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Anomalous Long Time Tails Due to Trapping

Jonathan Machta[1]

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A new mechanism is described for producing slow decays in the velocity correlation function of diffusive systems with directed trapping. If the directions for entering and leaving a trap are correlated and if the distribution of trapping times has a long tail then the velocity correlation function will have a corresponding long time tail. This new long time tail decays like $t^{-(2+\alpha)}$, where α is an exponent characterizing the tail of the distribution of trapping times. A simple random walk model which illustrates this mechanism is analyzed.

KEY WORDS: Random walks; trapping; disordered materials; long time tails; mode coupling.

1. INTRODUCTION

The purpose of this paper is to describe a new mechanism for producing slow decays in the velocity correlation function of a particle moving in a disordered diffusive medium. This mechanism depends upon the presence of directed traps. A trap is a region of space which is difficult to leave; it is "directed" if the directions for entering the trap are correlated with the directions for leaving it. If the characteristic time for a given directed trap is τ then the velocity of the particle will be correlated over a time τ as it enters and leaves the trap. Power law decays of the velocity correlation function (VCF) will arise if there is a distribution of trapping times with a power law tail.

Power law decays or long time tails in the VCF are a general feature of transport in disordered diffusive systems.[1-3] They occur in models governed by classical dynamics such as the Lorentz gas,[2,5-8] and in the motion of a quantum mechanical particle in a disordered potential.[9] They

[1] Department of Physics and Astronomy, The University of Massachusetts, Amherst, Massachusetts 01003.

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also occur in purely stochastic models (so long as the "velocity" is appropriately defined).[2,4,10] A variety of methods including exact solutions, mode coupling theory, kinetic theory, renormalization group methods, and effective medium theory have been used to derive the long time tails in these models. Excepting the quantum mechanical case,[9] all of these theories yield the result that the VCF decays like $t^{-(1+d/2)}$ for long times. The most general of these theories is the mode coupling theory[1,2] which shows that the $t^{-(1+d/2)}$ decay of the VCF results from long wavelength variations in the local diffusion coefficient of the system. The mode coupling theory identifies the amplitude of the long time tail with the mean squared fluctuations in the diffusion coefficient from one realization to another. Harrison and Zwanzig[4] have shown that the mode coupling expression for the long time tail is exact for a wide class of hopping models. On the other hand, we shall see that the mode coupling theory fails to predict long time tails due to directed trapping.

Random walk models with variety of random symmetric traps have been studied in the past.[11–15] A general argument given in Ref. 11 shows that symmetric trapping cannot lead to long time tails in the VCF. On the other hand, symmetric trapping does contribute to slow decays of Burnett and higher-order velocity correlation functions.[12–14] Although it was not explicitly stated there, the analysis of the Burnett correlation function given in Ref. 14, hereafter referred to as MNNE, leads to results which disagree with the mode coupling theory.

In this paper we study a simple hopping model with directed trapping. This model is similar to the one studied in MNNE and we use the methods developed there to analyze it. In Section 2 the model is defined and analyzed. In Section 3 the results are contrasted to those of the mode coupling theory and general conclusions are drawn.

2. RANDOM WALK MODEL

Consider a random walk on a d-dimensional hypercubic lattice with lattice spacing l. Associated with each lattice site there are two states, a conduction state and a trapping state. From the conduction state at site $\mathbf{n}$ the walker may hop to any of its near-neighbor conduction states at a rate ν or it may enter the associated trapping state at a rate $1/\tau_{\mathbf{n}}$. From the trapping state the particle may only return to the corresponding conduction state, again at the rate $1/\tau_{\mathbf{n}}$. Directionality is introduced into the model by having the trapping state displaced an amount $l\mathbf{x}_{\mathbf{n}}$ from the conduction state. This random walk model is conveniently described by the master equation:

$$dP_{\mathbf{n},+}(t)/dt = -v \sum_{\mathbf{nm}} \theta_{\mathbf{nm}} P_{\mathbf{m},+}(t) + (1/\tau_{\mathbf{n}})[P_{\mathbf{n},-}(t) - P_{\mathbf{n},+}(t)] \tag{1a}$$

$$dP_{\mathbf{n},-}(t)/dt = -(1/\tau_{\mathbf{n}})[P_{\mathbf{n},-}(t) - P_{\mathbf{n},+}(t)] \tag{1b}$$

where $P_{\mathbf{n},+}(t)$ and $P_{\mathbf{n},-}(t)$ refer, respectively, to the occupation probabilities of the conduction state and the trapping state associated with lattice site $\mathbf{n}$ at time t. The matrix $v\theta_{\mathbf{nm}}$ describes nearest-neighbor hopping among the conduction states with $\theta_{\mathbf{nm}}$ given by

$$\theta_{\mathbf{nm}} = \sum_{\mathbf{a}} (\delta_{\mathbf{n},\mathbf{m}} - \delta_{\mathbf{n},\mathbf{m}-\mathbf{a}}) \tag{2}$$

where the sum is over the $2d$ lattice directions. The number of sites in the lattice is M and at the end of the calculation the limit, $M \to \infty$ is taken.

Disorder is introduced into the model by allowing $\tau_{\mathbf{n}}$ and $\mathbf{x}_{\mathbf{n}}$ to be independent, identically distributed random variables. Interesting effects occur for trapping time distributions with power law tails of the form

$$\text{Prob}\{\tau_{\mathbf{n}} > t\} \sim At^{-\alpha} \qquad \text{as} \quad t \to \infty \tag{3}$$

and these are the distributions considered explicitly here. Note that these distributions are well-defined for $\alpha > 0$ but have no mean if $\alpha \leqslant 1$. The trap displacements are taken to have zero mean and fluctuation σ,

$$\langle \mathbf{x}_{\mathbf{n}} \rangle = 0 \tag{4a}$$

$$\langle \mathbf{x}_{\mathbf{n}} \cdot \mathbf{x}_{\mathbf{m}} \rangle = \sigma^2 \delta_{\mathbf{n},\mathbf{m}} \tag{4b}$$

The model described above is very similar to the system studied in MNNE. The crucial difference is that, in the present model, entering a trap is associated with a displacement whereas in MNNE, this is not the case. In this work we do not include a bias field or break detailed balance between the traps and the conduction states as was done in MNNE (in the notation of MNNE we have $\varepsilon = 0$ and $\lambda = 1$). In the present work we have taken random displacements; however, the results would be qualitatively the same if the traps were displaced in an ordered way.

The formal solution to the master equation (1) was obtained in MNNE and, for a given realization of the disorder, takes the form

$$\begin{pmatrix} \mathscr{P}_{\mathbf{n},+}(z) \\ \mathscr{P}_{\mathbf{n},-}(z) \end{pmatrix} = \sum_{\mathbf{nm}} \begin{pmatrix} G(\mathbf{n},+\,|\,\mathbf{m},+) & G(\mathbf{n},+\,|\,\mathbf{m},-) \\ G(\mathbf{n},-\,|\,\mathbf{m},+) & G(\mathbf{n},-\,|\,\mathbf{m},-) \end{pmatrix} \begin{pmatrix} P_{\mathbf{m},+}(0) \\ P_{\mathbf{m},-}(0) \end{pmatrix} \tag{5}$$

where the script character indicates a Laplace transform of the corresponding function of time and z is the Laplace transform variable. The components of the Green's function are given by

$$\mathbf{G}(+\mid+)=[z\mathbf{K}+v\boldsymbol{\theta}]^{-1}\equiv\mathbf{G} \tag{6a}$$

$$\mathbf{G}(+\mid-)=\mathbf{G}\mathbf{W}[z\mathbf{1}+\mathbf{W}]^{-1} \tag{6b}$$

$$\mathbf{G}(-\mid+)=[z\mathbf{1}+\mathbf{W}]^{-1}\,\mathbf{W}\mathbf{G} \tag{6c}$$

$$\mathbf{G}(-\mid-)=[z\mathbf{1}+\mathbf{W}]^{-1}+[z\mathbf{1}+\mathbf{W}]^{-1}\,\mathbf{W}\mathbf{G}\mathbf{W}[z\mathbf{1}+\mathbf{W}]^{-1} \tag{6d}$$

where we have used matrix notation to suppress the site indices. The matrix $\boldsymbol{\theta}$ is defined in Eq. (2) and the $\mathbf{W}$ and $\mathbf{K}$ are diagonal matrices defined by

$$W_{\mathbf{nm}}=\delta_{\mathbf{nm}}/\tau_{\mathbf{n}} \tag{7a}$$

$$K_{\mathbf{nm}}=\delta_{\mathbf{nm}}(z\tau_{\mathbf{n}}+2)/(z\tau_{\mathbf{n}}+1) \tag{7b}$$

The fundamental quantity of interest to us is the mean squared displacement, $\mu_2(t)$ of a walker chosen from the stationary distribution, $P^s_{\mathbf{n},+}=P^s_{\mathbf{n},-}=1/2M$. From $\mu_2(t)$ we can obtain the VCF, the generalized diffusion coefficient and, given the AC Einstein relation, the frequency-dependent conductivity. In terms of the components of the Green's function defined above, the Laplace transform of the mean squared displacement can be expressed in the form

$$\mu_2(z)=\sum_{\mathbf{m},\mathbf{n}}\sum_{\substack{a=+,-\\ b=+,-}}\langle l^2[\mathbf{m}-\mathbf{n}+\mathbf{x}_{\mathbf{m}}\delta_{a,-}-\mathbf{x}_{\mathbf{n}}\delta_{b,-}]^2\,G(\mathbf{m},a\mid\mathbf{n},b)\,P^s_{\mathbf{n},b}\rangle \tag{8}$$

where the angular brackets indicate an average over realizations of the random variables, τ and $\mathbf{x}$. By expanding the quantity in the square brackets and averaging over the variable $\mathbf{x}$ we may separate the expression for the mean squared displacement into two terms

$$\mu_2(z)=\mu_2^{(0)}(z)+\mu_2^{(1)}(z) \tag{9a}$$

where

$$\mu_2^{(0)}(z)=\sum_{\mathbf{m},\mathbf{n}}\sum_{\substack{a=+,-\\ b=+,-}}\langle l^2[\mathbf{m}-\mathbf{n}]^2\,G(\mathbf{m},a\mid\mathbf{n},b)\,P^s_{\mathbf{n},b}\rangle \tag{9b}$$

and

$$\mu_2^{(1)}(z)=\sum_{\mathbf{m},\mathbf{n}}\sum_{\substack{a=+,-\\ b=+,-}}\sigma^2l^2[\delta_{a,-}+\delta_{b,-}-2\delta_{a,-}\delta_{b,-}\delta_{\mathbf{m},\mathbf{n}}]\times\langle G(\mathbf{m},a\mid\mathbf{n},b)\,P^s_{\mathbf{n},b}\rangle \tag{9c}$$

Physically, $\mu_2^{(0)}(z)$ accounts for intersite displacements while $\mu_2^{(1)}(z)$ accounts for displacements between the conduction and trapping states. $\mu_2^{(0)}(z)$ was calculated for $d=1$ in MNNE and that calculation is easily generalized to $d>1$ to yield, in the time domain,

$$\mu_2^{(0)}(t) = 2d\,Dt \tag{10a}$$

with

$$D = l^2 \nu/2 \tag{10b}$$

Note that the only effect of the traps in Eqs. (10) is to reduce the diffusion coefficient by a factor of 2 over its value in a system without traps. This is because the walker spends half of its time immobile in a trap. The distribution of trap times does not enter the expression for the diffusion coefficient.

The quantity $\mu_2^{(1)}(z)$ can be simplified using Eqs. (6), an exact expansion for $\mathbf{G}$,

$$\mathbf{G} = (z\mathbf{K})^{-1} - \nu(z\mathbf{K})^{-1}\,\boldsymbol{\theta}(z\mathbf{K})^{-1} + \nu^2(z\mathbf{K})^{-1}\,\boldsymbol{\theta}\mathbf{G}\boldsymbol{\theta}(z\mathbf{K})^{-1} \tag{11}$$

and the fact that, for fixed $\mathbf{n}$,

$$\sum_{\mathbf{m}} \theta_{\mathbf{nm}} = \sum_{\mathbf{m}} \theta_{\mathbf{mn}} = 0 \tag{12}$$

The result is that

$$\mu_2^{(1)}(z) = l^2\sigma^2[(1/z) - \mathscr{P}(z) - \mathscr{Q}(z)] \tag{13a}$$

where

$$\mathscr{P}(z) = \langle \tau_0/(z\tau_0 + 1)\rangle \tag{13b}$$

and

$$\mathscr{Q}(z) = \langle (\mathbf{K}-1)^2\,\mathbf{G}(z)\rangle_{00} \tag{13c}$$

The three terms in the square brackets of Eq. (13a) have simple physical interpretations in the time domain. The first term is the sum of the probabilities, each 1/2, that the walker is trapped initially or finally. $P(t)$ is the probability that the walker stays in a single trap during the interval 0 to t. $Q(t)$ is the probability that the walker is trapped initially and finally in the same trap and that during the time interval from 0 to t has visited a conduction site at least once.

The asymptotic behavior of $P(t)$ is easily evaluated using a Tauberian theorem and the probability distribution of the trap times, Eq. (3),

$$P(t) \sim A\Gamma(1+\alpha)\, t^{-\alpha} \tag{14}$$

The asymptotic expansion of $\mathscr{Q}(z)$ can be developed by the methods of Section 4 of MNNE. The basic idea is to expand $\mathbf{G}$ in powers of $\delta\mathbf{K} = \mathbf{K} - \langle \mathbf{K} \rangle$ and to show that this is equivalent to a small z expansion. Since $\langle K_{nn} \rangle \sim 2 - (\text{const})\, z^{\alpha}$ the leading small z behavior of $\mathscr{Q}(z)$ is obtained by setting $\mathbf{K} = 2\mathbf{1}$ in Eqs. (6a) and (13c). Thus $\mathscr{Q}(z) \sim [(2z + \nu\boldsymbol{\theta})^{-1}]_{00}$ which is one half the Laplace transform of the probability of being at the origin of an ordinary random walk with diffusion coefficient D. To leading order then

$$Q(t) \sim (l^2/4\pi D t)^{d/2}/2 \tag{15}$$

The velocity correlation function, $\phi(t)$, is formally defined as one half the second derivative of the mean squared displacement. The leading long time tail of the VCF depends upon α and d and takes the form

$$\phi(t) \sim -d(d+2)\, l^{2+d}\sigma^2(\pi D)^{-d/2}(4t)^{-(2+d/2)} \qquad \text{for} \quad d/2 < \alpha \tag{16a}$$

or

$$\phi(t) \sim -\alpha l^2 \sigma^2 A\Gamma(2+\alpha)\, t^{-(2+\alpha)}/2 \qquad \text{for} \quad d/2 > \alpha \tag{16b}$$

3. DISCUSSION

We have studied a hopping model with trapping and determined the long time tail of the velocity correlation function. Let us contrast our result to the predictions which the mode coupling theory makes for our model. The mode-coupling theory predicts that the leading long time tail in a disordered diffusive system decays like $t^{-(1+d/2)}$ with an amplitude proportional to the fluctuations in the diffusion coefficient from one realization to another. In the present model, the diffusion coefficient is independent of the trap parameters $\mathbf{x}_m$ and τ_m [see Eq. (10)]. Thus there are no fluctuations in the diffusion coefficient and the mode coupling theory predicts that the long time tail is less singular than $t^{-(1+d/2)}$. Hence for the present model with $\alpha < (-1 + d/2)$, the mode coupling theory fails.

Roughly speaking, within the mode coupling theory long relaxation times, τ, are associated with long wavelength diffusive modes, i.e., $\tau \sim 1/q^2 D$ and q small. These modes are coupled to VCF via local fluctuations in the diffusion coefficient. On the other hand, in the present model there are also localized slow modes associated with traps with long relaxation times. The trap displacements couple these modes to the VCF. Indeed, the $t^{-(2+\alpha)}$ long time tail in the present model is independent of the diffusion process between conduction states.

The crucial feature of the model which leads to the anomalous long time tail is the presence of directed traps having a broad distribution of relaxation times. Other diffusive systems with this feature should also have a contribution to the VCF which decays like $t^{-(2+\alpha)}$. One example of this is the overlapping Lorentz gas where configurations of scatterers which almost completely enclose a region of space form directed traps. In Ref. 16 it is shown that the tail in the trapping time distribution has exponent $\alpha = 1/(d-1)$. Thus for $d > 3$ we expect the long time tail in the VCF to be dominated by trapping rather than ring events and to decay like $t^{-[2+1/(d-1)]}$. These ideas should also apply to the frequency-dependent conductivity in materials characterized by the "Swiss-cheese" model discussed recently by Halperin, Feng, and Sen.[17] Here overlapping spherical holes are randomly placed in a uniform conducting medium and traps are formed by configurations of holes which almost completely enclose a region of space.

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