Institute for Atmospheric and Earth System Research

UNIVERSITY OF HELSINKI
FACULTY OF SCIENCE

Towards understanding heterogeneous ice nucleation on realistic silver iodide surfaces from atomistic simulation

Bernhard Reischl, Golnaz Roudsari, Siiri Turtola, Olli H. Pakarinen and Hanna Vehkamäki

Institute for Atmospheric and Earth System Research (INAR) / Physics, University of Helsinki, Finland

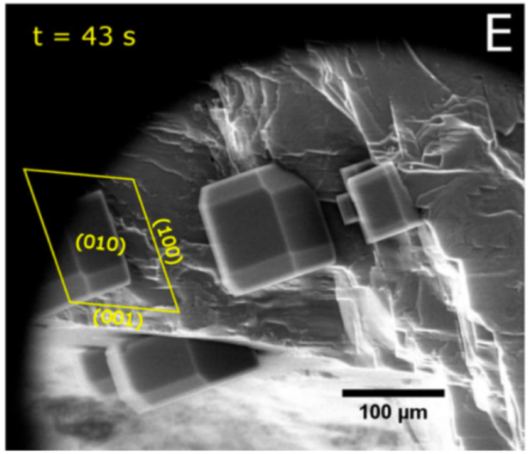
EGU General Assembly 2020 – Sharing Geoscience Online – May 2020

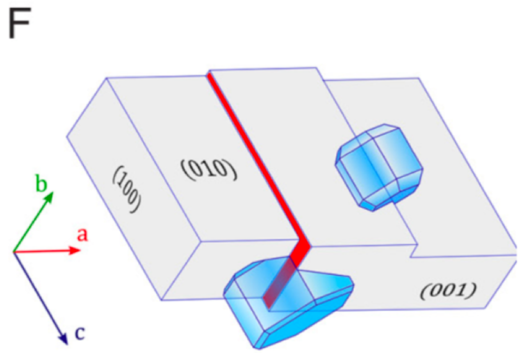
bernhard.reischl@helsinki.fi

G. Roudsari, B. Reischl, O. H. Pakarinen and H. Vehkamäki, "Atomistic Simulation of Ice Nucleation on Silver Iodide (0001) surfaces with defects", J. Phys. Chem. C **124**(1), 436-445 (2020).

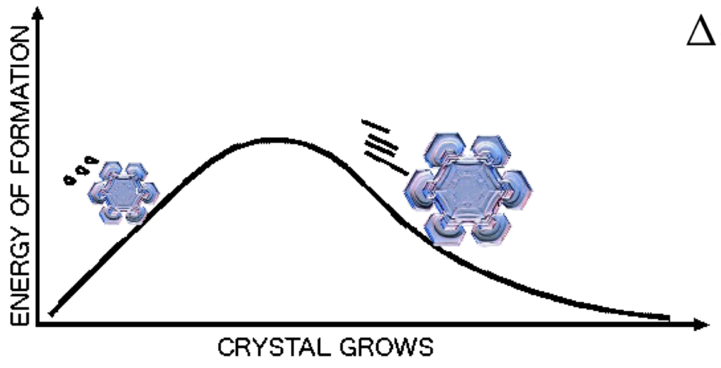
Heterogeneous ice nucleation

- Important to understand ice cloud formation and dynamics for global climate models or rain seeding applications (”geoengineering”)
- Homogeneous ice nucleation at -40°C ; mixed ice and water clouds form at -15°C
- Nucleation catalyzed by a foreign solid surface (e.g. aerosol particle)
- Interpretation of experiments typically with classical nucleation theory
- **Challenging to study atomistic details of ice nucleation on active sites both experimentally and computationally!**





Kiselev, et al., Science, 355, 367 (2017), Heterogeneous ice nucleation on K-rich Feldspar particles



$$\Delta G(r) = f(\theta)\left(\frac{4}{3}\pi r^3 \rho_l \Delta\mu + 4\pi r^2 \gamma_{lg}\right)$$

$$f(\theta) = \frac{1}{2} - \frac{3}{4}\cos(\theta) + \frac{1}{4}[\cos(\theta)]^3,$$

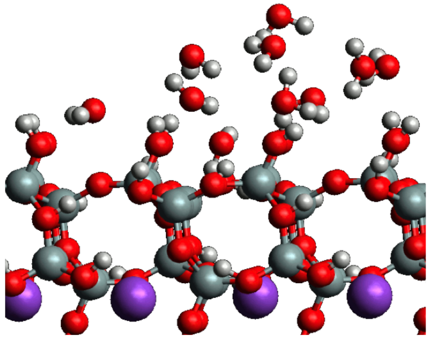
contact angle term lowers the free energy barrier

Which surfaces promote ice crystal formation effectively?

- Depends on surface morphology (crystal structure, confined geometries) and chemistry (hydrophilicity)
- For atmospheric ice nucleation: organic aerosol, microorganisms, **mineral dust particles**, …
- Molecular Dynamics simulations, at different levels of accuracy, can help understand / predict ice nucleation ability
- For many systems, time scale of nucleation is too long for unbiased MD -> seeded MD or enhanced sampling

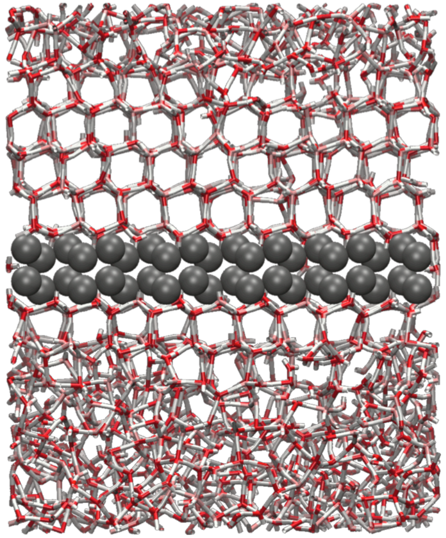
Quantum chemistry

- “a few” H_2O molecules
- Very short or no time evolution



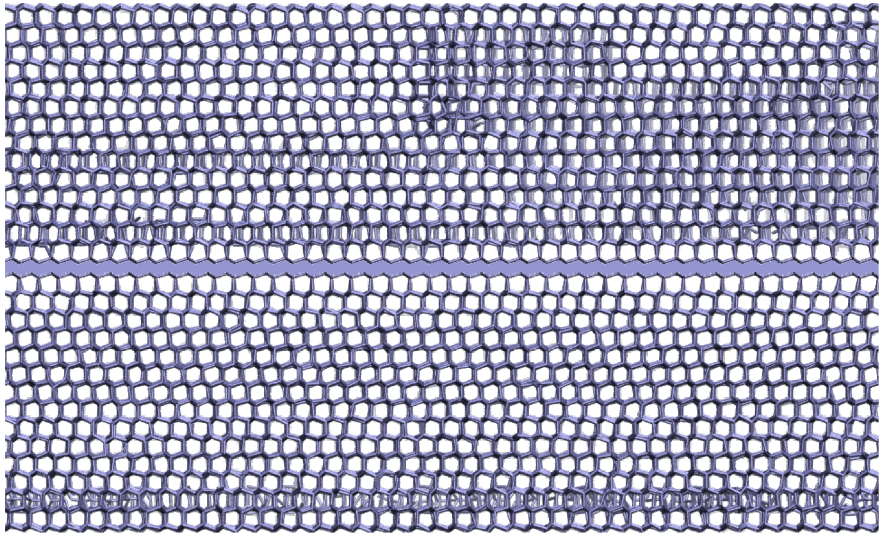
TIP4P/ice all-atom potential

~ 1000 H_2O molecules

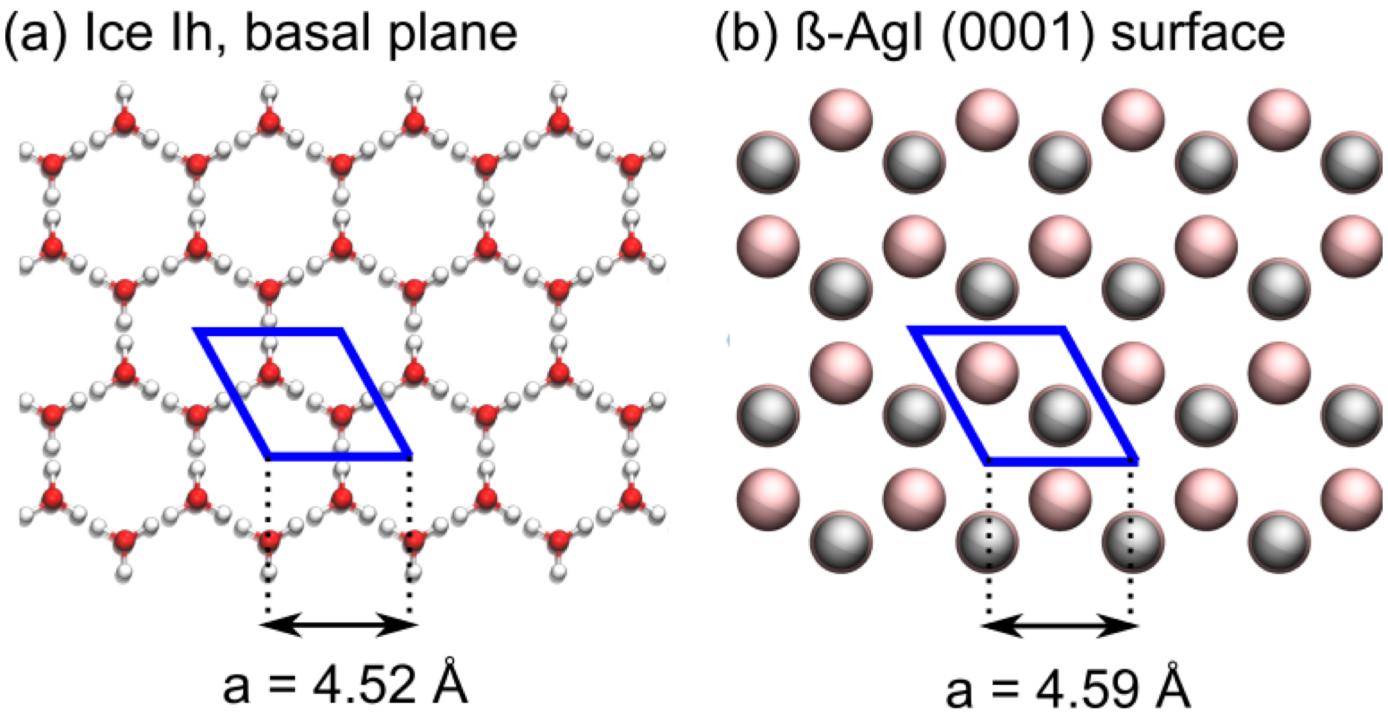


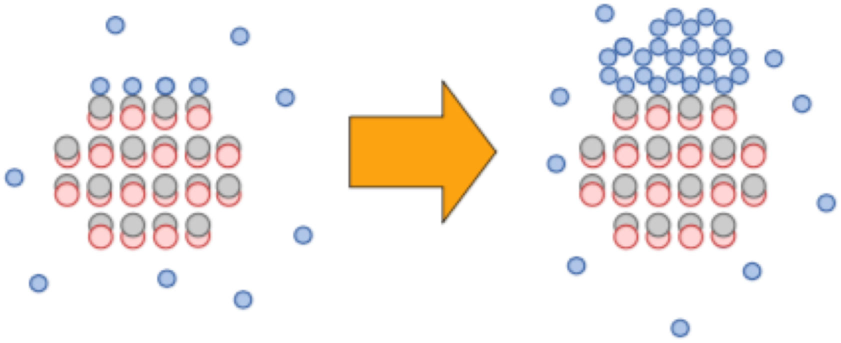
Monatomic water (mW) potential

~ 100 000 ‘H_2O’ molecules



Heterogeneous ice nucleation on silver iodide particles





- Silver iodide has been used as a rain seeding agent for decades
- Lattice mismatch between β-AgI (0001) and Ice Ih (0001) is only 2%
- Ice nucleation can be observed in unbiased molecular dynamics
- **(0001) is a polar surface! Defects and reconstructions should be common!**

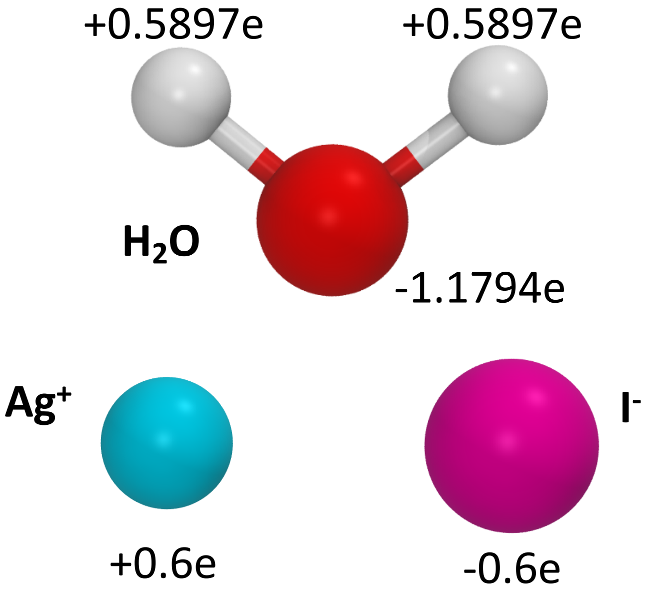
Simulation details

- Classical force field, Lennard Jones and Coulomb pair potentials:

$$U(r_{ij}) = U_{LJ} + U_{Coul} = \sum_{i<j} 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{1}{4\pi\epsilon_0}\frac{q_i q_j}{r_{ij}}$$

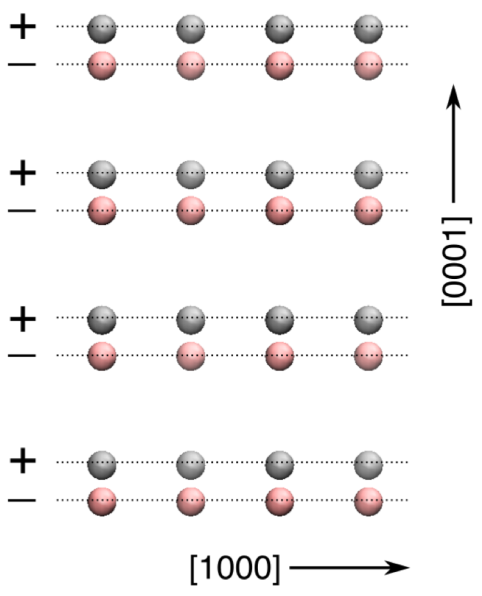
- All Ag^+ and I^- ions fixed to bulk positions
- H_2O modeled with TIP4P/ice potential [1]
- AgI – H_2O interactions by Hale and Kiefer [2], originally fitted to ST2 water

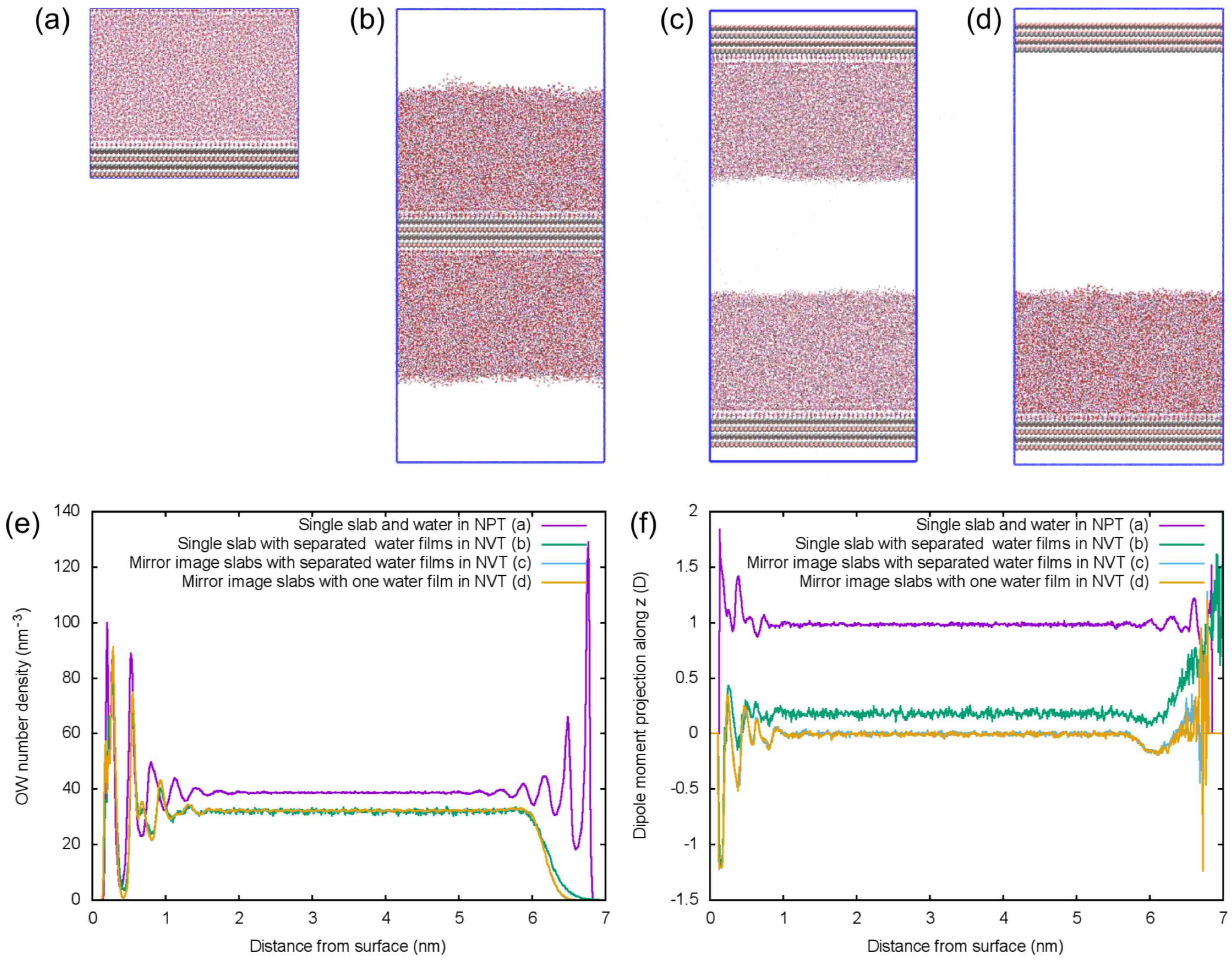
- GROMACS version 5 MD code (single precision), NVT (or NpT) ensemble
- Time step Δt = 2 fs
- Nosé-Hoover thermostat, τ = 0.4 ps
- Lennard-Jones and real-space electrostatics cut-off r_c = 8.5 Å (from TIP4P/ice)
- Long range electrostatics from particle-mesh Ewald scheme (PME)
- H_2O molecule rigid geometry enforced with SETTLE algorithm
- 3D periodic boundary conditions



[1] J. L. F. Abascal, E. Sanz, R. G. Fernández, and C. Vega, J. Chem. Phys. 122, 234511 (2005).
[2] B. N. Hale and J. Kiefer, J. Chem. Phys. 73, 923–933 (1980).

AgI (0001) has Tasker type 3 dipole: simulation setup?

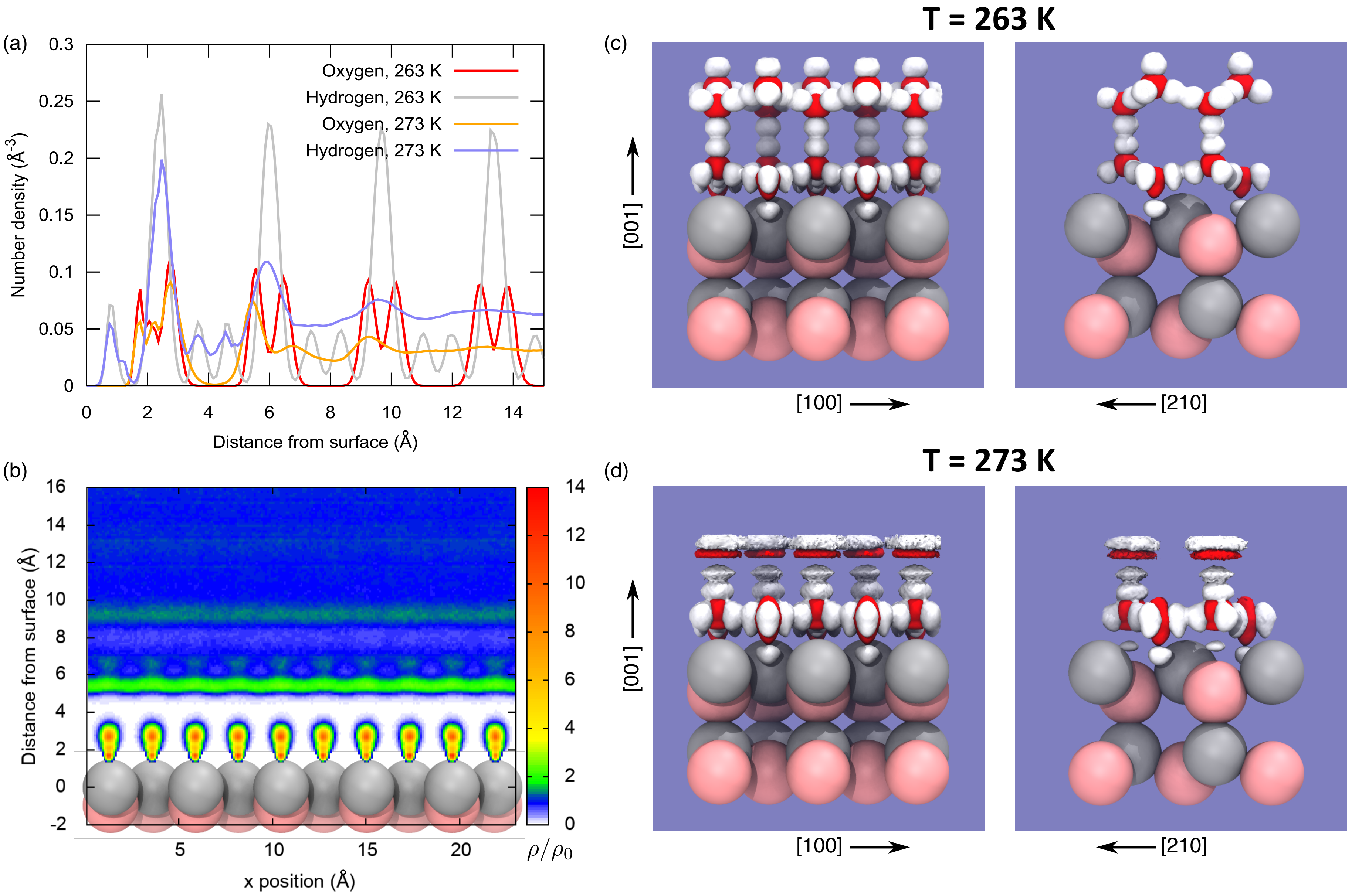




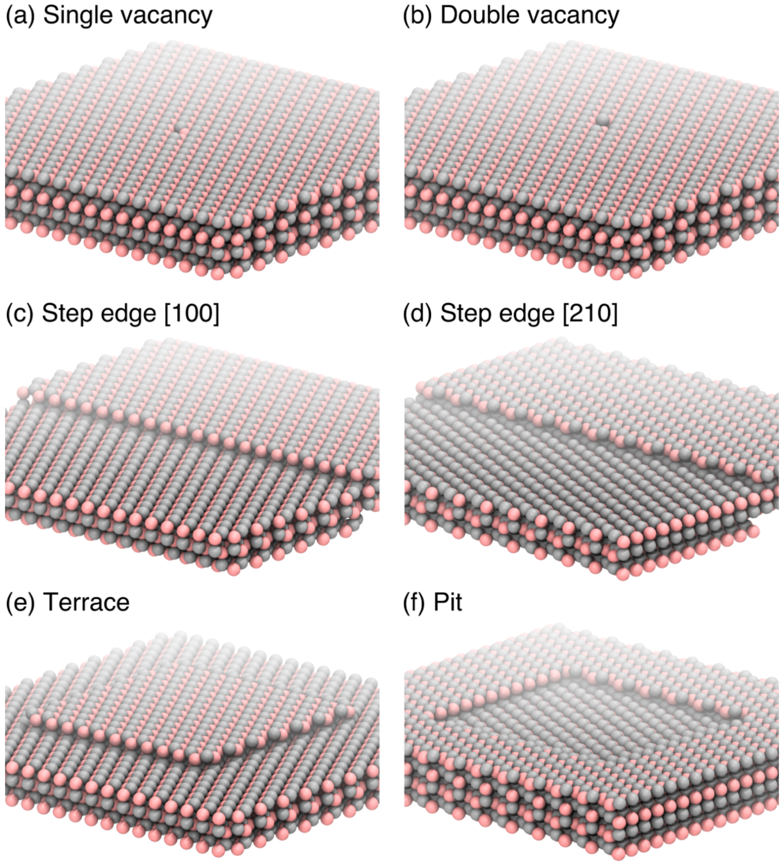
- Dipole field causes artefacts in traditional simulation setup with periodic boundary conditions (a-b)
- All simulations carried out with the ”mirror image slab” setup (d) in order to cancel dipole fields

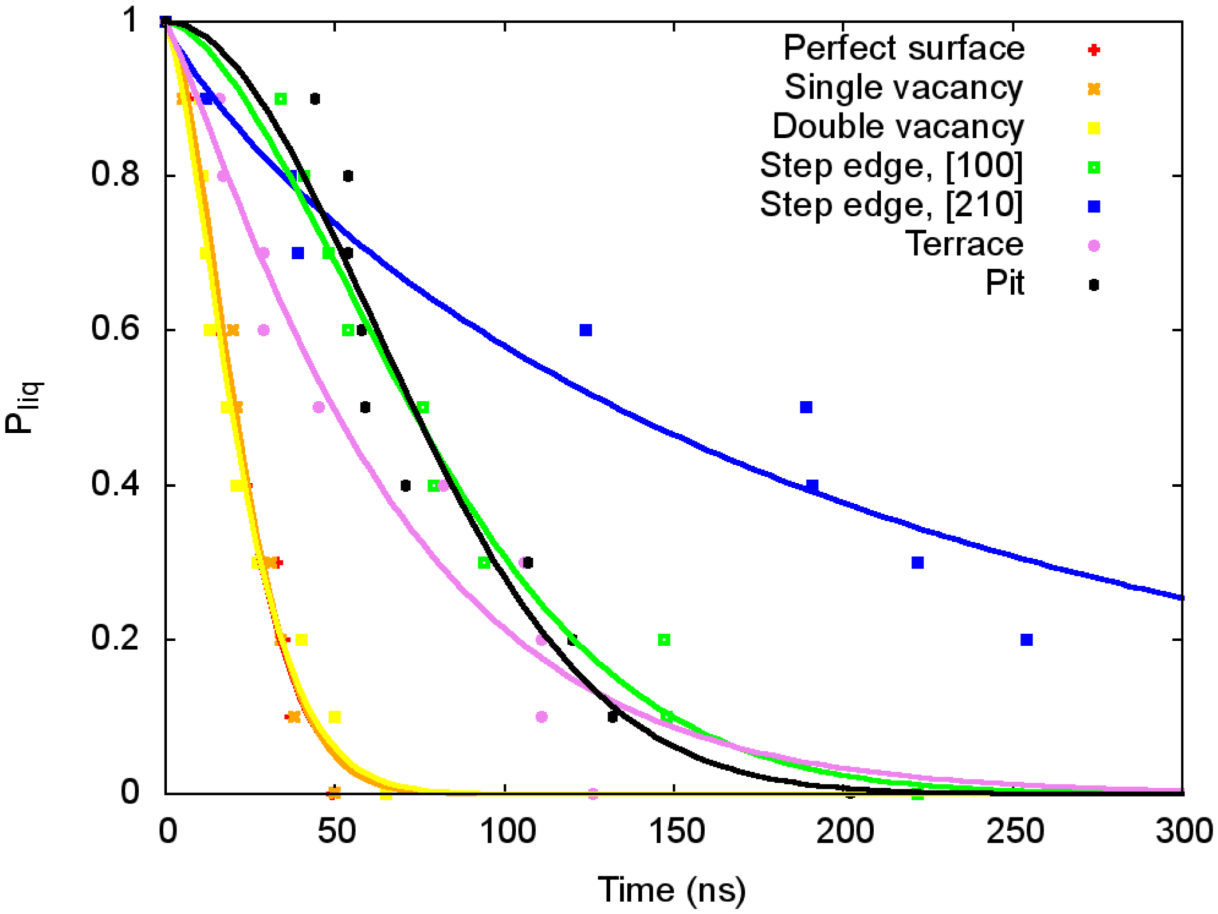
AgI (0001) hydration layer structure and dynamics

- Structure of first hydration layer (HL1) at 273 K on AgI (0001) very similar to basal plane of ice Ih, and to first layer of ice on AgI (0001) at 263 K.
- However, at 273 K water exchange in HL1 still occurs on a nanosecond time scale!
- Stabilizing the structure of HL2 marks the beginning of ice growth on the flat surface.



Ice nucleation rates from MD simulations at T = 263 K



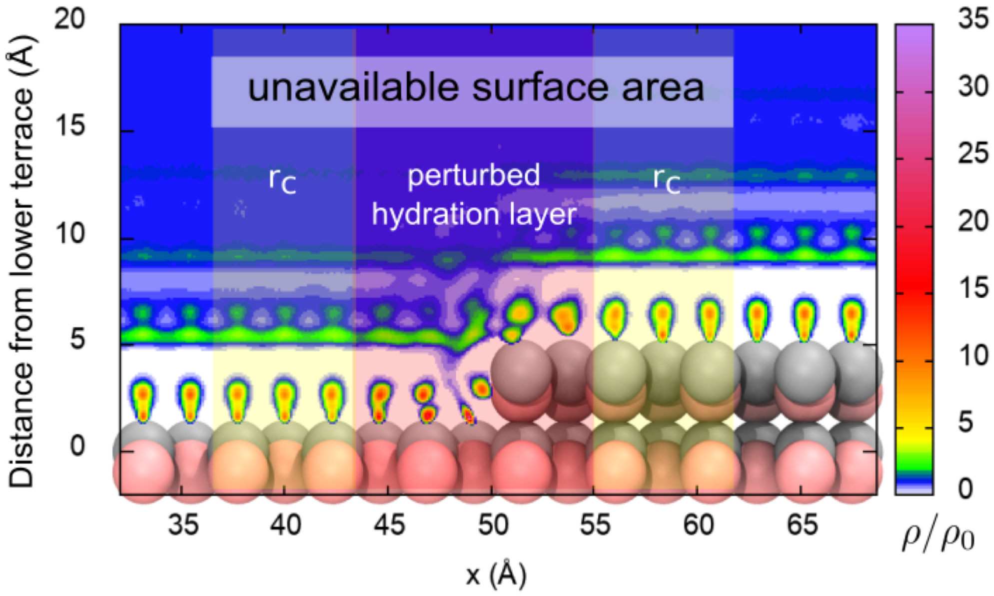


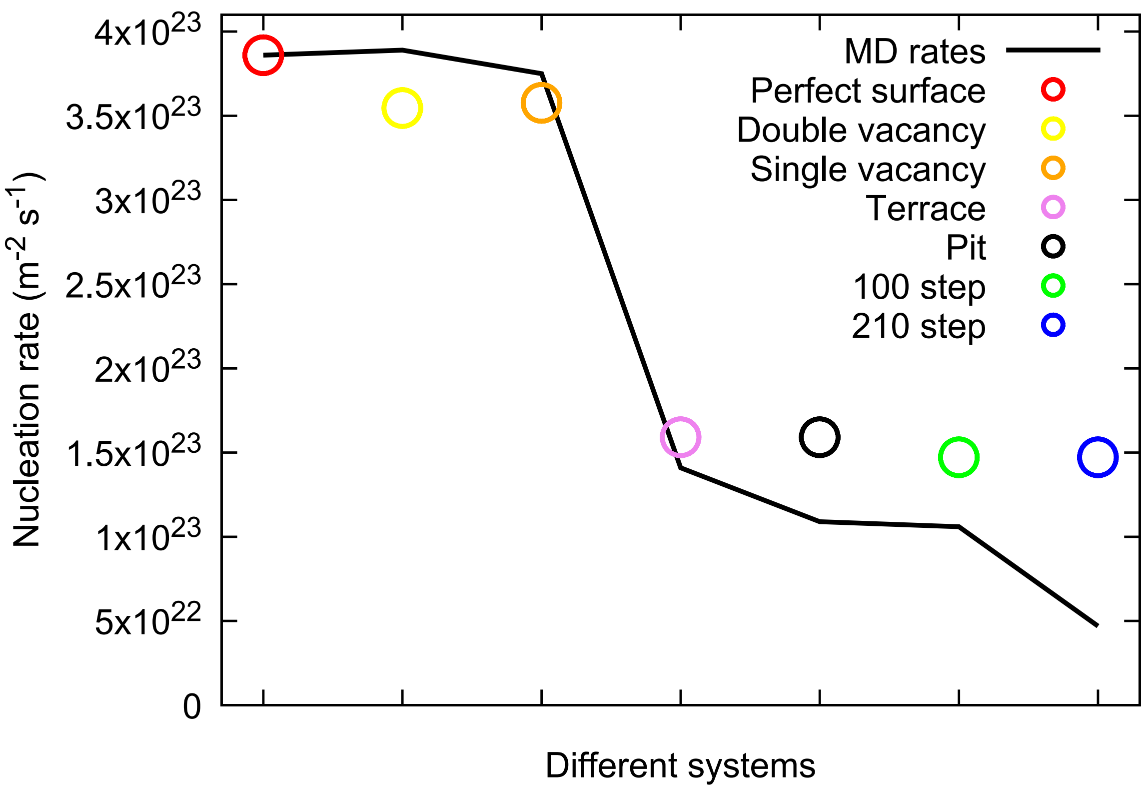
- We consider six different (0001) surfaces with defects (a-f)
- 10 independent MD simulations for each system
- Nucleation rates from fit to P_{liq} from induction times in MD simulations

$$P_{liq}(t) = \exp[-(Rt)^{\gamma}]$$

Effect of defects on ice nucleation on AgI (0001) surfaces

System	Nucleation rate ($\times 10^{23}$ m^{-2} s^{-1})
Perfect surface	3.86 ± 0.13
Single vacancy	3.75 ± 0.12
Double vacancy	3.89 ± 0.23
Step edge [100]	1.06 ± 0.04
Step edge [210]	0.47 ± 0.05
Terrace	1.41 ± 0.12
Pit	1.09 ± 0.06

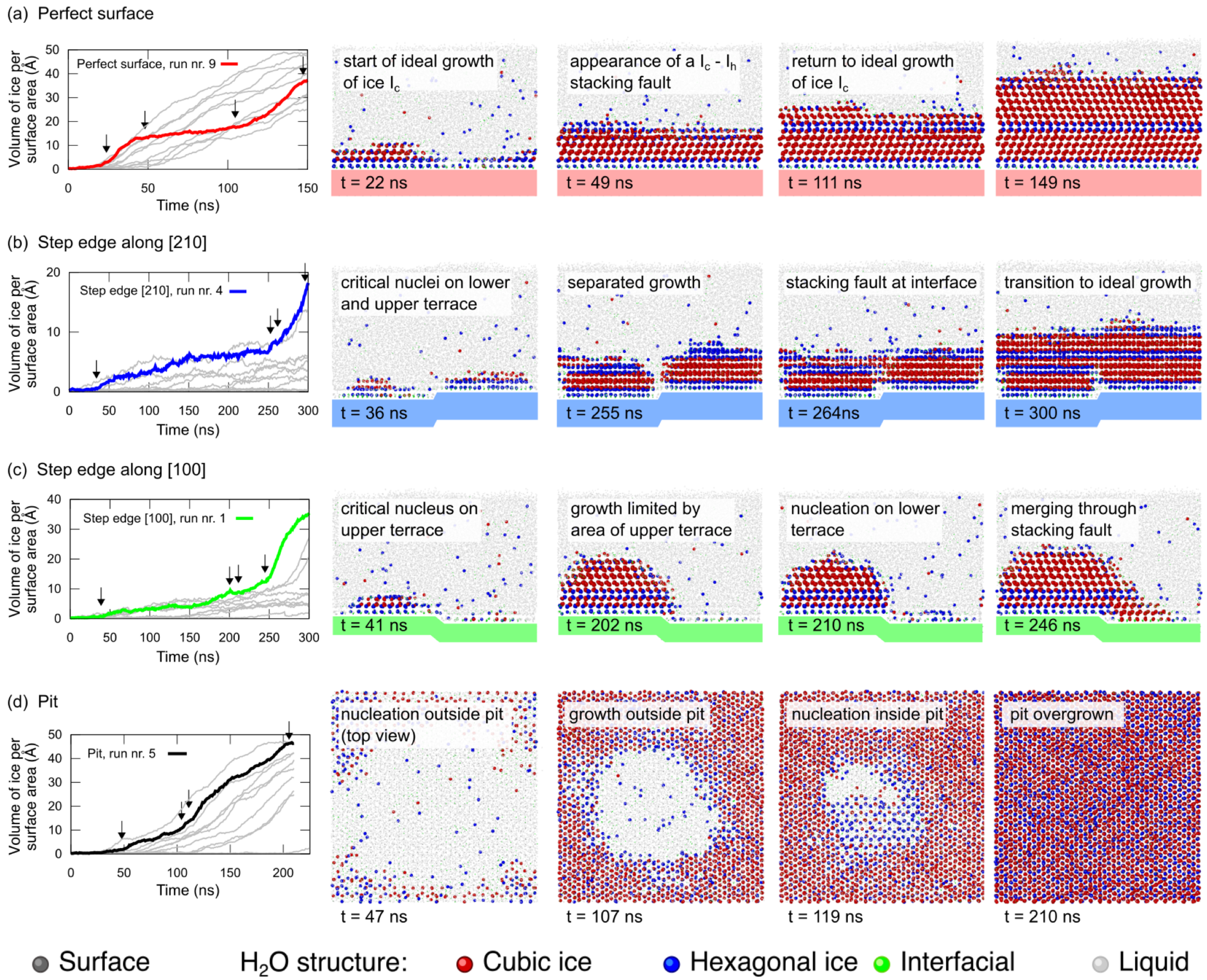




- Perfect AgI (0001) surface exhibits the highest nucleation rate
- Hydration layer perturbation around defects hinders formation of ice nuclei
- Nucleation rate on perfect surface scaled by accessible surface area (circles) predicts nucleation rates from MD (lines) on surfaces with defects well!

Atomistic details of ice growth mechanisms

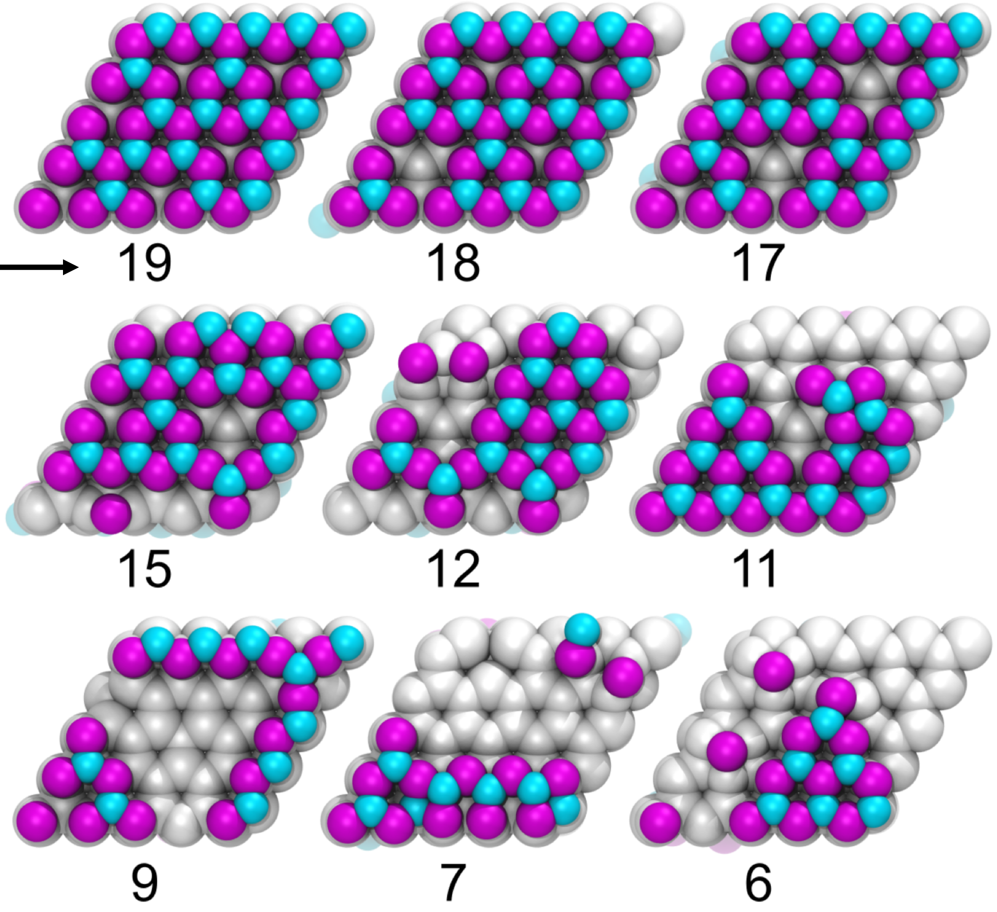
- Analysis of ice structure with the CHILL+ algorithm [1]
- Ideal growth rate corresponds to layer-by-layer growth of either hexagonal (Ih) or cubic (Ic) ice
- Stochastic appearance of stacking faults temporarilly reduces ice growth rate (a)
- Presence of defects can also increase the probability for stacking faults to occur (b-d)
- Stochastic nature of these processes requires study of many individual MD trajectories!

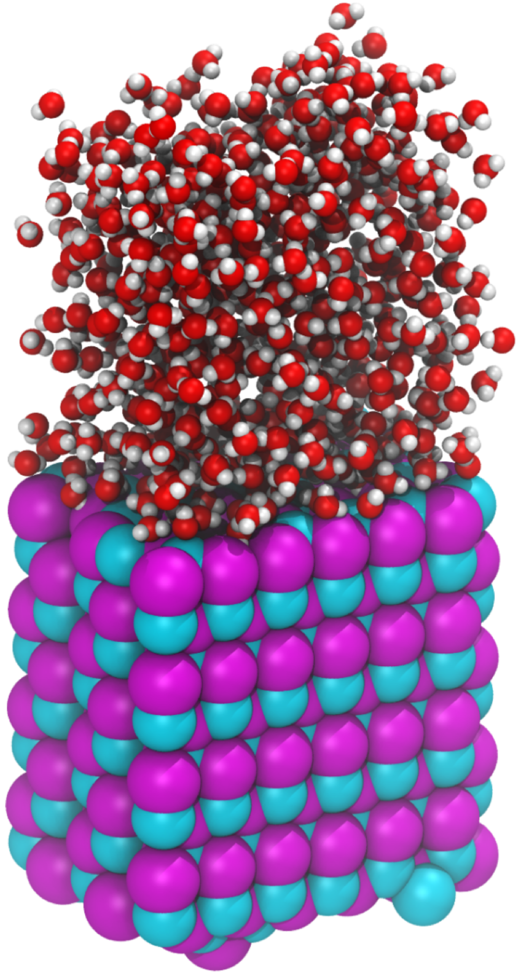


[1] A. H. Nguyen and V. Molinero, J. Phys. Chem. B, 119, 9369 (2015)

Outlook: AgI (0001) with (5x5) surface reconstruction

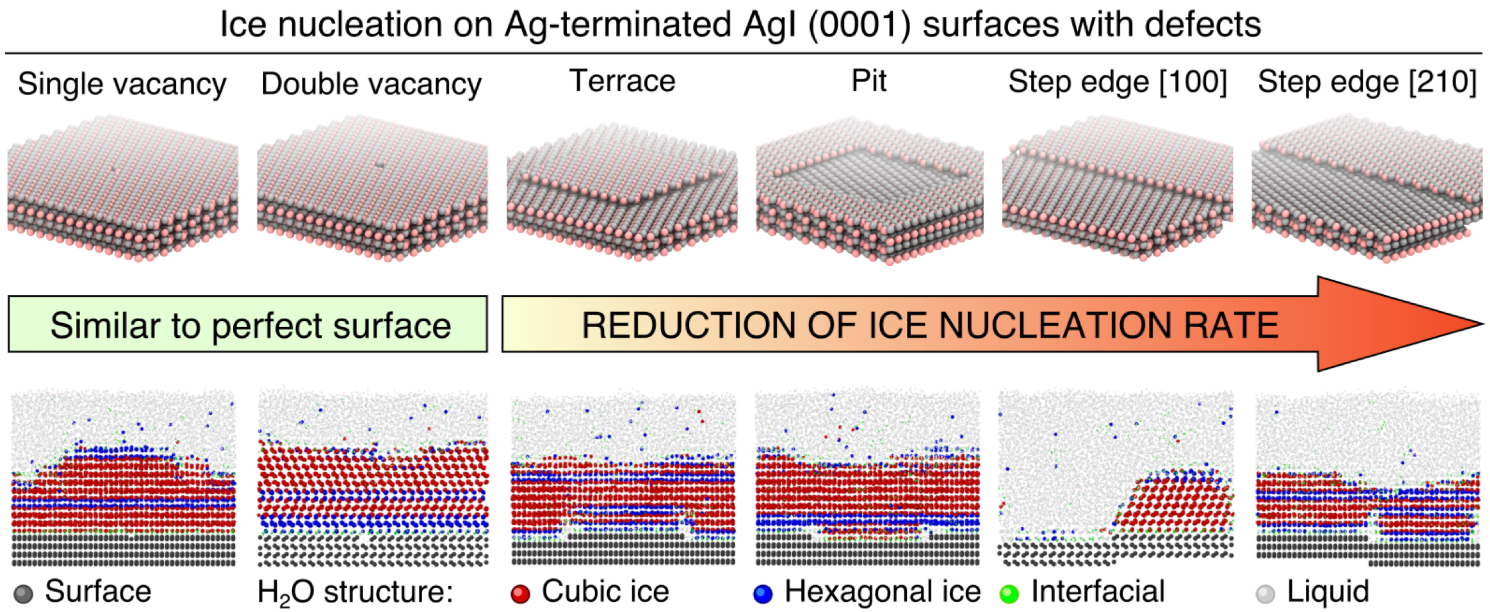
Number of Ag^+ ions in the 5x5 surface supercell





- In each (5x5) supercell, Ag and I ions have been moved from the top to the bottom of the slab to cancel the dipole
- Based on work on polar ZnO (0001) surfaces: Mora-Franz et al., Chem. Mater. 29, 5306 (2017)
- No nucleation after 250 ns at T = 253 K -> seeded MD simulations or enhanced sampling necessary!

Summary



- AgI (0001) is an excellent ice nucleating surface, but its dipole makes it unstable in nature - and tricky to simulate
- Nucleation rates on surfaces with defects can be explained by simple model where rate on perfect surface is scaled by effective surface area available for ice nucleation in defect systems, but this model fails to explain atomistic differences (e.g. step edges along two different crystallographic directions)
- Ideal ice growth is slowed down by stochastic appearance of stacking disorder between ice Ih and Ic, which is increased in the presence of some defects
- Now considering more realistic surfaces with reconstructions that eliminate, or reduce the dipole!

G. Roudsari, B. Reischl, O. H. Pakarinen and H. Vehkamäki, "Atomistic Simulation of Ice Nucleation on Silver Iodide (0001) surfaces with defects", J. Phys. Chem. C **124**(1), 436-445 (2020).

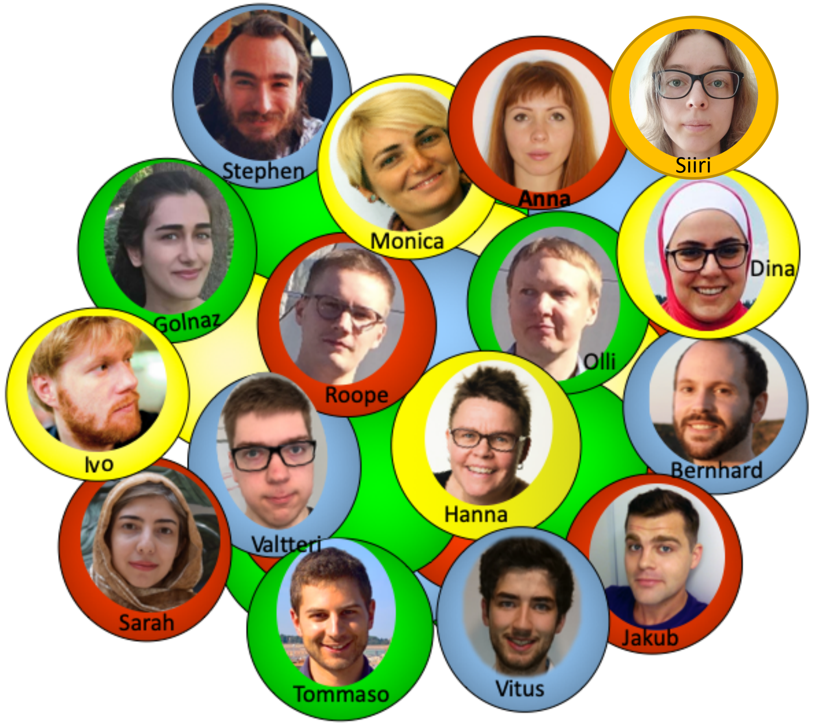
Acknowledgments

Computational Resources

CSC

FGCI - Finnish Grid and Cloud Infrastructure

The Computational Aerosol Physics Group



Funding

ACADEMY OF FINLAND

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

European Research Council
Established by the European Commission

Any opinions, findings and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the National Center of Meteorology, Abu Dhabi, UAE, funder of the research.