The Many Faces of Heterogeneous Ice Nucleation

Insights from Molecular Dynamics Simulations

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• 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

Outline
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
Simulating heterogeneous 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

Surface morphology
- J. Appl. Phys. 18, 593 (1947)
- Surface Science 601, 5378 (2007)

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


- 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 $a_{\text{fcc}}$ [3.52 - 4.66 Å] (surface morphology)
- Different water-surface interaction (LJ potential) strength $E_{\text{ads}}$ [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 $a_{\text{fcc}}$ and $E_{\text{ads}}$:
15 nucleation events (1 to 500 ns needed)
The tools of the trade

Nucleation rates $J$ from survival probability

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

![Graph showing the survival probability equation](Image)

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

**FIG. S2.** Stretched exponential fitting results for two dissimilar nucleation events.
Results

Simple models, complex behaviours

FIG. 5 a. Heat maps representing the values of ice nucleation rates on top of the four different surfaces considered plotted as a function of the adsorption energy $E_{\text{ads}}$ and the lattice parameter $a_{\text{fcc}}$. The lattice mismatch $\delta$ on $\{111\}$ is indicated below the graph. The values of the nucleation rate $J$ are reported as $\log_{10}(J/J_0)$ where $J_0$ refers to the homogeneous nucleation rate at the same temperature. b. Sketches of the different regions (white areas) in the $E_{\text{ads}}$-$a_{\text{fcc}}$ space in which we observe a significant enhancement of the nucleation rate. We label each region according to the face of $I_h$ nucleating and growing on top of the surface (basaly prismatic or $\{11\bar{2}0\}$) together with an indication of what it is that enhances the nucleation. “temp”, “buck” and “high $E$” refer to the in-plane template of the first overlay, the ice-like buckling of the contact layer, and the nucleation for high adsorption energies on compact surfaces as explained in section III B.

III. RESULTS

A. No Simple Trend for Nucleation Rates

The nucleation rates on the four surfaces considered are shown as bi-dimensional heat maps as a function of the lattice constant and adsorption energy in Figure 5a. Regions in the 2D plots for which a strong enhancement of the nucleation rates is observed are sketched in Figure 5b and snapshots of representative trajectories for all the classified regions can be found in the SI (Figures S4 to S7). Before even considering any microscopic details of the water structure or nucleation processes, several general observations about the data shown.
### Results

Simple models, complex behaviours

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

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![Graph showing heat maps with adsorption energy ($E_{\text{ads}}$) and lattice parameter ($a_{\text{fcc}}$) for different surfaces (111), (100), (110), (211).](image_url)
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
Inhibition and nucleation away from the surface

In some cases (typically weak $E_{\text{ads}}$) $J_{\text{het}} < J_{\text{homo}}$
Ice-like nuclei tend not to form on the crystalline surface
(~water-air interface)

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

![Diagram showing different ice faces and their growth on the (211) surface](image)

**Hexagonal overlayer**
- Basal face
- Terrace

**Rectangular overlayer**
- Prism face
- (11\(\bar{2}0\)) face

Different a\textsubscript{fcc} → Different templating → Different ice faces

**E\textsubscript{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

- 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

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

**Enhanced sampling simulations**

**Brute force molecular dynamics won’t work**

**Methods:**

- **Correct dynamical properties** at strong supercooling
- **Reliable force fields** needed for complex interfaces
- **Methods:**
- Brute force molecular dynamics won’t work
- **Enhanced sampling simulations** are still challenging

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The whole story

M. Fitzner, G.C. Sosso, S.J. Cox & A. Michaelides, JACS, just accepted

10.1021/jacs.5b08748