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Optical imaging and magnetophoresis of nanorods

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ABSTRACT

Peclet number analysis is performed to probe the convective motion of nanospheres and nanorods under the influence of magnetophoresis and diffusion. Under most circumstances, magnetophoretic behaviour dominates diffusion for nanorods, as the magnetic field lines tend to align the magnetic moment along the rod axis. The synthesis and dispersion of fluorophore-tagged nanorods are described. Fluorescence microscopy is employed to image the nanorod motion in a magnetic field gradient. The preliminary experimental data are consistent with the Peclet number analysis.

One of the advantages of magnetic particles in biology and biomedicine is the ability to control their movement with external fields. Magnetic particles (100 nm–1 μm) [1,2] are already in use for bioseparations. The magnetophoretic behaviour of micron size magnetic beads and long (micrometer length) nanowires has been investigated [3]. However, much less work has been done on magnetophoresis of particles in the nanoscale regime. Control of nanoscale motion could be a valuable tool for exploration within living cells. Nanoscale resolution would allow the use of magnetic nanoparticles for studies of biological processes at the subcellular level [4]. Since cells are typically microns in size, the larger magnetic particles that show strong magnetophoresis are not suited for this purpose. The ability to control the spatial evolution of nanoparticles while imaging it in submicron scale could be very important, for example in understanding intracellular trafficking and gene transfection for gene therapy [5], where nanoparticles are employed as DNA carriers [6]. To guide the motion of nanoparticles, magnetic forces must overcome viscous drag forces and Brownian diffusion.

Achieving magnetophoresis with nanoscale magnetic particles is more difficult than for larger particles because of enhanced drag forces. In the low Reynolds number regime [7], there is almost no inertial force for the nanoparticles undergoing magnetophoresis and hence, extremely large magnetic field gradients [8] are needed to induce nanoparticle motion. Our previous observations [9] of single particle dynamics using gold-coated particles and dark field optical microscopy showed that Brownian motion of the nanoparticles could be an even greater problem.

Here, we examine the role of nanoparticle shape on magnetophoresis and Brownian diffusion, enabling the design of optical nanoparticles for magnetically guided motion within a living cell. This is described in terms of a Peclet number, which is the ratio of convection (here the magnetophoresis) to diffusion (Brownian motion). This kind of analysis is useful because nanoparticles are much more susceptible to random thermal motion, compared with microbeads. We envision that accurate motion control of single nano-objects could be achieved within a living cell by using a feedback control system [10]. After presenting theoretical results for the motion of spherical and rod-shaped nanoparticles, we describe some preliminary experimental results for nanorods. We describe the preparation of fluorophore-labelled biocompatible magnetic nanorods, and characterize their size distribution by dynamic light scattering (DLS). We compare their magnetophoresis and diffusion based on fluorescence microscopy imaging.

1. Magnetophoresis and diffusion of nanorod and nanosphere

Controlling the motion of small nanoparticles with an applied magnetic field gradient is challenging, both because of large drag forces, compared to the magnetic forces and also due to Brownian motion. In previous work [9], we observed significant thermal diffusion of individual 30 nm nanoparticles. Within one second such particles can diffuse across a distance of 250 particle diameters (~8 μm). This could be problematic for applications that require the precise manipulation of small nanoparticles. The relative importance of magnetophoresis and Brownian diffusion effects are quantified by the Peclet number, which is defined

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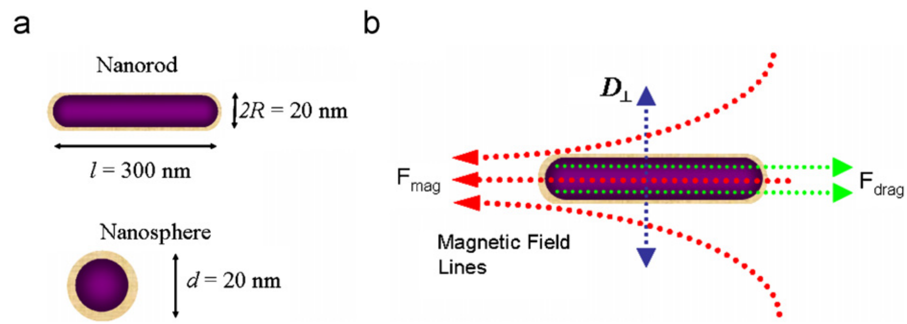

Fig. 1. (a) Dimensions of the nanosphere and nanorod described in this study. (b) Orientation of a nanorod along its long axis due to magnetic forces (F_{mag}) with the Stokes drag force (F_{drag}) opposing the magnetic force. In addition, random forces due to collisions with solvent molecules lead to Brownian diffusion, with a characteristic diffusion constant. If the rod is aligned as shown only diffusion perpendicular to the rod axis $D_\perp$ will alter the average velocity of the rod.

Table 1
Measured and calculated properties for both nanorods and nanospheres [9] used in this study.

	Nanosphere	Nanorod
Physical dimension Diameter Length	 20 nm	 20 nm 300 nm
Experimentally measured mean-square displacement in one second	8 μm	8–12 μm
Experimentally measured magnetophoretic velocity	Cannot be determined due to Brownian motion [9]	28 μm/s
Calculated magnetophoretic velocity at magnetic field gradient of 100 T/m	4.52 μm/s	27 μm/s
Peclet number at magnetic field gradient of 100 T/m	0.0018 (diffusion dominated)	1.19 (magnetophoresis stronger than diffusion)

as [11]

$$Pe = \frac{u_{mag} L}{D}. \tag{1}$$

Here L is a characteristic length scale, which is the diameter for a nanosphere or the length for a nanorod. u_{mag} is the magnetophoretic velocity and D is the diffusion coefficient of the nanoparticles. For $Pe > 1$, convective magnetophoresis is stronger, while if $Pe < 1$, diffusion is stronger. In the diffusion dominated regime, even though the particles on average move toward the higher magnetic field gradient, large diffusive steps make it difficult to track and control the particle trajectory.

We consider the magnetophoretic motion of a nanorod with length $l = 300$ nm and diameter $2R = 20$ nm and a nanosphere with $2R = d = 20$ nm in diameter (Fig. 1). All the critical calculated and measured parameters presented in this work are given in Table 1. The dimensions are chosen for convenience in comparing our previous experimental observations on nanospheres with 20 nm magnetic cores [9] and current experimental work on nanorods. Both move towards a higher magnetic field gradient region due to the balance of the magnetic force F_{mag} and the viscous drag force F_{drag}. The magnetic flux density, B, and its gradient ∇B were simulated for a solenoid using FEMlab 3.0® (Comsol, Ltd. 1999–2005). Here, the coil length was 0.4 m, with 400 turns, and the coil radius was 0.01 m with 400 turns. The current I was varied to determine the field and field gradient at distances along the axis of the solenoid. At magnetic field B and magnetic field gradient ∇B, the magnetic force on a spherical nanoparticle is

$$F_{mag} = \frac{\Delta\chi V_p}{\mu_0}(\nabla B)B, \tag{2}$$

where μ_0 is the vacuum permeability, V_p is the particle volume and $\Delta\chi$ is the difference in magnetic susceptibility between the particle and the fluid. The viscous drag force for a sphere is given by

$$F_{drag} = 3\pi\eta d u_{mag}, \tag{3}$$

where η is the viscosity of the suspending medium. Equating the magnetic and the drag forces, the magnetophoretic velocity for a sphere is then [12]

$$u_{mag} = \frac{\Delta\chi V_p}{3\pi\eta d\mu_0}(\nabla B)B. \tag{4}$$

For a nanorod, the analysis becomes slightly more complicated. Due to their shape anisotropy, nanorods have more stable magnetic moments, which help in alignment and enhance the magnetophoretic velocity. The nanorods studied here have been used as magnetic tape media, and therefore have a stable magnetic moment at room temperature. The propagation direction of a nanorod under magnetophoresis will be with its long axis oriented along the magnetic field lines, and only the viscous drag parallel to the nanorod axis hinders magnetophoresis. This drag force which is applicable to the rod-like structure with aspect ratio close to 20 is given by [13]

$$F_{drag\parallel} = \frac{2\pi\eta l u_{mag\parallel}}{\ln(l/2R) - 0.72}. \tag{5}$$

Combining Eqs. (4) and (5), we obtain the magnetophoretic velocity of the nanorod along its long axis

$$u_{mag\parallel} = \frac{\Delta\chi V_p[\ln(l/2R) - 0.72]}{2\pi\eta l\mu_0}(\nabla B)B. \tag{6}$$

Fig. 2a shows a comparison of the velocities of the nanosphere and nanorod as a function of the magnetic field gradient. The nanorod speed is almost six times higher than a nanosphere of the same diameter. This difference is mostly due to the differences in the magnetic volume rather than particle shape. From geometrical arguments, Zalich and coworkers [14] predicted that for the same radius R, the magnetophoretic mobility of a nanorod increases with increasing aspect ratio.

However, comparison of these velocities ignores the importance of thermal forces that lead to diffusion. Diffusion of a sphere