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Ageing single file motion

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Abstract. The mean squared displacement of a tracer particle in a single file of identical particles with excluded volume interactions shows the famed Harris scaling $\langle x^2(t)\rangle \simeq K_{1/2}t^{1/2}$ as function of time. Here we study what happens to this law when each particle of the single file interacts with the environment such that it is transiently immobilised for times τ with a power-law distribution $\psi(\tau) \simeq (\tau^\star)^\alpha$, and different ranges of the exponent α are considered. We find a dramatic slow-down of the motion of a tracer particle from Harris' law to an ultraslow, logarithmic time evolution $\langle x^2(t)\rangle \simeq K_0 \log^{1/2}(t)$ when $0 < \alpha < 1$. In the intermediate case $1 < \alpha < 2$, we observe a power-law form for the mean squared displacement, with a modified scaling exponent as compared to Harris' law. Once α is larger than two, the Brownian single file behaviour and thus Harris' law are restored. We also point out that this process is weakly non-ergodic in the sense that the time and ensemble averaged mean squared displacements are disparate.

1 Introduction

The mean squared displacement of a single tracer particle in a simple liquid is typically of the linear form

$$\langle x^2(t)\rangle = 2dK_1t, \tag{1}$$

the characteristic scaling for a Brownian particle, where d is the embedding dimension and K_1 the diffusion coefficient. For a random walker on a d dimensional lattice with lattice spacing a, $K_1 = a^2/[2d\tau_0]$, where τ_0 is the typical time for a single jump. In three dimensions, as long as the density of particles is not overly large, the motion of individual particles with excluding volume interactions will still be governed by Brownian motion, as the probability of particle-particle encounters is relatively small. However, when we confine the motion of the particle to one dimension, particles will eventually bump into each other. The resulting many-body interactions severely alter

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the Brownian law. As shown by Harris in 1965, the motion of a tracer particle in such a *single file* of particles is characterised by the square-root scaling

$$\langle x^2(t)\rangle \simeq K_{1/2}t^{1/2} \tag{2}$$

of the mean squared displacement [1]. Here $K_{1/2}$ is an anomalous diffusion coefficient of dimension cm/sec$^{1/2}$ and the symbol $\simeq$ denotes the asymptotic equality up to a constant prefactor. In the scenario discussed below, the Harris result (2) corresponds to a continuous time random walk process with an exponential distribution of waiting times.

Experimentally, single file motion was shown to be realised for colloidal particles moving in circular groves [2], an experiment in which also the asymptotic Gaussian character of the probability density of the particle position was demonstrated. Channels can also be realised by help of optical tweezers [3], and the motion of excluded volume particles in such channels exhibits a turnover from initial free diffusion to single file motion with the $t^{1/2}$ scaling of the mean squared displacement [4]. Also in this experiment the Gaussian nature of the propagator was shown [4]. Apart from these direct single particle tracking assays, single file diffusion was also demonstrated by pulsed field gradient NMR in zeolite structures, so-called molecular sieves [5] and further analysed by simulations [6]. Single file diffusion is also characteristic for molecular biological processes, for instance, the transport of biomolecules through cell membranes [7]. Moreover, this type of motion is observed in microchannel setups [8] as well as in nanochannels [9].

Single file diffusion has been studied extensively by analytical and simulations approaches, see, for instance, Refs. [10–14] with respect to the influence of various physical parameters such as the density of single file particles. More recently, the field of single file diffusion has received renewed attention. We mention the description of single file diffusion on a finite interval [15], the effect of the particle density [16], as well as single file motion of externally driven particles [17,18]. A major step forward in the understanding of a tagged particle in a single file is the harmonisation approach of Ref. [19], which shows that the motion of the particle is described by a fractional Langevin equation.

Here we consider the generalisation of the single file dynamics to a case when the particles in the single file interact with a disordered environment. Consider a single file of functionalised colloidal particles moving in a channel whose surface is functionalised complementarily to the colloidal particles, effecting transient sticking of the colloids to the wall of the channel with a power-law distribution $\psi(\tau) \simeq (\tau^\star)^\alpha$. The existence of such power-law distributed sticking times was indeed shown experimentally for colloids, which bind transiently to a wall [20]. This scenario gives rise to a logarithmic growth of the mean squared displacement instead of Harris' law (2). We stress that the approach taken herein–based on the physical scenario of sticky colloid-wall interactions–is different from that of previous works [21–23].

2 Ultraslow single file diffusion

Consider first a single particle, which successively becomes immobilised for periods τ, which are distributed according to the power-law probability density

$$\psi(\tau) = \frac{\alpha}{\tau^\star[1+\tau/\tau^\star]^{1+\alpha}} \simeq \frac{(\tau^\star)^\alpha}{\tau^{1+\alpha}}, \tag{3}$$

where the scaling exponent $\alpha > 0$ and $\tau^\star$ is a microscopic time scale. When $0 < \alpha < 1$ the distribution $\psi(\tau)$ does not possess a finite characteristic time scale

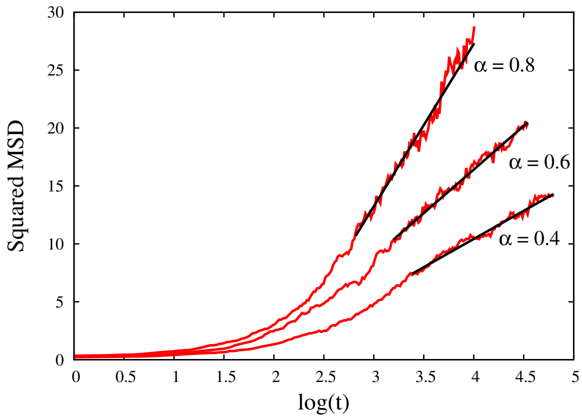

Fig. 1. Square of the mean squared displacement (red lines) for a labelled particle in a single file governed by the waiting time distribution (3) with $\alpha = 0.4$, 0.6, and 0.8. Note the logarithmic abscissa. The straight behaviour indicates the $\langle x^2(t)\rangle \simeq K_0 \log^{1/2}(t)$ scaling, where the prefactor depends on the scaling exponent α. The black solid lines are fitted by $\langle x^2(t)\rangle = c_1\sqrt{\log t + c_2}$. Parameters: we present an average over 5×10^3 runs for each α, on a lattice of size 100, occupied by $N = 31$ particles.

$\langle \tau \rangle = \int_0^\infty \tau\psi(\tau)d\tau$. The resulting particle motion is subdiffusive with $\langle x^2(t)\rangle \simeq K_\alpha t^\alpha$ [24]. This continuous time random walk scenario [25] leads to weakly non-ergodic behaviour in the sense that the process exhibits a disparity between ensemble averaged mean squared displacement and the corresponding time averaged mean squared displacement [26,27]. Moreover, the process is ageing: the dynamics of the traced particle depends explicitly on the time difference between the initiation of the particle and the start of the measurement [28–31]. In the trajectory of the particle, the scale-free nature of the waiting time distribution (3) effects longer and longer, single waiting times such that on average the particle appears increasingly immobile [30,31]. An important feature of this ageing is the following. If we start measuring the particle some time t_a after its motion was initiated, the times τ_1 to see the particle make its first jump after start of the measurement are not distributed according to the law (3), but follows the forward waiting time distribution [32]. When t_a is long, the forward waiting times τ_1 can become quite long, as well, and influence the motion of the particle until the measurement is much longer than t_a [28–31]. In the Brownian limit with $\alpha = 1$ normal diffusion is restored, the process is ergodic and non-ageing.

What happens when we use the waiting time distribution (3) in a single file of excluded volume particles in our scenario when each particle can independently bind to the functionalised surface and become immobilised? Consider first the scale-free case with scaling exponent $0 < \alpha < 1$ and follow a specific particle. Its diffusive motion in the channel can become interrupted by binding to the channel surface, and occasionally the associated sticking time can become very long, in analogy to the trajectory of a single, free particle in the continuous time random walk. However, when the particle is in a mobile phase, its motion can also be blocked by one of its nearest neighbours, when that neighbour is in a long immobile period. As the typical length of the sticking times τ increases as the whole system evolves in time, a mobile particle will run into a blocking particle characterised by longer and longer immobile periods.

Figure 1 shows results from simulations of a single file system, in which each particle is independently immobilised according to the power-law distribution (3) with diverging characteristic waiting time. As the data follow a straight line for the

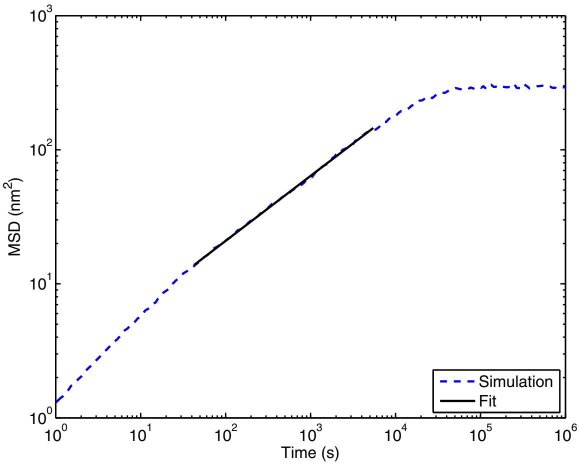

Fig. 2. Recovery of Harris' 1/2-scaling of the mean squared displacement, corresponding to the slope indicated by the black line.

specific scaling used in Fig. 1, the observed diffusion of the tagged particle is ultraslow and follows the logarithmic law [33]

$$\langle x^2(t)\rangle \simeq K_0 \log^{1/2}(t/t_0). \tag{4}$$

The prefactor on the right hand side remains a function of the scaling exponent α, as can be seen from the different slopes in Fig. 1. Note that here we introduce the ultraslow diffusion coefficient of physical dimension cm^2, and t_0 is a fundamental time scale. How can this result be rationalised? We first note that if we were representing the mean squared displacement as function of the number of steps of the particle and not of the actual time elapsing until this number of steps are performed, the result would be the Harris' law

$$\langle x^2(n)\rangle \simeq a^2 n^{1/2} \tag{5}$$

on a lattice with spacing a. To connect between this result and the logarithmic law (4) we use the following argument. At sufficiently long times, the motion of the labelled particle is dominated by long blocking events by a nearest neighbour. Apart from local motion, the labelled particle can only perform significant motion events once the blocking neighbour itself starts to move again. The progress of our labelled particle therefore corresponds to the forward waiting time of its neighbour. After some time, the tracer runs into another blockage, i.e., also its next time-limiting step is governed by the forward waiting time of a neighbour. The difference is that the time since the initial preparation of the system has increased, so statistically the new blocking neighbour's motion has continued to age and the forward waiting time typically becomes even longer. In this simple picture *every* time-limiting jump of the tracer particle is dominated by the forward waiting time, and the distribution governing this forward waiting time is progressively ageing.

This is exactly the scenario investigated in a recent study [34], in which a counting process $n(t)$ is considered. Each step $n \to n+1$ occurs with the forward waiting time, while the system is ageing. The result for the evolution of the mean number of jumps with time for $0 < \alpha < 1$ is given by [34]

$$\langle n(t)\rangle \simeq \mu^{-1}\log(t/t_0) \tag{6}$$

where $\mu = -\Gamma'(\alpha)/\Gamma(\alpha) - \gamma$ involving the complete Gamma function $\Gamma(\alpha)$ and the Euler constant $\gamma = 0.5772\ldots$. In particular, it can be shown that the relative fluctuations of $n(t)$ versus the mean $\langle n(t)\rangle$ decay as function of time and in this sense $n(t)$ becomes deterministic. With this argument we explain the logarithmic evolution (4) demonstrated in Fig. 1 through replacing n by $\log(t)$ in Eq. (5) [33].

A more intricate situation arises when the scaling exponent assumes intermediate values, $1 < \alpha < 2$. Here, the mean of the counting process, $\langle n(t)\rangle$, remains of the same order as the standard deviation. A more sophisticated argument to connect between the scaling exponent α of the waiting times and the time dependence of the mean squared displacement of the tracer particle in the single file is needed to explain the observed non-universal power-law scaling [33]. When $\alpha > 2$, the Harris' law (2) for the tracer particle is recovered [33]. Figure 2 shows the initial convergence of the tracer motion to the 1/2-scaling indicated by the black line. Eventually the tracer motion is limited by the finite size of the simulations box, effecting the plateau at longer times.

3 Discussion

Single file dynamics occurs quite widely in microscopic systems in both biology and technology. From a physics point of view the single file dynamics is of fundamental interest, as it combines stochastic motion with the interactions of a many-body system. We here showed that when the single file system is put in a strongly disordered environment, the famed Harris' scaling of the mean squared displacement changes drastically to an ultraslow, logarithmic scaling as function of time. For technological applications, this effect would offer the possibility of long-time storage of molecules in a narrow channel without the need to engineer removable lids, thus significantly improving the regular single file result described in Ref. [9]. While some molecules at the ends of the channel will diffuse out of the channel, the ultraslow motion of the remaining particles effect a massive retention, as shown here in the simulations for a relatively small system.

For the counting process $n(t)$ discussed above it can be shown that the dynamics is weakly non-ergodic in the sense that the scaling of the mean number $\langle n(t)\rangle$ of counts (6) as function of time differs from the scaling of the corresponding time average as function of the lag time. If we use the counting process as a timer for a random walk process in dimension $d = 3$, the mean squared displacement in the interesting range $0 < \alpha < 1$ according to Eq. (6) would be ultraslow, $\langle x^2(t)\rangle \simeq K_0 \log(t/t_0)$. Concurrently, the time averaged mean squared displacement $\overline{\delta^2(\Delta)} = \frac{1}{t-\Delta}\int_0^{t-\Delta}\left[x(t'+\Delta)-x(t')\right]^2 dt'$ used to evaluate sufficiently long single particle trajectories, would exhibit the scaling $\langle\overline{\delta^2(\Delta)}\rangle \simeq \log(t/t_0)\Delta/t$ as function of the lag time Δ and the length t of the corresponding time series [27]. The angular brackets in the latter expression denote an average over an ensemble of trajectories [27]. The inequivalence between the two kinds of averages will also affect the behaviour of the single file system governed by the distribution (3) of immobilisation times.

Generally, weakly non-ergodic behaviour is discussed in terms of the disparity $\langle x^2(\Delta)\rangle \neq \lim_{t\to\infty}\overline{\delta^2(\Delta)}$ of the ensemble averaged mean squared displacement $\langle x^2(t)\rangle$ and the time averaged mean squared displacement $\overline{\delta^2(\Delta)}$ even in the limit of long measurement times t [26,27,35–38]. Such behaviour was originally studied in the context of the inhomogeneous exploration of phase space in a single trajectory of processes governed by scale-free waiting time distributions of the kind (3) such that long waiting times effect the particle to remain longer in some areas even in the long time limit [39–43]. However, similar weakly non-ergodic behaviour was found in numerous other anomalous diffusion systems, including subdiffusive continuous time random walks with superimposed noise [44], diffusion with space-dependent [45–48] or time-dependent [49–51] diffusivities, continuous time random walk processes with correlated waiting times [52,53], strong anomalous diffusion systems [54], and even superdiffusive Lévy walks [55,57–59]. The cognisance of the weakly non-ergodic behaviour is relevant for the understanding of single particle tracking data in complex fluids, including the crowded cytoplasm and membranes of biological cells [27,60–64].

Weakly non-ergodic behaviour, apart from its experimental relevance, touches upon the fundamental concepts of statistical mechanics. To find out how diverging time scales due to the power-law waiting time distribution $\psi(\tau)$ with $0 < \alpha < 1$ and many-particle interactions conspire and which effects will arise, will certainly be interesting. The current generalised single file system could be an excellent basis for such studies. How this can be done exactly, is currently under investigation.

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