Determination of Ferrofluid Structure by Neutron Polarization Analysis

Roger Pynn and John B. Hayter
Institut Max von Laue–Paul Langevin, F-38042 Grenoble Cedex, France
and
Stuart W. Charles
University College of North Wales, Bangor LL57 2UW, United Kingdom

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Neutron polarization analysis is combined with small-angle scattering for the study of a concentrated cobalt ferrofluid. The geometry of the cobalt particle core and surrounding surfactant layer has been determined and an anomalous magnetic layer found at the cobalt surface. The interparticle structure factor, measured for the first time in a magnetically aligned ferrofluid, agrees well with a recent theory. Magnetic fluctuations, measured as a function of applied field, are found to be predominantly paramagnetic.

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Magnetic ferrofluids are stable colloidal suspensions of fine, superparamagnetic particles, each coated with a nonmagnetic, molecular, surfactant layer.[1,2] Partial information on the structure of such fluids has been obtained by bulk magnetization measurements, electron microscopy, Mössbauer spectroscopy,[3] small-angle x-ray scattering,[4] photon correlation, and small-angle neutron scattering.[5] In this Letter we demonstrate that supplementing the latter method with neutron polarization analysis[6] permits complete information to be obtained by a single technique. The experiments reported here were performed on the IN11 spectrometer at the Institut Laue-Langevin.[7]

Neutron polarization analysis distinguishes neutrons scattered without spin flip from those whose spins are flipped during a scattering process. The technique permits model-free separation of scattering due to fluctuations of particle number density and magnetization density, since these couple to the neutron through different mechanisms. *Nuclear* coherent scattering, which measures fluctuations in particle number density, is spin-nonflip (snf). *Magnetic* scattering is caused by components of the magnetization density, $\vec{M}_\perp(\vec{r})$, which are perpendicular to the neutron momentum transfer $\hbar\vec{q}$. Those components of $\vec{M}_\perp(\vec{r})$ which are perpendicular to the magnetic field $\vec{H}$ applied to the sample cause spin-flip (sf) scattering while the component of $\vec{M}_\perp$ parallel to $\vec{H}$ yields snf scattering. Measurement of scattered intensity with $\vec{q}$ perpendicular ($I_\perp$) and parallel ($I_\parallel$) to $\vec{H}$ thus allows separation of nuclear and magnetic contributions. Specifically, for a fully aligned ferrofluid, the *coherent* snf scattering is given by[8]

$$I_\parallel^{\mathrm{snf}}(q) = \alpha F_N^2(q) S_\parallel(q), \tag{1}$$

$$I_\perp^{\mathrm{snf}}(q) = \alpha [F_N(q) + F_M(q)]^2 S_\perp(q). \tag{2}$$

Here $F_N(q)$ and $F_M(q)$ are the nuclear and magnetic form factors of the ferrofluid particles while $S_\parallel(q)$ and $S_\perp(q)$ are the structure factors for $\vec{q}$ parallel and perpendicular to $\vec{H}$. α is a density-dependent constant into which are included spectrometer efficiency and sample self-shielding effects.

The ferrofluid used in these experiments was composed of small cobalt particles suspended in a saturated hydrocarbon solvent, Isopar-M, of average chain length C_{12}. Stabilization was achieved by using Monoxol-OT (anionic) surfactant with Imidrol-OC (cationic) cosurfactant in a 3:1 ratio. Electron-micrograph studies indicated that the cobalt particles were approximately spherical with an average radius of 2.8 ± 0.3 nm. The distribution of core radii about the mean value has a half-width of 0.6 nm; numerical calculations indicate that this polydispersity will not affect our later conclusions. Nuclear and magnetic scattering-length densities $B(r)$ for the cobalt core, surfactant shell, and solvent are shown in Fig. 1(a) as a function of distance r from the particle center. The value of B shown for the surfactant has been calculated under the assumption of a random packing of surfactant molecules. The solvent has been deliberately chosen to have a lower value of B than the surfactant since the inverse choice, used in some earlier neutron studies,[5] leads to significant structure in $F_N(q)$ and comcomitant difficulty in measuring $S(\vec{q})$. Since

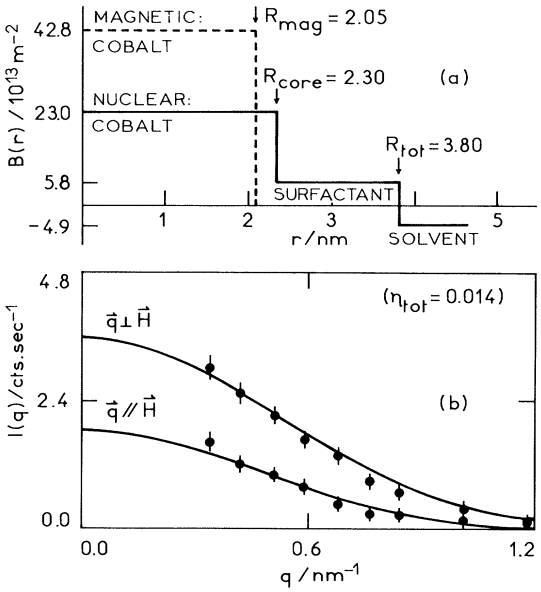

FIG. 1. (a) Neutron-scattering-length densities and geometrical parameters for the model ferrofluid particle. (b) Measured values (filled circles) of coherent snf intensities as a function of wave vector q for the dilute ferrofluid in a field $H = 0.5$ T (corresponding to 91% of saturated bulk magnetization) at 298 K. The volume fraction of particles is $\eta_{tot} = 4\pi R_{tot}^3 \rho/3$ where ρ is the particle number density. The lines are calculated from Eqs. (1) and (2) with the parameters of (a).

the volume fractions of cobalt and surfactant used in preparing the ferrofluid are known, the core radius R_{core} and the total radius R_{tot} are related, provided all surfactant surrounds cobalt particles. This assumption is tested by our experiment.

The coherent, snf scattering obtained with a dilute ferrofluid [$S(\vec{q}) \approx 1$] in an applied field of 0.5 T is shown in Fig. 1(b). Data for $\vec{q}$ parallel to $\vec{H}$ involve only nuclear scattering and may thus be fitted by adjusting the scaling factor α (called α_d for the dilute system) and the particle radius R_{tot}. The fit obtained, under the assumption that all surfactant resides on the cobalt particles, is shown by the lower curve in Fig. 1(b). If the surfactant head groups were all localized on the cobalt surface, the surfactant tails and the solvent would have similar scattering length densities so that R_{tot} would be much larger than the region of the particle which scatters neutrons. Although a fit to $I_{\parallel}(q)$ for the dilute system can be obtained in this case, the value deduced for R_{tot} (5.0 nm) yields a calculated structure factor for our concentrated ferrofluid whose peak position is completely at variance with the measurements. A similar inconsistency is observed if we assume significant penetration of solvent into the surfactant layer or less than 80% of total surfactant on the particles.[9] Our analysis, based on the model of random surfactant packing, yields $R_{core} = 2.3$ nm and good agreement between theory and experiment for concentrated systems. Once $F_N(q)$ has been obtained, $F_M(q)$ may be deduced from $I_{\perp}(q)$ in Fig. 1(b) by means of using Eq. (2). Since the scale parameter α_d is already determined, the only unknown is R_{mag}, the radius of that part of the cobalt core which contributes to magnetic scattering. We find R_{mag} to be at least 0.25 nm smaller than R_{core}, indicating that the outer layer, approximately one cobalt atom thick, does not contribute to magnetic scattering. Similar effects have been observed in Ni powders.[10] They may result from moment reduction such as has been observed when H_2 is chemisorbed on Ni,[11] or may reflect the presence of an oxide layer. A surface configuration of the Co spins which preserves the moment but which does not contribute to bulk magnetization is also possible. Such a configuration has been proposed for Co and Ni ferrite ferrofluid particles.[3] We draw attention to the fact that a symmetric arrangement of radially pinned spins would not contribute to magnetic neutron scattering.

A model for the structure factor $S(\vec{q})$ of a concentrated, fully aligned ferrofluid has been proposed by Hayter and Pynn.[12] For a particular particle structure and fluid density the theory involves no free parameters. Thus direct comparison with experiment may be made once the scale parameter α_c has been determined for the concentrated system by matching the theoretical and experimental peak values of $I_{\perp}(q)$ for the largest applied field [cf. Fig. 2(a)]. The value of α_c so obtained, which is used for *all* calculations of the concentrated system, is ~15 times the value α_d found for the (twenty times less concentrated) dilute system.

Figure 2(a) shows the coherent snf scattering obtained with the concentrated ferrofluid in a 0.5-T field. The two theoretical curves (full and dashed) in this figure correspond respectively to the inclusion or exclusion of short-range attractive forces. The latter, which are predominantly of van der Waals type,[13] have been modeled by a Yukawa potential of depth $0.7k_BT$ and range $0.4R_{tot}$. Such particle "stickiness" has little effect on the agreement between experiment and theory, which is good in either case. In contrast with previous

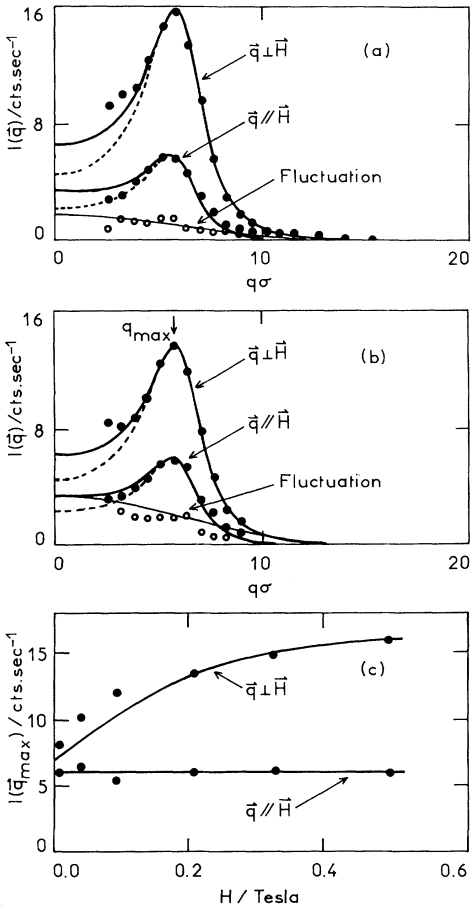

FIG. 2. (a) Measured values of coherent snf scattering (filled circles) and fluctuation scattering (open circles) for the concentrated ferrofluid (η_{tot}= 0.27) in a field of 0.5 T at 298 K. The abscissa is scaled by the particle diameter $\sigma = 2R_{tot}$. Calculated lines are discussed in the text. (b) As for (a) but with the applied field reduced to 0.2 T. Calculated curves are based on Eqs. (1), (4), and (5). (c) Measured (filled circles) and calculated coherent snf scattering at $q = q_{max}$ [cf. (b)] as a function of applied magnetic field for the concentrated system.

neutron studies,[5] the peaks shown in Fig. 2(a) represent particle correlations rather than oscillations in the particle form factor. Thus these data provide the first test of our model for $S(\vec{q})$ of an aligned ferrofluid. However, the reduced dipole moment is $\mu^* \simeq 0.4$ [12] for our ferrofluid, so that the model $S(\vec{q})$ is nearly isotropic and the corresponding pair correlation function $g(\vec{r})$ shows little evidence of particle chaining.

The open symbols displayed in Fig. 2(a) have been obtained from the measured spin-flip scattering as

$$I_{fluc}(q) = 3[I_{\parallel}^{sf}(q) - I_{\perp}^{sf}(q)]. \quad (3)$$

Nuclear-spin incoherent scattering (from both hydrogen and cobalt) is the same in both field geometries and cancels from this expression. The intensity given by Eq. (3) arises from fluctuations of those components of sample magnetization which are perpendicular to $\vec{H}$[6]; it thus measures departure from complete magnetic alignment. The dependence of the fluctuation scattering on wave vector q is similar to that of $F_M^2(q)$ at all applied fields < 0.5 T, indicating that the magnetization fluctuations are, as nearly as we can tell, paramagnetic. For such a system the standard Langevin treatment yields

$$I_{fluc}(q) = 3\alpha_c F_M^2(q) L(m)/m, \quad (4)$$

where $m = \mu H/k_B T$ [μ is the calculated particle moment and $m = 5.8$ in Fig. 2(a)] and $L(m) = \coth m - 1/m$. As Figs. 2(a) and 2(b) demonstrate, Eq. (4) provides a good description of the fluctuation scattering at applied fields of 0.5 and 0.2 T. If magnetic fluctuations are paramagnetic and $S(q)$ isotropic, an expression for the coherent snf intensity in a partially aligned sample can easily be obtained:

$$I_{\perp}^{snf}(q) = \alpha_c[F_N(q) + L(m)F_M(q)]^2 S(q) + F_M^2(q)[1 - 2L(m)/m - L^2(m)]. \quad (5)$$

At the highest field ($H = 0.5$ T) there is little difference between results obtained from Eqs. (2) and (5) justifying, *a posteriori*, the use of the former even in the presence of measurable fluctuation scattering. For intermediate fields, Eq. (5) provides a reasonable description of the snf scattering (cf. Fig. 2). At the lowest fields Eq. (5) underestimates slightly the snf scattering [cf. Fig. 2(c)] and Eq. (4) predicts less fluctuation scattering than is observed.

We conclude that polarization-analysis, small-angle neutron scattering provides an excellent tool for studying ferrofluids. In the cobalt suspension studied, we have determined the particle structure and found a magnetically anomalous layer in the cobalt at the interface with the surfactant, together with a surfactant arrangement which precludes purely head-in packing. R_{tot} depends sensitively on the position of the peak in data taken with the concentrated ferrofluid and is well determined by our measurement. Further, R_{mag} is accurately obtained from the difference between $I_{\parallel}(q)$ and $I_{\perp}(q)$ for the dilute system. The

boundary between cobalt and surfactant (R_{core}) is less well defined, however. The measurements generally confirm the model $S(\vec{q})$ used to interpret the data for concentrated, highly aligned suspensions, and show that moment fluctuations in these suspensions are essentially paramagnetic.

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