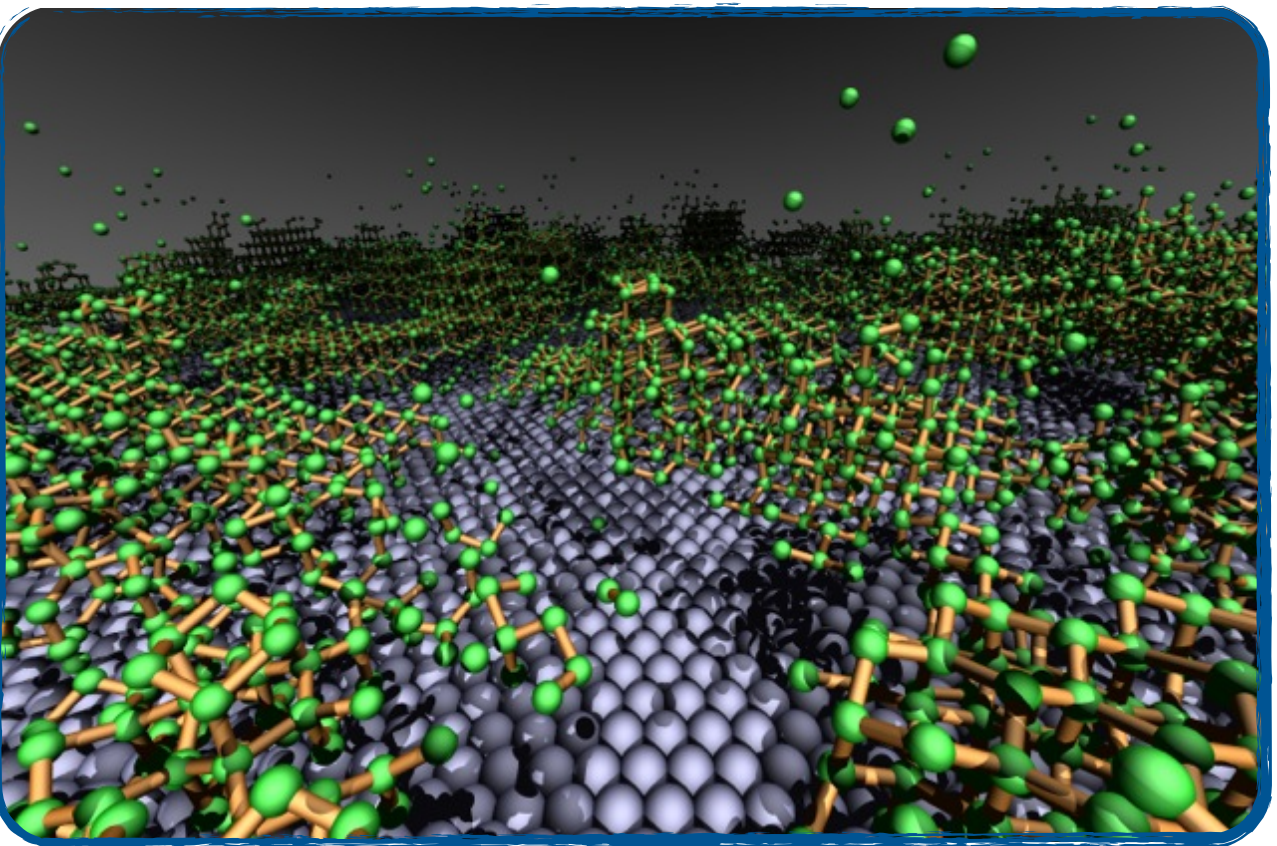
The Many Faces of Heterogeneous Ice Nucleation

Insights from Molecular Dynamics Simulations



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Trieste, Oct. 2016

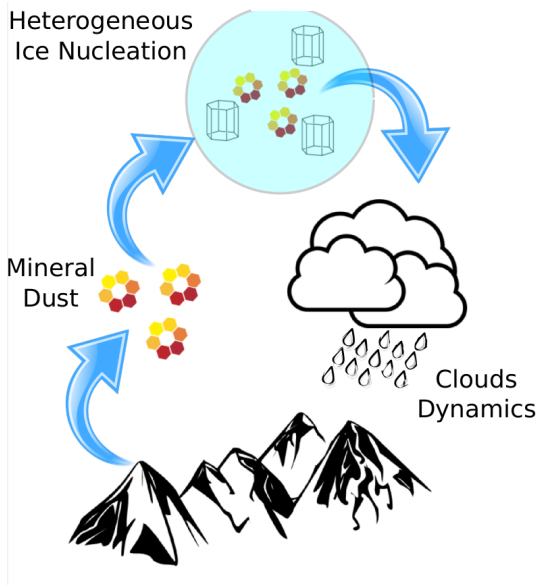
Outline

- **Heterogeneous Ice Nucleation**
  - Why do we care?
  - Open Issues: Hydrophobicity vs surface morphology
- **The tools of the trade**
  - Coarse grained water on ideal crystalline surfaces
  - Brute force molecular dynamics simulations: getting nucleation rates
- **Results**
  - Simple models, complex behaviours
  - Boosting nucleation rates: three microscopic motivations
- **What's next**
  - Current limitations & future perspectives
- **People & acknowledgments**

Heterogeneous Ice Nucleation

Homogeneous vs Heterogeneous nucleation

Why do we care?



Atmospheric science:

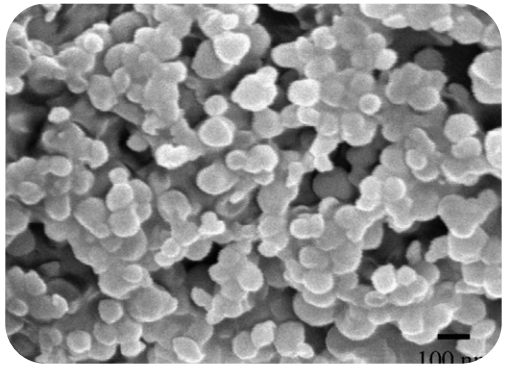
Clouds formation and dynamics

(climate change)

Cryobiology:

Intracellular freezing

(cryotherapy and cryopreservation)



Ice formation on top of lipid bilayers

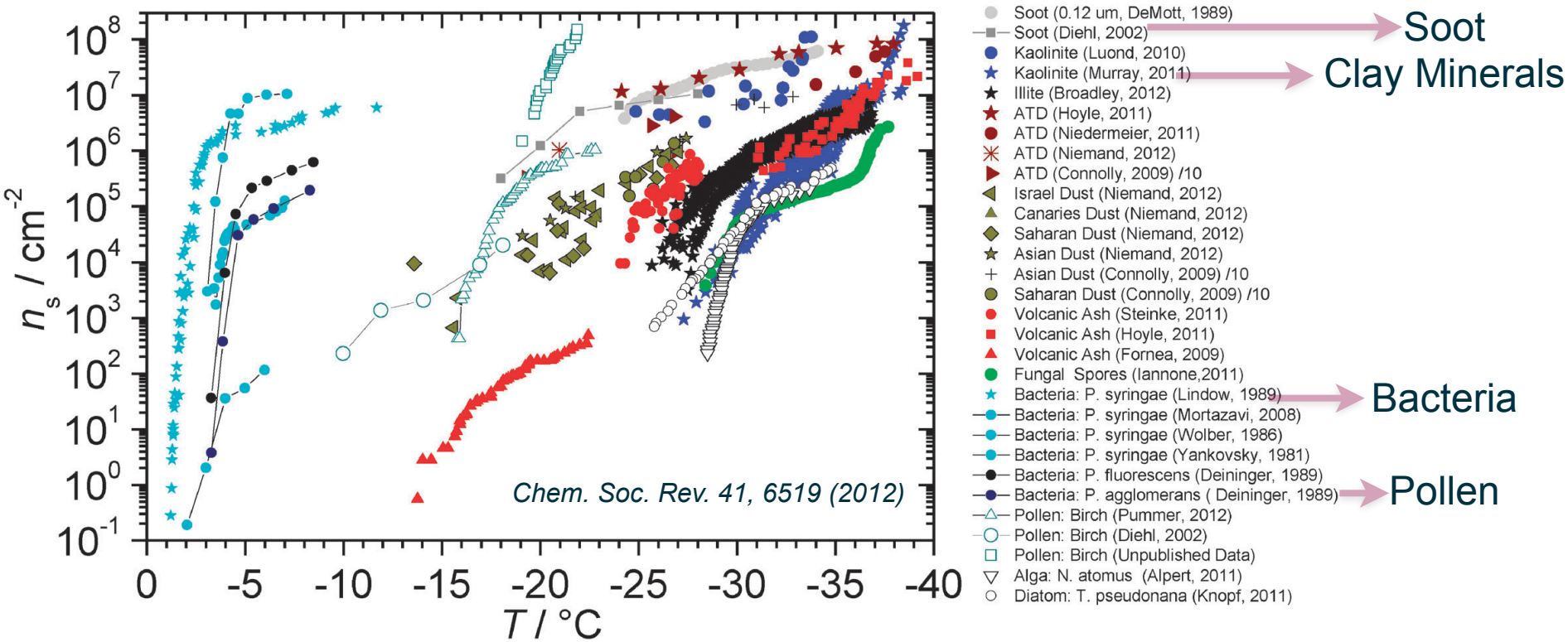
Cryobiology, 55, 210 (2007)

Heterogeneous Ice Nucleation

What makes a material a good Ice Nucleating Agent (INA)?

1. Long-standing and 2. Complex question

Experiments can now quantify the activity of many different INA:



But **we lack insights at the molecular level**

Heterogeneous Ice Nucleation

Atomistic simulations could help…

Simulating heterogenous ice nucleation is still a formidable task:

- It is difficult to describe water at interfaces properly
- Nucleation is a rare event (enhanced sampling techniques needed)
- Even the simplest scenarios are debated

Would a generic crystalline surface promote nucleation?

Most importantly: **why and how?**

Hydrophobicity

J. Phys. Chem. A 118, 7330 (2014)

J. Am. Chem. Soc. 136, 3156 (2014)

J. Chem. Phys. 142, 184705 (2015)

Surface morphology

J. Appl. Phys. 18, 593 (1947)

Surface Science 601, 5378 (2007)

J. Chem. Phys. 142, 184705 (2015)

In here:

Systematic investigation of the interplay between the two

The tools of the trade

Back to the basics…

Simple system → **General trends**

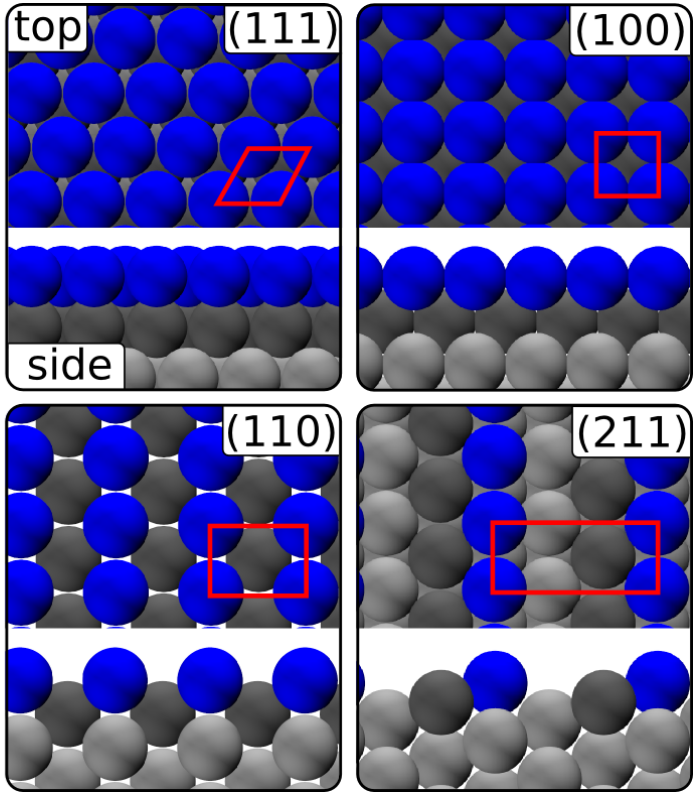
Coarse grained (mW) water

J. Phys. Chem. B 113, 4008 (2009)

- Computationally fast
- Fast water dynamics even at strong supercooling

on top of

Ideal FCC crystal (LJ particles, frozen)



- (111), (100), (110) and (211) surfaces (surface morphology)
- Different lattice parameters a_{fcc} [3.52 - 4.66 Å] (surface morphology)
- Different water-surface interaction (LJ potential) strength E_{ads} [0.2-12 kcal/mol] (hydrophobicity)

The tools of the trade

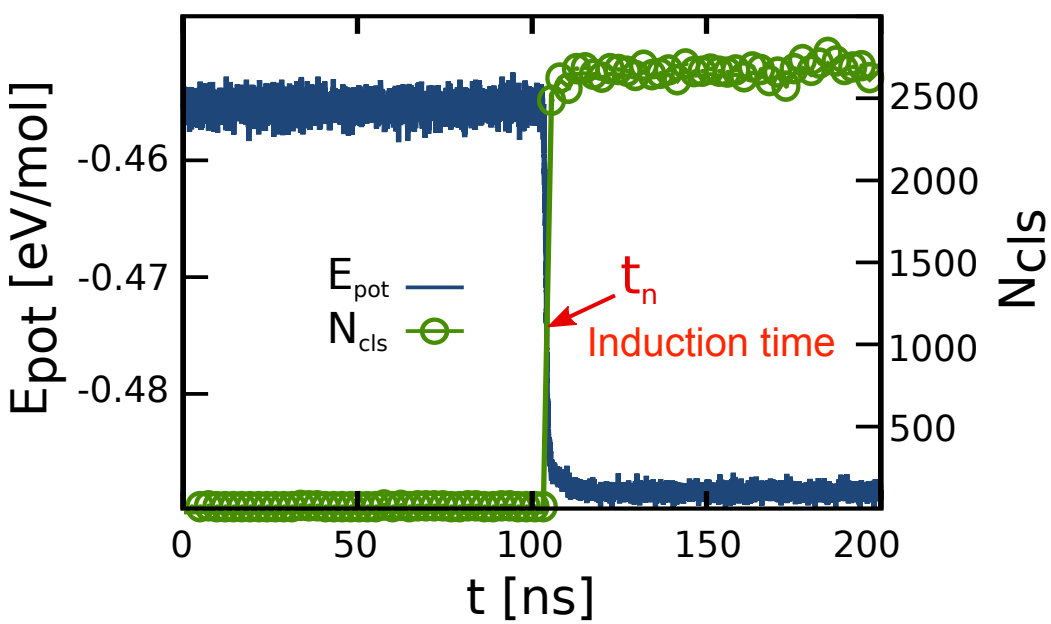
The method:

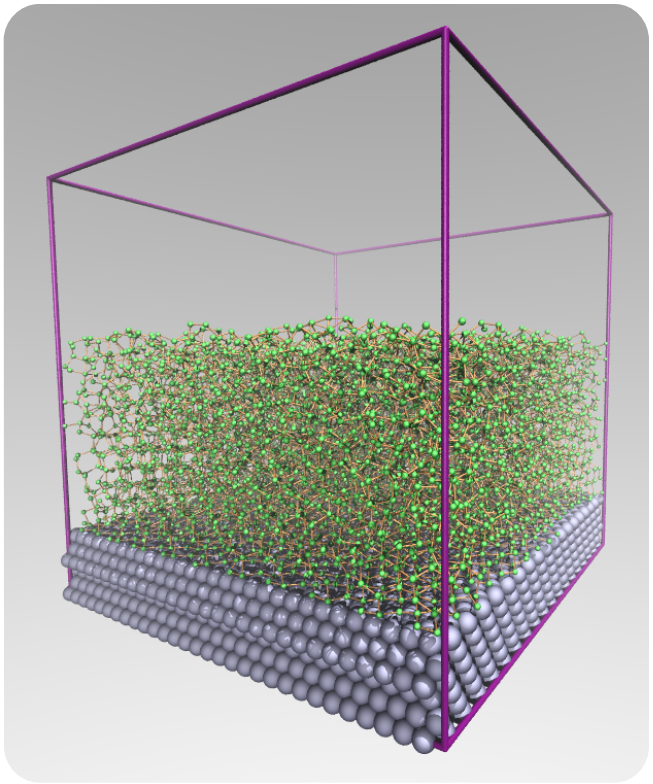
Brute force molecular dynamics simulations at 205 K

Code: LAMMPS. NVT ensemble (Nose-Hoover thermostat). Timestep = 2 fs Geometry: Slab

For each combination of a_{fcc} and E_{ads}:

15 nucleation events (1 to 500 ns needed)

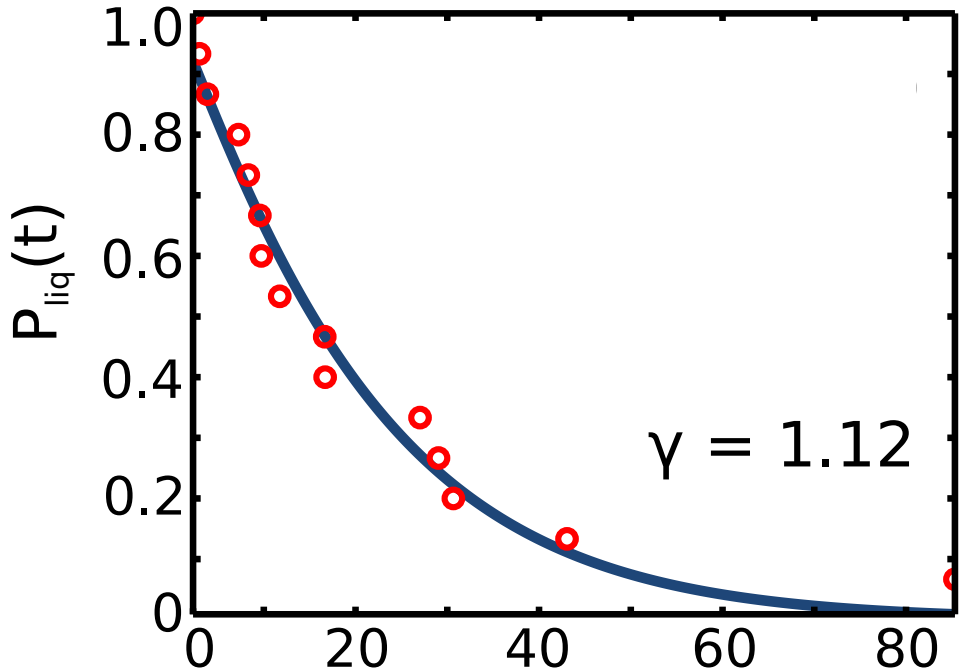




The tools of the trade

Nucleation rates *J* from survival probability

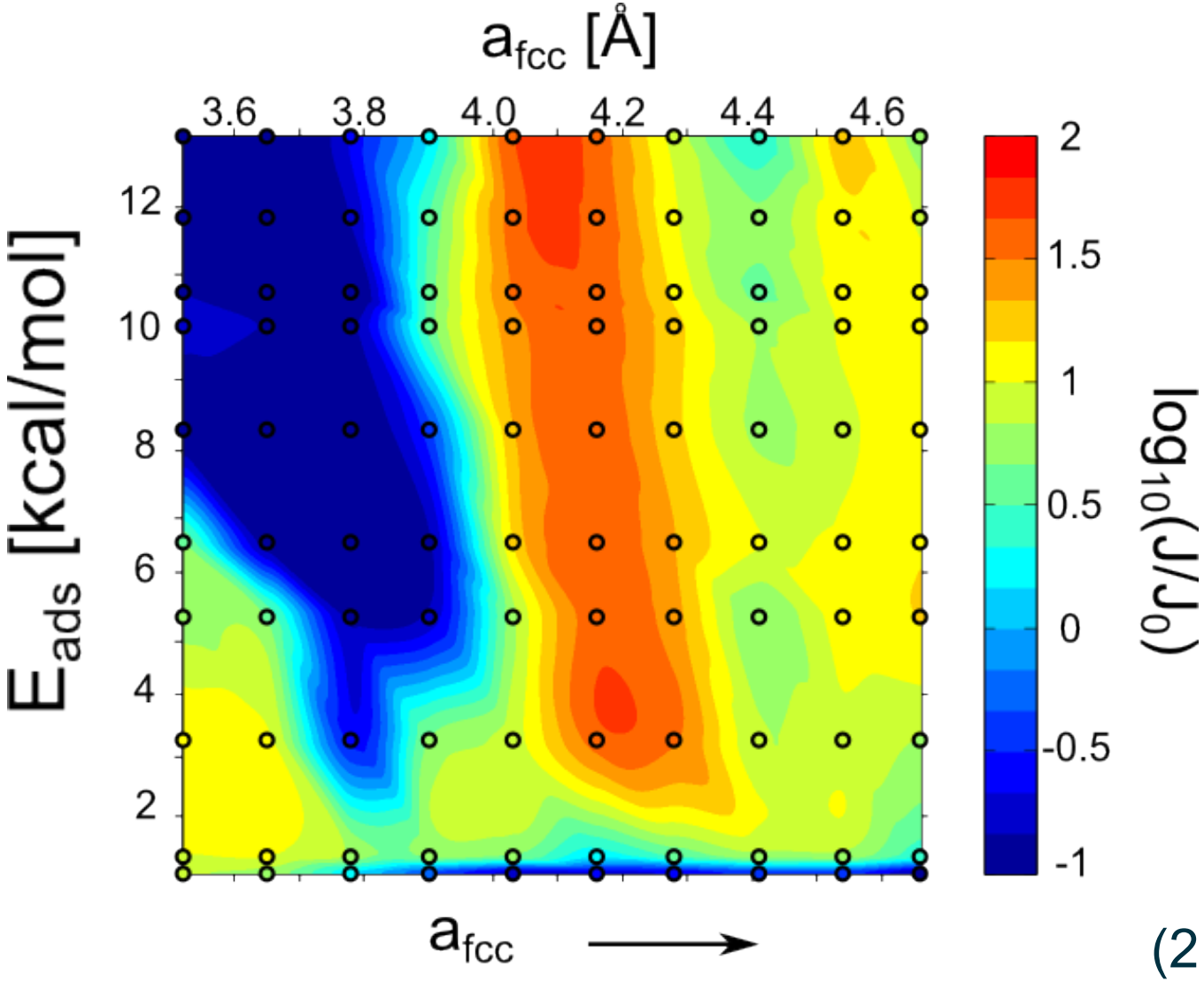
$$P_{liq}(t) = 1 - \frac{1}{N_{sim}} \sum_{i=1}^{N_{sim}} \Theta(t - t_n^{(i)})$$



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

Results

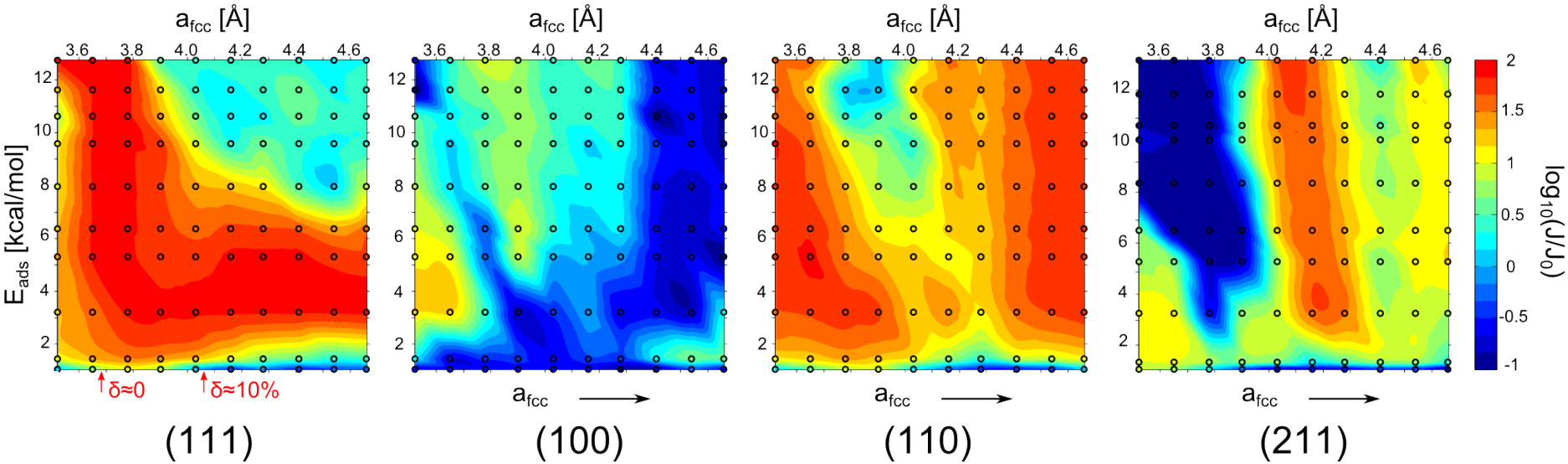
Simple models, complex behaviours



(211) face

Results

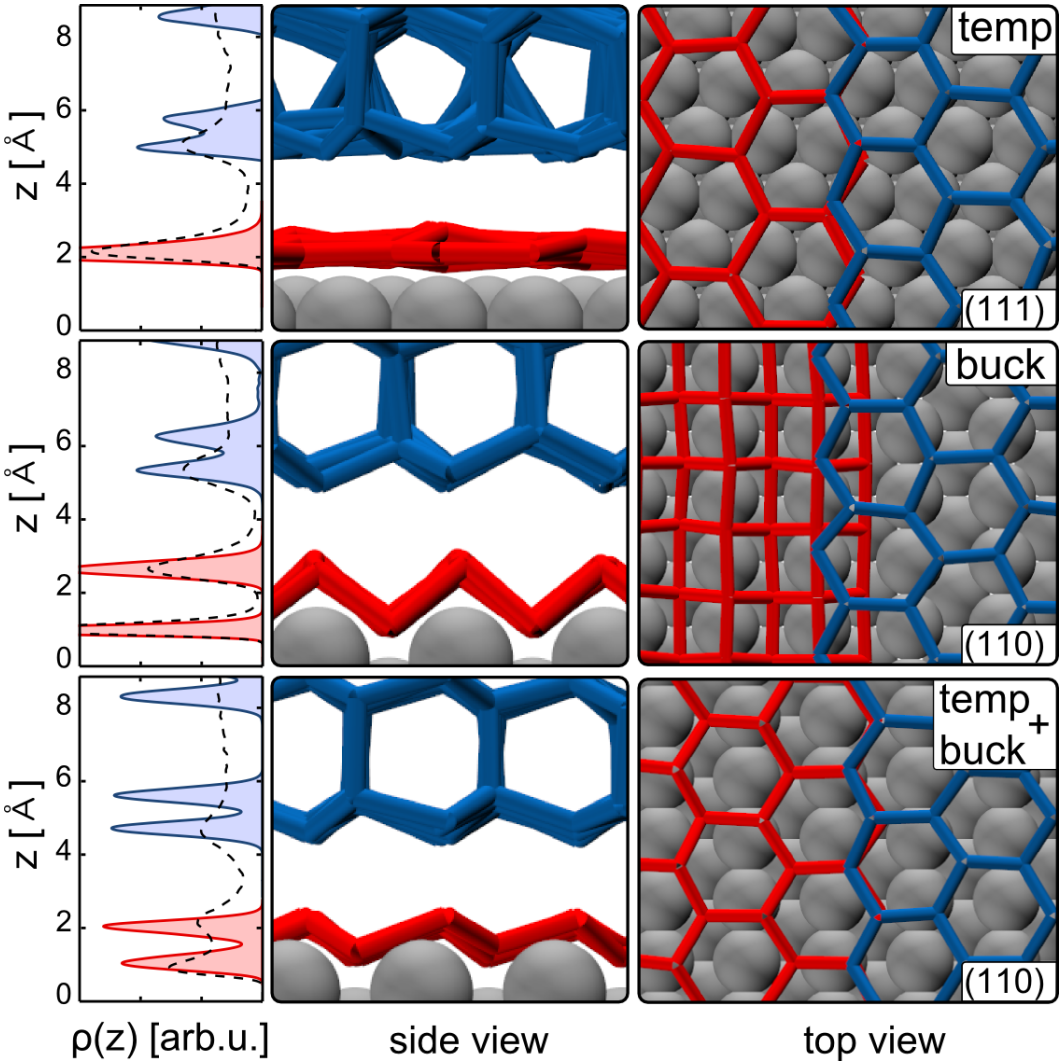
Simple models, complex behaviours



- The crystalline surfaces mostly do promote nucleation compared to homogeneous nucleation.
- Both a_{fcc} and E_{ads} do not influence nucleation on top of each surface in the same manner.
- There is no optimal value for E_{ads}, but nucleation rate is generally inhibited for very low adsorption energies
- The lattice mismatch δ cannot be regarded as the only requirement for an INA

Results

Boosting nucleation rates: three microscopic motivations



In-plane templating
of the first water overlayer

Buckling
of the first water overlayer

In-plane templating + Buckling
of the first water overlayer

Results

Inhibition and nucleation away from the surface

In some cases (typically weak E_{ads}) $J_{het} < J_{homo}$

Ice-like nuclei tend not to form on the crystalline surface

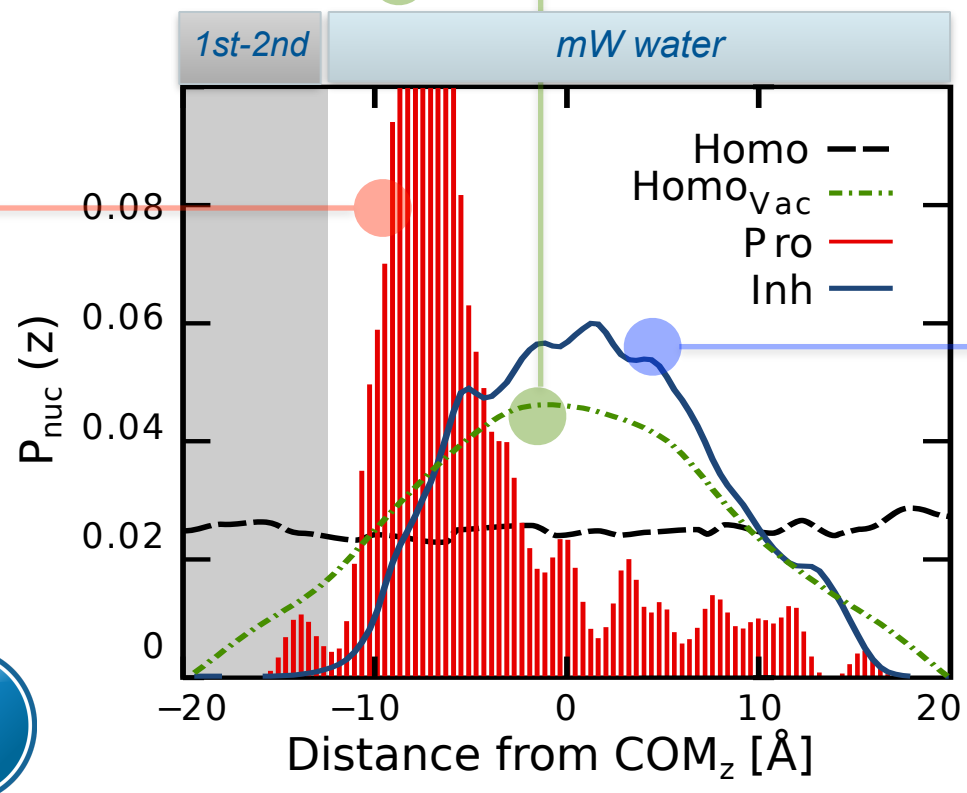
(~water-air interface)

Phys. Chem. Chem. Phys. 16, 25916 (2014)

In other cases $J_{het} > J_{homo}$

even when nothing happens

within the contact layer



Water dynamics at interface

and [ice] nucleation

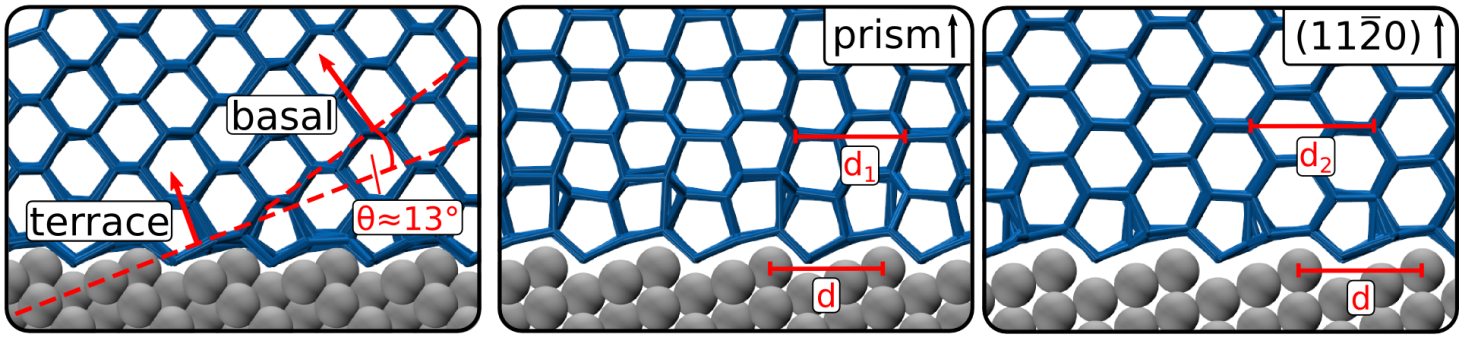
Results

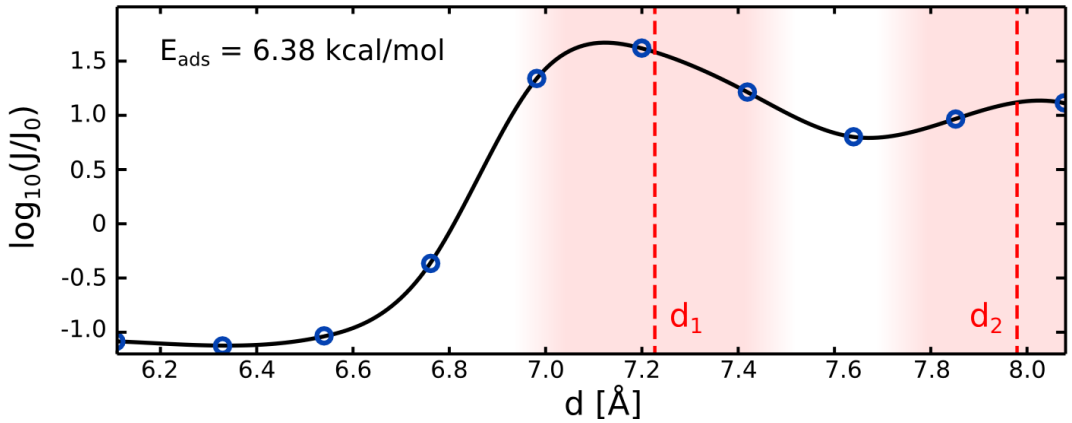
Different ice faces on top of the very same surface

e.g. : the (211) face

Hexagonal overlayer

Rectangular overlayer





Different a_{fcc} → Different templating → Different ice faces

E_{ads} not that important for (211), but **each surface has its own story to tell**

Results

Summary

- Even on top of the simplest substrates (frozen LJ particles), the **interplay between hydrophobicity and surface morphology** can affect heterogeneous ice nucleation in many different ways

- Lattice mismatch can play a role, but there is **so much more going on in the contact layer and even quite far away from the interface**

- Simple trends are nice and useful, but:
  - It looks like every surface has its story to tell
  - **Can we get closer to reality?**

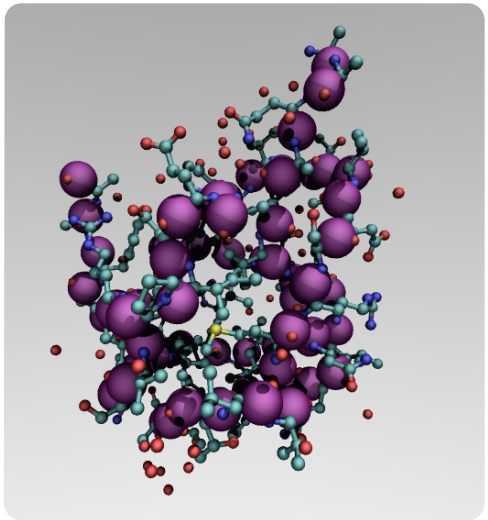
What's next

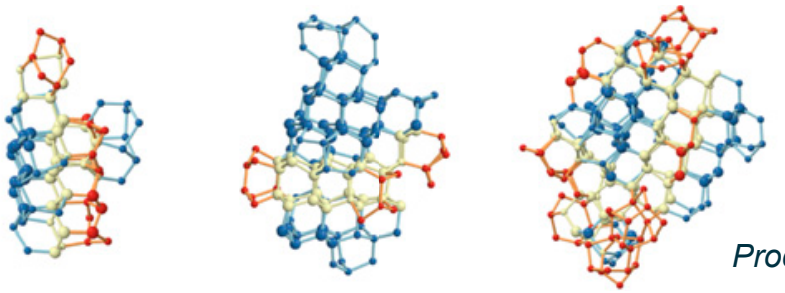
MB-pol (Paesani), NN (Dellago, Morawietz)

- Realistic surfaces:
  Reliable force fields needed for complex interfaces

- Fully atomistic models of water:
  Correct dynamical properties at strong supercooling

- Methods:
  Brute force molecular dynamics won't work
  Enhanced sampling simulations are still challenging





Proc. Nat. Acad. Sci. 112, 10582 (2015)

People & acknowledgements

People

Computational resources

archer

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The whole story

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10.1021/jacs.5b08748