Nonergodicity Mimics Inhomogeneity in Single Particle Tracking

Ariel Lubelski, Igor M. Sokolov, and Joseph Klafter

School of Chemistry, Raymond & Beverly Sackler Faculty of Exact Sciences, Tel-Aviv University, Tel Aviv 69978, Israel
Institut für Physik, Humboldt-Universität zu Berlin, Newtonstrasse 15, D-12489 Berlin, Germany

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Most statistical theories of anomalous diffusion rely on ensemble-averaged quantities such as the mean squared displacement. Single molecule tracking measurements require, however, temporal averaging. We contrast the two approaches in the case of continuous-time random walks with a power-law distribution of waiting times \( \psi(t) \propto t^{-1-\alpha} \), with \( 0 < \alpha < 1 \), lacking the mean. We show that, contrary to what is expected, the temporal averaged mean squared displacement leads to a simple diffusive behavior with diffusion coefficients that strongly differ from one trajectory to another. This distribution of diffusion coefficients renders a system inhomogeneous: an ensemble of simple diffusers with different diffusion coefficients. Taking an ensemble average over these diffusion coefficients results in an effective diffusion coefficient \( K_{\text{eff}} \sim T^{\alpha-1} \) which depends on the length of the trajectory \( T \).

In order to distinguish between systems with normal and anomalous diffusion, one typically looks at the mean squared displacement. Single molecule tracking measurements require, however, temporal averaging. We contrast the two approaches in the case of continuous-time random walks with a power-law distribution of waiting times \( \psi(t) \propto t^{-1-\alpha} \), with \( 0 < \alpha < 1 \), lacking the mean. We show that, contrary to what is expected, the temporal averaged mean squared displacement leads to a simple diffusive behavior with diffusion coefficients that strongly differ from one trajectory to another. This distribution of diffusion coefficients renders a system inhomogeneous: an ensemble of simple diffusers with different diffusion coefficients. Taking an ensemble average over these diffusion coefficients results in an effective diffusion coefficient \( K_{\text{eff}} \sim T^{\alpha-1} \) which depends on the length of the trajectory \( T \).

Thus, although the discrimination between normal diffusion and subdiffusion according to Eqs. (1) and (3) seems simple, in practice, however, the situation is quite involved. It is not always clear what kind of averaging should be applied in the anomalous case to be compared with Eq. (1).

The problem, as we show, is grave in the cases when the subdiffusion stems from a nonstationary process as is the case in continuous-time random walks (CTRWs) [3,10] with power-law tails and in random potential models [13]. As we proceed to show, an improper averaging procedure in such cases might lead to wrong conclusions about the transport properties of the system.

We use the CTRW to describe the motion of particles. In this model, particles move randomly by performing jumps whose length follows the probability density function (PDF) \( \lambda(x) \) and the waiting times between jumps follow the PDF \( \psi(t) \) (see the inset in Fig. 1 for a two-dimensional CTRW). The jump lengths and the waiting times are assumed to be independent from each other [3,10,14]. If the jump lengths and waiting times have finite second and first moments, respectively, the motion of the particles corresponds to normal diffusion. If the second moment of jump lengths still exists but the waiting-time PDF follows asymptotically a power law \( \psi(t) \propto t^{-1-\alpha} \), with \( 0 < \alpha < 1 \) (lacking the first moment), the MSD at time \( t \) defined as the ensemble average over many realizations of the process behaves as \( \langle x^2(t) \rangle_{\text{ens}} \propto t^{\alpha} \), i.e., follows a subdiffusive pattern [3,15].

Now imagine that we track experimentally particles moving under just this type of CTRW and obtain several records of very long trajectories of motion of the particles. Examples of three such trajectories \( x(t) \) in a one-dimensional CTRW are given in Fig. 1. As is often done in experiments assuming homogeneous random processes (simple diffusion), a temporal moving average is performed over the trajectory according to Eq. (2), the implicit assumption being that the type of averaging (ensemble vs
temporal) does not matter and the temporal averaging produces smoother curves in the case when the number of realizations is small. In the language of statistical mechanics, it means that one assumes the system to be ergodic.

The results obtained for particles performing CTRW with $\psi(y) \sim y^{-3/2}$. The inhomogeneous nature of the system is obvious and is further emphasized in Fig. 4. Inset: The CTRW model on a two-dimensional lattice. The waiting times are symbolized by circles whose area is proportional to the waiting time a walker spends at a lattice point before the next jump event occurs. The jumps lengths are equidistant.

FIG. 1 (color online). Three single-particle trajectories calculated from a CTRW with an asymptotic power-law distribution $\psi(y) \sim y^{-3/2}$. The inhomogeneous nature of the system is obvious and is further emphasized in Fig. 4. Inset: The CTRW model on a two-dimensional lattice. The waiting times are symbolized by circles whose area is proportional to the waiting time a walker spends at a lattice point before the next jump event occurs. The jumps lengths are equidistant.

The results obtained for particles performing CTRW with $\alpha = 0.8$ are shown in Fig. 1. Counterintuitively, we see that $\langle x^2(t) \rangle_T$ grows linearly in time and does not show the anticipated $\langle x^2(t) \rangle_{\text{ens}} \propto t^{0.8}$ behavior. Figure 2 contrasts these two types of behaviors. In the case of temporal averaging, we can determine the diffusion coefficient $K$ for each trajectory since its temporal MSD grows linearly. As demonstrated in Figs. 2 and 3, the diffusion coefficients for different trajectories differ strongly, so that one might conclude that a variety of particles of different sorts are observed, each of them showing a different diffusive behavior: Some are hardly mobile, and some are highly diffusive. This inhomogeneous type of behavior resembles strongly experimental findings in Refs. [1,2,7,11] although the mechanism there might be different. From Fig. 2, it is clear that the behavior of the mean squared displacement in the case of CTRW with power-law waiting-time distributions lacking the mean crucially depends on the type of averaging used. Therefore, the conclusion of a regular diffusion on the basis of temporal averaging might be erroneous since the system displays ergodicity breaking typical of such CTRW models. Ergodicity breaking in CTRW and equivalent systems has been discussed in several works [16–18], but the very basic aspect of the MSD has not been dealt with. The ergodicity breaking is intimately related to the aging property of the CTRW process with power-law waiting times [17,19] meaning that the rate of performing steps decreases with time as $k(t) \sim t^{-1}$ in contrast to a constant rate in the case of waiting times possessing a mean characteristic time.

As mentioned, the mean squared displacements as obtained by moving temporal averaging for different trajectories differ (see Fig. 3), even when the averaging times are long enough. This is translated into a relatively broad distribution of the diffusion coefficients $P(K)$ for single trajectories for the case of $\alpha = 0.8$, $T = 2 \times 10^6$, and $t = 500$. The red crosses, green stars, and cyan triangles show the time-averaged MSDs of three different single trajectories. The time-averaged MSDs increase linearly with time, $\langle X^2(t) \rangle_T = 2Kt$ with different $K$ values. The trajectories have to be long enough to allow for many steps. In the time averaging simulations, a distribution of exponents $\alpha$ is obtained around $\alpha = 1$ manifesting another aspect of inhomogeneity. The magenta solid curve is a time-averaged curve with the average diffusion coefficient, and the black dashed curve is the ensemble-averaged MSD which follows $\langle X^2(t) \rangle_{\text{ens}} \sim t^{0.8}$.

FIG. 2 (color online). Time-averaged and ensemble-averaged MSDs for $\alpha = 0.8$, $T = 2 \times 10^6$, and $t = 500$. The red crosses, green stars, and cyan triangles show the time-averaged MSDs of three different single trajectories. The time-averaged MSDs increase linearly with time, $\langle X^2(t) \rangle_T = 2Kt$ with different $K$ values. The trajectories have to be long enough to allow for many steps. In the time averaging simulations, a distribution of exponents $\alpha$ is obtained around $\alpha = 1$ manifesting another aspect of inhomogeneity. The magenta solid curve is a time-averaged curve with the average diffusion coefficient, and the black dashed curve is the ensemble-averaged MSD which follows $\langle X^2(t) \rangle_{\text{ens}} \sim t^{0.8}$.

FIG. 3 (color online). The distribution $P(K)$ of diffusion coefficients obtained from time-averaged single trajectories for the case of $\alpha = 0.8$, $T = 2 \times 10^6$, and $t = 500$. Note the inhomogeneous nature of observation, leading to relatively broad distribution of $K$ values.
trjectories characterized by a width which is of the order of the mean. Over this distribution, the mean diffusion coefficient $K$ can be determined, which describes the behavior of the double (temporal and ensemble) average of the data as given by $\langle (x^2(t))_{\text{ens}} \rangle$. Let us now turn to the theoretical description of the behavior of this quantity.

The ensemble mean squared displacement in a CTRW with finite mean squared displacement per step $\int_0^\infty x^2 \lambda(x) dx = a^2$ is governed by the mean number of steps performed [20] up to time $t$

$$\langle x^2(t) \rangle_{\text{ens}} = a^2 \langle n(t) \rangle_{\text{ens}}. \quad (4)$$

In the CTRW discussed above, the mean number of steps performed up to time $t$ grows as $\langle n(t) \rangle_{\text{ens}} \approx A t^\alpha$, with $A$ being a numerical prefactor [3,20]. The mean squared displacement between times $t_1$ and $t_2 > t_1$ is given by [21]

$$\langle (x(t_2) - x(t_1))^2 \rangle_{\text{ens}} = a^2 \langle [\langle n(t_2) \rangle_{\text{ens}} - \langle n(t_1) \rangle_{\text{ens}}] \rangle_{\text{ens}}, \quad (5)$$

as it follows from the independence of the spatial and the temporal aspects of the walk. Since the sequence of the temporal and of the ensemble average can be interchanged, we get [19]

$$\langle (x^2(t))_{\text{T}} \rangle_{\text{ens}} = a^2 \frac{1}{T} \int_0^T [\langle n(t') \rangle_{\text{ens}} - \langle n(t') \rangle_{\text{ens}}] dt'$$

$$= a^2 A \frac{T}{T} \int_0^r [(t' + t)^\alpha - t'^\alpha] dt', \quad (6)$$

where we have assumed that $T \gg t$. By expanding the expression in square brackets and performing the integration, we get

$$\langle (x^2(t))_{\text{T}} \rangle_{\text{ens}} = a^2 A T^{\alpha-1} t, \quad (7)$$

which is essentially the result for normal diffusion but with the effective diffusion coefficient $K_{\text{eff}}(T) = a^2 T^{\alpha-1}/2$ explicitly dependent on the exponent $\alpha$ and length of trajectory. The latter dependence disappears when $\alpha = 1$ as expected for normal diffusion. We stress that the CTRW-type subdiffusion can be obtained from the time average of single-particle trajectories if one carefully analyzes the prefactors as a function of the length of the trajectory.

Two caveats are in place. First, averaging over too short times might lead to the dependencies which are either sub- or superlinear, as observed in simulations. Second, to obtain a larger ensemble, one should not cut one trajectory into several smaller pieces, unless one knows explicitly the instances of jumps, since this produces yet another statistics. Starting a new part of a trajectory with a jump is allowed.

The dependence predicted in Eq. (7) is indeed observed in our numerical simulations. Figure 4 shows the behavior of $K_{\text{eff}}(T)$ for three different values of $\alpha$: namely, for $\alpha = 0.5, 0.6,$ and $0.8$. The results are compatible with Eq. (7).

The nonergodic behavior observed is not specific to subdiffusion and should be observed in superdiffusion as described by Lévy walks [22,23]. In the latter case the ensemble average leads to $\langle x^2(t) \rangle \propto t^\beta$, with $1 < \beta \leq 2$, while in the time average only the ballistic behavior $\beta = 2$ is observable. This type of nonergodic behavior allows for discriminating between different underlying origins of anomalous diffusion. The nonergodicity of subdiffusive systems discussed in this Letter stems from the nonstationary nature of the CTRW process with power-law tail waiting times. In systems governed by stationary increments such as fractional Brownian motion [24] and in the case of diffusion on fractals and on percolation clusters [25,26], ergodicity is expected. Namely, the ensemble and time averages coincide.