

# Magnetically tunable optical absorbance in a colloidal system

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We study the optical absorbance from a magnetically arranged colloidal structure, and investigate the possibility of creating a magnetically controlled optical sensor using this system. The colloids form chains when exposed to an external magnetic field, which tend to collapse and form a more random particle arrangement when the field is removed. We show that a small magnetic field is able to change the sensor's reflection coefficient by more than 30%, and investigate in detail the relaxation mechanism when the field is turned off.

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## I. INTRODUCTION

In recent years there has been a tremendous interest in the use of ordered magnetic colloidal systems in various technological and biomedical applications. Magnetic particles are readily manipulated by external magnetic fields, thus making them ideal for separation of biomolecules, as biomarkers in magnetic resonance imaging techniques, as mediators of heat for cancer therapy and as carriers for drug delivery [1–3]. In the past few decades a significant amount of research has been put into designing new micromachines and sensors based on paramagnetic colloids. In Refs. [4–7] it was demonstrated how local magnetic potentials visualized by optical techniques can be used to create tunable microstirrers as well as guiding systems for paramagnetic colloids and magnetotactic bacteria. Optical sensors based on magnetic colloids are particularly promising as they allow us to miniaturize the systems and to use weak external fields as control parameters. It has been found that systems composed of ferrofluid thin films have the ability to change their optical transmittance when exposed to a magnetic field, mainly due to field-induced structural arrangements [8–11]. A number of optical sensors have resulted from these studies, thus holding a great promise for future applications [12–15].

Here we investigate the possibility of creating a colloidal system with tunable magnetorelectance using micron-sized paramagnetic colloids inserted into a liquid cell. It is known that such colloids form clusters in dynamic or static fields [16–19], thus allowing a well-defined control over their structural arrangement. By applying a magnetic field aligned with the earth's gravitational field, we create long magnetic chains. When the magnetic field is turned off, the magnetic dipolar force binding the spheres together disappears, and the chains start to collapse such that all of the colloids sink toward a glass plate and form a two-dimensional system. A light beam passes perpendicular to the glass slides, and in the chain state the colloids cover minimum amount of area and therefore tend to absorb little light. When the field is turned off, the colloids cover a large area on the substrate and subsequently absorb more light. We show that the colloidal system is able to change its reflection coefficient by more than 30% as controlled by the magnetic field, and investigate in detail the collapse mechanism and the time scales involved using fiber optic detection and optical microscopy. The optical sensor presented here has several useful features which would allow it to be implemented also in practical systems.

First, a small magnetic field modulation ( $<4$  mT) results in a large change ( $>30\%$ ) in reflectance using only  $10\ \mu\text{L}$  of colloidal solution (costs approximately 1 U.S. dollar), which means that the optical element used here is rather cheap to test and develop. Second, the paramagnetic colloids are easily visualized in the microscope, thus allowing us to observe their structural arrangements and allowing us to provide a better theoretical understanding of the sensor. Finally, the paramagnetic colloids are used to bind biomolecules (proteins, cells and DNA), which makes the system biocompatible and adaptable for possible integration in biosensors.

## II. EXPERIMENT

Our experimental system consists of paramagnetic spheres dispersed in pure water and confined in a cell of area  $0.5\ \text{cm}^2$  and thickness  $100\ \mu\text{m}$  between two glass slides, see also Ref. [20] for a picture of the sample cell. We used glass slides purchased from Electron Microscopy Sciences, partially covered with Teflon of thickness  $100\ \mu\text{m}$ . A circular hole of radius  $4\ \text{mm}$  was not covered with Teflon, and therefore allowed confinement of the beads above the glass slide. The paramagnetic colloids used here were purchased from Dynal (Dynabeads M270), had a diameter  $2a = (2.8 \pm 0.2)\ \mu\text{m}$ , were coated with a carboxylic acid (COOH) group and supplied at a density of  $\sim 2 \times 10^9$  beads/ml and a zeta potential  $\sim -45$  mV. The colloidal solution was diluted by adding ultrapure water ( $>18\ \text{M}\Omega\ \text{cm}$ ) until the desired particle density was reached. The temperature during the experiments was approximately  $300\ \text{K}$ . We typically inserted  $10\ \mu\text{L}$  colloidal solution into the experimental cell using a pipette. The sample cell was sealed by gently setting a cover glass on top of the  $10\ \mu\text{L}$  colloidal solution, such that a sample cell of thickness comparable to that of the Teflon film was formed. After letting the system equilibrate, one observes that the beads sink to the lower glass surface (due to gravity) where they form a more or less ordered two-dimensional system depending on the concentration of colloids. Due to their negative charge, the colloids are repelled by the negatively charged glass surface and are therefore levitating a small distance above it. A convincing demonstration of this is presented in Refs. [21,22], where the colloids were used as microlenses and shown to fluctuate about an equilibrium height  $<1\ \mu\text{m}$  above the glass surface. Since all the colloids have

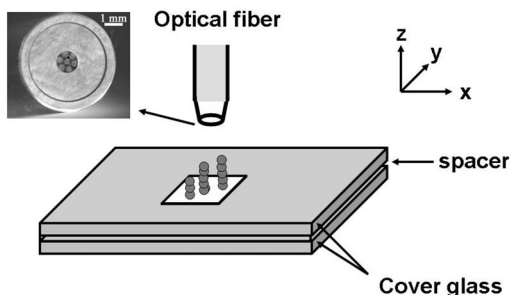


FIG. 1. Schematic drawing of the fiber-optical setup for measuring reflectance from the sample.

the same negative charge, they repel each other and therefore move around randomly without forming clusters, see also Ref. [19].

The glass slides were placed on a reflecting, white background and monitored using an optical fiber as seen in Fig. 1. Light from a Halogen lamp was passed through the center fiber cable, while six surrounding collector fibers (mounted in the same housing) collected the light reflected back from the white background after passing through the light-absorbing colloidal system. The light intensity was recorded using an Ocean Optics fiber spectrometer equipped with OOIBase32 Spectrometer Operating Software. It should be noted that this system measures a combination of transmission and reflection properties. The reason for selecting such a measurement system is that it allows easy integration into practical devices. Moreover, it improves the light economy in the system such that a high power illumination lamp (resulting in excessive heating) is unnecessary. In order to calibrate the system, we first measured the light reflectance  $R$  versus colloid (volume) concentration  $C$  as seen in Fig. 2. Since the paramagnetic colloids contain iron oxide nanograins, they absorb light, and less light is reflected from the white, diffuse background with increasing concentration of colloids. For lower concentrations the reflectance can be approximated by a linear curve,  $R=1-aC$  ( $a=0.14 \times 10^8$  ml/beads), whereas for higher concentrations the concentration dependency becomes slightly nonlinear. The reflectance at lower concentrations is not unexpected, as each colloid contributes linearly to the absorbance. At higher concentrations, the colloids come closer and even form multilayers on the glass substrate, and one cannot expect a simple

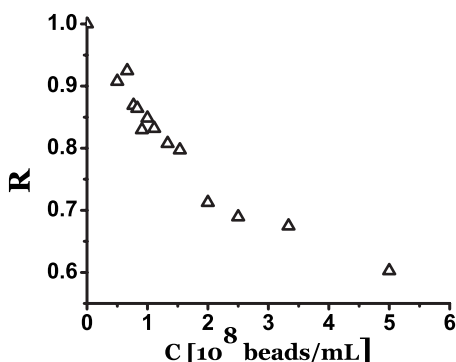


FIG. 2. The reflectance versus colloidal concentration.

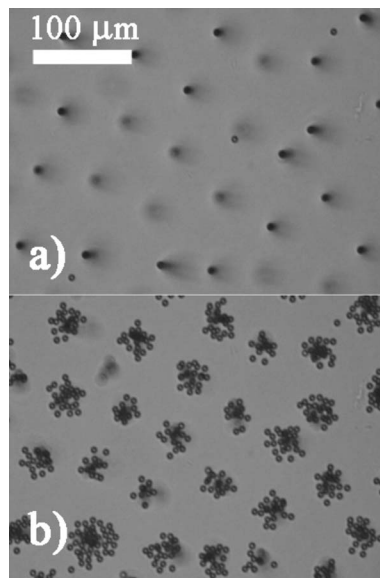


FIG. 3. (a) Colloidal chains in a magnetic field. (b) Upon removing the magnetic field the chains collapse and block a larger part of the light beam. (b) is taken about 4 s after removal of the magnetic field.

relationship between colloid concentration and reflectance. Upon applying a magnetic field, the colloids first rearrange into a more ordered lattice before they start to jump on top of each other and form chains (above a certain critical field). This behavior was reported in detail in Ref. [19], and such chains can be seen in the optical micrograph of Fig. 3(a). Upon removing the magnetic field the chains collapse and block a larger part of the light beam, see Fig. 3(b).

### III. RESULTS

Figure 4 shows a typical reflectance spectrum for a sample of concentration  $5 \times 10^8$  beads/ml without (thin black line) and with (thick black line) magnetic field. Note that upon changing the magnetic field from 0 to 14 mT, the corresponding reflectance changes from about 30% to 70%. Except for a peak near 600 nm, possibly caused by diffraction due to the nearly close-packed colloids lying on the

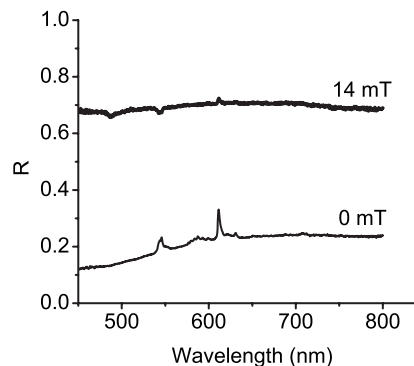


FIG. 4. The reflectance versus wavelength with (thick black line) and without (thin black line) magnetic field.

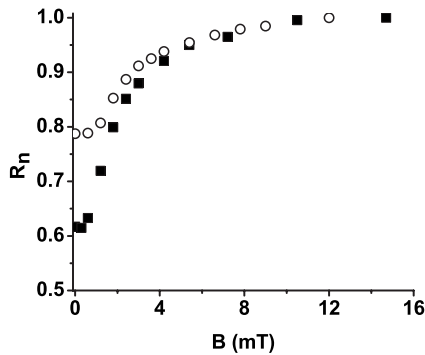


FIG. 5. The normalized reflectance versus magnetic field for concentrations of  $10^8$  beads/ml (open circles) and  $5 \times 10^8$  beads/ml (black squares).

glass substrate, which nearly vanishes in the high field state, the reflectance spectrum is nearly uniform, thus allowing us to study the system independent of wavelength in the visible region. It is in principle possible to check whether the peak is caused by diffraction using Bragg's scattering law. The fiber has a finite acceptance angle (typically  $10^\circ$ ), thus allowing several forward (or back) scattered Bragg wavelengths to be collected by the fiber. We calculate a Bragg wavelength of the order of 600 nm for a scattering angle of  $5^\circ$  for a close-packed system. However, it should also be pointed out that since the fiber collects a range of different scattering angles, the Bragg peaks are necessarily smeared out, and they are mostly overcome by absorbance and direct (unscattered) transmission. Figure 5 shows the reflectance (in the flat region of the spectrum) normalized to each concentration, i.e.,  $R_n = I/I_{\max}$  ( $I$  is the measured reflected intensity and  $I_{\max}$  the maximum reflected intensity for large fields for the same sample) versus magnetic field for concentrations of  $10^8$  beads/ml (open circles) and  $5 \times 10^8$  beads/ml (black squares). The wavelength was here selected to be 560 nm, although very similar results are found for other wavelengths where the peaks in Fig. 4 do not play a role. It is seen that for small magnetic fields the reflectance does not change much as the colloids are just rearranging in two dimensions without forming chains. However, above a certain critical field the colloids start to jump on top of each other and form chains, thus blocking less light from being reflected from the white background. In Ref. [19] it was demonstrated that the critical field decreases with colloidal density  $\rho$  (colloids/ $\mu\text{m}$  at the glass substrate) as  $\rho^{-3/4}$ , in qualitative agreement with the observations of Fig. 5. We also note that for fields between typically 1 and 3 mT the reflectance increases linearly with field until it reaches saturation at about 5 mT. The largest change in reflectance with magnetic field is seen for the largest colloidal concentrations, since these block more light when no magnetic field is applied. We see from Fig. 5 that a reflectance change of more than 30% occurs upon changing the magnetic field from 1 mT to 5 mT.

Figure 6 shows the normalized reflectance versus time after turning off the magnetic field for colloidal concentrations  $5 \times 10^7$  beads/ml (open squares),  $8 \times 10^8$  beads/ml (black squares) and  $5 \times 10^8$  beads/ml (open triangles). It is seen that the relaxation time back to nominal reflectance is

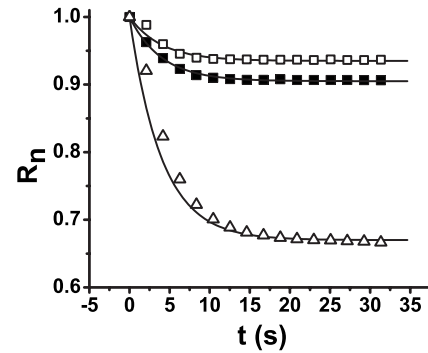


FIG. 6. The normalized reflectance versus time after the magnetic field has been turned off. Note that the reflectance is normalized to each colloidal concentration. See text for details.

typically a few seconds and independent of concentration. If we reapplied a magnetic field after waiting for a period much larger than the relaxation time, no hysteresis was observed, since the colloidal system had relaxed back to its original configuration at the glass plate. In order to get a better understanding of the relaxation process, we need to understand the forces acting on the colloids. When colloidal particles are dispersed in an aqueous solution, gravity, hydrodynamic drag, hydrodynamic and electrostatic interactions act on the colloidal system. However, here we expect gravity and hydrodynamic drag acting on the spheres to play the most important roles, since the electrostatic forces are relatively short range. It is known that the electrostatic interaction energy between the colloidal surfaces is given by  $E_E \sim B \times \exp(-z/\lambda_D)$  [22], where  $z$  is the distance between the colloidal surfaces,  $B$  is a constant depending on the surface charge and  $\lambda_D = \sqrt{\epsilon \epsilon_0 k_B T / 2e^2 c}$ , where  $\epsilon$  is the relative permeability,  $\epsilon_0$  is the permeability of vacuum,  $k_B$  is Boltzmann's constant,  $e$  is the electron charge, and  $c$  is the concentration of ions. For pure water  $\lambda_D \sim 0.9 \mu\text{m}$ , which means that the charged colloids will not interact significantly unless they are very close to each other. After turning off the magnetic field the spheres may not be in close contact any more due to the fact that the solutions used here are relatively dilute, and we do not expect electrostatic interactions to play a major role in the kinetics of the chain collapse. For spherical particles of radius  $a = 1.4 \mu\text{m}$  moving in a liquid of viscosity  $\eta = 1 \text{ mPas}$  at a velocity  $v$ , the drag is given by  $f\eta av$ . On the other hand, the gravity is given by  $mg$ , where  $m = (4\pi/3)a^3(\rho_c - \rho_w)$ ,  $\rho_c = 1600 \text{ kg/m}^3$  is the density of the colloids,  $\rho_w = 1600 \text{ kg/m}^3$  is the density of water, and  $g = 10 \text{ N/kg}$ . Using Newton's second law, we find that it takes a spherical particle of the order of microseconds to reach the terminal velocity given by

$$v_T = \frac{4\pi a^2(\rho_c - \rho_w)g}{3f\eta}, \quad (1)$$

which is found to be  $v_T = 2.6 \mu\text{m/s}$  if the sphere is freely moving such that  $f = 6\pi$ . Using this information, we can now obtain a simple equation characterizing the kinetics of the chain collapse. Assume that the particles move independently of each other at the terminal velocity (i.e., we neglect

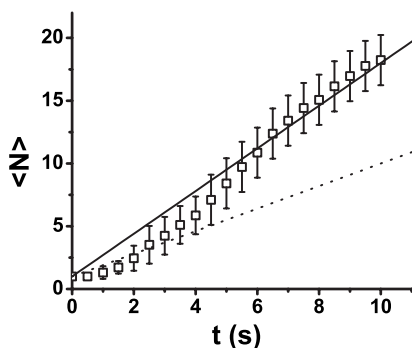


FIG. 7. The average number of colloids reaching the substrate as a function of time after turning off the magnetic field.

interactions between the particles). If we further assume that the particles stand exactly on top of each other right before the chain collapses, the second particle needs a time  $2a/v_T$  before it reaches the ground, the third particle needs  $4a/v_T$ , and the  $N$ th particle needs  $t=2a(N-1)/v_T$ . Thus, after a time  $t$  we find that

$$N = 1 + \frac{v_T}{2a}t \quad (2)$$

colloids can reach the glass substrate. Using an optical microscope in transmission mode, equipped with a charge-coupled device camera providing a frame rate of 8 fps, we measured the average number  $\langle N \rangle$  of colloids reaching the glass slide after the field was turned off. Typical images are seen in Fig. 3, and our corresponding measurements of  $\langle N \rangle$  are reported in Fig. 7. The error bars represent the standard deviation representing the spread in the cluster size seen in Fig. 3(b), and are rather large due to the difficulty of providing an exact count of  $N$  versus time. At  $t=0$ , we have  $N=1$  since only the lower colloid in the chain is in close proximity with the glass surface. For  $t < 5$  s, we found that  $\langle N \rangle$  could be well described by Eq. (2), with  $f=6\pi$  (dashed line in Fig. 7). However, for  $t > 5$  s, the assumption  $f=6\pi$  appears to break down, and we found that  $f=10$  would better describe the time evolution (solid line in Fig. 7). This means that the drag force has been reduced to almost one-half of the initial drag. One possible explanation for this observation is drag force reduction due to the altered flow field behind the falling chain, as modeled by Gluckman *et al.* [23], who showed that a drag reduction factor of 0.6 can be achieved for chains composed of many spheres moving in array. This could also be the case here. Initially, the spheres move at low velocities as they fall out of the chain at nearly terminal velocity. When some of the lower spheres move away, the upper spheres may move downwards experiencing a lower hydrodynamic drag in the flow field created by the lower spheres. This may resemble the migration of birds, which use each others flow fields to experience reduced friction. We have also assumed that the particles move independently of each other at the terminal velocity (i.e., we neglect interactions between the particles) in order to be able to describe the average number of particles system using a simple kinetic model [Eq. (2)]. It should also be pointed out that if the

particles are in contact with each other, the velocity may be significantly smaller than the terminal velocity. However, the fit of our model to the experimental data suggests that our assumption is reasonable.

In order to gain further insight into how the reflectivity changes with time after turning off the magnetic field, we will assume that the rate  $dM/dt$  of colloids available for blocking the light path is proportional to the available colloids,  $M_0 - M$ , where  $M_0$  is the total number of colloids blocking the light path when  $t \rightarrow \infty$ . Naturally, all the colloids block the light path, but chains consisting of more than two colloids do not block the light more efficiently than two colloids on top of each other (which are estimated to block most of the light). Thus, it is reasonable to assume that the effective number of colloids blocking the light path is given by

$$\frac{dM}{dt} = -\frac{M - M_0}{\tau}, \quad (3)$$

where  $\tau$  is the characteristic time required for the colloids to move out of the shadow of the chain. We expect that the minimum value for this characteristic time,  $\tau_{\min}$ , is found by assuming that the colloids need to move at least a distance  $2a$  in the  $x$  or  $y$  direction at a velocity comparable to the terminal velocity of the colloids, which means that  $\tau_{\min} = 2a/v_T = 1$  s. After integrating Eq. (4) we obtain

$$M(t) = M_0 - M_1 \exp\left(-\frac{t}{\tau}\right), \quad (4)$$

where  $M_0 - M_1$  is the initial number of colloids effectively blocking the light path. Since the reflectivity can be approximated by  $R(t) = 1 - bM(t)$ , where  $b$  is a constant, we may use Eq. (4) to derive

$$R(t) = R_0 + R_1 \exp\left(-\frac{t}{\tau}\right), \quad (5)$$

where  $R(t=0) = R_0 + R_1$  and  $R(t \rightarrow \infty) = R_0$ . The solid lines of Fig. 6 show fits of Eq. (5) to the experimental values of the reflectance for colloidal concentrations  $5 \times 10^7$  beads/ml,  $8 \times 10^7$  beads/ml, and  $5 \times 10^8$  beads/ml. We have used a single time constant,  $\tau=4$  s, to fit Eq. (5) to the experimental data. The good overlap between curve fits and experimental data points suggest that our theory is reasonable. It should also be noted that  $\tau=4$  s is larger than our estimate of  $\tau_{\min}$ , which is not unexpected since the colloids move in the  $x$  and  $y$  direction at velocity smaller than  $v_T$ . Electrostatic interactions may also play a role in facilitating a reduced falling velocity.

#### IV. CONCLUSION

In conclusion, we have studied a magnetic colloidal system that can undergo severe structural changes upon increasing the dipolar interactions between the colloids. We used this phenomenon to create an optical sensor, which allowed us to control the reflectivity by tuning a magnetic field. The sensor could be integrated into microfluidic systems, thus allowing one to probe other quantities in addition to magnetic fields.



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