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Report:
What we understand so far of the solidification of colloidal suspensions is derived primarily from the analogies with dilute alloys systems, or the investigated behaviour of single particles in front of a moving interface and is still a subject of intense work. A more realistic, multi-particles model should account for the particles movement, the various possible interactions between the particles and the multiple interactions between the particles and the solid/liquid cellular interface. Attempts towards modelling the system out of equilibrium with a non-planar interface are extremely complex. Direct experimental observations on which further theoretical analyses could be built and validated are still lacking, preventing further progress in this field.
The motivation for this proposal is therefore to investigate the solidification of colloidal suspensions in situ by X-ray radiography and tomography, with well-known and controlled suspensions, to assess the relationships between the freezing conditions and the final microstructures, and interpret the phenomenon in terms of interactions between the solidification front and the inert ceramic particles, in the case of highly concentrated ceramic suspensions.
During this experiment, we focussed on two aspects of the solidification: the initial transitory regime and the steady state. We have been able to perform systematic investigations of the interface kinetics, crystal growth morphology and particle redistribution behaviour, using a series a optimized colloidal suspensions.

Initial transitory regime The X-rays radiography and tomography observations of the freezing of alumina suspensions with different compositions during initial instants have bring new interesting elements on the transitional zone formation. We showed the composition of suspension influences the freezing temperature. The lower the freezing temperature, the greater the degree of supercooling. To catch up with the equilibrium temperature, found where the supercooling disappears, ice crystals must grow faster. Two ice crystals populations define the transitional zone : lamellar Z-crystal, oriented according to the thermal gradient, and R-crystals, randomly oriented ice crystals. We show that R-crystals correspond to the large dendritic ice crystals growing faster than the freezing front observed on radiography. These ice crystals should correspond to the first nucleus transformed into ice crystals. The position in suspension where they stop corresponds to the end of the transitional zone. By changing the composition of the suspensions and more accurately the counter-ion in our case, we change the microstructure of transitions zone with a dominance of cellular ice-crystals and modify the height of the transition zone. This study brings news elements to control the transitional zone undesirable for applications of porous materials obtained by ice-templating. These results are the object of a paper to be submitted in the coming weeks.

Steady state In steady state, the morphology of the ice crystals and the concentrated particles region is controlled by the ionic strength of the suspension, the presence of a binder, the viscosity and the cooling rate. Suspensions with low ionic strength solidifies with an island-like structure, instead of the usual cellular structure. The increase of ionic strength due to the local concentration of surfactants is destabilizing the particles. This phenomenon leads to the presence of a concentrated particles layer ahead of the ice front and the formation of a depletion zone, ahead of the concentrated particles layer. It is ultimately responsible for the formation of localized and globalized ice lenses, perpendicular to the growth direction. Eventually, the interface is totally destabilized, and the cellular structure turns into the island-like structure. These results highlights the critical importance of controlling the particles interactions and the formulation of the suspension. Surprisingly, the suspensions with the optimal dispersion state turn out to be the least interesting for the process. These results are the object of a paper to be submitted in the coming weeks.