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Aggregation in ferrofluids studied by Neutron Small Angle Scattering

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Résumé. — On a utilisé la technique de diffusion aux petits angles des neutrons pour étudier l'état d'aggrégation dans des ferrofluides à basse température et pour des aimantations variées. Des grains de cobalt, qui sont stabilisés dans le toluène par différents produits chimiques comme surfactant, ont donné un signal de diffusion neutronique d'un système bien groupé. Il existe une anisotropie de forme dans les échantillons après application d'un champ magnétique intense à basse température. On n'a pas trouvé d'anisotropie magnétique pour les échantillons de petites particules après suppression du champ magnétique mais les systèmes de grandes particules ont conservé cette anisotropie dans l'état solide.

Abstract. — Neutron Small Angle Scattering has been used to follow processes of particle aggregation in ferrofluids under various conditions of temperature and externally applied magnetic field. Cobalt particles, stabilized in toluene by one of two surfactant materials, showed neutron scattering characteristic of highly aggregated systems. Low temperature quenching in a strong magnetic field caused physical shape anisotropy to be fixed in the samples. A smaller particle system revealed no magnetic anisotropy after removal of the magnetic field whereas the larger particle system did retain anisotropic magnetic characteristics while held in the solid state.

1. Introduction. — Magnetic liquids (or « ferrofluids ») consist of suspensions of small (50-100 Å) magnetic particles such as Fe, Co or Fe₃O₄ in various carrier liquids. Aggregation of the particles due to magnetic and van der Waals' forces is prevented by using a surfactant coating and making the particle size sufficiently small so that the size of magnetic interactions are smaller than those of thermal energies. If significant aggregation occurs in a ferrofluid particle sedimentation will occur. This problem of aggregation would not be present in an intrinsically ferromagnetic liquid but such liquids are not known to exist.

In recent years considerable interest has been shown in the use of magnetic liquids in a wide range of applications [1]. Their use in rotating shaft seals, exclusion seals for computer disk drives and in loudspeakers is now well established. In these applications the liquids are subjected to high magnetic fields and magnetic field gradients (~ 10 kOe cm⁻¹) which, if any significant aggregation of the particles is present, would lead to a rapidly forming particle concentration gradient and sedimentation. This would render the liquid less effective for most applications. It is therefore important to obtain information of the degree of aggregation in magnetic liquids and determine the effect of temperature and externally applied magnetic fields.

Electron micrographs of magnetic particles, obtained from grids upon which magnetic liquids had been allowed to dry, show the presence of aggregates (chaining) especially for large (~ 150 Å) magnetic particles [2]. However it may not be realistic to assume that the degree of aggregation found in the liquid phase is the same as that on drying. X-ray scattering [3] has been used to study particle structure and grain correlations in ferrofluids and so too has light scattering [4]. Both these in situ methods have shown evidence of anisotropic particle clustering along the applied magnetic field direction. A further method of observing the process of aggregation in the liquids in situ, namely Neutron Small Angle Scattering (NSAS), is used here to help make a realistic evaluation of the suitability of magnetic liquids for various applications.

Some previous studies [5] using Neutron Small
Angle Scattering have shown that useful information can be obtained about the magnetic particles in magnetic liquids. This paper presents the results of an in situ study of aggregation in magnetic liquids containing cobalt particles in toluene using NSAS.

2. Experimental. — 2.1 Sample preparation. — The cobalt colloids were prepared [2] by the thermal decomposition of cobalt octacarbonyl in toluene-Hg held at its boiling point. The particle size was controlled by the presence of a surfactant which, for the two types of sample studied here, were Sarkosyl (an N-acyl sarcosine surfactant,

\[
\text{CH}_3\text{(CH}_2\text{)}_{10}\text{CON(CH}_3\text{)}\text{(CH}_2\text{)}\text{COOH}
\]

and Monoxol-OT (MOT, sodium di-octyl sulphonosuccinate). The samples, which were liquid and of low viscosity (≈ 10 cP) at room temperature, were contained in flat cells of optical quality quartz which had a path length in the sample of exactly 1 mm.

2.2 Neutron small angle scattering. — For unpolarized neutrons the coherent cross-section for a magnetic sample is the sum of nuclear and magnetic scattering contributions. The intensity is given by

\[
I(Q) = I_S(Q) + \{1 - (\mathbf{h} \cdot \mathbf{q})^2\} I_M(Q),
\]

where \( \mathbf{h} \) and \( \mathbf{q} \) are unit vectors in the directions of the magnetization and scattering vector, \( Q \) respectively.

When the magnetic moments are randomly oriented the orientational term \( \{1 - (\mathbf{h} \cdot \mathbf{q})^2\} \) involving \( \mathbf{h} \) and \( \mathbf{q} \) takes the value \( 2/3 \). \( I_M(Q) \) becomes isotropic and thus only \( |Q| \) dependent. In any other situation the magnetic contribution may be highly anisotropic. One extreme would be at saturation when all moments are aligned. Then for the scattering direction where \( Q \) is parallel to \( \mathbf{h} \), \( \mathbf{h} \cdot \mathbf{q} = 1 \), the appearance of magnetic scattering is suppressed.

Under normal circumstances when particle systems are made of particles in random orientation \( I_M(Q) \) is isotropic. This is true even if the particles themselves are anisometric in some way. \( I_M(Q) \) can become anisotropic in the event that alignment of anisometric particles occurs. For instance anisotropic scattering results if, say, rod-like particles lie with their major axes in one predominant direction.

To investigate the mixture of magnetic and physical effects, which may be anisotropic, in the magnetic liquid system NSAS experiments were carried out using the D17 instrument at the high flux reactor at the Institut Laue-Langevin, Grenoble [6]. In these experiments neutron scattering was detected over a range of momentum transfers, \( Q \). These ranges were achieved by selecting a particular wavelength, \( \lambda \) (with a distribution \( \delta \lambda / \lambda \sim 10\% \)) and setting the neutron detector at a given distance, \( D \) from the sample. We have

\[
|Q| = \frac{4\pi}{\lambda} \sin \left(\frac{\phi}{2}\right) \sim \frac{2\pi}{\lambda} \frac{r}{D},
\]

where \( \phi \) is the total scattering angle and \( r \) is the distance away from the undeviated incident beam. See figure 1.

Two series of experiments were carried out, the first at room temperature (≈ 300 K) and the second at low temperatures (77 < \( T < 300 \) K).

(a) At room temperature the measurements were made on a sample prepared with MOT as surfactant at various concentrations of particulate material. Two patterns were recorded for each specimen: one in zero field and one in a high field (≈ 8 kOe). The direction of the applied field with respect to the scattering geometry is pictorially represented in figure 1. For these experiments \( \lambda = 8.87 \) Å and \( D = 1.45 \) m with the subsequent realisation of \( Q \) values of 0.03 < \( Q < 0.18 \) Å\(^{-1}\).

(b) The low temperatures were achieved by using a liquid helium cryostat with the sample mounted between the pole faces of the electromagnet. In such an arrangement fields of up to only 4 kOe could be applied. The following sequence of temperature steps, field applications and sample geometry rearrangement was followed for samples containing MOT as surfactant and Sarkosyl as surfactant:

1. At room temperature the high field was applied to the sample.
2. The temperature was lowered in stages.
3. After a measurement at low temperature the sample was rotated through 90° about an axis colinear with the incident neutron beam.
4. The field was removed.
5. The sample was rotated by −90°.

The above sequence was repeated for different specimens of each of the samples except that the temperature was lowered without the initial application of the field (step (1)). Fields were applied only after the samples’ temperatures had been reduced to 77 K (step (3)).

Neutron scattering patterns were collected for the samples after each change of environment in the sequence. For the MOT sample \( \lambda = 6.97 \) Å and \( D = 1.52 \) m (0.05 < \( Q < 0.18 \) Å\(^{-1}\)) and for the Sarkosyl sample \( \lambda = 10.07 \) Å and \( D = 1.52 \) m.
(0.03 < Q < 0.12 Å⁻¹). Measurements on both samples were also made with λ = 9.94 Å and with D = 2.82 m (0.01 < Q < 0.07 Å⁻¹).

Finally all samples which had been subjected to either (or both) magnetic field or low temperature were measured at room temperature in the liquid state. This was done to check that no permanent changes had occurred in the sample.

2.3 Data Reduction. — Samples which gave isotropic scattering were exposed to the radiation for periods of about 15 min. Data collected thus were of good statistical quality and improved by computer radial summation procedures. Data collected from samples giving anisotropic scattering patterns however could not be treated in this manner and so exposure times were lengthened in order to achieve a reasonable number of counts compatible with the time taken to do a good experiment. The scattering patterns were corrected for the background scattering of the toluene and calibrated against the nominally flat incoherent scattering from water which was also used to correct for solid angle effects etc. [7]. For samples held in the high fields, which showed nuclear isotropic scattering, the magnetic, IM(Q) and nuclear, IN(Q), scattering intensities were extracted from the intensity components perpendicular and parallel to the applied field as explained previously [5].

3. Results. — 3.1 Room Temperature Measurements. — Room temperature measurements were made in zero and high (~ 8 kOe) fields. The contour plots for the zero field cases were all circularly symmetric in shape centred around the beam-stop. These patterns alone were radially summed and were replotted as I₀(Q) against Q. For the MOT sample measurements were made on samples at different magnetic volume fractions, φm, in the range from 0.0027 to 0.0214. These are shown in figure 2.

The scattering patterns for these same samples in high field were very anisotropic. There was a clear emergence of interference peaks in the perpendicular direction as φm increases, and slightly less so in the parallel direction. From the anisotropic patterns the scattering functions IM(Q) and IN(Q) for the sample with MOT as surfactant in the high field case for each of the volume fractions measured. Intensities have been scaled to volume fraction. The magnetic volume fractions, φm = M₀/I₀, where I₀ = 1.740 emu cm⁻³ for cobalt.

3.2 Low Temperature Measurements. — For these experiments data were preserved as contour plots of the whole detector. Patterns at each point in the sequence, described earlier, are shown in figure 4 for the MOT sample and figure 5 for the Sarkosyl sample. General attention is drawn to the striking anisotropy found in all cases. Particular note should be made of the changes in the form of scattering at low Q values (around the central beam-stop) from step to step and the persistence of the crescent shaped interference peaks while the field is on.

Fig. 2. — Plots of radially averaged, isotropic scattering for samples with MOT as surfactant in zero magnetic field. The measurements were taken at room temperature.

Fig. 3. — These plots show the components IM(Q) and IN(Q) for the sample with MOT as surfactant in the high field case for each of the volume fractions measured. Intensities have been scaled to volume fraction. The magnetic volume fractions, φm = M₀/I₀, where I₀ = 1.740 emu cm⁻³ for cobalt.

Fig. 4. — Changes in scattering pattern with change in temperature, field and sample orientation for the MOT surfactant cobalt sample (M₀ = 500 G). The magnitude of the magnetic field applied was ~ 4 kOe in the direction indicated as « H ». The direction « S » on the figure shows the direction of the first magnetic field during the quench from room temperature. (λ = 6.97 Å, D = 1.52 m, Qₑ = 0.190 Å⁻¹, where Qₑ = Q at the edge of the box representing the two dimensional detector.)
4. Discussion. — 4.1 Room Temperature Measurements. — For the most dilute ($\phi_m = 0.0027$) cobalt/toluene fluid with MOT as surfactant, no obvious interference features are observed for the zero field and high field cases. Assuming then that no aggregation was apparent the scattering intensity data, $I_m(Q)$ and $I_n(Q)$, were analysed on the basis that scattering resulted from a system of homogeneous spherical particles of magnetic diameter $D_m$ in the first case and nuclear (physical) diameter $D_n$ in the second. A lognormal distribution of the volume fraction of particle sizes was incorporated into the fitting procedures. This is a similar procedure to that used before [5] where particle interaction is neglected.

The values of $D_m$, $D_n$ and $\sigma$, the standard deviation of the distribution, are in satisfactory agreement with the magnetic and electron microscopy measurements. See table I. The difference between the values of $D_m$ and $D_n$ is quite general and has been found in Fe$_3$O$_4$ suspensions as well as cobalt suspensions. The difference has been attributed to the difficulty of magnetically saturating the systems because of « pinning » of the spins on the surface of the particles, resulting in an effectively low value of the saturation magnetization and here in an apparent reduced magnetic size [8]. In addition, for the cobalt system surface oxidation may also be a contributory factor.

For the more concentrated samples, in both zero and high field cases humps become more apparent in $I_{iso}(Q)$, $I_m(Q)$ and $I_n(Q)$ for $\phi_m = 0.0214$. Further there is also a marked increase in $I_m(Q \rightarrow 0)$ and $I_n(Q \rightarrow 0)$ at higher densities. This type of behaviour in the scattering functions can be explained in terms of the formation of clusters or aggregates of the primary particles. The increase in intensity at low $Q$ results from an enhancement in scattering from large particles (aggregates) and the increase in intensity of the interference peak results from a large number of individual particles constituting each aggregate. The real-space distance, $d$, giving rise to the peak at $Q \sim 0.075 \text{Å}^{-1}$ is $2 \pi Q \sim 85 \text{Å}$. This corresponds well with a centre-to-centre distance, for particles with $D_n = 47 \text{Å}$ coated with a layer of MOT molecules of extended length $\sim 19 \text{Å}$.

Further evidence showing that size of an aggregate is increased on application of a magnetic field is found by recreating the isotropic scattering pattern from the anisotropic components. To do this the components $I_{iso}(Q)$ and $I_m(Q)$ isolated from the anisotropic pattern as already explained are added in the ratio 1 : 2/3 the added components are then compared with the zero field isotropic pattern for the same sample. Figure 3 shows quite clearly that a severe change has taken place at low $Q$ i.e. in the region sampling large distances and where larger aggregates would show up. At high $Q$ where short distances are probed the curves superimpose which simply means that the composition of the individual particle remains unchanged by the application of a field.

4.2 Low Temperature Measurements. — The cobalt samples chosen had quite different particle sizes and thus a significant difference in magnetic moments. The sample containing the larger particles was stabilized with Sarkosyl and that with the smaller particles was stabilized with MOT. The size of the particles are given in table II.

A gradual change in the NSAS contours occurred

| Table I. — Parameters measured for the MOT surfactant cobalt sample used in the room temperature experiments. The standard deviation of the size distribution is given as $\sigma$. |
| --- | --- | --- |
| $D_m$/Å | $D_n$/Å | $\sigma$ |
| NSAS | 46.0 ± 2 | 47.7 ± 2 | ~ 0.2 |
| Electron Microscopy | — | 56 ± 6 | ~ 0.18 |
| Magnetization | 50 ± 5 | — | ~ 0.2 |

| Table II. — Particle sizes measured for the MOT and Sarkosyl surfactant cobalt samples used in the low temperature experiments. Sizes obtained by neutron scattering are the radii of gyration for the overall particles, this value therefore includes both magnetic and nuclear contributions. The equivalent diameter is that obtained from $R_g$ assuming the particle to be a homogeneous sphere. As such the equivalent diameter lies between values of $D_n$ and $D_m$ obtained from neutron scattering data. |
| --- | --- | --- |
| NSAS : | MOT | Sarkosyl |
| $R_g$/Å | 16.9 ± 0.7 | 33.3 ± 1.2 |
| equivalent diameter/Å | 43.6 | 85.9 |
| Electron Microscopy and magnetization : | | |
| $D_n$/Å | 64.0 ± 6 | 78.5 ± 8 |
| $D_m$/Å | 42.0 ± 4 | 62.0 ± 6 |
| $\sigma$ | ~ 0.18 | ~ 0.18 |
Changes in scattering pattern as the temperature of the Sarkosyl surfactant cobalt sample ($M_s = 317 \text{ G}$) is lowered in a high magnetic field. ($\lambda = 9.94 \text{ Å}, D = 2.82 \text{ m}, Q_e = 0.072 \text{ Å}^{-1}$). The regions marked « high » and « low » on 6f refer to scattered intensities at that point.

(Figs. 6 and 7) for both samples on cooling in the field. The appearance and intensification of an anisotropic interference pattern is illustrated in figure 6 for the Sarkosyl sample. These changes observed for both colloids are attributed to the formation of aggregates on lowering the temperature. As the temperature is lowered thermal effects become progressively less efficient in overcoming aggregation due to the magnetostatic interactions between particles. There is strong experimental [9] and theoretical [10] evidence that the aggregates exist in the form of chains. See figures 8 and 9.

On rotation of the solidified colloids (at low temperature) through $90^\circ$ in the presence of and with respect to the magnetic field applied during quenching, the anisotropic interference pattern followed the change in field direction. This contribution to the scattering is therefore consistent with magnetic scattering of the neutrons by the aligned magnetic moments within the particles.

It would appear that the interference pattern due to nuclear scattering of the neutrons by the chains or aggregates is significantly weaker than that of the magnetic scattering. If the two effects had been comparable, the interference pattern as observed for the sample after rotation through $90^\circ$ should have been roughly isotropic.

At low $Q$ there appears to be some quenched-in anisotropy i.e. the anisotropy is fixed in the sample and is not dependent on subsequent changes in the field direction. This quenched-in anisotropy is attributed to the nuclear scattering of the aggregates present. In addition, at low $Q$, there is also an anisotropy attributed to magnetic scattering. This is clearly illustrated in figures 7d and 7e for the MOT sample. In figure 7d the magnetic and nuclear anisotropies enhance each other whereas in figure 7e...
after the sample has been rotated by 90°, the anisotropies are at right angles to each other resulting in a rather isotropic-looking pattern. On removal of the magnetic field, the dominant anisotropy is clearly seen to be due to nuclear scattering (see Fig. 7f).

The increase in the intensity of neutrons scattered to low Q, for MOT colloids in figure 7d compared to figure 7a arises because of the presence of aggregation. For the Sarkosyl stabilized colloid containing the larger cobalt particles, the anisotropic interference pattern does not disappear when the field is removed (Fig. 6f). This arises because the magnetic moments of the particles remain partially aligned even on removal of the field whereas for the MOT sample the moments become randomly oriented, i.e. the Sarkosyl sample would be expected to have a remanence at low temperature whereas the MOT sample would not.

The explanation of these observations is quite straightforward. The magnetic moments of single domain particles tend to align themselves in the direction of an easy-axis of magnetization. The barrier to rotation (Neel rotation [11]) of the moment from an easy-axis direction to another or opposite direction is given by $K V$ where $K$ is the effective magnetic anisotropy constant and $V$ is the volume of the particle. $K$ will depend not only on the crystalline anisotropy but also on the presence of any particle-shape anisotropy [12]. Above a certain particle volume $V_p$ the thermal energies will be insufficient to allow the moment to overcome the barrier to rotation and thus follow changes in the direction of a small applied magnetic field. In this situation the moments are considered « blocked ». Thus solidified colloidal suspensions that are initially saturated in a magnetic field will possess a remanence when the field is removed. However for particles with volume less than $V_p$ the moments are essentially free to rotate within the particle and the system is said to be superparamagnetic and will not possess a remanence. The value of $V_p$ is temperature dependent. A more detailed discussion of this subject is given in a review of magnetic liquids by Charles and Popplewell [13]. For the conditions used on the NSAS measurements the majority of the particles in the colloid sample containing the smaller particles are expected to be superparamagnetic at 77 K and therefore the sample is expected to have little or no remanence as found, even though there is clear evidence of aggregation from the interference pattern. However for the colloid containing the larger particles a greater number of the particles would be « blocked » at 77 K with the result that the sample would possess a remanence as found.

Confirmation of the explanations has been provided by direct magnetic measurement of the two colloidal systems studied using a vibrational sample magnetometer [14]. The colloidal sample containing the smaller particles has only a very small remanence at 77 K whereas the colloid containing the larger particles has a significant remanence at 77 K which is approximately 0.1 of the saturation magnetization of the colloid.

The colloids quenched down to 77 K in zero magnetic field showed none of the quenched-in anisotropic effects. Interference effects from particles within aggregates were observed.

Observation of the room temperature, zero field scattering patterns taken for each sample after all other steps showed no differences to those prior to the main experiment. It is concluded that no permanent effects remained in any sample after raising the temperature back up.

5. Summary. — In summary these experiments have demonstrated, for the first time using NSAS, that it is possible to observe in situ the formation of aggregate clusters in cobalt/toluene ferrofluids. The tendency to form aggregates containing larger number of particles is increased as the temperature is reduced. Further, NSAS reveals an anisotropy in the shape of the aggregate which is quenched-in as the temperature is reduced in the field. This is in agreement with results from earlier X-ray [3] and light [4] scattering experiments. In addition a distinction can be made between samples which contain small particles and are therefore superparamagnetic and those containing larger particles which are ferromagnetic, by making observations at low temperature i.e. in the solid.

Further work is in progress on these systems and in particular measurements are being undertaken at low Q to determine the molecular weight and aspect ratio of the aggregates (chains).

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