Superdiffusive-like motion of colloidal nanorods

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In recent experiments, the temporal average $C(t)$ of the mean square displacement for nanorods moving through a chemical monolayer was explored. The results showed a scaling $C(t)\sim t^{1.6}$, which suggest the existence of superdiffusive motion for these particles. In this paper, we interpret these results by means of a continuous-time random walk (CTRW) model from which we can reproduce the exponent 1.6 and the curve $C(t)$ versus time found in the experiments. We show that the behavior observed arises as a consequence of the superposition of different transport mechanisms: directional propulsion plus translational and rotational diffusion. Our model reveals that this superdiffusive-like scaling may also be found in other systems as in chemotactic biological motion, provided that the characteristic times for translational and rotational diffusions are very different. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3102096]

The synthesis of controllable nanoscale motors for technological applications is becoming a major topic nowadays.[1] Many of these artificial devices consist of particles, which exploit reaction processes to convert chemical energy into mechanical work for self-propulsion. It results in an autonomous directional motion of the particles. Different examples of such propelled machines have been either theoretically proposed[2] or synthesized[3] recently.

In this paper, we focus our interest on rod-shaped nanoparticles with reaction-driven motion, which have received exhaustive attention since the works by Paxton *et al.*[4] In these systems, bimetallic (Pt–Au) asymmetric rods, as shown in Fig. 1 (inset), are introduced in a H_2O_2 solution. The platinum acts as a catalyst for the reaction $H_2O_2\rightarrow H_2+O_2$, so that this reaction generates an oxygen concentration gradient between the ends of the rod, which results in a propelled motion along the rod axis (we denote this direction by $\mathbf{x}_\parallel$ in the inset of Fig. 1, while $\mathbf{x}_\perp$ is the corresponding normal direction). The specific physical mechanisms driving the motion of these devices are not completely understood yet.[5] However, the analysis of the individual trajectories and the collective dynamics of these systems are of great interest in order to determine their applicability. Such tracking data have served, for example, to provide the first evidence of a nonbiological chemotactic dynamics at nanoscale.[6]

Recently, Dhar *et al.*[7] explored the characteristics of individual trajectories for these Pt–Au nanorods in Gibbs monolayers prepared by adding Sodium dodecyl sulfate to the H_2O_2 solution. This setup allows the rods to move throughout a two-dimensional (2D) interface, where each particle is characterized by its position vector $\mathbf{x}(t)$ and its fluctuating orientation angle $\theta(t)$ (see Fig. 1, inset). In Ref. 7, the authors studied the correlation function (CF)

$$C(t)=\frac{1}{T}\int_0^T[\mathbf{x}(t'+t)-\mathbf{x}(t')]^2dt' \tag{1}$$

for individual trajectories. This CF represents the temporal average of the mean square displacement (MSD) of the nanorods. Similarly, one can define the CF for the motion in the direction $\mathbf{x}_\parallel$ by $C_\parallel(t)=(1/T)\int_0^T[s_\parallel(t'+t)-s_\parallel(t')]^2dt'$, where $s_\parallel(t)$ is the total distance moved by the particle in the direction $\mathbf{x}_\parallel$ after a time t. As expected, the behavior found experimentally was $C_\parallel\sim t^2$, it is a ballistic motion along the rod axis due to chemical propulsion. Additional experiments (where the propelled motion was partially suppressed) also revealed the existence of an underlying diffusive behavior $C_\parallel\sim t$, probably caused by the fluctuating interactions between the particle and the surrounding media. On the other side, it was found that the nanorods hardly moved in the direction $\mathbf{x}_\perp$. So that, the behavior of $C(t)$ would be expected to show a statistics, which is in consonance with that found for $C_\parallel$. Surprisingly, in Ref. 7 the authors observed the emergence of superdiffusive motion $C(t)\sim t^\alpha$, with an exponent $\alpha=1.6$ similar to that found for Levy walks.[8]

At the sight of this intriguing result we have built a specific model to understand the emergence of the noninteger exponent α. Our analysis suggests that the behavior reported there could correspond to an intermediate region of times $t_1<t<t_2$ where the MSD resembles very much a power law but it is not. Below, we present our model in detail, compare our results to experimental data, and discuss the generality of our approach.

We consider a continuous time random walk (CTRW) process in 2D, which is a variant of the *velocity model* analyzed in Ref. 10. We consider that particles with orientation θ move with constant velocity v along the direction $\mathbf{x}_\parallel$ during a certain sojourn time t, randomly distributed according to the probability distribution function $\varphi(t)$ (*motion events*). Simultaneously, the particle experience during those sojourn times

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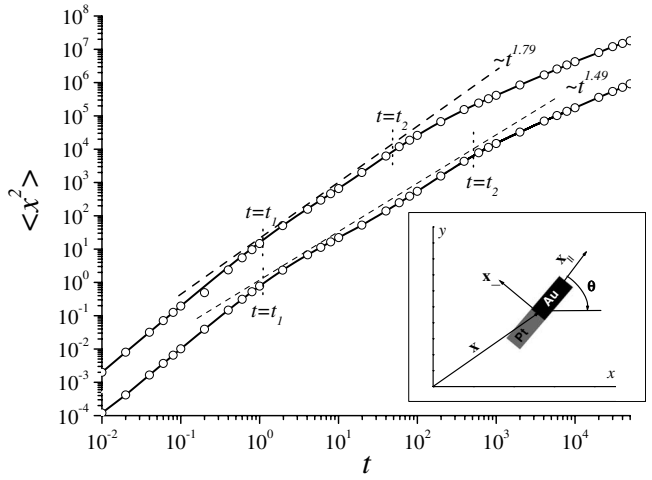

FIG. 1. Log-log plot of the MSD vs time. Solid lines correspond to the expression (8) with arbitrary parameters $v=2$, $v_D=4$, $\lambda=1$, $\sigma^2=0.02$ (upper case) and $v=0.2$, $v_D=1$, $\lambda=1$, $\sigma^2=0.002$ (lower case). Circles represent the corresponding results from the Monte Carlo simulations. For each case, the vertical dotted lines mark the values of t_1 and t_2 and the dashed lines represent the power law, which fits the results in the region $t_1<t<t_2$. Inset: Coordinate system used to describe the motion of rods in the current 2D model.

a diffusive motion determined by a characteristic velocity v_D in the same direction $\mathbf{x}_\parallel$. So that, after each random time [drawn from the distribution $\varphi(t)$] the particle chooses with probability 1/2 one of these two velocities (denoted by the sign + or −)

$$\mathbf{v}^{\pm} = ((v \pm v_D)\cos\,\theta, (v \pm v_D)\sin\,\theta). \tag{2}$$

After every sojourn time, the particle changes instantaneously its orientation from θ to a new value θ' (*turning events*) according to a probability distribution function $T(\theta' - \theta)$, and starts a new sojourn time traveling in the new direction. As these turning events are instantaneous, it allows us to take in our model (see equations below) consecutive motion and turning events as a single motion+turning event whose duration is determined by $\varphi(t)$. Assuming turning events as uncorrelated in time (Markov process), the distribution $\varphi(t)=\lambda e^{-\lambda t}$ will be used for these motion+turning events. This choice has been made in accordance to the exponential decay found experimentally for the angular correlations (see Fig. 2b in Ref. 7). So, note that we do not introduce in our model any memory effect or heavy-tailed distribution, as is done in standard models of superdiffusion.[9]

Now, we will find the corresponding master equation for this process. According to the prescriptions from the velocity model,[10] the probability density $j(\mathbf{x},\theta,t)$ of a particle starting a new motion event at the point $\mathbf{x}=(x,y)$ at time t is given by

$$j(\mathbf{x},\theta,t) = \int d\mathbf{x}' \int_0^{2\pi} d\theta' \int_0^t dt' j(\mathbf{x}-\mathbf{x}', \theta-\theta', t-t') \times \psi(\mathbf{x}', \theta-\theta', t')T(\theta') + \frac{\delta(\mathbf{x})\delta(t)}{2\pi}, \tag{3}$$

where the second term represents the contribution from the initial conditions. For simplicity, we consider that initially all the particles starts from the origin (0, 0) with a random value θ uniformly distributed. The function $\psi(\mathbf{x},\theta,t)$ in Eq. (3) gives us the probability distribution to move between two points separated by the vector $\mathbf{x}$ in time t for a single motion event. For the case of the propelled and diffusive particles described above, this function has the form $\psi(\mathbf{x},\theta,t) = \varphi(t)\Phi(\mathbf{x},\theta,t)$, with

$$\Phi(\mathbf{x},\theta,t) = \tfrac{1}{2}[\delta(\mathbf{x}-\mathbf{v}^+t) + \delta(\mathbf{x}-\mathbf{v}^-t)]. \tag{4}$$

On the other side, the probability density $P(\mathbf{x},\theta,t)$ for the particle to be at location $\mathbf{x}$ with orientation θ at time t is

$$P(\mathbf{x},\theta,t) = \int d\mathbf{x}' \int_0^t dt' j(\mathbf{x}-\mathbf{x}', \theta, t-t')\Psi(\mathbf{x}', \theta, t'). \tag{5}$$

The function $\Psi(\mathbf{x}',\theta,t')$ determines the probability to have moved so far a distance $\mathbf{x}$ with orientation θ in time t since the last turning event. This is closely related to $\psi(\mathbf{x}',\theta,t')$ by the expression $\Psi(\mathbf{x},\theta,t)=\Phi(\mathbf{x},\theta,t)\int d\mathbf{x}' \int_t^\infty dt' \psi(\mathbf{x}',\theta,t')$. For the specific case of uncorrelated events we are considering here, this relation simplifies to $\psi(\mathbf{x},\theta,t)=\lambda\Psi(\mathbf{x},\theta,t)$.

In general, our model [Eqs. (3) and (5)] cannot be solved due to the explicit dependence of the functions ψ and Ψ on the orientation angle θ. However, we shall show that for the specific purposes of the present paper a complete analytical treatment is possible. First, we need to consider that the turning distribution $T(\theta)$ is a rapidly decaying function of θ (it is, only small changes in orientation are allowed in a single turning event). So, Eq. (3) can be approximated by a Taylor expansion around $\theta'=0$ (diffusion approximation) and then it can be easily transformed from the real space $(\mathbf{x},\theta,t)$ into the Fourier–Laplace coordinates $(\mathbf{q},\theta,s)\equiv(q_x,q_y,\theta,s)$. From now on, we will use for simplicity the hat $\hat{f}$ to denote the Fourier–Laplace transform of f. So that, the system [Eqs. (3)–(5)] turns now into

$$\hat{j} = \hat{j}\hat{\psi} + \sigma^2 \frac{\partial^2}{\partial\theta^2}(\hat{j}\hat{\psi}) + \frac{1}{2\pi}, \quad \hat{P} = \hat{j}\hat{\Psi} \tag{6}$$

with $\sigma^2 \equiv \frac{1}{2}\int_0^{2\pi}\theta^2 T(\theta)d\theta$ being the second moment of $T(\theta)$ (the first moment is equal to 0 because we consider that the reorientation process is isotropic). Note that, according to the assumption done of small changes in the reorientation process, we must require that $\sigma^2 \ll 1$ is fulfilled.

Now, by introducing into Eq. (6) the explicit forms of ψ and Ψ given above, we obtain a closed equation for $\hat{P}$ in the form

$$0 = \sigma^2\lambda\frac{\partial^2\hat{P}}{\partial\theta^2} - [s + iv(q_x\cos\,\theta + q_y\sin\,\theta)]\hat{P} - \frac{v_D^2(q_x\cos\,\theta + q_y\sin\,\theta)^2}{s+\lambda+iv(q_x\cos\,\theta+q_y\sin\,\theta)}\hat{P} + \frac{1}{2\pi}. \tag{7}$$

This is a generalized wave equation with periodic coefficients. Although there exists a vast literature on resolution techniques for such kind of equations,[11] note that we do not need here to find the explicit solution of Eq. (7), as we are essentially interested in the determination of the MSD. So, we will derive the exact expression for the ensemble average of the MSD $\langle\mathbf{x}^2\rangle \equiv \int \mathbf{x}^2 P(\mathbf{x},\theta,t)d\mathbf{x}$. To do this, first we need

to integrate Eq. (7) over the whole spatial domain by evaluating that equation at $q_x=0$, $q_y=0$. As a result, a simple ordinary differential equation arises whose solution is $\hat{P}_0=1/2\pi s$ (we use the subindex $_0$ to denote that the function is being evaluated at $q_x=q_y=0$). This solution for $\hat{P}_0$ simply tells us that the total number of particles is conserved in time. Now, we can differentiate Eq. (7) with respect to q_x or q_y and use the same idea to find an explicit expression for $(\partial\hat{P}/\partial q_x)_0$ or $(\partial\hat{P}/\partial q_y)_0$, by knowing that these expressions vanish for $t=0$ (i.e., for $s\to\infty$). Then, after second differentiation we can also obtain $\langle \mathbf{x}^2\rangle(s)=-(\partial^2\hat{P}/\partial q_x^2)_0-(\partial^2\hat{P}/\partial q_y^2)_0$. After inverting the Laplace transform and integrating over all possible orientations θ, one has

$$\langle \mathbf{x}^2\rangle(t)=2\left(\frac{v_D}{\lambda}\right)^2\xi(t)+2\left(\frac{v}{\sigma^2\lambda}\right)^2\xi(\sigma^2 t) \tag{8}$$

with $\xi(t)=e^{-\lambda t}+\lambda t-1$. Equation (8) represents the key result of the present paper. Let us first discuss the asymptotic regimes of that expression, which can be summarized as

$$\langle \mathbf{x}^2\rangle(t)=\begin{cases}(v_D^2+v^2)t^2, & t\ll \min[\lambda^{-1},(\sigma^2\lambda)^{-1}]\\ 2\left(v_D^2+\dfrac{v^2}{\sigma^2}\right)\dfrac{t}{\lambda}, & t\gg \max[\lambda^{-1},(\sigma^2\lambda)^{-1}].\end{cases} \tag{9}$$

According to Eq. (9), for the limit of short times one finds a ballistic motion $\langle \mathbf{x}^2\rangle\sim t^2$. This is a consequence of the velocity model used in our approach; initially all the particles depart from the origin (0, 0) with constant velocity $v\pm v_D$, which results in a convective behavior. On the contrary, the long-time region yields a diffusive behavior $\langle \mathbf{x}^2\rangle=4Dt$. The first contribution to D comes straightforward from the diffusive speed v_D we have introduced in the model. The second contribution, where the directional speed v appears, is due to rotational diffusion, since after a very long time the particle has explored statistically all possible orientation angles θ with equal probability. From Eq. (9), we can deduce that the temporal behavior of our model is governed by two different characteristic timescales, $t_1=\lambda^{-1}$ and $t_2=(\sigma^2\lambda)^{-1}$, which have very different values because of the slow reorientation process considered (i.e., $\sigma^2\ll 1$). It implies the existence of an intermediate region $t_1<t<t_2$ separating the ballistic and the diffusive regimes. The interesting result we have found by studying graphically and numerically expression (8) is that, for a wide range of the values of the parameters, the behavior in this intermediate region resembles very much a power law $\langle \mathbf{x}^2\rangle\sim t^\alpha$, as we show in Fig. 1 for two specific cases. This could lead experimentally to the deceptive interpretation that the MSD is really a power law and so the diffusion is anomalous.

In order to confirm the validity of this result we have also performed Monte Carlo simulations where a large number of individual particles (typically 10^5) are allowed to evolve in time according to the microscopic behavior described in our model (i.e., a superposition of directional propulsion, translational motion, and slow angle reorientation). The corresponding results are also presented in Fig. 1 (circles) and show an excellent agreement with expression (8). Also, note that in the analytical derivation above we have used implicitly the idea that the temporal average $C(t)$ and the ensemble average $\langle \mathbf{x}^2\rangle$ of the MSD are equivalent. This can be done here because in our model we consider only Markov processes in time, so the system is ergodic and $C(t)=\langle \mathbf{x}^2\rangle(t)$. This is in contrast with standard CTRW models for anomalous diffusion,[9] where the existence of long-tailed distributions of waiting times lead to ergodicity breaking[12] due to aging effects. Our Monte Carlo simulations have also confirmed numerically the equivalence between the temporal and the ensemble averages in our model.

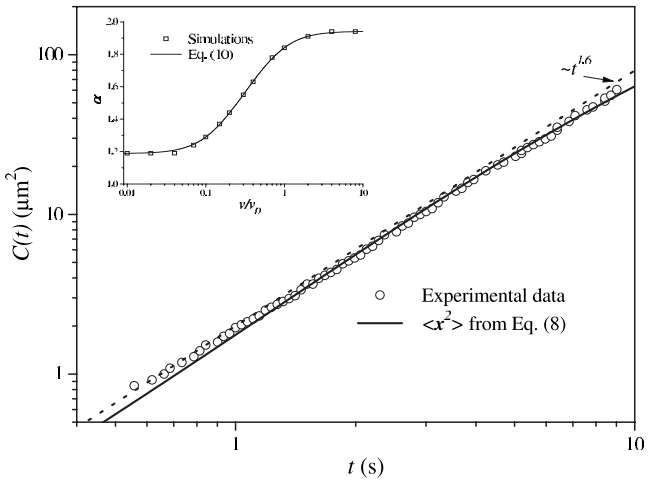

FIG. 2. Comparison between the experimental data (circles) for the CF of nanorods and the analytical expression (8) for the MSD predicted by our model, evaluating the parameters from the data in Ref. 7 (no adjustable parameters have been used). We also plot the behavior $C(t)\sim t^{1.6}$ (dashed line) found from the fitting of experimental data in Ref. 7. Inset: Plot of the analytical result Eq. (10) and the Monte Carlo simulations for the exponent α as a function of the quotient v/v_D. The parameters used are $\lambda=1$ and $\sigma^2=5\times10^{-3}$.

To facilitate the comparison between the results from our model and the experimental data, we can provide an expression for the exponent α as follows. We assume, according to the results from our simulations, that the power-law-like behavior extends over the whole region $t_1<t<t_2$. So that, we can evaluate $\langle \mathbf{x}^2\rangle$ from Eq. (8) at the points $t=(\sigma^2\lambda)^{-1}$ and $t=\lambda^{-1}$, and connect these two points by a power law $\ln[\langle \mathbf{x}^2\rangle]=\beta+\alpha\ln t$. The solution of the corresponding algebraic system leads to

$$\alpha=\frac{\ln\left[\dfrac{(v/v_D)^2(e^{-\sigma^2}+\sigma^2-1)+\sigma^4e^{-1}}{(v/v_D)^2e^{-1}+\sigma^2(\sigma^2e^{-1/\sigma^2}-\sigma^2+1)}\right]}{\ln\sigma^2}, \tag{10}$$

which is independent of the characteristic rate λ. Note that this expression predicts values of α, which are always in the region $1<\alpha<2$, so the model always yields superdiffusive-like motion. In the inset of Fig. 2, we compare the value of the exponents predicted by Eq. (10) with those derived from our Monte Carlo simulations. Again, the agreement found between numerical and analytical results is excellent in the whole region of the parameters examined. Let us stress that for the case $v/v_D\to0$ the results derived from our model are almost indistinguishable from the corresponding power law; only in the region $v/v_D\to\infty$ we find that this resemblance becomes poorer.

Now, from the data available in Ref. 7 we can try to evaluate the exponent α. There, the translational diffusion coefficient $D_{\|}$ was explored, so we could estimate $D_{\|}=v_D^2/2\lambda=0.12\pm0.02$ $\mu m^2/s$. On the other side, the decay rate of angular correlations in time gives us the value of $\sigma^2\lambda$, which reads $\sigma^2\lambda=0.38\pm0.02$. Also, we obtain $\sigma\lambda=2.64\pm0.26$ s^{-1} by evaluating the total angular distance covered by a particle during the experiments. Finally, we take for the propelled velocity the typical value $v=1.2$ $\mu m/s$. From all this, we estimate the parameters in Eqs. (8) and (10), which leads us to $\alpha=1.66\pm0.06$, in really good agreement with the exponent 1.6 reported in Ref. 7. Our model is even able to reproduce the whole experimental plot for $C(t)$ versus time in the superdiffusive-like region. This is shown in Fig. 2, where the circles represent the experimental data (redrawn from Fig. 2a in Ref. 7) and the lines correspond to our Eq. (8) (solid) and to the behavior $t^{1.6}$ (dashed) reported in the original work by Dhar *et al.*[7] It can be seen that both the power law and our analytical expression fit very well the experimental data, but our model has the advantage that it provides a physical interpretation of these results, as it has been derived from the microscopic behavior of individual nanorods.

As a whole, we have studied a system where the motion of particles is governed by directional propulsion and two different diffusion mechanisms (translational and rotational) in the case where one of the two diffusion processes is much slower than the other one. This implies the existence of an intermediate region of times for which the MSD shows often a power-law-like behavior, as that found in superdiffusion. The analysis of the expression (8), together with the results from our Monte Carlo simulations, summarize our findings, which are also in agreement with experimental results. Strictly speaking, the behavior resulting from our model cannot be called superdiffusive or anomalous. This is because the MSD found from this combination of propulsion and diffusion mechanisms is not a power law but *a function which resembles very much a power law* in some regimes. That is why we have coined the term superdiffusive-like to describe the behavior observed. Note that this point is of great importance for the correct interpretation of experimental data in general.

We stress that our expression (8) is not particular to the specific situation discussed here. A similar behavior is expected to be found for any situation where two or more simultaneous diffusion mechanisms govern the motion of the particles, each with a very different characteristic time. We note, for example, that similar patterns of motion to those described here arise in stratified flows[13,14] or bacterial motion, where it is known from simulations that the motion of individuals turns from ballistic (for short times) to diffusive (for long times).[15] For the widely studied case of *Escherichia coli*, it is known that the bacteria move in space by alternating run (with near-straight line motion) and tumbling (angle reorientation) periods.[16] So, these individual trajectories could also be described by the model presented here, or the equivalent three-dimensional version. However, the assumption of small changes in the orientation angle does not usually hold for these bacteria, since they can even turn 180° in a single tumbling process. So, it would be more difficult to observe for bacterial motion the power-law-like behavior reported in the present paper, unless large angle shifts in the tumbling process are inhibited somehow.

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