Aix*Marseille université
Initiative d'excellence

Ecole Doctorale des Sciences Chimiques ED250

Contrats Doctoraux **2020**

Intitulé du Sujet de Thèse : Experimental investigation of flocculation and new material synthesis by suspension freezing

Laboratoire : MADIREL

Equipe : INPACT

Directeur de thèse : Mickaël ANTONI

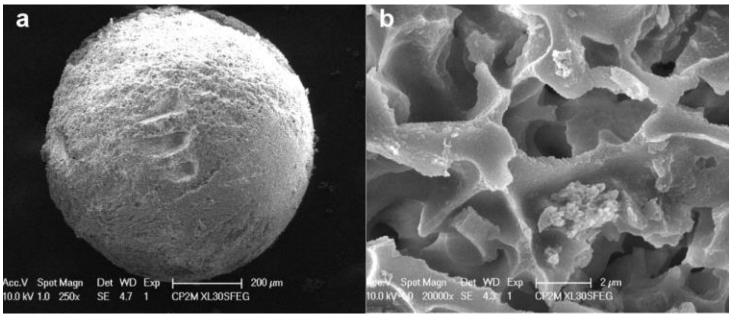
Co-Encadrant : Mathieu NESPOULOUS

email : m.antoni@univ-amu.fr

Frame of the study

The freezing of colloidal suspensions is of fundamental interest in material science, metallurgy, food preservation or in aerosol science. A two-step freezing scenario was recently evidenced in undercooled suspensions: First a fast adiabatic growth of dendrites that turns completed within a few milliseconds. Then a slower process driven by the release of solidification latent heat that sets in for several seconds [1].

Surprisingly, after a thawing back to room temperature, flocculated microstructures show up. The original suspensions are therefore modified from nano-dispersed to micro-dispersed [2]. When a second freeze/thaw cycle is performed, microstructures further flocculate and generate, for sufficiently dense suspensions, porous materials (see figure). This scale change is explained by the interplay of at least four different contributions: The electrostatic interaction between charged nanoparticles and charged ice front [3], DLVO forces that operate between nanoparticles and create an osmotic pressure, the disjoining forces between ice and nanoparticles, and viscous drag forces that hinder the displacement of nanoparticles [4].



(a) Scanning electron microscopy pictures of an aqueous droplet composed by 300 g/L silicon oxide nanoparticles produced after two freeze/thaw cycles. Scale bar is 200 µm. (b) Zoom-in showing the porous structure. Scale bar is 2 µm.

Performing freeze/thaw cycles to flocculate particles in a suspension is a simple methodology that opens interesting perspectives and a broad range of applications. New synthesis routes to incorporate active ingredients in porous structures, not by post modification, but by including them could for example be investigated with emulsified suspensions. The drastic granulometry modifications triggered by freeze/thawing could also help to address fundamental questions in aerosol science. Among them, the properties of atmospheric fine particles when evolving in a saturated moisture environment and in temperature conditions close 0 °C.

Project description

This PhD thesis intends to provide a better understanding into the properties of freezing suspensions. In this frame, the candidate will focus on experimental investigations with the objective to describe the flocculation dynamics of particles in freezing suspensions and to characterize the resulting flocculated materials by optical transmission tomography, scanning electron microscopy, dynamic light scattering, calorimetry, mercury porosimetry, BET surface analysis and impedancemetry. Suspensions will consist in mixtures of water, nanoparticles and surfactants that will be dispersed in either liquid matrices, emulsified suspension systems, or in gas phases to create aerosols.

Emulsified suspensions of silicon oxide nanoparticles have been recently investigated at the MADIREL laboratory for different concentrations [2]. The possibility of new routes for the synthesis of original materials has been validated. The next step, proposed in the frame of this PhD thesis, is to proceed with increasing complexity of the composition of the colloidal suspensions to synthetize materials with targeted properties. Specific nanoparticles (aluminum oxide, titanium oxide...) modified or not by surfactants (CTAB, SDS...) will be investigated. The produced materials will be characterized with the objective to understand the link between their properties and the experimental protocols followed for their synthesis. In this frame, emphasis will also be put on the conditions to create monodisperse populations of spherical flocculated particles such as the one displayed in figure (a).

This thesis work will also focus on the freezing of suspensions in aerosols, i.e. drop populations containing particles in a continuous phase no longer liquid, as in emulsions, but gaseous. The basic assumption is that the phenomena involved in both systems have strong similarities.

The phenomena of freezing in aerosols are a major issue, particularly in the field of cloud microphysics and climatology. An increase in the concentration of atmospheric aerosols indeed modifies the radiative properties of clouds, properties which happen to be the most uncertain component of global radiative forcing since the beginning of the industrial period.

The candidate will work in a research team focusing on chemical properties of dispersed systems (emulsions, porous media, suspensions) and chemical-physics of interfaces. She/He should hence demonstrate knowledge in thermodynamics, physics and chemistry of interfaces. Interest in instrumental developments as well as for optics and data treatment would be strongly appreciated.

References

[1] Nespoulous, M., Denoyel, R., Antoni, M., *Microstructure Formation in Freezing Nanosuspension Droplets*, J. Phys. Chem. letters, **(2018)**, 9(10), 2714-2719

[2] Nespoulous, M., Antoni, M., Chassigneux, C., Denoyel, R., *Porous silica beads produced by nanofluid emulsion freezing*, Microporous and Mesoporous Materials, 305, **(2020)**, 110362, *DOI: 10.1016/j.micromeso.2020.110362*

[3] M. A. Azouni and P. Casses. *Thermophysical properties effects on segregation during solidification*. Adv. Colloid Interface Sci. **(1998)**, 75, 83-106

[4] N. Kallay and D. Cakara. *Reversible charging of the ice–water interface. Measurement of the Surface Potential*. J. Colloid Interface Sci. **(2000)**, 232, 81-85