

# Kinetics of aggregation and magnetic separation of multicore iron oxide nanoparticles: effect of the grafted layer thickness

Olivier Sandre, Gauvin Hemery, Vincent Manin, Hinda Ezzaier, Cyrille Caludet, Pavel Kuzhir

## ► To cite this version:

Olivier Sandre, Gauvin Hemery, Vincent Manin, Hinda Ezzaier, Cyrille Caludet, et al.. Kinetics of aggregation and magnetic separation of multicore iron oxide nanoparticles: effect of the grafted layer thickness. International Conference Self-Assembly of Colloidal Systems (SACS2018), Sep 2018, Pessac, France. 2018. hal-01879138

HAL Id: hal-01879138

<https://hal.archives-ouvertes.fr/hal-01879138>

Submitted on 22 Sep 2018

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



## Kinetics of aggregation and magnetic separation of multicore iron oxide nanoparticles: effect of the grafted layer thickness

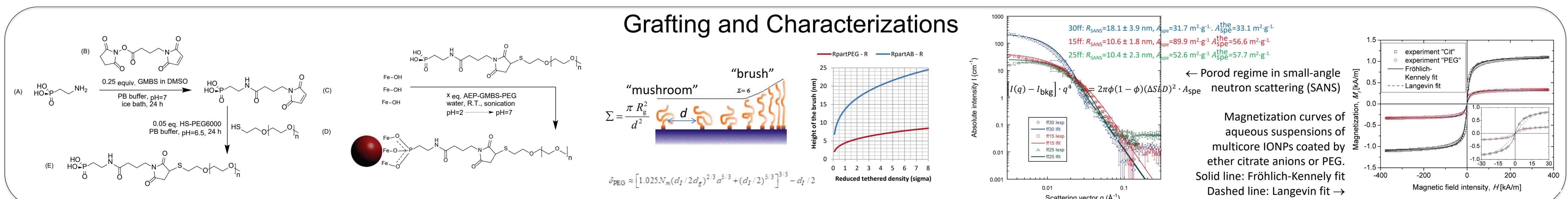
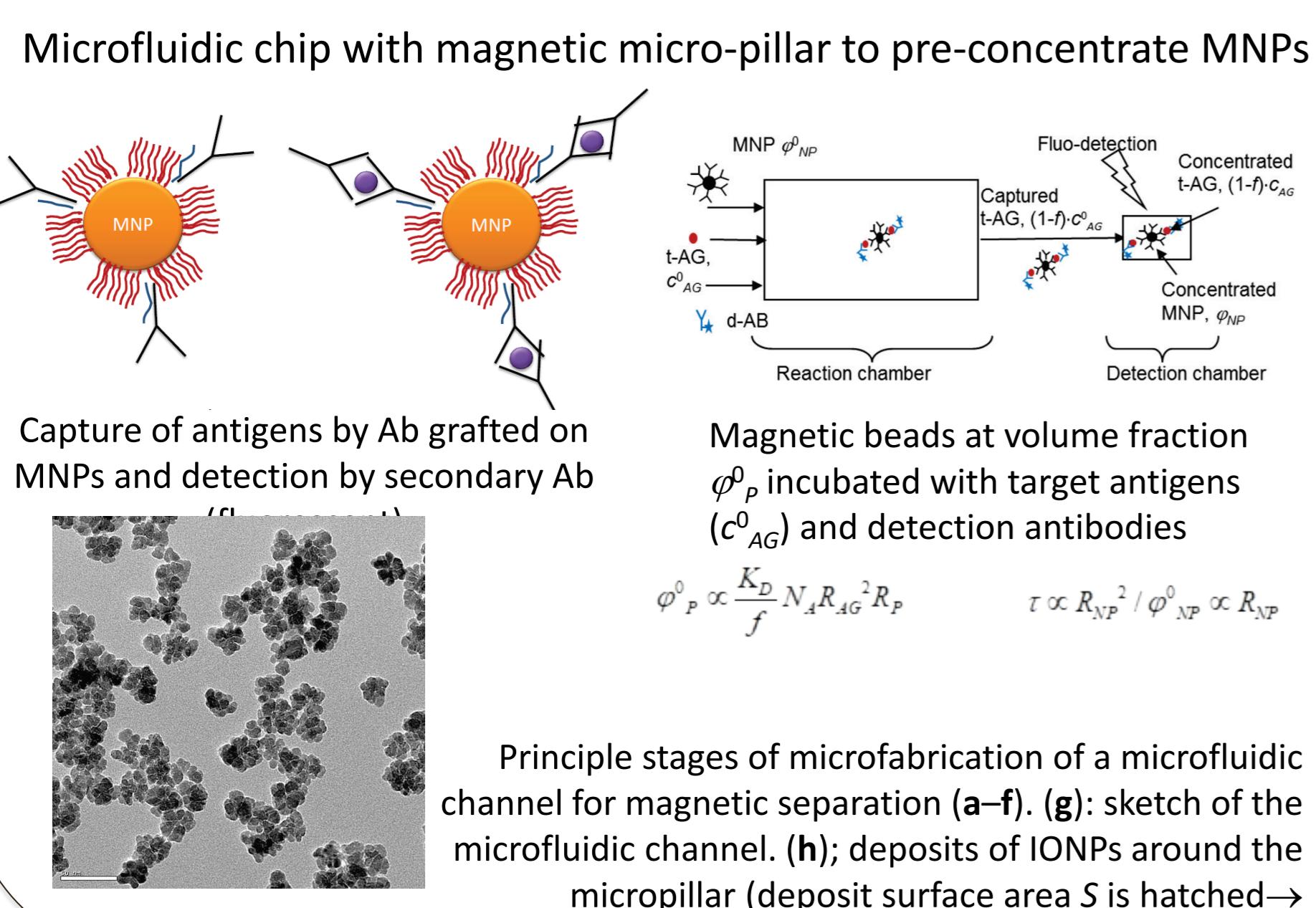
O. Sandre,\*<sup>1</sup> Gauvin Hémery,<sup>1</sup> Vincent Manin,<sup>1</sup> Hinda Ezzaier,<sup>2</sup> Cyrille Caludet,<sup>2</sup> Pavel Kuzhir\*<sup>2</sup>

[olivier.sandre@enscbp.fr](mailto:olivier.sandre@enscbp.fr), [pavel.kuzhir@unice.fr](mailto:pavel.kuzhir@unice.fr)

**Abstract:** Magnetic microbeads are commonly used in immunoassays to detect trace levels of antigens. Despite weaker magnetic attraction, we aim at developing efficient magnetic capture of multi-core magnetic nanoparticles (MNP) also called nanoflowers,[1] of outer diameter 30-60 nm, by using moderate magnetic field strengths. Recent work by some of us showed that magnetic interactions between MNPs of this size can still be strong enough to induce a reversible phase separation in the presence of a magnetic field  $B$  as weak as 10 mT.[2] During this phase separation, MNPs are gathered into micron-sized drop-like aggregates whose magnetic interaction with the applied field is much stronger than between individual nanoparticles and larger than thermal agitation  $k_B T$ . These fluid-like aggregates can then be separated from the solvent much more easily than single MNPs. Moreover, it is beneficial in continuous filtration to assemble the aggregates well before they are captured by magnetized collectors, by conveying the MNP suspension to the micro-filter across a microchannel submitted to a uniform external magnetic field  $H_0$ . This communication establishes the mechanisms of multi-core MNP capture in microfluidic channels under magnetic and flow fields, and presents a phase diagram in terms of Mason number, dipolar coupling constant, and thickness of the organic coating wrapping the multi-core MNPs: short citrate molecules or PEG chains.[3,4]

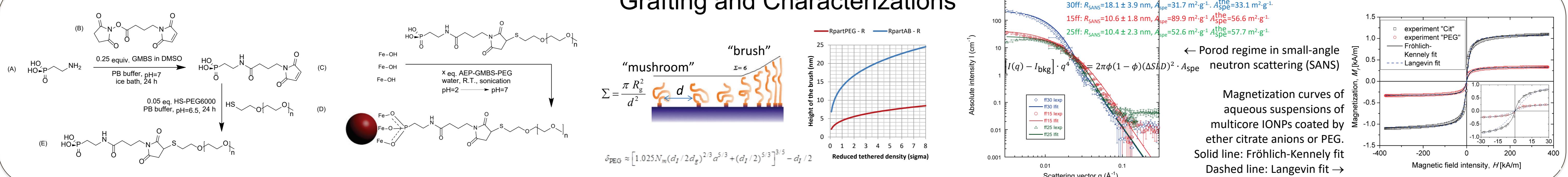
**Keywords:** Multi-core magnetic Nanoparticles, Magnetic attraction, Micropillars, Microfluidics.

### ImmunoMag project (funded by UCA<sup>JEDI</sup> IdEx)



- References
- [1] H. Ezzaier, J. Alves Marins, S. Schaub, B. H. Amara, P. Kuzhir, *J. Mag. Mag. Mat.* 2018, 459, 350
  - [2] G. Hemery, A. Keyes, E. Garaio, I. Rodrigo, J. A. Garcia, F. Plazaola, E. Garanger, O. Sandre, *Inorg. Chem.* 2017, 56, 8232
  - [3] G. Hemery, C. Genevois, F. Couillaud, S. Lacomme, et al. *Mol. Sys. Eng.* 2017, 2, 629-639
  - [4] H. Ezzaier, J. Marins, C. Claudet, G. Hemery, O. Sandre, P. Kuzhir, *Nanomaterials* 2018, 8, 623

### Grafting and Characterizations

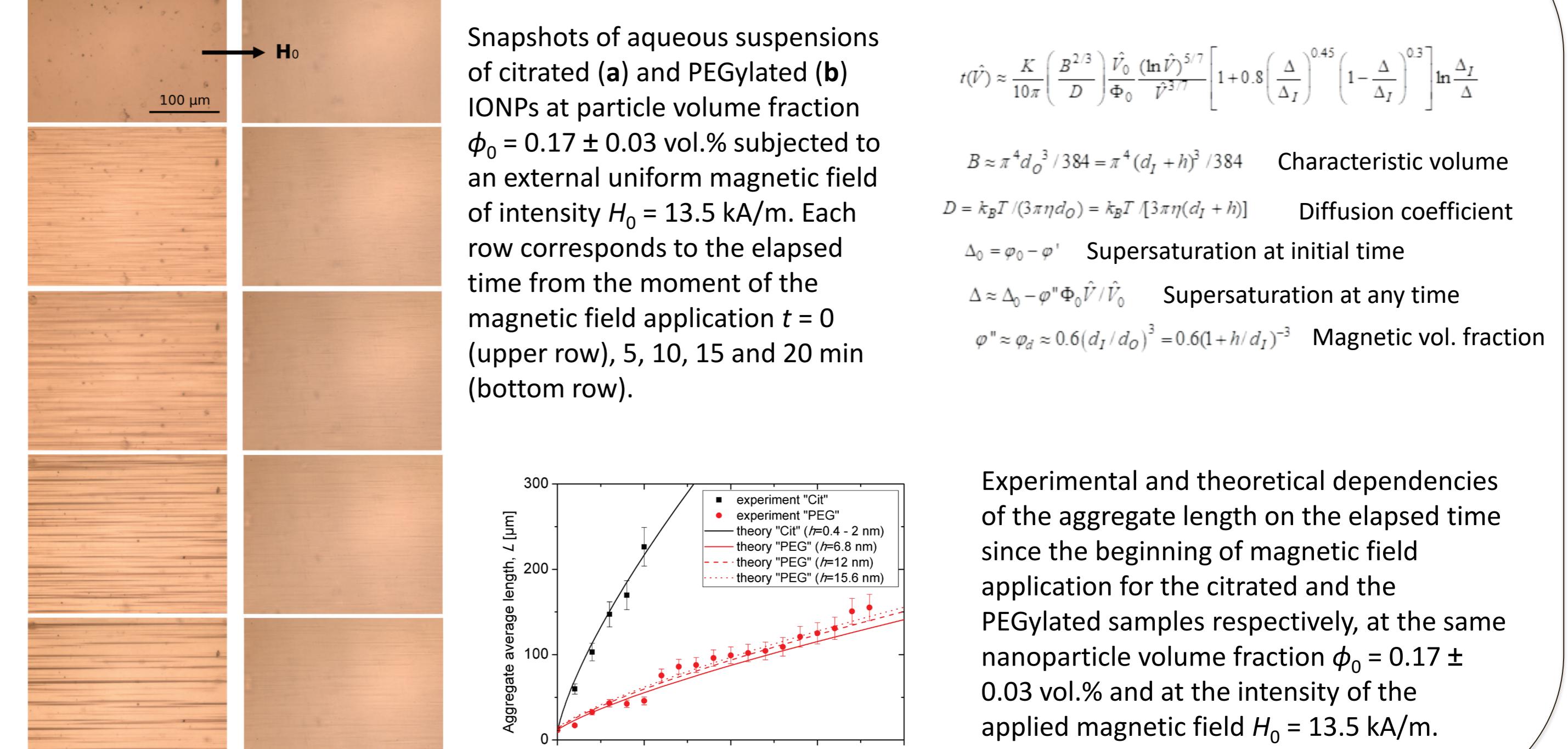


### Parameters of DLVO and magnetic dipolar interactions

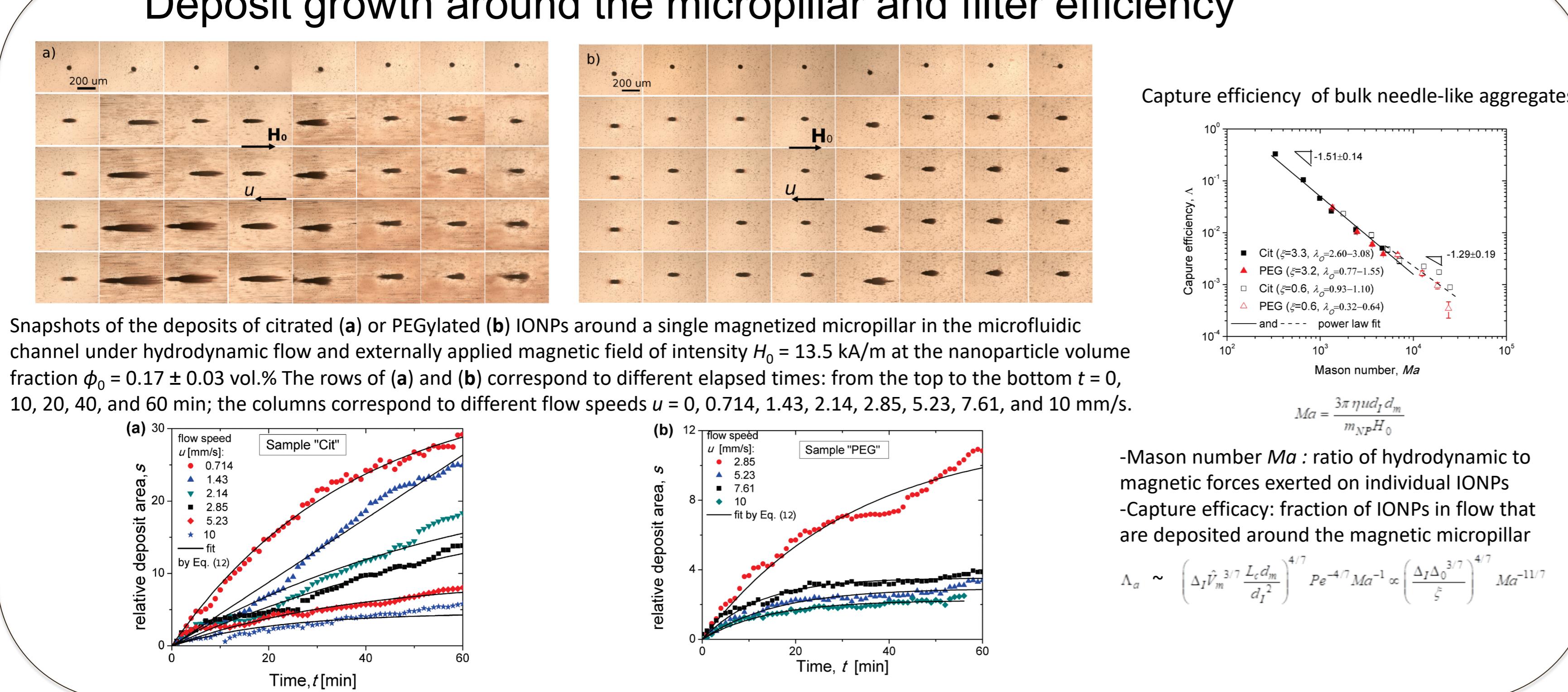
Coating	Separation between IONPs $h = 26$ (nm)	Debye Length $\kappa^{-1}$ (nm)	Charge Density $q$ (mC/m <sup>2</sup> )	Van der Waals Energy $ U_{vdw} /k_B T$		Electrostatic Energy $U_e/k_B T$	
				11.6	25.4	2.3	7.5
Cit	0.4	2.3	9.5	11.6	25.4	2.3	7.5
	2.0			2.3	7.5		
PEG	6.8 (mushroom)	4.0	3.4	0.7	0.6	0.4	0.15
	12.0 (DLS-TEM)			0.4	0.15	0.3	0.06
	15.6 (brush)						

Coating	Separation between IONPs, $h$ [nm]	$H_0 = 4.2$ kA/m			$H_0 = 13.5$ kA/m		
		Moment $m_{NP} X_{10^{24}}$ [T × m <sup>3</sup> ]	Langevin parameter $\xi$	Dipolar parameter $\lambda_i$	Moment $m_{NP} X_{10^{24}}$ [T × m <sup>3</sup> ]	Langevin parameter $\xi$	Dipolar parameter $\lambda_i$
Cit	0.4 (a)	1.22	0.62	1.15	1.10	2.04	3.33
	2.0 (b)			0.93	0.64	3.22	2.60
PEG	6.8 (c)			0.64	1.25	1.98	3.04
	12.0 (d)	1.27	0.64	0.42	1.25	3.23	1.55
	15.6 (e)			0.32			1.01

### Kinetics of Aggregation: Aggregate Size



### Deposit growth around the micropillar and filter efficiency



- Conclusions
- Thinner citrate layer on the IONP surface promotes faster & stronger field-induced aggregation, resulting in longer & thicker needle-like aggregates as compared to those obtained with a thicker PEG layer. This is explained by an increase of the aggregation rate thanks to increased initial supersaturation  $\Delta_0$  of the suspension as the magnetic interaction dipolar coupling parameter  $\lambda_o$  becomes stronger for IONPs covered with a thinner molecular layer.
  - Magnetic separation of MNPs realized in a microfluidic channel equipped with a single magnetizable micropillar. Measurements of the size of the nanoparticle deposits around micropillars allowed determining the capture efficiency  $\Lambda$  and the retention capacity  $\Delta_m$ , both decreasing with increasing Mason number due to stronger hydrodynamic/weaker magnetic forces hindering attraction of IONPs to the micropillar. Both theory and experiments confirm initial hypothesis that capture efficiency is significantly improved if MNPs undergo field-induced aggregation, whose timescale (several minutes) was comparable to travel time through the microfluidic separator.
  - Retention capacity is higher for the IONPs covered by a thinner citrate layer than for IONPs covered by a thicker PEG. This phenomenon is attributed to the fact that at same Mason number, dipolar coupling parameter of the Cit sample is about 2–3 times higher than for the PEG sample ( $\lambda_o = 2.60$ – $3.08$  vs.  $0.77$ – $1.55$ ). Stronger dipolar magnetic interactions between citrated MNPs allow to better resist against rupturing hydrodynamic forces on deposit surface.
  - On the contrary, the capture efficiency appears to be almost the same for thick PEG and thin citrate layers on the IONPs surface over the wide range of Mason numbers studied ( $300 < Ma < 10^4$ ). A small difference between both samples is explained by the fact that only a small portion of MNPs composes aggregates. Theoretical model developed in this work predicts a power-law trend of the Mason number dependency for the capture efficiency with exponent  $11/7 = 1.57$  in agreement with the experimental dependency at  $300 < Ma < 10^4$ .
  - Finally, current work clearly shows that multicore IONPs of ~30 nm size synthesized by the polyol route show good potential for biomedical sensor uses where efficient magnetic separation at low-field is required. One needs to find a compromise between biological functionalities of the adsorbed molecular layer and magnetic separation efficiency.