

## 'The Birth of a Crystal': Atomistic Simulation Studies of Crystal Nucleation

Agnieszka Kawaska, Oliver Hochrein, and Dirk Zahn

The nucleation and growth of crystals both from the melt and solution reflect phenomena of fundamental interest in physics, chemistry and materials science. At the macroscopic and mesoscopic scale, crystal solidification and melting processes have been the subject of a vast number of experimental studies. However, this does not apply to the microscopic scale, which is much more difficult to access through experiments. Computer simulations have proven to be a very powerful tool for understanding mechanisms at the atomic level of detail. Molecular dynamics or Monte-Carlo simulations can easily achieve atomistic resolution and hence appear particularly suitable for detailed mechanistic studies.

Nevertheless, the investigation of phase transitions still constitutes a considerable challenge to molecular simulations. Indeed, on the picosecond scale of a molecular dynamics study most crystallization processes are extremely slow. Crystal nucleation from the melt or from highly concentrated solutions is typically related to a large activation barrier, which causes nucleation to occur only rarely. We successfully adopted the transition path sampling approach (see also "Extending the Scope of 'In Silico Experiments': Theoretical Approaches for the Investigation of Reaction Mechanisms, Nucleation Events and Phase Transitions") to explore transition routes crossing such energy barriers. From this procedure dynamic pathways are obtained which allow studying crystal formation processes at the atomistic level of detail.

A snapshot from a characteristic trajectory of NaCl crystallization from the melt as obtained from our simulations is illustrated in Fig. 1. The solidification process is initiated by the formation of a small aggregate of 'solid-like' ions consisting of  $[\text{NaCl}_6]^{5-}$  or  $[\text{ClNa}_6]^{5+}$  octahedra. Such motifs of the bulk crystal also occur in the melt, however in the liquid state the octahedra only reflect temporal features and are excluded by our definition of 'solid-like' particles. The initial nuclei comprise of only 1-2 octahedra for which no preference for  $[\text{NaCl}_6]^{5-}$  or  $[\text{ClNa}_6]^{5+}$  constellations was observed. Subsequent aggregate growth was found to occur on a picosecond scale and after only about 20 ps

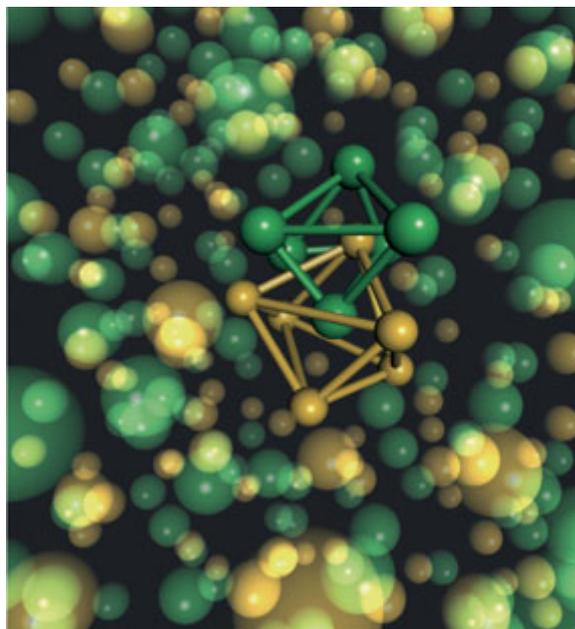


Fig. 1: Snapshot taken from a solidification trajectory of molten NaCl. The picture reflects a very early stage of crystal formation which involves only a few 'solid' ions.  $\text{Na}^+$  (yellow) and  $\text{Cl}^-$  (green) ions of the melt are illustrated by a semi-transparent representation.

the whole simulation cell (540 ions) was transformed to the crystalline structure [1].

We also studied the formation of NaCl aggregates from a super-saturated aqueous solution, which allowed unique insights in the structure of an 'embryonic' crystal formed in salt solution. The core of this  $[\text{Na}_x\text{Cl}_y]^{x-y}_{\text{aq}}$  aggregate in aqueous solution is formed by an entirely non-hydrated sodium ion (highlighted in purple in Fig. 2). In fact, all nucleation trajectories exhibited at least one sodium ion having no or at most one water molecule in the first coordination sphere. Non-hydrated chloride ions could not be observed in the small aggregates obtained from the simulations. The non-hydrated sodium ion was found to be 6-fold coordinated by chloride ions, arranged as a slightly deformed octahedron. These arrangements agree well with the ion coordination in the crystal structure and appear to be a common feature of the aggregate core. In a few simulation runs growth of these motifs is observed [2].

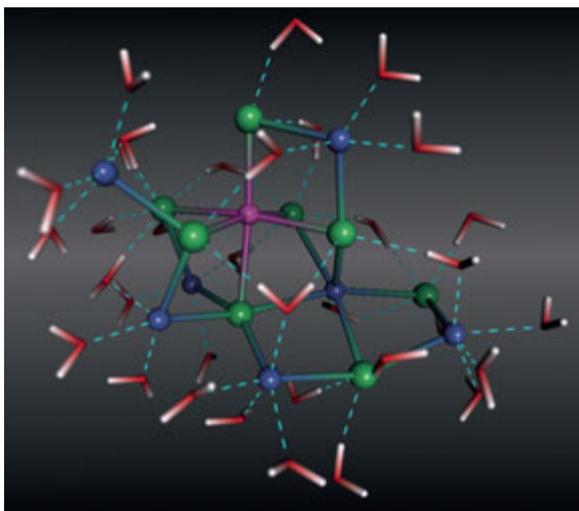


Fig. 2: Configuration of a selected  $[\text{Na}_8\text{Cl}_8]^0$  aggregate at the end of the 1 ns simulation run. Sodium and chloride ions are represented as blue and green balls, respectively. The water molecules in the first coordination sphere of the displayed ions are shown as stick models, all other molecules were cut.

Nucleation processes in heterogeneous systems — like crystallization from solution — are typically complicated by the need to tackle very large simulation systems. Depending on the concentration of the crystallizing compound, a considerable number of solvent molecules needs to be included in the model. In our recent work on the aggregation of NaCl from a slightly super-saturated aqueous solution, this ratio was relatively favorable: the simulation model of an aqueous solution comprised 35  $\text{Na}^+$  and 35  $\text{Cl}^-$  ions and 275 water molecules. While the computational demand related to the investigation of nucleation events in this small system is already considerably high, the investigation of the crystallization of compounds with lower solubility implies dramatically larger numbers of solvent molecules. For such systems both transition path sampling and free energy approaches are quite ineffective and there is a strong motivation for the formulation of alternative methods.

Making specific use of the characteristics related to crystallization processes of compounds of low solubility we developed an atomistic simulation scheme for investigating crystal growth from solution. Our method reflects an iterative scheme which combines a Monte-Carlo type approach for the identification of ion adsorption sites and — after each growth step — structural optimization of the ion cluster and the solvent by means of molecular dynamics simulation runs. An important approxi-

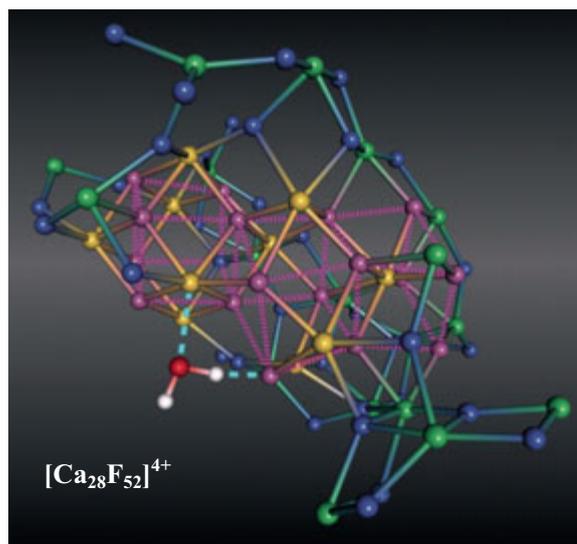


Fig. 3: Characteristic  $[\text{Ca}_{28}\text{F}_{52}]^{4+}$  aggregate generated in aqueous solution. The configuration of the highlighted ions in the interior of the cluster clearly exhibits motifs of the bulk material. The fluoride ions colored in purple form three adjacent cubes. The cubes are connected via a common face (right) and an edge (left). The latter contact reflects an incomplete cube, which is stabilized by a water molecule of the solvent. The calcium ions adjacent to the  $\text{F}^-$  cubes are highlighted in yellow. The location of these  $\text{Ca}^{2+}$  ions above/below the centers of the cube faces qualitatively corresponds to the alternating occupation of the cubes formed by fluoride ions by calcium ions as in the crystal structure of bulk  $\text{CaF}_2$ .

mation of our method is based on assuming full structural relaxation of the aggregates between each of the growth steps. This concept only holds for compounds of low solubility. To illustrate our method we studied the  $\text{CaF}_2$  aggregate growth from aqueous solution, which may be taken as a prototype for compounds of very low solubility.

While the overall configurations of the modeled  $[\text{Ca}_x\text{F}_y]^{2x-y}$  aggregates varied considerably, a series of common features can be identified which are predominantly observed in the inner core of the aggregates. In the initial stage of growth practically all ions have to be considered as part of the nucleus surface. However, in agglomerates of around 20 ions one can already observe the formation of regular structures. In fig. 3 these are indicated by the dotted lines connecting 8 fluoride ions which are arranged on the corners of a cube. The calcium ions are observed in the center of every second of these cubes. These motifs are also present in the crystal structure of fluorite. With increasing aggregate size a structured inner core can be distinguished from the more irregular outer regions of the ion clusters.

**References**

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