Application of a new unifying stochastic ice nucleation model to examine isothermal and cooling rate dependent immersion freezing

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Motivation

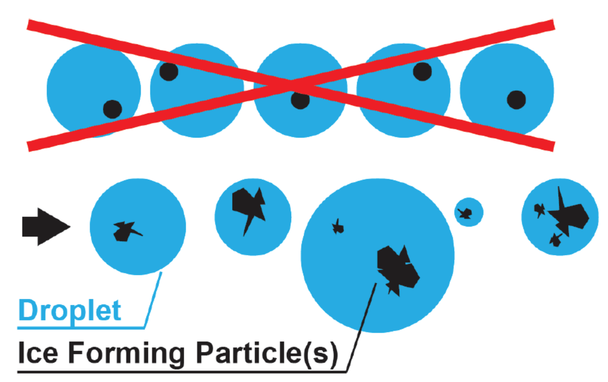
Immersion freezing represents the dominant ice nucleation process in mixed-phase clouds. Different immersion ice nucleation parameterization exists. Most of previous parameterizations are fit-derived representations of laboratory ice nucleation data sets invoking various mathematical concepts to reproduce the data. These concepts are usually not founded on physical theory or observable parameters. Extrapolation of fit-parameterized descriptions to atmospheric conditions can be challenging. **The goals of this study are:**

1. Represent immersion freezing data determined in the laboratory using only physical observables, i.e. parameters accessible in experiment.
2. The method should be applicable to any ice nucleation measurement technique.
3. The method should give insight if classical nucleation theory involving a stochastic and time dependent nucleation process can be used to describe observed freezing data.
4. Evaluate the importance of surface area of the ice nucleating particle for data interpretation and representation.
5. Evaluate if isothermal and cooling rate dependent immersion freezing data are in concert with classical nucleation theory.
6. Provide a quantitative measure to evalaute uncertainty in immersion freezing kinetics.

How to address these goals?

We use a stochastic freezing model based on a binomial distribution. This model is run via a Monte Carlo simulation to repeat an actual freezing experiment 100000 times to derive uncertainties and to evaluate the significance of particle surface area uncertainty in data interpretation. This Monte Carlo simulation is applied to isothermal (fixed temperature) and cooling rate dependent immersion freezing experiments.

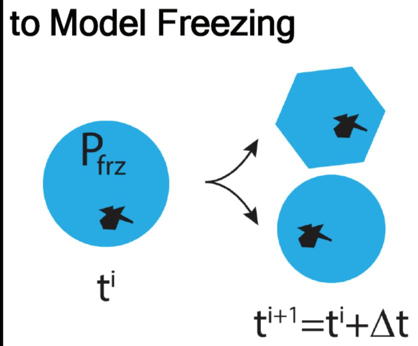
Model Setup and Treatment of Particle Surface Area



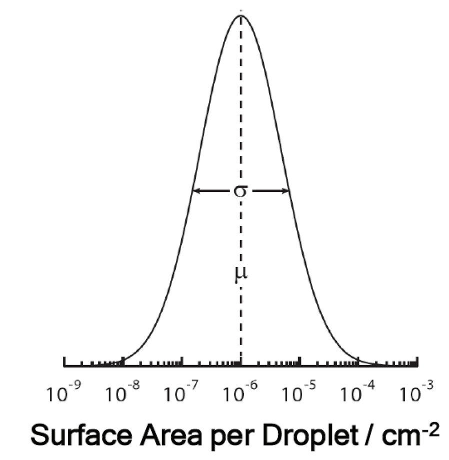
Particle Size: Measureable, Not Assumed, *e.g. Hartmann et al., 2016.*

Uniformity of Particle Surface: Not Assumed

Use Binomial Distribution to Model Freezing

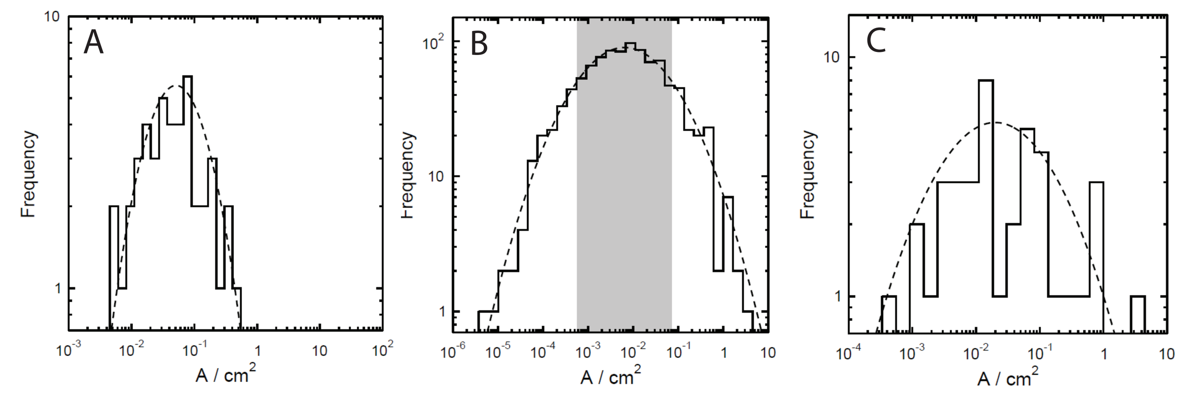


P_{frz} - Exponential Decay Law

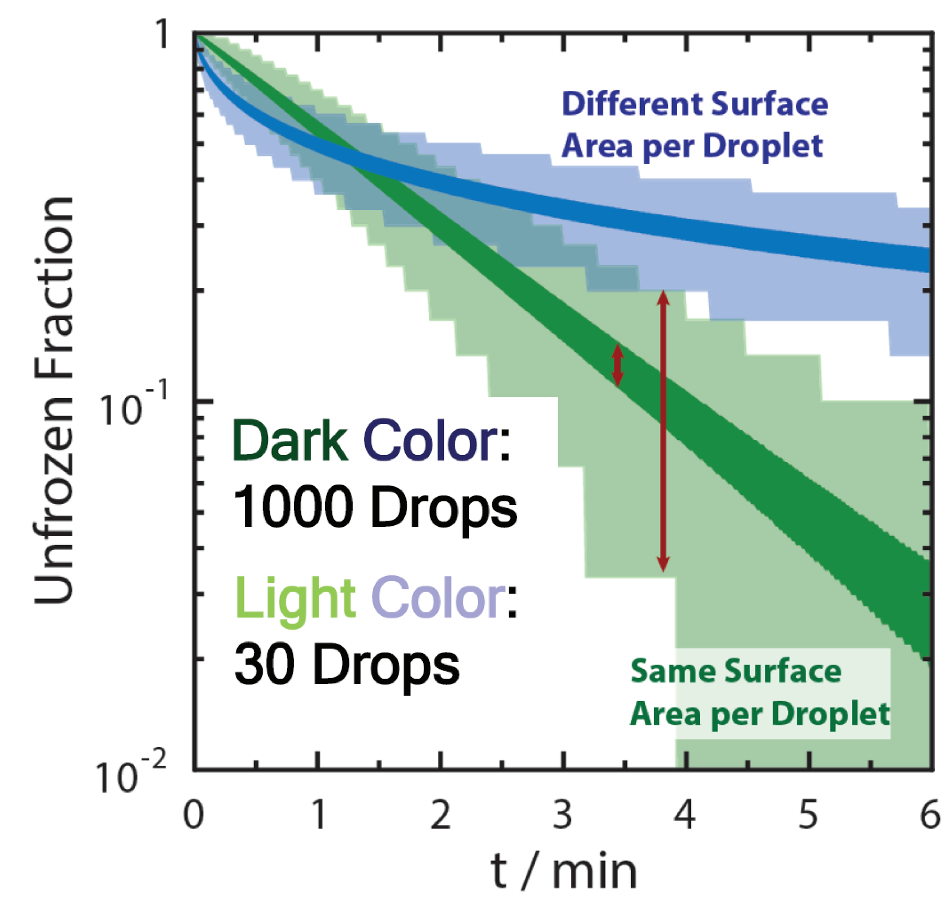


Assume INP surface area varies around mean with certain width.

Examples of random sampled INP surface areas per droplet from the lognormal distributions used in Diehl et al., ACP, 2014 (A), Wright and Petters, ACP, 2013 (B), and Herbert etal. ACP, 2014 (C).



Monte-Carlo Based Isothermal Immersion Freezing Model



100000 simulations per experiment with either 1000 or 30 freezing droplets.
Experiments shown correspond to Iso1 to 4 given in table below.

Unfrozen fraction trajectories appear either straight or curved on a log-linear plot, dependent primarily on the surface area variation, σ.

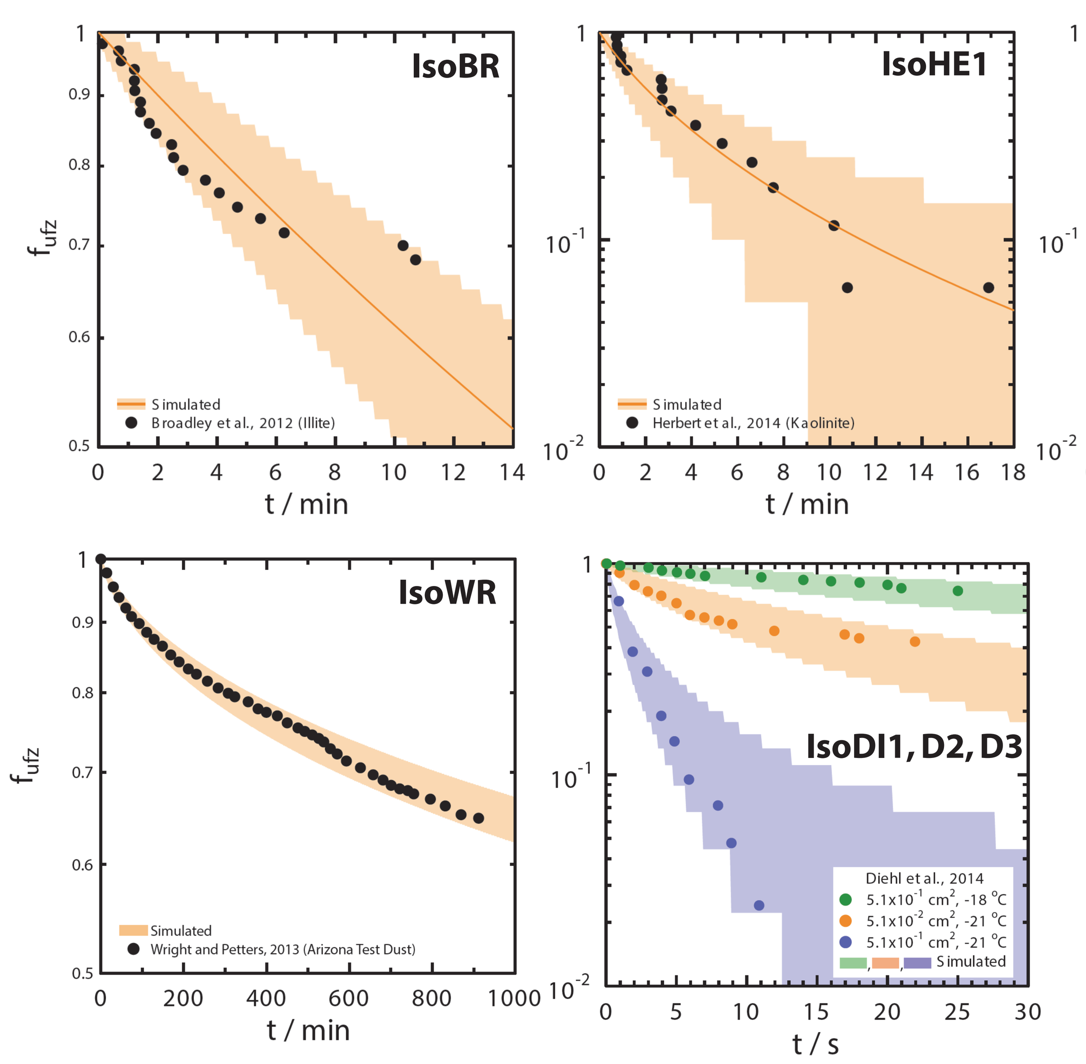
Shaded area shows 5 and 95 percentiles from the multiple simulations.

When lower total number of particles are used (N_{tot}), the uncertainty increases.

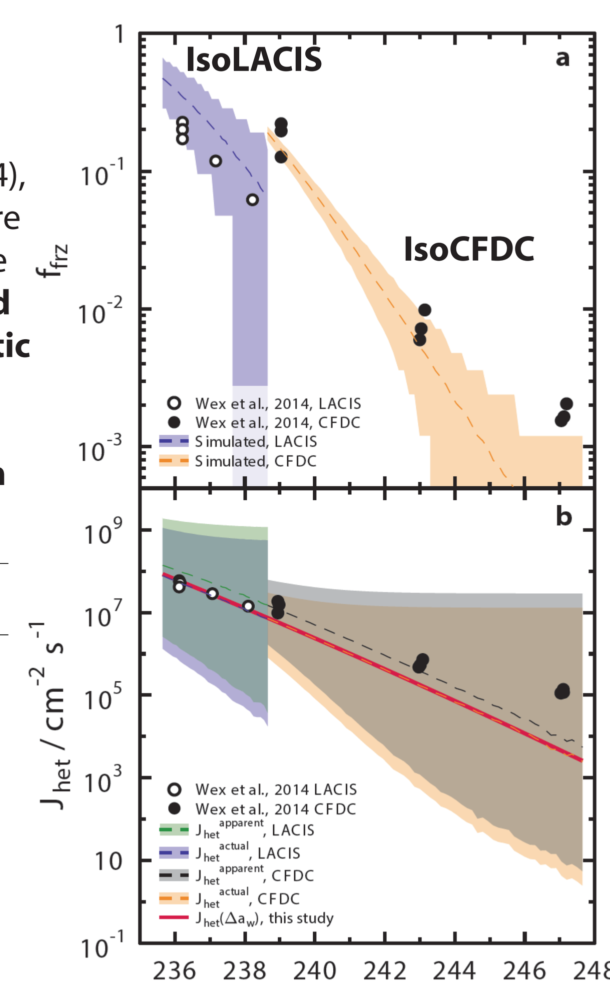
The effects of σ and N_{tot} on unfrozen fraction are independent of each other.

All displayed curves use same fixed J_{het} value. No need to invoke the presence of more and less active sites on particle surface.

Isothermal Immersion Freezing Model - Experimental Data Evaluation

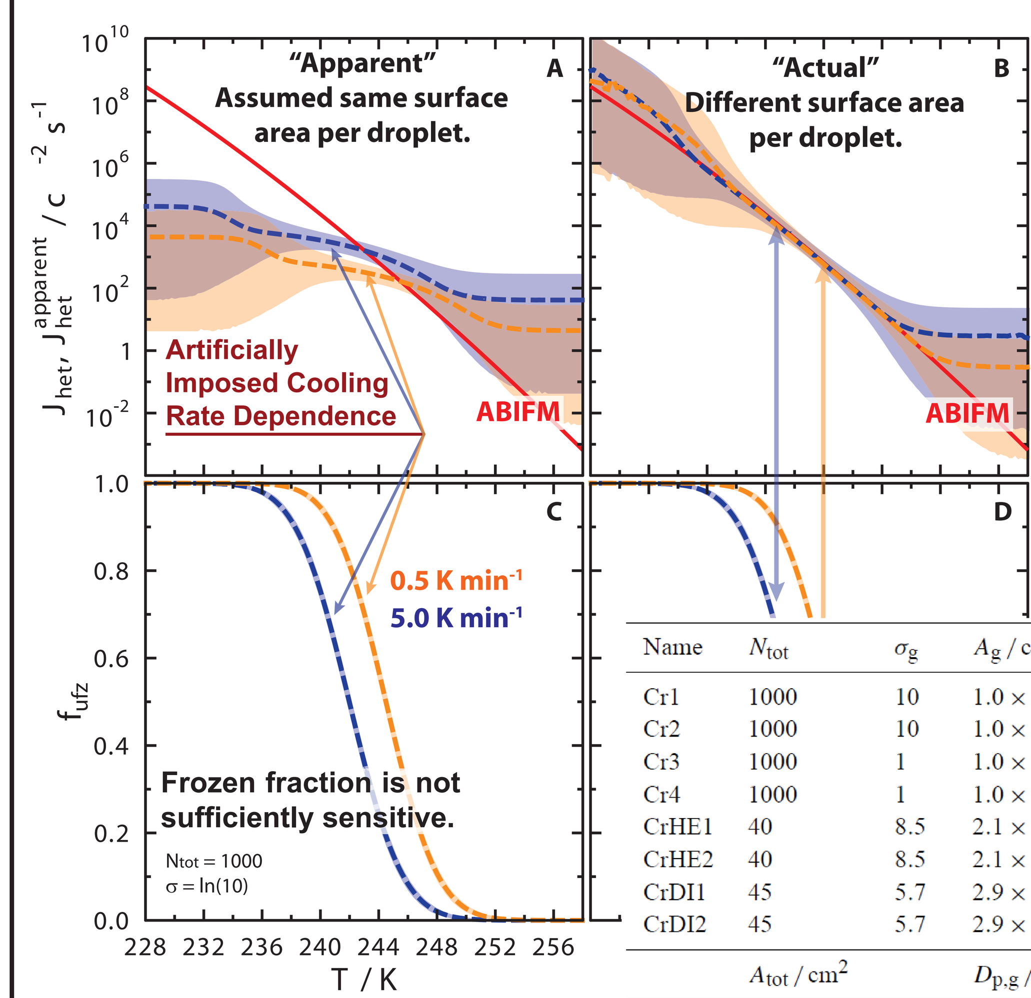


Simulated published immersion freezing data sets by Broadley et al (2012), Herbert et al. (2014), Wright and Petters (2013), Diehl et al. (2014), Wex et al. (2014). The simulations are using the parameters given in table below. **All data can be reproduced using a fixed J_{het} value and realistic assumptions of particle surface area variance. No need to invoke presence of special particles with special active sites.**



Name	N_{tot}	σ_g	A_g / cm²	T / K	J_{het} / cm^{-2} s^{-1}	INP Type	Figure	Color
Iso1	1000	1	1.0×10^{-5}	–	1.0×10^{3}	–	1a	dark green
Iso2	30	1	1.0×10^{-5}	–	1.0×10^{3}	–	1a	light green
Iso3	1000	10	1.0×10^{-5}	–	1.0×10^{3}	–	1a	dark blue
Iso4	30	10	1.0×10^{-5}	–	1.0×10^{3}	–	1a	light blue
IsoWR	1000	9.5	6.4×10^{-3}	251.15	6.0×10^{-4}	ATD[a]	1b	orange
IsoBR	63	U-pdf[b]	2.6×10^{-7}	243.3	2.8×10^{3}	illite	2a	orange
IsoHE1	40	2.2	1.2×10^{0}	255.15	4.1×10^{-3}	kaolinite	2b	orange
IsoHE2	40	8.5	2.0×10^{-2}	262.15	2.0×10^{-2}	feldspar	2c	orange
IsoDI1	45	3.2	5.1×10^{-1}	255.15	1.8×10^{-2}	illite	3	green
IsoDI2	45	3.2	5.1×10^{-2}	252.15	1.0×10^{0}	illite	3	orange
IsoDI3	45	3.2	5.1×10^{-1}	252.15	1.0×10^{0}	illite	3	blue
IsoCFDC	833	MCD[c]	MCD	238.65–247.65[d]	ABIFM[e]	kaolinite	7	orange, black
IsoLACIS	21	MCD	MCD	235.65–238.65[d]	ABIFM	kaolinite	7	blue, green

Cooling Rate Dependent Immersion Freezing Model



Simulations CR1 to 4 are shown.

Simulations demonstrate that differences in J_{het} (or n_s) are only due to the assumption that each droplet possesses same particle surface area. Accounting for each droplet's actual particle surface area avoids this apparent contradiction to classical nucleation theory: as expected, J_{het} is independent of cooling rate.

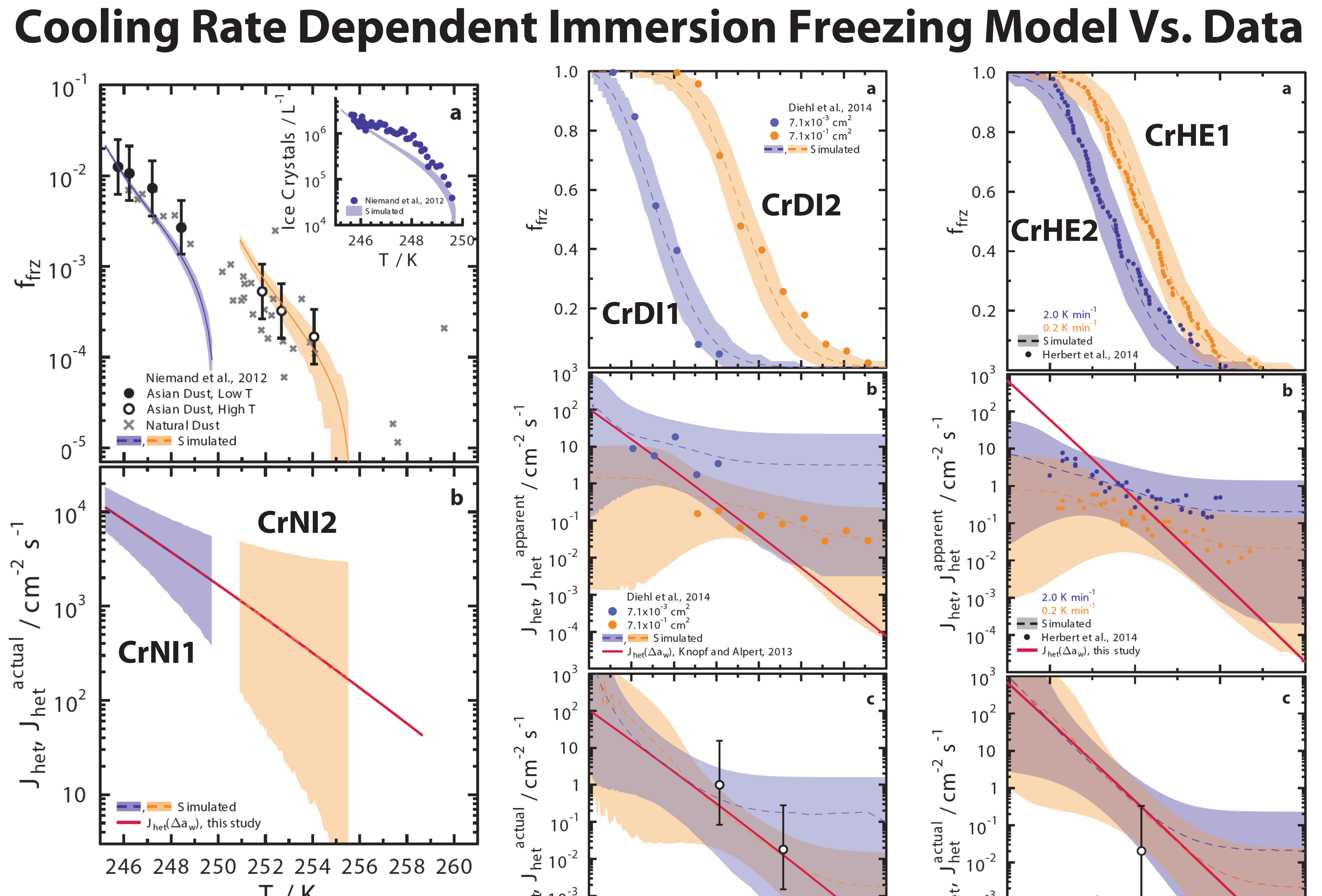
$$J_{het}^{apparent}(T) = \frac{n_{frz}(T)}{n_{ufz}(T) A_g \frac{\delta T}{r}}$$

versus

$$J_{het}^{actual}(T) = \frac{n_{frz}(T)}{\sum A_j \frac{\delta T}{r}}$$

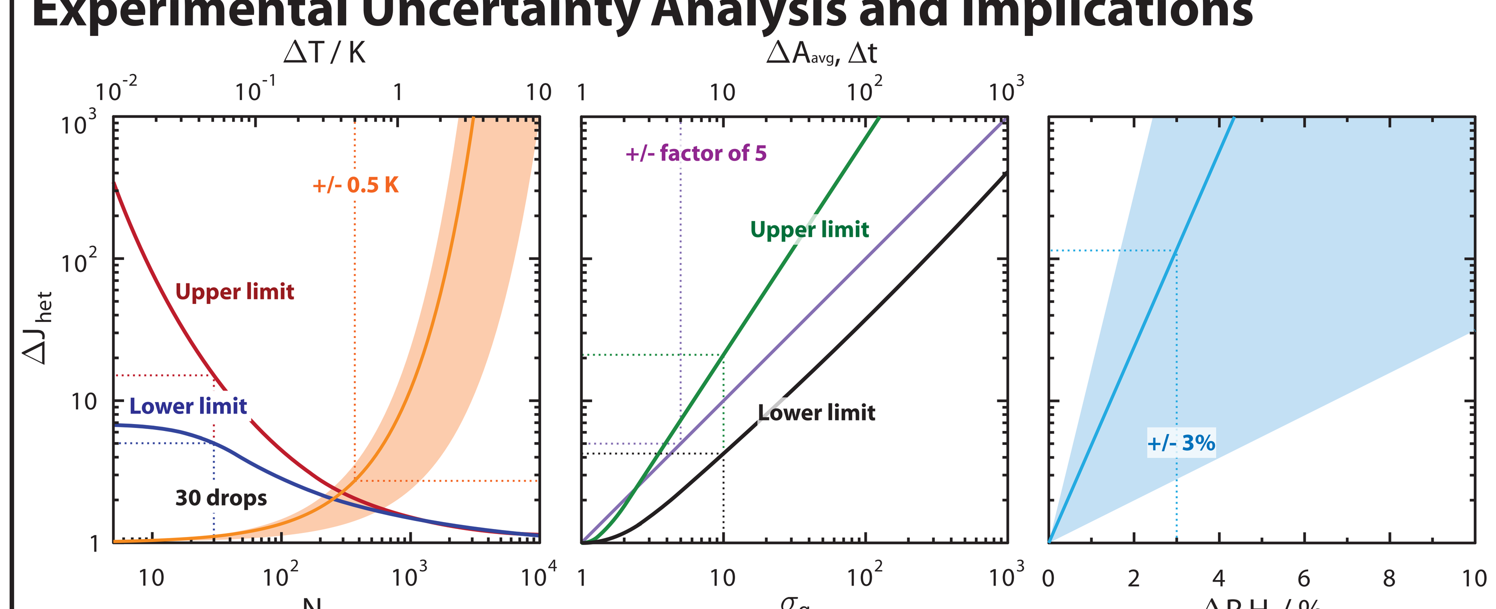
Name	N_{tot}	σ_g	A_g / cm²	m	c	r / K min^{-1}	INP Type	Figure	Color
Cr1	1000	10	1.0×10^{-5}	54.48	−10.67	0.5	illite	4	orange
Cr2	1000	10	1.0×10^{-5}	54.48	−10.67	5.0	illite	4	blue
Cr3	1000	1	1.0×10^{-5}	54.48	−10.67	0.5	illite	S7	black
Cr4	1000	1	1.0×10^{-5}	54.48	−10.67	5.0	illite	S7	green
CrHE1	40	8.5	2.1×10^{-2}	122.83	−12.98	0.2	feldspar	5	orange
CrHE2	40	8.5	2.1×10^{-2}	122.83	−12.98	2.0	feldspar	5	blue
CrDI1	45	5.7	2.9×10^{0}	54.48	−10.67	non-linear[a]	illite	6	orange
CrDI2	45	5.7	2.9×10^{-2}	54.48	−10.67	non-linear[a]	illite	6	blue
	A_{tot} / cm²		$D_{p,g}$ / µm						
CrNI1	6.5×10^{-4}	1.72	0.42	22.62	−1.35	non-linear[b]	ND[c]	8	blue
CrNI2	5.4×10^{-4}	1.69	0.40	22.62	−1.35	non-linear[b]	ND[c]	8	orange

Cooling Rate Dependent Immersion Freezing Model Vs. Data



Simulations predict the trend and numbers of observed ice-crystal numbers in AIDA chamber.

Experimental Uncertainty Analysis and Implications



Example errors are given as dotted lines in all panels. Propagated error yields ±2 orders of magnitude uncertainty .

At median frozen fraction, when N_{tot}<100 or σ~ln(10), J_{het} uncertainty is ~±1 order of magnitude. This uncertainty is significantly larger for frozen fractions <0.5 and >0.5 since less droplets freeze outside median temperature range.

$\Delta J_{het}(T)$ and $\Delta J_{het}(RH)$ errors are derived from a range of J_{het} values corresponding to different particle types such as mineral dust, marine biogenic, pollen, and humic soils.

Uncertainty in RH (in particular when studying immersion freezing at subsaturated conditions) can be the largest source of error for J_{het} derivations.

This analysis is capable to reproduce the majority of observed uncertainty in n_s of about ±2 orders of magnitude during the AIDA inter-comparison study (Hiranuma et al., 2015).

Summary and Conclusions

- Newly developed immersion freezing model simulations based on fundamental statistical principles and routed in classical nucleation theory (CNT).
- Model simulations reproduce previous immersion freezing data for a variety of studies, methods, and particle types including isothermal and cooling rate experiments.
- **Ice nucleating particle surface areas immersed in liquid droplets prepared in the laboratory are likely not identical. Assuming a monodisperse surface area can lead to misinterpretation of freezing data** (e.g. apparent cooling rate dependence and invoking active sites)**.**
- **Observation of too few ice formation events or performing a single experiment results in highly uncertain results.** Our analysis suggests that future experiments consider N_{tot}>100 and perform 3 independent experiments.
- Application of CNT allows derivation of J_{het}, a theoretical and physically defined parameter **applicable outside of laboratory time and surface area scales.**
- **Measured frozen fractions do not reflect J_{het} values or uncertainty properly.** The results suggest to not apply frozen fraction data for derivation of ice nucleation kinetics.
- **All shown results are in agreement with and captured by the water activity based immersion freezing model (ABIFM) by Knopf and Alpert, Faraday Discuss., 2013.** We recommend implementation of J_{het} in cloud resolving models making use of the ABIFM framework.

Article presented on this poster:

Peter A. Alpert and Daniel A. Knopf, Analysis of isothermal and cooling-rate-dependent immersion freezing by a unifying stochastic ice nucleation model, *Atmos. Chem. Phys.*, 16, 2083–2107, 2016 www.atmos-chem-phys.net/16/2083/2016/ doi:10.5194/acp-16-2083-2016

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