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Translational and rotational coupling in Brownian rods near a solid surface

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An anisotropic macromolecule confined between two surfaces displays Brownian motion predominantly in the plane parallel to these surfaces. It can be expected that both the rotational and translational diffusion coefficients are strongly affected by hydrodynamic interactions with the walls. This work studies the more extreme case in which a rodlike particle comes into contact with a wall or in very close proximity (order of 100 nm). Experimental data have been gathered and analyzed demonstrating the rod tethering on a surface. This is compared with numerical simulations to allow estimates of proximity to the surface. The experimental data show that particle tethered motion is subject to varied degrees of constraining which imply subtle deviations in the Brownian dynamical behavior. The key finding is that a rotational-translational coupling occurs which is markedly different from the translational and rotational movements normally predicted for anisotropic macromolecules.

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I. INTRODUCTION

The relation between diffusion and frictional coefficients of Brownian particles was first established by Einstein [1,2] and Smoluchowski [3] in the context of spherical particles. More recently, considerable advances have been made into understanding the motion of spheres in confined spaces [4]. The interaction between rotational and translational Brownian diffusions in anisotropic macromolecules which results in differentiated diffusion constants parallel and perpendicular to the particle's long axis in the short term, on the other hand, was first postulated by Perrin [5,6] and established in experiments using isolated ellipsoids in suspension over 70 years later [7]. An understanding of these short-term differentiated directional diffusions holds promise of exploitation in microparticle assembly for improved functionality. It was reported recently [8] that the influence of hydrodynamic interactions with a nearby wall on the Brownian dynamics of carbon nanofibers is such that the diffusion constants are significantly reduced. One characteristic that was uncovered was that the translational diffusion coefficient perpendicular to the rod axis tends to reduce more than the translational diffusion coefficient along the axis when encountering such interactions. A description of the mechanics for this was furnished via experiments using differing chamber thicknesses and thus degrees of constraining [9]. An implicit assumption in the conduct of these experiments is that the particles have Brownian motion predominantly in the plane parallel to the surface alone (i.e., the x - y plane in Fig. 1 for state A) and that they never contact the surface. Approximately neutrally buoyant ellipsoidal Brownian particles have been observed to populate the central plane of a thin fluid chamber [7], which is an entropic effect: the number of possible orientations is reduced when the center of mass of an elongated

particle is close to a wall [10]. Besides such equilibrium effects, there are also dynamical effects. Consideration of the simple case of a hard sphere shows that if a mismatch in density between the particle and suspending medium exists, resistance to the particles movement varies according to how close it is to a wall. When the gap width between the sphere and wall, h , is small enough the friction opposing motion perpendicular to the wall increases with $1/h$ [11]. Hence, theoretically under a single constant force such as gravity, the sphere should not settle on a perfectly smooth horizontal surface. In reality this is, of course, not the case as Brownian fluctuations and forces such as the van der Waals force cause contact to occur. Likewise, Brownian rods, after an extended period of time (depending on parameters), can be found copiously attached to the surface of small fluid chambers (state C in Fig. 1). As with the sphere, the friction on the rod will increase with proximity to the wall. However, a difference in the case of the rod is that the transition needs not necessarily be directly from a free to attached state. It is possible that one end attaches first. Paradoxically once this has occurred, it is the high drag forces at the surface that severely slow down a return to the free state. So, an intriguing question to uncover is whether sticking occurs directly (state A to C in Fig. 1) or through an intermediate path with one end tethered first (state A to B to C in Fig. 1). Such an intermediate step would involve a regime in which the translational and

FIG. 1. (Color online) Description of a Brownian rod (state A) in close proximity to a surface which may attach directly (state A to C) or via an intermediate tethered mode (state A to B to C).

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rotational diffusions of the rod are strongly coupled. This would manifest itself as a breaking of the symmetry of the diffusive paths of the two ends of the rod: in bulk the two ends diffuse with similar characteristics, whereas a rod tethered at one end would not show such symmetry. By further consideration of this process, we can hypothesize that this coupling need not be an abrupt transition occurring when contact is first made with the wall. If the rod approaches the wall with a slight inclination, the distance between wall and rod surface varies along the length of the rod, and so do the hydrodynamic interaction effects. Hence, it can be expected that the symmetry is broken as a gradual process as an inclined rod moves toward the wall, finally resulting in a clearly observable rotation dominated motion when contact is made.

In this work, we will give experimental evidence of a free-to-tethered transition of carbon nanofibers including detailed time records of the diffusion dynamics. We will show that the nanofiber tethers at one end to the surface as an intermediate step. Results from a computational model developed to investigate rod to wall interactions [12] were also used to confirm the behavioral inferences.

II. EXPERIMENTAL PROCEDURE AND DATA ANALYSIS METHODS

Observations were made of carbon nanofibers diluted in a de-ionized water suspension and placed in a chamber formed between a glass slide and a cover slip. In most instances (except where otherwise described) the fluid cell was created by placing 1.5 μl of the suspension in between a square cover slip measuring 18 mm and a microscope slide, resulting in a fluid thickness of approximately 4.5 μm . This fluid filled cell was then sealed with varnish in order to avoid evaporation. Such an approach has been used for investigating bacterial movement [13], creating fluidic channels [14], and particle collection [15]. Isolated carbon nanofibers were then observed using a 100 $\times$ microscope objective on an Olympus BX51 optical microscope, with recordings made with a Hitachi HV-D30 charge-coupled device camera operating at 25 frames per second interfaced to a DVD recorder

FIG. 2. (Color online) (A) Image (cropped) of a nanofiber, annotated with the axes used in the subsequent analysis. (B) A shish-kebab rod consisting of ten consecutive spheres in a slit of height L_z , as used for the computational model. The longest rod axis is aligned in the yz plane and is (almost) parallel to the confining walls. The distance h indicates the closest distance between wall and rod, and l' is the pivot to centroid length, as explained in the text.

and a personal computer via a National Instruments 1411 frame grabber card. A suitable recording for analysis would require that (a) no neighboring nanofibers stray in, (b) the nanofiber remains fully within the recording window, and (c) ambient disturbances are minimized. Coupled with the inability to change brightness, focal distance, and position once recording commenced, it is evident that finding recordings suitable for analysis is onerous. Analysis of the images was performed using an algorithm developed to locate the centroid $x(t_n)$, $y(t_n)$ of the nanofiber in the laboratory frame, as well as its angular orientation with respect to the x axis $\theta(t_n)$, which are depicted in Fig. 2(A). The images were first processed by (i) subtracting each frame from the background frame, (ii) applying a dynamical threshold, and (iii) median filtering to remove spatial noise. Then the centroid was found using an algorithm in which the angle of rotation was determined by analyzing successive pixels on a circular trajectory around the centroid.

In an approximately two-dimensional system, such as a very thin fluid film sandwiched between solid surfaces, the dynamics of a Brownian rod is often modeled by three Langevin equations:

$$\begin{bmatrix} \dot{x} \\ \dot{y} \end{bmatrix} = \begin{bmatrix} \sqrt{2D_a} \cos^2 \theta + \sqrt{2D_b} \sin^2 \theta & (\sqrt{2D_a} - \sqrt{2D_b}) \cos \theta \sin \theta \\ (\sqrt{2D_a} - \sqrt{2D_b}) \cos \theta \sin \theta & \sqrt{2D_a} \sin^2 \theta + \sqrt{2D_b} \cos^2 \theta \end{bmatrix} \begin{bmatrix} \xi_x \\ \xi_y \end{bmatrix},$$

$$\dot{\theta} = \sqrt{2D_\theta} \xi_\theta, \quad (1)$$

where an overdot indicates a time derivative and $\xi_{x,y,\theta}$ are time derivatives of a δ -correlated random Wiener process: $\langle \xi_x(t) \xi_x(t') \rangle = \delta(t-t')$. In such a model the translational movement arises purely from translational random

increments (ξ_x, ξ_y) , and similarly rotational motion is related to ξ_θ . As such the uncoupled translational and rotational motion is characterized by the diffusion coefficients D_a , D_b , and D_θ , which describe the long length translation, short length

translation, and rotation of the rod, respectively. *In bulk*, the values for these diffusion coefficients are given approximately by [16]

$$D_a = \frac{k_B T [\ln(2r) - 0.5]}{2\pi\eta_s L}, \quad D_b = \frac{k_B T [\ln(2r) + 0.5]}{4\pi\eta_s L},$$

$$D_\theta = \frac{3k_B T [\ln(2r) - 0.5]}{\pi\eta_s L^3}, \quad (2)$$

where k_B is Boltzmann's constant, T is the temperature in kelvin, $r=L/d$ is the aspect ratio (L and d are the length and the diameter of the fiber, respectively), and η_s is the viscosity of water at T . *In an approximately two-dimensional system*, highly confined in the third dimension (i.e., with a small height component), the actual values of the diffusion coefficients are considerably lower than these bulk values due to hydrodynamic interactions with walls [8,12]. Even when a particle is relatively far away from walls the hindering effects are still felt through the long-ranged hydrodynamic interactions. As a consequence the values of the translational and rotational diffusion coefficients in the plane parallel to the walls decrease significantly as the particles come nearer to the walls. It should be noted that the model represented by Eq. (1) does not allow for coupling between rotation and translation; we merely present it here to contrast with the data presented. We will measure the diffusion parameters (D_a , D_b , and D_θ) and examine the data to elucidate the coupling which occurs.

First, to determine the rotational diffusion coefficient experimentally, we considered the ensemble average of the differenced angular positions with time via

$$\langle [\Delta\theta(t)]^2 \rangle = 2D_\theta t. \quad (3)$$

The left-hand term is the mean squared difference and a quantity which is determinable directly from the image analysis. Similar expressions are applicable to D_x (related to Δx), D_a (related to Δa), and D_b (related to Δb), with the latter two being found from the centroid movement using

$$\begin{bmatrix} \Delta a \\ \Delta b \end{bmatrix} = \begin{bmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{bmatrix} \begin{bmatrix} \Delta x \\ \Delta y \end{bmatrix}. \quad (4)$$

As the rod progresses toward the solid surface we expect to witness a change in behavior. Therefore, a method is required to observe the alteration of the diffusion coefficients as a function of time. To do this the time data were broken into segments of N frames. For the segment consisting of frames i to $i+N$, the diffusion coefficient was then calculated independently. In this way, which is akin to a short-term Fourier transform, rather than having a single diffusion value for the whole data set, we obtain a value for the diffusion constant as a function of time. Clearly, it is important to ascertain a value of N that enables the diffusion trends to be revealed.

In order to detect a possible suppression of the motion of a tethered end of the nanofiber, it is useful to depict the trajectories in terms of the centroid locations (which should be in the form of arcs for perfect tethering) and the tethered end locations (in the form of spots) in time. The latter was

calculated using the nanofiber's pivot-to-centroid length l' and angle θ information relative to the centroid's Cartesian coordinate location x, y via

$$x_{end} = x - l' \cos \theta, \quad y_{end} = y + l' \sin \theta. \quad (5)$$

The value of l' was measured from the image data and essentially constituted the length minus the diameter of the nanofiber divided by 2. This is consistent with the assumption that the fibers have a cylindrical body with hemispherical ends, and that the tethering point is located on one of these hemispherical ends.

III. SIMULATION RESULTS

The translational and rotational diffusion coefficients of a particle in the presence of a wall are difficult to obtain theoretically. Analytical expressions in the creeping flow limit (applicable to small particles undergoing Brownian motion) are known, but are limited to the case of a spherical particle [11,17] or to a nonspherical particle whose major (hydrodynamic) axes are aligned with the wall and which is far removed from the wall [18,19]. In the general case, as encountered in this work, particles are not aligned with the wall and/or may not be far removed from it. One then has to resort to experiment or numerical evaluation to obtain the diffusion tensor or its inverse, the friction tensor. In the experimental section we will report on observations of significant decreases in translational and rotational diffusion coefficients compared to the expected (bulk) values. These findings will be confirmed by computer simulations in this section.

Numerical evaluation of the friction on a particle can be performed in several ways: by numerical summation of the forces due to a large number of Stokeslets distributed over the walls and surfaces of the particles [20,21], possibly including image singularities to efficiently capture the effect of the wall [22–24], or by a multipole expansion of the force densities induced on the spheres, also with an image representation to account for the wall [25,26].

In this paper we will use an alternative and particularly simple way to determine the friction on a colloidal particle, using molecular-dynamics simulations which explicitly include the solvent particles [12]. Because of the large difference in length scales between a colloidal particle and a solvent molecule, it is impossible to perform such simulations in full atomistic detail. Some form of coarse graining is necessary. Here, we choose the stochastic rotation dynamics (SRD) method to effectively represent the solvent [27]. The solvent interacts with walls and colloidal particles through excluded volume interactions [28–30]. Stochastic stick boundaries are implemented as described in [29]. In short, SRD particles which overlap with a wall or colloid are bounced back into the solvent with tangential and normal velocities from a thermal distribution. The change in momentum is used to calculate the force on the boundary. We note that despite the fact that the boundaries are taken into account through stochastic collision rules, the *average* effect is that of a classical stick boundary as often employed in (Stokesian) continuum mechanics. Because we determine

FIG. 3. (Color online) Computed translational diffusion coefficients as a function of normalized closest distance h/L_z for an untethered shish-kebab rod of $6 \mu\text{m}$ length and $0.6 \mu\text{m}$ diameter, lying almost parallel to the walls of a slit of height $L_z = 4.5 \mu\text{m}$ filled with water ($\eta = 10^{-3} \text{ Pa s}$). Different directions are indicated by different symbols: translations along the longest rod axis ($\sim y$; circles), translations perpendicular to the rod but along the wall ($\sim x$; squares), and translations perpendicular to the rod and perpendicular to the wall ($\sim z$; diamonds). Open (closed) symbols are for an angle of 80° (90°) between wall normal and rod axis. Dashed lines indicate the rod diffusion coefficients D_a and D_b in bulk.

frictions by taking long time averages, the average flow velocities close to the boundaries will be effectively zero in all directions. We have shown previously that this method accurately resolves the hydrodynamic fields and forces to distances as small as $d/16$ [12,29,30].

Specifically, here we study the friction on a shish-kebab model of a rod of aspect ratio 10, i.e., ten touching spheres on a straight line, as a function of distance to planar walls for (nearly) parallel configurations [see Fig. 2(B)]. The two planar walls are 7.5 rod diameters (or 0.75 rod lengths) apart. The friction components are obtained by analyzing the auto-correlations of the constraint forces and torques needed to constrain the colloidal configuration. We have chosen our simulation parameters such that, in SI units, our rod has a length of $6 \mu\text{m}$ and a diameter of $0.6 \mu\text{m}$, and the solvent has a viscosity of 10^{-3} Pa s (equal to that of water). More details on the simulation method, parameters, and constraints are given in the Appendix to this paper. For validation of its accuracy, we refer the reader to Ref. [12]. Although the aspect ratio of 10 and the shish-kebab shape are not exactly the same as those of the rods studied in the experiment, the similarity is close enough to draw valid qualitative conclusions.

In the bulk and in the absence of walls, the measured diffusion coefficients are $D_a = 0.160 \mu\text{m}^2/\text{s}$ and $D_b = 0.110 \mu\text{m}^2/\text{s}$, respectively, for our chosen simulation parameters (see [12]). We observe that all components of the diffusion tensor are reduced compared to the bulk values due to hydrodynamic interactions with nearby walls. Figure 3 shows the calculated translational diffusion coefficients as a function of the closest distance h between rod surface and wall, for 80° and 90° angles between the long rod axis and wall normal (i.e., 90° corresponds to the case where the rod lies parallel to the wall). Circles denote D_a and squares denote D_b ; values measured in bulk are indicated by black (up-

per) and red (lower) dashed lines, respectively. In agreement with experimental observations [8], the diffusivity perpendicular to the rod (D_b) is relatively more reduced by wall-induced hydrodynamic interactions than the diffusivity parallel to the rod (D_a). This statement remains valid for all distances to the wall.

Although in the current experimental setup the diffusion coefficient toward and away from the wall is very difficult to measure, the computations offer us insight into its dependence on the closest distance h . We observe that diffusion perpendicular to the wall is greatly reduced even at relatively large distances from the wall when the rod lies parallel to the wall (filled diamonds in Fig. 3). At small distances h the diffusion coefficient appears to scale linearly with h , in agreement with the expected asymptotic scaling from lubrication theory. This significant reduction in diffusion away from the wall may explain why, once a nanofiber is located close to one of the walls (which in itself may have taken a long time), it takes prohibitively long to escape back toward the center of the chamber.

The rotational diffusion is also influenced by the presence of confining walls. It is important to distinguish between rotation around the centroid and rotation around one of the rod's ends. A full discussion on rotations around the centroid may be found in Sec. IVB of Ref. [12]. Here, we limit ourselves to noting that the computational model predicts a bulk rotational diffusion coefficient around the centroid of 0.035 s^{-1} , and that the rotational diffusion generally decreases when the closest distance h between rod and wall is decreasing.

In the current work we focus on tethered behavior, where the rotations take place around a location closer to one of the rod's ends. A naive estimate for the rotational friction around one of the rod's ends would be to view it as a rotation around the centroid plus a matching translation, perpendicular to the rod's longest axis, on a circular path of radius $l/2$. Through the inverse relationship between friction and diffusion, this leads to $(D_\theta^{\text{end}})^{-1} \approx (D_\theta^{\text{cen}})^{-1} + (L/2)^2 (D_b)^{-1}$. Using the bulk values mentioned above this leads to a bulk rotational diffusion around an end of 0.0091 s^{-1} .

To check the above estimation and to study the effect of nearby walls in more detail, we have performed simulations corresponding to a rod one of which ends is fixed (tethered) to a specific location. Figure 4 shows the rotational diffusion coefficient for rotations around the fixed end as a function of closest distance h between rod and wall, for 80° and 90° angles between rod and wall. Again we observe that all diffusion components are reduced compared to the bulk value because of hydrodynamic interactions with the wall. Experimentally, only rotations around the axis perpendicular to the wall (around the z axis; squares in Fig. 4) are observable. The simulations show that for a rod lying parallel to the wall (closed symbols) the rotational diffusion around this axis is somewhat reduced as h is decreased, but not as strongly as the rotational diffusion around the x axis. The latter corresponds to rotations which bring one part of the rod closer to and another part further away from the wall. Again a linear lubrication-type scaling is observed at small h . These simulations clearly show that, once a nanofiber is located close to one of the walls, there is a significant reduction in *both* trans-

FIG. 4. (Color online) Computed rotational diffusion coefficients for rotations around the sphere located at the rod end which is closest to the wall [see Fig. 2(B)] as a function of normalized closest distance h/L_z . Rotations around the x axis are indicated by circles, and rotations around the z axis are indicated by squares. Open (closed) symbols are for an angle of 80° (90°) between wall normal and rod axis.

lational and rotational diffusions away from the wall. Again this explains why it takes prohibitively long to escape back toward the center of the chamber. We will use these simulation results to interpret our experimental observations in the next section.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

A. Observations of the transition from a free to a tethered rod

By laboriously tracking the motion of nanofibers over long durations it is possible to witness the transition from a free state to an end tethered state. Figure 5 depicts the time-based record of centroid positions [Fig. 5(A)] and angular positions [Fig. 5(B)] of a nanofiber $6.81 \times 0.93 \mu\text{m}^2$ in dimension that progressed from free movement to tethering. The centroid positions [Fig. 5(A)] do not reveal any obvious directional characteristic prior to tethering. This record, and others that we have examined, also do not indicate preferred locations where tethering occurs. The condition of tethering is evidenced in Fig. 5(A) by an arc-shaped trajectory. The

figure includes an inset in which four images of the tethered nanofiber recorded 40 s apart are overlaid to visually indicate the nature of the motion observed. Unlike the case of the centroid, the angular positions [Fig. 5(B)] do not indicate any characteristic behavior at the onset of tethering. This implies the tethering point allows considerable rotational freedom. These findings also allow us to infer that tethering is not due to the fiber end getting entangled or jammed onto a coarse surface defect, but more likely due to contacting the surface and remaining tethered by interaction with gentle surface roughness and possibly van der Waals forces. Also, this permits for a motion model to be adopted in which the end can be taken as a contacting hemisphere.

Clearly the result in Fig. 5 shows that the transition from state A to C (with reference to Fig. 1) goes through an intermediate step B. Further analysis will now be performed on the data (using the tools described in Sec. II) to examine the evolution of the diffusive behavior during this transition.

Figure 6 provides diffusion coefficient plots over time of the particle trajectory presented in Fig. 5. The length of the segment for diffusion analysis (see Sec. II) is set to 8000 images, which is a compromise between obtaining a sufficient data set to obtain a quantification of the stochastic process and retaining enough information on the time evolution. Figures 6(A) and 6(B) show the evolution of D_x and D_a , respectively. In describing the diffusive behavior it is more useful to consider D_a with its inherent link to the body frame of the rod. Figure 6(B) is divided into three regions. Region I refers to the case where the rod is moving freely. Tethering began immediately at the end of region I. This corresponds with a sharp drop in the diffusion coefficient value. However, due to the moving window approach in calculating the diffusion coefficients, and the resultant averaging over time, the start of the segment must move 8000 images beyond the onset of tethering before tethering behavior is measured fully. The fact that region II is of this length indicates a sudden transition from the free to the tethered state. It is, thus, in region III that the diffusion coefficients of the tethered case are obtained. Figures 6(C) and 6(D) give the evolution of D_b and D_θ . If Figs. 6(B) and 6(C) are observed together, it can be seen that a trough in values in region I occurs at approximately frame 30 000 in both plots. We sur-

FIG. 5. (Color) (A) The plot of the motion of the centroid of a rod undergoing the transition from free random movement (blue) to tethered arc like movement (red); (B) the associated angular values which complete the data set.

FIG. 6. (Color online) The diffusion coefficient calculated by segmenting the full data set into windows consisting of 8000 sequential images, with the window being moved in steps of 100 images, hence giving plots of (A) D_x , (B) D_a , (C) D_b , and (D) D_z against time. In (B) the different regimes are shown: region I indicates a free rod, region II is a transitional stage which comes about due to the length of the window, and region III is a tethered rod.

mise that at this time the rod has moved closer to the wall hence reducing diffusion. There is a general correlation in the observed rises and falls in both translational diffusion coefficients in the free regime. This then would be expected to correspond to a fluctuation of rod height within the chamber, even though the angular orientation [about the x axis in Fig. 2(B)] will also play a role.

The computational model demonstrates a decline of translation diffusion as the height of the rod decreases (Fig. 3). This decline occurs steeply within the lubrication layer at very low heights. The experimental data in regime I, the free state, show D_a averaging at $0.0347 \mu\text{m s}^{-1}$ and D_b of $0.0214 \mu\text{m s}^{-1}$. When compared with the bulk values [using Eq. (3)] of 0.205 and $0.149 \mu\text{m s}^{-1}$, respectively, these represent 83% and 86% reductions. To obtain such a degree of reduction, the computational model results call for a rod parallel to the chamber surface (Fig. 3) to be as close as 60 nm from the nearest surface. If the rod is inclined then one end will be closer than this. The movement of rods closer to the surface is a gravity effect and can be contrasted to previous experimental results for free rod diffusion, in which a polymer rod (which can be expected to have a very small density mismatch with the surrounding fluid) would stay predominately within the central horizontal plane of the chamber [7]. The value of D_a is observed to vary over a range from 0.028 to $0.040 \mu\text{m s}^{-1}$, while that of D_b is rela-

tively more restricted, varying as it does over a range of 0.019 – $0.024 \mu\text{m s}^{-1}$. This is consistent with the computational results, as can be seen from Fig. 3 by the slope of the lines depicting the translational diffusion coefficients at low heights, which find the slope of D_a to be significantly steeper than for D_b indicating that any change in height will effect D_a more strongly. While the height is likely to be altering during free diffusion, it is reasonable to assume this fluctuation to be rather limited. In fact the linear relationship between diffusion coefficients and height within the lubrication layer should translate to relative changes in D_a ($\pm 17\%$) and D_b ($\pm 12\%$) being similar to relative changes in the gap width h (errors arise due to the stochastic nature of the process and angular changes out of viewing plane). The small range of heights is consistent with the very low diffusion coefficient in the z direction, D_z . Once tethering occurs, a sharp reduction in the translational diffusion is observed and a more gradual reduction in the rotational diffusion. The latter will be inspected in more detail in the next section by analyzing the long time sequence data of tethered rods.

In summary, comparison between computed and experimental translational diffusion coefficients of a free rod has indicated that the rod is moving in very close proximity to the glass surface of the fluid chamber. In such a regime all the diffusion coefficients become very low. This may appear contradictory to the observation of tethering which requires a

FIG. 7. (Color) Spatial trajectories of the centroid (arcs) and tethered ends (spots) for carbon nanofibers measuring (A) 5.56×0.87 (length $\times$ diameter) μm^2 and (B) 7.50×1.04 μm^2 . Color coding has been used to split the data into time segments; in the case of (A) the segment lengths are chosen to highlight the movement of the tethered end, while in (B) the segments are equal in length. While both nanofibers are end tethered, they exhibit subtle differences which have important ramifications for the Brownian dynamics at play.

rotation or height change to occur such that one end tethers at the glass and for this transition to occur rapidly. While these relatively large fluctuations toward the surface are rare, one should still be able to locate them under a painstaking effort. This reconciliation of the apparent contradiction is consistent with experimental experience. Apart from the difficulty in finding the presence of such rods, one has to also contend with the need to obtain long periods of data in which the location surrounding the tethered rod remains clear of the presence of other suspended material. If the probability of finding tethered rods is rare, the probability of observing a transition to tethering is considerably still smaller.

B. Trajectories and rotational diffusion of tethered rods

We have observed and discussed the transition from a rod moving in both translational and rotational manners to one in which the rotational movement is by far the dominant. Now attention is turned to investigating the nature of the latter case by studying what we term “tethered” rods. Figures 7(A) and 7(B) depict the trajectories of two separate nanofibers. The locations of the centroid positions (in the form of arcs) and the tethered end (spots) are plotted over time. The two data sets used are from 5.56×0.87 (length $\times$ diameter) μm^2 [Fig. 7(A)] and 7.50×1.04 μm^2 [Fig. 7(B)] carbon nanofibers with trajectory recordings each lasting approximately 30 min. Color coding was used to split the data into different time segments. In Fig. 7(A) these segments are chosen such as to highlight the moving tether, while in Fig. 7(B), where this movement does not occur, the segments are of equal length. Two notable differences are observed. First in Fig. 7(A) the angle of spread is larger than in Fig. 7(B), with complete rotations occurring in the former. We postulate that this indicates a stronger and so more restrictive tethering in the case of Fig. 7(B). Second, the tethering location of Fig. 7(A) can be seen to move in a slip-stick manner, while that of Fig. 7(B) does not, again pointing to the postulated difference in tethering strength. The fact that the apparent tethering point can move in one of the cases

FIG. 8. (Color online) The rotational mean square difference parameter calculated for two carbon nanofibers, 5.56×0.87 (length $\times$ diameter) μm^2 in blue (upper) line [case (A)] and 7.50×1.04 μm^2 in green (lower) line [case (B)], both of which exhibit end tethered behavior. For case (A) the data are linear, while for case (B) a loss of linearity occurs at larger time intervals.

points to the fact that the tether is not created by a single larger protrusion from the surface.

To investigate the nature of the tether further, in Fig. 8 we show the mean square difference of the angle for each of the two cases. The data indicate a rotational diffusion coefficient of 0.013 s^{-1} for the nanofiber in case (A) compared with a theoretical value (free rod far from a wall) of 0.0458 s^{-1} . For the nanofiber in case (B), these values are 0.0035 s^{-1} (estimated for correlation times $< 1 \text{ s}$) and 0.0202 s^{-1} , respectively. This represents reductions to 28% and 17% of the bulk values. In case (B) the rotational diffusion coefficient can only be estimated because no true linear relation (slope of 1 on the double-logarithmic scale) between the mean square displacement (MSD) and time is observed. This implies that the movement is not purely diffusive for case (B), as does the incomplete circle describing the centroid movement (although this is not conclusive statistically). It is likely that the tether imposes a restriction on rotational movement, as well as preventing translation of the tethered end. By contrast, the MSD plot for case (A) is linear and a full sweep of angular locations is covered.

C. Translation-rotation coupling

In the introduction the hypothesis was stated that when contact is made with a solid surface there would be a coupling between translational and rotational diffusions leading to an asymmetry in the movements of each end of the rod. We most clearly observe this in data set (B). It was also stated that this transition from symmetric motion of the ends to asymmetric motion does not require contact with the solid surface. When the rod is very close to the surface and slightly inclined, the height difference along the length of the rod leads to differences in the degree of hydrodynamic interaction and hence an asymmetry. Concurrent with this, a coupling between the translational and rotational diffusion coefficients will emerge. Under such conditions it would be

expected (i) that a full range of rotational angles could be achieved (as there is no contact with the surface to impose a restriction), (ii) that the behavior would be fully diffusive, and (iii) that due to out of viewing plane alterations the nature of the tether may change over time. These three points are all consistent with the data collected from data set (A).

It can be expected that data set (A) will make a better comparison with the simulated model because the rotation appears less restricted. The model presents diffusion coefficients for rotation around a tethered at different heights of this end above the surface. In the experimental case we would expect the end to be at or extremely close to the wall. For a rod inclined at 90° to the normal, the simulation model predicts a value close to zero, while at 80° the predicted diffusion is on the order of 15% of the bulk rotational value. In the experimental case (A) the tethered rotational diffusion is 28% of the bulk value. In this case, the translational data indicate that the rod is within 60 nm of the wall prior to tethering, suggesting that the inclination of the rod is above the 80° value modeled. It appears that even if we take the 80° value, the reduction in rotational movement is overestimated when we compare it to the experimental data. This can be explained by the modeling approach used which assumes perfect end-sticking conditions, with the center of rotation on the rod end closest to the wall. However, our hypothesis states that when the rod is approaching the wall there is a gradual change in the location of the center of friction from the centroid toward the end closest to the wall. The center of rotation may not fully shift to the end of the rod, in which case the model will underestimate the actual rotational diffusion coefficient.

Further evidence for the coupling can be obtained from the experimental data by considering the time progression of rod (A) in the body frame, wherein Δa and Δb are the changes in location of the centroid between successive time frames. If we consider a tethered rod we obtain the further equation $\Delta b = l \Delta \theta$ from the small-angle approximation, where l is defined by this relationship. Previously a value l' has been defined as the expected pivot-to-centroid length, based on the expectation that the pivot should occur at the end of the cylindrical section of the rod assuming that contact takes place with the wall. Indeed if the rod is constrained at this point then $l' = l$. Figure 9(A) depicts the time evolution of the angular position of the nanofiber in (A). Rather than considering l as the ratio of the differential values of b and θ , an integral was performed instead. This has the effect of rendering the data less noisy, albeit it requires the angle of the rod to be nonzero. For the data of the nanofiber in (A), the calculation of l was done 350 s after the experiment was started, over a period in which the angle was nonzero. These data are presented in Fig. 9(B). In the case of the nanofiber in (A), l' is $2.35 \mu\text{m}$. Figure 9(B) shows that the value of l is consistently lower than l' . Hence, for any given $\Delta \theta$ value, Δb would be lower than what would be expected under perfect end-sticking conditions. This shows that slip occurs with respect to the surface in opposite direction to the sense of rotation of the nanofiber. This consistent slipping together with the larger scale movement of the tethered end shown in Fig. 7, and the diffusive nature of the data, implies that the rod does not make contact with the surface. This shows that

FIG. 9. (Color online) (A) Time evolution of the angular position θ (degrees) and (B) the calculated radius of rotation l (μm) for the case of the carbon nanofiber measuring 5.56×0.87 (length $\times$ diameter).

the coupling is due to hydrodynamic interaction based effects, with the center of rotation moving toward the end of the rod and located at distance l without reaching the rod end (l').

V. CONCLUDING REMARKS

The tethering motion of Brownian rods in close proximity or contact to a surface has been identified, demonstrated, and characterized. Sedimentation brings the rods investigated into close proximity to the lower chamber surface, an analytical comparison suggests as little as 60 nm. From this state a transition has been witnessed experimentally, which causes the rod to appear tethered at one end, with all further motion almost entirely rotational. The exhibition of two different modes, one in which the rotation is not purely diffusive suggesting a rotational friction due to the tether itself and a second in which the behavior remains diffusive, sheds light on the interesting nature of the tether. The former suggests direct contact with the surface. The latter, which manifests infrequent movement of the tethering location, alternatively appears to indicate a tether dominated by fluid friction effects.

The stick-slip response of the end tethered nanofiber shown here may provide some insight as to how some rod-like organisms are able to evolve the means to tether [31–33] and even move near surfaces. Apart from serving as a model to explain biophysical activity, the tethered carbon nanofiber

offers advantageous means in providing important localized information of the medium in which it resides. The merits of such a sensor include its minimal disturbance to the evolution of the measured quantity around the localized environment [34] and an absence of any input energy to drive the probe. Apart from temperature, some recent clever adaptations have been made to measure parameters such as magnetic susceptibility [35], viscosity [36], and surface forces [37]. While fluctuations in the Brownian motion using freely translating particles should provide significant information, there is the problem of these particles drifting away from the venue of measurement as well as colliding with other particles. Hence, the advantage of a tethered entity is clear. Nevertheless, challenges remain in relating to any physical activity since such a relationship is governed by knowledge of ζ_r , the rotational drag coefficient, which is influenced by the nearby wall in a complicated way. Generally, the tethered rods demonstrate a coupling between translational and rotational diffusive effects. Simulations to investigate this coupling are an obvious extension to the work presented here, which furnishes experimental evidence of Brownian mediated end tethering behavior of rods.

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APPENDIX: DETERMINATION OF THE HYDRODYNAMIC FRICTION ON A ROD BY CONSTRAINED SIMULATION

In this appendix we provide some details on the simulations we performed of a rod near a solid surface. Because of the large difference between time and length scales of solvent molecules and the solute (in this case a rod), it is advantageous to treat the solvent on a mesoscopic level. In this work we have used SRD [27–30], which is a particle-based simulation scheme in which the solvent-solvent interactions are coarse grained in time and space, while an “atomistic” description is adopted for the solvent-solute interactions.

In SRD the solvent is represented by a very large number of point particles (typically millions). The coarse-grained dynamics of the solvent is made up of two steps: streaming and collision. In the streaming step, the position $\mathbf{r}_i$ and velocity $\mathbf{v}_i$ of a solvent particle i are propagated for a time δt by solving Newton’s equations of motion. In the collision step the solvent is subdivided into cubic cells of size a_0 . Then a stochastic rotation of the solvent particle velocities is performed according to

$$\mathbf{v}_i \mapsto \mathbf{u} + \Omega\{\mathbf{v}_i - \mathbf{u}\},$$

where $\mathbf{u}$ is the center-of-mass velocity of the particles within a cell and Ω is a matrix which rotates velocities by a fixed angle α around a randomly oriented axis. Through the stochastic rotation of the velocities, the solvent particles can

efficiently exchange momentum without introducing direct forces between them during the streaming step. As the collision step preserves mass, linear momentum, and energy, the correct hydrodynamical behavior of the solvent is obtained on the mesoscopic scale [27,28]. Analytical solutions are known for the hydrodynamic properties of the solvent, such as its viscosity [38]. These properties depend on the choice of parameters: particle mass m , cell size a_0 , temperature kT , rotation angle α , collision interval δt , and average number of particles per collision cell. In our work we use m , a_0 , and kT as units of mass, length, and energy. The number density is set to five particles per collision cell, the rotation angle is $\alpha = \pi/2$, and the collision interval is $\delta t = 0.1t_0$, with time units $t_0 = a_0(m/kT)^{1/2}$. In our units, these choices mean that the solvent viscosity takes the value $\eta = 2.5m/(a_0t_0)$, and the kinematic viscosity is $\nu = 0.5a_0^2/t_0$. The Schmidt number Sc , which measures the rate of momentum (vorticity) diffusion relative to the rate of mass transfer, is given by $Sc = \nu/D_f \approx 5$, where D_f is the fluid particle self-diffusion constant [30]. In a gas $Sc \approx 1$, momentum is mainly transported by moving particles, whereas in a liquid Sc is much larger and momentum is primarily transported by interparticle collisions. For our purposes, it is only important that vorticity diffuses faster than the particles do.

The coupling of the solvent with walls and embedded objects, such as the shish-kebab rod studied here, is achieved as follows. During the streaming step, when a solvent particle overlaps with a wall or embedded object, it is moved back to the impact position $\mathbf{r}_i^{imp}$, and the solvent particle is displaced with a new velocity for the remaining part of the time step. To mimic thermal no-slip boundary conditions this new velocity is extracted from the following distributions for the tangent (v_t) and normal (v_n) components of the velocity, with respect to the surface velocity:

$$p(v_t) = \sqrt{\frac{m}{2\pi kT}} \exp\left(-\frac{mv_t^2}{2kT}\right),$$

$$p(v_n) = \frac{mv_n}{kT} \exp\left(-\frac{mv_n^2}{2kT}\right).$$

All changes in solvent particle velocities, $\Delta \mathbf{v}_i$, are summed and used to update the force $\mathbf{F}$ on the embedded object: $\mathbf{F} = -(m/\delta t)\sum_i \Delta \mathbf{v}_i$, where the sum runs over all particles that have collided with the object during the time step and the minus sign arises from Newton’s third law. Similarly, the torque on the embedded object is given by $\mathbf{T} = -(m/\delta t)\sum_i \mathbf{r}_i^{imp} \times \Delta \mathbf{v}_i$. Note that in this work the torque was determined with respect to the pivoting point, i.e., $\mathbf{r}_i^{imp}$ was determined relative to the location of the bead closest to the wall.

The hydrodynamic friction on a rod near a wall depends sensitively on its location and orientation. Diffusional processes, however, cause this location and orientation to change continuously. We therefore choose to measure the friction while keeping the position and orientation of the rod fixed. The advantage of such an approach is that the constraint force $\mathbf{F}^c$ and constraint torque $\mathbf{T}^c$ needed to keep the rod at a fixed position and orientation can be recorded over a

very long time interval, in our work typically $10^6 t_0$. These data can then be used to calculate the translational and rotational friction matrices (tensors) Ξ and Z through the Green-Kubo relations [12]:

$$\Xi_{\alpha\beta} = \lim_{t \rightarrow \infty} \frac{1}{kT} \int_0^t \langle F_\alpha^c(\tau+t) F_\beta^c(\tau) \rangle_\tau,$$

$$Z_{\alpha\beta} = \lim_{t \rightarrow \infty} \frac{1}{kT} \int_0^t \langle T_\alpha^c(\tau+t) T_\beta^c(\tau) \rangle_\tau,$$

where $\alpha, \beta \in \{x, y, z\}$ and the pointy brackets indicate an average over many time origins τ . The translational and rotational diffusion tensors are obtained by inverting these matrices (and multiplying by a trivial factor kT). In this work, with the rod lying nearly parallel to the y axis and the wall normal along the z axis [as shown in Fig. 2(B)], the diffusion coefficient D_a can be read off as the yy component and D_b as

the xx component of the translational diffusion tensor, while D_θ can be read off as the zz component of the rotational diffusion tensor.

Finally, we note that despite the large number of solvent particles, at any time the rod interacts with a much lower number of solvent particles than would be the case for a real colloidal rod. This leads to a somewhat larger diffusivity of the simulated rod. One can quantify this effect exactly and correct for it, as explained fully in Ref. [12].

In previous works we have confirmed that the above approach leads to a correct friction and flow field for a colloidal sphere if the radius of this sphere is greater than $2a_0$ [29,30]. To be on the safe side, as in Ref. [12], we have chosen a radius of $4a_0$ for the spheres in our shish-kebab rod model. We have validated this method of determining the friction by comparing the measured friction on a sphere near a wall with known theoretical expressions [12]. Good agreement was found for gap widths between sphere and wall ranging from many sphere diameters to as small as 1/16th sphere diameter.

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