FL, F, LF* and *FLF*.

Let us now introduce the primary $L \rightleftharpoons F$ transition probabilities, and quantities related to them. We view each possible sequence ...*LFLF*... as a realization of a stochastic process with holding time distributions $p(t)$ and $q(t)$ respectively for the $L$ and $F$ states. In other words, given that the diffusing particle has just fallen into an $L$ state (*i.e.*, become localized about a site) at some epoch $t_0$, the probability that

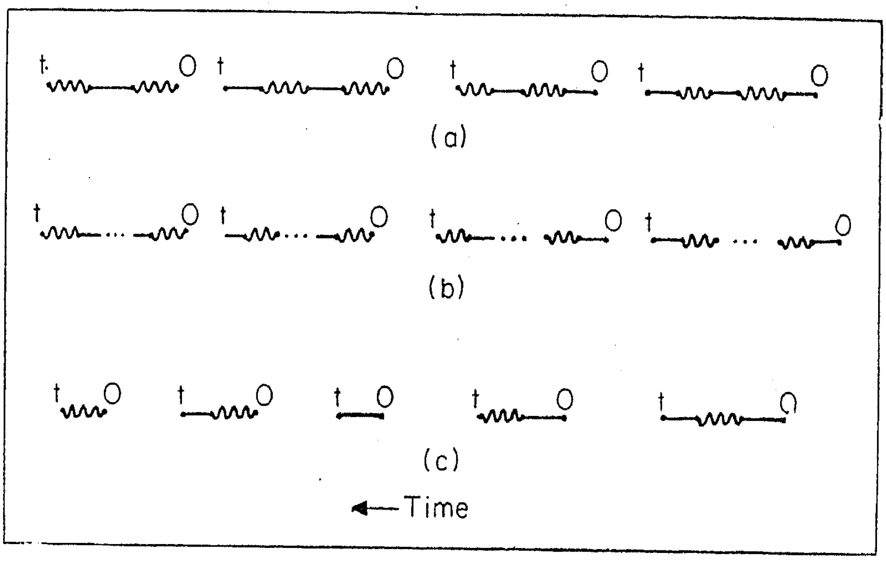


**Figure 1.** The diagrams contributing to (a) the one-step probability, $W(1, t)$; (b) the n-step probability, $W(n, t)$, $n > 1$; (c) the zero-step probability, $W(0, t)$. Wavy lines denote localized states, straight lines denote flight states.

the same state persists at epoch $(t_0+t)$ is given by $p(t)$. The distribution $q(t)$ is defined analogously for the state $F$. Evidently, $p(0)=q(0)=1$, and $p(t)$, $q(t)$ are non-increasing, positive functions of $t$ satisfying $p(\infty)=q(\infty)=0$. Further, using a prime to denote differentiation, $-p'(t)dt$ is the probability that a transition from $L$ to $F$ occurs in the time interval $(t_0+t, t_0+t+dt)$. Similarly, $-q'(t)dt$ is the analogous $F\to L$ transition probability. The mean residence time at a site is the mean time spent in the state $L$, and is equal to

$$w_0 = \int_0^\infty dt\, t\, (-p'(t)) \Big/ \int_0^\infty dt\, (-p'(t)) = \int_0^\infty dt\, p(t). \tag{17}$$

Likewise, the mean flight time is

$$w_1 = \int_0^\infty dt\, q(t). \tag{18}$$

Now, in setting up probabilities for sequences such as *LFLF*... from a randomly chosen origin of time labelled $t=0$, one has no precise knowledge of how long the initial state has persisted prior to $t=0$. Therefore the holding-time distribution for the *first* state in the sequence is distinct from $p(t)$ (if this state is $L$) or $q(t)$ (if this state is $F$). The first-waiting-time distributions for $L$ and $F$ respectively are given by (Feller 1966; see also the remarks in Balakrishnan 1980)

$$p_0(t) = (1/w_0) \int_t^\infty dt_1\, p(t_1), \quad q_0(t) = (1/w_1) \int_t^\infty dt_1\, q(t_1). \tag{19}$$

The corresponding first transition probabilities per unit time are of course*

$$-p_0'(t) = p(t)/w_0, \quad -q_0'(t) = q(t)/w_1. \tag{20}$$

Next, we must specify the relative *a priori* probabilities for the particle to be in the $L$ and $F$ states respectively at a randomly chosen origin of time. These are quite evidently determined by the mean lifetimes in the two states, and are given by $w_0/(w_0+w_1)$ and $w_1/(w_0+w_1)$ respectively. For $n \geqslant 1$, therefore, one can write

$$W(n, t) = \frac{w_0}{(w_0+w_1)}(W_{L\leftarrow L}(n, t) + W_{F\leftarrow L}(n, t))$$

$$+ \frac{w_1}{(w_0+w_1)}(W_{L\leftarrow F}(n, t) + W_{F\leftarrow F}(n, t)), \tag{21}$$

where the subscripts on $W$ refer to the initial and final states in the sequences. The construction of the quantities $W_{L\leftarrow L}(n, t)$, *etc.*, is straightforward. We find

$$W_{L\leftarrow L}(n, t) = \int_0^t dt_{2n} \ldots \int_0^{t_2} dt_1\, p(t-t_{2n})\, q'(t_{2n}-t_{2n-1})\, p'(t_{2n-1}-t_{2n-2}) \ldots$$

$$q'(t_2-t_1)\, p_0'(t_1),$$

$$W_{F\leftarrow L}(n, t) = -\int_0^t dt_{2n+1} \ldots \int_0^{t_2} dt_1\, q(t-t_{2n+1})\, p'(t_{2n+1}-t_{2n})$$

$$q'(t_{2n}-t_{2n-1}) \ldots q'(t_2-t_1)\, p_0'(t_1),$$

$$W_{L\leftarrow F}(n, t) = -\int_0^t dt_{2n+1} \ldots \int_0^{t_2} dt_1\, p(t-t_{2n+1})\, q'(t_{2n+1}-t_{2n})$$

$$p'(t_{2n}-t_{2n-1}) \ldots p'(t_2-t_1)\, q_0'(t_1),$$

$$W_{F\leftarrow F}(n, t) = \int_0^t dt_{2n+2} \ldots \int_0^{t_2} dt_1\, q(t-t_{2n+2})\, p'(t_{2n+2}-t_{2n+1})$$

$$q'(t_{2n+1}-t_{2n}) \ldots p'(t_2-t_1)\, q_0'(t_1). \tag{22}$$

*These expressions, and indeed the entire development of this section, can be summarized in technical terms (see Cox 1967) as follows: the sequences....*LFLF*....are realizations of an *equilibrium alternating renewal process* with distinct holding time distributions.

It remains to specify $W(0, t)$. Recalling the five contributory sequences referred to earlier (figure 1), we have

$$W(0, t) = \frac{w_0}{(w_0+w_1)}\left[p_0(t) - \int_0^t dt_1\, q(t-t_1)\, p_0'(t_1)\right] + \frac{w_1}{(w_0+w_1)}\left[q_0(t) - \int_0^t dt_1\, p(t-t_1)\, q_0'(t_1) + \int_0^t dt_2 \int_0^{t_2} dt_1\, q(t-t_2)\, p'(t_2-t_1)\, q_0'(t_1)\right]. \quad (23)$$

Further, $W(n, 0) = \delta_{n,0}$.

We may now compute the generating function $H(z, t)$. It is obviously convenient to work with the Laplace transform $\tilde{H}(z, s)$. Let $\tilde{p}(s)$, $\tilde{q}(s)$ denote the respective transforms of $p(t)$ and $q(t)$. After some algebra, we obtain the following compact result:

$$\tilde{H}(z, s) = \frac{1}{s} + \frac{(z-1)\,(1-s\,\tilde{q}(s))\,(\tilde{p}(s) + \tilde{q}(s) - s\,\tilde{p}(s)\,\tilde{q}(s))}{s(w_0+w_1)\,D(z, s)}, \quad (24)$$

where $\quad D(z, s) = 1 - z\,(1-s\,\tilde{p}(s))\,(1-s\,\tilde{q}(s)). \quad (25)$

This is the required solution. Since $H(1, s) = 1/s$, no sequences have been left out in the counting, and $W(n, t)$ is a normalized probability. The solution is of very general applicability. It encompasses complicated memory effects and correlations in the pulse sequences that cause the $L \rightleftharpoons F$ transitions. The case of exponential holding time distributions is the one of greatest physical relevance. It corresponds to uncorrelated sequences of transitions, and is studied in detail subsequently.

## 4. Explicit solution in one dimension

Before proceeding with the general theory, we record here the explicit solution for the conditional density $P(m, t)$ (or rather, its Laplace transform) in the case of a one-dimensional random walk. This involves the summation over $n$ expressed in (5), after the Laplace transform of $W(n, t)$ is obtained from the generating function (24). Let $\tilde{}\,(m, s)$ be the transform of $P(m, t)$. Write $\tilde{p}$, $\tilde{q}$ for $\tilde{p}(s)$ and $\tilde{q}(s)$ respectively, for brevity. After a considerable amount of algebra, we arrive at the following final result:

$$\tilde{P}(m, s) = \left[\frac{1}{s} - \frac{(\tilde{p}+\tilde{q}-s\,\tilde{p}\,\tilde{q})}{s\,(w_0+w_1)\,(1-s\,\tilde{p})}\right]\delta_{m,0} + (r/l)^{m/2}\left\{\frac{(\tilde{p}+\tilde{q}-s\,\tilde{p}\,\tilde{q})^2}{(w_0+w_1)\,(1-s\,\tilde{p})\,(1-h^2)^{1/2}}\right\}\,[(1-(1-h^2)^{1/2})/h]^m, \quad (26)$$

where $\quad h = h(s) = 2\,(rl)^{1/2}\,(1-s\,\tilde{p})\,(1-s\,\tilde{q}). \quad (27)$

This expression is valid for $m\geqslant 0$. For negative integral $m$, we must let $m\to -m$ and interchange $r$ and $l$ in the above. In principle, (26) is an exact, closed form solution to our two-state random walk problem on a one-dimensional lattice. If one sets $\tilde{q}=0$, $w_1=0$ in the above, the corresponding solution in the class of instantaneous jump models is obtained. On the other hand, setting $\tilde{p}=0$, $w_0=0$ yields the solution for the case of 'free' diffusion. As a quick check, let us set $m=0$ and evaluate $P(0, t)$ in the case $\tilde{q}=w_1=0$, $p(t)=\exp(-t/\tau_0)$. Making use of the appropriate inverse Laplace transforms (Oberhettinger and Badii 1973), we find from (26) and (27) that

$$P(0, t) = \exp(-t/\tau_0)\, I_0\,(2\,(rl)^{1/2}\, t/\tau_0), \tag{28}$$

where $I_0$ is the modified Bessel function of order zero. Equation (28) is in agreement with the general result (52) to be derived below. Similarly, if we set $\tilde{p}=w_0=0$ and $q(t)=\exp(-t/\tau_1)$, we find

$$P(0, t) = \exp(-t/\tau_1)\left[1+\int_0^t d\,\xi\, I_0\,(2\,\xi\,(rl)^{1/2})\right], \tag{29}$$

which is consistent with the general result (71).

The expressions in (26) and (27) simplify somewhat when $r=l=\frac{1}{2}$. The asymptotic $(t\to\infty)$ behaviour of $P(m, t)$ for fixed $m$ is then easily deduced. We expect a fall-off proportional to $t^{-1/2}$, characteristic of diffusion in one dimension. Examining (26) and (27) near $s=0$, we find a leading $s^{-1/2}$ behaviour owing to the factor $(1-h^2)^{-1/2}$ in curly brackets in (26). This leads to

$$P(m, t) \sim [(w_0+w_1)/2\pi t]^{1/2}, \tag{30}$$

as conjectured. In the next section, we consider the asymptotic behaviour of $P(\mathbf{m}, t)$ in further detail.

## 5. Asymptotic behaviour of $P(\mathbf{m}, t)$

Returning to diffusion in $d$ dimensions, let us establish first the asymptotic $(t\to\infty)$ behaviour of the conditional density $P$ for fixed (finite) $\mathbf{m}$. In contrast to the $t\sim 0$ regime, there is no simple scaling of variables in the multiple integrals constituting $W(n, t)$ that enables one to deduce the longtime behaviour of $W$, $H$ and $P$ directly. For this, it is necessary to know the nature and location of the leading singularities of $\tilde{p}(s)$ and $\tilde{q}(s)$. If $p(t)\exp(\lambda_0 t) = O$ and $q(t)\exp(\lambda_1 t) = O(1)$ as $t\to\infty$, these are simple poles at $s=-\lambda_0$ and $s=-\lambda_1$ respectively. We shall subsequently (in § 9) determine $H(z, t)$ in closed form in the case when these are the *only* singularities of $\tilde{p}(s)$ and $\tilde{q}(s)$. Even in that special case, $H(z, t)$ is rather complicated in appearance.

Even without a detailed knowledge of the singularity structure of $\tilde{p}(s)$ and $\tilde{q}(s)$, it is possible to prove that $P(\mathbf{m}, t) = O(t^{-d/2})$ as $t\to\infty$, in the absence of bias. An extra multiplicative exponential damping factor occurs when bias is introduced. To deduce these results, we begin with equation (23) for $\widetilde{H}(z, s)$, to find

$$\left[\frac{\partial^n \widetilde{H}(z, s)}{\partial z^n}\right]_{z=1} = \frac{n!\,(1 - s\widetilde{p})^{n-1}\,(1 - s\widetilde{q})^n}{(w_0 + w_1)\,s^{n+1}\,(\widetilde{p} + \widetilde{q} - s\widetilde{p}\,\widetilde{q})^{n-1}}. \tag{31}$$

Provided $\widetilde{p}(s)$ and $\widetilde{q}(s)$ are regular* at $s = 0$, the *leading* asymptotic behaviour in $t$ of the inverse transform of the left hand side in (31) comes from the term $(st)^n/n!$ in the expansion of the factor $\exp(st)$ occurring in the inverse transform. Therefore, as $t \to \infty$,

$$(\partial^n H(z, t)/\partial z^n)_{z=1} \sim t^n/(w_0 + w_1). \tag{32}$$

*Assuming* that summing over the foregoing leading behaviour of each term in the Taylor series about $z = 1$ of $H(z, t)$ gives the leading asymptotic behaviour of $H(z, t)$ itself, we get

$$H(z, t) \sim \exp\,[t(z - 1)/(w_0 + w_1)]. \tag{33}$$

Therefore the generating function for $P(\mathbf{m}, t)$ behaves as

$$L(z_1, \ldots, z_d, t) \sim \exp\,[t(g(z) - 1)/(w_0 + w_1)] \tag{34}$$

where $g(z)$ is the single-step generating function already defined in (3). $L$ thus factors into a product of $d$ exponentials, each of which is the generating function for a modified Bessel function. Since only the leading asymptotic behaviour in each of these must be retained, we obtain finally

$$P(\mathbf{m}, t) \sim \left(\frac{w_0+w_1}{4\pi t}\right)^{d/2} \exp\left(-\frac{b_d t}{w_0+w_1}\right) \prod_{i=1}^{d} (r_i/l_i)^{m_i/2}\,(r_i l_i)^{-1/4}, \tag{35}$$

where $$b_d = 1-2\sum_{i=1}^{d} (r_i l_i)^{1/2}. \tag{36}$$

Clearly $b_d \geqslant 0$, the equality sign obtaining when $r_i = l_i = (2d)^{-1}$. The foregoing shows how the expected $t^{-d/2}$ tail is modulated by an exponential damping factor when diffusion occurs in the presence of bias in any direction. When there is no bias, (35) reduces to

$$P(\mathbf{m}, t) \sim \left[\frac{(w_0+w_1)d}{2\pi t}\right]^{d/2}. \tag{37}$$

*This analyticity is essential for the 'conventional' asymptotic behaviour of $P$ to be realized. The circumstances under which non-analyticity at $s=0$ may arise are discussed briefly at the end of §7, and in greater detail in Balakrishnan (1981).

## 6. The mean square displacement

We turn now to the determination of that basic quantity in any theory of diffusion, the mean square displacement. We have already established (see (13)) that

$$\langle \mathbf{m}^2(t) \rangle = \nu(t) \tag{38}$$

for an unbiased random walk. (Recall that the lattice constant has been set equal to unity.) It is therefore $\nu(t)$, the mean number of complete steps executed in time $t$, that remains to be computed. An elegant expression for $\nu(t)$ can be obtained from (24). Evaluating $\partial \tilde{H}/\partial z$ at $z = 1$ and inverting the Laplace transform, we find

$$\nu(t) = \frac{1}{(w_0 + w_1)} \Big[ t - \int_0^t dt_1 \, q(t_1) \Big]. \tag{39}$$

Equation (39) may be re-cast in the form

$$\nu(t) = \frac{t}{(w_0 + w_1)} - \frac{w_1}{(w_0 + w_1)} (1 - q_0(t)), \tag{40}$$

in order to clarify the meaning of the various terms. The linear dependence is the familiar asymptotic behaviour in the purely diffusive limit (*i.e.*, when $t$ is much greater than the correlation time of the velocity), and is of course obtained as the asymptotic behaviour in simple random walk theory as well. The second term in (40) is the 'correction' that emerges when one drops the assumption that the flights from site to site occur instantaneously. It is again well known that the Langevin equation treatment of Brownian motion yields a specific form for this term: if $\gamma$ is the friction coefficient, the velocity of the diffusing particle is a stationary Gaussian Markov process with correlation time $\gamma^{-1}$, and the mean square displacement has a time-dependence given by $(\gamma t - 1 + \exp(-\gamma t))$. Equation (39) or (40) is the generalization of this result, valid even for lattice diffusion, derived within the framework of CTRW theory. The quantity $1 - q_0(t)$ is the no-transition probability (from a randomly chosen origin of time) in the flight state. The deviation of $\nu(t)$ from its asymptotic proportionality to $t$ is therefore given by the product of the foregoing no-transition probability and the *a priori* probability for the particle to be in the state of flight. This is the physical interpretation of the result derived above. This term is absent in all jump diffusion models (§ 7).

The second term in (39) actually dominates $\nu(t)$ for very *small* values of $t$. In general, $q(t)$ must be a non-increasing function of $t$ as $t$ varies from 0 to $\infty$. We therefore obtain the leading behaviour

$$\nu(t) \sim \tfrac{1}{2} (w_0 + w_1)^{-1} \, | q'(0) | \, t^2. \tag{41}$$

This leading quadratic $t$-dependence is of course required on physical grounds. The role played by a finite $q'$ in the emergence of this result is noteworthy. All jump models lead to an unphysical ($\sim t$) short-time behaviour of $\nu(t)$.

For a biased random walk, the mean square displacement depends on the second factorial moment $\nu_2(t)$ as well (see (13)). The leading short-time behaviour of this quantity is

$$\nu_2(t) \sim \frac{1}{12}(w_0 + w_1)^{-1} \,|\, p'(0) \,|\, (q'(0))^2\, t^4, \tag{42}$$

showing that the bias affects the rms displacement only from the $t^3$ term onwards in its short-time expansion.

## 7. Jump diffusion models

Although the assumption that the diffusing particle jumps instantaneously from site to site cannot be strictly valid, there are many situations in which it is a good approximation, when $w_0$ is much larger than $w_1$. Instantaneous jumps correspond to letting $-q'(t) \to \delta_+(t)$ the foregoing, with consequent alterations in the expression for $W(n,t)$. However, the final result is easily reproduced by simply setting $\tilde{q}(s)=0$ in (23) and (24). We have then

$$\tilde{H}(z, s) = \frac{1}{s} + \frac{(z-1)\,\tilde{p}(s)}{s w_0[1-z\,\{1-s\tilde{p}(s)\}]}. \tag{43}$$

Therefore $\nu(t) = t/w_0$, (44)

regardless of the actual functional form of $p(t)$. It is evident that (44) is unphysical at short times, as already mentioned. Once again, the asymptotic ($t\to\infty$) form of $P(\mathbf{m}, t)$ may be found following the steps in §5, provided $\tilde{p}(s)$ is not singular at $s=0$. The result, as expected, corresponds to setting $w_1=0$ in (35).

As a check on the formalism, consider the case of a *constant* residence time $\tau_0$ at each site. Then $p(t)=\theta\,(1-t/\tau_0)$ $(t \geqslant 0)$,

and $$\tilde{H}(z, s) = \frac{1}{s} + \frac{(z-1)\,(\exp(s\tau_0) - 1)}{s^2\,\tau_0\,(\exp(s\tau_0) - z)}. \tag{45}$$

Inverting the Laplace transform (Oberhettinger and Badii 1973), we get

$$H(z, t) = z^n \left[1 + (z-1)\left(\frac{t}{\tau_0} - n\right)\right] \quad \text{for } n\,\tau_0 \leqslant t \leqslant (n+1)\,\tau_0, \quad n=0, 1, 2, .. \tag{46}$$

This is precisely the result expected on physical grounds. At $t = n\tau_0$, we have $H(z, t) = z^n$, so that the generating function for the random walk is

$$L(z_1, \ldots, z_d, n\tau_0) = (g(z))^n, \tag{47}$$

as expected. At $t=(n+1)\tau_0$, $H(z, t)=z^{n+1}$, and $n\to n+1$ in (47). The changeover from the former value to the latter one is *continuous* as $t$ increases from $n\tau_0$ to $(n+1)\tau_0$. This physical feature is a consequence of the inclusion of the appropriate first-waiting-time distribution.

With this verification out of the way, we turn to a very important special case in which an explicit solution for the self-correlation function is possible. If each jump of the particle is the result of a large number of Bernoulli trials, then (see, *e.g.*, Feller 1966), using the symbol $\tau_0$ for the mean residence time $w_0$,

$$p(t)=\exp(-t/\tau_0). \tag{48}$$

Equation (48) implies that the random pulses which cause the particle to jump from site to site form an uncorrelated (Poisson) sequence. Further, the distinction between $p(t)$ and $p_0(t)$ *disappears in this case* (and *only* in this case). We find

$$\tilde{H}(z, s) = \tau_0/(1+s\tau_0-z) \tag{49}$$

and therefore

$$H(z, t) = \exp(t(z-1)/\tau_0), \tag{50}$$

which is the generating function for the Poisson distribution

$$W(n, t) = (1/n!)\,(t/\tau_0)^n \exp(-t/\tau_0) \tag{51}$$

with mean $\nu(t)=t/\tau_0$. This is the distribution assumed for $n$ in the treatment of the diffusion of hydrogen interstitials in metals by Gissler and Rother (1970). The jump diffusion model of Chudley and Elliott (1961) also follows from (51). Using the relation between the generating functions $H$ and $L$, we find

$$P(\mathbf{m}, t)= \exp(-t/\tau_0) \prod_{i=1}^{d} (r_i/l_i)^{m_i/2}\, I_{m_i}(2t(r_il_i)^{1/2}/\tau_0), \tag{52}$$

where $I_m$ is the modified Bessel function of order $m$. This is essentially the Chudley-Elliott result, extended to include bias in the random walk. In one dimension, it reduces to (28) as required. In figure 2, we have plotted the simple case that obtains when $d=1$, $m=0$, and further $r=l=\frac{1}{2}$. It is easily shown that (52) is the solution to the following Markovian master equation for biased jump diffusion on a $d$-dimensional lattice:

$$\frac{\partial}{\partial t}P(\mathbf{m}, t) = (1/\tau_0)\sum_{i=1}^{d} [r_i\,\{P(m_i-1, t)-P(m_i, t)\} + $$
$$+ l_i\,\{P(m_i+1, t) - P(m_i, t)\}]. \tag{53}$$

Here $(m_i\pm1)$ in the argument of $P$ is meant to denote a unit increment (or decrement) in the $i$th coordinate alone, *i.e.*, $P(m_2+1, t)\equiv P(m_1, m_2+1,\ldots, m_d, t)$. The

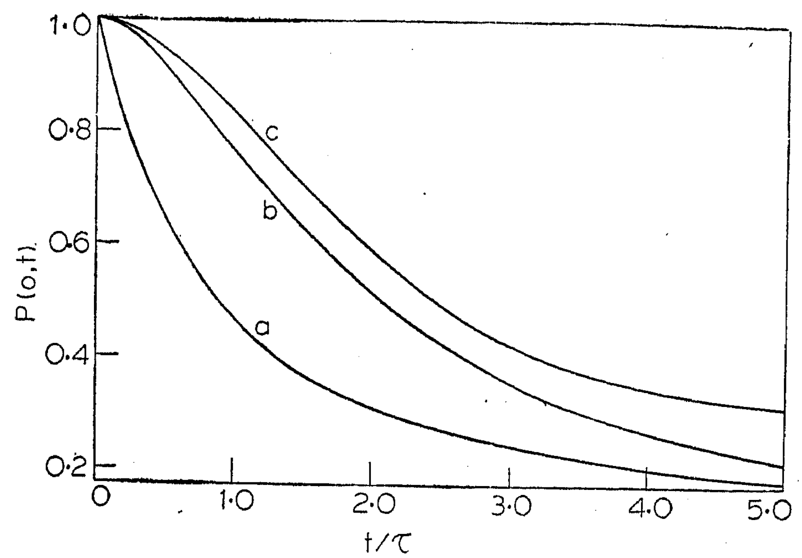


**Figure 2.** Probability $P(0, t)$ of return to the origin at time $t$, for an unbiased one dimensional random walk: (a) jump model with residence time distribution $p(t) = \exp(-t/\tau)$; (b) zero-residence time model with flight time distribution $q(t) = \exp(-t/\tau)$; (c) model with finite mean residence and flight times, with $p(t) = q(t) = \exp(-t/\tau)$.

initial condition is $P(\mathbf{m}, 0)=\delta_{\mathbf{m},\,\mathbf{0}}$, and $(1/\tau_0)$ is the mean rate of jumps. The foregoing clarifies the connection between the master equation and CTRW approaches, and the conditions under which the latter reduces to the former: (i) instantaneous jumps, (ii) exponential holding time distribution, or, equivalently, a Poisson sequence of jump-triggering pulses.

It is instructive also to pass to the limit when the difference equation (53) goes over into a partial differential equation. This happens when the step length $a\to 0$ and, simultaneously, the mean jump rate $(1/\tau_0)\to\infty$, keeping the ratio $a^2/\tau_0$ finite, as is familiar in diffusion theory. In the biased case, we must further let $(r_i - l_i)\to 0$ such that

$$\lim a\,(r_i - l_i)/\tau_0 = f_i \;(= \text{finite}). \tag{54}$$

Also set

$$\lim a^2\,(r_i + l_i)/2\,\tau_0 = D_i. \tag{55}$$

Then, replacing $P(\mathbf{m}, t)$ by $P(\mathbf{R}, t)$, it is seen that (53) goes over into

$$\begin{aligned}\frac{\partial P}{\partial t}(\mathbf{R}, t) &= \sum_{i=1}^{d}\{-f_i\,(\partial P/\partial R_i) + D_i\,(\partial^2 P/\partial R_i^2)\}\\ &= -\mathbf{f}\cdot\nabla P + \nabla\cdot\boldsymbol{D}\cdot\nabla P\end{aligned} \tag{56}$$

in an obvious notation, $D_i$ being the components of the diagonal diffusion tensor $\boldsymbol{D}$. The Smoluchowski equation for anisotropic diffusion in a constant force field is thus recovered. In the simpler situation of isotropic diffusion, (56) reduces to the conventional diffusion equation with the familiar Gaussian solution

$$P(\mathbf{R}, t) = (4\pi Dt)^{-d/2}\exp(-\mathbf{R}^2/4Dt). \tag{57}$$

The discrete solution (52) is transformed to the above on taking the appropriate limits in the parameters, and using the limit

$$\lim_{\zeta\to\infty} \zeta I_{\zeta x}(z\zeta^2)\exp(-z\zeta^2) = (2/\pi z)^{1/2}\exp(-x^2/2z). \tag{58}$$

An idea may be obtained of the extent to which the discrete solution $P(\mathbf{m}, t)$ deviates from a normal distribution by evaluating the excess of kurtosis, $\gamma_2(t)$. Using (16) and (50) for $H(z, t)$, we get

$$\gamma_2(t) = (\tau_0/t) - 2(d-1)/d. \tag{59}$$

For $t \ll \tau_0$, therefore, the distribution has a broader tail than the corresponding Gaussian. As $t$ increases, the distribution approaches normality. For $d=1$, the approach is asymptotic. In higher dimensional lattices, on the other hand, the 'extra' directions available enable this to be attained at a finite value of $t$, and for larger values of $t$ the distribution in fact becomes platykurtic.

We conclude this section on jump diffusion models with a brief discussion of an important generalization of the case of an exponential holding time distribution. This is a continuous superposition of exponentials, namely,

$$p(t) = \int_0^\infty d\tau\, \rho(\tau)\exp(-t/\tau), \tag{60}$$

where $\rho(\tau)$ is some spectral weight function. It is evident that (60) is a representation of considerable generality that can arise in numerous physical circumstances. If the jumps are caused by the simultaneous action of a *set* of mutually uncorrelated pulse sequences, for example, one may expect a departure from (48) that can be written as in (60). Again, if the potential barriers separating the 'localized' states have a distribution of heights (as in disordered media, for example), (60) results. Whatever the cause, certain general conclusions can be drawn when $p(t)$ is given by (60). The transform of this expression is

$$\tilde{p}(s) = \int_0^\infty d\tau\, \tau\rho(\tau)/(1+s\tau). \tag{61}$$

For a normalized distribution $\rho(\tau)$, we then have

$$\tilde{H}(z, s) = \frac{1}{s} + \frac{(z-1)\int_0^\infty d\tau\, \tau\rho(\tau)/(1+s\tau)}{sw_0\left[1 - z\int_0^\infty d\tau\, \rho(\tau)/(1+s\tau)\right]}, \tag{62}$$

where $$w_0 = \int_0^\infty d\tau\, \tau\rho(\tau). \tag{63}$$

The point we wish to make is as follows. While $v(t)$ is still given by $t/w_0$, a host of possibilities exists as regards the behaviour of $H(z, t)$, and hence that of $P(\mathbf{m}, t)$. The emergence of 'non-analytic' behaviour from an infinite summation or continuous superposition of 'regular' terms is of course well known, examples ranging from Regge behaviour to rock magnetism. In the present context, it is evident from (61) that $\tilde{p}(s)$ may have a part that is non-analytic* at $s = 0$. Under suitable circumstances, this leads to an unconventional asymptotic ($t \to \infty$) behaviour of $P(\mathbf{m}, t)$, different from that deduced in § 5 (see Balakrishnan 1981). The dynamic structure factor would then exhibit corresponding deviations from the standard $\omega^{d/2-1}$ behaviour near $\omega = 0$. In general, the asymptotic behaviour of $H$ and $P$ in such non-analytic cases may be deduced with the help of powerful Tauberian theorems, given a distribution $\rho(\tau)$ (or at least its asymptotic behaviour) based on the underlying physical processes.

## 8. Zero halt time models

The general theory may also be reduced to another physically interesting special case, complementary to that of § 7. 'Free' diffusion may occur, in the sense that the particle does not spend any time at all in the localized state while hopping from site to site. This amounts to passing to the limit $-p'(t) \to \delta_+(t)$ in the formalism of § 3. The resulting generating function $\tilde{H}(z, s)$ is given by

$$\tilde{H}(z, s) = \frac{1}{s} + \frac{(z-1)\,\tilde{q}(s)\,(1-s\,\tilde{q}(s))}{s w_1\,[1-z\,(1-s\,\tilde{q}(s))]}. \tag{64}$$

As far as $v(t)$ and hence the mean square displacement are concerned, the expressions derived in § 6 and the related discussion remain valid, with $w_0$ set equal to zero.

Once again, consider first the case of a constant flight time $\tau_1$ for each step, as a check on the formalism. Setting $q(t) = \theta(1-t/\tau_1)$ $(t \geqslant 0)$, we get, transforming back to the time variable,

$$H(z, t) = \begin{cases} 1 \text{ for } 0 \leqslant t \leqslant \tau_1 \\ z^{n-1}\left[1+(z-1)\left(\dfrac{t}{\tau_1} - n\right)\right] \text{ for } n\,\tau_1 \leqslant t \leqslant (n+1)\,\tau_1\ (n=1, 2, \ldots). \end{cases} \tag{65}$$

As in (46) *ff.*, this is just the required answer. Recall that a complete step, labelled by $n$, requires that each $F$ be adjoined by $L$ on either side. This is why $z^{n-1}$ in (65) plays the role of $z^n$ in (46).

Next, we turn to the functional form

$$q(t) = \exp(-t/\tau_1), \tag{66}$$

---

*If the variance of $p(t)$ diverges, for instance, then $\tilde{p}(s) = w_0 + cs + ds^{\alpha} + \ldots\ldots$ near $s=0$, where $1 < \alpha < 2$. This is precisely the sort of behaviour that leads to $1/f^{\alpha}$ noise effects in certain problems (Tunaley 1976), power-law tails in velocity correlation functions (Alder and Wainwright 1970), etc.

which is again of special interest. It implies that a Markov process governs the continued stay of the particle in the same state of flight at time $t$ that it entered at $t=0$. We find

$$H(z, t) = \left[1 - \frac{1}{z} + \frac{1}{z}\exp(tz/\tau_1)\right]\exp(-t/\tau_1), \tag{67}$$

so that

$$W(n, t) = \left[\delta_{n,0} + \frac{1}{(n+1)!}\left(\frac{t}{\tau_1}\right)^{n+1}\right]\exp(-t/\tau_1). \tag{68}$$

The mean square displacement follows from

$$\nu(t) = (t/\tau_1) - 1 + \exp(-t/\tau_1), \tag{69}$$

which has the correct behaviour for both small $t$ and large $t$ ($\sim t^2$ and $t$ respectively), as discussed in § 6. Now (69) is exactly what is obtained in the standard Langevin equation model of diffusion, $\tau_1$ being identified with the correlation time of the velocity, $\gamma^{-1}$. It is to be noted that this result is now attained by a *random walk* method, as a special case. In view of the above equivalence, we may regard this case as a basic model of free diffusion in the time-dependent random walk approach. What (67) describes is the time development of the ' steps ' (transitions) in the process. The subsequent linking of $H(z, t)$ to the conditional density of the displacement (or any other physical random variable) depends on the particular system of interest—*e.g.*, a lattice, or a continuous medium, or an irregular array of points, etc.

A closed expression for $P(\mathbf{m}, t)$ may be derived from (67). A trivial re-writing of that equation shows that the generating function for $P$ has the structure

$$L(z_1, \ldots, z_d, t) = \left[1 + \int_0^{t/\tau_1} d\xi \exp\{\xi g(z)\}\right]\exp(-t/\tau_1), \tag{70}$$

where $g(z)$ is given by (3). Since the exponential in curly brackets factors into a product of exponentials, we arrive at the solution

$$P(\mathbf{m}, t) = \left[\delta_{\mathbf{m},0} + \int_0^{t/\tau_1} d\xi \prod_{i=1}^{d} (r_i/l_i)^{m_i/2} I_{m_i}(2\xi(r_i l_i)^{1/2})\right]\exp(-t/\tau_1). \tag{71}$$

Once again, this reduces to (29) in one dimension. Figure 2 contains a plot of the special case $d=1$, $m=0$, $r=l=\frac{1}{2}$ as obtained from (71), and this should be compared with the corresponding plot for the jump diffusion model of § 7. It is interesting to note that, in one dimension, $P(m, t)$ has the alternative representation

$$P(m, t) = \left[\delta_{m,0} + \left(\frac{r}{l}\right)^{m/2}(rl)^{-1/2}\sum_{n=0}^{\infty}(-1)^n I_{m+2n+1}(2t(rl)^{1/2}/\tau_1)\right] \exp(-t/\tau_1). \tag{72}$$

The solution (71) should be compared with that of the zero *jump* time model, equation (52). The ' superposition ' implied by the integration over $\xi$ intuitively suggests an improvement in the short-time behaviour of the theory, a feature already discussed earlier. The master equation of which (71) is the solution makes the point even more explicit. For notational simplicity, consider the one-dimensional, unbiased case. We find

$$\frac{\partial}{\partial t} P(m, t) = (1/2\,\tau_1)\,[\{P(m+1, t) + P(m-1, t) - 2\,P(m, t)\}$$
$$- \{\delta_{m+1,0} + \delta_{m-1,0} - 2\,\delta_{m,0}\} \exp(-t/\tau_1)]\ . \tag{73}$$

Thus $\partial P(m, t)/\partial t \to 0$ as $t \to 0$, and the desired feature follows. Note that $P(m, 0) = \delta_{m,0}$ is the initial condition on $P$.

The deviation from a normal distribution of the solution $P$ (**m**, $t$) for an unbiased random walk may again be judged by the excess of kurtosis. We find, for $d$=3,

$$\gamma_2(t) = \left[\nu(t) + 3\left(1 - 2\frac{t}{\tau_1}\exp(-t/\tau_1) - \exp(-2\,t/\tau_1)\right)\right] \Big/ \nu^2(t), \tag{74}$$

where $\nu(t)$ is given by (69). Thus $\gamma_2(t)$ has the same leading behaviour as $1/\nu(t)$ for both $t \ll \tau_1$ and $t \gg \tau_1$, and becomes negligible for $t \gg \tau_1$.

## 9. Model with exponential holding times $p(t)$, $q(t)$

The natural extension of the special cases discussed in § § 7 and 8 is a model in which

$$p(t) = \exp(-t/\tau_0), \quad q(t) = \exp(-t/\tau_1), \tag{75}$$

where $\tau_0$ and $\tau_1$ are in general distinct. The scope of applicability of the theory is now increased, as there do occur situations in which $\tau_0$ and $\tau_1$ are comparable*. The analytic solution to be presented shortly for $H(z, t)$ displays the roles played by finite halt and flight times in the diffusion process.

We use (75) in (24) and invert the Laplace transform. After some tedious algebra, we obtain the following result. Let $\lambda_0 = 1/\tau_0$, $\lambda_1 = 1/\tau_1$, and

$$\eta(z) = [\tfrac{1}{4}(\lambda_0 - \lambda_1)^2 + \lambda_0\lambda_1 z]^{1/2}. \tag{76}$$

Then
$$z(\lambda_0 + \lambda_1)H(z, t) = \lambda_0(z-1)\exp(-\lambda_1 t) + [(\lambda_0 + \lambda_1 z)\cosh \eta t$$
$$+ (1/2\eta)\{(\lambda_0 - \lambda_1)(\lambda_0 - \lambda_1 z) + 4\lambda_0\lambda_1 z\}\sinh \eta t]$$
$$\exp\{-\tfrac{1}{2}(\lambda_0 + \lambda_1)t\}. \tag{77}$$

---

*The Singwi-Sjölander (1960) model for diffusion in liquids uses the choice (75). Although the first-waiting-time complication is ignored, no consequences ensue as a result because only the exponential forms for $p(t)$ and $q(t)$ are employed in that work.

It is easily verified that $H(1, t) = 1$, as required, and that $H(z, t)$ is an entire function of $z$. If $\tau_1 \to 0$, we have

$$\eta(z) \to (1/2\tau_1) + (z - \tfrac{1}{2})/\tau_0 + O(\tau_1), \tag{78}$$

and therefore

$$H(z, t) \to \exp\,[t(z-1)/\tau_0], \tag{79}$$

yielding the jump model of (50) *ff.* While if $\tau_0 \to 0$, we find

$$\eta(z) \to (1/2\tau_0) + (z - \tfrac{1}{2})/2\tau_1 + O(\tau_0), \tag{80}$$

and hence

$$H(z, t) \to [1 - (1/z) + (1/z)\exp(zt/\tau_1)]\exp(-t/\tau_1), \tag{81}$$

thus reproducing the free diffusion model of (67) *ff.*

Returning to (75) to (77), we find (using (39), for instance)

$$\nu(t) = [t - \tau_1 + \tau_1 \exp(-t/\tau_1)]/(\tau_0 + \tau_1). \tag{82}$$

It is evident that the mean square displacement has the correct short-time behaviour. The diffusion constant for unbiased random walk in three-dimensions is given by

$$D = a^2/6(\tau_0 + \tau_1), \tag{83}$$

as expected. In part 2, we shall see how (83) is modified in the presence of a local mode.

The structure of the 'interference' between the $L$ and $F$ states is made more transparent by considering the special case $\tau_0 = \tau_1 = \tau$, which lies halfway between the extremes studied earlier. Equation (77) now simplifies somewhat, and we obtain

$$H(z, t) = \frac{1}{2}\left[\left(1 - \frac{1}{z}\right) + \left(1 + \frac{1}{z}\right)\cosh(t\sqrt{z}/\tau) + (2/\sqrt{z})\sinh(t\sqrt{z}/\tau)\right]\exp(-t/\tau). \tag{84}$$

The corresponding probability $W(n, t)$ is given by

$$W(n, t) = \frac{1}{2}\left[\delta_{n,0} + \frac{(t/\tau)^{2n}}{(2n)!} + \frac{2(t/\tau)^{2n+1}}{(2n+1)!} + \frac{(t/\tau)^{2n+2}}{(2n+2)!}\right]\exp(-t/\tau). \tag{85}$$

Equation (85) should be compared with (51) (corresponding to $\tau_1 = 0$) and with (68) (which obtains when $\tau_0 = 0$). Compact as (85) is, however, there does not appear to be a simple closed form for $P(\mathbf{m}, t)$ in this instance, even in one dimension. This is itself an indication of the non-trivial ' mixing ' caused by the random alternation (in time) of the $L$ and $F$ states. For the sake of comparison, we have again computed (numerically) the quantity $P(0, t)$ for the case $d=1$, $m=0$, $r=l=\frac{1}{2}$, and plotted the result in figure 2. We note that the flat behaviour near $t=0$ persists, a consequence of the finite mean flight time in the model. The asymptotic ($t/\tau \to \infty$) behaviour of the model is of course already explicit, from the general discussion.

Other combinations of $p(t)$ and $q(t)$ can be studied, depending on the physical motivation. One such possibility is

$$p(t) = \exp(-t/\tau_0), \quad q(t) = \theta(1 - t/\tau_1), \tag{86}$$

corresponding to *flights* of a fixed time $\tau_1$ between two neighbouring lattice sites, interrupted by residence times distributed exponentially (as in the foregoing). This choice is related to the ' finite flight time ' model of Gissler and Stump (1973) for the diffusion of interstitial hydrogen. The formalism of the earlier sections can be applied to this case in a straightforward manner.* A distribution of flight times (such as the exponential distribution of (75)) is of course a more general consideration than the assumption of a constant flight time.

## 10. Summary and concluding remarks

We have developed a comprehensive two-state random walk model for the diffusion of a particle on a lattice. The outcome is a picture of the diffusion process that synthesises in a natural manner features of the two extremes of jump diffusion and fluid-like diffusion. The latter emerge as clearly identified limiting cases. Various models extant in the literature have been shown to correspond to special cases that obtain under additional assumptions. The general theory also enables one to isolate features that are common to whole classes of models (*e.g.*, instantaneous jump models) regardless of their finer details.

As the important results of this paper we may list the following: Equation (24) for the generating function of the steps of the random walk, which, in conjunction with (25) and (8), yields the generating function for the conditional probability, $P(\mathbf{m}, t)$; the explicit solution (26) for the linear lattice; the compact formula (39) (or (40)) for the mean square displacement of the particle; the unconventional asymptotic behaviour and other (' non-analytic ') effects caused by a continuous superposition of exponential holding time distributions, as discussed in § 7; the continuum-diffusion-like result of (69) for the mean square displacement in lattice diffusion, when a finite mean flight time is allowed for; the corresponding closed-form solution for $P(\mathbf{m}, t)$ exhibited in (71); and the strong mixing of the flight and residence states in general, (84) being a particular manifestation of the effect.

As already stated in § 2, we have focussed our attention in this paper on the interplay of the two characteristic times $w_0$ and $w_1$ (the mean residence and flight times). The details of the motion of the particle while in the localized state about a lattice site would also bring in the third characteristic time, the inverse of the local mode frequency. Besides, for certain calculations such as that of the structure factor, we should have to augment the temporal propagators $-p'(t_i-t_j)$ and $-q'(t_i-t_j)$ used

*In this case, the two-state random walk problem essentially simplifies to a single-state one with a displaced exponential distribution $p(t) = \exp(-(t - \tau_1)/\tau_0)$, $(t \geqslant \tau_1)$.

in constructing the sequences $W(n, t)$ in § 3 with concurrent spatial propagators for displacements within a cell and between cells. This would be similar to the procedure used by Singwi and Sjölander (1960) for diffusion in liquids. We may take the motion of the particle to be described by an isotropic, three-dimensional, classical oscillator of frequency $\omega_0$ whenever it is in the localized state. The propagator required is the conditional density for a displacement **r** within a cell in the time interval $t$. We may use for this quantity the self-correlation function given by Vineyard (1958), namely,

$$g(\mathbf{r}, t) = \left[\frac{m\omega_0^2}{4\pi k_B T(1-\cos \omega_0 t)}\right]^{3/2} \exp\left[-\frac{m\omega_0^2 \mathbf{r}^2}{4k_B T(1-\cos \omega_0 t)}\right] \tag{87}$$

The resultant convolution of such factors can be handled by supplementing the Laplace transform (with respect to the time variable) with a spatial Fourier transform. However, our somewhat different objective in the present paper was better served, in the interest of clarity, by keeping out this aspect of the problem. In paper 2, we concentrate on the dynamic mobility $\mu(\omega)$. We shall see that the oscillatory motion of the particle plays a significant role in determining the structure of this quantity.

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