Monte Carlo and Experimental Study of the Magnetic Behaviour of Superparamagnetic Iron Oxide Nanoparticles

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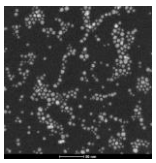
The magnetic field-dependent magnetisation of superparamagnetic iron oxide nanoparticles is probed through Monte Carlo simulations and compared to experimental results obtained on a Vibrating Sample Magnetometer with two different nanoparticle samples. The simulations are performed using the particle size distribution obtained from STEM images. Simulations and experiments are in good agreement for the sample with the smaller particles (R_0 = 3,21 nm) but not the second sample (<R> = 6,81 nm).

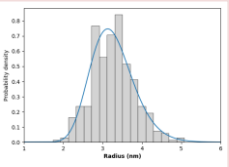
I. Introduction and research context

- Iron oxide nanoparticles are useful in a wide range of applications, especially in the biomedical field. Their characterization relies notably on their magnetisation curves.[1]
- Magnetisation curves are assumed to be equilibrium curves. Therefore, the Metropolis algorithm, which allows to compute the equilibrium properties of physical systems[2], is a method of choice to reproduce those curves through numerical simulations.
- However, very few studies compare results from such simulations to actual measurements.[3] This is our goal.[4]

II. Methods

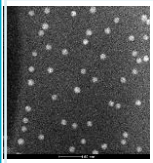
II. a. Experimental samples

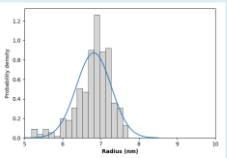




- Log-normal size distrib.
- R_0 = 3,21nm
- σ_L = 0,16
- [Fe] = 19,8 mM

Both samples :
- Oleic acid coating
- Suspended in toluene





- Normal size distrib.
- $\langle R \rangle$= 6,81 nm
- σ_N = 0,46 nm
- [Fe] = 19,7 mM

The magnetisation curves were obtained on a Vibrating Sample Magnetometer at 300K.

II. b. Simulations

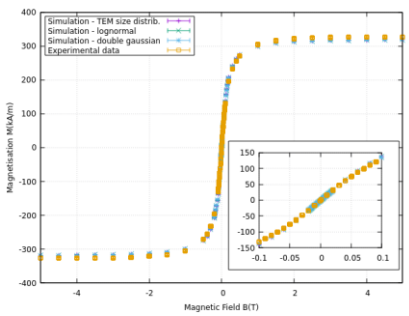
- A Metropolis algorithm based on the energy model :

$$E = -\vec{\mu}\cdot\vec{B} - KV\overrightarrow{1_A}\cdot\overrightarrow{1_B} - \frac{\mu_0}{4\pi}\sum_{i\neq j}\left[\frac{3(\overrightarrow{\mu_i}\cdot\overrightarrow{r_{ij}})(\overrightarrow{\mu_j}\cdot\overrightarrow{r_{ij}})}{r_{ij}^3} - \frac{\overrightarrow{\mu_i}\cdot\overrightarrow{\mu_j}}{r_{ij}^5}\right]$$

Zeeman energy | Anisotropy energy (unniaxial) | Magnetic dipole-dipole interaction energy

- Two evolution processes coexist : Néel relaxation (i.e. reorientation of $\overrightarrow{\mu_i}$) or Brown relaxation (i.e. reorientation of $\overrightarrow{1_A}$).
- Dipole-dipole interactions are considered only for particles within a certain cutoff radius of one another.

III. Results at 300K

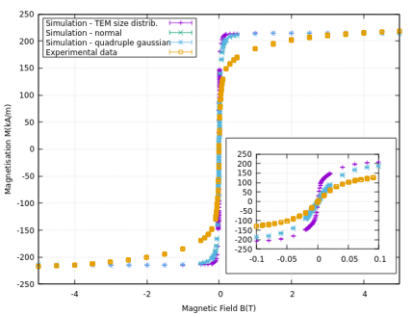


Particles with a median radius of 3,21 nm

The size dispersion of the experimental sample was considered in the algorithm in three different ways:

- The radii measured on the STEM were directly used;
- The radii were randomly sampled from the log-normal or normal distribution fitted from the histograms ;
- The radii were randomly sampled from a superposition of normal peaks fitted from the histograms.

The three cases superimpose for the first sample, less so for the second. This disagreement between the three simulations is however small compared to the disagreement between the simulations and the experimental data for that sample.



Particles with a mean radius of 6,81 nm

The agreement between the Monte Carlo simulations and the experimental data, is excellent for the first sample. On the other hand, the simulation completely fails to reproduce the experimental data for the second sample.

IV. Prospects

- The **strong disagreement** between the simulations and the experimental data for the second sample remains to be explained.
- The dynamics of those particles, and in particular the influence of dipolar interactions on the Néel time, should be studied. Indeed, if the Néel time is considerably heightened by these, the particles' magnetic moment perhaps does not have enough time to reach equilibrium over a characteristic measurement. This could explain the failure of the model observed for the bigger particles.
- Another possibility is that there is a need to refine the anisotropy model. Indeed, the uniaxial scheme is simplistic.

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[2] N. Metropolis et al., Equation of state calculations by fast computing machines, The Journal of Chemical Physics 21 (1953) 1087–1092. doi:10.1063/1.1699114.
[3] V. Schaller et al., Monte Carlo simulation of magnetic multi-core nanoparticles, Journal of Magnetism and Magnetic Materials 321 (2009) 1400-1403. doi:10.1016/j.jmmm.2009.02.047
[4] É. Martin et al., Monte Carlo simulations of the magnetic behaviour of iron oxide nanoparticle ensembles: taking size dispersion, particle anisotropy, and dipolar interactions into account, EPJB 95 (2022) 201. doi:10.1140/epjb/s10051-022-00468-w

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