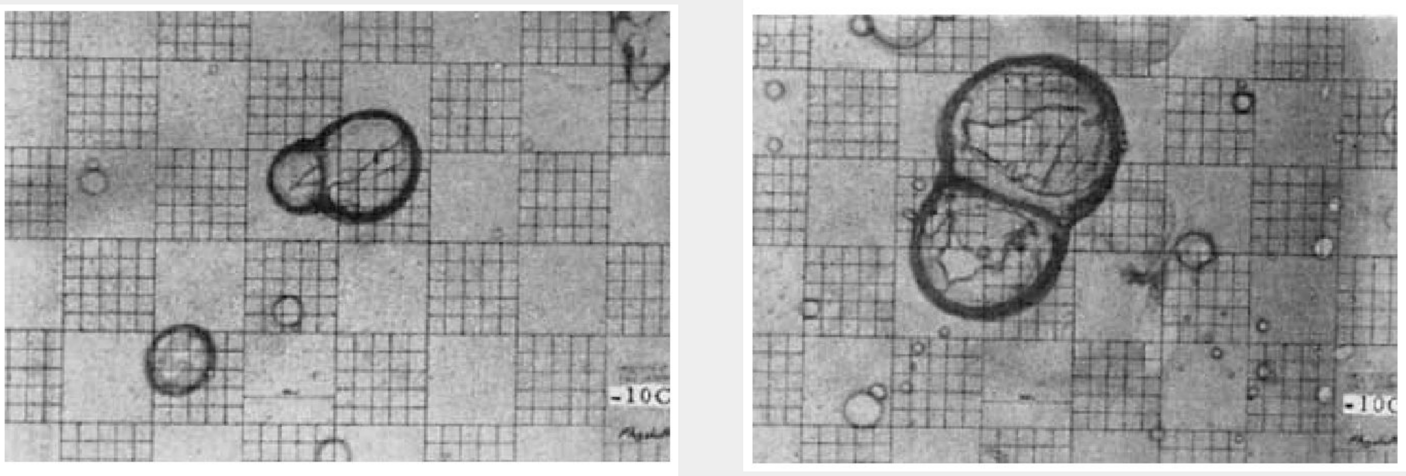
Do supercooled droplets freeze during collisions and breakup?



Molecular simulations show that water under tension increases its freezing temperature.

Elise Rosky, Will Cantrell, Tianshu Li, Issei Nakamura, Raymond Shaw

UNIVERSITY OF MICHIGAN
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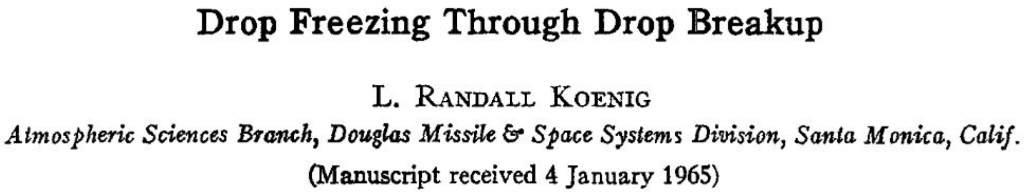
WASHINGTON, DC

Oct 28, 2024

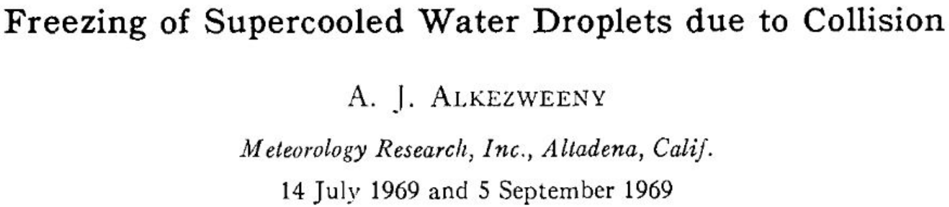
Speculation on droplet freezing during collision and breakup 1960 - 1980



Drop Freezing Through Drop Breakup

L. RANDALL KOENIG
Atmospheric Sciences Branch, Douglas Missile & Space Systems Division, Santa Monica, Calif.

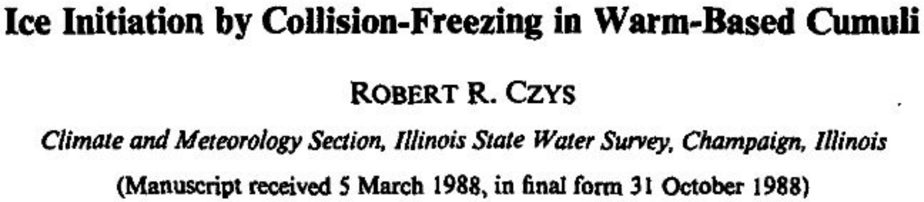
(Manuscript received 4 January 1965)



Freezing of Supercooled Water Droplets due to Collision

A. J. ALKEZWEENY
Meteorology Research, Inc., Altadena, Calif.

14 July 1969 and 5 September 1969



Ice Initiation by Collision-Freezing in Warm-Based Cumuli

ROBERT R. CZYS
Climate and Meteorology Section, Illinois State Water Survey, Champaign, Illinois

(Manuscript received 5 March 1988, in final form 31 October 1988)

During “mechanically-induced” ice nucleation, temperature is constant yet nucleation rate increases.

Violent motion of supercooled water will prompt the water to freeze; and the more violent the motion, the higher the probability of freezing. (Dorsey 1948)

The ice nucleation rate equation is predominantly temperature dependent.

$$j = A \exp\left(\frac{-C}{T\Delta\mu^2}\right)$$

j = nucleation rate ($m^{-3}s^{-1}$)
μ = chemical potential
A, C = constants

$$\Delta\mu = \frac{l_f(T_m - T)}{T_m}$$

Adding pressure dependence could explain constant temperature phenomena

$$j = A\exp\left(\frac{-C}{T\Delta\mu^2}\right)$$

$$\Delta\mu = \frac{l_f(T_m - T)}{T_m} + \Delta p\Delta v_{ls}$$

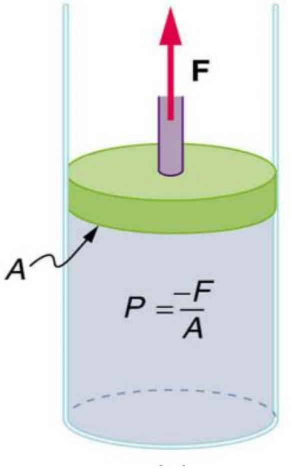
Neměc 2013

Δv_{ls} = volume difference between liquid and solid $(v_s - v_l < 0)$

T_m = melting temperature

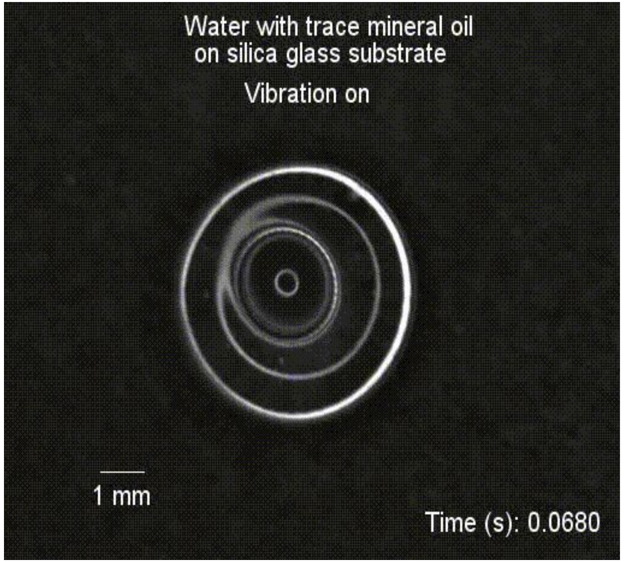
l_f = latent heat release

Negative pressure = Water is under tension

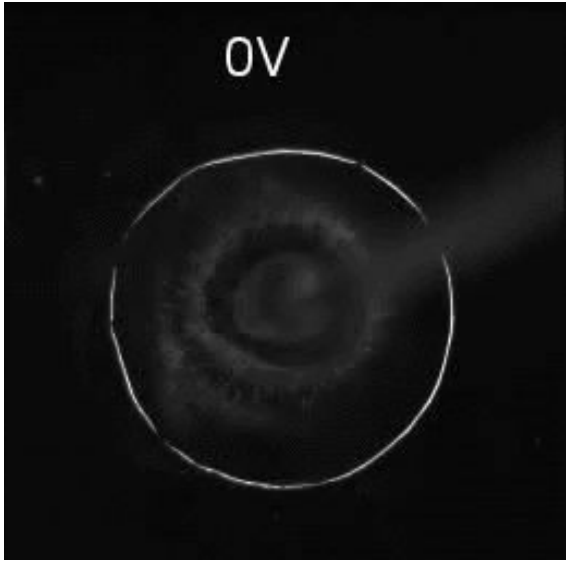


Experiments highlight the role of the air-water interface during mechanically-induced ice nucleation

Increased ice-nucleation is only observed when the surface of the droplet is stretched from its equilibrium shape, inducing curvature at the air-water interface.

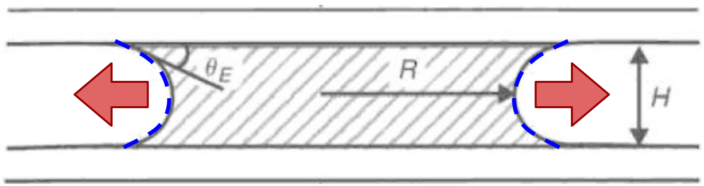


Fan Yang, Kostinski, et. al. PRE 2018



Yang et. al. APL (2015)

Curvature of the air-water interface creates Laplace pressure.

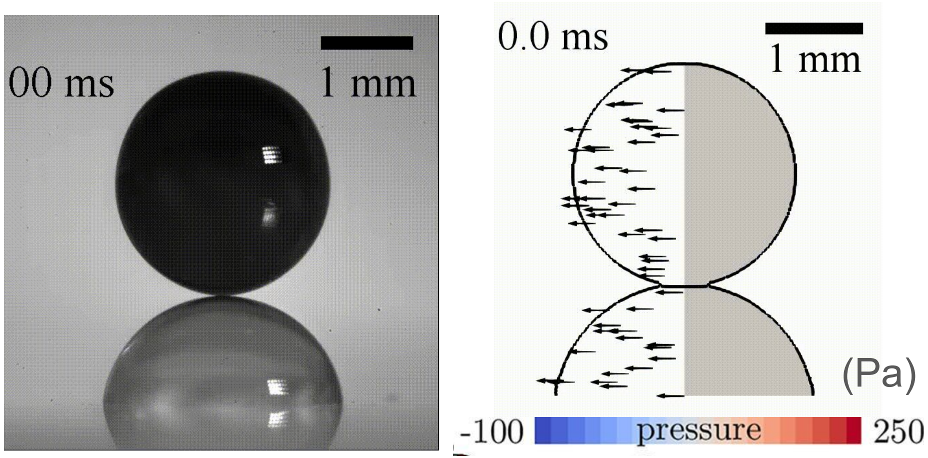


Negative Laplace pressure is produced by concave water surfaces.

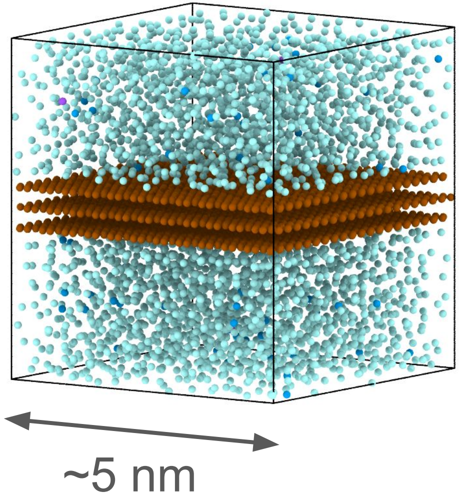
No mechanical motion is required to produce negative Laplace pressure.

During droplet coalescence, the air-water interface experiences high degrees of curvature with regions of negative pressure

Sykes et. al. 2020, Langmuir

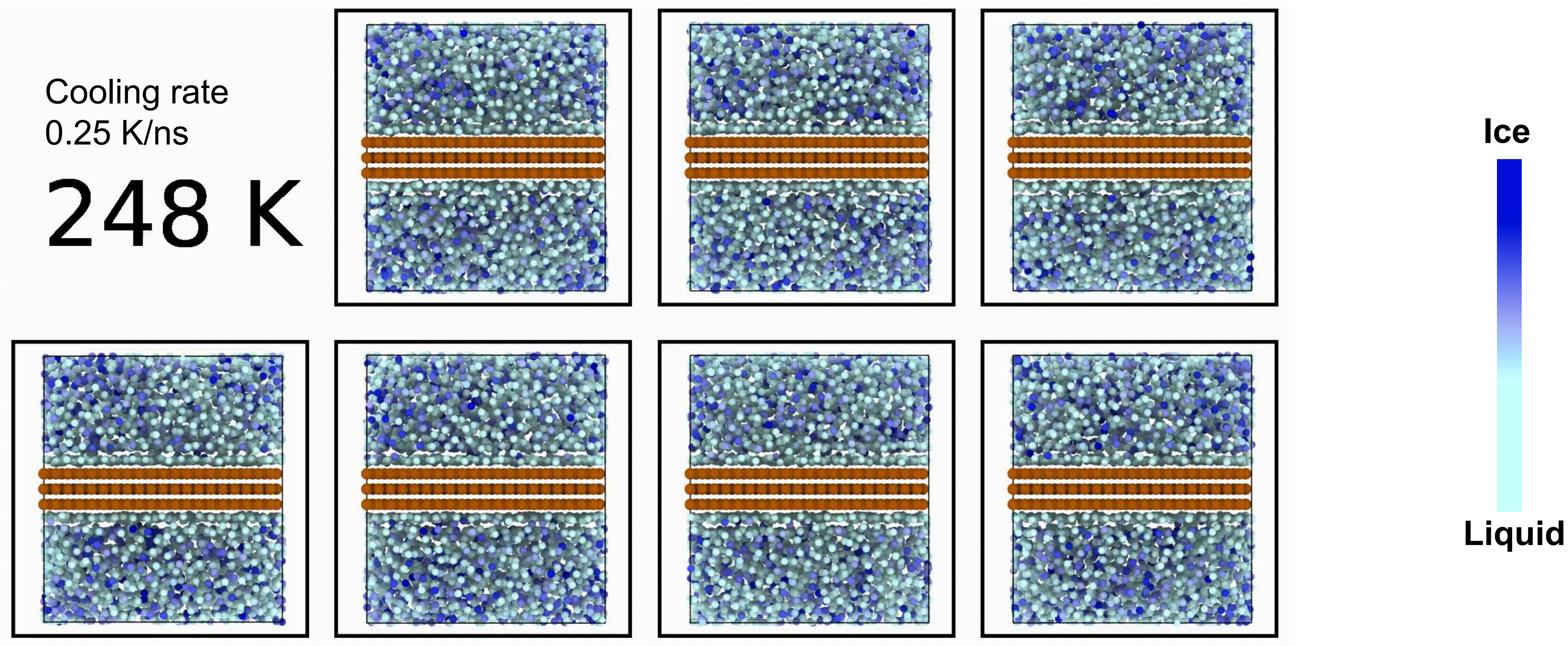


Molecular simulations demonstrate a direct quantitative link between negative pressure and increased ice nucleation rates.

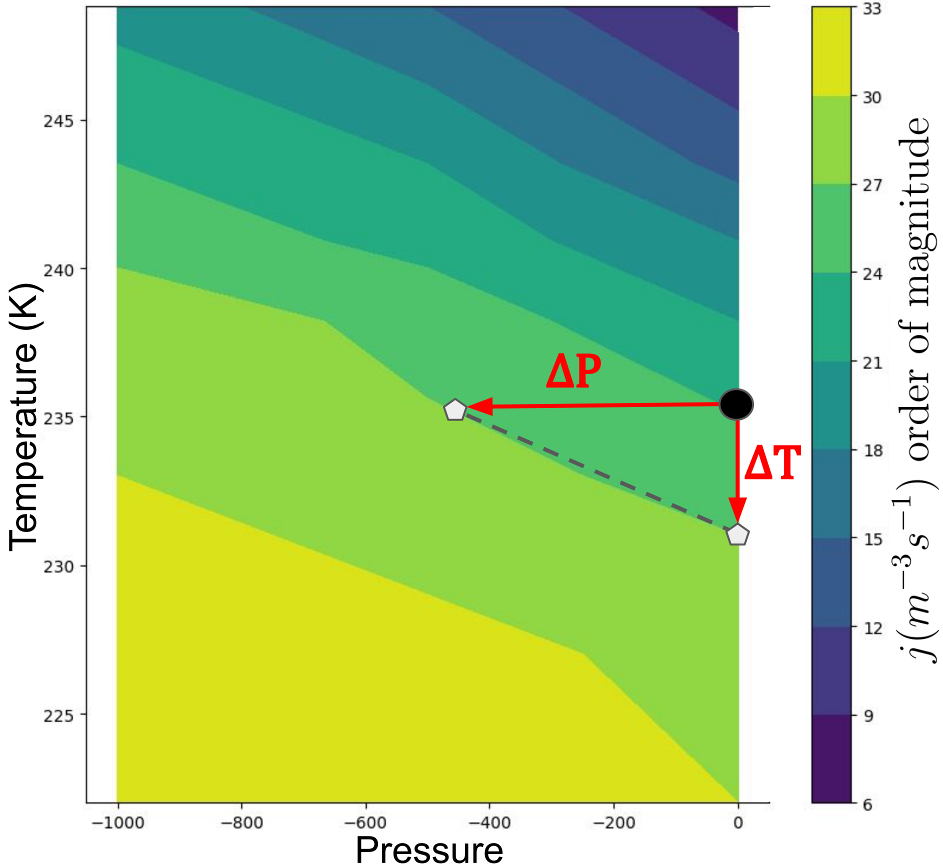


- Cyan = water
- Brown = hydrophilic substrate
- Periodic boundary conditions
- LAMMPS simulation software (Sandia National Lab)

Ice nucleation rates are found by simulating an ensemble of freezing events at each pressure.



The simulations show that negative pressure can increase nucleation rate without changing the temperature.



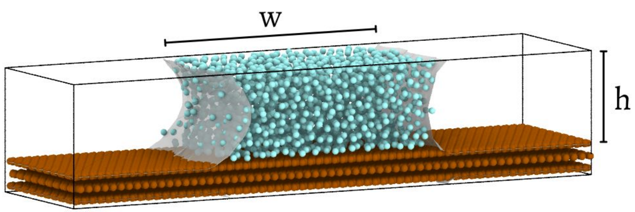
$$\boxed{\frac{\Delta T}{\Delta P} = \frac{T_m \Delta \nu_{ls}}{l_f}}$$

Δv_{ls} = volume difference $(v_s - v_l < 0)$
T_m = melting temperature
l_f = latent heat release

$$\frac{\Delta T}{\Delta P} \approx 0.007 \text{ K/atm}$$

Rosky et al. 2022, Chem. Phys. Lett.

Negative Laplace pressure in capillary bridges produce the expected increase of freezing temperature.



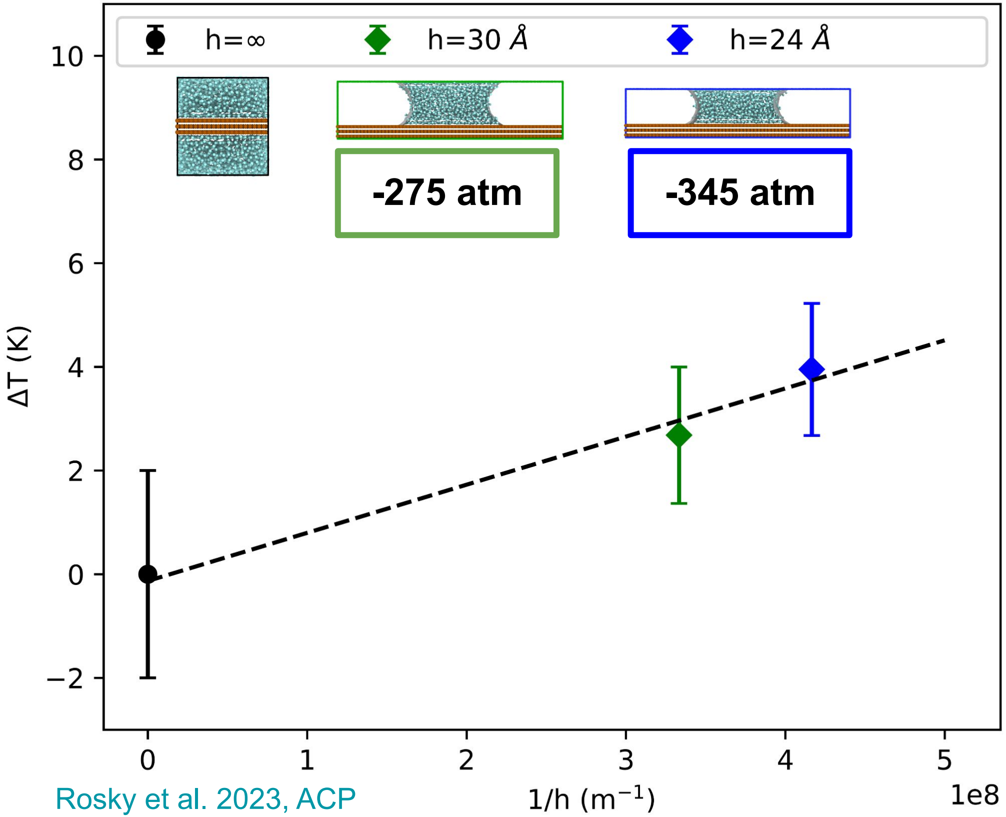
h = height of capillary bridge

Laplace pressure in the capillary bridge:

$$\Delta P_L = -\frac{2\sigma\cos(\theta)}{h}$$

Expected increase in freezing temp:

$$\Delta T = \frac{T_m \Delta \nu_{ls}}{l_f} \Delta P_L$$



Rosky et al. 2023, ACP

A pressure enhancement factor can quantify the impact of negative pressure on active INP concentrations.

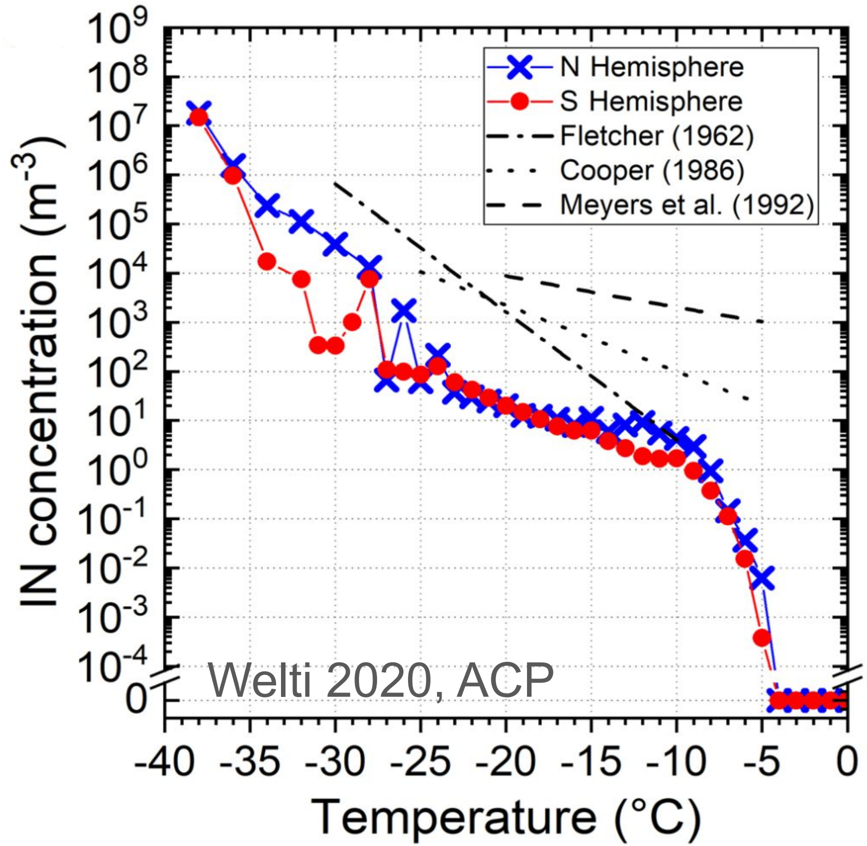
$N_i(T)$ Number of active INP as a function of temperature.

$\Delta T_p = 0.007 \Delta P$ Increase in INP activation temperature due to negative pressure (atm) from Rosky et. al. 2023.

$\Delta N_i(T) = \frac{\delta N_i(T)}{\delta T} \cdot \Delta T_p$ Increase in number of active INP due to increase in activation temperatures.

$\mathcal{E}_p(T) = \frac{\Delta N_i}{N_i}$ Pressure enhancement factor: number of pressure-activated INP compared to original INP

Enhancement values >1 mean that active INP concentration is more than doubled.



Welti 2020, ACP

$$\mathcal{E}_p(T) = \frac{\Delta N_i}{N_i} = \frac{1}{N_i(T)} \frac{\delta N_i(T)}{\delta T} \cdot \Delta T_p$$

Example using Fletcher 1962:

Negative pressure of ~200 atm results in enhancement $\mathcal{E}_p = 1$ at all temperatures.

(Surface curvature of ~10 nm)

Sources of negative pressure in cloud droplets have yet to be investigated.

Any source of negative pressure in water can lead to higher ice nucleation rates.

Uncertain what sources of negative pressure are active in the atmosphere.

- Droplet coalescence
- Contact nucleation
- Hydrophobic INP at the air-water interface
    - Pandey et. al. 2017
    - Bieber and Borduas-Dedekind 2024

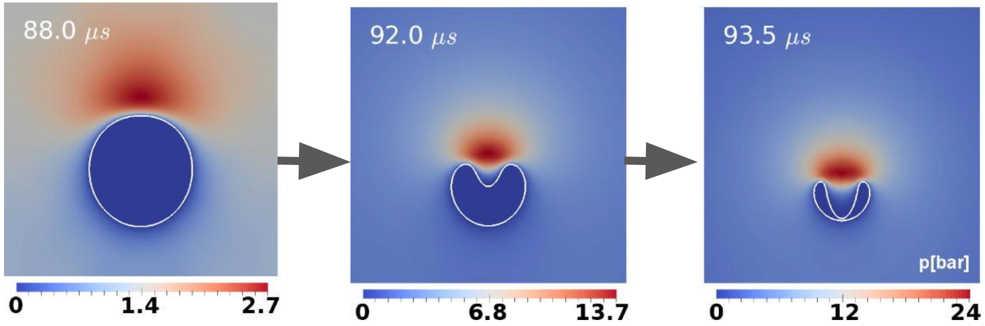
Nanometer-scale surface curvature produces hundreds of atmospheres of negative Laplace pressure → associated with high levels of enhancement in active INP.

Backup Slides

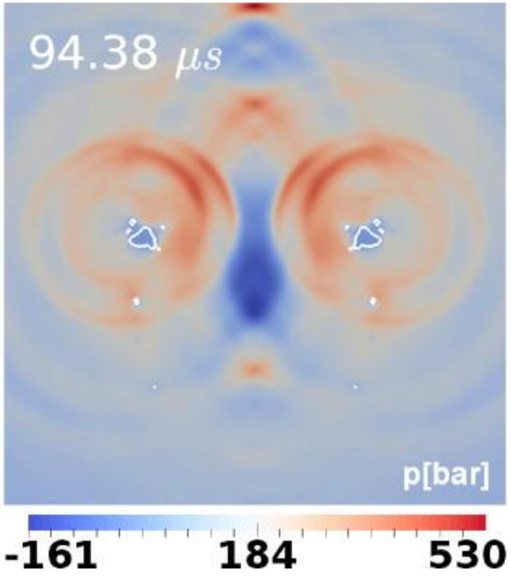
Negative pressure in water after air bubbles collapse.

Hunt and Jackson (1966) proposed that bubbles form during mechanical agitation, and that **negative pressure** following bubble collapse increases the freezing point.

Bubble collapsing

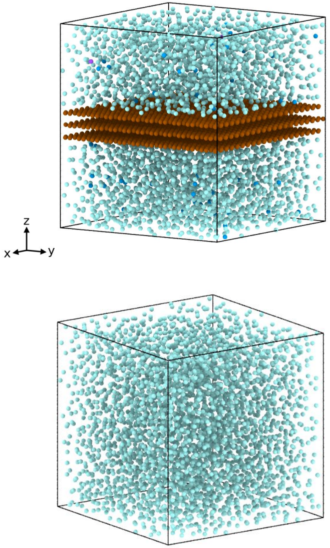


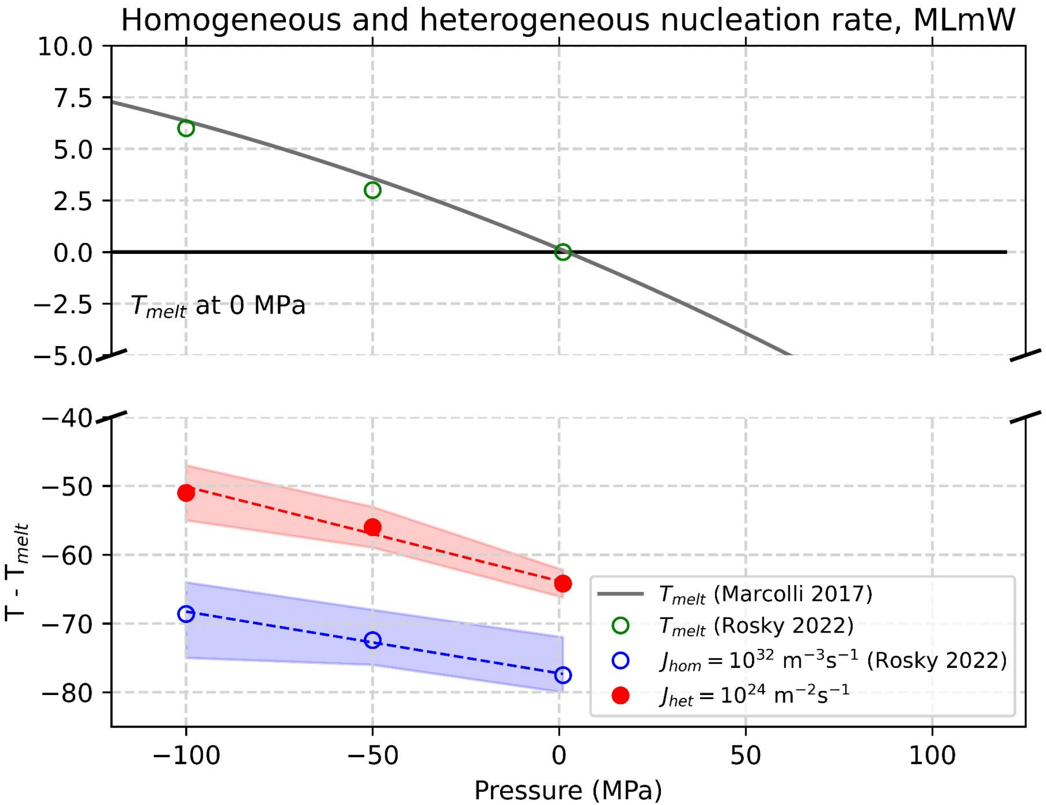
Lechner et. al. (2017)
The Journal of the Acoustical Society of America



Hundreds of bars negative pressure

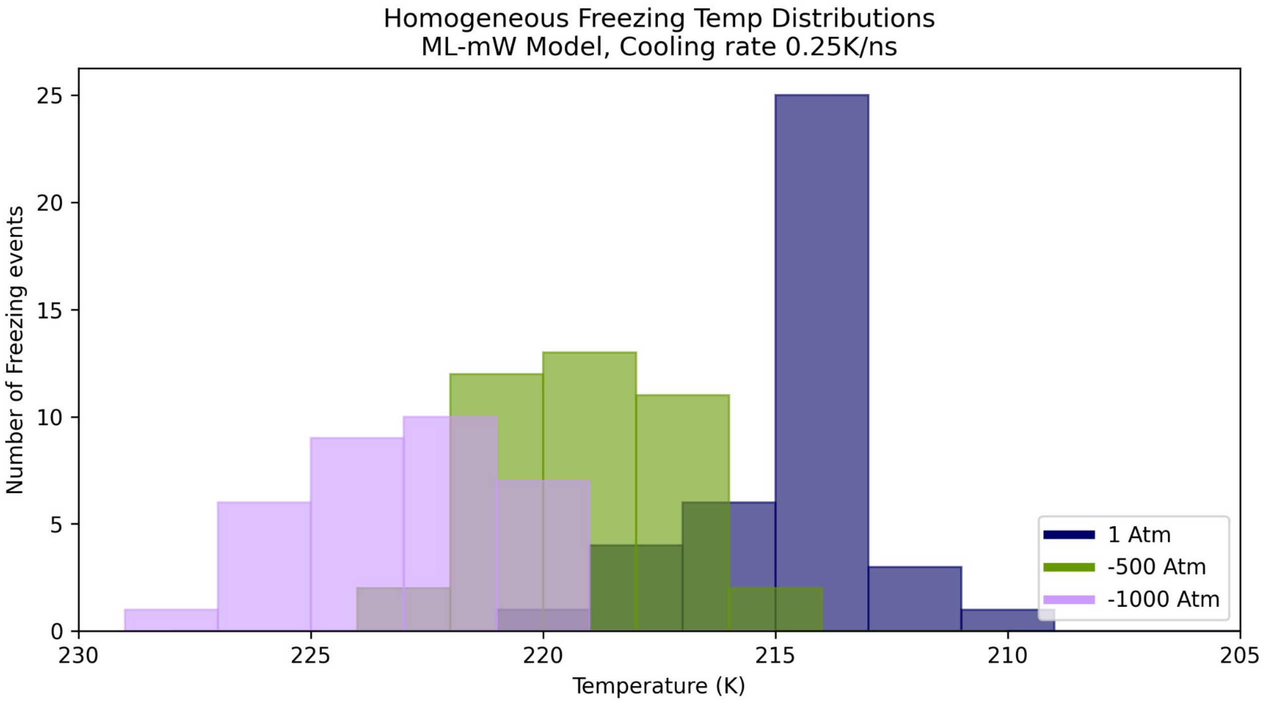
True for both homogeneous and heterogeneous ice nucleation





Rosky et al. 2023, ACP

Freezing temperature distributions are converted into nucleation rate in each temperature bin.



Rosky et al. 2022, Chem. Phys. Lett.