Temperature and size dependence of volume and surface nucleation rates for homogeneous freezing of supercooled water droplets

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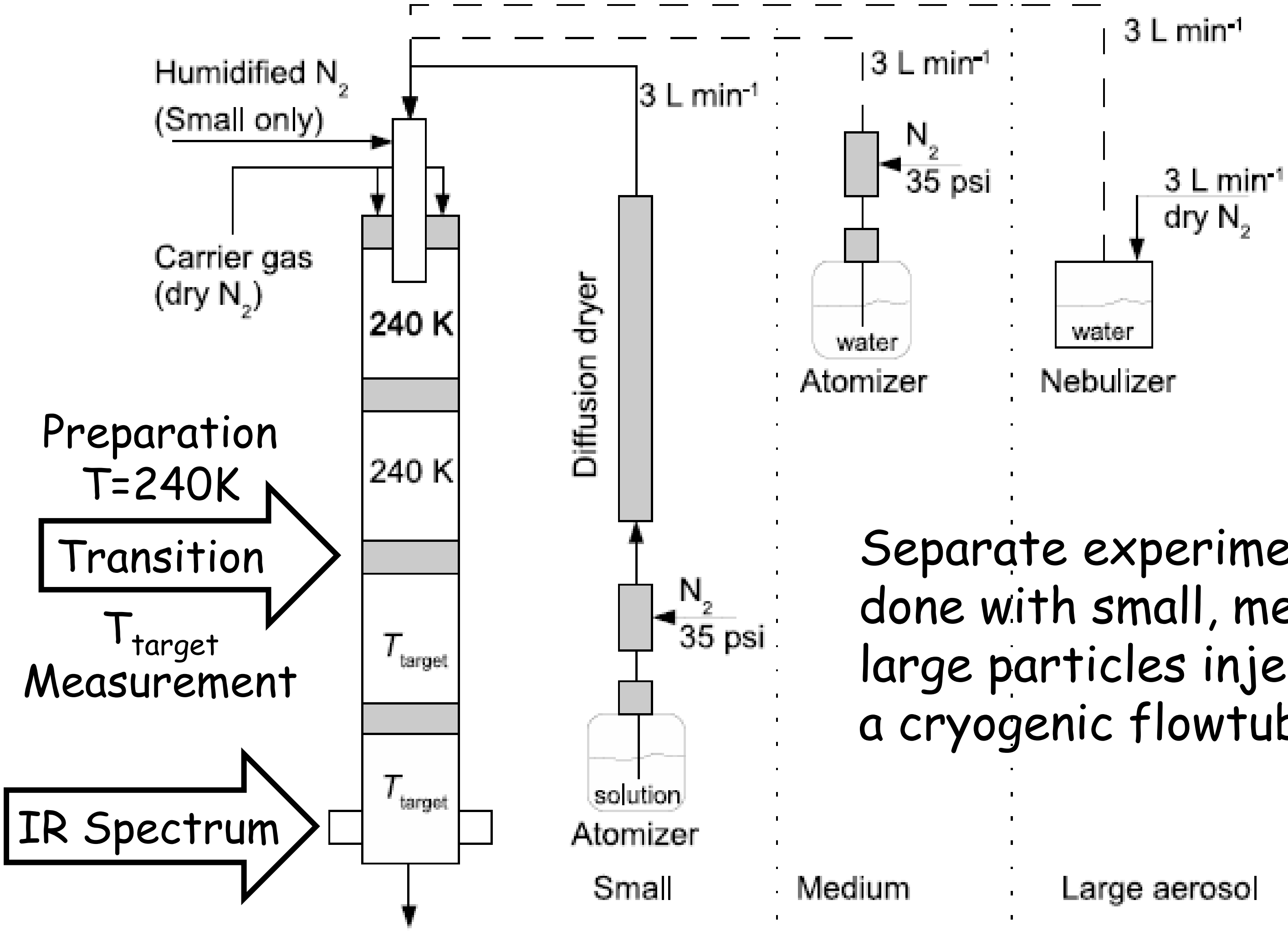
Procedure

- Experimental
  - Generate different sizes of ice particles in a flow tube at low (~ 235-240 K) temperatures
  - Measure infrared spectra of the particles during freezing
- Analysis
  - Invert spectra to obtain (volume) size distributions
  - Predict volume size distributions with parameterized nucleation/growth model
  - Extract nucleation rates for volume and surface nucleation mechanisms by comparing with measurements

Cryogenic Flowtube - Ice Particle Generation and Measurement



Separate experiments were done with small, medium and large particles injected into a cryogenic flowtube

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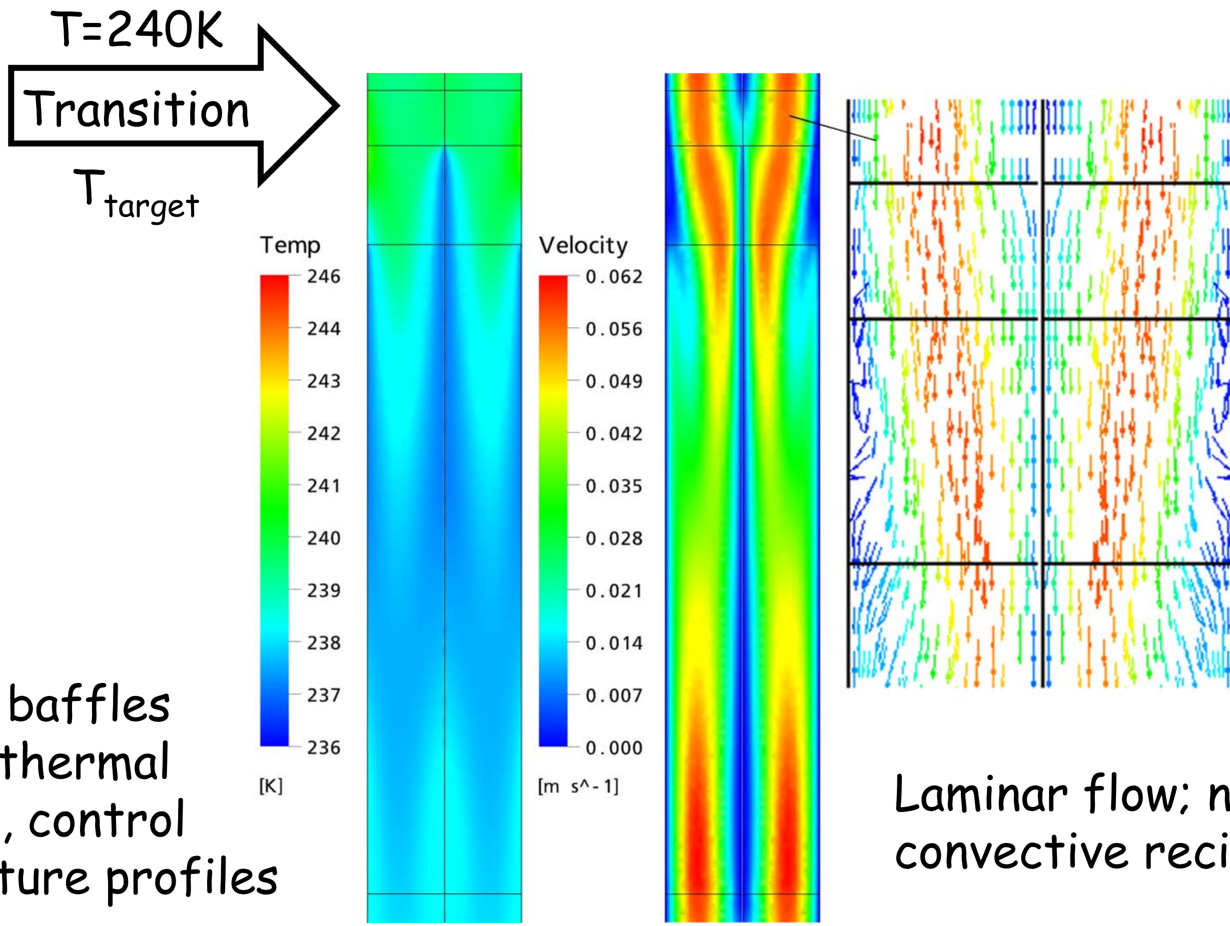
Flowtube Conditions from CFD Analysis



Interior baffles improve thermal transfer, control temperature profiles

Laminar flow; no convective recirculation

Calibrated CFD temperatures (error less than ±0.5 K)

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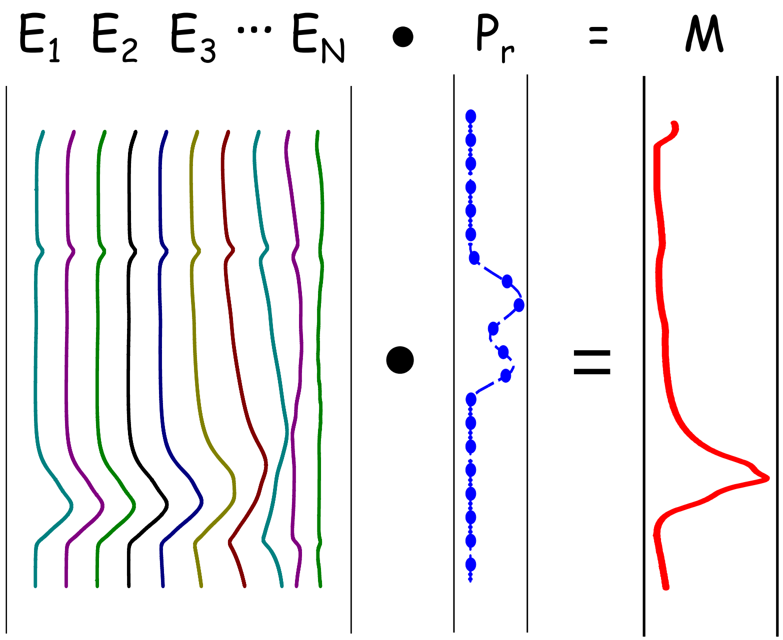
Determination of Size Distribution by Inversion of Measured Aerosol Spectrum



- Least Squares Fitting of Reference Spectra to the Measured Spectrum

E_r Monodisperse extinction spectra for radii r, calculated from measured indices of refraction

P_r Size distribution obtained by the fitting procedure

M Measured spectrum

Direct Fit: No Assumption about distribution shape.

<u>Procedure:</u>

$$\min_{\mathbf{P}} \left\{ \left| \mathbf{E} \cdot \mathbf{P} - \mathbf{M} \right|^2 \right\}^{1/2}$$

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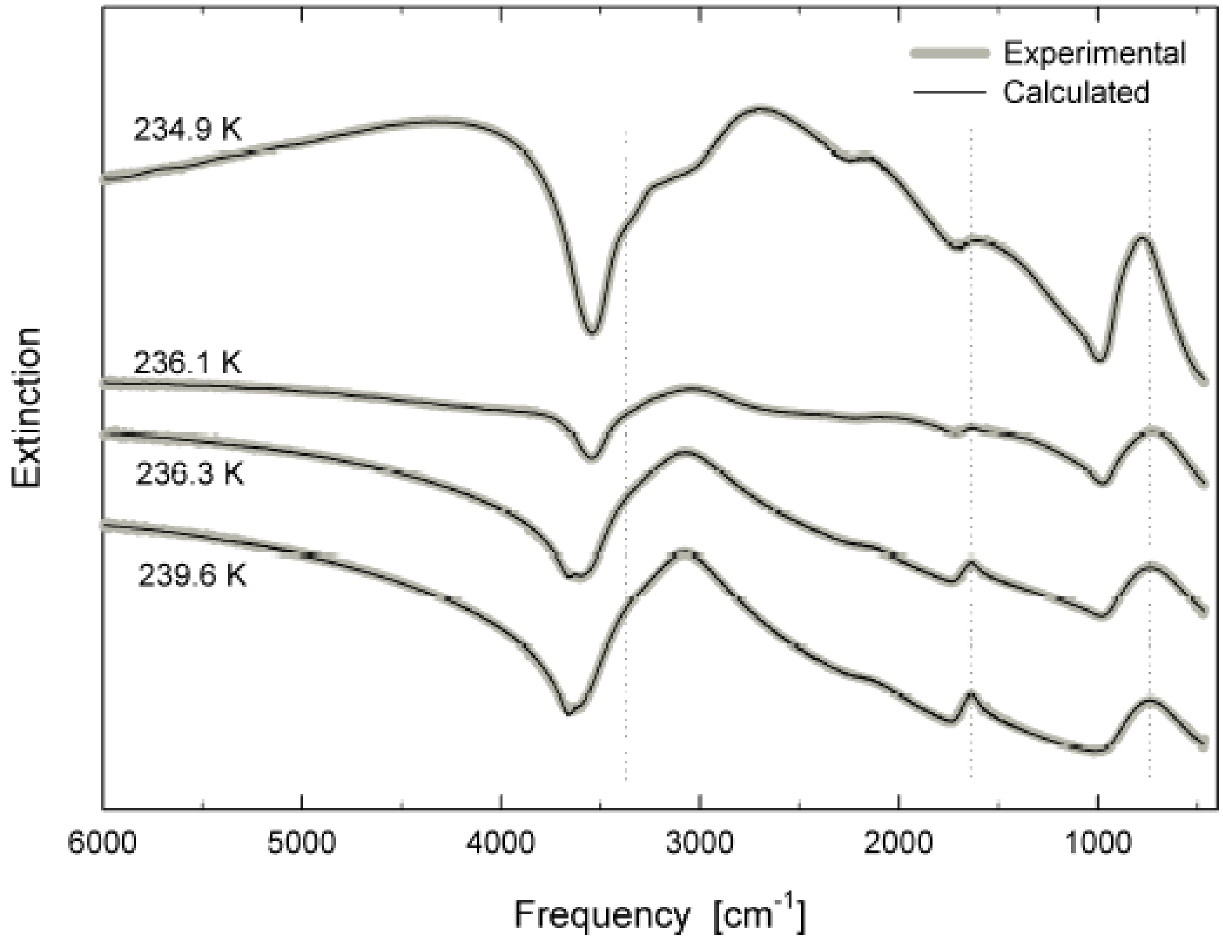
Typical Results of Spectral Inversion

- Ice + water spectra calculated from retrieved size distribution, compared with measured spectra.



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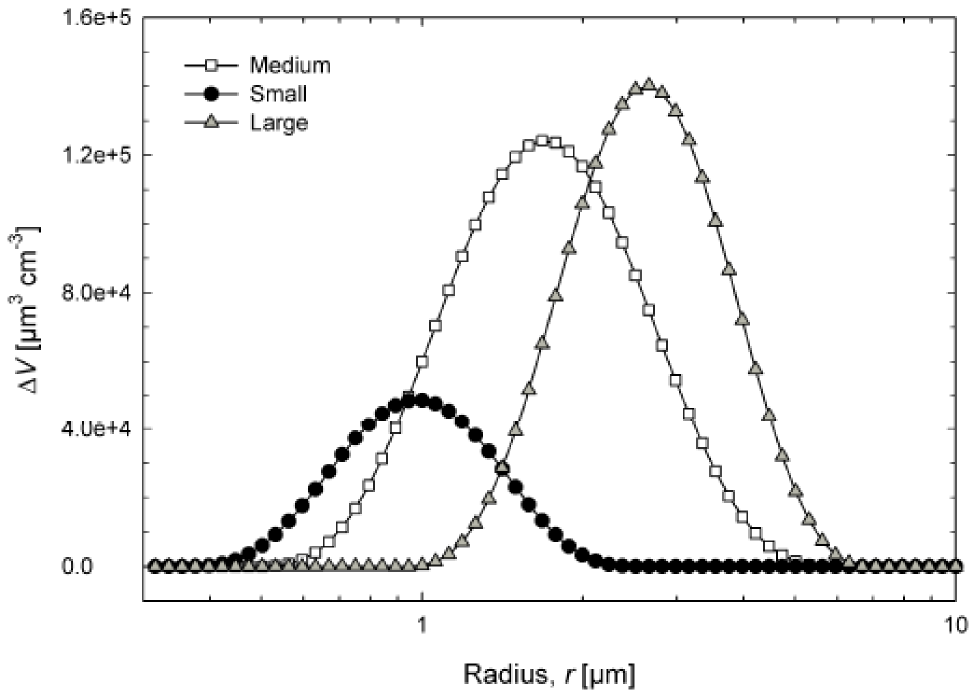
Determining Surface and Volume Nucleation Rates

- Experimental information available:
  - Temperature and velocity profiles (from CFD)
  - Measured number and size distributions of 240 K water droplets before the experiment and water/ice particles afterwards

Initial volume distributions of three sizes of water droplets at 240 K



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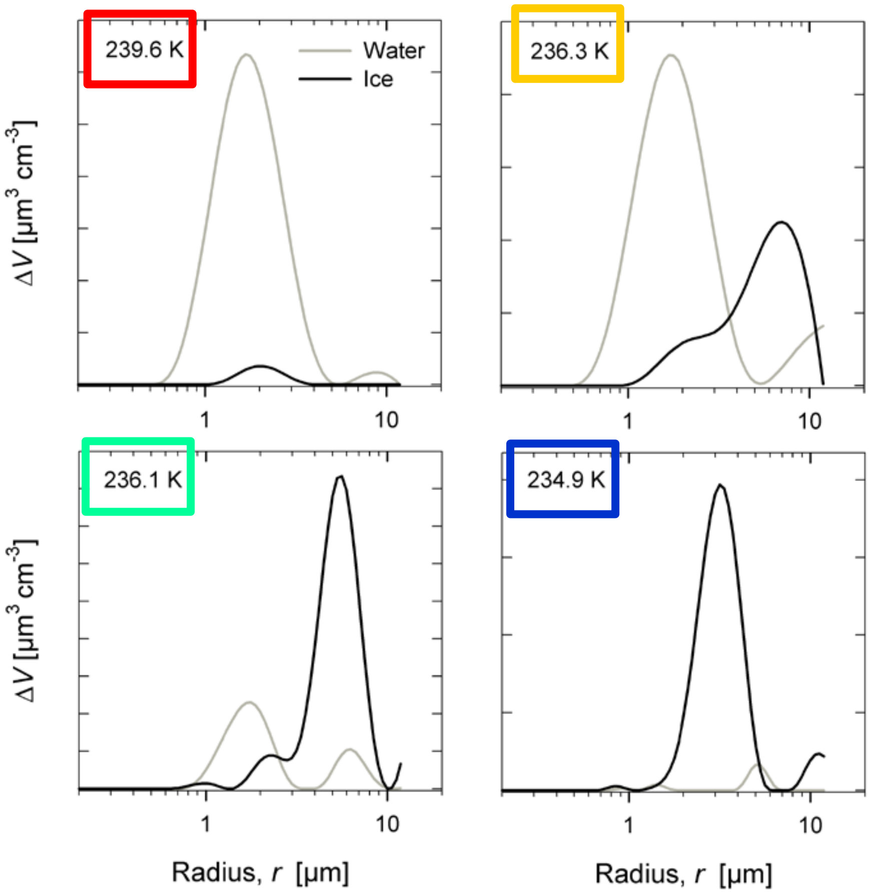
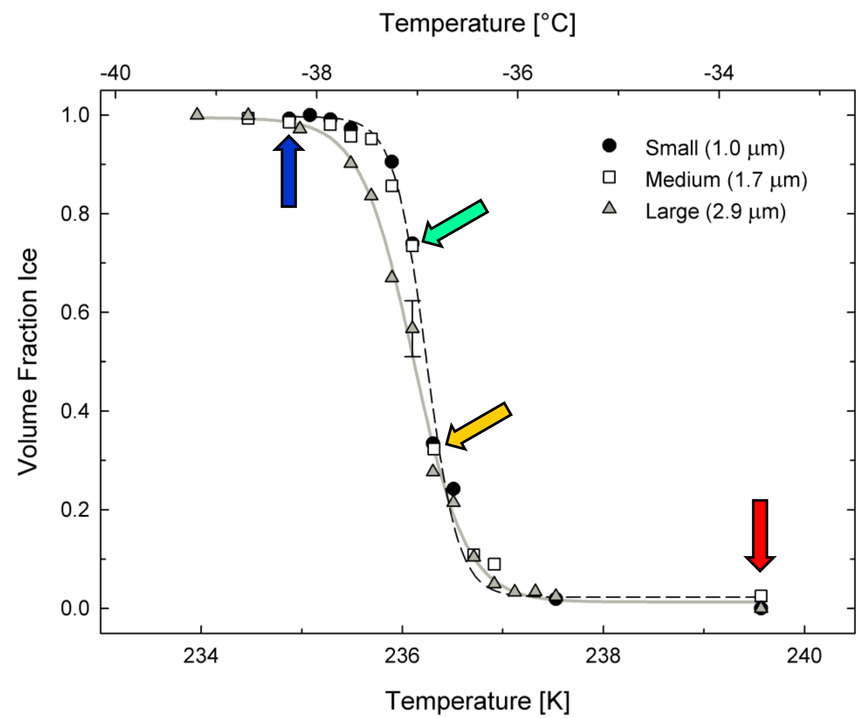
Measured Water and Ice Size Distributions

Temperature dependent volume distributions (medium particles)



Volume fraction frozen



Note shift to larger radius on freezing, due to mass transfer from water to ice

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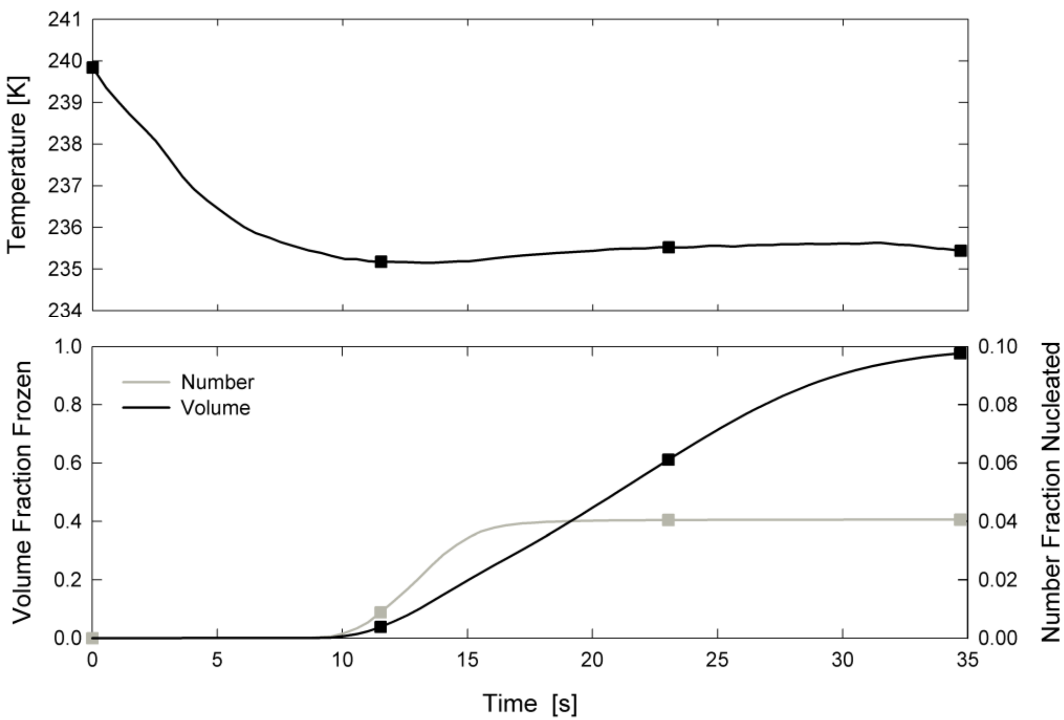
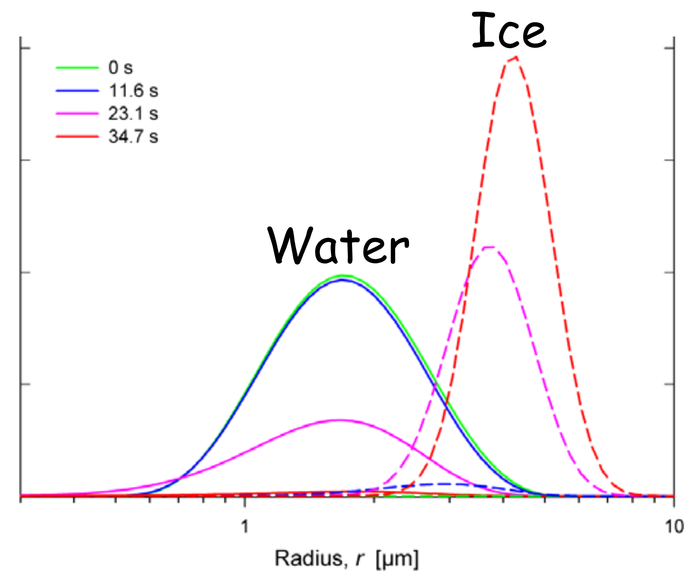
Particle Evolution from Microphysical Model

- Temperature profile calibrated by axial measurements
- Model prediction: nucleation from 10-15 s; growth from 10 to 35 s
- Predicted number and volume distributions of water and ice compared with spectral inversion measurements after 35 s





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Microphysical Nucleation/Growth Model[1]

- Separate volume and surface nucleation $J_t = J_V V + J_S S$
  - Classical nucleation formalism $J_{V/S}(T) = N_{V/S} \frac{kT}{h} exp\left(-\frac{\Delta F_{V/S}}{kT}\right)$
  - Djikaev *et al.*[2] theory for J_S: germ forms in a thin surface layer
  - Nucleation model rates:

Parameters: A_V, B_V, A_S, B_S

$$\begin{cases} J_V(T) = N_V \frac{kT}{h} exp\left(-\frac{A_V - B_V T}{kT}\right) \\ J_S(T) = N_S \frac{kT}{h} exp\left(-\frac{A_S - B_S T}{kT}\right) \end{cases}$$

- Size distribution binned; includes diffusion-limited mass transfer (condensation and evaporation), Kelvin effect corrections and wall losses
- Vary parameters to fit measured size/volume distributions

[1] Th. Kuhn, *et al.* ACP **11** 1 (2011); M. Earle *et al.* ACP **10**, 7945 (2010)

[2] J. Phys. Chem. A, **106**, 10247–10253, (2002)
ibid **112**, 6592–6600 (2008)

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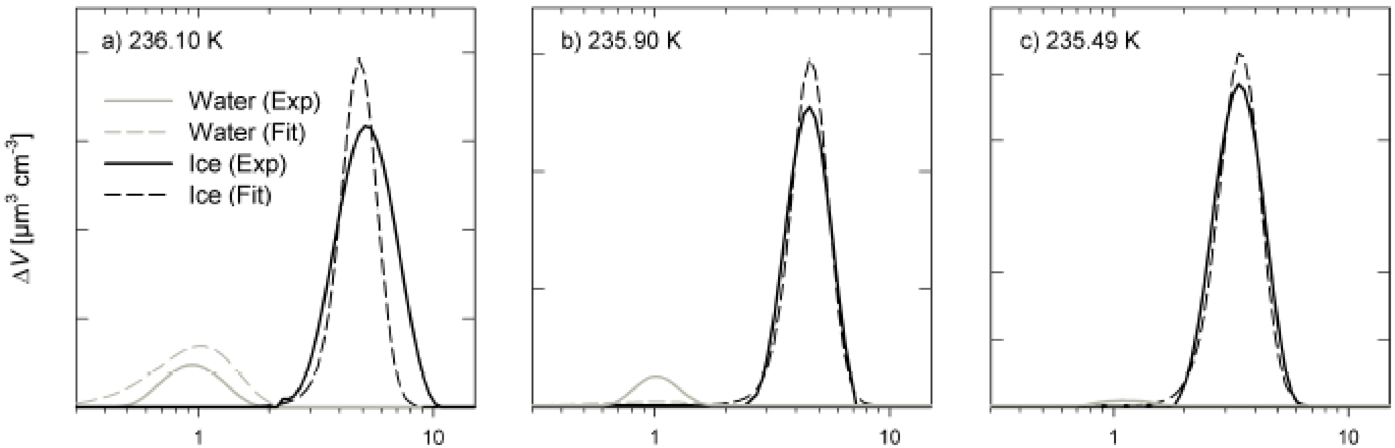
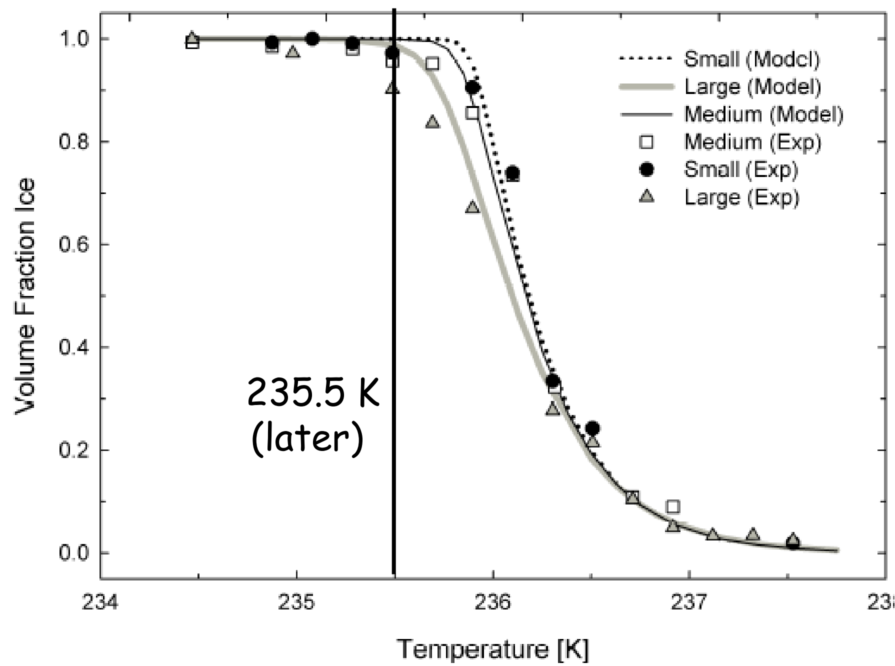
Converged Model Predictions *vs.* Measurements



- Water & ice size distributions and fraction frozen agree well with measurements (~30 experiments with S, M, L particles at various temperatures)

⇒ Model is accurate



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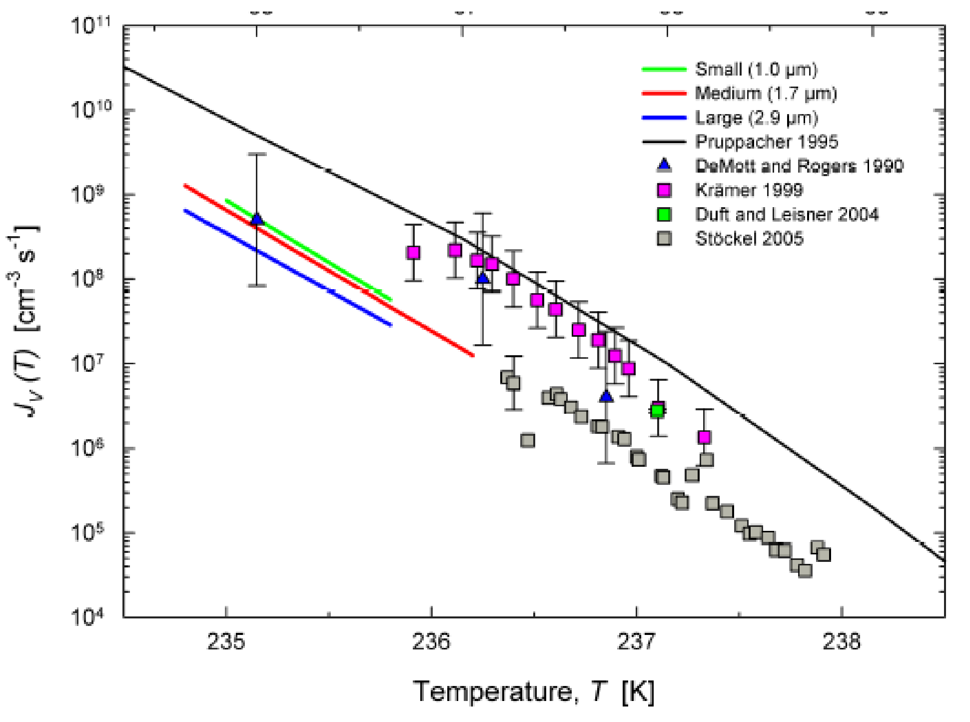
Result: Total Nucleation Rate

- Compares well with Stöckel *et al.* (2005)*; Not well with some others
  - Difficult measurements (nucleation rate changes by nearly a factor of 100 per degree



*Stöckel, P., *et al.*, Rates of homogeneous ice nucleation in levitated H2O and D2O droplets, J. Phys. Chem. A, 109, 2540-2546, 2005

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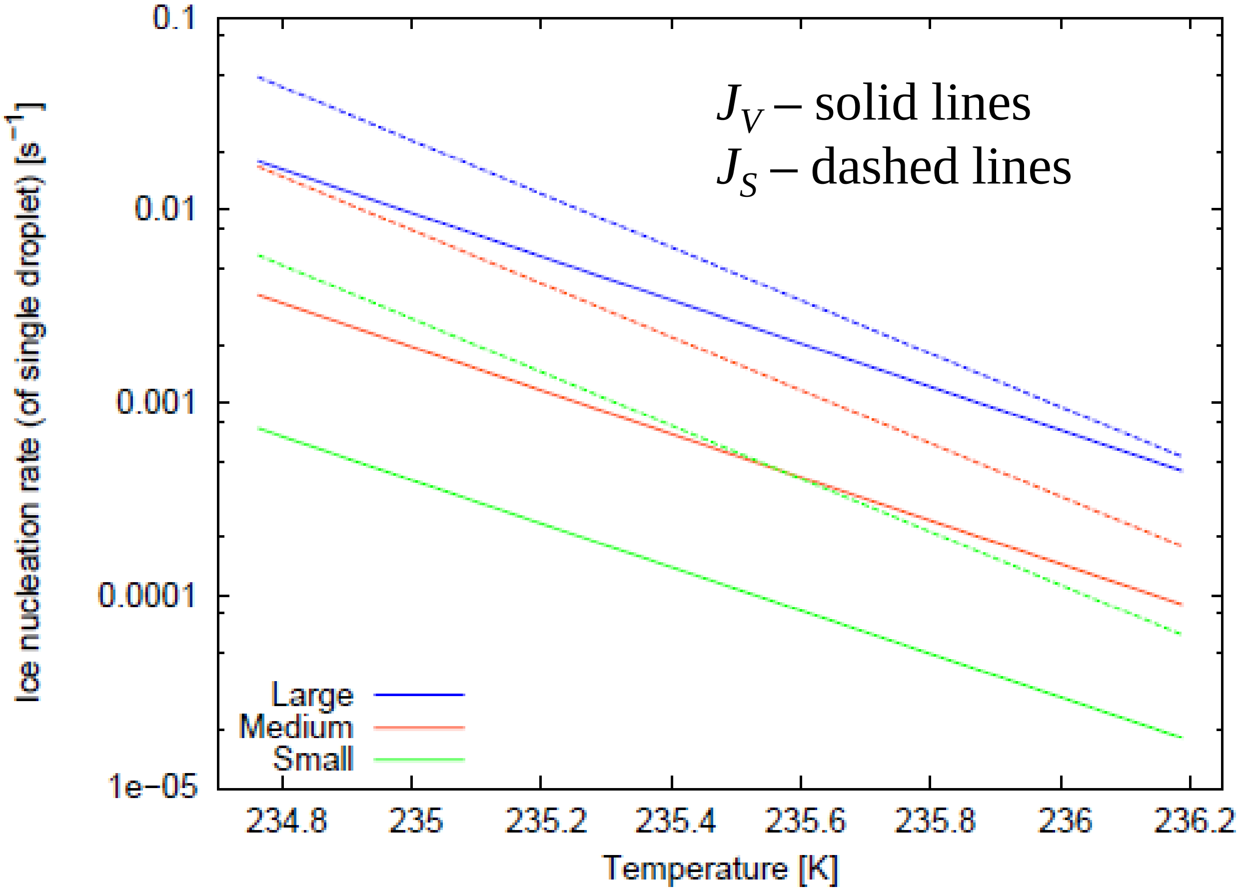
Surface and Volume Nucleation Rates Separated

- Surface nucleation rates are higher than volume for these sizes
- Difference is larger for smaller particles



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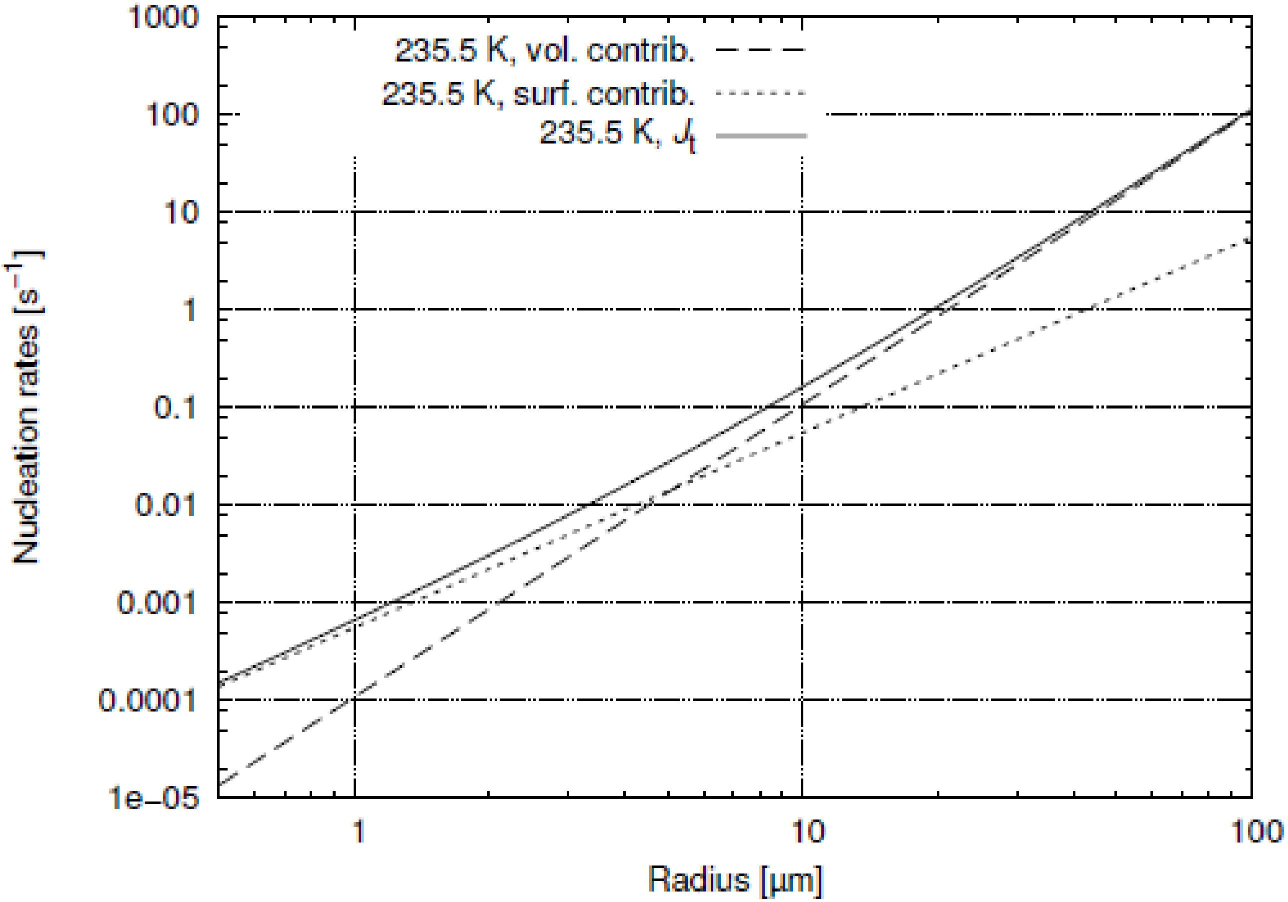
Relative Contributions of Volume and Surface Nucleation

Surface nucleation predominates for r < 5μm



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