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Subdiffusion of mixed origins: When ergodicity and nonergodicity coexist

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Single particle trajectories are investigated assuming the coexistence of two subdiffusive processes: diffusion on a fractal structure modeling spatial constraints on motion and heavy-tailed continuous time random walks representing energetic or chemical traps. The particles' mean squared displacement is found to depend on the way the mean is taken: temporal averaging over single-particle trajectories differs from averaging over an ensemble of particles. This is shown to stem from subordinating an ergodic anomalous process to a nonergodic one. The result is easily generalized to the subordination of any other ergodic process (i.e., fractional Brownian motion) to a nonergodic one. For certain parameters the ergodic diffusion on the underlying fractal structure dominates the transport yet displaying ergodicity breaking and aging.

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Bulk measurements of particles' movement do not always give a detailed enough picture of the underlying physical mechanisms. Widely used methods such as fluorescence correlation spectroscopy and fluorescence recovery after photobleaching reveal only apparent values of the diffusion coefficients. Single-particle tracking (SPT) measurements provide better insight into the movement properties of particles by analyzing individual trajectories [1]. Usually analyzed is the mean-squared displacement (MSD) of the particle [1],

$$\langle r^2(t)\rangle = K_\gamma t^\gamma, \tag{1}$$

where a linear dependence, i.e., $\gamma=1$, is considered a fingerprint of normal diffusion. Any other value of γ corresponds to anomalous diffusion. Here we focus on the case of subdiffusion, $0<\gamma<1$, which is widespread in physical and biological systems [1–6]. A question arises regarding the nature of the average in Eq. (1). This can be interpreted either as an ensemble average $\langle\,\rangle_{ens}$ over many trajectories, or as a time average $\langle\,\rangle_T$, i.e., a moving average over a single trajectory of time length T,

$$\langle r^2(\tau)\rangle_T \equiv \frac{1}{T-\tau}\int_0^{T-\tau} dt[r(t+\tau)-r(t)]^2. \tag{2}$$

When using SPT one is usually limited to a relatively small number of trajectories, naturally leading to the choice of temporal rather than ensemble averaging. The two are equal if the underlying mechanism of motion is *ergodic*. An erroneous assumption that all physical processes are ergodic, namely that the two averages always coincide, might give rise to misleading results. Understanding ergodicity of different transport mechanisms is therefore essential.

Subdiffusive motion can appear due to geometric [7] and/or energetic disorder [8–10]. An example is the synergy of geometrical restrictions modeled by fractals (percolation cluster and Sierpinski gasket) and of "chemical" residence times represented by continuous time random walks (CTRWs) with heavy tails, each leading to subdiffusion. In biological cells the motion of proteins can be hindered either by molecular crowding (geometric restraints modeled by fractals) or by chemical binding [3,4,6] (residence times represented by CTRWs with heavy tails). Essentially, both mechanisms can coexist. In this Rapid Communication we consider the synergy of a nonergodic process (heavy-tailed CTRW) on a fractal and discuss the properties of the MSD as obtained via ensemble and time averages.

We start with random walks on fractal structures. We follow numerically the trajectories of a walker on deterministic (Sierpinski gasket) and statistical (percolation cluster at criticality) fractals. In both cases a simple random walk was considered: every time unit the walker makes exactly one step to one of the nearest neighboring sites of the structure. Thus, the time t is essentially equivalent to the number of steps n of the walker. The particles' MSD was examined by performing ensemble and temporal averaging and was found to follow

$$\langle r(t)^2\rangle_{ens} = \langle r(t)^2\rangle_T = \widetilde{K}_\beta n^\beta = K_\beta t^\beta, \tag{3}$$

where K_β is the generalized diffusion constant with units of length^2/time$^\beta$. The two averages are equal, displaying ergodicity, as shown in Fig. 1. The theoretical value of β on a percolation cluster is 0.697 [7], the ensemble average produces 0.692 and the temporal average gives 0.697. The diffusion constant K_β is 1.555 from the ensemble average and 1.553 from the temporal. The theoretical value of β for a random walk on the Sierpinski gasket is 0.861 [7]. The numerical value obtained through the ensemble average is 0.855 while temporal averaging results in 0.880. The diffusion constant K_β is 0.835 from the ensemble average and 0.950 from the temporal. The larger discrepancy in the case of the Sierpinski gasket originates from its regularity which introduces hierarchical oscillations and requires averaging over extremely large samples.

CTRW is generally characterized by the distributions of step sizes and waiting times. Waiting-time and step-size dis-

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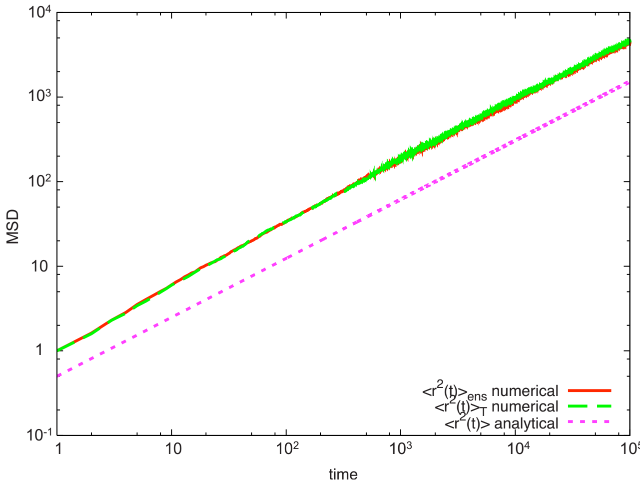

FIG. 1. (Color online) Ensemble and temporal averaging of MSD of diffusion on a percolation cluster at criticality. The MSDs are plotted on a log-log scale, where the slope is equivalent to the time exponent β. The plots of the ensemble and the temporal averaging coincide displaying ergodicity. The percolation cluster was generated using site percolation on a square lattice of size 250×250, with periodic boundary conditions, at critical concentration $p_c=0.592\,746$. Note that due to the overlap of the curves it is difficult to distinguish between the ensemble and temporal averages plots. The theoretical slope with $\beta=0.697$ appears as a guide.

tributions with finite mean and variance correspondingly lead to normal diffusion. A *heavy-tailed* CTRW refers to a power-law probability density function (PDF) of waiting times with a diverging first moment [1,2],

$$\psi(t) \sim \frac{\tau_0^\alpha}{t^{1+\alpha}}, \quad 0<\alpha<1. \tag{4}$$

Space and time decoupled CTRW with such a waiting time PDF leads to subdiffusion, namely, $\langle r^2(t)\rangle_{ens}=K_\alpha t^\alpha$, if the variance of the step size exists.

It has been shown [11–13] that this heavy-tailed CTRW exhibits nonergodicity: the ensemble MSD displays a subdiffusive behavior $\langle x^2(t)\rangle_{ens}\propto t^\alpha$ while the temporal MSD is linear in time $\langle x^2(t)\rangle_T\propto t$, mimicking normal diffusion. It should be noted that the prefactor of t (effective diffusion coefficient) in the temporal MSD fluctuates strongly over different trajectories. One therefore applies an additional ensemble average to this temporal average determining the mean diffusion coefficient K_α. This one was found to depend on the exponent α and on the length of the trajectory T, $K_\alpha(T)=AT^{\alpha-1}$ [12,13] so that

$$\langle\langle r^2(\tau)\rangle_T\rangle_{ens}=AT^{\alpha-1}\tau. \tag{5}$$

These two examples (fractals and CTRW) correspond to two typical sources of subdiffusion as caused by geometrical and energetic disorder.

Let us now combine these processes and consider heavy-tailed CTRWs on fractal structures. Such a CTRW on a Sierpinski gasket is illustrated in Fig. 2, where the sum of the random walker's coordinates, $x+y$, is plotted as a function of time to elucidate the sequence of steps. The long waiting times are clearly observed. The ensemble average in this case is obtained by generating a time subordination of the regular random walk on a fractal structure [14,15]. As in Eq. (3), the MSD of a random walker on a fractal structure is given by

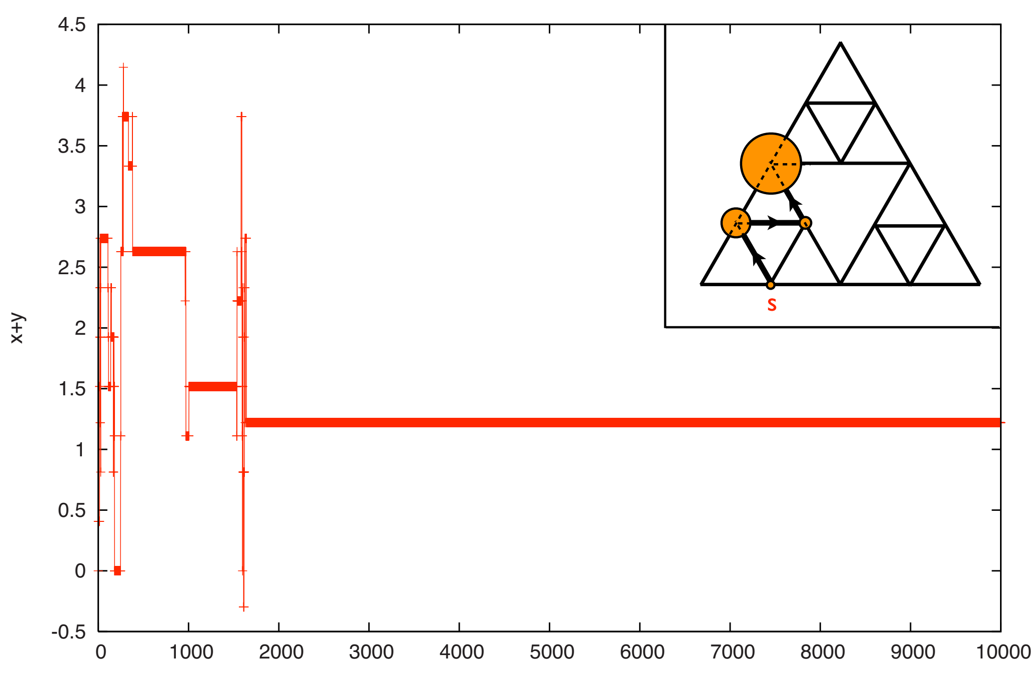

FIG. 2. (Color online) Heavy tailed CTRW on a Sierpinski gasket. Plot of the sum of coordinates of the RWs position $x+y$ as a function of time. In the inset a schematic representation of the process is shown, where circles represent different waiting times. In our simulations we used a Sierpinski gasket of 11th generation in two dimensions.

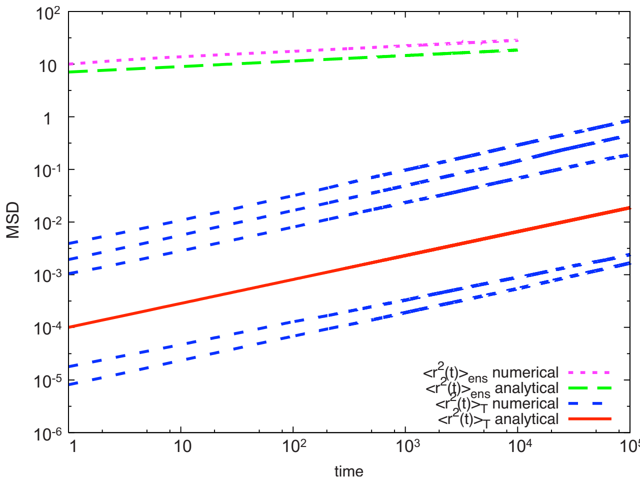

FIG. 3. (Color online) A log-log plot of the temporal and ensemble MSDs of a CTRW (α=0.3) on a percolation cluster at criticality. The distribution of diffusion constants is apparent for the temporal MSDs of different trajectories. The theoretical slopes are given as a guide for the eye. The numerically calculated ensemble average, at the top, fits the given theoretical slope. The same can be said for the different numerically calculated temporal MSDs, shown at the bottom part of the plot.

$\langle r_n^2\rangle \sim n^\beta$ in terms of the number of steps n. Unlike the previous case of a simple random walk, the number of steps n cannot be simply translated into the time t. Now the dependence of time t on the number of steps n is a random process characterized by the probability $\chi_n(t)$ to perform exactly n steps up to the time t. Therefore

$$\langle r^2(t)\rangle_{ens} = \sum_{n=0}^{\infty} \langle r_n^2\rangle \chi_n(t) \sim \sum_{n=0}^{\infty} n^\beta \chi_n(t) = \langle n^\beta(t)\rangle_{ens}. \quad (6)$$

The asymptotic form of $\chi_n(t)$ is given by [16]

$$\chi_n(t) \simeq \frac{t}{\alpha\tau_0} n^{-1/\alpha-1} L_\alpha\left(\frac{t}{\tau_0 n^{1/\alpha}}\right), \quad (7)$$

where $L_\alpha(t)$ is the one-sided Levy function [1,16].

Let us substitute Eq. (7) into Eq. (6), approximate the sum by an integral and make a change of variable $y=t'/\tau_0 n^{1/\alpha}$. Using the fact that $\int_0^\infty y^\eta L_\alpha(y)dy=\frac{\Gamma(1-\eta/\alpha)}{\Gamma(1-\eta)}$ [14] we get

$$\langle r^2(t)\rangle_{ens} \sim \left(\frac{t}{\tau_0}\right)^{\alpha\beta} \frac{\Gamma(1+\beta)}{1+\alpha\beta} \simeq t^{\alpha\cdot\beta}. \quad (8)$$

The two subdiffusive exponents α and β characterizing the heavy-tailed CTRW and the fractal random walk correspondingly, enter multiplicatively.

We now turn to the temporal average. As mentioned for CTRWs before, single trajectory temporal averages vary strongly from one measurement of the MSD to another exhibiting a broad distribution of coefficients [12], as illustrated in Fig. 3. We therefore take the ensemble mean of such temporal averages. Since the two averaging procedures are interchangeable, we have

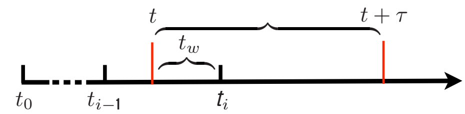

FIG. 4. (Color online) Schematic picture of events for the construction of the forward waiting time distribution, Eq. (11) and the averaging in Eq. (9).

$$\langle\langle r^2(\tau)\rangle_T\rangle_{ens} = \langle\langle r^2(\tau)\rangle_{ens}\rangle_T = \langle\langle n^\beta(\tau)\rangle_{ens}\rangle_T. \quad (9)$$

The r.h.s. of Eq. (9) can be explicitly written as

$$\langle\langle n^\beta(\tau)\rangle_{ens}\rangle_T \equiv \frac{1}{T-\tau}\int_0^{T-\tau} dt \langle (n(t+\tau)-n(t))^\beta\rangle_{ens}. \quad (10)$$

Special care has to be taken when calculating the integrand in Eq. (10) since the heavy-tailed CTRW process ages; i.e., the number of steps performed after some time t explicitly depends on t.

Let us look at time interval $[t,t+\tau]$, and let t_i denote the time of the first step taken in this interval. The time till the first step $t_w=t_i-t$ is called the *forward waiting time*. Figure 4 illustrates these definitions. The distribution of the forward waiting time differs from the one of further regular steps, given by $\psi(t)$. Note that we do not know how much time has passed between the time of the last step t_{i-1} before the observation started and the beginning of observation t. From the first step on, the usual connection between the elapsed time $t'=\tau-t_w$ and the mean number of steps holds. Thus the correct form of the desired ensemble average is expressed by averaging $\langle n^\beta(t')\rangle$ of the ordinary renewal process over the forward waiting times [17],

$$\langle (n(t+\tau)-n(t))^\beta\rangle_{ens} = \int_0^\tau \langle n^\beta(\tau-t_w)\rangle_{ens}\psi_1(t_w|t)dt_w. \quad (11)$$

The distribution of the forward waiting time t_w is known [17],

$$\psi_1(t_w|t) = \frac{\sin(\pi\alpha)}{\pi}\frac{t^\alpha}{t_w^\alpha(t+t_w)}, \quad (12)$$

which in the long time limit $t_w/t \ll 1$ is

$$\psi_1(t_w|t) \sim \frac{\sin(\pi\alpha)}{\pi}\frac{t^{\alpha-1}}{t_w^\alpha}. \quad (13)$$

Performing the average in Eq. (11), by substituting Eqs. (8) and (13) we get

$$\langle (n(t+\tau)-n(t))^\beta\rangle_{ens} = \frac{\Gamma(1+\beta)}{(a+\alpha\beta)}\frac{\sin(\pi\alpha)}{\pi}\frac{t^{\alpha-1}}{t_0^\alpha}\int_0^\tau \frac{(\tau-t_w)^{\alpha\beta}}{t_w^\alpha}dt_w. \quad (14)$$

The integral in Eq. (14) equals to $\tau^{1-\alpha+\alpha\beta}\Gamma(1+\alpha\beta)\times\Gamma(1-\alpha)/\Gamma(2-\alpha+\alpha\beta)$. Thus,

$$\langle (n(t+\tau)-n(t))^{\beta}\rangle_{ens} = C\cdot \tau^{1-\alpha+\alpha\beta}t^{1-\alpha}, \tag{15}$$

with $C=[\Gamma(1+\beta)\Gamma(1-\alpha)/\Gamma(2-\alpha+\alpha\beta)]\sin(\pi\alpha)/\pi\tau_0^{\alpha\beta}$. Performing temporal integration in Eq. (10) we now get

$$\langle\langle r^2(\tau)\rangle_{ens}\rangle_T \sim \langle\langle n^{\beta}(\tau)\rangle_{ens}\rangle_T = \frac{C}{\alpha}T^{\alpha-1}\tau^{1-\alpha+\alpha\beta}. \tag{16}$$

This result has to be contrasted with the ensemble MSD as given by Eq. (8). The exponent of the temporal MSD is no longer a product of the corresponding exponents of the single processes. Moreover, the prefactor, giving the corresponding generalized diffusion coefficient, depends explicitly on the length of trajectory which can be tested experimentally for different lengths of trajectories. Performing an ensemble average only cannot unravel possible coexistence of ergodic and nonergodic underlying processes.

Numerical results support our analytical derivations. We simulated a CTRW with $\alpha=0.3$ on both a percolation cluster at the critical threshold ($\beta=0.697$), and on a Sierpinski gasket embedded in two dimensions ($\beta=0.861$). For the Sierpinski gasket, the theoretical ensemble exponent is $\alpha\beta=0.258$. We simulated $5\cdot 10^4$ walkers over 10^4 time steps, resulting in an exponent 0.251. The theoretical temporal exponent, following Eq. (16), is $1-\alpha+\alpha\beta=0.958$. The temporal MSD was calculated for 200 trajectories, while the time exponent was taken from the linear fit to the log-log plot of the MSD vs time. Only trajectories with good linear fits were taken into consideration (with $R^2>0.999$). An average was taken over the exponents of the remaining 121 trajectories, resulting in 0.949 ± 0.038. The theoretical exponent for the ensemble MSD on the percolation cluster is 0.209. Simulations of 10^5 random walkers resulted in an exponent of 0.212. The theoretical temporal exponent is 0.909. The simulations here lead to the exponent 0.924 ± 0.060. The ensemble and temporal MSDs for the percolation cluster are plotted in Fig. 3. Note the spread in values of the diffusion coefficient in temporal average for different trajectories.

Taking $\alpha\to 0$ in Eq. (16) leads to an almost linear time dependence of the temporal MSD of the subordinated process independent of the underlying fractal structure. On the other hand $\alpha\lesssim 1$ will lead to a subdiffusive exponent dominated by the fractal nature. Thus, we have a process that recovers temporal exponents of the MSD close to the fractal ones, yet characterized by ergodicity breaking.

The results in this Rapid Communication may be generalized to the subordination of any two processes, as long as one is ergodic, i.e., fractional Brownian motion, and the other not.

Based on the processes discussed above we note that care should be taken when describing ergodic processes by using time fractional derivatives [1,18,20]. Given the success of the fractional Fokker-Planck equation (FFPE), derived from heavy-tailed CTRW [1], in modeling subdiffusive behavior, attempts have been made to use it to describe the subdiffusion of a random walk on a fractal structure [19]. One should note that FFPE is intrinsically nonergodic. It cannot describe processes characterized by ergodicity even if subdiffusive. Random walks on fractal structures are not hindered due to temporal constraints, but rather due to geometric constraints and are therefore ergodic. The application of FFPE to the fractal case or any other ergodic process is therefore erroneous.

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