Shape Discrimination with Hexapole Dipole Interactions in Magic Angle Spinning Colloidal Magnetic Resonance.

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Magic Angle Spinning (MAS) is a powerful technique in solid state NMR which allows to time average the magnetic dipolar interactions between the nucleons and, in turn, increases the spectral resolution[1]. Dipolar interactions and chemical shift are both first order anisotropies which are proportional to the second order Legendre polynomial $P_2(\cos\vartheta)$, and vanish when applied the magnetic field sample is spun at the "magic angle", ϑ_{magic} = 54.74º, with respect to a fixed axis. However, second order anisotropies such as quadrupolar and hexapole-dipole interactions, do not vanish at ϑ_{magic} since they are proportional to the fourth order Legendre Polynomial $P_4(\cos\vartheta_{magic})$=-7/18≠0 and can cause small but finite spectral broadening. Effects due to high order multipole moments play an important role in many other systems such as in Rare Earth Conpounds[2], antiferroelectric liquid crystal[3], nematic molecules[4], electrorheological fluids[5] and nematic emulsions[6]. It has been shown that liquid dispersions of paramagnetic colloidal particles can be used as a model system in Condensed Matter[7,8]. When subjected to an external magnetic field, the dipolar interactions between the particles can be precisely tuned. However these particles have spherical shapes and thus cannot cause magnetic anisotropy and large multipolar interactions. Here we use dipole-dipole and dipole-hexapole interactions for a shape sensitive active control, assembly and sorting of microscopic colloidal particles.

We study the interactions between magnetically driven DNA-linked, anisotropic and isotropic colloidal rotors interacting via induced magnetic dipolar and multipolar forces. Anisotropic colloidal doublets were realized by using two streptavidin coated polystyrene paramagnetic spherical particles having different radii, a_1 = 1.4 μm and a_2 = 0.5 μm (Dynabeads). The two particles were linked with two complementary single-stranded DNA sequences having 25 base pairs (see[9] for details). A water drop containing ~10^6 doublets/ml was placed on top of a glass plate, see Fig. 1(a). Gravity and electrostatic interactions between the doublets and the negative charged glass surface confine the particles to float a few nanometers above the surface. An external magnetic field was provided by using three coils with their axes perpendicular to each other. In comparison to MAS, where spinning is achieved by mechanically rotating a tilted sample, our magnetic field precesses with frequency Ω and precession angle ϑ about an axis normal to the glass plate supporting the rotors. The coil normal to the substrate was connected to a DC current source (TT*i* EX1810R), while the two horizontal coils were connected to a waveform generator (TT*i* TGA1242) fed by a current amplifier (ONKYO M-282). The particles were observed with a 100X oil immersion objective mounted on an optical microscope (Leica DMPL) equipped with a CCD color camera (Basler A311F). Videos for image analysis were recorded at a rate of 30 frames per second. At low frequencies $\Omega < 75.4\ s^{-1}$, the colloidal rotors resonate and synchronously rotate with the field.

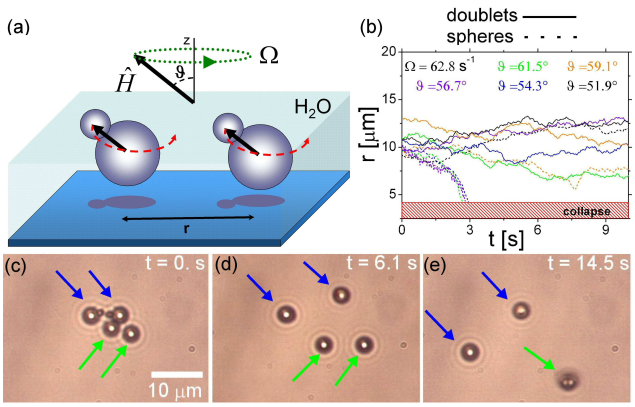

Figure 1. (a) Scheme of two doublets rotated by an external magnetic field **H** precessing around the *z* axis with frequency Ω and precession angle ϑ. (b) Time evolution of the interparticle distance *r* for two interacting doublets (continuous lines) and two isotropic spheres (dashed lines) at different precession angles ϑ for $\Omega = 62.8\ s^{-1}$ and H=1300 A/m. (c-e) Images of the colloidal doublets (blue arrows) and of isotropic spheres (green arrows). The precession angle is originally set to $\vartheta = 0$ such that all rotors separate as from (c) to (d). In d) we switch the precession angle to $\vartheta = 61.5^o$ and the doublets remain separated while the spheres collapse (e). The doublet shape visible in fig. 1(c), can only be resolved for doublets at rest. A corresponding movie is deposited in the supporting information.

Mainly odd ($m_1=(\chi_1 V_1+\chi_2 V_2) H$, $m_3=3(a_1+a_2)^2\chi_1 V_1 \chi_2 V_2\ H/(\chi_1 V_1+\chi_2 V_2)$) magnetic multipole moments[10] m_l $(l=1,2,3..)$ are induced in each rotor and the rotors start to magnetically interact with each other. Here V_1,V_2, are the volumes of the individual spheres composing the doublet and $\boldsymbol{H}=\hat{H}[\cos\vartheta \boldsymbol{e}_z + \sin\vartheta (\cos(\Omega t)\boldsymbol{e}_x+\sin(\Omega t)\boldsymbol{e}_y)]$ is the precessing magnetic field. χ_1=0.4 and χ_2=1.1 are the effective volume magnetic susceptibilities of the spheres. Higher moments only occur in rotors with anisotropic shape, and this allows us to discriminate between rotors of isotropic and anisotropic shape close to ϑ_{magic}.

In the supporting information[9] we provide a detailed description of the dynamics of an individual doublet with respect to the frequency of the precessing field. Since here we are interested in the interactions between two rotors, all following measurements were taken at low frequency where the rotors move synchronously with the magnetic field. Using video microscopy and particle tracking routines, we analyze the time evolution of the relative displacement between the rotors. In Fig. 1(b) we show the interparticle distance between two doublets at different precession angles for $\Omega = 62.8\ s^{-1}$. Similar data under the same field conditions are shown as dashed lines for a pair of isotropic spheres. In the shaded red region in Fig. 1(b) rotors merge to form a single rotating cluster. Changing the precession angle of the field allows varying the dipolar interaction between the rotors from net attractive, where all the particles collapse into a single rotating cluster, to net repulsive, where isotropic spheres and anisotropic doublets diffuse close to each other but do not collapse. Isotropic rotors are repulsive below and attractive beyond the magic angle ($\vartheta_{magic} = 54.7^o$). Isotropic rotors therefore are well described by a dipolar coupling. Anisotropic doublets, however, repel even above the magic angle, e.g. for $\Omega = 62.8\ s^{-1}$ up to an angle $\vartheta > 61.5^o$. In the discriminating range of precession angles $\vartheta_{magic} < \vartheta < 61.5^o$ isotropic particles can be extracted from a mixture of shapes because they all collapse into one rotating super cluster, Fig. 1 (c)-(e). We attribute the stronger repelling tendency of anisotropic rotors to repulsive hexapole-dipole interactions[11]. We explore the range of precession angles to discriminate particles with different shape by first applying a magnetic field precessing at an angle $\vartheta < \vartheta_{magic}$ where the four rotors separates as in Fig. 1 (c)-(d), and then switching to a precession angle of $\vartheta = 56.7^o$. In this case isotropic particles collapse, while the rotating doublets repel and remain separated. In[9] a movie is available showing the separation dynamics of all four rotors as well as the consecutive collapse of the spheres but not the doublets after switching to $\vartheta = 56.7^o$.

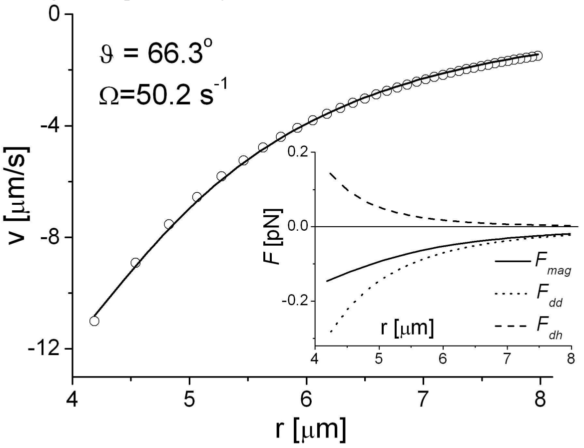

Figure 2. (a) Collapse velocity of two doublet under an external field with $\vartheta = 66.3^O$ and $\Omega = 50.2\ s^{-1}$. The continuous line is a fit by following equation 2. The small inset shows the corresponding dipolar (dotted line) and Hexapole - dipole (dashed line) contribution to the total magnetic force (continuous line) between the doublets.

We explain the interaction between the rotating doublets by considering both the dipole-dipole ($F_{dd} \sim r^{-4}$), and dipole-hexapole ($F_{dh} \sim r^{-6}$) contributions to the total magnetic force:

$$F_{mag} = \frac{\mu_0}{4\pi}\left[3\frac{m_1^2 P_2(\cos\vartheta)}{r^4} - 15\frac{m_1 m_3 P_4(\cos\vartheta)}{r^6}\right] \qquad (1)$$

where m_1, and m_3 are the dipolar and hexapole moments of the doublet. If we neglect hydrodynamic interactions between both rotors the magnetic force on each rotor is balanced by the viscous drag $F_{visc} \approx 6\pi a \eta\, v/2$ on each rotor, where $a \approx a_1 + a_2 cos^2 \vartheta/2$ is the hydrodynamic radius of the spinning rotor, $\eta = 10^{-3}\ Ns/m^2$ is the viscosity of water, and ν is the relative velocity between both rotors. Such an approximation holds for larger separations and we obtain the attraction or repulsion velocity of the rotors as:

$$v = \frac{\mu_0 m_1^2}{4\pi^2 \eta a^5}\left[\frac{P_2(\cos\vartheta)}{(r/a)^4} - 5\frac{m_3}{m_1 a^2}\frac{P_4(\cos\vartheta)}{(r/a)^6}\right] \qquad (2)$$

In the regime $\vartheta_{magic} < \vartheta < 61.5^o$ two anisotropic rotors will separate until they reach an equilibrium separation:

$$r_{equ} = \sqrt{5 m_3 P_4(\cos\vartheta) / m_1 P_2(\cos\vartheta)} \qquad (3)$$

We determined a ratio of $m_3/m_1 = 3.4\ \mu m^2$ at the precession angle of $\vartheta = 56.7^O$ from the equilibrium separation $r_{equ} = 11.3\ \mu m$ of the doublets. When we increase the precession angle $\vartheta > 61.5^o$ the equilibrium radius becomes smaller than the hydrodynamic radius and the doublets collapse into a single rotating cluster. Fig. 2 shows the experimental collapse velocity (open circles) for two doublets when subjected to an external magnetic field precessing with frequency $\Omega = 50.2\ s^{-1}$ and at an angle $\vartheta = 66.3^O > \vartheta_{magic}$. The solid line is a fit to equation (2) with a dipole moment $m_1 = 3.4 \cdot 10^{-14}\ Am^2$ and a hexapole moment $m_3 = 1.35 \cdot 10^{-25}\ Am^4$ corresponding to a ratio between the hexapolar to the dipolar magnetic moment of $m_3/m_1 = 3.9\ \mu m^2$. As shown in the small inset, the dipole-dipole attraction F_{dd} overcomes the dipole-hexapole repulsion F_{dh} leading to a net attraction. A theoretical estimation of the ratio between the hexapole and dipole moment gives m_3/m_1=1.1 μm^2 which close to the experimental value. The remaining factor 2 could arise either from depolarization effects due to the polymer matrix of the colloidal particles or to asymmetric distribution inside the colloids of the superparamgnetic iron oxide grains.

In summary, we realized micron-sized magnetically driven isotropic and anisotropic colloidal rotors. We showed that a balance between magnetic dipole-dipole and dipole-hexapole interactions near the magic angle allows a separation between spherical and anisotropic magnetic colloidal rotors. The shape separation of externally controlled rotating micro-objects might be interesting for technological applications such as assemblies of stirrers for microfluidic devices[12], micro-technological tools[13] or as "reconfigurable" mechanical systems[14].

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Supporting Information Available: Realization of colloidal doublets, doublet rotation under a magnetic field, derivation of equation (1) and (2), three movies (mpeg1) showing the motions of the doublets and spherical particles under a precessing magnetic field. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Details are given in the Supporting Information.
(10) For axisymmetric rotors the magnetic multipole susceptibilities are scalar numbers defined with respect to the figure axis of the rotor.
(11) Dipole-quadrupole interactions vanish because the precession axis is normal to the rotor separation.
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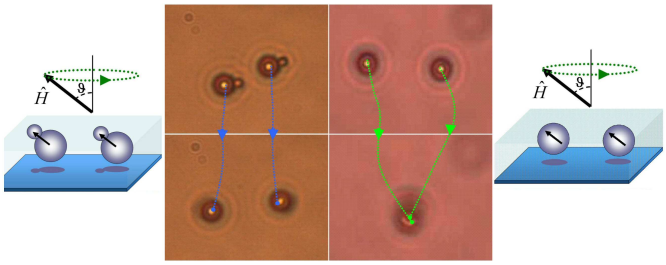

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