Brine Rejection from Freezing Salt Solutions
A Molecular Dynamics Study

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Brine Rejection

Freezing of salt water causes rejection of salt (badly soluble in ice) to the surroundings, creating water with very high salt content – brine.

macroscopic picture of the freezing front – instabilities

freezing of KCl solution

Project motivation

Brine rejection

- Thundercloud electrification
  - laboratory experiments and computer simulations

- Arctic / Antarctic water masses ventilation
  - direct observation in the Okhotsk Sea

- Molecular level insight needed
- Computationally challenging project
Theoretical Studies

Ice–water interfaces
- work of Haymet et al.

Water freezing
- crystallization in electric field
- confined water
  Koga et al., *Nature* 2000, 408, 564
- freezing "from scratch"
- Monte Carlo studies
  Radhakrishnan and Trout, *J. Am. Chem. Soc.* 2003, 125, 7743

Effect of NaCl on water freezing
- No published simulation results so far
"Experimental" Setup

- simulation cell
- density profile
- layer of cubic ice as a template
- SPC/E water model
- melting temperature 215 K (0 °C)
- 3D periodic boundary conditions
- anisotropic constant pressure coupling
- long simulations (100 ns –)
- temperature range -15 °C to +35 °C
- addition of salt
Neat Water Freezing

- freezing at -5° in 50 ns
- large template
- independent interfaces (?)
- freezing at -15° in 315 ns
- realistic growth rate
- melting at any temperature above -15° (0° – 60 ns)
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Salt Water Freezing and Brine Rejection

2 NaCl ion pairs (0.15 M)

4 NaCl ion pairs (0.3 M)
Salt Water Freezing and Brine Rejection

2 NaCl ion pairs (0.15 M)

4 NaCl ion pairs (0.3 M)
Salt Water Freezing and Brine Rejection

Snapshots from the MD simulation

1 ns
Salt Water Freezing and Brine Rejection

Snapshots from the MD simulation

1 ns

200 ns
Salt Water Freezing and Brine Rejection

Snapshots from the MD simulation

1 ns

200 ns

400 ns
Snapshots from the MD simulation

1 ns

400 ns

200 ns

600 ns

Salt Water Freezing and Brine Rejection

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Brine rejection

EMSI 2005
Summary

- 1\textsuperscript{st} reported simulations of the brine rejection process
- Atomic resolution (unlike the experiments)
- Proposed order: \textit{salt concentration fluctuation} – \textit{freezing}
- Larger scale simulations are needed
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Thank You for Your Attention