

Direct observation of dipolar chains in iron ferrofluids by cryogenic electron microscopy

K. BUTTER¹, P. H. H. BOMANS², P. M. FREDERIK², G. J. VROEGE¹ AND A. P. PHILIPSE*¹

¹Van 't Hoff Laboratory for Physical and Colloid Chemistry, Debye Institute, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

²EM Unit, Department of Pathology, University of Maastricht, Universiteitssingel 50, 6229 ER Maastricht, The Netherlands

*e-mail: a.p.philipse@chem.uu.nl

Published online: 12 January 2003; doi:10.1038/nmat811

A key issue in research on ferrofluids (dispersions of magnetic colloids) is the effect of dipolar interactions on their structure and phase behaviour^{1,2}, which is not only important for practical applications³ but gives fundamental insight in dipolar fluids in general. In 1970, de Gennes and Pincus⁴ predicted a Van der Waals-like phase diagram and the presence of linear chains of particles in ferrofluids in zero magnetic field. Despite many experimental studies^{5–7}, no direct evidence of the existence of linear chains of dipoles has been reported in the absence of magnetic field, although simulations^{8–11} clearly show the presence of chain-like structures. Here, we show *in situ* linear dipolar structures in ferrofluids in zero field, visualized on the particle level by electron cryo-microscopy on thin, vitrified films of organic dispersions of monodisperse metallic iron particles. On systematically increasing the particle size, we find an abrupt transition from separate particles to randomly oriented linear aggregates and branched chains or networks. When vitrified in a permanent magnetic field, these chains align and form thick elongated structures, indicating lateral attraction between parallel dipole chains. These findings show that the experimental model used is well suited to study the structural properties of dipolar particle systems.

Evidence for the presence of dipolar chains in ferrofluids in zero field has historically been difficult to obtain; for example, scattering patterns in zero field are always isotropic, and their interpretation requires additional assumptions. Direct imaging on the particle level by conventional transmission electron microscopy (TEM) provides no direct proof for the actual arrangement of particles in the liquid phase, because the microstructure may be severely distorted due to drying. An additional problem is that dipole–dipole interactions in the most commonly used magnetite (Fe₃O₄) ferrofluids are fairly weak⁶ and cannot be varied due to the method of synthesis¹², making it questionable whether chain formation in zero field occurs in these dispersions. However, the more advanced cryogenic TEM (cryo-TEM, discussed below) technique can now be fruitfully applied to a more versatile model ferrofluid consisting of metallic iron colloids.

The magnetic dipole moment of a single-domain sphere of radius r and bulk saturation magnetization M_s is $\mu = 4\pi r^3 M_s / 3$. The dipole–dipole interaction between two magnetic particles at contact, scales as $\mu^2 / \sigma^3 \propto r^6 / \sigma^3$ (σ being the effective hard-sphere diameter, consisting of the core diameter and the thickness of the surfactant layer)¹³, so that the ferrofluid microstructure should be very sensitive to particle size. For this study, we therefore chose iron dispersions where

dipole–dipole interactions can be tuned by particle size variation¹⁴ and are much stronger than for magnetite, because M_s is larger for iron¹³. Synthesis methods of iron dispersions are limited to apolar organic solvents, but this is advantageous for studying the effect of dipolar interactions, because electrostatic interactions will be practically absent. In addition, our particles are coated with a thick surfactant layer to minimize the effect of Van der Waals attractions. These properties make iron dispersions suitable for systematically studying dipolar structures in ferrofluids as a function of particle size. Cryo-TEM is a technique that studies vitrified, thin, liquid films in low-dose TEM. A fast temperature quench of films of dispersions vitrifies the solvent, arresting the diffusion of particles on the timescale of glass formation. Thus, this method preserves the arrangement of particles in the solvent, which can subsequently be imaged on the particle level. The resolution we obtain is sufficient to clearly distinguish particles as small as 2 nm (Fig. 1). Most cryo-TEM work has been done on aqueous samples¹⁵ where the film stability is based on a balance of attractive Van der Waals forces between the air–liquid interfaces and electrostatic repulsions between charged surfactants organized at these interfaces¹⁶. Making stable, glassy films of organic solvents is not trivial¹⁵ and only a few reports have appeared (for example, ref. 17). We found that thin films of iron dispersions in decalin are surprisingly stable, despite the absence of charged surfactants, and that they can readily be vitrified in liquid nitrogen.

We synthesized dispersions (see Methods) of single-domain, superparamagnetic iron particles¹³ with low polydispersity, surrounded by a stabilizing shell of modified polyisobutene¹⁸. The composition of

Table 1 Characterization of iron dispersions.

Code	a_{TEM}^* (nm)	a_{SAXS}^\dagger (nm)	a_{M}^\ddagger (nm)	μ_{AGM}^\S (Am ² × 10 ¹⁹)
A	2.1 ± 0.3	2.17	1.3	0.123
B	6.0 ± 0.74	4.88	4.1	4.149
C	6.6 ± 1.1	6.03	5.1	8.38
D	6.9 ± 1.0	8.82	6.0	13.19
E	8.2 ± 1.5	9.54		

*Particle radius measured from TEM-micrographs. †Particle radius determined from Guinier curves of SAXS measurements. ‡Magnetic radius determined from magnetization curves. §Dipole moment $\mu = 4\pi a_{\text{M}}^3 M_s / 3$ with $M_s = 1.49 \times 10^6$ Am⁻¹ (bulk value for Fe_{0.75}C_{0.25}, of which our particles consist)¹⁹.

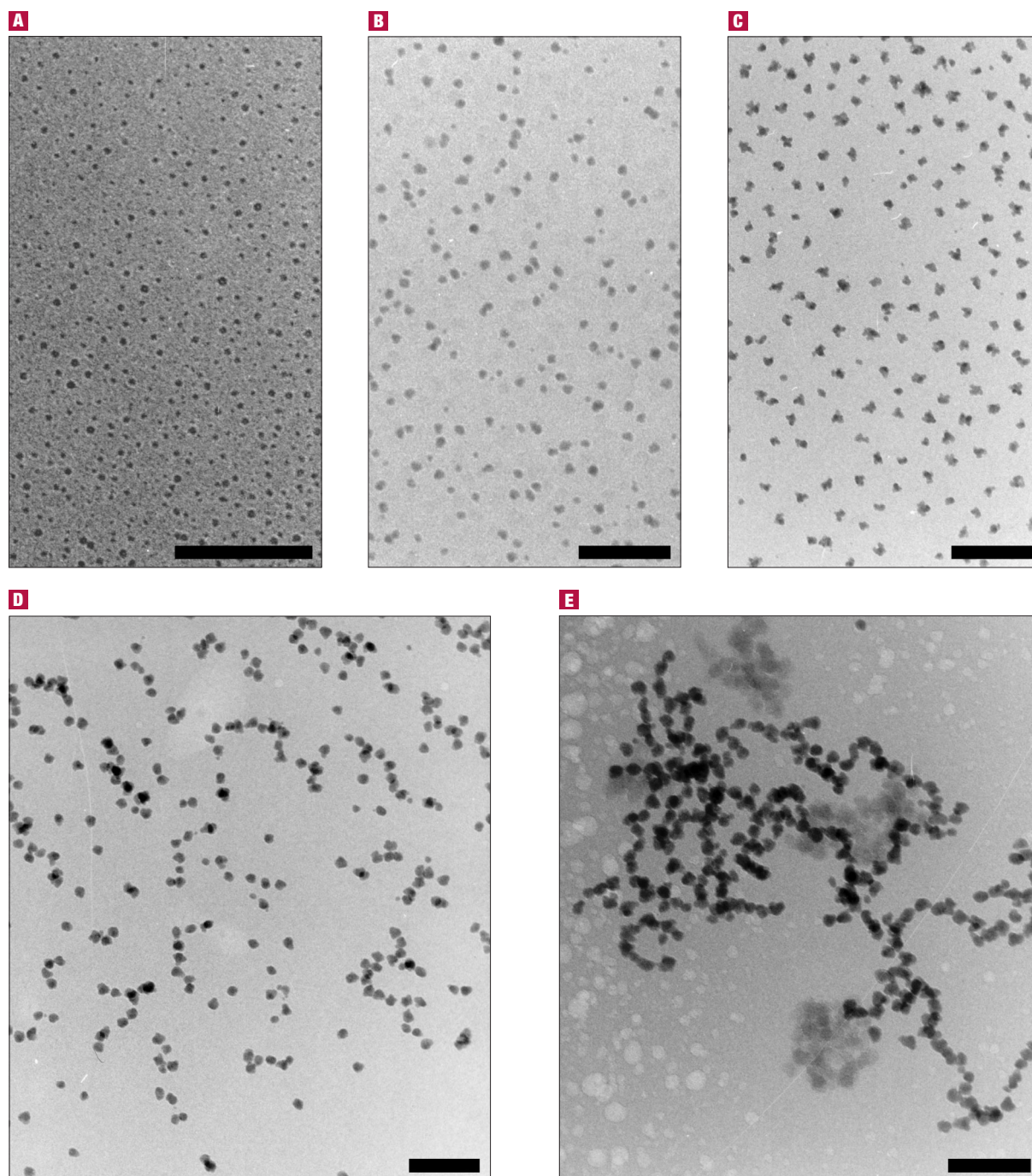


Figure 1 Typical cryo-TEM images of iron dispersions with increasing average particle radius, labelled according to Table 1. The samples were made from dispersions with equal volume fractions (0.0006) of iron. In E, the white objects on the left and top right, and the three larger structures with poor contrast are artefacts. Scale bars = 100 nm.

the particles is discussed elsewhere¹⁹. Particle sizes, determined by different measuring techniques, as well as particle dipole moments, for five dispersions A–E are presented in Table 1, and their cryo-TEM images in Fig. 1. Susceptibility measurements as a function of height confirm that all dispersions are stable and do not phase separate.

In marked contrast to magnetite dispersions⁶, in our ferrofluids we clearly observe linear structures in zero magnetic field for sufficiently large iron particles (dispersion D in Fig. 1). Their anisotropy provides supporting evidence that these aggregates are caused by dipole–dipole interactions, favouring a head-to-tail orientation. Note that chains are

not aggregated to larger ‘superclusters’; chain–chain interactions are obviously weak, as is confirmed in simulations¹⁹. The presence of many individual particles in Fig. 1D indicates that we observe a snapshot of dynamic clusters, which are easily disrupted by thermal motion. For larger particles we indeed see the effect of stronger dipoles: cluster sizes increase considerably, and the number of single particles is reduced (Fig. 1E). Smaller particles, which have weaker dipoles, stay separated (Fig. 1A–C) because the dominant interaction is the isotropic repulsion by the polymer shell. Note that Van der Waals attractions are weak in our dispersions; owing to their thick surfactant layers, the particles do not

form isotropic clusters (see Fig. 1A–C), as are found in dispersions of oleic-acid-coated magnetite (Fe_3O_4) particles⁶. Because the Van der Waals interaction is a function of r/σ only, whereas the dipolar interaction has a stronger volume dependence²⁰, Van der Waals attractions will become relatively less important on increasing the particle size (dispersions D and E). Dipolar interactions are very sensitive to particle radius, as expected^{4,13} from their scaling for particles at contact as r^6/σ^3 , and the structure formation predicted by de Gennes and Pincus⁴ is clearly observed above a critical particle size. It must be noted that we study ferrofluids in thin films—having thickness of the order of a particle diameter, as determined from electron energy loss spectra (EELS)²¹—which ought to be considered as two-dimensional. Simulations of comparable systems in two dimensions^{8,10,11} do indeed show very similar particle structures (tortuous, branching chains) to those in Fig. 1D, although in some recent simulations flux closure rings are found¹¹, which we did not observe in our samples.

The existence of anisotropic structures is not limited to thin films, as is shown by preliminary measurements of the complex susceptibility as a function of frequency, from which brownian relaxation times (τ_b) can be determined by previously reported methods²². For dispersions D and E we find much larger values for τ_b than expected for single particles, whereas for smaller particles (dispersion C) τ_b corresponds to their particle size. These measurements clearly confirm the presence of larger structures in the (three-dimensional) dispersions D and E, in agreement with what we found in two-dimensional liquid films.

If the linear structures, as in Fig. 1D, are truly due to dominant dipolar forces, they should align in the direction of an externally applied magnetic field. To verify this, dispersion D was vitrified in a saturating magnetic field, giving a film that was extremely susceptible to electron beam radiation damage. The stability of the film increased considerably by the addition of small particles A. For comparison, the same mixtures have also been vitrified in the absence of a magnetic field, which gives similar pictures (Fig. 2a) as samples without particles A (Fig. 1D). In a magnetic field however, the structures of particles D are straightened and aligned in the field direction (Fig. 2b), confirming that our aggregates indeed consist of dipoles. Another striking effect of the magnetic field is the enormous increase of the cluster dimensions in the lateral direction. Very similar structures are found in magneto- and electro-rheological fluids^{23,24} and dispersions of non-magnetic particles in ferrofluids in magnetic fields²⁵, where they have been explained in terms of lateral aggregation. Indeed, chain–chain interaction between fluctuating parallel dipolar chains, aligned by a magnetic field, can give rise to attraction perpendicular to the field direction²⁶. The resemblance with the systems described above, where dipolar interactions prevail, shows that dipolar forces indeed also dominate in our ferrofluids. Note, however, that all cases observed previously involve induced dipoles, which do not form chains in zero field. In our case, we see the transition between relatively small chains of permanent dipoles in zero field and much larger aggregating chains in high fields.

The smaller particles A were distributed homogeneously within the film (as can be seen in the background of the micrographs in Fig. 2) and their moments were presumably aligned by the magnetic field, but evidently dipole–dipole interactions were too weak to cause field-induced aggregates. The stability behaviour observed suggests that the mere presence of homogeneously distributed particles is sufficient to stabilize the film. This rationalizes the observation that films of particles D are stable without a magnetic field, but only marginally stable with a large magnetic field where big clusters are formed, leaving large areas without any particles. In this hypothesis, the addition of the much less magnetic particles A then leads to stabilization by ensuring that particles remain distributed throughout the film.

Our experiments support several theories^{4,9,27} and simulations^{8–11}, demonstrating a structural change in a ferrofluid for increasingly strong dipoles, going from single particles to randomly oriented anisotropic clusters. As in many simulations on dipolar hard spheres^{1,8}, we do not

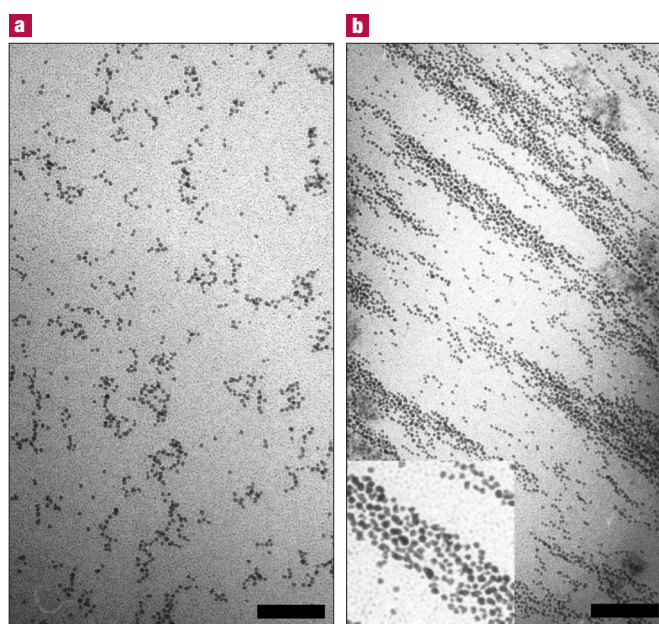


Figure 2 Cryo-TEM images of a mixture of dispersions D and A (with iron volume fractions of particles of 0.0006 and 0.0004, respectively). **a**, in zero field, and **b**, in a saturating magnetic field. The insert is an enlargement (4 times) of a part of the complete picture. Because particles have been in air only for a very short time, the images do not show the oxidized layers around the iron cores, which we observed for particles exposed to air for a few hours. Chains, already existing in zero field, align in the magnetic field. Scale bars = 200 nm.

find a phase transition. Our results in zero field qualitatively agree with results from simulations, showing chain-like structures for sufficiently large dipoles that thermally dissociate then recombine^{1,8–10}. Chain formation for simulations in three dimensions¹ roughly starts at a dimensionless reduced dipole moment μ^* of 2–2.5 with an average chain length varying from 1.4 to 10 particles for a concentration ρ^* of 0.3. This value is similar to our experimental results, where chain formation starts for iron particles in dispersion D with a value of 2.4 for μ^* (using the dipole moment and TEM radius from Table 1 with a surfactant layer¹⁸ of 6 nm) and a mean cluster size of 2.49 for a comparable concentration. Quantitative results from two-dimensional simulations are known for similar μ^* values, but only for much lower concentrations ρ^* than in our samples¹¹, showing longer mean chain lengths, and the presence of ring-like structures that were not observed in our ferrofluids.

Structural information from cryo-TEM is clearly of importance to interpret for example, small angle neutron or X-ray scattering (SANS or SAXS) curves measured on the same dispersions. A combination of techniques (SANS, SAXS, complex susceptibility measurements and cryo-TEM) may provide us with a complete picture of the behaviour of dipolar fluids. Iron colloids, where dipolar interactions can be tuned both by changing particle sizes and by varying minimum particle distances (using surfactants with different lengths¹⁸), may well be the experimental equivalent of computer simulations on dipolar spheres with a variable ratio of isotropic and dipolar interaction¹.

METHODS

SYNTHESIS OF IRON DISPERSIONS

The iron dispersions were synthesized by thermal decomposition of $\text{Fe}(\text{CO})_5$ in decalin in the presence of modified polyisobutene (PIB) as described previously¹⁸ and always stored under nitrogen atmosphere.

Average particle radii were varied by changing the Fe(CO)₅/PIB ratio. Particles D and E were grown from particles C, by adding extra Fe(CO)₅ afterwards¹⁸. Similar susceptibility measurements as in ref. 28 confirm that all dispersions are stable and do not phase separate.

VITRIFICATION OF FILMS

Vitrified films of dispersions were made on grids coated with holey carbon film (R2/2, Quantifoil Micro Tools, Jena, Germany) using a vitrobot²⁹ in an oxygen-poor atmosphere (approximately 0.4 vol.% O₂) to prevent particle oxidation. Photographs were taken from the carbon film holes with a Philips CM12 TEM (Eindhoven, The Netherlands) at 120 kV using low-dose techniques. For measurements in an external magnetic field, the grid, fixed between the poles of a small permanent magnet³⁰ (1.6 tesla), was blotted by hand in air. Vitrification was performed by plunging the magnet in liquid nitrogen while the grid stays fixed between the magnet poles.

Received 12 July 2002; accepted 9 December 2002; published 12 January 2003.

References

- Teixeira, P. I. C., Tavares, J. M. & Telo da Gama, M. M. The effect of dipolar forces on the structure and thermodynamics of classical fluids. *J. Phys. Condens. Matter* **12**, R411–R434 (2000).
- Thusty, T. & Safran, S. A. Defect-induced phase separation in dipolar fluids. *Science* **290**, 1328–1331 (2000).
- Berkovski, B. & Bashtovoy, V. (eds) *Magnetic Fluids and Applications Handbook* (Begel House, New York, 1996).
- de Gennes, P. G. & Pincus, P. A. Pair correlations in a ferromagnetic colloid. *Phys. Kondens. Mater.* **11**, 189–198 (1970).
- Shen, L., Stachowiak, A., Fateen, S. K., Laibinis, P. E. & Hatton, T. A. Structure of alkanolic acid stabilized magnetic fluids. A small-angle neutron and light scattering analysis. *Langmuir* **17**, 288–299 (2001).
- Donselaar, L. N. *et al.* Visualisation of particle association in magnetic fluids in zero-field. *J. Magn. Mater.* **201**, 58–61 (1999).
- Cebula, D. J., Charles, S. W. & Popplewell, J. Aggregation in ferrofluids studied by neutron small angle scattering. *J. Physique* **44**, 207–213 (1983).
- Weis, J. J. Orientational structure of quasi-two-dimensional dipolar hard spheres. *Mol. Phys.* **93**, 361–364 (1998).
- Tavares, J. M., Weis, J. J. & Telo da Gama, M. M. Strongly dipolar fluids at low densities compared to living polymers. *Phys. Rev. E* **59**, 4388–4395 (1999).
- Chantrell, R. W., Bradbury, A., Popplewell, J. & Charles, S. W. Agglomerate formation in a magnetic fluid. *J. Appl. Phys.* **53**, 2742–2744 (1982).
- Tavares, J. M., Weis, J. J. & Telo da Gama, M. M. Quasi-two-dimensional dipolar fluid at low densities: Monte Carlo simulations and theory. *Phys. Rev. E* **65**, 061201 (2002).
- Massart, R. Preparation of aqueous magnetic liquids in alkaline and acidic media. *IEEE Trans. Magn.* **17**, 1247–1275 (1981).
- Rosensweig, R. E. *Ferrohydrodynamics* (Cambridge Univ. Press, Cambridge, 1985).
- Griffiths, C. H., O'Horo, M. P. & Smith, T. W. The structure, magnetic characterization, and oxidation of colloidal iron dispersions. *J. Appl. Phys.* **50**, 7108–7115 (1979).
- Talmon, Y. Transmission electron microscopy of complex fluids: The state of the art. *Ber. Bunsenges. Phys. Chem.* **100**, 364–372 (1996).
- Frederik, P. M., Stuart, M. C. A., Schrijvers, A. H. G. J. & Bomans, P. H. H. Thin film formation and the imaging of phospholipids by cryo-electron microscopy. *Scanning Microscopy* **3**, 277–284 (1989).
- Oostergetel, G. T., Esselink, F. J. & Hadziioannou, G. Cryo-electron microscopy of block copolymers in an organic solvent. *Langmuir* **11**, 3721–3724 (1995).
- Pathmamanoharan, C., Zuiverloon, N. L. & Philips, A. P. Controlled (seeded) growth of monodisperse sterically stabilised magnetic iron colloids. *Progr. Colloid Polym. Sci.* **115**, 141–145 (2000).
- Goossens, A. *et al.* Monodisperse magnetic iron colloids grafted with polyisobutene: a model system for Fischer-Tropsch catalysts? *Hyperfine Interact.* **141/142**, 381–386 (2002).
- Scholten, P. C. in *Magnetic Properties of Fine Particles* (eds Dormann, J. L. & Fiorani, D.) 277–286 (Elsevier, Amsterdam, The Netherlands, 1992).
- Reimer, L. *Transmission Electron Microscopy: Physics of Image Formation and Microanalysis* 2nd edn Vol. 36 (Springer, Heidelberg 1989).
- Fannin, P. C., Scaife, B. K. P. & Charles, S. W. New technique for measuring the complex susceptibility of ferrofluids. *J. Phys. E* **19**, 238–239 (1986).
- Fermigier, M. & Gast, A. P. Structure evolution in a paramagnetic latex suspension. *J. Magn. Mater.* **122**, 46–50 (1993).
- Gast, A. P. & Zukoski, C. F. Electrorheological fluids as colloidal suspensions. *Adv. Colloid Interface Sci.* **30**, 153–202 (1989).
- Skjeltorp, A. T. One- and two-dimensional crystallization of magnetic holes. *Phys. Rev. Lett.* **51**, 2306–2309 (1983).
- Halsey, T. C. Electrorheological fluids. *Science* **258**, 761–766 (1992).
- Osipov, M. A., Teixeira, P. I. C. & Telo da Gama, M. M. Structure of strongly dipolar fluids at low densities. *Phys. Rev. E* **54**, 2597–2609 (1996).
- van Ewijk, G. A., Vroege, G. J. & Kuipers, B. W. M. Phase behavior of magnetic colloid-polymer mixtures: 2. A magnetic sensing coil study. *Langmuir* **18**, 382–390 (2002).
- Frederik, P. M., Bomans, P. H. H., Laeven, P. E. J. & Nijpels, F. J. T. *Device for Preparing Specimens for a Cryo-electron Microscope* (Netherlands Industrial Property Office (RO/NL) PCT/NL02/00189 2002).
- Oldenbourg, H. & Philips, W. C. Small permanent magnet for fields up to 2.6 T. *Rev. Sci. Instrum.* **57**, 2362–2365 (1986).

Acknowledgements

Marc Storms and Felix de Haas from FEI Electron Optics, Eindhoven, The Netherlands, are thanked for performing the EELS-measurements. Ben Ern  and Thido Arts are thanked for their help with the susceptibility measurements. Financial support was granted by the Dutch Technology Foundation (STW) with financial aid from the Council for Chemical Science of the Netherlands Organization for Scientific Research (CW/NWO).

Correspondence and requests for materials should be addressed to A.P.P.

Competing financial interests

The authors declare that they have no competing financial interests.