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

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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!

\[ \Delta G(r) = f(\theta) \left( \frac{4}{3} \pi r^3 \rho_1 \Delta \mu + 4 \pi r^2 \gamma_g \right) \]

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

contact angle term lowers the free energy barrier

Kiselev, et al., Science, 355, 367 (2017), Heterogeneous ice nucleation on K-rich Feldspar particles
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$_2$O molecules
- Very short or no time evolution

### TIP4P/ice all-atom potential
- ~ 1000 H$_2$O molecules

### Monatomic water (mW) potential
- ~ 100 000 ‘H$_2$O’ molecules
Heterogeneous ice nucleation on silver iodide particles

• Silver iodide has been used as a rain seeding agent for decades
• Lattice mismatch between β-Agl (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:

\[ U(r_{ij}) = U_{LJ} + U_{Coul} = \sum_{i<j} 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r_{ij}} \]

- All Ag and I ions fixed to bulk positions
- H₂O modeled with TIP4P/ice potential [1]
- AgI – H₂O 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)
- H₂O molecule rigid geometry enforced with SETTLE algorithm
- 3D periodic boundary conditions

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

(a) Number density [Å⁻³] vs. Distance from surface [Å]
- Oxygen, 263 K
- Hydrogen, 263 K
- Oxygen, 273 K
- Hydrogen, 273 K

(b) Heat map of density [ρ/ρ₀] vs. Distance from surface [Å] and x position [Å]

(c) Images at T = 263 K
- [010] orientation
- [100] orientation

(d) Images at T = 273 K
- [010] orientation
- [100] orientation

Time scale for water exchange in HL1 ~ 2 ns
Ice nucleation rates from MD simulations at $T = 263$ K

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

$$P_{\text{liq}}(t) = \exp[-(Rt)\gamma]$$
Effect of defects on ice nucleation on AgI (0001) surfaces

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

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

- start of ideal growth of ice $l_2$
- appearance of a $l_1 - l_2$ stacking fault
- return to ideal growth of ice $l_2$
- critical nuclei on lower and upper terrace
- separated growth
- stacking fault at interface
- transition to ideal growth
- critical nucleus on upper terrace
- growth limited by area of upper terrace
- nucleation on lower terrace
- merging through stacking fault
- nucleation outside pit
- growth outside pit
- nucleation inside pit
- pit overgrown
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

- 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!
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