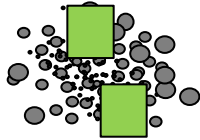# A Theory of Immersion Freezing
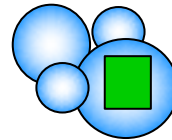
Donifan Barahona

Global Modelling and Assimilation office
NASA Goddard Space Flight Center
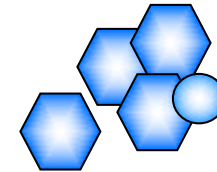Greenbelt, MD, USA.

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).

National Aeronautics and Space Administration

# Classical Nucleation Theory

Liquid

Ice
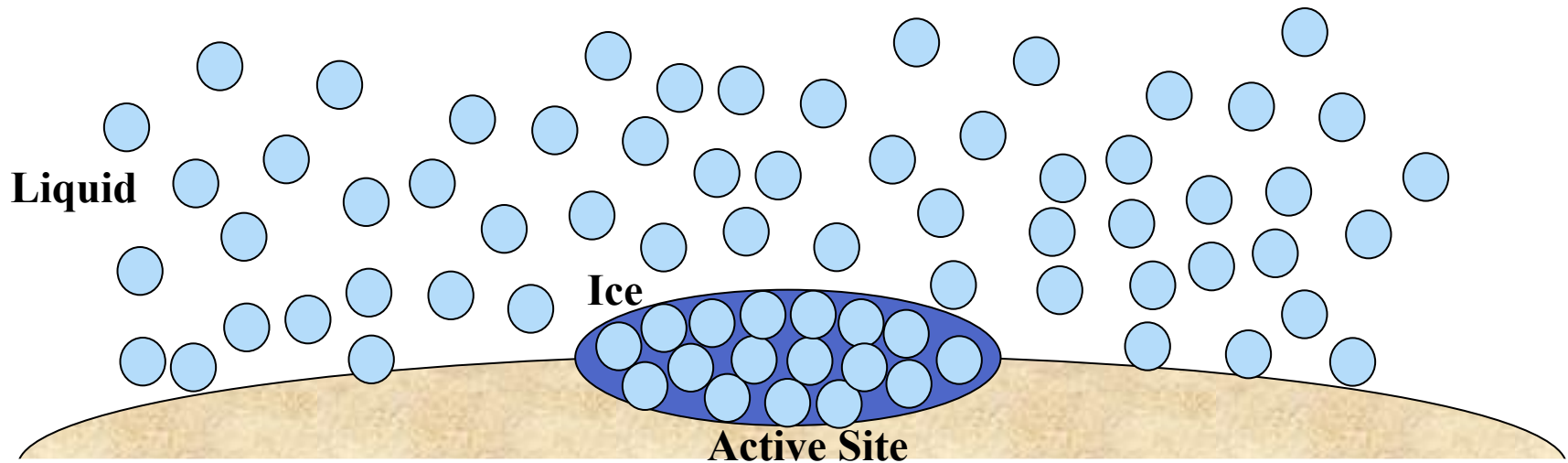
Active Site

- Active site = adsorption site

- Water has uniform properties up to the dividing line

- Ice germ is implicitly considered denser than the liquid

GMAO

Vicinal Water Differs from Bulk Water

- **Vicinal water may exist in a ordered state (Ice-Like) near the solid-liquid interface** and that such ordered structures may propagate over hundreds to thousands of molecular diameters (Drost-Hansen, 1969, Zheng et al., 2006).

- Presence of ordered found in water near interfaces in biological (Snyder et al., 2014), metallic (Michot et al., 2002) and clay (Yu et al., 2001). 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). Increased viscosity may be a necessary condition for ice nucleation since structural ordering is not possible in a fluid with low viscosity (Anderson, 1967).

- **The work of nucleation and the enhancement of the viscosity of the vicinal water are tightly linked.**

Nucleation within a Dense Liquid
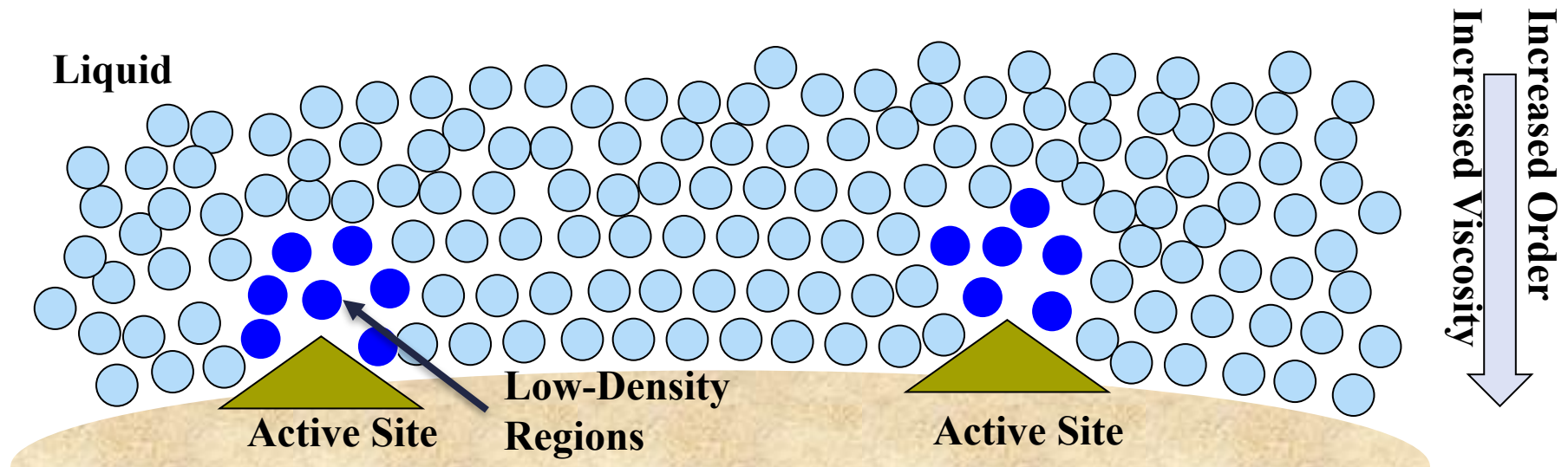
1. Description of the properties of vicinal water

2. Relate vicinal water thermodynamics to the work of ice nucleation

3. Description of the effect of the particle on the interfacial flux, hence on the nucleation rate

1-Thermodynamics of Vicinal Water

| Bulk Liquid | μ_w, a_w |

Vicinal Water

LL   IL, μ_{IL} LL   LL

IL   IL $\mu_{LL}, a_{w,\,eff}$

Particle
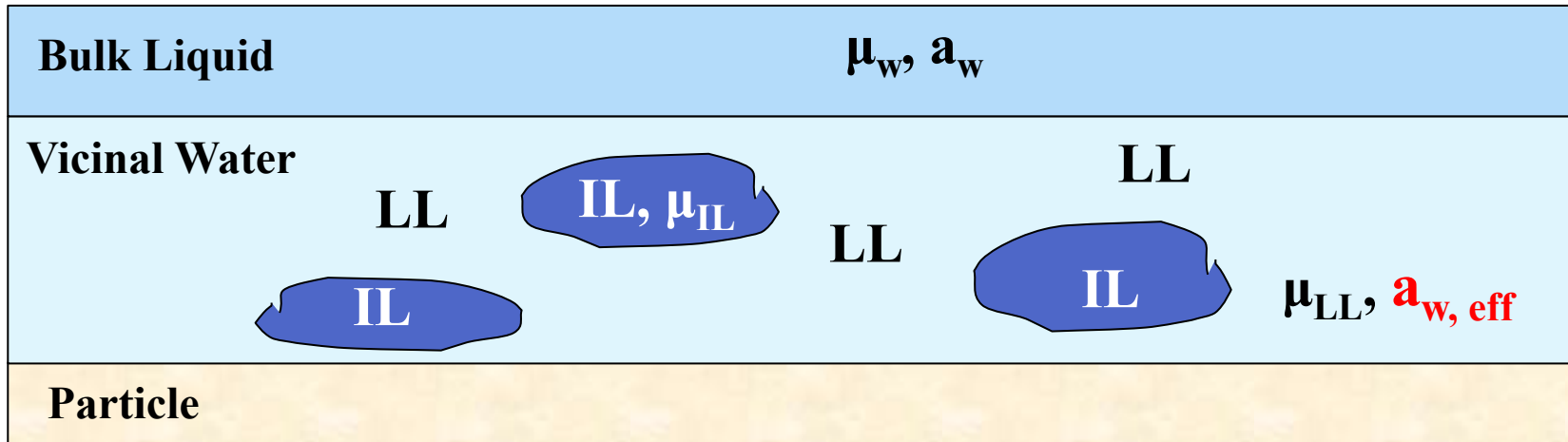
ζ = Fraction of Ice-Like regions in the vicinal water (i.e., Templating Factor).
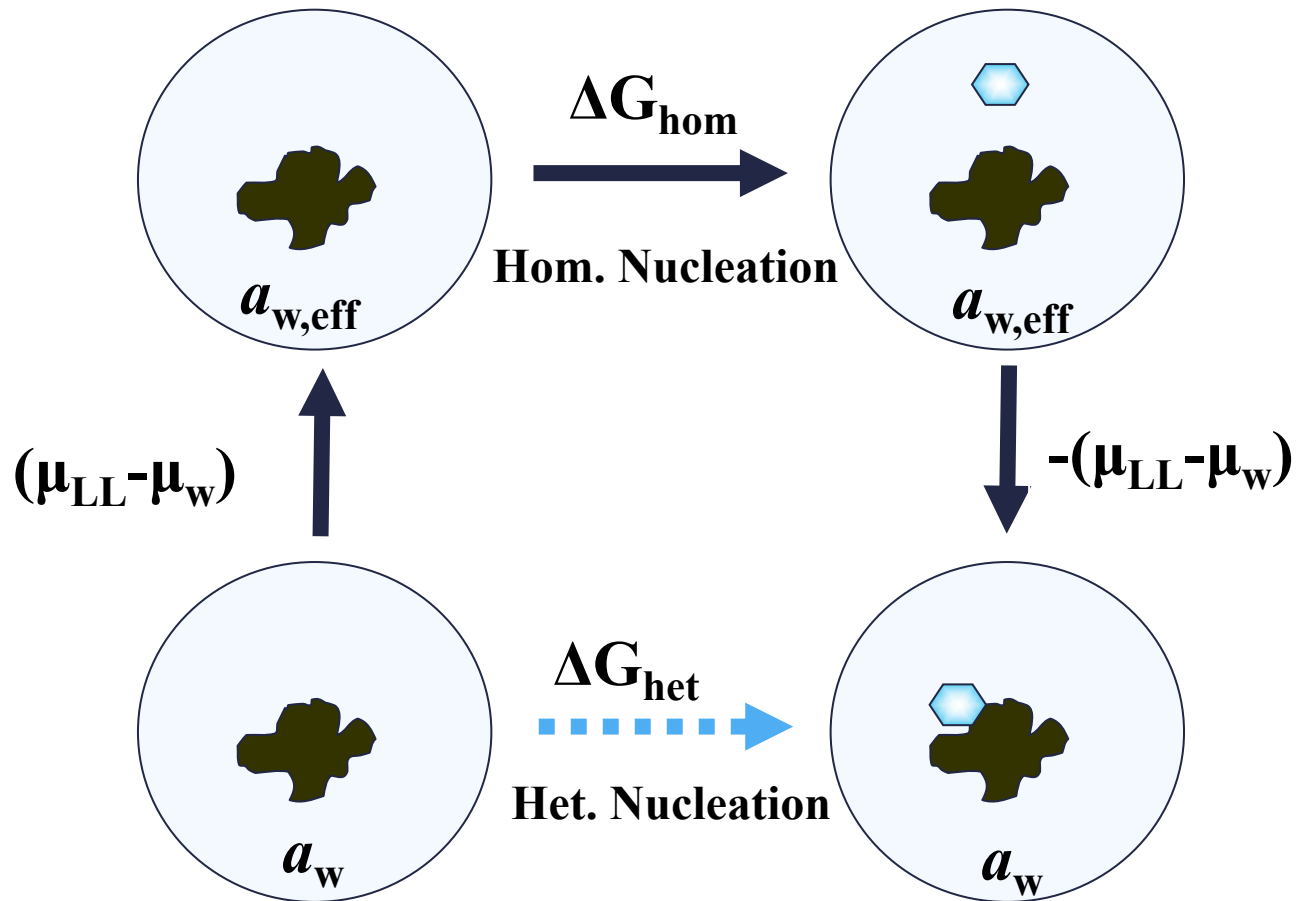
For homogeneous nucleation $\zeta = 0$

Two state model: Regular solution of Liquid Like (LL) and Ice Like (IL) regions, in equilibrium with the bulk liquid

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

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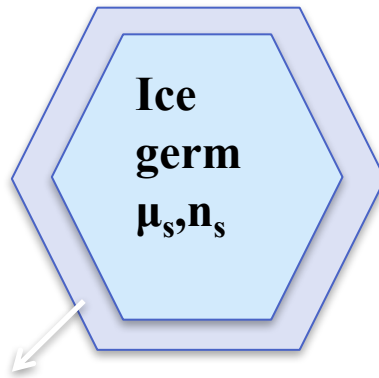Tc, N = Critical parameters

2-Work of Nucleation

Nucleation modeled as occurring *Homogeneously* in the LL regions

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

Homogeneous Ice Nucleation

Bulk liquid

$$N_w \atop \mu_{w,1} \quad \rightarrow \quad \mu_{w,2} \atop N_w - n$$

Ice germ μ_s, n_s

interface

$\mu_{w,ls}$
n_{ls}

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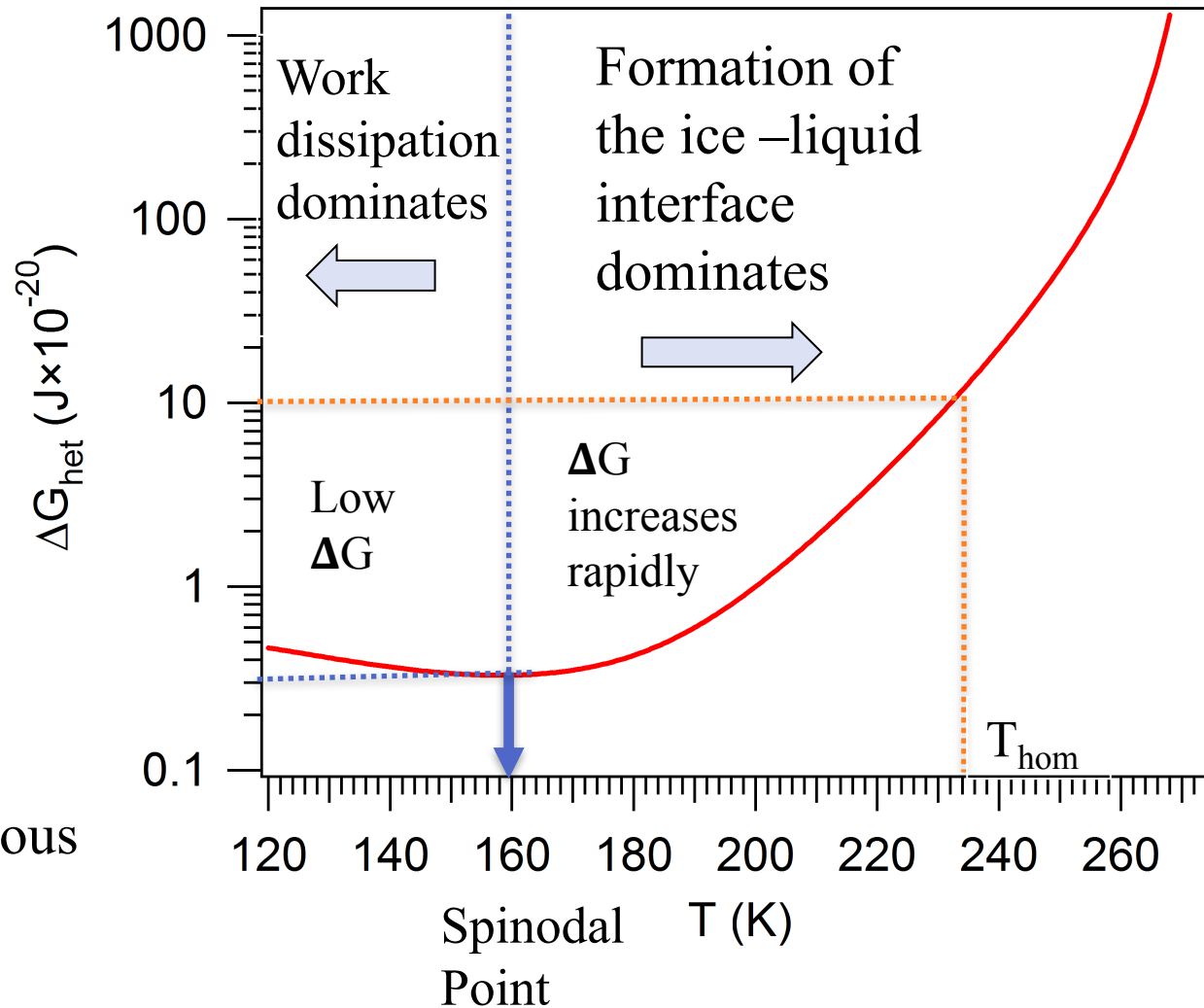s: Lattice geometry (1.105)

- 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

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

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

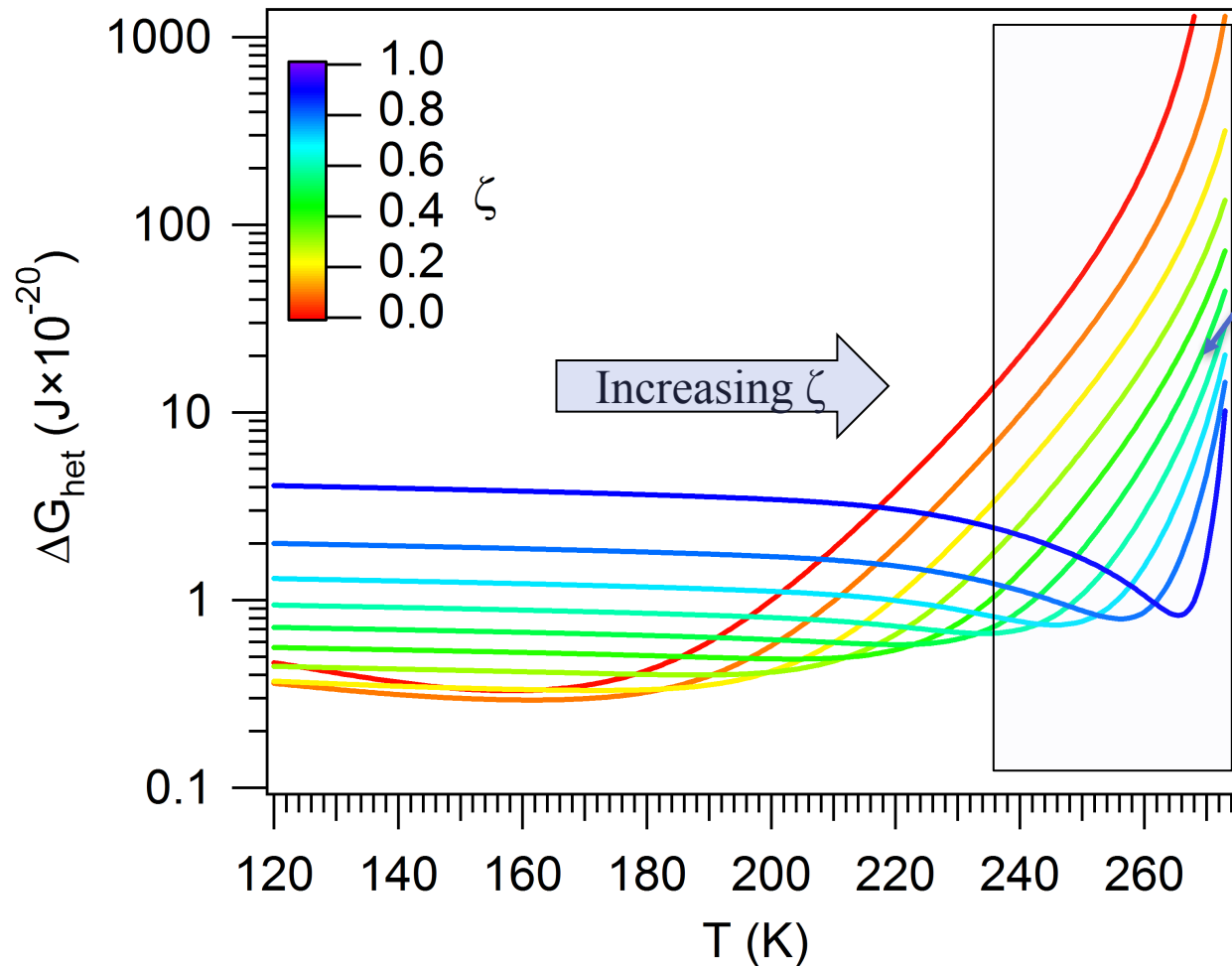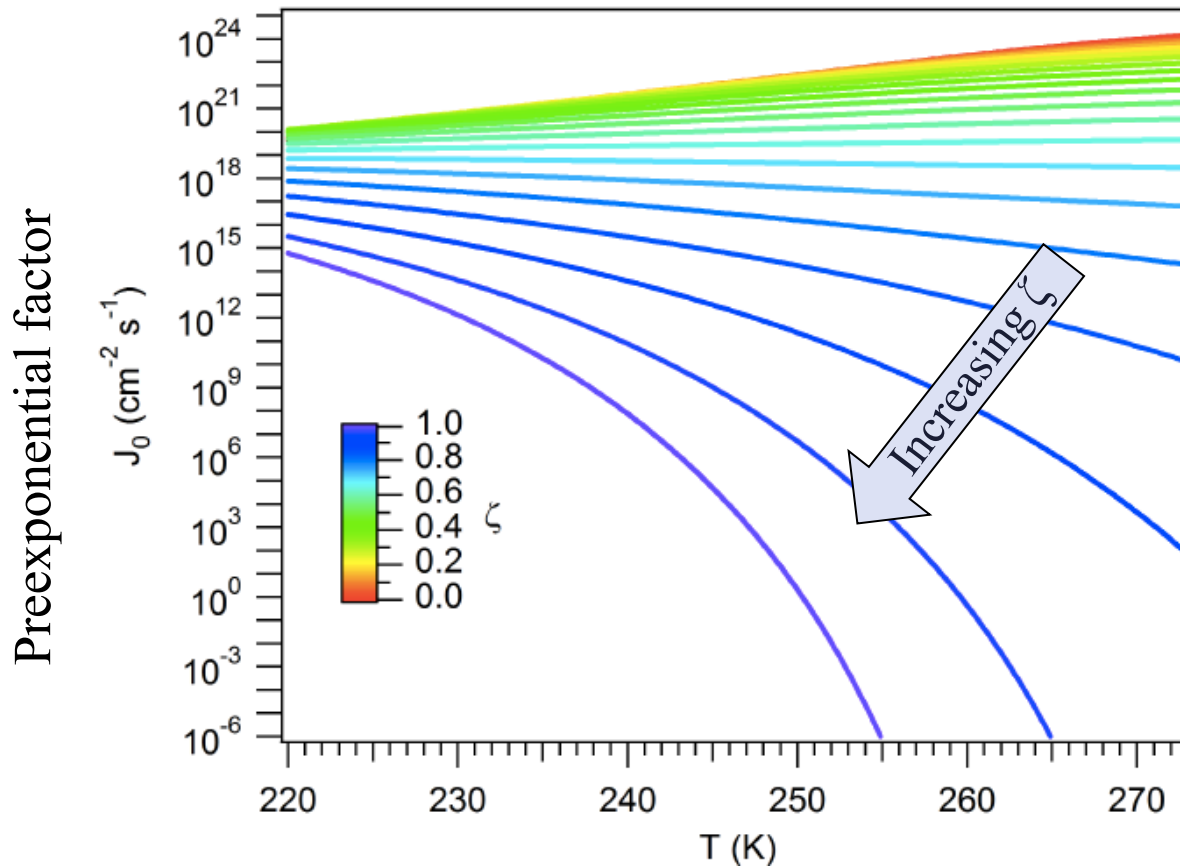# Work of nucleation: Spinodal Regime

Work of nucleation: Spinodal Regime

Particles with $\zeta > 0.7$ may display spinodal behavior for immersion freezing T

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

3-Dynamics Of Ice Germ Growth

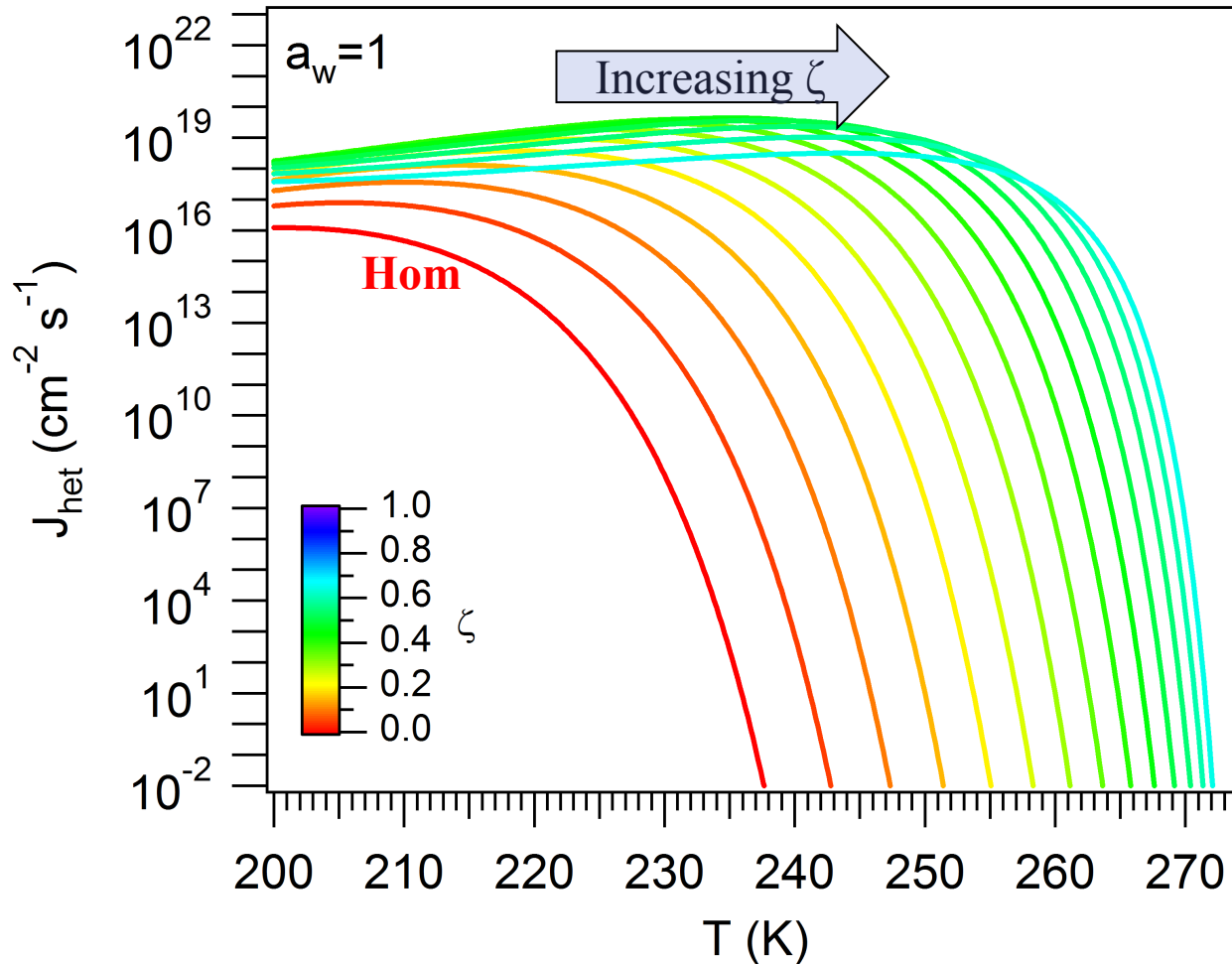$$D \propto \exp\left(-\frac{A}{TS_c}\right)$$

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
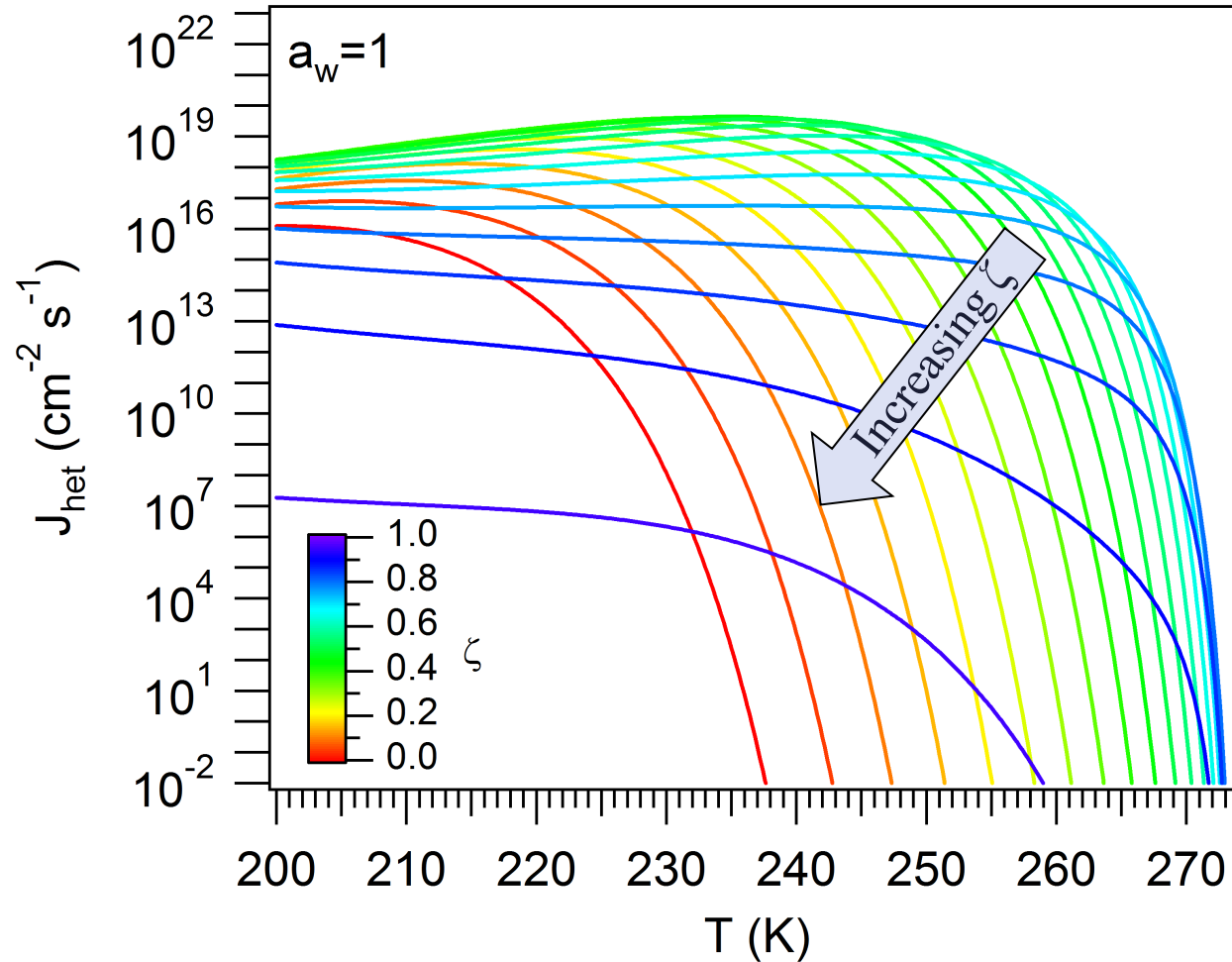
Nucleation rate: Dynamic and Thermodynamic Factors

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
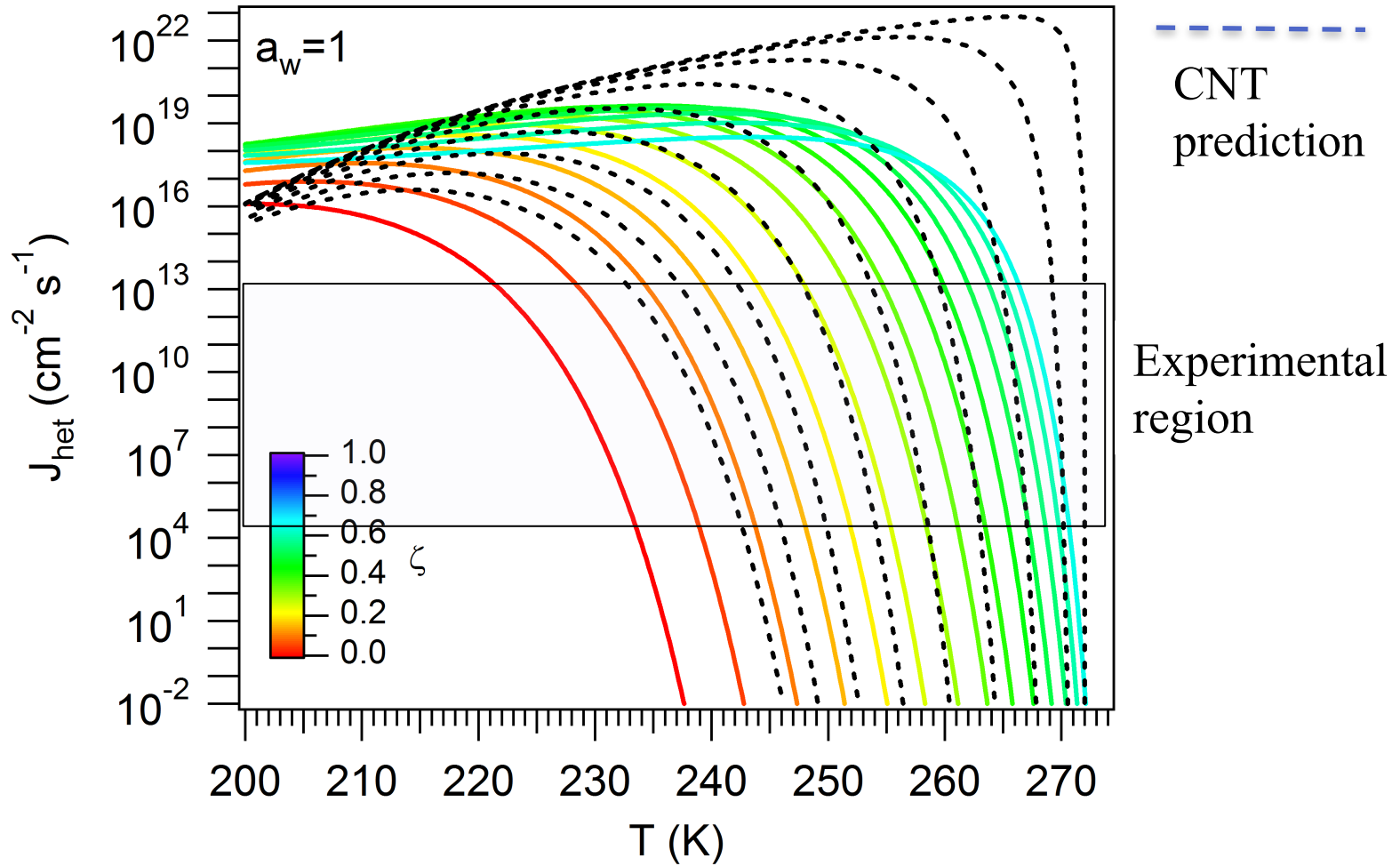
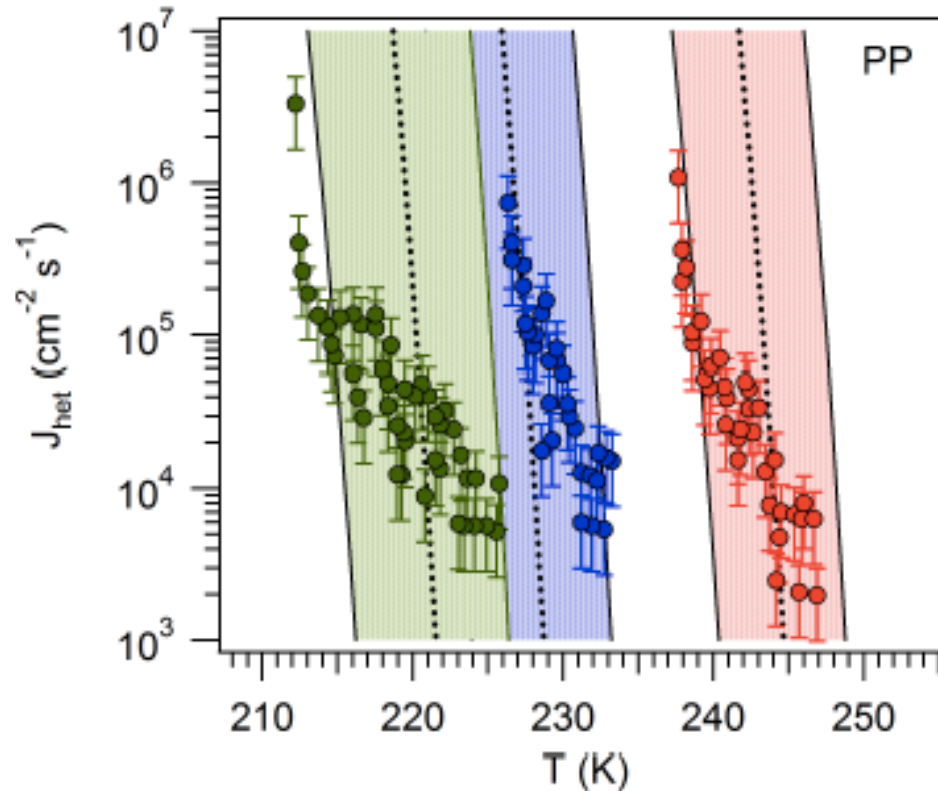# Nucleation rate: Dynamic and Thermodynamic Factors

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). $\Delta a_{w,het} = 0.2466 \pm 0.025$

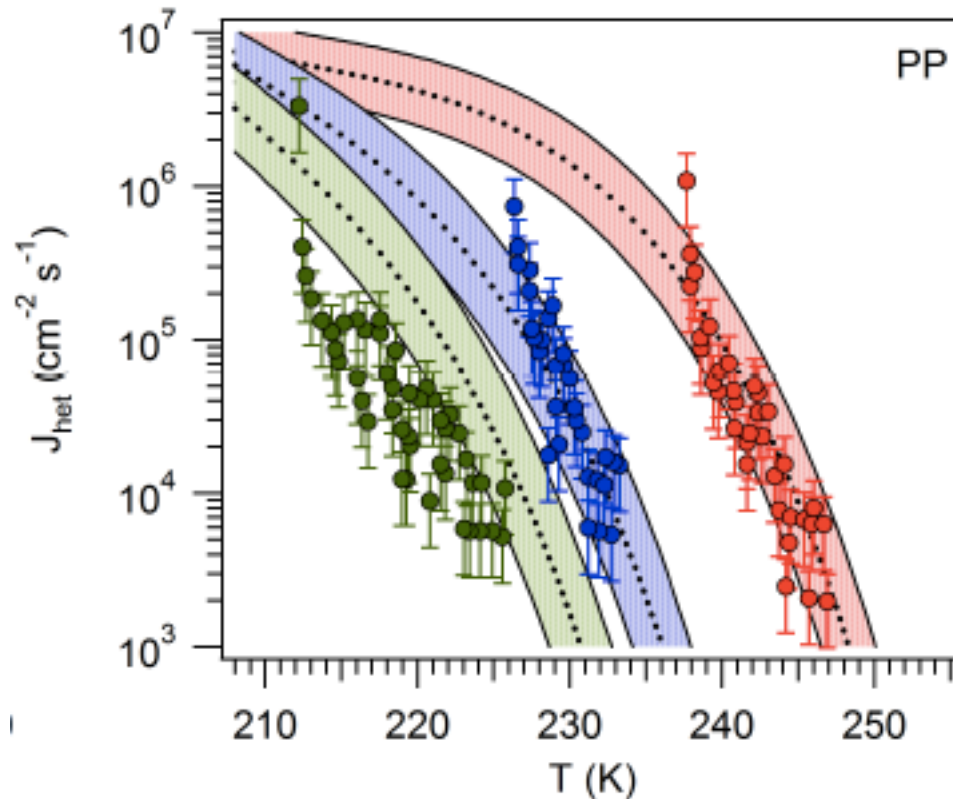Shaded area: Model predictions for $a_w = 0.86$, 0.91, and 1.0.

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

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

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

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

Spinodal Ice Nucleation

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

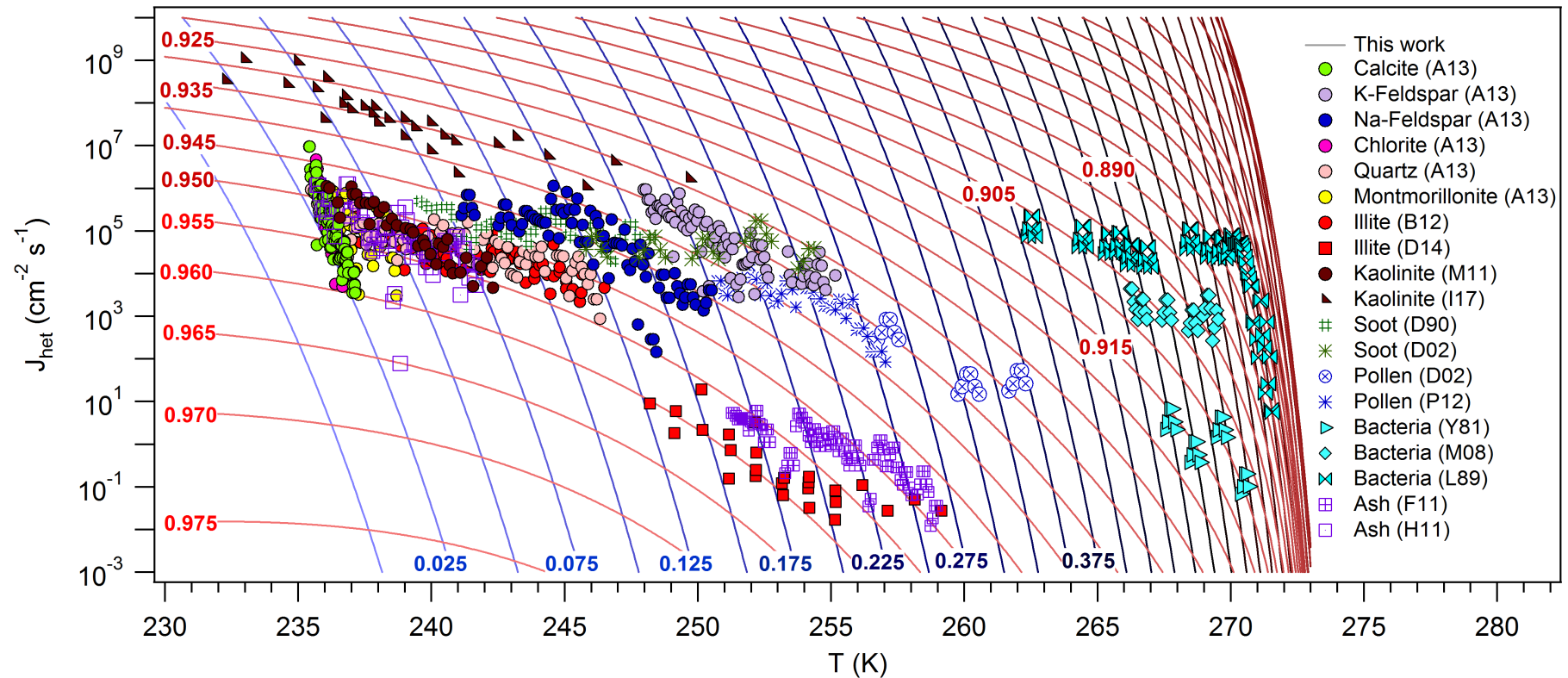Shaded area: Model predictions for a_w = 0.86, 0.91, and 1.0.

Better agreement in dJ_{het}/dT.

Dynamical effects may play a significant role in this case.

Find ζ 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!

Water Activity Criterion
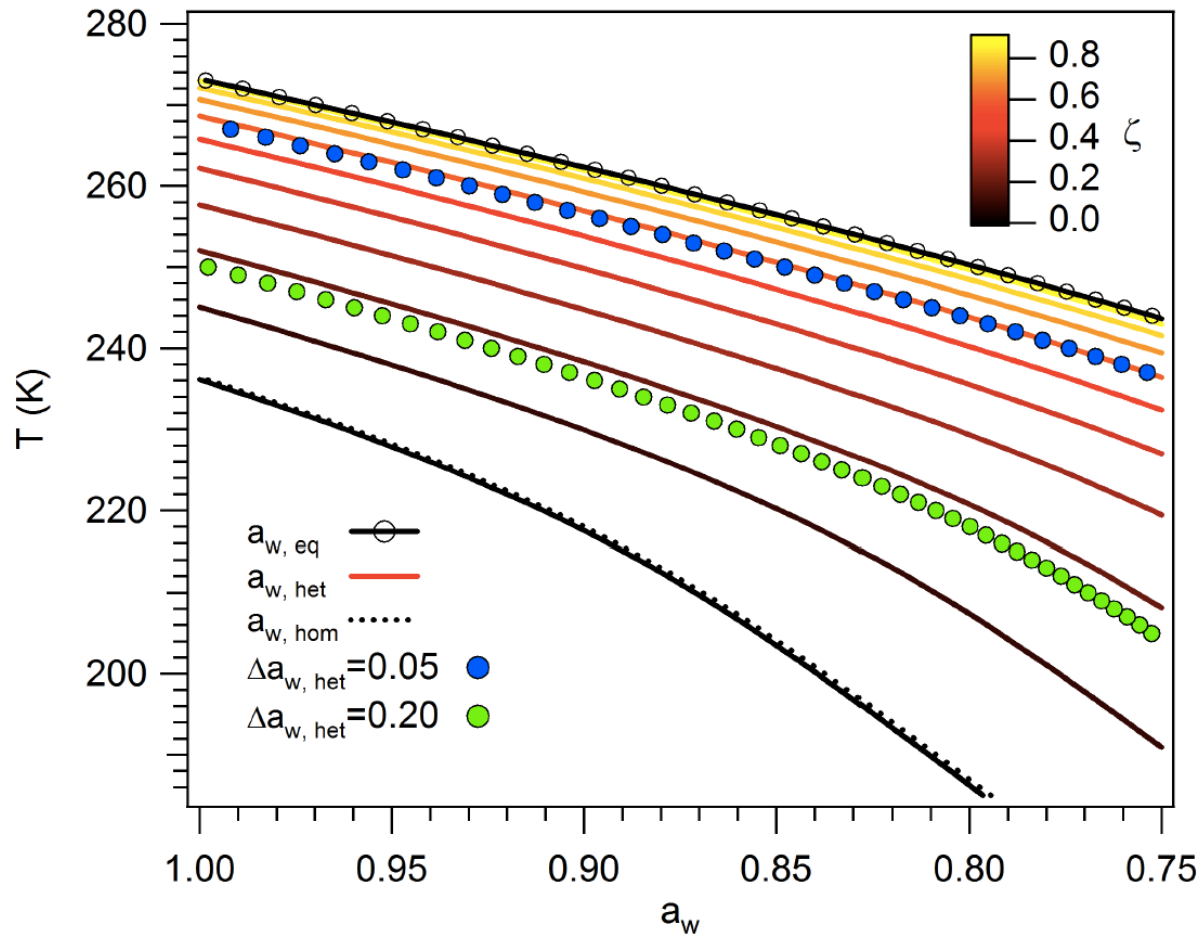
Direct correspondence between ζ and Δa$_{w,het}$