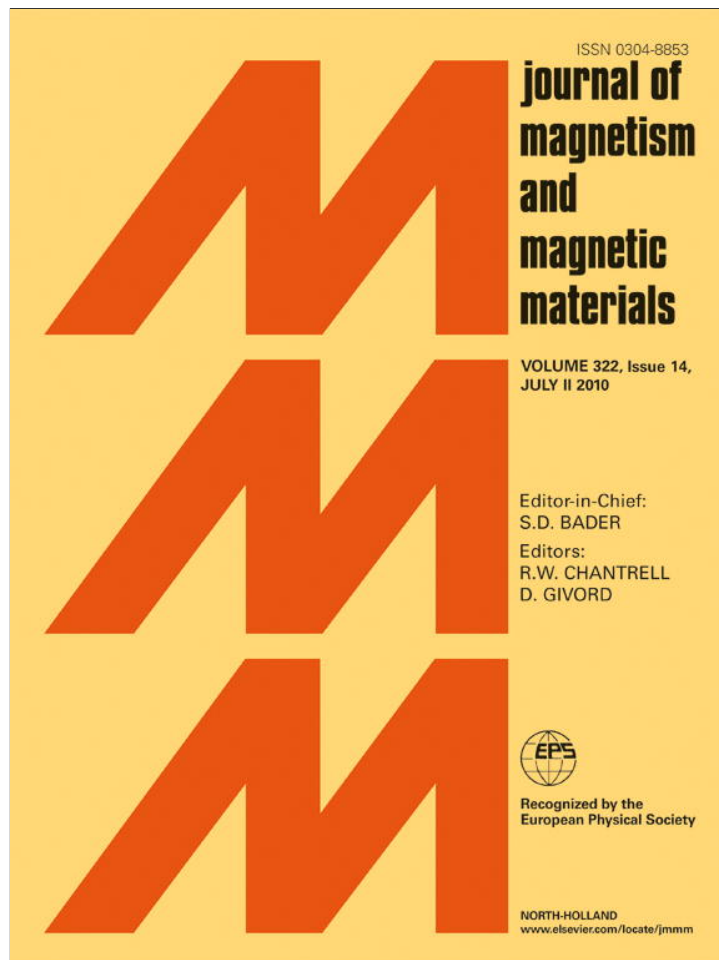


Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Magneto-controlled illumination with opto-fluidics

Serhiy Z. Malynych^{a,b,c,1}, Alexander Tokarev^{a,b}, Stephen Hudson^c, George Chumanov^{b,c}, John Ballato^{a,b}, Konstantin G. Kornev^{a,b,*}

^a School of Materials Science and Engineering, 161 Sirrine Hall, Clemson University, Clemson, SC 29634, USA

^b Center for Optical Materials Science and Engineering Technologies (COMSET), Clemson University, Clemson, SC 29634, USA

^c Department of Chemistry, 116 BRC, Clemson University, Clemson, SC 29634, USA

ARTICLE INFO

Article history:

Received 18 August 2009

Available online 7 January 2010

Keywords:

Iron oxide nanoparticle

Ferrofluid

Light scattering

Optofluidic

ABSTRACT

Imaging of micro- and nanofluidics is a challenge since the size of the channels is so small that the installment of additional optical and mechanical switches is very difficult. The size of the device and associated increase in viscous dissipation constitute another constraint. In response to these limitations, this work proposes and demonstrates the manipulation of light by adding a functional lens to control the light on demand. In the present work, this lens is realized by filling a hollow fiber with a colloid of superparamagnetic Fe₃O₄ nanoparticles. When the propagation of light is perpendicular to the magnetic field, this lens stretches the circular beam into a ribbon yielding a larger visible area. Potentially, one can apply a rotating magnetic field thus illuminating a larger spot size or creating other beam geometries. Such composite fibers might also be of value for Faraday isolation and other magneto-optic effects in optical fibers.

Published by Elsevier B.V.

1. Introduction

Magnetic fluids are colloids of subdomain paramagnetic particles that are dispersed in a liquid carrier [1–4]. Since their discovery, numerous interesting optical phenomena have been observed [4–6] and there has been a growing interest in applications of optical effects in magnetic fluids over the last decade. The promising applications include magnetic dichroism, magnetically induced birefringence, Faraday rotation and ellipticity, as well as field-affected light scattering [4,7–11]. Philip et al. [12,13] have observed a decrease in the light intensity transmitted through the iron oxide (Fe₃O₄, magnetite) nanoparticle suspension. The authors reported a dependence of the transmission coefficient on magnetic field, not specifying its time dependence. To interpret the experimental results, the authors proposed to take into account the light retardation caused by standing waves in the nanoparticles. However, the effect of chain formation in the suspension, which depends on time and magnetic field, has shown to be important [14]. An elegant study on time dependent anisotropic scattering induced by magnetic field in chemically stabilized Fe₃O₄ nanoparticles were analyzed in detail in Ref. [14]. Light scattering patterns were simultaneously recorded for light beams oriented along and across

magnetic field. Only the experiment with the light polarization orthogonal to the magnetic field is lacking and in our paper we consider these effects.

A diffraction pattern, resembling that produced by a wire (Fig. 1A), was observed in magnetic fluids [5,13–15]. When a laser beam passes through a magnetic fluid placed in a magnetic field it undergoes diffraction producing a characteristic pattern, such as that shown in Fig. 1B. This pattern is different from that produced by a wire because individual fringes are not separated in the former whereas they are clearly distinguished in the latter. Traditionally, diffraction has been studied in magnetic fluids at low concentration of magnetic carriers [1,2,8,16]. The observed patterns were interpreted assuming that magnetic particles form chains in an external magnetic field. It is known that the diffraction pattern from a chain represents a linear series of fringes like those observed with a wire. Light intensity in these fringes decays with the distance from the center spot. The position of these maxima at normal incidence is given by the equation $\sin \theta_n = n(\lambda/d)$, where θ_n is the diffraction angle, $n=0, \pm 1, \pm 2, \dots$ is the diffraction order, and d is the chain diameter [4,6,10].

The absence of well-defined spacing between fringes from magnetic fluids suggests that the observed pattern most likely is caused by multiple diffraction. When the light enters a magnetic fluid it diffracts from the first layer of the chains. This diffracted light undergoes second diffraction from the next layer and so on (Fig. 2). Thus, light diffracted by a spatial grating of magnetic chains is an integral sum of diffraction events from individual chains and the observed pattern can be interpreted as a combination of diffraction and interference.

* Corresponding author.

E-mail address: kkornev@clemson.edu (K.G. Kornev).

¹ On leave from V.E Lashkaryov Institute for Physics of Semiconductors, NAS of Ukraine, 41 Prospect Nauki, Kyiv 03028, Ukraine

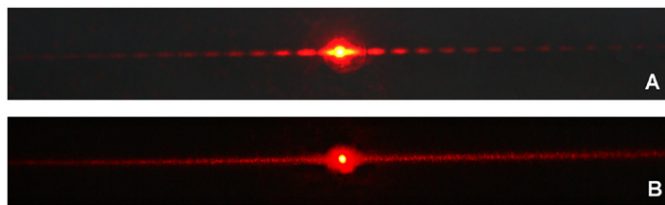


Fig. 1. Diffraction pattern from a single wire (A) and assemble of chains in magnetic fluid exposed to a magnetic field (B).

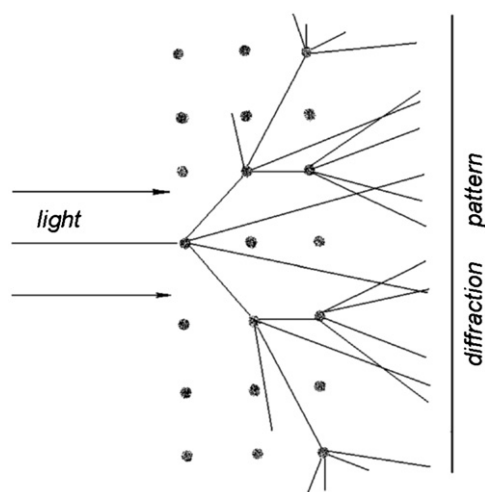


Fig. 2. Multiple diffraction in magnetic fluid. The chains and the direction of magnetic field are normal to the page. Diffraction pattern results from the interference between all possible diffraction orders.

Kuhlow and Lambeck [17] presented a rigorous theory of multiple diffraction from similar structures formed by magnetic domains in thick crystals. The diffraction is proposed to depend on the light polarization caused by Faraday rotation. In this work, the diffraction patterns and polarization dependence of light transmission measured at the center of laser beam was studied. The kinetic behavior of transmission coefficients then is related to multiple diffraction and light scattering. It was concluded from the experiments that the transmission coefficients depend on the polarization of light. This observation suggests that the Kuhlow–Lambeck theory can be extended to magnetic chains as well. We also propose a potential application of the diffraction effects in magnetic fluids for optofluidics.

2. Experiments

An aqueous suspension of 10 nm Fe_3O_4 nanoparticles with 0.0012 volume fraction was used in magneto-optic experiments. Iron oxide nanoparticles were synthesized by mixing 1 M ferric chloride and 2 M ferrous chloride in 2 M HCl with 500 ml of 0.7 M ammonia solution. After 10 min of stirring the solution was magnetically decanted and 2 M solution of perchloric acid was added to the reaction flask followed by vigorous stirring. The solution was then centrifuged and decanted again. Finally, the precipitate was redispersed in de-ionized water. No surfactants or stabilizers were added to the colloid. The stability of the colloid was provided by electrical double layer surrounding each nanoparticle. Details of the synthesis can be found elsewhere [18]. Concentration of nanoparticles was measured by thermogravimetric analysis. TEM was utilized to determine the nanoparticle size.

A standard spectrophotometer glass cuvette with 10 mm optical path was used in all magneto-optical experiments. The cuvette with the nanoparticles was placed between the poles of a water-cooled, DC magnet (GMW Associates). The gap between magnet poles was set to the minimum determined by the size of the cuvette allowing us to reach the magnetic flux densities up to 0.72 T. A Hall probe was used to measure the intensity and uniformity of the magnetic field. The uniformity of the magnetic field within the sample volume was within 0.1%. A He–Ne laser with a 632.8 nm wavelength was used as a light source. The measurements were performed for the transverse geometry (light propagation perpendicular to the magnetic field) with polarization plane being parallel and orthogonal to the applied magnetic field. We have not observed noticeable diffraction patterns for the longitudinal geometry when the light beam was parallel to the magnetic field and was guided through the 5 mm holes drilled in the magnetic poles. Hence, this effect is not discussed here. Glan–Thompson polarizer (Thorlabs) was used to define the polarization state. Light intensity was measured by a Si photodetector equipped with a ground glass diffuser to ensure uniform illumination of the detector. The signal was processed in the LabVIEW environment. Diffraction patterns were observed visually through a translucent screen and recorded with a CCD camera.

3. Results and discussion

Fig. 3 depicts the time evolution of the relative transmission coefficient after the sample was exposed to a magnetic field of various intensities. Relative transmission coefficient T is defined as $T=I/I_0$, where I_0 and I are transmitted light intensities measured before and after the field application, respectively. The light beam was orthogonal to the direction of the magnetic field. The plane of polarization was chosen perpendicular (Fig. 3A) and parallel (Fig. 3B) to the magnetic field. The kinetic behavior of the relative transmission coefficient is similar to that reported in [19,20]. Here, we extend studies to include a detailed analysis of the observed kinetic behavior on the basis of the diffraction phenomenon.

Each kinetic curve in Fig. 3 can be divided into three characteristic regions that are particularly pronounced at higher magnetic fields. The first region corresponds to a rapid increase of the transmitted light intensity (increase of T) immediately after the field was turned on, as is noticed from a spike on the kinetic curves. The origin of this spike is currently unknown and is under investigation. The second region is between the end of the spike and time t_1 when the intensity in the central spot reached minimum. The third region between t_1 and t_2 corresponds to a relatively slow increase of the signal until it plateaus.

It was concluded that the minimum of light intensity in the central spot measured at t_1 was due to the formation of chain-like structures from magnetic nanoparticles. Because of multiple diffraction from these structures light would ‘spread’ into a thin line causing the intensity reduction in the central spot. In other words, the energy redistribution between zero-order and higher-orders diffraction maxima leads to the decrease of the intensity of the transmitted light measured by the detector. A similar behavior is expected even in dilute colloids, for which the diffraction fringes are well-separated because multiple diffraction is small.

The increase of light intensity in the third region between t_1 and t_2 can be explained by slow coagulation of individual chains [21]. The magnetic dipole moments of individual particles inside the chain are canceled and only magnetic ‘charges’ at the end of the chain remain. This makes the entire chain behave as a large

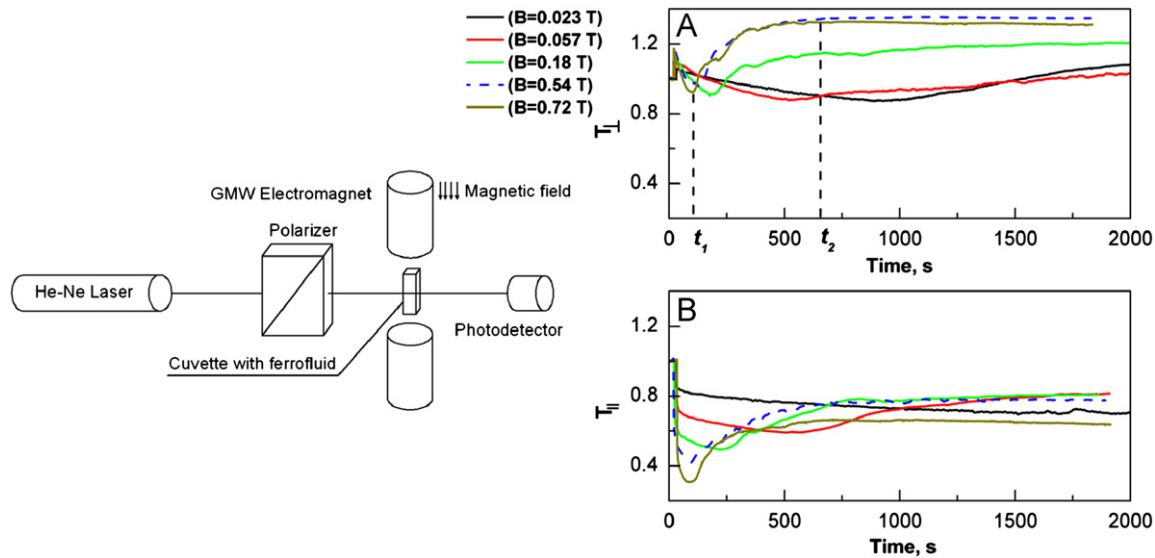


Fig. 3. Experimental set-up and time evolution of relative transmission coefficients in magnetic fluids. (A) The plane of light polarization is perpendicular to the magnetic field and (B) the plane of light polarization is parallel to the magnetic field. Incident beam is always perpendicular to the magnetic field.

magnetic dipole. When the distance between the chains is not much larger than the size of the chains, they experience a near-field interaction that decays with the distance as $1/R$ as opposed to $1/R^3$ expected for dipole–dipole interaction at the distances much larger than the size of the dipoles. This ‘slowly’ decaying near-field interaction caused a relatively long-distance attraction and, consequently, the coagulation of the chains. As the chains coalesced, the spacing between them increases, the multiple diffraction decreases and more light is transmitted. This explanation is corroborated by the simultaneous observation of ‘fainting’ of the diffraction line as the intensity in the central spot increased during the time period between t_1 and t_2 . The interaction between chains at long distances is similar to that between magnetic nanoneedles [21]. As was shown in experiments with magnetic nanoneedles, their coalescence took longer time because of their lower mobility [21].

It was also noted that the diffraction pattern persisted for over an hour after the magnetic field was switched off, particularly for magnetic fields stronger than 0.2 T. This observation indicated that the chain structures remained stable for long time and therefore may also yield interesting opportunities for optical cache memories. The long-term stability can be explained by the prevailing effect of dipole–dipole attraction between the particles as compared to electrostatic repulsion due to electrochemical double layer. The critical condition for stability follows from a natural modification of the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory [22], $U(h)=dU/dh=0$, where U is the interaction energy of two magnetic nanoparticles with diameter d separated by thickness h :

$$U = A_{\text{DLVO}} e^{-\kappa_D h} - \frac{\pi \mu_0 M^2 d^6}{72 (h+d)^3} \quad (1)$$

A_{DLVO} is the electrochemical constant used in the DLVO theory [22], μ_0 is the permeability of free space, M is the particle magnetization, and $1/k_D$ is the Debye length. From the DLVO conditions $U(h)=dU/dh=0$ we immediately obtain the critical separation distance $h_c=3/k_D-d$. For example, in pure water at pH 7, $1/k_D \sim 1 \mu\text{m}$, therefore, if the nanoparticles come closer, they are expected to form stable pair. As the Debye length decreases, the stability condition becomes dependent on the nanoparticle size. Substituting the critical distance into the condition $U(h_c)=0$, we see that the critical magnetic moment depends on the electro-

chemical conditions:

$$M = \sqrt{\frac{72 A_{\text{DLVO}} e^{-3+\kappa_D d}}{\pi \mu_0 d^5}} \left(\frac{3}{\kappa_D}\right)^3 \quad (2)$$

As the Debye length decreases, the critical magnetic moment decreases as well, leading to formation of more stable chains at weaker field.

The particle magnetization M in magnetic fluids nonlinearly depends on the field through the Langevin formula [1,2], suggesting that the magnetic moment depends on temperature and the applied field. Brownian rotation of the magnetic moment becomes insignificant in strong fields therefore longer particle chains are formed. The local field from the neighbors in long chains could freeze the magnetic moment resulting in the observed stability of the chains and the diffraction pattern after removing the external field.

Another noticeable effect is that the transmission coefficients demonstrate the dependence on the light polarization. In Fig. 3 A, the transmission coefficient is shown for the light polarized in the plane perpendicular to the magnetic field. In this case, the electric field vector is perpendicular to the chain axis. As the magnetic field increased, larger and faster (smaller t_1 and t_2) changes of the transmission coefficient were observed. At 0.54 T field, the transmission coefficient reached minimum at ca. 0.88 in about $t_1=120$ s and fully recovered to its maximum value of ca. 1.28 after 700 s. However, when the field was reduced ten times (0.057 T), the minimum was reached in ca. 500 s and the overall change of the transmission coefficient was only 0.1. The observed changes of the transmission coefficient with time and applied field were due the formation kinetics of the nanoparticle chain, as described above. First, a large number of relatively small chains were formed causing strong scattering of light and the reduction of the intensity in the central spot. With time and in stronger fields, chains became larger and agglomerated into bundles spaced at relatively large distances from each other. In this case, multiple diffraction of light took place leading to the formation of a characteristic line with larger intensity in the central spot. When light polarization was parallel to the magnetic field and the electric vector aligned along the chain axis, the cross-section for the interaction with light was increased and the observed changes of the transmission coefficient were larger (Fig. 3B). According to the theory of field-induced anisotropy in magnetic fluids [9–

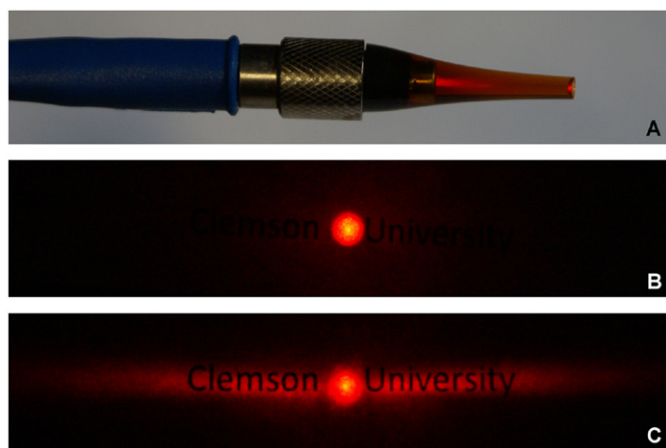


Fig. 4. Optical fiber with a capillary tip filled with magnetic fluid (A); light pattern on a screen before (B) and after (C) the magnetic field was switched on. Central spot corresponds to direct laser beam (zero-order diffraction); diffracted line is slightly bent due to the imperfections in optical alignment.

11,23,24] the differences in light transmission result from modifications of refractive index associated with the chain formation. In turn, the intensity of light diffracted by the chains and projected on the screen depends on the light polarization. This effect opens up another way of controlled illumination.

The transmission of light through the magnetic fluid in a magnetic field depends on the polarization of light. A stronger magnetically induced diffraction as well as larger intensity changes in the central spot was observed when measurements were performed with the polarization vector parallel rather than perpendicular to the applied magnetic field (Fig. 3).

Magnetically induced diffraction inspires a practical application of this phenomenon, in which light can be manipulated with magnetic field. The light beam from a laser can be coupled to the optical fiber with a tip filled with a magnetic fluid. Without magnetic field, the light goes through the tip forming a round spot on the screen. When the field is applied perpendicularly to the fiber, it deforms the spot thus illuminating a larger area. In order to check this idea, a 15 mm long conical tip cut from a glass pipette was mounted at the end of 0.2 mm multimode optical fiber (Fig. 4A). The inner diameter of the narrowest part of the tip was about 2 mm. The tip was then gently filled with the Fe_3O_2 magnetic fluid and placed between the poles of GMW magnet. A strip of paper was used as a screen.

Turning on magnetic field resulted in the instant appearance of a diffraction line with gradually increasing brightness. The maximum level of the brightness was achieved after about 20–30 s (Fig. 4C). The same effect was also observed when a small droplet of the magnetic fluid was attached to the end of the fiber. Turning magnetic field on and off allowed one to rapidly change the shape of the illuminated spot.

4. Conclusions

We observed the time dependent variations of the optical transmission of a colloid of Fe_3O_4 nanoparticles exposed to magnetic field of differing strengths. The transmission coefficient measured at the center of the laser beam decreased to a minimum and then slowly increased to a saturation level. This dependence was explained by multiple diffraction of light on magnetic chains formed in magnetic fluid. This means the radiation energy is redistributed over the center of the laser beam and diffraction wings thus

reducing the measured transmission coefficient. This effect also depends on the direction of the polarization of light relative to the direction of the magnetic field. This behavior is explained by the field-induced changes in refractive index of the magnetic fluid. The observed diffraction effects may find practical applications in optofluidics where the light beam can be stretched, intensified, or deemed by applying magnetic field or changing polarization.

Acknowledgments

We thank Dr. B. Zdyrko for his assistance in LabVIEW programming. The authors are also grateful for the financial support from the Clemson Center for Optical Materials Science and Engineering Technologies (COMSET), United States Department of Energy, Grant no. DEFG02-06ER46342, and National Science Foundation, Grants CMMI 0826067 and CMMI 0825832.

References

- [1] E. Blums, A. Cebers, M.M. Maiorov, in: *Magnetic Fluids*, Walter de Gruyter, New York, 1997.
- [2] R.E. Rosensweig, in: *Ferrohydrodynamics*, Cambridge University Press, Cambridge, 1985.
- [3] S. Laurent, et al., *Magnetic iron oxide nanoparticles: synthesis, stabilization, vectorization, physicochemical characterizations, and biological applications*, *Chemical Reviews* 108 (2008) 2064–2110.
- [4] B.M. Berkovskii, V.G. Bashstovoi (Eds.), *Magnetic Fluids and Applications Handbook*, Begell House Publishers, New York, 1996.
- [5] W.E.L. Haas, J.E. Adams, *Diffraction effects in ferrofluids*, *Applied Physics Letters* 27 (1975) 571–572.
- [6] C.F. Hayes, *Observation of association in a ferromagnetic colloid*, *Journal of Colloid and Interface Science* 52 (1975) 239–243.
- [7] H.W. Davies, J.P. Llewellyn, *Magneto-optic effects in ferrofluids*, *Journal of Physics D—Applied Physics* 13 (1980) 2327–2336.
- [8] J.C. Bacri, et al., *Transient grating in a ferrofluid under magnetic-field-effect of magnetic-interactions on the diffusion-coefficient of translation*, *Physical Review E* 52 (1995) 3936–3942.
- [9] V. Socoliuc, et al., *Agglomerate formation in moderately concentrated ferrofluids from static magneto-optical measurements*, *Journal of Magnetism and Magnetic Materials* 191 (1999) 241–248.
- [10] S. Taketomi, M. Ukita, M. Mizukami, H. Miyajima, S. Chikazumi, *Magneto-optical effects of magnetic fluid*, *Journal of the Physical Society of Japan* 56 (1987) 3362–3374.
- [11] V. Socoliuc, *Investigation of concentration and surfactant quality influence on magnetic particle agglomeration in ferrofluids from static linear dichroism experiments*, *Journal of Magnetism and Magnetic Materials* 207 (1999) 146–157.
- [12] J. Philip, J.M. Laskar, B. Raj, *Magnetic field induced extinction of light in a suspension of Fe_3O_4 nanoparticles*, *Applied Physics Letters* 92 (2008) 221911.
- [13] J.M. Laskar, J. Philip, B. Raj, *Light scattering in a magnetically polarizable nanoparticle suspension*, *Physical Review E* 78 (2008) 031404.
- [14] C. Rablau, et al., *Magnetic-field-induced optical anisotropy in ferrofluids: a time-dependent light-scattering investigation*, *Physical Review E* 78 (2008) 051502.
- [15] A.K. Bentley, A.B. Ellis, G.C. Lisensky, W.C. Crone, *Suspensions of nickel nanowires as magneto-optical switches*, *Nanotechnology* 16 (2005) 2193–2196.
- [16] J.E. Martin, K.M. Hill, C.P. Tigges, *Magnetic-field-induced optical transmittance in colloidal suspensions*, *Physical Review E* 59 (1999) 5676–5692.
- [17] B. Kuhlow, M. Lambeck, *Consideration of multiple diffraction in magneto-optical imaging*, *Journal of Magnetism and Magnetic Materials* 4 (1977) 337–343.
- [18] R. Massart, *Preparation of aqueous magnetic liquids in alkaline and acidic media*, *IEEE Transactions on Magnetics* 17 (1981) 1247–1248.
- [19] J. Li, et al., *Field-induced transmission of light in ionic ferrofluids of tunable viscosity*, *Journal of Physics D—Applied Physics* 37 (2004) 3357–3360.
- [20] J. Li, et al., *Field modulation of light transmission through ferrofluid film*, *Applied Physics Letters* 91 (2007) 253108.
- [21] K.G. Kornev, D. Halverson, G. Korneva, Y. Gogotsi, G. Fridman, *Magnetostatic interactions between carbon nanotubes filled with magnetic nanoparticles*, *Applied Physics Letters* 92 (2008) 233117.
- [22] J.N. Israelachvili, in: *Intermolecular and Surface Forces*, Academic Press, New York, 1987.
- [23] J.J.M. Janssen, J. Perenboom, *Magneto-optical phenomena in magnetic fluids—the influence of orientation of anisotropic scatterers*, *Journal of Magnetism and Magnetic Materials* 81 (1989) 14–24.
- [24] E.S. Kooij, A.C. Galca, B. Poelsema, *Versatile transmission ellipsometry to study linear ferrofluid magneto-optics*, *Journal of Colloid and Interface Science* 304 (2006) 261–270.