Thermodynamic and Dynamic Aspects of Ice Nucleation

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Determines phase partitioning in mixed-phase stratus and convective clouds

Plays a very important role in the evolution of Arctic clouds

May affect climate sensitivity (Tan et al. 2016).

Immersion Ice Nucleation

Soluble and Insoluble Aerosol Ice Nuclei (INP)
Mostly dust, soot, and biological material

Immersion Freezing

Ice crystal population

- INP completely immersed
- Thermodynamic equilibrium
- Could happen at RH<100%
Water-Particle Interactions

- **Vicinal water may exist in a ordered state (Ice-Like) near the solid-liquid interface.** Ordered structures may propagate over hundreds to thousands of molecular diameters (Drost-Hansen, 1969, Zheng et al., 2006). Found in biological (Snyder et al., 2014), metallic (Michot et al., 2002) and clay (Yu et al., 2001) interfaces. Also supported by MD simulations (Cox et al., 2015).

- **Strong evidence of ice formation several molecular diameters away from the clay-water interface:** “ice formation does not require an ice germ attached to the substrate” (Anderson, 1967).

- **The viscosity of interfacial water regulates the ice nucleation activity** (Li et al., 2014). **The work of nucleation and the enhancement of the viscosity of the vicinal water are tightly linked.**
Nucleation within a Dense Liquid

Bulk Liquid

Vicinal water

Active Site

Active Site

Low density water (ice precursor)

+ Order
+ Viscosity
Nucleation within a Dense Liquid

Goal: To describe immersion freezing as determined by the effect of the particle on the vicinal water

Steps:
1. Model the properties of vicinal water
2. Relate vicinal water thermodynamics to the work of ice nucleation
3. Describe of the effect of the particle on the interfacial flux, hence on the nucleation rate
1-Thermodynamics of Vicinal Water

<table>
<thead>
<tr>
<th>Bulk Liquid</th>
<th>$\mu_w$, $a_w$</th>
</tr>
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<tbody>
<tr>
<td>LL</td>
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Two state model: Vicinal water as a regular solution of Liquid-Like (LL) and Ice-Like (IL) regions, in equilibrium with the bulk liquid and the particle.

$\zeta = \text{Fraction of Ice-Like regions in the vicinal water (Templating Factor).}$

Material - specific.

For homogeneous nucleation $\zeta = 0$
# 1-Thermodynamics of Vicinal Water

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Two state model: Vicinal water as a regular solution of Liquid-Like (LL) and Ice-Like (IL) regions, in equilibrium with the bulk liquid and the particle.

\[ \zeta = \text{Fraction of Ice-Like regions in the vicinal water (Templating Factor).} \]

Material specific.

For homogeneous nucleation \( \zeta = 0 \)

\[ \mu_w = \mu_{LL} + \zeta \Delta \mu_s - \frac{2 k_B T_c}{N} \zeta (1 - \zeta). \]

\( \Delta \mu_s \): Free energy of fusion

\( T_c, N \) = Critical parameters

**Heterogeneous Ice Nucleation** can be modeled as occurring

**Homogeneously** in the LL regions

\[ \Delta G_{\text{het}}(a_w) = \Delta G_{\text{hom}}(a_{w,\text{eff}}). \]

\( a_{w,\text{eff}} = a_w \) in the LL regions
Homogeneous Ice Nucleation

- Neg-entropic Nucleation Framework, NNF:
  - Emphasizes entropic changes across the interface.
  - The interfacial energy and the activation energy are explicit functions of $a_w$ and $T$.
  - Accounts for *dissipation* effects during ice germ formation

[Diagram showing the process of homogeneous ice nucleation, including a core-shell structure for the ice germ and molecular fluctuation in the liquid phase leading to the loss of a small amount of work.]

Barahona, ACP, 2014, 2015
Work of nucleation: Spinodal Regime

\[ \zeta = 0, \]
Homogeneous nucleation

Formation of the ice–liquid interface dominates
Work dissipation dominates

For typical hom the dissipated work is negligible

\[ \Delta G \text{ increases rapidly} \]

\[ \Delta G_{\text{het}} (\times 10^{-20}) \]

\[ \begin{align*}
\text{Low } & \Delta G \\
120 & \text{ Spinodal Point} \\
120 & \text{ } T (K) \\
240 & \text{ } T_{\text{hom}} \\
1000 & \end{align*} \]
Particles with $\zeta > 0.7$ may display spinodal behavior for immersion freezing $T$.

Spinodal point moves towards higher $T$ for $\zeta > 0$. 

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**Work of nucleation: Spinodal Regime**

- $\Delta G_{\text{net}}$ (J x $10^{-20}$)
- $T$ (K)
- $\zeta$

Increasing $\zeta$
Dynamics Of Ice Germ Growth

The presence of the particle decreases the diffusivity of interfacial water by reducing the configurational entropy:

Only water in LL regions can diffuse

INP that efficiently reduce the work of nucleation ($\zeta > 0.7$) also tend to decrease the molecular flux to the ice germ

\[ D \propto \exp\left(-\frac{A}{TS_c}\right) \]

Adam and Gibbs, 1965
Nucleation rate: Dynamic and Thermodynamic Factors

Classical regime ($\zeta<0.6$): High $\Delta G$, and high $J_0$. Limited effect of the particle on vicinal water. Steep $dJ/dT$. 

Increasing $\zeta$
Classical regime: Overlap with CNT predictions. The contact angle and $\zeta$ carry similar information
Two very different INP can display the same freezing temperature with very different sensitivities to cooling rate and surface area.

Spinodal regime ($\zeta > 0.7$): Negligible $\Delta G$, and low $J_0$. Strong kinetic limitations.

Shallow $dJ/dT$
Application: Immersion Freezing by Humic INP

Markers: Data from Rigg et al (2013). $\Delta a_{w,het} = 0.2466 \pm 0.025$

Shaded area: Model predictions for $a_w = 0.86, 0.91,$ and $1.0$.

$\zeta \sim 0.05$. Classical germ forming regime.

Reasonable agreement in $J_{het}$ but $dJ_{het}/dT$ seems off.

Thermodynamic correspondence between $\zeta$ and $\Delta a_{w,het}$
Spinodal Ice Nucleation

Markers: Data from Rigg et al (2013). $\Delta a_{w,het} = 0.2466 \pm 0.025$

Shaded area: Model predictions for $a_w = 0.86$, $0.91$, and $1.0$.

Better agreement in $dJ_{het}/dT$. Dynamical effects may play a significant role in this case.

Find $\zeta$ fitted in a region corresponding to spinodal ice nucleation to ($\zeta \sim 0.955$).
Spinodal Ice Nucleation may be Common

Blue Lines: Classical regime
Red Lines: Spinodal regime
Markers: Derived and measured ice nucleation rates
Conclusions

• Current immersion freezing theory relies on a view that mimics ice formation from the vapor, neglecting several **interactions unique to the liquid.** A comprehensive approach is developed to account for such interactions.

• Instead of being purely driven by thermodynamics, heterogeneous ice nucleation in the liquid phase is a process determined by the **competition between thermodynamic and kinetic constraints** to the formation and propagation of ice.

• Accounting for the effect on the particle of the vicinal water suggests the **existence of a spinodal regime where dynamics controls the ice nucleation rate.** Preliminary data suggest that it may be common in nature.

• Paper under discussion: “On the Thermodynamic and Dynamic Aspects of Immersion Ice Nucleation”. ACPD.
THANKS!
Classical Nucleation Theory

- CNT provides the basis for the semi-empirical modeling of ice nucleation in clouds models
- Key assumptions:
  - Active site = adsorption site
  - Water has uniform properties up to the dividing line
  - Ice germ is implicitly considered denser than the liquid
  - IN activity depends only on the surface properties
Nucleation modeled as occurring Homogeneously in the LL regions.

$$\Delta G_{het}(a_w) = \Delta G_{hom}(a_{w, eff}).$$
Water Activity Criterion

Direct correspondence between $\zeta$ and $\Delta a_w,_{het}$
Nucleation within a Dense Liquid

Bulk Liquid

- Active Site

+ Order
+ Viscosity

Low density water (ice precursor)
Homogeneous Ice Nucleation

- Neg-entropic Nucleation Framework, NNF:
  - Emphasizes entropic changes across the interface.
  - Obviates the explicit parameterization of the interfacial energy and the activation energy.
  - Accounts for *dissipation* effects during ice germ formation

\[
\Delta G_{\text{nuc}} = \frac{4}{27} \frac{[\Gamma_w s (\Delta h_f - \Gamma_w k_B T \ln a_w)]^3}{[k_B T \ln \left( \frac{a_w}{a_{w,eq}} \right)]^2}
\]

\[
\Delta G_{\text{act}} = k_B T \left[ \frac{E}{(T - T_0)} + n_t \ln \left( \frac{a_w}{a_{w,eq}} \right) \right]
\]

- **Bulk liquid**
  - \( N_w \rightarrow \mu_w, N_w-n \)

- **Ice germ**
  - \( \mu_s, n_s \)

- **Interface**
  - \( \mu_{w,ls}, \Gamma_w \)

- \( \Delta h_f \): Enthalpy of fusion
- \( a_w \): Water activity
- \( \Gamma_w \): Interface thickness (1.46)
- \( s \): Lattice geometry (1.105)