A Random Walk to a Non-Ergodic Equilibrium Concept

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Random walk models, such as the trap model, continuous time random walks, and comb models exhibit weak ergodicity breaking, when the average waiting time is infinite. The open question is: what statistical mechanical theory replaces the canonical Boltzmann-Gibbs theory for such systems? In this manuscript a non-ergodic equilibrium concept is investigated, for a continuous time random walk model in a potential field. In particular we show that in the non-ergodic phase the distribution of the occupation time of the particle on a given lattice point, approaches $U$ or $W$ shaped distributions related to the arcsin law. We show that when conditions of detailed balance are applied, these distributions depend on the partition function of the problem, thus establishing a relation between the non-ergodic dynamics and canonical statistical mechanics. In the ergodic phase the distribution function of the occupation times approaches a delta function centered on the value predicted based on standard Boltzmann–Gibbs statistics. Relation of our work with single molecule experiments is briefly discussed.

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I. INTRODUCTION

There is growing interest in non-ergodicity of systems whose dynamics is governed by power law waiting times, such a way that a state of the system is occupied with a sojourn time whose average is infinite. Such non-ergodicity, called weak ergodicity breaking [4], was first introduced in the context of glassy dynamics. It has found several applications in Physics: phenomenological models of glassy dynamics [3], laser cooling [1], blinking quantum dots [3–4], and models of atomic transport in optical lattice [5]. For example single blinking quantum dots, when interacting with a continuous wave laser field, turn at random times from a bright state in which many fluorescent photons are emitted, to a dark state. It is found that the distribution of dark and bright times follows power law behavior. Somewhat similar statistical behavior is found also for laser cooling of atoms, where the atom is found in two states in momentum space, a cold trapped state and a free state, the sojourn time probability density function has a power law behavior $\psi(\tau) \propto \tau^{-(1+\alpha)}$ with $\alpha < 1$. For such systems the time average of physical observable, for example the time average of fluorescence intensity of single quantum dots, is non-identical to the ensemble average even in the long time limit. From a stochastic point of view such ergodicity breaking is expected, since the condition to obtain ergodicity is that the measurement time $t$ be much longer than the microscopic time scale of the problem. However the microscopic time scale in our examples is infinite, namely the mean trapping times or the mean dark and bright times diverge. When these characteristic time scales are infinite, namely $\alpha < 1$, we can never make time averages for long enough times to obtain ergodicity.

It is important to note that the concept of a waiting (i.e. trapping) time probability density function (PDF) $\psi(\tau)$, with diverging first moment, is widespread and found in many fields of Physics [2–4, 5, 6, 7]. It was introduced into the theory of transport of charge carriers in disordered material [11], in the context of the continuous time random walk (CTRW). The CTRW describes a random walk on a lattice with a waiting time PDF of times between jump events $\psi(\tau)$. The model exhibits anomalous diffusion [11] and aging behaviors [16, 17, 18], when $\alpha < 1$, which are related to ergodicity breaking. The CTRW found many applications in the context of chaotic dynamics [12, 13, 18], tracer diffusion in complex flows [14, 15], financial time series [20], diffusion of bead in a polymer network [21], to name a few [4, 5, 6]. The dynamics of CTRW is similar to the dynamics of the comb model [8] and the annealed version of the trap model [16]. In turn the trap model is related to the random energy model [22]. All these systems and models can be at-least suspected of exhibiting non-ergodic behavior, and hence constructing a general theory of non-ergodicity for such systems is in our opinion a worthy goal.

Systems and models exhibiting anomalous diffusion, and CTRW behaviors can be divided into two categories. Systems where the random walk is close to thermal equilibrium, where the temperature of the system is well defined at least from an experimental point of view, and non-thermal systems. The ergodicity breaking of thermal CTRW models, is in conflict with Boltzmann–Gibbs ergodic assumption. As far as we know, there is no theory characterizing the non-ergodic properties of the CTRW for either thermal or non-thermal type of random walk.

Hence one goal of this manuscript is to obtain the non-ergodic properties of the well known CTRW model on a lattice. Secondly we investigate ergodicity breaking and its relation to Boltzmann–Gibbs statistics. Using rather general arguments and using a CTRW model we investigate the distribution of the total occupation times of a lattice point or a state of the system. We show that
in the limit of long measurement time and in the ergodic phase the occupation times are obtained using the Boltzmann–Gibbs canonical ensemble, provided that detailed balance conditions are satisfied. In the non-ergodic phase we obtain non-trivial distribution of the occupation times, which are related to the arcsin law. These limiting distributions are unique in the sense that they do not depend on all the dynamical details of the underlying model. Further the distributions we obtain depend on Boltzmann’s probability namely on the temperature $T$ and the partition function $Z$. Thus a connection is established between non-ergodic dynamics and the basic tool of statistical mechanics.

The study of occupation times in the context of classical Brownian motion was considered by P. Lévy. Consider a Brownian path generated with $\dot{x}(t) = \eta(t)$, where $\eta(t)$ is Gaussian white noise, in the time interval $(0, t)$, and with free boundary conditions. The total time $t_+$, the particle spend on the half space $x > 0$ is called the occupation time of the positive half space. The fraction of occupation time $p^+ = t_+ / t$ is distributed according to the celebrated arcsin law \[ f(p^+) = \frac{1}{\pi \sqrt{p^+ (1 - p^+)}}, \]
where $0 \leq p^+ \leq 1$. In contrast to naive expectation, it is unlikely to find $p^+ = 1/2$, which would mean that the particle remains half of the time in $x > 0$. Instead $f(p^+)$ diverges on $p^+ = 0$ and $p^- = 1$, indicating that the Brownian particle tends to stay either in $x > 0$ or in $x < 0$ for long times of the order of the measurement time $t$. Hence $f(p^+)$ has a $U$ shape. Such a behavior is related to the survival probability of the Brownian particle. The probability of a Brownian particle, starting at $x > 0$ to remain in $x > 0$ without crossing $x = 0$, decays like a power law $t^{-1/2}$. The average time the particle remains in $x > 0$, before the first crossing of $x = 0$, is infinite. Similar $U$ shape distributions, in far less trivial examples, are investigated more recently in the context of random walks in random environments \cite{22}, renewal processes \cite{26}, stochastic processes \cite{27}, zero temperature Glauber spin dynamics \cite{28}, diffusion equation \cite{31}, two dimensional Ising model \cite{30}, and growing interface \cite{29}.

The study of non-ergodicity within the CTRW framework is timely due to recent single molecule \cite{32} type of experiments. In many experiments anomalous diffusion, and power law behavior was observed using single particle tracking techniques \cite{3, 21, 33, 34, 35} (e.g. single quantum dots \cite{4}). An interesting example is the diffusive motion of magnetic beads in an actin network \cite{21}. The latter exhibit a CTRW type of behavior while the system has a well defined temperature $T$, namely the random walk seems close to thermal equilibrium and the particle is coupled to a thermal heat bath. In particular, long tailed $t^{-(1+\alpha)}$ waiting time distributions were recorded and anomalous sub-diffusion $(\langle x^2 \rangle \sim t^{\alpha})$ with $\alpha < 1$, was observed. While clearly ensemble average classification of the anomalous process, e.g. the mean square displacement, are important, it is the time averages of single particle trajectories which distinguish the single particle measurement from standard ensemble average type of measurement. And stochastic theories of non-ergodicity can help with the fundamental question in single molecule experiments: are time averages recorded in such experiment identical to the corresponding ensemble averages? and if not how do we classify the non-ergodic phase?

This paper is organized as follows. In Sec. \textbf{III} we discuss a possible generalization of Boltzmann–Gibbs statistics for non-ergodic dynamics. In Sec. \textbf{IV} we introduce the CTRW model, which yields the non-ergodic dynamics. Sec. \textbf{V} is the main technical part of the paper, in which we obtain first passage time properties of the CTRW. The relation of these properties to the non-ergodic behavior is shown. In Sec. \textbf{VI} we give the main results and compare between the non-ergodic framework and standard Boltzmann–Gibbs statistics. A brief summary of our results was published recently \cite{22}.

\section{II. FROM BOLTZMANN STATISTICS TO NON-ERGODICITY}

In this section we discuss a possible non-ergodic generalization of Boltzmann–Gibbs theory, without attempting to prove its validity.

The basic tool in statistical mechanics is Boltzmann’s probability $P^B_x$ of finding a system in a state with energy $E_x$,
\begin{equation}
P^B_x = \frac{\exp(-E_x/T)}{Z},
\end{equation}
where $T$ is the temperature and $Z = \sum_x \exp(-E_x/T)$. In Eq. (2) we use the canonical ensemble and assume a classical system, with discrete energy states $\{0 \leq E_1 \leq E_2 \cdots \}$. To obtain the average energy of the system, we use
\begin{equation}
\langle E \rangle = \sum_x E_x P^B_x,
\end{equation}
and similarly for other physical observables like entropy, free energy etc. Eq. (6) is an ensemble average. When measurement of a single system is made, a time average of a physical observable is recorded. Consider a system randomly changing between its energy states $\{E_x\}$. At a given time the system occupies one energy state. Let $t_x$ be the total time spent by the system in energy state $E_x$, within the total observation period $(0, t)$. The system may visit state $E_x$ many times during the evolution, hence $t_x$ is composed in principle from many sojourn times. We define the occupation fraction
\begin{equation}
\tau_x = \frac{t_x}{t}, \quad \text{and the time average energy is} \quad \bar{E} = \sum_x E_x \tau_x.
\end{equation}
According to statistical mechanics, once the ergodic hypothesis is satisfied, and within the canonical formalism
The probability density function (PDF) of \( \mathbf{p}_x \) is

\[
\mathbb{E} = \langle E \rangle,
\]

and similarly for other physical observables. More generally, the occupation fraction \( \mathbf{p}_x \) is a random variable, whose statistical properties depend on the underlying dynamics. If Boltzmann’s conditions hold the probability density function (PDF) of \( \mathbf{p}_x \) is

\[
f(\mathbf{p}_x) = \delta(\mathbf{p}_x - \mathbf{p}_x^B)
\]

in the thermodynamic limit. The last Eq. is a restatement of the ergodic hypothesis.

In this manuscript we discuss a possible generalization of the ergodic hypothesis. Our proposal is that the PDF of \( \mathbf{p}_x \), for certain models described by CTRW type of dynamics, is described by a \( \delta \) function

\[
f(\mathbf{p}_x) = \delta_\alpha(\mathbf{R}_x, \mathbf{p}_x) = \frac{\sin \alpha \pi}{\mathbf{R}_x^{\alpha} + 1 - \mathbf{p}_x \alpha^{\alpha}}
\]

This PDF was obtained by Lamperti [36] in the context of the mathematical theory of occupation times (and see Appendix A for details). For \( \mathbf{R}_x = 1, \alpha = 1/2 \) we have the arc-sin law. Here we claim that when local detailed balance condition is satisfied

\[
\mathbf{R}_x = \frac{\mathbf{p}_x^B}{1 - \mathbf{p}_x^B},
\]

and \( 0 < \alpha < 1 \). When \( \alpha = 1 \) we get usual ergodic behavior defined in Eq. [4]. Eq. [5] is valid only in the limit of long measurement time. In the non-ergodic phase \( \alpha < 1 \) Eqs. [6,7] establish a relation between the ergodicity breaking and Boltzmann–Gibbs statistics. The exponent \( \alpha \) is the anomalous diffusion exponent in the relation \( \langle x^\alpha \rangle \propto t^\alpha \).

For CTRWs not satisfying detailed balance condition a more general rule holds. We will show that the PDF of the fraction of time spent on lattice point \( x \), \( \mathbf{p}_x \), is still given by Eq. [4]. However now

\[
\mathbf{R}_x = \frac{P_x^{eq}}{1 - P_x^{eq}},
\]

where \( P_x^{eq} \) is the probability that a particle occupies lattice point \( x \) in equilibrium (an equilibrium is obtained for system of finite size). Here \( P_x^{eq} \) and \( P_x^B \) are probabilities in ensemble sense, namely if we consider an ensemble of \( N \) non interacting particles (or systems) satisfying some dynamical rule, \( P_x^{eq} \) and \( P_x^B \) yield in principle the probability that a member of the ensemble occupies state \( x \) in equilibrium, which is not identical to \( \mathbf{p}_x \) for non-ergodic systems.

Let us give some general arguments for the validity of Eqs. [6,7]. Consider a particular energy state of the system and call it \( E_x \). At a given time the system is either in energy state \( E_x \) or is in any of the other energy states. When the system does not occupy state \( x \) we will say that the system is in state \( nx \) (not \( x \)). Assume that sojourn times in states \( x \) and \( nx \) are not correlated. Thus we imagine the system occupying state \( x \) then occupying state \( nx \), then again state \( x \) etc. The amplitudes \( A_x \) and \( A_{nx} \) will generally depend on the particular dynamics of the system. We show in Appendix A that Eq. [10] holds with \( \mathbf{R}_x = A_x/A_{nx} \). Generally it seems a hopeless mission to calculate the ratio \( A_x/A_{nx} \) from any microscopical model. However a simple physical argument yields the ratio \( \mathbf{R}_x \). Assume that for an ensemble of systems Boltzmann–Gibbs statistical mechanics holds. Such an assumption means that on average we must have

\[
\langle \mathbf{p}_x \rangle = \mathbf{p}_x^B,
\]

where \( \mathbf{p}_x^B \) is Boltzmann’s probability of finding a member of an ensemble of systems in state \( x \). On the other hand, Eq. [10] yields

\[
\langle \mathbf{p}_x \rangle = \int_0^1 \mathbf{p}_x f(\mathbf{p}_x) d\mathbf{p}_x = \frac{\mathbf{R}_x}{1 + \mathbf{R}_x}.
\]

Using Eq. [10,11] we obtain Eq. [12].

Our work, is related to the concept of weak ergodicity breaking, suggested by Bouchaud [1]. In standard statistical mechanics, one divides the phase space of the system, into equally sized cells, and the system is supposed to visit these cells, with equal probability under certain constrains (e.g. the energy of the system is constant for the micro-canonical ensemble). Strong ergodicity breaking means that in order to leave one phase space cell to another, one has to cross a barrier (e.g. an energy barrier) which becomes infinite, in the thermodynamic limit. In this case the time it takes for the system to move from one state to the other is infinite. It is worth while thinking of such a process, in terms of a distribution of escape times, \( \psi(\tau) = \Gamma \exp(-\Gamma \tau) \), where \( \Gamma t \) is small and \( t \) is the measurement time (e.g. an activation over a very high energy barrier). In that case the particle/system simply remains in a certain domain of phase space, for the whole period of observation, and the system does not explore its entire phase space available for ergodic systems. A very different scenario was suggested by Bouchaud, in the context of glassy dynamics and the trap model. If the distribution of sticking times, follows power law behavior, the average escape time diverges

\[
\langle \tau \rangle \propto \int_0^\infty \tau \tau^{-1-a} d\tau = \infty
\]

when \( a < 1 \). Note that also for the strong non-ergodicity case we may have an infinite waiting time \( \langle \tau \rangle = 1/\Gamma \) when \( \Gamma \to 0 \). However for power law waiting times the system or particle may still explore its phase space.
Or in other words, exponential waiting times and power law waiting times, yield very different type of dynamics, even if for both the average waiting time is infinite. Thus, roughly speaking, for weak non-ergodicity and for ensemble of particles we may still get Boltzmann–Gibbs statistics, since from any initial condition the phase space is totally covered. However the system remains weakly non-ergodic, since during its evolution, the system will randomly pick one state, which it will occupy for a very long period (but it still visits all the other states) and then time averages are not equal to ensemble averages. The goal of this manuscript is to show that the strong assumptions we used are correct within a specific model, the well known CTRW model.

III. CTRW IN FORCE FIELD

We consider a one dimensional CTRW walk on a lattice. The lattice points are labeled with index \( x \) and \( x = -L, -L + 1, ..., 0, ..., L \), hence the system size is \( 2L + 1 \). On each lattice point we define a probability \( 0 < Q_R(x) < 1 \) for jumping right, and a probability for jumping left \( Q_L(x) = 1 - Q_R(x) \). Let \( \psi(\tau) \) be the PDF of waiting times at the sites, this PDF does not depend on the position of the particle. If the particle starts at site \( x = 0 \), it will wait there for a period \( \tau_1 \) determined from \( \psi(\tau) \), it will then jump with probability \( Q_L(0) \) to the left, and with probability \( Q_R(0) \) to the right. After the jump, say to lattice point 1, the particle will pause for a period \( \tau_2 \), whose statistical properties are determined by \( \psi(\tau) \). It will then jump either back to point 0 or to \( x = 2 \), according to the probability law \( Q_R(1) \). Then the process is renewed. We consider reflecting boundary conditions, namely \( Q_L(L) = Q_R(-L) = 1 \).

The case of a long tailed waiting time distribution, where \( \psi(\tau) \propto \tau^{-(1+\alpha)} \) when \( \tau \to \infty \) and \( 0 < \alpha < 1 \) yields a non-ergodic behavior. In this case the average waiting time is infinite. The Laplace transform of \( \psi(\tau) \) is

\[
\hat{\psi}(u) = \int_0^\infty e^{-u\tau} \psi(\tau) d\tau.
\]

As-usual according to Tauberian theorem [24], the small \( u \) behavior is

\[
\hat{\psi}(u) \sim 1 - Au^\alpha + \cdots
\]

and \( A > 0 \) is a constant.

Choose a specific lattice point \( x \), then define \( \theta_x(t) = 1 \) if the particle is on \( x \), otherwise it is zero. We define the occupation fraction as the time average of \( \theta_x(t) \),

\[
\overline{\theta}_x = \frac{\int_0^t \theta_x(t') dt'}{t},
\]

namely \( \overline{\theta}_x = t_x/t \) where \( t_x \) is the total time spent on lattice point \( x \) (i.e., the occupation time of site \( x \)). We will later calculate the PDF of \( \overline{\theta}_x \).

Two special cases are the unbiased CTRW, where \( Q_L(x) = Q_R(x) = 1/2 \), and the biased CTRW with \( Q_L(x) = q \). In these cases all transition probabilities do not depend on the position of the random walker \( x \), besides on the boundaries of course. In the language of random walks these cases describe symmetric diffusion process, and diffusion with a drift. Note that in our model \( Q_L(x) \) are not random variables, rather they are included in the model to mimic a deterministic potential field acting on the system. For detailed discussion of CTRW models see [2].

The case of diffusion with a constant drift, i.e., \( q \neq 1/2 \) is used many times to model diffusion under the influence of a constant external driving force \( F \). If the Physical process is close to thermal equilibrium the condition of detailed balance is imposed on the dynamics, in order that for an ensemble of particles Boltzmann equilibrium is reached [see further discussion after Eq. (18)]. The potential energy at each point \( x \), due to the interaction with the external driving force is \( E(x) = -F ax \) and \( a \) is the lattice spacing. The condition of detailed balance then reads

\[
\frac{Q_L(x)}{Q_R(x)} = \exp \left(-\frac{Fa}{T}\right)
\]

where \( T \) is the temperature, and the right hand side of Eq. (16) is independent of lattice coordinate. Since \( Q_L(x) = q \) is independent of \( x \) we have

\[
q = \frac{1}{1 + \exp(Fa/T)}.
\]

More generally we define an energy profile for the system \( \{E_{-L}, E_{-L+1}, ..., E_1, \cdots\} \). The general detailed balance condition is then

\[
\frac{Q_L(x)}{1 - Q_L(x - 1)} = \exp \left(-\frac{E_{x-1} - E_x}{T}\right)
\]

The choice of detailed balance condition means that for an ensemble of particles standard Boltzmann-Gibbs statistics holds. Thus for example if we observe many independent particles, and look at their density profile in equilibrium, we will see a profile which is determined by Boltzmann equilibrium. On the other hand if we consider a trajectory of a single particle, and from it find \( \overline{\theta}_x \), we are not likely to find the value of \( \overline{\theta}_x \) close to Boltzmann’s probability, when \( \alpha < 1 \). Thus ergodicity breaking is found on the level of a single particle. Note that there is an interesting transition between one particle information and many particle behavior, however this is not the subject of our work [31].

IV. FIRST PASSAGE TIMES

The problem of ergodicity breaking is related in this section to the problem of first passage times.
The process $\theta_2(t)$ is a two state process, with state $x$ denoting particle on lattice point $x$ and state $nx$ indicating that the particle is not on $x$. Obviously the waiting times in state $x$ are given by $\psi_x(\tau) = \psi(\tau)$. To obtain the PDF of waiting times in state $nx$, $\psi_{nx}(\tau)$ we must calculate statistical properties of first passage times. After the particle leaves point $x$ it is located either on $x + 1$ or $x - 1$ with probabilities $Q_R(x)$ and $Q_L(x)$, respectively. Let $t_L$ denote the time it will take the particle to return to $x$ starting at point $x - 1$, i.e. the first passage time from $x - 1$ to $x$. Let $t_R$ be the first passage time to reach $x$ starting from $x + 1$. Let $f_R(t_R)$, $[f_L(t_L)]$ be the PDF of the first passage time $t_R$, $t_L$ respectively. Then the PDF of times in state $nx$ is given by

$$\psi_{nx}(\tau) = Q_R(x)f_R(\tau) + Q_L(x)f_L(\tau). \quad (19)$$

In principle once the long time behavior of the PDFs of first passage times is obtained, we have $\psi_{nx}(\tau)$ and $\psi_x(\tau)$, and then we may use the formalism developed in Appendix A to obtain the PDF of the occupation fraction $\tau_x$. We now investigate the first passage times PDFs for biased and unbiased CTRW, using an analytical approach. The reader not interested in mathematical details, may skip to Sec. [V].

### A. Relation Between Discrete Time and continuous time RWs

For convenience we define a new lattice. We consider the CTRW in one dimension, on lattice points $x = 0, 1, 2, \ldots, \bar{L}$. Point $x = 0$ is a “sticky” absorbing boundary, namely once the particle reaches point $x = 0$ it remains there for ever. Point $\bar{L}$ is a reflecting boundary, and initially at time $t = 0$ the particle is on $x = 1$. Let $S_{CT}(t)$ be the survival probability of the CTRW particle, and the subscript CT indicates CTRW. The object of interest is the PDF of first passage time $f_{CT}(t)$, which is minus the time derivative of $S_{CT}(t)$. The solution is possible due to an important relation between the CTRW first passage time problem and that of discrete time random walks. In the first passage time problem with CTRW dynamics with exponential waiting times was considered.

Point 0 of the new lattice is point $x$ in the original problem and $\bar{L} = \bar{L} - x$ and similarly for the other $\bar{L} - 1$ points of the new lattice. Hence the calculation of the first passage PDF on the new lattice $x = 0, 1, 2, \ldots, \bar{L}$ yields $f_R(t_L)$. With straight forward change of notation we may consider also $f_L(t_L)$.

Let $S_{CT}(t)$ be the survival probability of the CTRW particle in the interval $x = 1, \ldots, x = \bar{L}$. Let $S_{dis}(N)$ be the probability of survival after $N$ jumps events, for a particle starting at $x = 1$, the subscript dis stands for discrete. Then

$$S_{CT}(t) = \sum_{N=0}^{\infty} S_{dis}(N)P(N,t) \quad (20)$$

where $P(N,t)$ is the probability for $N$ steps, in time $t$, in a CTRW process. In Laplace, $t \rightarrow u$ space it is easy to show using the convolution theorem of Laplace transform that

$$\hat{P}(N,u) = \frac{1 - \hat{\psi}(u)}{u} \hat{\psi}(u)^N \quad (21)$$

where $\hat{\psi}(u)$ is the Laplace transform of $\psi(\tau)$. In this work the discrete Laplace transform of an arbitrary function $G(N)$, also called the $z$ transform is defined as

$$\hat{G}(z) = \sum_{N=0}^{\infty} z^N G(N) \quad (22)$$

Using Eqs. (20),(21) we find

$$\hat{S}_{CT}(u) = \frac{1 - \hat{\psi}(u)}{u} \hat{S}_{dis} \left[ \hat{\psi}(u) \right]. \quad (23)$$

This equation establishes the relation between the discrete and continuous time problems.

Let $P_x(N)$ be the probability of occupying site $x$ after $N$ jumps and $P_x(0) = \delta_{x,1}$. The Master equation describing the discrete time problem is given by

$$P_0(N + 1) = Q_L(1)P_1(N) + P_0(N)$$

since the origin 0 is absorbing

$$P_1(N + 1) = Q_L(2)P_2(N)$$
$$P_2(N + 1) = Q_R(1)P_1(N) + Q_L(3)P_3(N)$$
$$P_x(N + 1) = Q_R(x - 1)P_{x-1}(N) + Q_L(x + 1)P_{x+1}(N)$$
$$P_{L-1}(N + 1) = P_L(N) + Q_R(L - 2)P_{L-2}(N)$$
$$P_L(N + 1) = Q_R(L - 1)P_{L-1}(N). \quad (24)$$

The probability to be absorbed for the first time at $x = 0$ after $N + 1$ jumps (the discrete time) is

$$F_{dis}(N + 1) = Q_L(1)P_1(N). \quad (25)$$

The discrete survival probability is given by

$$S_{dis}(N) = 1 - P_0(N). \quad (26)$$

Using Eq. (24)

$$S_{dis}(N) = 1 - \left[ Q_L(1)P_1(N - 1) + P_0(N - 1) \right], \quad (27)$$

and from Eq. (25)

$$S_{dis}(N) = 1 - \left[ F_{dis}(N) + P_0(N - 1) \right]. \quad (28)$$

Using Eq. (25) we have

$$S_{dis}(N) - S_{dis}(N - 1) = -F_{dis}(N), \quad (29)$$
which simply means that the change in the survival probability at step \(N\) is equal to minus the probability of first passage. Using the \(z\) transform Eq. (22) of Eq. (24) we find
\[
\hat{S}_{\text{dis}}(z) = \frac{1 - \hat{F}_{\text{dis}}(z)}{1 - z}.
\]
Hence from Eq. (22)
\[
\hat{S}_{\text{CT}}(u) = \frac{1}{u} \left\{ 1 - \hat{F}_{\text{dis}} \left[ \tilde{\psi}(u) \right] \right\}.
\]
Let \(f_{\text{CT}}(t)\) be the first passage time PDF of the CTRW problem. As-usual
\[
f_{\text{CT}}(t) = -\frac{d}{dt}S_{\text{CT}}(t).
\]
which is the continuous pair of Eq. (29). If the random walker always returns to the origin, then \(\int_0^\infty f_{\text{CT}}(t)dt = 1\), and Eq. (32) yields
\[
\hat{f}_{\text{CT}}(u) = -u\hat{S}_{\text{CT}}(u) + 1
\]
and using Eq. (31)
\[
\hat{f}_{\text{CT}}(u) = \hat{F}_{\text{dis}} \left[ \tilde{\psi}(u) \right].
\]
This is the most important equation of this sub-section. At-least in some cases the solution of the discrete time first passage time problem, in \(z\) space is possible, and then we can transform the solution to Laplace \(u\) space of the seemingly more difficult case of continuous time. Note that our assumption that the random walk is recurrent is valid only when the system size is finite, and \(Q_L(x) > 0\) for any \(x\) besides on the boundary.

**B. First Passage Time for Unbiased Case**

We now find the first passage time distribution for the unbiased CTRW in Laplace space. For the unbiased random walk we have \(Q_L(x) = Q_R(x) = 1/2\), for \(x \neq 0\), \(x \neq \bar{L}\). And as mentioned \(x = 0\) is the absorbing boundary condition, while \(L\) is a reflecting wall. As shown we may consider the first passage time for the discrete time random walk Eq. (24) and the transformation Eq. (32) to obtain the corresponding CTRW first passage time. Using Eq. (22) the \(z\) transform of Eq. (24) is
\[
\hat{P}_0(z) = \frac{z}{2} \hat{P}_1(z) + z \hat{P}_0(z)
\]
using the initial conditions \(P_1(0) = 1\),
\[
\hat{P}_1(z) - 1 = \frac{z}{2} \hat{P}_2(z),
\]
for \(x = 2, \ldots, L - 2\),
\[
\hat{P}_x(z) = \frac{z}{2} \left[ \hat{P}_{x-1}(z) + \hat{P}_{x+1}(z) \right],
\]
\[
\hat{P}_{L-1}(z) = \frac{z}{2} \hat{P}_L(z) + \frac{z}{2} \hat{P}_{L-2}(z)
\]
and using Eq. (26)
\[
\hat{F}_{\text{dis}}(z) = \frac{z}{2} \hat{P}_1(z).
\]
To solve these equations we use a recursive solution method. We define \(\phi_x(z)\) using the relation
\[
\hat{P}_x(z) = \phi_x(z) \hat{P}_{x-1}(z),
\]
and it is easy to show using Eqs. (35, 37)
\[
\phi_L(z) = \frac{z}{2} \quad \phi_{L-1}(z) = \frac{(z/2)(1 - z^2/2)}{1 - z \phi_x(z)/2}
\]
The function \(\phi_x(z)\) also satisfies the recursion relation
\[
\phi_{x-1}(z) = \frac{(z/2)}{1 - z \phi_x(z)/2}
\]
which is easy to obtain from Eq. (42). Let
\[
\phi_x(z) = g_x(z) \frac{h_x(z)}{h_x(z)}
\]
and using Eq. (39)
\[
\left( \begin{array}{c}
g_{x-1}(z) \\
\frac{h_{x-1}(z)}{h_x(z)}
\end{array} \right) = \left( \begin{array}{cc}
0 & \frac{z}{2}
\end{array} \right) \left( \begin{array}{cc}
g_x(z) \\
\frac{h_x(z)}{h_x(z)}
\end{array} \right)
\]
Since we are interested only in the ratio \(g_x(z)/h_x(z)\) we may set \(h_{L-1}(z) = 1\) and \(g_L(z) = z/2\) using Eq. (38). Eq. (42) gives the seeds for the iteration rule Eq. (43): \(h_{L-1}(z) = 1 - z^2/2\) and \(g_{L-1}(z) = z/2\), which yield \(h_{L-2}(z); g_{L-2}(z)\) etc. Let
\[
h_x(z) = B_+ (\Lambda_+)^{L-x} + B_- (\Lambda_-)^{L-x}
\]
and from \(h_L(z) = 1\) we have \(B_+ + B_- = 1\). \(\Lambda_\pm\) are eigen values of the matrix in Eq. (43)
\[
\Lambda_\pm = \frac{1 \pm \sqrt{1 - z^2}}{2}.
\]
Using \(h_{L-1}(z) = 1 - z^2/2\) it is easy to show
\[
B_- = \frac{1 - z^2/2 - \Lambda_+}{\Lambda_- - \Lambda_+}
\]
and \(B_+ = 1 - B_-\). Using
\[
\hat{P}_1(z) = \frac{1}{1 - z \phi_x(z)/2}
\]
and \(\phi_x(z) = z h_3(z)/2 h_2(z)\) and Eqs. (42, 42) we find
\[
\hat{P}_{\text{dis}}(z) = \frac{z/2}{1 - z^2 B_+ \Lambda_+^{L-3} + B_\Lambda_+^{L-3} - B_\Lambda_-^{L-3} + \Lambda_+^{L-2} - \Lambda_-^{L-2}}
\]
This equation is important since it yields the discrete first passage time probability with which the CTRW PDF of first passage time can be obtained. Using the Laplace transform of the waiting time PDF Eq. (41) and Eqs. (44) we obtain the small $u$ behavior
\begin{equation}
\hat{f}_{\text{CT}}(u) \sim 1 - (2\tilde{L} - 1)Au^\alpha + \cdots.
\end{equation}

To summarize Eq. (47) yields the Laplace transform of the first passage times of the unbiased CTRW with reflecting boundary condition on $\tilde{L}$, absorbing on the origin, and initial location of the particle on $x = 1$.

### C. First Passage Time for Uniform Bias

We now find the first passage time distribution for the biased CTRW in Laplace space, skipping many of the algebraic details. Now the probability to jump left is $Q_L(x) = q$ and hence the probability to jump to the right is $Q_R(x) = 1 - q$, for $x \neq 0$, $x \neq \tilde{L}$. The two boundary conditions are: $x = 0$ is absorbing, while $\tilde{L}$ is a reflecting wall. Like the unbiased case we treat the problem of the discrete time random walk and then use the transformation Eq. (53) to obtain the corresponding CTRW first passage time distribution.

In this case the $z$ transform of the master Eq. (44) is
\begin{equation}
\tilde{P}_0(z) = zq \tilde{P}_1(z) + z\tilde{P}_0(z)
\end{equation}
\begin{equation}
\tilde{P}_1(z) - 1 = zq \tilde{P}_2(z)
\end{equation}
\begin{equation}
\tilde{P}_x(z) = z(1-q) \tilde{P}_{x-1}(z) + zq \tilde{P}_{x+1}(z)
\end{equation}
\begin{equation}
\tilde{P}_{\tilde{L}-1}(z) = z\tilde{P}_{\tilde{L}}(z) + z(1-q) \tilde{P}_{\tilde{L}-2}(z)
\end{equation}
\begin{equation}
\tilde{P}_{\tilde{L}}(z) = z(1-q) \tilde{P}_{\tilde{L}-1}(z).
\end{equation}

And using Eq. (40)
\begin{equation}
\tilde{F}_{\text{dis}}(z) = zq \tilde{P}_1(z).
\end{equation}

The solution of the biased master equation follows the same procedure as for the unbiased and yields
\begin{equation}
\tilde{F}(z) = \frac{qz}{1 - q(1-q)z^2B_+\lambda_{-}^{-3} + B_-\lambda_+^{-3}},
\end{equation}
where
\begin{equation}
\lambda_{\pm}(z) = \frac{1 \pm \sqrt{1 - 4qz^2(1-q)}}{2},
\end{equation}
$B_+ + B_- = 1$, and
\begin{equation}
B_+(z) = \frac{1 - \lambda_+ - z^2(1-q)}{\lambda_+ - \lambda_-}.
\end{equation}

Using Eq. (40) one can show that $\tilde{F}_{\text{dis}}(z = 1) = 1$, for any finite $\tilde{L}$ and $q \neq 0$, namely if we wait long enough the particle always reaches the sticky boundary on $x = 0$.

We now return to the CTRW problem. We use the relation Eq. (44) and insert in Eq. (51) the small $u$ behavior of the Laplace transform of the waiting time PDF Eq. (41). In the limit of $u \to 0$ we find the Laplace transform of the PDF of the first passage time of the CTRW particle
\begin{equation}
\hat{f}_{\text{CT}}(u) \sim 1 - \frac{Au^\alpha}{2q - 1} \left[ 1 - 2(1-q) \left(\frac{1-q}{q}\right)^{\tilde{L}-1} \right] + \cdots.
\end{equation}

This is the main result of this section, since it will yield the non-ergodic properties of the biased CTRW. We see that for $q = 1$ or $L = 1$, $\hat{f}_{\text{CT}}(u) \sim 1 - Au^\alpha$ as expected since then $\hat{f}_{\text{CT}}(u) = \psi(u)$. The second term on the right hand side of Eq. (53) will diverge when $q < 1/2$ and $L \to \infty$, as expected for an infinite system, and for a random walker moving against the average drift. We see from Eq. (53), that the PDF of first passage times $f_{\text{CT}}(t) \propto t^{-(1+\alpha)}$, in the limit of long times, when $\alpha < 1$. In the limit $q \to 1/2$ the solution for the biased case Eq. (55), reduces to the unbiased solution Eq. (41).
V. MAIN RESULTS

A. Non- Thermal random walks

First consider the unbiased one dimensional CTRW on a lattice \( x = -L, \ldots, L \). The PDF of the fraction of occupation time \( \overline{\psi}_x = \overline{t}_x/t \) on a lattice point \( x \), excluding the boundary points, is obtained using Eqs. (19, 44). The general idea of the proof is to note that \( \psi_x = u \) for \( u \to 0 \) and hence using Appendix A we find

\[
\psi_{nx}(u) \sim 1 - A (2L - 1) u^\alpha
\]

for \( u \to 0 \) and hence using Appendix A we find

\[
\lim_{t \to \infty} f(\overline{\psi}_x) = \delta_u \left( \frac{(2L - 1)^{-1}}{\overline{\psi}_x} \right).
\]

Where the \( \delta_u \) function was defined in Eq. (54). Eq. (55) does not depend on the position \( x \) of the observation point, reflecting the symmetry of the problem. From Eq. (55) we see that the amplitude ratio satisfies \( \mathcal{R}_x = 1/(2L - 1) < 1 \) when \( L > 1 \). This inequality means that we are less likely to find the particle on the particular lattice point \( x \) under observation (state \( x \)), if compared with the probability of finding the particle on any of the other lattice points (state \( nx \)).

\[
\mathcal{R}_x = \left\{ \frac{2}{2q - 1} \left[ q^2 \left( \frac{q}{1 - q} \right)^{L+x-1} - (1 - q)^2 \left( \frac{1 - q}{q} \right)^{L-x-1} \right] - 1 \right\}^{-1}.
\]

The latter Eqs. (58, 59) and the results obtained in Appendix A indicate that the PDF of fraction of occupation time is

\[
f(\overline{\psi}_x) = \delta_u \left( \mathcal{R}_x, \overline{\psi}_x \right)
\]

with \( \mathcal{R}_x \) given in Eq. (59).

As expected the PDF of the fraction of occupation time, for the biased CTRW, depends on the location of the site under consideration. As-usual if \( q < 1/2 \) the particle prefers to stick to the right wall. In our case this behavior implies that if \( q < 1/2 \) and \( x \approx -L \) (\( L \) is large) then \( \mathcal{R}_x \to 0 \), which means that the lattice point \( x \) is never occupied, as expected.

B. Equilibrium–Ergodicity Breaking Relationship

Eqs. (58, 59) describe the non-ergodic properties of the CTRW for biased and unbiased cases. We will now consider a relation of the problem of non-ergodicity with the equilibrium of the process. Consider an ensemble of independent random walkers performing the CTRW process, in the finite domain. After a long period of time an equilibrium will be reached, for which the density of particles is found in a steady state profile. Such an equilibrium is obtained after each individual member of the ensemble made many jump events (one can easily prove that such an equilibrium is reached). We denote the probability of finding such a random walker on point \( x \) with \( P^e_x \). It is straightforward to obtain \( P^e_x \), though some care must be made when we take into consideration the boundary conditions of the problem. In equilibrium

\[
P^e_x = \frac{(1-q)^x}{Z}
\]

and on the boundaries

\[
P^e_{L} = \frac{(1-q)(1-q)^{L-1}}{Z}
\]
\[ P_{eq}^{x} = \frac{q (1-q)}{Z} \]  \quad (62)

And \( Z \) is then obtained from \( \sum_{x=-L}^{L} P_{eq}^{x} = 1 \). Here \( Z \) is a normalization constant of the problem, not necessarily related to Boltzmann–Gibbs statistics.

Using the equilibrium properties of the system, after a short calculation of the normalization constant and some algebra, we find that Eqs. \((58\) [59] [60]) may be written in a more elegant form

\[ f(\bar{p}_x) = \delta_\alpha \left( \frac{P_{eq}^{x}}{1 - P_{eq}^{x} \overline{p}_x} \right) . \]  \quad (63)

Note that \( P_{eq}^{x} \) yields the equilibrium properties of many non-interacting random walkers, or the density profile of large number of particles. Hence the single particle non-ergodicity is related to statistical properties of the equilibrium of many particles. The fact that we find such a relation should be anticipated, since if we average the harmonic potential field, and hence \( f(x) \) must be clearly related to \( P_{eq}^{x} \). And the requirement \( \bar{p}_x = P_{eq}^{x} \) implies that \( \mathcal{R}_x = P_{eq}^{x} / (1 - P_{eq}^{x}) \) as we indeed found (and similar to our discussion in Sec. 11). For the unbiased case, \( q = 1/2 \) we have \( P_{eq}^{x} = 1/2L \), which leads to 55. Note that the equilibrium population on the boundaries \( x = \pm L \) is half the value of that found on \( x \neq \pm L \), and hence \( Z = 2L \) even though we have \( 2L + 1 \) lattice points.

A possible extension of our result: we believe that if we consider the occupation times on \( M < 2L + 1 \) lattice points, Eq. 56 is still valid and \( P_x^B = M/(2L) \) when \( L \) is large. A proof of 56 based on the calculation of the first passage time for such a case is cumbersome, if we consider a general configuration of \( M \) lattice points under observations, however we did verify this result numerically.

C. Thermal Random Walks

If the CTRW particle is interacting with a thermal heat bath, we can relate the non-ergodicity to Boltzmann–Gibbs statistics. For the free particle we recall that Boltzmann probability of occupying a lattice point is simply

\[ P_x^B = \frac{1}{Z} \]  \quad (64)

and as mentioned \( Z = 2L \) is the normalization condition, or the partition function of the problem. Hence rewriting Eq. 63

\[ f(\bar{p}_x) = \delta_\alpha \left( \frac{P_x^B}{1 - P_x^B \overline{p}_x} \right) . \]  \quad (65)

The factor \( P_x^B / (1 - P_x^B) \) means that with probability \( P_x^B \) the particle is in state \( x \), and with probability \( 1 - P_x^B \) the particle is in state \( n \) i.e., the rest of the system (here we mean probability in the ensemble sense).

For biased CTRW when detailed balance condition Eq. 14 holds, we find once again

\[ f(\bar{p}_x) = \delta_\alpha \left( \frac{P_x^B}{1 - P_x^B \overline{p}_x} \right) . \]  \quad (66)

and now

\[ P_x^B = \frac{\exp \left( \frac{-V(x)}{T} \right)}{Z}, \]  \quad (67)
where $x$ is the lattice site under observation, $V(x) = -Fax$ is the potential field, and $a$ is the lattice spacing. Here the partition function is

$$Z = 2 \left[ q^2 \left( \frac{1-a}{q} \right)^{-L+1} - (1-q) \left( \frac{1-a}{q} \right)^{-L+1} \right] \frac{2q-1}{2q-1}.$$ (68)

which is easily verified once proper reflecting boundary conditions are applied, and using Eq. (17).

### D. Numerical Demonstration

In previous sections we considered the cases of biased and unbiased CTRWs. We see however that our results may be more general, and valid also for random walks in a general deterministic external field. We decided to check this issue using the example of a random walk in an Harmonic trap. For that aim we used numerical simulations, since calculations of the first passage time are cumbersome. The problem of anomalous diffusion in Harmonic potential was considered in the context of fractional Fokker–Planck equations [40] and in single particle experiments [34]. Anomalous diffusion in harmonic field was also investigated using fractional Langevin equations [41, 42]. It would be interesting to test if such stochastic equations yield an ergodic behavior.

The potential field we choose is $V(x) = Kx^2$, and $K = 1$. We used: (i) the condition of detailed balance Eq. (18), and (ii) at bottom of the well, point $x = 0$, we used the symmetry of the potential and choose $Q_L(0) = Q_R(0) = 1/2$. These two conditions yield $Q_L(x)$. In simulations we generate random waiting times, according to the normalized power law waiting time PDF $\psi(\tau) = \alpha\tau^{-(1+\alpha)}$, for $\tau > 1$.

We first checked that Boltzmann equilibrium is reached for an ensemble of particles. In these simulations we build histograms of the position of $N = 10^8$ particles, after each particle evolves for a time $t = 10^6$. In Fig. 4 we find good agreement between our simulations and Boltzmann statistics when many particles are considered. The Fig. illustrates that an observer of a large number of particles cannot detect ergodicity breaking, and the single particle limit is essential for our discussion.

We then consider one trajectory at a time. We obtain from the simulations, the total time spent by the particle on lattice point $x = 0$, namely at the minimum of the potential. This time is $t_x$ and the fraction of occupation time $\bar{p}_x = t_x/t$. In the ergodic phase and long time limit $\bar{p}_x$ will approach the value predicted by Boltzmann statistics. While in the non-ergodic phase we test if our prediction Eq. (14) hold. In Figs. 2–4 we consider three values of $\alpha$, $\alpha = 0.3, 0.5, 0.8$ and fix the temperature $T$. All figures show an excellent agreement between our theoretical predictions Eqs. (6,7) and numerical simulations. It is more important however to understand the meaning of the figures.

For small $0 < \alpha < 1$ we expect that the particle will get stuck on one lattice point during a very long period, which is of the order of the measurement time $t$. This trapping point, can be either the point of observation (e.g., $x = 0$ in our simulations) or some other lattice point. In these cases we expect to find $\bar{p}_x \simeq 1$ or $\bar{p}_x \simeq 0$ respectively. Hence the PDF of $\bar{p}_x$ has a $U$ shape. This case exhibits large deviations from ergodic behavior, in the sense that we have a very small probability for finding the occupation fraction close to the value predicted based on Boltzmann’s ergodic theory. As shown in Figs. 2–4 such $U$ shape behavior is found for the cases $\alpha = 0.3$ and $\alpha = 0.5$. We also plotted the prediction made using
the ergodic assumption (the arrows in the Figures) to demonstrate the fact that a measurement is not likely to yield the average which is located on $P^B_x$.

When we increase $\alpha$ we anticipate a more ergodic behavior, in particular in the limit $\alpha \to 1$. An ergodic behavior means that the PDF of the occupation fraction $\overline{p}_x$ is centered on the Boltzmann’s probability. In Fig. 4 where $\alpha = 0.8$ we start seeing a peak in the PDF of $\overline{p}_x$ centered in the vicinity of the ensemble average value. Note however that the PDF $f(\overline{p}_x)$ still attains its maxima on $\overline{p}_x = 0$ and $\overline{p}_x = 1$. Hence we find a weaker non-ergodic behavior if compared with the cases $\alpha = 0.3, 0.5$, and a $W$ shape of the PDF.

In Fig. 4 we consider the example of a particle in an Harmonic field, we fix $\alpha = 0.8$ and vary temperature, using Eqs. (6,7). The observation point remains $x = 0$. At temperature $T \approx 1.3$ (solid line) we see that the PDF of $\overline{p}_x$ is symmetric. This happens when $P^B_x = 1/2$, namely for a case that there is probability half of occupying the observation point, and probability half to be out of this point. When the temperature is very low, we expect to find the particle, in the ground state, namely on $x = 0$. Hence the PDF of $\overline{p}_x$ is tilted towards $\overline{p}_x \approx 1$ when temperature is lowered (see Fig 5 when $T = 0.8$). In contrast when the temperature is high, we expect the probability of occupying the observation point $x = 0$ to be reduced (as-usual entropy wins at high temperature). And indeed we observe that when $T = 3$ the PDF of $\overline{p}_x$ is more tilted towards the left namely to $\overline{p}_x \approx 0$.

E. Validity of main Eqs. (6,7)

Our numerical work as well as our analytical solutions for the bias and non-bias CTRW show the validity of Eqs. (6,7). What happens for more general type of potential fields? Can we claim, that Eq. (6) has a wider applicability? Consider the CTRW with potential profile, \{...$E_x$...\}, with the dynamics satisfying detailed balance condition. We claim, but have no rigorous proof, that if for $\psi(\tau)$ with finite moments, the system is ergodic, then for the same energy profile but when the waiting time has a long tail, Eqs. (6,7) hold. Our reasoning is that we can think of $\alpha$ as a control parameter, which we can vary between $0 < \alpha \leq 1$. And since for the case $\alpha = 1$ we have $R_x = P^B_x/(1 - P^B_x)$ also for $0 < \alpha < 1$ this relation must hold (since $P_B$ does not depend on $\alpha$). Further the transformation $s(\tau) \to As^\alpha$ in the small $s$ behavior of the waiting time seems to indicate that the behavior we found has a general validity.

A way to understand the ergodicity breaking laws, Eqs. (6,7), is to consider the number of times $n_x$ the particle visits lattice point $x$, during a long measurement time. In that case the particle visits $x$ many times, and we assume that the fraction of number of visits satisfies

$$\frac{n_x}{n} = \exp \left[ -\frac{V(x)}{T} \right],$$  

where $n$ is the total number of jumps made by the particle. If the first moment of the waiting time distribution is finite, we have $t_x/t = n_x/n$, since the average time spent on $x$ is $n_x$ times the mean waiting time. When the average waiting time is infinite $\alpha < 1$, one can show that the PDF of $t_x/t$ is given by Eq. (6) if condition Eq. (69) holds. Eq. (69) should be tested in more detail, for example using numerical simulations.

VI. SUMMARY AND DISCUSSION

We obtained the non-ergodic properties of biased and unbiased continuous time random walks. In particular the distribution of the occupation fraction $\overline{p}_x$ was found. Our results are valid both for thermal and non-thermal cases. In both cases the non-ergodicity is described using the $\delta_x(R_x, \overline{p}_x)$ PDF Eq. (6). Where $\alpha$ is the anomalous diffusion exponent $(\alpha^2) \sim t^\alpha$. Both for thermal and non-thermal random walks the parameter $R_x$ is related to the ensemble averaged equilibrium properties of the system, Eqs. (63, 66) respectively. If the system is in vicinity of thermal equilibrium, the equilibrium of the system is the Boltzmann–Gibbs equilibrium, in the ensemble sense. Such behavior is found when detailed balance conditions are applied. In this case the characterization of the non-ergodic properties of the occupation times is related to the partition function, and temperature. The non-ergodicity manifests itself when time average of single particle observables is considered. In particular the occupation time, in a given energy state, or on a particular lattice point. Hence the non-ergodicity might reveal itself in single particle experiments.

Models and systems describing anomalous diffusion are wide spread. In most cases ensemble average properties of such processes are investigated, both in theory and in experiment. For single particle experiments, where the problem of ensemble averaging is removed, we may either: i) reconstruct the ensemble averages, by repeating the single molecule experiment many times, or ii) investigate the ergodic properties of the system, by considering fraction of occupation time in a particular state, and obtaining its distribution. It is the second type of measurement which is considered here, which yields insight into single particle properties which differ from the standard ensemble measurement, provided that a non-ergodic phase is investigated. And while the theory of anomalous diffusion processes is now vast, the non-ergodic properties of such processes are still not well understood. Investigation of this topic beyond the CTRW approach is left for future work.

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VII. APPENDIX A: THE $\delta_n (R_x, \overline{\theta}_+)$ FUNCTION

In this Appendix we re-derive the limit theorem Eq. 6. While this goal was accomplished long time ago 36, we believe that it is worth while re-deriving this result using methods similar to those used today in statistical Physics community 26. We also derive an exact distribution for the occupation fraction of a two state process in Laplace space Eq. 31 32.

Consider a system evolving between two states, + and −, corresponding to states $x$ and $nx$ respectively. Let $\theta(t)$ = 1 when the system is in state + otherwise $\theta(t)$ = 0 and the system is in state −. A schematic diagram of $\theta(t)$ is shown in Fig. 6. Let $\{t_i\}$ denote dots on the time axis on which transition events between state + to state − or vice versa is made. Let $\{\tau_i\}$ be sojourn times either in state + or state −. If the process starts with state +, then $\tau_i$ is a + state if $i$ is odd. We also denote the total number of jumps, in the measurement time interval $(0, t)$ with $n$. We assume that the sojourn times are independent identically distributed random variables. The PDF of sojourn times is $\psi_+(\tau)$ and $\psi_-(\tau)$ for states + and − respectively. Such a simple process is called a two state renewal process. As-usual it is convenient to analyze such a stochastic process using the Laplace transforms

$$\hat{\psi}_\pm(s) = \int_0^\infty e^{-st} \psi_\pm(\tau) d\tau.$$  

(70)

While we will consider general properties of the stochastic process, we will eventually focus on two main cases. First consider the case where all moments of $\psi_+(\tau)$ are finite, e.g. exponential PDFs belong to this category. Then the following small $s$ expansion holds

$$\hat{\psi}_\pm(s) \sim 1 - s\langle \tau_\pm \rangle + \cdots.$$  

(71)

Here $\langle \tau_\pm \rangle$ are the mean sojourn times in states $\pm$. A second generic case is:

$$\hat{\psi}_\pm(s) \sim 1 - s^\alpha A_\pm + \cdots.$$  

(72)

with $0 < \alpha < 1$. For example the one sided Lévy PDF $\hat{\psi}_+(s) = \exp(-A_+ s^\alpha)$ belongs to this class. In the time domain these PDFs behave like

$$\psi_\pm(t) \sim \frac{A_\pm}{\Gamma(-\alpha)} t^{1+\alpha}$$  

(73)

when $t$ is large, namely for this family of PDFs the average waiting times in both states diverges.

Let $t_+$ be the total time spent in state +, within the time period $(0, t)$. Then the occupation fraction in state + is

$$\overline{\theta}_+ = \frac{t_+}{t} = \frac{\int_0^t \theta(t') dt'}{t}.$$  

(74)

We now consider statistical properties of $t_+$ focusing on the scaling limit $t \rightarrow \infty$. Let $I_{n,t}^+_+(t_+)$ be the PDF of $t_+$ conditioned that $n$ renewal (i.e. jumps) events occurred in the time interval $(0, t)$, and that the start of the process is in state +.

Consider the case $n$ odd, $n = 2k + 1$ with $k = 0, 1, \ldots$. Then since we start with state +, $t_+ = \sum_{i=1, \text{odd}}^n \tau_i$ where the summation is only over odd $i$’s. Also we have $n < t < n+1$, where $n+1$ is a renewal event which occurs after end of measurement (see Fig. 6). Hence

$$I_{n,t}^+_+(t_+) = \langle \delta \left( t_+ - \sum_{i=1, \text{odd}}^n \tau_i \right) I(t_n \leq t \leq t_{n+1}) \rangle,$$  

(75)

where $\delta(x)$ is the Dirac delta function, and

$$I(t_n \leq t \leq t_{n+1}) = \begin{cases} 1 & \text{If condition in parenthesis is true} \\ 0 & \text{otherwise.} \end{cases}$$  

(76)

In Eq. 60 $\langle \cdots \rangle$ denotes an average over the stochastic process, soon to be specified in more detail. Later we will consider the case $n$ even, and then sum over $n$ to obtain the PDF of $t_+$.

Let $s$ be the Laplace pair of $t$, and $u$ of $t_+$. It is convenient to consider the double Laplace transform $\tilde{I}_{n,s}^+_+(u)$ of $I_{n,t}^+_+(t_+)$

$$\tilde{I}_{n,s}^+_+(u) = \int_0^\infty e^{-t_+u} \int_0^\infty e^{-st} I_{n,t}^+_+(t_+) dt_+ dt =$$

$$\langle \int_0^\infty \int_0^\infty e^{-ut_+ - st} \delta \left( t_+ - \sum_{i=1, \text{odd}}^n \tau_i \right) I(t_n \leq t \leq t_{n+1}) dt_+ dt \rangle$$

$$= \left( \frac{e^{-st_n} - e^{-st_{n+1}}}{s} - \frac{e^{-st_n} \sum_{i=1, \text{odd}}^{n-1} \tau_i}{s} \right),$$  

(77)

where we made use of Eq. 61. Now we may consider the average $\langle \cdots \rangle$, using $t_n = \sum_{i=1, \text{odd}}^n \tau_i + \sum_{i=2, \text{even}}^{n-1} \tau_i$ and similarly for $t_{n+1}$. Recalling that $\tau_i$ with odd (even)
\[ i + (-) \text{ states respectively we find after averaging over the } \{ \tau_i \} \text{s} \]

\[ \hat{f}_{n,s}^+(u) = \hat{\psi}_{n}^k(s + u) \hat{\psi}_{n}^k(s) \frac{1 - \hat{\psi}_-(s)}{s} \]

where \( n = 2k + 1 \). For even \( n \) such that \( n = 2k, k = 1, 2, \cdots \) we obtain

\[ \hat{f}_{n,s}^+(u) = \hat{\psi}_{n}^k(s + u) \hat{\psi}_{n}^k(s) \frac{1 - \hat{\psi}_+(s + u)}{s + u} \]

Note that for even \( n \) the last + interval falls on \( t \), and we must define \( \tau_n = t - t_n \) as the time difference between end of the measurement and last jump in the sequence (see Fig. \ref{fig:}). We are ready to obtain the double Laplace transform of \( f_{s,n}^+(t_n) \), i.e., the PDF of \( t_n \) when the process starts in + state,

\[ \hat{f}_s^+(u) = \sum_{k=0}^{\infty} \left[ \hat{f}_{2k,n,s}^+(u) + \hat{f}_{2k+1,n,s}^+(u) \right]. \]

Using Eqs. \ref{eq:81}, \ref{eq:82}, we obtain the exact solution to the problem in Laplace \( s, u \) space

\[ \hat{f}_s^+(u) = \left[ \frac{1 - \hat{\psi}_+(s + u)}{s + u} + \frac{1 - \hat{\psi}_-(s)}{s} \right] \frac{1}{1 - \hat{\psi}_+(s + u) \hat{\psi}_-(s)}. \]  

Eqs. \ref{eq:81}, \ref{eq:82} yield in principle the exact expression for the occupation fraction, which might be useful in determining the pre-asymptotic behavior, for example using numerical inverse Laplace transform.

For the generic case Eq. \ref{eq:72}, in the limit of \( s \to 0 \) and \( u \to 0 \) their ratio remaining arbitrary, Eqs. \ref{eq:81}, \ref{eq:82} yield

\[ \hat{f}_s^+(u) \sim \frac{\mathcal{R}(s + u)^{\alpha-1} + s^{\alpha-1}}{\mathcal{R}(s + u)^{\alpha} + s^{\alpha}} \]

with

\[ \mathcal{R} = \frac{A_+}{A_-}. \]

The amplitude ratio \( \mathcal{R} \) determines the degree of symmetry in the problem. Note that in this scaling limit the initial state of the process, i.e., process being in state + or − at initial time, is not important.

The small \((s, u)\) limit considered in Eq. \ref{eq:83} corresponds to large measurement time \( t \) and occupation time \( t_n \) limit. We invert Eq. \ref{eq:83} using a method given in \ref{eq:84}. The method states that if in the limit \( s, u \to 0 \) a double Laplace transform behaves like

\[ \hat{f}_s(u) = \frac{1}{s} g \left( \frac{s}{u} \right) \]

then the PDF of the scaled variable \( \bar{\tau} = t_n/t \) is in the long time \( t \) limit

\[ f(\bar{\tau}) = -\frac{1}{\pi Re} \lim_{\epsilon \to 0} \text{Im} \left( -\frac{1}{x + i\epsilon} \right) |_{x=\bar{\tau}}. \]

Using Eq. \ref{eq:86} we find the PDF of the fraction of occupation time \( \bar{\tau} = t_n/t \)

\[ f(\bar{\tau}) = \delta(\mathcal{R}, \bar{\tau}) = \frac{\sin \pi \alpha}{\pi} \frac{\mathcal{R} \bar{\tau}^{\alpha-1} (1 - \bar{\tau}^\alpha)^{\alpha-1}}{\mathcal{R}^2 (1 - \bar{\tau}^\alpha)^{2\alpha} + \mathcal{R}^2 \bar{\tau}^{2\alpha} + 2 \mathcal{R} (1 - \mathcal{R})^\alpha \bar{\tau}^{\alpha} \cos \pi \alpha}. \]

The PDF is normalized according to

\[ \int_0^1 f(\bar{\tau}) d\bar{\tau} = 1; \]

it is valid only in the long time \( t \) limit and is independent of it. In this sense an equilibrium is obtained. In particular when \( A_+ = A_- \) and \( \alpha = 1/2 \) we find the arcsin distribution. It is easy to show that the average

\[ \langle \bar{\tau} \rangle = \frac{\langle t_n \rangle}{t} = \frac{A_+}{A_+ + A_-}. \]

In the limit \( \alpha \to 1 \) we obtain

\[ f(\bar{\tau}) = \delta(\mathcal{R} \bar{\tau} - \langle \tau \rangle_+, \mathcal{R} \bar{\tau} + \langle \tau \rangle_-), \]

where \( \langle \tau \rangle_\pm \) are the average waiting times when the waiting time PDFs have finite moments. We identify this
behavior with an ergodic behavior, since according to Eq. (3) \( \overline{p}_+ \) is a time average of \( \theta(t) \), which is equal to the ensemble average value when moments of \( \psi_{\pm}(\tau) \) are finite.

From Eq. (5) we see that the PDF of \( \overline{p}_+ \) is not narrowly centered on the ensemble average value when \( \alpha < 1 \). Hence the case \( \alpha < 1 \) is called the non-ergodic phase. Indeed any measurement of \( \theta(t) \) will remain random even in the long time limit.

\[ \lim_{t \to \infty} f(\overline{p}_+) = 0 \quad \text{or} \quad \lim_{t \to \infty} f(\overline{p}_+) = 1. \]

1. Hence the case \( \alpha < 1 \) is called the non-ergodic phase. Indeed any measurement of \( \theta(t) \) is unlikely to yield the average, and \( f(\overline{p}_+) \to 0 \) or \( \overline{p}_+ \to 1 \). The latter behavior corresponding to systems in state – or state + during nearly all the measurement time, respectively. The reason for non-ergodic behavior is that in a measurement time interval \( (0, t) \) we expect to obtain a few sojourn times of the order of \( t \), these can be either + times or – times or both. In each measurement we make these large sojourn times will be different than those found in a second measurement. Hence the time average of \( \theta(t) \), the occupation fraction \( \overline{p}_+ \) will remain random even in the long time limit.

[1] J. P. Bouchaud, J. De Physique I 2 1705 (1992).
[2] F. Bardou, J. P. Bouchaud, A. Aspect, and C. Cohen-Tannoudji L’Evy Statistics and Laser Cooling Cambridge University Press (2002).
[3] X. Brokmann, J. P. Hermier, G. Messin, P. Desbiolles, J. P. Bouchaud, M. Dahan Phys. Rev. Lett. 90 120601 (2003).
[4] G. Margolin, E. Barkai Phys. Rev. Lett. 94 080601 (2005).
[5] E. Lutz, Phys. Rev. Lett. 93 190602 (2004)
[6] J. P. Bouchaud and A. Georges, Phys. Reports 195 127 (1990)
[7] G. Metzler and J. Klafter, Phys. Rep. 339 1 (2000).
[8] D. ben-Avraham, and S. Havlin, Diffusion and Reactions in Fractals and Disordered Systems Cambridge University Press (2000).
[9] Eric Bertin, François Bardou, cond-mat/0503150 (2005).
[10] J. Klafter, M. F. Shlesinger, and G. Zumofen Physics Today 49 33 (1996).
[11] H. Scher and E. Montroll, Phys. Rev. B 12 2455 (1975).
[12] G. Zumofen, and J. Klafter Phys. Rev. E 47 851 (1993).
[13] G. M. Zaslavsky, Physics Report 371 461 (2002).
[14] T. H. Solomon, E. R. Weeks, H. L. Swinney, Phys. Rev. Lett. 71 3475 (1993).
[15] H. Scher, G. Margolin, R. Metzler, J. Klafter, and B. Berkovitz Geophysical Research Letters 29 1061 (2002).
[16] C. Monthus, and J. P. Bouchaud, J. of Phys. A Mathematical and General 29 3847 (1996).
[17] E. Barkai, and Y. C. Cheng J. of Chemical Physics 118 6167 (2003).
[18] E. Barkai, Phys. Rev. Lett. 90 104101 (2003).
[19] P. Allergini, G. Aquino, P. Grigolini, et al Phys. Rev. E 68 056123 (2003).
[20] F. Mainardi, M. Roberto, R. Gornflo, E. Scalas Physica A 287 468 (2000).
[21] I. Y. Wong, M. L. Garbel, D. R. Reichman, E. R. Weeks, M. T. Valentine, A. R. Bausch, D. A. Weitz Phys. Rev. Lett. 92 178101 (2004).
[22] G. Bel, E. Barkai, Phys. Rev. Lett. (in press).
[23] G. Ben Arous, A. Bovier, V. Gayrard, Phys. Rev. Lett. 88 087201 (2002).
[24] W. Feller, An introduction to probability theory and its applications, Volume 2 John Wiley and Sons, New York (1971).
[25] S. N. Majumdar, and A. Comtet, Phys. Rev. Lett. 89 060601 (2002).
[26] C. Godreche, and J. M. Luck. J. of Statistical Physics 104 489 (2001).
[27] A. Dhar, and S. N. Majumdar, Phys. Rev. E 59 6413 (1999).
[28] I. Dornic, and C. Godreche, J. Phys. A 31 5413 (1998).
[29] Z. Torockzai, T. J. Newman, and S. Das Sarma, Phys. Rev. E R1115 (1999).
[30] J. M. Drouffe, and C. Godreche, J. Phys. A 31 9801 (1998).
[31] T. J. Newman, W. Loinaz, Phys. Rev. Lett. 86 2712 (2001).
[32] E. Barkai, Y. Jung and R. Silbey, Annual Review of Physical Chemistry 55 457 (2004).
[33] I. M. Tolic-Norrelykke, E. L. Munteanu, G. Thon, L. Oddeshede, K. Berg-Sorensen Phys. Rev. Lett. 93 078102 (2004).
[34] H. Yang, G. B. Lou, P. Karnchanaphanurach, T. M. Louie, I. Rech, S. Cove, L. Y. Xun, and X. Xie Science 302 5643 (2003).
[35] A. R. Bizzarri, S. Cannistraro, Phys. Rev. Lett. 94 068303 (2005).
[36] J. Lamperti, Trans. Amer. Math. Soc. 88 380 (1958).
[37] G. H. Weiss, and P. P. Calabrese, Physica A 234 443 (1996).
[38] S. Redner, A Guide to First passage Process Cambridge University Press New York (2001)
[39] I. Goldhirsh, and Y. Gefen, Phys. Rev. A 33 2583 (1986).
[40] R. Metzler, E. Barkai, and J. Klafter Phys. Rev. Lett. 82 3563 (1999).
[41] S. C. Kou, and X. S. Xie, Phys. Rev. Lett. 93 180603 (2004)
[42] R. Kopferman J. of Statistical Physics 114 291 (2004).