

Brine Rejection from Freezing Salt Solutions: A Molecular Dynamics Study

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The atmospherically and technologically very important process of brine rejection from freezing salt solutions is investigated with atomic resolution using molecular dynamics simulations. The present calculations allow us to follow the motion of each water molecule and salt ion and to propose a microscopic mechanism of brine rejection, in which a fluctuation (reduction) of the ion density in the vicinity of the ice front is followed by the growth of a new ice layer. The presence of salt slows down the freezing process, which leads to the formation of an almost neat ice next to a disordered brine layer.

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There is a striking difference between liquid water and ice in terms of salt solubilities. On one hand, water is an excellent solvent which is capable of dissolving molar amounts of common inorganic salts such as NaCl. On the other hand, salts are almost insoluble in ice, with solubilities in the micromolar range at best [1,2]. This fact is behind a very interesting natural phenomenon—brine rejection from freezing aqueous salt solutions. For temperatures above the eutectic point of a given salt (e.g., -21.1°C for NaCl [3]) the solution freezes as neat ice with salt ions being rejected into the unfrozen part of the system. As the freezing process progresses a salt concentration gradient, as well as a temperature (due to latent heat release) gradient is established across the freezing front. This leads to macroscopic instabilities due to which an originally planar freezing front becomes corrugated [4–6].

The well-known fact that sea ice is less salty than sea water is a direct consequence of the above effect. Moreover, brine rejected from freezing sea water increases the density of the underlying water masses. This triggers massive ocean circulations which influence the global climate [7,8]. Analogous brine rejection occurs also during impact freezing of supercooled cloud water droplets, which contain salt ions originating from the soluble cloud condensation nuclei. Such a process has recently been invoked in a suggested new mechanism of thundercloud electrification via transfer of salt ions during collisions of ice crystals with the brine covered surface of graupels [9].

Motivated by the atmospheric and technological (desalination) implications, as well as by fundamental scientific curiosity, the macroscopic features of brine rejection have been intensely investigated both experimentally [10] and theoretically [4]. However, the detailed microscopic mechanism of brine rejection remains elusive, since it is experimentally hardly feasible to follow individual atomic motions during this process. In this situation, molecular dynamics (MD) simulations can play a unique role as an exploratory tool for elucidating the molecular mechanism of brine rejection. It is the principal aim of this Letter to communicate such results. Based on previous MD studies of neat water freezing and processes at the ice-water

interfaces [11–16] we first establish a computational protocol for reproducibly freezing water in contact with an ice layer. In the second and most important step we apply this procedure to molecular simulations of brine rejection from a freezing aqueous salt solution. This allows us to follow the dynamics of the brine rejection process with atomic resolution and address questions concerning the interplay between salt ion motions and the progression of the freezing front.

In the MD simulations, periodic boundary conditions were employed with a unit cell with approximate dimensions of $22 \times 23 \times 43 \text{ \AA}^3$, consisting of 720 water molecules and a variable number of salt ions. One fourth of the volume was constructed as a proton disordered cubic ice [17] while the rest was initially in the liquid phase (see Fig. 1). For the construction of the system we followed the procedure proposed by Hayward and Haymet [18]. 3D periodic boundary conditions were applied, creating an

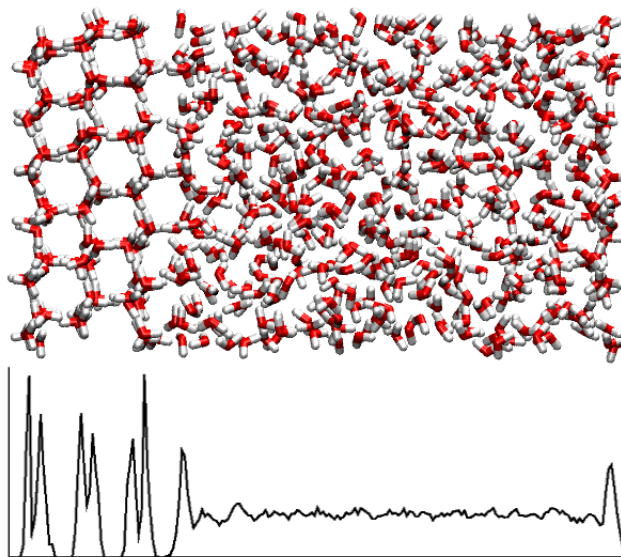


FIG. 1 (color online). The simulation cell and the water oxygen density profile at the beginning of the simulation. The unit cell is periodically repeated in all three dimensions.

infinite patch of cubic ice in the xy plane surrounded by liquid water, with two (111) ice-water interfaces perpendicular to the z axis per unit cell. Salt was introduced into the system by replacing randomly chosen liquid phase water molecules by the appropriate number of sodium and chloride ions. In this way, systems of approximately $0.15M$ (2 NaCl ion pairs) and $0.3M$ (4 NaCl ion pairs) salt concentrations were created.

All simulations were carried out using the PMEMD program [19,20]. A standard nonpolarizable rigid-monomer force field was employed for water [extended simple point charge (SPC/E) potential] and ions [21,22]. Classical equations of motion were propagated numerically with a time step of 1 fs. A cutoff distance of 9 Å was used for van der Waals and Coulomb interactions, and a smooth particle mesh Ewald procedure [23] was applied for accounting for the long-range electrostatic interactions. Temperature was kept constant using the Berendsen coupling scheme [24], in which the velocities of all particles are frequently rescaled to maintain the desired temperature. Pressure was maintained at 1 atm. Anisotropic pressure scaling was employed due to the inherent anisotropy of the initial ice-water layered structure. However, this anisotropy is rather weak, especially if compared to the large pressure fluctuations inherent to almost incompressible systems such as water.

To equilibrate the ice-water interface, we adapted for our purpose the procedure described in detail in Ref. [18]. Several consecutive constant volume runs with increasing time steps (ranging from 0.1 to 1.0 fs) and temperature were used to remove potential bad contacts introduced during the construction of the simulation cell. Consequently, a 50 ps constant volume run, followed by a 100 ps constant pressure simulation was used to provide a relaxed system (Fig. 1). Positions of ice phase water molecules were kept fixed during this initial equilibration process. Note that heating and equilibration eventually lead to partial melting of the ice surface in contact with liquid water. Very long production runs of hundreds of nanoseconds, during which all atoms in the system were allowed to move, followed. Simulations at different temperatures were performed, the investigated temperature range being -15 to $+15$ degrees from the melting point of the SPC/E water (215 K, *vide infra*).

The resulting trajectories were analyzed in terms of density profiles. The simulation box was divided into 0.2 Å thick slices parallel to the interface and distributions of oxygen atoms, Na^+ , and Cl^- ions were recorded. The initial oxygen density profile (Fig. 1) exhibits a characteristic double-peaked behavior in the left part, arising from the presence of the oxygen bilayers in ice, while it is unstructured in the liquid water part of the cell.

We have investigated the freezing of water and salt solutions in contact with a layer of cubic ice Ic. Cubic ice has very similar properties (structure, density, heat capacity, etc.) to the most common hexagonal ice Ih, of which it is a metastable form. Moreover, there are impor-

tant processes where cubic rather than hexagonal ice is formed. Morishige and Uematsu [25] reported freezing to cubic ice for water confined in nanopores. This type of ice is also present in the upper atmosphere and can play an important role in cloud formation [26–28]. Moreover, cubic ice was recently reported as the phase being predominantly formed during the freezing of water droplets with radii up to 15 nm or water films up to 10 nm [29], i.e., comparable in thickness to that of the initial ice patch in our systems.

In computer simulations, melting temperature is a sensitive function of the employed force field. Clearly, none of the water potentials is perfect and they are known to exhibit different melting temperatures, which are typically below the experimental value of 0°C . Melting temperatures of ice described by different water models were published recently and for the SPC/E potential a value of 215 K was estimated [30]. Despite this deficiency, the relatively simple and computationally efficient SPC/E model captures well most of the physical properties of water and ice [15]. We, therefore, introduce a relative temperature scale where the melting point is assigned the value of 0° .

We performed a series of freezing/melting simulations of the ice layer in contact with neat water for a range of temperatures below and above 0° . Figure 2(a) demonstrates the results of a typical simulation of melting of an ice layer in contact with liquid water at the estimated melting temperature of SPC/E water [30]. We see that for about 50 ns the two phases coexisted with each other, after which the ice phase melted within several nanoseconds. The delayed melting is primarily connected with the limited efficiency of the heat bath to provide the necessary latent heat at temperatures close to the melting point. Figure 2(b) shows a typical freezing simulation at -15° . From the very beginning we see an onset of freezing accompanied in some cases by subsequent remelting of layers adjacent to the original ice phase. Eventually, after about 150 ns massive freezing starts and the whole sample freezes within additional 100 ns.

The most important message from these simulations is the establishment of a procedure and time scale for reproducibly freezing and melting ice-water systems. Previous simulation studies of the coexistence of an ice layer with liquid water employing SPC/E or similar water models were done on the time scale of hundreds of picoseconds to 2 ns [15,18,31]. It follows from the present simulations, that hundreds of nanoseconds are necessary to capture freezing of SPC/E water in the nanometer-scale cell (which nicely correlates with experimental ice growth rates of the order of millimeters to centimeters per second [32]) and even melting close to 0° takes several to tens of nanoseconds [see Fig. 2(a)]. The only previous simulation of freezing employing comparable time scales involved ice formation from liquid water “from scratch,” i.e., without a contact with an ice layer [13]. Most recently, the situation has, however, somewhat changed thanks to the appearance

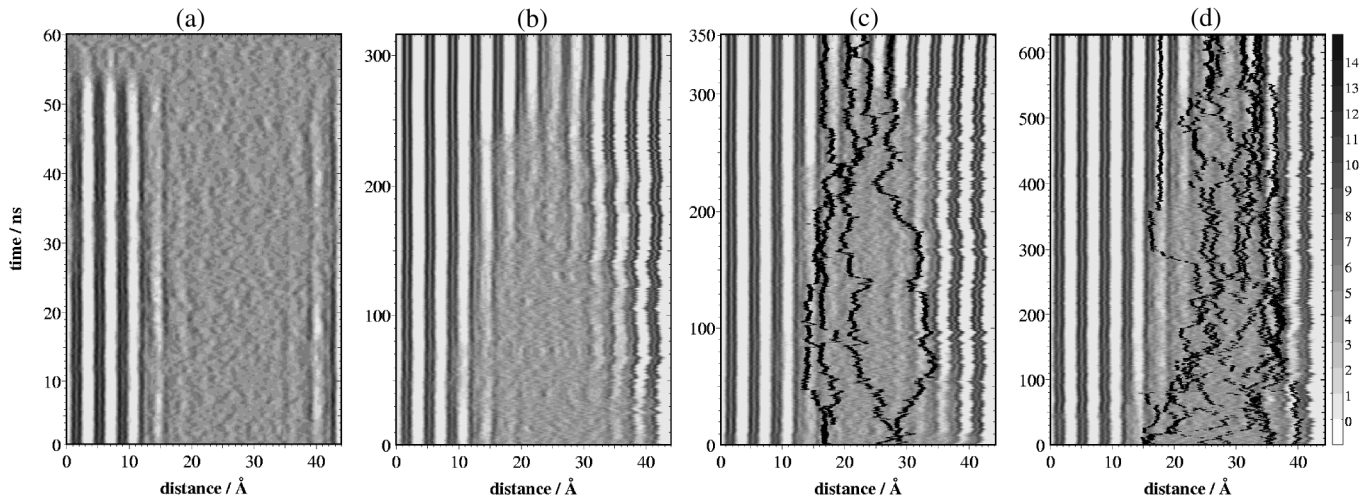


FIG. 2. Time evolution of the water oxygen density profiles and positions of sodium and chloride ions. The density scale (in arbitrary units) is on the right hand side. (a) Ice melting simulation. Note the melting process of the structured ice phase on the left hand side after about 50 ns. (b) Water freezing simulation. Note the gradual freezing of the unstructured liquid water phase taking hundreds of nanoseconds. (c) Salt water (0.15M) freezing. (d) Salt water (0.3M) freezing. Trajectories of Na^+ and Cl^- ions are shown as black lines. Note in (c) and (d) the rejection of the ions as the freezing front progresses.

of new water models leading to faster freezing at temperatures closer to 0°C [33–35].

After establishing a robust computational protocol for neat water freezing we could proceed to the main topic, i.e., molecular simulations of brine rejection from freezing salt solutions. Figs. 2(c) and 2(d) show the time evolution of the density profiles for systems containing 2 or 4 NaCl ion pairs, respectively. Both simulations were performed with temperature fixed 15° below the melting point, consistently with the study of neat water freezing. It can be seen that the time scales of the freezing process increase with increasing salt concentration, from about 250 ns in neat water to more than $0.5\ \mu\text{s}$ for the most concentrated solution. This is a direct demonstration at the molecular level of the kinetic antifreeze effect of the added salt.

From the time-dependent density profiles as well as from the simulation snapshots (see Fig. 3 for representative snapshots for the most concentrated system) it is clear that both sodium and chloride ions are rejected by the advancing freezing front into the remainder of the liquid phase. Eventually, the system freezes as neat ice almost completely, the ions being expelled into a small volume of concentrated brine. This region with high salt concentration (over $1M$) has a glassy character and we see a very slow tendency for incorporation of further water molecules into the ice lattice. However, on the time scale of the present calculations (which is extremely large for MD simulations) complete steady state situation between the ice and brine regions is not established yet.

A simulation with higher salt concentration shows that an ion can be sometimes trapped inside the ice crystal [Fig. 2(d)], in qualitative accord with the low solubility of salts in ice. The fact that we observe a chloride anion (but not a sodium cation) deposited in the top layer of ice also nicely correlates with results of recent simulations of

NaCl ions placed at the ice surface, which also suggested a certain degree of charge separation [36]. In light of the persisting controversy concerning the magnitude of the measured transient electrical potential across the freezing front (the so-called Workman-Reynolds effect) [37,38] it would be desirable to try to better characterize this effect in the simulations. However, due to the low solubilities of salt ions in ice, extremely large unit cells (which are currently computationally prohibitive) would be required for obtaining statistically significant data.

The present molecular simulations allow us to address questions concerning the detailed dynamical mechanism of brine rejection. From the trajectories of the ions [Figs. 2(c) and 2(d)] we see that the progression of the ice front and the expulsion of the ions into the unfrozen volume are highly correlated. Upon closer inspection, it becomes clear

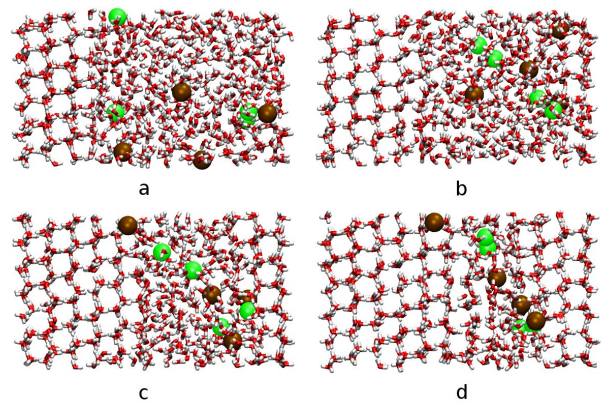


FIG. 3 (color online). Snapshots from the freezing simulation of the 0.3M salt solution. (a) 1 ns, (b) 200 ns, (c) 400 ns, (d) 600 ns. Na^+ and Cl^- are given as light (green online) and dark (brown online) spheres, respectively.

that the usual scenario is a fluctuation (reduction) of the salt density close to the ice front, which is followed by a buildup of a new ice layer [see, e.g., a freezing event between 200 and 300 ns in Fig. 2(c)]. Many more extremely time demanding simulations are needed to fully quantify this observation, but the atomic picture is emerging already from the present results.

In summary, we investigated by means of extensive molecular dynamics simulations the freezing of water and salt solutions in contact with an ice layer. A procedure for reproducibly freezing neat water next to an ice layer was established, together with the relevant (>100 ns) time scale. This time scale, which can to some extent depend on the particular choice of a water model, is consistent with the naturally occurring macroscopic freezing rates. Brine rejection was observed in systems with varying salt concentration for temperatures below melting and above the eutectic point. We showed at the molecular level that NaCl acts as an antifreeze agent and proposed a mechanism correlating local fluctuations of salt concentration with the progression of the freezing front. A detailed description of the molecular mechanism of brine rejection aims at our better understanding of this important natural phenomenon. With the present rapid improvements of water models and computational resources it is desirable to perform simulations employing larger unit cells and/or longer time scales with water which freezes close to 0°C . Work in this direction is in progress in several groups. The present molecular dynamics simulations open a way to quantitative modeling of brine rejection in atmospherically relevant systems (e.g., freezing of the sea surface in polar regions or riming of supercooled droplets in thunderclouds) and to explore efficient strategies to control this process in technological applications such as desalination.

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