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Universality of anomalous diffusion in extremely disordered systems

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Abstract

The universal time-dependence of the mean-square displacement for motion in a random energy landscape with equal minima is evaluated analytically and numerically in the percolation path approximation (PPA), which was recently shown by extensive computer simulations in two and three dimensions [Dyre and Schrøder, cond-mat/9601052] to be more accurate than the standard effective medium approximation (EMA). According to the PPA the universal mean-square displacement in dimensionless units as function of time varies as $1/\ln^2(t^{-1})$ for $t \rightarrow 0$. This implies a quite different short-time behavior than predicted by the EMA, where the universal mean-square displacement varies as $1/\ln(t^{-1})$ at short times [Dyre and Jacobsen, Phys. Rev. E 52 (1995) 2429].

1. Introduction

The study of motion in rugged energy landscapes is relevant in a number of contexts [1,2]. Examples include models for dc [3-5] and ac conduction in disordered solids [6-9], protein dynamics [10-12], viscous flow of liquids close to the glass transition [13,14], diffusion in random flows [15], or rate processes controlled by the anomalous diffusion of reactants [16-20]. Usually, the complexity of a system is represented by some sort of randomness of the energy landscape. Recently, interest has focussed on the extreme disorder limit arrived at by letting the temperature go to zero [21-23]. In this limit the rates for jumps across energy barriers cover more and more decades of frequency. According to the effective medium approximation (EMA), in the extreme disorder limit a universality arises: The frequency-dependent diffusion constant becomes independent of the energy barrier probability distribution [21]. The existence of universality was confirmed by computer simulations in two dimensions [21]. However, more extensive simulations in two and three dimensions have shown that the EMA is not quantitatively accurate [24]. Instead, a new approximation - the percolation path approximation (PPA) - has been proposed [24] and shown to work better than the EMA.

The purpose of this paper is to evaluate the universal time-dependence of the mean-square displacement in the PPA, supplementing our earlier calculation of the mean-square displacement in the EMA [25]. This is done in Section 3 after setting up the model and reviewing basic concepts in Section 2. Section 4 studies the asymptotic behavior of the universal mean-square displacement at short and long times according to both the EMA and the PPA. Section 5 contains the conclusion.

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2. Model and basic concepts

In most cases it is realistic to model the motion of a "particle" (representing the state of the system) in a rugged energy landscape in d dimensions by a Langevin equation for motion in a potential that is random in some sense. Usually, one would assume that the potential is randomly Gaussian with some finite spatial correlation, for example with an exponentially decaying autocorrelation. In this case correlations beyond the correlation lenght may be ignored, leading to a hopping model with random jump rates as studied below.

At low temperatures the "particle" spends most time vibrating in potential energy minima. Occasionally, by thermal excitation the "particle" acquires enough energy to "jump" between two minima. Thus, the low-temperature behavior may be described by a discrete so-called hopping model [6,26,27] characterized by an ordinary master equation for the probability to stay at some site. For simplicity it will be assumed that the sites lie on a d-dimensional cubic lattice, that all sites have the same energy (Model A of Ref. [22]), and that the values of the barriers to be overcome in hopping from one site to a neighboring site are uncorrelated from link to link. Assuming rate theory, the jump frequency for jumps along a particular link, Γ, is given by $\Gamma = \Gamma_0 \exp[-E/(k_B T)]$ where the activation energy E is chosen randomly according to some probability distribution, $p(E)$.

The quantity of interest is the mean-square displacement in an axis direction i as function of time, $\langle \Delta X_i^2(t) \rangle$. The frequency-dependent diffusion constant $D(s)$ is defined [28] by [where a convergence factor $\lim_{\epsilon \to 0} e^{-\epsilon t}$ ($\epsilon > 0$) is implicitly understood in the integral]

$$D(s) = \frac{s^2}{2} \int_0^\infty \langle \Delta X_i^2(t) \rangle e^{-st} \, dt . \tag{1}$$

Here s denotes the "Laplace" (imaginary) frequency: $s = i\omega$. For ordinary diffusion, where $\langle \Delta X_i^2(t) \rangle = 2Dt$, Eq. (1) implies $D(s) = D$. In disordered systems the mean-square displacement at short times varies more rapidly than this. This implies [25] that $D(s)$, if considered as function of *real* s, is an increasing function.

Throughout this paper dimensionless units are used: The units of length and time are chosen such that the DC limit of $D(s)$ is 1 and the frequency marking the onset of frequency-dependence of $D(s)$ is one. It is sometimes convenient to regard the "particle" as charged; if the unit of charge is suitably chosen the fluctuation-dissipation theorem implies $\sigma(s) = D(s)$, where $\sigma(s)$ is the frequency-dependent conductivity.

3. Universality in the extreme disorder limit

The hopping model may be mapped to an electrical network consisting of resistors [equal to the inverse jump rate], identical capacitors, and a large number of voltage generators [21,29]. In the zero-frequency limit the network reduces to a simple resistance network. At low temperatures the DC current flows on the "percolation cluster" [30,31], the set of links with activation energy below E_c, where E_c in terms of the link percolation threshold p_c is defined by

$$\int_0^{E_c} p(E) \, dE = p_c . \tag{2}$$

The physical background for the universality of the frequency-dependent diffusion constant (or equivalently, of the time-dependent mean-square displacement) is the fact [21] that low-frequency AC diffusion is also dominated by percolation. More precisely: At any given temperature percolation effects dominate AC diffusion for a finite frequency-range around the frequency marking the onset of frequency-dependence of $D(s)$ [equal to one in our unit system]; however, this range of frequencies covers more and more decades as the temperature is lowered towards zero.

Because of the dominance of percolation at low temperatures, the details of $p(E)$ are unimportant if $p(E)$ is smooth at E_c and $p(E_c) \neq 0$, as is assumed throughout this paper. In these cases the EMA leads [21] to the following equation for the universal $D = D(s)$:

$$D \ln D = s . \tag{3}$$

This equation was first derived by Bryksin in 1980 [32] in a paper discussing the frequency-dependent conductivity in the dilute limit of the "r-hopping model" for tunneling between randomly placed sites in a d-dimensional solid. If one defines the two functions

$$E(\theta) = \frac{\theta}{\sin\theta} \, e^{-\theta\cot\theta} \tag{4}$$

and

$$F(\theta) = \left(\cos\theta - \frac{\sin\theta}{\theta}\right)^2 + \sin^2\theta , \tag{5}$$

the solution of Eq. (3) is [25]

$$D(s) = 1 + \frac{1}{\pi}\int_0^\pi F(\theta) \, \frac{sE(\theta)}{s + E(\theta)} \, d\theta . \tag{6}$$

The time-dependence of the mean square displacement is given [25] by

$$\langle \Delta X_i^2(t) \rangle_{\rm EMA} = 2t + \frac{2}{\pi}\int_0^\pi F(\theta) \left(1 - e^{-tE(\theta)}\right) d\theta . \tag{7}$$

At long times ($t \gg 1$) Eq. (7) implies ordinary diffusion, $\langle \Delta X_i^2(t) \rangle = 2t$. At short times ($t \ll 1$) Eq. (7) implies $\langle \Delta X_i^2(t) \rangle \simeq 2/\ln(t^{-1})$ [25]. This result is derived in a more general setting in the next section.

The percolation path approximation (PPA) [24] is based on the following naive picture of "conduction" on the percolation cluster. Ignoring the fractal nature of the percolation cluster, the conducting paths are regarded as one-dimensional. In high dimensions this point of view leads to the correct percolation threshold. In two or three dimensions a large part of the percolation cluster does not contribute to low-frequency conduction. Only the "backbone" of the cluster is relevant here. In fact, on the backbone the so-called "red" bonds carry all current flowing through the cluster. The set of red bonds has a fractal dimension close to one (3/4 in two dimension and 1.2 in three dimensions) [15], thus justifying the use of the PPA also in two or three dimensions.

Since the criterion for a link of the lattice belonging to the percolation cluster is that the activation energy for the link jump rate is below E_c, we model a percolation path as a one-dimensional path with a randomly chosen activation energy below E_c. Thus, according to the PPA diffusion in the extreme disorder limit is modelled as an effectively one-dimensional process that involves the same activation energy probability distribution as that of the d-dimensional lattice, $p(E)$, but with a sharp cut-off at $E = E_c$. Unfortunately, even this simple one-dimensional model cannot be solved analytically. The solution of the one-dimensional model *in the EMA* [24] is

$$\sqrt{D} \, \ln\left[1 + \sqrt{sD}\right] = \sqrt{s} . \tag{8}$$

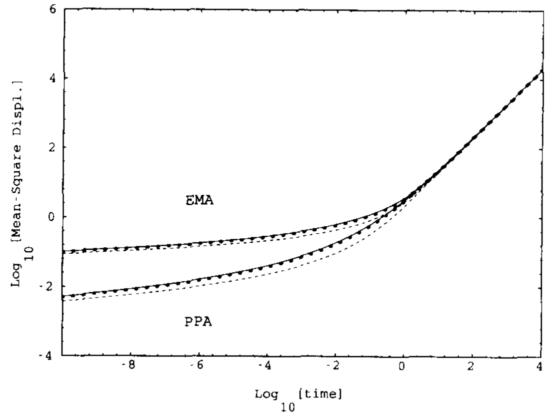

Fig. 1. Log-log plot of the universal mean-square displacement in dimensionless units according to the effective medium approximation (EMA) and the percolation path approximation (PPA). The full curves give the exact mean-square displacement as function of time [Eqs. (7) and (12)], the dashed lines give the rough analytical approximations [Eqs. (31) and (32)], and the dots give the approximation $\langle \Delta X_i^2(t) \rangle \cong 2tD(t^{-1})$, where $D(s)$ is the frequency-dependent diffusion constant defined in Eq. (1).

Since the motivation for constructing the PPA is the fact that the EMA is inaccurate, it may seem strange to use the EMA for approximately solving the one-dimensional model behind the PPA. However, in Ref. [24] it was shown by computer simulations that Eq. (8) works very well for systems with a sharp activation energy cut-off in one dimension. Note that we here have an unusual example of a mean-field theory (EMA) that works better in one dimension than in two or three dimensions.

To calculate the mean-square displacement in the PPA, Laplace inversion of Eq. (1) is undertaken:

$$\langle \Delta X_i^2(t) \rangle = \frac{1}{2\pi i} \oint \frac{2\,D(s)}{s^2}\, e^{st}\, ds\,. \tag{9}$$

Here, as usual for Laplace inversions, it is understood that the integration contour goes from $-i\infty$ to $i\infty$ to the right of all poles of the integrand. Introducing the variable $z = 1 + \sqrt{sD}$, Eq. (8) implies

$$(z-1)\ \ln z = s\,, \tag{10}$$

and Eq. (9) becomes

$$\langle \Delta X_i^2(t) \rangle_{\mathrm{PPA}} = \frac{1}{2\pi i} \oint \frac{2\,(z(s)-1)^2}{s^3} e^{st}\, ds\,. \tag{11}$$

Since $ds = [(z-1)/z + \ln z]\, dz$ we may now eliminate the transcendental equation Eq. (10) and transfer Eq. (11) into an ordinary complex contour integral:

$$\langle \Delta X_i^2(t) \rangle_{\mathrm{PPA}} = \frac{1}{2\pi i} \oint 2 \left(\frac{1}{(z-1)\ln^2 z} + \frac{1}{z \ln^3 z} \right) e^{[(z-1)\ln z]t} dz\,. \tag{12}$$

In the numerical evaluation of Eq. (12) we have used the integration contour given by the straight line in the complex plane through the number $a = \alpha + \beta/t$ parallel to the imaginary axis with $\alpha = 1.01$ and $\beta = 0.05$, associated with cut-offs at $a \pm ib$ for $b = 10 + 10/t$.

Fig. 1 shows the mean-square displacement (full curves) according to the EMA (Eq. (7)) and to the PPA (Eq. (12)). Clearly, at short times the two approximations give quite different results. This is verified analytically in the following section.

4. Asymptotic behavior of mean-square displacement

The mean-square displacement at short times is dominated by the contributions from $D(s)$ at large s. Eq. (3) implies that $\ln D/\ln s \to 1$ as $s \to \infty$ and therefore we have the following expression for the asymptotic behavior of $D(s)$ in the EMA,

$$\text{EMA}: \quad D(s) \sim \frac{s}{\ln s} \quad (s \to \infty) . \tag{13}$$

Eq. (8) also implies $\ln D/\ln s \to 1$ as $s \to \infty$ and just as above

$$\text{PPA}: \quad D(s) \sim \frac{s}{\ln^2 s} \quad (s \to \infty) . \tag{14}$$

Granted that the mean-square displacement in the EMA and PPA is positive and monotone the Tauberian theorem of Ref. [33] applies: If the Laplace transform $\tilde{u}(s) = 2D(s)/s^2$ of a positive monotone function $u(t) = \langle \Delta X_i^2(t) \rangle$ for some $\rho > 0$ and all $\lambda > 0$ satisfies

$$\frac{D(s\lambda)}{\lambda^2 D(s)} = \frac{\tilde{u}(s\lambda)}{\tilde{u}(s)} \to \frac{1}{\lambda^\rho} \quad \text{for } s \to \infty \text{ (resp. 0)} \tag{15}$$

then

$$\frac{\langle \Delta X_i^2(t) \rangle}{2tD(t^{-1})} = \frac{u(t)t}{\tilde{u}(t^{-1})} \to \frac{1}{\Gamma(\rho)} \quad \text{for } t \to 0 \text{ (resp. } \infty) . \tag{16}$$

If Eq. (15) holds for all nonnegative complex λ (as in our case) one may argue heuristically for Eq. (16) via the inversion formula: By the change of variable $z = st$ Eq. (9) implies

$$\frac{\langle \Delta X_i^2(t) \rangle}{2tD(t^{-1})} = \frac{1}{2\pi \mathrm{i}} \oint \frac{D(t^{-1}z)}{z^2 D(t^{-1})} \mathrm{e}^z \, \mathrm{d}z , \tag{17}$$

and from Eq. (15) for complex $\lambda = z$ then follows

$$\frac{\langle \Delta X_i^2(t) \rangle}{2tD(t^{-1})} \to \frac{1}{2\pi \mathrm{i}} \oint \frac{\mathrm{e}^z}{z^\rho} \mathrm{d}z = \frac{1}{\Gamma(\rho)} \quad \text{for} \quad t \to 0 \text{ (resp. } \infty) . \tag{18}$$

Since both Eq. (13) and Eq. (14) entails Eq. (15) with $\rho = 1$ for $s \to \infty$, it follows by Eq. (16) that the short-time asymptotic behavior of the mean-square displacement is given by

$$\text{EMA}: \quad \langle \Delta X_i^2(t) \rangle_{\text{EMA}} \sim 2tD(t^{-1}) \sim \frac{2}{\ln(t^{-1})} \quad (t \to 0), \tag{19}$$

$$\text{PPA}: \quad \langle \Delta X_i^2(t) \rangle_{\text{PPA}} \sim 2tD(t^{-1}) \sim \frac{2}{\ln^2(t^{-1})} \quad (t \to 0). \tag{20}$$

The expression $2tD(t^{-1})$ also gives the leading term in the long-time behavior of the mean-square displacement: Since $D(s) \to 1$ for $s \to 0$ (by definition of the unit system), Eq. (15) holds with $\rho = 2$ for $s \to 0$, so that by Eq. (16)

$$\langle \Delta X_i^2(t) \rangle \sim 2tD(t^{-1}) \sim 2t \quad (t \to \infty). \tag{21}$$

In fact, as is clear from Fig. 1, the expression $2tD(t^{-1})$ (dotted curves) approximates the mean-square displacement well over the entire time scale: For the EMA the deviation is less than 7.5% and for the PPA it is less than 9%.

As expected, at long times the mean-square displacement varies dominantly as $2t$. More precisely, in the EMA Eq. (7) implies [25]

$$\langle \Delta X_i^2(t)\rangle_{\mathrm{EMA}} = 2t + 2 \quad (t \to \infty)\,. \tag{22}$$

A closer investigation of the PPA, to be detailed below, reveals that

$$\langle \Delta X_i^2(t)\rangle_{\mathrm{PPA}} = 2t + \frac{2}{\sqrt{\pi}}\sqrt{t} + \frac{1}{12} \quad (t \to \infty)\,. \tag{23}$$

This will be used in an analytical approximation presented in the conclusion. To arrive at Eq. (23) we expand $D(s)$ into a power series in $\sqrt{s}$ at $s = 0$ as follows. Let $w = \sqrt{sD}$. Then $D(s) = w^2(s)/s$, where w is defined as an analytic function of s off the negative real axis by

$$s = w \ln(1 + w)\,. \tag{24}$$

Here w takes values in the complex plane to the right of the curve defined by $w\ln(1 + w)$ being real and non-positive. The right hand side of Eq. (24) may be expanded

$$s = w^2 - \frac{w^3}{2} + \frac{w^4}{3} - \frac{w^5}{4} + \cdots, \tag{25}$$

from which it follows that

$$\sqrt{s} = w - \frac{w^2}{4} + \frac{13w^3}{96} - \frac{35w^4}{384} + \cdots. \tag{26}$$

The above series may be inverted,

$$w = s^{1/2} + \frac{s}{4} - \frac{s^{3/2}}{96} + 0 \cdot s^2 + \cdots, \tag{27}$$

thus giving

$$D(s) = \frac{w^2}{s} = 1 + \frac{s^{1/2}}{2} + \frac{s}{24} - \frac{s^{3/2}}{192} + \cdots. \tag{28}$$

Inserting this expansion of $D(s)$ into Eq. (9), and using the well-known formula (used also above in Eq. (18))

$$\frac{1}{2\pi \mathrm{i}} \oint s^{-n} \mathrm{e}^{st}\, \mathrm{d}s = \frac{t^{n-1}}{\Gamma(n)}, \tag{29}$$

which for $t > 0$ holds for all real n when the integration contour encircles the negative real axis, we obtain the following asymptotic expansion valid for $t \to \infty$:

$$\begin{aligned} \langle \Delta X_i^2(t)\rangle_{\mathrm{PPA}} &= \frac{1}{2\pi \mathrm{i}} \oint \left(2s^{-2} + s^{-3/2} + \frac{s^{-1}}{12} - \frac{s^{-1/2}}{96} + \cdots\right) \mathrm{e}^{st}\, \mathrm{d}s \\ &= 2t + \frac{2}{\sqrt{\pi}} t^{1/2} + \frac{1}{12} - \frac{1}{96\sqrt{\pi}} t^{-1/2} + \cdots. \end{aligned} \tag{30}$$

Truncating this series after the third term we obtain the approximation in Eq. (23), with an error given dominantly by the fourth term as $t \to \infty$.

The approximation in Eq. (23) is accurate within 0.2% for $t \geqslant 1$ and within 2.5% for $t \geqslant 0.1$.

5. Conclusion

We have calculated the universal mean-square displacement within the PPA for an extremely disordered system with equal energy minima. Asymptotically, at short times the universal mean-square displacement according to the EMA varies as $1/\ln(t^{-1})$, while in the PPA it varies as $1/\ln^2(t^{-1})$. From the asymptotic behaviors it is possible to construct rough analytical expressions, that at long times give a mean-square displacement equal to $2t$. For the EMA a rough analytical approximation is given [25] by

$$\langle \Delta X_i^2(t) \rangle_{\mathrm{EMA}} \cong \frac{2}{\ln(1+t^{-1})} . \tag{31}$$

This expression is valid within 33% for all t. For the PPA the following expression is easily shown to have the correct short and long time behaviors to leading order:

$$\langle \Delta X_i^2(t) \rangle_{\mathrm{PPA}} \cong \frac{2}{\ln^2(1+t^{-1})} - 2t^2 . \tag{32}$$

This expression is valid within 51% for all t. The two approximate expressions are shown by dashed curves in Fig. 1. A more accurate analytical approximation to the EMA universal mean-square displacement is given in Ref. [25]; for the PPA the following approximation is accurate within 3.5%

$$\langle \Delta X_i^2(t) \rangle_{\mathrm{PPA}} \cong \begin{cases} \dfrac{2}{\ln^2[1+t^{-1}/\ln(\mathrm{e}+t^{-1})]} - 2t^2 - \dfrac{4}{\mathrm{e}}t, & \text{for } t \leqslant 0.1 , \\[2ex] 2t + \dfrac{2}{\sqrt{\pi}} t^{1/2} + \dfrac{1}{12}, & \text{for } t \geqslant 0.1 . \end{cases} \tag{33}$$

The model studied in the present paper is somewhat artificial in the sense that all minima are assumed to be equal. Future work should look into the possible existence of universality for the more general class of models dealing with hopping between energetically inequivalent sites (Model B of Ref. [22]). We conjecture that, if there is a lowest allowed energy, these models exhibit the same sort of universality as found in the above studied "symmetric" hopping model in the low-temperature [extreme disorder] limit: At sufficiently low temperatures only the very lowest energies close to the ground state energy are populated and diffusion may effectively be regarded as a symmetric hopping between these very low-energy sites.

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