Magnetic confinement of Brownian rotation to a single axis and application to Janus and cluster microparticles

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(Received 9 July 2010; accepted 10 August 2010; published online 7 October 2010)

We present an experimental, one-dimensional, Brownian rotation system in which the free rotation is confined to a single axis. Control of the rotational diffusion of a single microparticle, or particle aggregate, around a chosen axis, was performed by using a static 1.0 mT external magnetic field. The confined object rotated freely around the chosen axis, and that axis was confined to within 3.9°. This method presents several advantages and may have wide applicability in biological and physical systems of interest. © *2010 American Institute of Physics*. [doi:10.1063/1.3485296]

Brownian translation and rotation, as models for the study of diffusion mechanisms, have been of historic and fundamental importance to a plethora of fields, including physics, nanoscience, chemistry, biology, and economics.[1–3] Rotational Brownian motion was discovered by Brown in 1827,[4] later described by Einstein in 1906 using thermodynamics,[5] and implemented by Perrin to determine Avogadro's number in 1909.[6,7] While translational Brownian motion is better known and more often used, Brownian rotation is also important to many fields (e.g., biology[8] and astrophysics[9]). Constructing a strictly one-dimensional Brownian rotation system, as demonstrated here, is of practical importance and potentially of theoretical interest.

In contrast to Brownian translation where Einstein's analytical formalism is rigorous, regardless of the number of dimensions of motion, the Einstein rotational formalism[5] is only rigorous for one-dimensional Brownian rotation.[10] One dimensional Brownian rotation has been observed experimentally in the past;[11] however, there has been a lack of direct measurements for unrestricted one-dimensional Brownian rotation systems, i.e., systems that rotate freely about a single fixed axis. For example, Kappler[12] created a torsion balance by suspending a mirror from quartz fibers. Cheng and colleagues[13,14] trapped disk-like colloids in optical tweezers. In these experiments, the observable body that undergoes one-dimensional rotation is hindered from freely rotating, e.g., it experiences a potential that hinders its one-dimensional rotation. In the case of Kappler, the mirror cannot turn freely. In the case of Cheng *et al.*, a potential resisting free rotation is created by the optical trap. More recently, Altintas and colleagues were able to implement magnetic clamping to confine the diffusion of individual nanorods.[11] Additionally, systems with asymmetric particles have been used to study the coupling between translational and rotational diffusion.[15,16] However, all of the above systems require a significant restriction on the Brownian motion around the rotational axis (i.e., a "passive" restoring force that hinders the rotation). Furthermore, these systems sometimes cannot be performed on a single spherical particle, but require more than one particle.

In this paper, we demonstrate and experimentally validate one-dimensional rotational diffusion, without restrictions along the diffusion axis, for a single particle, as well as for an aggregate. To create and actively control a one-dimensional rotator that is free to diffuse through all angles in a single plane, we implement magnetic Janus particles,[17–19] see Fig. 1. Janus particles have two chemically or physically different hemispheres and have been useful for a variety of applications and measurements.[19] Here, we orient such a magnetic particle in a static magnetic field so that the rotational diffusion of single particles and particle aggregates can be observed with standard bright-field microscopy.

Janus particles were fabricated from spherical polystyrene particles with a 2 μm diameter that were dispersed onto a glass substrate and coated by evaporating a 200 nm nickel layer (this process is described in more detail in Ref. 20). Alternatively, commercially available magnetic particles can be half coated with aluminum or other materials to fabricate Janus particles.[18] The metallic layer of the Janus particle provides optical asymmetry and, depending on the rotational axis, creates a modulated intensity (with magnetic field applied parallel to the imaging plane) or a constant intensity with changing angular orientation [magnetic field applied perpendicular to the imaging plane—as shown in Figs. 1 and 2(a)]. Using this method, the rotational axis can be actively

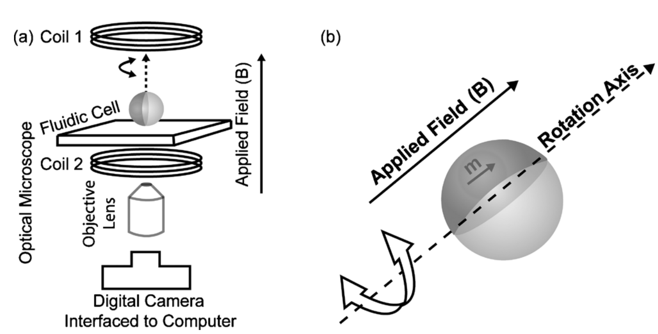

FIG. 1. Schematic representation of (a) the experimental optical microscopy setup and set of Helmholtz coils used to observe the one-dimensional rotation of a single Janus particle and (b) the concept underlying the one-dimensional rotation of a magnetic microsphere, where the particle rotates around a chosen and fixed axis determined by the orientation of the applied magnetic field.

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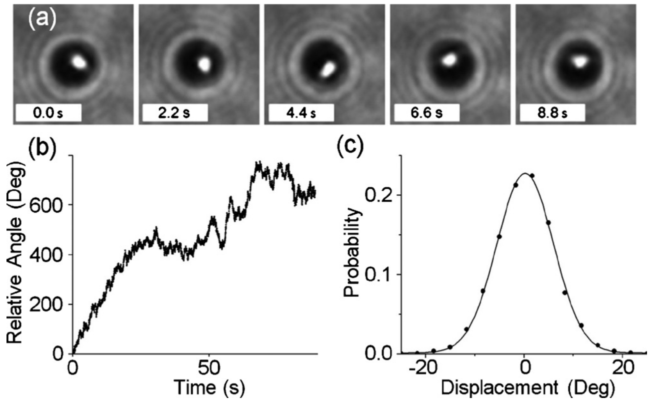

FIG. 2. (a) Bright field microscopy images of one-dimensional Brownian rotation of a single 2.0 μm diameter microsphere magnetized through the equator and rotating around a 1.0 mT fixed axis that is parallel to the optical axis (perpendicular to the imaging plane). The images are shown for every 100th frame (2.2 s intervals) at a frame rate of 45 frames per second, where the image size is approximately 5×5 μm^2. The bright spot in the image is caused by transmitted light passing through the noncoated hemisphere of the microsphere that does not have a thin nickel film (a similar particle is shown in a real-time video online). (b) Angular orientation in time for the particle shown in part (a) and (c) the resulting angular step displacement probability distribution function: circles are experimental values and the line is a Gaussian fit (enhanced online). [URL: http://dx.doi.org/10.1063/1.3485296.1]

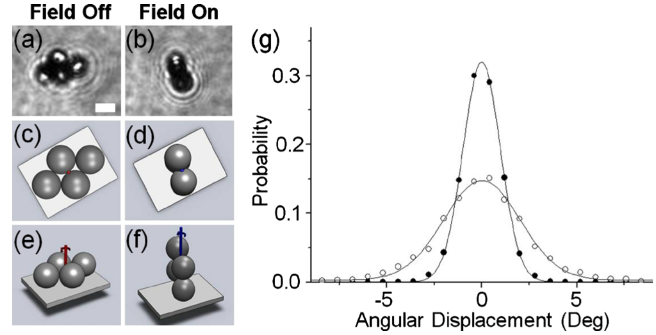

FIG. 3. (Color online) Microscopy images of a four particle aggregate with (a) no applied magnetic field and (b) with a 1.0 mT field applied along the optical axis (in the direction perpendicular to the imaging plane), where the scale bar is 2 μm. Schematic illustrations of the same aggregate oriented on the glass-fluid interface with (c) and (e) "field off" (gravitational forces determine the axis of free rotation) and (d) and (f) "field on" (magnetic forces determine the axis of free rotation). (g) Probability distribution function for the aggregate shown in (a) and (b), where the open circles denote data for "field on," the closed circles denote data for "field off," and the lines are Gaussian fits. The widths of the Gaussian fits are 0.98° and 2.0°, which give diffusion coefficients of 21.7 deg^2/s and 90.2 deg^2/s, respectively, using the described probability distribution equation.

isolated and arbitrarily chosen. This depends on the initial orientation of the magnetic moment of the particle and the orientation of the applied field.

The magnetic particles were suspended in deionized water with <0.5% sodium dodecyl sulfate to minimize stiction. Custom made fluidic cells with a 100 μm thickness were used to prevent convection and evaporation. The fluidic cells allow for measurement of biologically interesting samples, such as magnetic beads attached to single bacterial cells.[21] A static magnetic field was established with two pairs of Helmholtz coils (a total of four air core electromagnets) to control the orientation of the particle with a field strength of 0–1.4 mT. Images were obtained using an inverted Olympus (IX71) microscope with a 100× oil immersion objective, in bright-field mode, and with a Coolsnap digital camera. Each particle's bright and dark hemispheres [see images in Fig. 2(a)] were tracked using an ImageJ routine, MultiTracker. From the tracking values, the orientation of the particle could be measured in time—Fig. 2(b). To further minimize surface interactions, or any effects from having a center of mass slightly off-center, we applied a magnetic field along the optical axis (instead of in the imaging plane) when observing Brownian motion.

The extent of confinement to a single axis was quantified by applying a magnetic field parallel to the image plane and using a magnetic particle with a 100 nm nickel layer, magnetized through the poles—as is commonly done with magnetic Janus particles[18] (the particle was magnetized so that when a field was applied in the imaging plane, the particle aligned with the nickel hemisphere and the polystyrene hemisphere in-line with the field, e.g., through the poles). The measured standard deviation from alignment with a 1.0 mT applied magnetic field was 3.9 degrees. This deviation decreases with increased magnetic field amplitude, as expected from the kT/mB thermal energy consideration, where k is the Boltzmann constant, T the temperature, m the magnetic moment of the particle, and B the magnetic field amplitude.

When the particle is magnetized along its equator and a magnetic field is applied perpendicular to the imaging plane (e.g., along the optical axis), as shown in Fig. 1, the particle diffuses in the imaging plane as shown in Fig. 2(a). In this configuration, it is straightforward to measure the time-dependent angular orientation of the particle. Figure 2(b) shows the relative angular orientation of a typical particle. From this data, the angular displacement can be calculated and the probability distribution can be determined,[22,27] which is given by $P(d)=1/2\pi\sigma^2[\exp(-d^2/2\sigma^2)]$, where d is the angular displacement and $\sigma=\sqrt{(2D_r t)}$ is the distribution's root mean square deviation—see Fig. 2(c). The fit is in good agreement with the rotational probability function and suggests free Brownian diffusion for the observed one dimensional rotation. The diffusion coefficient, $D_r=\sigma^2/2t$, can be determined from the fit in Fig. 2(c), and is 727.5 deg^2/s. By using $\tau=1/2D_r$, where $D_r=kT/\kappa\eta V$, κ is the shape factor, η the dynamic viscosity, V the volume, and τ the rotational correlation time, we obtain $\tau=2.26$ s. These numbers compare reasonably well with analogous systems in water.[23,24] By changing the direction of the static field, it is also possible to allow for rotational diffusion around different rotational axes (relative to the sample plane), such as parallel to the imaging plane. Being able to control how the particle rotationally diffuses with respect to an interface or object, could lead to further studies, such as investigation of molecular interactions at interfaces.[25] The ability to control rotation in this manner, also addresses the potential limitation of using the optical intensity to approximate the angle, as previously done for rotational diffusion.[18,23,26–28]

One potential application of confining Brownian rotation to a single dimension is the ability to measure rotational diffusion around different axes. We thus measured the rotational diffusion of a rigid four-particle aggregate about two different axes: one with no applied field ("field off"), where the rotation was restricted to one dimension by the glass-fluid interface, and the other with an applied magnetic field

("field on"), where the rotation was restricted to one dimension by the magnetic field—see Figs. 3(a)–3(f). The diffusion coefficients calculated from the fits were 21.7 $\deg^2/s$ with "field off" and 90.2 $\deg^2/s$ with "field on," i.e., $D_r^{on}/D_r^{off}=4.16$. The corresponding change in drag can arise from either interface effects (e.g., effective viscosity) or from the difference in shape factor, κ, when rotation occurs around different axes. Comparison of this diffusion ratio to the Hydro++ simulation[29] is underway.

Summarizing, we designed and implemented an experimental system that enables strictly one-dimensional Brownian rotation, i.e., genuine Brownian rotation around a single, conserved, rotation axis. The results demonstrate a method for handling rotational Brownian motion in a controlled way, and are rigorously describable by the Einstein analytical formalism,[5] in contrast to unrestricted Brownian rotation.[10] The methodology presented in this letter could be applied to the study of rotational diffusion, such as near interfaces, in complex fluids, and in biological environments.

The authors would like to acknowledge Rodney Agayan, Jeffrey Anker, and Dan Youngstrom for useful discussions. This work was supported by NSF/DMR under Grant No. 0455330.

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