Thermodynamic and Dynamic Aspects of Ice Nucleation

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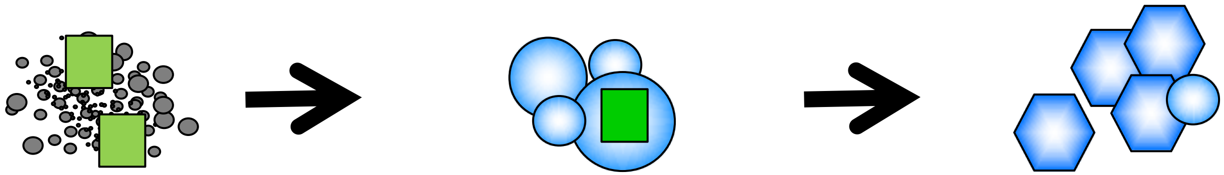
Immersion Ice Nucleation



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%

- 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).

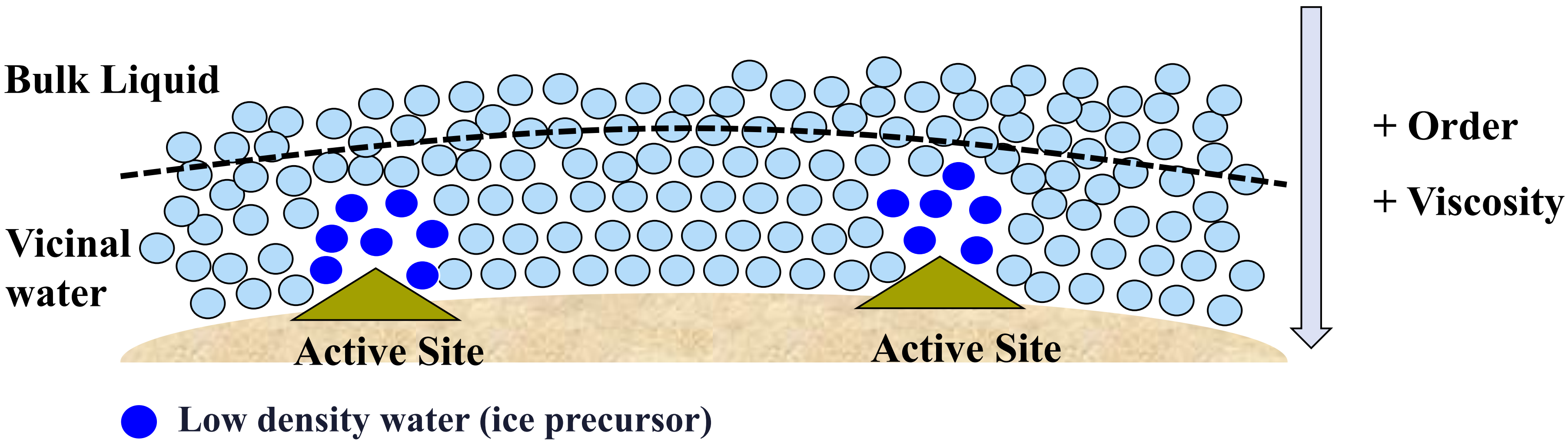
Water-Particle Interactions

- **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



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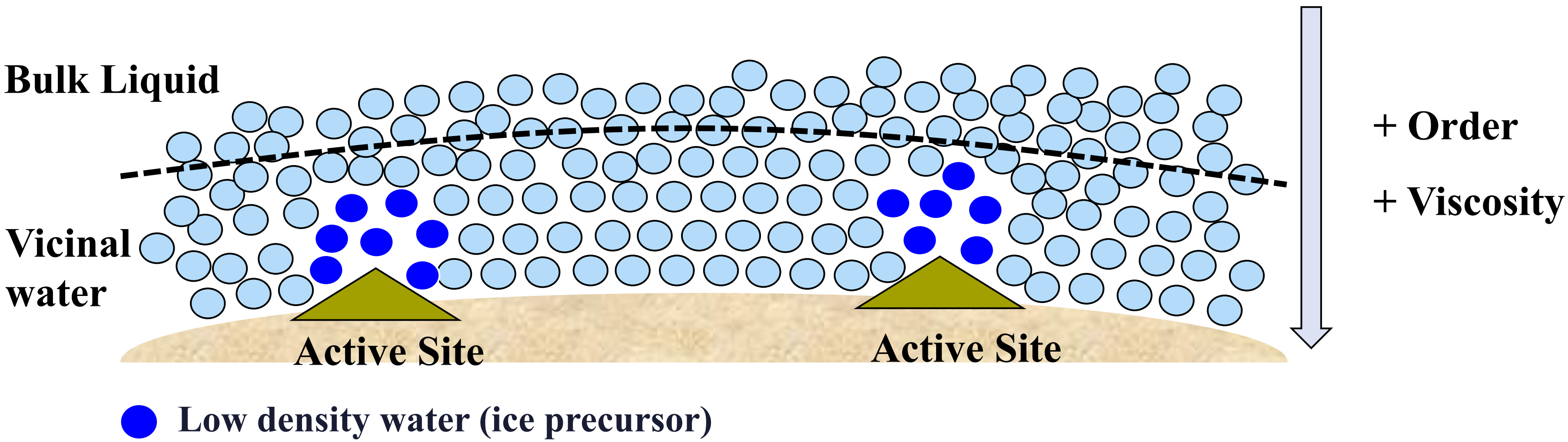
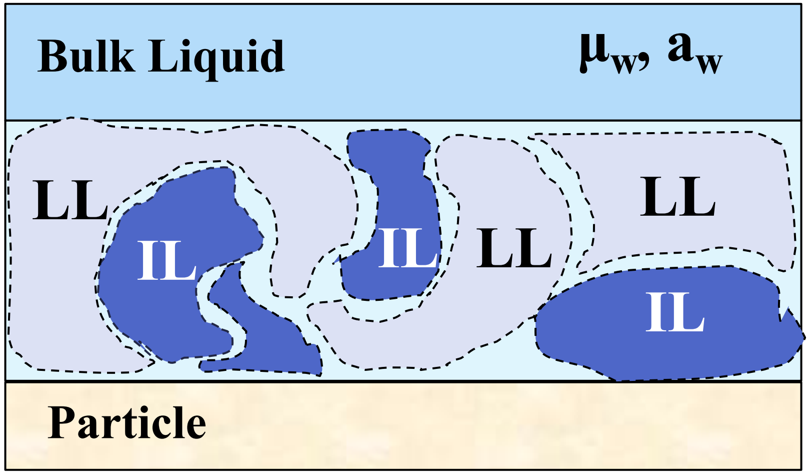


Goal: To describe immersion freezing as determined by the effect of the particle on the vicinal water

- 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

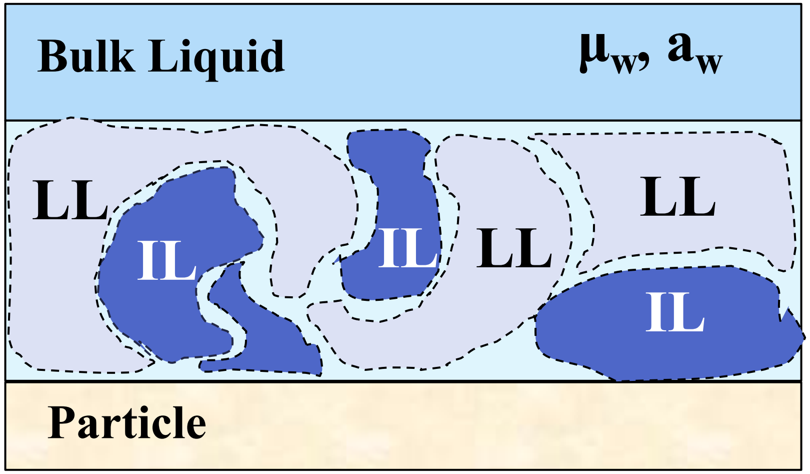


Two state model: Vicinal water as a regular solution of Liquid-Like (LL) and Ice-Like (IL) regions, in equilibrium with the bulk liquid and the particle.

ζ = Fraction of Ice-Like regions in the vicinal water (Templating Factor). Material –specifc.

For homogeneous nucleation $\zeta = 0$

1-Thermodynamics of Vicinal Water



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Direct relation between the water activity in the bulk and in the LL regions

$$\mu_{\mathrm{w}} = \mu_{\mathrm{LL}} + \zeta \Delta\mu_s - \frac{2k_{\mathrm{B}}T_c}{N}\zeta(1-\zeta).$$

$\Delta\mu_s$: Free energy of fusion
Tc, N = Critical parameters

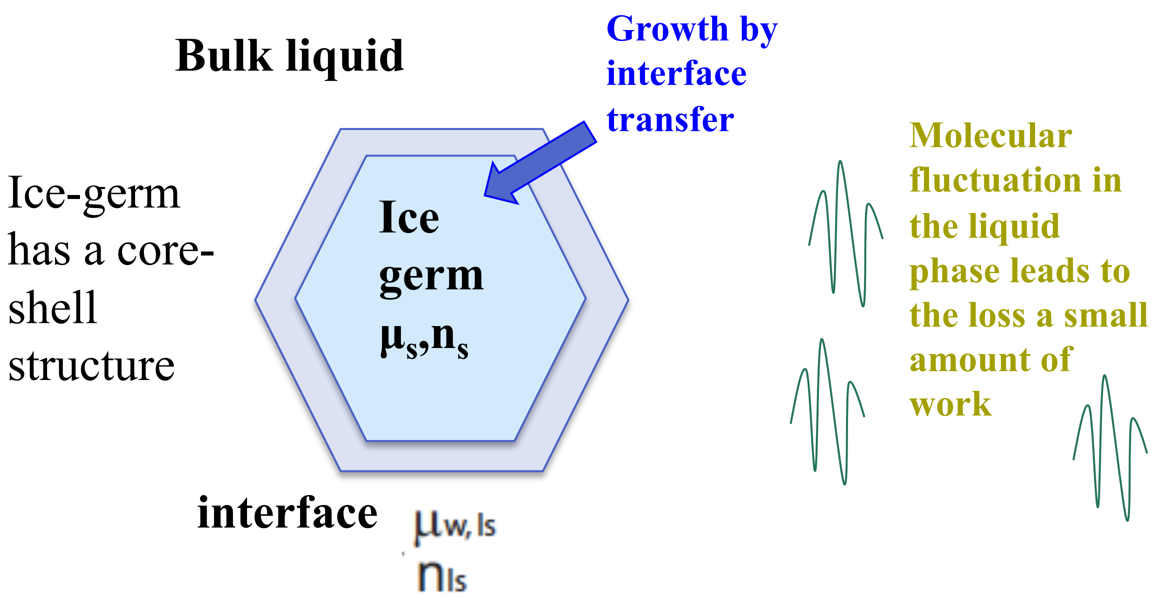
Heterogeneous **Ice Nucleation can be modeled as occurring** ***Homogeneously*** **in the LL regions**

$$\Delta G_{\mathrm{het}}(a_{\mathrm{w}}) = \Delta G_{\mathrm{hom}}(a_{\mathrm{w,\,eff}}).$$

$\mathbf{a_{w,\,eff}}$ = a_w in the LL regions

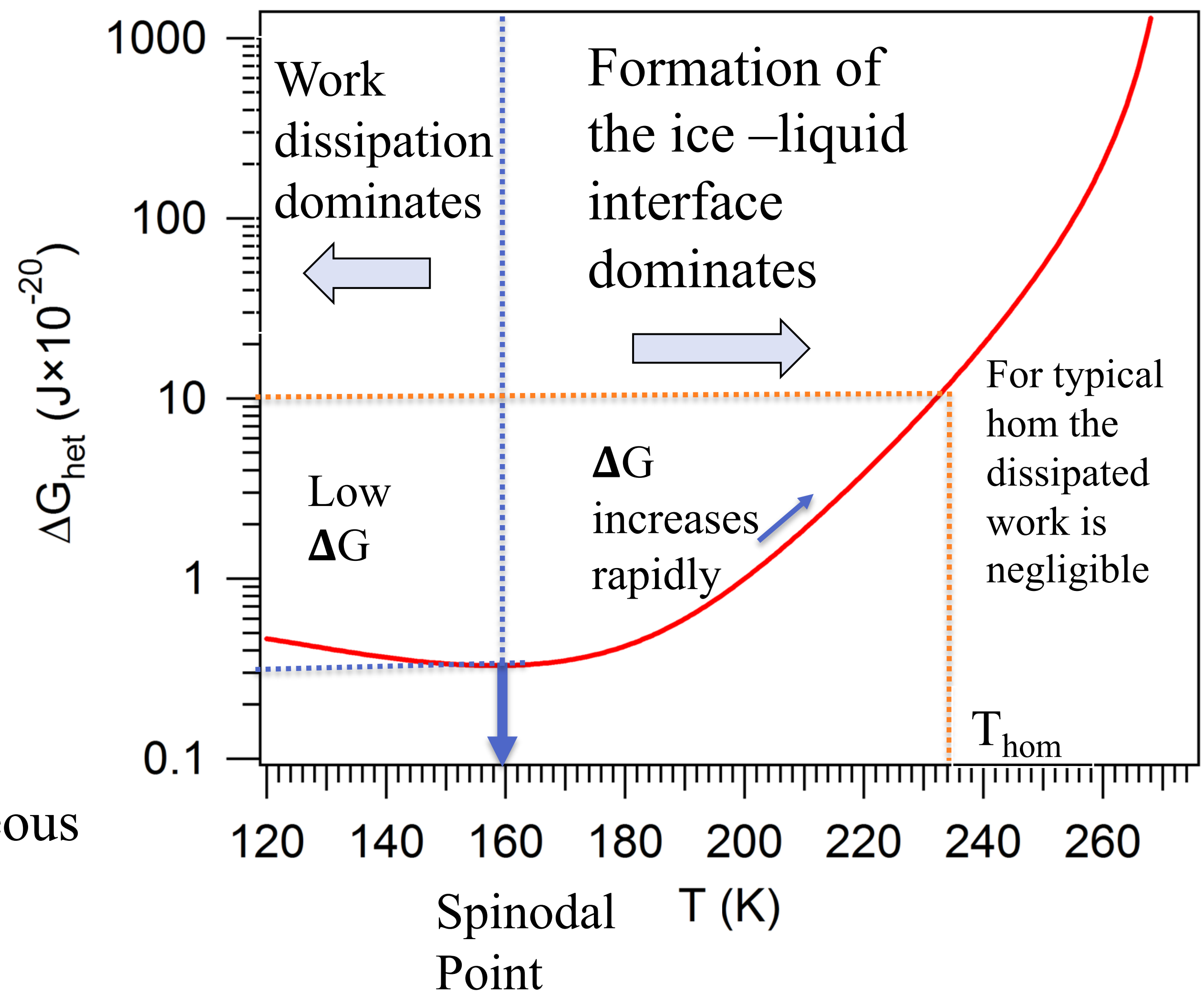
Homogeneous Ice Nucleation

- 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



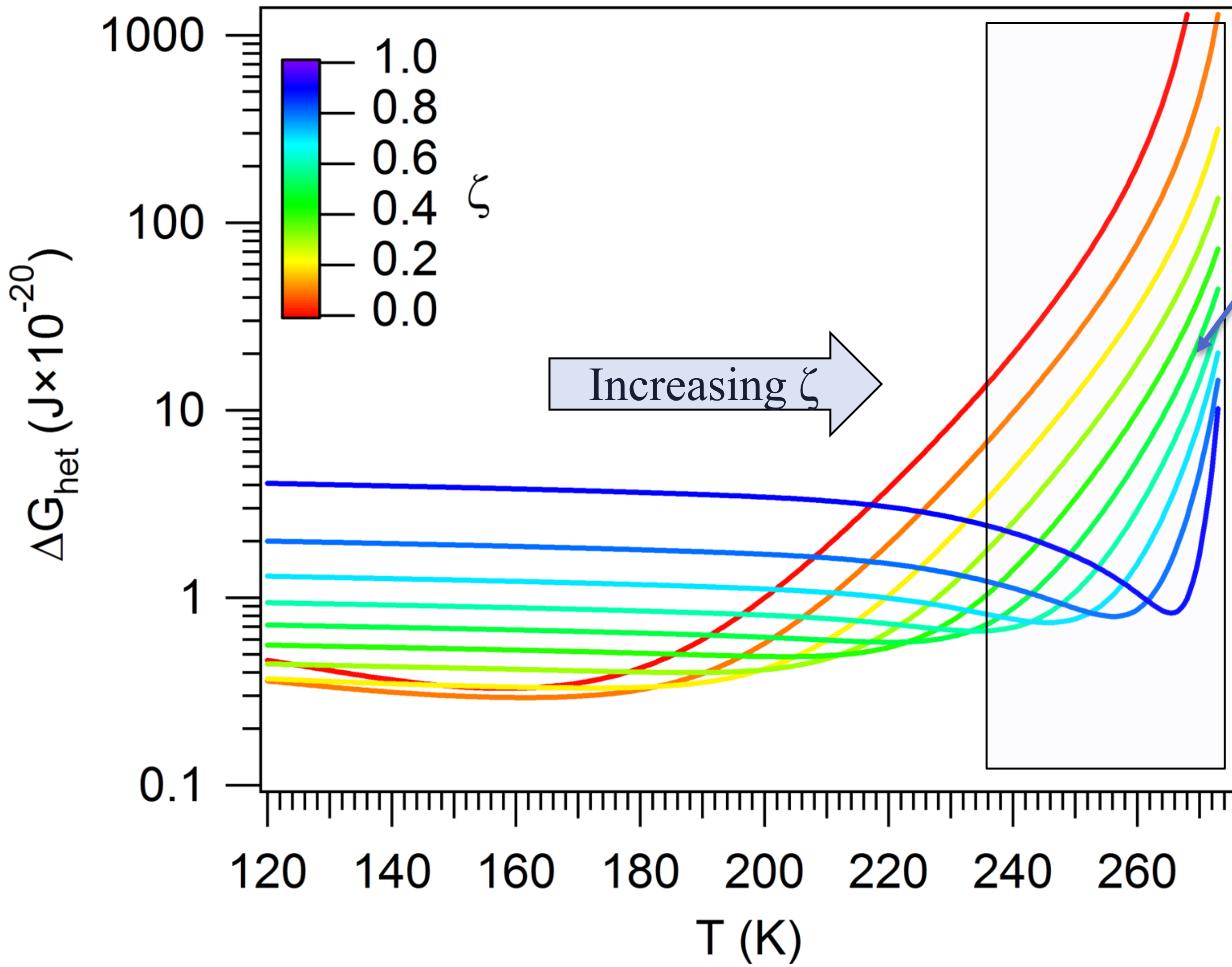
Barahona, ACP, 2014, 2015

Work of nucleation: Spinodal Regime



$\zeta = 0$,
Homogeneous nucleation

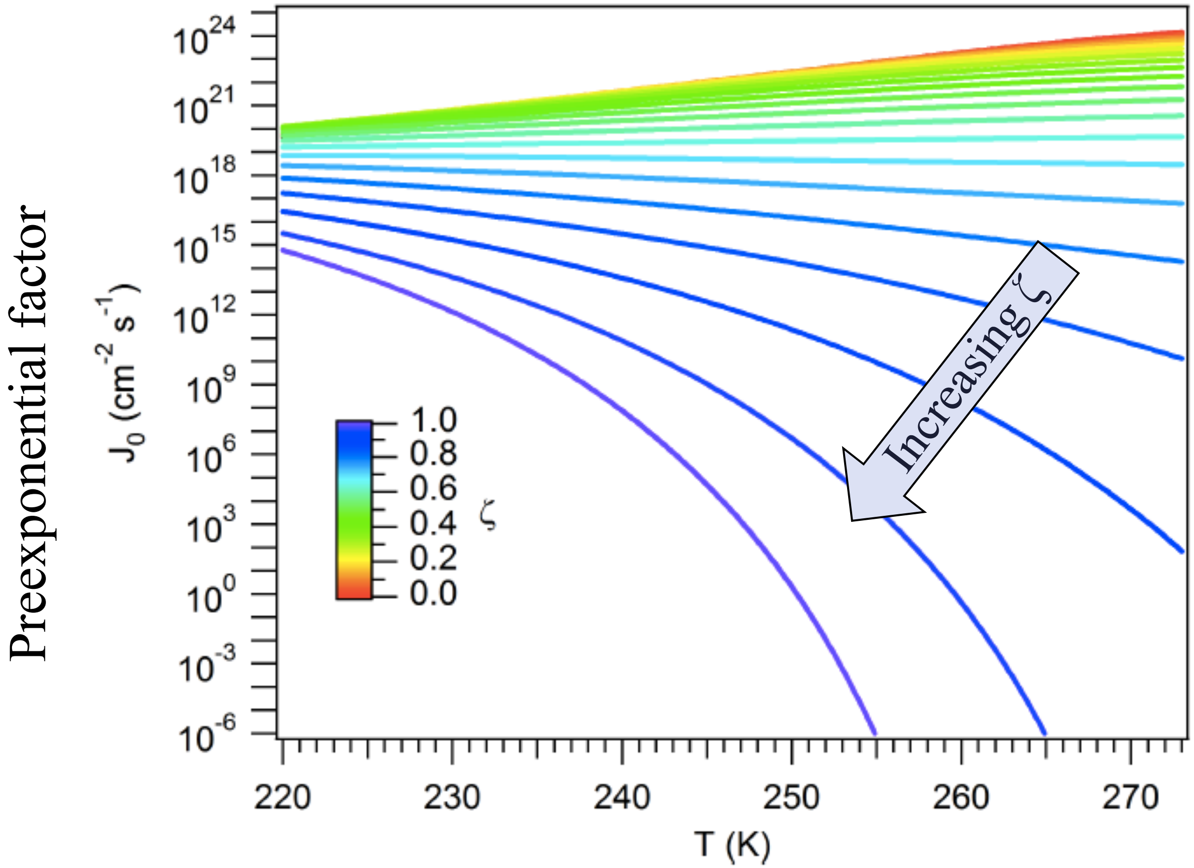
Work of nucleation: Spinodal Regime



Particles with ζ > 0.7 may display spinodal behavior for immersion freezing T

Spinodal point moves towards higher T for ζ > 0

3-Dynamics Of Ice Germ Growth



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

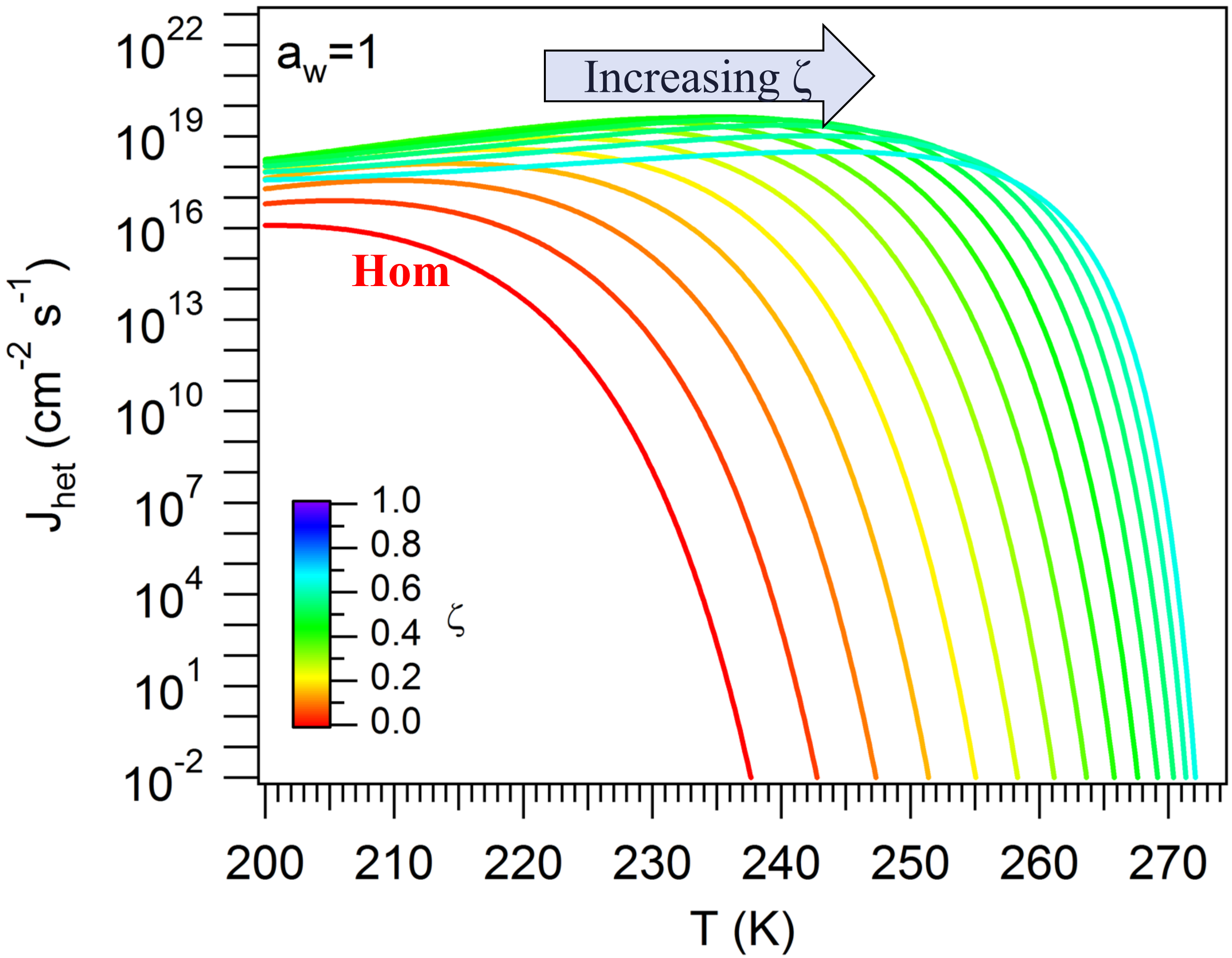
Adam and Gibbs, 1965

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

Only water in LL regions can diffuse

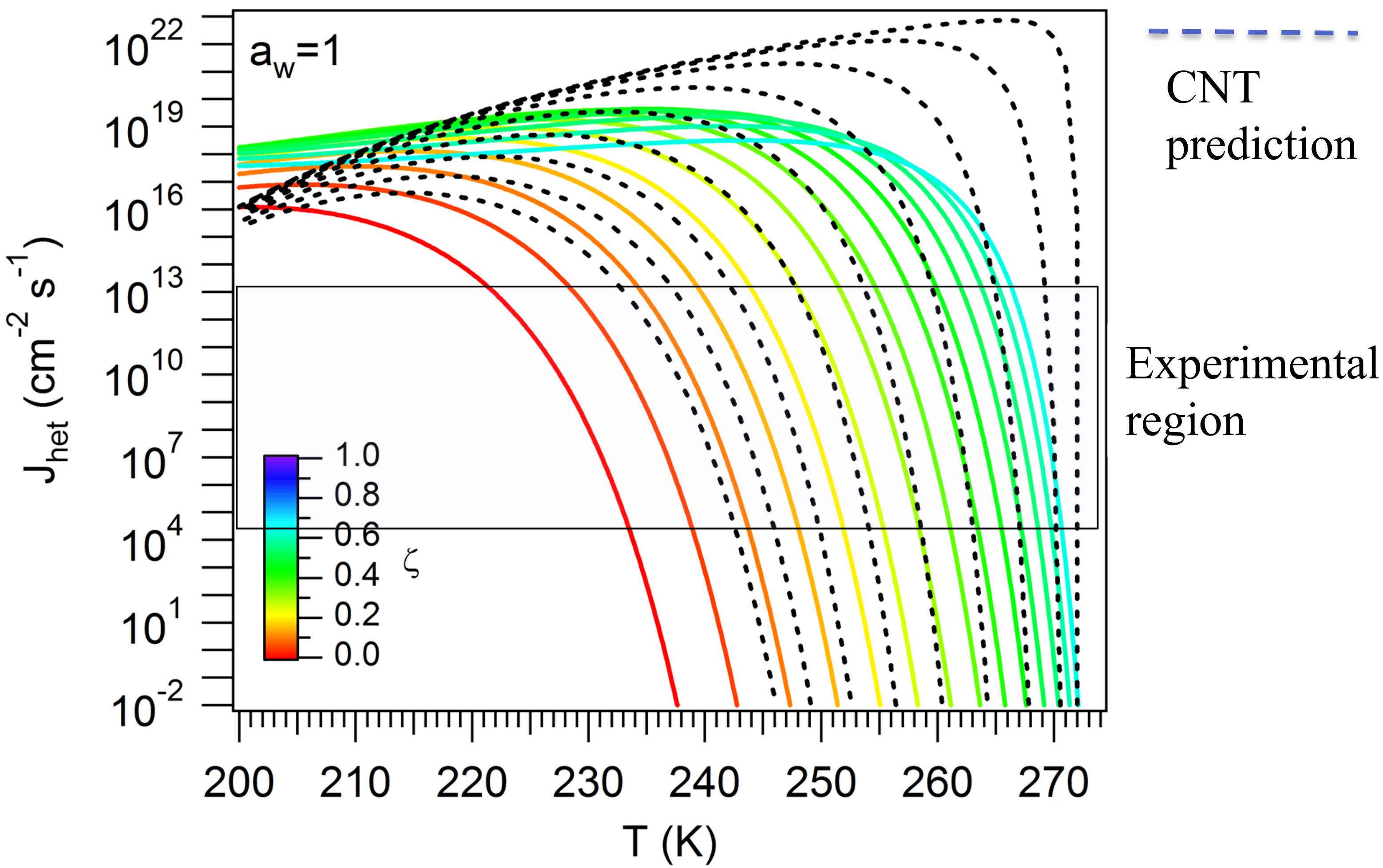
INP that efficiently reduce the work of nucleation ($\zeta > 0.7$) also tend to decrease the molecular flux to the ice germ

Nucleation rate: Dynamic and Thermodynamic Factors



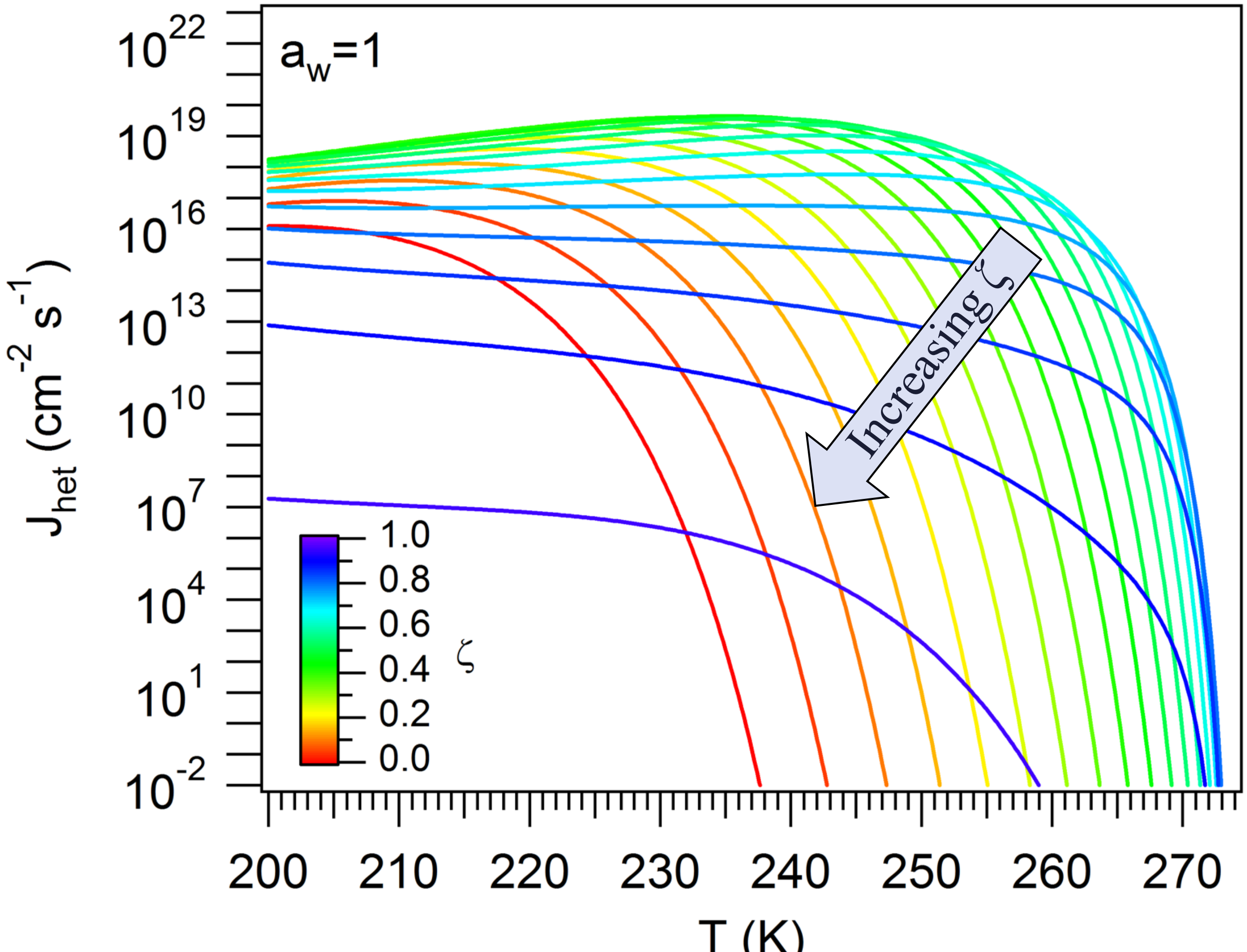
Classical regime (ζ<0.6): High ΔG, and high J_0. Limited effect of the particle on vicinal water. Steep dJ/dT.

Nucleation rate: Dynamic and Thermodynamic Factors



Classical regime: Overlap with CNT predictions. The contact angle and ζ carry similar information

Nucleation rate: Dynamic and Thermodynamic Factors

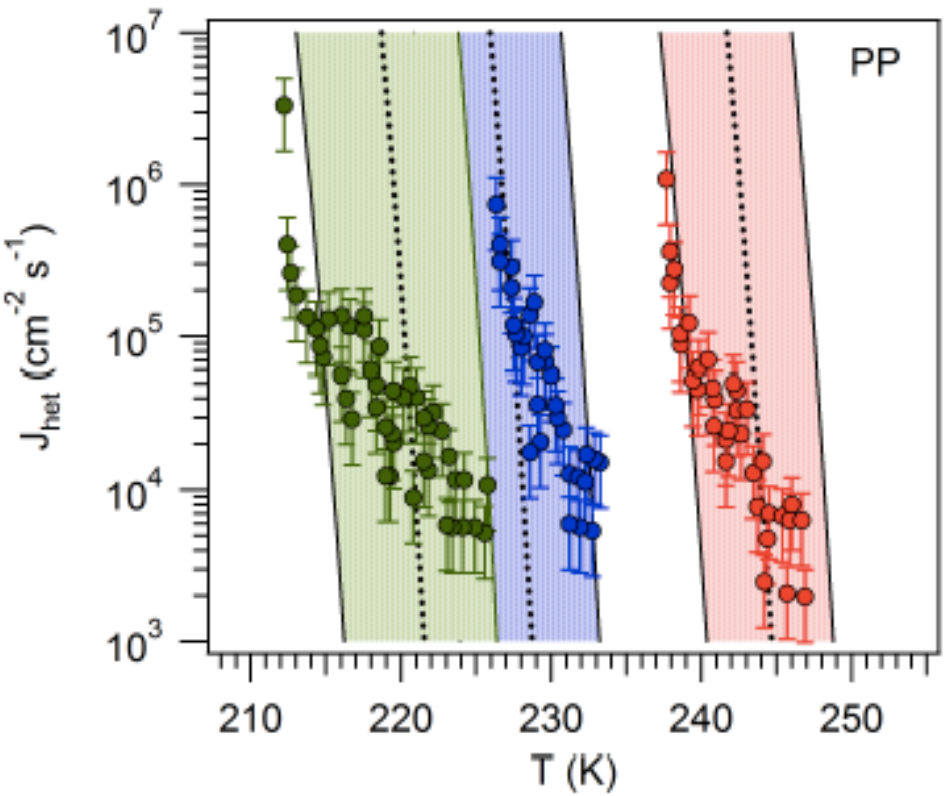


Two very different INP can display the same freezing temperature with very different sensitivities to cooling rate and surface area

Spinodal regime (ζ>0.7): Negligible ΔG, and low J_0. Strong kinetic limitations.

Shallow dJ/dT

Application: Immersion Freezing by Humic INP



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

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

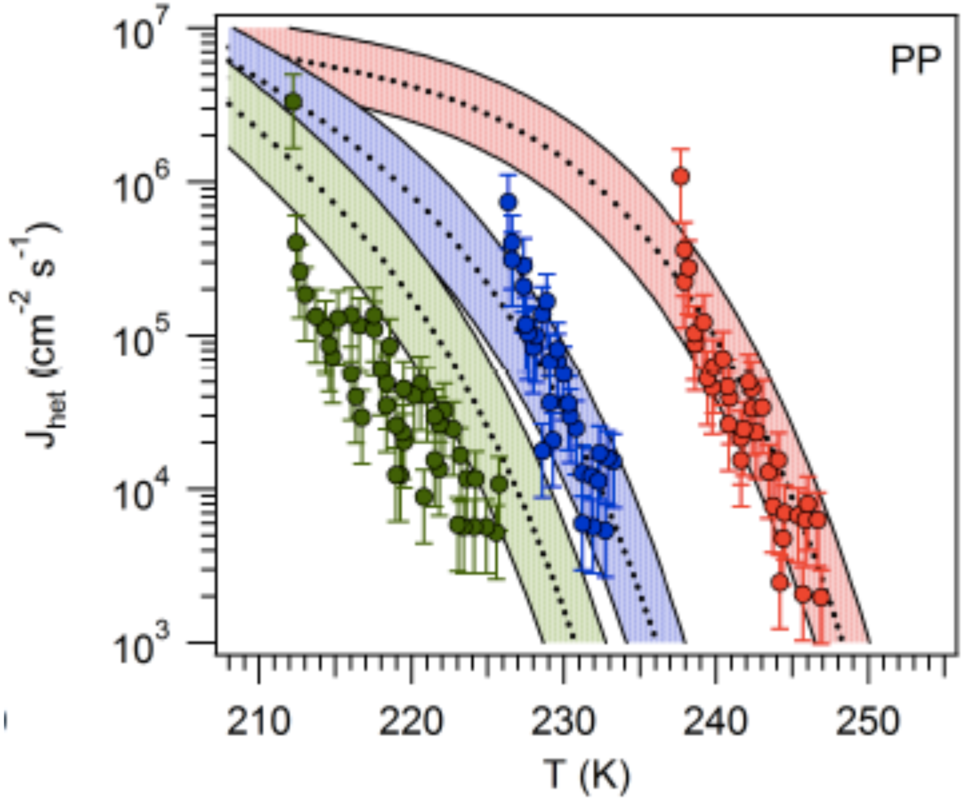
ζ~ 0.05. Classical germ forming regime.

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

$$\zeta^2 - \zeta\left(1 - \frac{\Delta a_{\mathrm{w,\,hom}}}{\Lambda_{\mathrm{E}}}\right) - \left(\frac{\Delta a_{\mathrm{w,\,hom}} - \Delta a_{\mathrm{w,\,het}}}{\Lambda_{\mathrm{E}}}\right) = 0.$$

Thermodynamic correspondence between ζ and $\mathbf{\Delta} a_{w,het}$

Spinodal Ice Nucleation



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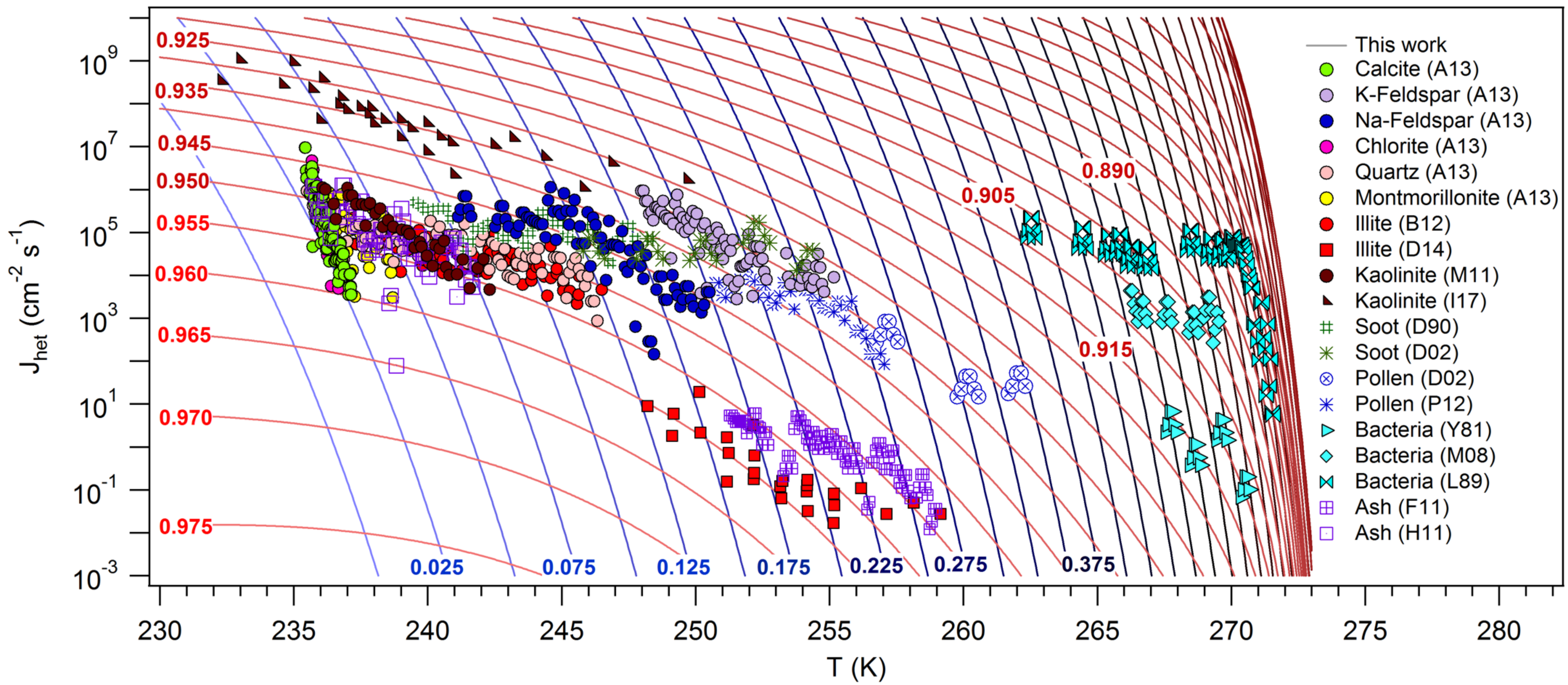
Shaded area: Model predictions for a_w = 0.86, 0.91, and 1.0.

Better agreement in dJ_{het}/dT.

Dynamical effects may play a significant role in this case.

Find ζ fitted in a region corresponding to spinodal ice nucleation to (ζ ~ 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.

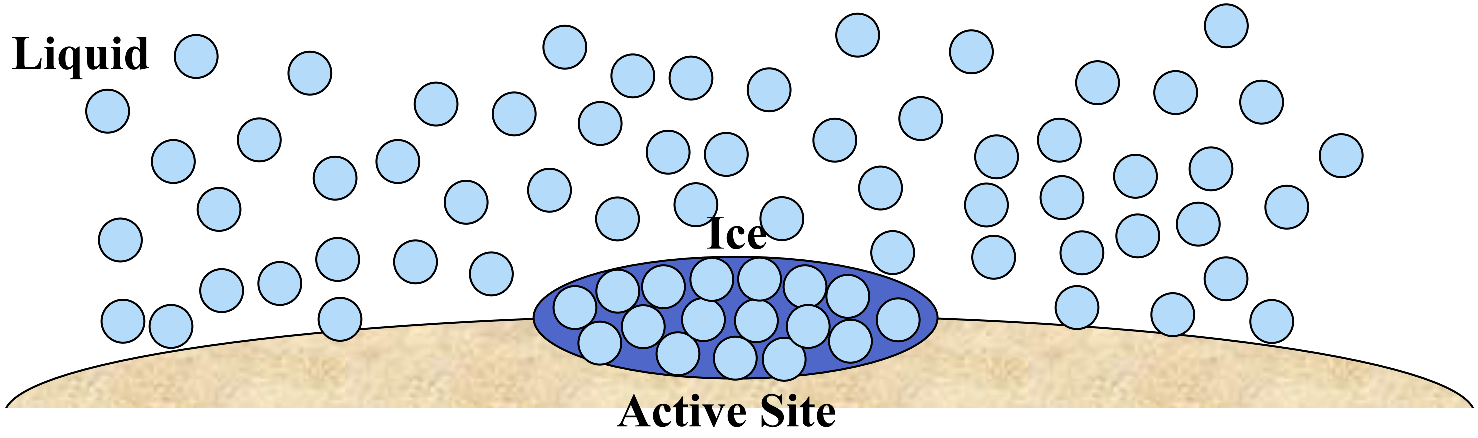
- Instead of being purely driven by thermodynamics, heterogeneous ice nucleation in the liquid phase is a process determined by the **competition between thermodynamic and kinetic constraints** to the formation and propagation of ice.

- 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.

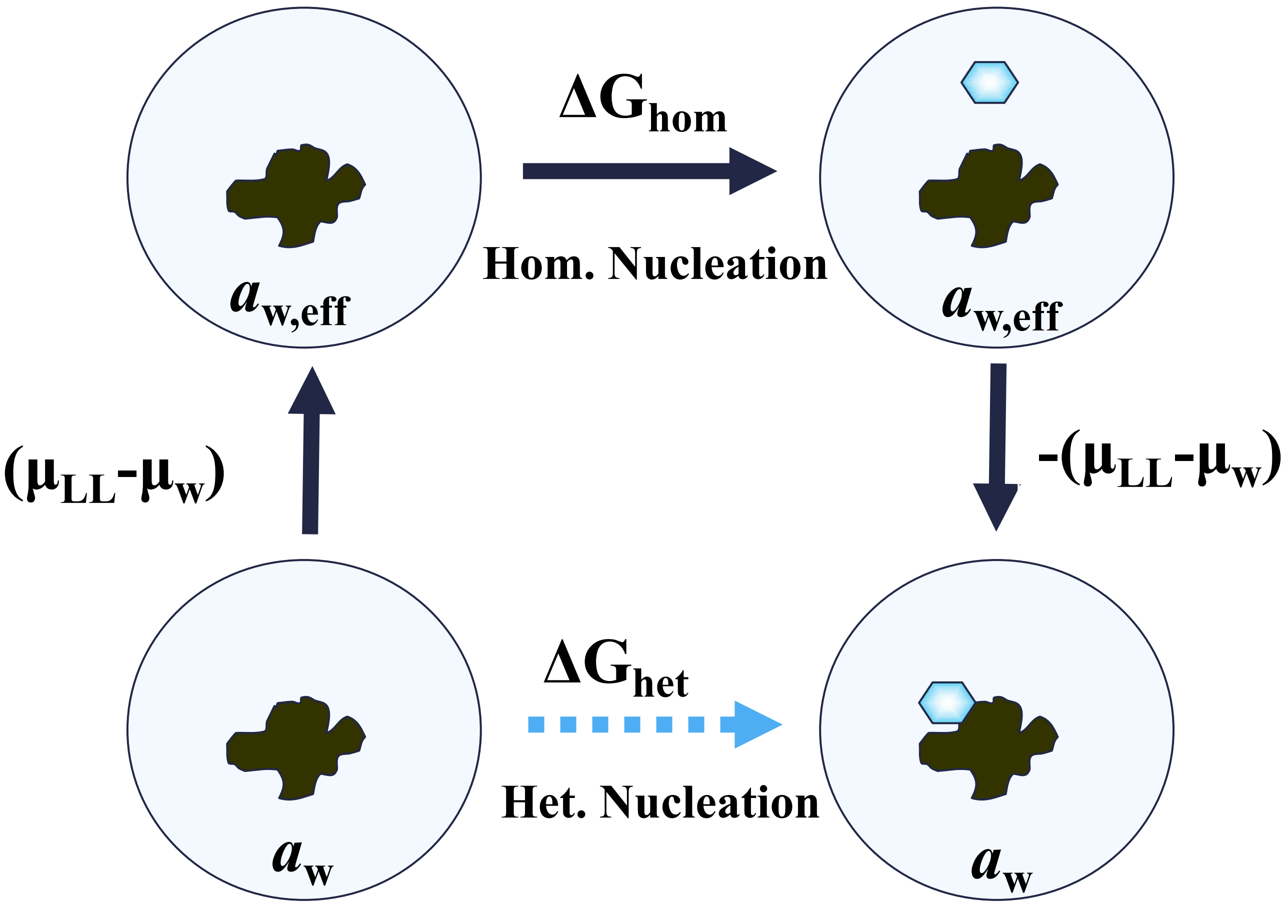
THANKS!

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

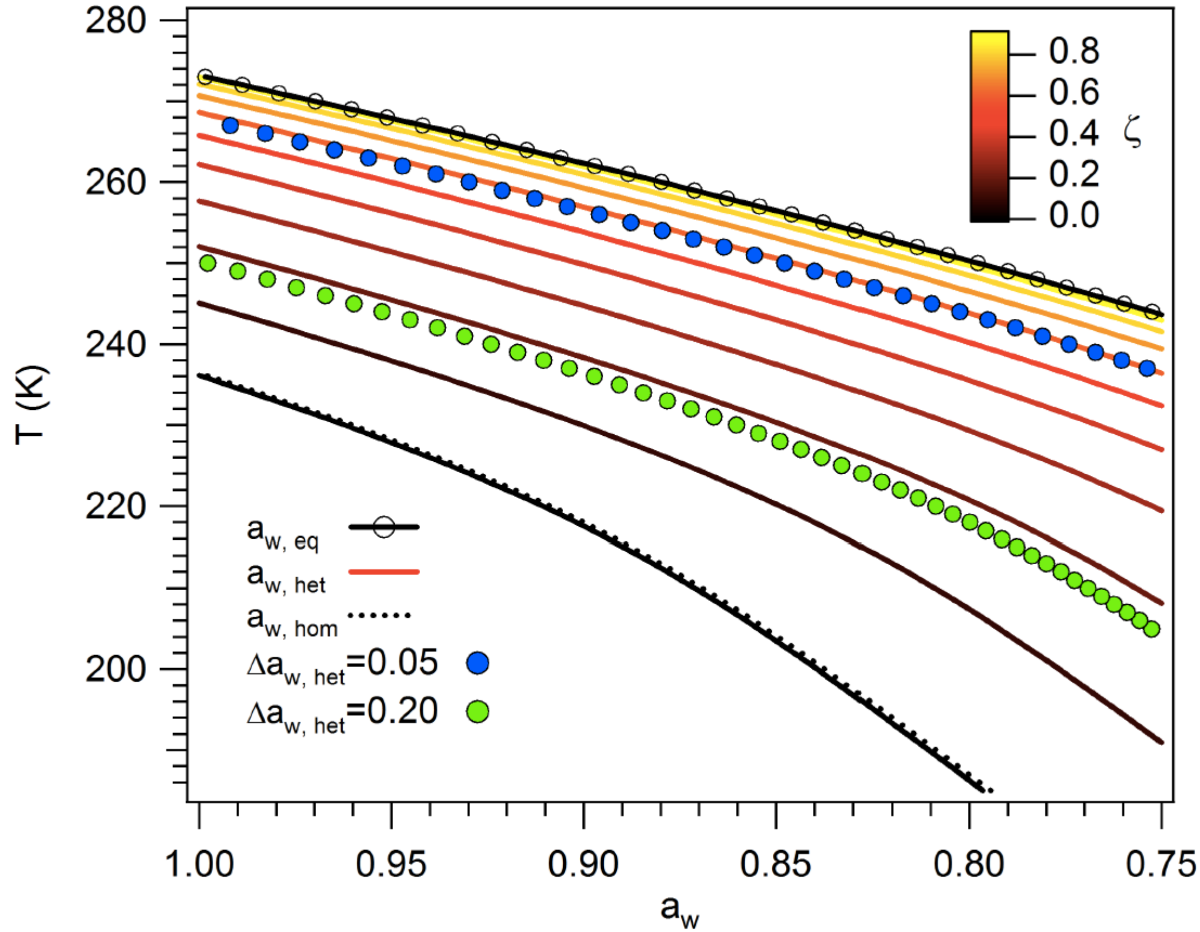
2-Work of Nucleation



Nucleation modeled as occurring *Homogeneously* in the LL regions

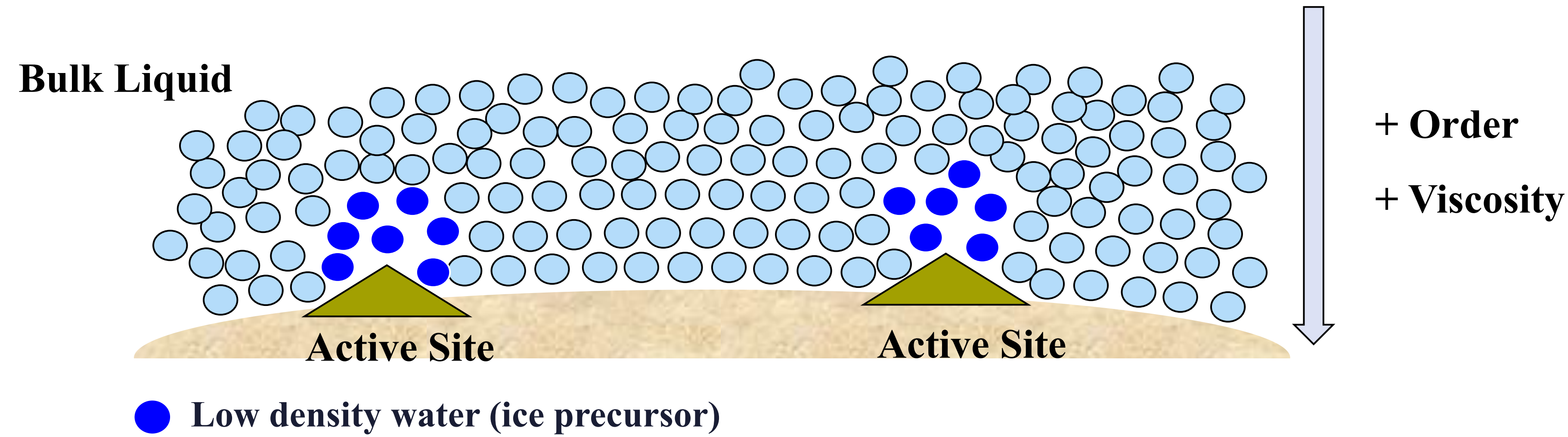
$$\Delta G_{het}(a_w) = \Delta G_{hom}(a_{w,\,eff}).$$

Water Activity Criterion

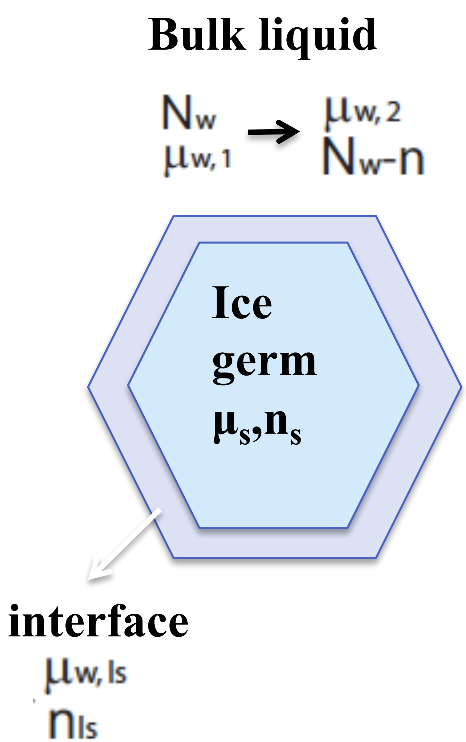


Direct correspondence between ζ and $\Delta a_{w,het}$

Nucleation within a Dense Liquid



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

$$\Delta G_{\mathrm{nuc}} = \frac{4}{27}\frac{\left[\Gamma_{\mathrm{w}} s\left(\Delta h_{\mathrm{f}} - \Gamma_{\mathrm{w}} k_{\mathrm{B}} T \ln a_{\mathrm{w}}\right)\right]^3}{\left[k_{\mathrm{B}} T \ln\left(\frac{a_{\mathrm{w}}^2}{a_{\mathrm{w,eq}}}\right)\right]^2}.$$

$$\Delta G_{\mathrm{act}} = k_{\mathrm{B}} T\left[\frac{E}{(T-T_0)} + n_{\mathrm{t}} \ln\left(\frac{a_{\mathrm{w}}}{a_{\mathrm{w,eq}}}\right)\right].$$

Δh_f: Enthalpy of fusion
a_w: Water activity
Γ_w: Interface thickess (1.46)
s: Lattice geometry (1.105)

Barahona, ACP, 2014, 2015