Particle interaction in polydisperse magnetic fluids: Experimental aspects of small-angle neutron scattering applications

Mikhail V. Avdeev *

Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Joliot-Curie str. 6, 141980 Dubna, Moscow Reg., Russia

ARTICLE INFO

ABSTRACT

The paper considers the experimental aspects of the observation of interaction effects in magnetic fluids with size polydisperse nanoparticles by means of small-angle neutron scattering (SANS). The possibilities of the method are discussed for different regimes of interaction predicted by the theory of dipolar fluids. The typical effects related to the experimentally observed structure-factor under different conditions, as well as possible ways of its theoretical description are analyzed.

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1. Introduction

Colloidal stability of magnetic fluids (MFs) is achieved by coating quasi-spherical magnetic nanoparticles placed in liquid carriers with stabilizing layers of surfactants or/and ions. This procedure effectively decreases or compensates the dipole–dipole interaction between magnetic moments of one-domain particles in MFs, thus preventing their unregulated coagulation, especially under external magnetic fields. In an ideal case, when the dipole–dipole interaction is totally suppressed, the particles follow the so-called superparamagnetic behavior characterized by the Langevin-type magnetization with the renormalization to the magnetic moment per nanoparticle and determined by thermal orientation fluctuations of the magnetic moments in the solution. The deviations from this regime have an impact on the macroscopic properties of magnetic fluids, which is actively employed in practice in many technical applications (for a current overview and examples see [1,2]). The fundamental and rather uneasy task to describe a strongly anisotropic dipole–dipole interaction in this case faces a problem for real MFs, where nanoparticles are highly polydisperse. This hinders the application of the theoretical approaches considering mainly monodisperse systems. One more difficulty is connected with the colloidal nature of MFs, where chemical interactions between various components of the solutions are also important factors influencing their stability. This restricts the variation of thermodynamic parameters (temperature, concentration) of the systems with the retention of the same particle structure and fluid stability. Also, non-equilibrium colloidal aggregation after the synthesis often cannot be neglected and significantly affects the interaction characteristics.

The present paper concerns the experimental aspects of the observation of interaction effects in polydisperse MFs. The scattering methods such as small-angle neutron scattering (SANS) are the most direct tools for this purpose. The examples of their use as a part of complex approaches, which combine different complementary techniques, can be found elsewhere (e.g. reviews [3,4]). Here we restrict our consideration to the problems of the polydispersity effect in the interpretation of the SANS curves. While recent advances in the synthesis of magnetic fluids make it possible to produce special systems with various types of magnetic particles and interactions, the particle polydispersity still remains a somewhat inner property of these systems and reflects the fact that the production of monodisperse magnetic fluids is an extremely difficult and expensive procedure for comprehensive investigations. In this connection the development of both theoretical and experimental methods to characterize the polydisperse complex systems is of current interest. The theoretical approaches developed so far for suspensions of magnetic nanoparticles in liquids can be experimentally tested to some extent by means of SANS. The present paper aims at specifying the possibilities and restrictions of the method with respect to different kinds of correlations in magnetic colloidal systems. Several classes of problems are distinguished together with the current level of understanding and prospects for their solution.

2. Principles of small-angle neutron scattering

The general expression for the differential scattering cross-section of neutrons from spherical monodisperse nanoparticles and their isotropic distribution in some homogeneous medium (solvent) is represented by

* Tel.: +7 4962162674; fax: +7 4962165484.
  E-mail address: avd@nf.jinr.ru.

a function $I(q)$ of the modulus of the momentum transfer $q = (4\pi/\lambda)$ $\sin(\theta/2)$, where λ is the neutron wavelength and θ is the scattering angle. It comprises two factorized contributions:

$$I(q) \sim P(q)S(q), \tag{1}$$

where $P(q)$ is the form-factor and $S(q)$ is the structure-factor. Both factors are determined by the Fourier transforms of the correlation functions describing the scattering length distribution (SLD) within a single particle (form-factor) and the distribution of the particle locations (structure-factor). The particle form-factor is usually defined as

$$P(q) = F^2(q), \tag{2}$$

$$F(q) = 4\pi \int_0^{R_{max}} (\rho(r) - \rho_s) \frac{\sin(qr)}{qr} r^2 dr \tag{3}$$

where $F(q)$ is the scattering amplitude, $\rho(r)$ is the SLD distribution profile in the particle, ρ_s is the solvent SLD, and R_{max} is the outer particle radius. The structure-factor operates with the radial distribution function $g(r)$ as

$$S(q) = 1 + 4\pi n \int_0^\infty (g(r) - 1) \frac{\sin(qr)}{qr} r^2 dr, \tag{4}$$

where n is the particle number density, which is directly determined by the volume fraction of the scattering particles.

The essential point is that in a system with magnetic nanoparticles there are two kinds of neutron scattering corresponding to the interactions of neutrons with atomic nuclei (nuclear scattering) and atomic magnetic moments (magnetic scattering). As a first approximation, one can use just the sum of both contributions in the following way [5]:

$$I(q) \approx nF_N^2(q)S_N(q) + (2/3)nF_M^2(q)S_M(q) \tag{5}$$

where indexes 'N' and 'M' denote the nuclear and magnetic scattering, respectively. The nuclear scattering contribution describes effectively the correlations between atoms in a particle ('nuclear' form-factor) and between particles ('nuclear' structure-factor), while the magnetic scattering contribution describes the correlations between orientations of magnetic moments of the atoms in a particle (magnetic form-factor) and between orientations of magnetic moments of the particles (magnetic structure-factor). The additional factor of 2/3 in the magnetic term of Eq. (5) is the result of the fact that the magnetic scattering length of the neutron depends on the mutual orientation of the momentum transfer and the magnetic moment; the well-known sine-squared dependence of the corresponding angle gives the discussed coefficient after averaging over the isotropic distribution of particle magnetic moment orientations in non-magnetized magnetic fluids.

Here we consider only sterically stabilized magnetic fluids, where the electrostatic interaction between the surfactant shells is minimal, so the interaction potential is the sum of the hard/soft sphere interaction and the dipole–dipole interaction between magnetic moments of nanoparticles.

The characterization of nanoparticles themselves (no interaction) in magnetic fluids by SANS is performed for diluted solutions (volume fraction of magnetic material $\varphi \sim 1\%$), when the scattering structure-factors in Eq. (5) are close to unity. The scattered intensity depends strongly on the solvent SLD, which can be varied by using different mixtures of usual H- and deuterated D-solvents. A specific change in the scattering curves over a typical interval of the solvent SLD (restricted by H- and D-solvents) is followed in Fig. 1 for polydisperse magnetic fluids with well-defined core–shell nanoparticles. Additionally, the map of a typical distribution of SLD for the components of magnetic fluids is given in the inset of Fig. 1. One can see that because of this distribution a specific
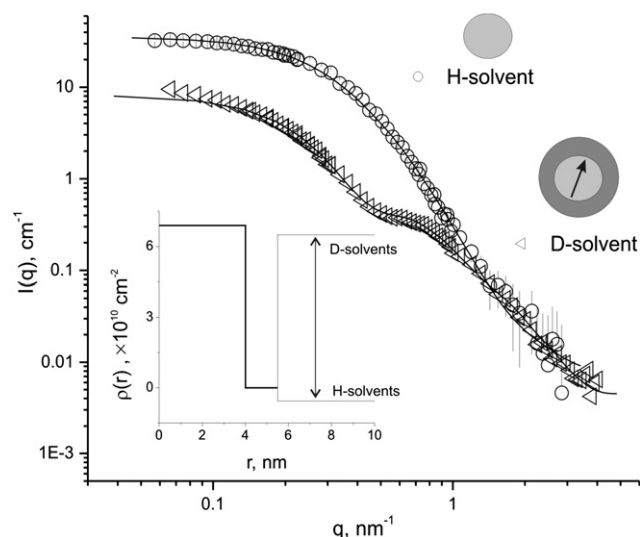

Fig. 1. Characteristic experimental SANS curves (Budapest Neutron Center) for diluted MFs with well defined separated nanoparticles (magnetite coated with fatty acids in non-polar organic solvent) on H- and D-carriers with the illustration of what kind of information one gets for the systems with different rates of solvent deuteration. Here, an example is given for oleic acid coating, $\varphi = 1\%$. The solid lines show the model form-factors averaged over a log-normal particle size distribution ($R_0 = 3.4$ nm, $S = 0.38$). The determined thickness of the surfactant shell is 1.4 nm. The inset contains the particle SLD profiles for H- and D-cases.
The experimental data are obtained from the Budapest Neutron Center.

change in the character of the curve takes place when varying the solvent from H- to D-case. The principal information obtained for the limiting (from the viewpoint of deuteration) cases is illustrated in Fig. 1. In the case of H-solvents the contrast between the surfactant shell and the solvent is close to zero, so the nuclear scattering occurs only from the magnetic core. The contrast between the core and the solvent is so high that this scattering is much larger than the magnetic scattering contribution; consequently the latter can be neglected. The nuclear scattering contribution in this case is well described by the particle form-factor (Eq. (2)) corresponding to a homogeneous sphere ($\rho(r) = \text{const}$) averaged over the particle size distribution function $D_n(R)$:

$$I(q) = n \int_0^{R_{max}} P(q, R) D_n(R) dR \tag{6}$$

thus proving that $S_N(q)$ is close to unity over the whole covered q-interval. As a result, one obtains the parameters of the $D_n(R)$ function, which is usually assumed to be of the log-normal type. In the opposite case of D-solvents the shell effect is well observed in the scattering as a specific band in the curve, which is well fitted by the polydisperse 'core–shell' model. Again, it shows that $S_N(q) = 1$. The magnetic scattering is no longer small, but, as it will be shown below, it affects the curves mainly at small q-values because of the specific structure-factor $S_M(q)$ (see deviation of the experimental points from the core–shell model of independent non-magnetic particles).

Below the cases where the scattered intensity can be considered in terms of Eq. (5) are discussed regarding the experimental possibilities of the analysis of $S_N(q)$ and $S_M(q)$ factors in polydisperse magnetic fluids. Eq. (5) suggests that the two kinds of structure-factors are isotropic. The important point is that they do not interfere, thus suggesting that the magnetic interaction is not so strong. To some extent this approximation can be used for magnetic fluids under external magnetic fields. When the magnetic interaction is strong, an additional factor is the formation of aggregates, which affects the particle radial distribution function. When the fraction of aggregates is large then the structure-factors can be considered with respect to the particle location in the aggregates.