

MOLECULAR SIMULATIONS OF WATER FREEZING: BRINE REJECTION AND HOMOGENEOUS NUCLEATION

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1 INTRODUCTION

Water is probably the most important and the most intensely studied substance on Earth. It is the solvent of life and it is also of vital importance in many aspects of our existence, ranging from cloud microphysics to its key role as a solvent in many chemical reactions. The familiar process of water freezing is encountered in many natural and technologically relevant processes. In this contribution, we discuss the applicability of the methods of computational chemistry for the theoretical study of two important phenomena. Namely, we apply the molecular dynamics (MD) simulations to the study of brine rejection from freezing salt solutions and the study of homogeneous nucleation of supercooled water.

Sodium chloride and other common inorganic salts are very poorly soluble in ice, with solubilities in the micromolar range at best.^{1,2} Liquid water, however, is capable of dissolving molar amounts of these salts. This property is clearly demonstrated by the fact that the salinity of the sea ice is much smaller than that of seawater. When the aqueous NaCl solution freezes above its eutectic temperature ($-21.1\text{ }^{\circ}\text{C}$)³ it solidifies as almost pure ice. The salt is rejected into the surrounding unfrozen solution. Salt concentration and temperature gradients due to latent heat release are established across the freezing front as freezing proceeds. This results in the formation of macroscopic instabilities and the initially planar freezing front becomes corrugated.^{4,6}

When freezing occurs on the surface of the ocean, the rejected salt increases the density of underlying water masses. This leads to massive circulations in the ocean influencing the global climate.^{7,8} Brine rejection is also proposed to play important role in the thundercloud electrification.⁹ Supercooled cloud water droplets containing salt particles originating from the soluble cloud condensation nuclei can freeze upon impact. Dissolved salt is then rejected from the freezing water and concentrates on the surface of the graupel. The electrification then occurs via the collisions between neat ice crystals and salt-covered graupels.

Brine rejection is thus an extremely interesting and also important process with wide natural, atmospheric, and technological consequences (with desalination as a prominent example). It has, therefore, been subject to experimental¹⁰ as well as theoretical research.¹¹ In most cases, water in nature freezes heterogeneously, i.e., in contact with crystallization nuclei such as small pieces of ice or minerals. When such contact is avoided, water can be supercooled to very low temperatures (up to $-30\text{ }^{\circ}\text{C}$) before homogeneous freezing takes

place.¹² Droplets of supercooled water are known to be formed in the stratosphere and upper troposphere.^{13,14} Homogeneous nucleation is the controlling mechanism for the formation of cirrus and polar stratospheric clouds, affecting directly the radiative balance of the Earth.

There exists an ongoing scientific debate whether homogeneous nucleation starts at the surface or rather in the bulk of the water droplet. The experimental evidence in this case is ambiguous. It has been concluded recently that, based on existing thermodynamic nucleation models, as well as laboratory and atmospheric data, ice nucleation at the surface can be neither confirmed nor disregarded.¹⁵ Recent laboratory experiments indicate that homogeneous ice freezing is a volume-proportional process with surface nucleation being potentially important for small droplets with radii below 20 μm .¹⁶ On the contrary, higher freezing temperatures and faster freezing rates were observed for droplets with an ice-forming nucleus placed close to the surface compared to a bulk location.¹⁷ It has been suggested recently that molecular simulations could provide further information concerning the surface-initiated homogeneous nucleation.¹⁸

Thanks to advancement of the computer technology computer simulations of processes related to water freezing are becoming feasible. The greatest advantage of the calculations is that they can provide insight to the structure and dynamics of the system at an atomic level, with resolution often inaccessible to experimental techniques.

Crystallization usually involves very long time scales (at least when compared to time scales of routine calculations) and complicated potential energy landscapes. Computer simulations of this process are, therefore, considered to be difficult in general. In a series of papers, Haymet and coworkers investigated the structure and dynamics of the ice/water interface.¹⁹⁻²¹ In their approach, the pre-built patches of water and ice were put together to create the interface. The necessity to simulate the highly improbable creation of the crystallization nucleus was thus avoided. Similar setup was used by other groups to assess various properties of the ice/water interface.²²⁻²⁶

These simulations can be easily extended to systems containing solutes, namely simple salts. However, most of the reported simulation studies concerned only the behavior of the solute at the stable ice/water interface.^{27,28} Only recently results of successful simulations of the brine rejection process involving a moving ice/solution boundary have been reported.^{11,29,30}

Water freezing was observed in simulations of systems subjected to an electric field,³¹ in confined water,³² and in (non-dynamic) Monte Carlo calculations.³³ However, there are to the best of our knowledge only two successful MD simulations of water freezing "from scratch", i.e., without any bias introduced by initial conditions (existing crystallization nucleus or external electric potential).^{34,35}

A key point in the simulations is the choice of the interaction potential. There exist many different water models optimized for different purposes.³⁶ Each model shows better or worse agreement with particular water properties. These models are mostly fitted to describe liquid water. Therefore, their use for the simulations of ice can be tricky. Namely, one of the properties that is often described incorrectly is the melting temperature. A comprehensive comparison of the most common water models with respect to the melting temperature of water has been published recently.³⁷ Values in the wide range of 190 – 270 K were obtained. It is, therefore, always necessary to choose between the computer efficiency of the model and the quality of the description of water properties, although a more complicated model does not always mean better description.

We applied the MD technique to the simulation of brine rejection from freezing salt solutions employing the rigid 3-site simple point charge (SPC/E) water model^{38,39} to obtain the microscopic picture of this very important natural process. Further, we used a recently

proposed 6-center water potential⁴⁰ (abbreviated NE6) for simulation of the water freezing "from scratch" performed in a slab geometry. The ultimate goal was to provide a computational view on the surface-induced homogeneous nucleation.

2 COMPUTATIONAL METHODOLOGY

2.1 Brine rejection

Our calculations can be viewed as an extension of the work of Bryk and Haymet.²⁷ They studied the behavior of the Na⁺ and Cl⁻ ions at the static ice/water interface on the nanosecond timescale. We were interested in the solidification process itself and in the expulsion of the ions into the remaining liquid. This required using longer simulation times (hundreds of nanoseconds). For the purpose of our research, we used the SPC/E water potential.³⁸ Potential parameters for sodium and chloride ions were taken as the non-polarizable set from Ref. 41.

For the construction of the simulation cells we employed the approach of Hayward and Haymet.²⁰ A brief outline of the procedure is given below while a more detailed description can be found in our recent papers.^{11,29} Pre-equilibrated cells of liquid water and ice were combined together to create systems with alternating solid/liquid phases. Salt ions were then introduced into the liquid. After the application of the periodic boundary conditions, infinite slabs in the xy-plane of ice next to a liquid salt solution were formed. We then let these cells to evolve at different temperatures and observed the time needed to freeze the remaining liquid part of the sample. We also monitored the positions of the ions.

After the equilibration of the simulation cells, the production runs were performed at the target temperatures with the timestep of 1 fs. Long-range electrostatic interactions were treated using the smooth particle mesh Ewald method (SPME). Calculations were run in the NPT ensemble, with anisotropic pressure coupling and target pressure of 1 atm, using Berendsen barostat. The total length of the simulations ranged from several hundreds of nanoseconds to a microsecond.

2.2 Homogeneous nucleation

We used the newly proposed six-center water potential (NE6) for the simulations.⁴⁰ A simulation cell with approximate dimensions 13.5 x 15.5 x 30.0 Å³ containing 192 water molecules was elongated in the z-direction to 100 Å. Replication of the original unit cell twice and three times in the z-direction and elongation to 180 and 270 Å provided the simulation cells with 384 and 576 water molecules, respectively. Subsequent application of periodic boundary conditions yielded infinite slabs in the xy-plane, each possessing two air/water interfaces perpendicular to the z-axis.

The production runs followed the system preparation and adjustment of the target temperature. Newtonian equations of motion were solved with a time step of 1 fs, with the total length of simulations in the range of 100 – 500 ns. The calculations were run in the NVT ensemble, with long-range electrostatics treated again using the SPME method. The melting temperature of the NE6 water model is estimated to be close to 0 °C. The simulations of the smallest cell performed at different temperatures indicated that supercooling the sample to 250 K provided the fastest freezing rates. Therefore, simulations of the larger systems were performed at this temperature as well.

3 RESULTS AND DISCUSSION

3.1 Brine rejection

We have simulated freezing of a salt solution in contact with a patch of cubic ice Ic. The properties of this ice form (density, heat capacity, etc.) are very similar to those of the most common hexagonal ice Ih. Ice Ic is actually a metastable form of the ice Ih. There exist several important processes where cubic rather than hexagonal ice is formed. This type of ice is present in the upper atmosphere and can play important role in cloud formation.⁴²⁻⁴⁴ It was also reported that freezing in nanopores leads preferentially to cubic ice.⁴⁵ Very recently, cubic ice was reported to be the dominant ice crystal modification during the freezing of water droplets (with radius up to 15 nm) and thin water films (up to 10 nm thick).⁴⁶ These dimensions are comparable to the initial thickness of the ice patch in our simulations.

We performed series of simulations for a range of temperatures around the melting point of the SPC/E water model (215 K, i.e., significantly below the experimental value).³⁷ Despite this deficiency, this very simple model provides very reasonable description of other water and ice properties.²¹ Below, we introduce a relative temperature scale with the melting point assigned a value of 0°.

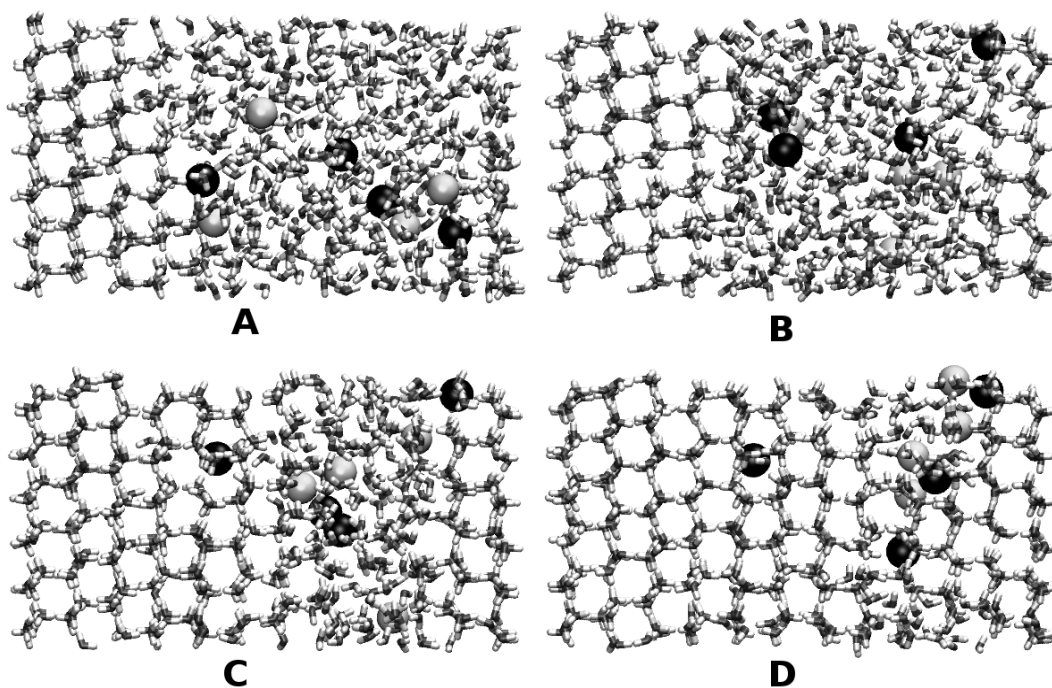


Figure 1 Snapshots from the MD simulation of the brine rejection with 4 NaCl pairs. Na^+ and Cl^- are given as light and dark spheres, respectively. Snapshots correspond to A) 200 ns, B) 400 ns, C) 600 ns, D) 815 ns simulation time.

First, it was necessary to establish a robust simulation protocol for reproducible freezing of neat water in contact with a patch of ice. The results can be summarized as follows. In previous studies of the ice/water coexistence rather short simulation times were used (up to 2 ns).^{20,21,46} Our simulations show, however, that hundreds of nanoseconds are needed to freeze the nanometer-scale unit cell of SPC/E water and even melting close to 0° takes several to tens of nanoseconds.^{11,29} Depending on the size of the system melting was observed in the temperature range of -10 - 0°.

Then simulations of salt solutions in contact with ice were performed. In general, melting temperature decreased and freezing was observed at -15°. Also, the time needed to freeze the sample grew dramatically with increasing salt concentration. These are direct demonstrations of the kinetic and thermodynamic antifreeze effects of the added salt at the molecular level.

Representative snapshots from brine rejection simulations are given on Figure 1. It can be clearly seen that both sodium and chloride are rejected by the freezing front into the remaining liquid solution (save a single chloride which got trapped in the ice lattice). At the end of the simulation, a thin layer of unfrozen concentrated brine solution with glassy character is formed. There is a slow tendency to incorporate more of the remaining water molecules into the ice lattice; however this process exceeds the time scale of present simulations.

A more detailed analysis revealed that the freezing proceeds by the following mechanism. First, there is a fluctuation (decrease) of salt density near the freezing front followed by the buildup of the new ice layer.

3.2 Homogeneous nucleation

We have also simulated homogeneous freezing of slabs of neat water. The main outcome of the simulations is shown in Figure 2. It shows snapshots from the MD simulation of the medium-sized simulation cell. Only water molecules in the central unit cell are displayed. When periodic boundary conditions are employed, an extended slab is formed. In the figure, it is easy to locate the interfacial regions (top and bottom of the picture) and the bulk region located between the two interfaces.

The first crystallization nucleus forms in the subsurface approximately at 45 ns. The second subsurface nucleus occurs 110 ns after the beginning of the simulation. Freezing proceeds independently from both nuclei and the freezing fronts meet at 160 ns, forming a somewhat disordered contact zone. Cubic ice Ic forms predominantly in the simulations and many defects can be identified in the ice lattice. Freezing to cubic ice is consistent with the recent findings that small droplets and thin water films prefer this crystal modification over hexagonal ice Ih.⁴⁷

Similar results were also obtained for other simulations of systems of varying sizes. In all cases the initial crystallization nucleus forms in the subsurface and freezing then proceeds towards the bulk.

In one case we observed concurrent formation of two ice nuclei; one in the subsurface and one in the bulk. The freezing then proceeded from both nuclei. Figures displaying snapshots from these simulations and further analysis can be found elsewhere.⁴⁸

The preferred nucleation in the subsurface can be due to several factors. First, the volume change upon the phase transition (change in the molar volume upon freezing is positive for water) will direct the process to the region of lower density, i.e., towards the interface. However, the water molecules at the very interface are very disordered and undercoordinated and cannot freeze.

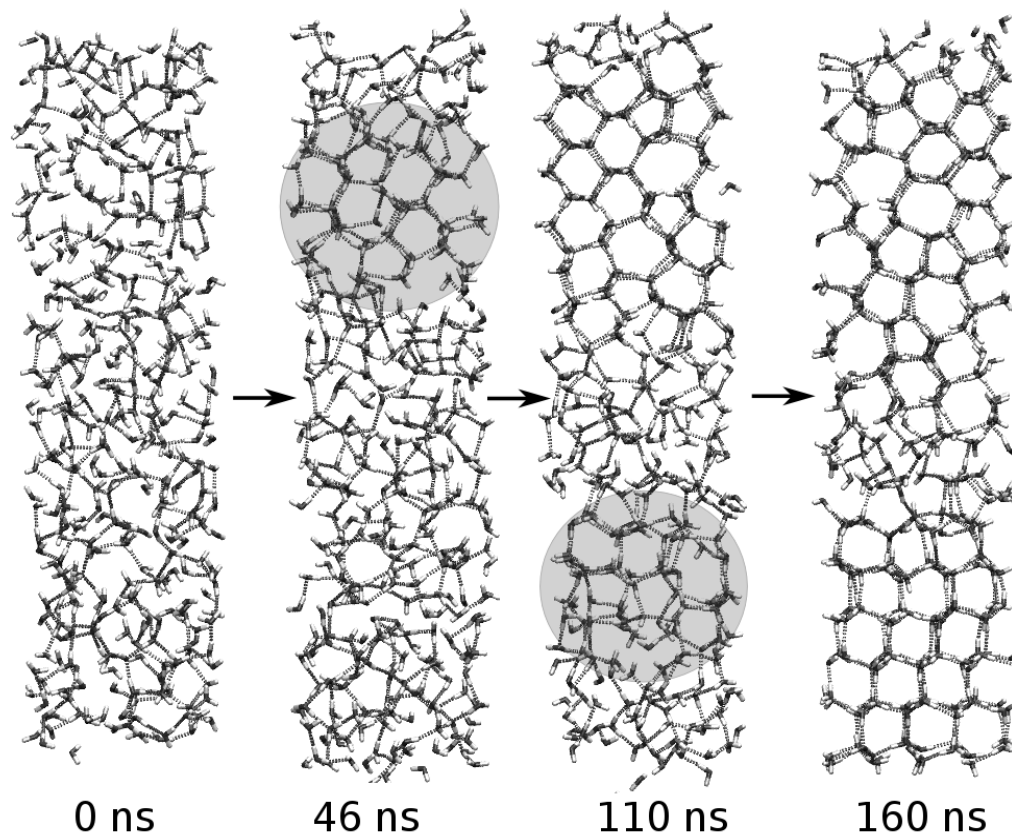


Figure 2 Snapshots from the MD simulation of the slab with 384 water molecules. Both crystallization nuclei (shaded regions) form in the subsurface. Water freezes mostly as cubic ice, with many defects.

There exists an electric field at the interface establishing the surface potential estimated to be in the order of 100 mV.^{49,50} Such potential difference across the sub-nanometer wide interfacial region is equivalent to very strong electric field. It has been shown recently that such field can be used to enable ice nucleation.³¹

Molecules at the interface and in the subsurface also have larger mobility than those in bulk phase. Their reorientation into positions corresponding to ice lattice can be expected to be faster than in the bulk. This can be viewed as a kinetic advantage for the creation of the ice nucleus near the interface.

4 CONCLUSION

This contribution shows how molecular simulations can be used to provide better insight into highly relevant natural and technological processes of ice nucleation and freezing.

We investigated freezing of water and salt solutions by means of molecular dynamics simulations. We first established a robust simulation protocol for water freezing and then applied this approach to the study of the brine rejection process. Brine rejection was observed for a series of systems with varying salt concentration. We showed the anti-freeze

effect of the salt on the molecular level and proposed a mechanism correlating local fluctuations in the salt ion density and the progression of the freezing front.

Computer simulations were also used to show that the crystallization nucleus is more likely to form in the subsurface than in the bulk phase of the water slab. This result can have far reaching atmospheric implications. It has been suggested that formation of an ice nucleus at the interface would be hampered by contamination of the surface by organic surfactants.¹² The effect of the adsorbed material will surely propagate towards the subsurface as well, however it will be smaller than in the topmost layer. Therefore, the anthropogenic emissions should have an effect on the radiative balance of the Earth atmosphere. This effect should, however, be smaller than predicted using the assumption of surface nucleation.

Acknowledgements

We would like to thank the **META**Centrum project for generous allocation of computer time. Support from the Czech Ministry of Education (grant LC512) is gratefully acknowledged. L.V. acknowledges the support from the granting Agency of the Czech Republic (grant 203/05/H001).

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