

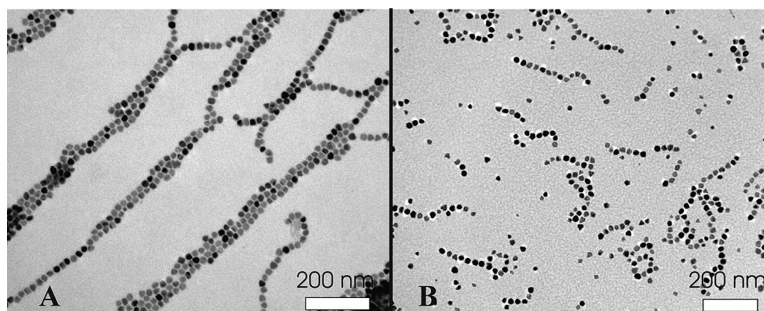
Communication

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Direct Imaging of Zero-Field Dipolar Structures in Colloidal Dispersions of Synthetic Magnetite

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Magnetite (Fe₃O₄) forms the basis of most dispersions studied in the field of magnetic fluids and magnetic colloids.^{1,2} Despite extensive theory and simulations on chain formation in dipolar fluids in zero field,^{3,4} such structures have not yet been imaged in laboratory-made magnetite dispersions. Here, we present the first direct observation of dipolar chain formation in zero field in a ferrofluid containing the largest synthetic single-domain magnetite particles studied so far.

Magnetite ferrofluids comprise sterically or charge stabilized particles in water or organic solvents. The first preparation method involved grinding of magnetite mineral in a surfactant solution.⁵ This was followed by chemical precipitation methods⁶ which are still widely applied. However, these methods have serious drawbacks when it comes to studying the fundamental physical chemistry of dipolar fluids. First, they result in fairly polydisperse particles, and control over the average particle size is limited. Second, the maximum average particle diameter is typically only 10 nm, which is insufficient for significant dipolar structure formation in zero field. Dipolar structure formation is expected when the dipolar potential exceeds thermal fluctuations; that is, for a dipolar coupling constant $\lambda > 2$, where $\lambda = \mu_0 \mu^2 / (4\pi k_B T \sigma^3)$ and $\mu_0 = 4\pi \times 10^{-7}$ J A⁻² m⁻¹, μ is the magnetic moment of one particle (equal to its magnetic volume times 4.8×10^5 A m⁻¹ for magnetite²), k_B is the Boltzmann constant, T the absolute temperature, and σ the hard sphere diameter. Since $\lambda \approx 0.3$ for 10 nm magnetite particles coated with a 2 nm thick organic surfactant layer, any aggregation in zero field is most likely due to isotropic van der Waals attractions between iron oxide cores.⁷ For strongly magnetic particles, simulations such as by Chantrell et al.⁴ (Figure 1) predict the formation of dipolar chains and flux-closure rings.^{8,9} Due to the relatively small particle sizes, such dipolar structures have not been observed or imaged (in zero field) in conventional magnetite fluids, not even with in situ cryogenic transmission electron microscopy (cryo-TEM).⁷ A possibility to obtain larger magnetite particles is to harvest them from magnetotactic bacteria.⁹ Indeed, such particles form the chain structures expected for strongly dipolar particles. The yield of bacterial magnetite, however, is low, and the colloids are difficult to purify from organic residue.⁹ Moreover, this biomineralization does not allow adjustment of the particle size.

Recently, a novel organometallic synthesis method was reported by Sun et al.¹⁰ to produce fairly monodisperse magnetite particles. We have examined this method extensively but found it quite difficult to reproduce a particular particle size and, in addition, to reach diameters beyond 16 nm ($\lambda > 2$) required for dipolar chain formation. It was necessary to develop a modified procedure (see below) to obtain such large particles in a high yield. Our procedure

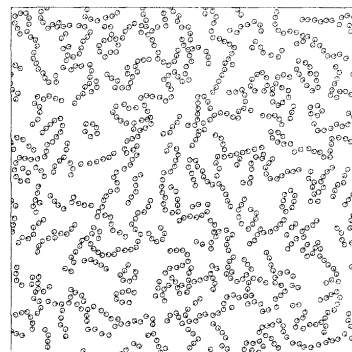


Figure 1. A two-dimensional Monte Carlo simulation on 15 nm magnetic Co particles ($\lambda \approx 22$) by Chantrell et al.,⁴ showing the formation of dipolar chains and flux-closure rings in zero field. Reprinted with permission from ref 4. Copyright 1980 Institute of Physics Publishing.

resulted in a controlled and reproducible growth of magnetite particles that exhibit dipolar structure formation in zero field.

Seed particles (4 nm diameter) were prepared following Sun et al.¹⁰ The seed solution was washed by adding at most 20 mL of ethanol and precipitated within minutes using a small magnet (1000 G), recovering approximately 95% of the material. The sediment was redispersed in diphenyl ether (20 mL) by shaking, adding 50 μ L of oleic acid and 50 μ L of oleylamine, and ultrasonicing for several minutes, and a dispersion was obtained that was used for further growth. The dispersion was transferred to a reaction flask, and while stirring, the same amounts of precursors were added as in the seed synthesis. The mixture was gradually heated to reflux in 15 min and refluxed for an additional 30 min. Finally, the washing procedure with ethanol was repeated, and the product was transferred to diphenyl ether, or to Decalin if no further growth was required. The 21 nm particles were prepared by repeating this method up to seven times, starting with the addition of extra surfactants and subsequent ultrasonication. An advantage of several growth steps is the low polydispersity (<10%) and improved sphericity of the large particles.

X-ray diffraction was used to verify the crystal structure of the colloids.¹¹ The position and relative intensity of all diffraction peaks match well with the pattern for magnetite (Fe₃O₄).^{10,12} Line broadening in the two systems agrees with the diameters of the particles from TEM, indicating that the particles are single crystals. Magnetization curves¹³ of dilute dispersions yield magnetic diameters of 15 and 20 nm, confirming that the particles are single magnetic domains.

Dynamic susceptibility spectra¹⁴ reveal that the magnetic moment was free to rotate inside the 16 nm particles (N el relaxation with a characteristic frequency above 100 kHz) but fixed inside structures obtained with the 21 nm particles (Brownian rotation with a

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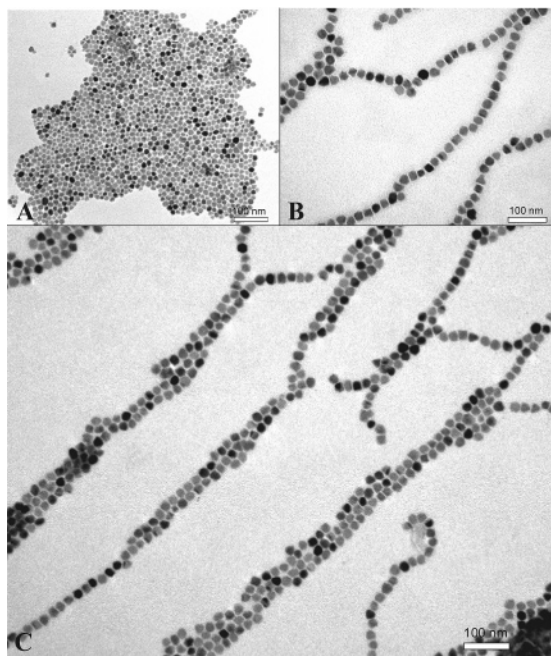


Figure 2. Representative TEM bright field images (zero field) of magnetite particles deposited from Decalin dispersions on polymer-coated, carbon-sputtered copper grids. (A) The 16 nm particles are fixed in droplet-shape islands with an isotropic internal structure. (B and C) All of the 21 nm particles are present in long dipolar chains. Scale bars: 100 nm.

characteristic frequency of <100 Hz, well below the characteristic frequency of several kHz for single particles and, therefore, indicative of large structures). The same measurements indicate that the chain length decreases upon dilution, which apparently results from a dynamic equilibrium.

Conventional TEM (Figure 2) and direct (in situ) cryogenic imaging (Figure 3) clearly show the growing effect of dipolar attractions for increasingly large magnetite particles. Figure 2 presents conventional TEM images of 16 and 21 nm magnetite particles. The 16 nm particles form droplet-shape structures expected for particles with dominant isotropic interactions ($\lambda \approx 2$), while the 21 nm particles show linear chains as a result of prevailing magnetic interactions ($\lambda \approx 7$).

Cryo-TEM images of vitrified Decalin dispersions¹⁵ are displayed in Figure 3. The dispersion of 16 nm particles is distinguished by isotropic repulsion between the surfactant-coated colloids. The 21 nm magnetite particles display single and branched chains as well as flux-closure structures in striking resemblance with those shown in Figure 1. The anisotropic features are due to dipole-dipole interactions, favoring a head-to-tail orientation. The dipolar chains consist of up to 20 particles. Panels B and C of Figure 3 clearly are snapshots of a dynamic equilibrium between single particles and wormlike structures. By comparison, Panels B and C of Figure 2 demonstrate the substantial effect of drying the dispersions for conventional TEM; single particles are absent, and extensive parallel chains are formed, which according to cryo-TEM, are not present in the dispersion.

We have shown that synthetic magnetite colloids can be prepared sufficiently large to exhibit rich dipolar structure formation in zero field, which can be imaged by cryo-TEM. To our knowledge, this is the only ferrofluid system available at present that allows quantifying chain length and ring-size distributions of dipolar structures as a function of concentration and particle size. In contrast to conventional magnetite fluids, these dispersions are very promising for the experimental study of the morphology and thermodynamics of dipolar fluids.¹⁶

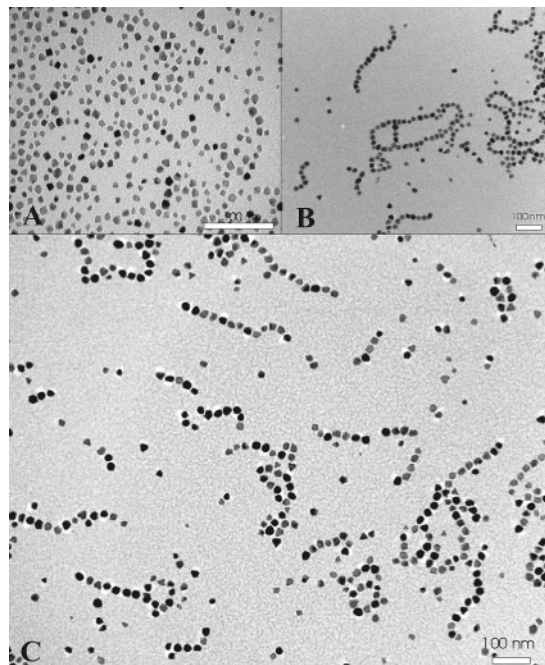


Figure 3. Typical in situ cryo-TEM images (zero field) of vitrified magnetite dispersions. (A) The 16 nm particles (surface fraction including organic layer: 0.64) appear to repel each other. (B and C) The 21 nm particles (surface fraction including organic layer: 0.17) form dynamic structures comparable to those of the simulations in Figure 1. Scale bars: 100 nm.

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