Stochastic Ergodicity Breaking: a Random Walk Approach.

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The continuous time random walk (CTRW) model exhibits a non-ergodic phase when the average waiting time diverges. Using an analytical approach for the non-biased and the uniformly biased CTRWs, and numerical simulations for the CTRW in a potential field, we obtain the non-ergodic properties of the random walk which show strong deviations from Boltzmann–Gibbs theory. We derive the distribution function of occupation times in a bounded region of space which, in the ergodic phase recovers the Boltzmann–Gibbs theory, while in the non-ergodic phase yields a generalized non-ergodic statistical law.

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The ergodic hypothesis is a cornerstone of statistical mechanics. It states that ensemble averages and time averages are equal in the limit of infinite measurement time. Starting with the work of Bouchaud, there is growing interest in stochastic ergodicity breaking (SEB) which finds applications in a wide range of physical systems: phenomenological models of glasses, laser cooling, blinking quantum dots, and models of atomic transport in optical lattices. SEB is found for systems, whose dynamics is characterized by power law sojourn times, with infinite average waiting times. In such systems the microscopical time scale diverges, for example the average trapping time of an atom in the theory of laser cooling. The relation between SEB and diverging sojourn times can be briefly explained, by noting that one condition to obtain ergodicity is that the measurement time is long, compared with the characteristic time scale of the problem. However this condition is never fulfilled if the microscopical time scale, i.e. the average trapping time, is infinite. It is important to note that the concept of trapping time probability density function (PDF) $\psi(t)$, with diverging first moment, is wide spread and found in many fields of physics. It was introduced into physics by Scher and Montroll in the context of continuous time random walk (CTRW) [10]. This well known model exhibits anomalous sub-diffusion $\langle r^2 \rangle \sim t^\alpha$ with $\alpha < 1$, and aging behaviors which are related to SEB.

Clearly if the CTRW is non-ergodic, Boltzmann–Gibbs statistics is not valid, in a way defined precisely later. The goal of this letter is to obtain a generalization of Boltzmann–Gibbs statistical mechanics, for CTRW models. Besides its theoretical importance this goal is timely due to recent observations on the single particle level of CTRW type of dynamics, for example anomalous diffusion of a single magnetic bead in a polymer network with a well defined temperature $T$. In single particle experiments, the many particle averaging, i.e. the problem of ensemble averaging, is removed. Hence a fundamental question is whether time averages of single particle trajectories yield information identical to ensemble averages. The large number of applications of the CTRW model, and related models like the trap model and the comb model, make us believe that constructing a general non-ergodic theory for such systems is worthy.

Before introducing the model, recall that the basic tool in statistical mechanics is Boltzmann’s probability $P_B(x)$ of finding a system in a state with energy $E(x)$, using the canonical ensemble

$$P_B(x) = \frac{\exp \left( -\frac{E(x)}{T} \right)}{Z},$$

where $T$ is the temperature and $Z = \sum_x \exp[-E(x)/T]$ is the normalizing partition function. Here for simplicity we assume a discrete energy spectrum. To obtain the ensemble average of a physical observable, for example the energy of the system, we use $\langle E \rangle = \sum_x E(x) P_B(x)$, and similarly for other physical observables like entropy, free energy etc. When measurement of a single system is made, a time average is recorded. Consider a system randomly changing between its energy states $\{E(x)\}$. Let $t_x$ be the total time spent by the system in energy state $E(x)$, within the total observation interval $(0, t)$. We define the occupation fraction

$$\overline{p}_x = \frac{t_x}{t},$$

and the time average energy is $\overline{E} = \sum_x E(x) \overline{p}_x$.

According to statistical mechanics, once the ergodic hypothesis is satisfied, and within the canonical formalism $\overline{p}_x = P_B(x)$ and then $\overline{E} = \langle E \rangle$, and similarly for other physical observables. Thus for ergodic systems the fraction of occupation time is non-random, in the thermodynamic limit of long measurement time. For non-ergodic systems the occupation fraction $\overline{p}_x$ is a random variable, even in the long time limit. Thus, an important goal of the theory of SEB is to calculate the distribution function of the random variable $\overline{p}_x$. We will show below, in the context of CTRW models, that a rather general distribution function, describes statistical properties of the fraction of occupation times in the non-ergodic phase. And that this distribution function is related to the partition function of the problem.
The lattice points are labeled with index \(x\) each lattice point we define a probability \(Q_L(x)\) and \(Q_R(0)\) 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 \(t\), which is equal to \(t = 0\) or to \(t = 2\). As the particle leaves lattice point \(x\) it is either on \(x + 1\) or on \(x - 1\). Let \(t_R(t)\) be the random time it takes the particle starting on \(x + 1\) \((x - 1)\) to return to \(x\), and \(f_R(t)\) \([f_L(t)\]) the corresponding PDF of the first passage time respectively. Then the PDF of times in state \(-\) is

\[
\psi_-(t) = Q_R(x)f_R(t) + Q_L(x)f_L(t).
\]

We will later find explicit expressions for \(\psi_-(t)\), however for the time being let us assume that in the limit of long \(t\) it behaves like

\[
\psi_-(t) \sim \frac{A_x t^{-(1+\alpha)}}{\Gamma(-\alpha)},
\]

where \(A_x > 0\) will depend on model parameters. Let \(t_x\) be the total time spent on point \(x\), within the time period \(0, t\). Then the occupation fraction is \(R_x = t_x/t = \int_0^t \theta_x(t')dt'/t\). A calculation, whose details will be given elsewhere, shows that the PDF of the occupation fraction in the limit of infinite measurement time is

\[
f(\bar{R}_x) = \delta_\alpha(R_x, \bar{R}_x),
\]

where \(\bar{R}_x = A/A_x\) and \(\delta_\alpha(R_x, \bar{R}_x) \equiv \sin \pi \alpha \frac{R_x \bar{R}_x^{\alpha-1} (1 - \bar{R}_x)^{\alpha-1}}{\pi (1 - \bar{R}_x)^{2\alpha} + \bar{R}_x^{2\alpha} + 2 R_x (1 - \bar{R}_x)^{\alpha} \bar{R}_x \cos \pi \alpha}.

This equation indicates SEB since the occupation fraction remains a random variable, even in the limit of long measurement times. The PDF Eq. (6) is normalized according to \(\int_0^1 \delta_\alpha(R_x, \bar{R}_x) d\bar{R}_x = 1\). When \(R_x = 1\), Eq. (6) was obtained by Lamperti [14] in the context of the mathematical theory of occupation times [17], and see [3] for a physical application in the context of blinking quantum dots. In particular when \(R_x = 1\) and \(\alpha = 1/2\) we find the arc sinus distribution. More generally the amplitude ratio \(R_x\) determines the degree of symmetry in the problem as we will demonstrate later.

We use a general physical argument to obtain \(R_x\). Assume that the random walker is in contact with a thermal heat bath, with temperature \(T\), and interacting with an external potential field \(E(x)\). For an ensemble of particles Boltzmann Gibbs statistics must hold. In particular the probability that a single member of an ensemble of particles, will occupy the lattice point \(x\), is given by \(P_B(x)\) Eq. (4). Eq. (6) shows that \(\bar{R}_x\) is a random variable, however when we ensemble average the occupation fraction we must obtain Boltzmann-equilibrium statistics

\[
\langle \bar{R}_x \rangle = \int_0^1 \bar{R}_x f(\bar{R}_x) d\bar{R}_x = P_B(x).
\]

On the other hand Eq. (5) yields

\[
\langle \bar{R}_x \rangle = \frac{R_x}{1 + R_x}.
\]
Hence we find
\[ \mathcal{R}_x = \frac{P_B(x)}{1 - P_B(x)} = \frac{\exp \left( - \frac{E(x)}{T} \right)}{Z'}, \quad (9) \]
where \( Z' = \sum_y \exp(-E(y)/T) \) and the sum is over all energy states excluding state \( x \). Eqs. (9) describe the relation between the non-ergodic dynamics and the partition function of the problem. Thus we established an explicit relation between SEB and the basic tool of equilibrium statistical mechanics. The remaining goal of this Letter is to prove our physical picture, based on the CTRW model.

We now consider the unbiased one dimensional CTRW on a lattice \( x = -L, \ldots, L \), with \( Q_L(x) = Q_R(x) = 1/2 \). Such a process describes sub-diffusive motion. We obtained the long time behaviors of PDFs \( f_R(t) \) and \( f_L(t) \) (details are left for longer publication), and then obtained the PDF of the fraction of occupation time \( \overline{\tau}_x \) on a lattice point \( x \), excluding the boundary points,

\[ \lim_{t \to \infty} f(\overline{\tau}_x) = \delta_\alpha \left( (2L - 1)^{-1}, \overline{\tau}_x \right). \quad (10) \]

Eq. (10) does not depend on the position \( x \) of the observation point, reflecting the symmetry of the problem.

The biased CTRW yields anomalous diffusion with a drift. For this case the probability of jumping left is \( Q_L(x) = q \), and right is \( 1 - q \) where \( q \neq 1/2 \). Unlike the unbiased case now clearly different locations along the lattice, have different distributions of the fraction of occupation time. A detailed calculation of the first passage times, shows that in the long time limit,
\[ f(\overline{\tau}_x) = \delta_\alpha [\mathcal{R}_x, \overline{\tau}_x] \quad (11) \]
with \( \mathcal{R}_x = \frac{2}{2q - 1} \left[ q^2 \left( \frac{q}{1 - q} \right)^{L+x-1} - (1-q)^2 \left( \frac{1-q}{q} \right)^{L-x-1} \right] - 1 \)^{-1}. (12)

Note that Eq. (11) is not sensitive to the short time behavior of the waiting time distribution. When \( q = 1/2 \) we recover Eq. (10).

The biased CTRW is used to model anomalous diffusion under the influence of a constant external driving force \( \mathcal{F} \), e.g. [10]. If the physical process is close to thermal equilibrium, the condition of detailed balance is imposed on the dynamics. This standard condition implies that for an ensemble of particles Boltzmann’s equilibrium is obtained. The potential energy at each point \( x \), excluding the reflecting boundaries, due to the interaction with the external driving force is \( E(x) = -\mathcal{F}ax \) and \( a \) is the lattice spacing. The condition of detailed balance then reads
\[ q = \frac{1}{1 + \exp \left( \frac{\mathcal{F}a}{T} \right)} . \quad (13) \]

Using Eqs. (12) we can rewrite the solution in an elegant form
\[ f(\overline{\tau}_x) = \delta_\alpha \left( \frac{P_B(x)}{1 - P_B(x)}, \overline{\tau}_x \right) . \quad (14) \]

where \( P_B(x) \) is the canonical Boltzmann factor Eq. (1). When the external force is zero we have \( P_B(x) = 1/Z \) and \( Z = 2L \). Eq. (14) proves that our physical arguments leading to Eq. (9) are valid, at-least for the uniformly biased and unbiased random walks. More generally, for
CTRWs far from thermal equilibrium, Eq. (13) is still valid however one must replace $P_B(x)$ with the corresponding equilibrium probability.

Eq. (13) shows that the fluctuations $\overline{p}_x$ are vast, in particular in any single measurement we are not likely to measure the averaged value $P_B(x)$ (see details below). In the limit $\alpha \to 1$ our theory reduces to the standard canonical theory, since then $f(\overline{p}_x) = \delta[\overline{p}_x - P_B(x)]$. Using Eq. (13) we can explain the meaning of the asymmetry parameter $R_x$ in Eq. (9). The numerator of $R_x$ is $P_B(x)$, namely the probability (in ensemble sense) of finding the system in state $+$ (i.e. $\theta_x(t) = 1$) while the denominator $1 - P_B(x)$ is the probability of finding the particle in state $-$ (i.e. $\theta_x(t) = 0$). This interpretation suggests to us that Eq. (13) has a more general validity, beyond the biased and non-biased CTRW.

More generally we define an energy profile for the system $\{E_{-L}, E_{-L+1}, \ldots, E_x, \ldots\}$. The well known detailed balance, relates between density of particles at equilibrium $N_{eq}(x)$ at points $x$ and say $x - 1$ according to

$$N_{eq}(x)Q_L(x) = N_{eq}(x-1)\left[1 - Q_L(x-1)\right]$$  \hspace{1cm} (15)

where $N_{eq}(x)/N_{eq}(x-1) = \exp\left(\frac{E_{x-1} - E_x}{T}\right)$ and hence we get the constrain on the transition probabilities $Q_L(x)/[1 - Q_L(x-1)] = \exp\left(-\frac{E_{x-1} - E_x}{T}\right)$. For a general energy field we postulate that, if the energy profile yields a Boltzmann–Gibbs ergodic behavior for a waiting time distribution with finite moments (e.g., exponential waiting times), then for the same energy profile and a long tailed waiting time PDF $\psi(t)$ given in Eq. (2), our central Eq. (13) is still valid. Now $P_B(x)$ depends of course on the specific energy profile under investigation.

We check numerically the generality of Eq. (13), using the example of a random walk in an harmonic potential. The problem of anomalous diffusion in harmonic field was considered in the context of fractional Fokker–Planck equations [12] and in single protein experiments [13]. As a byproduct, our work shows that fractional Fokker-Planck equations [8] can be used to describe density of many particles and not time average quantities, in this sense the fractional kinetic framework is very different than the standard Fokker-Planck equations.

The potential field we choose is $E(x) = Kx^2$, with $K = 1$, and $T = 3$. Eq. (15) and the symmetry condition $Q_L(0) = 1/2$ define the set of transition probabilities $\{Q_L(x)\}$ for the problem. In Fig. 1 we check that our simulations yield Boltzmann equilibrium in the Harmonic field for an ensemble of particles. We then consider one trajectory at a time. We obtain from the simulations, the total time $t_x$ spent by a particle on the lattice point $x = 0$, namely at the minimum of the potential, and then construct histograms of the occupation fraction $\overline{p}_x = t_x/t$.

We consider the case $\alpha = 0.3$ in Fig. 2 and show an excellent agreement between our non-ergodic theory Eq. (14) and numerical simulations. The figure exhibits a $U$ shaped PDF. To understand this behavior, note that for $\alpha << 1$ 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 $\overline{p}_x \approx 1$ or $\overline{p}_x \approx 0$, respectively. Hence the PDF of $\overline{p}_x$ has a $U$ shape. This is a strong non ergodic behavior, in the sense that we have a very small probability for finding occupation fraction close to the value predicted based on Boltzmann’s ergodic theory (the arrow).

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 (i.e. the arrows in the Figs). In Fig. 3 we set $\alpha = 0.8$ and observe 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 maximum on $\overline{p}_x = 0$ and $\overline{p}_x = 1$.

More generally, Eqs. (6, 9) yield the non-ergodic statistical mechanical theory of the CTRW model, in the sense that our theory gives the distribution of $\overline{p}_x$, while the ergodic Boltzmann–Gibbs theory states $\overline{p}_x = P_B(x)$. Our arguments leading to Eqs. (6, 9) are general, hence our theory might not be limited to CTRW models. The mathematical foundation of the theory is the limit theorem (10) related to the arcsine law. The physical input is the anomalous diffusion exponent $\alpha$. A connection between the non-ergodic dynamics and the partition function was found, which enables us to find non-trivial SEB properties of the underlying random walk, in particular the random walk in a potential field.

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