ERC Starting Grant
Research proposal (Part B1)

Freezing Colloids

FreeCo

- Dr. Sylvain DEVILLE
- CNRS

- Project 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 biomimetic 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 phenomenon through in situ observations and mathematical modelling, to exert a better control on the processing route and achieve the full potential of this novel class of biomimetic materials. Materials will be processed and their structure/properties relationships optimized, while focussing on a case study: microreactors for the removal of pollutants for indoor air quality, indoor air pollution being one of the top human health risks. If satisfying progress is made, such knowledge will be applied to the more complex situations of emulsions and foams, with implications in cryobiology.

This project 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 in ceramics for biomedical applications, and in particular in ceramics containing yttria-stabilized zirconia (YTZP). Such ceramics could suffer a slow phase transformation at the sample surface in a humid atmosphere, followed by microcracking and a loss in strength, referred to as ageing. The zirconia manufacturers assumed that the problem of ageing under an in vivo situation was irrelevant until 2001, when several hundreds of hip prosthesis failures were reported in a very short period, quickly related to ageing. Even if limited in time and number and clearly identified to be process controlled, these events have had a catastrophic impact on the use of zirconia. New interpretations of ageing were made possible during my PhD by the development or improvements of techniques that allow monitoring of low temperature degradation from the atomic to the macroscopic scale, in particular with the application of atomic force microscopy to the monitoring of the early stages of ageing. A particular achievement of this work was the identification of ageing mechanisms in ceramic composites such as zirconia-toughened alumina, which promoted the interest for these materials. Such ceramics 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, and temporarily shifted my focus from dense to porous materials. My work at the LBNL was primarily concerned with the development of a new biomimetic processing route for porous ceramic, based on the freezing of colloids. 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. The simplest ideas being often the best, we quickly infiltrated these unique materials with a secondary organic phase and demonstrate how complex composites could be processed this way, with structure strongly reminding those of natural ones such as the nacre of seashells, such architectures exhibiting unique toughening mechanisms. 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. I consequently introduced simple ideas for controlling the freezing of colloids through templating and additives, for instance.

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 radiography and tomography, which provides real time in situ observations of crystal growth and particle redistribution. The feasibility experiments turned out very successful. In particular, we shed a new light on the nucleation and growth behaviour during the initial instants of freezing. More important was the recent discovery of metastable and unstable states of cellular solidification in such systems. We characterized these interface instabilities and proposed a mechanism to account for the experimental observations. These results have important implications for anyone involved in the solidification of colloidal suspensions, and are especially important for the materials scientists using the phenomenon to process porous materials, and should lay down solid foundations for further theoretical elaboration.

ii. Recognition and diffusion

The quality, originality and multidisciplinary nature of my work have been recognised at multiple levels, from the scientific community to the funding agencies and the public. Evidences of this recognition are multiple and briefly described below.

Publications and citations – I have been able to publish my work in the multidisciplinary peer-reviewed journals with the highest impact such as *Science*, or in leading journals in materials science such as *Nature Materials* (IF 23,1)*, Nanoletters* (IF 10,3)*, Advanced Materials* (IF 8,2)*, Annual Review of Materials Research* (IF 7,9) or *Biomaterials* (IF 6,6). These 27 papers resulted in over +380 citations to date, including +200 citations regarding the postdoctoral work (Scopus data, self-citations of all authors removed).

Results dissemination to the public – Of particular importance was the work on the solidification of colloidal suspensions, and its use in materials science as a novel processing route for biomimetic porous materials. The first paper was published in *Science* at the end of 2006, and attracted at that time a lot of attention from the scientific community and the public, through papers in the press, such as the New York Times, Daily Telegraph, Die Zeit, Frankfurter Allgemeine Zeitung, 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* with a paper by Philip Ball. A long popularization paper ("Artifical bone: the exploit coming from the cold") was published in the French science journal "Science et Vie" (monthly circulation: 335 000).

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 work on freezing was initially carried out within a NIH funded project. The research path opened by these results lead to a second paper in *Science* in 2008 ("Tough, bioinspired hybrid materials") by my former colleagues after my return to France. The exciting perspectives opened by these two 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 ANR (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. At the same time, I also applied at the ESRF to obtain some beam time at the synchrotron to investigate in situ the solidification of colloidal suspension by X-ray radiography and tomography. The application was successful and the four days access we obtained in 2008 to perform feasibility and preliminary experiments yielded already three papers, including a recent one in *Nature Materials*, validating the interest of the technique and already providing exciting new results.

Conferences – Consequently to this work, I was invited to deliver several invited talks in major international conferences in my field, such as the 10th European Ceramic Society Meeting (Berlin, 2007, "The materials that came in from the cold: nacre-like bioceramics through freezing"), and the 11th European Ceramic Society Meeting (Krakow, 2009, "Understanding and controlling freeze-casting of porous ceramics"). In addition, I have also been solicited to contribute to conferences organisation (MSE 2010, ECERS 2011), or to be part of the advisory board (ECERS 2009, CIMTEC 2010).

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 (Science, Nature Materials, Biomaterials or the Journal of the American Ceramic Society), an invited chapter in the Handbook of Biomineralization (Wiley-CH), the variety of journals soliciting me for reviewing papers (Phys Rev Lett, Angew Chem, Crystal Growth and Design, Journal of the American Ceramic Society, Biomaterials or Biomacromolecules) or an invited talk at the 2nd annual Orthopaedic Manufacturing technology exposition and conference (Rosemont, IL,USA, 2006, "Biomimetics as inspirational tools for tissue engineering"). To promote more actively this approach in the case of the investigations of colloids freezing, I am currently co-organizing 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. The workshop will take place in Avignon, France, in September 2010, and should gather researchers from materials science, geophysics, mathematics, cryobiology or food engineering. The feedback so far is extremely positive and we are looking forward to this exciting event.

iii. Assessment of the specific stage of my career

With a PhD defended 5 years ago, 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 permanent position at CNRS, since November 2006. To support my research activity, I have been able to hire a PhD thanks to the ANR grant. Owing to the complexity of the scientific problem to investigate and the promising perspectives open by the research, setting up a team with 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 France and in Europe. The ERC Starting grant would therefore be the optimal solution for such evolution.

1(b) Curriculum Vitae

Background

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)

- Biomimetic composites and nature-inspired approaches for materials processing
- Solidification of colloidal suspensions
- Atomic force microscopy of ceramics
- Mechanical properties and reinforcement mechanisms of porous and dense ceramics
- Degradation mechanisms in zirconia-based ceramics for biomedical applications: multiscale approaches

Scientific production

- 27 peer-reviewed papers
- 9 talks and 4 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 one PhD student (begun in 2008, expected to end in 2011)
- undergraduate students: 2 to 3 per year since PhD, for short term projects (3 to 6 months)
- supervising a technician (half time) in the lab.

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
- **Contributing editor** for the Journal of the American Ceramic Society
- **Referee** for the French Research Agency (ANR) in 2008 and 2009
- **Advisory board** for ECERS 2009 and CIMTEC 2011
- **Session organiser** for the ECERS 2011, on emerging colloidal processing route
- **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

- **French National Research Agency**: 350 k€ for 3 years (ending in Nov. 2010). Initiator and coordinator of the project.
- 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 leaded to new large scale project in **7thFP** (**project Nanoker**: "Structural Ceramic Composites for Top-End Functional Applications").

1(c) Early Achievement-Track-Record

i. Selection of publications

The publications marked with an asterisk (*) were not co-authored by my PhD supervisor. Citations data from Scopus (self-citations of all authors removed).

	Publication	Citations
1.	C. Pecharromán, J.F. Bartolomé, J. Requena, J.S. Moya, **S. Deville**, J. Chevalier, G. Fantozzi, R. Torrecillas, Percolative mechanism of ageing in zirconia containing ceramics for medical applications, *Adv. Mater.*, 15 [6] 507-511 (2003)	10
2.	**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)	8
3.	J. Chevalier, **S. Deville**, G. Fantozzi, J. Bartolomé, C. Pecharroman, J. Requena, S. Moya, R. Torrecillas, Nano-structured ceramics oxide with a slow crack growth resistance close to covalent materials, *Nanoletters*, 5(7) 1297-1301 (2005)	11
4.	**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)	18
5.	***S. Deville**, E. Saiz, R. K. Nalla, A. P. Tomsia, Freezing as a path to build complex composites, *Science*, 311 515-518 (2006)	114
6.	***S. Deville**, E. Saiz, A. P. Tomsia, Freeze-casting of hydroxyapatite scaffolds for bone tissue engineering, *Biomaterials* 27 5480–5489 (2006)	64
7.	***S. Deville**, E. Saiz, A. P. Tomsia, Ice-templated porous alumina structures, *Acta Mater* 55(6) 1965-1974 (2007)	21
8.	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)	12
9.	***S. Deville**, Freeze-casting of porous ceramics: a review of current achievements and issues, *Adv Eng Mater,* 10(3) 155-169 (2008)	14
10.	*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)	
11.	***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.* (accepted, available online 07/09/09)	
12.	***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.* (accepted, available online 09/24/09)	
13.	***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* (accepted Oct. 9th, 2009)	

ii. Patents

- One patent application in the US: Fabrication of Three-Dimensional Organic/Inorganic Scaffolds by Robocasting, US Patent 60/984,299, E. Saiz, J. Russias, S. Deville, A. P. Tomsia.
- Two patent applications pending in France (title not disclosed, but related to colloids freezing)

iii. Invited conference

- 107th Annual Meeting of the American Ceramic Society, "New information's on the surface tetragonal to monoclinic transformation in zirconia", S. Deville, J. Chevalier **2005**
- 2nd Annual Orthopaedic Manufacturing & Technology Exposition and Conference , Rosemont, Illinois (USA), "Biomimetics as inspirational tools for tissue engineering", S. Deville **2006**
- 10th European Ceramic Society Meeting, Berlin, "The materials that came in from the cold: nacre-like bioceramics through freezing", S. Deville **2007**
- 11th European Ceramic Society Meeting, Krakow, Poland, "Understanding and controlling freeze-casting of porous ceramics", S. Deville **2009**

iv. Awards and prizes

- Winner of the poster contest, 8th Conference of the European Ceramic Society, Istanbul, Turkey **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, Portoroz, Slovenia **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", 311, p.479-480 (2006)
- Nature Materials, "Material witness: cold comfort", 5, p.174 (2006)
- Journal of the American Dental Association, "New strategy found for creating artificial bone", 137(3) p.308 (2006)
- American Ceramic Society Bulletin, "Secrets of the sea yield stronger artificial bone", 85(4), p.4 (2006)
- Materials Today, "Seashell provides blueprint for composites", 9(3), p.10 (2006)
- Materials Today, "Ice template defines porous ceramics", 10(6), p.13 (2007)

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

- New York Times (US), "Secrets of Shells and Ceramics",
- Business Week (US), "A Sea Change For Artificial Bones?"
- Times (UK), "Frozen sea of possibilities for joints"
- Financial Times (UK) (science news of the week)
- Sueddeutsche Zeitung (Germany) (science news of the week)
- Frankfurter Allgemeine Zeitung (Germany) (science news of the week)
- Die Zeit (Germany) "Von Muscheln lernen" (*Learning from Seashells*)
- Daily Telegraph (UK) (science news of the week)
- Science News (US): "Mother-of-Pearl on Ice: New ceramics might serve in bones and machines"
- The Tribune (India), "Ceramics for bone"
- Chemistry and Industry Magazine (UK), "Tougher, lighter and as cool as ice"
- Courrier International (France, circulation>270 000), "Inspirée de la nature, une céramique plus solide" (*Inspired by nature, a stronger ceramic*)
- American Scientist (US), "Secrets in the shell", 95(5) (2007)
- Science et Vie (France, circulation >335 000), "Os artificiel, l'exploit qui vient du froid" (*Artificial bone : the exploit coming from the cold*), June 2006, p. 100-103
- L'Usine Nouvelle (France, circulation >70 000), "Des microscomposites qui s'inspirent de la nature" (*Nature inspired microscomposites*), n°3000, March 2006

Section 1d: ***Extended Synopsis of the project proposal***

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

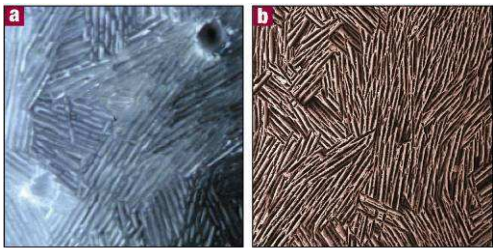

Fig. 2: Brine channels in sea ice and porous ceramics through colloids freezing

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 dense composite, if infiltrated with a suitable second phase. Using composites is a method to take advantage of both polymer and ceramics

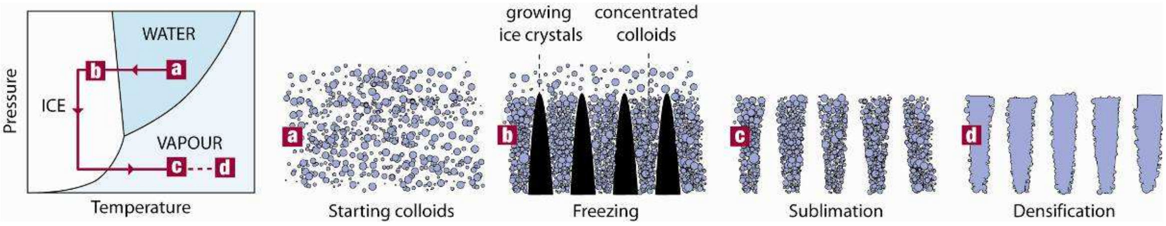

Fig. 3: Freezing colloids, a bioinspired materials processing route.

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**[1].

The preliminary results we published in *Science* in 2006[2] 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.

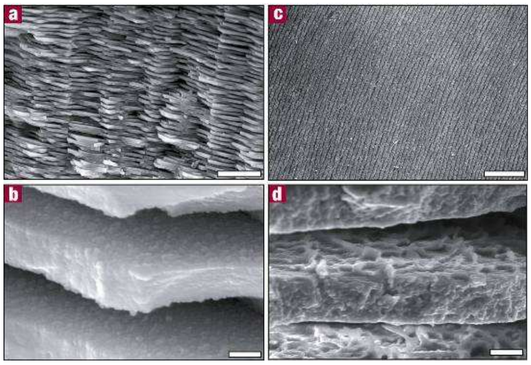

Fig. 4: (a-b) Nacre of the abalone shell and (c-d) nacre-like structures obtained with colloids freezing. Scale bars a: 10 µm, b: 0.3 µm, c: 300 µm, d: 10 µm

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[3] 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 and extensive work is still needed to assess the structure/properties relationships in this unique class of hierarchical materials.

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 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

[1] S. Deville et al., in Handbook of Biomineralization, Vol. 2, Wiley-VCH, Weinheim, 2007.
[2] S. Deville et al., Freezing as a path to build complex composites, *Science*, 311 515-518 (2006).
[3] S. Deville (2006), Ibid.; E. Munch et al., Tough, bio-inspired hybrid materials, *Science*, 322[5907] 1516-1520 (2008).

system out of equilibrium).

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:

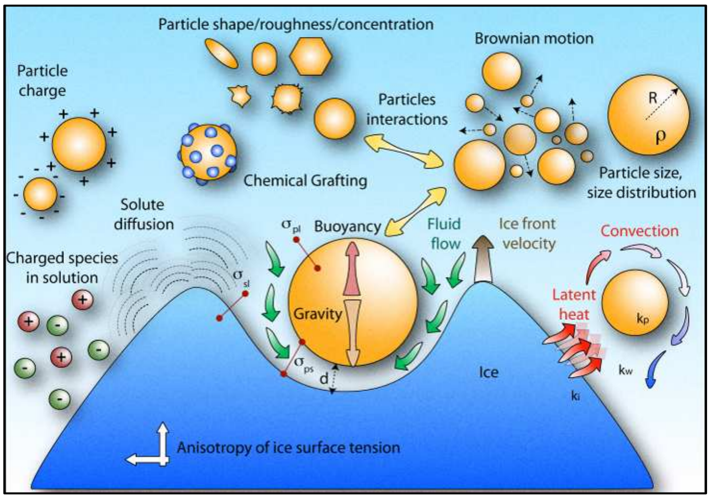

Fig. 5: Freezing colloids, schematic representation of the process and identification of the main parameters to take into account.

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 scientific problem.

b. 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 three subprojects, namely **observing, modelling** and **controlling** the freezing of colloids. Lessons learned from this cycle will be applied in materials science to

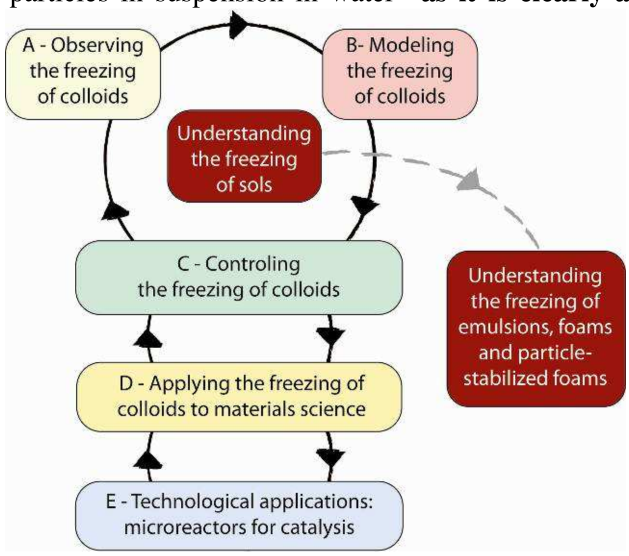

Fig. 6 : Project workflow

characterize and optimize the 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 and materials processing and characterization strategies. In particular, if satisfying progresses are made towards understanding and controlling the freezing of hydrosols, such knowledge will be applied to the more complex situations of emulsions and foams, with implications in cryobiology.

A - Observing the freezing of colloids in situ

A thorough experimental observation approach will be followed, using inorganic 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**:

- **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.
- **Confocal microscopy** with a cold stage, using model silica colloids marked in fluorescence to provide **in situ particle tracking possibilities**.
- **X-rays radiography and tomography**, which provides quantitative kinetic and structural observations. Our recent previous results, including a paper in *Nature Materials*, are raising 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. **We will investigate the possibility of adding markers** to assess more precisely local particle redistribution effects and individual particles trajectory.

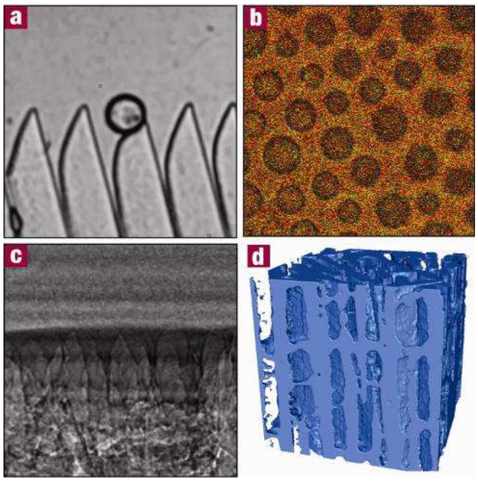

Fig. 7: Observing the freezing of colloids. Experimental techniques considered in this project includes optical microscopy in confined space (a), confocal microscopy (b), X-ray radiography (c) and X-ray tomography (d).

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 encourageing and promising.

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

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. We propose to explore a few of these promising emerging approaches, such as a**pplying external constraints and fields** (currents, electric field, magnetic field, pressure and temperature gradients), **templating, adding additives** or **impurities** to control the morphology if the ice crystals**,** and **modifying the colloids characteristics** (morphologies, size and surface state).

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 of the structure/properties relationships. We aim to progress here by combining three approaches: **processing porous ceramic materials, and subsequently infiltrating them with an organic phase** (to obtain biomimetic porous and dense composites), **characterizing the structure and properties of such materials and assessing their structure/properties relationships**, including attempts for in-situ identification of the toughening mechanisms using in situ testing under X-ray tomography, and **optimizing the structure** through 3D finite element modelling and image processing. All these characterizations will aim at establishing relationships between processing microstructural parameters and mechanical properties to optimize the functional properties.

E - Technological applications of colloids freezing, a case study: microreactors for the removal of pollutants

Applications of such uniquely structured materials are multiple. Of particular interest is the directionality of the structure, which can provide unique directional functional properties such as heat or mass transport or mechanical response. Such properties, combined with state of the art functionnalization of the surface, can potentially revolutionize several technological applications. **We propose to focus here on one case study, of particular technological, environmental and economical importance: microreactors for catalysis technology**, a key technology in achieving sustainable chemical processes and pollution control. Although more than 80% of the processes in the chemical industry depend on catalytic technologies, the sustainability as well as the catalytic and economic efficiency of such processes are often limited. It is currently estimated that as much as **30% of the fine chemicals and drugs currently in production could be made more efficiently using microreactors**. We propose to apply colloids freezing to the processing of microreactors and investigate their potential in the context of the **removal of pollutants for indoor air quality (IAQ)**. Volatile organic compounds (VOCs), present in buildings or cars, are wide-ranging classes of chemicals such as formaldehyde. Their release has widespread environmental implications, and has been linked to the increase in photochemical smog, the depletion of atmospheric ozone and the production of ground-level ozone. Environmental Protection Agency has validated that **indoor air pollution is one of the top human health risks**. The removal of formaldehyde is vital for improving IAQ and human being's health due to a carcinogenic risk. Current photocatalytic approaches require UV lights and are kinetically limited, leading difficult their utilization with very high space velocity (high air flow). On the other hand, active carbon sorbents need to be regularly replaced and are not selective. An alternative is to implement catalytic combustion of VOC at low temperatures. The objective of this case study will be to **develop microstructured reactors, using the colloids freezing processing route** as well as nanostructured catalysts with highly dispersed clusters of active metallic sites **for removal of formaldehyde at room temperature**.

Generalizing the freezing of hydrosols to emulsions, foam and particle-stabilized foams

We focussed so far on the freezing of hydrosol: solid colloidal particles in suspension in water. Although already remarkably complex, solid colloids present an intrinsic characteristic which simplify the analysis: the particles are not deformable. If the previous part of the project is successful **we propose to extend the previous approach and analysis to the case where the colloids can be deformed**. The whole category of hydrocolloids is now concerned, depending on the nature of the dispersed phase: **emulsions, foams and eventually particle-stabilized foams**. Although considerably more complex, the implications and applications are also much broader. In particular, bubbles –either solid or liquid– can be considered as an **analogue to biological cells**, so that we can potentially expect to gain new insights on the behaviour of cells during cryopreservation. Finally, when applying these concepts to the processing or porous materials, we can expect a whole new range of architectures and more freedom in the control of their structure.

Conclusions: opportunities and breakthroughs

This multi-disciplinary project offers a unique integration of approaches, competences and resources in materials science, chemistry, physics and mathematics. The proposed iterative approach, running from the most fundamental understanding of the physical mechanisms to technological applications 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 damages to plants through breaking and desiccation, and to roads, pavement and building foundation. The damages 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 the ice crystals 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 from 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 at 42 billion US$. 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

[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).

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 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 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 is still a subject of intense work. **Little has been made regarding the case of concentrated colloids**, although recent progress has been made for the situation of low interface velocity with a planar morphology.

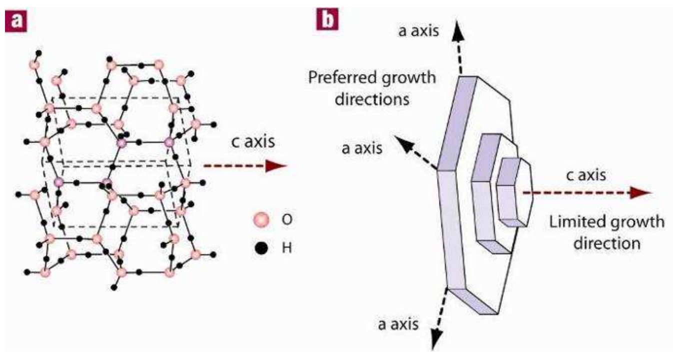

Fig. 2: Hexagonal structure of ice under the usual conditions of temperature and pressure, and anisotropy of growth kinetics.

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).

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

Hence, the freezing of colloids has long been 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 analysed (so far) nor understood. The unknowns of the phenomenon can be gathered in three categories:

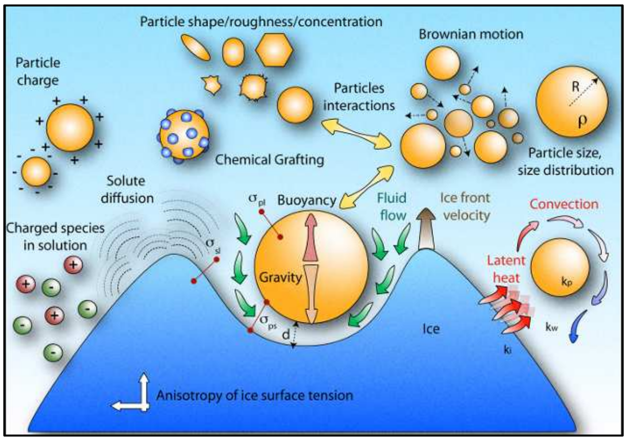

Fig. 3: Freezing colloids, schematic representation of the phenomenon and identification of the main parameters to take into account.

- **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.

Modelling the freezing of colloids: a necessary challenge

Theoretical approaches to modelling freezing colloids have focused 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 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. 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.

* **Linear/nonlinear stability analysis** – In previous research we demonstrated that ice segregation in colloidal systems occurs as a result of a morphological instability of the ice—colloid interface. In that 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 excellent agreement with experiment. 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

[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* (2009).

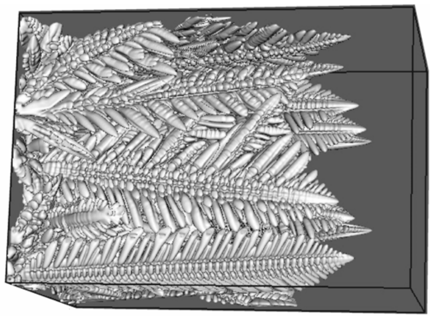

Fig. 4: Phase field modelling of directional dendritic growth of a Mg–Al alloy. After J. Eiken, Int. J. Cast Met. Res. (2009)

additional transitions including the pushing/trapping boundary in concentrated systems. Further generalizations, 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: an innovating bioinspired processing route... for biomimetic materials

Among the many possible applications of colloids freezing, its potential use as a processing route for biomimetic 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**.

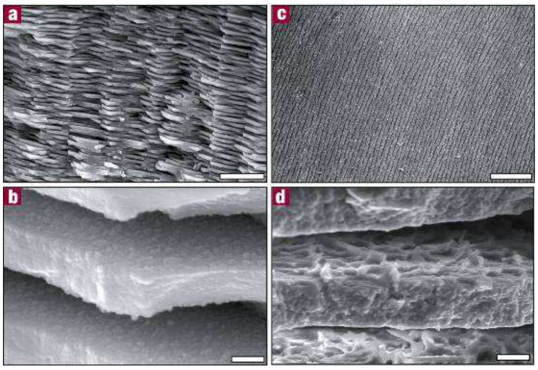

Fig. 5: Nacre of the abalone shell and nacre-like structures obtained with colloids freezing.(a-b): Structure of nacre of abalone shells, (c-d): structure of ice-templated materials, inorganic/organic composite (c) and details of inorganic porous structure (d). Scale bars a: 10 μm, b: 0.3 μm, c: 300 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 bio-inspired 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 biomimetic, environmentally-friendly processing route for biomimetic 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

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

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 and environmentally-friendly templating agent[7].**

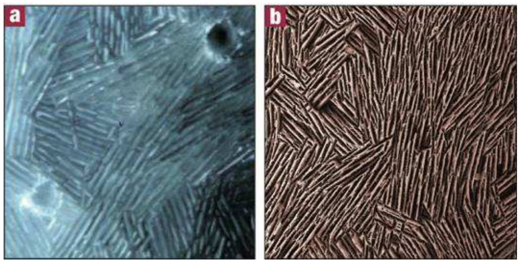

Fig. 6: Brine channels in sea ice and porous ceramics through colloids freezing

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. The resulting ceramic part is 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. **Using composites is a method to take advantage of both polymer and ceramics qualities, ideally to achieve materials with high stiffness and high toughness.** Nature is again clearly showing the path to follow, and the unique properties of natural materials such as nacre, bone or teeth are usually encountered through the unique combination of organic and inorganic phases, combined in sophisticated and complex structures whose properties far exceed what could be expected from a simple mixture of their components. 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, replicating its multilayer structure and other structural features (fig 5) such as roughness or inorganic bridges.

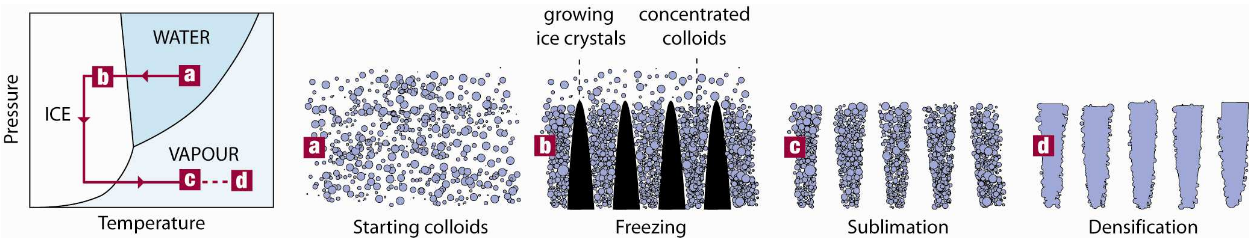

Fig. 7: Freezing colloids, a bioinspired materials processing route.

The preliminary results we published in *Science* in 2006 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. Advantage can be taken of the knowledge associated with other fields involved in colloids freezing or other solidification processes, described earlier. 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, catalysis, gas pump (oxygen, hydrogen), detectors, 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.

*** A unique biomimetic hierarchical structure**

The structures obtained here are unique, both in terms of structure and control of the structure. The multilayered structure revealed a strong texture arising from the structure of the ice[8]. Under proper freezing conditions, ice crystals are continuous throughout the samples, resulting in highly anisotropic materials. Besides the multilayer aspects, ten degrees of structural hierarchy have already been identified (fig 8), throughout all the

[7] S. Deville et al., Freezing as a path to build complex composites, *Science*, 311 515-518 (2006).
[8] S. Deville et al., Ice-templated porous alumina structures, *Acta Mater.*, 55 1965-1974 (2007).

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.

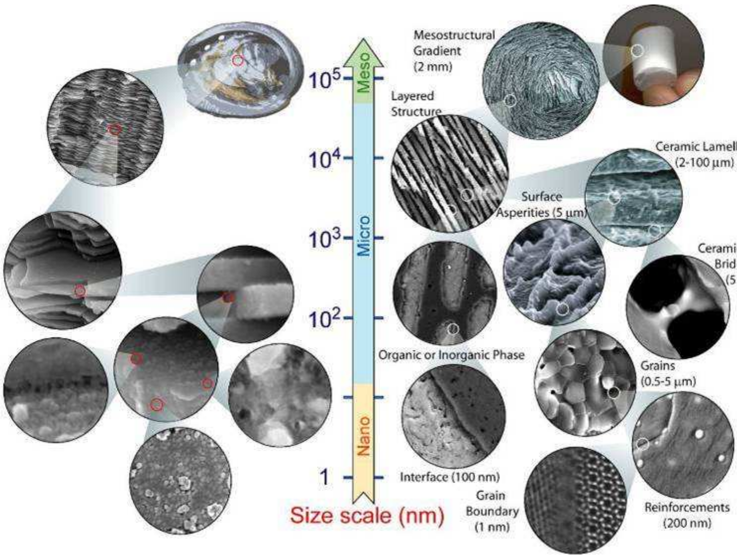

Fig. 8: Hierarchical structure of nacre (left) and freeze-casted materials (right)

*** 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. The process is nevertheless not limited to porous materials. Natural composites achieve strength and toughness through complex hierarchical designs that are extremely difficult to replicate synthetically. These porous structures can be in a further step partially or completely infiltrated with a second phase.

However, 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 structures and systems observed in nature are most of the time multifunctional, such as wood, providing structural stiffness, strength and toughness, along with nutrient transport to the leaves. **The structural hierarchy of these materials can be used to introduce, fulfil and enhance one or several particular functions**, like stiffness (associated with orientation gradients), gas transport (through directionality of the pores), structural resistance (through fine grains and reinforcement), ionic conductivity (along grain boundaries) and chemical reactivity (defined by surface chemistry). Such aspects have not been investigated so far, and could yield considerable improvements of some of the functional properties. The objective of this part of the project is therefore to assess the structure/properties relationships in this unique class of porous hierarchical materials.

Technological applications of colloids freezing, a case study: biomimetic microreactors for catalysis

Applications of such uniquely structured materials are multiple. Of particular interest is the directionality of the structure, which can provide unique directional functional properties such as heat or mass transport or mechanical response. Such properties, combined with a proper functionnalization of the surface, can potentially revolutionize several technological applications. **We propose to focus here on one case study, of particular technological, environmental and economical importance: microreactors for catalysis technology**, a key technology in achieving sustainable chemical processes and pollution control. Although more than 80% of the processes in the chemical industry depend on catalytic technologies, the sustainability as well as the catalytic and economic efficiency of such processes are often limited, in particular in case of heterogeneously catalyzed chemical processes. Pressed by margin shrinkage and environmental considerations to streamline costs and reduce environmental damage, **many of the biggest names in fine chemicals, specialty chemicals, pharmaceuticals and consumer products are developing applications for microreactors**. Some companies are already using them for commercial production, and typical applications of microreactors technology include ethylene via the oxidative dehydrogenation of ethane, dimethylether directly from syngas, the Fischer-Tropsch process, steam methane reforming, hydrocracking, higher alcohols from syngas, and the production of methanol, styrene, vinyl acetate monomer, formaldehyde and ethylene oxide. It is currently estimated that as much as **30% of the fine chemicals and drugs currently in production could be made more efficiently using microreactors**.

Issues related to mixing –heat transfer, mass transfer and hydrodynamics– which slow transformations and allow side reactions in large reactors, are **effectively eliminated in microreactors**, where mixing is essentially

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

instantaneous, hence the speed. **Reaction kinetics becomes the only factor limiting progress** and rates can increase dramatically. More selective and reliable chemistry results from greater process control. Flow rate, channel length and extremely efficient heat transfer can all be adjusted in microreactors to optimize reaction time and temperature. One benefit is less waste, which in turn lowers costs. The proposed project deliberately addresses two key issues to overcome current restrictions in microreactors technology by:

- **Designing a new generation of nanostructured microreactors** based on the freezing of ceramics colloids offering a wide range of variable functionalities on the nano, micro and meso scale.
- **Tailoring surface functionalities of these biomimetic microreactors** by controlled immobilization (heterogenization) of highly efficient catalytic sites such as metallic clusters.

The ice-templated ceramics and associated technology offer a unique combination of fast, economic and environmentally friendly process, structure and properties, which we believe can induce real breakthroughs if used as microreactors. These advantages will be achieved by the characteristics of the ice-templated porous ceramics and the corresponding production process, given in table 2.

Table 2: Features of the freezing approach and expected functional improvements in microreactors technology.

Unique features of the freezing approach	Functional property, expected advantages
Directional porosity and structure	Reduce heat and mass transport limitation
Very high specific surface area	Optimal reactivity and access of reagents to the catalytic sites
Easy tuning of porosity characteristics: pore shape, size, surface roughness, porosity amount	Facilitate the optimisation of functional properties
Large pore size in channels, combined with directionality	Reduce limitations due to clogging of catalysts under repeated use.
Very high strength	Long term mechanical performance
Versatility of the processing route	The nature of the microreactor can be adjusted as a function of specific requirements associated to the corresponding chemistry
One-pot synthesis is possible with the sol-gel approach: no high temperature consolidation step	The catalyst can be incorporated from the beginning of the process.

These advanced continuous catalytic processes will be applied to indoor air quality (IAQ). Volatile organic compounds (VOCs), present in buildings or cars, are wide-ranging classes of chemicals and currently over 300 compounds are considered as VOCs by US EPA[10]. **Their release has widespread environmental implications**, and has been linked to the increase in photochemical smog, the depletion of atmospheric ozone and the production of ground-level ozone. Formaldehyde, acetaldehyde, and acrolein are highly reactive compounds released from several sources into the indoor environment. Formaldehyde is released by various building materials, including pressed wood products made with urea–formaldehyde resins or phenol–formaldehyde resins, conversion varnishes, and latex paints. Some carpets also emit formaldehyde and acetaldehyde. In addition, formaldehyde, acetaldehyde, and acrolein are combustion products; they are present in wood smoke and in tobacco smoke. Environmental Protection Agency has validated that **indoor air pollution is one of the top human health risks**. The studies on IAQ have been transited gradually to indoor volatile organic compounds (VOCs). The removal of formaldehyde is vital for improving IAQ and human being's health due to a carcinogenic risk. The objective of this case study will be to **develop microstructured reactors as well as nanostructured catalysts with highly dispersed clusters of active metallic sites for removal of formaldehyde at room temperature**. Present air purification technologies for VOC trace contaminant degradation use photocatalysts or active carbon filters. The photocatalytic processes require UV lights and are kinetically limited, leading difficulties in their utilization with very high space velocity (high air flow). On the other hand, active carbon sorbents need to be regularly replaced and are not selective. An alternative is to implement catalytic combustion of VOC at low temperatures. This technology could be combined with active carbon filters.

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

[10] US EPA, Characterizing air emissions from indoor sources, EPA report: EPA/600/F-95/005, US Environmental Protection Agency, Washington, DC, 1995

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 strong 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 to investigate the colloid redistribution occurring during freezing. The corresponding space (submicronic) and velocity (tens to hundreds of microns/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. In the case of concentrated colloids, similar approaches cannot be used and new experimental approaches must 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 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 concentration of colloids, such as the freezing temperature curve and a dependence of particle diffusivity upon concentration and temperature. The situation becomes even more complex –if possible– when deformable colloids such as cells or bubbles are considered.
- **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[11].
- **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

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

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 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.

Progress will be accomplished through iterative cycles of three subprojects, namely observing, modelling and controlling the freezing of colloids. Lessons learned from this iterative approach will be applied to materials science in a threefold approach. Control of the porous architecture will benefit from the knowledge learned during the observation/modelling/control cycle. The first objective is to better assess and understand the structure/properties relationships of these ice-templated materials and composites. The second objective is to optimize the porous architectures through a dialog between finite element (FE) modelling of the obtained architectures and the modification of these architectures by image processing constrained by the results of FE. The third objective is a case study of the application of such materials to overcome important technological issues in catalysis. 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. In particular, if satisfying progress is made towards understanding and controlling the freezing of hydrosols, such knowledge will be applied to the more complex situations of emulsions, foams and particle-stabilized foams.

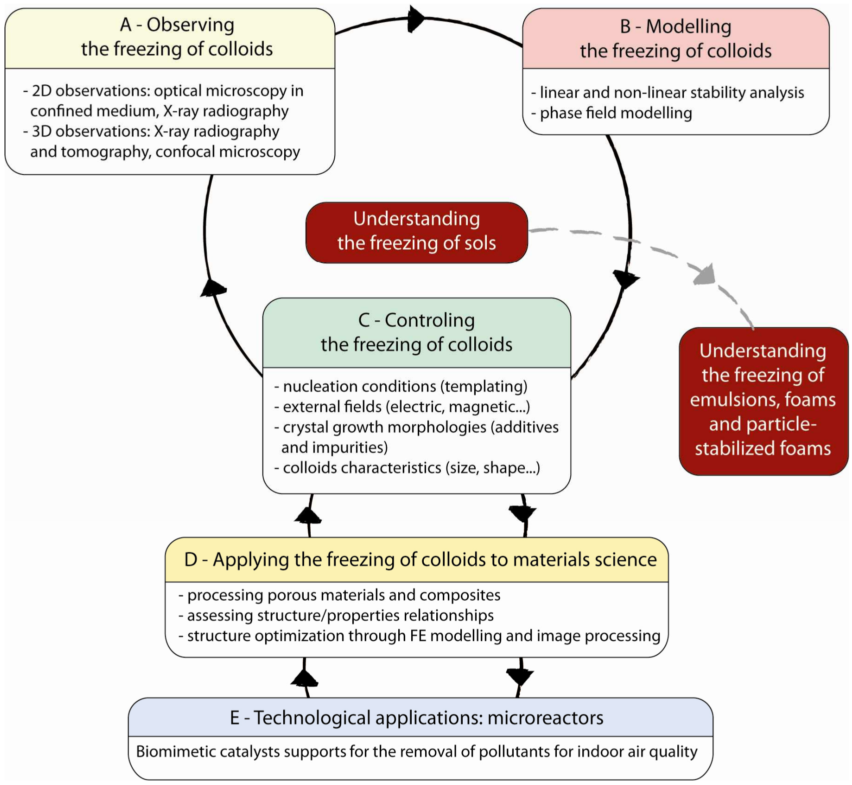

Fig. 9: Project workflow

A - Observing the freezing of colloids in situ

This project is based on a hands-on approach. 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 inorganic colloids such as ceramic particles or clay. A variety of in situ observation techniques will be used to follow the crystals nucleation and growth and corresponding particles redistribution (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.

– **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)[12]. 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.
– **Confocal microscopy** with a cold stage will be used, using model silica colloids **marked in fluorescence** (red and green) and exhibiting **adapted surface chemistries**, to provide **in situ particle tracking possibilities**. Preliminary results were again encouraging (not published, fig 10b), but further developments of the technique are necessary to work under correct, if not optimal, conditions.

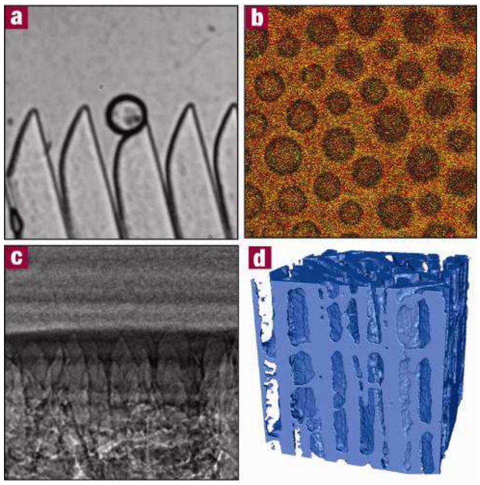

Fig. 10: Observing the freezing of colloids. Experimental techniques considered in this project includes optical microscopy in the bulk (a) and in confined space (b), confocal microscopy (c), X-ray radiography (d) and X-ray tomography (e).

– **X-ray radiography and tomography**, which provides quantitative kinetic and structural observations (fig 10c-d). Our recent previous results[13], including a paper in *Nature Materials*[14], 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. **We will investigate the possibility of adding markers** –particles of similar size but with a very different coefficient of X-rays absorption, such as CeO_2– to assess more precisely local particle redistribution effects and individual particles trajectory. The solidification experiments will be conducted in very thin capillaries to limit the overlapping effects of particles through the sample thickness.

A PhD student will be hired to work full time on this part of the project. 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 –** A thermodynamic model will be developed of the nonequilibrium phase diagram of colloids. This will replace the equilibrium diagram used in our previous models[15]. 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 separating stable from unstable states. When possible the calculations will be performed analytically – in more complex cases the eigenvalue problem will be solved numerically.

(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. The experiments will guide the theoretical modelling choices –which parameters are most important to include in the modelling– and vice versa.

C - Controlling colloids freezing

Whether for its potential use or to control its detrimental consequences, the freezing of colloids will greatly benefit from a better control of its process. Such control can be achieved through a variety of techniques, and we

[12] M. Georgelin et al., Onset of sidebranching in directional solidification, *Phys. Rev. E*, 57 3189-3204 (1998).
[13] 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.
[14] S. Deville et al. (2009) Ibid.
[15] S.S.L. Peppin et al. (2008) Ibid.

propose here to explore a few of these promising emerging approaches, such as:

- **Applying external constraints and fields – currents** (liquid flow)**, electric field, magnetic field, pressure and temperature gradients**. A good example of the trans-disciplinary approach at work here is the influence of hydrodynamic currents on the orientation of the growing crystals[16]. The c-axes are sometime perpendicular to the plane of the ice platelets composing sea ice and, over distances of many kilometres, are found to be aligned about a particular direction in the horizontal plane. Laboratory and field results indicate that this alignment is due to the flow of sea water at the ice-water interface which forces the c-axes to lie parallel to the current. We propose to apply this effect to control the orientation of the ice crystals in colloids in the laboratory, by applying various types of flow, in order to gain further control over the hierarchical structure of the resulting materials.
- **Templating –** The idea of templating the growth of crystals by controlling their nucleation is of course not new, but can nevertheless find a fresh take in this context. Little is known about the nucleation and growth conditions in the concentrated colloidal suspensions, and we propose to try to address some of these issues here. We already reported experiments with proof of principles for templating[17], although plenty of room for improvements is available, and the actual behaviour of the system in the presence of templates was far from being understood. Particularly puzzling was the observation that crystals were found to grow **perpendicular** to the template. The importance of nucleation conditions, or seeding, has also been clearly revealed for sea or lake ice growth[18], and can again serve as inspiration in our approach.
- **Adding additives and impurities –** 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. Of particular interest is the effect of additives or impurities on the growth of the ice crystals, substances usually referred to as cryoprotectants in the cryoengineering literature. The choice of additives is nevertheless not limited to commonly used cryoprotectants, and we recently demonstrated[19] how common substances such as sugar or salt could be used to control the growth morphologies. Little is understood about the effect of such substances, and we propose to focus on a few of these to further investigate their mechanism on ice growth. **In particular, we propose to investigate the effect of common cryoprotectants on the growth of ice in concentrated colloids**, such as DMSO, ethylene and propylene glycol or antifreeze proteins, **and to investigate the binding mechanisms of such substances at the water/ice interface**, using direct observations of ice growth in colloids.
- **Playing with colloids characteristics –** The characteristics and properties of the colloids, such as their size, shape, aspect ratio, or surface energy could be of tremendous importance in regards of the mechanisms controlling particle redistribution in front of the solidification interface. The existence of a critical size of particle above which all particles are entrapped has already been widely demonstrated. The influence of colloids characteristics is nevertheless not limited to this critical velocity, and **we propose to investigate this in deeper details, by using model colloids of controlled morphologies, size and surface state**.

  A PhD 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[20] toughness (K_{IC}) of more than 20 MPa.m$^{1/2}$ on alumina – polymer composites, increased by a factor of 5 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:

- **Processing porous ceramic materials, and subsequently infiltrating them with an organic phase**, to obtain biomimetic composites. Two categories of composites will be processed: porous composites, where the porous ceramic scaffold is just functionalised with a thin polymer coating (fig 11), and dense composites, where the polymer is completely filling the porous ceramic structure.

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[16] P. J. Langhorne et al., Alignment of crystals in sea ice due to fluid motion, *Cold Regions Sci. Tech*, 12[2] 197-214 (1986).
[17] E. Munch et al., Architectural control of freeze-cast ceramics through additives and templating, *J. Am. Ceram. Soc.*, 92[7] 1534-1539 (2009).
[18] A. J. Gow, Orientation textures in ice sheets of quietly frozen lakes, *J. Cryst. Growth*, 74[2] 247-258 (1986).
[19] E. Munch et al. (2009) Ibid.
[20] E. Munch et al., Tough, bio-inspired hybrid materials, *Science*, 322[5907] 1516-1520 (2008).

– **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:
    - **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. 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 porous, anisotropic materials. The use of image correlation should increase the probability of success.
    - **very advanced characterisation: in-situ identification of the toughening mechanisms**: in-situ mechanical testing in an X-Ray tomography may allow us to understand and quantify the toughening mechanisms: role of the sliding of the elementary bricks, 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 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[21]. In situ double torsion is already feasible using resources part of the project (see part c, resources, p.14). 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, at the present moment) will be developed and implemented. This part is a bit risky, but even failing it would provide formidable insight for the use of these techniques on simpler materials. We plan to limit the risk by investigating crack growth both in porous materials and porous and dense composites, obtained through infiltration of the porous ceramics. The crack observation in dense composites is much easier and should allow us to properly design the setup and the experimental conditions for the in situ testing.

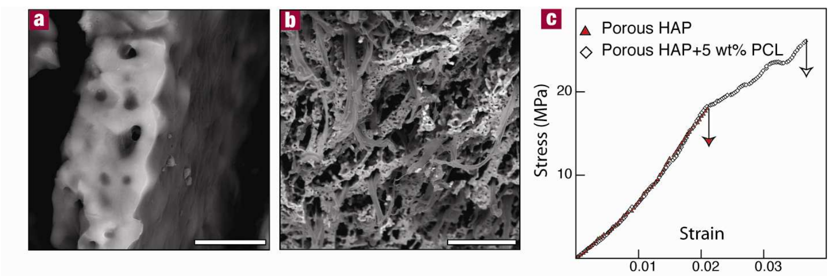

Fig. 11: Reinforcing porous ceramics with a polymer coating. Preliminary results showing an improvement both in flexural strength and strain. (a) Detail of a ceramic wall showing the polymer coating (b) fracture surface revealing crack bridging by polymer fibrils. Scale bars: (a) 10 µm, (b) 100 µm

– **Optimization of the structure through 3D finite element modelling and image processing** – The 3D images of the actual architectures produced during the project by tomography can also be regarded as starting points for improving the optimisation of different properties. **Mechanical properties can for instance be optimised by a dialog between FE calculations on the obtained architectures, and the modification of these architectures by image processing** (mathematical morphology) constrained by the result of the FE. The resulting "modified" microstructure should exhibit optimal mechanical properties. Similar optimisation ways could also be derived for parameters such as the specific surface (catalysis) or the tortuosity (fluid or gas transport properties). A work in such a direction would allow us to design a tool for microstructure optimisation. This tool could provide the information of the modification to apply to the architecture could be used as a guideline to improve or adjust the process in an iterative approach, in view of a specific application, through a modification of the processing conditions or colloids formulation, for example. It could also suggest new application possibilities for the produced structures.

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

[21] F. Hild et al., Three dimensional analysis of a compression test on stone wool, *Acta Mater* 57 3310-3320 (2009).

for the materials design optimisation in an iterative process. **Two postdocs will be hired** to perform these analyses: one with an expertise in materials processing, mechanical characterization and X-rays tomography, and a second one with an expertise in finite element modelling and image processing.

E - Technological applications of colloids freezing: removal of pollutants for indoor air quality

This part of the project will address different scientific and technological challenges in the fields of **materials science, catalytic chemistry and chemical engineering**. The key objective of this subproject is to make use of the versatile, fast and environmentally benign process of freezing colloids for preparing biomimetic ceramic materials to **develop novel tailor-made nanostructured ceramic microreactors acting as catalyst supports**. These supports, which can be made from any type of ceramic powder, have to meet the requirements of both catalytic chemistry and continuous process design. The contribution to catalytic chemistry is based on the creation of tailored surface functionalities being able to immobilize catalytic active species through physical interaction and/or chemical bonding. With respect to process design, the high and hierarchical porosity can be used to manage aspects of fluid dynamics through the support (e.g. flow and residence time distribution) providing minimized flow resistance (macroporosity) and increased accessibility to catalytic sites (mesoporosity).

We propose to use **biomimetic catalysts obtained by freezing** for achieving **ceramic-based microreactors for catalytic combustion of VOCs**, which could significantly:

- improve the management of the temperature with autothermal process in the range 50-100°C, without air preheating,
- increase the dispersion of metallic active sites by developing a ceramic structure which combines reasonable mechanical properties and large specific surface areas,
- promote the interactions between reactants and active sites by confining the reaction in micrometric size channels of the ceramic microreactor,
- increase the flexibility of the air treatment system in terms of size and utilization.

The aim is to develop **ceramic-based microreactors from alumina, zirconia, titania and ceria with high specific areas**. **The metallic active sites will be gold nanoparticles dispersed in the porosity**. Gold is active for VOC combustion at low temperatures but must be used on the nanoscale. The hierarchical structure of the biomimetic honeycomb will be adjusted in order to stabilize extremely low the size of gold particles coupled with a good accessibility of the polluted air.

Systematic investigations will be conducted to achieve a deliberate variation of material properties as a result of different preparation methods and process conditions. The goal is to deliberately adjust internal geometries and surfaces of the porous ceramics which can be directly correlated to the specific requirements defined by the different catalytic reactions (surface areas, surface functionalities, pore sizes, flow through characteristics, mechanical strength, etc.). **Ceramic samples which already contain additional ceramic or metallic components as catalytic active materials will be elaborated**. All samples will be analyzed and characterized in detail by various physical, optical and chemical techniques. On basis of these data, the most interesting and promising ice-templated ceramic systems will be selected that will be tested as catalyst support material in the next step.

Catalytic activity measurements for VOC combustion in air will be performed at atmospheric pressure in a specific continuous flow reactor. Catalytic performances will be carried out in a low temperature range: 20-100°C and for reactive mixtures containing synthetic air and traces of VOCs. A first series of experiments will be performed with a single VOC, i.e. formaldehyde (from few ppm to 100 ppm) in order to select the most effective ceramic-based microreactors. The impact of the space velocity both on VOC conversion and by-products formation will be deeply analyzed. Reactants and products will be analyzed with a micro-gas chromatography and on-line Infra-Red analysers for CO and CO_2. Possible presence of by-products will be checked with a gas chromatograph coupled with a mass spectrometer (GC-MS) or with a PTR-MS (Proton Transfer Reaction Mass Spectrometer) which allows the on-line VOCs detection at the ppb level.

Secondly, the most effective ceramic-based microstructure honeycombs associated with gold nanoparticles will be involved in a **more realistic polluted air containing several VOCs**. Formaldehyde, acetaldehyde, toluene and dichloromethane will be mixed at the ppm level in air. The catalytic performances will be measured at very high space velocity in order to simulate indoor air treatment.

Generalizing the freezing of hydrosols to emulsions, foam and particle-stabilized foams

We focussed so far on the freezing of hydrosol: solid colloidal particles in suspension in water. Although already remarkably complex, solid colloids present an intrinsic characteristic which nevertheless simplify the analysis: the particles are not deformable. If the previous part of the project is successful, i.e. good progress has been made in understanding and modelling the freezing of colloids, **we propose to extend the previous approach and analysis to the case where the colloids can be deformed**. **The whole category of hydrocolloids is now**

concerned, depending on the nature of the dispersed phase: emulsions, foams and eventually particle-stabilized foams[22] (fig 12). Although considerably more complex –deformable interface, temporal stability to take into account– the implications and applications are also much broader. In particular, bubbles –either solid or liquid– can be considered as an analogue to biological cells, so that we can potentially expect to gain new insights on the behaviour of cells during cryopreservation. Predictive models built from such experiments can then potentially be used to develop novel protocols to preserve cells and tissues for transplantation. **Using bubbles instead of cells present several advantages**: size more easily tuned, little if no degradation during observations –the influence of the X-ray beam for example can be particularly deleterious in the case of cells–, and possible control of the interfacial properties via the surface tension to name a few. In addition, when applying these concepts to the processing of porous materials, we can reasonably expect a whole new range of architectures and more freedom in the control of their structure. **A postdoc will be hired to investigate this approach**.

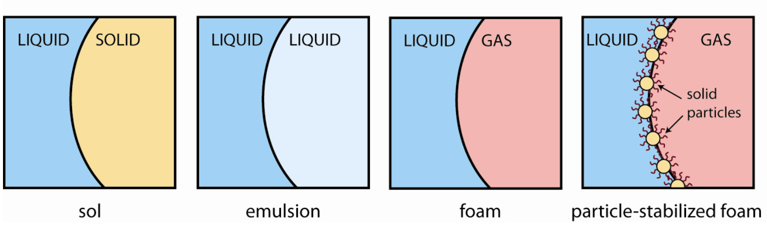

Fig. 12: Various types of hydrocolloids.

Conclusions

This **multi-disciplinary** project 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, but also biomaterials or energy production, and open a whole **new field of research**. The proposed iterative approach, running from the most fundamental understanding of the physical mechanisms to technological applications 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, from the most fundamental understanding of the freezing of colloids to the technological applications, requires a **unique combination of expertise** –in several disparate fields such as materials science, chemistry and mathematics–, **research environment** and **equipment**. The PI laboratory in Cavaillon 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, mechanical testing, X-ray diffraction) and **mechanical testing** (flexural and compressive strength, hardness). In addition, a platform with all the necessary equipment for **catalytic tests** is already available in the lab (micro-gas chromatography, on-line Infra-Red analysers for CO and CO_2, gas chromatograph coupled with a mass spectrometer (GC-MS), Proton Transfer Reaction Mass Spectrometer), since catalysis is the main application focus of the lab. Additional resources not located in the lab but available through the CNRS include a **confocal microscope equipped with a cold stage** –which will be used with calibrated model silica particles marked in fluorescence)– and a highly specific **directional solidification set-up for thin layers**. **Beam time** –corresponding to the subcontracting costs– will be bought to secure access to the **synchrotron at the ESRF**.

Since the necessary resources and equipment are already present in the lab, the majority of the budget is devoted to hiring students and postdocs to carry out the experiments. Overall, **two PhD students and six postdocs will be hired** during the duration of the project. 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: three researchers outside of the PI laboratory will contribute to very specific aspects of the project, X-ray tomography, mathematical modelling and slow crack growth experiments.

- **Dr. Eric Maire** (from CNRS, 93 papers, +1250 citations) is among the world leaders of X-ray tomography applied to materials science. He will bring his expertise on tomography to the project through co-coaching of a PhD and a postdoc, and contribute to the structure optimisation through FE modelling and image processing, based on the tomography data. Available additional resources include a **tomograph** (laboratory based).
- **Dr. S. S. L. Peppin** will be in charge of the modelling development. Benefiting from a world-class research

[22] U. T. Gonzenbach et al., Ultrastable particle-stabilized foams, *Angew. Chem*, 45 [21] 3526-3530 (2006).

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, **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**[23], 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.

- Finally, one challenging key aspect of the characterization of the mechanical properties of the biomimetic materials is the identification of the toughening mechanisms by slow crack growth experiments. Although the mechanical characterization will be performed in the PI lab, the project will benefit for these particular experiments from the expertise of a member of the ceramic group of the MATEIS laboratory (CNRS), recognized as the **world leader in slow crack growth experiments on ceramics** and the project will benefit from their equipment to perform such experiments, which include a specifically designed stage for in situ double torsion testing under the tomograph.

	Cost Category	Year 1	Year 2	Year 3	Year 4	Year 5	Total (Y1-5)
Direct Costs:	*Personnel:*						
	PI	52786	53572	54357	55143	55929	271787
	Senior Staff						
	Post docs	74862	101930	122200	24910	50760	374662
	Students	16500	67320	68640	52470	0	204930
	Other						
	Total Personnel:	144148	222822	245197	132523	106689	851379
	Other Direct Costs:						
	Equipment						
	Consumables	21912	62913	59000	45000	13000	201825
	Travel	16727	16728	9000	9000	9000	60455
	Publications, etc		1288				1288
	Other						
	Total Other Direct Costs:	38639	80929	68000	54000	22000	263568
	Total Direct Costs:	182787	303751	313197	186523	128689	1114947
Indirect Costs (overheads):	Max 20% of Direct Costs	36557	60750	62639	37305	25738	222989
Subcontracting Costs:	(No overheads)	40000	40000	40000	40000	0	160000
Total Costs of project:	(by year and total)	259344	404501	415836	263828	154427	1497936
Requested Grant:	(by year and total)						1497936

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

[23] 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*, in press (2009), On diffusion and permeation, *J Non-Equ. Thermo.*, in press (2009).

d. Ethical issues

	Research on Human Embryo/ Foetus	YES	NO
	Does the proposed research involve human Embryos?		X
	Does the proposed research involve human Foetal Tissues/ Cells?		X
	Does the proposed research involve human Embryonic Stem Cells (hESCs)?		X
	Does the proposed research on human Embryonic Stem Cells involve cells in culture?		X
	Does the proposed research on Human Embryonic Stem Cells involve the derivation of cells from Embryos?		X
	DO ANY OF THE ABOVE ISSUES APPLY TO MY PROPOSAL?		X

	Research on Humans	YES	NO
	Does the proposed research involve children?		X
	Does the proposed research involve patients?		X
	Does the proposed research involve persons not able to give consent?		X
	Does the proposed research involve adult healthy volunteers?		X
	Does the proposed research involve Human genetic material?		X
	Does the proposed research involve Human biological samples?		X
	Does the proposed research involve Human data collection?		X
	DO ANY OF THE ABOVE ISSUES APPLY TO MY PROPOSAL?		X

	Privacy	YES	NO
	Does the proposed research involve processing of genetic information or personal data (e.g. health, sexual lifestyle, ethnicity, political opinion, religious or philosophical conviction)?		X
	Does the proposed research involve tracking the location or observation of people?		X
	DO ANY OF THE ABOVE ISSUES APPLY TO MY PROPOSAL?		X

	Research on Animals	YES	NO
	Does the proposed research involve research on animals?		X
	Are those animals transgenic small laboratory animals?		X
	Are those animals transgenic farm animals?		X
	Are those animals non-human primates?		X
	Are those animals cloned farm animals?		X
	DO ANY OF THE ABOVE ISSUES APPLY TO MY PROPOSAL?		X

	Research Involving Developing Countries	YES	NO
	Does the proposed research involve the use of local resources (genetic, animal, plant, etc)?		X
	Is the proposed research of benefit to local communities (e.g. capacity building, access to healthcare, education, etc)?		X
	DO ANY OF THE ABOVE ISSUES APPLY TO MY PROPOSAL?		X

	Dual Use	YES	NO
	Research having direct military use		X
	Research having the potential for terrorist abuse		X
	DO ANY OF THE ABOVE ISSUES APPLY TO MY PROPOSAL?		X

Other Ethical Issues	YES	NO
Are there **OTHER** activities that may raise **Ethical Issues**?		X
If **YES** please specify:		

Section 3: *Research Environment*

a. PI's Host institution: CNRS

The Centre National de la Recherche Scientifique (National Center for Scientific Research) is a government-funded research organization, under the administrative authority of France's Ministry of Research, whose mission is to carry out all research capable of advancing knowledge and bringing social, cultural, and economic benefits for society. 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.

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, designs, manufactures and distributes building materials, providing innovative solutions to meet growing demand in emerging countries, for **energy efficiency and for environmental protection**. Research and innovation are the driving of Saint-Gobain's strategy; resources dedicated to research have been increasing by 10% every year since 2004 and 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. Saint-Gobain is of course particularly interested in the colloids freezing route.

The joint lab (Laboratory of Synthesis and Functionnalisation of Ceramics) comprised around 20 people (tenured researchers, technicians, postdocs and students), working in collaboration in four teams, with a strong expertise on ceramic powders synthesis, colloidal suspensions preparation and characterization and subsequent shaping of ceramic pieces. The main application focuses of the lab are **catalysis and electrochemistry,** and an entire testing platform is available for such application tests, with state of the art equipment.

b. Additional institution: Oxford Centre for Collaborative Applied Mathematics

The mathematical modelling and numerical work will be undertaken within OCCAM, the Oxford Centre for Collaborative Applied Mathematics. OCCAM was established in 2009 with substantial funding from the KAUST Global Research Partnership. The Centre, which is part of the Mathematical Institute, is allied to a global network of mathematicians and is based on the **use of innovative mathematics, novel numerical algorithms and powerful computers to foster and advance interdisciplinary research**. Aiming to meet the ever-increasing global demand for quantitative understanding of complex scientific phenomena, OCCAM has been built on the strength of four pre-existing groups of applied and computational mathematicians working in Oxford: the Oxford Centre for Industrial and Applied Mathematics, the Centre for Mathematical Biology, the Numerical Analysis Group and the Computational Biology Group.

Members of the Mathematical Institute have extensive experience in tackling moving boundary problems and phase field models in materials science. The Computing Laboratory network 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.