Mesocrystals and Nonclassical Crystallization

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Preface

Crystallization is certainly among the most studied processes in science and also of great practical importance. This is because the properties of many solid bodies and materials depend on their crystal structure, the crystal shape and their mutual texture. In addition, crystallization is an elemental separation technique, one of the most simple self-assembly processes to create order from the atomic to the macroscopic scale. Finally, it creates beautiful objects of esthetical value, which fascinate humankind already for centuries.

It is not astonishing that crystallization processes are already studied for a long time, beginning with alchemy (where crystallization was one of the ''elemental operations''), and in a systematic, scientific fashion since the end of the 18^{th} century. One might think that a process of such scientific and technological importance is well known down to the finest details after such intense studies for more than a century, but this is not true. It is true that a ''classical'' picture of crystallization has been established, supported by a pleiora of experimental work. It describes crystallization as a layer-wise deposition of atom/ion/molecules on the surfaces of a crystal nucleus, amplifying it within the constraints dictated by the crystal unit cell. Nevertheless, it is also well known that this classical model does not apply for many ''real-life'' crystallization processes (i.e. beyond conditions chosen which are especially good to observe the ''classical'' growth). It is still mostly not possible to quantitatively predict crystallization processes as well as the formed intermediates. Application of crystallization theories fails often even for most simple systems, and thus the modelling of crystallization processes. After 200 years of systematic scientific work, one might also state that the understanding of crystallization beginning from the atomar level is still rather restricted, as well as it is for the interface of a crystal with solvent and the other dissolved compounds.

Apart and apparently separated from synthetic crystallization processes, crystalline biominerals have been analyzed, which have nothing in common with the conception of a single crystal, anymore. Despite physical single crystal properties, they exhibit curvature as a common feature, e.g. as sea urchin spines. Up to now, their precise formation is often still unknown. Such structures are a true challenge for the classical crystallization model, which simply by no means can explain the formation of such structures. Amorphous precursor phases as well as nanoparticle based crystallization pathways were recently identified to contribute to the formation processes of Biominerals, and this knowledge could be folded back to the growth of synthetic crystals. Reanalyzing the literature, this

turns out to be a ''rediscovery'', as it seems that many important original observations are meanwhile forgotten and hidden in the past literature, as they simply did not comply with the classical crystallization model.

It is interesting to guess how crystallization processes were perceived in the early days. Natural scientists were quite universally trained and did not differentiate between biological and inorganic matter to an extent which is common nowadays. It was therefore ''clear'' to observe their scientific objects with an interdisciplinary view – a skill which is weak nowadays and indeed is worth to be rediscovered. As a tutorial exercise, we will start this book with the early descriptions of Biominerals and other crystals, which do not agree with the classical view on crystallization. These old papers already contain the keys towards a deeper understanding of crystal complexity – even if the analytical techniques to probe the assumptions made were often not yet developed. For example the philosopher and biologist Ernst Haeckel carefully observed the complexity of crystallization in the presence and absence of biomolecules and coined notations as ''living crystal field'' and ''diseased crystals''. These words do not sound as exact science in todays language, but in fact already indicate the importance of long-ranged physical fields or additives for crystallization processes. It was presumably the biggest challenge of this book that we seriously tried to gather all available information from historical colloid studies together, which are often only available in german language, and to refresh them for modern use.

The early observations of crystallization pathways well beyond the classical crystallization model (which is much younger) were followed by experimental evidence from the last decade for nanoparticle based formation mechanisms of single crystals, and nowadays this evidence is literally exploding. An increasing number of densified concepts like ''Oriented Attachment'' or ''Mesocrystal formation'' as well as elucidation of the role of amorphous precursor particles, also in Biominerals, was following. This explosion of knowledge can certainly be attributed to the increasing interest in nanotechnology and colloid science, but is to our opinion mainly due to the improved analytical possibilities as compared to those available only 20 years ago. For example, tactoids, which are oriented nanoparticle assemblies, were described as early as 1925 by Zocher but could only be analyzed by light microscopy. A detailed analysis with modern methods would certainly have changed crystallization models as such.

It is also the intention of this book to present the whole wealth of experimental observations available meanwhile, and to formulate mechanisms of non classical crystallization in an attempt to extend the classical textbook knowledge on crystallization. This is especially important in view of the fact that all more general textbooks, e.g. for physical chemistry, still only consider the classical atom/ion/molecule mediated crystallization pathway. In this book, we will try to summarize the classical and non classical crystallization pathways not only by experimental evidence but also with a comprehensive discussion of possible formation mechanisms and features of the various crystallization pathways as well as the necessary analytics. It is a go for a comprehensive treatment of modern crystallization science, and we know well that it is impossible at the present stage of knowledge to provide detailed and well backed up mechanisms for all non classical crystallization pathways which are discussed in this book. We nevertheless hope to provide the necessary toolbox for all scientists who work in the many areas related to modern crystallization to gain a better understanding of their systems; the book

hopefully gives some guidelines how to deal with these often highly complex crystal systems.

The emerging crystallization picture is a more open one where the borderlines between crystallization schemes leading to single crystals and polycrystalline aggregates as well as those between liquid crystalline systems and solid crystals vanish. There appears to be a unifying crystallization picture, which combines all well known observations of the past so far attributed to different mechanisms. A comprehensive treatment of classical and non classical crystallization will catalyze future progress in the field since it helps to identify mechanisms on the base of their typical features and by suitable analytical techniques.

It is a special wish that also students and young researchers can confront themselves with the ''self-organization'' view of crystallization since up to now, there is no equivalent densified treatment of non classical crystallization. The expectations for the future are high: The gain of basic knowledge in the field of organized crystalline arrays will lead to highly sophisticated crystalline materials of the future, covering topics such as hierarchical organic-inorganic hybrid structures, better understanding of biomineralization processes, enhanced predictive tools of crystallization events, new morphosynthesis strategies, new hybrid materials combining the physical properties of different nanoparticles in a single crystalline material, and many more.

We have structured our book into 12 chapters. After the introduction, we introduce the existing crystallization theory (Chapter 2), opposed by the presentation of crystals challenging this classical textbook view on crystallization (Chapter 3). Some non classical particle mediated crystallization pathways are presented afterwards. (Chapter 4). Their foundations are discussed with a treatment of self organization (Chapter 5), colloidal crystals (Chapter 6) as well as the mesocrystal concept and properties (Chapter 7). Formation mechanisms of mesocrystals are discussed in chapter 8, as well as the analytical tools to study such mesocrystals (Chapter 9). Possibilities for the tuning of mesocrystal properties are delineated in (Chapter 10). Finally, a unifying crystallization scenario combining classical and non-classical crystallization will be presented (Chapter 11), and the analogy between hierarchically structured crystals and biopolymers as well as oriented Aggregation and polymers will be discussed (Chapter 12). An outlook to the future with a short glance of what might be possible with an extended toolbox of crystallization will be given. We are deeply indebted to Annette Pape for her enduring assistance during the writing process of this book. We also thank Profs. Lennart Bergström, Stockholm and Shu Hong Yu, Hefei for the useful discussions on the content of this book.

Finally we would like to acknowledge our families who have supported us through all the years of doing science, but especially during the two years of writing this book. It is clear that an active scientist has no time to write such book predominantly at the normal working hours, and many weekends and nights were sacrificed for the writing process. We are therefore extremely grateful to our wives Steffi and Sigrun as well as to our children for their patience to accept passionate science as it is.

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