Atomistic Mechanism of NaCl Nucleation from an Aqueous Solution

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Despite great technological relevance, the initial steps of nucleation and crystal growth from solution are still poorly understood. While experimentally difficult to access, simulations in principle may provide insight at the atomic level. However, in most cases the computational demand dramatically exceeds the scope of current hardware. Since crystallization usually occurs on time scales much larger than the few ns of a molecular dynamics simulation, special techniques for the study of rare events are of particular interest. In the present work the nucleation of sodium chloride aggregates from aqueous solution is investigated from path sampling molecular dynamics simulation. The introduced simulation schemes appear to be widely applicable.

Introduction.—Crystal nucleation and growth from solution is a frequently observed phenomenon in both physics and chemistry. Though macroscopically well described, little knowledge is available at the atomic level of detail [1,2]. The early stage of nucleus formation may involve only a few ions and is thus hard to access from experiment. Molecular dynamics simulation may achieve microscopic resolution; however, in many cases the time scale of nucleation drastically exceeds the scope of direct simulation. Recently, Frenkel and co-workers were able to study homogeneous nucleation from computer simulation [3–5]. While this corresponds to crystallization from the melt, the investigation of crystallization from solution from molecular dynamics simulation was believed to be impossible for a long time. A pioneering study of the crystallization of a model solution by computer simulation was recently published by Anwar *et al.* [2]. While their Lennard-Jones–type solute-solvent system did not correspond to a realistic system, it is the aim of this Letter to investigate the initial steps of nucleation within a realistic solution.

Sodium chloride — in its crystalline form as well as in aqueous solution — is widely spread in everyday life. Solutions of NaCl were subject to many studies in both experiment and theory [6,7]. In their computer simulations, Koneshan and Rasaiah were able to observe the aggregation of NaCl in supercritical aqueous solution [8]. However, the microscopic mechanism of NaCl nucleation at normal conditions remained elusive so far. A related field is the study of interfaces of solid sodium chloride and water [9–11]. Oyen and Hentschke studied NaCl(001) interfaces in contact with aqueous sodium chloride solutions of various concentrations [11]. In their work, the highest sodium chloride concentration investigated is more than twice the saturation value. Within a 9 ns simulation run, some of the solute sodium and none of the chloride ions were observed to adsorb on the crystal surface; however, no growth of crystal layers or crystal nucleation from solution could be observed. In contact

with solid NaCl the oversaturated solution could be expected to crystallize even faster. However, the presumably still rather large difference in time scales of the crystallization processes and computer simulations prevented such observations. The existence of NaCl ion clusters was observed experimentally even at undersaturated concentrations [12].

While the investigation of the formation of macroscopic crystals is computationally too demanding, molecular dynamics simulations may have better chances to offer insight into the very early stage of nucleation, involving only a few ions. However, also for small simulation systems, the time-scale problem remains crucial. In the present work the path sampling method, developed for the study of rare events by Chandler and co-workers is applied to this issue [13,14].

Simulation details.—Molecular dynamics simulations were carried out using the DLPOLY package [15]. The model parameters of the NaCl solution were taken from the literature [9]. Ewald summation using a real space cutoff of 10 Å was applied to the electrostatics. In order to improve time reversibility a relatively small time step of 0.5 fs was chosen.

The aggregation trajectories are collected using the path sampling method developed by Chandler and co-workers [13,14]. Starting from a trajectory in which the process of interest is observed, new trajectories are obtained in an iterative way. This is accomplished by selecting a configuration from the preceding trajectory and slightly modifying the atomic momenta. Velocity changes are incorporated in a manner conserving the total energy, momentum, and angular momentum, respectively. The modified configuration is propagated in both directions of time. The resulting trajectory is then checked for the process of interest. In case the desired event takes place, the trajectory is used for generating a new trajectory, repeating the above procedure.

Results.—From experimental investigations, crystallization of NaCl is known to occur at sodium chloride

concentrations larger than 5.4 mol/L [16]. In the present simulations, a box of 275 water molecules and 35 ions of each, Na^+ and Cl^-, is used. This corresponds to an oversaturation of 30%. In the initial configuration of the solution the ions were placed at random positions, with a minimum distance of 5 Å between each ion. After 100 ps equilibration, the system was propagated by 1 ns applying constant pressure and temperature using standard conditions. For each ion the number of neighboring water molecules was calculated as a function of time. This was accomplished by counting the oxygen atoms within a threshold distance of 3.125 and 3.875 Å for Na^+ and Cl^-, respectively. The values of the threshold distances were chosen according to the first minima of the related radial distribution functions. During the 1 ns simulation run, the majority of Na^+ and Cl^- ions were coordinated by 5–6 and 7–8 water molecules, respectively. However, for some ions much lower coordination numbers could be observed. The duration of such partial dehydration ranged from some hundreds of femtoseconds to a few picoseconds. The lowest number of neighboring water molecules was found to be 3 (Na^+) and 4 (Cl^-), respectively. This effect cannot be regarded as nucleation. However, considering the low extent of oversaturation and the small size of the simulation box, one surely needs much longer runs than 1 ns in order to have a reasonable chance to observe crystal nucleation within the simulation.

Despite presumably having to wait for a long time before the formation of a NaCl nucleus starts, the nucleation process itself may occur on a much smaller time scale. Thus it would be feasible to focus our simulations on the nucleation process only and entirely skip the waiting time. The path sampling method developed by Chandler and co-workers allows such a simulation strategy [13,14].

Before path sampling iterations may be started, a first trajectory is needed as a prerequisite. In case of rare events such as crystal nucleation, the waiting time for observing just one event may exceed the scope of molecular dynamics simulations. It is then necessary to model a putative transition state and try to find a first trajectory from propagation in both directions of time. While for low dimensional systems this may be achieved from intuition, in the present case a systematic strategy—as outlined in the following—appears more feasible. The rate of crystallization is strongly dependent on the hydrophilicity of the solute. Thus by altering the ion-water interactions one obtains an artificial system, which may crystallize much faster. Indeed, by increasing the van der Waals radii of the ion-water oxygen atom interactions ($\sigma_{Na-O} = 2.72$ Å, $\sigma_{Cl-O} = 3.55$ Å) by 0.5 Å, the solution crystallizes within a few tens of picoseconds. Though the resulting trajectory does not correspond to a realistic model of a NaCl solution, it may still be used for guessing transition-state configurations related to the proper model. The modified solution was propagated in

the canonical ensemble. Therein the box length was fixed to the average value observed from the 1 ns run of the NaCl solution described in the beginning of this section. A thermostat is used to constrain the temperature to 300 K and thus damp the kinetic energy resulting from switching the interaction parameters. Intermediate configurations were taken from the crystallization trajectory of the modified solution. These were propagated in both directions of time in molecular dynamics simulations applying the proper interaction parameters. A Newton algorithm is used to obtain a trajectory — corresponding istic model of the NaCl solution — in which nucleation is observed.

In the simulation schemes described above one is required to define a quantitative measure in order to decide whether nucleation takes place or not. The choice of this order parameter should be done carefully, since a too rigorous criterion may result in predefining the process mechanism. In the present work the loss of more than half of the number of hydration water molecules of at least one ion (i.e., $N_{hyd} \leq 3$ for Na^+ and $N_{hyd} \leq 4$ for Cl^-) was used as one of two nucleation criteria. While obviously being a necessary condition for nucleation, this criterion also holds for short-living aggregates of ions. Using just the hydration number criterion, path sampling yielded a large number of aggregates, which decomposed after a few picoseconds. Irrespective of whether crystal growth occurs via the growth of a single nucleus, by merging of multiple nuclei or as a combination of both, aggregates may surely be expected to exhibit much larger lifetimes in order to be considered as potential nuclei. By demanding the hydration number criterion to apply for at least 25 ps, an upper limit of the decay rate of the ion aggregates was established. Applying both conditions as nucleation criteria, aggregates of a much larger lifetime were obtained. Indeed the most unstable aggregate remained for a peroid of 95 ps. Since the observed lifetimes dramatically extend the 25 ps sampling criterion applied, the aggregate stability may not be considered as an artifact caused by the nucleation criteria.

The path sampling iterations may be interpreted in terms of a Monte Carlo simulation in the ensemble of dynamical pathways of the nucleation process. Thus even if the initial trajectory is not a likely one, the iterations will converge towards more favorable pathways. The path sampling procedure was applied to trajectories of 150 ps. Because of the iterative nature of the method, subsequent trajectories may not be considered as independent from each other. However, by comparing the aggregate size and shape at the final configuration of each trajectory, about five iterations were found to be sufficient to ensure decorrelation. The first 50 trajectories were ignored in order to avoid memory effects to the transition state of the first trajectory, obtained from modified interaction parameters. In the production run every tenth trajectory was considered. The following analysis is based on 20 independent trajectories.
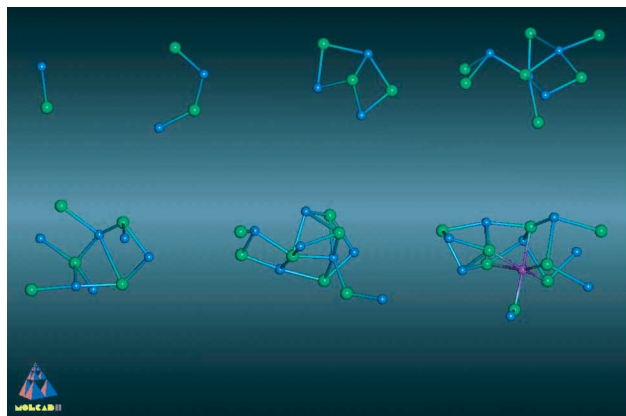
FIG. 1 (color). Formation of a $[Na_xCl_y]^{x-y}_{aq}$ aggregate in water (not shown) as observed in a 150 ps trajectory obtained from path sampling. Sodium and chloride ions are colored blue and green, respectively. Entirely nonhydrated ions are highlighted in purple. Snapshots are taken in intervals of 25 ps.

A typical trajectory as obtained from the path sampling procedure is illustrated in Fig. 1. The core of this $[Na_xCl_y]^{x-y}_{aq}$ aggregate in aqueous solution is formed by an entirely nonhydrated sodium ion (highlighted in purple). In fact, all nucleation trajectories exhibited at least one sodium ion having no or at most one water molecule in the first coordination sphere. Nonhydrated chloride ions could not be observed in the small aggregates obtained from the simulations. The nonhydrated sodium ion was found to be sixfold coordinated by chloride ions, arranged as slightly deformed octahedra. These formations nicely agree with the ion arrangement in the crystal structure.

Each of the 20 trajectories obtained from path sampling was further propagated by 1 ns. During this period only one aggregate decomposed, exhibiting a total life-time of 95 ps. Figures 2(a)–2(c) show the final configuration of three representative aggregates. While size and form of the aggregates vary considerably a common characteristic is the existence of at least one sodium ion with only one [Fig. 2(a)] or without any [Fig. 2(b)] hydration water molecule. The majority of simulation runs exhibited a nonhydrated sodium ion, which was found to be octahedrally coordinated by six chloride ions throughout. *We propose these formations as centers of stability of the aggregates.* However, in none of the trajectories produced could a single sodium ion, surrounded by six chloride ions, be observed without further aggregation. Additional Na^+ and Cl^- ions were found next to the Cl^- octahedra. The total charge the $[Na_xCl_y]^{x-y}_{aq}$ aggregates varied from -4 to $+1$.

The proposed concept of centers of stability is supported from the observation of growth of such solidlike structures in two of the hydrated $[Na_xCl_y]^{x-y}_{aq}$ aggregates. Figure 2(c) shows an aggregate having two nonhydrated Na^+ ions. Both are nicely octahedrally coordinated by chloride ions, as observed in solid sodium chloride. It is noteworthy that in both cases the two octahedra are connected via three common chloride ions. In the bulk crystal structure, the octahedra share only two ions at maximum. We relate the unusual connectivity to a lack of ions in the small aggregates.

The structures of $[NaCl]_n$ and $[Na_{n+1}Cl_n]^{+1}$ aggregates in vacuum were investigated from both experiment and model calculations [17,18]. Despite some structural similarities to the aqueous aggregates presented in the present work, the vacuum clusters typically are more compact and symmetric.

Conclusions and discussion.—It is somewhat daring to propose "the" nucleus of NaCl crystallization from aqueous solution. Despite the large number of degrees of freedom in $[Na_xCl_y]^{x-y}_{aq}$ aggregate formation, the
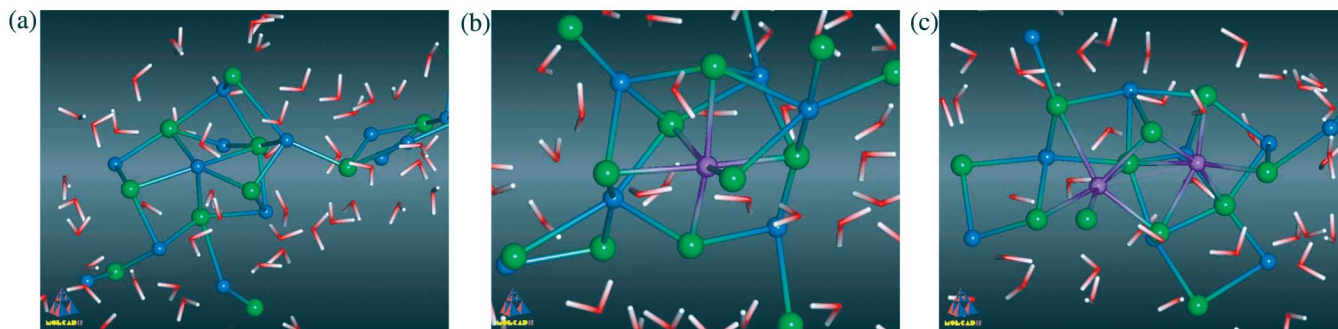

FIG. 2 (color). (a) Configuration of a selected $[Na_xCl_y]^{x-y}_{aq}$ aggregate at the end of the 1 ns simulation run. Sodium and chloride ions are represented as blue and green balls, respectively. The water molecules of the first coordination sphere of the displayed ions are shown as sticks; all other molecules were cut. (b) Configuration of a selected $[Na_xCl_y]^{x-y}_{aq}$ aggregate at the end of the 1 ns simulation run. As observed in the majority of our simulation runs, one sodium ion (purple) is entirely free of hydration water molecules. The coordination by chloride ions is similar to those in the crystal structure, though the Cl-Na-Cl angles may deviate by $\pm 10°$ from the ideal $90°$. The Na-Cl distances vary from 2.8 to 3.1 Å and thus tend to be larger than in the crystal structure. (c) Configuration of one out of two $[Na_xCl_y]^{x-y}_{aq}$ aggregates, exhibiting two nonhydrated sodium ions (purple) at the end of the 1 ns simulation run. The distance of these sodium ions is 0.1 Å larger than in the crystal structure. The Cl^- octahedra coordinating two nonhydrated sodium ions are strongly distorted. The corresponding Cl-Na-Cl angles range from $75°$ to $110°$.

presence of nonhydrated sodium ions appears to be a common feature. For such Na$^+$ ions the coordination by Cl$^-$ was always found to be very similar to that in the crystal structure. This also holds for the sodium ions having one water molecule in its first coordination sphere. Those sodium ions were observed to be coordinated by five chloride ions [Fig. 2(a)]. Consequently, formations of nonhydrated sodium ions coordinated octahedrally by chloride ions are proposed as centers of stability of the aggregates. This concept is supported by the observation of growth of such structures in two of our simulation runs. Since the number of ions in the simulation box is limited, growth is hindered with increasing aggregate size. The investigation of aggregate growth to large ion clusters would thus require much larger model systems. While this would result in a considerable increase in the computational demand, the presented simulations offer insight into the very early stage of nucleation processes.

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