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Visualisation of particle association in magnetic fluids in zero-field

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Abstract

We report direct visual evidence for the association of particles in stable magnetic fluids in zero magnetic field, observed with cryo-transmission electron microscopy. The rather isotropic shape of the reversible associates indicates that isotropic (van der Waals) attraction is at least partly responsible for the particle association. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Colloidal stability of magnetic fluids (in zero-field) requires a repulsion between suspended particles, usually generated by electrical double layers and/or surfactants or polymers on the particle surface. This stability does not necessarily imply that magnetic or van der Waals attractions are completely masked. These long-range attractions may produce a 'secondary minimum' in the interaction potential. A weak minimum allows *temporary* (reversible) association of particles without loss of colloidal stability (i.e. without phase separation or irreversible aggregation).

Association in fluids in zero-field has been studied theoretically [1] as well as with Monte Carlo simulations [2]. Recently, we found experimental indications for reversible associates of weakly attractive particles in sedimentation [3] and light scattering [4] studies on dilute fluids. However, no direct visual evidence for the zero-field association of magnetic grains has, to our knowledge, yet been reported. The aim of this work is to investigate whether indeed particle association occurs in zero magnetic field using electron microscopy. Transmission electron microscopy (TEM) is a common technique for examining colloidal particles. However, one observes dried structures in a high vacuum, which yields little information about the spatial distribution of particles in the starting fluid. Therefore we also use cryo-TEM, where an extremely fast cooling rate is applied,

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which keeps colloidal structures in a fluid in their original state [5]. We focus here on some illustrative and representative (cryo) TEM results. More details can be found elsewhere [4].

2. Experimental

Three magnetic dispersions (Table 1) were prepared following Refs. [6–8]. The stabilisation of FFAq and FFPe particles is due to both double layer and steric interaction [3]. The FFO1 grains are only stabilised by a surfactant layer. For the stabilisation of the FFAq dispersion an excess of tetra methyl ammonium hydroxide (TMA) is used. The second surfactant layer of the FFPe-particles is weakly adsorbed, so there are also free dodecylbenzenesulfonic acid molecules present. All fluids exhibited long-term stability with no visible signs of flocculation.

Three methods [4] were used to prepare samples for the transmission electron microscope (TEM). Samples obtained by using the method A are observed with TEM at room temperature. The grids prepared by methods B and C were examined with cyro-TEM at a temperature of -172°C.

A. Samples were made by dipping 200 mesh Cu-grids, coated with a formvar/carbon film, in dilute dispersions. Then the samples were dried at room temperature. TEM was carried out with a Philips CM10H electron microscope at 60 kV.

B. A small sample droplet was placed on a TEM-grid. By blotting the liquid with filter paper a thin film was obtained. Then the specimen was plunged into the cryogen. As cryogen liquid ethane or liquid nitrogen was used depending on the solvent of the samples. The grid was transferred under liquid nitrogen and mounted in a cyro-TEM holder, which was inserted into the TEM Philips CM12 and examined at -172°C at 120 kV.

C. As in B, but now using a holey carbon film-coated copper grid.

For cryo-TEM, cooling of the sample must be fast to prevent rearrangement of the colloidal particles due to crystallisation of the liquid. Therefore ethane was used as a cryogen for the aqueous samples. Since toluene dissolves in liquid ethane, we used liquid nitrogen to freeze the FFO1 samples. We tried to perform cryo-TEM on the pentanol dispersion FFPe. Unfortunately it was not possible to obtain a film thin enough to be examined.

3. Results and discussion

An electron micrograph of the magnetic dispersion FFO1 dried in zero-magnetic field is shown in Fig. 1. The individual particle surfaces do not touch but are separated by a small distance of about 1 nm, which is probably due to the stabilising layer (oleic acid and for the FFPe particles oleic acid and DBS). The particle structure on a micrograph as in Fig. 1, as noted earlier, is not a reliable image of structures in a fluid. Nevertheless, all cryo-TEM results [4] confirm that particles tend to group together. We will briefly discuss some representative cryo-results.

Fig. 2 shows a distribution of particle associates in sample treated according to method C. It is difficult to get an accurate picture of the distribution because of variation in vitrified film thickness

Table 1
Particle radii from TEM (a_{TEM}) and magnetisation measurements (a_{mag}) of the magnetic disperisons

	a_{TEM}[nm]	a_{mag}[nm]	Stabilising layer	Solvent
FFAq	5.2 ± 2.5	5.3 ± 2.5	Tetra methyl ammonium hydroxide	Water, pH ≈ 10
FFO1	5.5 ± 2.5	5.7 ± 2.8	Oleic acid	Toluene
FFPe	5.2 ± 2.4	5.2 ± 2.1	Double surfactant layer: oleic acid and dodecylbenzenesulfonic acid (DBS) [7,8]	Pentanol

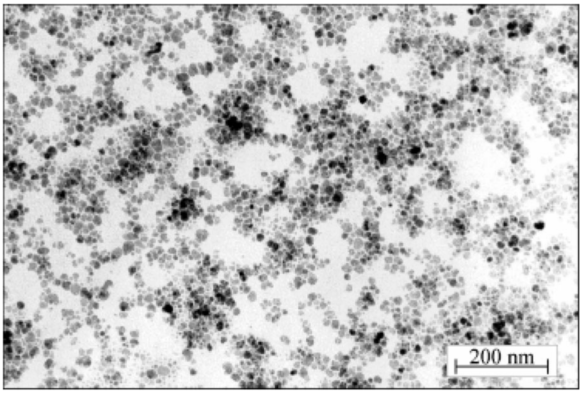

Fig. 1. Transmission electron micrograph of the magnetic magnetite particles FFO1 stabilised with oleic acid in toluene (method A).

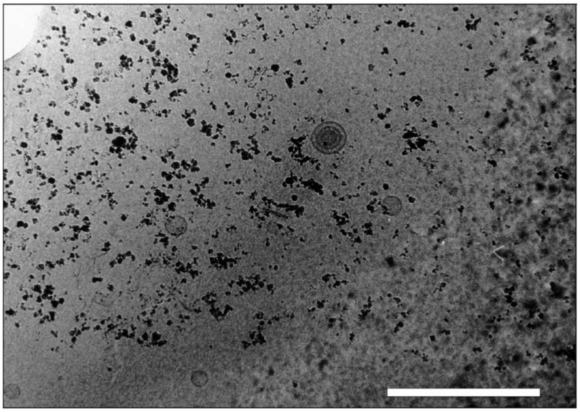

Fig. 2. A cryo-transmission electron micrograph of a FFAq sample on a holey carbon grid (method C). In the upper left corner a part of a hole is visible. The bar is 500 nm.

and the concomitant segregation of cluster sizes [5]. The presence of associates is nevertheless clear.

Figs. 3 and 4 depict a representative selection of results from method B, again showing a variety of associates in aqueous (Fig. 3) as well as non-aqueous fluids (Fig. 4). In Fig. 4a we observe a dense texture of magnetite particles in the most concentrated sample (volume fraction $\phi = 5\%$). Separate associates are difficult to identify here. However, at much lower concentration $\phi = 0.05\%$) we clearly observe a heterogeneous distribution of magnetite particles. Particles group together in associates which are separated by empty solvent regions with occasionally single particles (Fig. 4b–Fig. 4d). The clusters in Fig. 4 vary in size from 2 to about 50 singlets.

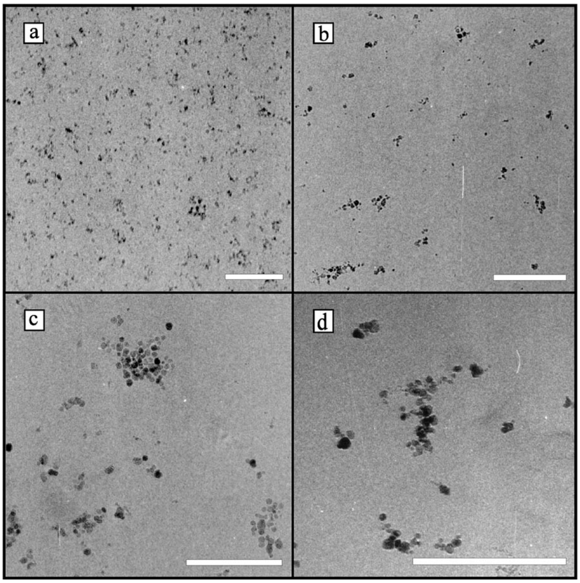

Fig. 3. Cryo-electron micrographs of aqueous FFAq dispersion (method B) with volume fractions 0.5% (a) and 0.05% (b–d). Bar is 200 nm.

It would be hard to judge from the cryo-TEM pictures – without further information – that the depicted particles have a magnetic moment. There are no clear signs of the linear chains expected for particles with dominant anisotropic interactions [1,2,9]. Instead the associates have a rather isotropic morphology, indicating that the dipole interaction is weak. It is also very likely that the isotropic van der Waals attraction contributes significantly. For example, the van der Waals attraction between two magnetite spheres with diameter 11 nm and a surfactant layer thickness of 1 nm may equal one to several kT at particle contact, depending on the Hamaker constant which here is of order $A \approx 10^{-19}$ J. Add to this a weak magnetic attraction and one can easily understand why particles tend to form (weak) associates. Only for stronger magnetic interactions one finds growth of linear chains, as observed for cobalt particles [9].

4. Conclusions

Cryo-TEM micrographs of vitrified (dilute) ferrofluids in zero-field show that particle associates

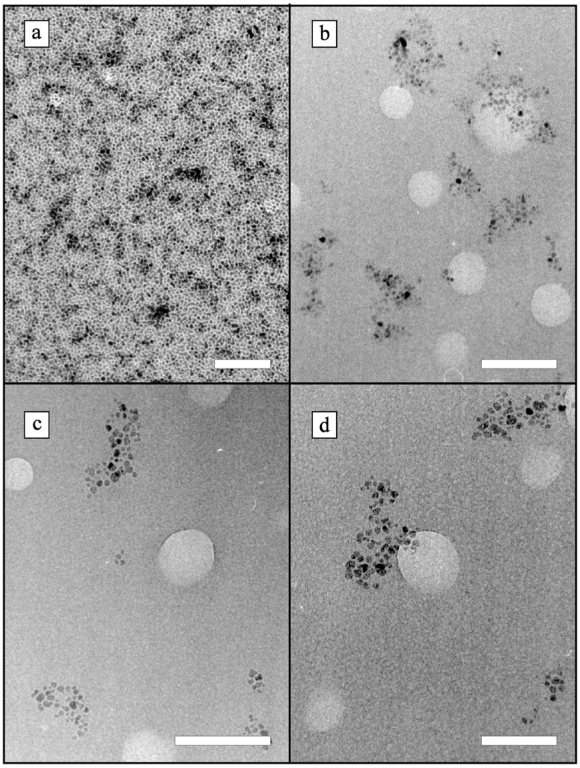

Fig. 4. Cryo-electron micrographs of FFO1 particles in toluene (method B). Volume fractions are 5% (a) and 0.05% (c–d). White spots are due to radiation damage. Bar is 200 nm.

are present in all investigated samples. The isotropic morphology of the associates suggests that van der Waals attractions cannot be neglected as is often done [1,2]. Dipolar attractions apparently are not strong enough to induce clearly anisotropic clusters (chain formation requires larger magnetite particles). Our conclusion confirms the work of Dubois et al. [10], who explain phase separation in zero-field as a consequence of isotropic particle interaction.

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