European Research Council

ERC Starting Grant
Research proposal (Part B section 1 (B1))
(to be evaluated in Step 1)

Freezing Colloids

FreeCo

- Dr. Sylvain Deville
- CNRS
- Proposal duration: 60 months

Proposal summary:
The freezing of colloids is an amazingly common phenomenon encountered in many natural and engineering processes such as the freezing of soils, food engineering or cryobiology. It can also be used as a bioinspired, versatile and environmentally-friendly processing route for bioinspired porous materials and composites exhibiting breakthroughs in functional properties. Yet, it is still a puzzling phenomenon with many unexplained features, due to the complexity of the system, the space and time scales at which the process should be investigated and the multidisciplinary approach required to completely apprehend it.
The objective is to progress towards a deep understanding of the freezing of colloids through novel in situ observations approaches and mathematical modelling, to exert a better control on the processing route and achieve the full potential of this novel class of bioinspired materials. Hierarchical porous composites materials will be processed and their structure/properties relationships investigated and optimized.
This project, at the borderline of materials science, offers a unique integration of approaches, competences and resources in materials science, chemistry, physics, mathematics and technological developments of observation techniques. For materials science only, the versatility of the process and its control could yield potential breakthroughs in numerous key applications of tremendous human, technological, environmental and economical importance such as catalysis, biomaterials or energy production, and open a whole new field of research. Far-reaching implications beyond materials science are expected, both from the developments in mathematics and physics, and from the implications of colloids freezing in many situations and fields of research.

Section 1: *The Principal Investigator*
1(a) Scientific Leadership Potential

i. Early scientific contributions to the research field

My early work (PhD) was focused on the investigation of the reinforcement of the mechanical properties and degradation mechanisms (ageing) in ceramics for biomedical applications. A particular achievement of this work was the identification of ageing mechanisms in ceramic composites, which are now increasingly considered as the new gold standard in orthopaedics and are undergoing considerable developments, both in orthopaedics and dental applications. Following my interest in biomaterials, I joined the group of Dr. A. P. Tomsia in the Materials Science Division of the Lawrence Berkeley National Laboratory. I demonstrated how the solidification of colloidal ceramic suspensions could be mastered to elaborate porous bioinspired ceramic architectures, exhibiting a 400% increase in compressive strength, in comparison to state of the art materials. Complex composites could be derived, with structure and properties strongly reminding those of natural ones such as the nacre of seashells. This was not only a radically new approach for materials processing, but we could benefit from the knowledge accumulated in revolving fields such as cryobiology, geophysics or food engineering. Back to France, I focussed on understanding the freezing of colloids, and in particular introduced a novel experimental approach to investigate the process, using X-rays imaging, which provides real time in situ observations. The most important results was the discovery of metastable and unstable states of cellular solidification in such systems, which have important implications for anyone involved in the solidification of colloidal suspensions, and are especially important when processing porous materials. These observations should lay down solid foundations for further theoretical elaboration.

ii. Recognition and diffusion

Publications and citations – I have been able to publish my work in multidisciplinary peer-reviewed journals with the highest impact such as *Science*, or in leading journals in materials science such as *Nature Materials* (IF 29,5), *Nanoletters* (IF 10,3), *Advanced Materials* (IF 8,4), *Annual Review of Materials Research* (IF 7,9) or *Biomaterials* (IF 7,4). These 30 papers resulted in over +580 citations to date, including +320 citations regarding the postdoctoral work (Scopus data, self-citations of all authors removed).

Results dissemination to the public – The early work on colloids freezing attracted a lot of attention from the scientific community and the public, through papers in the press, such as the New York Times, Times, Business Week, or even the Financial Times. The paper was accompanied by a perspective paper in *Science* and mentioned in other scientific journals such as *Nature Materials*. The PI of my group at the Lawrence Berkeley National Laboratory was cited as one of the *top 50 technology leaders* of the year by the journal *Scientific American* for my results on freezing and the perspectives they opened.

Funding agencies and opportunities– The research path opened by my results lead to a second paper in *Science* in 2008 ("Tough, bioinspired hybrid materials") by my former LBNL colleagues after my return to France. These results and papers resulted in a new substantial grant by the NIH (8M$ for a 5 years project) for my former PI. Back to France, I obtained a 3 years grant (350k€) by the French National Research Agency to proceed with this work, providing me with an opportunity to launch this field of research in Europe and obtain proof of principles results on many approaches on which the current project is based.

Conferences –I was invited to deliver several invited talks in major international conferences in my field. In addition, I have been solicited to contribute to conferences organisation or to be part of the advisory board.

Multidisciplinary nature and impact of the research activities – I have always been a fervent partisan of the multidisciplinary approach in scientific investigations, and my current research interests are strongly driven by this motivation. This has been recognised at multiple levels, from the wide variety of nature of the journals I published in to the variety of journals soliciting me for reviewing papers. To promote more actively this approach in the case of the investigations of colloids freezing, I organized in 2010 the first international and multidisciplinary workshop on the solidification of colloidal suspensions with a colleague of the Mathematical Institute at the University of Oxford, UK, an event that gathered around 60 researchers from a wide variety of backgrounds. The feedback was so good that another one will be organized in 2 years.

iii. Assessment of the specific stage of my career

I consider myself as a **starter**, according to the ERC criteria. After having successfully launched a new field of research in the US, which I subsequently brought back to Europe, I am now one of the world leaders of these investigations in materials science, with plenty of ideas and approaches to implement and yet little means to do so. I am currently holding a tenure position at CNRS, with currently two PhD students to support this activity. Setting up a team with a critical mass and multiple competencies in the domains involved here –materials science, mathematics, physics, cryoengineering, chemistry– is the next logical step to make substantial progress, and anchor this field of research as a standalone activity in Europe. The ERC Starting grant would therefore be the optimal solution for such evolution.

1(b) Curriculum Vitae

Background

32 year old (born in 1978) Engineer and master's degree in Materials Science and Engineering from the National Institute of Applied Science (INSA) in 2001.

Professional Academic Experience

–	Researcher (tenure)	CNRS, Cavaillon, France	**2006-today**
–	Postdoc	Materials Science Division, Lawrence Berkeley National Lab., USA	**2004-2006**
–	PhD	INSA Lyon, France	**2001-2004**

Research interest and activities (past and present)

- Bioinspired composites and nature-inspired approaches for materials processing
- Solidification of colloidal suspensions
- X-rays imaging techniques
- Atomic force microscopy of phase transformation in ceramics
- Mechanical properties and reinforcement mechanisms of porous and dense ceramics
- Degradation mechanisms in zirconia-based ceramics for biomedical applications: multiscale approaches

Scientific production

- 30 peer-reviewed papers, in *Science, Nature Materials, Nanoletters, Advanced Materials, Annual Review of Materials Research, Biomaterials*, etc…
- 11 talks and 5 invited talks in international conferences
- 6 peer-reviewed proceeding of international conferences
- 1 invited chapter in Handbook of Biomineralization (Wiley-CH)

Students and PhD supervision

- supervising two PhD students (begun in 2008 and 2011)
- supervising two technicians and an engineer in the lab
- undergraduate students: 2 to 3 per year since PhD, for short term projects (3 to 6 months)

Scientific community activity

- **Referee** for peer-reviewed journal: Physical Review Letters, Angewandte Chem., Advanced Materials, Advanced Functional Materials, Biomaterials, Journal of Materials Research, Materials Research Bulletin, Surface and Coatings Technology, Composites Part A, Crystal Growth and Design, Journal of the American Ceramic Society, Chemical Engineering Journal, International Journal of Applied Ceramic Technology, Biomedical Materials, International Journal of Materials Research, Polymer, Ceramics International, Biomacromolecules, Journal of the Royal Society Interface, Journal of Microscopy, Journal of Chemical Technology & Biotechnology, Acta Materiala, Journal of the European Ceramic Society
- **Contributing editor** for the Journal of the American Ceramic Society
- **Referee** for the French National Research Agency (ANR, 2008 and 2009), NSF career program (2010)
- **Advisory board** for ECERS 2009 and CIMTEC 2011
- **Initiator and co-organizer** of the 1st International and Multidisciplinary Workshop on the Solidification of Colloidal Suspensions (2010, Avignon, France). Co-organized by the CNRS, Saint-Gobain and the University of Oxford

International Collaboration

- Lawrence Berkeley National Laboratory, USA
- Mathematics Institute, Univ. of Oxford, UK

Funding ID (note: no ongoing application)

- **French National Research Agency**: 350 k€ for 3 years (ending May. 2011). Initiator and coordinator of the project. Assessment of techniques to investigate the freezing of colloids and investigations of the importance of colloidal suspension stabilization.
- **CIFRE fellowship**, for the PhD of Florian BOUVILLE (Oct. 2010-2014), 300 k€ for 3 years.

Investigation of the behaviour of anisotropic colloidal particles during the freezing of colloids.

- **JECS Trust fund**, 10k€, to support participation of students to the 1st International and Multidisciplinary Workshop on the Solidification of Colloidal Suspensions (2010, Avignon, France).
- **European Synchrotron Radiation Facility**, 3 and 5 days beamtime access (2008 and 2010), equiv. 30k€ and 50k€.
- Participation to **6thFP** (**project Bioker**: "Extending the life span of orthopaedic implants: development of ceramic hip and knee prostheses with improved zirconia toughened alumina nanocomposites", Project n° GRD1-2000-25039). PhD results contributed to launch a new large scale project (**Nanoker**: "Structural Ceramic Composites for Top-End Functional Applications") in **7th FP**.

1(c) Early Achievement-Track-Record

i. Selection of publications (main author) in peer-reviewed journals (20 out of 30)
The publications marked with an asterisk (*) were not co-authored by my PhD supervisor. Citations data from Scopus (self-citations of all authors removed).

	Citations
1. **S. Deville**, J. Chevalier, G. Fantozzi, J. F. Bartolomé, J. Requena, J. S. Moya, R. Torrecillas, L. A. Díaz, Low-temperature ageing of zirconia-toughened alumina ceramics and its implication in biomedical implants, *J. Eur. Ceram. Soc.*, 23 2975-2982 (2003)	19
2. **S. Deville**, J. Chevalier, Martensitic relief observation by atomic force microscopy in yttria stabilized zirconia, *J. Am. Ceram. Soc.*, 86 [12] 2225-2227 (2003). (front cover)	5
3. **S. Deville**, G. Guénin, J. Chevalier, Martensitic transformation in zirconia. Part I: Nanometer scale prediction and measurement of transformation induced relief, *Acta Mater*, 52 5697–5707 (2004)	8
4. **S. Deville**, G. Guénin, J. Chevalier, Martensitic transformation in zirconia. Part II : Martensite growth, *Acta Mater.*, 52 5709–5721 (2004)	6
5. **S. Deville**, J. Chevalier, H. El Attaoui, Atomic force microscopy study and qualitative analysis of martensite relief in zirconia, *J. Am. Ceram. Soc.* 88(5) 1261-1267 (2005)	9
6. **S. Deville**, H. El Attaoui, J. Chevalier, Atomic force microscopy of transformation toughening in ceria-stabilized zirconia, *J. Eur. Ceram. Soc.* 25(13) 3089-3096 (2005)	10
7. **S. Deville**, J. Chevalier, C. Dauvergne, G. Fantozzi, J. F. Bartolomé, J. S. Moya, R. Torrecillas, Microstructural investigation of the aging behavior of (3Y-TZP)-Al_2O_3 composites *J. Am. Ceram. Soc.* 88(5) 1273-1280 (2005)	9
8. **S. Deville**, L. Gremillard, J. Chevalier, G. Fantozzi, A critical comparison of methods for the determination of the ageing sensitivity in biomedical grade yttria stabilized zirconia, *J. Biomed. Mater. Res.* , 72B(2) 239-245 (2005)	21
9. **S. Deville**, J. Chevalier, L. Gremillard, Influence of residual stresses and surface finish on the ageing sensitivity of biomedical grade 3Y-TZP, *Biomaterials*, 27(10) 2186-2192 (2006)	26
10. ***S. Deville**, E. Saiz, R. K. Nalla, A. P. Tomsia, Freezing as a path to build complex composites, *Science*, 311 515-518 (2006)	179
11. ***S. Deville**, E. Saiz, A. P. Tomsia, Freeze-casting of hydroxyapatite scaffolds for bone tissue engineering, *Biomaterials* 27 5480–5489 (2006)	95
12. ***S. Deville**, E. Saiz, A. P. Tomsia, Ice-templated porous alumina structures, *Acta Mater* 55(6) 1965-1974 (2007)	40
13. J. Chevalier, L. Gremillard, **S. Deville**, Low temperature degradation of zirconia and its implication on biomedical implants, *Ann Rev of Mater Res*, 37 1-32 (2007)	26
14. ***S. Deville**, Freeze-casting of porous ceramics: a review of current achievements and issues, *Adv Eng Mater,* 10(3) 155-169 (2008)	29
15. *E. Munch, E. Saiz, A. P. Tomsia, **S. Deville**, Architectural control of freeze-casted ceramics through additives and templating, *J. Am. Ceram. Soc.* 92 [7] 1534–1539 (2009)	4
16. ***S. Deville**, E. Maire, A. Lasalle, A. Bogner, C. Gauthier, J. Leloup, C. Guizard, In situ X-ray radiography and tomography observations of the solidification of aqueous alumina particles suspensions, Part I: initial instants, *J. Am. Ceram. Soc.* 92(11) 2489-2496 (2009)	

17. ***S. Deville**, E. Maire, A. Lasalle, A. Bogner, C. Gauthier, J. Leloup, C. Guizard, In situ X-ray radiography and tomography observations of the solidification of aqueous alumina particles suspensions, part II: steady state, *J. Am. Ceram. Soc.* 92(11) 2497-2503 (2009)
18. ***S. Deville**, E. Maire, G. Bernard-Granger, A. Lasalle, A. Bogner, C. Gauthier, J. Leloup, C. Guizard, Metastable and unstable cellular solidification of colloidal suspensions, *Nature Materials* 8(12) 966-972 (2009) 1
19. ***S. Deville**, E. Maire, A. Lasalle, A. Bogner, C. Gauthier, J. Leloup, C. Guizard , Influence of particle size on ice nucleation and growth during the ice-templating process, *J. Am. Ceram. Soc.* 93(9) 2507-2510 (2010)
20. ***S. Deville**, Freeze-casting of porous biomaterials: structure, properties and opportunities, *Materials*, 3 1913-1927 (2010)

ii. Patents

- "Fabrication of Three-Dimensional Organic/Inorganic Scaffolds by Robocasting" (US Patent 60/984,299)
- "Tubular porous materials" (French patent application n°10/52485)
- "Microreactors" (French patent application n°10/52486)

iii. Invited conferences and presentations

- Invited seminary at *Ecole Polytechnique Fédérale de Lausanne* (EPFL), "Atomic force microscopy study of the tetragonal to monoclinic phase martensitic transformation of zirconia" (2004)
- 107th Annual Meeting of the American Ceramic Society, "New Information's on the Surface Tetragonal to Monoclinic Transformation in Zirconia" (2005)
- 2nd Annual Orthopaedic Manufacturing & Technology Exposition and Conference, Rosemont, Illinois (USA), "Biomimetics as Inspirational tools for Tissue Engineering" (2006)
- Xth European Ceramic Society Meeting, Berlin, "The materials that came in from the cold: nacre-like bioceramics through freezing" (2007)
- Seminars on Theoretical Geophysics, *University of Cambridge*, "Porous ceramics by controlled solidification of colloidal suspensions" (2008)
- XIth European Ceramic Society Meeting, Cracovie, Poland, "Understanding and controlling freeze-casting of porous ceramics" (2009)
- Industrial and Interdisciplinary Workshops, *University of Oxford*, Mathematical Institute, "Investigating the freezing of colloids by X-rays radiography and tomography: recent results, limitations and potential for further progress" (2009)
- Mathematical Geoscience Seminars, *University of Oxford*, Mathematical Institute, Oxford Centre for Industrial and Applied Mathematics, "The freezing of colloids: the implications and applications in materials science and geophysics" (2009)
- 8th International Workshop on Interfaces, Santiago de Compostela (Spain), title t.b.a. (2011)

iv. Awards and prizes

- Winner of the poster contest, 8th Conference of the European Ceramic Society (2003)
- Award for the best PhD of the year, French Ceramic Society (2005)
- Winner of the student speech contest, 9th Conference of the European Ceramic Society (2005)
- Young Researcher Award, City of Lyon, France (2006)

v. Articles referencing the work in scientific journals

Science, "Materials science: making better ceramic composites with ice" (2006), Nature Materials, "Material witness: cold comfort" (2006), Journal of the American Dental Association, "New strategy found for creating artificial bone" (2006), American Ceramic Society Bulletin, "Secrets of the sea yield stronger artificial bone" (2006), Materials Today, "Seashell provides blueprint for composites" (2006), Materials Today, "Ice template defines porous ceramics" (2007)

vi. Articles referencing the work in generic press in 2006, following the Science paper

New York Times, Business Week, Times, Financial Times, Sueddeutsche Zeitung, Frankfurter Allgemeine Zeitung, Die Zeit, Daily Telegraph, Chemistry and Industry Magazine, American Scientist, L'Usine Nouvelle, etc…

Section 1d: *Extended Synopsis of the project proposal* (max 5 pages)

Colloids everywhere

Colloids are often seen as big atoms that can be directly observed in real space. They are therefore playing an increasingly important role as model systems to study processes of interest in condensed matter physics such as melting, freezing and glass transitions. The presence of and the interest for colloids is not restricted to physics and materials science, and **colloids are present in many natural or engineering process or substances**, in domains as diverse as biology (blood, enzymes, fumic and humic substances), environment (fog, mist, cloud), geophysics (clay particles, silicates), filtration (pollutants), food (milk, mayonnaise, whipped cream, gelatin) or engineering (styrofoam, aerogel) to name a few. A colloidal dispersion is a system in which particles of colloidal size (1nm-1μm) of any nature (solid, liquid or gas) are dispersed in a continuous phase of a different composition or state. More specifically, **this project is focussing on hydrocolloids**: colloidal system wherein the solid colloidal particles or objects are dispersed in water.

Freezing colloids, a common phenomenon

The solidification or freezing of colloidal suspension or colloids is commonly encountered in a variety of natural processes such as the **freezing of soils** in northern regions and the **growth of sea ice**, or everyday life and engineering situations such as **food engineering** (fabrication of ice cream)**, materials science, cryobiology, filtration** or **water** purification and the **removal of pollutants** from waste (fig. 1). It is therefore an amazingly common phenomenon, of stupendous impact in natural, physical, social and technological environments. The associated costs (degradation of roads) or benefits (climate control, cryopreservation protocols and tissue engineering scaffolds) are of tremendous importance.

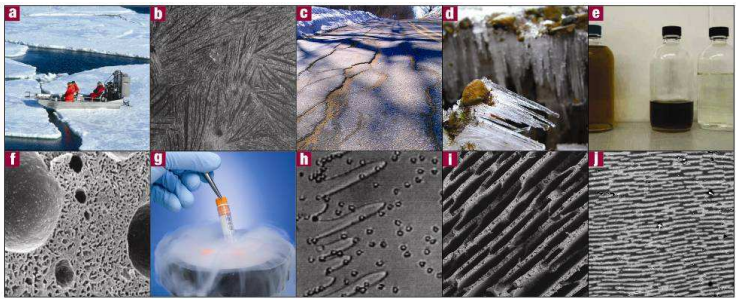

Fig. 1: Colloids freezing situations: (a-b) sea ice and brine channels formation, (c-d) soils freezing and frost heave, (e) removal of pollutants by freezing, (f) ice cream manufacturing, (g) cryopreservation of reproductive cells (h) and red blood cells, (i) porous ceramics and (j) composites obtained through colloids freezing.

Freezing colloids: an innovating bioinspired processing route... for biomimetic materials

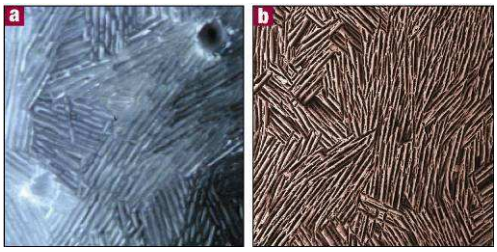

Fig. 2: Brine channels in sea ice and porous ceramics through colloids freezing

Among the many applications of colloids freezing, its potential use as a processing route for biomimetic porous materials is particularly innovating and exciting. For some years now, the design of biomimetic materials and systems has been the focus of increased attention. The properties, functions and structures encountered in nature are increasingly appealing for non-biological applications, and often arising from complex structures defined at several length scales. **Applying nature's blueprints to advanced materials could yield a brand new range of materials with properties orders of magnitude above the currently available solutions**. Tangible applications of biomimetics are nevertheless and surprisingly still very scarce. The underlying reason for this lies in the **lack of processing routes to implement the bio-inspired designs** into materials and systems and yet, the message from biology here is clear – there is a need in the design of new materials to develop mechanisms at multiple length scales in order to create new hybrid materials with unique functional properties.

The freezing of colloids can be used as a self-assembly process inspired by a natural occurrence of colloids freezing, the freezing of sea ice. Pure hexagonal ice platelets are formed, and the various impurities originally present in seawater (salt, biological organisms) are expelled from the forming ice and entrapped within the brine channels between the ice crystals (fig. 2). **Using ceramic colloidal particles instead of biological impurities, we take advantage of this natural segregation principle, while using ice as a natural and environmentally-friendly templating agent** (fig 3)**.** The ice is then removed by sublimation. The final result is a scaffold with a complex and usually anisotropic porous microstructure generated during freezing, this structure being a replica of the ice structure before drying. This ceramic scaffold can then be used as a basis for porous or dense composite, if infiltrated with a suitable second phase. Using composites is

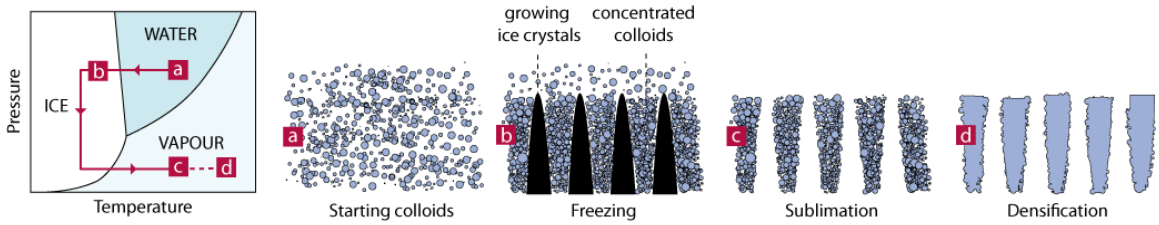

Fig. 3: Freezing colloids, a bioinspired materials processing route.

a method to take advantage of both polymer and ceramics qualities, ideally to achieve materials with high stiffness and high toughness. The porous scaffolds and dense composites obtained by this process exhibit striking similarities to the macro- and micro-structure of the inorganic component of nacre (fig 4), including a **complex and highly hierarchic structure defined at several length scales**.

The preliminary results we published in *Science*[1] have raised considerable attention on the freezing process, both from academic and industrial partners such as BMW, PPG or Saint-Gobain. The freezing route is indeed an appealing process due to its simplicity, with no equivalent at the moment, both in terms of process –environmentally-friendly, with no solvent but water– and structures obtained –highly directional. Structuring bulk materials at submicronic scales usually yields unrealistic processing time, hindering further realistic development. Samples a few centimetres thick can be processed within a few minutes with the freezing approach. Besides, the equipment required is readily available and has been developed, tested and used for years in various fields including cryopreservation, food or materials engineering. Finally, and of uttermost importance, **the freezing process is extremely versatile**, unlike the vast majority of the biomimetic routes developed so far which often rely on highly specific interfacial compatibilities. The structural formation mechanisms involved here are based mostly on physical interactions; **any type of ceramic, metallic of even polymer particles can be used. The range of potential applications derived from this approach is therefore extremely wide**: filtration, catalysis, gas pump (oxygen, hydrogen), scaffolds for biomaterials, high temperature superconducting ceramics (resistive superconducting fault-current limiters), impact resistant materials for armour applications, heat exchangers (microelectronics), heat guides, wear resistant materials for cutting tools, and so forth.

Promising properties, potential breakthroughs

As expected from the unique structure, unprecedented properties are exhibited by such materials. We demonstrated for example a 400% increase in compressive strength of hydroxyapatite scaffolds for bone substitutes compared to materials obtained through state of the art techniques. **The structural anisotropy can also be highly beneficial for a wide range of other applications involved with mass, gas or species transport.** The process is nevertheless not limited to porous materials, and the preliminary results of the mechanical response of derived composites[2] are also unprecedented. It is nevertheless clear that we only scratched the surface of the potentialities offered by the freezing process. Much ground is yet to be covered before the full potential of this approach can be clearly assessed, and in particular an extensive work is still needed to assess the structure/properties relationships in this unique class of hierarchical materials.

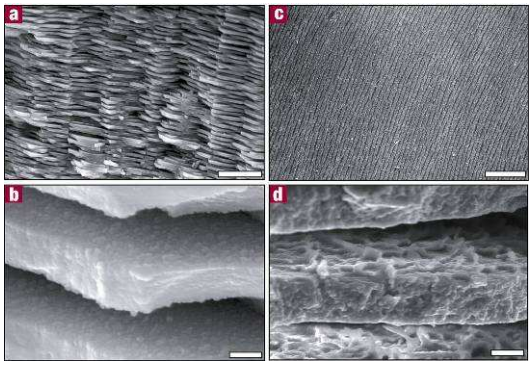

Fig. 4: (a-b) Nacre of the abalone shell and (c-d) nacre-like structures obtained through colloids freezing. Scale bars a: 10 µm, b: 0.3 µm, c: 300 µm, d: 10 µm

Freezing colloids: what we do not (and would like to) know

The phenomenon by itself is disappointingly simple to describe: the water/ice interface is propagating through a colloidal suspension of particles, cells or micro-organisms. **This simplicity is nevertheless only apparent** and the freezing of colloids is still a puzzling phenomenon, with many unexplained features. **A very large number of disparate parameters should be accounted for when trying to understand and model the freezing of colloids** (fig 5). The unknown of the phenomenon can be gathered in three categories: parameters related to the **colloids** (content, diffusivity, interactions, physical properties of the colloids, etc..), parameters related to the **crystal growth** (dynamics of crystal formation and growth morphology in presence of colloids, relative importance of latent heat, anisotropy of crystal growth, role of impurities on the growth

[1] S. Deville et al., Freezing as a path to build complex composites, *Science*, 311 515-518 (2006).
[2] S. Deville (2006), Ibid.; E. Munch et al., Tough, bio-inspired hybrid materials, *Science*, 322[5907] 1516-1520 (2008).

of crystals) and parameters related to the **system as a whole** (the interactions between the colloids and the propagating interface, and the behaviour of the system out of equilibrium).

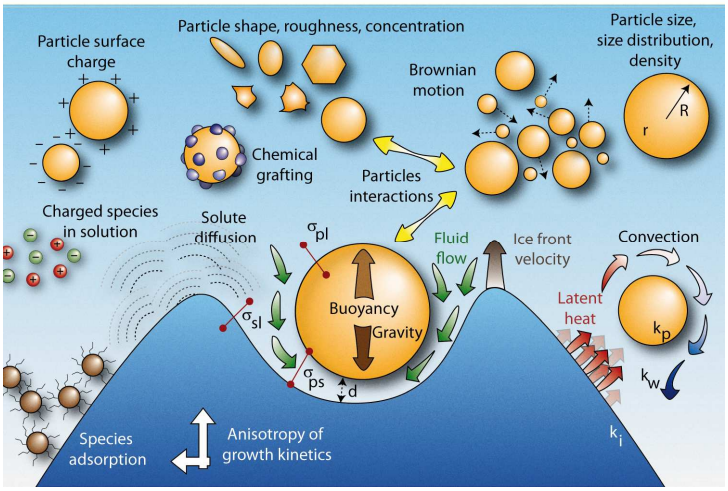

Fig. 5: Freezing colloids, schematic representation of the main parameters to take into account.

Challenges ahead

The underlying reasons for such lack of knowledge are the previously mentioned complexity of the system, and the challenges in observing, modelling and controlling the phenomenon. Several sets of scientific and technical challenges can be identified:

1- Multi-disciplinary approach required – Understanding the core of the process required cross-disciplinary approaches, using knowledge from ice physics, mathematics, engineering, materials science, geophysics and cryobiology, making the problem a truly exciting multi-disciplinary challenge.

2- Experimental and modelling challenges – A strong experimental foundation on which further theoretical developments can be built and validated is of course a preliminary and strong requirement. Ideally, we would need in situ real time three-dimensional observations of both the crystal growth and colloids movement in the suspensions, with individual colloidal particle tracking to investigate their redistribution during freezing. The corresponding space (submicronic) and velocity (tens to hundreds of microns/s) scales severely restrict the choice of experimental techniques. The nature of the colloid-interface interaction should be assessed and taken into account, with a possible local thermodynamic equilibrium at the interface.

3- Complexity and specificities of the system – The number of parameters that should be accounted for is staggering, as described previously. In addition, colloids exhibit various non-linear physical properties dependence with the concentration of colloids, making the underlying physics even more complex. The effects of colloids on the dynamics of the system are still largely unclear (possible asymptotic regime of the interface, morphological instabilities specific and/or similar to that of alloys). The parameters triggering the instabilities must possibly be assessed at several length scales, from the colloid to the dendrites, and colloids agglomerates.

4- From the lab to the real world: boundary conditions and space and time scales – The experimental results have to be compared with the natural and technological occurrences of colloids freezing. The boundary conditions in these systems can be tremendously different, implying strong variations in both space and time scales, from large scale (soils, ocean) to intermediate scale (materials science, cryobiology, food engineering) and confined scale (microfluidics, biology).

In summary, this is an excellent and exciting scientific problem!

Methodology

The core objective of the project is the progress towards a deeper understanding of the freezing of colloids and in particular here of hydrosols –solid colloidal particles in suspension in water– **as it is clearly a necessary step towards a better control of the derived materials processing route associated to colloids freezing**. This project integrates **materials science, chemistry, physics, mathematics** and **technological developments of observation techniques.** To guarantee the success of the project, the research plan has been designed with a highly iterative approach, the basic lessons learned after each iteration will be applied in the design and control of the process of the next cycle. To overcome the complexity of the modelling of the process, progress towards further understanding will be accompanied by in situ experimental observations of the freezing of colloids, using several different and complementary techniques. Progresses will thus be accomplished through iterative cycles of four subprojects, namely **observing, modelling**, **controlling** and **using** the freezing of colloids. Lessons learned from this cycle will be applied to materials science to characterize and optimize the porous structure and their functional properties (fig 6). **This project has been designed to incorporate a gradient of risk at several levels**, by combining conventional and novel approaches in observation techniques, modelling, materials processing and characterization strategies.

A - Observing the freezing of colloids

A thorough experimental observation approach will be followed, using model colloids. A variety of in situ observations techniques will be used to follow the crystal nucleation and growth and corresponding particle redistribution (fig 7). **Each of these techniques has its own advantages, drawbacks and limitations, and will provide a picture of the system at different length and time scales**:

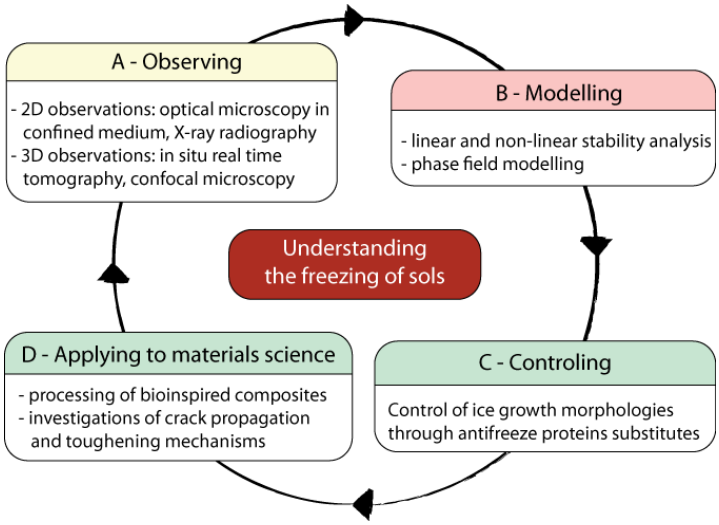

Fig. 6: Project workflow

(a) Optical observations in confined space in a 20 μm layer, using a dedicated solidification stage, to specifically test the predictions of the mathematical models resulting from the modelling of colloids freezing. In situ non-intrusive observation of the freezing process can be achieved by observing the solidification interface at various magnifications ranging from the micrometric scale of dendrite tips to the millimetre scale of a whole dendritic pattern. Real-time observation of the coupled dynamics between the solidification interface and the colloid particles can be achieved in regimes going from the slow planar interface to the rapid well-developed dendrites.

(b) Confocal microscopy provides a way to overcome many of the problems in conventional microscopy caused by multiple scattering of objects which are out of focus, and prevents imaging deep within a sample. In addition, it might provide a complementary alternative to X-rays imaging, where the effects of interaction between the very energetic beam and colloids are largely unknown, and the current spatial resolution does not allow individual particle imaging. **Confocal microscopy** with a cold stage, using model colloids marked in fluorescence, will provide **in situ particle tracking possibilities and real particles packing determination**.

(c) X-rays radiography and tomography, which provides quantitative kinetic and structural observations. Our recent previous results, including a paper in *Nature Materials*, raised a strong interest for this technique, which is now ready to be used in a more systematic approach to investigate the relative importance of several of the parameters mentioned previously. Our objective in the present project is to use imaging techniques able to give a **5 Hz temporal resolution** in tomography, to observe for the first time the **evolution of the morphology of the freezing front in 3D**, and possibly quantify the local particle concentration and redistribution.

These experiments, if successful, will provide us a 3D vision of the evolution of crystal growth morphology during the solidification, which can be **compared with the output of the phase field model**, developed in the other part of the project. We should also get a 3D representation of the colloid concentration profile, which again can be **compared with the output of the modelling**.

All these experimental observations will be compared and linked when possible to that obtained in natural situations, such as the growth of sea ice or the freezing of soils, to get the most complete picture of the phenomenon to date. The risk is relatively limited since many preliminary results we obtained on these techniques are really encouraging and promising.

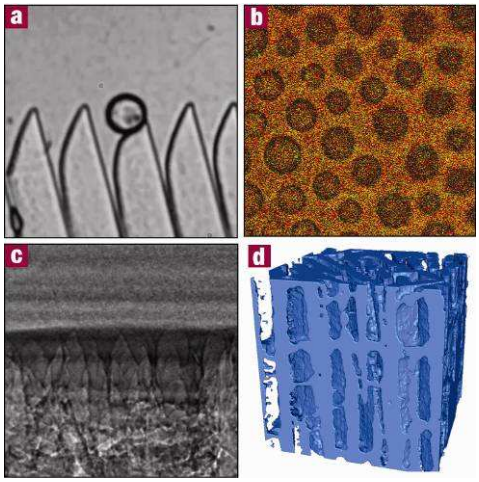

Fig. 7: Observing the freezing of colloids. Experimental techniques considered in this project includes optical microscopy in confined space (a), confocal microscopy (b), X-ray radiography (c) and X-ray tomography (d).

B - Modelling the freezing of colloids: a necessary challenge

Theoretical approaches to modelling freezing colloids have focused so far on the interaction of an isolated particle with an advancing ice front. Many geological, biological and industrial systems involve concentrated particle systems. Owing to their neglect of particle-particle interactions, **isolated particle models are not able to quantify the critical dependence of the final ice crystal morphologies on initial colloid concentration** – a crucially important operating parameter for industrial applications. A new mathematical framework has been developed that accounts quantitatively for such interactions. The approach treats a

colloidal suspension as a non-ideal two-component "alloy" in which the solute particles are vastly larger than the solvent, and exploits the physical basis for the dynamics and thermodynamics of pre-melting between the particles and the frozen solvent. A distinct advantage of this approach is that it enables mathematical techniques developed for studying pattern formation in far-from-equilibrium systems to be applied (with proper modifications) to freezing colloids. In this project **we will apply two such techniques, stability analysis** and **phase field models**, to quantify solidification structures observed in experiments on freezing colloids undertaken concurrently. The new models will lead to more general morphology diagrams capable of predicting additional transitions including the pushing/trapping boundary in concentrated systems. **Phase field modelling** can yield exceptional insight into microscale pattern formation, and giving good quantitative agreement with experiment. No phase field model has yet been developed for colloidal systems, despite wide-ranging potential benefits. It is the goal of this work to **develop the first thermodynamically rigorous phase field model of a freezing colloid**. We are confident the new model is feasible, owing to our successful derivation of equations describing the morphological instability of an ice-colloid interface at low velocity.

C - Controlling colloids freezing: effect of antifreeze proteins substitutes

Whether for its potential use or to control its detrimental consequences, the freezing of colloids will greatly benefit from a better control, which can be exerted through a variety of techniques. The objective here is to gain a **more specific and predictable control of the porous morphologies through a specific control of the ice crystal growth morphologies**. Antifreeze proteins, naturally present in living species such as fishes, insects and plants, act through several mechanism to inhibit ice nucleation and/or severely control ice growth, through a specific adsorption on particular crystalline planes of the ice crystals (fig 8). Little is understood about the effect of such substances in concentrated colloids, and we propose here to focus on **the effect of antifreeze proteins substitutes on the growth of ice in concentrated colloids and to assess their potential for controlling the porous morphologies** of ice-templated materials, using the direct observations methods of ice growth in colloids developed in the other part of the project.

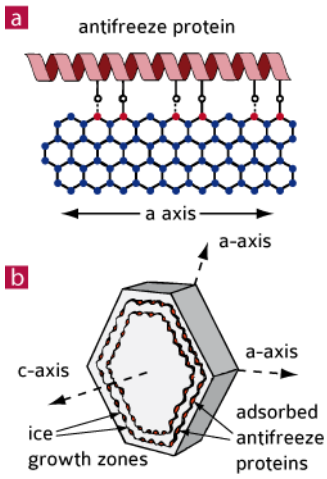

Fig 8: (a) Adsorption of antifreeze protein at the surface of ice. (b) Illustration of how antifreeze proteins inhibit ice crystal growth according to the adsorption-inhibition theory.

D - Applying colloids freezing to materials science

Materials obtained through the freezing of colloids may present unique and outstanding mechanical properties. Apart from the preliminary results we published previously, little is known about the properties of such materials and their structure/properties relationships. We aim to progress here by combining two approaches: **processing porous ceramic materials, and subsequently infiltrating them with an organic phase** to obtain bioinspired porous composites, and **characterizing the structure and properties of such materials to assess their structure/properties relationships.** This includes attempts for in-situ identification of the toughening mechanisms in porous materials and complex composites using in situ testing under X-ray tomography. All these characterizations will aim at establishing relationships between processing microstructural parameters and mechanical properties to optimize the functional properties.

Conclusions: opportunities and breakthroughs

This multi-disciplinary project, at the borderline of materials science, offers a unique integration of approaches, competences and resources in materials science, chemistry, physics and mathematics. The proposed iterative approach, focussed on the most fundamental understanding of the physical mechanisms, should allow for progressive and substantial progresses into the complex phenomenon of colloids freezing. Members of the team for this project have contributed numerous milestones toward several key steps of the project, and preliminary proofs of principles results offer a reasonable confidence in the successful outcome of the project. For materials science only, the versatility of the process, associated to its proper control, could yield **potential breakthrough in numerous key applications** of tremendous human, technological, environmental and economical interest such as catalysis, biomaterials or energy production, and open a whole new field of research. **Far-reaching implications beyond materials science** are expected, both from the development of new approaches and tools in mathematics and physics, and from the implications of colloids freezing in many situations and fields of research.

ERC Starting Grant
Research proposal (Part B2)

a. State-of-the-art and objectives

Colloids everywhere

Colloidal particles are often seen as big atoms that can be directly observed in real space. They are therefore playing an increasingly important role as model systems to study processes of interest in condensed matter physics such as melting, freezing and glass transitions. The possible direct observation of colloidal particles may provide valuable insights into the basic solidification, melting, freezing or glass transition mechanisms, observations extremely difficult to achieve otherwise. **The presence of and the interest for colloids is not restricted to physics and materials science, and colloids are present in many natural or engineering process or substances**, in domains as diverse as biology (blood, enzymes, fumic and humic substances), environment (fog, mist, cloud), geophysics (clay particles, silicates), filtration (pollutants), food (milk, mayonnaise, whipped cream, gelatin) or engineering (styrofoam, aerogel) to name a few.

The term colloidal refers to a state of subdivision, implying that the molecules, polymolecular particles or more generally objects (such as biological cells) dispersed in a medium have at least in one direction a dimension roughly between 1 nm and 1µm, or that in a system discontinuities are found at distances of that order. A colloidal dispersion is a system in which particles of colloidal size of any nature (solid, liquid or gas) are dispersed in a continuous phase of a different composition or state (table 1). The term colloid will be used here as a short synonym for colloidal system. More specifically, **this project is focussing on hydrocolloids**: colloidal system wherein the solid colloidal particles or objects are dispersed in water.

*Table 1: Classification of colloids. * All gases are mutually miscible.*

Medium/phases		Dispersed phase		
		Gas	**Liquid**	**Solid**
Continuous phase	**Gas**	(none)*	Liquid aerosol	Solid aerosol
	Liquid	Foam	Emulsion	Sol
	Solid	Solid foam	Gel	Solid sol

Freezing colloids, a common phenomenon

The solidification or freezing of colloidal suspension or colloids is commonly encountered in a variety of natural processes such as the freezing of soils in northern regions and the growth of sea ice, or everyday life and engineering situations such as food engineering, materials science, cryobiology, filtration or water purification and the removal of pollutants from waste (fig 1).

The process associated with the **freezing of soils** (clay colloids) is usually known as *frost heave*, and induces deformation and thrust of the ground surface, which in turn induces potential damage to plants through breaking and desiccation, and to roads, pavement and building foundation. The damage and the associated costs of frost heave can be considerable in areas susceptible to low temperatures. **The growth of fresh sea ice** in the oceans is another natural occurrence of colloids freezing. The ocean salt and various micro-organisms and algae are rejected from the growing ice crystals and entrapped between these in brine channels. These brine channels comprise highly salt concentrated water, denser than usually, and have an important influence on the ocean overturning circulation. In addition, the brine channels play an important role in the thermal exchanges between the ocean and the atmosphere. The greatly increased salinity of brine channels, inducing a lower solidification temperature (below -50°C), might also have permitted an extended amount of time during which the life on Mars could have evolved[1]. The behaviour of biological colloids subjected to freezing is also a process of tremendous importance in the **cryopreservation of cells and tissues**, including blood, stem cells, reproductive cells, tissue and organs. The lowering of the temperature is sought for its effect in stopping the biochemical reactions, therefore preventing cells' death. Nevertheless, controlling the interaction between the ice and the cells is essential to prevent any fatal damage that could be inflicted to the cells during the freezing and thawing stages. Complex protocols, including cryoprotectants, have been developed to overcome these problems, although there is still plenty of room for improvements. Food engineers and kids (in particular mine) are also greatly interested in freezing or frozen colloids, the most common application being the fabrication of **ice cream**, a market estimated in 2008 to be of 42 billion US$ value. From a materials science point of view, ice cream is an amazingly complex material, comprising solid, liquid and gas components. The right combination of ingredients and process parameters lead to proper lightness, softness, sweetness and taste, resulting from the proper control of the microstructure of ice crystals, air bubbles, fat droplets and matrix. The freezing stage of this complex colloidal medium is of course central and of tremendous importance and still the object of intense research. Engineers are finally more and more

[1] D. D. Wynn-Williams et al., Brines in seepage channels as eluants for subsurface relict biomolecules on Mars?, *Astrobiology*, 1[2] 165-184 (2001).

interested in the solidification of colloids, for their implications in various processes such as the **processing of particle-reinforced alloys and composites, the removal of water pollutants** by controlled directional solidification or the **processing of porous materials** using the freezing of colloidal suspensions, which is described in more detail hereafter. Freezing colloids is therefore an amazingly common phenomenon, of **stupendous impact in natural, physical, social and technological environments**. The associated costs (degradation of roads) or benefits (climate control, cryopreservation protocols and tissue engineering scaffolds) are of tremendous importance.

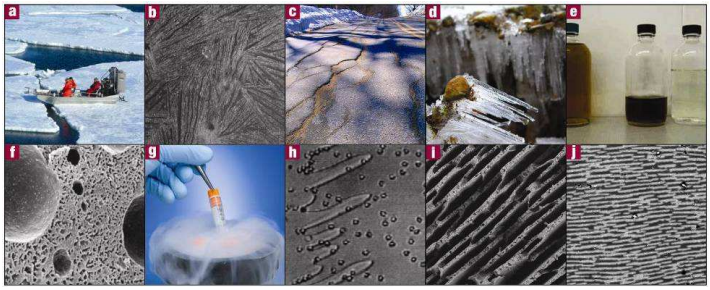

Fig. 1: Colloids freezing situations: (a-b)sea ice and brine channels formation, (c-d) soils freezing and frost heave,(e) removal of pollutants by freezing, (f) ice cream manufacturing, (g) cryopreservation of reproductive cells (h) and red blood cells, (i) porous ceramics and (j) composites obtained through colloids freezing.

Freezing colloids: what we do know

The phenomenon by itself is disappointingly simple: a solidification interface, usually the water/ice interface, is propagating through a colloidal suspension of particles, cells or micro-organisms. **This simplicity is nevertheless only apparent** and we are still far from a correct understanding and control of the phenomenon. 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 (or cells) in front of a moving interface and it is still a subject of intense work. **Little has been made regarding the case of concentrated colloids**, although recent progress has emerged for the situation of low interface velocity with a planar morphology.

Probably the most important characteristic of colloids freezing is the existence of a **critical interface velocity** beyond which colloids are entrapped by the moving interface. Inversely, a critical particle size exists at a given interface velocity, dictating the rejection or the engulfment of the colloid. Depending on the morphology of the solidification interface –flat, cellular, lamellar– and the colloids size, different behaviours can be observed, ranging from total rejection of the colloids –the basic effect upon which the solidification of colloidal suspensions is used to remove pollutants from water– to total encapsulation of the colloids at very high velocities. A wide variety of intermediate situations exist, with complex dynamics of crystal growth and colloids redistribution by the interface. The morphology of the solidification interface is of course critical, and mostly depends on the imposed solidification conditions. The simplest case, albeit of limited practical interest – except for the removal of pollutants– is the lowest interface velocity (<1 µm/s), with a flat interface. When the velocity increases, the morphology of the interface evolves as a function of not only the cooling conditions but also the colloids characteristics. Of all the solvents being considered in the above mentioned processes, **water is the most commonly encountered, but also the most peculiar**. Several specificities of water and ice must be taken into account. For example, under the usual temperature and pressure conditions, ice exhibits a very high anisotropic crystal growth. The hexagonal structure of ice results in the formation of platelets or lamellae, the ice growth kinetics in the basal plane being orders of magnitude larger than perpendicular to the basal plane (fig 2). This anisotropy is the underlying reason for the peculiar morphology of the brine channels in sea ice (fig 1b, fig 6a).

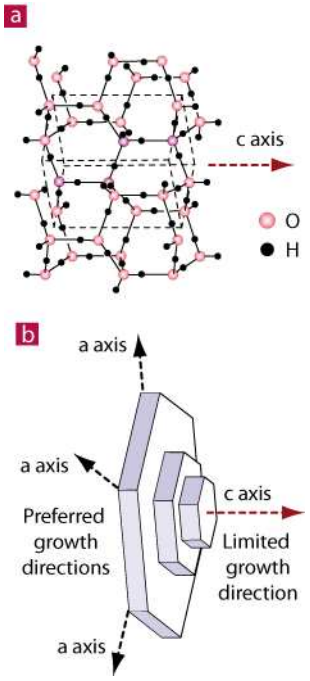

Fig. 2: Hexagonal structure of ice under the usual conditions of temperature and pressure (a), and anisotropy of growth kinetics (b).

Freezing colloids: what we do not (and would like to) know

Hence, the freezing of colloids has long been and is still a puzzling phenomenon, with many unexplained features, inter alia the presence and the onset of interface instabilities at high velocity or the morphology of the growing crystals in the presence of concentrated colloids. **A very large number of disparate parameters should be accounted for when trying to understand and model the freezing of colloids** (fig 3). The characteristics of the colloidal suspension are often critical to the behaviour of the system during freezing, and to a large extent neither have been analysed (so far) nor understood. The unknowns of the phenomenon can be gathered in three categories:

- **Parameters related to the colloids**, such as the relative importance of colloids' characteristics, including the colloids content, their diffusivity, the interactions between the colloids, the physical properties of the colloids such as their interface with water (roughness, surface tension, hydrophobicity or hydrophilicity), the difference

of thermal conductivity between the ice and the colloids, etc...

- **Parameters related to the crystal growth**, such as the dynamics of crystal formation and growth morphology in presence of colloids, the relative importance of latent heat, the anisotropy of crystal growth, the role of impurities on the growth of ice crystals.
- **Parameters related to the system as a whole**: the interactions between the colloids and the propagating interface, and the behaviour of the system out of equilibrium, i.e. at rapid velocities (this is not understood so far).

The numerous difficulties and challenges associated with the investigations of these parameters and effects will be described later on.

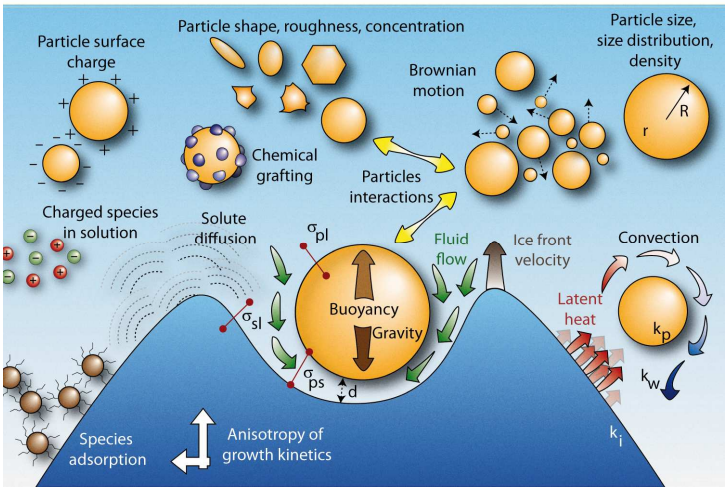

Fig. 3: Freezing colloids, schematic representation of the main parameters to take into account.

Modelling the freezing of colloids: a necessary challenge

Theoretical approaches to modelling freezing colloids have, for the past 50 years, focused almost exclusively on the interaction of an isolated particle with an advancing ice front[2]. Such models have explained important aspects of colloids freezing, such as the critical freezing velocity below which isolated particles are pushed ahead of the ice, and above which the particles are trapped into the ice lattice. Many geological, biological and industrial systems involve concentrated particle systems. Owing to their neglect of particle-particle interactions, **isolated particle models are not able to quantify the critical dependence of the final ice crystal morphologies on the initial colloid concentration** – a crucially important operating parameter for industrial applications. A new mathematical framework has been developed that accounts quantitatively for such interactions[3]. The approach treats a colloidal suspension as a non-ideal two-component "alloy" in which the solute particles are vastly larger than the solvent, and exploits the physical basis for the dynamics and thermodynamics of pre-melting between the particles and the frozen solvent. A distinct advantage of this approach is that it enables mathematical techniques developed for studying pattern formation in far-from-equilibrium systems[4] to be applied —with proper modifications— to freezing colloids. We have compared predictions of this model to X-rays radiography measurements[5] of particle concentration profiles in the colloid and ice phases and obtained good qualitative and quantitative agreement. In this project **we will apply two mathematical techniques, stability analysis and phase field models**, to further quantify solidification structures observed in experiments on freezing colloids undertaken concurrently.

* **Solidification model and stability analysis** – In previous research we have demonstrated that ice and particle segregation in colloidal systems occurs as a result of a morphological instability of the ice–colloid interface. In this work the ice–colloid interface was treated as locally in equilibrium (slow freezing velocities). A morphology diagram was constructed to predict critical operating parameters (e.g., freezing velocity) beyond which a planar interface becomes unstable, yielding good agreement with experiments. Recent evidence indicates that at higher freezing velocities nonequilibrium effects at the interface are important[5]. In the present work **we will allow for nonequilibrium effects** such as kinetic undercooling, kinetic anisotropy and particle trapping, and **explore their effect on quantitative predictions of instability wavelengths and critical operating parameters**. Accounting for kinetic effects and particle trapping in this manner will complement and generalize previous modelling of instabilities and isolated particle effects. The new model will lead to more general morphology diagrams capable of predicting additional transitions including the pushing/trapping boundary in concentrated systems. Further generalizations,

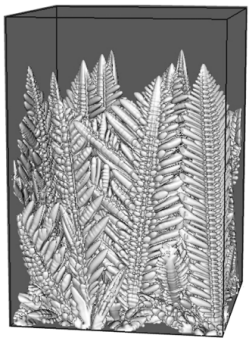

Fig. 4: Phase field modelling of dendritic growth of a Mg–Al alloy.

[2] D. R. Uhlmann et al., Interaction between particles and a solid/liquid interface, *J. Appl. Phys.*, 35 2986–2992 (1964); J.C.T. Kao et al., Particle capture in binary solidification, *J. Fluid Mech.*, 625 299–320 (2009)
[3] S. S. L. Peppin et al., Solidification of colloidal suspensions, *J. Fluid Mech.*, 554 147-166 (2006), Morphological instability in freezing colloidal suspensions, *Proc. R. Soc. London A*, 463[2079] 723-733 (2007); Experimental verification of morphological instability in freezing aqueous colloidal suspensions, *Phys. Rev. Lett.*, 100[23] 238301-238304 (2008)
[4] M. C. Cross et al., Pattern formation outside of equilibrium, *Rev. Mod. Phys.*, 65 851 (1993)
[5] S. Deville et al., Metastable and unstable cellular solidification of colloidal suspensions, *Nature Materials*, 8(12) 966-72 (2009).

such as the effects of salt ions and fluid flow on the instabilities, will also be explored.

*** Phase field modelling** – The phase field technique is a powerful method for simulating the evolution of complex morphologies[6]. By introducing a phase field variable that varies continuously across phase boundaries, complex shapes can be simulated without having to explicitly track a deforming interface. In alloy systems, phase field models are used to simulate the growth of dendrites in solidifying materials (fig 4), yielding exceptional insight into microscale pattern formation, and giving good quantitative agreement with experiment. No phase field model has yet been developed for colloidal systems, despite wide-ranging potential benefits. It is the goal of this work to **develop the first thermodynamically rigorous phase field model of a freezing colloid**. This will require non-trivial new mathematics, owing to the highly nonlinear dependence of colloid physicochemical properties on the particle fraction. We are confident the new model is feasible, owing to our successful derivation of equations describing the morphological instability of an ice-colloid interface.

Freezing colloids in materials science: a bioinspired processing route... for bioinspired materials

Among the many possible applications of colloids freezing, its potential use as a processing route for bioinspired porous materials is particularly innovating and exciting.

*** The undelivered promises of biomimetics**

For some years now, the design of biomimetic materials and systems has been the focus of increased attention. The properties, functions, and structures encountered in nature are increasingly appealing for non-biological applications: control of the structure at different levels, adaptation to the environment, soft processing conditions, use of biodegradable materials, or the ability to self-repair. The range of functions achieved by such biological routes is extremely wide, and the solutions encountered in nature result from millions of years of evolution and can indeed be seen as an optimum for the targeted functions. Nature has nonetheless a very limited range of materials with which it works, and is limited in its processing and use to a low temperature and low pressure environment. Materials scientists and engineers, on the other hand, have access to a much wider range of advanced materials suitable for severe experimental conditions. **Applying nature's blueprints to advanced materials could yield a brand new range of materials with properties orders of magnitude above the currently available solutions**.

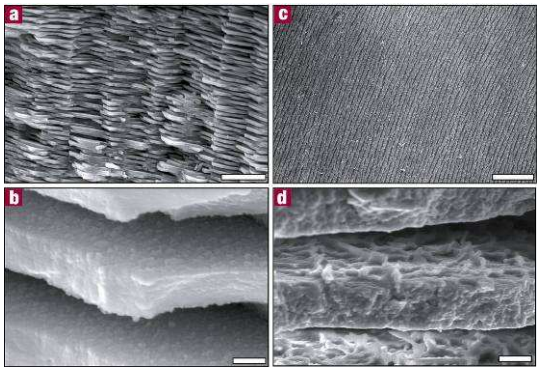

Fig. 5: Nacre of the abalone shell (a-b) and nacre-like structures obtained with colloids freezing(c-d) Scale bars a: 10 µm, b: 0.3 µm, c: 300 µm, d: 10 µm

Tangible applications of biomimetics are nevertheless and surprisingly still very scarce, and besides the well-known example of Velcro, very few of these principles have found their way to manufactured products. The underlying reason for this lies in the **lack of processing routes to implement the bioinspired designs** into materials and systems, which is very frustrating indeed considering that the blueprints are now available…

Nacre, the iridescent material thickly coating many shells and molluscs (fig 5a-b), is a school-case example for biomimetic inspiration. The unique hierarchical architecture of nacre represents the optimum of how to **overcome intrinsic materials weakness by hierarchical design to strengthen and toughen structures**. The work of fracture of abalone nacre is indeed about 1000 to 3000 times greater than that of a single crystal of the pure mineral, stupendous properties arising from its complex hierarchical architecture. Few if no structural engineering materials have such a hierarchy of structure, yet the message from biology here is clear – there is a need in the design of new materials to develop mechanisms at multiple length scales in order to create new hybrid materials with unique functional properties.

*** Freezing colloids: a bioinspired, environmentally-friendly processing route for bioinspired materials**

The freezing of colloids can be used as a bulk self-assembly process inspired by a natural occurrence of colloids freezing, the freezing of sea ice, which occurs at the surface of the Earth's polar oceans. In sea ice, pure hexagonal ice platelets are formed, and the various impurities originally present in seawater (salt, biological organisms, etc.) are expelled from the forming ice and entrapped within the channels between the ice crystals (fig 6). **Using ceramic particles instead of biological impurities, we take advantage of this natural segregation principle, while using ice as a natural**

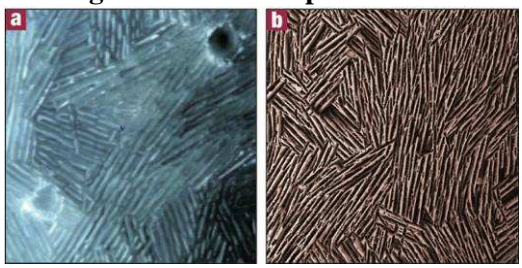

Fig. 6: Brine channels in sea ice and porous ceramics through colloids freezing

[6] W. A. Boettinger et al., Phase-field simulations of solidification, *Annu. Rev. Mater. Res.*, 32 163-194 (2002).

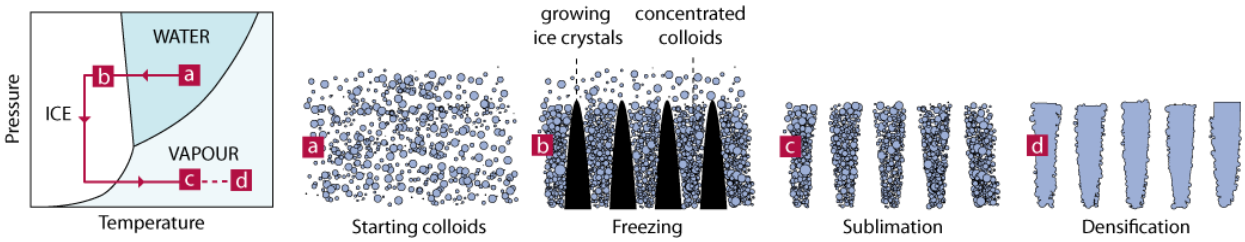

Fig. 7: Freezing colloids, a bioinspired materials processing route.

and environmentally-friendly templating agent[7]. The process takes advantage of the water-ice phase diagram (fig 7). Freezing of the ceramic colloids is performed under controlled conditions to build an interpenetrating scaffold of ice and ceramic particles. The ice is then removed by sublimation and the resulting ceramic part sintered at high temperature. The final result is a scaffold with a complex and usually anisotropic porous microstructure generated during freezing, this structure being a replica of the original ice structure. This ceramic scaffold can then be used as a basis for dense composite, if infiltrated with a suitable second phase. The dense complex composites obtained by this process exhibit **striking similarities to the macro- and micro-structure of the inorganic component of nacre**, replicating its multilayer structure and other structural features (fig 5) such as roughness or inorganic bridges, and with **properties which far exceed what could be expected from a simple mixture of their components[8]**. Ten degrees of structural hierarchy have already been identified (fig 8), throughout all the length scales, making the structure a very unique one. Most important is the fact that a very wide range of techniques and parameters can be used to control the structure and each of these degrees of hierarchy, which might be used either to promote a single property (e.g., mechanical strength), or to introduce several functionalities, associated with each of the degrees of hierarchy. We believe that through the exposed freezing process we can control and tailor functional properties for a wide spectrum of applications.

The preliminary results we published in *Science* have raised considerable attention on the freezing process, both from academic and industrial partners such as BMW, PPG or Saint-Gobain. The freezing route is indeed an appealing process due to its simplicity, with no equivalent at the moment, both in terms of process and structures obtained. The process is **environmentally-friendly**, with no solvent involved but water, and does not require a highly specific processing environment. Structuring bulk materials at the nanometre or submicron scales usually yields unrealistic processing time, hindering further development. The freezing process follows the exact opposite path: getting finer structure is achieved through increased freezing kinetics. Samples a few centimetres thick can be processed within a few minutes. The process being based on the freezing technology, the equipment required is readily available and has been developed, tested and used for years in various fields including food or materials engineering. Understanding and controlling the underlying phenomena associated with the freezing route make it a truly interdisciplinary scientific challenge. Finally, and of uttermost importance, **the freezing process is extremely versatile**. The vast majority of the biomimetic routes developed so far often rely on highly specific interfacial compatibilities. The structural formation mechanisms involved here being based mostly on physical interactions —between the solidification front and the particles— **any type of ceramic, metallic of even polymer particles can be used**. The range of potential applications derived from this approach is extremely wide: filtration, catalysts support, scaffolds for biomaterials, heat guides, wear resistant materials for cutting tools, and so forth.

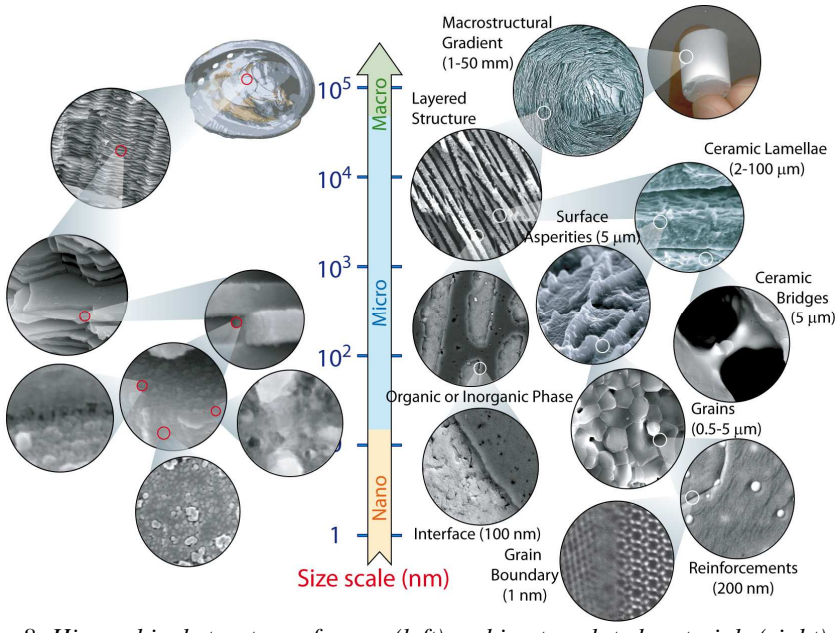

Fig. 8: Hierarchical structure of nacre (left) and ice-templated materials (right)

[7] S. Deville et al., Freezing as a path to build complex composites, *Science*, 311 515-518 (2006).
[8] E. Munch et al., Tough, bio-inspired hybrid materials, *Science*, 322 1516-1520 (2008).

*** Promising properties, potential breakthrough**

As expected from the unique structure, some unique properties are exhibited by such materials. In particular, the strong anisotropy can considerably enhance functional properties in one direction when needed, e.g., mechanical properties, electrical or thermal conductivities. We demonstrated for example a 400% increase in compressive strength of hydroxyapatite scaffolds for bone substitutes compared to materials obtained through state of the art techniques[9]. **Such anisotropy can be highly beneficial for a wide range of other applications involved with mass, gas or species transport,** and yet, very little is known about the specific properties and structure/properties relationships of such materials. It is clear that we have only scratched the surface of the potentialities offered by the freezing process. Much ground is yet to be covered before the full potential of this approach can be clearly assessed. **The objective of this part of the project is therefore to assess the structure/properties relationships in this unique class of porous hierarchical materials**, which combine toughening mechanisms acting at multiple scales. Previous results highlighted the tremendous potential of the bioinspired approach and suggested promising strategies for structural optimization, some of which will be explored in this project.

Challenges ahead

The freezing of colloids has long been a puzzling phenomenon with many unexplained features. One obvious reason for this situation is the previously mentioned complexity of the system, and the challenges in observing, modelling and controlling the phenomenon. Five sets of scientific and technical challenges can be identified.

1- Cross-disciplinary approach required

Apprehending the process of colloids freezing requires an advanced understanding in disparate areas, which implies differences in the concepts, approaches, analysis and vocabulary. The different contexts, from materials processing to soils freezing, yield sometime different interpretations of the experiments. **Understanding the core of the process requires cross-disciplinary approaches, using knowledge from ice physics, mathematics, engineering, materials science, geophysics and cryobiology**, making the problem a truly exciting cross-disciplinary challenge.

2- Experimental challenges

A solid experimental foundation on which further theoretical developments can be built and validated is of course a preliminary and strong requirement. If the various manifestations of colloids freezing can be observed in numerous occurrences in natural or technological situations, precise and quantitative observations are required for understanding the process. **Ideally, we would need in situ real time three-dimensional observations of both the crystals growth and colloids movement in the suspensions**, with individual colloid tracking and concentration measurement to investigate the colloid redistribution occurring during freezing. The corresponding space (submicronic) and velocity (tens to hundreds of μm/s) scales severely restrict the choice of experimental techniques. Tracking optically individual particles has been used for situations where a single particle is interacting with a solidifying interface. However, in the case of concentrated colloids, these approaches suffers from the same problem of light scattering, that is **multiple scattering from objects** (colloids) that are out of focus within the illuminated region prevents imaging deep within a sample. New experimental approaches must therefore be considered. As is often the case, a single experimental technique is not sufficient to characterize the process. In addition, any interaction between the observation technique (such as the X-ray beam) and the sample should be carefully assessed. We plan to tackle this challenge by using a variety of complementary in situ observation techniques.

3- Complexity and specificities of the system

If the process by itself could seem rather trivial –colloids in front of a propagating solidifying interface– the number of parameters that should be accounted for is staggering. These parameters are related both to the crystals growth and the colloids, and the interactions between both. In addition, several specificities of the components of the process increase further its complexity.

- **Ice growth** – Water, whether under its solid, liquid or gas form, is one of the most peculiar known substances. Any theoretical development should account, for instance, for the anisotropic crystal growth of ice, the latent heat, the density fluctuations of water with temperature, diffusion and thermal diffusion (regelation) in the ice phase to name a few.
- **Colloids –** An excellent knowledge of the colloidal suspension state is required, such as the presence of colloids agglomerate, the surface charge of colloids or the water affinity of the colloids surface. In addition, unlike alloys, colloidal suspensions exhibit various non-linear physical properties dependence with the

[9] S. Deville et al. (2006), Ibid.

concentration of colloids, such as the freezing temperature curve and a dependence of particle diffusivity upon concentration and temperature.

- **Interactions between the solidification interface and colloids –** Such interactions can take place at several length and time scales, and both individual interactions and bulk interactions should be taken into account. Besides, a variation of the segregation coefficient with the interface velocity must be incorporated.
- **Role of impurities –** Impurities, whether introduced voluntarily (additives) or not (pollutants) can have a tremendous influence over the process, such as a modification of crystal growth through a possible absorption at the crystal surface, which in turn affects the crystals morphology and surface energy. The presence of impurities, in particular salt ions, can induce a possible electromigration, leading to a modification of the effective diffusion coefficient of the colloids[10].
- **Kinetics** – At high interface velocity, the system is usually out of thermodynamic equilibrium. Kinetic aspects must therefore be accounted for. This results in an increased complexity of the modelling approach, described hereafter.

4- Modelling challenges

All –or at least all major of– the above mentioned parameters must be incorporated in any realistic model of the system. This in turn results in a need to build new mathematical models, with non linear partial differential equations to be solved. We can already mention the role of highly anisotropic crystal growth –which could be modelled via a surface energy depending on orientation, hydrodynamic effects in the suspension, the temperature dependence of diffusion coefficient, diffusion and thermal diffusion in the ice and a velocity-dependent segregation coefficient. The complexity of the model can be progressively increased to incorporate all the essential parameters previously cited.

5- From the lab to the real world: boundary conditions and space and time scales

Confronting lab and modelling results to real world situations will inevitably face numerous challenges. In particular, difficulties might be expected with the scaling of the identified mechanisms occurring during the freezing. The experimental results will have to be compared with the natural and technological occurrences of colloids freezing, where the boundary conditions can be tremendously different, from large scale (soils, ocean) to intermediate scale (materials science, cryobiology, food engineering) and confined scale (microfluidics, biology). This implies strong variations in both **space scale,** from the nanometre (interaction between colloidal particle and interface) to the meter (typical sea ice or frozen soils thickness) and kilometres (hydrodynamic currents, which can influence the crystals orientation), and **time scale** – from seconds (rejection of particles, nucleation of crystals) to months (crystals growth, long distance diffusion).

In summary, this is an excellent and exciting scientific problem!

b. Methodology

The core objective of the project (fig 9) **is the progress towards a deeper understanding of the freezing of colloids** and in particular here of hydrosol –solid colloidal particles in suspension in water– **as it is clearly a necessary step towards achieving a better control of the derived materials processing route**. **This project integrates materials science, chemistry, physics, mathematics and technological developments of observation techniques.** To limit the risk and guarantee the success of the project, the research plan has been designed with a highly iterative approach, the basic lessons learned after each iteration will be applied in the design and control of the process of the next cycle. To overcome the complexity of the modelling of the process, progress towards further understanding will be based on in situ experimental observations of the freezing of colloids, using several different and complementary techniques, providing insights in the phenomenon at different length and time scales.

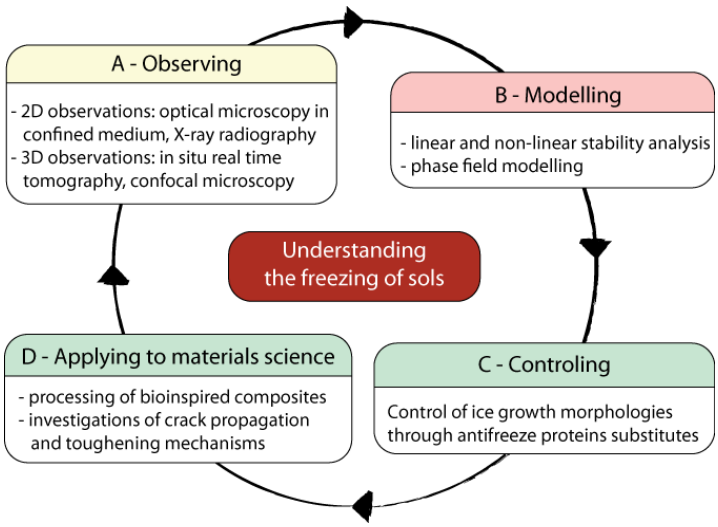

Fig. 9: Project workflow

Progress will be accomplished through iterative cycles of four subprojects, namely observing, modelling,

[10] B. Abécassis et al., Boosting migration of large particles by solute contrasts, *Nature Materials*, 7[10] 785-789 (2008).

controlling and applying the freezing of colloids to materials science. Control of the materials complex architecture will hence benefit from the knowledge learned during the previous steps. The first objective is to better assess and understand the structure/properties relationships of these ice-templated materials and composites. These various objectives and the proposed methodology will be described below.

This project has been designed to incorporate a gradient of risk at several levels, by combining conventional and novel approaches in observation techniques, modelling and materials processing and characterization strategies. The time $\mathbf{T_0}$ mentioned in the timelines corresponds to the **effective beginning** of the project.

A - Observing the freezing of colloids in situ

This part of the project is focussed on experimental observations. To progressively apprehend the complexity of the system and take the number of parameters into account, a thorough experimental observation approach will be followed, using both organic and inorganic colloids.

The simplest model system is the **hard-sphere system**, in which the colloids are non-interacting at all separations beyond their radius and infinitely repulsive on contact. When colloids exhibit a surface charge, this changes the interparticle potential from hard-sphere-like to soft. The modification of the interparticle potential can potentially greatly affect the particle redistribution and interactions with the freezing front during the solidification of concentrated colloids. We will investigate here two different systems, a **hard-sphere system with calibrated silica spheres** (with a fluorescent core), and a **soft-sphere system, with calibrated PMMA particles** (also marked in fluorescence).

A variety of in situ observation techniques will be used to follow the crystals nucleation and growth and corresponding particles redistribution at relevant time and space scales (fig 10). **Each of these techniques has its own advantages, drawbacks and limitations, and will provide a picture of the system at different length and time scale.** Different categories of techniques will be used, namely optical microscopy, confocal microscopy and X-ray radiography and tomography.

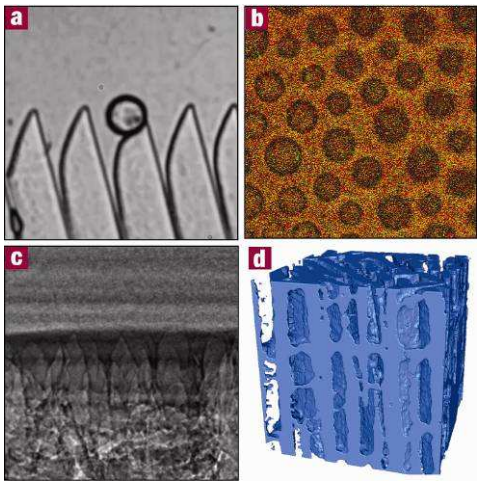

Fig. 10: Observing the freezing of colloids. Experimental techniques considered in this project includes optical microscopy in the bulk (a) and in confined space (b), confocal microscopy (c), X-ray radiography (d) and X-ray tomography (e).

(a) **Optical observations in confined space.** Preliminary experiments with proof of principles (fig 10a) have been achieved on a highly specific directional solidification set-up originally designed for the study of the solidification of transparent alloys on thin samples (20 μm)[11]. In situ non-intrusive observation of the freezing process can be achieved by observing with an optical microscope the solidification interface at various magnifications ranging from the micrometric scale of dendrite tips to the millimetre scale of a whole dendritic pattern. Real-time observation of the coupled dynamics between the solidification interface and the colloid particles can be achieved in regimes going from the slow planar interface to the rapid well-developed dendrites. Samples are thin enough to exhibit a single layer of dendrites, thus enabling the accurate observation of inter-dendritic segregation of colloids on well-resolved dendrites. **A postDoc will be hired for one year to work full time on this part of the project.**

Objectives
- investigate the role of concentration of both particles and additives on the interface
- investigate particle redistribution by the interface in 2D
- modification of the morphology of the interface induced by the interactions with the particles
- investigate interface dynamics and clarify its relationship to the instabilities of solidification interface in solutions

Materials and experimental conditions: unidirectional solidification in a thin film (20 μm) through transparent samples

Experimental developments: need to upgrade the cold stage, in particular to control the condensation at the observation surface through anhydrous gas flush

Milestones and timeline (total: 12 months) **– Begins at $\mathbf{T_0}$+6 months**
- setup upgrade: **2 months**. Successful if temperature down to -30°C and no condensation
- effect of particles and additives on interface dynamics and morphology: **6 months**
- identification and characterization of interface dynamics: **4 months**

Expected difficulties, alternatives
- control of particle sedimentation in a thin layer when lowering additives concentration. Alternative: use of

[11] M. Georgelin et al., Onset of sidebranching in directional solidification, *Phys. Rev. E*, 57 3189-3204 (1998).

smaller size, control of surface chemistry and surface charge.
- control of the desired particles concentrations when preparing samples. Alternative: specific sample filling, use of smaller size.

(b) **Confocal microscopy** with a cold stage will be used, to provide **in situ particle tracking possibilities and detailed characterization of particles packing between the crystals**. Preliminary results, performed in a CNRS partner lab, were again encouraging (not published, fig 10b), but further developments of the technique are necessary to work under correct, if not optimal, conditions. Confocal microscopy, with point by point illumination of the sample and rejection of out of focus light, provides a way to overcome many of the problems in conventional microscopy caused by multiple scattering of objects which are out of focus, and prevents imaging deep within a sample. In addition, it might provide a complementary alternative to X-rays imaging, where the effects of interaction between the highly energetic beam and colloids are largely unknown, and the current spatial resolution does not allow individual particle imaging. For confocal microscopy, it might be useful to use a model colloidal suspension using preferentially **silica** spherical colloids where the **refractive index between the colloids and the solution is matched** (index matching technique). This reduces **strongly the scattering** and allows images to be obtained in depth inside the solution which is itself doped with a small amount of fluorescent agent to increase the contrast between water and silica.

Objectives: **investigate colloidal particles packing** in the frozen body and **in situ crystal growth and particle tracking** during solidification
Materials and experimental conditions: laser scanning confocal microscope (*Leica TCS SP5 tandem*), directional solidification using a Peltier stage.
Experimental developments: develop a cold stage to upgrade the confocal microscope for in situ freezing experiments (already initiated, with a Peltier stage previously developed for atomic force microscopy experiments)
Milestones and timeline (total: 36 months, this subproject includes the X-rays tomography approach) **– Begins at T_0+6 months**
- upgrade of a cold stage to perform in situ freezing of the suspension, calibration of cooling conditions and sample dimensions: **6 months** (initiated before arrival of the PhD student). We have the experience of developing a similar stage for an atomic force microscope, where the observation conditions and constraints are somewhat similar.
- observation of frozen samples: **6 months**
- in situ observation of crystal growth and individual tracking of colloidal particles: **18 months**

Expected difficulties, alternatives:
- possible difficulty to do the *in situ* tracking in 3D. Alternative: follow in 2D in a horizontal plane perpendicular to the interface displacement direction. This is already a good approximation since most of the particle redistribution is expected to occur in this plane, due to the lateral growth of ice crystals.
- spatial resolution to follow submicronic colloidal particles. Alternative: use a larger colloidal system (1-5 μm).
- rapid decay of fluorescence signal during the observation. Need to fine-tune the experimental conditions.
- control of the cooling conditions, in particular to avoid ice condensation at the surface. Alternative: add an anhydrous gas flushing system to the setup.
- control of nucleation conditions to make sure we are observing the system in a steady state

(c) In situ freezing experiments will be followed by **X-rays tomography observations**, which provides quantitative kinetic and structural observations of the phenomena involved. The technique being limited in spatial resolution, it will clearly not allow us to identify single particles in the suspension. We have nevertheless proved that it was a very good tool to analyze the morphology of the ice crystals using a resolution of about 1 μm. Our recent previous results[12] (fig 10c-d), including a paper in *Nature Materials*[13], are raising a strong interest for this technique. The optimal experimental conditions have now been identified, and the technique is ready to be used in a more systematic approach, to investigate the relative importance of several of the parameters mentioned previously. Our objective in the present project is to use imaging techniques able to give a 5 Hz temporal resolution in tomography, to **observe for the first time the evolution of the morphology of the freezing front in 3D, and possibly quantify the local particle concentration and redistribution**. We have already successfully used X-rays radiography at similar frequencies during freezing and can of course continue in this way. The present project would allow us to go one step further. For this, tomography experiments with a 5 Hz frequency could be carried out at the ID15 beamline at the ESRF, one of the only sources in the world where the required high flux would allow us to perform such high speed experiments. This requires rotating the sample continuously (2.5 round

[12] S. Deville et al., In situ X-ray radiography and tomography observations of the solidification of aqueous alumina particles suspensions, Part I: initial instants, *J. Am. Ceram. Soc.* (2009); Ibid, part II: steady state.
[13] S. Deville et al. (2009) Ibid.

per second for 180° acquisition) and record images using a very fast CMOS type X-ray camera. Each scan requiring 1000 projections, the acquisition speed in radiography has to go up to 5000 Hz. We have already participated to experiments of that sort to prove the feasibility. **The PhD student will have to build a specific cryostat** able to rotate continuously during the tomography acquisition.

These experiments, if successful, will provide us a 3D vision of the evolution of crystal growth morphology during the solidification, which can be **compared with the output of the phase field model**, developed in the other part of the project. We should also get a 3D representation of the colloid concentration profile, which again can be **compared with the output of the modelling**.

Objectives: **evolution of the 3D morphology** of the ice crystals at a **5Hz frequency** and **3D measurement of the colloid particle concentration**

Materials and experimental conditions

- conditions: unidirectional solidification
- imaging: 5Hz tomography acquisition on beamline ID15 at the ESRF with a 1.5 μm spatial resolution.
- targeted interfacial velocity: 10 μm/s or less, the interface displacement during the acquisition must be limited to achieve a good imaging.

Experimental developments: need to develop a specific cryostat able to rotate continuously during the tomography acquisition

Milestones and timeline (total: 36 months, this subproject includes the confocal microscopy approach) **– Begins at T_0+6 months**

- successful development of new cryostat: **6 months**
- successful in situ tomography at 5Hz and local measurement of colloids concentration from beam absorption intensities: **8 months** (beamtime access will be concentrated on a few days)

Expected difficulties, alternatives

- control of cooling conditions compatible with the permanent unidirectional rotation of the cell. We have the experience of already developing a similar cell.
- control of cooling conditions to achieve a solidification interface velocity compatible with the desired 5Hz acquisition frequency
- limitation of side effects due to the relatively small size of the mould being used
- alternative: there is no alternative for this specific objective. Nevertheless, we have already participated to experiments at the ID15 beamline of that sort to prove the feasibility.

A PhD student will be hired to work full time on the confocal microscopy and tomography developments and investigations. All these experimental observations will be compared and linked when possible to that obtained in natural situations, such as the growth of sea ice or the freezing of soils, to get possibly the most complete picture of the phenomenon to date.

B - Modelling colloids freezing

(a) **Stability analysis –** The nonequilibrium phase diagram of a colloidal suspension will first be developed. This will generalize the equilibrium diagram used in previous models[14] allowing for particle trapping effects (quantified by a segregation coefficient). The presence of dissolved solutes will be modelled by introducing a coupled expression for mass conservation within a non-equilibrium thermodynamics framework. Fluid flow will be accounted for by including the Navier-Stokes equation as one of the governing equations, with a nonlinear colloid concentration-dependent viscosity. Linearization of the governing equations and ensuing stability analysis will lead to a characteristic equation relating operating parameters such as colloid concentration and freezing rate, and separating stable from unstable states. Predictions of this equation can be directly compared to experimental measurements of critical freezing rates. When possible the calculations will be performed analytically – in more complex cases the eigenvalue problem will be solved numerically.

Objectives: **construction of new non-equilibrium colloid phase diagram** and **generalization of solidification model and stability analysis**

Parameters to retrieve/predict from experiments

- initial particle concentration, solution pH, impurity concentration, temperature gradient, freezing rate (input)
- freezing rate at onset of instability, colloidal particle concentration profile (model prediction)

Milestones and timeline (total: 12 months) **– Begins at T_0**

- derivation of phase diagram: **3 months**
- derivation, solution of stability model + comparison to experiment: **6-9 months**

[14] S.S.L. Peppin et al. (2008) Ibid.

Expected difficulties, alternatives
- we will attempt to derive analytical expressions for critical freezing velocities as function of operating parameters - the high degree of nonlinearity in the governing equations will make this difficult.
- alternative: solve the eigenvalue problem analytically only in certain asymptotic limits, and solve numerically otherwise.

(b) **Phase field –** For the phase field model the governing equations developed for the stability analysis in (a) will be coupled with a nonlinear partial differential equation (pde) describing the phase field variable. This will enable a single set of pdes to describe the entire domain, dispensing with the need to explicitly track an interface. Owing to rapid variations in the phase field variable near interfaces, newly developed codes at Oxford for rapid solution of nonlinear pdes will be utilized. This part of the project will be undertaken in collaboration with members of the Oxford Computing Laboratory. Throughout the project, the results will be compared with contemporaneous experiments in France. Operating parameters such as the base and far-field temperatures, initial colloid concentration, and solution pH will be entered into the model. The model output will predict ice growth rates, colloid concentration profile, and 3D ice morphology, all of which can be directly compared with experimental tomography and confocal microscopy results. The experiments will guide the theoretical modelling choices –which parameters are most important to include in the modelling– and vice versa.

Objectives
- **derive a partial differential equation for the phase field variable** that is thermodynamically consistent with the non-equilibrium colloidal phase diagram.
- **solve the resulting phase-field equations numerically** to predict 3D ice crystal morphologies and colloid concentration profiles, and compare with experimental tomography results.

Parameters to retrieve/predict from experiments
- temperature or heat flux at base of sample cell, far-field laboratory temperature, initial particle concentration and pH of colloid (input)
- growth rate of ice phase, position of ice-colloid interfaces, 3D morphology of ice crystals, concentration profile of colloidal particles in the ice and suspension phases (predict)

Milestones and timeline (total: 12 months) **– Begins at T_0+12 months**
- derivation of new phase-field equations: **6 months**
- numerical solution of equations and comparison with experimental results: **6-9 months**

Expected difficulties, alternatives
- tracking the 3D interface morphology in the presence of temperature and colloid concentration gradients will yield a multi-scale and stiff numerical challenge. With access to supercomputers and state-of-the-art computational techniques at Oxford we are confident such challenges can be overcome.
- alternative: depending on numerical stability issues, it may be useful to solve the equations within a level set framework rather than phase field. We have experts in both these methodologies at OCCAM (eg Jonathan Whiteley, Colin Campbell).

A postDoc will be hired at OCCAM for two years to work full time on this part of the project.

C - Controlling colloids freezing: effect of antifreeze proteins substitutes

The morphology of ice crystals can be of uttermost importance, whether for its implications with the damages inflicted to tissues in cryopreservation or the resulting morphologies of the porous materials obtained through colloids freezing. A wide array of techniques is available to control the morphology of the growing crystals and we propose here to explore one specific among these promising emerging approaches: the control of ice growth morphologies through antifreeze proteins (AFPs) substitutes. We recently demonstrated[15] how common substances such as sugar or salt could be used to control the growth morphologies. The objective here is to gain a **more specific and predictable control of the porous morphologies through a specific control of the ice crystal growth morphologies**. Antifreeze proteins, naturally present in living species such as fishes, insects and plants, act through several mechanisms to inhibit ice nucleation and/or severely control ice growth, through a specific adsorption on

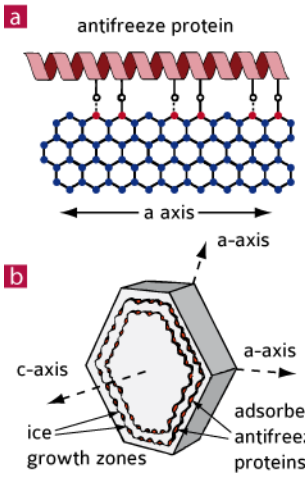

Fig 11: (a) Adsorption of antifreeze protein through Van der Waals and hydrogen bonding at the surface of ice. (b) Illustration of how antifreeze proteins inhibit ice crystal growth according to the adsorption-inhibition theory.

[15] E. Munch et al. (2009) Ibid.

particular crystalline planes of the ice crystals (fig 11)[16]. Little is understood about the effect of such substances in concentrated colloids, and we propose here to focus on **the effect of antifreeze proteins substitutes on the growth of ice in concentrated colloids**, **and to assess their potential for controlling the porous morphologies of ice-templated materials**, using the direct observations methods of ice growth in colloids developed in the other part of the project. We propose here to investigate the effect of substitutes and not AFPs, because of their availability and much lower price. For practical and economical considerations, AFPs cannot be considered as a viable processing aid for the developed processing route.

Objectives
- investigate the **effect of AFPs substitutes in the presence of colloids**. After a preliminary screening, the attention will probably focus on block copolymers such as double hydrophilic block copolymers based on poly-(ethylene oxide)-block-poly(1,4 butadiene) (PEO-b-PB), with hydroxyl or phosphate units in the side chain or polymers such as polyvinyl alcohol (PVA), which appears to be the most promising so far.

Materials and experimental conditions
- hard and soft spheres model (**PMMA and silica**) with controlled surface chemistry for the initial screening and fundamental investigations, and then eventually transfer to **alumina** for the control of the ice-templated materials.
- optical microscopy, confocal microscopy, X-rays tomography, DSC, XRD with cold stage to investigate ice crystals orientation patterns

Experimental developments: nothing specific, we take advantage here of the other developments of the project.

Milestones and timeline (total: 36 months) – **Begins at T_0+18 months**
- first screening of candidate substances through optical and confocal observations and materials processing to identify two or three promising substances: **6 months**
- measurement of ice crystals orientation and orientation pattern through XRD, measurement of ice unit cell in presence of AFPs substitutes: **6 months**
- compare the effect of AFPs substitute for hard (PMMA) and soft (silica) spheres systems: **12 months**
- use of these most promising substances to finely tune the characteristics of ice templated ceramics, preliminary assessment of mechanical properties: **12 months**

Expected difficulties, alternatives
- the exact mechanism(s) of action are still a matter of debate: hydrogen bonding, van der Waals bonding, entropy decrease, increase of the binding strength of internal hydrogen binding in ice, existence and role of a quasi-liquid layer (QLL), ordering of water molecules around the AFP, etc…
- AFPs substitutes can also interact with the colloids and therefore affect the observations. It might be necessary to observe the effect both in absence and in presence of colloids.
- AFPs substitutes can also modify several physical parameters of the system in presence of concentrated colloids, such as the suspension viscosity. Assessing the precise mechanism will therefore be difficult, although this might not be a requirement for the control of the porous structure.

A PhD student will be hired to work full-time on these aspects of the project. His work will greatly benefit from the development of the experimental observations techniques developed previously.

D - Applying colloids freezing to materials science

Materials obtained through the freezing of colloids may present unique and outstanding mechanical properties. Indeed, we have previously reported strength up to 160 MPa for porous hydroxyapatite –that is, **up to four times the strength usually reported** in the literature for HAP with similar porosity– while colleagues at LBNL proceeded with the work and obtained[17] toughness (K_{IC}) of more than 20 MPa.m$^{1/2}$ on alumina – polymer composites, increased by a factor of five as compared to monolithic, polycrystalline alumina. Apart from these preliminary results, little is known about the properties of such materials, and of the structure/properties relationships. We aim to progress here by combining three approaches:

(a) Processing porous ceramic materials, and subsequently **infiltrating them with an organic phase**, to obtain porous bioinspired composites. In these materials the porous ceramic scaffold is just functionalised with a thin polymer coating (fig 12).

(b) Characterizing the structure and properties of such materials and assessing their structure/properties relationships. These impressive results were obtained so far in the strongest direction of the tested materials, which are highly anisotropic. We aim also at mechanically characterising the materials in the other directions. The properties we seek to measure may be separated into three groups:

[16] P. L. Davies et al., Structure and function of antifreeze proteins, *Phil. Trans. R. Soc. Lond. B* 357, 927-935 (2002)
[17] E. Munch et al., Tough, bio-inspired hybrid materials, *Science*, 322[5907] 1516-1520 (2008).

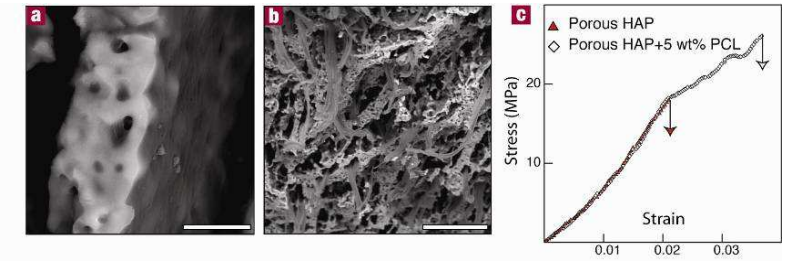

Fig. 12: Reinforcing porous hydroxyapatite with a polycaprolactone coating. Preliminary results showing an improvement both in flexural strength and strain. (a) Detail of a ceramic wall showing the polymer coating (b) fracture surface revealing crack bridging by polymer fibrils. Scale bars: (a) 10 µm, (b) 100 µm

- **basic mechanical properties: hardness, strength, load – displacement curve in traction, compression, torsion and bending, for static and dynamic conditions.** Indeed, for such architectured materials, even if they are based on ceramic, we do not expect plain linear, elastic – fragile behaviour: sliding of the elementary bricks may occur as it happens for example in nacre[18]. This part has a very high probability of success, since it uses classical methods, and only requires samples big enough (a few centimetres) for the tests.
- **advanced characterisation: measure of the crack-propagation behaviour in the different directions** (by single-edge notched beam and double torsion tests), **characterisation of the toughening mechanisms**. This part has a medium probability of success: this kind of measurement is mastered on dense materials, but to our knowledge it has never been conducted on porous materials, much less on **anisotropic**, porous materials. The use of image correlation should increase the probability of success.
- **very advanced characterisation: in-situ identification of the toughening mechanisms**: Stable crack growth during the R-curve measurements provides an opportunity to observe directly the toughening mechanisms and their relationship to the characteristic features of the microstructure. By performing these tests in situ in the scanning electron microscope or in the X-Ray tomograph, it is possible to measure the R-curve while simultaneously monitoring the evolution of damage mechanisms ahead of the crack tip and the extrinsic shielding mechanisms acting in the crack wake. We will then determine the role of the elementary bricks sliding, of their roughness, of the transverse connections between bricks… This requires the observation of the crack path, which may prove exceedingly difficult in porous materials. However, **two distinct methods for the crack observation in the tomograph will be tested**: direct observation thanks to a contrasting agent (infiltration with liquid with high X-Ray absorption), or indirect observation via measurement of the discontinuity of the displacement field obtained by 3D image correlation. This has been proved to be feasible on cellular materials[19]. In situ double torsion is already feasible using resources part of the project. This part is a bit risky, but even failing it would provide formidable insight for the use of these techniques on simpler materials.

All these characterizations will aim at **establishing relationships between processing microstructural parameters and mechanical properties and optimizing the functional properties**. The influence of parameters such as porosity (shape, size), roughness of the elementary bricks, amount of transverse links between the bricks, nature of a potential second phase, interfacial properties will be determined, and shall provide further guidelines for the materials design optimisation in an iterative process. **A PhD student will be hired to work full time on this part of the project**, with a formation in materials processing and mechanical characterization.

Objectives: processing – microstructure – mechanical properties relations, optimisation of the functional properties
Materials and experimental conditions

- porous alumina coated with polycaprolactone or poly lactic acid layers, in the shape of blocks typically 0.5 x 0.5 x 5 cm^3 to 0.5 x 3 x 5 cm^3
- indentation, traction, compression, torsion and bending, in static and dynamic conditions, double torsion ex-situ and in situ in a X-Ray tomograph

Experimental developments: Design of a novel stage to perform flexural tests in situ under the X-rays beam, at high resolution (local tomography inside a big sample could for instance be performed using a voxel size as small as 0.17 μm at the ESRF).
Milestones and timeline (total: 36 months) **– Begins at T_0+18 months**

- processing of porous ceramics and composites : **4 months**
- basic mechanical properties: **8 months**
- crack propagation behaviour: **10 months** (V-K_I curves are known for ceramics and composites)

[18] M.A. Meyers et al., Biological materials: Structure and mechanical properties *Progress in Materials Science,* 53 1–206 (2008).
[19] F. Hild et al., Three dimensional analysis of a compression test on stone wool, *Acta Mater* 57 3310-3320 (2009).

- in situ observations (in SEM and tomograph): **14 months** (toughening mechanisms are identified)

Expected difficulties, alternatives

- difficulties for in situ tomography observations in porous materials: alternative is investigating crack growth also in dense composites, which is easier and should allow us to properly design the setup and the experimental conditions.
- the desired size of the samples may be difficult to achieve: we may then work on smaller samples, with the risk of achieving lower quality results, the tested area not being completely representative of the overall material.

Conclusions

This **multi-disciplinary** project, at the borderline of materials science, offers a unique integration of approaches, competences and resources in materials science, chemistry, physics, mathematics and technological developments of observation techniques. For materials science only, the versatility of the process, associated to its proper control, could yield potential breakthroughs in numerous key applications of tremendous human, technological, environmental and economical interest such as catalysis, biomaterials or energy production, and open a whole **new field of research**. The proposed iterative approach, focussed on the most fundamental understanding of the physical mechanisms, should allow for progressive and substantial progresses into the complex phenomenon of colloids freezing. **Far-reaching implications beyond materials science are expected**, both from the development of new approaches and tools in mathematics and physics, and from the implications of colloids freezing in many situations and fields of research.

c. Resources

The unique integrated approach of this project, focussed on the most fundamental understanding of the freezing of colloids, requires a **unique combination of expertise** –in several disparate fields such as materials science, chemistry and mathematics–, **research environment** and **equipment**. The National Center for Scientific Research (CNRS) is a government-funded research organization, under the administrative authority of France's Ministry of Research. CNRS **encourages collaboration between specialists from different disciplines** in particular with the university thus opening up new fields of enquiry to meet social and economic needs. CNRS has developed **interdisciplinary programs** which bring together various CNRS departments as well as other research institutions and industry, and is thus a perfect fit for such a proposal.

CNRS laboratories are located throughout France, and employ a large body of tenured researchers, engineers, and support staff. A particular category of laboratories are the joint labs, where the CNRS is partnering with industry. The PI lab is such a **joint lab, partnering with Saint-Gobain**. Saint-Gobain, a French company, is the world leader in the habitat and construction markets. Saint-Gobain works with over 200 universities and research laboratories worldwide. **The joint lab is located in one of the largest R&D centre of Saint-Gobain**, in Cavaillon, France, and therefore benefits from the best of both worlds: easy networking and collaboration with CNRS laboratories and universities, with access to their resources and infrastructures, and the interest and support of a large company to convert the research breakthroughs into technological advancements. Like the CNRS, Saint-Gobain is of course particularly interested in the colloids freezing route. The laboratory already includes the majority of the necessary equipment for the project, including **suspensions characterization** (viscometer, zeta-potential, granulometry, IR spectrometer), **materials processing** (freezing stages, freeze-dryer, furnaces), **physical characterization** (BET, mercury porosimetry, SEM, dilatometer, X-ray diffraction) and **mechanical testing** (flexural and compressive strength, hardness).

Several additional resources are not located in the lab but available through the CNRS: a highly specific **directional solidification set-up for thin layers** (available at the IRPHE laboratory**,** UMR6594), a **tomograph** (laboratory based), which will be used to prepare the synchrotron experiments (available at the MATEIS laboratory, UMR5510), and specific mechanical testing stage for **slow crack growth experiments on ceramics,** which include a specifically designed stage for in situ double torsion testing under the tomograph (available also at the MATEIS laboratory). **Beam time** –corresponding to the subcontracting costs– will be bought to secure access to the **synchrotron at the ESRF** in Grenoble.

Since the necessary resources and majority of the equipment are already present in the PI lab in Cavaillon or through the CNRS, an important part of the budget is devoted to hiring students and postDocs to carry out the experiments. Overall, **three PhD students and two postDocs** will be hired during the entire duration of the project, **one postDoc being hired and coached directly at OCCAM in Oxford**. This should allow setting up a team with a critical mass to make substantial progress on this complex and multidisciplinary problem.

Members of the team for this project have contributed numerous milestones toward several key steps of the project. The team has been composed to make sure that all key aspects of the project can be tackled with the best expertise and resources available. In particular, one researcher outside of the PI laboratory will contribute to an

essential aspect of the project: **Dr. S. S. L. Peppin**, who will be in charge of the modelling development. Benefiting from a world-class research environment at the Mathematical Institute at the University of Oxford (UK), intellectual collaboration with Cambridge and Yale Universities, and good connexion with the soils and sea ice science communities, members of the Mathematical Institute have extensive experience in tackling moving boundary problems and phase field models in materials science. **Dr. Peppin, although just beginning his career, can be considered as the most advanced researcher worldwide on the topic of modelling of the solidification of colloidal suspensions**[20], and developed a new mathematical framework that accounts quantitatively for the particles interactions. **Dr. Peppin will hire and coach a 2-years postDoc** helping him in modelling developments. The Computing Laboratory network at OCCAM connects a variety of computers, including a large number of **Sun workstations** and PC-compatibles. For major computing projects (e.g. macroscale phase field modelling) OCCAM has **access to computers in the Oxford Supercomputing Centre**, as well as to a **222 teraflops supercomputer** at KAUST. These computing facilities combined with the dynamic collaborative atmosphere at the Mathematical Institute, provide an excellent setting within which to accomplish the mathematical modelling and numerical goals of the research.

	Cost Category	**Year 1**	**Year 2**	**Year 3**	**Year 4**	**Year 5**	**Total (Y1-5)**
Direct Costs:	*Personnel:*						
	PI	55 135	55 937	56 740	57 543	58 345	283 700
	Senior Staff	10 199	10 351	0	0	0	20 550
	Post docs	74 515	77 326	0	0	0	151 841
	Students	16 500	67 320	102 960	87 450	35 640	309 870
	Other						
	Total Personnel:	156 349	210 934	159 700	144 993	93 985	765 961
	Other Direct Costs:						
	Equipment	0	0	0	0	0	0
	Consumables	38 000	63 000	68 000	58 000	33 000	260 000
	Travel	16 652	17 804	9 000	9 000	7 000	59 456
	Publications, etc	638	650	0	0	0	1 288
	Other	0	4 160	0	0	0	4 160
	Total Other Direct Costs:	55 290	85 614	77 000	67 000	40 000	324 904
	Total Direct Costs:	211 639	296 548	236 700	211 993	133 985	1 090 865
Indirect Costs (overheads):	Max 20% of Direct Costs	42 327	59 308	47 340	42 399	26 797	220 171
Subcontracting Costs:	(No overheads)	40 000	40 000	40 000	40 000	0	160 000
Total Costs of project:	(by year and total)	293 966	395 856	324 040	294 392	160 782	1 469 036
Requested Grant:	(by year and total)	293 966	395 856	324 040	294 392	160 782	1 469 036

% of working time the PI dedicates to the project over the period of the grant:	**65%**

[20] S. S. L. Peppin et al., Pressure and relative motion in colloidal suspensions, *Phys. Fluids*, 17[5] 1-10 (2005). Solidification of colloidal suspensions, *J. Fluid Mech.*, 554 147-166 (2006), Morphological instability in freezing colloidal suspensions, *Proc. R. Soc. London A*, 463[2079] 723-733 (2007); Experimental verification of morphological instability in freezing aqueous colloidal suspensions, *Phys. Rev. Lett.*, 100[23] 238301-238304 (2008), Morphological instability of a nonequilibrium ice-colloid interface, *Proc. R. Soc. London A*, 466 (2113), pp. 177-194 (2009); On diffusion and permeation, *J Non-Equ. Thermo.*, 34 (4), pp. 355-369 (2009)

d. Ethical issues table

	Research on Human Embryo/ Foetus	YES	Page
	Does the proposed research involve human Embryos?		
	Does the proposed research involve human Foetal Tissues/ Cells?		
	Does the proposed research involve human Embryonic Stem Cells (hESCs)?		
	Does the proposed research on human Embryonic Stem Cells involve cells in culture?		
	Does the proposed research on Human Embryonic Stem Cells involve the derivation of cells from Embryos?		
	I CONFIRM THAT NONE OF THE ABOVE ISSUES APPLY TO MY PROPOSAL	yes	

	Research on Humans	YES	Page
	Does the proposed research involve children?		
	Does the proposed research involve patients?		
	Does the proposed research involve persons not able to give consent?		
	Does the proposed research involve adult healthy volunteers?		
	Does the proposed research involve Human genetic material?		
	Does the proposed research involve Human biological samples?		
	Does the proposed research involve Human data collection?		
	I CONFIRM THAT NONE OF THE ABOVE ISSUES APPLY TO MY PROPOSAL	yes	

	Privacy	YES	Page
	Does the proposed research involve processing of genetic information or personal data (e.g. health, sexual lifestyle, ethnicity, political opinion, religious or philosophical conviction)?		
	Does the proposed research involve tracking the location or observation of people?		
	I CONFIRM THAT NONE OF THE ABOVE ISSUES APPLY TO MY PROPOSAL	yes	

	Research on Animals	YES	Page
	Does the proposed research involve research on animals?		
	Are those animals transgenic small laboratory animals?		
	Are those animals transgenic farm animals?		
	Are those animals non-human primates?		
	Are those animals cloned farm animals?		
	I CONFIRM THAT NONE OF THE ABOVE ISSUES APPLY TO MY PROPOSAL	yes	

	Research Involving non-EU Countries (ICPC Countries)	YES	Page
	Is the proposed research (or parts of it) going to take place in one or more of the ICPC Countries?		
	Is any material used in the research (e.g. personal data, animal and/or human tissue samples, genetic material, live animals, etc) : a) Collected in any of the ICPC countries?		
	b) Exported to any other country (including ICPC and EU Member States)?		
	I CONFIRM THAT NONE OF THE ABOVE ISSUES APPLY TO MY PROPOSAL	yes	

	Dual Use	YES	Page
	Research having direct military use		
	Research having the potential for terrorist abuse		
	I CONFIRM THAT NONE OF THE ABOVE ISSUES APPLY TO MY PROPOSAL	yes	