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Asymptotic Solutions of Continuous-Time Random Walks

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The continuous-time random walk of Montroll and Weiss has a complete separation of time (how long a walker will remain at a site) and space (how far a walker will jump when it leaves a site). The time part is completely described by a pausing time distribution $\psi(t)$. This paper relates the asymptotic time behavior of the probability of being at site l at time t to the asymptotic behavior of $\psi(t)$. Two classes of behavior are discussed in detail. The first is the familiar Gaussian diffusion packet which occurs, in general, when at least the first two moments of $\psi(t)$ exist; the other occurs when $\psi(t)$ falls off so slowly that all of its moments are infinite. Other types of possible behavior are mentioned. The relationship of this work to solutions of a generalized master equation and to transient photocurrents in certain amorphous semiconductors and organic materials is discussed.

KEY WORDS: Random walks; non-Markovian; Tauberian theorems; stable (Lévy) distributions; generalized master equations; transport theory.

1. INTRODUCTION

The continuous-time random lattice walk (CTRW) of Montroll and Weiss[1-8] describes a walker hopping randomly on a periodic lattice with the steps

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occurring at random time intervals. We will assume that the random step lengths have a finite mean and variance. Independently of the step length, one introduces a pausing time distribution $\psi(t)$ to describe the random times when the walker hops. The probability that a walker jumps off of a site l that it reached at $t = 0$ in the time interval $(t, t + dt)$ is $\psi(t)\,dt$. The probability $\psi(t)$ is normalized to unity so the walker must eventually jump.

The purpose of this paper is to describe the asymptotic time behavior of the CTRW by investigating the asymptotic behavior of the pausing time distribution. This work was motivated by the papers of Montroll and Scher,[2,8] where several random walks are solved analytically for carefully chosen $\psi(t)$. We will find that the familiar Gaussian diffusion limit is not always obtained, even when the random step lengths are finite. Another very different type of behavior arises when the first and therefore all moments of $\psi(t)$ are infinite. This new type of behavior has been found useful for modeling transient photocurrents in certain amorphous materials.[8]

The main mathematical tool in investigating the asymptotic behavior of the CTRW will be a Tauberian theorem of Hardy and Littlewood (see Ref. 9) that has been generalized by Karamata (see Ref. 11), and will be used in the following form:

$$\text{if} \quad f(\mu) \sim \mu^{-k} A(1/\mu) \quad \text{as } \mu \to 0, \quad \text{with } k > 0 \tag{1a}$$

$$\text{then} \quad g(t) \sim t^{k-1} A(t)/\Gamma(k) \quad \text{as } t \to \infty \tag{1b}$$

where $\mathscr{L}[g(t)] = f(\mu)$, $\mathscr{L}$ is the Laplace transform, and A is a slowly varying function, i.e., for fixed $\lambda > 0$, $A(\lambda y)/A(y) \sim A(\lambda/y)/A(1/y) \sim 1$ as $y \to \infty$. From now on we will use the symbol $\sim$ to mean either $\mu \to 0$ or $t \to \infty$.

In Sections 2 and 3 we calculate the mean and dispersion of the random walker on an infinite periodic lattice, and then discuss some lattice statistics in Section 4. Section 5 adds an absorbing boundary, and Section 6 relates this work to solutions of a generalized master equation and to transient photocurrents in certain amorphous materials.

2. THE MEAN

We begin our discussion of the CTRW with an equation that includes several of the important stochastic functions of random walk theory on a lattice. It can be shown[2] that

$$\begin{aligned} \gamma(\mathbf{k}, t) &\equiv \sum_{\mathbf{l}} P(\mathbf{l}, t) \exp(-i\mathbf{l}\cdot\mathbf{k}) \\ &= \mathscr{L}^{-1}([1 - \psi^*(\mu)]\{\mu[1 - \lambda(\mathbf{k})\psi^*(\mu)]\}^{-1}) \end{aligned} \tag{2}$$

where $P(\mathbf{l}, t)$ is the probability of a walker being at site $\mathbf{l}$ at time t, $\psi^*(\mu)$ is the Laplace transform of $\psi(t)$, $\mathscr{L}^{-1}$ is the inverse Laplace transform, and

$$\lambda(\mathbf{k}) \equiv \sum_{\mathbf{l}} p(\mathbf{l}) \exp(-i\mathbf{l}\cdot\mathbf{k}) \tag{3}$$

and is called the structure function of the lattice. The probability that when a jump occurs it is of length and direction $\mathbf{l}$ is $p(\mathbf{l})$.

By differentiating (2) the moments of $P(\mathbf{l}, t)$ can be found[2,10),2]

$$\begin{aligned}\langle l(t)\rangle \equiv \sum_{\mathbf{l}} lP(l, t) &= i \left.\frac{\partial\gamma(k, t)}{\partial k}\right|_{k=0} \\ &= i \left.\frac{\partial\gamma(k, t)}{\partial\lambda}\right|_{\lambda=1} \left.\frac{d\lambda(k)}{dk}\right|_{k=0} \\ &= \bar{l} \left.\frac{\partial\gamma(k, t)}{\partial\lambda}\right|_{\lambda=1}\end{aligned} \tag{4}$$

where $\overline{l^n} \equiv \sum_l l^n p(l)$.

Using (2), we have

$$\begin{aligned}\langle l(t)\rangle &= \bar{l}\frac{\partial}{\partial\lambda}\left\{L^{-1}\left[\frac{1-\psi^*(\mu)}{\mu}\,\frac{1}{1-\lambda\psi^*(\mu)}\right]\right\}_{\lambda=1} \\ &= \bar{l}L^{-1}\frac{\psi^*(\mu)}{\mu[1-\psi^*(\mu)]}\end{aligned} \tag{5}$$

For convenience, we have limited our discussion to one dimension, since higher dimensionality will only affect the spatial scaling factor $\bar{l}$. However, the dimensionality will have a dramatic effect when we calculate lattice statistics. Note that no nearest-neighbor steps or similar approximation is used. We will only assume that $\bar{l}$ and $\overline{l^2}$ are finite.

The large-time behavior of $\psi(t)$ is determined by the small-μ dependence of $\psi^*(\mu)$. So we see from (5) that to investigate the asymptotic behavior of $\langle l(t)\rangle$, we must study the small-μ dependence of $\psi^*(\mu)$. We will study, in detail, two classes of behavior of $\psi(t)$ because of their physical significance. Other classes of behavior will be mentioned at the end of Section 3 and in Appendix A.

We will first study the case when the first two moments, $\bar{t}$ and $\overline{t^2}$, of $\psi(t)$ are finite, where

$$\overline{t^n} \equiv \int_0^\infty x^n\psi(x)\,dx$$

[2] The random walk is usually studied on a finite lattice with periodic boundary conditions. The wave number k is inversely proportional to the number of lattice sites. So setting $k = 0$ in Eq. (4) ensures we are working on an infinite lattice.

It is shown in Appendix A that when $\bar{t}$ and t^2 are finite then

$$\psi^*(\mu) \sim 1 - \mu\bar{t} + \tfrac{1}{2}\mu^2\overline{t^2} \tag{6a}$$

The second case we will discuss is when $\bar{t}$ is infinite and $\psi(t) \sim [t^{1+\alpha}\Gamma(1-\alpha)A(t)]^{-1}$, for $0 < \alpha < 1$, and thus[11]

$$\psi^*(\mu) \sim 1 - \mu^\alpha/A(1/\mu) \tag{6b}$$

where A is the slowly varying function defined in (1). For simplicity we can let $A(t) = A(1/\mu) = \text{const}$, and still discuss when $\bar{t}$ is infinite the cases when $\psi(t)$ falls off algebraically at long times. The introduction of the slowly varying function A allows one to include such cases as $\psi(t) \sim (t^{1+\alpha}\ln t)^{-1}$, or $\ln(\ln t)/t^{1+\alpha}$, etc. The asymptotic behavior of $\psi(t)$ in (6b) is the same as for a subset of a class of probabilities called stable (Lévy) distributions. We will see that this second class of behavior of the $\psi(t)$ distribution with the long tail leads to a new type of behavior for a random walk with applications to transport in certain amorphous materials.

So the small-μ behavior of $\psi^*(\mu)$ that we are considering falls into two classes depending on whether $\bar{t}$ is finite, hence splitting the asymptotic behavior of the moments of $P(l, t)$ into two classes. To calculate the mean of $P(l, t)$, we use (1), (5), and (6) and first let $\psi^*(\mu) \sim 1 - \mu\bar{t} + \frac{1}{2}\mu^2\overline{t^2}$,

$$f(\mu) = \psi^*(\mu)/\mu[1 - \psi^*(\mu)] \qquad \text{and} \qquad \bar{l}g(t) = \langle l(t)\rangle$$

Then one has

$$\begin{aligned} f(\mu) &\sim (1 - \mu\bar{t})(\mu^2\bar{t} - \tfrac{1}{2}\mu^3\overline{t^2})^{-1} \\ &\sim (\mu^2\bar{t})^{-1} + (\mu\bar{t})^{-1}[(\tfrac{1}{2}\overline{t^2}/\bar{t}) - \bar{t}] \end{aligned}$$

and thus

$$\langle l(t)\rangle \sim (\bar{l}/\bar{t})t + \bar{l}(\tfrac{1}{2}\overline{t^2}/\bar{t}^2 - 1) \sim (\bar{l}/\bar{t})t \tag{7}$$

A second type of behavior for the mean is found when $\psi^*(\mu) \sim 1 - \mu^\alpha/A(1/\mu)$, $0 < \alpha < 1$. Then

$$f(\mu) \sim [1 - \mu^\alpha/A(\mu^{-1})]/[\mu^{1+\alpha}/A(\mu^{-1})] \sim [\mu^{1+\alpha}/A(\mu^{-1})]^{-1}$$

thus

$$\langle l(t)\rangle \sim [\bar{l}/\Gamma(\alpha + 1)]t^\alpha A(t) \tag{8}$$

3. THE DISPERSION

The dispersion is given by

$$\sigma(t) \equiv [\langle l^2(t)\rangle - \langle l(t)\rangle^2]^{1/2}$$

It can be shown[2] that

$$\sigma^2(t) = \overline{l^2}\,\frac{\partial\gamma}{\partial\lambda}\bigg|_{\lambda=1} + \bar{l}^2\left[\frac{\partial^2\gamma}{\partial\lambda^2}\bigg|_{\lambda=1} - \left(\frac{\partial\gamma}{\partial\lambda}\right)^2\bigg|_{\lambda=1}\right] \tag{9}$$

Using (2) in (9), we obtain

$$\sigma^2(t) = \overline{l^2}L^{-1}\frac{\psi^*(\mu)}{\mu[1-\psi^*(\mu)]} + \bar{l}^2L^{-1}\frac{2\psi^{*2}(\mu)}{\mu[1-\psi^*(\mu)]^2} - \bar{l}^2\left\{L^{-1}\frac{\psi^*(\mu)}{\mu[1-\psi^*(\mu)]}\right\}^2 \tag{10}$$

As we saw in the calculation of the mean, it is only the behavior of $\psi^*(\mu)$ for small μ that will determine the moments of $P(l, t)$ at large times. We will again consider the two cases for which we calculated the mean. The first is where the first two moments of $\psi(t)$ exist, and the second is where $\psi(t)$ falls off so slowly that no moments exist.

First consider $\psi^*(\mu) \sim 1 - \mu\bar{t} + \frac{1}{2}\mu^2\overline{t^2}$. After applying (1) in Eq. (10), we find

$$\begin{aligned}\sigma^2 \sim{}& \overline{l^2}[(t/\bar{t}) + (\tfrac{1}{2}\overline{t^2}/\bar{t}^2) - 1]\\ &+ \bar{l}^2\{[2t^2/\bar{t}^2\Gamma(3)] + (4t/\bar{t})[(\tfrac{1}{2}\overline{t^2}/\bar{t}^2) - 1]\}\\ &- \bar{l}^2\{(t^2/\bar{t}^2) + (2t/\bar{t})[(\tfrac{1}{2}\overline{t^2}/\bar{t}^2) - 1]\}\end{aligned}$$

and thus

$$\sigma(t) \sim \{(\overline{l^2}/\bar{t}) + (2\bar{l}^2/\bar{t})[(\tfrac{1}{2}\overline{t^2}/\bar{t}^2) - 1]\}^{1/2}t^{1/2} \tag{11}$$

Note that for $\psi^*(\mu) \sim 1 - \mu\bar{t} + \frac{1}{2}\mu^2\overline{t^2}$ one obtains asymptotically a diffusion packet moving with a constant velocity $d\langle l(t)\rangle/dt$ and spreading as $t^{1/2}$ whether or not a bias is present.

For the second case, when $\psi^*(\mu) \sim 1 - \mu^\alpha/A(1/\mu)$, $0 < \alpha < 1$, then

$$\sigma^2(t) \sim \frac{\overline{l^2}t^\alpha A(t)}{\Gamma(1+\alpha)} + \bar{l}^2\left[\frac{2t^{2\alpha}}{\Gamma(1+2\alpha)} - \frac{t^{2\alpha}}{\Gamma^2(1+\alpha)}\right]A^2(t)$$

Thus

$$\sigma(t) \sim \begin{cases}\bar{l}\{[2/\Gamma(1+2\alpha)] - \Gamma^{-2}(1+\alpha)\}^{1/2}t^\alpha A(t) & \text{if } \bar{l} \neq 0 \quad \text{(12a)}\\ [\overline{l^2}/\Gamma(1+\alpha)]^{1/2}t^{\alpha/2}A^{1/2}(t) & \text{if } \bar{l} = 0 \quad \text{(12b)}\end{cases}$$

For this class of $\psi^*(\mu)$, with $\bar{l} \neq 0$, one obtains an unusual type of transport where the dispersion grows as quickly as the mean. We will discuss the applications of this in Section 6, but first we will discuss another possible type of behavior of the CTRW, some lattice statistics, and then introduce an absorbing boundary to our random walk.

A case we have not yet discussed is when $\bar{t}$ is finite, but $\overline{t^2}$ is infinite and $\psi(t)$ decays as $[t^{2+\alpha}A(t)]^{-1}$. Now $\psi^*(\mu) \sim 1 - \mu\bar{t} + \text{const} \times \mu^{1+\alpha}/A(\mu^{-1})$. We now find, using the same type of analysis as before, that

$$\langle l(t)\rangle \sim (\bar{l}/\bar{t})t + \text{const} \times t^{1-\alpha}/\bar{t}^2A(t)$$

$$\sigma^2(t) \sim \overline{l^2}(t/\bar{t}) + \text{const} \times \bar{l}^2t^{2-\alpha}/\bar{t}^3A(t)$$

When $\bar{l} = 0$ we recover the same asymptotic behavior as when all the moments of $\psi(t)$ exist. We will reserve the special cases $\psi(t) \sim t^{-2}$ and t^{-3} for Appendix A.

4. LATTICE STATISTICS

Let $S(t)$ be the average number of distinct lattice sites visited after a time t. Montroll and Weiss[1] have shown that

$$\mathscr{L}(S(t)) = \psi^*(\mu)/\mu[1 - \psi^*(\mu)]P(0, \psi^*(\mu)) \tag{13}$$

where $P(0, z) \equiv \sum_{n=0}^{\infty} p_n(0)z^n$, and $p_n(0)$ is the probability of returning to the origin after n steps. They further show in one, two, and three dimensions, respectively, for a symmetric ($\bar{l} = 0$) random walk with nearest-neighbor steps that

$$P(0, z) = (1 - z^2)^{-1/2} \qquad (1\text{D}) \tag{14a}$$

$$P(0, z) \sim -\pi^{-1} \log(1 - z) \qquad (2\text{D}) \tag{14b}$$

$$P(0, z) \sim P(0, 1) \quad \text{as} \quad z \to 1 \qquad (3\text{D}) \tag{14c}$$

Then assuming $\bar{t}$ is finite, and using (1), they find

$$S(t) \sim (8t/\pi\bar{t})^{1/2} \qquad (1\text{D}) \tag{15a}$$

$$S(t) \sim t/\bar{t}P(0, 1) \qquad (3\text{D}) \tag{15b}$$

The Tauberian theorem (1) can be used with $A(1/\mu) = \pi/\bar{t} \log(1/\mu\bar{t})$ to give

$$S(t) \sim \pi(t/\bar{t})/\log(t/\bar{t}) \qquad (2\text{D}) \tag{15c}$$

For our case when $\bar{t}$ is infinite, and $\psi^*(\mu) \sim 1 - \mu^\alpha/A(\mu^{-1})$

$$S(t) \sim t^{\alpha/2}A^{1/2}(t)/\Gamma(1 + \alpha/2) \qquad (1\text{D}) \tag{16a}$$

$$S(t) \sim \pi t^\alpha A(t)/\{\Gamma(1 + \alpha) \log[t^\alpha A(t)]\} \qquad (2\text{D}) \tag{16b}$$

$$S(t) \sim t^\alpha A(t)/P(0, 1)\Gamma(1 + \alpha) \quad \text{for} \quad 0 < \alpha < 1 \qquad (3\text{D}) \tag{16c}$$

As expected, when the mean pausing time is infinite a fewer number of sites are visited in a time t than if $\bar{t}$ were finite. However, the important fact to realize is that transport can still take place when the mean pausing time $\bar{t}$ is infinite. Since the probability $\psi(t)$ is normalized to unity, a finite median time to jump exists. So there is a probability of $\frac{1}{2}$ that the walker has jumped by the median time, even though the mean pausing time is infinite.

5. ABSORBING BOUNDARY

We define a mean current $I(t)$ by

$$I(t) \equiv d\langle l(t)\rangle/dt \tag{17a}$$

and current fluctuations $\Delta I(t)$ by

$$\Delta I(t) \equiv d\sigma(t)/dt \tag{17b}$$

When $\bar{t}$ is finite and $\bar{l} \neq 0$ we easily find that the mean current is constant and the current fluctuations decay as $t^{-1/2}$. When $\bar{t}$ is infinite and $\psi(t) \sim t^{-1-\alpha}$ both the mean current and its fluctuations decay as $t^{-1+\alpha}$.

In this section we calculate how a biased current of random walkers is modified by the presence of an absorbing boundary, assuming there is a positive bias for jumping toward the boundary. The equation for a CTRW with an absorbing boundary at lattice site N when a walker is initially at the origin is[2]

$$P(l, t) = P_0(l, t) - \int_0^t d\tau\, F(N, \tau) P_0(l - N, t - \tau) \tag{18}$$

where the subscript on P denotes the probability in the absence of a boundary, and $F(N, \tau)$ is the probability of reaching site N for the first time at time τ. The second term on the right subtracts all the paths that reach l by passing through the boundary. Multiplying both sides of (18) by $l - N$ and summing over all l yields

$$\langle l(t)\rangle = \langle l(t)\rangle_0 - \int_0^t d\tau\, F(N, \tau)\langle l(t - \tau)\rangle_0 \tag{19}$$

Before the walkers start to reach the boundary the first passage time probability distribution $F(N, \tau)$ is near zero, and thus $\langle l(t)\rangle$ is nearly the same as without the boundary. Now let us wait a long enough time for F to become important and calculate how the boundary affects the current. This is most readily done by working with the Laplace transform of (19), which is

$$\langle l^*(\mu)\rangle = \langle l^*(\mu)\rangle_0[1 - F^*(N, \mu)] \tag{20}$$

and then using the Tauberian theorem (1).

We will discuss the effect of the boundary for two classes of $\psi(t)$. For nearest-neighbor steps it is shown in Appendix B that when $\bar{t}$ and $\overline{t^2}$ are finite and a bias is present

$$F^*(N, \mu) \sim 1 - a\mu + b\mu^2 \tag{21a}$$

and when $\bar{t}$ is infinite and $\psi(t) \sim (t^{1+\alpha})^{-1}$

$$F^*(N, \mu) \sim 1 - a\mu^\alpha + b\mu^{2\alpha} \tag{21b}$$

where $a, b > 0$. It is hypothesized that a more general class of jumps will not affect the small-μ behavior of F^*. A study of the asymptotic time behavior of $F(N, t)$ for various $\psi(t)$ can be found in Appendix B.

When $\bar{t}$ and $\overline{t^2}$ are finite we know from (7) that $\langle l^*(\mu)\rangle_0 \sim \mu^{-2}$, and when $\bar{t}$ is infinite we know from (8) that $\langle l^*(\mu)\rangle_0 \sim \mu^{-1-\alpha}$. Let us use this, (20), and (21a) to consider the case when $\bar{t}$ and $\overline{t^2}$ are finite. We find $\langle l^*(\mu)\rangle \sim \text{const}/\mu$, which leads to $\langle l(t)\rangle \sim$ const and a mean current $I(t) \sim 0$. As expected, eventually all the walkers in this Gaussian diffusion packet, which is initially moving toward the boundary with a constant velocity, are absorbed.

For the case when $\bar{t}$ is infinite we can find that the initial mean current behavior of $I(t) \sim \bar{l}t^{-1+\alpha}$ changes to $I(t) \sim \bar{l}t^{-1-\alpha}$. Note that when $\bar{t}$ is infinite the mean current eventually goes to zero as $t^{-1+\alpha}$ even when no absorbing boundary is present!

6. DISCUSSION AND APPLICATIONS

One can continue to find the higher moments and get a complete asymptotic description of $P(\mathbf{l}, t)$ in terms of its moments. If one chooses $\psi(t) = \lambda e^{-\lambda t}$ for, say, a three-dimensional random walk biased in the x direction, then $P(\mathbf{l}, t)$ can be solved for exactly.[2] In the continuum limit it is a three-dimensional Gaussian diffusion probability distribution whose peak travels with a constant mean velocity in the x direction and diffuses in all directions, i.e.,

$$P(\mathbf{l}, t) = (4\pi Dt)^{-3/2} \exp[-(x - vt)^2 - y^2 - z^2/4Dt] \tag{22a}$$

where D is appropriately chosen, and

$$\langle l_x(t)\rangle \sim t, \qquad \langle l_y(t)\rangle = \langle l_z(t)\rangle = 0 \tag{22b}$$

$$\sigma_x(t) = \sigma_y(t) = \sigma_z(t) \sim t^{1/2} \tag{22c}$$

This is exactly the asymptotic behavior we find when the first two moments of $\psi(t)$ exist.

This Gaussian behavior breaks down when $\bar{t}$ is infinite. Then, even though the mean increases as t^α there will at long times still be a considerable probability that the walker is on its original site. Once a walker reaches any site it will have a considerable probability for remaining there a very long time. This gives rise to a long dispersive tail in the probability and in the mean current. In a sense, this long tail represents the memory of the CTRW. The absence of this long tail in the Gaussian distribution implies that asymptotically the random walker loses the memory of where it has been and the process becomes Markovian.

Another way to discuss the memory of the CTRW is to relate it to the memory $\phi(t)$ of a generalized master equation (GME). It has been shown by Kenkre *et al.*[4] that the CTRW, which is in general non-Markovian, is equivalent to the GME

$$dP(l, t)/dt = \int_0^t \phi(t - \tau)[-P(l, \tau) + \sum_{l' \neq l} p(l - l')P(l', \tau)]\, d\tau \tag{23a}$$

when

$$\phi^*(\mu) = \mu\psi^*(\mu)/[1 - \psi^*(\mu)] \tag{23b}$$

When (23b) is used the GME can be rewritten as

$$P(l, t) = \int_0^t \psi(\tau) \sum_{l' \neq l} p(l - l')P(l', t - \tau)\, d\tau + P(l, 0)\left[1 - \int_0^t \psi(x)\, dx\right] \tag{24}$$

So we have actually analyzed the asymptotic time behavior of these transport equations. It can also be easily shown[3,4] that if $\psi(t) = \lambda e^{-\lambda t}$, or equivalently $\phi(t) = \delta(t)$, then the GME corresponding to the CTRW reduces to the Markovian master equation. Therefore the preceding analysis shows that if $\psi(t)$ has at least two finite moments then as $t \to \infty$ the Markovian master equation will be a valid description of the CTRW. This generalizes the proof of Bedeaux *et al.*,[3] which states that when all the moments of $\psi(t)$ exist the Markovian master equation will asymptotically be a valid description of the CTRW. Of course, for short times the behavior of the non-Markovian CTRW may be quite different from that predicted by the Markovian master equation.

We have seen that when $\bar{l} = 0$ only the existence of the first moment of $\psi(t)$ is necessary to obtain Gaussian behavior asymptotically. A similar statement is made by Lakatos-Lindenberg and Bedeaux,[7] who show that the linear response from equilibrium, i.e., $\bar{l} = 0$, of a random walker on a lattice to forces which vary with frequency $\omega \ll 1/\bar{t}$ is the same as for the walker obeying a Markovian master equation.

In discussion renewal processes with nonexponential pausing times Feller[11] states, "It is hard to find practical examples besides the bus running without schedule along a circular route." We will now discuss a practical example where the pausing time $\psi(t)$ is not only nonexponential, but behaves as a stable distribution which does not even have a finite mean!

In transient photoconductivity experiments[8] in the amorphous semiconductor As_2Se_3 holes are injected near a positive electrode. The holes are then transported to a negative electrode where they are absorbed and the current they generate is measured. Experimentally, it is found that the holes do not move as a well-defined packet, but rather as a disturbance whose fluctuations grow as quickly as its mean. Furthermore, the current initially goes as $t^{-1+\alpha}$ and then changes its behavior to $t^{-1-\alpha}$. For amorphous As_2Se_3, $\alpha \simeq 0.5$, and for similar experiments with the organic compound TNF–PVK, $\alpha \simeq 0.8$.[8] This is just the type of transport we have discussed for the CTRW when $\psi(t)$ has no finite moments and decays as $t^{-1-\alpha}$. So we assume that the CTRW describes the hopping motion of charges between spatially random localized sites which act as deep traps. The randomization of the localized sites leads to a distribution of pausing times between jumps which we have described by $\psi(t)$. Tunaley[15] has discussed the natural appearance of infinite mean pausing times in certain amorphous systems.

That this type of transport could be described by the CTRW was first shown by Montroll and Scher.[2,8] They obtained analytic expressions for the first two moments of $P(l, t)$ for a carefully chosen $\psi(t)$ that decays as $t^{-3/2}$, to describe the transient photocurrents in amorphous As_2Se_3. Diagrams of $P(l, t)$, for different $\psi(t)$, and the currents involved can also be found in their work.

Since all the moments of $\psi(t)$ are infinite, it appears that the Markovian master equation cannot describe the hopping transport of charge carriers between the deep traps in certain amorphous materials. Only the GME description will suffice.

It is the $\psi(t)$ that asymptotically behave as stable distributions that lead to the new interesting behavior of the CTRW. Gnedenko and Kolmogorov[13] have remarked concerning stable distributions that, "It is probable that the scope of applied problems in which they play an essential role will become in due course rather wide."

APPENDIX A

We now study the small-μ behavior of $\psi^*(\mu)$, which is determined by the large-time behavior of its inverse Laplace transform $\psi(t)$. First, let us assume all the moments $\overline{t^n}$ of $\psi(t)$ exist. Then

$$\psi^*(\mu) \equiv \int_0^\infty e^{-\mu t}\psi(t)\,dt \tag{A.1}$$

$$\begin{aligned} &= \int_0^\infty \psi(t)\,dt - \mu\int_0^\infty t\psi(t)\,dt + \cdots + \frac{(-\mu)^n}{n!}\int_0^\infty t^n\psi(t)\,dt + \cdots \\ &= 1 - \mu\bar{t} + (\text{higher orders of } \mu) \end{aligned} \tag{A.2}$$

We now show that this small-μ behavior holds even when only $\bar{t}$ is finite. In general,

$$(-1)^n\, d^n\psi^*(\mu)/d\mu^n = \int_0^\infty e^{-\mu t} t^n \psi(t)\,dt \neq 0 \tag{A.3}$$

The finite mean time $\bar{t}$ is

$$\bar{t} = -d\psi^*(0)/d\mu \tag{A.4}$$

So $\psi^*(\mu) = \text{const} - \mu\bar{t} + (\text{higher orders of } \mu)$. The constant is one, since $\psi(t)$ is normalized. No lower orders of μ are possible or else $d\psi^*(0)/d\mu$ would diverge, yielding an infinite $\bar{t}$, which would violate our assumption.

In general, if the first n moments of $\psi(t)$ exist, then

$$\psi^*(\mu) = 1 - \mu\bar{t} + \cdots + [(-\mu)^n/n!]\bar{t}^n + (\text{higher orders of } \mu) \tag{A.5}$$

Now let us consider the class of $\psi(t)$ that fall off asymptotically as $[t^{1+\alpha}\Gamma(1-\alpha)A(t)]^{-1}$ as $t \to \infty$, with $0 < \alpha < 1$. The slowly varying function at infinity $A(t)$ was defined in (1) and discussed in the text. This class of pausing time distributions fall off so slowly at large times that all the moments of this class of $\psi(t)$ are infinite. A class of probabilities with the same asymptotic behavior is a subset of the stable (Lévy) distributions.[11-13] In general the stable distributions are defined on the domain $(-\infty, \infty)$ and are only known in terms of their Fourier transforms. By choosing an exponent α for $0 < \alpha < 1$ they are defined and normalized on $(0, \infty)$ and have the Laplace transform[11]

$$\mathscr{L}[\psi_\alpha(t)] = \exp[-\mu^\alpha/A(1/\mu)]$$

So the small-μ behavior of $\psi^*(\mu)$ for this class of pausing time probability functions is

$$\psi^*(\mu) \sim 1 - \mu^\alpha/A(1/\mu) \tag{A.6}$$

As a specific example, consider the Laplace transforms $F_n(\mu)$, which were discussed in Ref. 2, of repeated integrals of the complimentary error function, where

$$\psi(t) = f_n(t) = c_n a^2[\exp(a^2 t)]i^n \operatorname{Erfc}(at^{1/2})$$

$$i^n \operatorname{Erfc} z = (2/\pi^{1/2}n!)\int_z^\infty (y-z)^n \exp(-y^2)\, dy$$

and c_n is a normalizing constant. The function $f_2(t)$ has no finite moments since it falls off as $t^{-3/2}$ as $t \to \infty$, and has the Laplace transform

$$F_2(\mu) = (S^{1/2}+1)^{-2} \sim 1 - 2S^{1/2} \qquad \text{as} \quad S \to 0$$

where $S = \mu/a^2$, which is verified by (A.6). The function $f_4(t)$ has one finite moment since $f_4(t) \sim t^{-5/2}$ as $t \to \infty$, and

$$F_4(\mu) = (3S^{1/2}+1)(S^{1/2}+1)^{-3} \sim 1 - 3S \qquad \text{as} \quad S \to 0$$

which is verified by (A.5).

When $\bar{t}$ is infinite a case we have not yet discussed is when $\psi(t) \sim t^{-2}$. The behavior of $\psi^*(\mu)$ can be found by analyzing the small-μ behavior of

$$\mathscr{L}\left(\frac{2}{\pi}\frac{1}{1+t^2}\right) \sim 1 + \frac{2}{\pi}\mu \ln \mu - \frac{2}{\pi}(1-\gamma)\mu$$

where $\gamma = 0.577$ is the Euler–Mascheroni constant. Using this form of $\psi^*(\mu)$, we can find that

$$\langle l(t)\rangle \sim \bar{l}(t/\ln t) \tag{A.7}$$

and

$$\sigma^2(t) \sim \text{const} \times \overline{l^2}(t/\ln t) + \text{const} \times \bar{l}^2(t^2/\ln^4 t) \tag{A.8}$$

Finally, we discuss the case when $\bar{t}$ is finite, $\overline{t^2}$ is infinite, and $\psi(t) \sim t^{-3}$. Then $\psi^*(\mu) \sim 1 - \mu\bar{t} + \text{const} \times \mu^2 \ln \mu$, and we find

$$\langle l(t)\rangle \sim \bar{l}t/\bar{t} \tag{A.9}$$

and

$$\sigma^2(t) \sim (\overline{l^2}t/\bar{t}) + \text{const} \times \bar{l}^2(t \ln t)/\bar{t}^3 \tag{A.10}$$

APPENDIX B

We now study the small-μ behavior of $F^*(l, \mu)$. It can be shown[1] that

$$F^*(l, \mu) \equiv \mathscr{L}(F(l, t)) = \mathscr{F}(l, \psi^*(\mu)) \equiv \sum_{n=0}^{\infty} f_n(l)(\psi^*(\mu))^n \tag{B.1}$$

where $f_n(l)$ is the probability of reaching site l for the first time at the nth step. Feller[14] shows that in one dimension

$$\mathscr{F}(N, s) = \left[\frac{1 - (1 - 4pqs^2)^{1/2}}{2qs}\right]^N \tag{B.2}$$

when the walker starts at the origin, and takes nearest-neighbor steps to the right and left with probabilities p and q.

As shown in Appendix A, when $\psi(t) \sim t^{-1-\alpha}$ then $\psi^*(\mu) \sim 1 - c\mu^\alpha + d\mu^{2\alpha}$, and when $\bar{t}$ and $\overline{t^2}$ are both finite then $\psi^*(\mu) \sim 1 - \bar{t}\mu + \frac{1}{2}\overline{t^2}\mu^2$. Setting $s = \psi^*(\mu)$, we have $s^2 \sim 1 + \text{const} \times \mu^\alpha + \text{const} \times \mu^{2\alpha}$, where α can be chosen to fit either of the cases discussed above, and the constants are positive. Using the above in (B.2) when $p \neq q$, we have

$$\mathscr{F}^{1/N}(N\psi^*(\mu)) \sim \frac{1 - [1 - 4pq(1 - \text{const} \times \mu^\alpha + \text{const} \times \mu^{2\alpha})]^{1/2}}{2q} \tag{B.3}$$

Let $X = 4pq(1 - \text{const} \times \mu^\alpha + \text{const} \times \mu^{2\alpha})$; then

$$X^n \sim (4pq)^n - n[(4pq)^n(\text{const} \times \mu^\alpha - \text{const} \times \mu^{2\alpha})]$$

Expanding the square root in (B.3), we have

$$\begin{aligned}(1 - X)^{1/2} &= 1 - \frac{1}{2}X - \frac{1}{8}X^2 - \sum_{n=3}^{\infty} \frac{X^n}{2^n(n-1)!!} \\ &\sim (1 - 4pq)^{1/2} + (\text{convergent series}) \\ &\qquad (\text{const} \times \mu^\alpha - \text{const} \times \mu^{2\alpha})\end{aligned}$$

For small μ (B.3) becomes

$$[1 - (1 - 4pq)^{1/2} - \text{const} \times \mu^{\alpha} + \text{const} \times \mu^{2\alpha}]/2q$$
$$= \frac{1 - (1 - 2q)}{2q} - \text{const} \times \mu^{\alpha} + \text{const} \times \mu^{2\alpha}$$
$$= 1 - \text{const} \times \mu^{\alpha} + \text{const} \times \mu^{2\alpha} \tag{B.4}$$

Finally, (B.4) retains the same small-μ form when raised to the Nth power.

Further interesting facts about first passage time distribution can now be discussed. It is known[13,14] for a symmetric ($\bar{l} = 0$) random lattice walk with nearest-neighbor steps occurring at regular intervals, i.e., $\psi(t) = \delta(t - \bar{t})$, that, asymptotically, the first passage time distribution to any lattice site is the stable distribution with $\alpha = \frac{1}{2}$. This is called the Smirnov distribution, and is one of three stable distributions that are known analytically. The probability $f(N, m)$ of a first passage to N after m steps is

$$f(N, m) \sim [Nm^{-3/2}/(2\pi)^{1/2}] \exp(-N^2/2m) \qquad \text{as} \quad m \to \infty \tag{B.5}$$

Note that the mean first passage time (number of steps) is infinite.

We will now show that the Smirnov distribution appears under more general conditions. For a symmetric random walk, where the only other assumption is that $\overline{l^2}$ is finite, Montroll and Weiss[1] have shown that

$$\mathscr{F}(N, s) \sim \exp\{-N[2(1 - s)]^{1/2}/\overline{l^2}\} \qquad \text{as} \quad s \to 1 \tag{B.6}$$

By setting $s = \psi^*(\mu)$ and further assuming that $\bar{t}$ is finite, we find from (B.6) that

$$\mathscr{F}(N, \psi^*(\mu)) \sim 1 - N(2\bar{t}\mu)^{1/2}/\overline{l^2} \tag{B.7}$$

Using (B.1) and (A.6), we see that asymptotically $F(l, t)$ has a Smirnov distribution in time for a CTRW when $\bar{l} = 0$, and $\overline{l^2}$ and $\bar{t}$ are finite.

If a bias is present and nearest-neighbor steps are taken, we see from (B.4) that $F(N, t)$ will asymptotically have a Smirnov distribution in time when $\psi(t)$ does, and will have an α-stable distribution when $\psi(t)$ does, for $0 < \alpha < 1$.

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