

## From Ions in Solution to Nanocrystals and Composite Materials: Insights from Atomistic Simulations

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### Introduction

The investigation of crystal nucleation from solution poses a considerable challenge to atomistic simulations. Much more than sophisticated computer hardware, human resources, i.e. smart algorithms for tackling the time-length scale problem, are indispensable requirements. During the past 5-10 years, this field of research experienced exciting advances. The first papers from the late 90's were based on 'brute-force' molecular dynamics simulations using simple models such as solutions of spherical particles. Today, efficient methods allow the study of realistic crystal nucleation scenarios with a direct relation to solid state and materials chemistry. Starting from the association of single ions, accessible insights range from the mechanisms of motif formation [1], ripening reactions [2,3] and the self-organization of nanocrystals [3,4] to interactions with growth-controlling additives [5] and the formation of hybrid materials [6].

The very initial stage of the aggregation process corresponds to the association of a few tens of ions from the solution. Such small (and unstable) aggregates are practically elusive to direct experimental evidence. Nonetheless, for the understanding of ionic self-organization processes insights into the crystal's infancy are of crucial importance. So far, only indirect evidence could be obtained from complexes of ionic aggregates and ligand molecules. In case such additives form strong coordinating bonds to the aggregates further growth may be blocked and experimental characterization becomes accessible. In some cases, the resulting aggregate-ligand complexes can even be precipitated in a crystalline form and the atomistic structure may be determined by crystal structure analysis. But how much will the ligand molecules manipulate the structure of the aggregate? In particular for polymorphic inorganic phases, the comparison of different aggregate-ligand complexes indicates a close interplay of both components. For a profound understanding of this issue -and of the mechanisms of ion association and self-organ-

ization in embryonic aggregates in general- we believe atomistic simulations will play an essential role.

Indeed, molecular dynamics simulations may be performed at the atomistic level of detail and also offer the required time-resolution for profound in-situ studies. However, without confirmation from experimental evidence, insights obtained from computer simulations will receive only poor acceptance. Though seminal in method development, the early work on crystal nucleation could only address simplified models such as spherical particles or rigid dumbbells either by brute-force molecular dynamics simulations at strong thermodynamic driving or by inducing aggregate formation along a predefined reaction coordinate. More recently, unprejudiced simulation schemes were developed for bridging the time-length scale problem inherent to the simulation of self-organization processes. The methodical advances furthermore paved the way for the use of much more realistic simulation models of ionic solutions. Such models may also involve additive molecules as frequently used in precipitation experiments to control aggregate growth. On this basis, encouraging links to the available experimental evidence were established.

### ZnO and ZnO/polymer composites

The perspectives of such studies may be nicely illustrated by the example of ZnO nucleation from solution. Apart from its wide use for UV protection, nanocrystals of zinc oxide exhibit a large variety of interesting potential applications including room temperature UV lasers, LEDs, solar cells and sensors. Moreover, they also represent a prototype model for the exploration of oxide nanocrystal precipitation from solution. Most of the related sol-gel processes are based on alcoholic solutions of  $\text{Zn}^{2+}$  and  $\text{OH}^-$  ions (plus counter ions originating from the reactant materials). Nevertheless, stable  $\text{Zn}(\text{OH})_2$  crystals are typically not observed. Instead, the most common precipitation reactions

involve proton transfer leading to the formation of oxide ions and the crystallization of ZnO. As for many other compounds a full account of ionic self-organization from solution in the ZnO case study hence involves the investigation of ripening reactions at the aggregate-solvent interface.

The Kawska-Zahn approaches to atomistic simulations of aggregate growth from solution [3,4] reflects an iterative procedure which allows to investigate ion association and self-organization from the very beginning. Typically a single ion is chosen as the initial aggregate to which further ions are added one-by-one or as clusters. For each aggregate growth attempt, the first step i) is given by a docking-like approach for searching putative sites for ion association. The ionic species is chosen randomly according to the corresponding concentration in the solution. To mimic the effect of ion migration from solution the incoming ion is placed on the surface of a sphere in proximity of the aggregate. Keeping the ionic positions of the central aggregate fixed, the solvent molecules are removed and a putative site for ion association is identified from steepest descend minimization of the interactions of the aggregate and the incoming ion. This circumvents the drastic computational costs related to brute-force simulations of ion diffusion and association in moderately superconcentrated solutions. Instead we use an inexpensive, yet approximate approach for mimicking the uptake of further ions from the embedding solution in an implicit manner.

To reconcile the approximate nature of the docking step described above, after each ion association the obtained agglomerates are optimized by detailed atomistic simulations using explicit solvent models. In the following steps ii) and iii) structural relaxation based on simulated annealing is first applied to the solvent molecules only ii), and then to the whole system iii). The resulting configuration of step iii) is scanned for hydrogen bonds which might induce proton transfer reactions. In the iteration step iv) the OH $\cdots$ OH distances of the hydrogen bonds interconnecting the OH $^-$  ions are calculated and the shortest hydrogen bond is taken as a candidate for proton transfer. The putative reaction A-OH $\cdots$ OH $^- \rightarrow$  A-O $^{2-}$  + H $_2$ O (A = aggregate) is then explored by combined quantum/classical molecular mechanics calculations. For the sake of computational feasibility (the possibility of proton transfer is explored after every

ion association event) we only calculate the energy levels of the reactant and the product states. This covers the essential aspect of the putative reaction, i.e. whether proton transfer is exothermic or not. Both possible states are relaxed by simulated annealing before the energetically more favorable constellation is taken as the starting point for the next aggregate growth event.

The very initial stage of the aggregation process corresponds to the association of Zn $^{2+}$  and OH $^-$  ions from the ethanolic solution. Strikingly, self-organization may already be observed in aggregates counting less than 20 ions. In this premature ordering the zinc ions are coordinated by hydroxide ions arranged as (incomplete) octahedra similar to motifs of the rocksalt-type structure. In this constellation the hydrogen atoms of the OH $^-$  groups point to the solvent and H $^{\delta+}\cdots$ Zn $^{2+}$  contacts are avoided. Consequently, the formation of extended domains of such motifs is clearly hindered. Indeed, the pre-ordering represents a very temporary feature which changes dramatically in the course of local O $^{2-}$  ion formation. The first proton transfer event leading to Zn $_x$ OH $_y \rightarrow$  Zn $_x$ OH $_y$ O ripening is illustrated in Figure 1.

After the agglomeration of about 100 ions many ripening reactions have occurred and the beginning of ZnO ordering is observed in the aggregate center. At this stage of aggregate growth most of the 6-ring motifs are still randomly oriented. However, the two highlighted chair-type motifs exhibit a staggered arrangement and represent the onset of

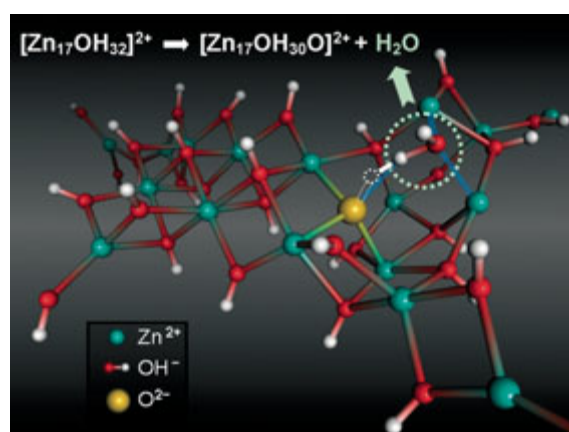


Fig. 1: Onset of ZnO formation by condensation reactions. A newly associated hydroxide ion experiences hydrogen bonding to the hydrogen atom of an adjacent OH ion. This hydrogen bond is used for proton transfer. The resulting water molecule migrates into the solvent, whereas the O $^{2-}$  ion remains within the aggregate.

orientation correlation between the 6-rings (Fig. 2). Indeed, the staggered arrangement does not undergo substantial changes during further crystal growth and is hence suggested as a center of stability. This assumption is supported by the observation of progressive ordering in the same manner starting from this motif.

The ion-by-ion study of crystal nucleation from solution is most suited for the very early stages of crystal formation, i.e. aggregate growth up to a few hundreds of ions. Once the key mechanisms of ion association, ripening and motif formation are explored, it is reasonable to transfer the observed building rules to later stages of surface growth. In this manner, realistic scale-up models may be prepared without explicit growth simulations.

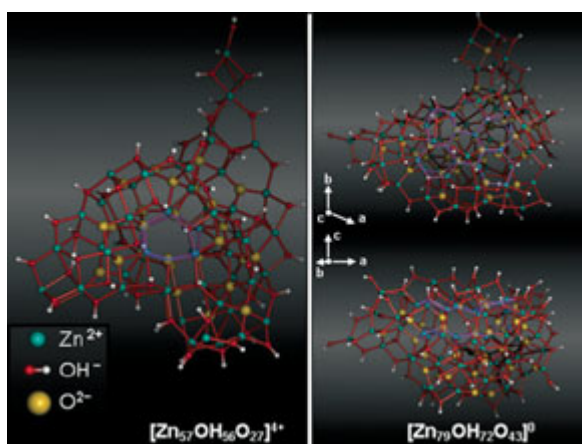


Fig. 2: Nucleation and growth of domains of the wurtzite-type structure. Adjacent to the staggered 6-ring motifs highlighted in the left, further chair motifs of matching orientation are formed. The ionic ordering of the ZnO nanocrystal hence nucleates in the center of the agglomerates and—in the course of further aggregate growth—propagates within the growing bulk domain.

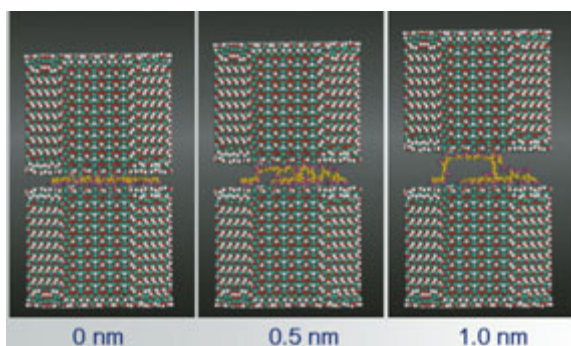


Fig. 3: Scale-up model of two ZnO nanocrystals linked by polyacrylate molecules under tensile load. With increasing strain the polymer-nanocrystal bonds are gradually broken. This process is reversible up to elongations by several nanometers.

An example for the use of such scale-up models is given by the investigation of polyacrylate-nanocrystal interactions. The nanorods illustrated in Figure 3 comprise around 25.000 ions that were arranged according to building rules derived from much smaller aggregates (~150 ions, Fig. 2). Apart from the analysis of shape control by different affinity to different crystal faces, simulation studies of such scale-up models may also form a basis for the understanding of nanocrystal-polymer composite materials. Current efforts are dedicated to the calculation of the stress-strain diagrams of nanocrystals linked by polyacrylate molecules. In cooperation with atomic force microscopy experiments, a profound understanding of hybrid materials and their mechanical properties is envisaged.

### Apatite/collagen biocomposites

Apatite-collagen composites belong to the most abundant biominerals in both humans and animal life forms. The importance of this material as the predominant component of bone and teeth motivated a large number of (biomimetic) experimental and theoretical studies [7,8]. Despite these efforts, we are still at the beginning of understanding biomineral formation. This motivated the development of biomimetic setups which reduce the complexity inherent to metabolic processes, while nevertheless describing the key aspects of composite nucleation [7].

In a somewhat similar fashion, atomistic simulations can throw light on model systems which account for aspects of the complex interplay of inorganic matter with biomolecules. For example, model studies mimicking the association of single ions to collagen fibers in aqueous solution provided an atomistic understanding of collagen stiffening or bending by calcium or phosphate pre-impregnation, respectively, which accounts for changes in the growth mechanisms governing the composites form development at the mesoscale [5].

In a subsequent study, we investigated the mechanisms of aggregate formation and growth-control by collagen fibers at the atomistic scale. The focus is dedicated to the embryonic stage of the nucleation process—both in water and in aqueous solutions containing collagen molecules. From this we explored the (self)organization in different environments and elaborate insights into

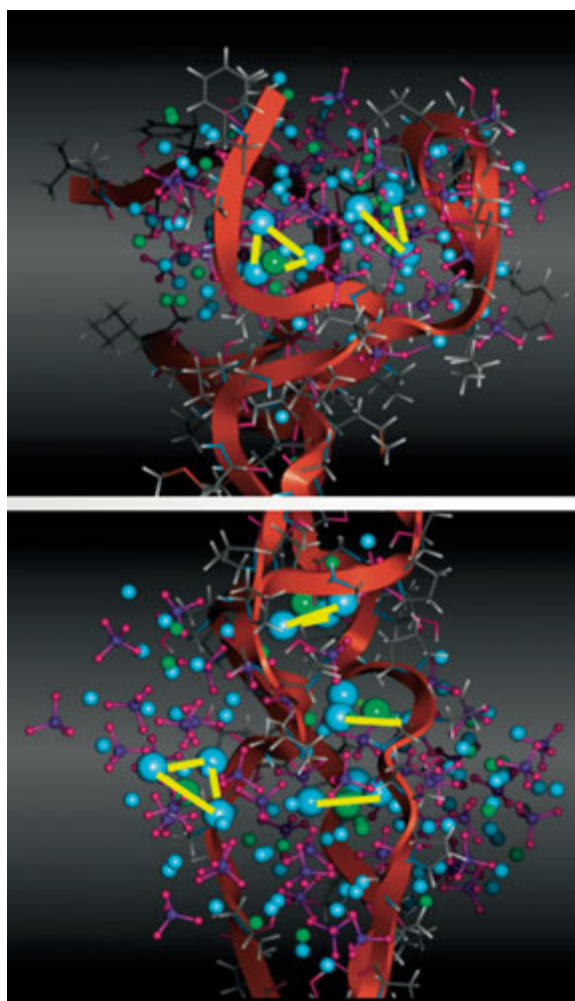


Fig. 4: Nucleation mechanisms of apatite/collagen composites at the atomistic level of detail. We identified peculiar motifs of the apatite crystal structure whose formation is promoted by ion association to the biomolecule. Apart from acting as a nucleation seed for ionic ordering, the collagen triple-helices also induce orientation control to these motifs.

the atomistic interplay governing the formation of apatite-collagen composites (Fig. 4). Our studies addressed ion aggregation promoted by the tails of a collagen fiber and calciumphosphate nucleation at the triple-helical backbone of collagen. Both aspects were explored in separate simulation setups and are contrasted to a third model system corresponding to calcium, phosphate and fluoride ion aggregation from aqueous solution in the absence of collagen molecules. From this comparative approach, we could identify the design of  $\text{Ca}_3\text{F}$  motifs to be induced by incorporation into the triple-helix during the embryonic stage of ion association. These motifs represent nucleation seeds for the formation of the apatite crystal structure oriented in accordance to the alignment of the collagen fibers [9]. Accordingly, ion association to collagen followed by motif design and orientation is suggested as an atomistic mechanism of growth control governing the nucleation of apatite-collagen composites [6,9].

## References

- [1] D. Zahn, Phys. Rev. Lett., 92 (2004), 40801. "Birth of a Crystal", Phys. Rev. Focus 2 (2004).
- [2] D. Zahn, Z. Anorg. Allg. Chem. **630** (2004) 1507.
- [3] A. Kawska, P. Duchstein, O. Hochrein, and D. Zahn, Nanoletters, **8** (2008) 2336.
- [4] A. Kawska, J. Brickmann, R. Kniep, O. Hochrein, and D. Zahn, J. Chem. Phys., **124** (2006) 24513.
- [5] H. Tlatlik, P. Simon, A. Kawska, D. Zahn, R. and Kniep, Angew. Chem., **118** (2006) 1939. Angew. Chem. Int. Ed., **45** (2006) 1905.
- [6] A. Kawska, O. Hochrein, J. Brickmann, R. Kniep, D. Zahn, Angew. Chem., Int. Ed., **120** (2008) 5060. "Building Bones", Nature Materials, **7** (2008) 517.
- [7] R. Kniep and P. Simon, Top. Curr. Chem. **270** (2006) 73.
- [8] D. Zahn, O. Hochrein, A. Kawska, J. Brickmann, and R. Kniep, J. Mater. Sci. **42** (2007) 8966.
- [9] P. Simon, D. Zahn, H. Lichte, and R. Kniep, Angew. Chem. **118** (2006) 1945; Angew. Chem. Int. Ed. **45** (2006) 1911.