Field-induced phase separation of a magnetic colloid under AC fields

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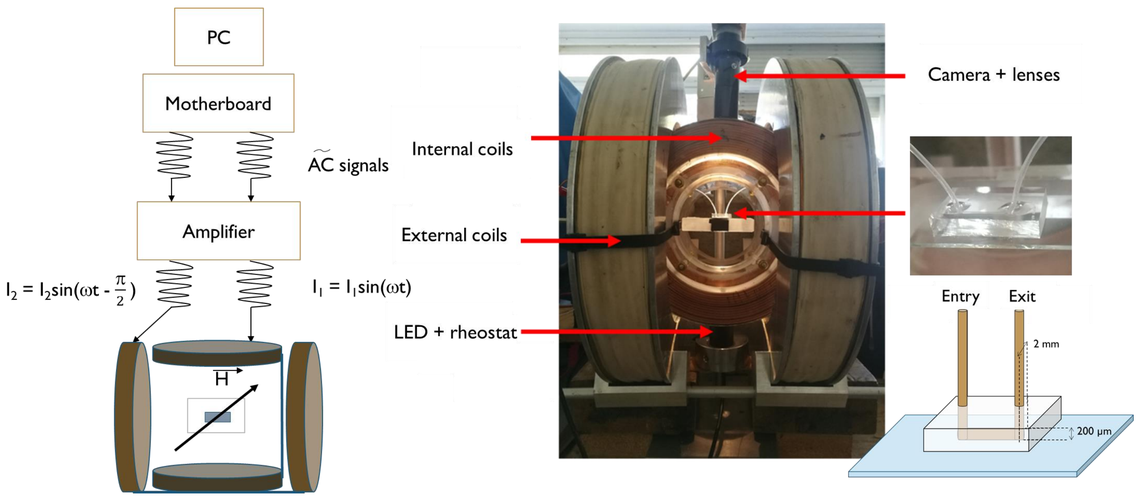
Introduction

This work is devoted to the experimental study of kinetics of phase separation of a magnetic colloid under AC rotating magnetic fields. To this purpose, we use citrate-coated maghemite nanoparticles (medium size 8 nm) dispersed in distilled water and slightly destabilized addition of salts screening electrostatic repulsion between nanoparticles and leading to primary aggregates. In the presence of an AC unidirectional sinusoidal magnetic field (5-10 kA/m), the primary isotropic aggregates are attracted to each other and form long needle-shape aggregates of a typical length of 0.1-0.5 mm during a timescale related to a translational diffusivity of nanoparticles and the suspension supersaturation. Once they reach a maximal length related to homogeneity of the chemical potential across the suspension, some aggregates coalesce with each other in order to decrease the surface energy, but the coalescence is strongly slowed down by repulsive magnetic dipolar interactions, such that in practice the phase separation is not accomplished during a few hours. However, when a rotating sinusoidal magnetic field of the same amplitude is applied, the needle-like aggregates (appearing a few minutes after switching on the field) grow very quickly due to their collisions with free nanoparticles as they synchronously rotate with the field. We focus on fundamental understanding of this phenomenon tuned by Mason and Péclet numbers, as well as by magnetic nanoparticle concentration and suspension supersaturation. From the practical point of view, the obtained results open new perspectives for controlling the field-induced aggregation which may be applied in co-operative magnetophoresis, immuno-agglutination assays and magnetically assisted thrombolysis.

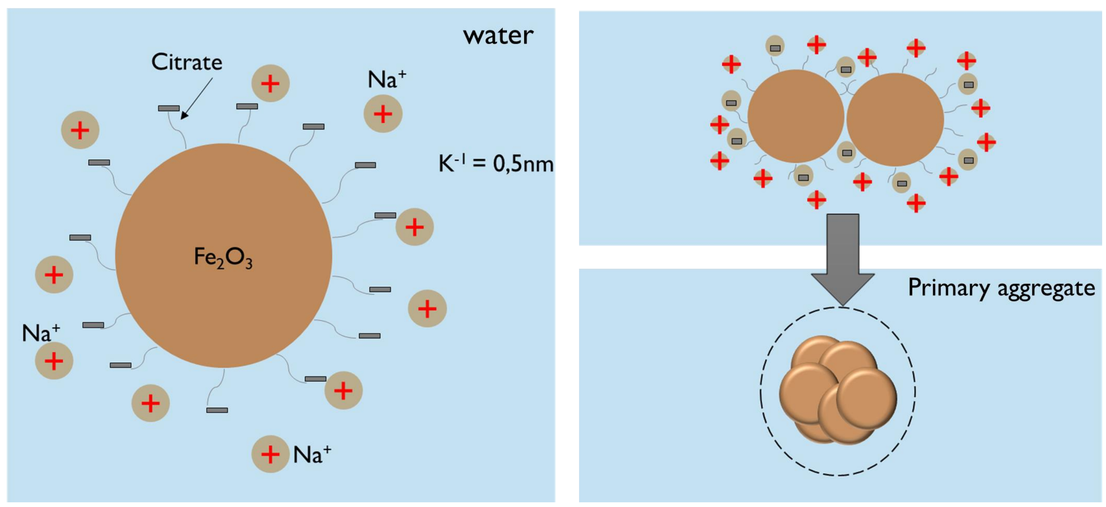
Methods

Experimental system

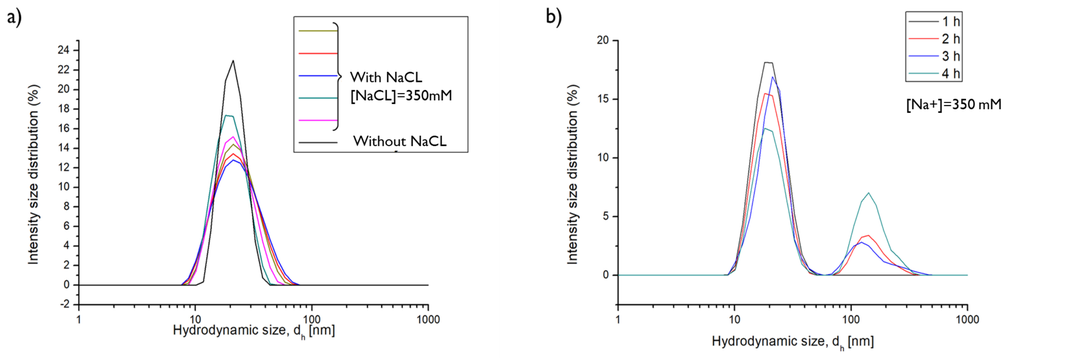
The system used for the experimental study consists of two nested Helmholtz coil pairs powered by a suitable alternating current to generate a rotating magnetic field and a microfluidic circuit within which the formation of rotating needle-like aggregates under rotating magnetic fields are observed.



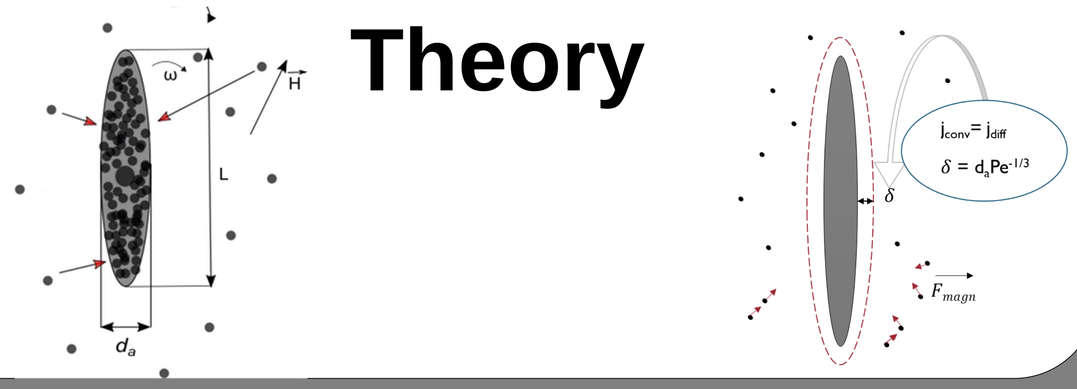
Suspension of nanoparticles



Caracterisation of Iron Oxyde nanoparticles in solution through DLS. Particle volumic fraction of 0,16%, addition of NaCl with $[Na^+]$ = 0,350mM and pH = 5,50. Aggreagation time without rotating field >> Aggregation time with rotating field



Theory



- Peclet's Number :
  $Pe \sim \frac{j_{conv}}{j_{diff}} = \frac{L\,\omega\,d_a}{D_p}$
- Particle flux $J = \varphi_i \frac{dV_a}{dt}$
- Diffusive Boundary Layer Theory: $J \sim D_p\, Pe^{1/3}\, (\varphi_\infty - \varphi')L$
- Particle Volume Conservation: $\varphi_\infty = \varphi_0 - \varphi_i n_a V_a$
  (number of agregates per unit volume n_a constant with time)
- Agregate Volume: $V_a = \frac{\pi}{6}\frac{L^3}{r_a^2}$
- Minimum of free energy of aggregate: $V_a \sim d_p^3 \frac{r_a^7}{ln^3 r_a}$

$\widetilde{V_a} = \frac{V_a}{V_m}$, $\widetilde{V_m} \sim \frac{\varphi_0 - \varphi'}{\varphi_i n_a d_p^3}$

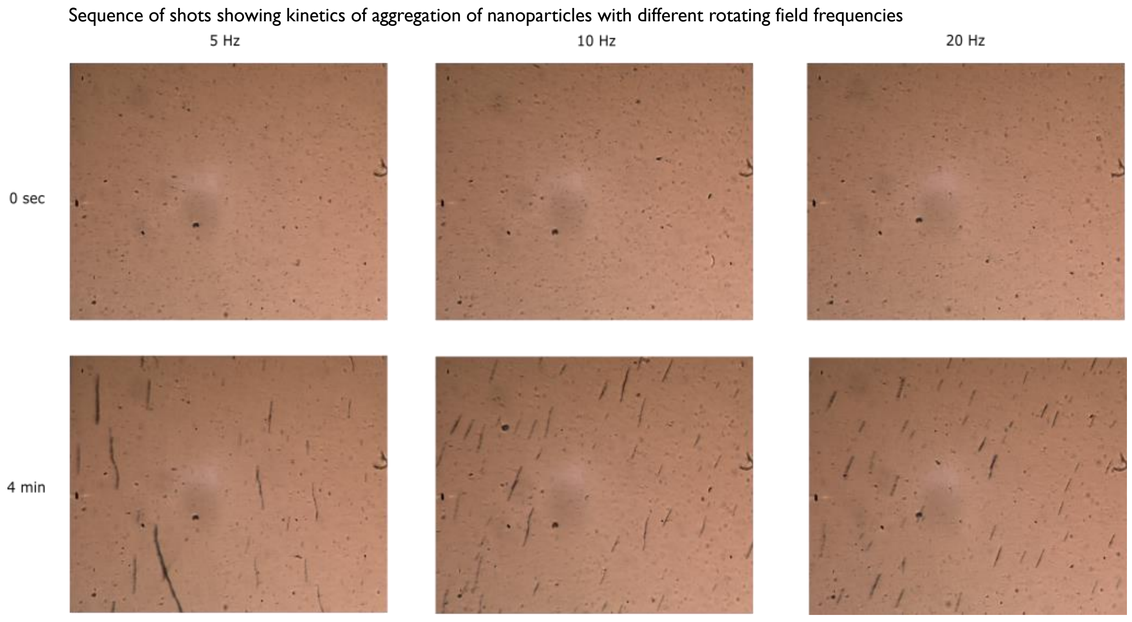
$\frac{d\widetilde{V_a}}{d\tilde{t}} \sim \frac{\varphi_0 - \varphi'}{\varphi_i \widetilde{V_m}^{1/3}} \widetilde{V_a}^{2/3}(1-\widetilde{V_a})$

$\tilde{t} = \frac{D_p^{2/3}\omega^{1/3}}{{d_p}^{4/3}} t$

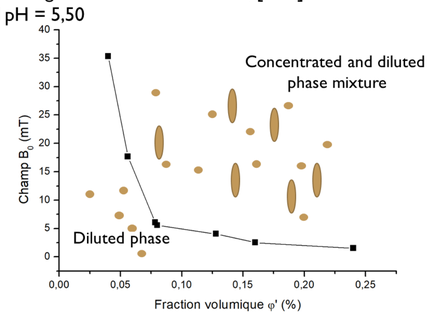
→ we find $\widetilde{V_a}(\tilde{t})$

Results

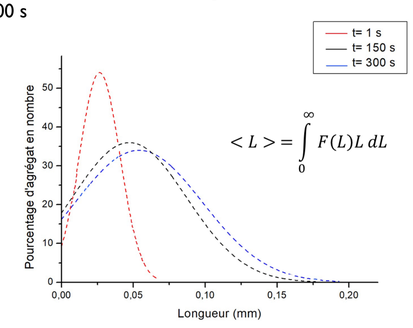
Sequence of shots showing kinetics of aggregation of nanoparticles with different rotating field frequencies

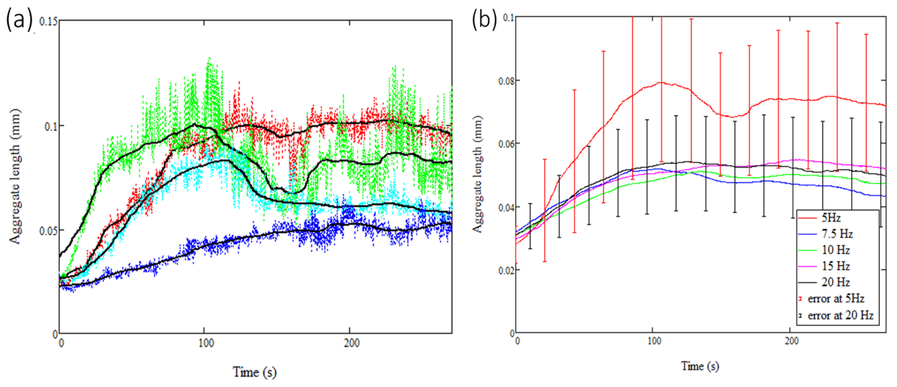


Phase diagram with NaCl constant, [Na+] = 350mM and pH = 5,50



Analysis of the size distribution at a given time, Time t = 1s, Time t = 150 s, Time t = 300 s

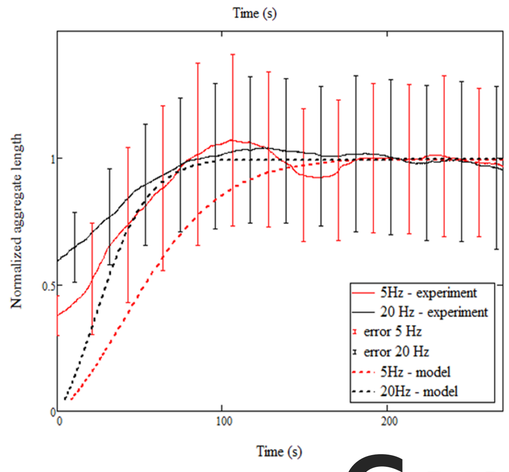




Experimental dependencies of the aggregate mean length (obtained from the size distribution) on the elapsed time.

(a) 4 raw experimental curves (dashed) and smoothed (continuous) for a frequency f = 5Hz,

(b) Length averaged over 4 measurements for each field frequency. The error bars are presented for f = 5Hz and f = 20Hz. For (a) and (b) the amplitude of the field is B_0 = 11mT



Experimental comparison of aggregate length normalized by maximum length as a function of time for two field frequencies. The model parameters: The supersaturation $\Delta_0 = \varphi_0 - \varphi'$= 0.16% -0.07% = 0.09% or 9.10^{-4}. The value φ'= 0.07% of the aggregation threshold comes from the phase diagram for the amplitude of the field B_0= 11mT; volume fraction of particles in the aggregate φ_i= 30%; average diameter of nanoparticles dp = 20nm; the maximum diameter of the aggregates d_a= 5 µm, the maximum length of the aggregate is directly measured at the stage of the experimental curves L (t).

Characteristic aggregation time:

$$t_{agr} = \frac{\varphi_i Vmax^{1/3} {d_p}^{1/3}}{{D_p}^{2/3}\omega^{1/3}(\varphi_\infty - \varphi')} \sim 100s$$

Conclusions

From the experiment:

At f=5 Hz: Aggregates longer than for any of f > 5 Hz and a faster aggregation rate

Explanation: Largest aggregates size at low frequency for the hydrodynamic forces exerted on the aggregates are smaller as their rotation speed is low.

Extremely fast aggregates creation (1min) (length 50-80 µm) rotating with the field

From theory :

$$\frac{dL}{dt} \sim \frac{L_{max}}{t_{agr}} \sim {L_{max}}^{2/9}.\,\omega^{1/3}$$

Aggregation speed is decreasing with the frequency as ${L_{max}}^{2/9}$ decreases faster than $\omega^{1/3}$ *increases*

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