EFFECT OF WATER CONFINEMENT ON HETEROGENEOUS ICE NUCLEATION

Olli Pakarinen, Golnaz Roudsari,
Bernhard Reischl, Hanna Vehkamäki

INAR, University of Helsinki, Finland

INAR

HELSINGIN YLIOPISTO
HELSINGFORS UNIVERSITET
UNIVERSITY OF HELSINKI

Institute for
Atmospheric and Earth
System Research

EGU General Assembly 2020 – Sharing Geoscience Online 6.5.2020

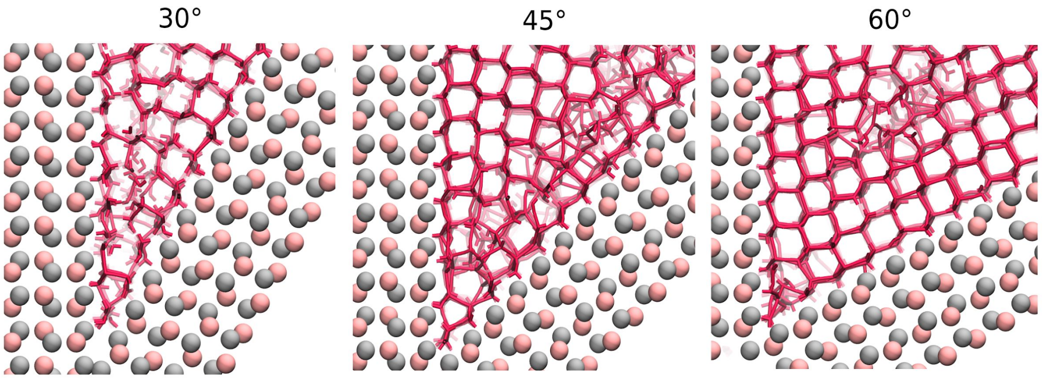
Highlights of research

In this work, we studied the role of water confinement on heterogeneous ice nucleation (IN) through Molecular Dynamics (MD).

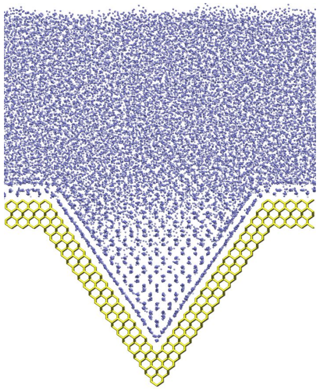
We found that IN enhancement by water confinement is active also at very low supercooling, enabling very IN active surface features, leading to ice crystallization at higher temperatures than any flat surfaces, close to the melting point of ice.

We found that water confinement in wedges and pits with different angles can significantly alter the ice nucleation rate. In particular, it is found that the angles which matches the ice lattice can promote ice nucleation substantially.

Non-monotonous enhancement as function of angle deviates from CNT.



Suitable defect structures or lattice match with ice enhance IN



Experimentally realizable etched pits in silicon

Using Molecular Dynamics simulations allows us to pinpoint where ice nucleation exactly occurs, look at the mechanisms and how ice grows in the simulation cell.

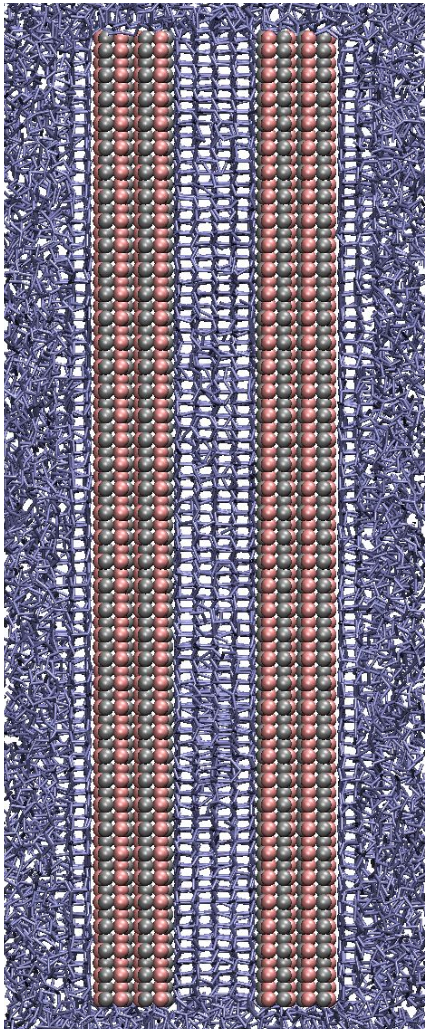
Motivation & introduction

- Understanding how surfaces control ice nucleation is important for many applications, but the detailed mechanism remains unclear
- Experiments have suggested surface irregularities, grooves or pits, as possible active sites on surfaces
- Earlier work has revealed ice nucleation mechanisms in a concave cavity at large supercooling - here we aim to study if this enhancement by water confinement is active also near the thermodynamic melting point of ice
- CNT predicts that a concave cavity is always favouring crystallization, because of smaller critical clusters
- Experiments show that ice nucleation also depends on other factors such as lattice match and surface chemistry
- Molecular Dynamics simulations can show the underlying of mechanism of ice growth in a concave wedge
- Here, we study ice nucleation on AgI slit systems, and AgI and Si pit and wedge geometries using both all-atom and coarse-grained Molecular Dynamics simulations

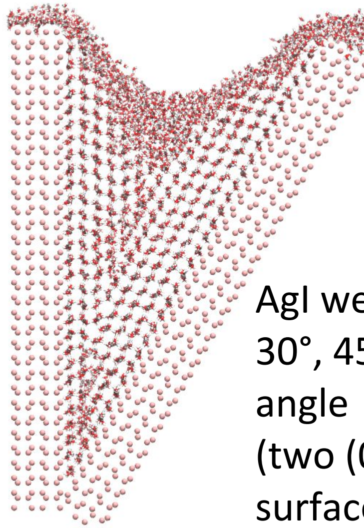
Studied systems: slit, wedge and pit geometries

Small supercooling for IN

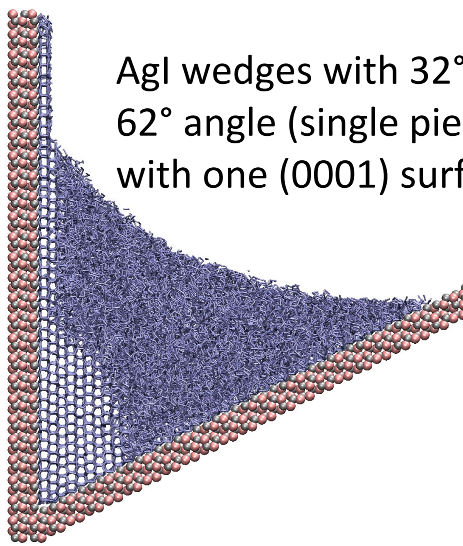
AgI slit system with mirrored Ag-terminated AgI(0001) surfaces



AgI wedge system



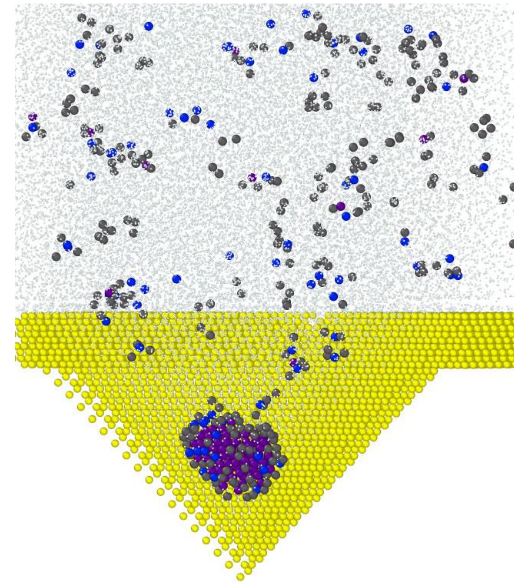
AgI wedges with 30°, 45° and 60° angle (two (0001) surfaces)



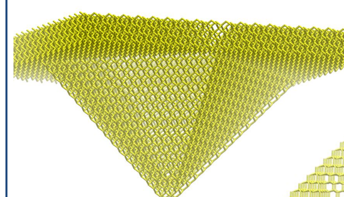
AgI wedges with 32° and 62° angle (single piece with one (0001) surface)

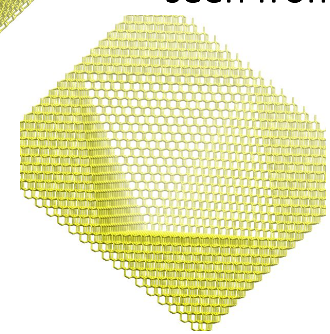
Large supercooling for IN

Water (32 000 mW molecules) in MD simulation on the **Si(100) pit**.



KOH-etched pit on the silicon (100) surface, seen from the side and top.

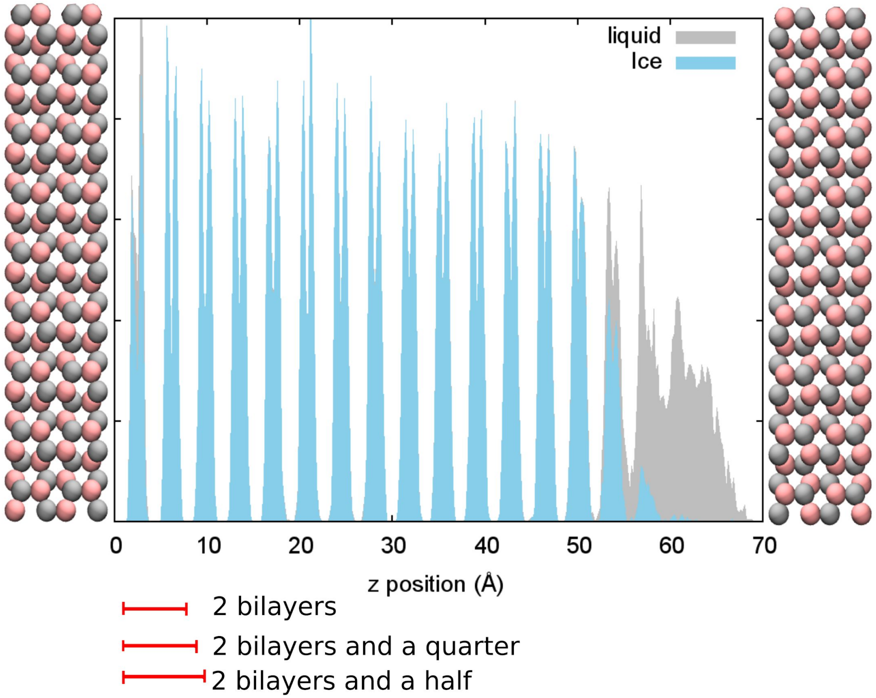




Pit structures realizable in experiments.

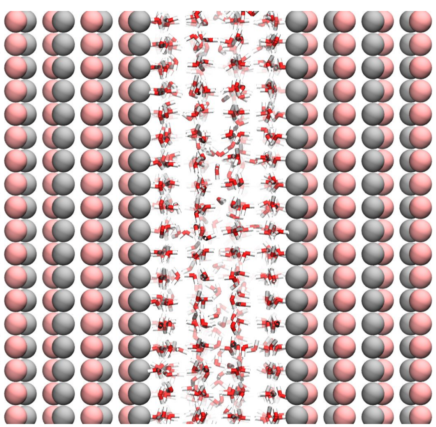
Colors in figures: mW water: blue / TIP4P O: red, H: white / Ag: silver / I: pink / Si: yellow

Results: AgI slit systems

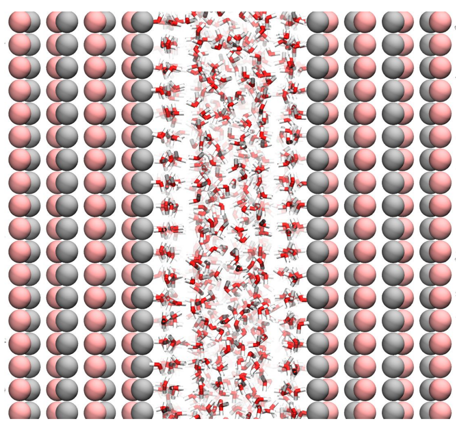


The role of confinement was studied with MD simulations performed on slit systems between 2 AgI (0001) slabs. The gap between 2 slabs is based on the width of ice bilayers. Here we defined three different sizes as they are shown in the figure. Our results show that ice formation between 0 ˚C and -10 ˚C is significantly affected by the width of the gap in slit systems.

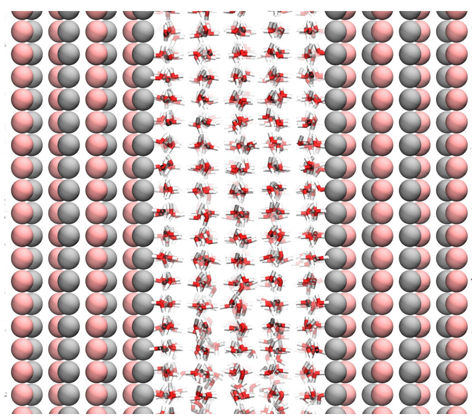
TIP4P/ice and mW models give identical results, ice forms only when there is space for integer number of ice bilayers.



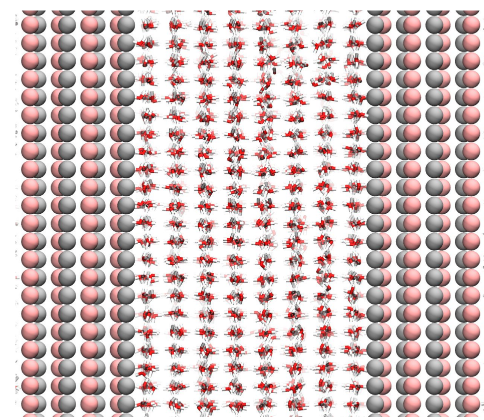
2 * 2 bilayers
Ice formation



2 * 2 bilayers and a quarter
No ice formation

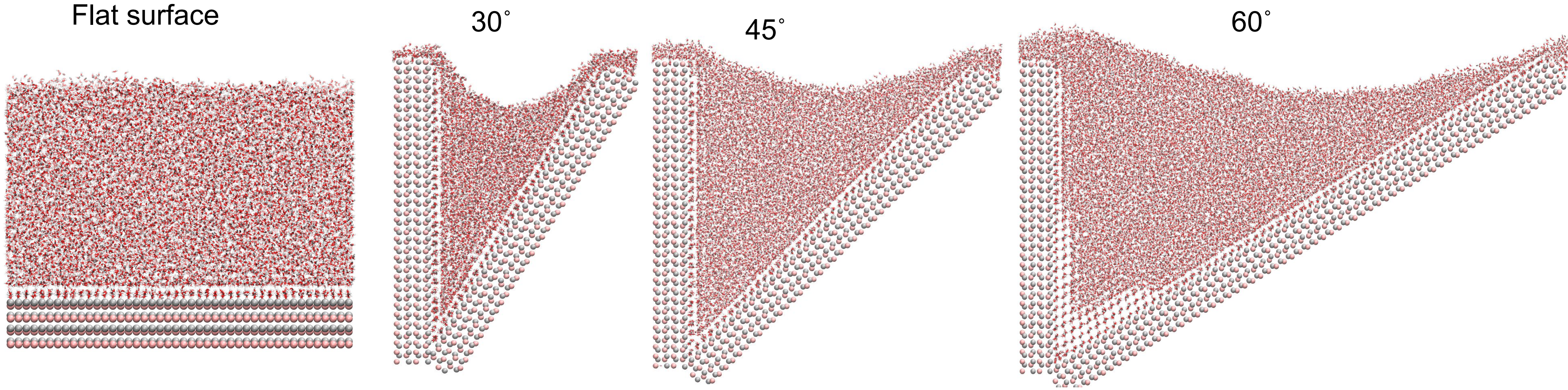


2 * 2 bilayers and a half
Ice formation



2 * 4 bilayers
Ice formation

TIP4P/ice results on AgI wedges (1/2)

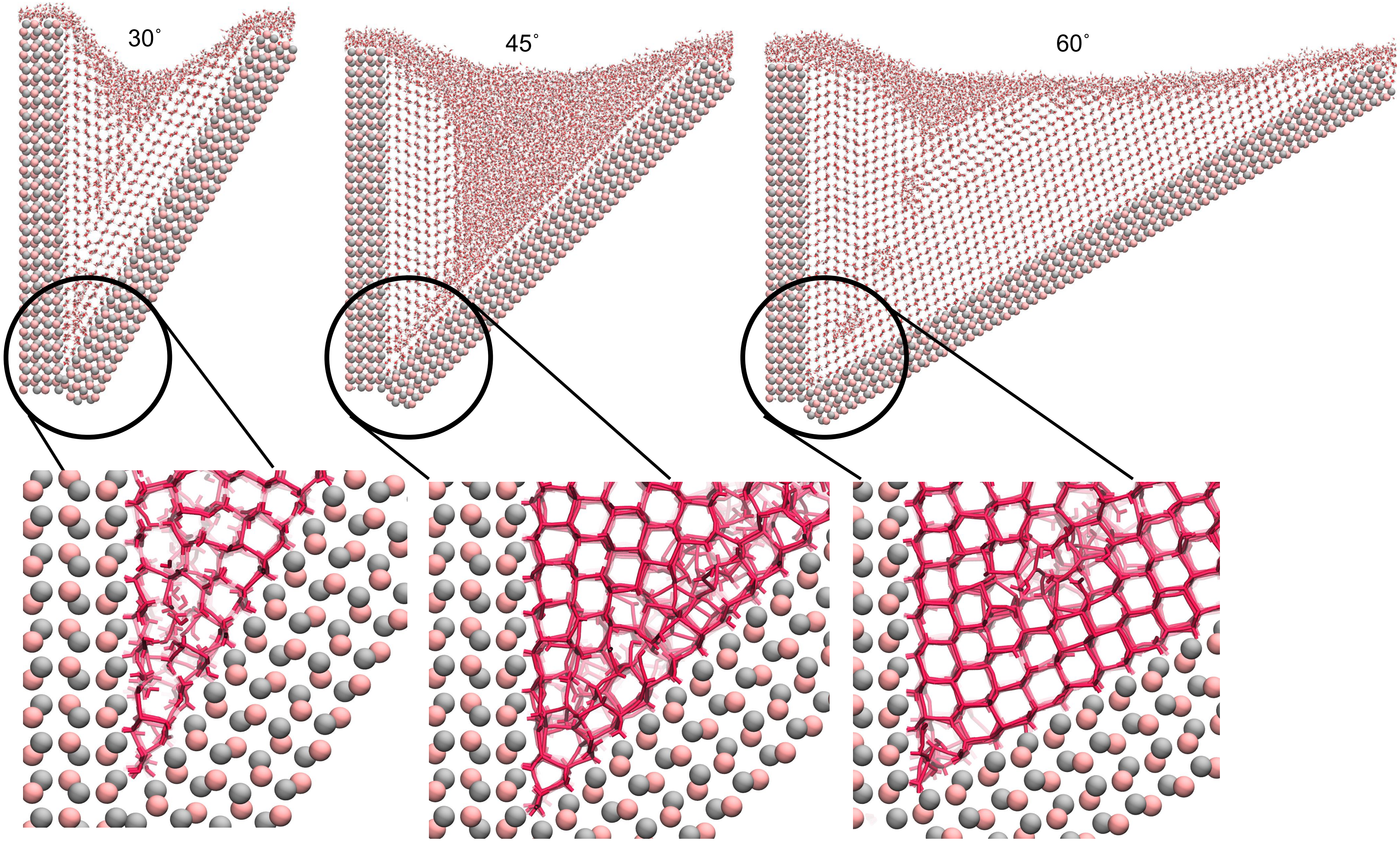


	Flat surface	Wedge 30˚	Wedge 45˚	Wedge 60˚
-10 ˚C	35 ns	55 ns	60 ns	15 ns
-8 ˚C	No nucleation	No nucleation	No nucleation	25 ns
-6 ˚C	No nucleation	No nucleation	No nucleation	25 ns

Table: Induction times for ice nucleation on flat surfaces and wedge systems at different supercooling

Studies showed that sharp, concave wedge of graphene can enhance ice nucleation (Bi, Cao & Li, 2016). Here, the role of confinement was studied on AgI(0001) at 263 K (-10 ˚C), 265 K (-8 ˚C) and 267 K (-6 ˚C) and with angles 30˚, 45˚ and 60˚. Our results show that wedge with 60˚ is greatly enhancing ice nucleation, compared to 30˚, 45˚ wedges and the flat AgI (0001) surface.

TIP4P/ice results on AgI wedges (2/2)

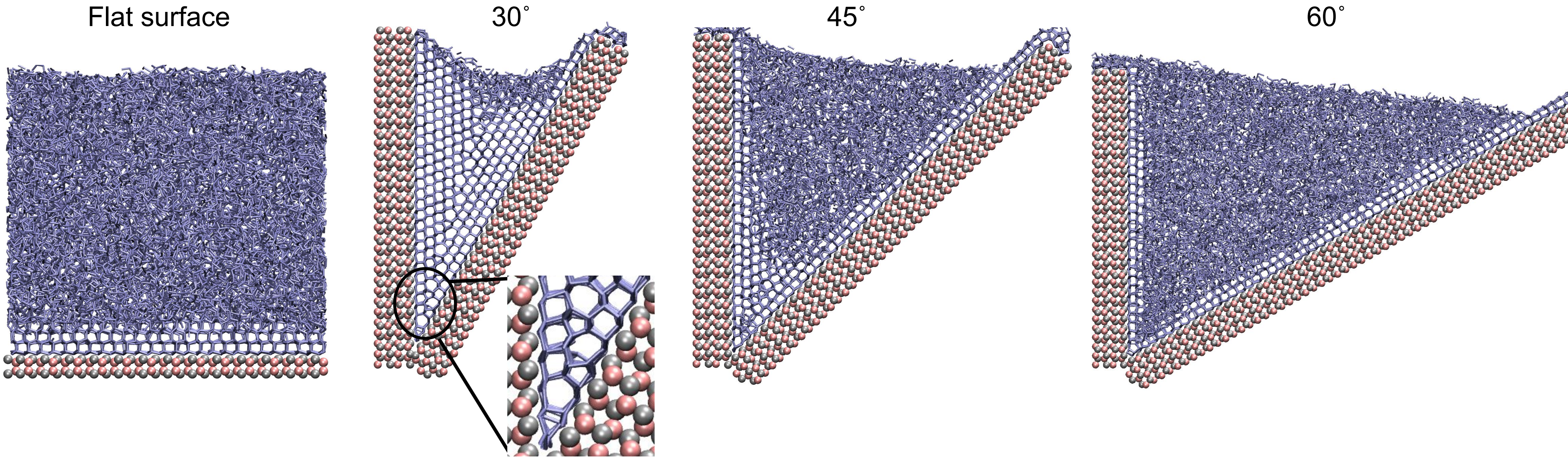


The enhanced ice nucleation within a 60˚ wedge can be explained as:

1) The geometry which constraints water molecules' movement and decreases the ice-water interfacial area
2) The 60˚ angle enables the ice-like layers on both (0001) surfaces to directly into a joint, nearly perfect ice lattice with a low number of defects

mW results on AgI wedges

Two AgI(0001) surfaces
Results after 20 ns at -10˚C



The flat AgI surface shows 2-3 layers of ice growth within 20 ns at -10 ˚C, and slow growth after that.

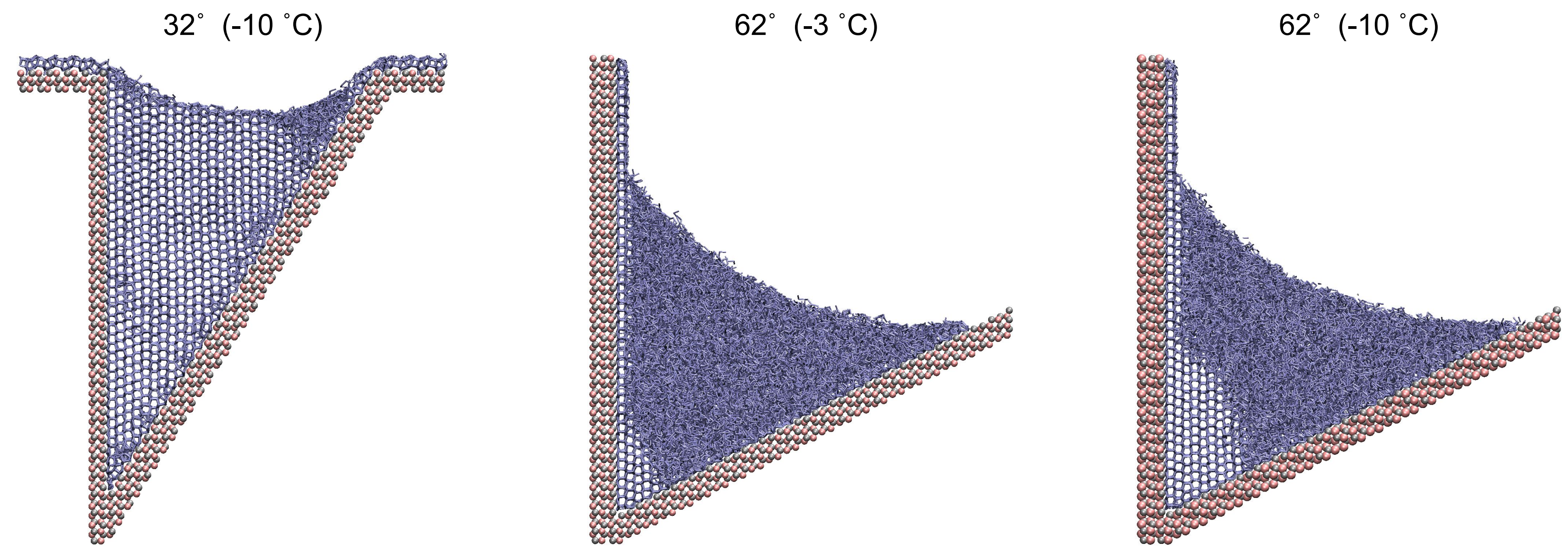
In the 30˚ wedge, ice grows to fill the system in roughly 8 ns at -10˚C . The lattice mismatch between ice growing from the two equal AgI surfaces is mediated by a coupled 5 - 7 ring structure (see inset), just as reported earlier for graphene surfaces (Bi, Cao & Li, 2016) at clearly larger supercooling.

In the 45˚ wedge, similar features can be seen, but only a few nm of ice grows from the bottom of the wedge within 20 ns at -10 ˚C .

In the 60˚ wedge, two layers of ice-like structure grows within 1 ns at -10 ˚C, but any further growth of ice is blocked by the mismatch (and a collection of 4,5,6 and 7 rings) at the bottom of the wedge structure for 20 ns.

mW results on single-piece AgI wedges

AgI(0001) on the left side
(Ongoing simulations)



In the 32˚ wedge, ice grows to fill the system in roughly 12 ns at -10˚C, despite some defects at the bottom of the wedge.

In the 62˚ wedge, ice cluster with 1 - 2 nm diameter grows to the bottom of the wedge within 20 ns at -3 ˚C

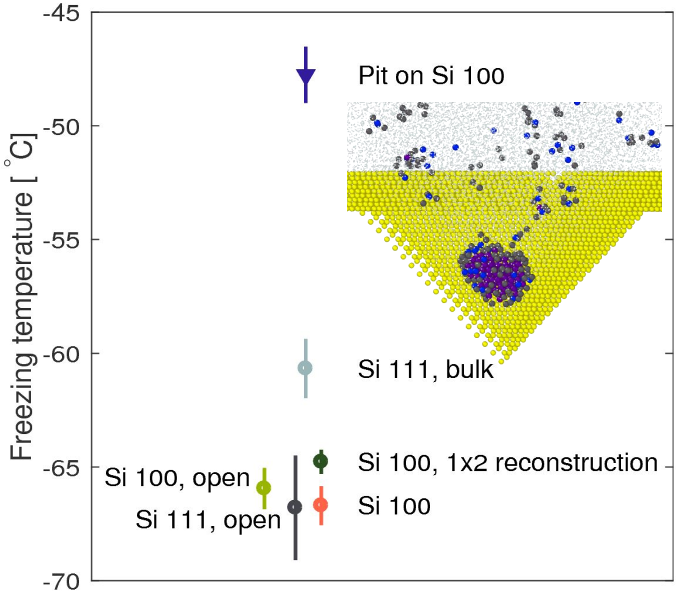
In the 62˚ wedge, when cooled to -10 ˚C (1 K / ns), a few nm of ice growth from the bottom of the wedge is seen.

Tiny differences in water bonding leads to clear differences in ice nucleation efficiency between the TIP4P/ice and mW water models. Both show large enhancement of IN due to confinement in a suitable wedge geometry, leading to nucleation very near the thermodynamical melting point.

Results: Silicon pits and wedges

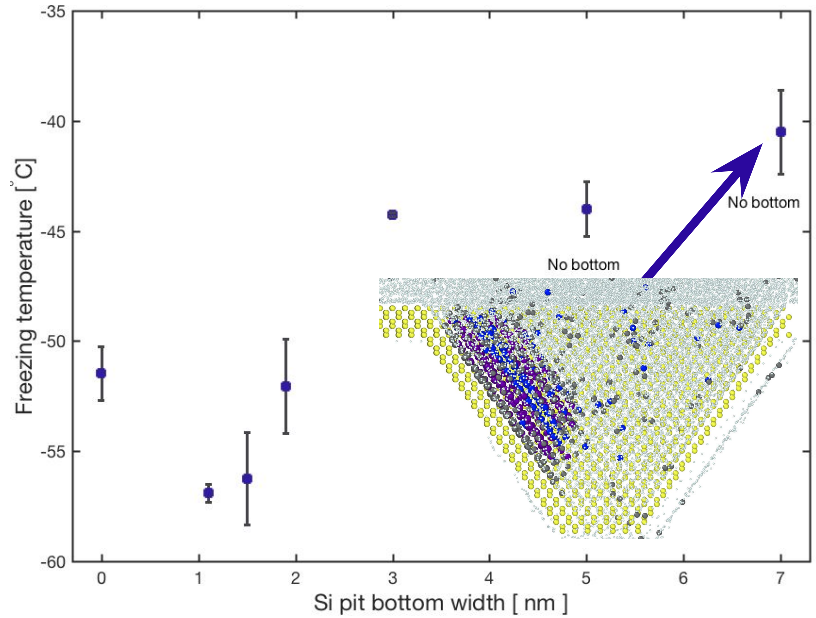
At large supercooling, confinement drastically increases IN efficiency of Si surfaces

Pit vs. flat Si surfaces



Freezing temperature for different cells: a clear 12.9 °C increase in freezing temperature in a pit, compared to the (111) surface (or 17.0 °C to the (100) surface).

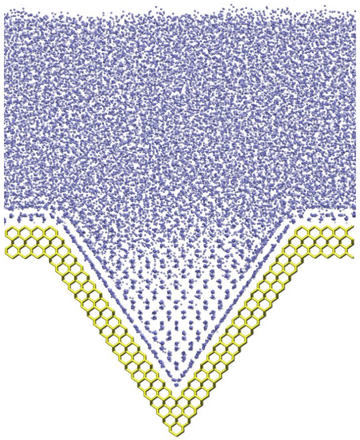
Effect of pit sharpness



Pit sharpness is not critical, the effect is clear also for pits with a flat pit bottom.

Nucleation occurs at the inside wall of pits, not at the bottom.

Si wedge



Wedge on Si(001) shows nucleation already at -40 °C, perfect growth of cubic ice.

Note: Flat Si surfaces show IN only near the homogeneous nucleation temperature of mW

Discussion and conclusions

Our results show that IN enhancement by water confinement is active also at very low supercooling, enabling very IN active surface features

At certain widths of slits and certain pit/wedge angles, clear enhancement of ice nucleation is observed. This non-monotonous enhancement as function of angle deviates from CNT, which expects monotonous behavior.

It is found that the angles which match the ice lattice or enable suitable defect structures can promote ice nucleation substantially.

Despite much stronger patterning of water by the AgI surfaces compared to graphite, surprisingly similar mechanisms and defect patterns in ice are found in both.

No differences between TIP4P/ice and mW results in the slit systems, but small differences in water bonding (probably at wedge bottom) lead to clear differences in ice nucleation efficiency in the wedge systems.

METHODS:

TIP4P/ice WATER MODEL

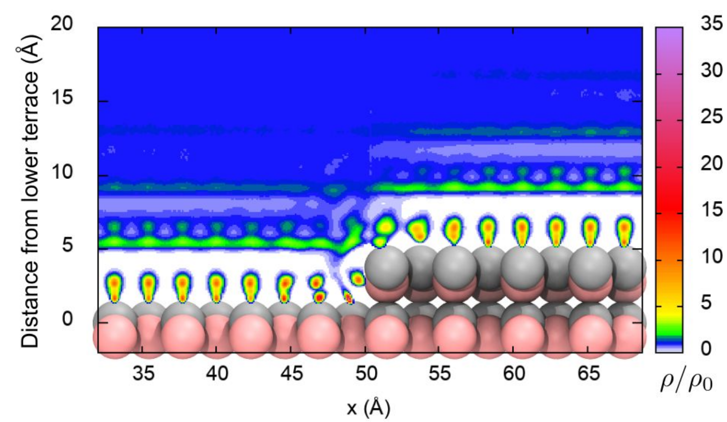
TIP4P/ice is good at describing the phase diagram of water and transformations between phases. Melting temperature ~ 270 K.

- Hale & Kiefer (1980) AgI-H_2O interactions
- Gromacs MD simulations with 5 fs timestep

mW COARSE-GRAINED WATER MODEL

For a reliable comparison to TIP4P/ice results, mW-AgI interactions were parameterized to accurately reproduce both the 273 K hydration structure of TIP4P/ice water on AgI surfaces, and the binding energy of ice I_h on AgI (0001).

- LAMMPS MD simulations
- 5 fs time step



Hydration layer structure of TIP4P/ice water on an AgI step

[G. Roudsari, B. Reischl, O. H. Pakarinen, and H. Vehkamäki, J. Phys. Chem. C. 124, 1 (2020)]

Presentation D3131 | EGU2020-7758

Acknowledgements

This material is based on work supported by the National Center of Meteorology, Abu Dhabi, UAE under the UAE Research Program for Rain Enhancement Science, the Academy of Finland Center of Excellence programme (grant no. 307331) and ARKTIKO project 285067 ICINA, by ERC Grant 692891-DAMOCLES, Univ. Helsinki ATMATH project and by supercomputing resources at CSC - IT Center for Science Ltd.

برنامج الإمارات لبحوث علوم الاستمطار
UAE Research Program for Rain Enhancement Science

European Research Council
Established by the European Commission

ACADEMY OF FINLAND

CSC