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Intermittent Brownian dynamics over a rigid strand: Heavily tailed relocation statistics in a simple geometry

P. Levitz,[1,*] M. Zinsmeister,[2] P. Davidson,[3] D. Constantin,[3] and O. Poncelet[4]
[1]*Physique de la Matière Condensée, Ecole Polytechnique, CNRS 91128 Palaiseau, France*
[2]*MAPMO, UMR 6628, Université d'Orléans, 45067 Orléans, France*
[3]*Laboratoire de Physique des Solides, Université Paris-Sud, CNRS, UMR8502, 91405 Orsay Cedex, France*
[4]*CEA/Grenoble LITEN DTNM L2T, Grenoble, France*

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We analyze the intermittent Brownian dynamics (a succession of adsorption and bulk relocation steps) of a test particle over a single strand. We propose an analytic expression of the relocation time distribution at all times. We show that this distribution has a nontrivial heavily tailed statistics at long time with a diverging average relocation time. In order to experimentally probe this first passage statistics, we follow the intermittent Brownian dynamics of water molecules over long and stiff imogolite mineral strands, using a field cycling NMR dispersion technique. Our analytic derivation is found to be in good agreement with experimental data on a large domain of observation. Implications for the efficiency of a search strategy on a single filament are then discussed and the importance of the confinement and/or the finite size effect is emphasized.

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I. INTRODUCTION

Intermittent Brownian dynamics (IBD) of diffusing particles over strands shows up in various interfacial systems such as colloidal suspensions or biological polymers. IBD is characterized by a succession of adsorption steps generally located nearby the interface (A) and relocation periods in the bulk phase (R). Recently, three specific examples involving isolated strands and/or associations of filaments were discussed in the literature. First, the optimal search strategy for a specific target site on DNA by a diffusing protein [1,2]. Second, the enhanced reaction kinetics in cytoskeleton filaments or tubular structures like axons and dendrites [3]. Third, the long-term dynamics of a monovalent counterion around isolated DNA strands [4]. To understand these phenomena, knowledge of the detailed structure of the IBD (the statistics of relocation and adsorption times) is essential. The simplest assumption is that the duration of each step, R and A, is exponentially distributed [2]. This exponential dependence implies a finite average relocation time. On the other hand, heavily tailed duration statistics (evolving asymptotically as an algebraic law) can lead to an infinite-mean relocation time [5]. This very puzzling situation was considered to be induced by anomalous confined motions [5,6].

In this Rapid Communication we show, both theoretically and experimentally, that such heavily tailed statistics actually occur in the simplest case, that of an isolated long filament. We propose an analytic expression for the probability density function (PDF) $\Psi_R(t)$ characterizing the relocation time. This first passage statistics is experimentally investigated, using a model system of long and stiff strands named imogolite, similar in many ways to fibrillar biopolymers such as DNA or F-actin. Field cycling NMR dispersion technique (NMRD) [7,8] is used to probe the intermittent Brownian dynamics of water molecules over these rigid strands. We show that our analytic derivation is in good agreement with the experimental data on a large time and/or frequency domain.

II. RELOCATION STATISTICS

During the intermittent Brownian dynamics over a rigid and infinite cylinder of radius r_{cyl}, the relocation process is a direct product of a one-dimensional (1D) Brownian trajectory along the strand axis and a two-dimensional (2D) Brownian motion in the orthogonal plane. Starting at a distance δ from the cylinder boundary (with $\delta \ll r_{cyl}$), this latter process ensures a recurrent encounter with the cylinder surface (the escape probability is zero). This property is essential for the search strategy along "1D" objects [2,3]. In the 2D plane, the Laplace transform $\hat{\Psi}_R(s)$ of $\Psi_R(t)$ is well-known and reads [9,10]

$$\hat{\Psi}_R(s) = \frac{K_0(r_{cyl}\sqrt{s/D})}{K_0[(r_{cyl}+\delta)\sqrt{s/D}]}, \tag{1}$$

where K_0 is the modified Bessel function of order zero and D the self-diffusion coefficient of the particle in bulk. Analytical inversion of Eq. (1) is not straightforward due to the strict positivity of the K_0 function, but it can be performed numerically. However, an analytical derivation is still possible if we split the relocation process in two consecutive time domains. At short time, $t < t_{cyl}$ with $t_{cyl} = r_{cyl}^2/2D$, the diffusing molecule probes locally the perimeter of the circle. This 2D Brownian trajectory can again be decomposed into a 1D motion almost parallel to the border and inefficient for the relocation and a second motion along the radius. The latter process is characterized by a well-known first passage probability to the origin for a diffusing particle that begins at δ in a semi-infinite interval [10]. In this time domain ($t < t_{cyl}$), $\Psi_R(t)$ reads

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[*] Corresponding author. FAX: +33 1 69 33 30 04. pierre.levitz@polytechnique.edu

$$\Psi_R(t) = \frac{\delta}{\sqrt{4\pi D t^3}} \exp\left(-\frac{\delta^2}{4Dt}\right). \qquad (2)$$

To explore the long time regime ($t > t_{cyl}$), we consider, in the 2D plane, the probability $S_R(r)$ of hitting the circle of radius ($r_{cyl}+r+\delta$) before the circle r_{cyl} when starting from the circle of radius $r_{cyl}+\delta$. The standard potential theory gives [10]

$$S_R(r) = \frac{\ln(1+\delta/r_{cyl})}{\ln(1+\delta/r_{cyl}+r/r_{cyl})}. \qquad (3)$$

The Brownian nature of the relocation bridge allows us to approximate the probability distribution function $\Psi_R(t)$ as [11]

$$\Psi_R(t) = \int dr' \left[-\frac{dS_R(r')}{dr'}\right] \delta\left(\frac{r'^2}{2D} - t\right). \qquad (4)$$

The change of variable $r'^2/2D = t'$ in the Dirac function δ gives

$$\Psi_R(t) = -\frac{D}{r}\frac{dS_R}{dr}\bigg|_{r=\sqrt{2Dt}}, \qquad (5)$$

we finally get

$$\Psi_R(t) = \frac{(\delta/r_{cyl})\sqrt{t/t_{cyl}}}{2t(1+\sqrt{t/t_{cyl}})\ln^2(1+\delta/r_{cyl}+\sqrt{t/t_{cyl}})}, \qquad (6)$$

Eq. (5) ensures the correct normalization of the PDF $\Psi_R(t)$. Finally, for $t \gg t_{cyl}$, $\Psi_R(t)$ simplifies to

$$\Psi_R(t) = \frac{2\delta/r_{cyl}}{t\ln^2(t/t_{cyl})}. \qquad (7)$$

As shown in Fig. 1 (for a set of parameters discussed later on), the analytical expression of $\Psi_R(t)$ [Eq. (2) for $t < t_{cyl}$ and Eq. (6) for $t > t_{cyl}$] closely follows the numerical inversion of Eq. (1). Almost no discontinuity is observed at $t = t_{cyl}$.

Equation (7) has several remarkable features: (i) This PDF is one of the most heavily tailed relocation statistics one can encounter; in particular, a $1/[t\ln(t/t_{cyl})]$ distribution is no longer normalized. (ii) $\Psi_R(t)$ does not possess finite moments, entailing that a mean relocation time cannot be defined. This property is encountered in other different geometries. For example, Bychuk and O'Shaughnessey [12] have extensively analyzed the relocation statistics over an infinite plane. In their case, a long $t^{-3/2}$ tail is predicted. As adsorption, desorption, diffusion in the bulk and readsorption are repeated many times, this specific exponent $3/2$ allows them to propose an analytic form of the effective surface propagator (exhibiting a Cauchy distribution on a large domain of time and space). To our best knowledge, there is no available analytic expression of this propagator for a relocation statistics given by Eqs. (2) and (6).

III. COMPARISON WITH EXPERIMENT

As a model system of filaments, we investigate colloidal suspensions of synthetic imogolite nanorods [13]. Imogolite

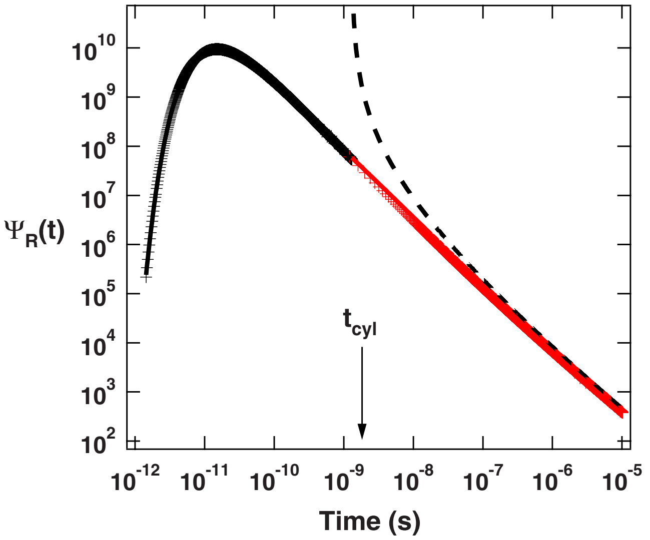

FIG. 1. (Color online) Evolution of the relocation time statistics over a single filament of radius $r_{cyl}=1.6$ nm, starting at distance $\delta = 0.3$ nm from the boundary of the cylinder. The self-diffusion coefficient of the particle is taken as $D=10^{-9}$ m^2/s. Cross symbols: numerical inversion of Eq. (1). Solid line: evolution of Eq. (2) for $t < t_{cyl}$ and Eq. (6) for $t > t_{cyl}$. Dashed line: evolution of Eq. (7) at long time, running as $1/[t\ln^2(t/t_{cyl})]$.

is a crystalized hydrous aluminosilicate mineral, of $Al_2SiO_3(OH)_4$ chemical formula. These very long, stiff and positively charged (at pH=5) nanotubes can easily be dispersed in water, yielding colloidal suspensions that show a liquid-crystalline nematic phase at high concentration. As previously reported, concentrated samples (volume fraction $\phi > 0.004$) are nematic whereas very dilute ones ($\phi < 0.002$) are isotropic [14]. In order to control the particle size and the degree of dispersion, we have performed an extended study of these colloidal suspensions using the small angle x-ray scattering technique (SAXS). The SAXS pattern (left part of Fig. 2) of a nematic suspension sucked into a capillary shows very anisotropic scattering oriented perpendicularly to the flow direction, which demonstrates that the

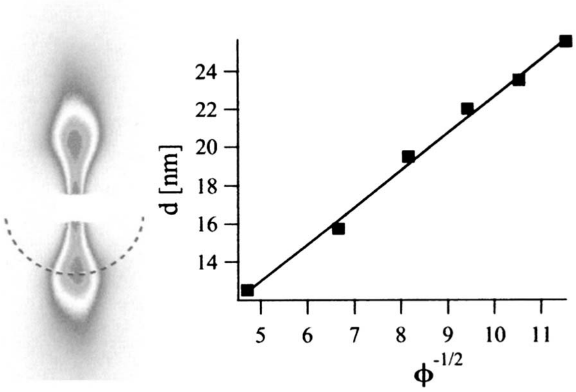

FIG. 2. Left: SAXS pattern of a flow-aligned nematic sample of imogolite suspension. The flow direction is horizontal. Right: Position of the first maximum in the radial distribution function $g(r)$ as a function of $\phi^{-1/2}$, obtained from the structure factors (symbols) and linear fit (line).

imogolite nanotubes were well aligned by the flow. The absence of any sharp reflections proves the nematic nature of these suspensions. The nematic order parameter S can be derived from a fit of the azimuthal profile of the scattered intensity by using well-established methods [15]. As expected for a lyotropic nematic phase of stiff rodlike colloids, the found value of S, mainly 0.78 ± 0.05, is fairly high. Moreover, the radial profile of the scattered intensity shows a diffuse scattering peak that arises from liquidlike positional order. We analyzed the SAXS patterns of a series of nematic samples with decreasing volume fraction ϕ. The intensity $I(q)$ recorded in the equatorial plane was divided by the form factor $|F(q)|^2$ obtained by the study of dilute isotropic samples to get the structure factor $S(q)$. Under the assumption of strong nematic order (rods oriented along z), the Fourier transform of $S(q)$ yields the radial distribution function $g(r)$ in the (x,y) plane. The position d of the first maximum in $g(r)$ is plotted as a function of $\phi^{-1/2}$ in the right part of Fig. 2. From the dilution law $d(\phi)$ and the analysis of the form factor, we infer that the rod surface is atomically smooth and that the outer diameter has a value of 3.2 nm, compatible with those given in the literature [16].

As shown by Kimmich *et al.* [7,8], it is possible to probe the intermittent dynamics of the water molecule near an interface by NMRD. In the case of a diluted colloidal suspension, the water proton intradipolar spin-lattice relaxation rate is driven by a fast molecular exchange process between bulk and interfacial regions. At low frequency $\omega = 2\pi f$, $R_1(\omega)$ can be split in three statistically independent contributions [18]:

$$R_1(\omega) = R_1^{bulk} + \phi[\tilde{R}_1^{slow}(\omega) + \tilde{R}_1^{fast}]. \tag{8}$$

R_1^{bulk} is the relaxation rate of the bulk water used in the experiment. $\tilde{R}_1^{fast}$ is related to local molecular dynamics on the interface and is almost constant at low frequency. $\tilde{R}_1^{slow}(\omega)$ depends on the intermittence between adsorption steps and relocation periods. There is almost two ways to analyze $\tilde{R}_1^{slow}(\omega)$. First, as proposed elsewhere [7], one can use the effective surface propagator which integrates adsorption and relocation events. As already mentioned, the analytical expression of this propagator is available for a flat surface, but apparently not for a thin cylinder. In this work, we will consider a second way [17], handling directly the adsorption and the relocation statistics.

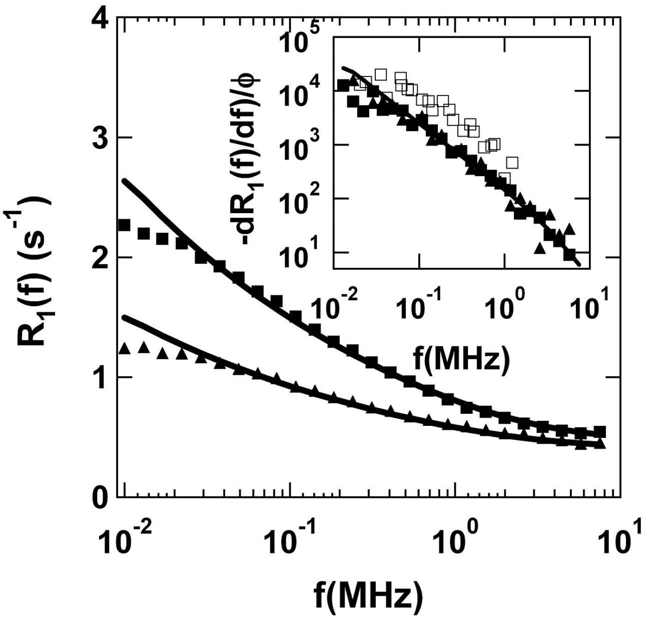

FIG. 3. Frequency dependence of water spin-lattice relaxation rate $R_1(f)$ in isotropic imogolite colloidal suspensions at 298 K. Proton NMRD at $\phi = 1.8 \times 10^{-3}$ (full squares) and at $\phi = 0.9 \times 10^{-4}$ (full triangles). Inset, frequency derivatives of the dispersion curves, normalized by the volume fraction. Open square: Deuterium NMRD in D_2O suspension at $\phi = 1.8 \times 10^{-3}$. In continuous lines: analytical model computed with Eqs. (8) and (10).

In the local framework of the cylinder, defined by the unit vector $\vec{n}_d$ oriented along the main axis, the slowest contribution of the magnetic noise $I(t)$ felt by a molecule adsorbed on the surface is related to the value of the second rank spherical harmonic function $Y_2^0(\pi/2)$ [18]. In this framework, this slowest contribution evolves as a stochastic succession of steps having the same height. $\tilde{R}_1^{slow}(\omega)$ is then equal to $\omega_d^2[\tilde{J}(\omega) + 4\tilde{J}(2\omega)]$. $\tilde{J}(\omega)$ is the time Fourier transform of the normalized correlation function $\langle I(t) * I(-t)\rangle / \langle I(0) * I(0)\rangle$ where the asterisk stands for the convolution operator. ω_d^2 is a constant taking into account the strength of the magnetic interaction in the adsorption step and the rotation transformation from the local to the laboratory framework. Following [17], $\tilde{J}(\omega)$ reads in the laboratory framework as

$$\tilde{J}(\omega) = \frac{1}{\tau_A \omega^2} \mathrm{Re}\left[\frac{[1 - \tilde{\Psi}_R(\omega)][1 - \tilde{\Psi}_A(\omega)]}{1 - \tilde{\Psi}_R(\omega)\tilde{\Psi}_A(\omega)}\right], \tag{9}$$

where $\tilde{\Psi}_R(\omega)$ and $\tilde{\Psi}_A(\omega)$ are the time Fourier transforms of the PDF characterizing the relocation, $\Psi_R(t)$, and the adsorption statistics, $\Psi_A(t)$, respectively. Equation (9) is sensitive to the two elementary steps of the intermittent dynamics. However, for smooth and homogeneous surfaces, $\Psi_A(t)$ usually evolves as $\tau_A^{-1} \exp(-t/\tau_A)$ where τ_A is the average adsorption time [17]. To sum up, Eq. (9) offers an interesting way of probing the relocation time statistics.

NMRD experiments were performed, at 298 K, on a fast field cycling spectrometer (Stelar Company). We have investigated very diluted isotropic suspensions. Each sample is characterized by only one spin-lattice relaxation time and the dispersion curves are shown in Fig. 3 for two volume concentrations ($\phi = 0.9 \times 10^{-4}$ and $\phi = 1.8 \times 10^{-3}$). The experimental accuracy on each point is on the order of 0.01. In the inset, we show the frequency derivatives of the dispersion curves, normalized by the volume fraction. The observed superimposition of proton dispersions curves allows one to check the hypothesis of a fast exchange mechanism. We also observed that proton (H_2O) and deuterium (D_2O) NMRD spectra evolve in a similar way. Relaxation processes are thus mainly due to a reorientation modulation of either an intramolecular dipole-dipole interaction for ^1H or a quadrupolar interaction for ^2H. This condition is required to assure the validity of Eq. (9).

We will now attempt to model the experimental data. $\Psi_R(t)$ shown in Fig. 1 is computed using the following experimental parameters: the measured radius of the imogolite strand $r_{cyl}=1.6$ nm, the size of a water molecule (0.3 nm) for δ, and the bulk diffusion coefficient of water $D=10^{-9}$ m^2/s. It is easy to check that in a time domain ranging from 5.0×10^{-9} s to 3×10^{-5} s, $\Psi_R(t)$ closely evolves as $\gamma/t^{(1+\mu)}$ with $\gamma=1.28$ and $\mu=0.31$. This time range largely overlaps the associated time domain of our NMRD experiments. This algebraic approximation of $\Psi_R(t)$ allows one to write $\tilde{J}(\omega)$ as [17]

$$\tilde{J}(\omega) = \frac{\tau_A}{a(1+b^2/a^2)\omega^{\mu} + (2\tau_A b\omega/a) + (\tau_A^2\omega^{2-\mu}/a)}, \quad (10)$$

with $a=|\Gamma(-\mu)|\cos(\pi\mu/2)\gamma$, $b=|\Gamma(-\mu)|\sin(\pi\mu/2)\gamma$, Γ standing for the gamma function. Equations (8) and (10) can then be used to fit the experimental data. R_1^{bulk} is directly measured on the bulk water batch used for particle dilution. Its value is 0.36 s^{-1}. The two linear parameters, $\tilde{R}_1^{fast}$ and ω_d^2 are found to be equal to 63.5 s^{-1} and 1.63×10^{10} s^{-2}, respectively. The only nonlinear parameter left is the average adsorption time τ_A. The best estimation is $\tau_A=3.6$ ns, a common value used for clay mineral surfaces [17]. Above 20 KHz, a good agreement with the experiment is observed in Fig. 3. Between 20 kHz and 1 MHz and looking at Eq. (10), we can predict an algebraic evolution of $R_1(\omega)$ characterized by the exponent μ. In the higher frequency regime, above 1 MHz, the contribution in Eq. (10) of the second term of the denominator induces a stronger decrease of $R_1(f)$ as observed in the inset of Fig. 3. Below $f_c=20$ kHz, our model overestimates the relaxation rate. Several causes can be proposed, among them, a finite persistence length l_c of the imogolite strand. In such a case and according to the relation $l_c=\sqrt{D/(\pi f_c)}$, l_c should be on the order of 130 nm. However, a more extended study is needed to characterize this last regime.

IV. CONCLUSION

In conclusion, we have presented a theoretical and an experimental study of an intermittent Brownian dynamics over a single filament. This process is characterized by one of the most heavily tailed relocation statistics that can be encountered. On one hand, the mean relocation time was shown to diverge for an infinite strand. On another hand, this mean time appears to be strongly sensitive to the finite size of the filament. Therefore a relocation strategy is only beneficial for an optimal search strategy when this heavy tail is suppressed, e.g., by a finite length effect or by a confinement induced, for example, by the neighboring strands in dense biological assemblies [3]. Our colloidal system offers an interesting way of controlling such a confinement by varying the concentration, in both the isotropic and nematic phases. How a cutoff and/or a crossover appear at long time, setting a finite mean relocation time, will be the subject of a future work.

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