[PHYSICS IN SPACE]

AGGREGATION AND CRYSTALLISATION IN SPACE

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C.E.A. Kirschhock [1], **F. Otálora** [2], **R. Piazza** [3] and **S. Mazzoni** [4],
[1] Centre for Surface Chemistry and Catalysis, Katholieke Universiteit Leuven, [2] Laboratorio de Estudios Cristalográficos IATC, CSIC, U Granada, [3] Dipartimento di Ingegneria Nucleare, Politecnico di Milano, [4] European Space Agency, Noordwijk, The Netherlands

Aggregation and crystal nucleation phenomena are among the subjects in condensed matter physics that still deserve a strong experimental effort to be fully grasped. This is in particular the case for macromolecular solutions or to dispersions of particles in the colloidal size range. Self-assembly, spontaneous ordering, structural organization on mesoscopic scales, are moreover key concepts for the design of nanostructured materials with specific functional properties. Although ground-based experiments performed on model systems have already shed light on many aspects of the latter phenomena, the presence of gravity often plays a noxious role. Density gradients induced by fast settling of large aggregates, or convective effects associated with the depletion zone around growing crystallites are just two well-known examples. But gravity often yields additional and rather unexpected effects.

To investigate these issues, ESA has recently promoted three distinct, related space projects. They are related, respectively, to the formation of synthetic zeolites, the aggregation and crystallisation of model colloidal systems, the nucleation and growth of protein crystals. These studies will benefit from the already planned development of a versatile light scattering (LS) setup to be installed on the International Space Station (ISS), allowing the use of novel sophisticated optical techniques. Further investigation methods such as confocal microscopy are also foreseen on the ISS, the implementation of rheological and particle manipulation would be an invaluable addition.

Zeolites

Synthetic zeolites are crystalline porous silicates with invaluable importance in a sustainable industrialised world. Zeolite adsorbents and catalysts are workhorses of petroleum and natural gas processing. They are also used in large volumes as detergent enhancer and as drying agents. Applications extend into a wealth of new areas including environmental protection, production of fine chemicals, serving as *e.g.* pharmaceuticals, nutriceuticals, fragrances, flavours, agrochemicals, and further as sensors, electro-optical devices, etc.

The industrial synthesis of zeolites is a slow process involving the lengthy hydrothermal conversion of a silicate-based hydrogel into crystalline material. Depending on the synthesis composition and the presence of structure directing agents (templates) in the form of cations or organic molecules, different pore topologies are obtained. How a specific structure is formed and why the crystallisation takes so long is presently poorly understood. Improved insight into the basic molecular mechanisms during zeolite formation is indispensable for the design and synthesis of tailor-made materials for numerous potential applications awaiting the development of an appropriate zeolite.

Zeolite formation is a complex interplay between silica, templates and solvent. The synthesis mixtures react very sensitively on changes in composition, pH, and convection. This circumstance makes *in situ* observation mandatory. The so-called clear solution synthesis, where no gel-formation occurs, is an ideal model system to study the processes leading up to crystalline zeolites. Specifically the formation of Silicalite-1 from tetraethylorthosilicate, tetrapropylammoniumhydroxide and water has been studied in detail by a number of research groups. Very early in clear solution formation 2-4 nm sized particles appear, which are thought to be precursors for the final zeolite structure [1,2]. They consist of a silica core enclosed by a template shell [3]. Over time silica-template interplay leads to successive structure optimization within these precursors. Suitable building units now start to aggregate into crystals. Such a process is a classical example of self-organisation on different time- and length-scales. Experiments under free-fall conditions aboard sounding rockets and the ISS clearly demonstrated that the nanosized precursors are already affected by the absence of gravity which is a manifestation of long range phenomena [4]. These results prompted an intensive on-ground study of the system focussing on the colloidal interactions which lead to the local enrichment of suitable building units for aggregation in so-called ordered liquid phases (OLPs). With this concept it was possible to re-direct the self-organization by addition of a secondary structure directing agent towards the formation of a new class of hierarchical porous materials [2].

Even though the understanding of zeolite formation has significantly progressed over the last few years, many open questions remain. Especially the initial organization of unstructured silica into specific precursors and the following integration into crystals needs attention. Space experiments are necessary to understand in detail the multi-scale aspects of the formation of precursors and their role in the overall aggregation mechanism. Future experiments are planned to answer these questions. The formation of precursors, their optimisation, enrichment and aggregation will be followed *in situ* aboard the ISS.

Biological macromolecules

The difficulties found with protein crystallisation by the end of the last century motivated many attempts to conduct protein crystal growth in space. Crystallisation of proteins in space has been a large effort since 1982, overwhelmingly based on the "serendipity" approach. Overall, from various evaluations, about 20% of the space-grown crystals showed improvements in diffraction quality, larger crystal volume, more regular visual morphology, or all of the above. Poor reproducibility of conditions, ambiguities in the meaning of "quality improvement" and large scattering of results make this improvement figure not fully reliable and render ambiguous most claims about the benefit of experimenting in space and the reasons for the expected/observed quality enhancements

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Besides the serendipity approach, attempts have been made to understand how a reduction in gravity might improve either the protein crystal quality or our basic knowledge on the operation and implications of the processes involved in protein crystal growth. This rational effort was much more limited in terms of number of experiments, but it brought about much better insight into the protein crystallisation. Fundamental research of biological macromolecule crystallisation reveals that these crystals grow by mechanisms similar to those known for small molecule crystals grown from solution, and contain defects similar to those existing in them. On top of this classical lattice disorder, intramolecular disorder (such as conformation variations or orientation misalignment of the molecules) [5] may be the most important factor limiting the quality of diffraction data and, therefore, the most interesting one for studies on crystal quality and space relevance.

Central to any study of the space relevant aspects of crystal growth is the recognition of the processes that could plausibly explain a different growth behaviour or crystal quality in microgravity. All intermolecular interactions are about 32 orders of magnitude stronger than that related to gravity. Also, Brownian motion velocity of protein molecules is sqrt(3kT/m) ≈ 3-30 m/s at room temperatures for molecules having a molecular weight of 10^4 -10^6 Da. These Brownian velocities are orders of magnitude larger than the 0.1 mm/s that we can assume as a maximum value for the bulk terrestrial convection. Therefore, only the macroscopic mass transport of protein molecules to the growing crystal surface and the interrelation of this transport with the protein incorporation processes at the crystal interface may explain any difference in growth behaviour or in crystal quality.

During the last 20 years, some European initiatives focused on the study of protein crystallisation in space on the basis of a rational understanding of the crystal growth physics. Currently the Topical Team on Solution Crystal Growth and the Science Team of the project selected in ESA's ELIPS programme are active in this direction. So far, these initiatives have concentrated on two main hypotheses on the gravity-dependent processes involved in crystal growth that can influence the quality of the crystals:

1. Protein depletion zone (PDZ) & low supersaturation growth [6, 7]: The rate at which the crystallising protein is transported, via pure or convectional diffusion, to the growing crystal surface may be comparable with the rate at which this protein is incorporated into the crystal lattice on this surface. Then, the supersaturation immediately at the crystal surface is lower than that in the bulk solution and steady, which is known to be beneficial for the quality of crystals grown from solution.

2. Impurity depletion zone (IDZ) & diffusion purification [8]: Impurity concentration trapped by the growing crystal is often larger than that in the surrounding mother solution. Therefore, a crystal just nucleated in solution purifies this solution around itself. The further portions of this crystal grow from a cleaner solution, and will also be cleaner (at the expense of its core). This means diffusion purification: each impurity molecule may reach the crystal surface only after filtering through the IDZ.

Nucleation has been more rarely studied. Interactions driving nucleation of macromolecular crystals are controlled by the precipitant concentration that in most cases turns out to be inhomogeneous due to macroscopic mass transport of the precipitant. Consequently, macroscopic solubility gradients exist, corresponding to concentration (*i.e.* density) gradients that are subject to buoyancy convection. Recent results on the amplification of concentration fluctuations at diffusion fronts in the absence of gravitational effects (GRAdient-Driven FLuctuation EXperiment onboard Foton-M3 mission) demonstrated the relevance of nucleation studies in space and triggered new efforts in this direction.

A series of papers showing our last results and the advances made in the definition of X-ray data quality, the PDZ effect, and the diffusion purification of impurities is in press [9].

Colloidal suspensions

Colloidal suspensions have been very successful model systems for testing basic predictions in statistical mechanics and condensed matter physics [10]. Many of the open questions in colloid science concern *solidification*, *i.e.*, the origin, formation, and dynamics of structures displaying a yield stress, such as colloidal crystals, glasses, and gels. Moreover, stress-yielding suspensions play a crucial role in many processes related to the food, oil, adhesive, paint, environmental, and pharmaceutical industry, as well as in making nano-structured materials such as photonic crystals and electro-rheological fluids, and even in biological structures.

Gravity may strongly influence the structural properties of colloidal suspensions: illustratively, experiments done in space have recently shown that gravity plays an important and not yet fully understood role even in the aggregation of nanometric colloids. The influence of gravity is even more important in colloid solidification, because gravitational stress can propagate on macroscopic length scales, therefore dictating not only the local properties, but also the global, macroscopic behavior of a sample. For dispersion of particles made of a dense material, the need for free-fall conditions is self-evident, since interesting structures such as loose colloidal gels cannot sustain gravitational stress. Yet, even when the density mismatch with the solvent is much less severe, gravity strongly affects colloidal aggregation. For instance, intriguing findings have been made concerning the growth of fractal aggregates of density-matched polystyrene particles, which has been found to be still limited by gravity on earth. By contrast, in space larger aggregates are obtained, whose size is ultimately limited by the stress due to thermal fluctuations.

We shall therefore take advantage of μ-gravity conditions to investigate some areas that are at the forefront of the current research on colloidal solids, such as the glass transition in hard-spheres systems, the dynamics and ageing of colloidal gels and glasses, the crystallisation of colloidal mixtures, and the behaviour of suspensions of anisotropic particles.

Our main approach relies both on using sophisticated optical methods, and on performing experiments on new particle systems presenting interesting structural or optical properties. Besides more 'traditional' colloidal systems, we shall indeed investigate colloidal suspensions of particles with complex geometries (ellipsoids, dumbbells, and rods), or exploit the peculiar optical properties of partially-crystalline colloids. As for the experimental methods, LS techniques possess many unique features that make them an extremely valuable tool for studying colloidal structure and dynamics. In particular, when compared to optical microscopy, LS is sensitive to motion on smaller scales (as small as a fraction of a nanometer for experiments in the highly multiple scattering limit, the Diffusing Wave Spectroscopy), allowing the study of smaller particles. Since all relevant dynamic time scales decrease with decreasing particle size, smaller particles are a premium when studying the very slow dynamics and aging of super-cooled or glassy suspensions. As stated before, besides already "standard" scattering methods, the new LS setup planned for the ISS will include novel techniques, such as Depolarized Dynamic Light Scattering [11], which allow the rotational dynamics of anisotropic particles, or spherical particles with an optically anisotropic composition, to be studied, and Time Resolved Correlation [12], which provides time and space-resolved information on the dynamics, yielding crucial information for structurally and dynamically heterogeneous samples such as gels or glasses.

However, direct visualization of colloidal structures, allowing one to track the coordinates of individual particles and their time evolution with a resolution of the order of a few tens of nanometers [13] would also be extremely useful. We are therefore investigating the possibility of having on board the ISS a confocal microscope, equipped with optical tweezers (to manipulate individual particles), a "dielectrophoretic bottle" (allowing one to tune the local volume fraction of a dispersion by the application of an inhomogeneous electric field), and a flat plate-shear cell, where the relative speeds of the upper and lower plate can be individually set, creating a plane of zero-velocity for optical observation.

Space experiments exploiting novel experimental methods and systems will then very likely increase our understanding of colloid solidification in relation to fundamental physics and biology research, industrial applications, and the preparation of new advanced materials. ■

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EDITOR'S NOTE

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