

# 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

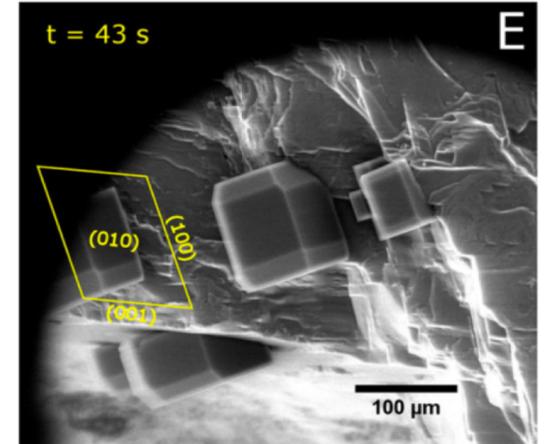
*Institute for Atmospheric and Earth System Research (INAR) / Physics, University of Helsinki, Finland*

IAMA 2019, UC Davis, December 4th, 2019

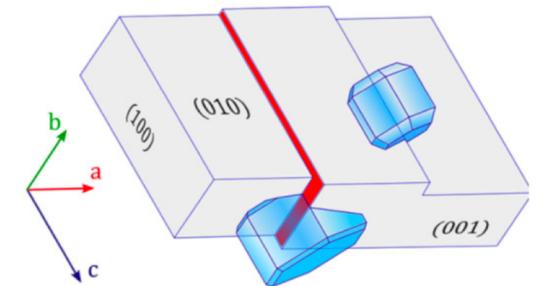
bernhard.reischl@helsinki.fi

# Heterogeneous ice nucleation

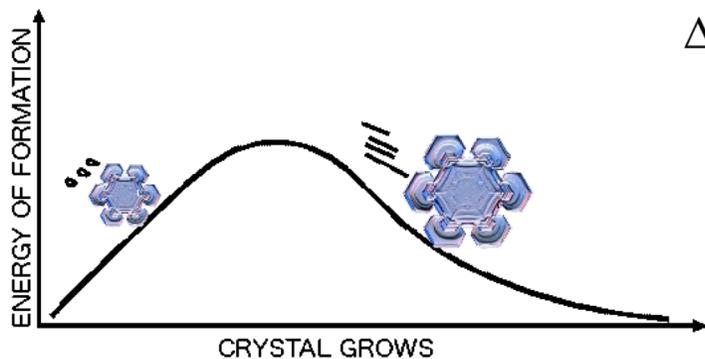
- Important to understand ice cloud formation and dynamics for global climate models or rain seeding applications ("geoengineering")
- Homogeneous ice nucleation at  $-40^{\circ}\text{C}$  ; mixed ice and water clouds form at  $-15^{\circ}\text{C}$
- Nucleation catalyzed by a foreign solid surface (e.g. 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!**



F



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



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

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

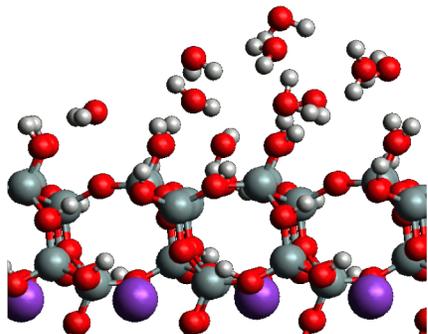
contact angle term lowers  
the free energy barrier

# 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

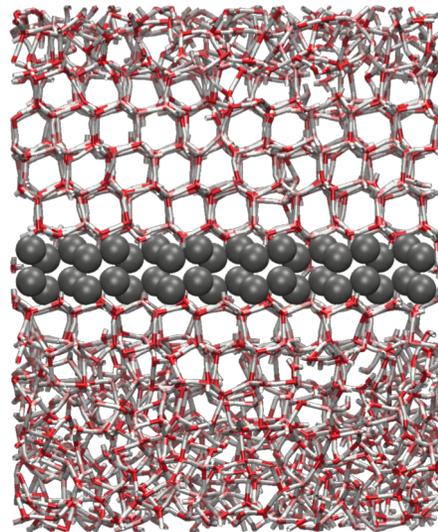
## Quantum chemistry

- “a few” H<sub>2</sub>O molecules
- Very short or no time evolution



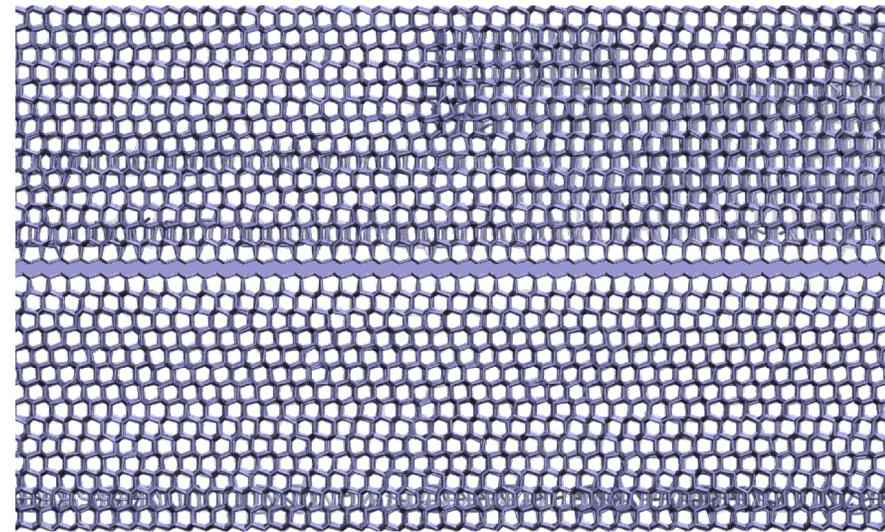
## TIP4P/ice all-atom potential

~ 1000 H<sub>2</sub>O molecules



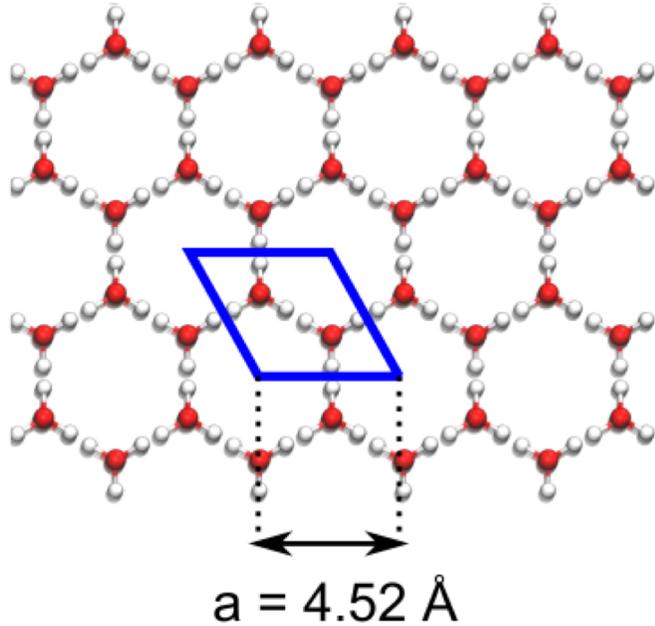
## Monatomic water (mW) potential

~ 100 000 'H<sub>2</sub>O' molecules

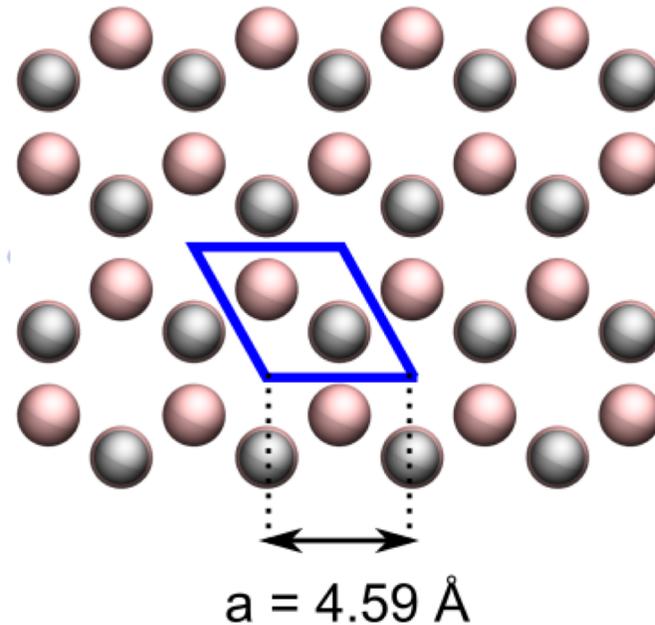


# Heterogeneous ice nucleation on silver iodide particles

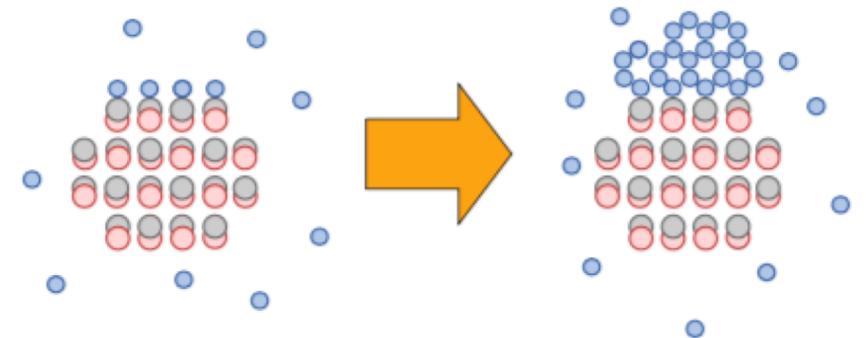
(a) Ice Ih, basal plane



(b)  $\beta$ -AgI (0001) surface



- Silver iodide has been used as a rain seeding agent for decades
- Lattice mismatch between  $\beta$ -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!**



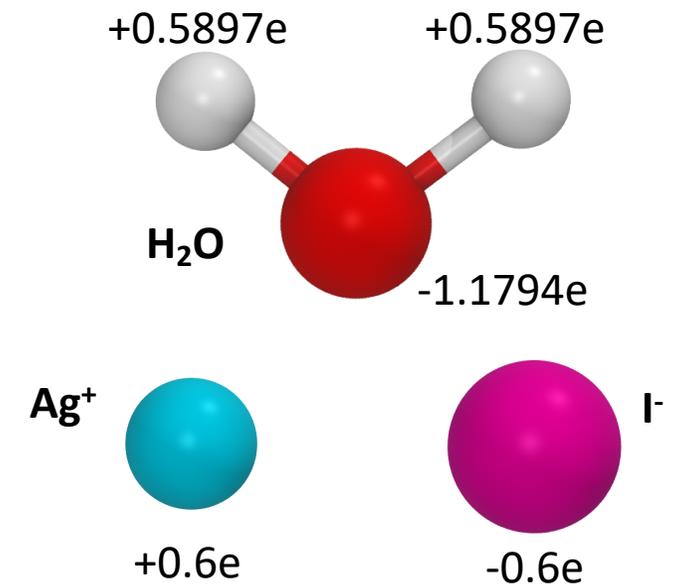
# Simulation details

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

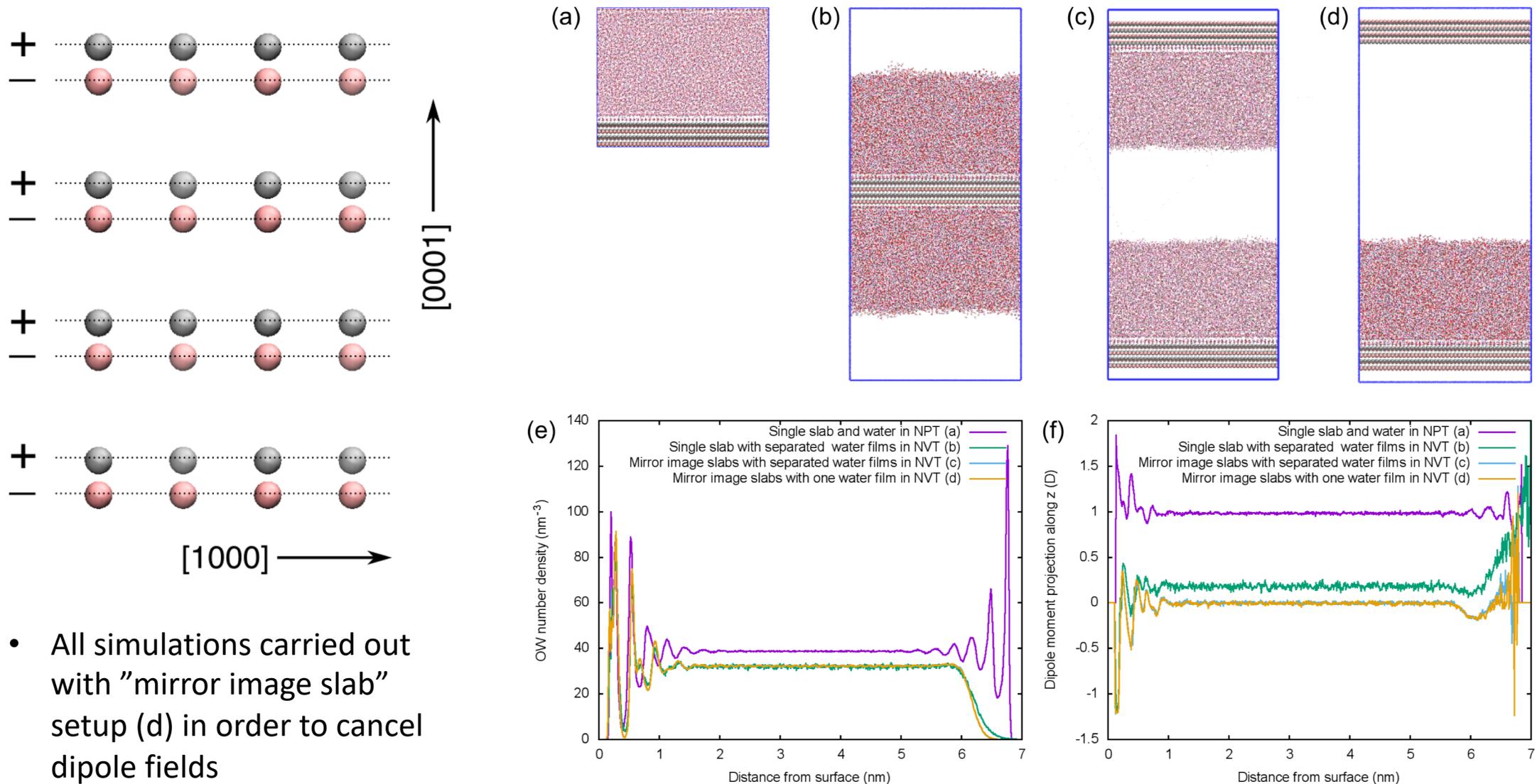
$$U(r_{ij}) = U_{LJ} + U_{Coul} = \sum_{i<j} 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}}$$

- All Ag and I ions fixed to bulk positions
- H<sub>2</sub>O modeled with TIP4P/ice potential [1]
- AgI – H<sub>2</sub>O interactions by Hale and Kiefer, originally fitted to ST2 water [2]
  
- GROMACS version 5 MD code (single precision), NVT (or NpT) ensemble
- Time step  $\Delta t = 2$  fs
- Nosé-Hoover thermostat,  $\tau = 0.4$  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<sub>2</sub>O 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).

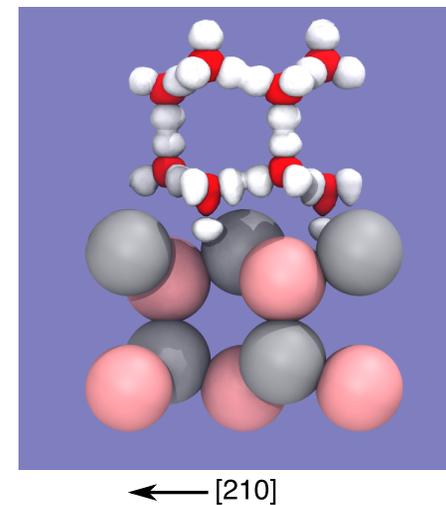
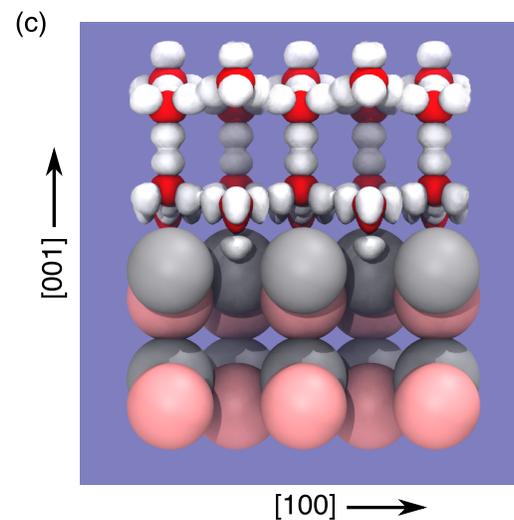
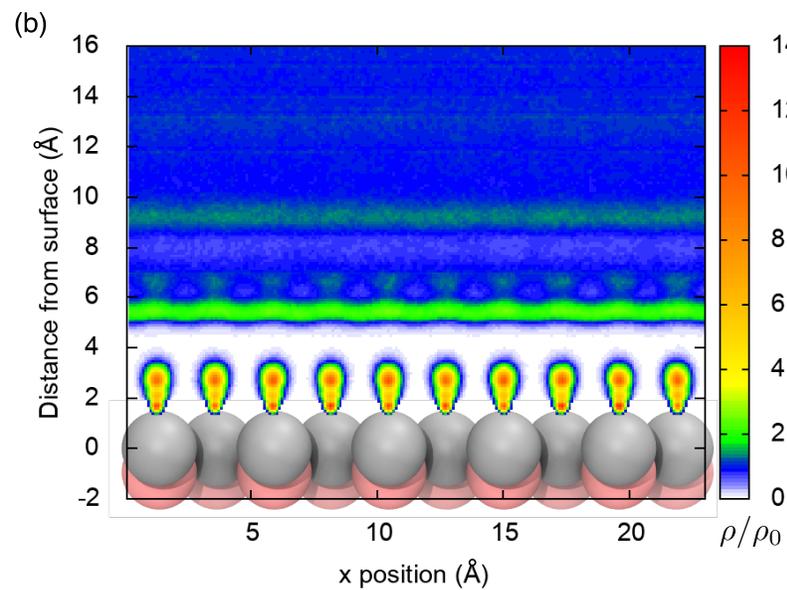
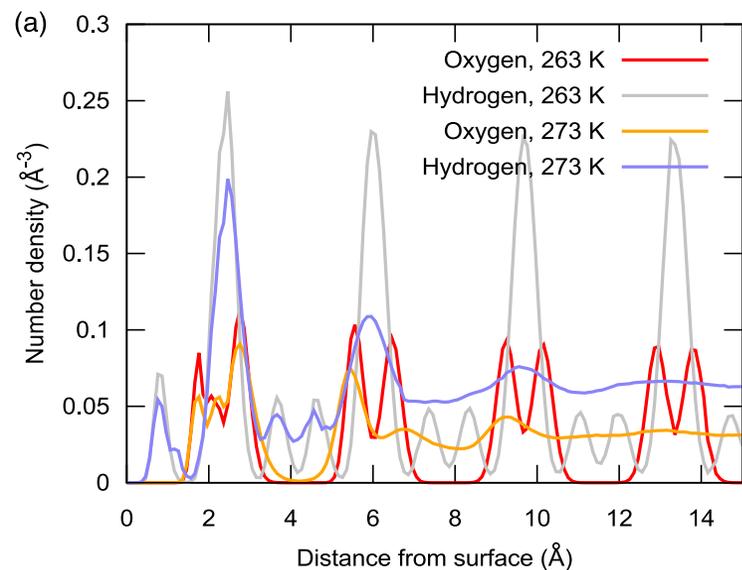


# AgI (0001) has Tasker type 3 dipole: simulation setup?

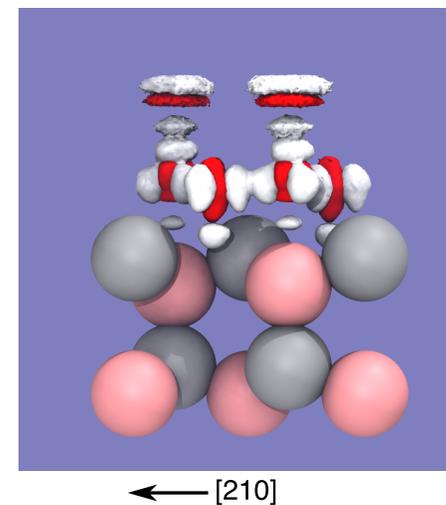
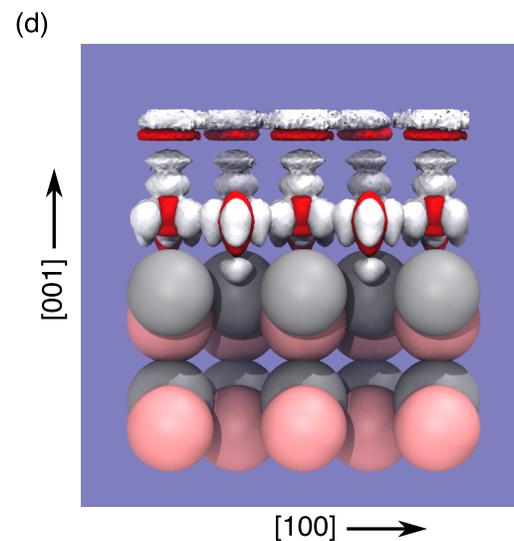


- All simulations carried out with "mirror image slab" setup (d) in order to cancel dipole fields

# AgI (0001) hydration layer structure and dynamics



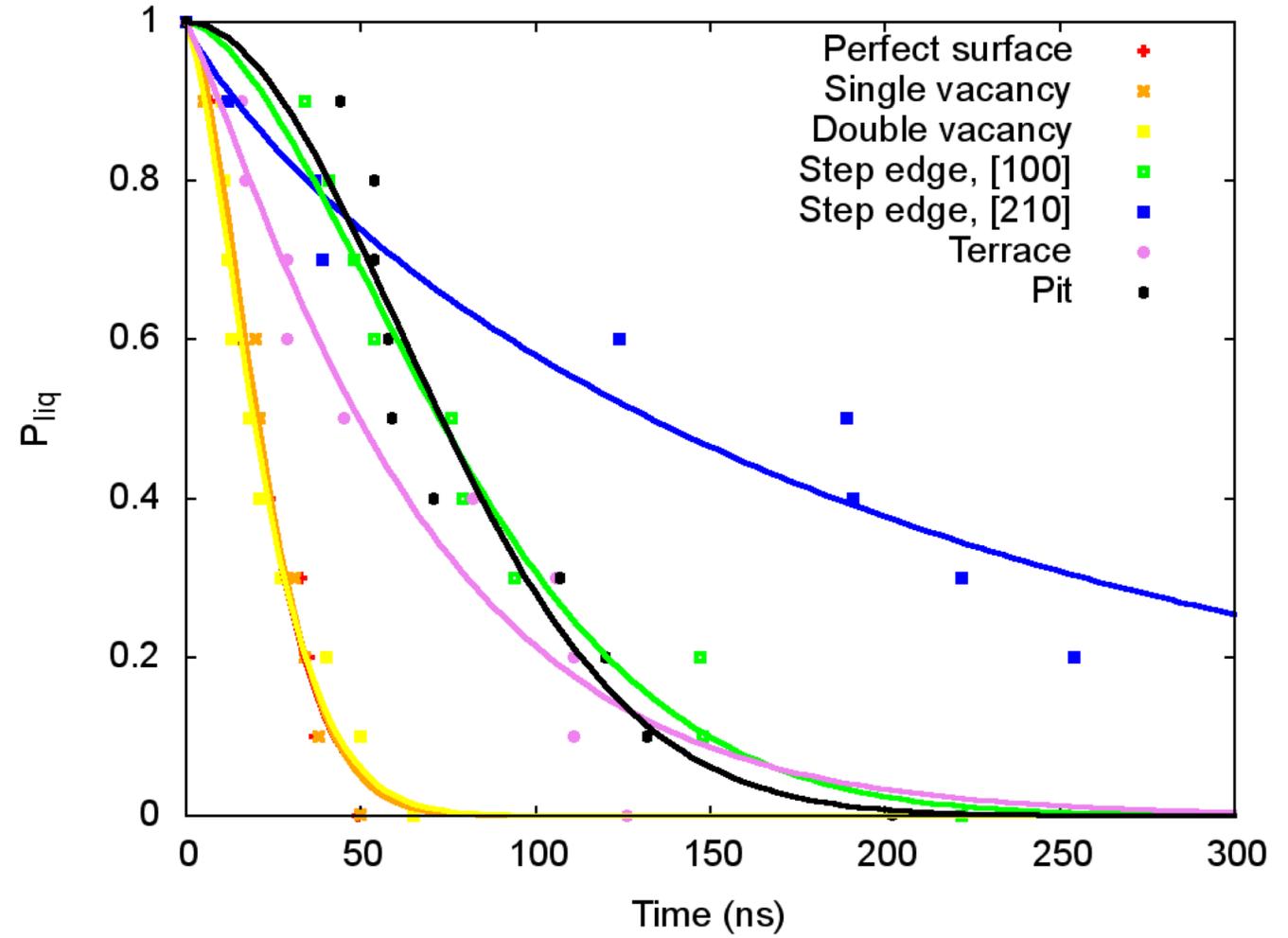
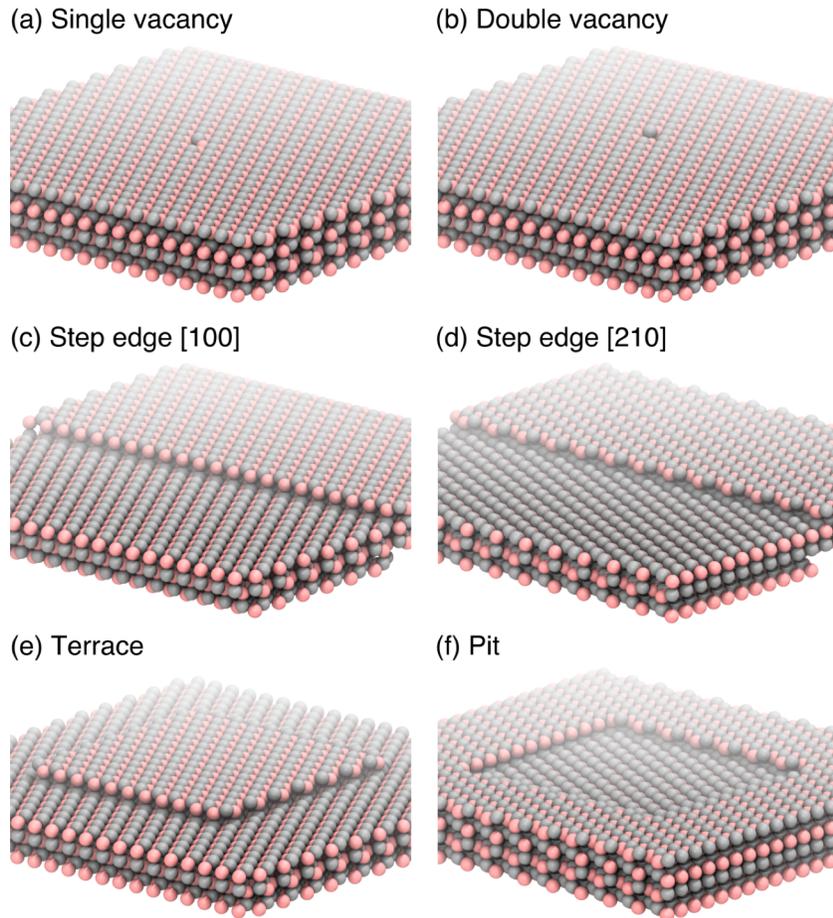
**T = 263 K**



**T = 273 K**

Time scale for water exchange in HL1  $\sim 2$  ns

# Ice nucleation rates from MD simulations at T = 263 K

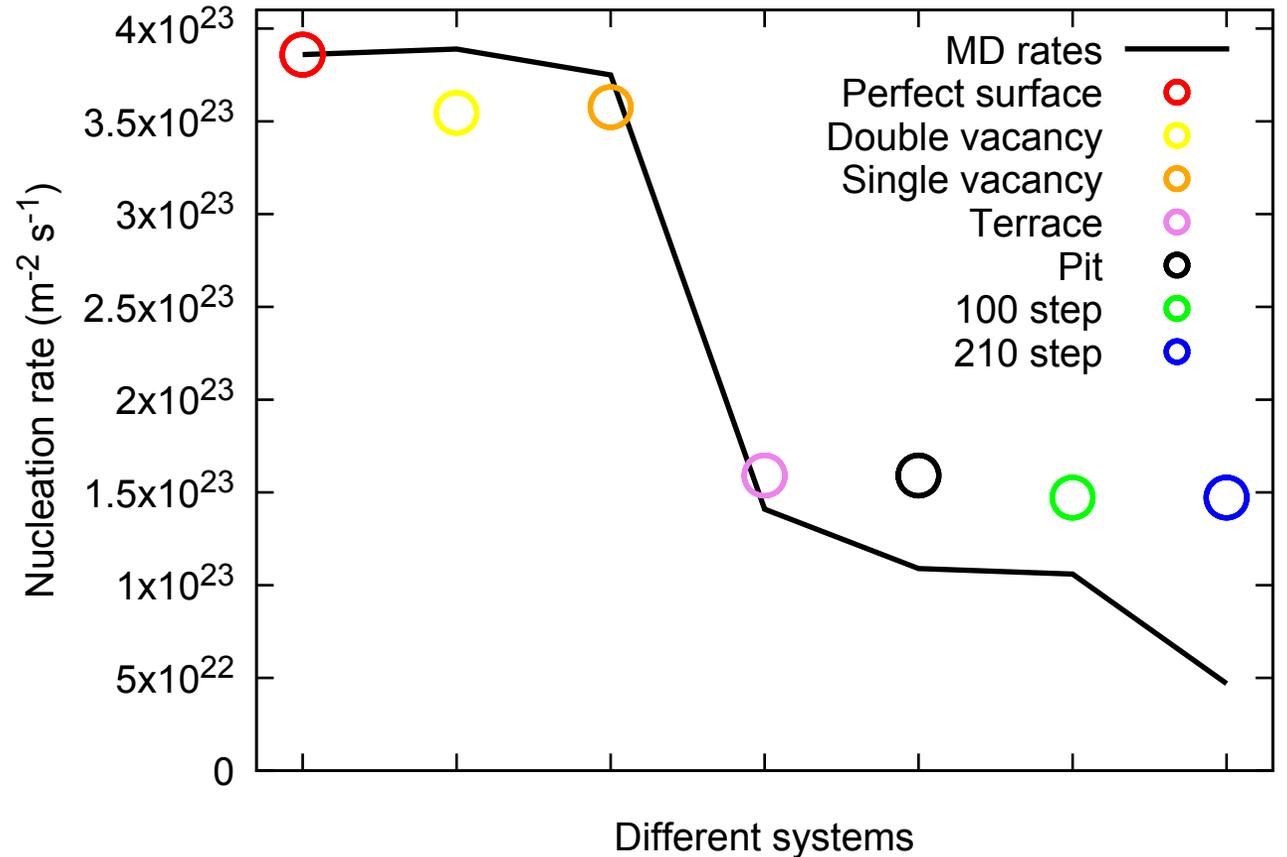
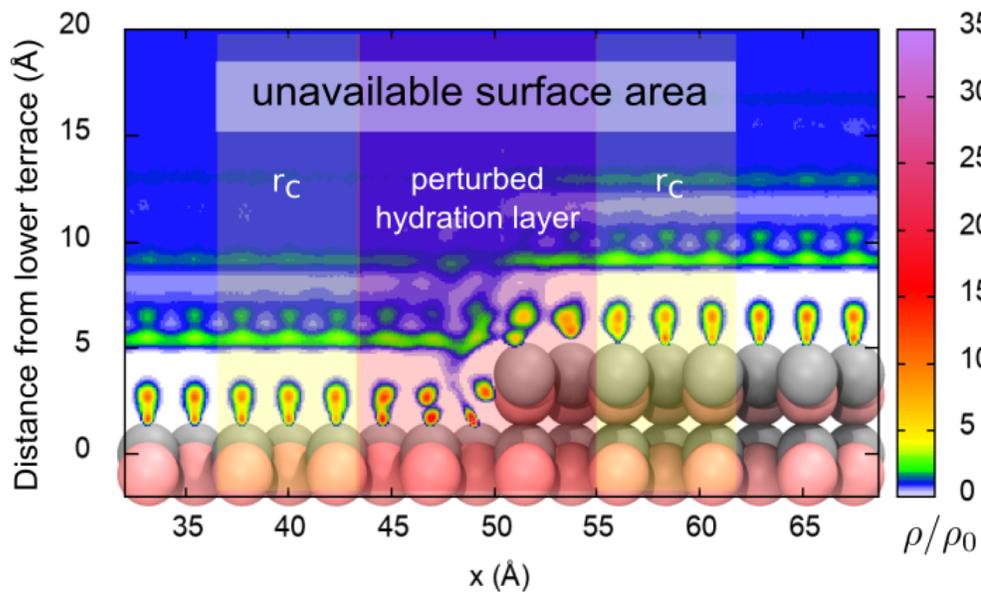


- 10 independent simulations per system,
- Nucleation rates from fit to  $P_{liq}$  from induction times in MD simulations

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

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

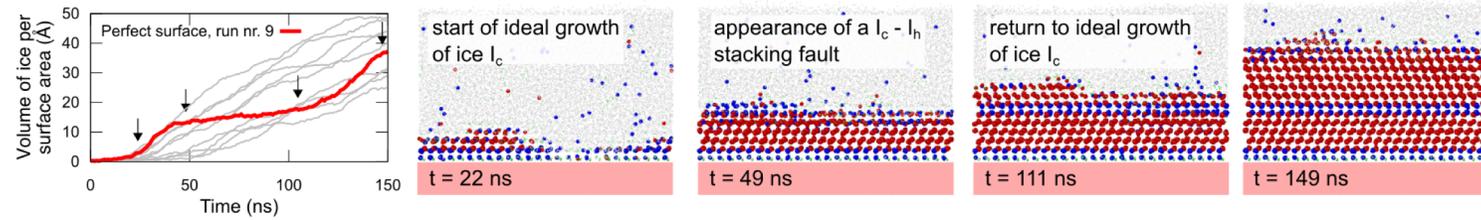
System	Nucleation rate ( $\times 10^{23} \text{ m}^{-2} \text{ s}^{-1}$ )
Perfect surface	$3.86 \pm 0.13$
Single vacancy	$3.75 \pm 0.12$
Double vacancy	$3.89 \pm 0.23$
Step edge [100]	$1.06 \pm 0.04$
Step edge [210]	$0.47 \pm 0.05$
Terrace	$1.41 \pm 0.12$
Pit	$1.09 \pm 0.06$



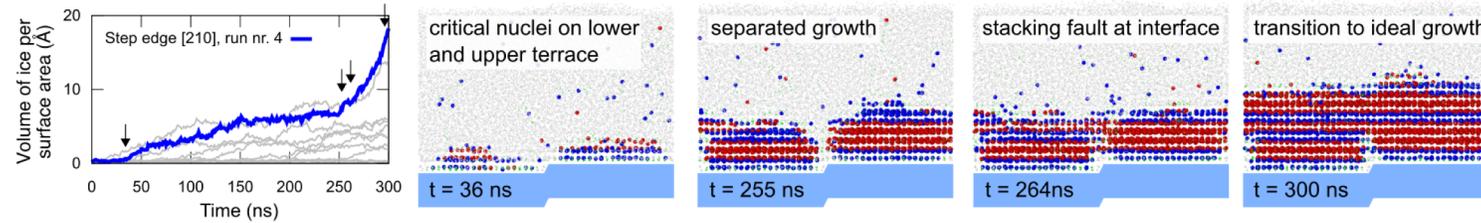
Nucleation rate on perfect surface scaled by accessible surface area predicts nucleation rates from MD on surfaces with defects well!

# Atomistic details of ice growth mechanisms

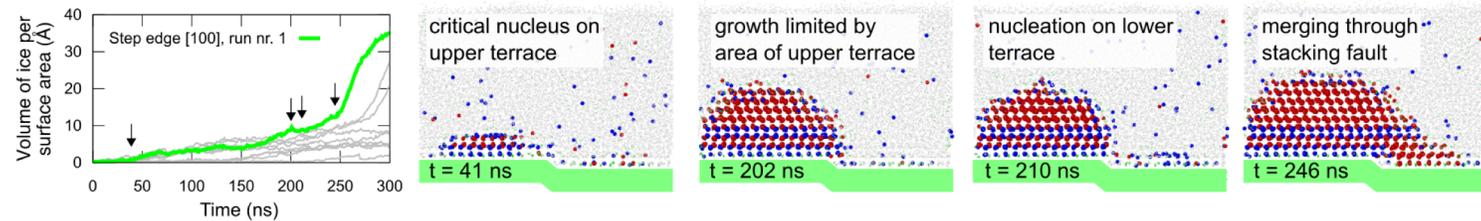
(a) Perfect surface



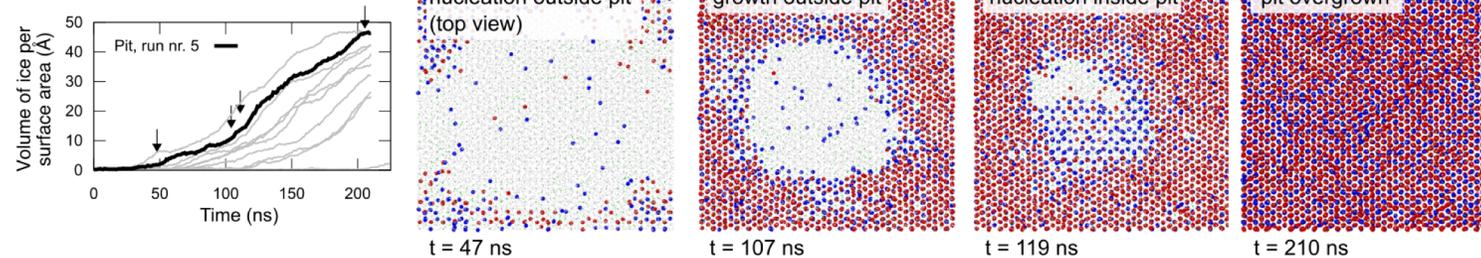
(b) Step edge along [210]



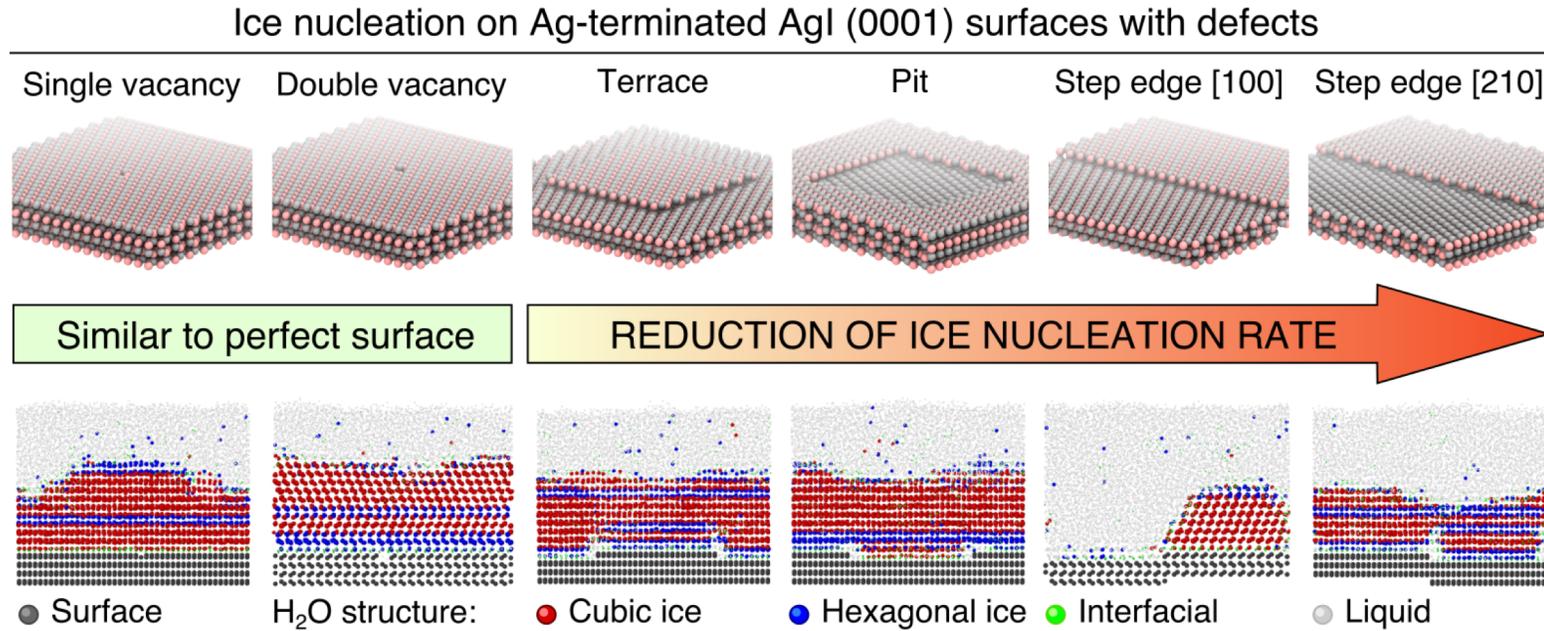
(c) Step edge along [100]



(d) Pit



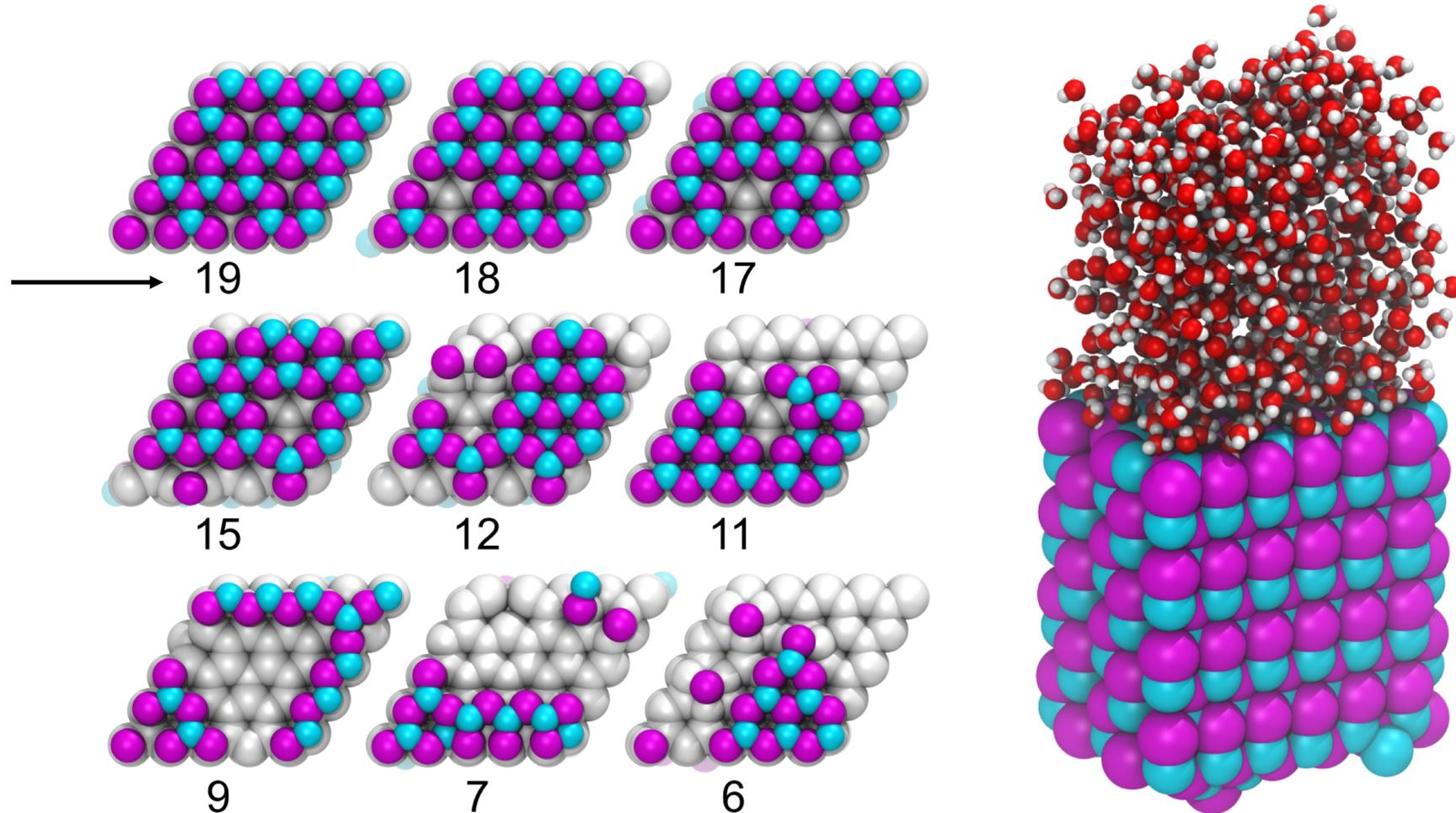
# Summary and Outlook



- Nucleation rate 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 model fails to explain atomistic differences
- Ideal ice growth is slowed down by stochastic appearance of stacking disorder between ice Ih and Ic, which is increased by some defects
- Problem of the polar surface remains! Now considering more realistic surfaces with reconstructions that eliminate/reduce dipole!

# AgI (0001) with (5x5) surface reconstruction

Number of  
 $\text{Ag}^+$  ions in  
the 5x5  
supercell  
surface



- 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!

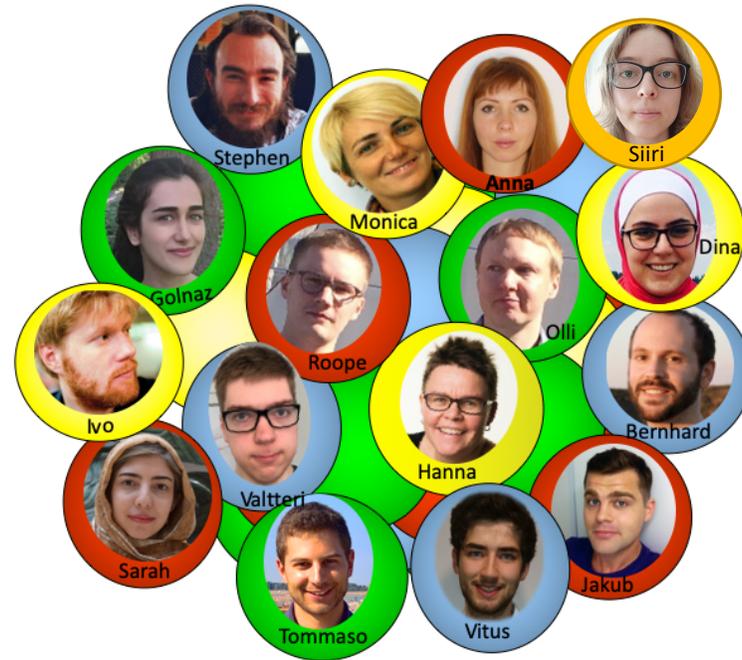
# Acknowledgments



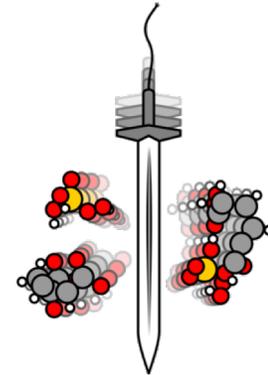
Computational Resources



The Computational Aerosol Physics Group



Funding



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