Towards Holonomic Control of Janus Particles in Optomagnetic Traps

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Janus particles generally refer to a class of colloids with two dissimilar faces having unique material properties.[1] The spherical asymmetry associated with Janus particles is the key to realizing many commercial applications, including electro- phoretic displays,[2,3] nanosviscometers,[4] and self-propelling micromachines.[5] These diverse functionalities were accomplished by using an external electric or magnetic field to control the particle orientation,[6–8] and in the process, modulate its reflectivity, hydrodynamic mobility, or direction of motion, respectively. However, these same asymmetries can interfere with optical trapping techniques that are used to control the translational degrees of freedom of a particle.[9] Optical fields present an effective method for controlling the three translational degrees of freedom for particles ranging from tens of nanometers[10] to micrometers in size.[11–13] Previously, optical fields have been used in combination with magnetic fields to control four degrees of freedom of an asymmetric particle or particle aggregate.[15–18] To achieve five or more degrees of freedom, magnetic Janus particles can theoretically be used; however, none so far have been stable in an optical trap. Controlling all six degrees of freedom of Janus particles, including three translational and three rotational, would open up new applications not only in biophysical force and torsion measurements, but also in microfluidics and material self-assembly.

Here we report on a new type of spherical Janus that can be manipulated by a combination of optical and magnetic fields. We demonstrate the ability to directly control five degrees of freedom of the particle’s motion (three translational and two orientational) while constraining the final sixth degree of freedom. Ultimately, this demonstration represents the most control ever achieved over freely suspended spherical colloidal particles and opens up many exciting applications; the most obvious being the exertion of torsional and linear forces on biomolecules. The main achievement reported here was to develop a method of synthesizing magnetically anisotropic Janus particles that are also compatible with conventional optical trapping systems. We developed a novel lithographic technique for forming so-called “dot” Janus particles, which have a metallic coating covering <20% of their surface area. The advantage of this approach is that the dot Janus particles behave more like normal dielectric particles in an optical trap, while also responding to magnetic forces and torques produced by an external magnetic field.

Purely dielectric and metallic Mie and Rayleigh particles have been optically trapped using a variety of techniques. Both dielectric microparticles and nanoparticles can be trapped in three dimensions with a high degree of spatial control.[11–13] Metallic nanoparticles can also be trapped in three dimensions because scattering from metallic and dielectric particles are similar in this size regime.[19] However, metallic microparticles can only be controlled in two dimensions, due to considerations previously documented by others.[20–23] For anisotropic Janus particles, such as dielectric particles that are partially covered by metal, the trapping stability in a focused optical beam depends to a great extent on the degree of metal coverage of the particle surface.

Here we propose a general explanation for why optical trapping is more easily accomplished with dot Janus particles than with half-coated Janus particles. In the Mie size regime, where the particle diameter is large compared with the trapping wavelength, λ, the momentum imparted by a focused optical beam can be described using geometric ray optics following Ashkin’s line of reasoning.[24] In brief, each light ray refracts and reflects at the particle/liquid interface according to Snell’s law, and the momentum change between the incident ray and the refracted/reflected ray is summed over all incident rays to determine the net force on the particle. Typically, the net force is artificially divided into a gradient force, arising from refraction through the particle, and a scattering force, arising from reflection at the particle surface. The gradient force tends to pull the particle towards the beam focus, whereas the scattering force tends to push the particle away from the emission source.

Figure 1 illustrates the incident light rays a and b refracted through the particle and the gradient forces $\vec{F}_a$ and $\vec{F}_b$ imparted on the particle due to each light ray. The ray optics approach reveals the importance of the symmetry of conjugate light rays in an optical trap. As long as the gradient force balances the scattering force, $\vec{F}_s$, the trap will remain stable. For particles partially coated by reflective metal, the symmetry of this process may be broken, leading to unbalanced torques and forces that will depend on the position and orientation of the particle.

As illustrated in Figure 1b, the metal coating inhibits light
transmission through half of the particle leading to unbalanced
gradient and scattering forces, consequently expelling a Janus
particle from the center of the trap. This effect was recently
observed experimentally. At low optical powers ($\leq 7$ mW), it was
demonstrated that Janus beads can be confined within an optical
trap, however, the trapping region in these cases is not strongly
localized and rotation of the particle can be observed about the
focal point. Optical trapping capability should theoretically be improved with dot Janus
particles, as illustrated in Figure 1c, because the momentum imbalance on opposing sides
of the particle is greatly reduced.

There are many methods to fabricate Janus particles including masking, directional evaporation, microcontact printing, and interfacial fluid techniques. Nano-meter-size metallic Janus particles have been fabricated using a convective assembly deposition technique followed by metal evaporation or through self-assembled grafting techniques. On the micrometer-size scale, metallic Janus particles are most commonly produced by directional metal evaporation onto colloidal monolayers. We used variants of this technique to produce both conventional half metallic Janus particles and dot Janus particles. In brief, 10-μm polystyrene particles in ethanol were pipetted onto glass microscope slides, which formed consistent regions of close-packed monolayers upon solvent evaporation. A thin 50-nm cobalt layer was directionally evaporated onto the substrate using conventional metal evaporation techniques. Next, the substrate was sonicated in water to resuspend the half Janus particles. The dot Janus particles are engineered from the same monolayer of particles, however, an intermediary step is required to partially mask the region of metal evaporation. This is accomplished by first spanning a 1.5-μm-thick layer of photoresist onto another glass slide. The two slides are pressed firmly together into a sandwich, causing the photoresist to fill the voids between the particles and both slides except in the region where steric forces between the top glass slide and the particles exclude the photoresist. Due to mass balance considerations, it is possible that the photoresist develops cavities in the interparticle regions. In any case, a uniform coating of the interfaces was reliably formed enabling protection of the particles by the photoresist except at the contact points between the particles and the top slide. The sandwich is cured by heating the sample at 90°C for 2 min, after which the two slides can be pulled apart. The particles remain anchored to the bottom slide due to stronger adhesion forces, leaving a small dot of $\sim 20\%$ uncoated surface remaining on each particle. A thinner 20-nm cobalt layer is evaporated onto the surface. Thinner metal films allow for easier lift-off when the sample is next developed to remove the photoresist and release the dot Janus particles into solution. The particles can then be transferred to an aqueous solvent for testing.
In order to test the optical compatibility of these Janus particles, each type of suspension was exposed to an optical trap. The optical trapping setup, identical to Jenness et al.,[35] used a 532-nm wavelength laser coupled with a spatial light modulator. Half Janus particles were immediately expelled from the beam focus when the laser was turned on (see Supporting Information, Video 1). Upon lowering the average beam power below a certain threshold (<8.0 mW), half Janus particles, though not trapped, would remain near the focal point. Occasionally, these proximal particles were observed to rotate around the focal point, consistent with previous results.[9] In some cases, heating of the particle was observed as substantiated by the formation of air bubbles nucleating on the particle surface, a phenomenon previously observed in colloidal suspensions of microparticles.[36–39] However, at these lower beam intensities, the optical traps could not overcome surface and gravitational forces to translate half Janus particles in a reliable fashion.

Alternatively, the dot Janus particles can be trapped in the focal point of the optical trap and subsequently controlled in three orthogonal spatial directions (x, y, z) (Fig. 3, see Supporting Information, Video 2). In the coordinate system defined in Figure 3a, the trapped dot Janus particle remains free to rotate in the ψ and φ directions, however, the optical trap effectively constrains the particle's motion in the θ direction in order to minimize interference of the cobalt dot with the transmission of the optical beam. While it is theoretically possible to directly control θ as well by using an optical beam that can be independently rotated, this is technically very challenging and was not demonstrated in this work. Trapping of both dot Janus and bare 10-μm particles was consistently observed with laser intensities in the range of 2 to 15 mW. The compatibility of the dot Janus particles with the full range of trapping laser intensities demonstrates that the metal coatings of dot Janus particles do not impair the optical trapping capability.

To test the magnetic response of both types of Janus particles, external magnetic fields were applied using iron-core solenoids. Cobalt is ferromagnetic, retaining a remnant magnetic moment, \( m_p \), in the absence of magnetic field. The magnetic moment of cobalt can be approximated from the magnetization of bulk cobalt, \( M_p = 5000 \text{emu} \), and the volume of the cobalt patch, \( V_p \), as \( m_p = M_p V_p \). Thin films of cobalt have large shape anisotropy, which causes the magnetic moment to be effectively pinned in the plane of the film. In the presence of an external field, \( H_{ext} \), the moment of the particle will feel a magnetic torque, \( \tau_m \), that aligns it along the external field direction, according to \( \tau_m = \mu_0 m_p \times H_{ext} \), where \( \mu_0 \) is the permeability of free space. For the 10-μm-diameter dot Janus particles fabricated here, the maximum magnetic torque in a 50 Oe magnetic field is calculated to be \( 2 \times 10^{-15} \text{ N} \cdot \text{m} \). For low Reynolds number systems, such as this one where inertial terms are negligible, the rotation frequency of the particle can be determined through the balance between magnetic torque and viscous drag, where \( J_{ROT} = 8\pi \eta m^3 \), is the torsional friction on a particle of radius a due to a fluid with viscosity \( \eta \). For sufficiently low rotation frequencies, the particle becomes phase-locked with the external field and follows the equations of motion of a non-linear harmonic oscillator, similar to systems studied by others.[41] For this system, we calculate the critical frequency to be on the order of hundreds of hertz, thus the angular velocity of the particle will nearly always be phase locked with the field. For the sake of comparison, the magnetic torque in our experimental system is three orders of magnitude larger than torques previously reported in similar optomagnetic systems,[17] which is a direct result of the large volume of ferromagnetic material on the surface of these dot Janus particles. This torque, of course, can be adjusted by changing the thickness of the cobalt dot, however, this additional control element was not tested here.

Although alignment in two dimensions can be achieved using a single uniform field, due to the axial symmetry of the field, the particle will have one remaining orientational degree of freedom that cannot be controlled. For example, if the field direction is \( \phi, \psi = 0^\circ \), then the magnetic moment will be constrained to the plane \( \phi, \psi = 0^\circ \). However, the particle is still free to rotate in θ (Fig. 4). It is possible to increase the control of the particle by using an optical trap in combination with external magnetic field. The optical trap can directly control three translational degrees of freedom of the particle while constraining one rotational degree of freedom (θ in this case). In addition, the magnetic field can directly control the remaining two orientational degrees of freedom leading to near holonomic control of a colloidal particle. To demonstrate this system, three iron-core solenoids are placed...
along orthogonal axes that are positioned 5 cm from the sample (Fig. 5a). A dot Janus particle is first optically trapped within the focal point allowing for control of x, y, z and a constraint of $\theta = 0^\circ$. An external magnetic field is applied to orient the particle in $\varphi$ and $\psi$ directions (see Supporting Information, Video 3).

In order to demonstrate the degree of particle control, a series of videos is provided as a visual aid. In one, a particle is moved in a circular path via a programmed optical beam while a 30 Gauss, 0.1 Hz horizontally rotating magnetic field simultaneously orients the particle in $\varphi$ and $\psi$ directions (see Supporting Information, Video 4). In another, a 30 Gauss, 1 Hz vertically rotating magnetic field is shown to rotate the particle’s orientation in $\varphi$. (Fig. 5c–e, see Supporting Information, Video 5). Theoretically, it is possible to use holograms generated by spatial light modulators to control multiple particles simultaneously. This approach may also be combined with local magnetic fields to achieve near holonomic control of an ensemble of particles. [42,43]

In this work, we have developed a new method for the controlled synthesis of dot Janus particles that have sufficiently small surface coverage of covalt film to allow compatibility with an optical trap. The near holonomic control over these spherical Janus particles opens up a new realm of advanced manipulation strategies that will have important ramifications in nanoengineering. The controlled manipulation of dot Janus particles affords new degrees of freedom in the measurement of mechanical properties of previously investigated molecules such as DNA, ankyrin, and many other biomolecules. Recent studies have also introduced the concept of manipulating and controlling cell function through the magnetic actuation of nanoparticles bound to the cell surface. [46,47] These potential biological applications as well as the ability to improve directed hierarchical particle assembly establish the broad reaching scientific value of the capabilities demonstrated here.

### Experimental

**Preparation of Colloidal Crystals** To deposit a single layer of colloids onto a glass slide, 10-μm polystyrene particles (Thermofisher, Waltham, MA) were transferred from aqueous solvent by spinning the particles down in a centrifuge at 2 units of relative centrifugal force for 1 min and resuspending them in ethanol. These particles were pipetted onto slightly tilted glass microscope slides, which formed consistent regions of close-packed monolayers via gravitation induced sedimentation combined with solvent evaporation.

**Development and Stabilization of Dot Janus Particles** After metal evaporation (Fig. 2f), the glass slide with dot Janus particles is placed in a small glass vial filled with M-351 (Microchem) for 5 min and sonicated for 10 s. With the dot Janus particles in suspension, the slide is discarded and the fluid is pipetted into microcentrifuge tubes and diluted ten-fold with 0.05% LiquiNox. The particles are spun down in a centrifuge at 2 units of relative centrifugal force for 1 min and resuspended in 0.05% LiquiNox. This step is repeated an additional time.

**Optical Trap Set-up** The laser was a pulsed Coherent Primsa Nd:YVO4, 512 nm. The microscope was a Zeiss Axiovert 200 microscope fit with Zeiss 100×, 40×, and 10× lenses. The SLM used was a HOLOEYE LCR 2500 and was run in phase only mode. The beam path was encoded in phase holograms to create the desired intensity distributions and played back in movie form to create preprogrammed paths. To prepare a sample for the optical trap, dilute Janus particle suspensions (~0.1% volume fraction) were placed between a microscope slide and a glass coverslip separated by a 120-μm-thick spacer (Invitrogen, Carlsbad, CA).

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