

Bottom-to-Top: Understanding Ion Association, Crystal Nucleation and Growth, the Formation of Hierarchical Composites and Materials Properties from Atomistic Simulations

Dirk Zahn¹, Patrick Duchstein¹, Theodor Milek², and Gotthard Seifert²

Recently, the field of crystal nucleation and growth has received a dramatic increase in researcher's attention as new classes of materials are accessible from nanocrystal fabrication and the production of composite materials by combination of nanocrystals with additional molecules. The abundant studies dedicated to the formation of nanocrystalline matter surely improved our knowledge of crystal nucleation in general. However, as far as the mechanisms of ion aggregation from solution and the self-organization of motifs are concerned, the key questions (that is the exploration of atomistic mechanisms) did not only remain largely unanswered, but became even more momentous.

This situation is particularly challenging as the synthesis of nanocrystalline matter includes 'bottom-to-top' approaches which make use of atomistic/molecular self-organization from solution to produce novel kinds of materials. While the age of man-made nanomaterials is still in its infancy, hierarchical biocomposites such as teeth, bone and exoskeletons already demonstrate the peculiar materials properties that are at reach.

At the macroscopic and mesoscopic scale both, crystal solidification from the melt and nucleation from solution, have been subjected to a vast number of experimental studies. However, this does not apply for the microscopic scale, which is much more difficult to access from experiment. Here, computer simulations have evolved to an increasingly attractive tool of investigation. However, whilst the potential for investigating crystal nucleation and growth by means of atomistic simulations is immense, there are technical challenges that need to be addressed carefully. Tackling the time- and length-scale problem inherent to both, crystal aggregation and growth, remains an ongoing challenge to molecular simulation algorithms.

Within a series of studies, we established the Kawska-Zahn method as a versatile simulation approach for the analysis of atom/molecule association, ripening reactions and the self-organization of aggregates [1,2]. Within an iterative procedure, aggregate formation is explored as a series of ion

association and aggregate relaxation events. Thus, our studies start with the association of only a pair of solutes and typically follow the evolution of forming aggregates up to several hundreds of atoms / molecules.

To cope with nucleation processes in dilute solutions we mimic diffusion processes in an approximate manner. While the uptake of solutes is modeled by a simple docking-type approach, incorporation into the aggregate is explored by detailed atomistic simulation. As an important feature, the applied relaxation procedure does not necessarily involve global energy minimization after each growth event, but instead describes crystal growth as a series of structurally related configurations which may also include local energy minima. In the spirit of Ostwald's step rule, a continuous evolution of the aggregate structure is observed during crystal growth [1,2].

From this, the infancy of a crystal may be investigated from continuous pathways starting from a pair of atoms/ions. By iterative modeling of subsequent growth steps, the evolution of aggregates may be analyzed as a function of size. Apart from the self-organization of a crystal structure, our simulations may also provide insights into the competition of different structural motifs (i.e. the foundations of non-classical nucleation and the Oswald step rule). This feature is demonstrated in Figure 1 for the experimentally well-characterized example of the development of copper clusters. In analogy to this case study, also the aggregation of calcium carbonate and calcium phosphate mesocrystals and their subsequent reorganization is accessible to our simulation approach [1,2].

Our studies of ion association and aggregate growth from solution comprise detailed analyses of the interplay of the solvent molecules with the forming aggregate. Moreover, a combined quantum/classical molecular dynamics scheme was developed to explore ripening reactions during crystal growth. A prominent example for such processes is given by the nucleation of ZnO from ethanolic $\text{Zn}^{2+} / \text{OH}^-$ solutions. In the embryonic

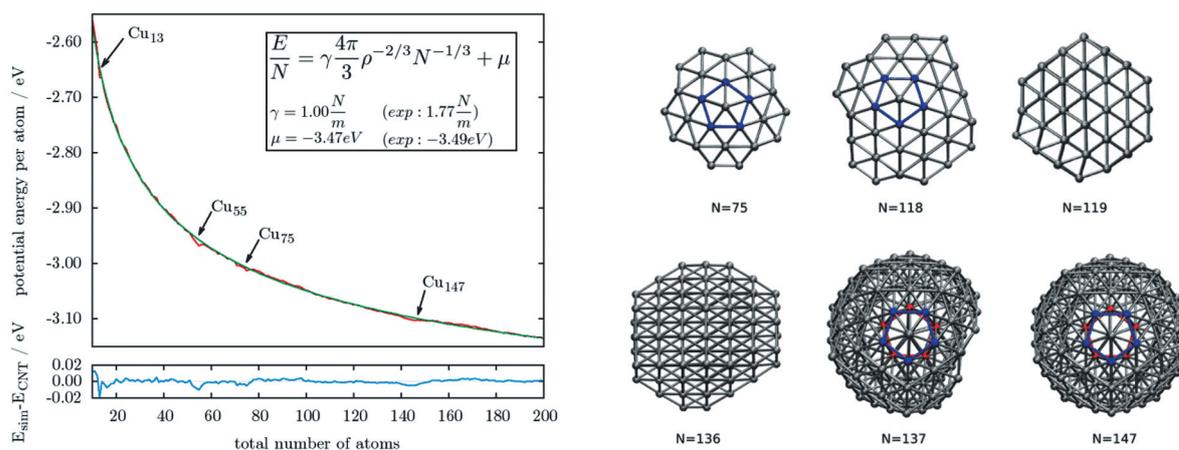


Fig. 1: Aggregation of Cu clusters from the vapor. Left: potential energy per particle as a function of aggregate size (red curve), and a fitted curve (green) based on classical nucleation theory. Right: structural evolution of an aggregate (from $N = 75$ to 147) exhibiting a competition of fcc-type motifs with icosahedral arrangements. The latter account for deviations from the classical nucleation pathway and are confirmed from experiments as particularly stable ‘magic number’ clusters.

stage of aggregate formation a metastable agglomerate of Zn^{2+} and OH^- ions is formed. However, instead of forming a $\text{Zn}(\text{OH})_2$ crystal, proton transfer reactions lead to the formation of O^{2-} ions (Fig. 2, left) and the nucleation of a ZnO domain in the aggregate core (Fig. 2, right) [3].

The implementation of additional molecules into the simulation models allows the detailed investigation of the mechanisms of growth control. So far, such studies were focused on collagen molecules (mostly using $(\text{Hyp-Pro-Gly})_n$ as a simple approximant) which directly change the nucleation mecha-

nism of apatite by acting as crystallization seeds. This allowed a unique level of insights into the interplay between the organic and the inorganic components of the forming composite [4].

An important finding from such studies is given by the detailed structural information that can be directly observed. Figure 3 shows the formation of Ca_3F triangle motifs induced by calcium ion association to collagen. These motifs were found to be very stable and their formation and growth was identified as the first level of ordering of what later becomes a collagen-apatite composite structure.

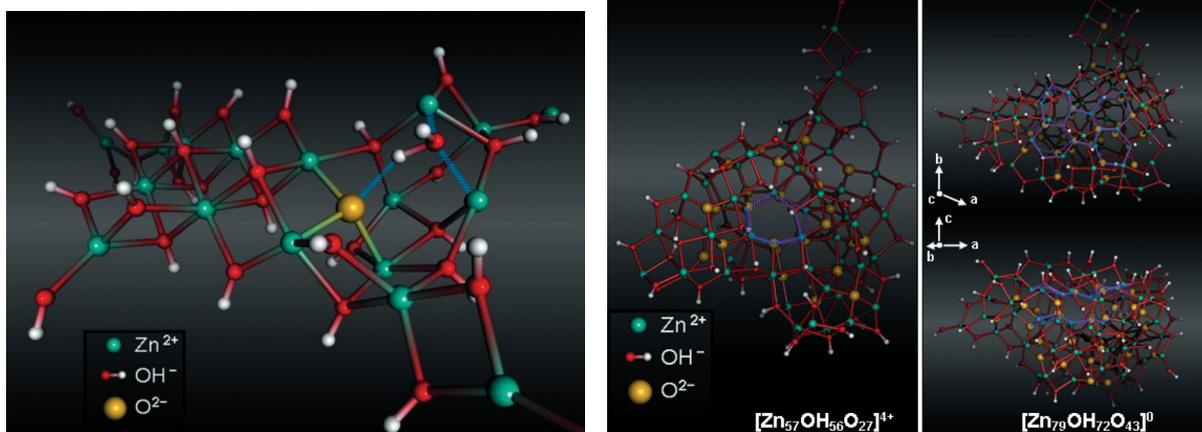


Fig. 2: Nucleation from solution. Left: Aggregation of Zn^{2+} and OH^- ions. Right: nucleation and growth of ZnO/Zn(OH)₂ core-shell nanoparticles. For clarity reasons solvent molecules are not shown.

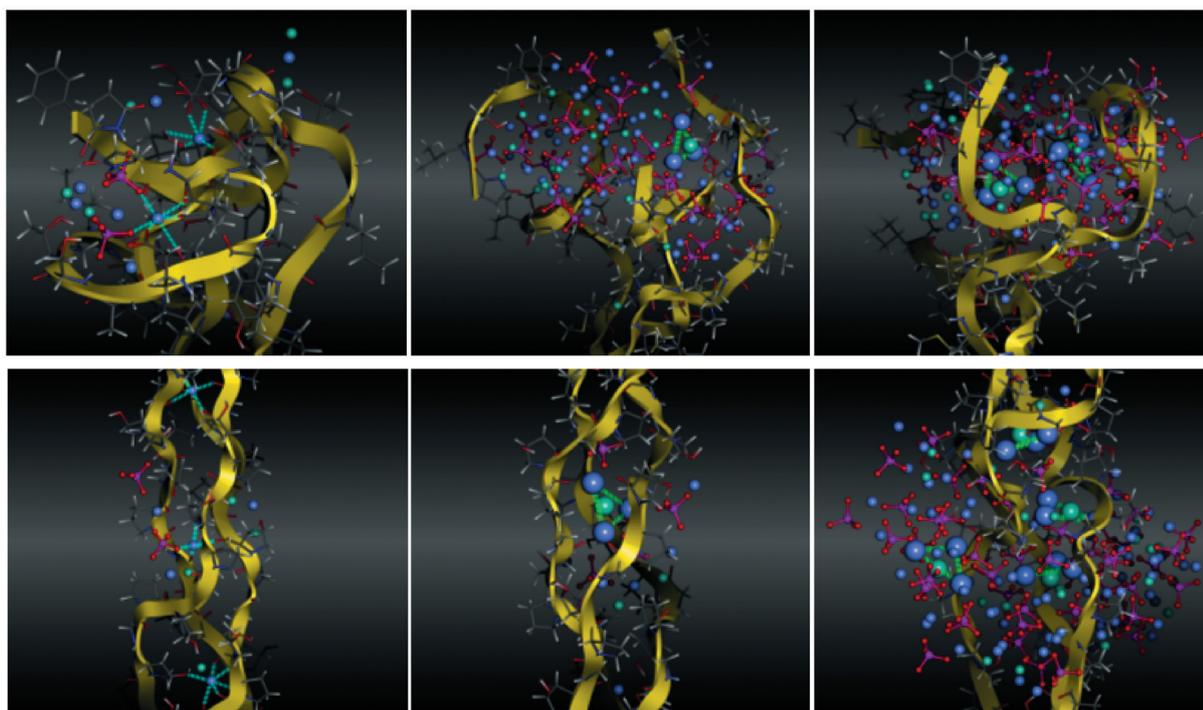


Fig. 3: Nucleation from solution including collagen as an additive. From left to right: Aggregation of calcium, phosphate and fluoride ions as well as nucleation and growth of apatite-type motifs induced by a collagen triple-helix. For clarity reasons water molecules are not shown. Colors: Ca^{2+} , F^- and PO_4^{3-} ions are shown in blue, green and red, respectively. The collagen backbone is highlighted by yellow ribbons.

Moreover, this interplay also induces orientation control to these motifs giving rise to the alignment of the *c* axis of the forming apatite crystallites along the triplehelices. The latter scenario is well-established from electron microscopy. Thus, the most relevant structural relationships between both components of the composites may be explored at the atomic level of detail.

To explore apatite-collagen composites at the 1 nm – 10 nm length-scale a scale-bridging concept was developed. In the long run, this shall allow the exploration of atomic processes that account for the unique structure and the mechanic properties of enamel, dentine and bone. As the atomic structure and composition of such complex biocomposites is only partially explored, the first step (i) of our studies is related to realistic crystal nucleation scenarios of apatite-collagen (biomimetic composites, dentine, bone) and apatite-amelogenin (enamel) systems employing a gradually increasing level of complexity and sophistication. Starting from the association of single ions, elaborated insights range from the mechanisms of motif formation, ripening reactions and the self-organization of nanocrystals

and their interplay with growth-controlling molecular moieties. On this basis, (ii) reliable building rules for scale-up models are being derived, allowing to create multi-million atom models which shall provide a realistic account of apatite-protein composites at the 10 nm – 100 nm length scale [5].

Thus, by bridging scales from nucleation and growth to bulk materials, our bottom-to-top approach opens a new perspective to the profound understanding of crystal nucleation, the formation of hierarchical composites including the characterization of their peculiar properties from atomistic simulation. Whilst maintaining the atomic level of detail, this paves the way to models mimicking fundamental aspects of teeth and bone, including their hierarchical structures and peculiar mechanical properties.

Using modern molecular dynamics protocols, we demonstrated the investigation of deformation and fracture processes for a variety of materials, spanning a range from ductile to brittle compounds [6,7]. As a first result related to hierarchical composites, a biomimetic hydroxyapatite-collagen composite model with similar protein content to

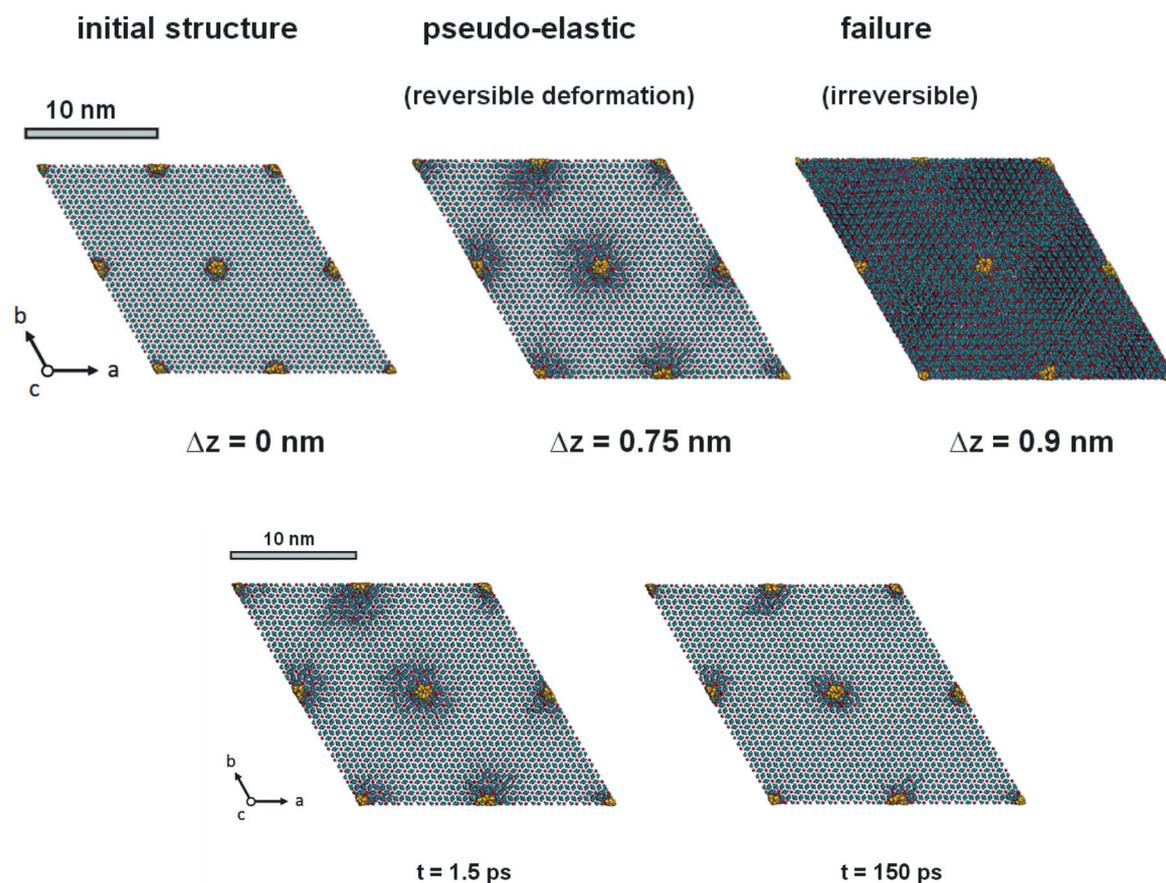


Fig. 4: Snapshots of the apatite-collagen composite model (comprising 212340 atoms) during compression along the c-axis. Before eventual failure, plastic deformation is initiated near the collagen molecules (highlighted in yellow) which are suggested to act as nucleation seeds to local „amorphisation“ of ionic ordering. Using this mechanism, the material may withstand a limited degree of inelastic deformation without losing overall structural integrity (failure). Because of the specific and local nature of the sacrifice of ionic ordering, *the composite deformation is pseudo-elastic, and may undergo self-healing* after releasing the mechanical load (see below).

enamel was subjected to deformation and fracture studies [8]. By means of molecular dynamics simulation, a peculiar route to sacrificing local ordering at the sake of global structural integrity was elaborated. Along this line, plastic deformation occurs in a pseudo-elastic manner (Fig. 4). Thus, when released from mechanical load, gradual reordering of apatite areas provides self-healing of the composite. This pseudo-elastic relaxation occurs on a much slower time scale (ns) compared to elastic response (ps) and thus temporarily retains shock energy which is then dissipated gradually. Our simulations hence revealed a molecular mechanism of transforming shock energy into heat [8].

References

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¹ Present address: Universität Erlangen, Erlangen, Germany

² Technische Universität Dresden, Dresden, Germany