Occupation Time Statistics in the Quenched Trap Model

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We investigate the distribution of the occupation time of a particle undergoing a random walk among random energy traps and in the presence of a deterministic potential field. When the distribution of energy traps is exponential with a width T_g, we find in thermal equilibrium a transition between Boltzmann statistics when $T > T_g$ to Lamperti statistics when $T < T_g$. We explain why our main results are valid for other models of quenched disorder, and discuss briefly implications on single particle experiments.

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Particles diffusing randomly in condensed phase environments, with a very broad distribution of trapping times, are found in diverse physical systems [1]. When the average trapping time is infinite, such processes lead to anomalous diffusion and relaxation which are well investigated, for example, in the context of dynamics of ensembles of charge carriers in amorphous semiconductors [2–4]. More recently, similar dynamics was investigated in single particle experiments, where the problem of ensemble averaging is removed [5–8]. Bouchaud [9] showed that annealed dynamical processes, described by power law trapping times with a diverging mean trapping time, break ergodicity and hence usual statistical mechanics does not apply [10]. Intuitively, one can argue that if the averaged trapping time diverges, measurements can never be made for time long enough, in order for usual statistical mechanics to apply. Since, in these days, single particle experiments exhibit power law trapping times, it is natural to ask what theory replaces the usual Boltzmann theory for such systems.

In this Letter we classify deviations from Boltzmann statistics, for random walks on a lattice with quenched disorder, in terms of statistics of occupation times. Consider first simple Brownian motion in a deterministic binding potential $U^{\mathrm{det}}(x)$. The occupation time t^{Occ} is the time the particle spends in the domain $x_1 < x < x_2$. For ergodic dynamics in thermal equilibrium, the occupation fraction $\bar{p} \equiv t^{\mathrm{Occ}}/t$ is given by Boltzmann statistics

$$\bar{p} \longrightarrow \frac{\int_{x_1}^{x_2} e^{-U^{\mathrm{det}}(x)/T} dx}{Z}, \tag{1}$$

in the limit of long measurement time t, $Z = \int_{-\infty}^{\infty} \exp[-U^{\mathrm{det}}(x)/T] dx$ is the normalizing partition function and T is the temperature. In many single particle experiments, in disordered systems, the potential energy sampled by the particle is random [5–7]. Majumdar and Comtet [11] considered the Sinai model and showed that the occupation fraction may exhibit large fluctuations from one sample of disorder to another. Here we consider the problem of the distribution of the occupation time, in the context of the quenched trap model, finding strong deviations from Boltzmann's theory. As we will show, the generality of our theory is based on the observation that random partition functions, of random systems which exhibit anomalous diffusion, are distributed according to Lévy statistics which leads to a new type of non-Boltzmann statistical law. Previously, nontrivial occupation times were measured for blinking quantum dots driven by a laser field [8], a system far from thermal equilibrium. Possible verification of our theory in the laboratory is discussed at the end of the Letter.

Quenched trap model.—We consider a particle undergoing a one-dimensional random walk on a quenched random energy landscape on a lattice [9,12,13]. Lattice points are on $x = 0, a, 2a, \ldots, L$, where a is the lattice spacing. On each lattice point a random energy E_x is assigned, which is minus the energy of the particle on site x, so $E_x > 0$ is the depth of a trap on site x. The energies of the traps $\{E_x\}$ are independent identically distributed random variables, with a common probability density function (PDF) $\rho(E) = (1/T_g)\exp(-E/T_g)$. Such density of states leads to anomalous diffusion [14,15], and aging [9,15–17] when $T < T_g$. The model was used to describe dynamics of many systems: transport of electrons in amorphous materials [2–4], single molecule pulling experiments [7], rheology of soft matter [18], e.g., emulsions, relaxation in glasses [9,12,19], and green fluorescent protein dynamics [20]. Because of an interaction with a heat bath, the particle may escape site x and jump to one of its nearest neighbors. The average time it takes the particle to escape from site x is given by Arrhenius law $\tau_x = \exp(E_x/T)$. Notice that small changes in E_x lead to an exponential shift in τ_x. In particular, it is easy to show that the PDF of the waiting times is

$$\psi(\tau) = \frac{T}{T_g} \tau^{-(1+T/T_g)} \qquad \tau \geq 1, \tag{2}$$

so when $T < T_g$ the average waiting time diverges. In addition to the random potential energy, a deterministic field may act on the particle, which leads to a biased random walk. Let q_x $(1 - q_x)$ be the probability of jumping left (right) from site x, respectively. The master equation for the population on site x, P_x is

$$\frac{dP_x}{dt} = -\frac{1}{\tau_x}P_x + \frac{q_{x+1}}{\tau_{x+1}}P_{x+1} + \frac{1-q_{x-1}}{\tau_{x-1}}P_{x-1}. \quad (3)$$

For nonbiased random walks $q_x = 1/2$, while for uniformly biased random walks $q_x \neq 1/2$ is a constant. The boundary conditions are reflecting $q_0 = 0$ and $q_L = 1$. The local bias q_x is controlled by a deterministic potential field $U_x^{\rm det}$. It is usually assumed that detailed balance conditions hold so that the dynamics of the populations reach thermal equilibrium, described by Boltzmann's canonical ensemble. For the trap model this well-known condition leads to

$$\frac{q_x}{1-q_{x-1}} = \exp\left[-\frac{(U_{x-1}^{\rm det} - U_x^{\rm det})}{T}\right]. \quad (4)$$

For example, if a constant driving force field $\mathcal{F}$ acts on the system $q_x = 1/[1+\exp(\mathcal{F}a/T)]$ [16].

We consider a single realization of disorder in the thermodynamic limit where the measurement time $t \to \infty$ before the system size is made large. One can show that the equilibrium of populations is described by Boltzmann statistics, which is not surprising since we used the detailed balance condition. The total time the particle spends in the domain $x_1 \leq x \leq L$ is the occupation time $t^{\rm Occ}$. This domain is called the observation domain. For a finite system, there exists a minimum of the energy, and the process is ergodic; hence, the occupation fraction for a single disordered system is

$$\bar{p} = \frac{t^{\rm Occ}}{t} \to \frac{Z^{\rm O}}{Z^{\rm O} + Z^{\rm NO}}, \quad (5)$$

where

$$Z^{\rm O} = \sum_{x=x_1}^{L} \exp\left[-\frac{(U_x^{\rm det} - E_x)}{T}\right] \quad (6)$$

is the partition function of the observation domain and $Z^{\rm NO} = \sum_{x=0}^{x_1-a} \exp[-(U_x^{\rm det} - E_x)/T]$ is the partition function of the rest of the system. The occupation fraction is a random variable which varies from one system to the other; the goal of this Letter is to calculate its distribution. However, first three comments are in place. (i) As mentioned, if we have only a single realization of disorder the occupation fraction is given by Boltzmann statistics. The question then is whether the occupation fraction a self-averaging quantity. Namely, we investigate many realizations of disorder, for each the occupation fraction is a random variable and hence we construct its distribution. This case corresponds to single molecule experiments where one may track independently a large number of individual molecules, each one interacting with a unique random environment [6]. (ii) The occupation time in Eq. (5) describes rather generally the occupation time of a particle in a random energy landscape and is not unique to the specific dynamics of the quenched trap model. For example, we could add random barriers [21], which would not alter the statistics of occupation times in equilibrium. (iii) Previous work [10] considered the occupation times of the continuous time random walk (CTRW) model (annealed model), unlike the quenched trap model, in the CTRW model ergodicity is broken and the system is not spatially disordered.

From Eq. (5) we see that the distribution of the occupation fraction $\bar{p}$ is obtained in principle from the distributions of two independent random partition functions $Z^{\rm O}$ and $Z^{\rm NO}$. Let $G_{Z^{\rm O}}(z)$ and $G_{Z^{\rm NO}}(z)$ be the PDFs of $Z^{\rm O}$ and $Z^{\rm NO}$, respectively. Then the PDF of the occupation fraction $f(\bar{p})$ is found using Eq. (5)

$$f(\bar{p}) = \int_0^\infty dz z G_{Z^{\rm NO}}[(1-\bar{p})z] G_{Z^{\rm O}}(\bar{p}z). \quad (7)$$

We now consider the problem of finding $G_{Z^{\rm O}}(z)$.

If the deterministic part of the field $U_x^{\rm det}$ is a constant, Eq. (6) shows that $Z^{\rm O}$ is a sum of independent identically distributed random variables, and then Gauss–Lévy limit theorems apply. In contrast, when $U_x^{\rm det}$ is not a constant then we are dealing with the problem of summation of nonidentically distributed random variables and, hence, in what follows we modify the familiar limit theorems for the case under investigation.

Let n be the number of lattice points in the interval $[x_1, L]$. We consider the scaled random variable $\tilde{Z}^{\rm O} = Z^{\rm O}/n^{1/\alpha}$ with $\alpha = T/T_g$ and $T < T_g$. The Laplace $z \to u$ transform of the PDF of $\tilde{Z}^{\rm O}$ is found using Eq. (6) and $\rho(E)$

$$\hat{G}_{\tilde{Z}^{\rm O}}(u) = \exp\left\{\sum_{x=x_1}^{L} \ln\left[\hat{\psi}\left(\frac{u e^{-T/U_x^{\rm det}}}{n^{1/\alpha}}\right)\right]\right\}, \quad (8)$$

where $\hat{\psi}(u) = \int_0^\infty \exp(-u\tau)\psi(\tau)d\tau$. We now consider the limit of large n. We use the small u expansion

$$\ln[\hat{\psi}(u)] \sim -{\rm A}u^\alpha + \frac{\alpha}{1-\alpha}u + \cdots, \quad (9)$$

where $A = \alpha|\Gamma(-\alpha)|$, and from Eqs. (8) and (9), we find

$$\hat{G}_{\tilde{Z}^{\rm O}}(u) \sim \exp\left\{-\frac{Au^\alpha}{n}\sum_{x=x_1}^{L} e^{-U_x^{\rm det}\alpha/T} + \frac{\alpha u}{(1-\alpha)n^{1/\alpha}}\sum_{x=x_1}^{L} e^{-U_x^{\rm det}/T} + \cdots\right\}. \quad (10)$$

In the continuum limit of $a \to 0$, $n \to \infty$, and $L - x_1 = an$ remaining finite, we may replace the summation with integration and find the stretched exponential

$$\hat{G}_{\tilde{Z}^{\rm O}}(u) \sim \exp\left[-A\frac{\int_{x_1}^{L} e^{-U^{\rm det}(x)/T_g}dx}{L-x_1}u^\alpha\right], \quad (11)$$

where $U^{\rm det}(x)$ is the deterministic field in the continuum limit. The inverse Laplace transform of Eq. (11) is the one-sided Lévy stable law.

A similar calculation is made for $Z^{\rm NO}$. We invert the Laplace transform in Eq. (11), switch back to the original variable $Z^{\rm O}$ instead of the scaled one $\tilde{Z}^{\rm O}$, and find using

Eq. (7)

$$f(\bar{p}) \sim \frac{1}{(\mathcal{R})^{1/\alpha}} \int_0^\infty dz z l_\alpha[(1-\bar{p})z] l_\alpha\left[\frac{\bar{p}z}{(\mathcal{R})^{1/\alpha}}\right], \quad (12)$$

with

$$\mathcal{R} = \frac{P_B(T_g)}{1 - P_B(T_g)}. \quad (13)$$

In Eq. (12) $l_\alpha(z)$ is the one-sided Lévy stable PDF whose Laplace pair is $\hat{l}_\alpha(u) \equiv \exp(-u^\alpha)$. $P_B(T_g)$ is Boltzmann's probability of finding the particle in the observation domain calculated using the deterministic field with a temperature T_g

$$P_B(T_g) = \frac{\int_{x_1}^L \exp(-U^{\rm det}(x)/T_g) dx}{Z(T_g)}. \quad (14)$$

Solving the integral Eq. (12), we find the Lamperti [22] PDF

$$f(\bar{p}) \sim \frac{\sin\pi\alpha}{\pi} \times \frac{\mathcal{R}\bar{p}^{\alpha-1}(1-\bar{p})^{\alpha-1}}{\mathcal{R}^2(1-\bar{p})^{2\alpha} + \bar{p}^{2\alpha} + 2\mathcal{R}(1-\bar{p})^\alpha \bar{p}^\alpha \cos\pi\alpha}. \quad (15)$$

Equations (13) and (15) are the main results of this Letter, soon to be discussed in detail, which are valid in the glassy phase $T < T_g$.

For $T > T_g$ and in the same limit we have the usual canonical behavior

$$f(\bar{p}) \sim \delta[\bar{p} - P_B(T)]. \quad (16)$$

Equation (16) shows that when $T > T_g$ the disorder plays no role, indicating the reproducibility of Boltzmann's statistics Eq. (1), when the disorder is weak.

Equations (13) and (15) give the distribution of the occupation time, which is the generalization of the usual Boltzmann law Eq. (16). The parameter $\mathcal{R}$ is called the asymmetry parameter, and if $\mathcal{R} = 1$, $f(\bar{p})$ is symmetric. The asymmetry parameter $\mathcal{R}$ is calculated by the usual type of integral over the Boltzmann factor; however, now the temperature T_g is the relevant temperature not T [see Eq. (13)]. Roughly speaking, there are two sources of fluctuations: the disorder characterized by T_g, and the temperature T. Hence when $T < T_g$ the relevant temperature is the "temperature of the disorder", that is T_g. For example using Eqs. (13), (15), and (16) the average occupation fraction has the following surprising behavior,

$$\langle \bar{p} \rangle = \begin{cases} P_B(T_g) & T < T_g \\ P_B(T) & T > T_g. \end{cases} \quad (17)$$

The average occupation fraction freezes in the colder glassy phase of $T < T_g$ in the sense that it does not depend on the temperature T, for any type of deterministic binding field.

In Fig. 1 we demonstrate our results comparing our theory with numerical simulations on a lattice. We consider the situation where the deterministic field is $U^{\rm det}(x) = \mathcal{F}x$ and $0 < x$, and the observation domain is $0 < x < T_g/\mathcal{F}$. In Fig. 1(a) with $T > T_g$ we see that the distribution of occupation fraction is very narrow with $\bar{p} = P_B(T = 3T_g) = 1 - e^{-1/3}$, indicating that the disorder is not important. In contrast, when $T < T_g$ the behavior of the occupation fraction changes dramatically and $\bar{p}$ is non-self-averaging and random.

Equation (15) shows that when $T/T_g \ll 1$ the PDF of occupation fraction is essentially composed of two delta functions centered on $\bar{p} = 1$ and $\bar{p} = 0$. Namely, for some samples of disorder, the particle is within the observation domain during all the observation time t ($\bar{p} = 1$) and in other samples the particle is never in the observation domain ($\bar{p} = 0$). This behavior is easy to understand, when $T \to 0$ the minimum of the random potential energy is the most populated, and this minimum can be found either in the observation domain or out of it. As shown in Fig. 1(c), for small but finite T we have a nontrivial bimodal U shape of the PDF, which reflects this low temperature behavior. As the temperature increases we start seeing a third peak in the PDF of the occupation fraction being developed [see Fig. 1(b)]; so when $T \to T_g$ the self-averaging phase is approached.

In Fig. 2 we show the averaged occupation fraction versus temperature T using the same deterministic poten-

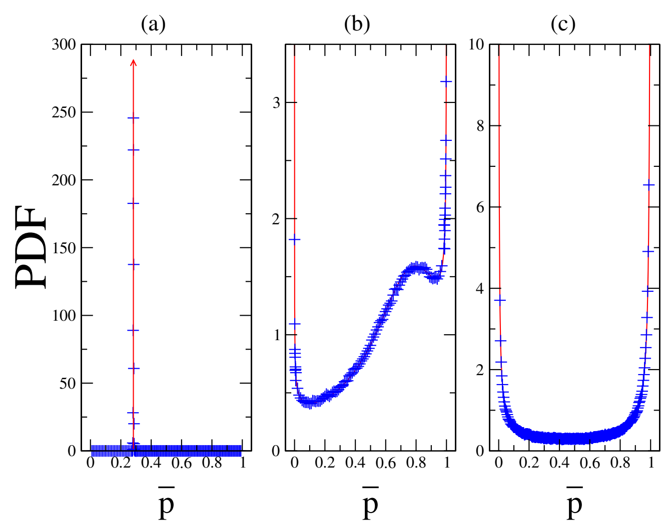

FIG. 1 (color online). The PDF of the occupation fraction for the deterministic field $U(x) = \mathcal{F}x$. (a) For $T = 3T_g$ we find a delta function centered on the value given by Boltzmann's statistics. When $T/T_g = 0.7$ [panel (b)] the nontrivial distribution of the occupation fraction has three peaks while for $T/T_g = 0.3$ [panel (c)] the distribution is bimodal. The + symbols are simulations and the curve is the theoretical prediction [Eq. (15)] without fitting. We used $\mathcal{F} = 1$, $T_g = 1$, $a = 10^{-5}$ the observation domain $0 < x < 1$, system size 20, and 3×10^4 disordered systems.

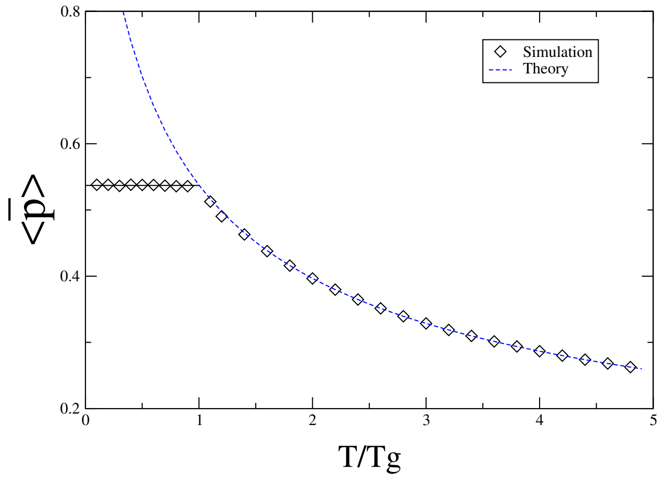

FIG. 2 (color online). The averaged occupation fraction versus T/T_g. When $T > T_g$, $\langle \bar{p} \rangle = P_B(T)$, namely, the usual Boltzmann theory applies, while for $T < T_g$, $\langle \bar{p} \rangle = P_B(T_g)$, which is independent of the temperature T. The lines are theoretical predictions [Eq. (17)] and the diamonds are simulation results with no fitting.

tial field as in Fig. 1. For $T > T_g$ the average occupation fraction is $P_B(T)$ and hence, as the temperature is decreased, the average occupation time increases, since the particles condensate closer to the minimum of the deterministic field which is on $x = 0$ as the temperature is reduced. However, when $T = T_g$ we see in Fig. 2 a type of phase transition in the behavior of the averaged occupation fraction, and it does not depend on T when $T < T_g$, as predicted by our theory Eq. (17).

Let us discuss the generality of our results beyond the quenched trap model. We have divided our system into two, the observation domain and the rest of the system. The partition functions of these domains are random variables, due to the randomness of the underlying Hamiltonian. Our results show that when the partition functions are distributed according to Lévy statistics, then the Lamperti distribution Eq. (15) describes the statistics of the occupation time. It is natural that partition functions of random systems are Lévy distributed [23], since a partition function is a sum over energy states and if these states are random and uncorrelated the Lévy limit theorems must apply. Indeed, as we will show in a future publication, our main result, Eq. (15), describes also occupation time statistics in models with quenched random geometry: the random comb model, which is a model of a random walk on a loopless random fractal; and models of anomalous diffusion of a particle on structures with distributed dangling bonds in the presence of bias [1,24,25]. Finally, we note that our theory is valid also in dimensions higher than 1.

It is interesting to verify in experiment our theoretical predictions, for example, using the experimental set up of Wong *et al.* [5]. There the anomalous diffusion of magnetic beads in a random polymer network was observed. The measured [5] exponent α for the power law distribution of the waiting times $\psi(\tau) \propto \tau^{-(1+\alpha)}$, depends on the ratio of the size of the bead and the linear size of the mesh of the network l (roughly a μm). We suggest adding an external binding field, for example, a harmonic trap, $U^{\text{det}}(\mathbf{x}) = k\mathbf{x}^2/2$. The dimensionless thermal length $\sqrt{T/k}/l$ should be larger than unity so that many traps are included in the observation domain. The occupation time of single particles can then be measured, and according to our theory for quenched disordered systems, its distribution is given by Eq. (15) with $\mathcal{R} = \frac{P_B(T_{\text{eff}})}{1-P_B(T_{\text{eff}})}$ with $1/T_{\text{eff}} = \alpha/T$ and not by Boltzmann's law. Besides the basic issue of a possible generalization of Boltzmann's law for disordered system, such measurement can provide insight into the nature of disorder, for example; whether it is quenched or annealed.

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