

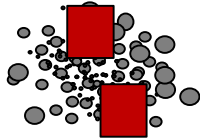
The role of composition and surface area variability in ice nucleation, and how to get rid of it

Donifan Barahona

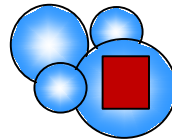
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Special thanks to Ben Murray and Tom Whale

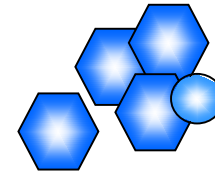
Immersion Ice Nucleation



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



Immersion Freezing

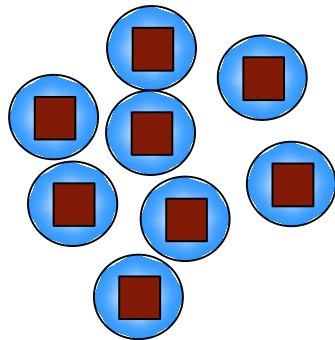


Ice crystal population

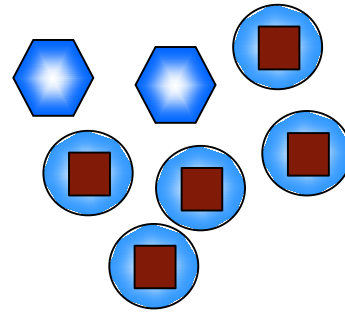
- INP completely immersed
- Thermodynamic equilibrium
- Could happen at $RH < 100\%$

- Plays a very important role in the evolution of Arctic and Convective clouds. May affect climate sensitivity (Tan et al. 2016).
- Parameterized by estimating ice nucleation efficiencies from laboratory data either in the form of active site density, or by constraining nucleation theories

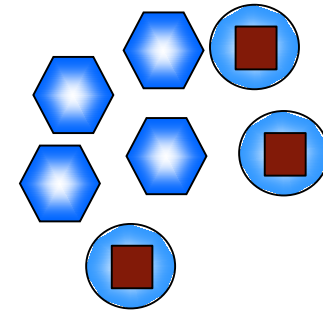
Immersion Ice Nucleation



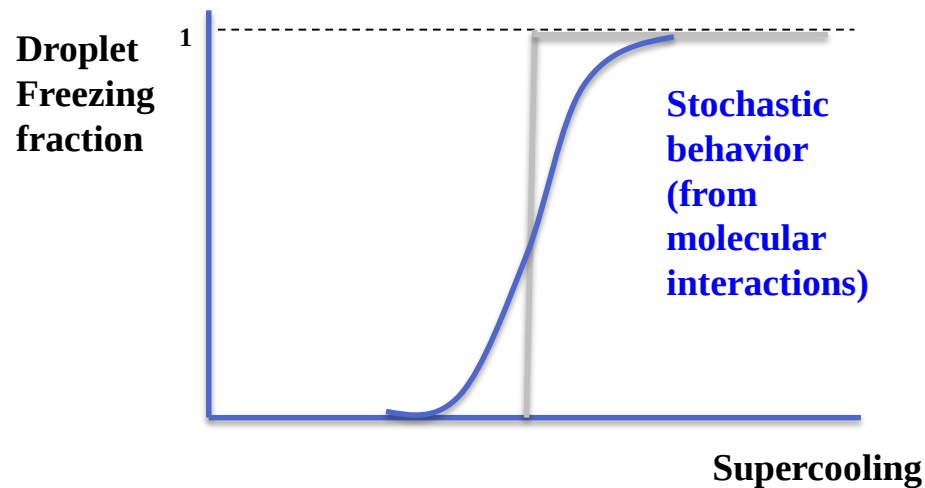
T1



T2



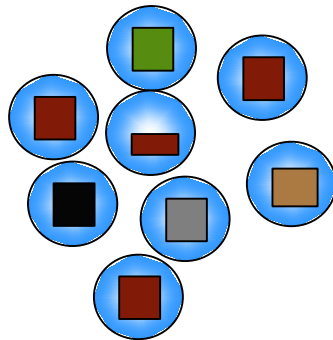
T3



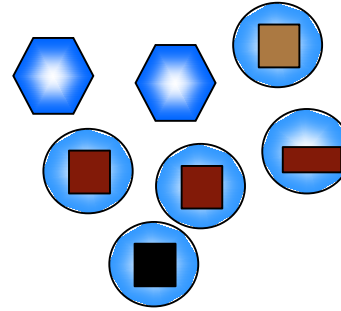
Active site density

Nucleation rate

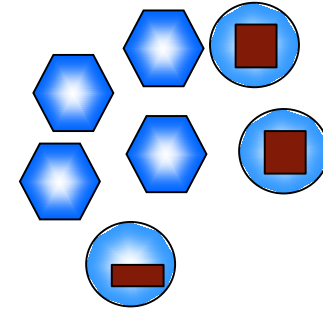
Immersion Ice Nucleation



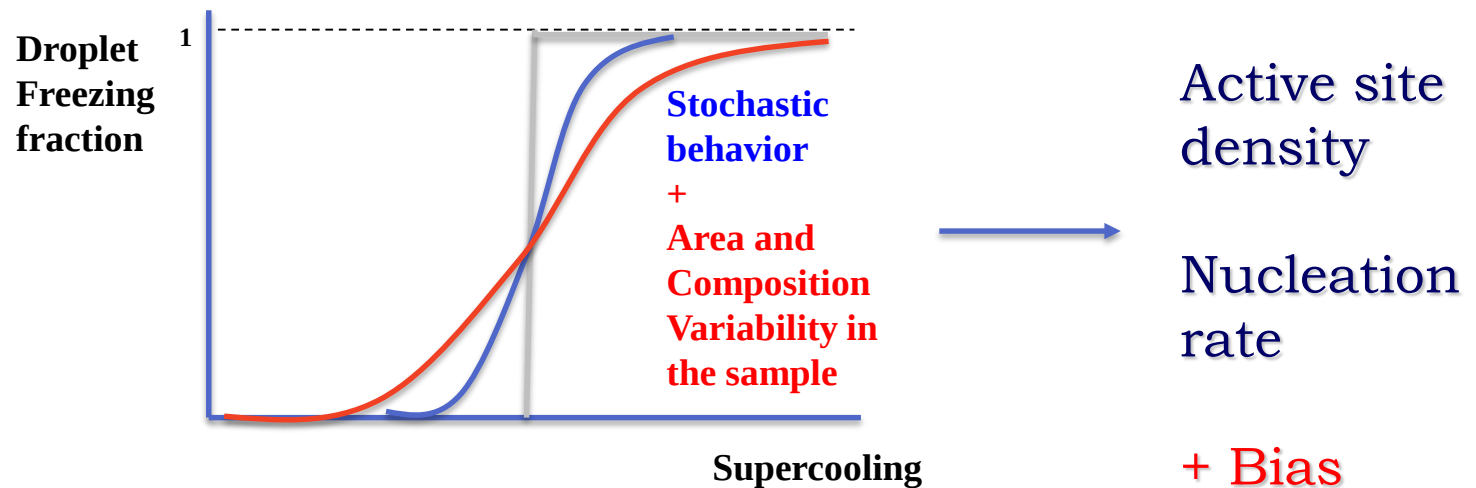
T1



T2



T3



Dealing with variability

- Singular approach: Typically neglected.
 - Variability in the sample is about the same as in the target population.
- Stochastic approach: Contact angle distribution $P(\theta)$ for the population (and sometimes for each particle).
 - Assumes CNT as correctly describing the underlying physical nucleation mechanism.
 - Cannot be used to validate nucleation theories.
 - $P(\theta)$ is not a fundamental property of the material as it carries information on sample variability

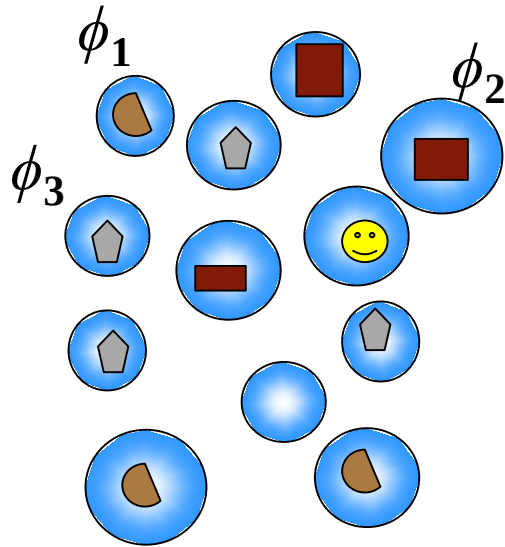
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How significant is the bias in active site density/nucleation rate introduced by neglecting variability?

How to remove it without assuming an specific mechanism (e.g., CNT)?

Modeling Variability



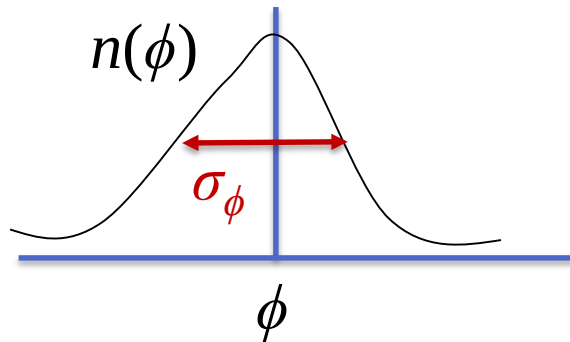
$$\phi = \text{area} \times \text{active site density} = J \times \text{area}$$

$$\phi \sim \# \text{ active sites per droplet}$$

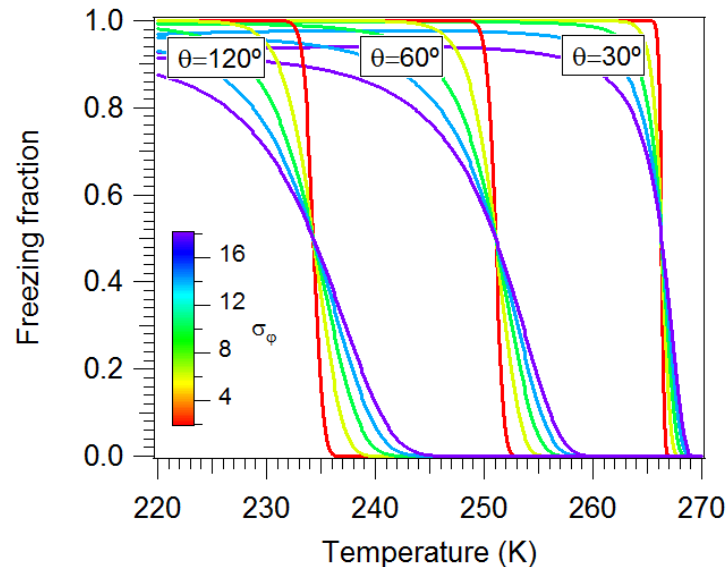
$$\text{Freezing fraction} = f_f = 1 - \int_0^{\infty} e^{-\phi} n(\phi) d\phi.$$

$$f_f = 1 - \mathcal{N}(\bar{\phi}, \sigma_{\phi})$$

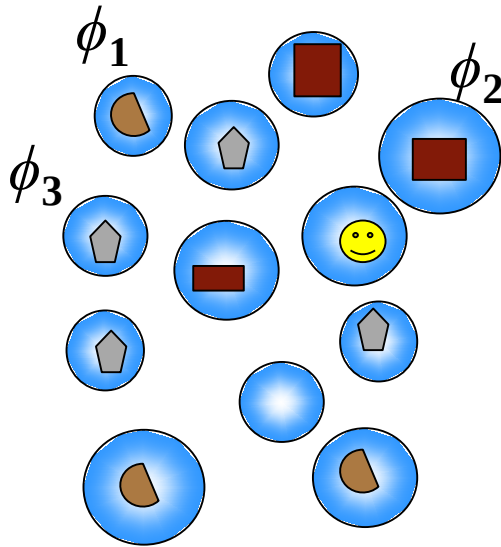
Laplace transform of $n(\phi)$
calculated at the mean ϕ



$n(\phi)$ is likely lognormal



Modeling Variability



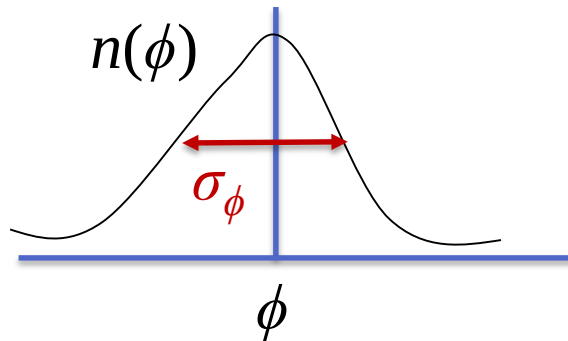
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Laplace transform of $n(\phi)$
calculated at the mean ϕ



$n(\phi)$ is likely lognormal

$$\sigma_{\phi} \rightarrow 0, \quad \bar{\rho}_{\text{as,app}} = -\frac{\ln(1 - f_f)}{\bar{s}_p}$$

Apparent active site density

Using Synthetic Data to Estimate the Effect of Variability

1- Use nucleation theory to find an “equivalent” active site density. This is the “true” value,

$$\rho_{as,true} \equiv \int_0^t J dt'$$

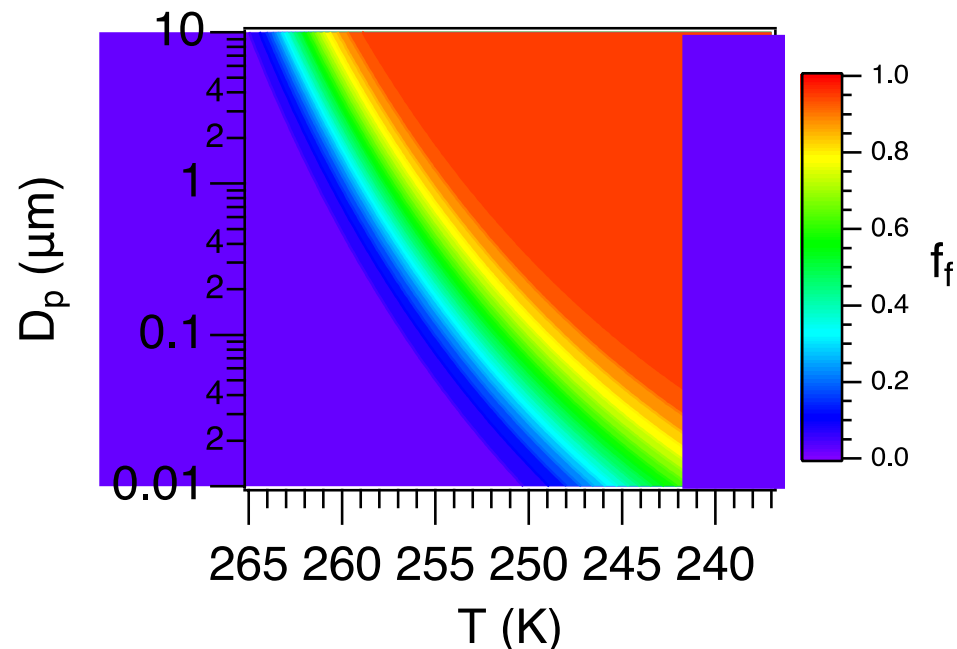
2- Find freezing fraction for a given σ_ϕ ,

$$f_f = 1 - \mathcal{N}(\bar{\phi}, \sigma_\phi)$$

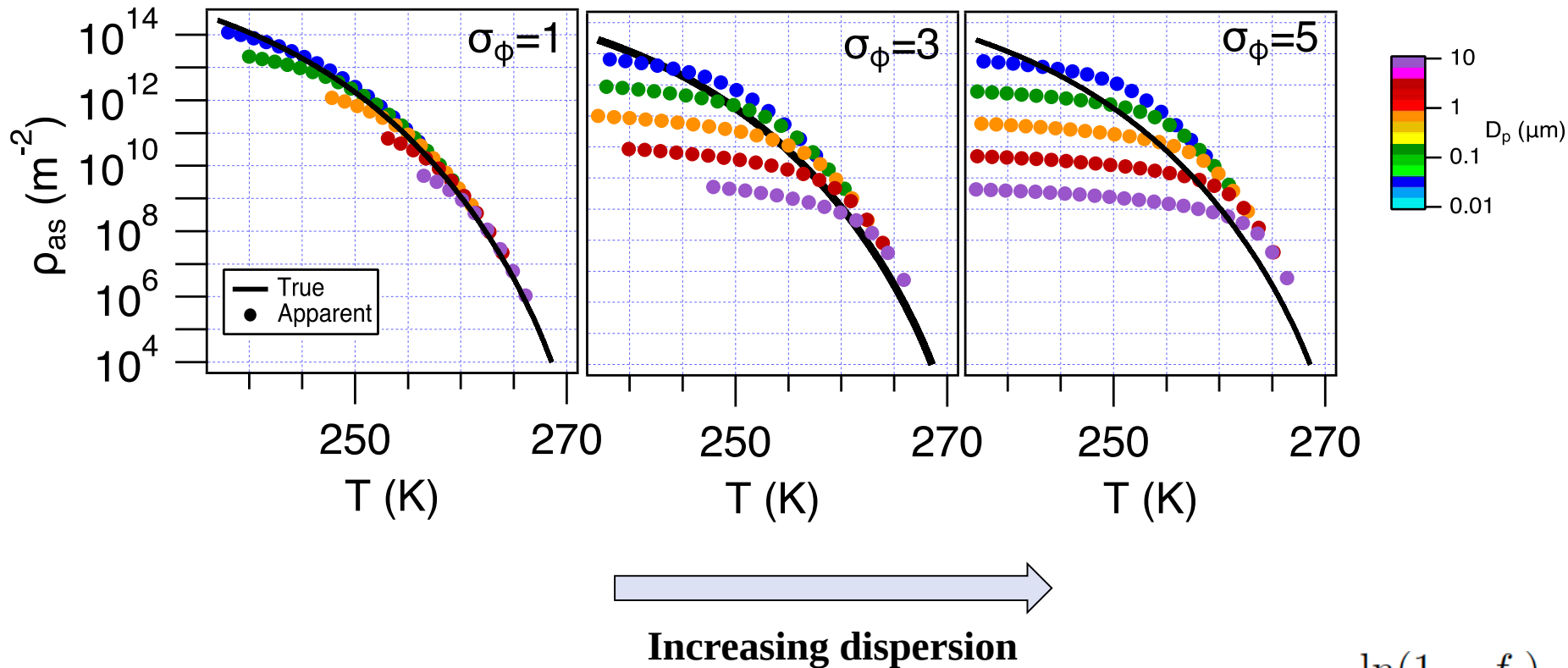
3- Compare $\rho_{as,true}$ Vs. $\rho_{as,app}$,

$$\bar{\rho}_{as,app} = - \frac{\ln(1 - f_f)}{\bar{s}_p}$$

Droplet freezing fraction for Microcline, $\sigma_\phi = 2$



How much does variability matter?



$\rho_{as,app}$ may underestimate the actual active site density by several orders of magnitude, and, it is not independent of surface area

$$\bar{\rho}_{as,app} = -\frac{\ln(1 - f_f)}{\bar{s}_p}$$

Eliminating the bias

We don't know σ_ϕ in advance

$$\boxed{f_f = 1 - \mathcal{N}(\bar{\phi}, \sigma_\phi)} \quad \longrightarrow \quad \boxed{\bar{\rho}_{\text{as}} = \frac{1}{\bar{s}_p} \mathcal{N}^{-1}(1 - f_f)}$$

Invert
(Quite difficult)

Eliminating the bias

We don't know σ_ϕ in advance

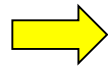
$$f_f = 1 - \mathcal{N}(\bar{\phi}, \sigma_\phi)$$



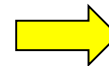
$$\bar{\rho}_{as} = \frac{1}{\bar{s}_p} \mathcal{N}^{-1}(1 - f_f)$$

Invert
(Quite difficult)

$$\frac{\partial f_f}{\partial T} = -\frac{d\mathcal{N}}{d\bar{\phi}} \frac{\partial \bar{\phi}}{dT}$$



$$\frac{\partial \bar{\phi}}{\partial T} - \alpha \frac{\partial \bar{\phi}}{\partial \ln \bar{s}_p} = 0$$



$$\frac{dg}{dT} - \alpha g = 0 \quad \Rightarrow \quad \ln \frac{g}{g_o} = \int \alpha dT$$

$$\frac{\partial f_f}{\partial \ln \bar{s}_p} = -\frac{d\mathcal{N}}{d\bar{\phi}} \frac{\partial \bar{\phi}}{\partial \ln \bar{s}_p}$$

$$\phi = s_p * \rho_{as} = s_p * g$$

$$\bar{\rho}_{as} = -\frac{\ln(0.5)}{\bar{s}_p} \exp\left(\int_{T_{50}}^T \alpha dT\right) \quad \alpha = \frac{\partial f_f}{\partial T} / \frac{\partial f_f}{\partial \ln \bar{s}_p}$$

T_{50} = Temperature at $f_f = 0.5$

s_p = mean surface area per droplet

Bias-Free Ice Nucleation Efficiency

$$\bar{\rho}_{as} = -\frac{\ln(0.5)}{\bar{s}_p} \exp \left(\int_{T_{50}}^T \alpha dT \right)$$

$$\alpha = \frac{\partial f_f}{\partial T} / \frac{\partial f_f}{\partial \ln \bar{s}_p}.$$

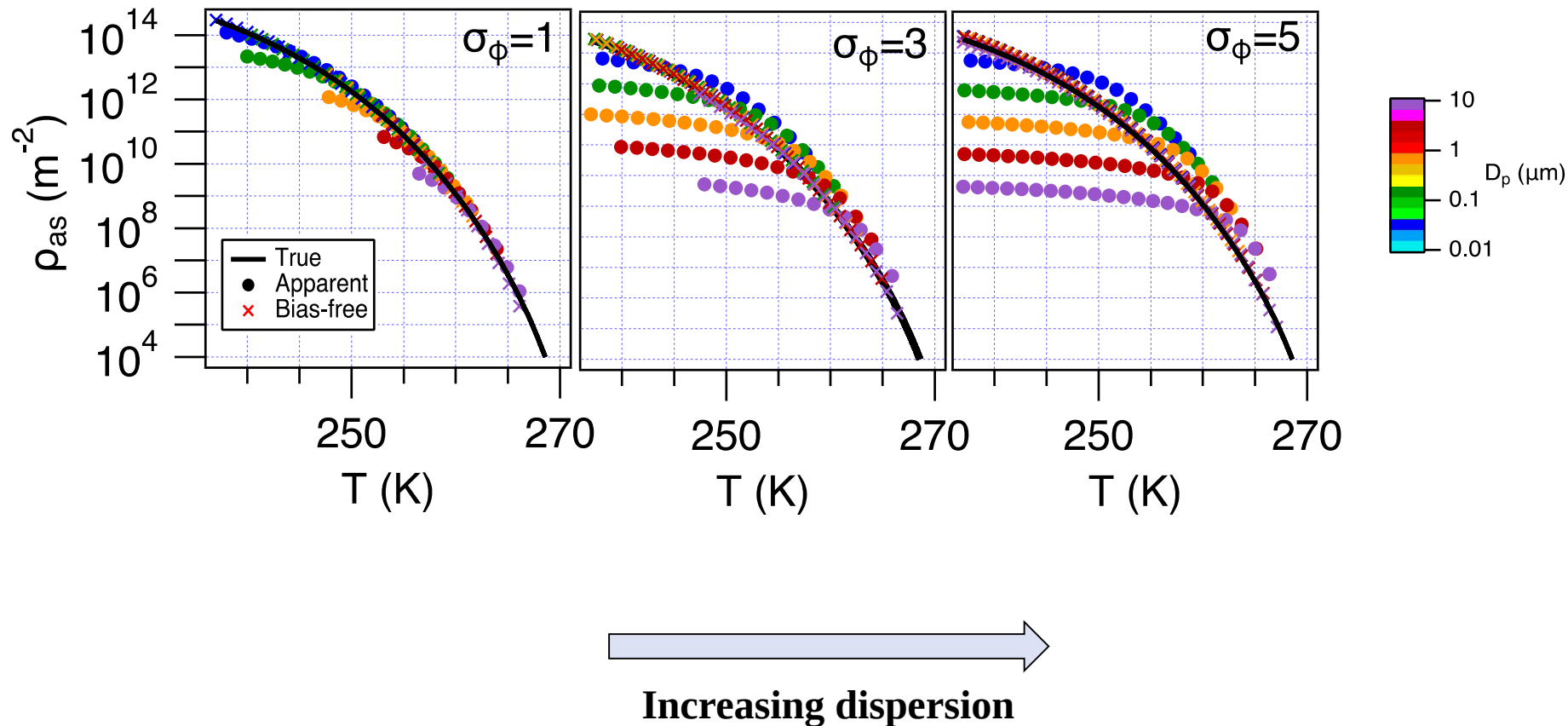
ρ_{as} = Active site density

T_{50} = Temperature at $f_f = 0.5$

s_p = mean surface area per droplet

By performing droplet freezing measurements as a function of both particle surface area and temperature, the intrinsic nucleation efficiency of a material can be obtained.

How much does variability matter?



The bias-free estimate always overlaps with the true value. Independent of variability. Corresponds to the actual efficiency.

$$\bar{\rho}_{as,app} = -\frac{\ln(1 - f_f)}{\bar{s}_p}$$

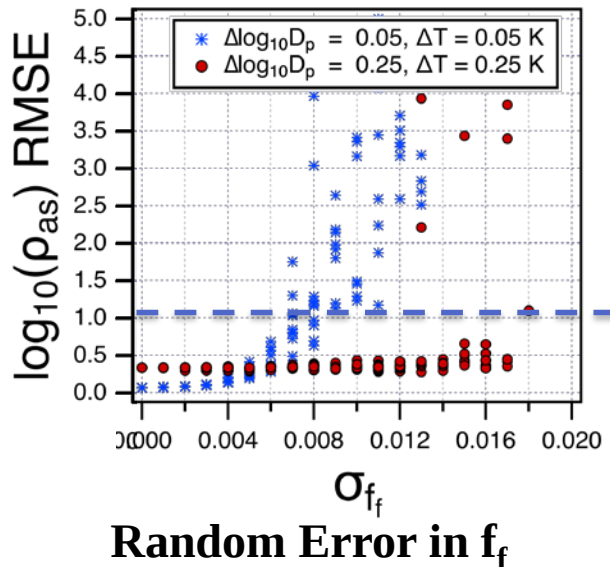
What about the real world?

$$\bar{\rho}_{as} = -\frac{\ln(0.5)}{\bar{s}_p} \exp\left(\int_{T_{50}}^T \alpha dT\right)$$

$$\alpha = \frac{\partial f_f}{\partial T} / \frac{\partial f_f}{\partial \ln \bar{s}_p}$$

Assumptions:

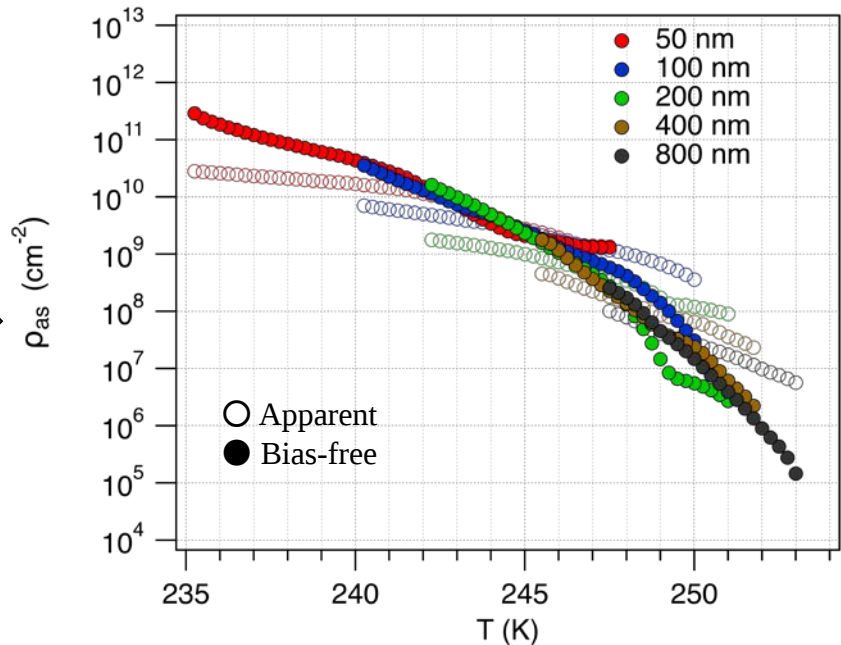
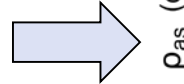
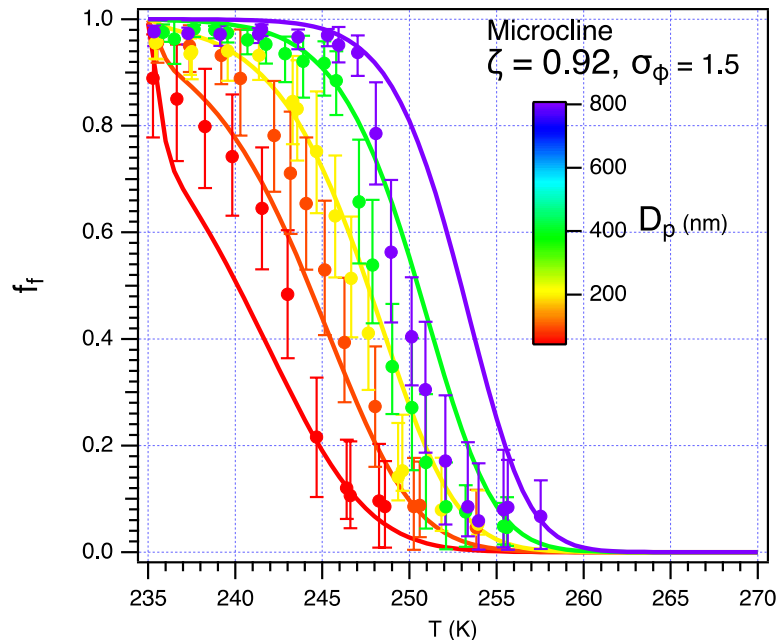
1. T_{50} is known
2. The partial derivatives of f_f can be accurately calculated



As a rule to keep the RMS error under one order or magnitude:

- $\Delta T \sim 0.5$ K
- $\Delta \log_{10} D_p \sim 0.5$
- $\sigma_{ff} < 5$ %
- Smooth spectra may accommodate larger error

Application to Existing Data Sets



*Data has been interpolated to 0.25 K
Estimated error is about one order of magnitude

$$\bar{\rho}_{as} = -\frac{\ln(0.5)}{\bar{s}_p} \exp \left(\int_{T_{50}}^T \alpha dT \right)$$

$$\bar{\rho}_{as,app} = -\frac{\ln(1 - f_f)}{\bar{s}_p}$$

The bias free estimate shows a more consistent trend than the apparent value

Conclusions

- Ice nucleation active site densities and nucleation rates obtained from droplet freezing experiments may be biased because variability is neglected.
- Such as bias may be significant reaching several orders of magnitude in parameterized active site density. It may translate to about 40% error in freezing fraction (~ 3 K in freezing threshold) when used in models.
- A method is introduced that for the first time allows to estimate the intrinsic ice nucleation efficiency of a give material. In many cases the accuracy of current experimental techniques is enough to improve estimates.
- The proposed method **amounts to a distinction between the “freezing rate” and the actual nucleation rate of a material.** It allows the validation of nucleation theories.



THANKS!

