Optics Communications 283 (2010) 1182–1187

Contents lists available at ScienceDirect

Optics Communications

journal homepage: www.elsevier.com/locate/optcom

The modulation of coupling in the relaxation behavior of light transmitted through binary ferrofluids

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ARTICLE INFO

Article history:
Received 20 September 2009
Received in revised form 21 October 2009
Accepted 8 November 2009

Keywords:
Ferrofluid
Transmission light
Relaxation behavior
Modulation

ABSTRACT

With an external magnetic field, a relaxation process is observed when the light transmit through binary ferrofluids composed of ferrimagnetic $CoFe_2O_4$ and paramagnetic p-$NiFe_2O_4$ nanoparticles similar to ferrofluids consisting only of $CoFe_2O_4$. Since only the ferrimagnetic nanoparticles are able to form field-induced chainlike structures for such binary ferrofluids by magnetic interaction between the particles, so the relaxation behavior of the transmitted light is caused mainly by the ferrimagnetic system. In the binary ferrofluids, the paramagnetic nanoparticles, regarded as magnetically polarized gas molecules, are restrained to occupy the space between the ferrimagnetic chains and distribute following the $CoFe_2O_4$ particle chains covering and diverging, producing a modulation effect on the relaxation behavior of the transmitted light. The modulation effect can be characterized by range and time parameters that describe the relationship of the relaxation behavior of the transmitted light to the properties of the binary ferrofluids and single $CoFe_2O_4$ ferrofluids.

1. Introduction

Generally, so-called ferrofluids are suspensions of strong magnetic (ferromagnetic or ferrimagnetic) nanoparticles with diameters of the order of 10 nm, dispersed in a carrier liquid [1]. Other similar suspensions are magneto-rheological fluids that comprise mesoscale (1–10 μm) ferromagnetic or ferrimagnetic particulates [2]. When a modest external magnetic field is applied, of the order of 10^2 Gs, the strong magnetic nanoparticles in the ferrofluids can form chainlike structures parallel to the field direction [3]. The chains will move under the influence of both the force towards the center from the magnetic field gradient (known as the "magnetic convergent force") and the repulsive force between chains (known as the "magnetic divergent force") for the magnetic fields used in technical devices with a non-uniformity of the order of 10^4–10^5 Gs/m [4]. So, the intensity of the light transmitted through a ferrofluid film will vary non-monotonically with time and display a relaxation process from the "geometric shadowing effect" [5–8], in which the intensity difference between the transmitted and incident light is regarded as resulting only from the opaque cross-section of the medium, since the scattering is far less than the absorption. Fig. 1 is a typical curve of the variation of the relative transmission coefficient T with time t during the application of a magnetic field to a ferrofluid prepared by Massart's method [9]. T is defined as

$$T = (I'/I_0)/(I/I_0) = I'/I \quad (1)$$

where I_0 is the intensity of incident light, $I'(I)$ is the intensity of transmitted light in the presence of a external magnetic field. In such a T–t curve, the minimum value T_2 with its corresponding time t_2, and the maximum value T_3 and its corresponding time t_3 are known as the characteristic parameters describing the relaxation behavior [6,10]. It can be seen yet from Fig. 1 that T could exceed 1. This means that in certain a short time of the field-induced relaxation process, the intensity of the transmission light could become larger than the one in the absence of magnetic field.

The properties of ferrofluids/magneto-rheological fluids with two dispersed phase have attracted significant research interest. For example, the formation of chainlike aggregates and the demixing phase transition have been theoretically studied by a model of a bi-dispersed magnetic system composed of "large" and "small" particles [11–14]. Patel et al. observed a novel magnetic-optical effect in composites consisting of magnetic or diamagnetic micron-sized particles suspended in the ferrofluids [15]. Ge et al. found that for magnetic colloids based on sub-micron-sized Fe_3O_4 particles, the tuning range of the diffraction can be further increased by mixing two samples with a large size difference [16]. Jeyadevan et al. and Masheva et al. investigated the magnetization behavior of mixtures with superparamagnetic and non-superparamagnetic particles [17,18]. Islan et al. explored the magnetic-field-induced ordering and micro-phase separation of aqueous mixtures of ferrofluids with non-magnetic latex spheres [19]. Mehta et al. considered magnetooptical effects in ferrofluids containing single

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doi:10.1016/j.optcom.2009.11.016

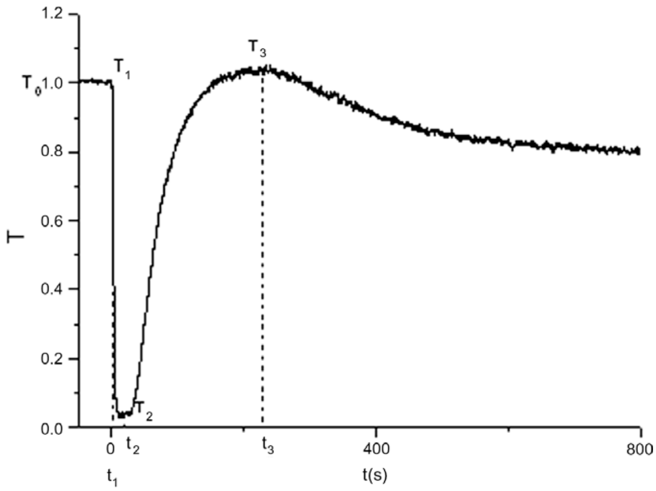

Fig. 1. The *T–t* curve for the $CoFe_2O_4$ ionic ferrofluid with particle volume fraction $\phi = 0.5\%$ in an applied magnetic field (1300 Gs). After the field is turned on (not ramped slowly) at $t = t_0(=0)$, T first increased quickly from $T_0(=1)$ up to the maximum level labeled T_1 during the time from $t_0(=0)$ to t_1, then decreased. However, $\Delta T(=T_1 - T_0)$ may be too weak to measure and $\Delta t(=t_1 - t_0)$ is far shorter than the relaxation process of the transmitted light, so T_1, t_1 can be regarded as equal to T_0 and t_0, respectively.

magnetic nanoparticles and large aggregates [20], as well as observed the phenomenon of field-induced trapping of visible light for a mixture of ferrofluid and micron-sized magnetic spheres [21]. Donatini et al. demonstrated that compatible ferrofluids, e.g. $CoFe_2O_4$ and Fe_3O_4, can be mixed in suitable proportions so as to cancel the circular dichroism at selected wavelengths [22]. In this paper, the relaxation behavior of light transmitted through binary ferrofluids composed of strong magnetic (ferrimagnetic) and weak magnetic (paramagnetic) nanoparticles, is reported.

Ferrimagnetic nanoparticles have permanent magnetic moments m, described by

$$m = \frac{\pi}{6} a^3 M_s \tag{2}$$

where a is the diameter of the particle and M_s is the saturation magnetization [1]. In the absence of magnetic field, the permanent magnetic moments are randomly oriented because of thermal motion. When a magnetic field is applied, the moments fixed inside the ferrimagnetic nanoparticles become oriented order and the interaction between the particles depends on the orientation. Paramagnetic nanoparticles do not have a permanent magnetic moment. However, application of an external magnetic field would induce a magnetic moment, as follows

$$m = \frac{\pi}{6} a^3 \chi H \tag{3}$$

where χ is the magnetic susceptibility and H is the applied magnetic field [23,24]. These particles interact pairwise with each other via the dipole–dipole interaction energy. The maximal dipolar attraction energy between dipoles m_i and m_j, E_M, occurs when they are in the head-to-tail configuration and is given by

$$E_M = -\frac{\mu_0 m_i m_j}{2\pi r_{ij}^3} \tag{4}$$

where μ_0 is the vacuum magnetic permeability and r_{ij} is the distance between the centers of particles i and j, i.e. the sum of radii of the two particles i and j. The strength of the dipolar interaction between the particles can be expressed by a coupling constant defined as the ratio of the maximal attraction energy between the particles and the thermal energy [25,26] as

$$\lambda = -\frac{E_M}{k_B T} = \frac{\mu_0 m_i m_j}{2\pi r_{ij}^3 k_B T} \tag{5}$$

where k_B is the Boltzmann constant and T is the absolute temperature. Eq. (5) is suitable for describing the interaction between different particles. If the magnetic dipole–dipole interaction energy between the particles exceeds the thermal energy k_BT, then the particles could arrange themselves into chains [27]. Because of thermal disorientation of the magnetic moments, the actual magnetic interaction energy is significantly smaller than $E_{M.}$ Application of an external magnetic field aligns the magnetic moments and increases the attractive interaction between the particles, so it is possible that an applied magnetic field induce the particles in a ferrofluid to aggregate [28]. In a binary system based on ferrimagnetic nanoparticles and paramagnetic nanoparticles, if $\lambda > 2$ between the ferrimagnetic particles, and $\lambda \leqslant 2$ between the paramagnetic particles as well as between the ferrimagnetic and paramagnetic nanoparticles, only the ferrimagnetic nanoparticles can form chainlike structures under the influence of an external magnetic field. In addition, the paramagnetic nanoparticles will act as a magnetically polarized molecular gas and distribute among the ferrimagnetic nanoparticle chains. Therefore, binary ferrofluids composed of ferrimagnetic and paramagnetic nanoparticles very closely model a magnetically bi-dispersed system [12]. For this reason, it not only has potential applications but can also be used as the subject of fundamental ferrofluid research.

2. Experiment

In the present work, the particles were prepared by co-precipitation technology. From electron micrographs, the particle size as well as the size distribution were obtained. This is regarded as the simplest measurement of nanoparticle size [29]. The strong magnetic particles consist of $CoFe_2O_4$, with median size 12.76 nm and standard deviation 0.35. The weak magnetic particles consist of ($Ni(OH)_2$:2FeOOH) which is the precursor to synthesized $NiFe_2O_4$ [30], and are written as p-$NiFe_2O_4$. Their median size is 4.37 nm with standard deviation 0.18. The magnetization curves of the particles were measured with the field from 0 to 10^4 Gs at room temperature using a vibrating sample magnetometer (VSM), as shown in Fig. 2. Obviously, the $CoFe_2O_4$ particles are ferrimagnetic and the p-$NiFe_2O_4$ particles are paramagnetic. From the results of magnetization, the average coupling constants at 300 K can be calculated as $\lambda = 4.10$ between $CoFe_2O_4$ particles,

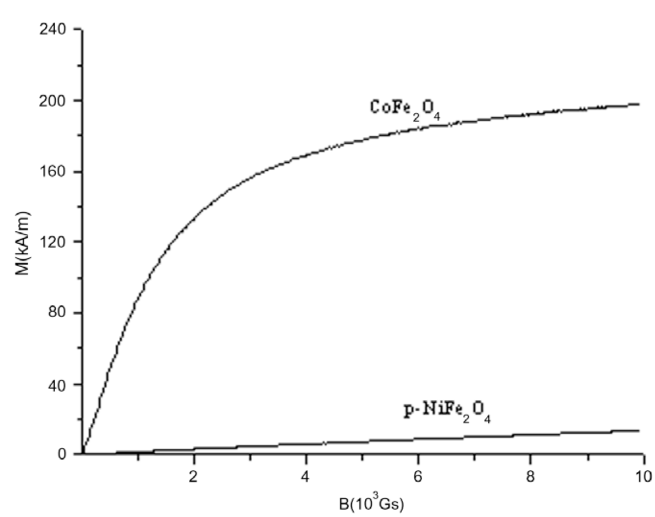

Fig. 2. The magnetization curves of (a) $CoFe_2O_4$ nanoparticles and (b) p-$MgFe_2O_4$ nanoparticles.