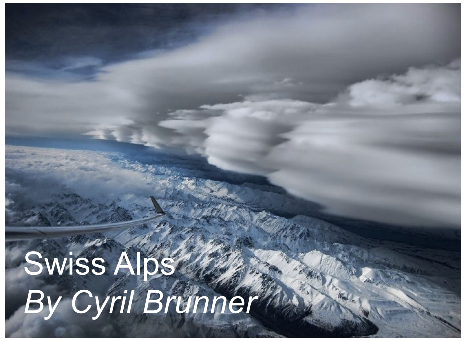
Watching super-cooled water droplets nucleate heterogeneously with high speed cryo-microscopy



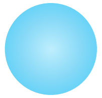
Dr. Nadine Borduas-Dedekind
Assistant professor
Department of Chemistry
University of British-Columbia

@nadineborduas
#NBDGroup

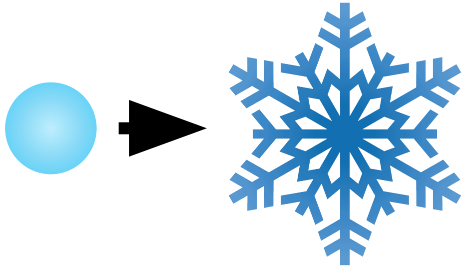
This work was conducted on the unceded, traditional and ancestral homelands of the xʷməθkʷəy̓əm nation.

Can We Even Observe Microphysics?

Cloud microphysics: Formation, growth, and transformation of cloud droplets and ice crystals



Condensation & evaporation
Collision & coalescence



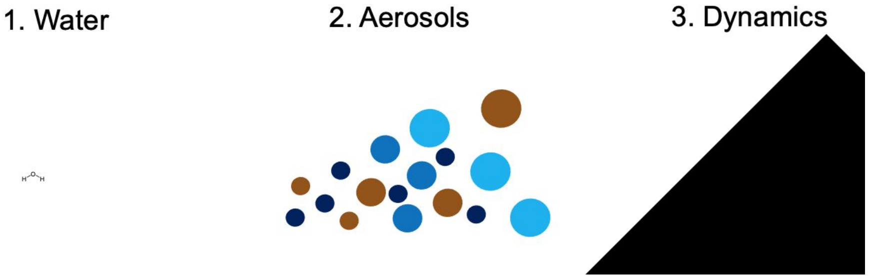
Nucleation:
- Homogeneous nucleation
- Heterogenous nucleation

Bergeron-Findeisen process

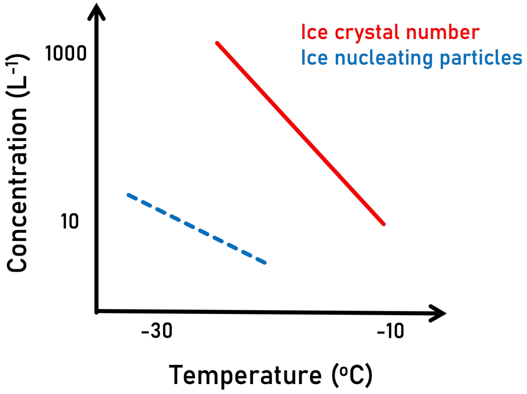
Deposition & sublimation
Ice aggregation
Riming
Secondary ice processes:
- Rime splintering (H-M)
- Collisional breakup
- Frozen droplet breakup

Research gaps in atmospheric ice nucleation from my perspective

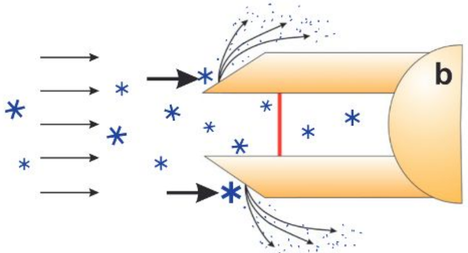
- Reconciliation of scales



- More ice crystals than ice nucleating particles

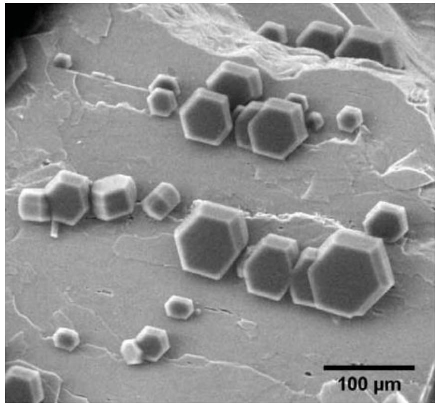


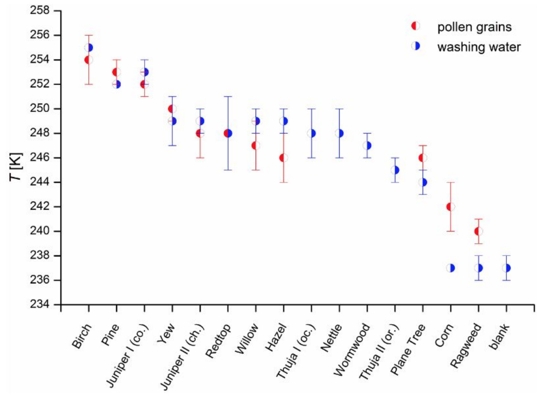
- Sampling techniques and instrumentation modify the original ice nuclei



Korolev, *J. Atmos. Oceanic Technol.*, **2013**

- No universal mechanism to predict the ice nucleating ability of a substance





Atmospheric ice nucleation by organic matter

Brennan et al., *Atmos. Chem. Phys.*, **2020**, *20*, 163

Müller, et al. *ACS Environ. Au*, **2023**, *3*, 164

Borduas et al, *Atmos. Chem. Phys.* **2019**, *19*, 12397

Thompson, et al. *Atmos. Chem. Phys*, **2024**, under review

Paul Bieber

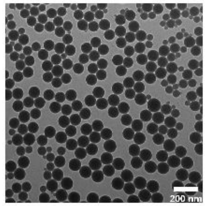
Émilie Payment

Emily Chiao

High speed images of freezing

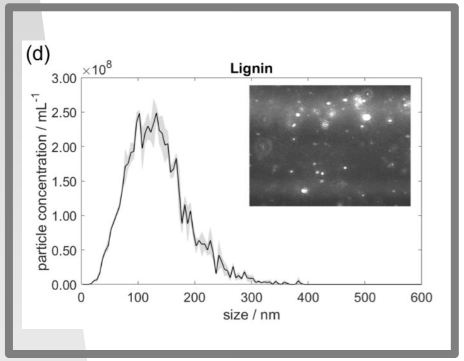
Bieber & Borduas, *Sci. Adv.* **2024**,

Miller, Brennan, et al., *Atmos. Meas. Tech.* **2021**, *14*, 3131



Lignin nanoparticle as INPs

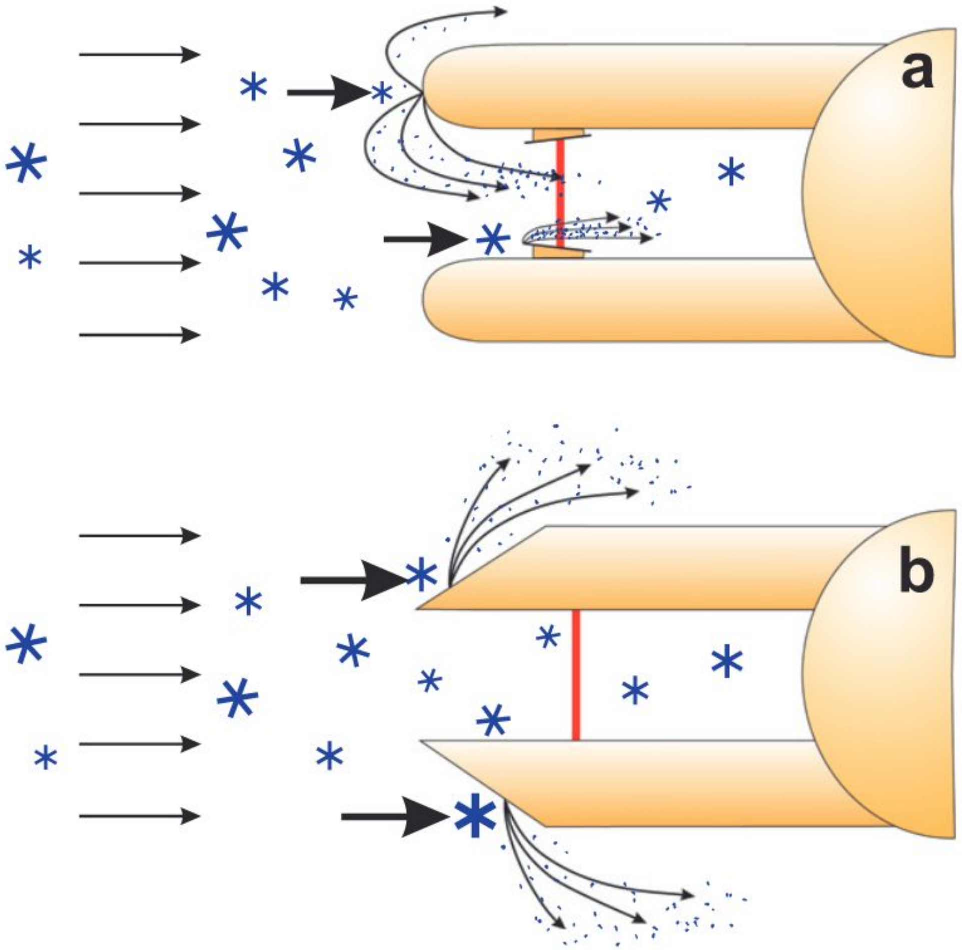
Zeleny et al., *ACS ES&T Air*, **2024**, revisions



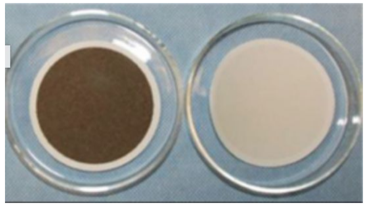
Bieber et al., *J. Chem. Phys.* **2024**,

Sampling techniques of aerosols, cloud droplets and ice crystals

Korolev tips for ice crystals



Korolev, Emery, Creelman.
J. Atmos. Oceanic Technol., **2013**, *30*, 690



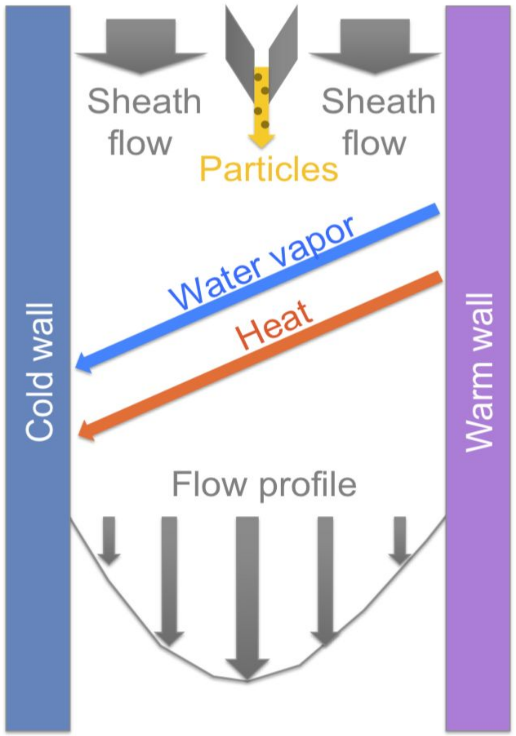
High volume sampler

Impinger

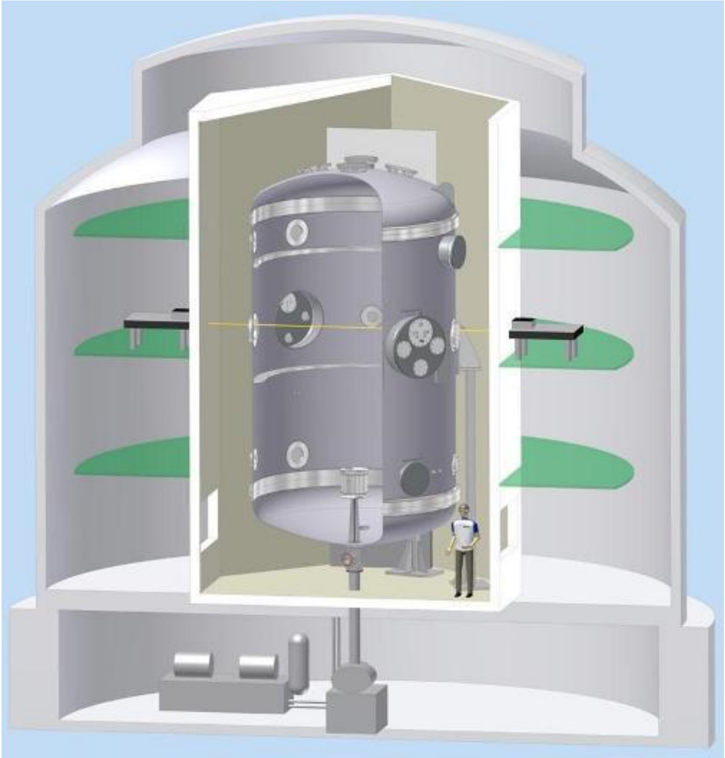
Cloud samplers
Jungfraujoch, Switzerland

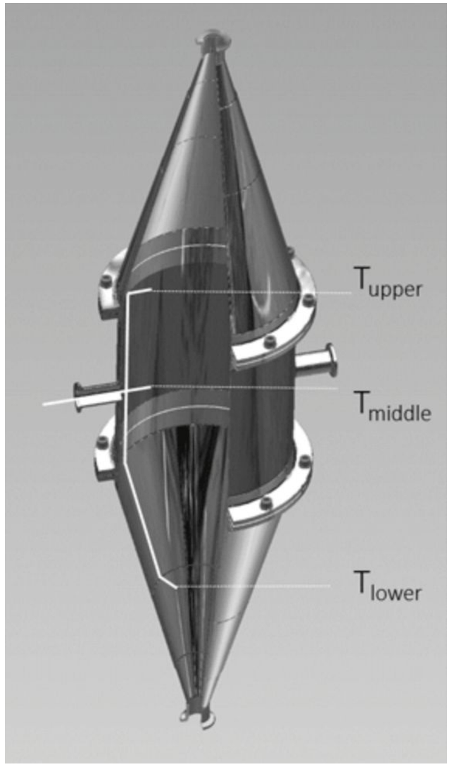
Online measurements of single ice nucleating particles

Continuous flow diffusion chambers



Expansion chambers



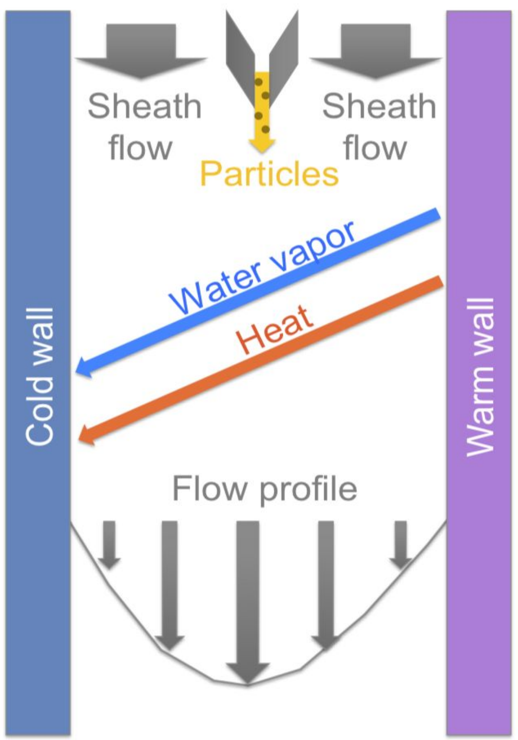


UT-CFDC: Kanji & Abbatt, *Aerosol Sci. Technol.*, **2009**, *43*, 730
SPIN: Garimella et al. *Atmos. Meas. Tech*. **2016**, *9*, 2781
HINC: Lacher et al., *Atmos. Chem. Phys.*, **2017**, *17*, 15199
HINC-Auto: Brunner & Kanji, *Atmos. Meas. Tech.*, **2021**, *14*, 269

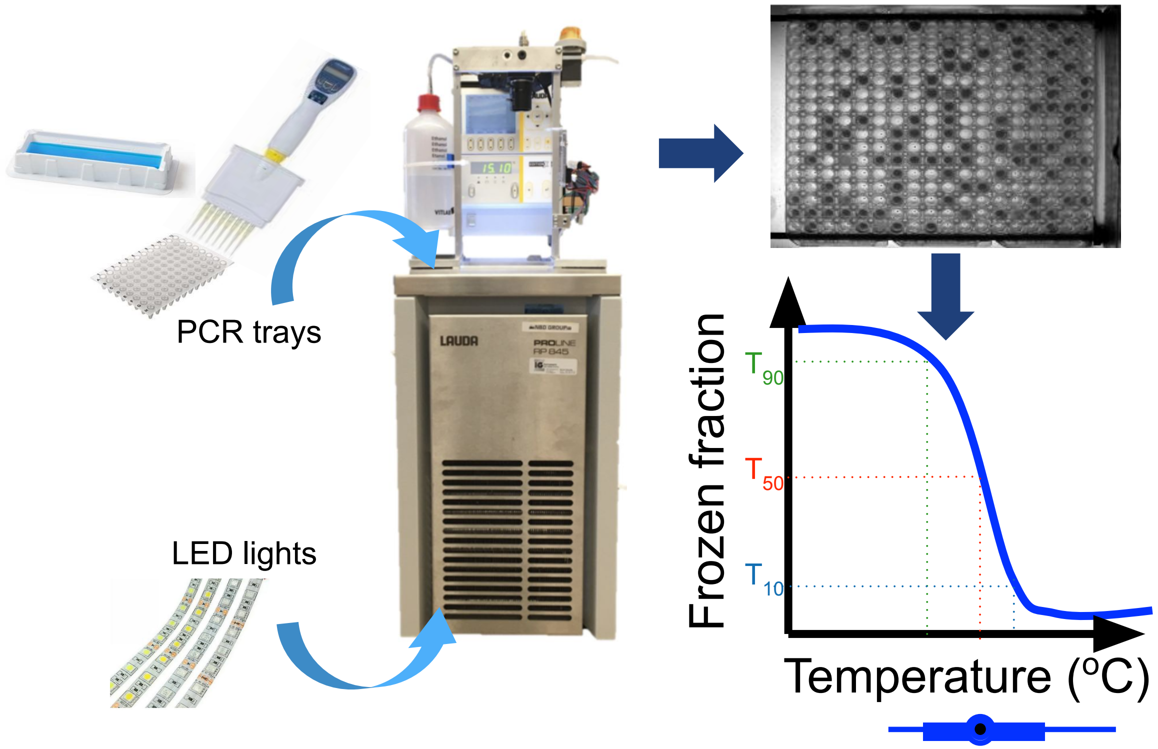
AIDA chamber: Möhler et al. *Atmos. Chem. Phys.*, **2003**, *3*, 211
LACIS: Hartman et al., *Atmos. Chem. Phys.*, **2011**, *11*, 1753
PINE chamber: Möhler et al., *Atmos. Meas. Tech*. **2021**, *14*, 1143

Online and offline measurements of ice nucleating particles

Single particle measurements



Bulk solution measurements



UT-CFDC: Kanji & Abbatt, *Aerosol Sci. Technol.*, **2009**, *43*, 730
SPIN: Garimella et al. *Atmos. Meas. Tech.* **2016**, *9*, 2781
HINC: Lacher et al., *Atmos. Chem. Phys.*, **2017**, *17*, 15199
HINC-Auto: Brunner & Kanji, *Atmos. Meas. Tech.*, **2021**, *14*, 269

Hill et al., *App. Environ. Microbiol.*, **2014**, *80*, 1256
Stopelli et al., *Atmos. Meas. Tech.*, **2014**, *7*, 129
Beall et al., *Atmos. Meas. Tech.*, **2017**, *10*, 2613
Miller, Brennan et al., *Atmos. Meas. Tech.*, **2021**, *14*, 3131

List of droplet freezing techniques (40+ and counting)

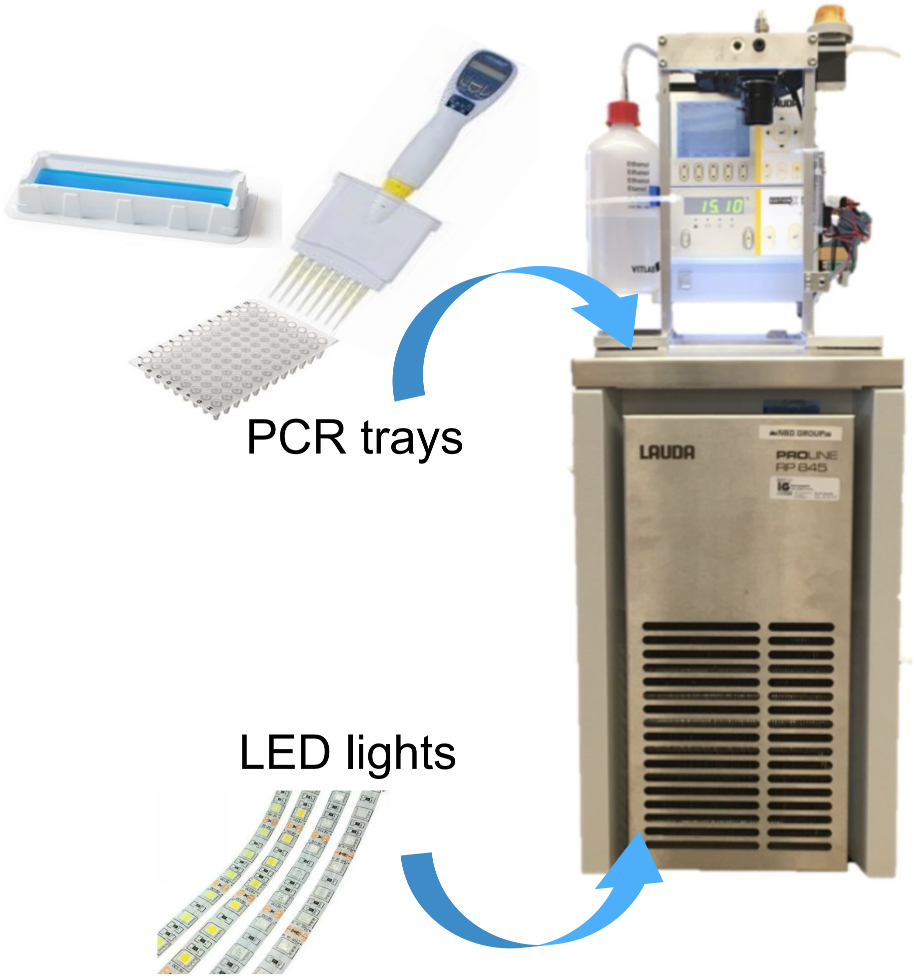
Instrument name	Brief description
Flow cell microscopy technique for aerosol phase transitions	Vapors condensed onto the bottom of a sample cell on aluminum cooling block; freezing monitored via microscope
Droplet freezing technique (DFT)	Particles deposited on a glass slide in a sample cell on a cold stage, with droplets grown by water vapor; freezing monitored via microscope
Microfluidic apparatus	Flow-focusing nozzle continuously produces droplets in a stream of fluorocarbon across a seven-temperature-zone cold plate; freezing monitored via microscope
FRankfurt Ice Deposition freezinG Experiment – Tel Aviv University (FRIDGE-TAU)	Pipetted drops onto Vaseline-coated Peltier cold stage in low-pressure diffusion chamber; freezing monitored via CCD camera
Picoliter and Nanoliter Nucleation by Immersed Particle Instrument (pico-NIPI, nano-NIPI)	Nebulized droplets encased in silicon oil on hydrophobic glass slides on aluminum cold stage; freezing monitored via microscope
Vienna Optical Droplet Crystallization Analyzer (VODCA)	Water–oil emulsion pipetted onto a glass slide on a Peltier cold stage, all contained in an airtight cell; freezing monitored via microscope
Drop freezing apparatus for filters	Filter cutouts placed inside small tubes with water, cooled in a water bath; freezing monitored by manual inspection
Microliter Nucleation by Immersed Particle Instrument (microL-NIPI)	Drops pipetted onto a hydrophobic glass slide in humidity-controlled enclosure on a cold stage; freezing monitored via camera
North Carolina State University cold stage (NC State-CS)	Emulsion of water in squalene placed on a glass slide resting in an aluminum dish on a thermoelectric element; freezing monitored via camera
Microfluidic device for homogeneous ice nucleation	Microfluidically produced water-in-oil emulsion on cryo-microscopy cold stage; freezing monitored via microscope (alternatively frozen with differential scanning calorimetry)
LED-based Ice Nucleation Detection Apparatus (LINDA)	Sample in tubes held in polycarbonate tray atop an LED array submersed in a water–glycerin cooling bath; freezing monitored via camera
Colorado State University Ice Spectrometer (CSU-IS)	Sample aliquots pipetted into two 96-well PCR trays cooled on custom cold blocks with N_2 flow; freezing monitored via camera
Bielefeld Ice Nucleation ARraY (BINARY)	Droplets pipetted onto a glass slide with separated compartments atop a Peltier cold stage, all enclosed in a, N_2-purged chamber; freezing monitored via camera
Water-Activity-Controlled Immersion Freezing Experiment (WACIFE)	Droplets pipetted onto a glass plate in a humidity-controlled aerosol conditioning cell, then sealed from ambient air and cooled on a cold stage; freezing monitored via microscope
National Institute of Polar Research Cryogenic Refrigerator Applied to Freezing Test (NIPR-CRAFT)	Drops pipetted onto a Vaseline-coated aluminum plate cooled on a cryogenic refrigerator stage; freezing monitored via camera
Karlsruhe Institute of Technology Cold Stage (KIT-CS)	Droplets printed on a silicon substrate by piezo-driven drop-on-demand generator, and drops then covered in silicone oil and placed on cold stage; freezing monitored via CCD camera
Microplate partially submersed in cooling liquid	Droplets contained in 96-well microplates partially submersed in a cooling water–alcohol bath; freezing monitored via infrared camera
Carnegie Mellon University Cold Stage (CMU-CS)	Droplets of water in oil on a substrate in aluminum chamber cooled with a thermoelectric element; freezing monitored via microscope
Microfluidic device and cold stage	Microfluidically generated drops in oil on a glass slide on a cryostage; freezing monitored via microscope camera
Automated Ice Spectrometer (AIS)	Drops in two 96-well PCR trays fitted into aluminum blocks fixed in a liquid cooling bath, all enclosed in an acrylic box; freezing monitored via camera
National Oceanic and Atmospheric Administration Drop Freezing Cold Plate (NOAA-DFCP)	Drops pipetted onto Vaseline-coated copper disk placed on a thermoelectric cold plate and covered in a plastic dome; freezing monitored optically
Peking University Ice Nucleation Array (PKU-INA)	Drops pipetted into compartments on a glass slide atop a cold stage in a N_2-purged box; freezing monitored via CCD camera
WeIzmann Supercooled Droplets Observation on Microarray (WISDOM)	Microfluidically produced droplet array on a PDMS surface placed on a cryostage purged with N_2; freezing monitored via microscope camera
Twin-plate Ice Nucleation Assay (TINA)	Droplets contained in four multiwell plates (2 × 96 and 2 × 384) placed on two custom aluminum cooling blocks; freezing monitored via infrared camera
Freezing on a chip	Drops loaded on a silicon plate with etched cavities and set on thermoelectric cooler in an N_2-flushed cell; freezing monitored via camera
InfraRed Nucleation by Immersed Particles Instrument (IR-NIPI)	Drops pipetted into 96-well plate on a cold stage enclosed in a chamber; freezing monitored via infrared camera
Ice Nucleation Droplet Array (INDA)	Samples placed in wells of a 96-well PCR tray cooled in a cooling bath; freezing monitored via CCD camera
Leipzig Ice Nucleation Array (LINA)	Droplets pipetted into compartments on a glass slide and cooled on a Peltier element; freezing monitored via CCD camera
Microfluidic droplet freezing assay	Microfluidically produced droplets in oil collected in microwells on glass slides placed on a Peltier cold stage in an airtight chamber; freezing monitored via microscope camera
Drop freeze assay experiment directly on exposed filters	Droplets pipetted onto filters placed on a glass slide and cold stage in an N_2-purged chamber; freezing monitored via camera
West Texas Cryogenic Refrigerator Applied to Freezing Test (WT-CRAFT)	Drops pipetted onto Vaseline-coated aluminum plate and cooled on a cryogenic refrigerator stage; freezing monitored via camera
DRoplet Ice Nuclei Counter Zurich (DRINCZ)	Droplets pipetted into 96-well PCR tray submersed in ethanol cooling bath; freezing monitored via camera
Cold stage to detect the most active INP in single crystals	Ice crystals placed with ultrapure water on a copper cold plate, melted, and refrozen; freezing monitored via manual inspection
“Store and create” microfluidic device	Microfluidically generated droplets in oil in microwells of a PDMS chip placed on a cold plate sealed with an acrylic lid; freezing monitored via microscope camera
Pyroelectric thermal sensor for ice nucleation	Drops pipetted onto Vaseline-coated pyroelectric polymer atop a cooling block; freezing monitored via pyroelectric thermal sensor
University of Toronto Drop Freezing Technique (UT-DFT)	Drops pipetted into multiwell PCR trays cooled in an ethylene glycol water bath; freezing monitored via camera
Ice Nucleation SpEctrometer of the Karlsruhe Institute of Technology (INSEKT)	Drops pipetted into two 96-well PCR trays cooled in custom cooling blocks; freezing monitored via camera
Lab-On-a-Chip Nucleation by Immersed Particle Instrument (LOC-NIPI)	Water-in-oil droplets mirofluidically generated in continuous flow and passed over a series of Peltier cold plates in an N_2-purged container; freezing monitored via microscope camera
Freezing Ice Nuclei Counter (FINC)	Drops pipetted into three 96-well Piko PCR trays submersed in ethanol cooling bath; freezing monitored via camera

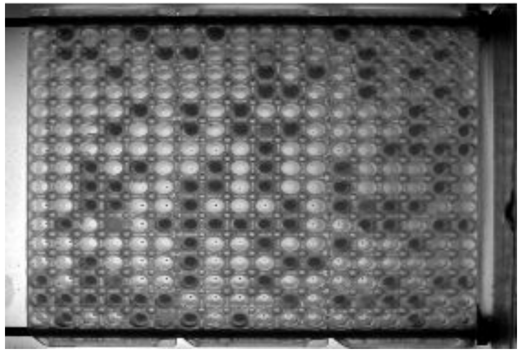
Characteristics:

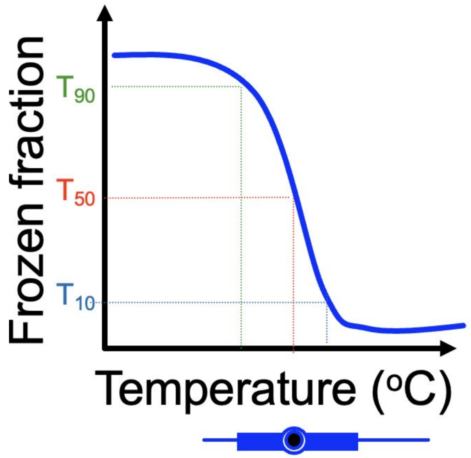
- droplet size
- number of droplets per experiment
- surface
- droplet shape
- low water background

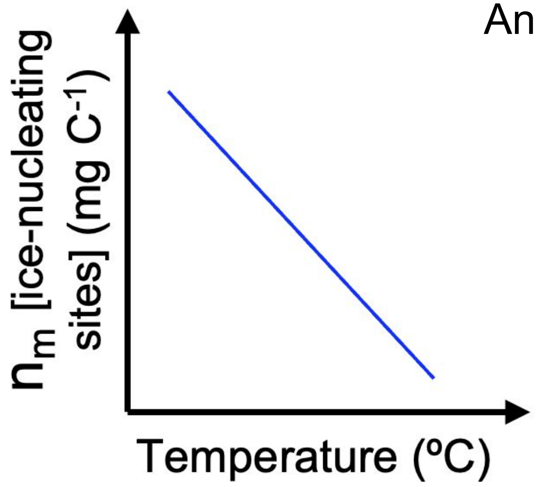
Miller, Brennan, Mignani, Wieder, David, Borduas-Dedekind, *Atmos. Meas. Tech.*, **2021**, *14*, 3131

Drop Freezing Ice Nuclei Counter (FINC)









Killian Brennan

Anna Miller

Miller, Brennan, Mignani, Wieder, David, Borduas-Dedekind, *Atmos. Meas. Tech.*, **2021**, *14*, 3131
David et al., *Atmos. Meas. Tech.* **2019**, *12*, 6865

How clean are our backgrounds and handling blanks?

Atmos. Meas. Tech., 11, 5315–5334, 2018
https://doi.org/10.5194/amt-11-5315-2018

Atmospheric Measurement Techniques
Open Access
EGU

Cleaning up our water: reducing interferences from nonhomogeneous freezing of "pure" water in droplet freezing assays of ice-nucleating particles

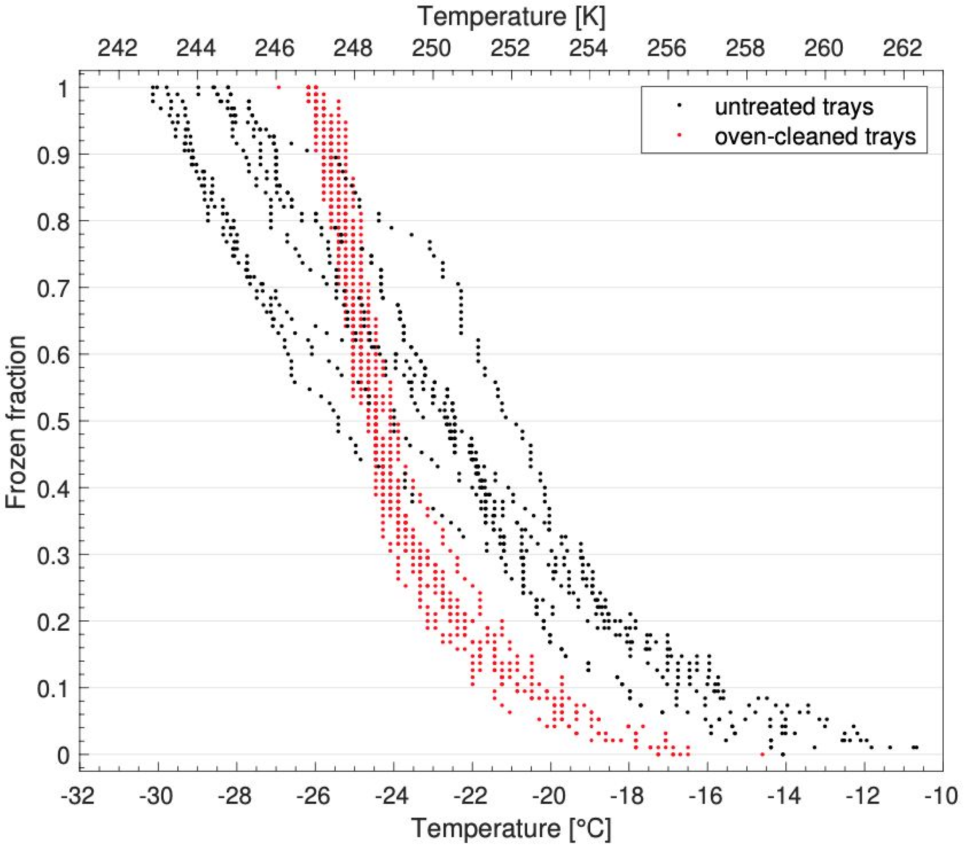
Michael Polen, Thomas Brubaker, Joshua Somers, and Ryan C. Sullivan
Center for Atmospheric Particle Studies, Carnegie Mellon University, Pittsburgh, Pennsylvania, USA

Atmospheric Research 250 (2021) 105419
Contents lists available at ScienceDirect
Atmospheric Research
journal homepage: www.elsevier.com/locate/atmosres
ELSEVIER

Check for updates

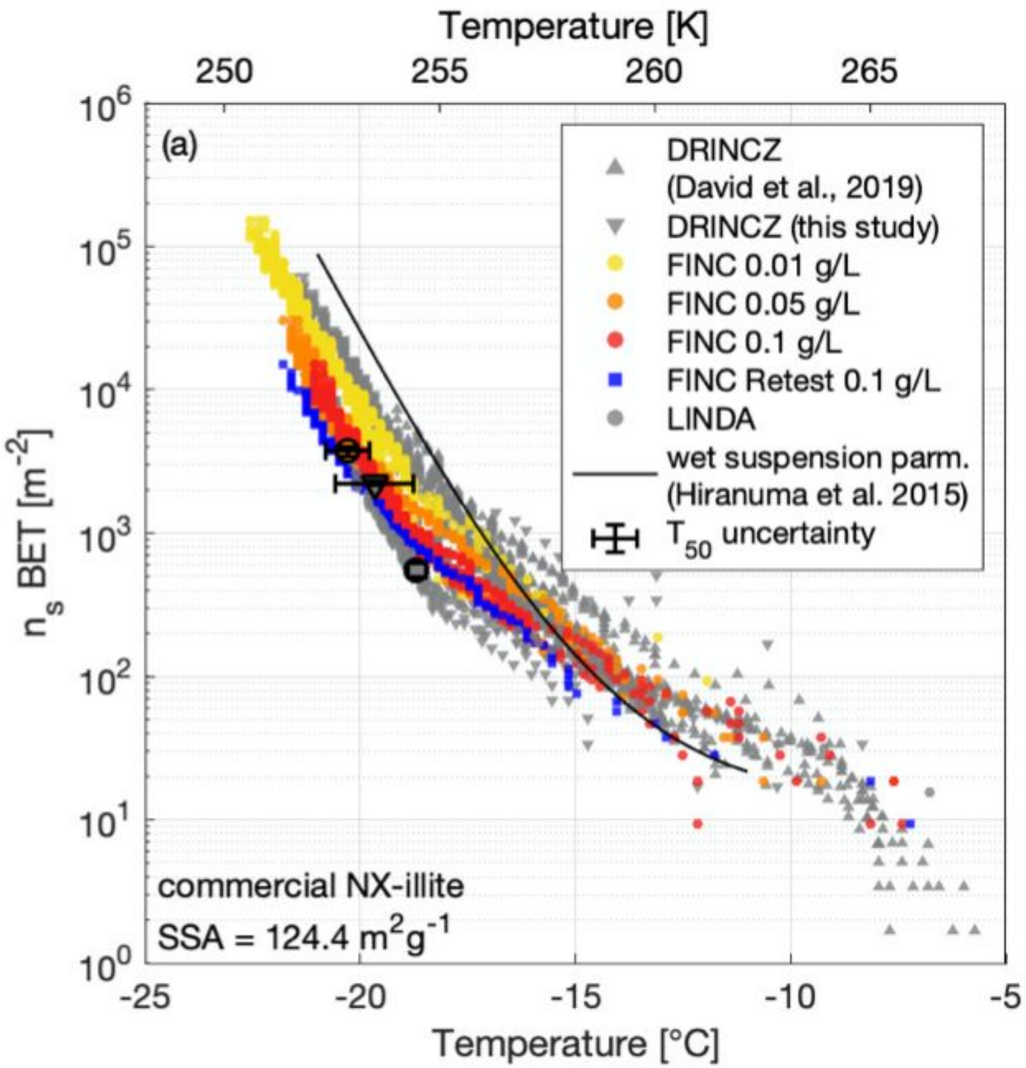
Pragmatic protocols for working cleanly when measuring ice nucleating particles

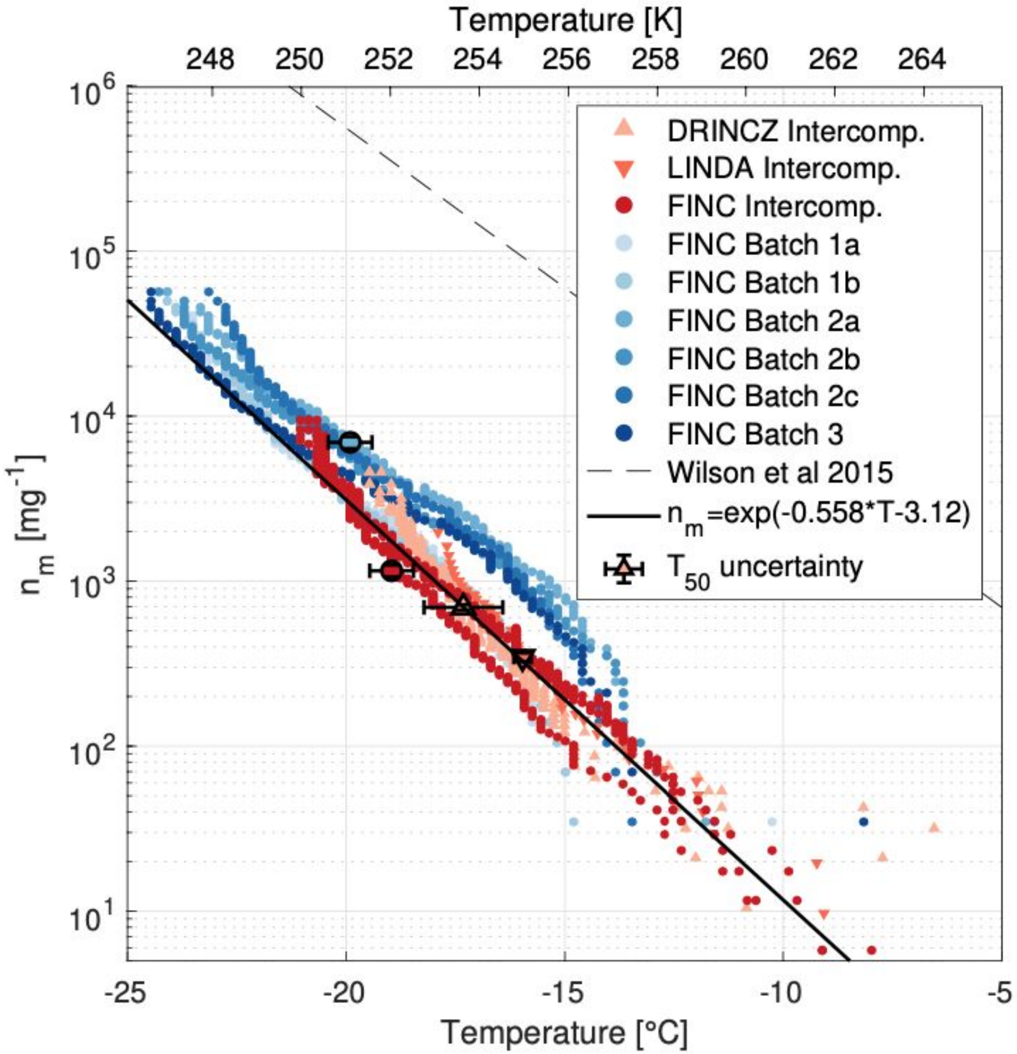
Kevin R. Barry[a,*], Thomas C.J. Hill[a], Conrad Jentzsch[b,c], Bruce F. Moffett[d], Frank Stratmann[b], Paul J. DeMott[a]



Miller, Brennan, Mignani, Wieder, David, Borduas-Dedekind, *Atmos. Meas. Tech.*, **2021**, *14*, 3131

FINC validation: Lignin as an immersion freezing standard



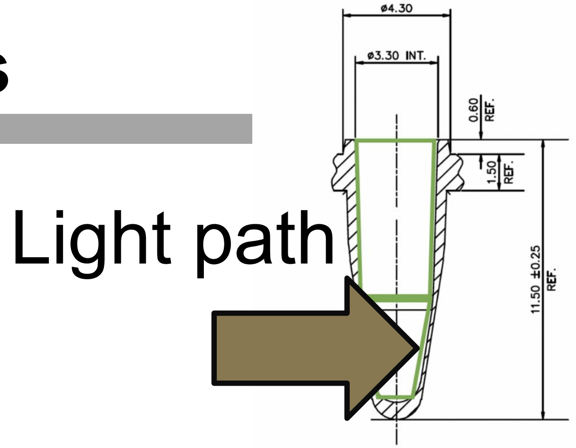



Killian Brennan

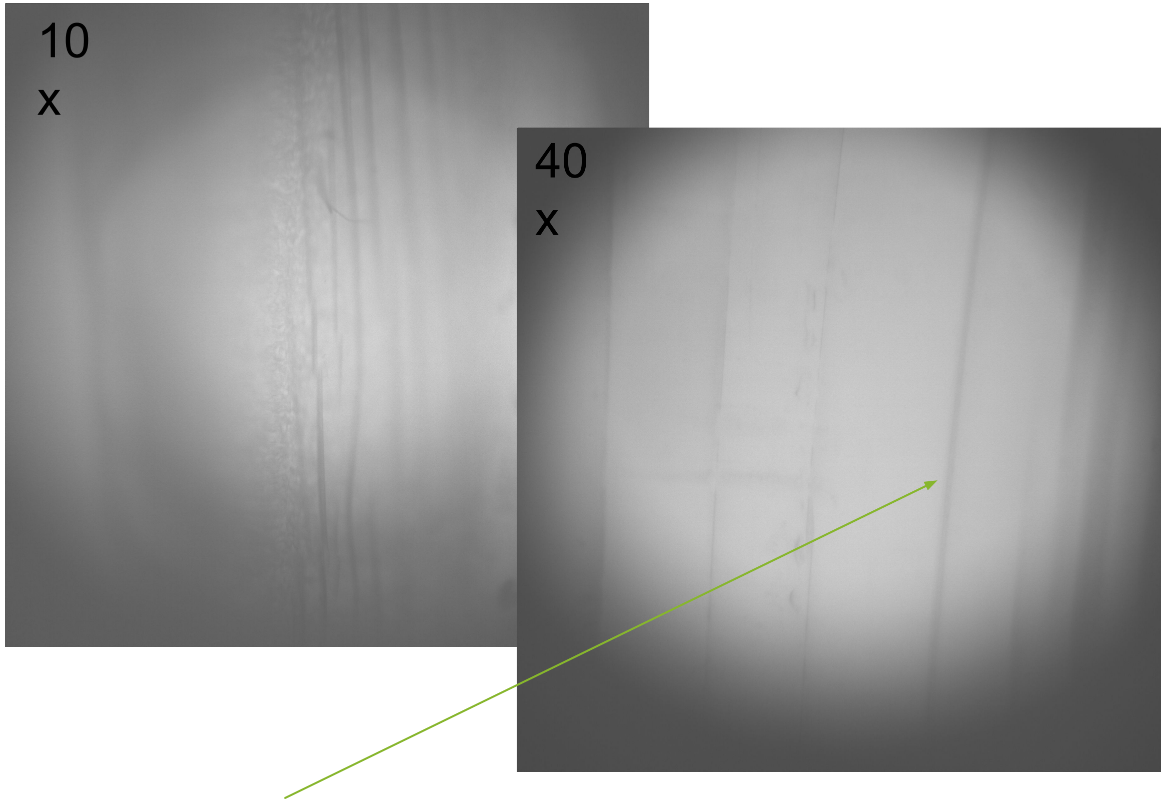

Anna Miller

Miller, Brennan, Mignani, Wieder, David, Borduas-Dedekind, *Atmos. Meas. Tech.*, **2021**, *14*, 3131

The role of the plastic/water and air/water interfaces

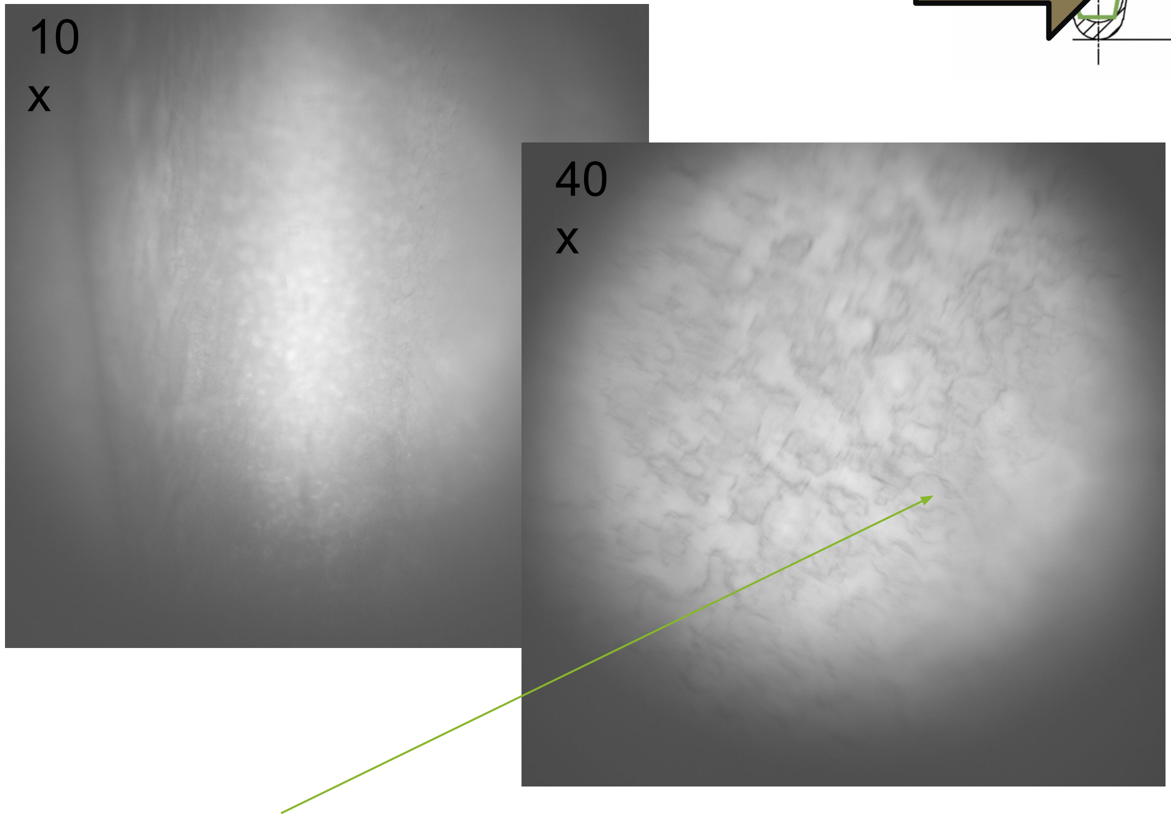


- Non heated



Gaps seen in the inner-surface of the PCR tray from the manufacturing process

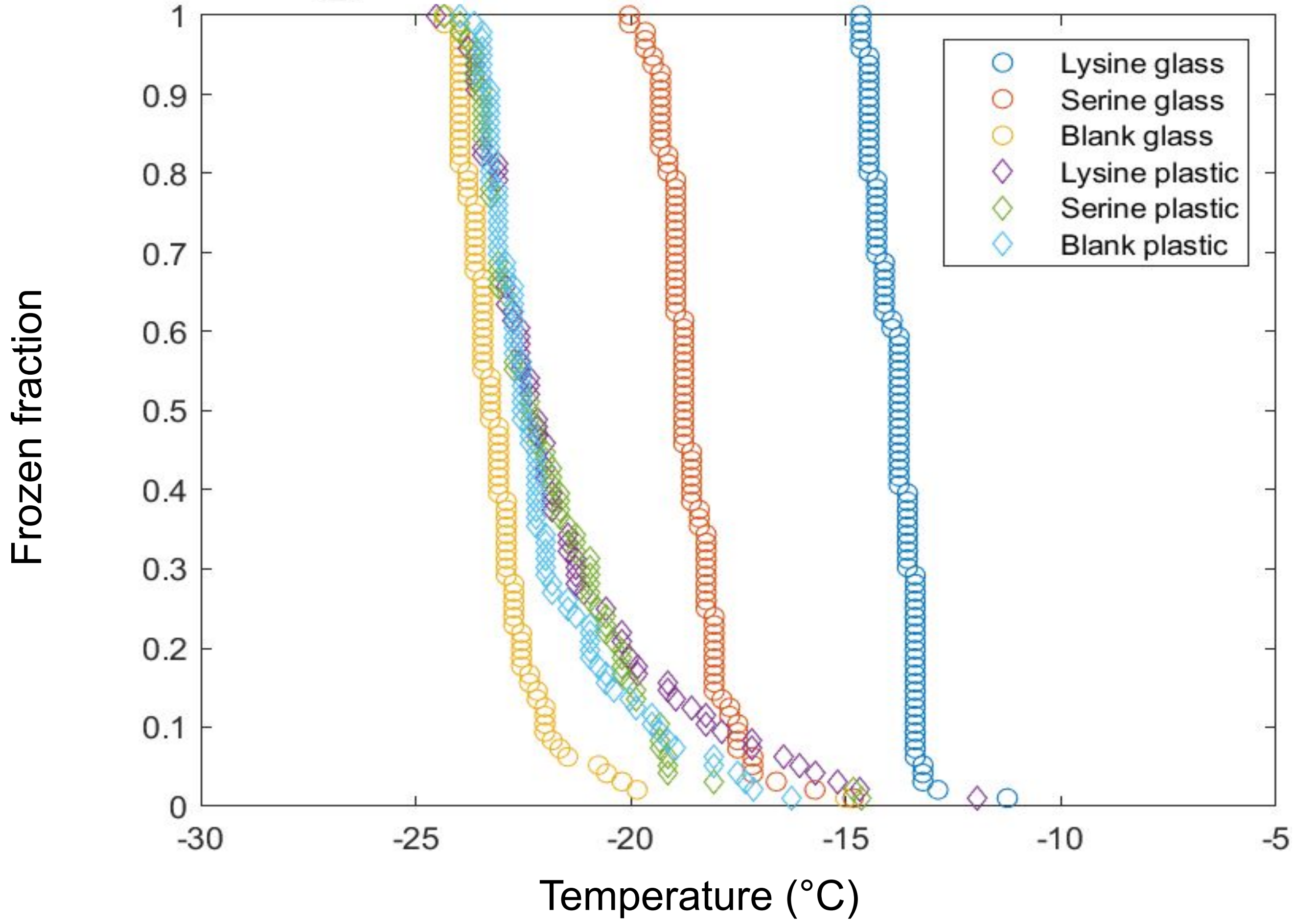
- Heated, 120 °C, 2 h

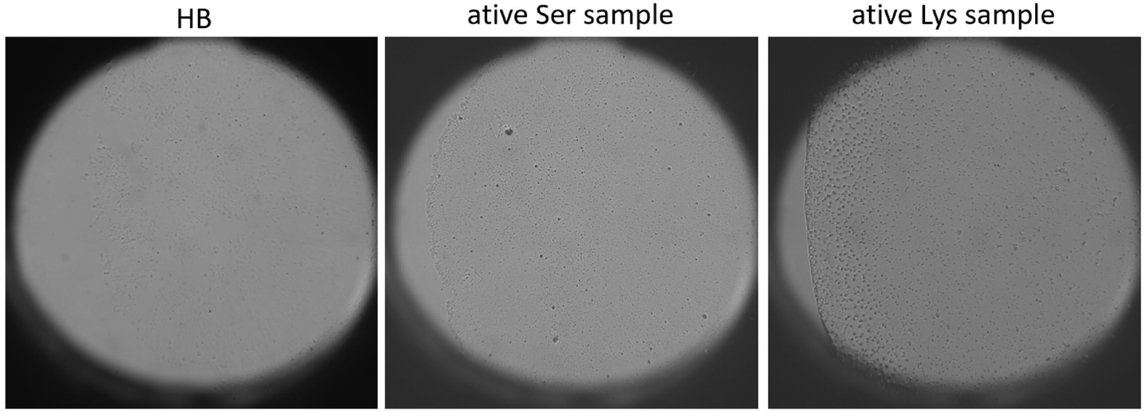


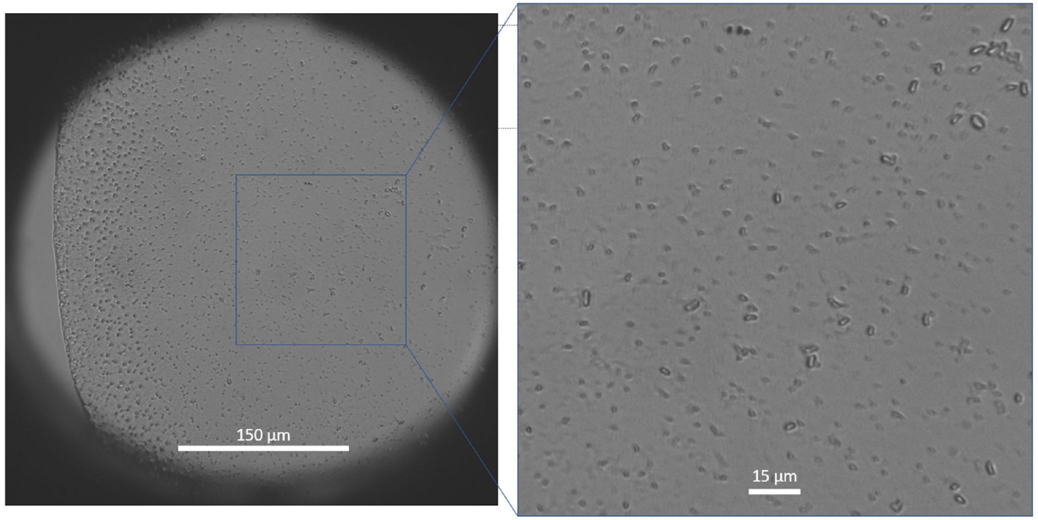
Gaps disappear following heat treatment

Avoid glassware!

Water + amino acids



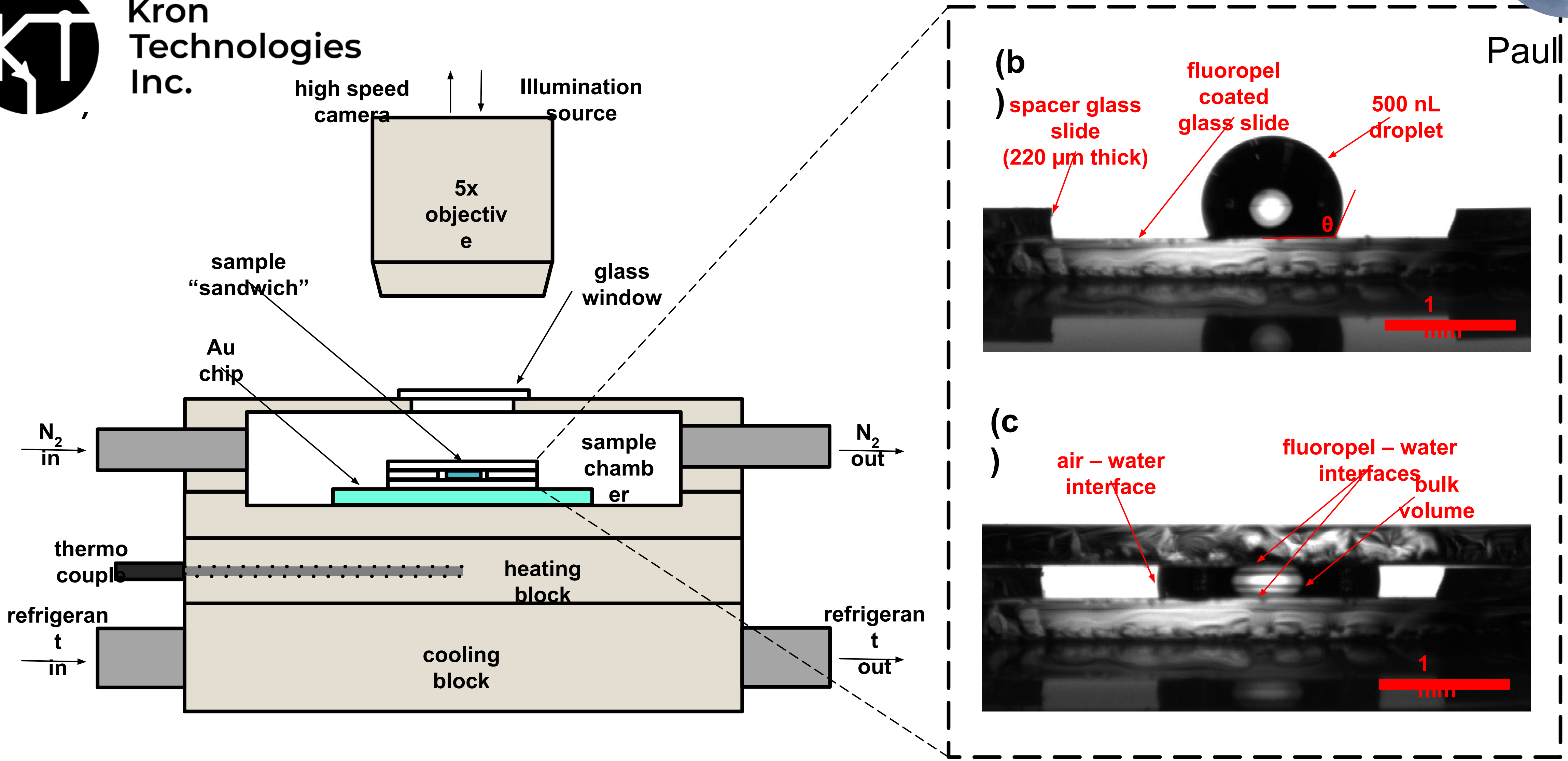




Probing the role of the air-water interface experimentally

Paul Bieber

Kron Technologies Inc.



High speed imaging of supercooled droplets (2100 f/s)

Paul Bieber

1-Docosanol

(positive control)

Birch pollen extract

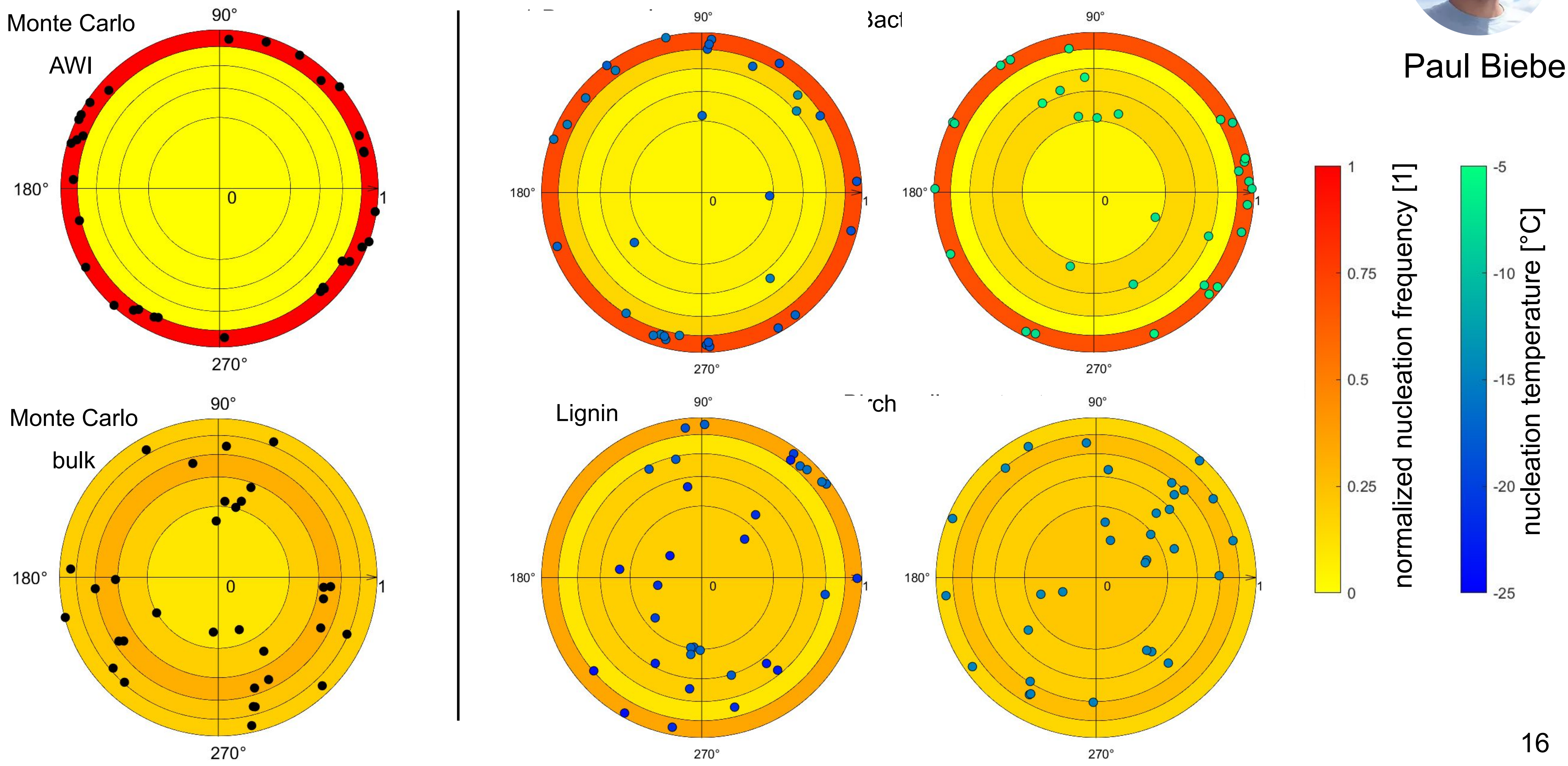
Betula pendula

Bacterial proteins

inaZ, *Pseudomonas syringae*

Statistics of nucleation at the air-water interface

Paul Bieber

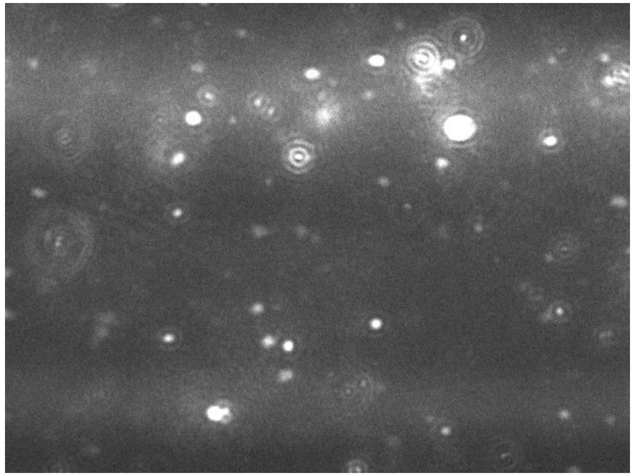


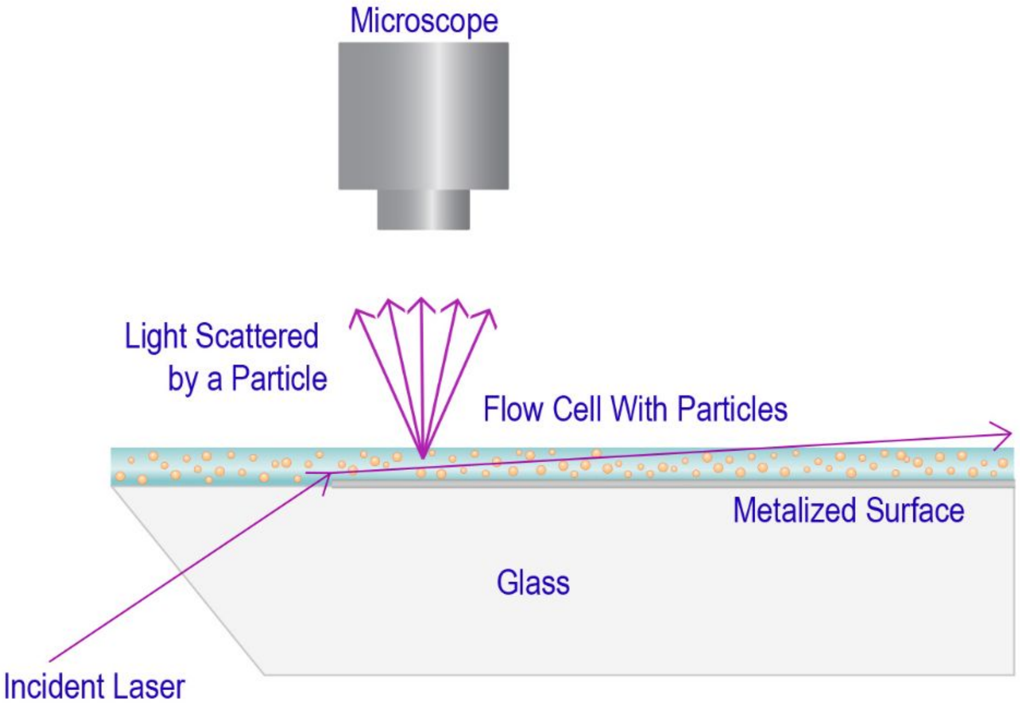
Further probing the aggregation of lignin

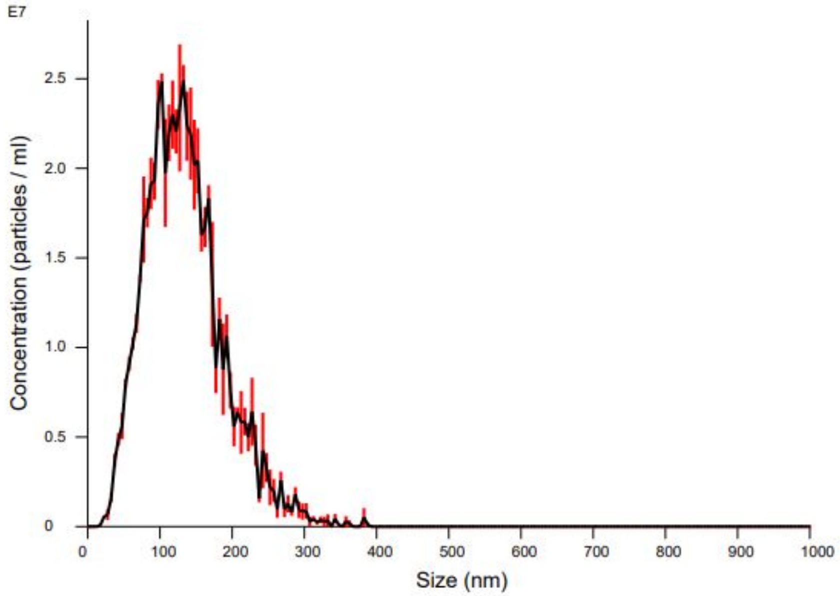
Paul Bieber

Nano Particle Tracking Analysis (NTA)

- Light scatters on nano mater sized particles in a solution
- The motion is proportional to the size of the particles

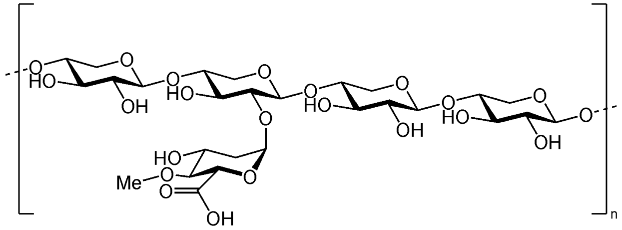




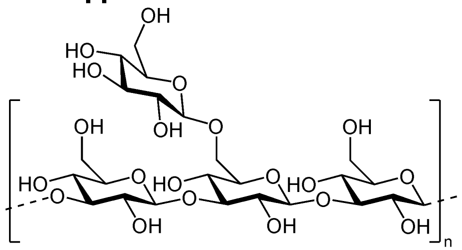


Ice nucleating (bio)organic macromolecules

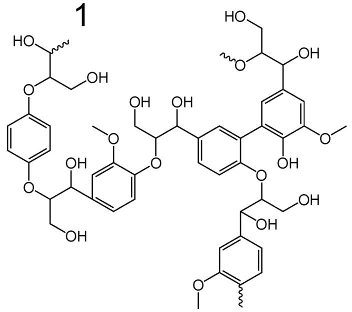
Xylan

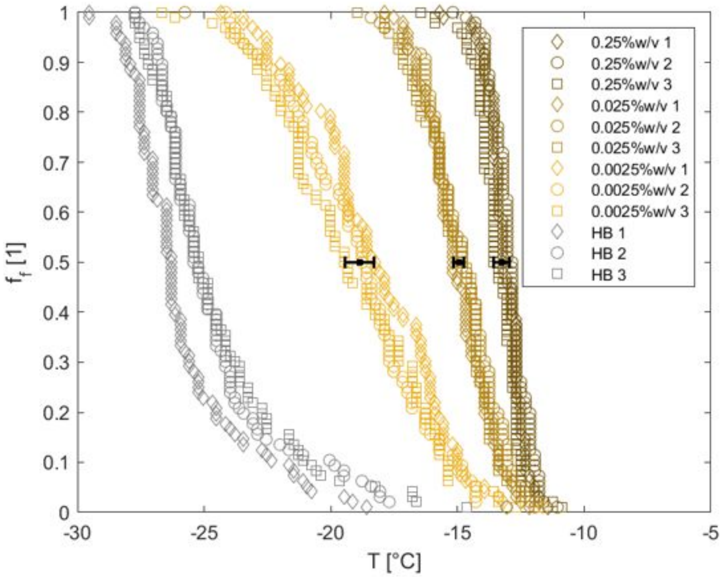


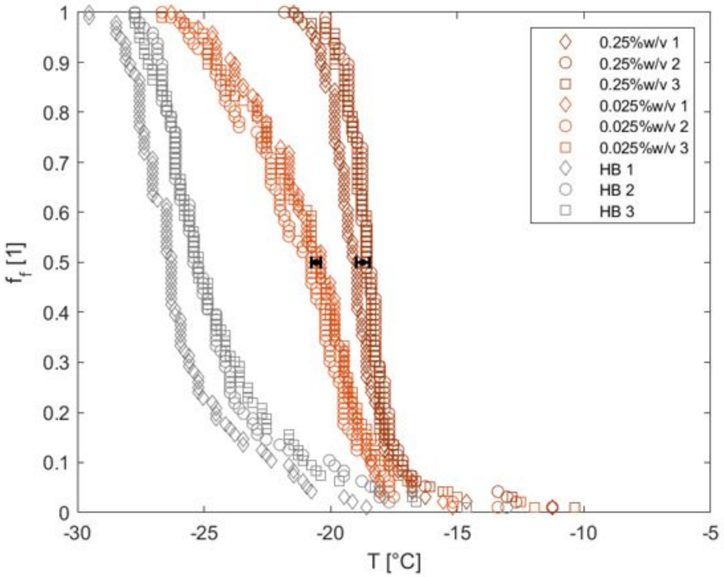
Laminarin

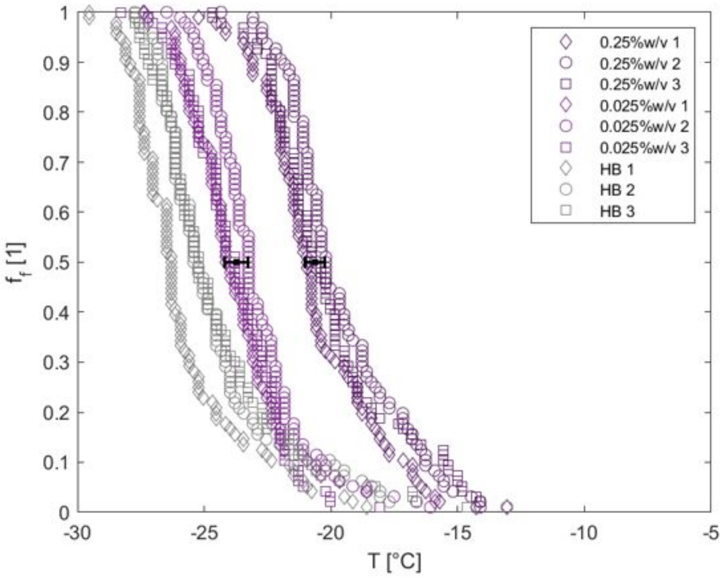


Lignin[1]







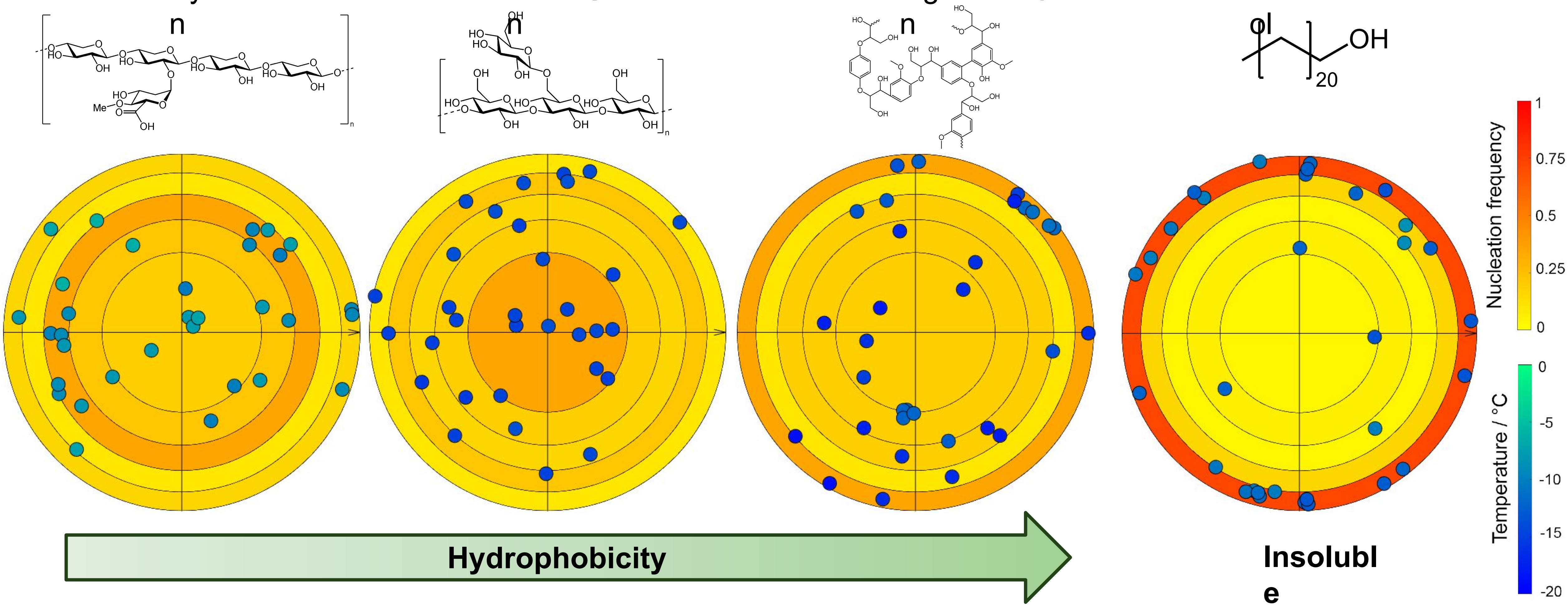


Bieber et al., *in prep.*

[1] Bogler & Borduas, *ACP*,

Ice nucleating (bio)organic macromolecules
High-speed microscopy

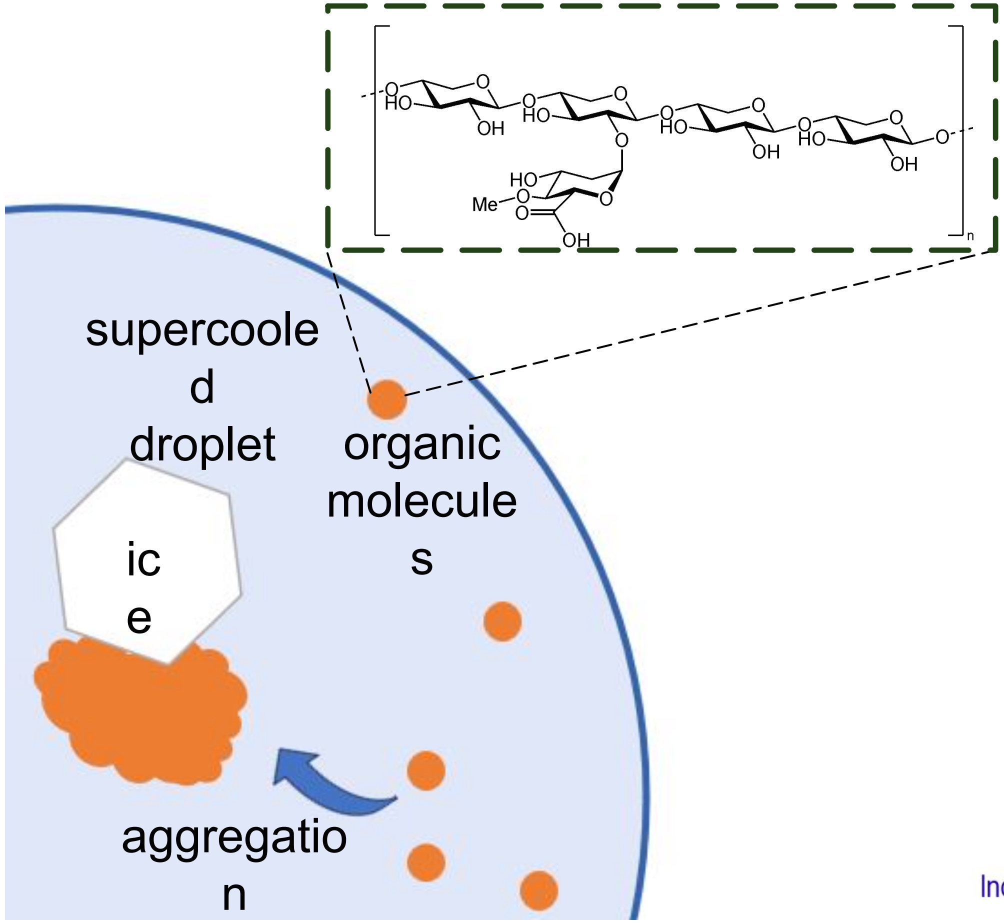
Xylan | Laminarin | Lignin | Docosanol



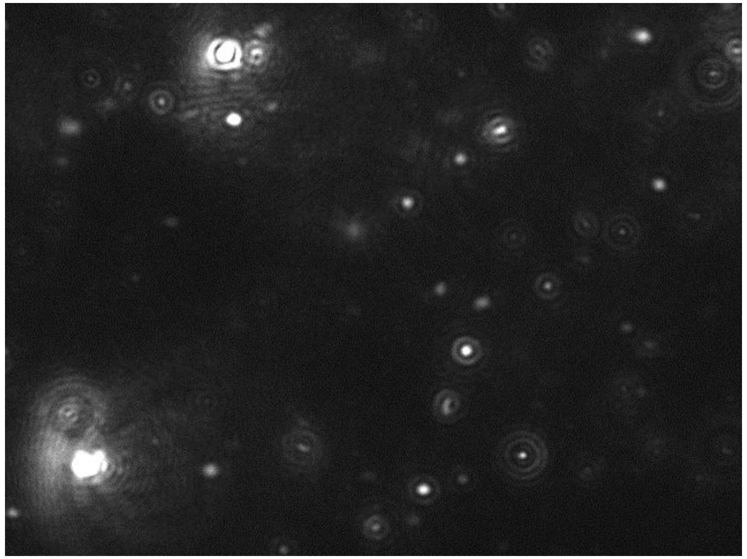
□ Dissolved organic material shows little or no affinity for ice nucleation at the air-water interface

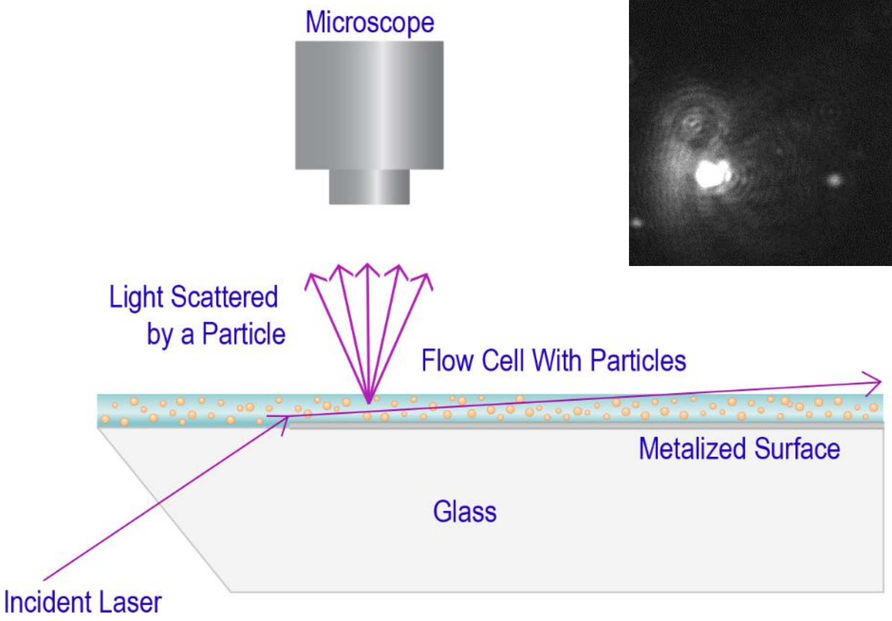
Bieber et al., in

Less hydrophobic organic nano aggregates nucleate ice in the bulk



Nanoparticle tracking analysis (NTA)





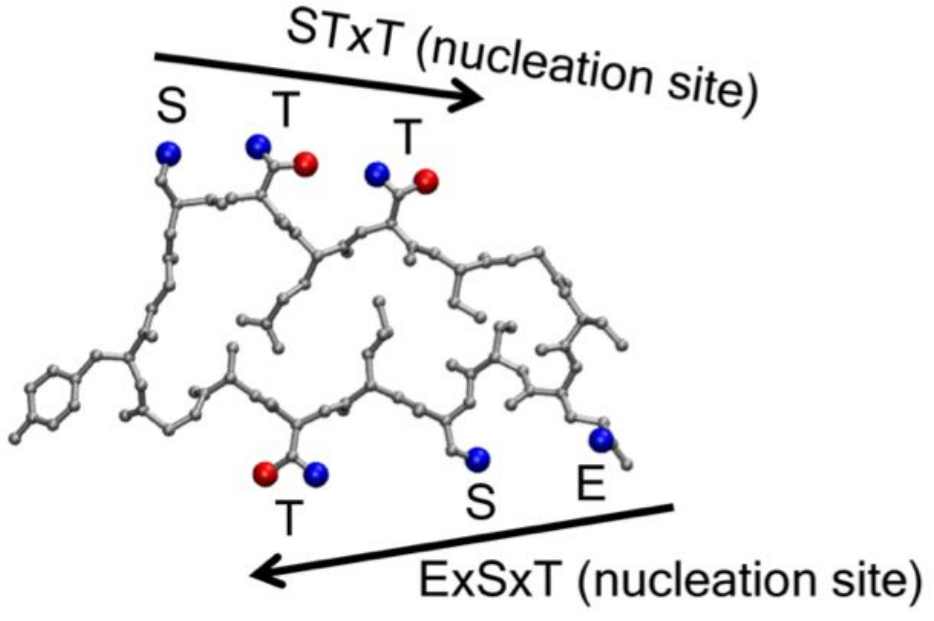
Bieber et al., in

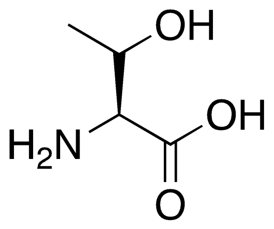
Adapted from https://particletechlabs.com/analytical-testing/nanoparticle-tracking-analysis/ accessed 30.03.23

Molecular dynamic simulations

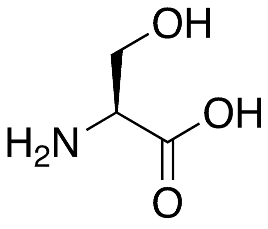
- Fundamental mechanism and H-bonding

  β-helix exposes water to a flat array of threonine (T) repeating unit TxT

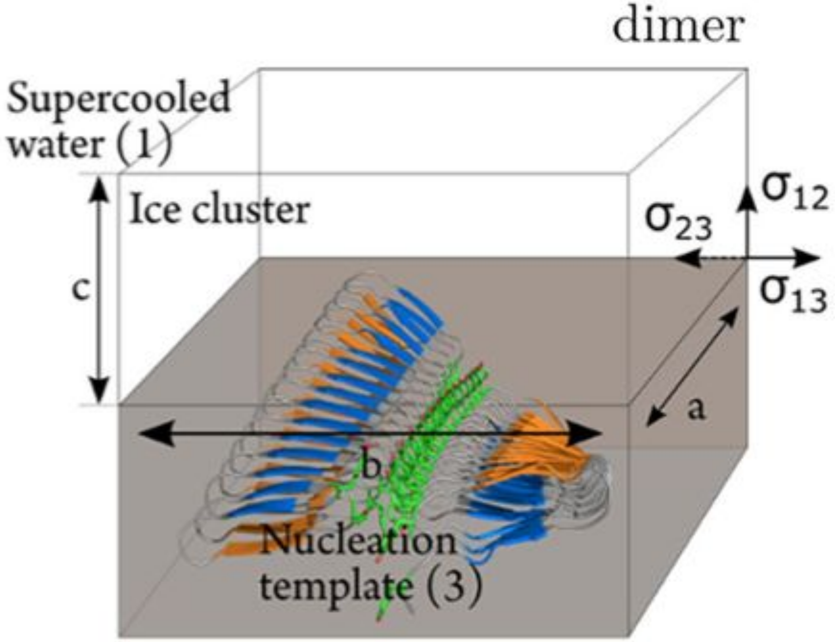




Threonine (T)



Serine (S)

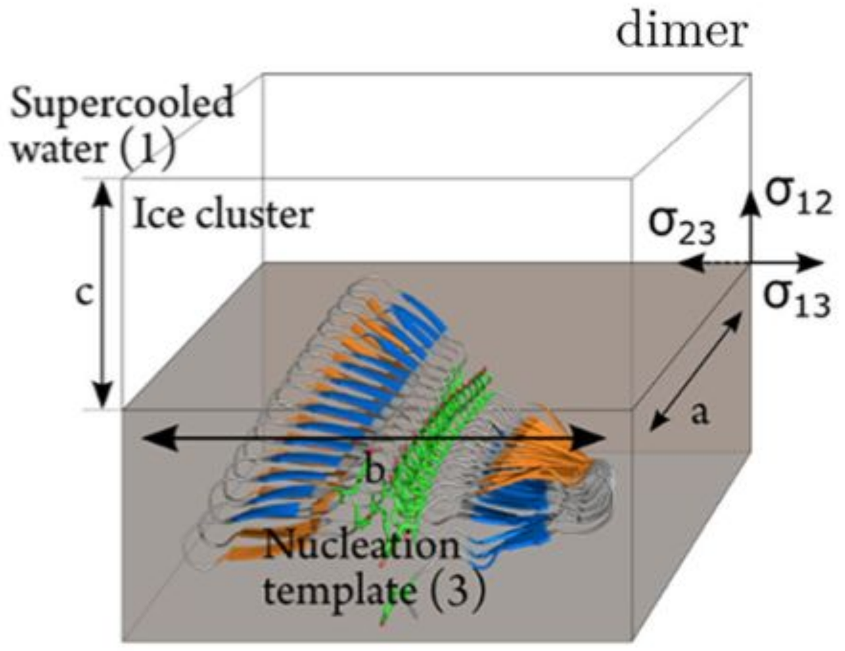


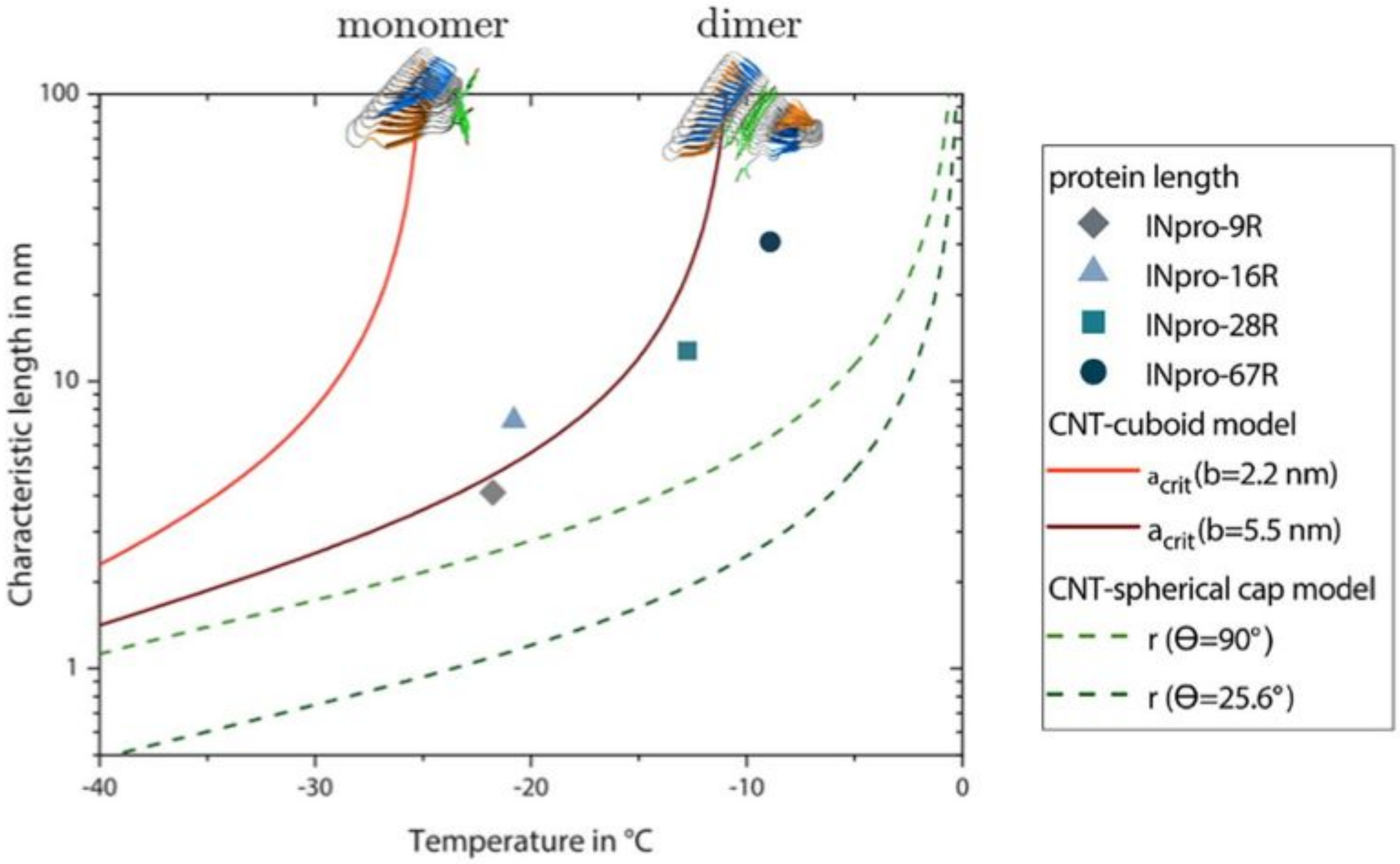
Hudait, Odendahl, Qiu, Paesani, Molinero, *J. Am. Chem. Soc.*, **2018**, *140*, 4905

Hartmann et al., *Front. Microbiol.*, **2022**, *13*, 872306.

Role of dimerization for the INAz protein to nucleate

Structure and Protein-Protein Interactions of Ice Nucleation Proteins Drive Their Activity





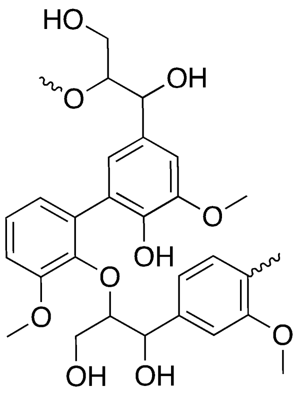
Hartmann et al., *Front. Microbiol.*, **2022**, *13*, 872306.

How does lignin nucleate ice?

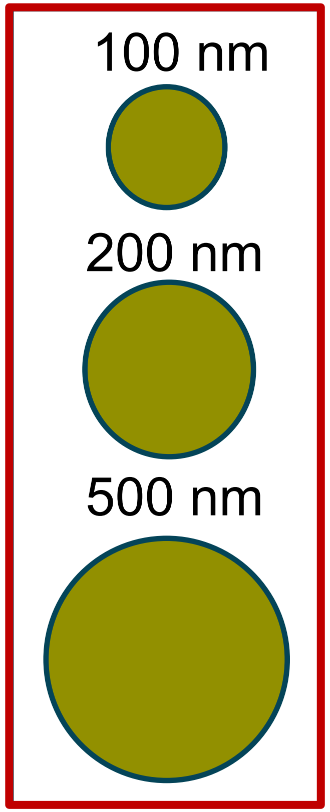
Anna Zeleny

A bottom-up approach to probe and understand ice nucleation mechanisms.

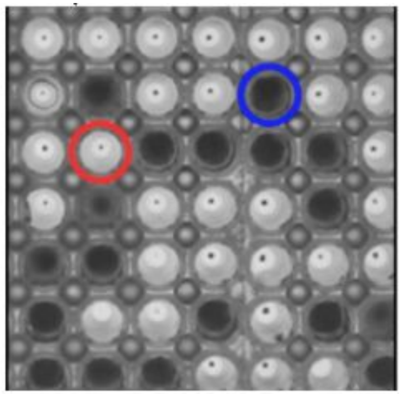
Dr. Jingqian Chen

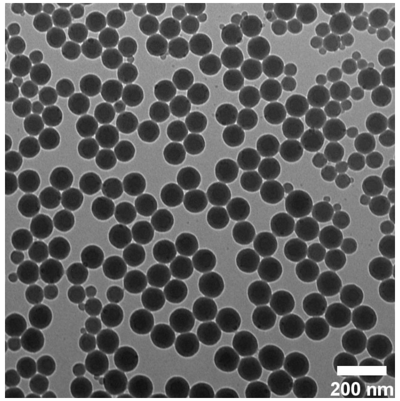


Synthesize



Measure

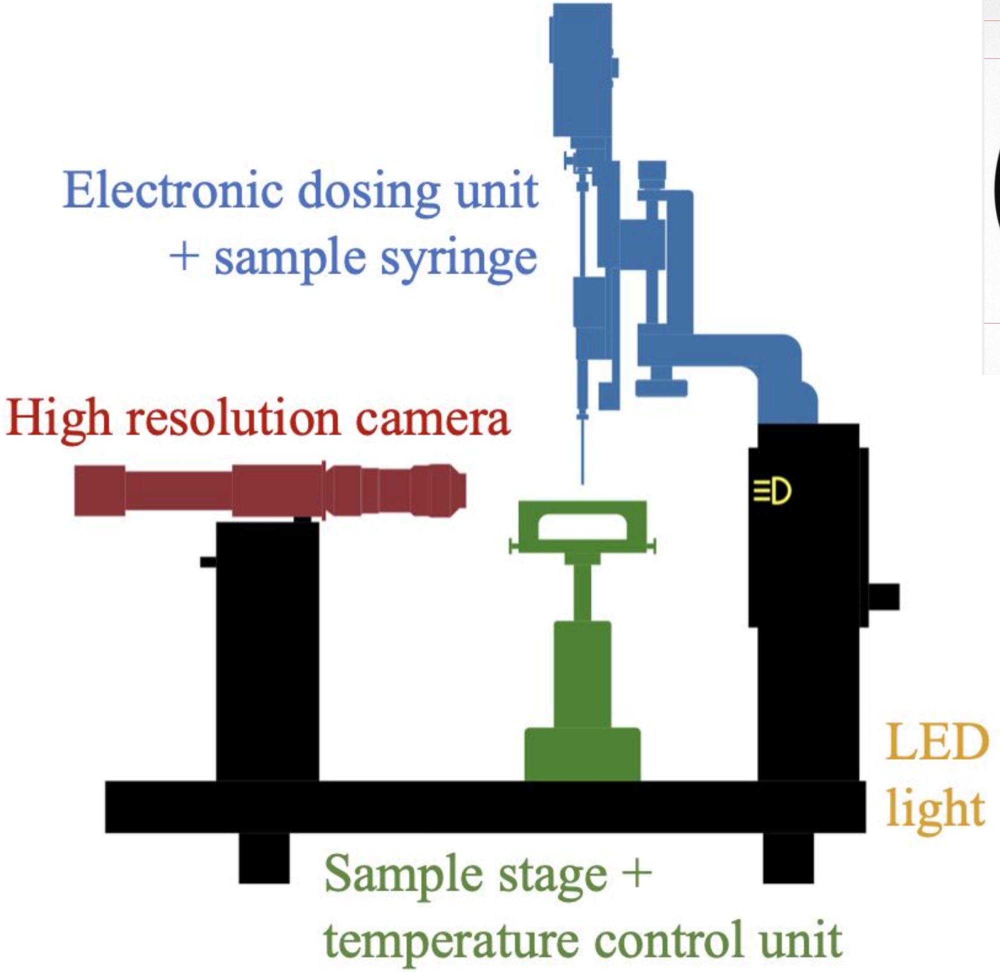


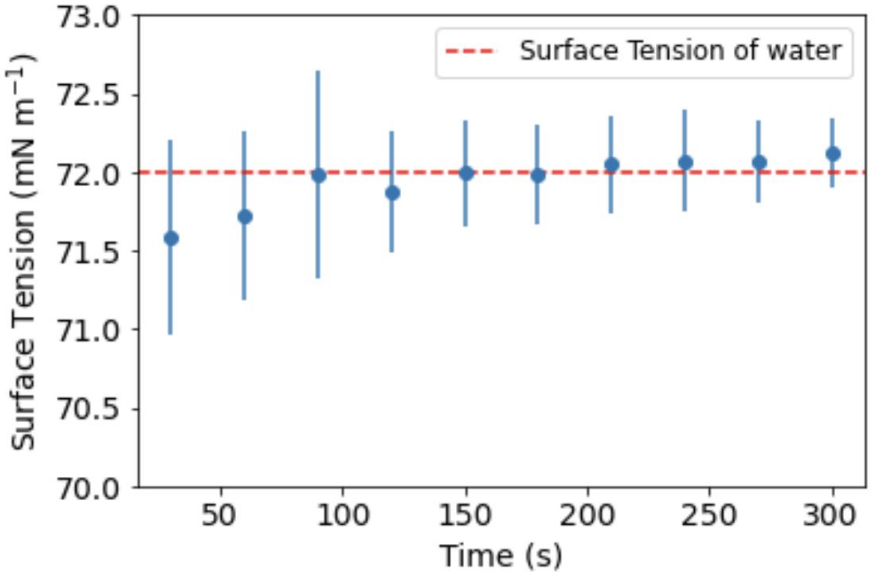


Inform

BrC

Optical Contact Angle (OCA) tensiometer



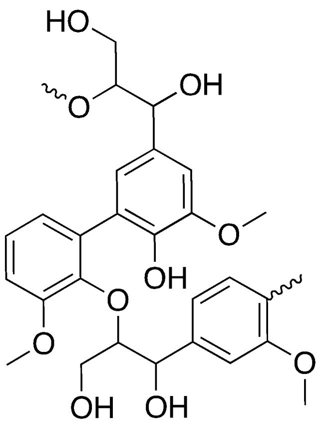


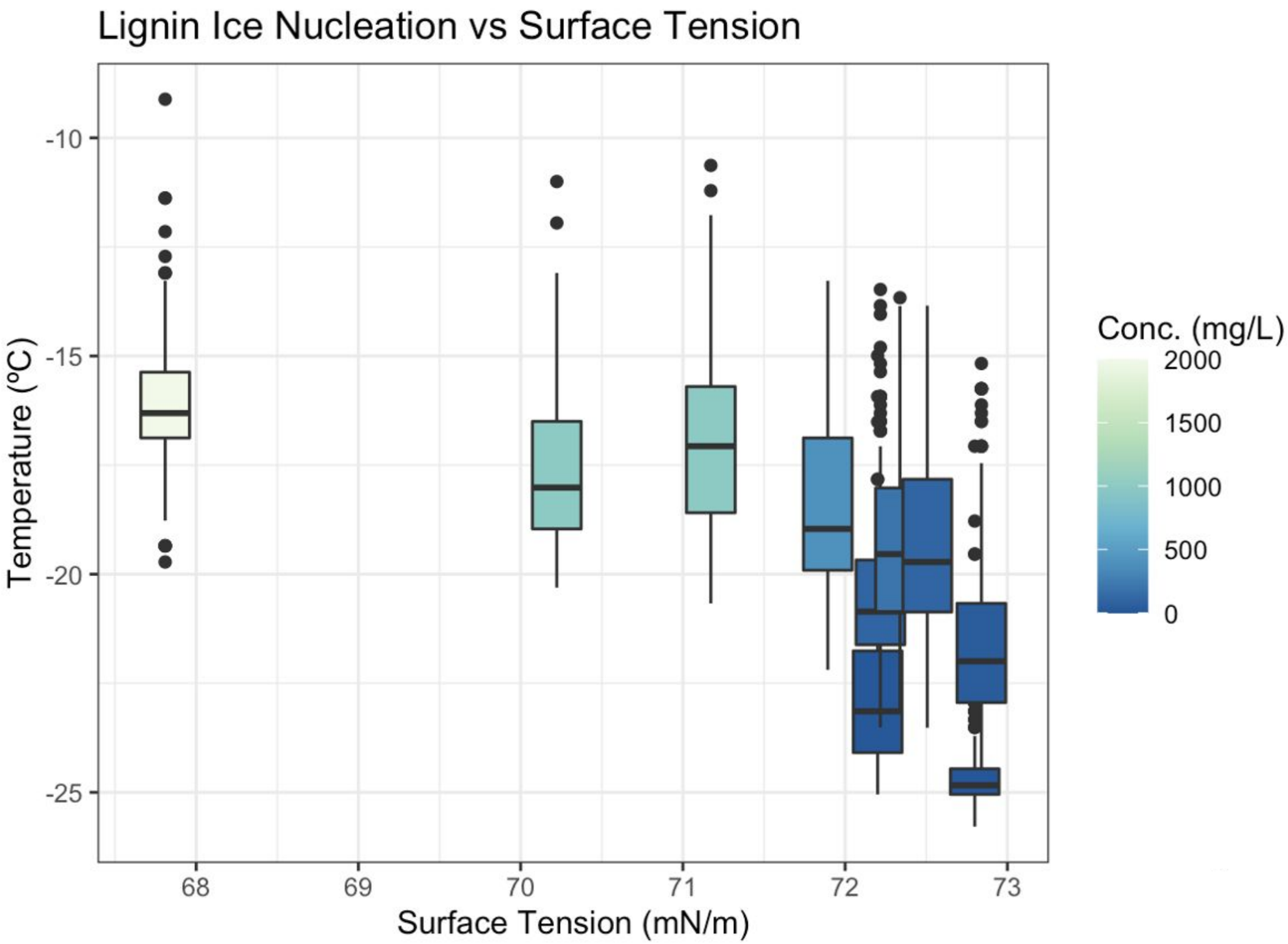
Katie Thompson
(U Leeds)

Nicole Link

Thompson, Link, Murray, Borduas-Dedekind, *in preparation*

Surface tension and ice nucleating ability of lignin





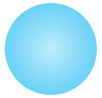
Katie Thompson (U Leeds)

Nicole Link

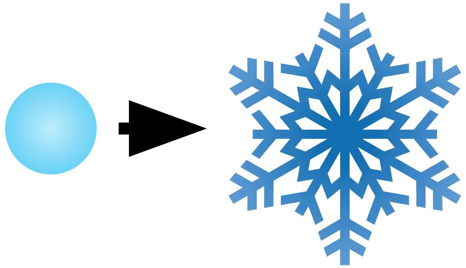
Thompson, Link, Murray, Borduas-Dedekind, *in*

Can We Even Observe Microphysics?

Cloud microphysics: Formation, growth, and transformation of cloud droplets and ice crystals



Condensation & evaporation
Collision & coalescence



Nucleation:
- Homogeneous nucleation
- Heterogenous nucleation

Bergeron-Findeisen process

Deposition & sublimation
Ice aggregation
Riming
Secondary ice processes:
- Rime splintering (H-M)
- Collisional breakup
- Frozen droplet breakup

Atmospheric ice nucleation by organic matter

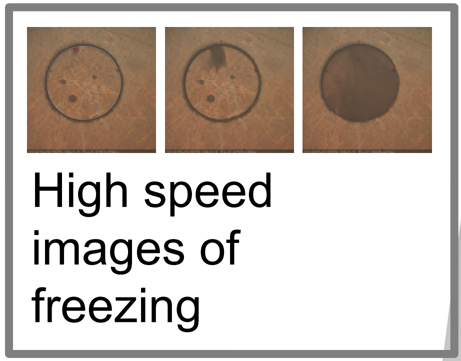
Brennan et al., *Atmos. Chem. Phys.*, **2020**, *20*, 163

Borduas et al, *Atmos. Chem. Phys.* **2019**, *19*, 12397

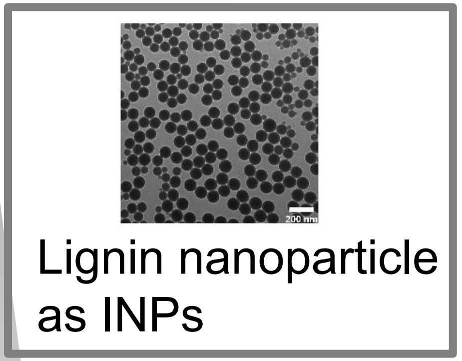
Paul Bieber

Émilie Payment

Emily Chiao



Bieber & Borduas, *Sci. Adv.* **2024**,

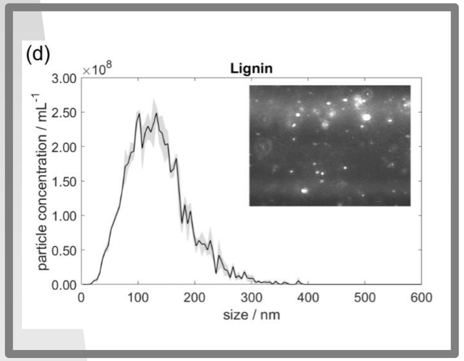


Zeleny et al., *ACS ES&T Air*, **2024**, revisions

Müller, et al. *ACS Environ. Au*, **2023**, *3*, 164

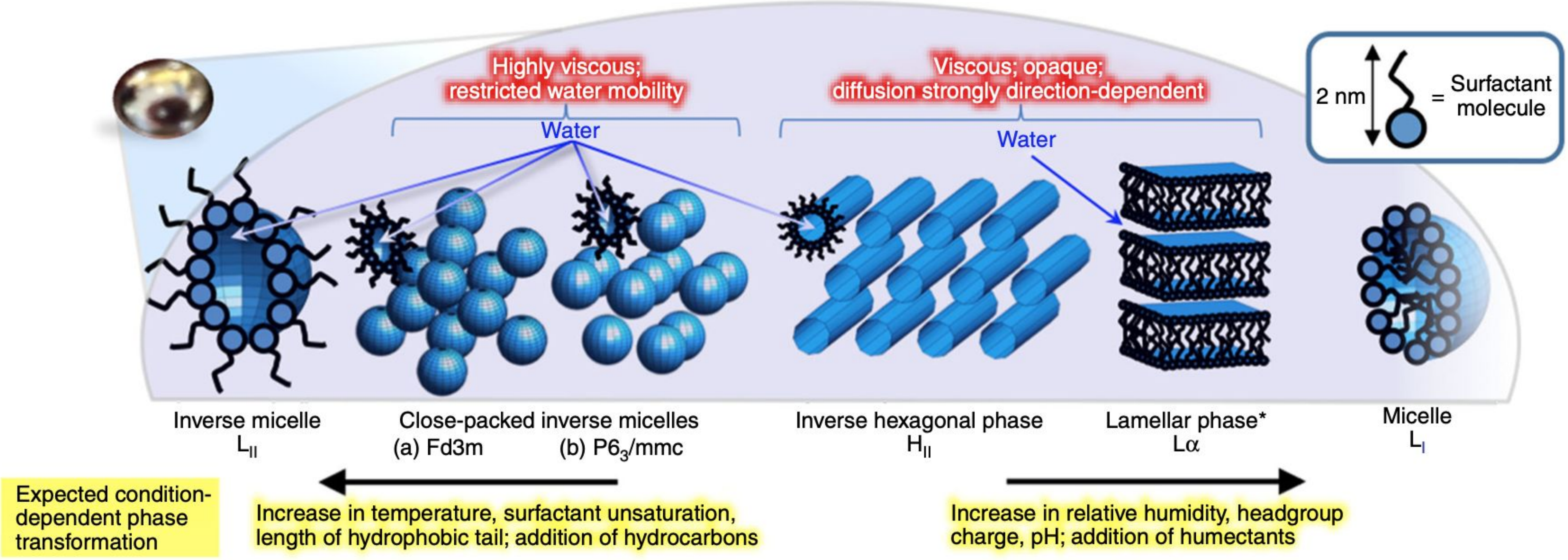
Thompson, et al. *Atmos. Chem. Phys*, **2024**, under review

Miller, Brennan, et al., *Atmos. Meas. Tech.* **2021**, *14*, 3131



Bieber et al., *J. Chem. Phys.* **2024**,

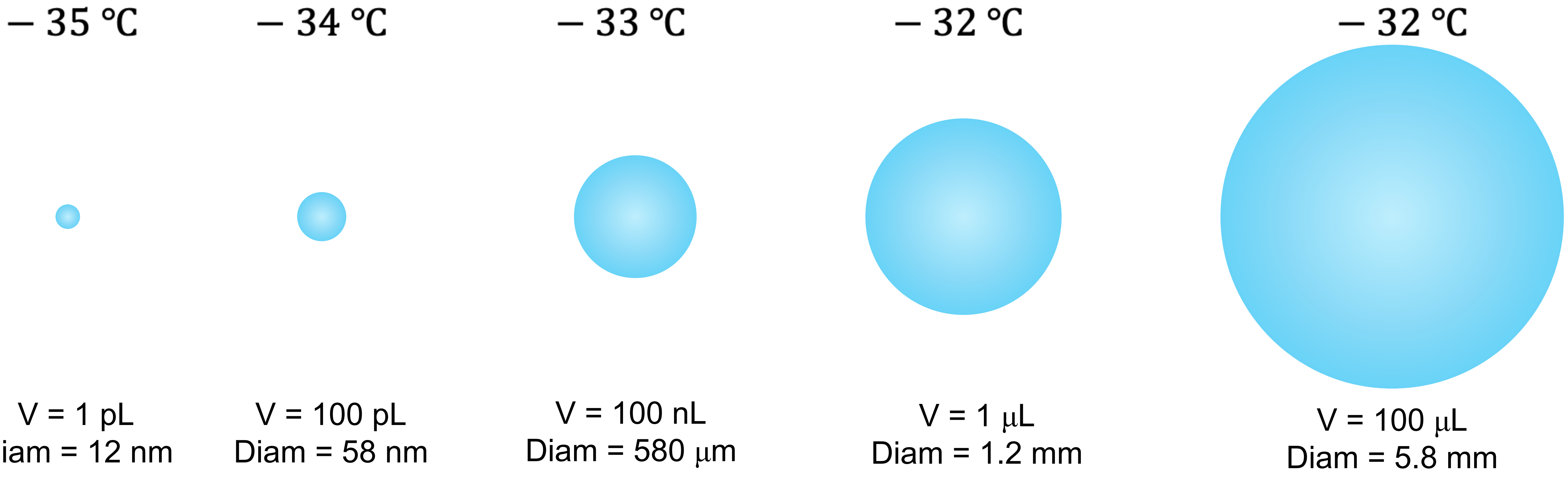
3D self-assembly in proxies for atmospheric aerosols



Pfrang, Rastogi, Cabrera-Martinez, Seddon, Dicko, Labrador, Plivelic, Cowieson, Squires, *Nature Comm.*, **2017**, *8*, 1724

Volume and rate of freezing

- When it takes < 1 s for 50% of spherical droplets to theoretically freeze homogeneously
- Nucleation is stochastic process from size fluctuations of the initial ice germ

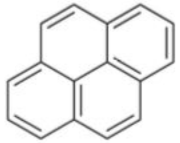


Pao K Wang, "Physics and Dynamics of Clouds and Precipitation: Chapter 7 Nucleation" **2013**

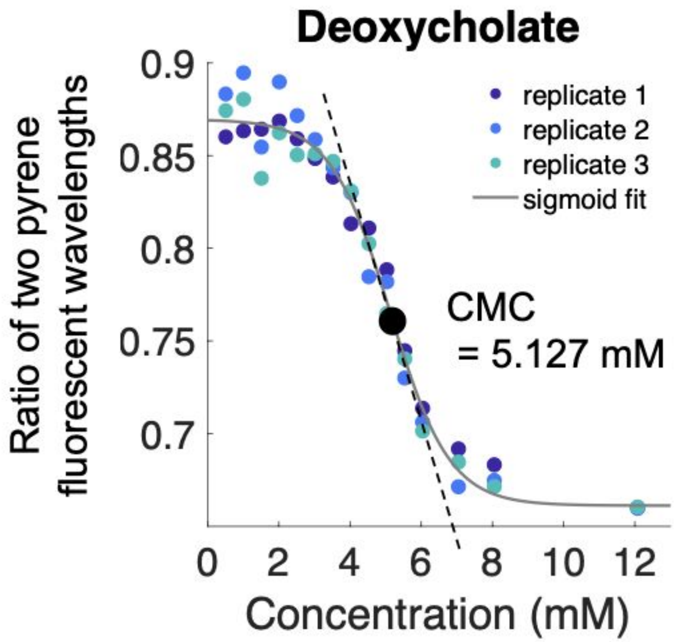
Role of micelle formation for ice nucleation of lignin

CMC determination

Pyrene fluorescence



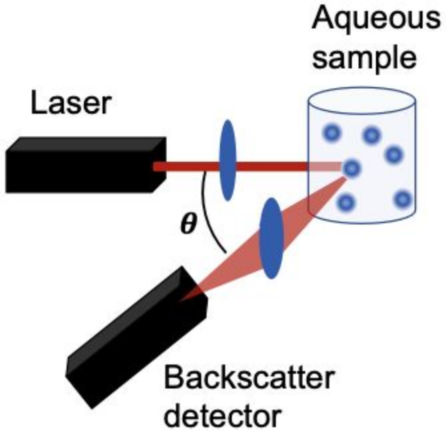
Pyrene fluoresces differently when in a polar (aqueous) vs. nonpolar (interior of micelle) microenvironment

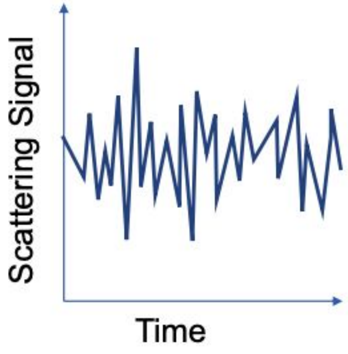


Anna Miller

Micelle size characterization:

Dynamic light scattering (DLS)

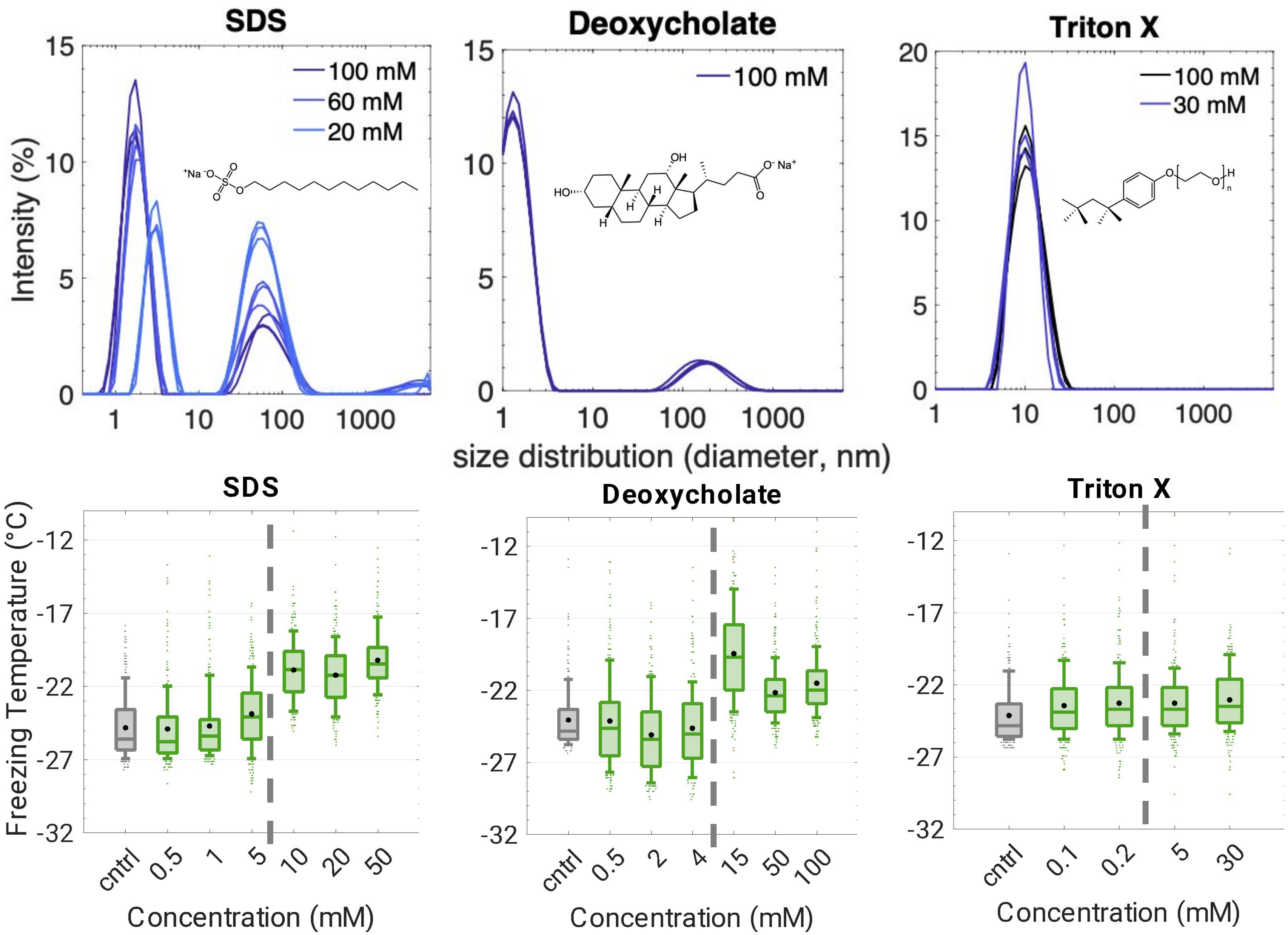




- measure of Brownian motion
- Hydrodynamic particle size
- Size distributions

Miller, Master Thesis, 2020

Micelle concentration and ice nucleating ability of aerosols

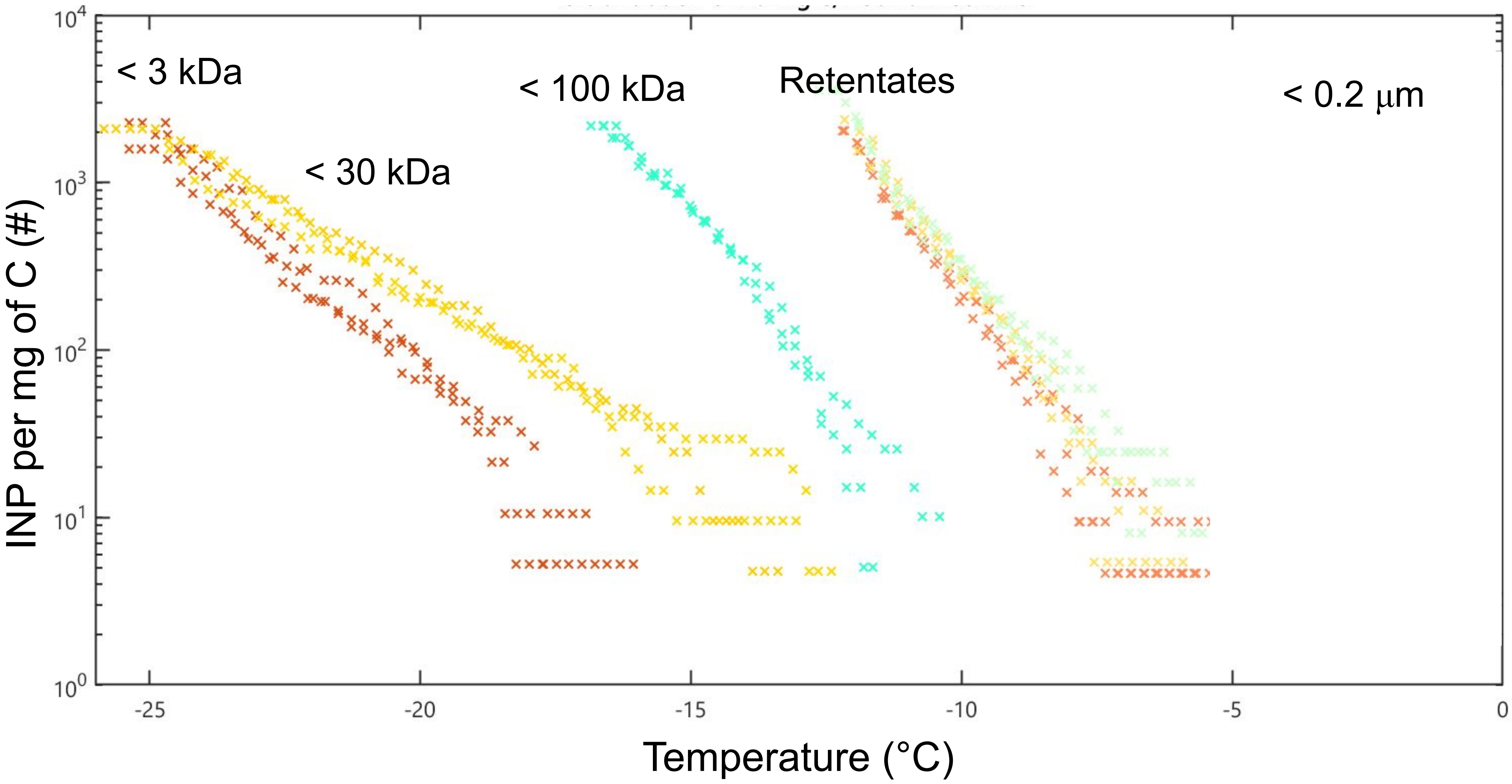


Anna Miller

Gérard et al. (*ES&T*, 2019) reported surfactant concentrations in aerosol >100 mM

- No CMC for lignin
- But how does CMC change with T?

Size fractionation of dissolved organic matter matters



Lin Boynton

Preliminary results using Suwannee River fulvic acid standard isolates