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# Ferrofluids from prism-like nanoparticles

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**Abstract**

Decomposition of iron pentacarbonyl in kerosene in the presence of octanoic acid and bis-2-ethylhexylamine leads to very monodisperse iron nanoparticles and thus to monodisperse magnetic nanoparticles. These latter can be spherical or appear as triangles on MET pictures. SAXS and AFM indicate that particles are more likely prisms. They can be dispersed in cyclohexane to produce ferrofluids.


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## 1. Introduction

Among the numerous routes that have been described to synthesize magnetic nanoparticles, some of them allow a precise control of the particle size, but the control of the particle shape is more difficult. Such a control has been recently described for silver [1,2], cadmium sulfide [3], palladium and nickel [4] nanoparticles.

Usual magnetic nanoparticles are either made of metals (Fe or Co) or are based on ferric oxide ($Fe_3O_4$, $\gamma$-$Fe_2O_3$, $Fe_2CoO_4$, $BaFe_{12}O_{19}$, etc.). Ferric oxide particles are usually obtained by alkaline condensation of iron salts, either in water [5], or in an organic solvent in the presence of a surfactant [6]. Such methods that lead to a large amount of material are moreover rapid and easy to carry out. They allow a rough control of the particles mean diameter in the nanometric range, but a real control of the polydispersity of the systems needs a further size sorting process [7], or is achieved by the use of microemulsions [8,9]. Anyway in the nanometric range, the shape of these particles is usually rock-like, except in the case of $BaFe_{12}O_{19}$ particles that can be obtained as hexagonal platelets [10].

Metallic magnetic nanoparticles have higher saturation magnetization than oxide ones but are quickly oxidized. They are obtained by several methods. One of them is the thermal decomposition of iron carbonyl or cobalt carbonyl in an organic solvent in the presence of a protecting agent [11]. Particles produced by this method are spherical ones, with usually a narrow size distribution.

We use here this method to synthesize monodisperse magnetic nanoparticles that can be either spherical or ''prism-like''. These particles are easily dispersed in oily media, allowing production of magnetic fluids.

## 2. Experimentals

### 2.1. Materials

Iron pentacarbonyl, octanoic acid (OA), bis-2-ethylhexylamine (BEA) and the kerosene are all bought from Aldrich and used as received.

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### 2.2. Synthesis of iron particles dispersed in cyclohexane

Kerosene (100 mL) was introduced in a 0.5 L four-neck round-bottom flask under nitrogen. It was stirred and degassed by nitrogen during half an hour. The stabilizing agent (OA and BEA) was then introduced and iron pentacarbonyl was added in one time using a Hamilton syringe. The mixture was then heated to 90 °C under nitrogen stream and kept at this temperature during one hour. It was then refluxed between 180 and 200 °C. During the decomposition of iron pentacarbonyl, orange fumes were observed. The end of the reaction was characterized by the end of these fumes and the solution turned black upon the formation of iron nanoparticles. This solution was cooled down to room temperature. A mixture of acetone and methanol (50/50 v/v) was added, allowing to get a black precipitate. This latter was isolated by magnetic separation and dispersed in cyclohexane allowing to obtain a ferrofluid. All the washing steps have to be carried out in a glove box, under nitrogen atmosphere in order to avoid oxidation. Even when oxidation is allowed the dispersion stays stable with regards to particles agglomeration.

### 2.3. Methods for characterization

Particle shape and size distribution were deduced from transmission electron microscopy (TEM): a drop of the dispersion, diluted by the solvent was deposited on the carbon grid and the solvent was evaporated. Observation was performed with a microscope JEOL 100 CX2. Electron diffraction allowed the determination of the nature of the particles. The experimental particles size distribution was fitted by a log-normal law characterized by the parameters $d_0$ and $\sigma$.

Atomic force microscopy (AFM) was performed in the taping mode (digital instruments). The sample was deposited on a carbon support.

Magnetization of the samples (dispersions or powders) was measured as a function of the magnetic field up to 1 T, using a home made vibrating magnetometer [12].

Small angle X-ray scattering (SAXS) on diluted dispersions of particles gives the form factor $P(q)$ charateristic of particles shape. It has been performed in the LURE laboratory using synchroton (beamline D22, Orsay, France). The dispersion placed between "captons windows" has a low volume fraction ($\phi < 1\%$) in order that the scattered intensity can be assimilated to the form factor $P(q)$.

## 3. Results

### 3.1. Macroscopic aspect of the samples

At the end of the synthesis stable dispersions are obtained. Their color ranges from black to red, depending on the oxidation of the particles. Even if most of the manipulations are performed in the glove box, oxidation is not completely avoided because of the very small size of particles.

### 3.2. Electron microscopy

Pictures of Fig. 1 show mixtures of spherical particles and triangle-like particles. Spherical particles are almost monodisperse (Fig. 1a). The diameters distribution is well described by a log-normal law of parameters $d_0 = 5.2$ nm and $\sigma = 0.1$. In some cases, almost only triangles are observed. The triangles look equilateral, of the same size as spherical particles, which means between 5 and 10 nm by side (Fig. 1b).

### 3.3. SAXS

SAXS provides an averaged description of the system [13]. Fig. 2 is the form factor of the dispersion corresponding to the TEM Fig. 1b. At low $q$, $P(q)$ reaches the Guinier plateau indicating that no aggregation occurs. The double-logarithmic plot shows a straight line in the intermediate $q$ domain, with a constant slope of $-3$. For comparison, solid lines are

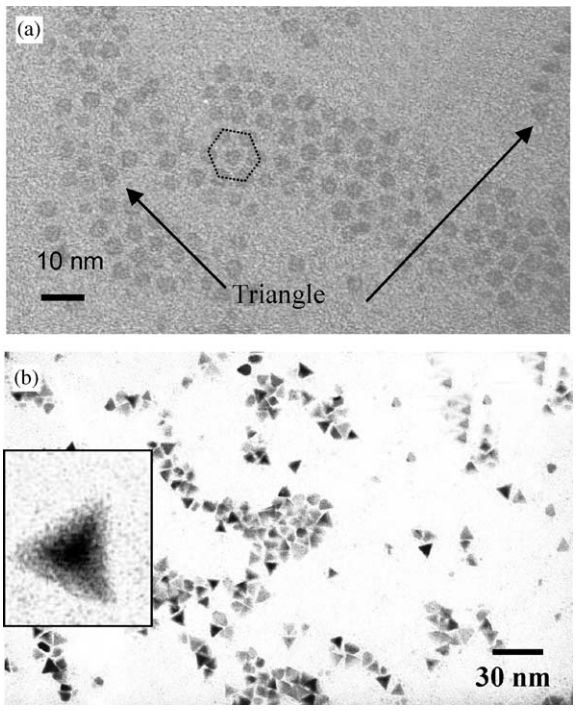


Fig. 1. TEM pictures: (a) of a mixture of spherical and triangular particles of diameter around 5 nm (hexagonal packing on the grid is observed attesting the monodispersity of the samples). (b) Of trigonal particles, an enlargement of a triangle illustrates that this latter looks equilateral.

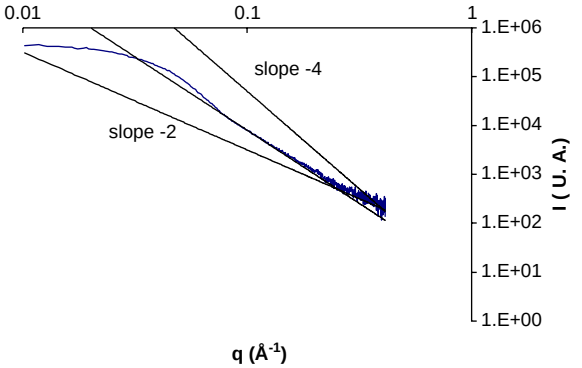


Fig. 2. Form factor obtained by SAXS for the dispersion of particles corresponding to Fig. 1b.

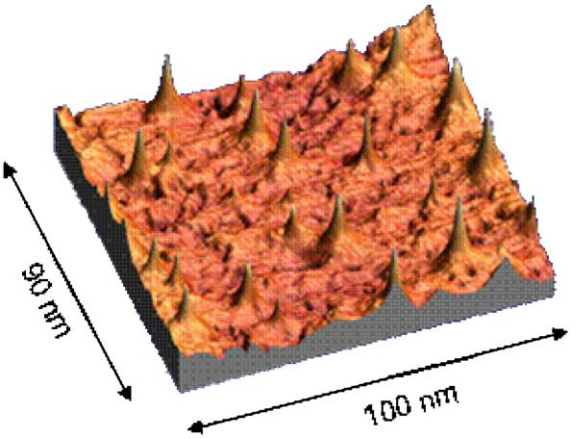


Fig. 3. AFM picture of particles corresponding to Fig. 1b.

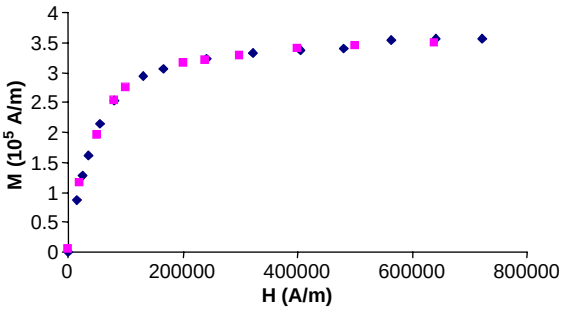


Fig. 4. Magnetization curve of a ferrofluid-based on prism-like iron nanoparticles.

plotted with slopes equal to −4 and −2, respectively, expected for spheres and platelets. As consequences, SAXS proves that the nanoparticles here are neither spheres nor platelets and thus a prismatic shape is possible.

### 3.4. Atomic force microscopy

AFM provides additional information on the particle shape. Fig. 3 is characteristic of the samples for which triangles appeared on TEM pictures. Such peaks are never observed for spherical particles, neither for plate-like particles. It indicates that particles are not discotic triangles deposited on the surface, but more likely prisms or pyramids (Fig. 3).

### 3.5. Magnetization measurements

The magnetization curves of the dispersions are in any case characteristic of a superparamagnetic behavior (Fig. 4). The ratio of the saturation magnetization to the iron concentration varies according to the oxidation state of the sample from $3.10 \times 10^5$ A/m/g of Fe to $5.27 \times 10^5$ A/m/g of Fe (pure Fe: $1.75 \times 10^6$ A/m/g of Fe).

## 4. Conclusion

We used the thermal decomposition of iron pentacarbonyl in kerosene, using OA and bis-2-ethylhexylamine in order to get cyclohexane magnetic fluids. As Butter et al. who used decomposition of iron pentacarbonyl in decalin with oleic acid and polyisobutene [13], we obtained monodispersed spherical particles but also prisms, in various proportions. Cheon et al. also described the shape evolution of iron oxide nanocrystal [14] but obtained only low percentage of non-spherical particles. Many have been proposed to explain the evolution of the particles shape: Ostwald ripening (in the case of silver particles obtained in the presence of light) [1], or self-assembly of small spherical particles that lead to triangular aggregates [15]. Such hypotheses are supported by getting triangles larger than the spherical particles. We did not observe this and think, as in Ref. [4], that the shape control is more likely related to a template effect due to the carboxylate surfactant used in large amount during the synthesis process. AFM and SAXS provided an additional indication on particles shape compared with TEM: particles are not plate triangles, but more likely prisms or pyramids.

These anisotropic particles can be dispersed in an organic solvent, producing dispersions that have a superparamagnetic behavior, and exhibit colloidal stability. The phase behavior of such dispersions of prisms will be studied in order to propose a method of separation of prisms from spheres in the mixtures.

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## Further reading

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