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Salt Crystallization from an Evaporating Aqueous Solution by Molecular Dynamics Simulations

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Molecular simulations of crystal nucleation and growth from an evaporating salt solution are presented. Despite the fact that crystallization from solution is the most common way of producing crystals in nature, it has not been simulated on a computer with molecular resolution. We show that such calculations are feasible both for clusters and for extended systems, containing initially an almost saturated solution of sodium chloride. Moreover, we demonstrate that, within a broad range of external conditions, the nanosecond time scale computer simulations robustly and reproducibly display the onset of salt crystallization from solution. We also provide analysis at an atomic resolution and establish the role of water molecules in the process. The present simulations provide unique information about the mechanism and dynamics of nucleation and crystal growth from an evaporating solution. Such information can be used for predictions of morphologies and growth rates of macroscopic crystals from first principles.

Introduction

Crystallization of salts from concentrated aqueous solutions by water evaporation is a familiar process occurring commonly in nature. Understanding the molecular mechanism of crystal nucleation and growth is highly desirable, but current experimental techniques can hardly provide the relevant dynamical information with an atomic scale resolution. In principle, computer simulations[1] are ideally suited for such a task. However, due to the complexity of the potential energy landscape[2] and long times scales involved in the process, the few successful simulations have been so far restricted to crystallizations from melt,[3−9] despite the fact that crystal growth from solution is typically the method of choice in technological applications. A notable exception is a recent simulation of crystallization from a binary solution of model Lennard-Jones particles.[10]

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Here, we present results from molecular dynamics simulations of evaporating aqueous NaCl solutions with realistic interaction potentials. For both isolated clusters and slabs with extended solution/vacuum interfaces we observe nucleation and growth of the cubic crystal lattice of rock salt on the nanosecond time scale. This robust and reproducible process is significantly accelerated by temperature elevation.

Method

Aqueous solution of rock salt reaches saturation at 6.1 M, which corresponds to roughly nine water molecules per one NaCl ion pair.[11] MD simulations of water evaporation and salt crystallization from saturated solutions were performed for two system geometries, a large isolated cluster and a slab embedded in a periodic box ($2.48 \times 2.48 \times 25.60$ nm^3 or $2.38 \times 2.38 \times 25.60$ nm^3). After equilibration at 280 K, evaporation has been induced by gradual heating of the system. A very weak coupling parameter to the heat bath of 200 ps was used, and the final

temperature (900, 500, or 300 K) was reached in about 1 ns. For Na$^+$ and Cl$^-$ ions we employed the same nonpolarizable force field as that in ref 12, that is, positive (Na$^+$) and negative (Cl$^-$) unit charges and the following Lennard-Jones parameters: $\sigma_{Na^+} = 0.273$ nm, $\epsilon_{Na^+} = 0.1$ kcal/mol, $\sigma_{Cl^-} = 0.431$ nm, and $\epsilon_{Cl^-} = 0.1$ kcal/mol. Two standard water models, SPC[13] and SPC/E,[13] were adopted for the cluster systems. Simulations showed that in both cases salt crystallization occurred via an identical mechanism. However, within the former model water evaporation and, consequently, salt crystallization took place on a shorter time scale. For this reason, we have adopted the SPC water model for the extensive slab calculations, while for the cluster systems we present here results with the SPC/E model. Internal degrees of freedom of water molecules were constrained using the SHAKE algorithm.[14] A time step of 1 fs was employed for the 5 ns simulations. For the extended slab systems, long range interactions were cut off at 1.1 nm and accounted for using the smooth particle mesh Ewald method.[15] All calculations were performed using the Amber program package.[16]

Results and Discussion

In our first molecular dynamics (MD) simulation, we have constructed an aqueous salt cluster close to saturation by mixing together 288 water molecules, 32 sodium cations, and 32 chloride anions. We have then equilibrated the system at 280 K for 0.2 ns. During this period almost no water evaporation occurred, and the cluster maintained the character of a concentrated liquid solution. This is demonstrated in Figure 1a, which shows a snapshot from the end of the equilibration run. 286 water molecules (two waters evaporated) are well mixed with the ions, which exhibit a disordered structure. The degree of (dis)order can be quantified via the radial distribution functions (RDFs), that is, the probabilities of finding a particular pair of species at a certain separation. Figure 1b displays the Na$^+$–Cl$^-$, Na$^+$–Na$^+$, and Cl$^-$–Cl$^-$ RDFs averaged over the second half of the equilibration run. All three functions exhibit a broad and almost structureless peak between 0.4 and 2.5 nm. This lack of long range structure is a clear signature of disordered species. The pronounced narrow peak of the Na$^+$–Cl$^-$ RDF around 0.3 nm reflects an extended pairing of ions with opposite charges, typical for concentrated salt solutions.[17−19]

A straightforward way to rapidly remove water molecules from the cluster and thus initiate salt nucleation and crystal growth is to gradually heat the system. Since rock salt melts only at 1074 K,[20] there is a broad temperature range where extensive water evaporation and salt crystallization can occur simultaneously. We use this fact to our advantage by heating within 1 ns the equilibrated cluster from 280 to 900 K. During this period water molecules evaporate vigorously. The rapid decrease of the number of water molecules, which remain bound to the ionic core, is shown in the upper panel of Figure 2. As a consequence of water evaporation, the concentration of the solution quickly exceeds saturation and salt starts to precipitate. Figure 1c shows a snapshot from the middle of the heating period. Most of the ions now form a compact core surrounded by the remaining 168 water molecules. At this point the sodium and chloride ions begin to exhibit an alternating pattern, although a long range order is still missing. This is clearly seen on the three ionic RDFs, averaged over the 0.4−0.6 ns of the simulation (Figure 1d). For separations below 1 nm, each of the RDFs shows peaks reflecting the nascent crystalline structure, while at larger interionic distances the signal becomes less resolved, preserving thus the signature of the earlier disorder. The gradual
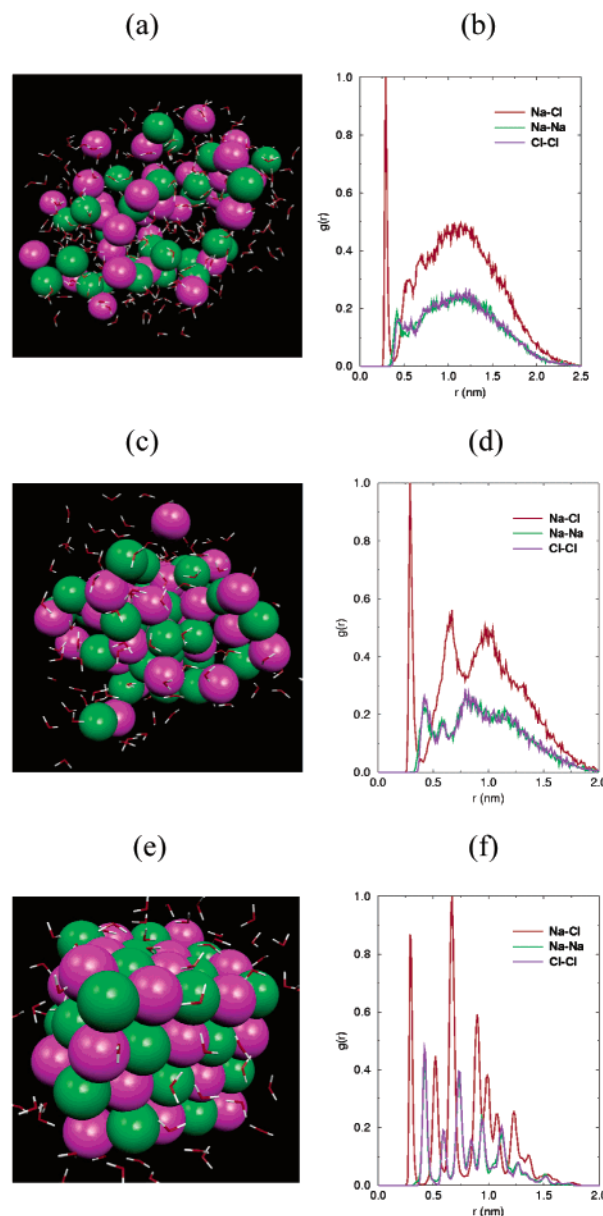
Figure 1. Snapshots from a molecular dynamics simulation of rock salt crystallization from an aqueous cluster: (a) initial aqueous solution at 280 K; (c) formation of an ionic core after 0.5 ns of heating to 900 K; (e) final crystal nucleus after a 5 ns run. The corresponding (unnormalized) Na$^+$–Cl$^-$, Na$^+$–Na$^+$, and Cl$^-$–Cl$^-$ radial distribution functions, which reflect the transition from a disordered state to a crystal, are shown in parts b, d, and f. Color coding: sodium, green; chloride, violet; water molecules, red and white sticks.

increase of the range of crystalline order is also displayed in the lower panel of Figure 2 and directly correlates with the decreasing size of the ionic core (see middle panel of Figure 2).

We have continued the MD simulation for a total time of 5 ns. Within the first 2 ns the ions frequently rearranged, finding eventually the optimal cubic crystal arrangement. After the crystal nucleated, very little ion dynamics takes place in the remainder of the simulation. A snapshot from the end of the whole run is displayed in Figure 1e. (Note that both parts c and e of Figure 1 are zoomed in with respect to Figure 1a, since the cluster size decreases during water evaporation.) The corresponding RDFs averaged over the last 1 ns are shown in Figure 1f. We see an almost perfect cubic lattice of the crystal nucleus. Remarkably, none of the ions is dislocated from the crystal

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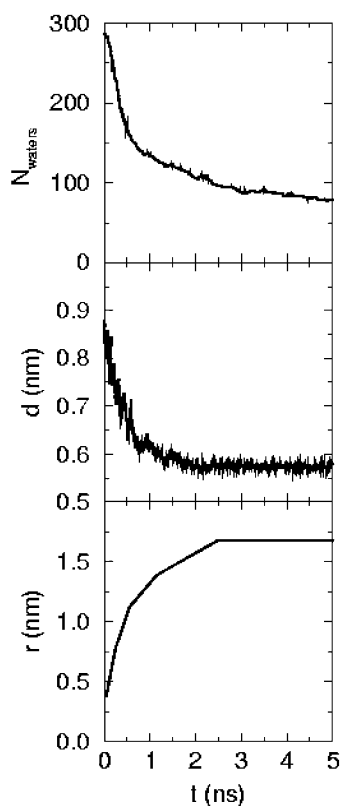
Figure 2. Time evolution of the number of water molecules bound to the ionic core (upper panel), of the size of the ionic core, defined as the mean distance of an ion from the center of mass of the ionic system (middle panel), and of the range of crystalline order of the crystal nucleus (lower panel). Note that rapid water evaporation precedes shrinking and subsequent crystallization of the ionic system.

lattice. Consequently, all three ionic RDFs show, for the whole 1.5 nm spatial extent of the crystal nucleus, pronounced, well resolved peaks, which form a pattern pertinent to the dual fcc lattice of rock salt.[21] The lattice constant of our crystal is less than 5% larger than the experimental value at ambient conditions of 0.564 nm,[21] which is due to the elevated temperature, finite size of the crystal, and small inaccuracies in the interaction potentials.

Despite the relatively high temperature, 79 water molecules still reside at the surface of the newly formed crystal at the end of the 5 ns simulation. This is due to the fact that these water molecules bind directly to the salt ions, and the water−ion interactions are much stronger than those between water molecules themselves. Analysis of the simulation shows that water molecules play an important role in the formation of the crystal nucleus from the evaporating solution. First, they prevent an initial disintegration of the forming ionic core. This can be proven by artificially removing, at the beginning of the simulation, all the water molecules. In that case no ionic core is created, but the ions rather form pairs or small clusters which fly away from each other. Moreover, the surface water molecules lower potential barriers for ion rearrangements,[22] facilitating thus gradual long range ordering. The role of water molecules is clear also from Figure 2, which shows that rapid water evaporation and consequent shrinking of the ionic core precede crystallization. The same pattern emerges also from the time evolution of interaction energies. While the ion−water potential energy diminishes as a consequence of water evaporation, the attractive ion−ion Coulomb interactions grow stronger upon shrinking and crystallization of the ionic core. Finally, we note that crystallization occurs in the present cluster also at temper-
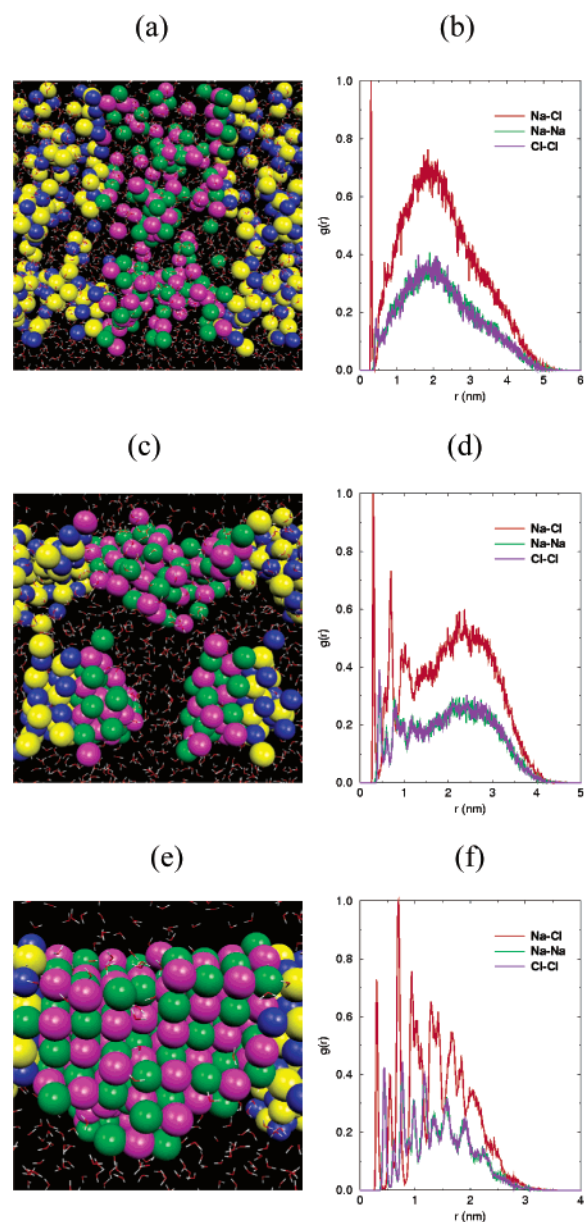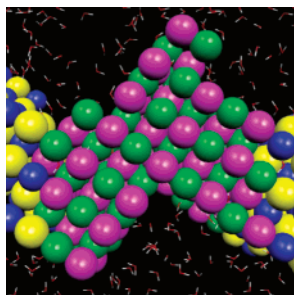

Figure 3. Snapshots from a molecular dynamics simulation of NaCl crystallization from an aqueous solution in an extended slab geometry: (a) initial solvated state at 280 K; (c) clustering of ions after 0.5 ns of heating to 500 K; (e) nascent crystal layer after a 1.5 ns run. The corresponding (unnormalized) ion−ion radial distribution functions, exhibiting the gradual transition from a disordered state to a crystal, are shown in parts b, d, and f. For particles in the central box the color coding is the same as that in Figure 1, while ions in the two neighboring boxes are displayed in blue and yellow.

atures lower than 900 K. The main effect of reducing temperature is that water molecules evaporate more slowly and crystal growth takes progressively longer times. Still, within 5 ns we observed formation of a crystal nucleus at 500 K, and even at only 300 K. These crystal nuclei appear to be slightly less perfect than that obtained at 900 K (due to slower water evaportaion there was less time for ionic rearrangements within the 5 ns simulation); however, the corresponding RDFs at different temperatures almost coincide.

Molecular dynamics techniques allow for simulations of extended systems using periodic boundary conditions.[1] The bulk phase can be modeled using, for example, a replicating cubic box. However, such a system is not suitable for our purpose, since it possesses no surface from which evaporation could

Figure 4. Final snapshots from 4 ns molecular dynamics simulations of salt crystallization from an aqueous solution in an extended slab geometry, with a box size reduced by 0.1 nm compared to the case displayed in Figure 3. Note that, due to the strain of the smaller box, a tilted crystal structure developed. (Color coding is the same as that in Figure 3.)

occur. Fortunately, a well-established procedure exists for modeling extended systems of a slab geometry with two infinite flat surfaces. The slab arrangement is achieved by significantly extending one of the box dimensions.[23] Figure 3 shows results of a MD simulation analogous to the cluster run, performed, however, for an extended slab with a unit box containing 864 water molecules, 96 sodium ions, and 96 chloride ions. Due to the larger size and slab geometry of the system the crystallization dynamics is more complex than that in the small cluster. In Figure 3a we see a well equilibrated slab of a 6.1 M aqueous salt solution at 280 K. The lack of long range ionic order reflects itself in the RDFs (taking into account, for more direct comparison with the cluster case, only particles in the central box) displayed in Figure 3b. Both the broad features and the sharp peak at 0.3 nm of the Na^+-Cl^- RDF are analogous to those of the cluster system at 280 K discussed above. Figure 3c presents the geometry of the system after 0.5 ns of heating to 500 K. During this period water molecules rapidly evaporated from the slab and the ions coalesced, forming two or several nuclei, each similar to the ionic core from the cluster simulation (see Figure 1c). Note that pockets filled with water remain between these nuclei. The RDFs averaged over the last 0.1 ns of the heating interval clearly show establishment of a short range ionic structure, while the long range disorder remains (see Figure 3d).

The crystal nuclei described above slowly move in the aqueous slab and, upon close encounters, coalesce. The frequency of these encounters depends sensitively on temperature and the rate of heating. For example, heating to 900 K typically resulted in creation of two salt crystal layers which did not coalesce on the time scale of the simulation, while at 500 K we obtained within 1 ns after the heating period a single layer of crystalline rock salt. The nascent crystal is covered with the remaining water molecules, which again play an important role in facilitating ion rearrangements. The newly formed crystal layer is displayed in Figure 3e. We clearly see a regular crystalline pattern, which is also confirmed by the characteristic peaks in the RDFs, displayed in Figure 3f. Note that water molecules reside now only at the outside of the crystal and in the gas phase. Once the crystal layer of rock salt is formed, the ionic dynamics becomes rather moderate, leading to further refining of the crystal. The number of ions in the box was intentionally chosen such as not to correspond to a completely filled crystal layer, so individual ions continue to slowly rearrange, but the structure of the NaCl layer remains crystalline. Finally, we note that the box size was chosen such as to conveniently accommodate four NaCl crystal layers. However, such a choice is not a necessary condition for a successful crystallization. This is demonstrated in Figure 4, which shows the final geometry after a 4 ns run in a box with dimensions reduced by 0.1 nm compared to the previous case. Again, crystallization took place but due to the strain imposed by the reduced box size a tilted structure of the crystal layer developed.

Conclusions

We have shown that salt nucleation and crystal growth from an evaporating aqueous solution can be simulated using molecular dynamics techniques, both in clusters and in extended slab systems. A broad range of physical conditions exists, where the computer simulations robustly and reproducibly display these phenomena. Our simulations provide a valuable insight with an atomic scale resolution into the mechanistic and dynamical aspects of the onset of crystallization. In particular, we have analyzed in detail the role of both the evaporating and surface water molecules in the creation of the ionic core and the subsequent growth of the salt crystal nucleus. Such information is an initial step for first principle predictions of growth rates and morphologies of macroscopic crystals.

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