

## Anomalous diffusion in ferrofluids

Alenka Mertelj,<sup>1</sup> Luka Cmok,<sup>1</sup> and Martin Čopič<sup>1,2</sup><sup>1</sup>*J. Stefan Institute, Jamova 39, SI-1001 Ljubljana, Slovenia*<sup>2</sup>*Department of Physics, University of Ljubljana, SI-1000 Ljubljana, Slovenia*

(Received 10 November 2008; revised manuscript received 30 January 2009; published 8 April 2009)

By dynamic light scattering we have studied suspensions of ferrimagnetic maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) nanoparticles in *n*-decane with attractive interparticle interaction. The measurements in the suspensions of different concentrations ranging from 0.21 to 25.8 wt % have been compared in zero external field and in the magnetic field of 270 mT. In all samples well-defined relaxation process was observed. In the absence of an external field the suspensions were homogeneous, while in the magnetic field most of the suspensions undergo phase separation in a needlelike islands of a very dense suspension surrounded by a dilute suspension. The underfield dynamical behavior is found to be anisotropic and diffusive in both directions at low concentration. For the more concentrated sample, in the direction parallel to the external field, it remains diffusive with a larger diffusion coefficient while it is not so in the perpendicular direction, in which the mean-squared displacement grows faster than linearly with time and the dependence of the relaxation rate on the scattering vector  $q$  is not quadratic. In this direction the dynamics of the system present similar features as glasses or gels close to the dynamical arrest.

DOI: [10.1103/PhysRevE.79.041402](https://doi.org/10.1103/PhysRevE.79.041402)

PACS number(s): 82.70.-y, 47.65.Cb, 78.35.+c, 66.10.C-

## I. INTRODUCTION

Ferrofluids, i.e., colloids of magnetic single-domain nanoparticles in solvents, show interesting external magnetic-field-dependent dynamical properties [1,2]. Among them the most interesting for application are field-dependent rheological properties (see, for example, Ref. [2]). Depending on the dipolar interaction parameter, magnetic particles in suspension in the absence of magnetic field may either chain or behave similarly as in any other suspension. In the presence of external magnetic field the magnetic interaction between the particles becomes more important and the system may undergo a phase-separation process leading to a liquidlike dense phase surrounded by the gaslike phase of individual particles [3] or may remain monophasic [4] depending on the global balance of interparticle interaction. If the polydispersity is low the dense phase can order in hexagonal crystal-like phase [5–7]. However usually the polydispersity is not very low. In the process of phase separation in the external magnetic field the largest particles, which are present in the polydisperse suspension and for which the magnetic interaction at contact exceeds the thermal energy  $k_B T$ , form chains and play the key role. In the early stages they form larger needlelike aggregates between which the interaction is anisotropic leading after ripening up to micron-sized elongated droplets. The rotational motion of these larger aggregates is suppressed by the external field and that cause the increase in the viscosity [8]. There are many experimental [9–11] and theoretical [12–16] studies on the phase separation and formation of the chains.

The particles in the ferrofluids are either sterically or electrostatically stabilized. In the latter, also called ionic ferrofluids, one can tune the electric repulsion and the magnetic dipolar interaction, so that the system in the external magnetic field does not undergo phase separation, but remains monophasic and may form some kind of repulsive glass at large concentration and large interparticle repulsion. The

properties of such a glass were studied by x-ray photon correlation spectroscopy in the absence of external magnetic field [17,18] and by neutron-scattering and quasielastic neutron spin-echo experiments [19–21]. The x-ray experiments show a so-called “anomalous diffusion behavior,” where the mean-square displacement increases faster than linearly with time, and the typical relaxation rate is not proportional to the square of the wave vector  $q^2$  but to  $q$  only [17]. These experiments were made at the high  $q$ , where one probes the dynamics in the range of the distance between the particles ( $1/q \sim$  distance between the particles). In the neutron spin-echo experiments the hydrodynamic function was measured and it exhibits peak at  $q$  where also the scattering intensity has a peak, which means that the correlated motion of the neighboring particles is probed. In this large- $q$  limit the Brownian motion is shown to be either significantly anisotropic [20] or just slightly anisotropic [21].

In monophasic ferrofluids, the diffusion in low- $q$  limit has been measured by forced Rayleigh (FRS) experiments [22–25]. By two strong laser beams one creates a grating of high and low intensities of the light field, and due to thermal Soret effect particles move to the region of high or low intensity (depending on the sign of the Soret coefficient) and create a density grating. After switching off the strong laser field, the decay of the induced grating is measured by weak probe laser beam, and the diffusion coefficients can be obtained. Also these experiments show that in monophasic samples under external magnetic field the translational dynamics is diffusive and strongly anisotropic [23].

Experiments on the translational dynamics of the samples that undergo phase separation in the external field are scarce. In the x-ray photon correlation spectroscopy study [26] the dynamics in the large- $q$  region (from  $2.1 \times 10^7$  to  $2.5 \times 10^9$  /m) was investigated. It was found out to be diffusive and that in the absence of the field the translational diffusion constant of the particles was significantly smaller than expected for free diffusing single nanoparticles. In the external magnetic field the translational diffusion constant perpen-

dicular to the external field was smaller than the parallel one, and both were smaller than the translational diffusion constant in the zero field.

If the ionically stabilized fluids, where there is no chaining in the external magnetic field due to strong repulsive electric interaction, are reasonably well understood, the experiments and the theory on the dynamics of diphasic ferrofluids are far from conclusive. Indeed less is known on the dynamical behavior of the ferrofluids that undergo the phase separation, i.e., they form chains, elongated aggregates. Those are the ferrofluids that show very interesting rheological behavior (see, for example, [2]). Ultrasound attenuation has been shown to be highly anisotropic in such systems [27]. Recently the hydrodynamic theory of polydispersed chain-forming ferrofluids has been proposed [28]. It predicts interesting orientational dynamics and explains the magneto-viscous effect. Equilibrium properties of bidispersed ferrofluid with chain aggregates have been studied theoretically and compared to the computer simulations in Ref. [29]. One of the interesting results of this study is that the presence of small particles suppresses the growth of the aggregates. What is the role of the polydispersity and how the phase separation and static structures that appear in the external magnetic field influence the diffusive dynamic is still an open question. In this paper we present dynamic light-scattering (DLS) experiments in a ferrofluid that undergoes phase separation in external field.

The dynamical behavior in low- and intermediate- $q$  regions is well covered by the DLS experiments, although those are rarely done in the ferrofluids. The main reason is that the ferrofluids absorb light in the visible range. In our experiments we overcame this problem by using low intensity of the laser beam. We chose the wavelength in the region where absorption of the magnetic particles is small and the samples were thin enough. By DLS we have studied the dynamics of maghemite nanoparticles in decane. We have measured the dependence of the translational dynamics on the concentration of the magnetic particles, on the external magnetic field, and on the scattering vector. The experiment and its results are described in Sec. II and are followed by discussion (Sec. III) and conclusions (Sec. IV).

## II. EXPERIMENT

The ferrofluid used in our experiments was suspension of maghemite ( $\gamma$ - $\text{Fe}_2\text{O}_3$ ) nanoparticles in  $n$ -decane. The suspension was sterically stabilized using oleic acid as a surfactant. We did not observe any sedimentation of the particles in suspension in the absence of the external magnetic field. The size distribution of nanoparticles in suspension was measured using DLS in dilute suspension (0.021 wt %) and the number distribution can be approximated by Schultz (also referred as gamma) distribution [30] with the mean particle hydrodynamic radius  $R$  of 8 nm and standard deviation of 3.6 nm. The corresponding average diffusion constant is  $3.2 \times 10^{-11} \text{ m}^2/\text{s}$ . The viscosity of  $n$ -decane at 297 K is  $\eta_0 = 0.84 \text{ mPa s}$ . The magnetic core of the particles is smaller by the length of the surfactant molecules and is approximately of the average radius of 5.5 nm, as was also deter-

mined from electron micrographs. The magnetization of the particles is  $3.1 \times 10^5 \text{ A/m}$ , so the magnetic moment  $p_m$  of the particles with the magnetic radius of 5.5 nm is  $2.2 \times 10^{-19} \text{ A m}^2$ . The dipolar interaction parameter  $\lambda^* = \frac{\mu_0 p_m^2}{4\pi k_B T (2R_c)^3}$  is defined for monodispersed suspension of particles [8], where  $R_c$  is the radius of the magnetic core plus the length of the surfactant molecule. In our case  $R_c$  is approximately the same as the hydrodynamic radius. The average  $\lambda_{\text{av}}^* = \int dR P_N(R) \lambda^*(R)$  calculated from the experimental number distribution function  $P_N(R)$  for our sample is approximately 1.4. The concentration of the particles with surfactant in different samples was 0.21, 2.1, 10, and 25.8 wt % of which approximately 17 wt % is the oleic acid, so the volume concentration of the magnetic particles was approximately 0.023, 0.24, 1.2, and 3.5 vol %. Less concentrated samples were obtained by dilution of the 25.8 wt % sample.

In our experiment we used a standard photon correlation setup using a He-Ne laser with wavelength of 632.8 nm and an ALV-6010/160 correlator to obtain the autocorrelation functions of the scattered light intensity. The laser wavelength used was chosen, so that the absorption of the maghemite particles was low, for example, at 632.8 nm the absorption of the particles is more than four times smaller than at 532 nm. The intensity of the laser beam was low and the measured correlation function did not depend on the intensity, so we conclude that no heating effects due to absorption were present in our measurements. The thickness of the samples was either 12  $\mu\text{m}$  for concentrations of 2.1, 10, and 25.8 wt % or 100  $\mu\text{m}$  for 0.21 wt % sample. The direction of external magnetic field and the scattering wave vectors were in all of our measurements in the plane of the sample; the scattering wave vector was either parallel or perpendicular to magnetic field. The direction of gravity was in the plane of the sample perpendicular to the scattering vector. The polarizations of the incoming and scattered light were vertical, i.e., either parallel or perpendicular to the magnetic field. There was no measurable signal in the depolarized scattering in the absence of and in the applied external magnetic field indicating that the scattering objects are optically isotropic in the absence of the field and in the external magnetic field the orientational motion of elongated objects was suppressed. The measured intensity autocorrelation function was nonexponential due to polydispersity of the particles. Due to the static structures in the samples (Fig. 1), most of the measurements were performed in mixed regime, that is, the intensity autocorrelation function  $g_2(t)$  is related to the field autocorrelation function  $g_1(t)$  by the relation  $g_2 = 1 + 2(1 - j_d)j_d g_1 + j_d^2 g_1^2$  with  $j_d$  being the ratio between the intensity of the light that is scattered inelastically and the total scattered intensity. We fitted  $g_2(t)$  using a stretched exponential function  $\exp[-(t/\tau_m)^s]$  for the field autocorrelation function  $g_1(t)$ . The average relaxation rate  $1/\tau$  shown in graphs was obtained using the relation  $\tau = \tau_m \Gamma(1/s)/s$  with  $\Gamma$  being the gamma function [31].

In the absence of the external field samples of all concentrations are homogenous on the scale of optical microscopy. In Fig. 2 the relaxation rate as a function of the square of the scattering vector  $q^2$  is shown for samples of different concentrations. For monodispersed noninteracting particles that

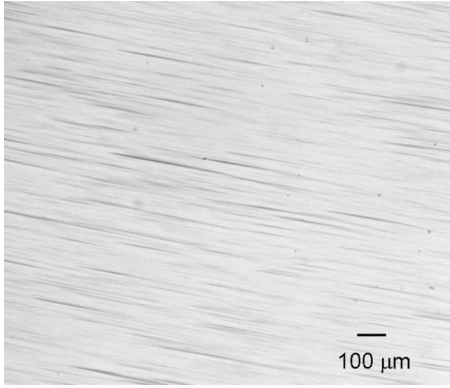


FIG. 1. Microscope image of the 10 wt % sample in the external magnetic field of 270 mT showing phase separation into needles and gas phase.

undergo Brownian motion the field autocorrelation function  $g_1(t)$  is a single exponential function with the relaxation rate given by

$$\frac{1}{\tau} = Dq^2 = \frac{k_B T}{6\pi\eta R} q^2, \quad (1)$$

where  $D$  is the diffusion constant of the particles,  $k_B$  is the Boltzmann constant,  $T$  is the temperature,  $\eta$  is the viscosity of the suspension, and  $R$  is the hydrodynamic radius of the particles. For polydispersed samples  $g_1(t)$  is a weighted sum of single exponential functions that results in a nonexponential function that decays slower than the single exponential function and in many cases including ours can be well fitted with the stretched exponential function  $\exp[-(t/\tau_m)^s]$  with the stretching exponent  $s$  smaller than 1. In the absence of the field the obtained stretching exponent  $s$  for all concentrations was typically 0.86. In the dilute 0.021 wt % sample, which was used in the size distribution measurements, the diffusion constant obtained from the stretched exponential fit is  $D(\phi \rightarrow 0) = 2.25 \times 10^{-11} \text{ m}^2/\text{s} (1 \pm 0.08)$  and is for a factor of 0.7 smaller than the average diffusion constant. The reason for the difference is that in the stretched exponential fit we do not take into account that the contribution of the particles with a given radius to the field autocorrelation function is weighted with the scattering cross section and that leads to smaller value of the diffusion constant. Since the stretching exponent was in most of our measurements approximately the same, also the factor between the average diffusion constant and the diffusion constant obtained from the stretched exponential fit is the same and the comparison between the diffusion constants obtained from the stretched exponential fit from different samples is possible. The diffusion constant in the 0.21 wt % sample is within experimental error the same as in the diluted (0.021 wt %) sample. In samples with concentrations of 2.1, 10, and 25.8 wt % the diffusion constant is smaller than in diluted samples, which is either due to the formation of aggregates or the interaction between the particles. In the denser 10 and 25.8 wt % samples there are rather large fluctuations in the relaxation rate in different measurements that cannot be attributed to the experimental error; however, the slope of the dependence of the relaxation rate on the scattering vector remains the same.

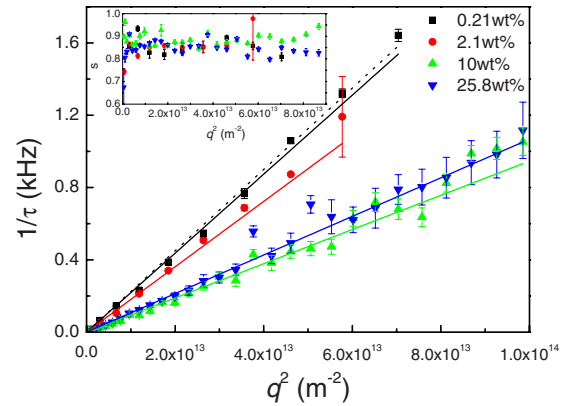


FIG. 2. (Color online) The dependence of the average relaxation rate of the correlation function on the square of the scattering vector for ferrofluids with different concentrations of magnetic nanoparticles in the absence of the external magnetic field. The lines are linear fits to the data. The dotted line is relaxation rate vs scattering vector extrapolated to zero concentration of magnetic particles. Inset: the stretching exponent versus the square of the scattering vector.

In the external magnetic field of 270 mT (of the permanent magnet) the most diluted sample (0.21 wt %) looks homogenous under an optical microscope as in the absence of the field, while the more concentrated samples undergo a phase separation into needlelike islands of a very dense phase surrounded by a diluted phase. Such a phase separation in dense liquidlike phase of nanoparticles surrounded by gaslike phase is typical for ferrofluids in the external magnetic field [3]. In the 2.1 wt % sample the needles are quite large (10–200  $\mu\text{m}$ ) but sparse and after the removal of the magnetic field they collapse into one or more spherical droplets that disappear in several hours. In the 10 wt % sample (Fig. 1) the needles are smaller but still clearly seen under the microscope and they disappear immediately after the removal of the field. In the 25.8 wt % sample there are some visible needles under field but most of them are too small to be seen under the microscope. Their existence can be deduced from the diffraction of the laser beam. The scattering of light is much stronger in the scattering plane perpendicular to the magnetic field indicating that the scattering is caused by elongated objects that are oriented along the magnetic field. The diffraction pattern disappears in a few minutes after the removal of the field, while when the external magnetic field is applied, it takes a few hours before the structure stabilizes, i.e., before the diffraction pattern becomes static. Also the part of dynamically scattered light is larger in the direction perpendicular to the field, which suggests that the diffusing objects are small needles or chains. The intensity of dynamically scattered light at larger  $q$  represents around 50%–60% of the whole scattered intensity at given  $q$ .

The phase-separation process is completely reversible and the measured autocorrelation function after the removal of the field is the same as before the sample was exposed to the external field. The needles are always oriented along the field and no rotational Brownian motion is observed. When a needle is far from other needles it undergoes translational



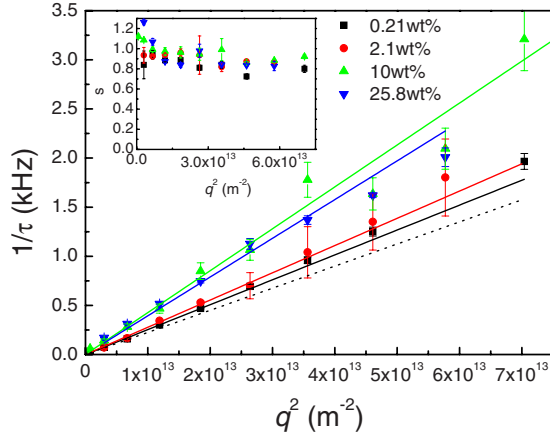


FIG. 3. (Color online) The dependence of the average relaxation rate of the correlation function on the square of the scattering vector for ferrofluids with different concentrations of magnetic nanoparticles parallel to the direction of the external magnetic field of 270 mT. The lines are linear fits to the data. The dotted line is relaxation rate vs scattering vector extrapolated to zero concentration of magnetic particles. Inset: the stretching exponent versus the square of the scattering vector.

Brownian motion, but when there are, for example, two needles and the distance between them is on the order of a length of the needles, there is attractive force between the two in the direction parallel to the field and the needles move, so that they coalesce with the opposite ends. In the direction perpendicular to the external magnetic field the approaching of the needles due to thermal motion stops at a certain distance between the needles, which is smaller than the length of the needles, due to the repulsive force between the needles. After initial rearrangement and growth of the needles due to the coalescence, they form a frustrated intercalated glassy structure where further motion and coalescence is suppressed by repulsive forces between the needles. The Brownian motion of the needles in the structure is suppressed and is not observable under the microscope. In the 2.1 wt % sample when the field is switched off and the needles collapse into spherical drops, the Brownian motion of these drops is clearly seen under the microscope. If the field is turned on again, the structure of needles reappears and the Brownian motion is again suppressed. This shows that in this case the magnetic interaction is considerably larger than the thermal energy  $k_B T$ . In the 2.1 wt % sample the large needles sediment and in the microscopy experiment they are at the bottom glass plate and the glassy structure described above is two dimensional (2D). In 10 wt % the repulsive force between the needles hinders sedimentation and after the formation of three-dimensional (3D) glassy structure we observe no sedimentation. In 25.8 wt % no sedimentation is observed in the time scale of our experiments.

The concentration dependence of the size of the needles can be understood in the following way. The formation of the disordered structure stops the coalescence when the average distance between the needles is comparable to the length of the needles. For more concentrated samples this condition is fulfilled for shorter needles. When the field is switched on,

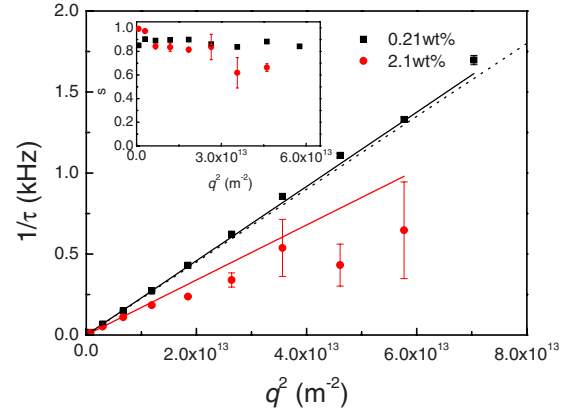


FIG. 4. (Color online) The dependence of the average relaxation rate of the correlation function on the square of the scattering vector for ferrofluids with the concentrations of magnetic nanoparticles of 0.21 and 2.1 wt % perpendicular to the direction of the external magnetic field of 270 mT. The lines are linear fits to the data. The dotted line is relaxation rate vs scattering vector extrapolated to zero concentration of magnetic particles. Inset: the stretching exponent versus the square of the scattering vector.

due to higher concentration of magnetic particles, also the initial concentration of the small needles is larger, and they form the disordered structure that stops the coalescence at earlier stage of phase separation than in less concentrated samples and consequently, in more concentrated samples, the needles are smaller. In the most concentrated sample the growth of the needles is suppressed at a very early stage and most of the needles are very small.

To test the diffusive nature of the dynamics, we have measured the intensity autocorrelation function as a function of scattering vector along (Fig. 3) and perpendicular (Figs. 4 and 5) to the direction of the magnetic field. The relaxation rate  $\tau^{-1}$  remains proportional to  $q^2$  in both directions in the less concentrated samples while it is not the case in the two more concentrated ones. For the diluted 0.21 wt % sample the diffusion constant is within the experimental error the same as in the absence of the field. In Fig. 6 the diffusion constants as a function of volume concentration is shown. For the 2.1 wt % sample the diffusion constant perpendicular to the field is about 10% smaller than in zero field while parallel to the field diffusion becomes faster by a factor of about 1.6. In this sample, as already mentioned, in the magnetic field there are needles that diffuse and also sediment and occasionally float through the scattering volume and make the contribution of the free nanoparticles (the gas phase) to the autocorrelation function sometimes unobservable. This is a problem especially at high  $q$ 's.

For the most concentrated 25 wt % sample in the direction along the field the relaxation rate can be fitted with  $aq^\beta$  and is by a factor of about 1.5 larger than the relaxation rate for the dilute 0.21 wt % sample. The stretching exponent  $s$  is larger than 1 for small scattering vectors, while for large  $q$  vectors it is similar to the case without the external field. In the direction perpendicular to the magnetic field the autocorrelation function shows two relaxations. The slow one has the relaxation rate similar as in the absence of the field, but the stretching exponent  $s$  is larger than 1 (Fig. 5). While the

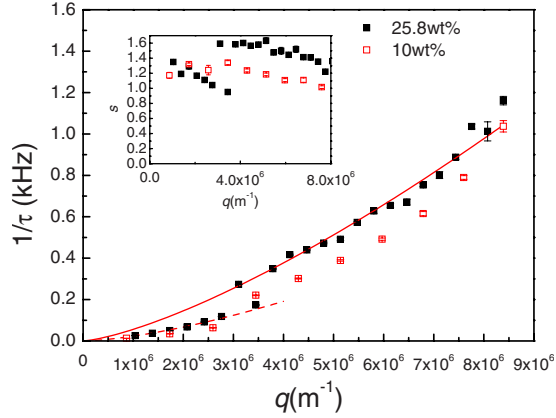


FIG. 5. (Color online) The dependence of the relaxation rate  $1/\tau_m$  (see text) of the correlation function on the scattering vector for ferrofluids with the concentrations of magnetic nanoparticles of 10 wt % (hollow symbols) and 25.8 wt % (full symbols) perpendicular to the direction of the external magnetic field of 270 mT. The line is the fit  $aq^\beta$  to the data for 25.8 wt % sample for  $q > q_c$  with obtained  $\beta=1.4$  and the dash line is the same fit for the  $q < q_c$  with obtained  $\beta=1.5$ . Inset: the stretching exponent versus the scattering vector.

stretching exponent  $s < 1$  can be attributed to the polydispersity of the system, the stretching exponent  $s > 1$  indicates the anomalous diffusion. In Fig. 5 we clearly see two regimes. In both the dependence of the relaxation rate on the scattering vector can be fitted with  $aq^\beta$  with  $\beta < 2$ . Below a region around  $q_c$  the exponent  $\beta \approx 1.5$ , while for scattering vectors larger than  $q_c$  the obtained exponent is  $\beta \approx 1.4$ . The change from one regime to the other is also clearly seen in the dependence of the stretching exponent on the scattering vector (inset of the Fig. 5). The wave vector  $q_c$  corresponds to the distance of approximately  $2 \mu\text{m}$ , which could be attributed to the typical distance between the needles of the static structure. The faster relaxation has much lower amplitude (about 5% of the total signal) and its relaxation rate of about 5–10 kHz does not show significant dependence on the scattering vector. Similar fast mode but with even lower amplitude is also observed in this sample in the absence of the field.

For the 10 wt % sample the situation is similar as for the most concentrated sample (Fig. 5). The relaxation rate along the field is for a factor of about 1.5 faster than in the dilute sample, while perpendicular to the field the relaxation rate remain approximately the same as for the same sample without the external field, only the nature of the dynamics, i.e., the stretching exponent, changes. Similarly as in the 2.1 wt % sample also in this case the large needles also diffuse and make the scattering experiment more difficult and the data less reliable.

In diluted samples and in concentrated samples in zero field, the only observed dynamics is diffusion of the nanoparticles and/or small aggregates. The time scale of the dynamics in the biphasic phase remains on the same order of magnitude as in the absence of the field, so we attribute it to the motion of the nanoparticles and small aggregates in the gas phase. We do not observe the dynamics of the nanoparticles in the concentrated phase (in the needles) because the concentrated phase is opaque.

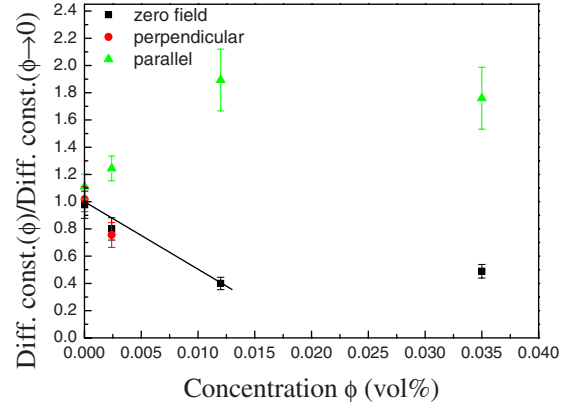


FIG. 6. (Color online) The dependence of the normalized diffusion constant on the volume concentration of the nanoparticles in the absence of the external field (squares), parallel (triangles), and perpendicular (circles) to the external magnetic field.  $B=270$  mT and  $D(\phi \rightarrow 0)=2.25 \times 10^{-11}$  m<sup>2</sup>/s. The line is the fit to the data according to Eq. (2).

### III. DISCUSSION

Our experiments show that in a dilute 0.21 wt % suspension of magnetic particles, as expected, the interparticle interactions do not influence the diffusion of the particles. In the external magnetic field the sample remains isotropic and the diffusion constant is the same as in the absence of the field. The measured diffusion constant corresponds to the single-particle hydrodynamic radius.

For the more concentrated samples we first look at the results in the absence of the external field. For those the diffusion constant is smaller than the diffusion constant of the free particles. There are two possibilities: the diffusion of the particles is slowed down either because of the interaction between the particles and/or the particles form aggregates. In a monophasic sample with interacting particles the diffusion constant at low volume fractions can be written as [23]

$$D = \frac{k_B T}{6\pi\eta R} [1 + (\kappa_T - \kappa_F)\phi], \quad (2)$$

where  $\phi$  is the volume concentration of the particles and the coefficients  $\kappa_T$  and  $\kappa_F$  account for thermodynamic and hydrodynamic interactions, respectively. The value of friction coefficient  $\kappa_F$  for hard spheres is 6.55 and  $\kappa_T - \kappa_F$  for hard spheres is 1.45 [32,33]. In our experiments the diffusion constant approximately linearly depends on concentration for less concentrated samples (Fig. 6) and the obtained value for  $\kappa_T - \kappa_F = -50 \pm 4$ . The negative  $\kappa_T$  is expected for attractive systems which our system is in the absence of the field. It has been shown theoretically that the dipolar interactions can lead to the strong suppression of the diffusion in ferrofluids in the absence of the field and that the diffusion constant then decreases monotonically with the concentration of the particles [34,35]. Our experimental results would correspond to the calculated case of monodispersed particles from Refs. [34,35] where the dipolar interaction coefficient  $\lambda^* \approx 2.5$ , which is larger than the average  $\lambda_{av}^* \approx 1.4$  of our polydispersed sample. This suggests that at least some of the de-

crease in the diffusion constant is due to the aggregation of the particles also in the samples with low concentration. For low volume fractions ( $\phi \lesssim 3$  vol %) the theoretically obtained dependence of the diffusion constant on the concentration is approximately linear and also in the experiments in other ferrofluids the dependence of the diffusion constant on the concentration was approximately linear up to 10 vol % [4,25]. In our experiments the diffusion constant for the most concentrated sample (25 wt % corresponds to 3.5 vol %) clearly deviates from linear behavior which also indicate that the particles aggregate. In such a case the magnetic interaction between multidomain aggregates is suppressed and correction to the diffusion constant due to concentration is smaller. Assuming that in the most concentrated sample the aggregates form and that the interaction between them is suppressed, so that the diffusion constant does not differ much from the diffusion constant of noninteracting particles, we can estimate that the aggregates consist of not more than five to ten nanoparticles.

In the external field the phase separation into a dense liquidlike phase surrounded by a gas phase takes place. The needlelike islands of liquid phase form some kind of (quasi)static 3D structure. A number of papers deal with the formation of such structures (for a recent review, see [3]). Here we focus on the dynamical behavior of such a system. The particles (or aggregates) that remain in the gaslike phase diffuse in the fluid around the structure of the liquidlike phase. In the 2.1 wt % sample, where the islands of the liquidlike phase are sparse, our results are similar as in the FRS experiments in the ionically stabilized ferrofluid that does not undergo the phase separation [23]. The diffusion along the field becomes faster than in the zero field, while perpendicular to the field it is slightly slower. We have to note that the concentration in our samples is much smaller than in FRS experiments, where the concentration of the particles was 10 vol %, while in our case the concentration of the particles is only about 0.24 vol %. Surprisingly the interparticle interaction seems to be strong enough already at such small concentration to affect the diffusion.

In more concentrated (10 and 25.8 wt %) samples the diffusion of the particles is also anisotropic and in addition in the direction perpendicular to the external field shows superdiffusive behavior, i.e., the mean-squared displacement increase faster than linearly with time,  $\langle \Delta R^2(t) \rangle = D_\alpha t^\alpha$  with  $\alpha > 1$ . The intensity of the dynamically scattered light is larger in the direction perpendicular to the field than parallel to the field, which means that moving particles are aggregates that are elongated and oriented along the magnetic field. If we assume that the aggregates form already in the absence of the field, a plausible scenario would be that in the field some of the aggregates form the dense phase and the others remain in the gas phase. In the absence of the field the aggregates are probably spherical since there is no depolarized scattering from the sample. In the external field those aggregates should reform into needlelike objects and the translation diffusion constant of the elongated object is anisotropic. From the diffusion constant we can estimate that the number of the particles in the aggregates is not larger than 10, and if they form a chain with the aspect ratio of approximately 10, the resulting anisotropy of translational diffusion constant

$D_{\parallel}/D_{\perp}$  would be 1.37 [36]. This is much smaller than measured in our samples, where even for 2.1 wt % sample the measured anisotropy  $D_{\parallel}/D_{\perp}$  is 1.7. In a simple rod system the maximal value for  $D_{\parallel}/D_{\perp}$  is 2, and only for the aspect ratio of more than 100  $D_{\parallel}/D_{\perp}$  is larger than 1.7. If the chains were larger, the diffusion constant would be smaller. From the values of the diffusion constant we conclude the aggregates are not larger than ten particles. So the shape of the aggregates can contribute to the anisotropy of diffusion but cannot explain the value of the measured anisotropy. We have to note that our samples are polydispersed and the two-dimensional x-ray scattering experiments in polydispersed samples have shown that the aggregates consist of both large and small nanoparticles [37], so that the aggregates are not nicely ordered chains but are more complex elongated objects. Their dipole moment is oriented along the field, and in the direction perpendicular to the field the interaction between them is repulsive, while along the field it is attractive.

While in normal diffusion that can be explained with Brownian motion of individual particles, the probability that a particle moves for a certain distance in a time  $t$  is a Gaussian with width equal to  $\sqrt{\langle \Delta R^2(t) \rangle} = \sqrt{6Dt}$ , the superdiffusion is usually connected with Levy flights or Levy walks [38], where the probability that the particle moves a certain distance in a time  $t$  is non-Gaussian with a finite probability also for long jumps that result in power-law dependence of the mean-squared displacement  $\langle \Delta R^2(t) \rangle$ . Such a distribution can arise from spatial or time inhomogeneous potential [38]. The spatial and dynamical heterogeneities, typical for glass, gels, and fragile systems, and their fluctuations near glass or jamming transition attract considerable attention in recent years. The anomalous diffusion and unusual dependence on the scattering vector  $q$  has been observed in many of such systems in three dimensions, to mention just few, in gels made from aggregated colloids [39–41], in nanoemulsions [42], and in nanoparticles suspended in supercooled liquid [43]. The x-ray experiments in the absence of the external magnetic field in dense (30 vol %) ionic ferrofluid, where there was no aggregation, suggest that also that system falls into the broad class exhibiting the heterogeneous dynamics [17,18]. The results of our measurements can also be understood in a similar way, although we must point out that our system largely differs from the one investigated in x-ray experiments. It is much less dense, the particles do aggregate, and the system is diphasic and auto-organized under field. Our concentrated system (the 25.8 wt % sample) shows similarity with the colloidal suspensions approaching the jamming transition [39,40]. In those systems the correlation function initially decays by a few percent to a plateau, which corresponds to the rattling of particles in the cages formed by their neighbors. At later times rearrangement of the cage leads to the final structural relaxation, allowing the particle to diffuse through the sample [44]. The autocorrelation function of this process can be fitted by a stretched exponential function  $A \exp[-(t/\tau_0)^\beta]$ , where stretching exponent  $\beta$  is larger than 1 at the volume fractions that are close to the volume fraction at which the jamming transition occurs and is smaller than 1 for lower volume fractions, i.e., further away from the jamming transition. Initially, the system shows the aging behavior, i.e., the relaxation time  $\tau_0$  grows

with time, and then a stationary regime is reached in which  $\tau_0$  exhibits large fluctuations but no overall increasing trend [40]. We also observe similar behavior in our measurements. In the absence of the field the stretching exponent and the  $q$  dependence look normal, but there are unusually large fluctuations in the relaxation rate that exceed 20%. We also observe an initial decay of the correlation function of a few percent. This relaxation does not depend on  $q$ . For the intracage diffusion the scattering-vector dependence of the relaxation rate is expected for scattering vectors that are larger than  $q_{\min} \sim \pi/d_c$ , where  $d_c$  is the cage size. For scattering vectors smaller than  $q_{\min}$  the measured relaxation rate would be  $\sim Dq_{\min}^2$  with  $D$  being the diffusion constant of a free particle. From our measured relaxation rate we can estimate the cage size to be on the order of 100 nm, which indeed is on the same order as the average distance between the particles in the concentrated samples. In the external magnetic field the situation is more complex. Perpendicular to the field direction, two distinctive regions in the  $q$  dependence show that the system is spatially heterogeneous also on this scale. The typical size of this heterogeneity is 1.6–2.2  $\mu\text{m}$  that we can attribute to the static structure of the larger needles. In both  $q$  regions the system behaves similarly. The stretching exponent is larger than 1 and the  $q$  dependence is not quadratic. The typical value of the stretching exponent for larger  $q$  region is  $\approx 1.5$  and this is a typical value also observed in above-mentioned systems. The  $q$  dependence in our case is different, which may be due to the lower dimensionality (2D plane perpendicular to the field) in which our samples show the behavior typical for the systems close to the dynamical arrest.

In the third dimension, i.e., parallel to the direction of the external field the interaction between the needles is attractive. Also in this direction the nature of the dynamics in the small- $q$  region differs from the large- $q$  behavior although transition is not that abrupt. (We have to note that the data in the direction parallel to the field are noisier than in the perpendicular direction since the scattered intensity in that direction is much smaller.) For larger- $q$  region the dynamical behavior looks like free diffusion but the diffusion constant

is even larger than expected for the free diffusion of the single nanoparticles. The attractive interaction between the needles obviously enhances the diffusion and on longer distances (probed in the small- $q$  region) also long jumps are stimulated leading to the Levy statistics [38] and, consequently, to the stretching exponent larger than 1. The enhancement of the diffusion of elongated magnetic objects in the direction parallel to the external field was also predicted by theory in [45].

#### IV. CONCLUSIONS

In conclusion, our measurements show that the dynamical behavior of the sterically stabilized ferrofluid depends on the concentration of the magnetic particles and is strongly influenced by the external field. In more concentrated samples in the external magnetic field strong anisotropy of the typical relaxation rate and also of the nature of the dynamics was observed. The diffusing objects are small elongated aggregates consisting of less than ten nanoparticles. The dependence of the relaxation rate on the scattering vector shows that there are spatial heterogeneities in the system, a point which is confirmed by optical microscopy. The nature of dynamics perpendicular to the field is different from that parallel to the field. In the perpendicular direction the system behaves as a kind of colloidal glass or gel close to the dynamical arrest, while in parallel direction it keeps the free diffusion behavior although the diffusion in this direction is rather fast. Also in the absence of the field in the more concentrated samples the fluctuations of the relaxation rate suggest that the system is close to the jamming transition.

#### ACKNOWLEDGMENTS

M.Č. and A.M. acknowledge the support from Ministry of Higher Education, Science and Technology of Slovenia (Grant No. P1-0192). We thank S. Gyergyek and M. Drogenik for providing the magnetic particles used in our measurements.

- 
- [1] R. E. Rosensweig, *Ferrohydrodynamics* (Dover, Mineola, NY, 1997).
  - [2] *Ferrofluids*, edited by S. Odenbach (Springer Verlag, Berlin, 2002).
  - [3] For a recent review, see C. Holm and J.-J. Weis, *Curr. Opin. Colloid Interface Sci.* **10**, 133 (2005).
  - [4] E. Dubois, R. Perzinsky, F. Boué, and V. Cabuil, *Langmuir* **16**, 5617 (2000).
  - [5] M. Klokkenburg, B. H. Erné, J. D. Meeldijk, A. Wiedenmann, A. V. Petukhov, R. P. A. Dullens, and A. P. Philipse, *Phys. Rev. Lett.* **97**, 185702 (2006).
  - [6] M. Klokkenburg, B. H. Erné, A. Wiedenmann, A. V. Petukhov, and A. P. Philipse, *Phys. Rev. E* **75**, 051408 (2007).
  - [7] A. Wiedenmann, A. Hoell, M. Kammel, and P. Boesecke, *Phys. Rev. E* **68**, 031203 (2003).
  - [8] S. Odenbach, *J. Phys.: Condens. Matter* **16**, R1135 (2004).
  - [9] K. Butter, P. H. Bomans, P. M. Frederik, G. J. Vroege, and A. P. Philipse, *Nature Mater.* **2**, 88 (2003).
  - [10] K. Butter, P. H. Bomans, P. M. Frederik, G. J. Vroege, and A. P. Philipse, *J. Phys.: Condens. Matter* **15**, S1451 (2003).
  - [11] M. F. Islam, K. H. Lin, D. Lacoste, T. C. Lubensky, and A. G. Yodh, *Phys. Rev. E* **67**, 021402 (2003).
  - [12] V. Cabuil, *Curr. Opin. Colloid Interface Sci.* **5**, 44 (2000).
  - [13] D. Lacoste and T. C. Lubensky, *Phys. Rev. E* **64**, 041506 (2001).
  - [14] A. Yu. Zubarev and L. Yu. Iskakova, *Phys. Rev. E* **68**, 061203 (2003).
  - [15] A. Yu. Zubarev and L. Yu. Iskakova, *Physica A* **335**, 325 (2004).
  - [16] T. Kristóf, J. Liszi, and I. Szalai, *Phys. Rev. E* **69**, 062106 (2004).



- (2004).
- [17] A. Robert, E. Wandersman, E. Dubois, V. Dupois, and R. Perzynski, *Europhys. Lett.* **75**, 764 (2006).
- [18] E. Wandersman, A. Duri, A. Robert, E. Dubois, V. Dupois, and R. Perzynski, *J. Phys.: Condens. Matter* **20**, 155104 (2008).
- [19] F. Gazeau, F. Boué, E. Dubois, and R. Perzynski, *J. Phys.: Condens. Matter* **15**, S1305 (2003).
- [20] F. Gazeau, E. Dubois, J.-C. Bacri, F. Boué, A. Cebers, and R. Perzynski, *Phys. Rev. E* **65**, 031403 (2002).
- [21] G. Méridet, E. Dubois, M. Jardat, A. Bourdon, G. Demouchy, V. Dupois, B. Farago, R. Perzynski, and P. Turq, *J. Phys.: Condens. Matter* **18**, S2685 (2006).
- [22] J. C. Bacri, A. Cebers, A. Bourdon, G. Demouchy, B. M. Heegaard, and R. Perzynski, *Phys. Rev. Lett.* **74**, 5032 (1995).
- [23] J. C. Bacri, A. Cebers, A. Bourdon, G. Demouchy, B. M. Heegaard, B. Kashevsky, and R. Perzynski, *Phys. Rev. E* **52**, 3936 (1995).
- [24] J. Lenglet, A. Bourdon, J. C. Bacri, and G. Demouchy, *Phys. Rev. E* **65**, 031408 (2002).
- [25] G. Méridet, E. Dubois, A. Bourdon, G. Demouchy, V. Dupois, and R. Perzynski, *J. Magn. Magn. Mater.* **289**, 39 (2005).
- [26] J. Lal, D. Abernathy, L. Auvray, O. Diat, and G. Grübel, *Eur. Phys. J. E* **4**, 263 (2001).
- [27] M. Shliomis, M. Mond, and K. Morozov, *Phys. Rev. Lett.* **101**, 074505 (2008).
- [28] S. Mahle, P. Ilg, and M. Liu, *Phys. Rev. E* **77**, 016305 (2008).
- [29] C. Holm, A. Ivanov, S. Kantorovich, E. Pyanzina, and E. Reznikov, *J. Phys.: Condens. Matter* **18**, S2737 (2006).
- [30] See, for example, P. J. Patty and B. J. Frisken, *Appl. Opt.* **45**, 2209 (2006).
- [31] C. P. Lindsey and G. D. Patterson, *J. Chem. Phys.* **73**, 3348 (1980).
- [32] G. K. Batchelor, *J. Fluid Mech.* **52**, 245 (1972).
- [33] G. K. Batchelor, *J. Fluid Mech.* **74**, 1 (1976).
- [34] K. I. Morozov, *J. Magn. Magn. Mater.* **122**, 98 (1993).
- [35] M. Hernandez-Contreras, P. Gonzalez-Mozuelos, O. Alarcon-Waess, and H. Ruiz-Estrada, *Phys. Rev. E* **57**, 1817 (1998).
- [36] M. M. Tirado, C. López Martínez, and J. García de la Torre, *J. Chem. Phys.* **81**, 2047 (1984).
- [37] T. Kruse, H.-G. Krauthäuser, A. Spanoudaki, and R. Pelster, *Phys. Rev. B* **67**, 094206 (2003).
- [38] J. Klafter, M. F. Shlesinger, and G. Zumofen, *Phys. Today* **49**(2), 33 (1996).
- [39] L. Cipelletti, S. Manley, R. C. Ball, and D. A. Weitz, *Phys. Rev. Lett.* **84**, 2275 (2000).
- [40] P. Ballesta, A. Duri, and L. Cipelletti, *Nat. Phys.* **4**, 550 (2008).
- [41] E. Del Gado and W. Kob, *Phys. Rev. Lett.* **98**, 028303 (2007).
- [42] H. Guo, J. N. Wilking, D. Liang, T. G. Mason, J. L. Harden, and R. L. Leheny, *Phys. Rev. E* **75**, 041401 (2007).
- [43] C. Caronna, Yu. Chushkin, A. Madsen, and A. Cupane, *Phys. Rev. Lett.* **100**, 055702 (2008).
- [44] E. R. Weeks and D. A. Weitz, *Phys. Rev. Lett.* **89**, 095704 (2002).
- [45] P. Ilg, *Phys. Rev. E* **71**, 051407 (2005).