Ice nucleation without supercooling: on the search for the most potent ice nucleants

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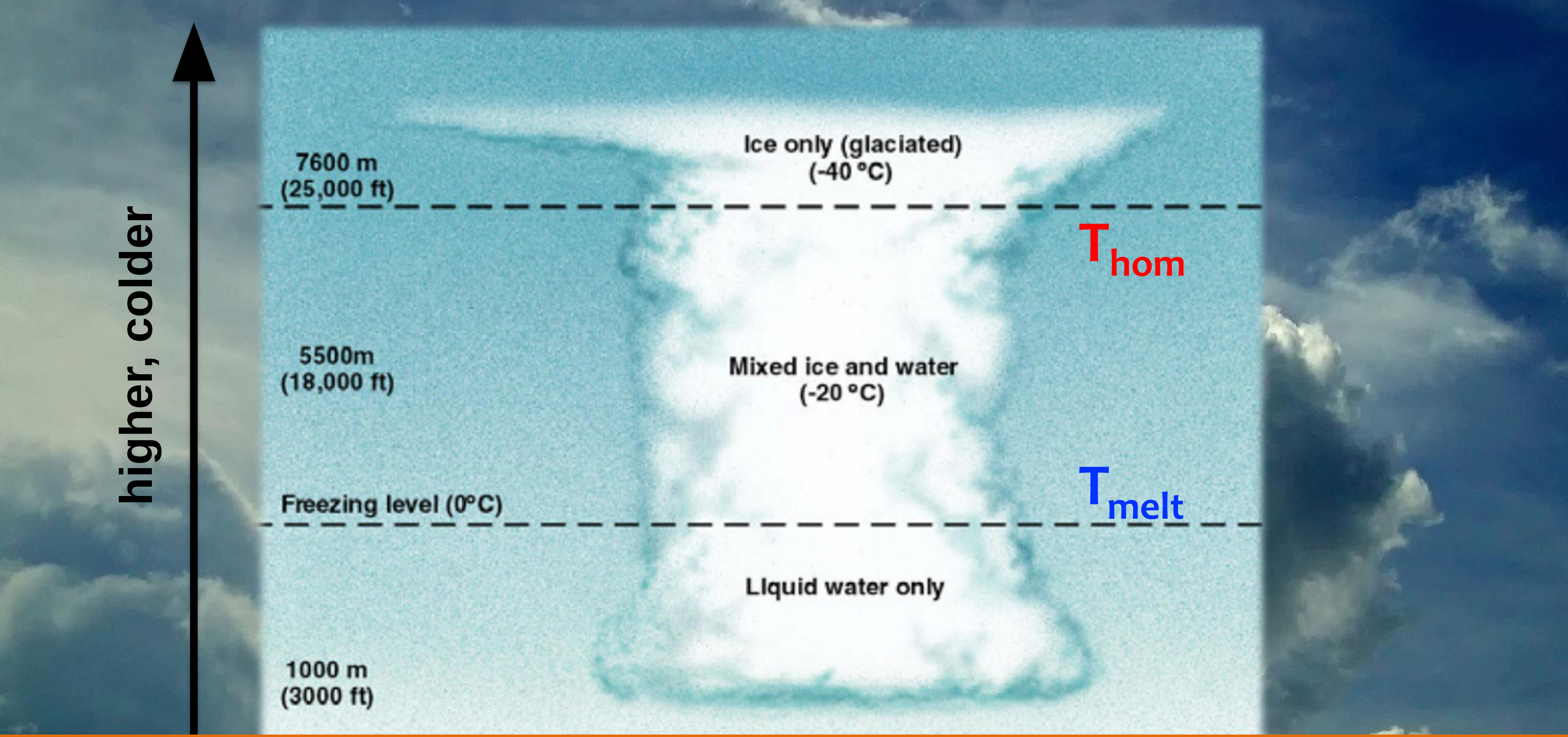
Atanu Metya

Arpa Hudait



Rain and snow are initiated by ice formation in clouds

Weather modification through cloud seeding was intensely pursued during the Cold War

1946
Ice seeding by dry ice in a cloud chamber
Followed by seeding of real clouds …

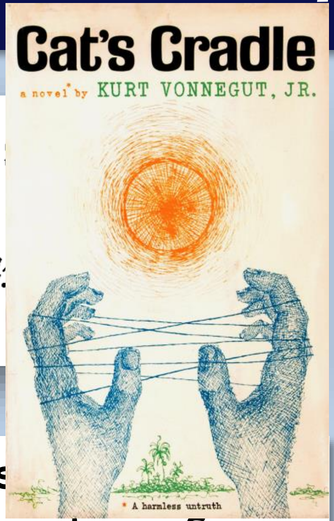
agricultural expansion

military interests (weather weapons)

Search for the most potent ice nucleants bloomed

The Nucleation of Ice Formation by

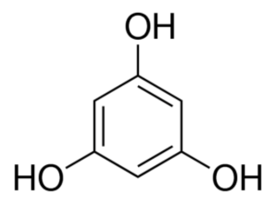
B. VONNEGUT
General Electric Research Laboratory, Schenectad
(Received March 17, 1947)



1963
"ice nine"

Investigation of certain s
as crystallization reagents of
supercooled fog
Bashkirova and Krasikov 1957

phloroglucinol



NATURE, JANUARY 28, 1967

L. F. EVANS

Two-dimensional Nucleation of Ice

THE customary theory for the nucleation of ice on a crystalline substrate is based on the probability that a spherical cap of ice will grow, by statistical fluctuations, to a size such that the volume free energy and the surface free energy counterbalance[1,2]. Although this model is mathematically tractable, its validity has been questioned[3,4] on the grounds that the macroscopic values of the physical properties of ice may not apply to aggregates of only a few molecules. No alternative theory has yet been proposed to describe the molecular process by which ice deposits on a substrate. It is the purpose of this communication to show that the first stage in the nucleation of ice on organic nucleators is the growth of monolayer patches of ice on the nucleator surface.

Experimental Studies of Organic Ice Nuclei

N. FUKUTA
Radiophysics Laboratory, CSIRO, Sydney, Australia
(Manuscript received 24 May 1965, in revised form 27 July 1965)

ABSTRACT

The ability of 329 selected organic compounds to nucleate ice has been tested by three methods. Their activity was found to depend strongly on the method of preparation. More than 20 compounds were found to nucleate ice at temperatures above −5C when freshly ground. Some meta and para derivatives of benzene showed excellent activity. Particles prepared by condensation were less active, the only newly-discovered material effective above −5C being 1,5-dihydroxynaphthalene. Its use as a cloud seeding agent is suggested.

Several organic crystals at high pressures nucleate ice
without supercooling!

US military was using cloud seeding as weather weapon to extend monsoon season and muddle the supply route of the Vietcong

1971 – comes out in the press
1972 – leaking of Pentagon papers
1973 – US Senate calls for treaty to ban weather modification as weapons

1978 – World treaty bans weather weapons

1950s – NUCLEATION THEORY

Entropy effect in ice crystal nucleation
NH Fletcher - The Journal of Chemical Physics, 1959 - aip.scitation.org
… which they expose. Large steps on basal faces expose prism faces, and are thus good **ice nucleation** sites … Such steps are therefore not particularly good **ice nucleation** sites, though all steps favor the condensation of water in the liquid form …
Cited by 65 Related articles All 3 versions

1960s – FUNDAMENTALS

Ice nucleation and the substrate-ice interface
DM Anderson - Nature, 1967 - nature.com
NATURE. VOL. 21 6, NOVEM EEE 1 1 , 1 g6 7 Fig. 3. Chain-like aggregate of the forms depicted in Fig. 2. It is conspicuous that the aggregate is situated on a crack within the rock. Note isolated elements in the surroundings (from Witwatersran quartzite as in Fig. 1 ; the line represents …
Cited by 87 Related articles All 3 versions

1970s – BIOLOGICAL ICE NUCLEATION

Ice nucleation induced by Pseudomonas syringae
LR Maki, EL Galyan, MM Chang-Chien… - Applied …, 1974 - Am Soc Microbiol
Broth cultures of suspensions of Pseudomonas syringae isolated from decaying alder leaves (Alnus tenuifolia) were found to freeze at very warm (-1.8 to-3.8 C) temperatures. T initiation of freezing appears associated with the intact cell and not with extracellular …
Cited by 598 Related articles All 8 versions

1980s – BIOLOGICAL ICE NUCLEATION

[PDF] The role of bacterial **ice nucleation** in frost injury to plants
SE Lindow - Annual review of phytopathology, 1983 - annualreviews.org
The science of plant pathology is largely a study of the mechanisms, quantifica tion, and alleviation of plant stresses due to biological agents. Of obvious importance are the stress to plants directly caused by infection by various plant pathogenic fungi, bacteria, viruses ..
Cited by 472 Related articles All 8 versions

1990s – CLOUD AND WEATHER MODELS

New primary **ice-nucleation** parameterizations in an explicit cloud model
MP Meyers, PJ DeMott… - Journal of Applied …, 1992 - journals.ametsoc.org
Two new primary **ice-nucleation** parameterizations are examined in the Regional Atmospheric Modeling System (RAMS) cloud model via sensitivity tests on a wintertime precipitation event in the Sierra Nevada region. A model combining the effects of deposition …
Cited by 892 Related articles All 11 versions

2000s –PARAMETERIZATIONS FOR WEATHER MODELS

[HTML] Water activity as the determinant for homogeneous **ice nucleation** in aqueous solutions
T Koop, B Luo, A Tsias, T Peter - Nature, 2000 - nature.com
The unique properties of water in the supercooled (metastable) state are not fully understood 1. In particular, the effects of solutes and mechanical pressure on the kinetics of the liquid-to-solid phase transition of supercooled water and aqueous solutions to ice have …
Cited by 1087 Related articles All 18 versions

[HTML] Molecular dynamics simulation of the **ice nucleation** and growth process leading to water freezing

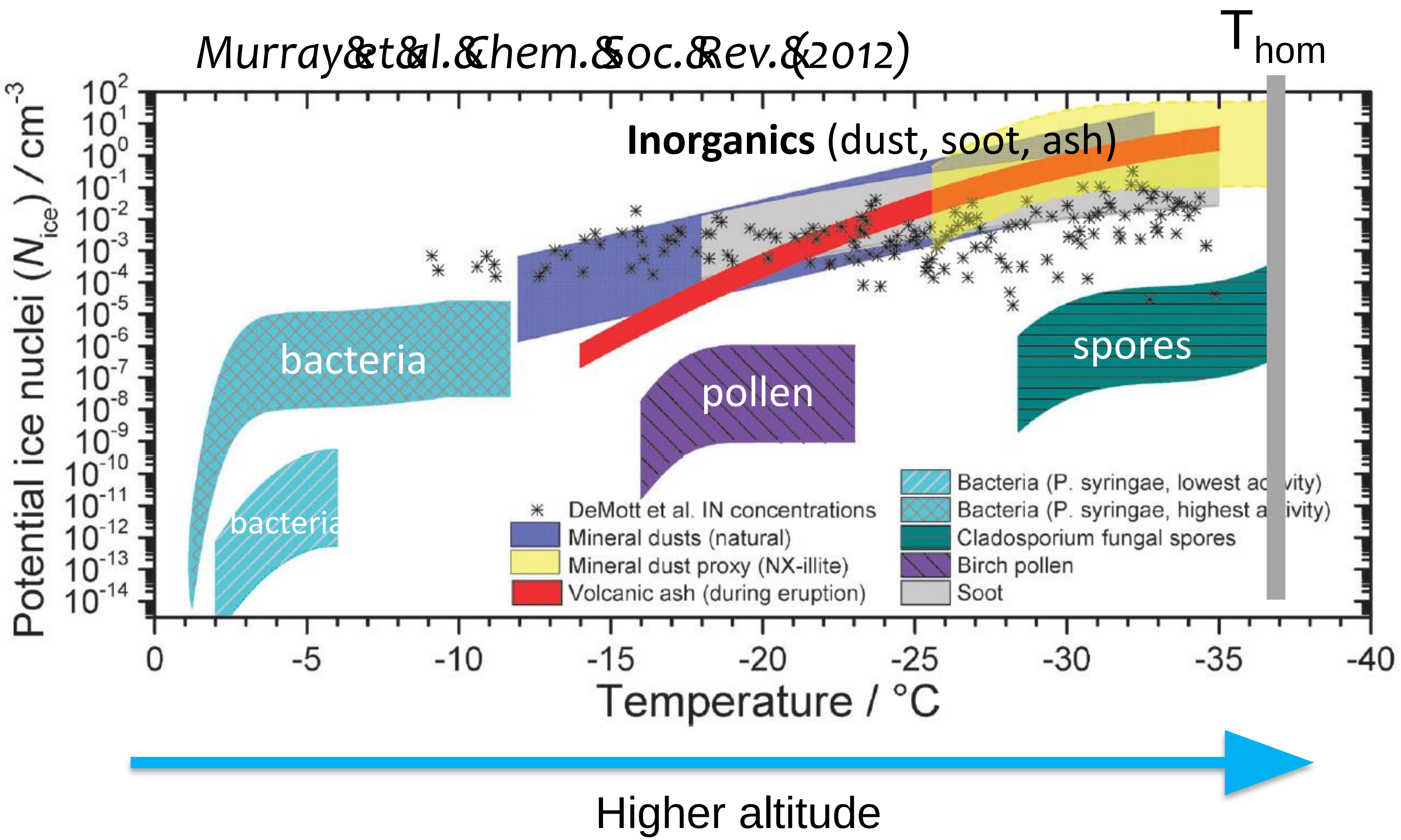
first computer simulation of ice nucleation!

M Matsumoto, S Saito, I Ohmine - Nature, 2002 - nature.com
Upon cooling, water freezes to ice. This familiar phase transition occurs widely in nature, yet unlike the freezing of simple liquids 1, 2, 3, it has never been successfully simulated on a computer. The difficulty lies with the fact that hydrogen bonding between individual water …
Cited by 770 Related articles All 13 versions

2010s – ATMOSPHERIC AEROSOLS / CLIMATE MODELS

[PDF] Heterogeneous **ice nucleation** on atmospheric aerosols: a review of results from laboratory experiments
C Hoose, O Möhler - Atmos. Chem. Phys, 2012 - core.ac.uk
A small subset of the atmospheric aerosol population has the ability to induce ice formation at conditions under which ice would not form without them (heterogeneous **ice nucleation**). While no closed theoretical description of this process and the requirements for good ice …
Cited by 743 Related articles All 10 versions

Bacteria act as ice nucleants in clouds



***Ps. syringae* bacteria are pervasive plant pathogens that nucleate ice through assemblies of proteins on their outer wall**

(dead) Ps. Syringae is used for making snow…

Outline

What makes bacterial proteins so good at ice nucleation?

Why do they have a distribution of nucleation temperatures?

How do organic crystals promote ice formation?

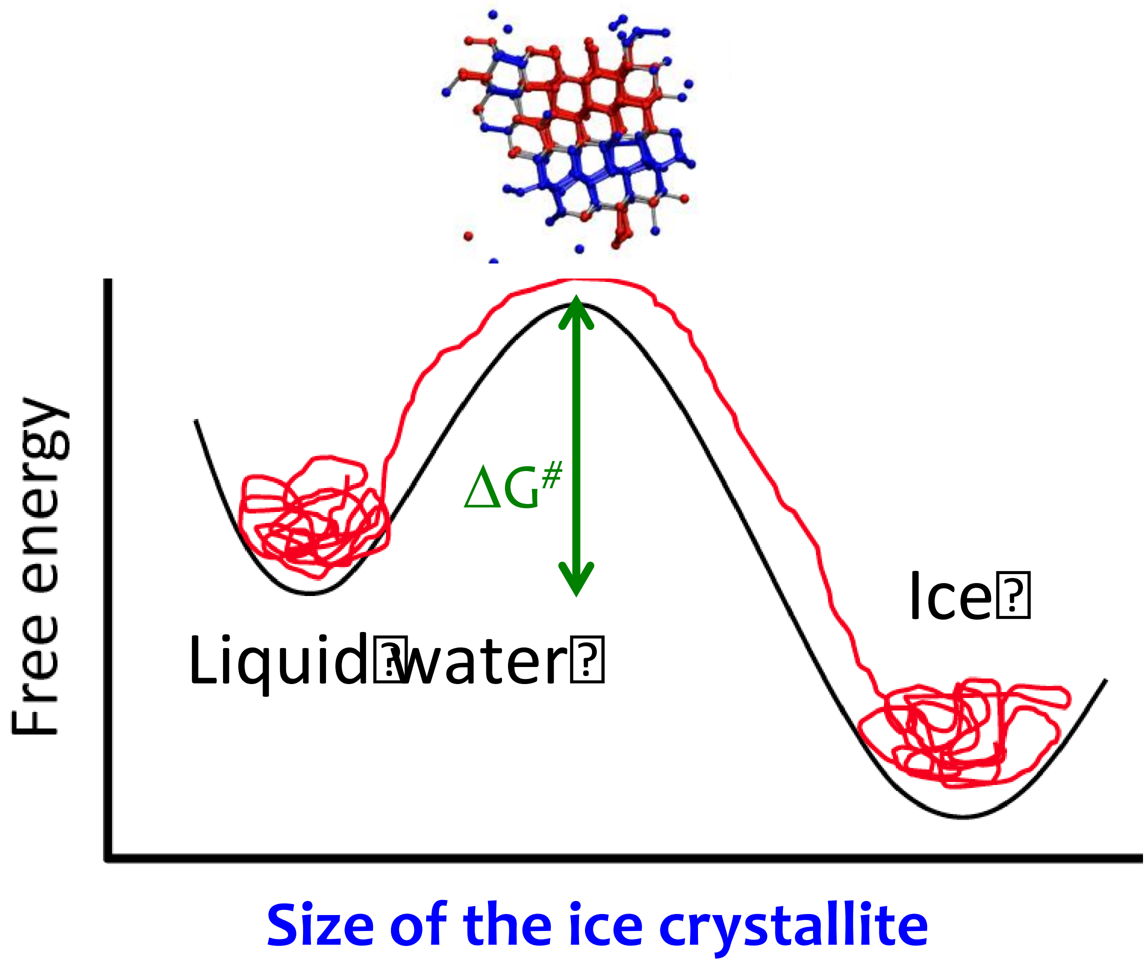
The search for the most potent ice nucleants:

Ice nucleation without supercooling

We address these questions using

molecular simulations with coarse-grained and united-atom models, nucleation theory, and thermodynamics

The crystallization of water is an activated process



Stable phase of nanoscopic ice is stacking disordered.
Different from that of bulk ice!

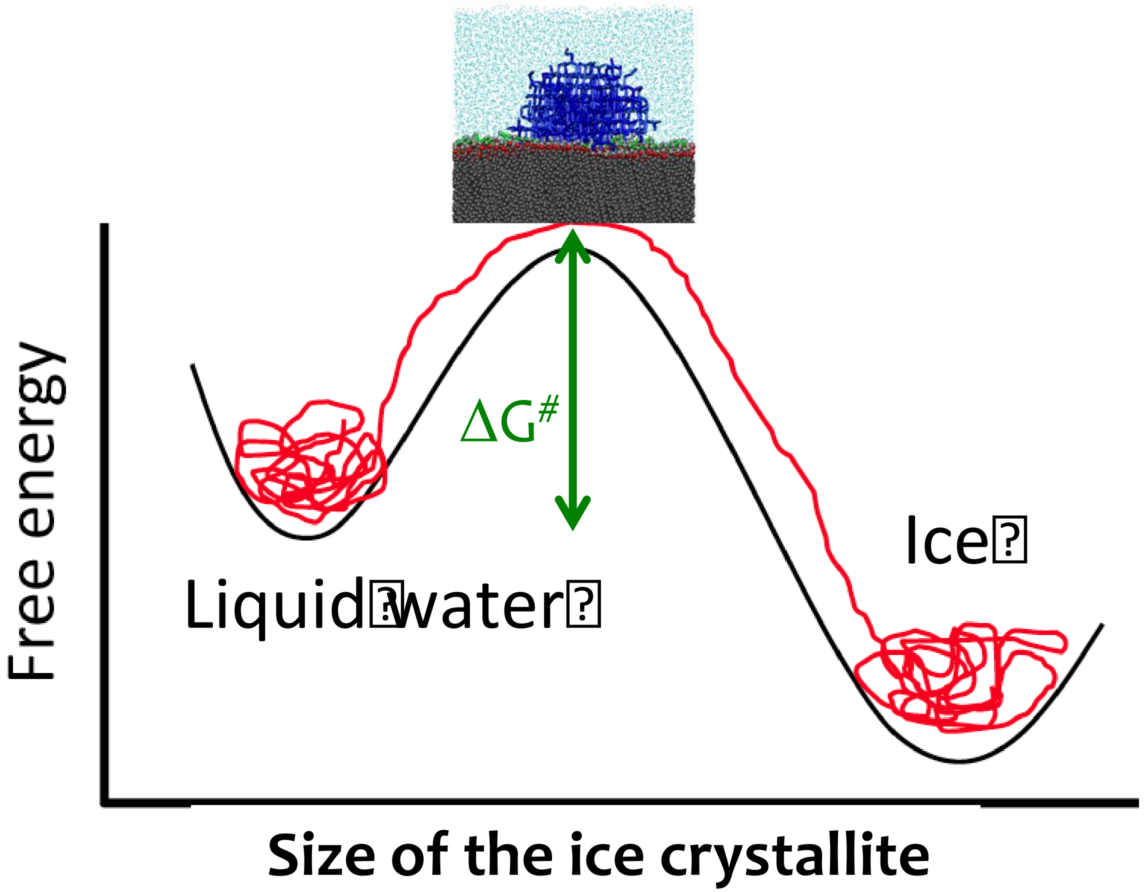
Lupi et al. Nature 2017

Barrier of nucleation arises from the cost of the ice interface

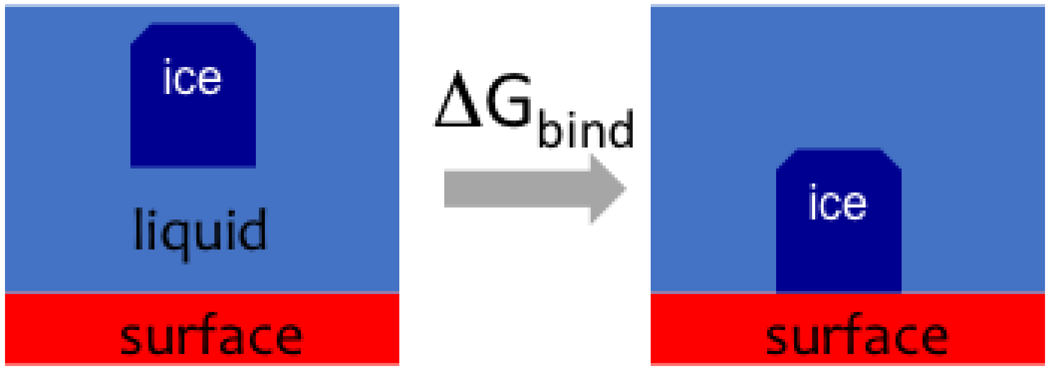
$$\Delta G^{\#} = c\,\gamma^3 / (\rho\Delta\mu)^2$$

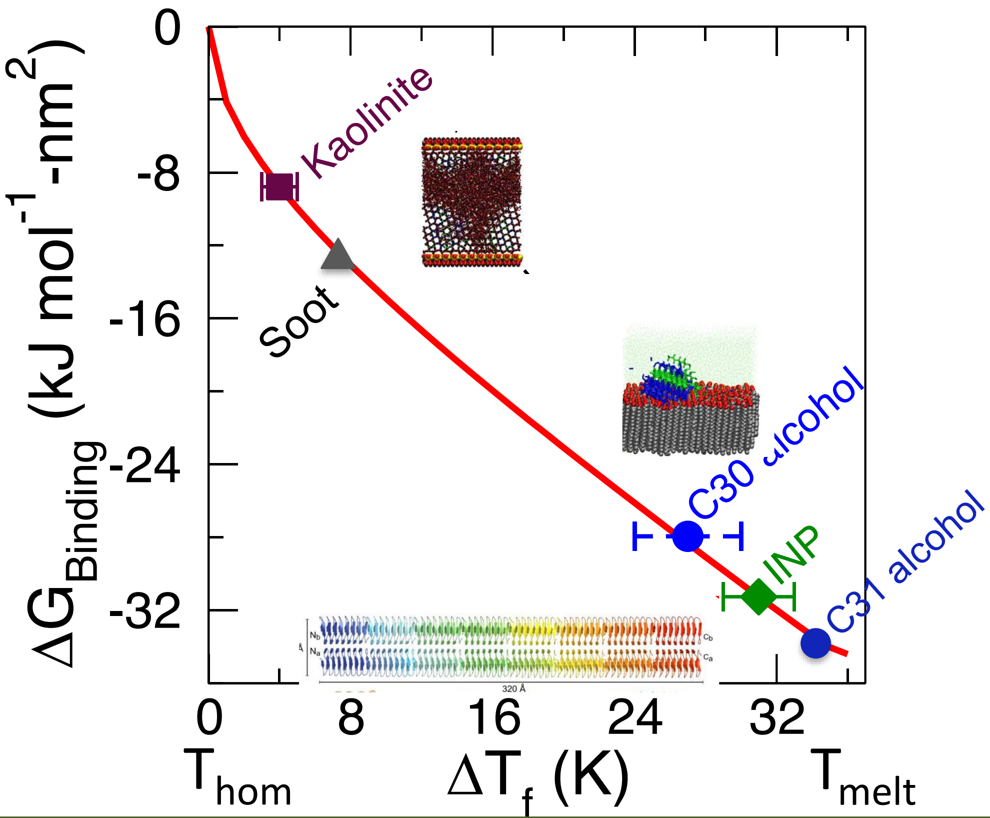
Lupi, Hudait, Peters, Gruenwald, Mullen, Nguyen and Molinero, Nature 2017

Surfaces and molecules promote the nucleation of ice by decreasing the cost of the ice surface



The binding free energy of ice to the surface determines the ice freezing temperature



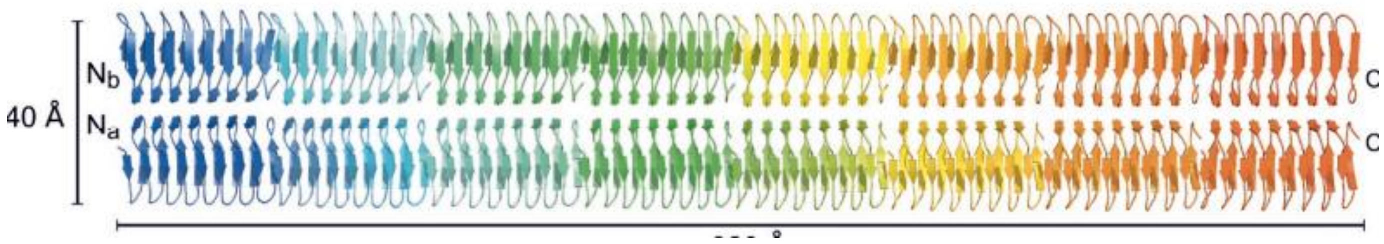


Ice binding proteins, alcohol monolayers and some organic crystals nucleate ice at very high temperatures.

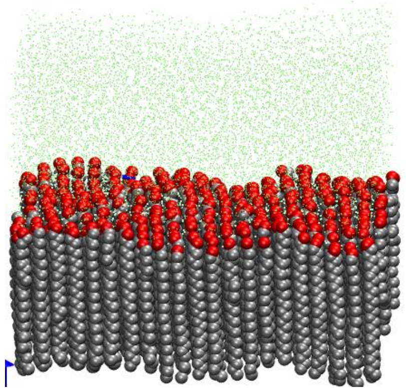
What makes them so efficient at binding ice?

Qiu, Odendahl, Hudait, Mason, Bertram, Paesani, DeMott & Molinero, JACS 2017

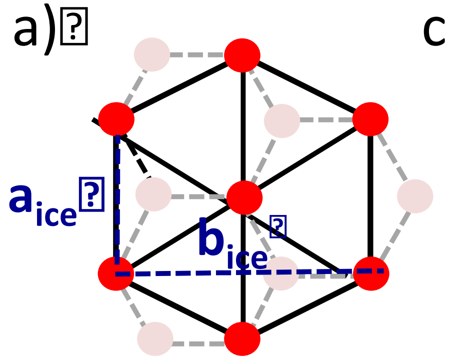
Molecules with OH groups ordered similar to water in ice planes are particularly efficient promoters of ice nucleation



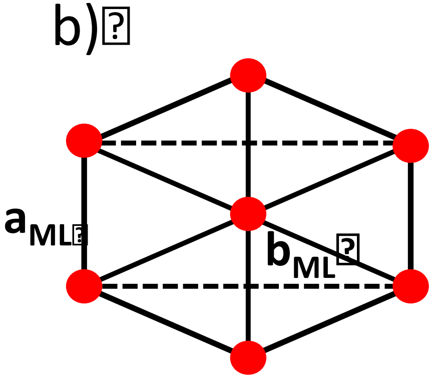
Ice Nucleating Proteins



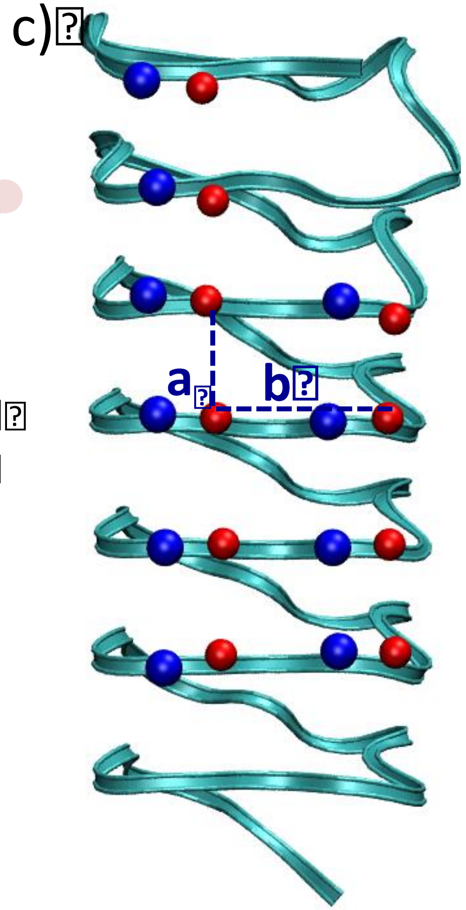
Monolayers of Alcohols



Hexagonal unit cell of hexagonal ice



Rectangular unit cell of alcohol or acid monolayers

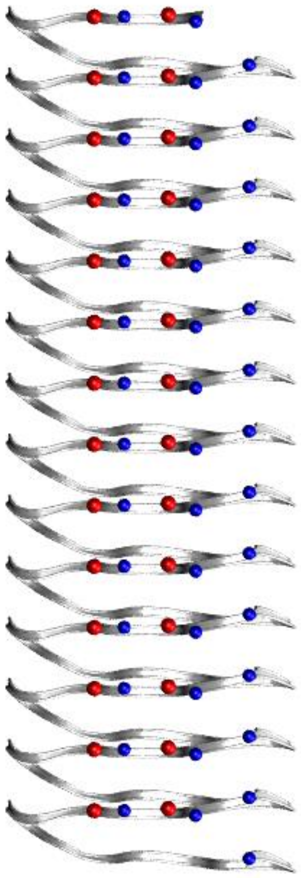


Binding sites of *TmAFP protein*

Qiu, Odendahl, Hudait, Mason, Bertram, Paesani, DeMott & Molinero, JACS 2017
Hudait, Odendahl, Qiu, Paesani, & Molinero, JACS 2018

Ice nucleating proteins bind to ice through an anchored clathrate motif that bridges hydrogen bonding order of binding surface and ice face

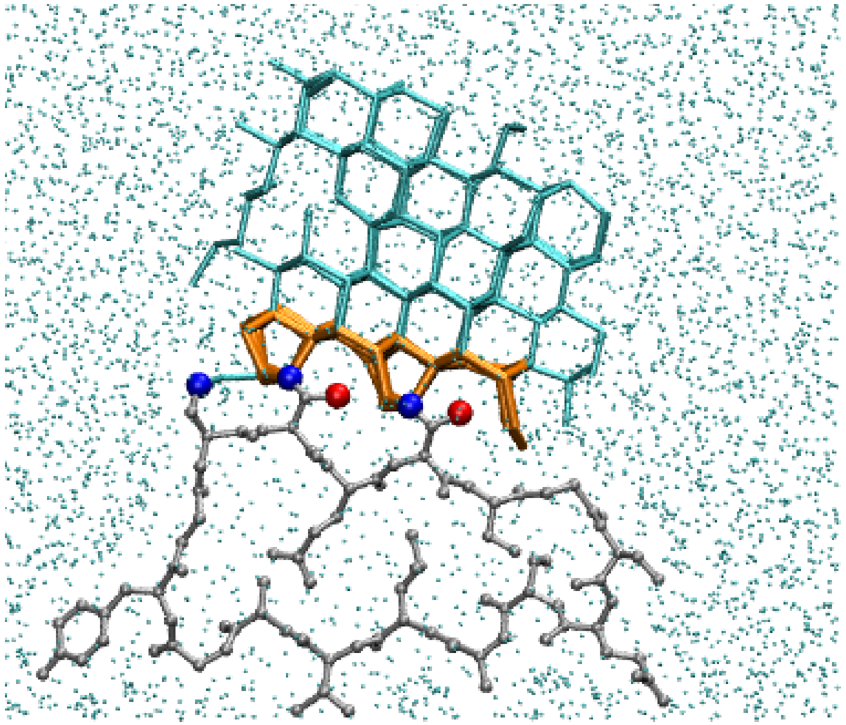
model INP

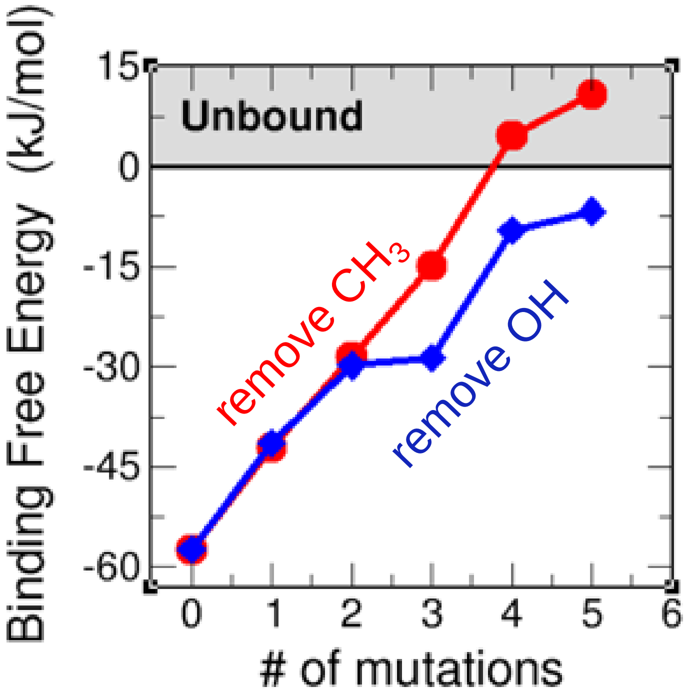


Conserved TxT arrays

Threonine exposes:
OH
CH_3

Binds the ice nucleus through anchored clathrate motif



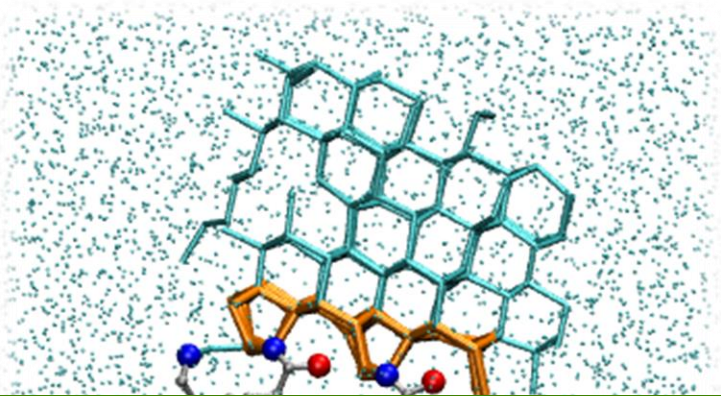


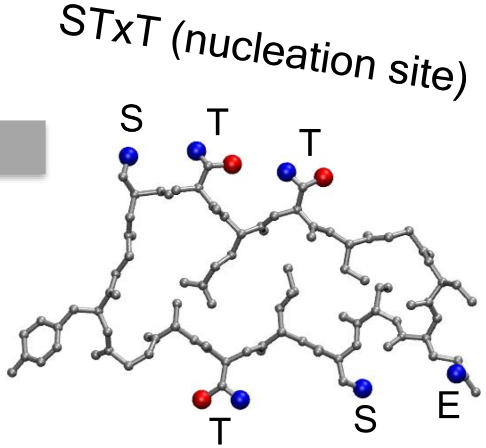
Hydrogen-bonding and hydrophobic groups contribute equally to the binding free energy of the proteins to ice

Hudait, Odendahl, Qiu, Paesani, & Molinero, JACS 2018
Hudait, Qiu, & Molinero, JACS 2019

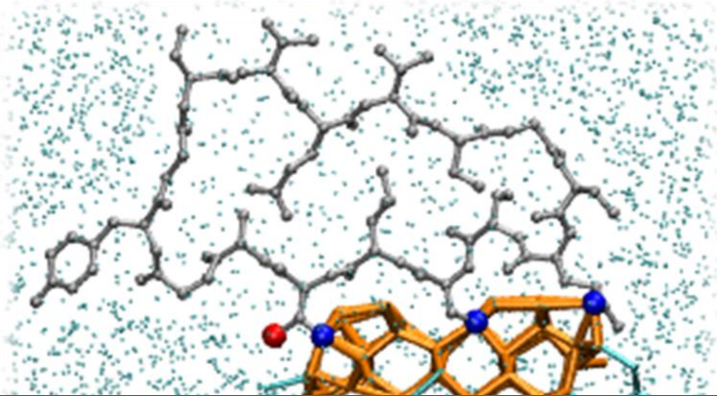
Ice nucleating protein of Ps. syringae has two ice binding sites with comparable ice nucleation efficiency

STxT side generates ice bound through **anchored clathrate motif**





ExSxT side generates ice bound through **ice-like motif**



Mixed hydrophobic and hydrogen bonding or only hydrogen bonding Interactions can be equally efficient at binding proteins to ice

ΔT_f = 14 ± 2 K

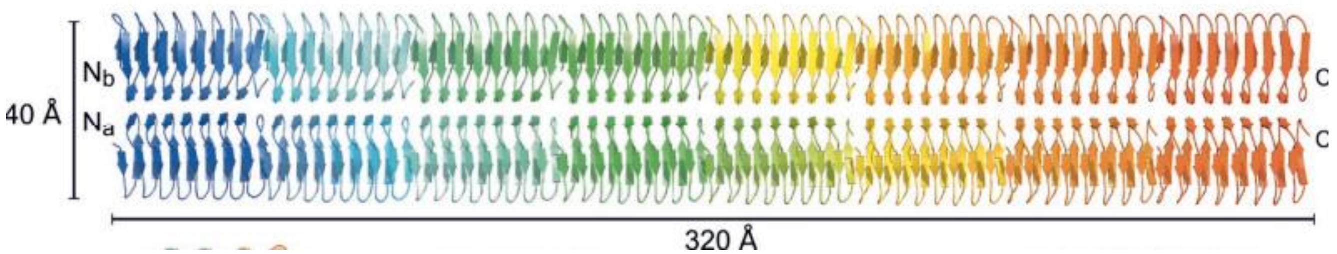
experiment
ΔT_f = 12 K

ΔT_f = 15 ± 2 K

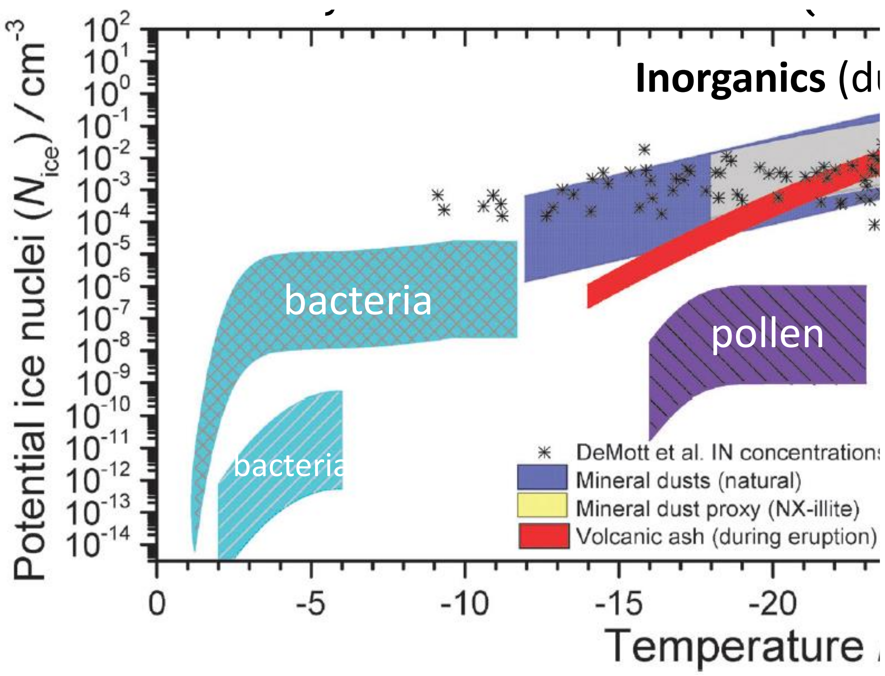
Ling et al. J. Geophys. Res.: Atmos. 2018

Hudait, Odendahl, Qiu, Paesani, & Molinero, JACS 2018

Ice nucleating proteins are large and they aggregate in the cell membrane

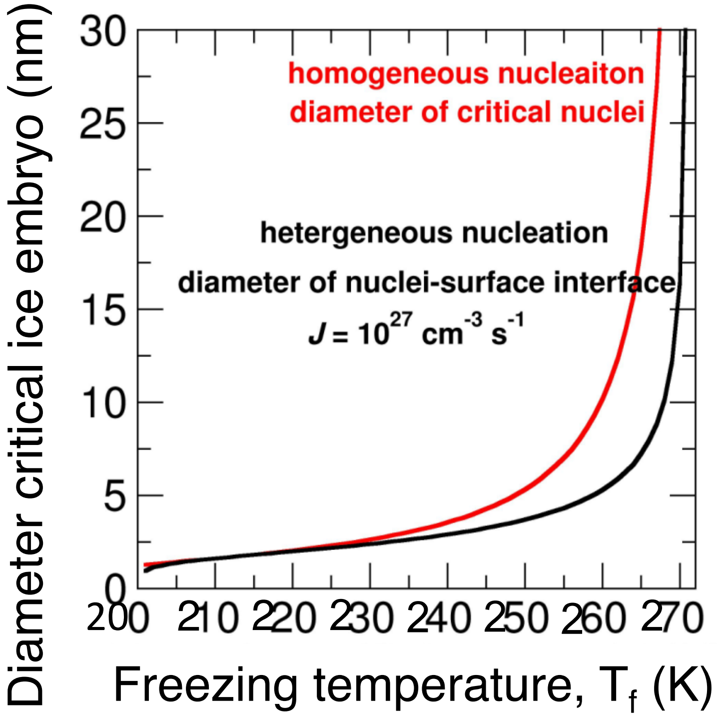


Experiments by Lindow and coworkers from 1980s suggest that the distribution of ice nucleation temperatures arises from assemblies with different number of ice nucleating proteins



How do size and aggregation of the proteins impact ice nucleation?

Ice nucleation requires the stabilization of a critical ice embryo: the higher the nucleation temperature, the larger the critical nucleus



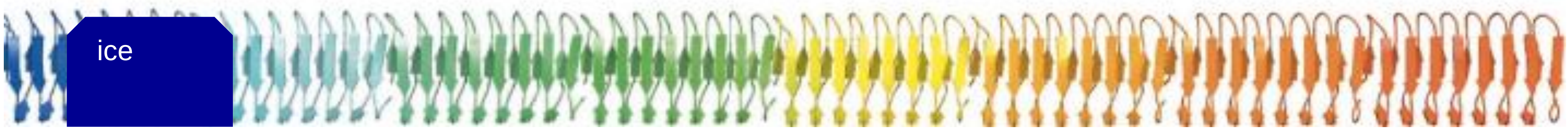
TmAFP has 4 TxT loops

AFPs bind strongly to existing ice,
but it can only stabilize a tiny embryo

***Tm*AFP nucleates ice just 2±1 K above T_{homo}**

Qiu, Hudait & Molinero, JACS 2019
Eickhoff et al. JPC Lett 2019

***Ps*INP monomer has 68 wider loops**

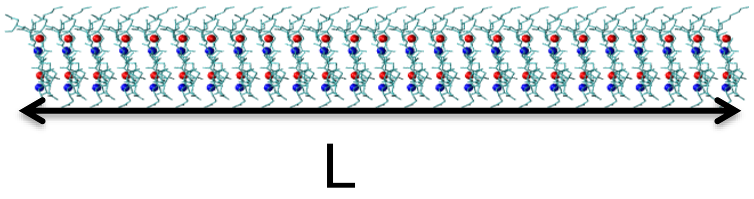


INP Monomer nucleates ice at 12 K above T_{homo}

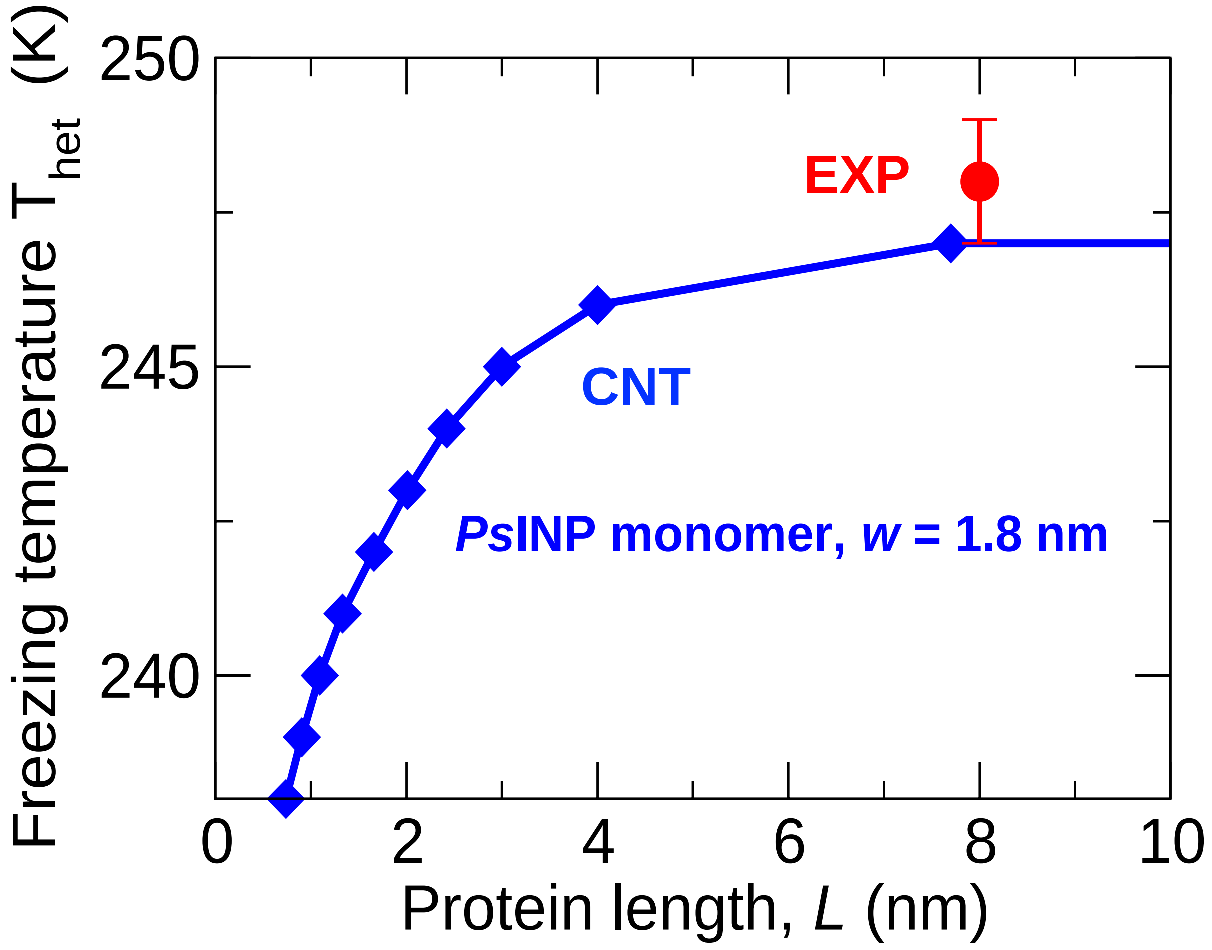
Ling *et al. J. Geophys. Res.: Atmos. 2018,*

Size of protein binding site controls ice nucleation temperature

We build proteins by adding loops of an ice binding protein

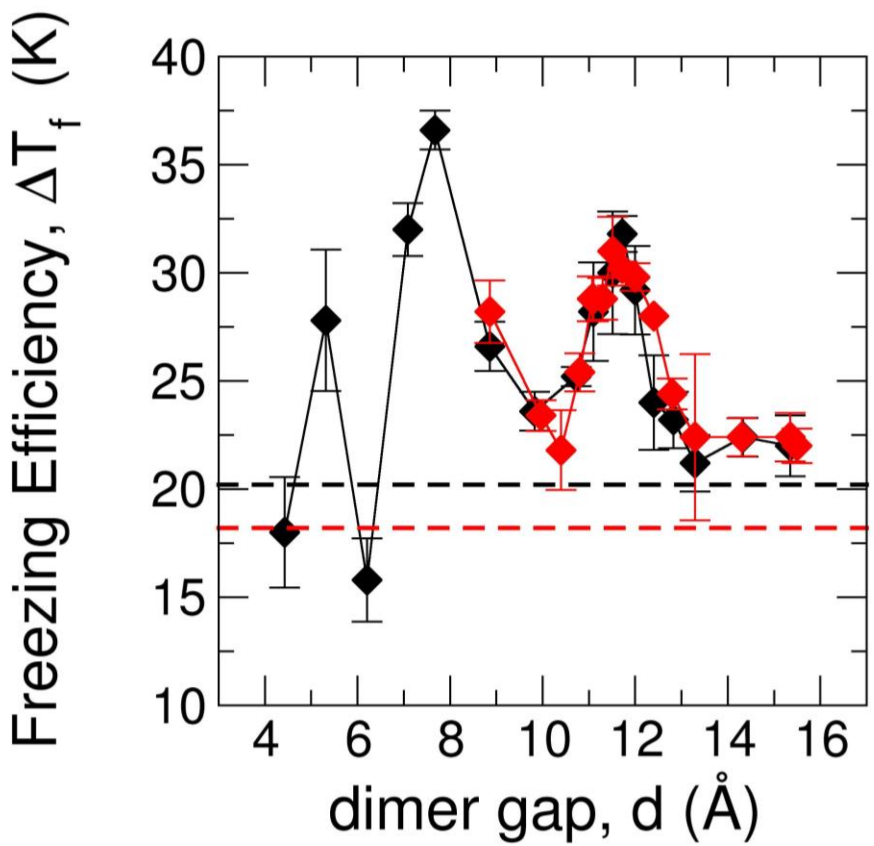


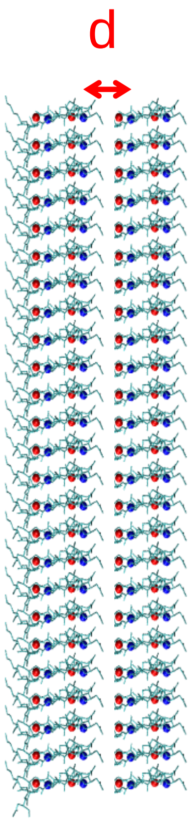
Qiu, Hudait & Molinero, JACS 2019

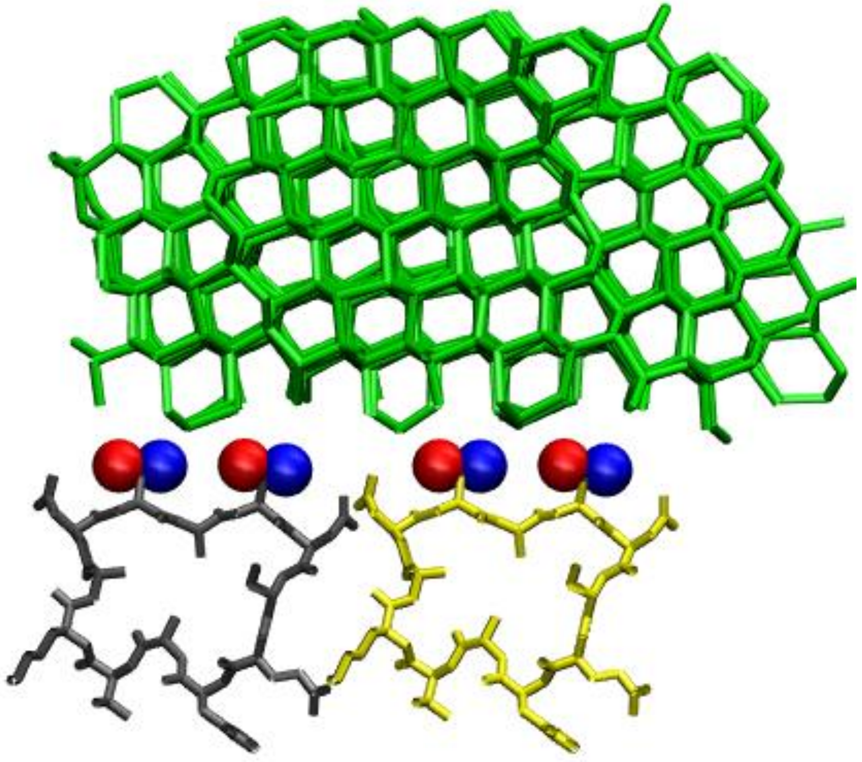


Width of the protein limits its ice nucleation efficiency:
Proteins must aggregate to reach their full nucleation potential

Optimal distances for protein aggregation are those that allow seamless connection of ice bound to all protein monomers



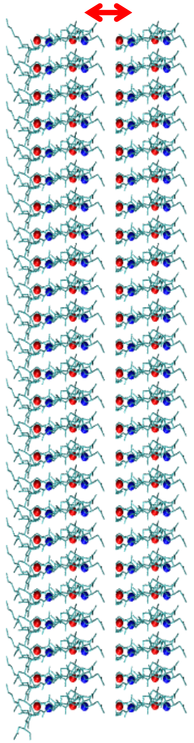




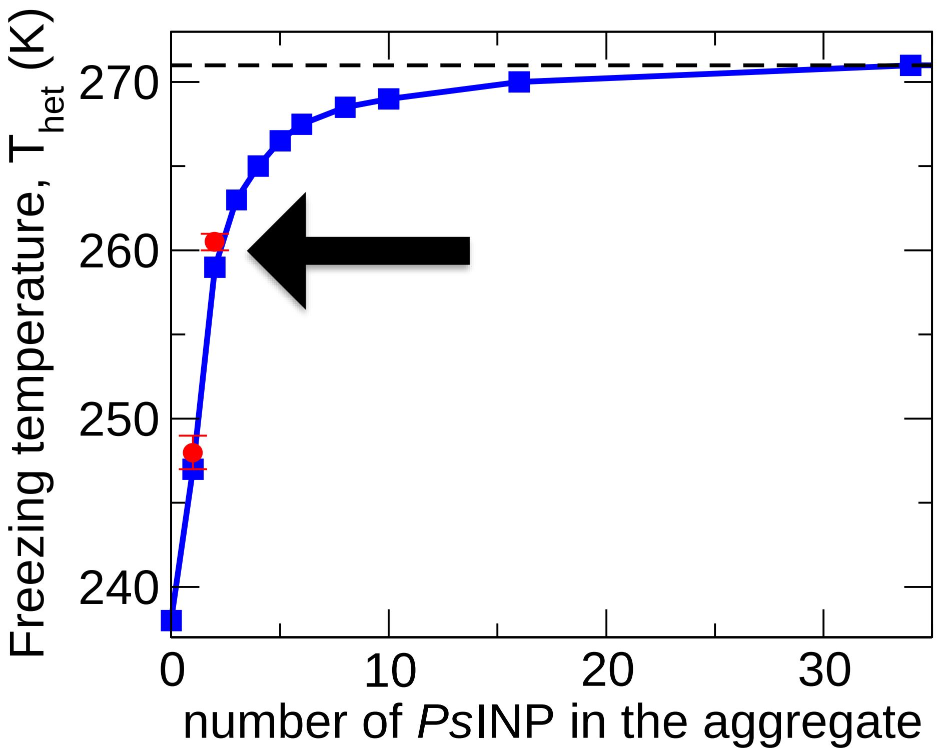
Bacteria must have exquisite control of the distance between ice-nucleating proteins in their cell membrane

Qiu, Hudait & Molinero, JACS 2019

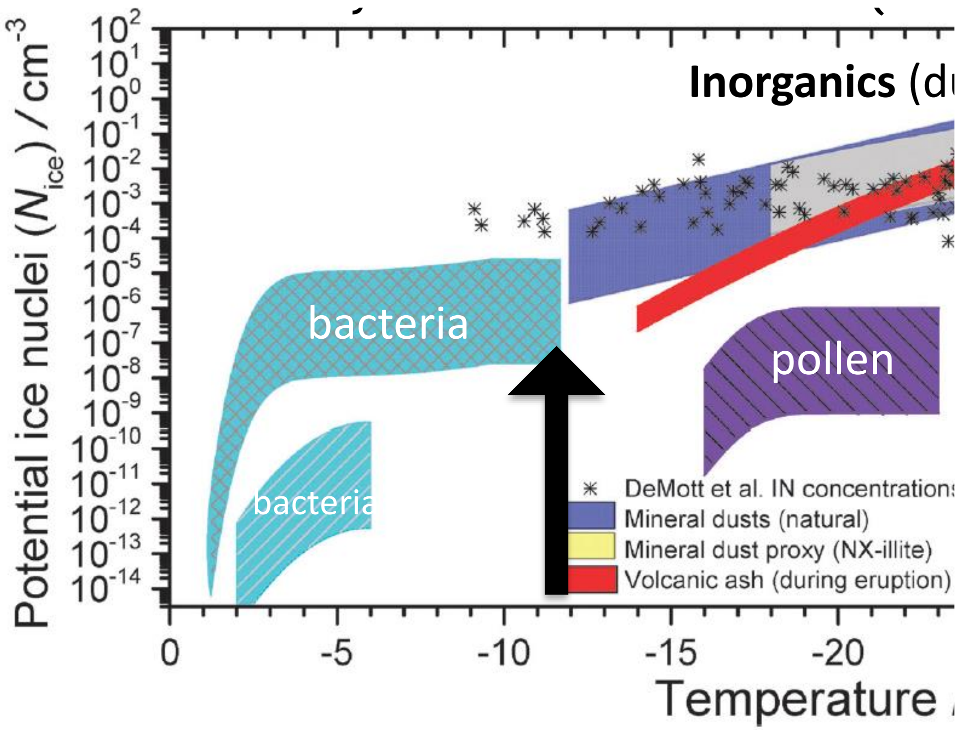
INP aggregates in Ps. syringae range from dimers to ~32 proteins



Theoretical prediction of freezing temperatures vs size of the protein aggregate



Density of nucleating bacteria in atmospherre vs temperature at which they nucleate ice



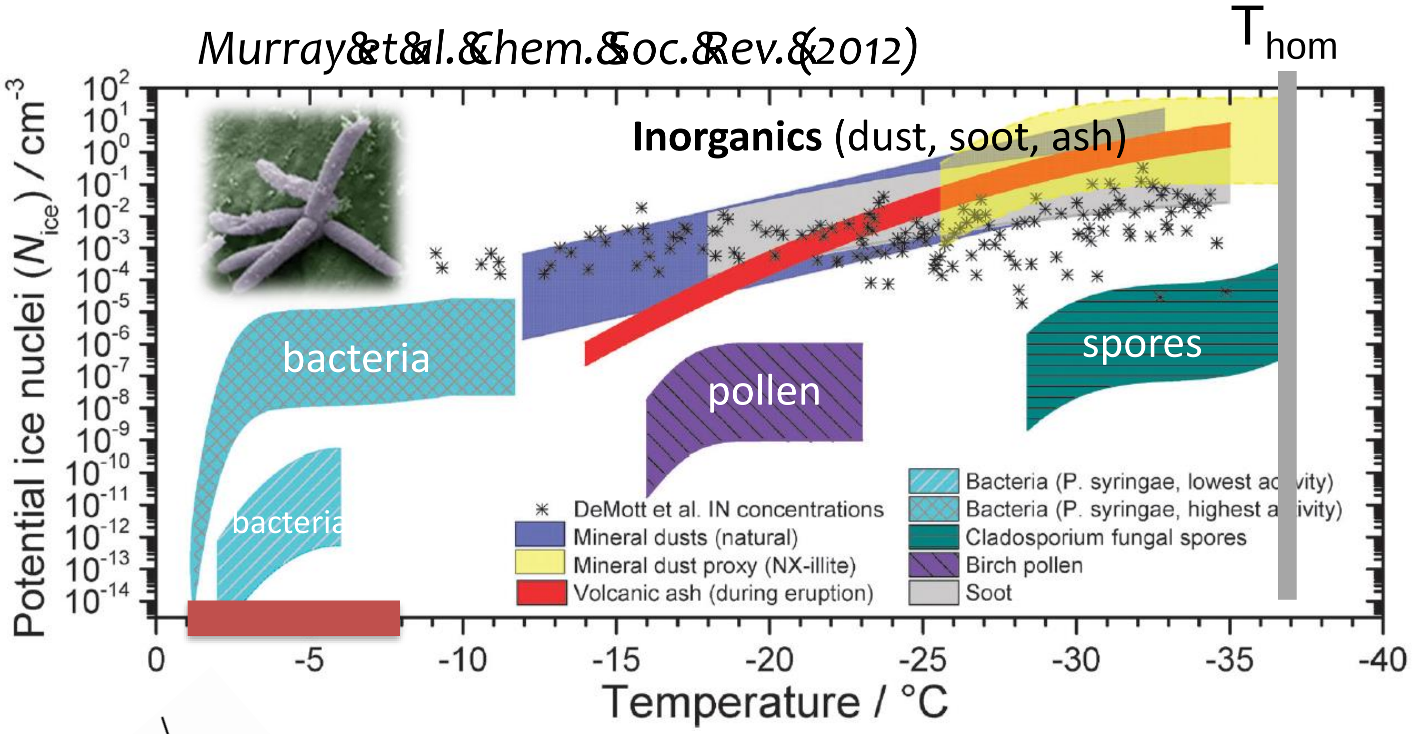
Bacterial ice nucleating proteins are as potent ice nucleants as ice itself

Qiu, Hudait & Molinero, JACS 2019

Proteins and organic crystals can be very efficient nucleants,
promoting water crystallization at very low supercooling

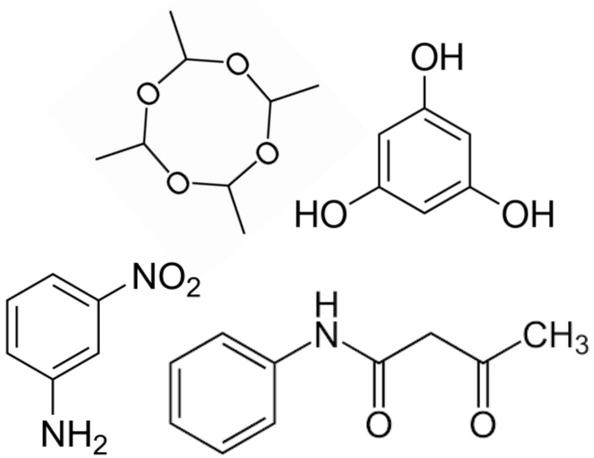
Ps. syringae bacteria are the most efficient ice nucleants in nature.

Bacterial ice-nucleating proteins bind ice at least as strongly as ice itself.



Crystals of simple organics can be as potent nucleants as Ps. Syringae

Organics are 20-90% mass of submicron atmospheric aerosols.



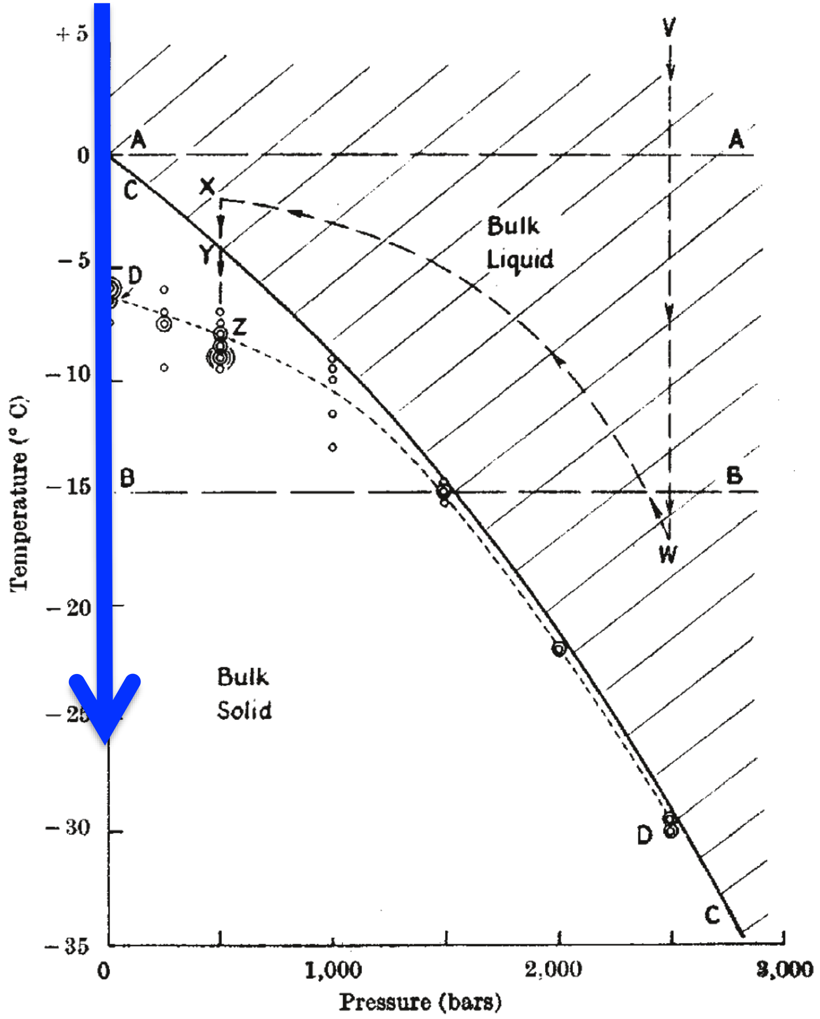
Hundreds of organic crystals were tested for ice nucleation in the 1960's – Several dozen nucleate ice at T > -5 ^{o}C

Head Nature 1961

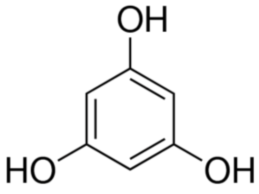
Fukuta Nature 1960 & J. Atm. Sci. 1966

Evans Nature 1967

Ice nucleation efficiency of most potent organic crystals rivals that of ice nucleating bacteria



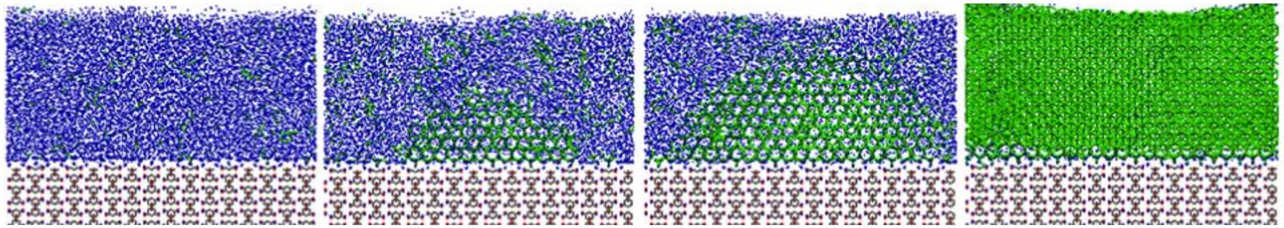
phloroglucinol



Two-dimensional Nucleation of Ice

Evans, Nature 1967

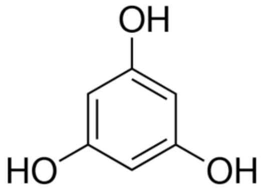
Evans proposed that the exceptional ice nucleation efficiency was due to the progressive formation of an ordered monolayer at the organic-water interface



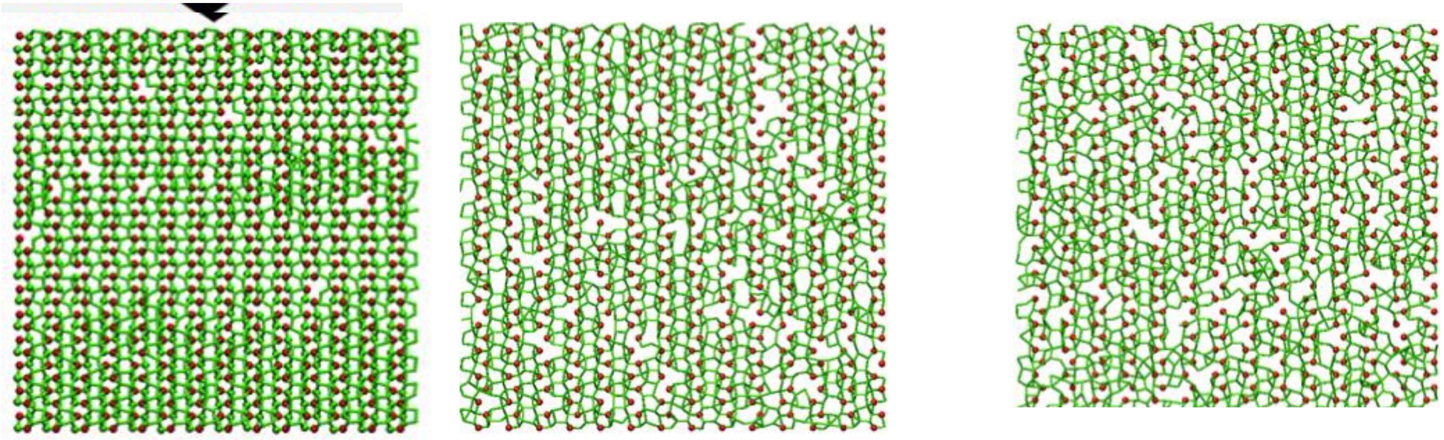
Simulations confirm there is a distinct water monolayer at the organic interface that orders progressively on cooling , but fully only after ice formation

All simulations at
1 bar @(010) face

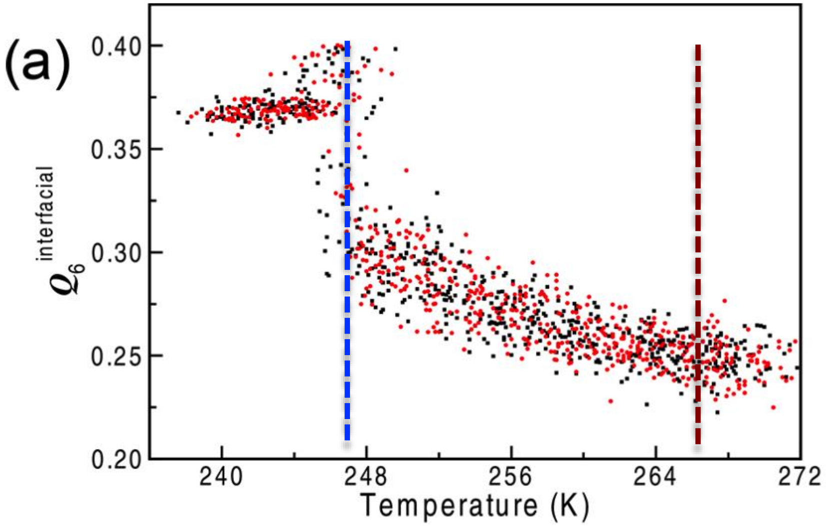
of phloroglucinol
dihydrate



crystallized interface | liquid interface @ 250 K | liquid interface @ 260 K



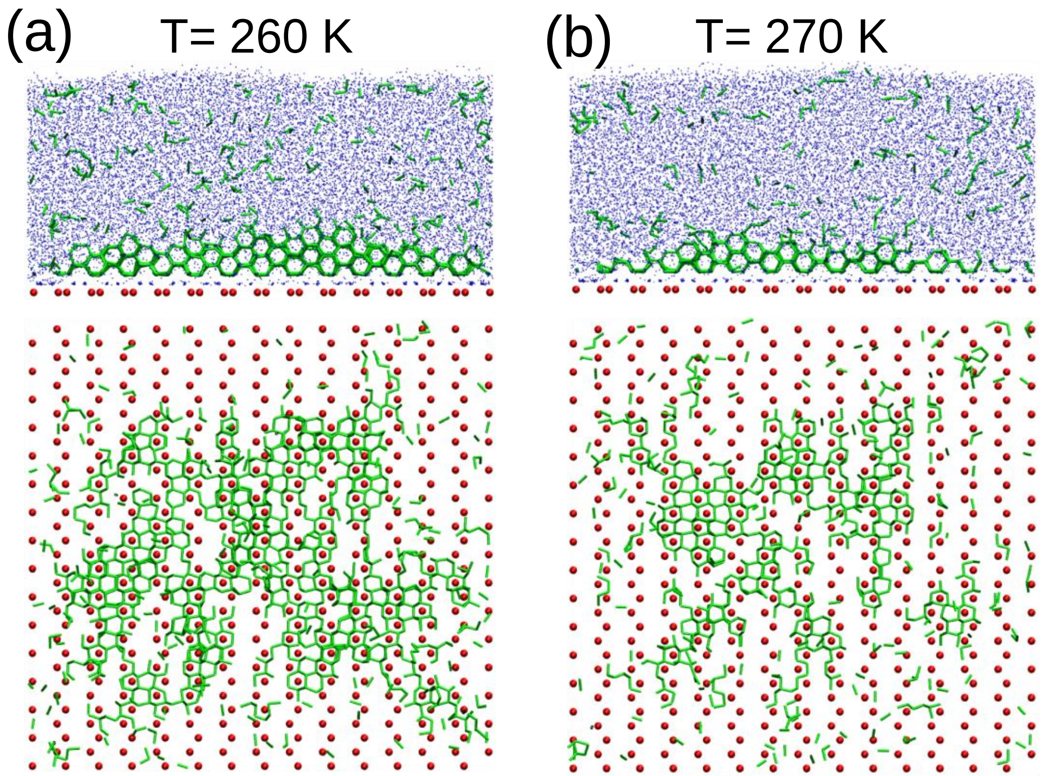
T_{het} = 248 K@10^9 K/s T_{het} = 266 K @0.1 K/s

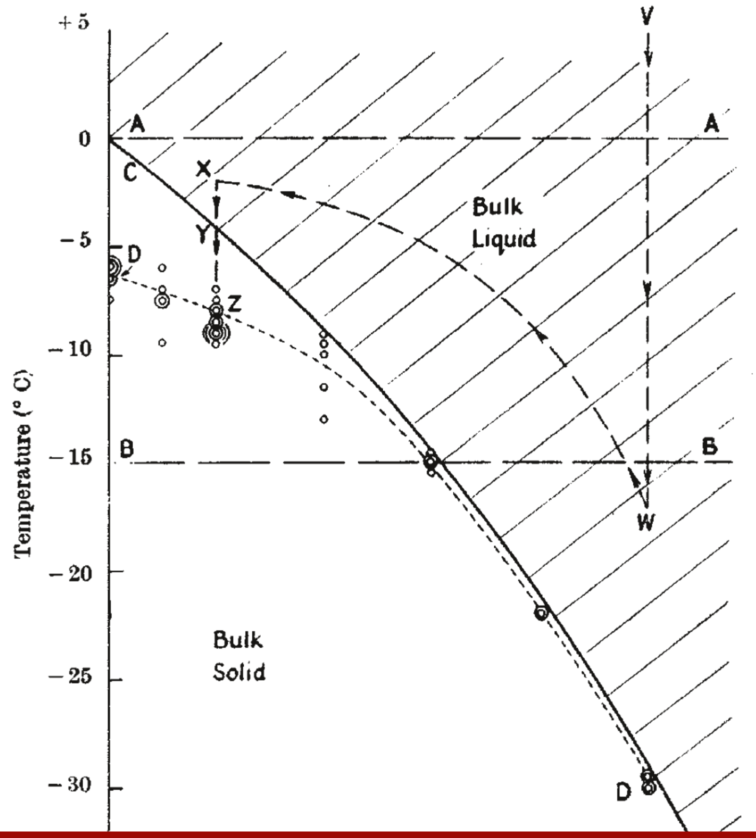


interfacial transition layer with 5- and 6-member rings bridges the distinct HB order of organic and ice face

Metya and Molinero, JACS 2021

Fully ordered monolayer would nucleate ice at T > -2ºC





Simulations restraining the amount of ice

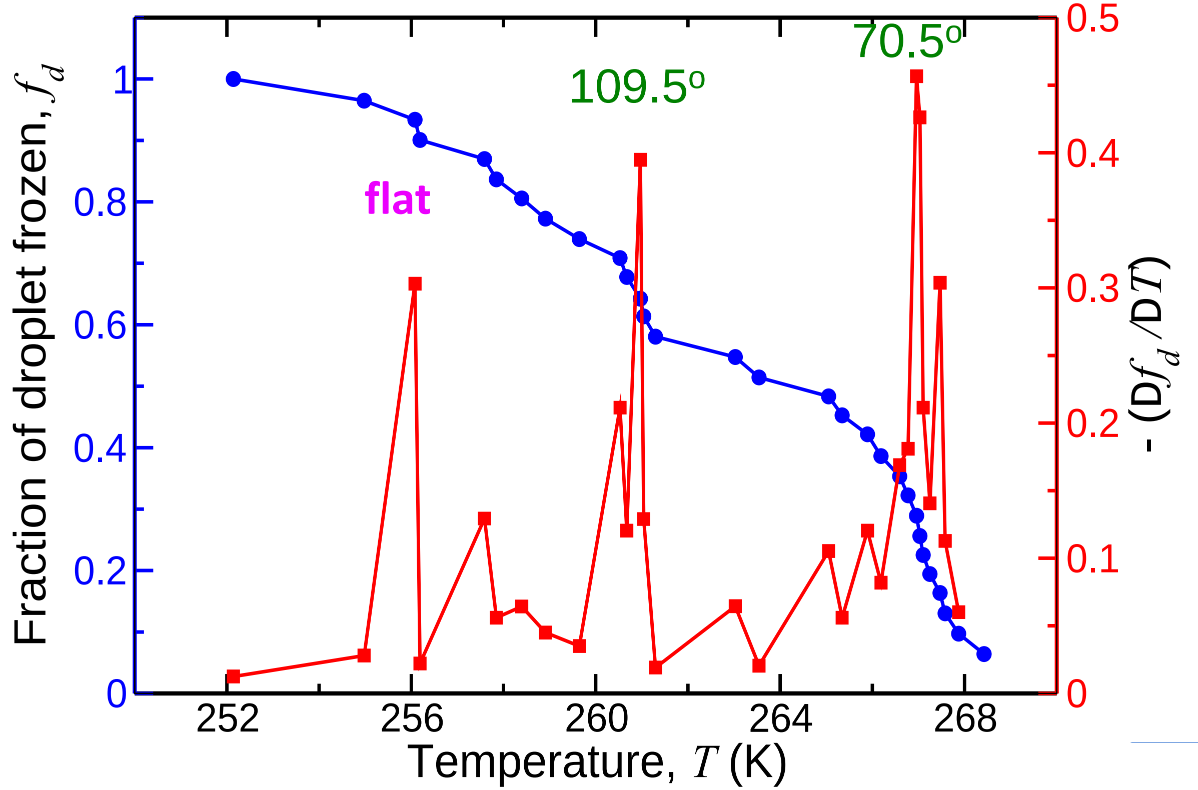
Intersection of temperature of formation of the monolayer and T_{melt} of ice could account for the outstanding ice nucleation at high pressures

Metya and Molinero, JACS 2021

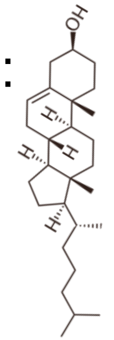
Not everything that shines is gold!!

Topographical defects can confer exceptional ice nucleation ability to mediocre nucleants

Nucleation by pure cholesterol monohydrate crystals



Cholesterol has a single hydroxylated surface: only that surface can bind ice.

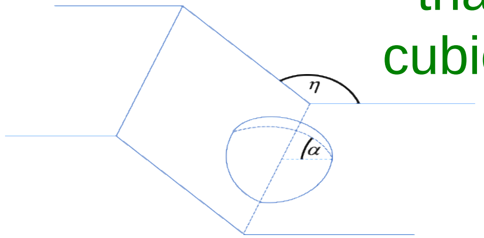


What is that's face T_{het} ?

What are the other peaks?

We use molecular simulations to assign the **nucleation by the flat cholesterol monohydrate surface to the 256 K peak**

We use nucleation theory to assign the **peaks around 261 and 267 K to ice nucleation on 109.5º and 70.5º wedges** that seamlessly accommodate cubic ice bound by its (111) face.



Experimental fd curve: Sosso et al. Chem. Sci. 2018

Metya, Qiu and Molinero, to be submitted

There may be defects with many angles in the crystals, but only a few wedge angles can accommodate ice without strain

Bi et al. Nat. Comm. 2017: ice nucleation in graphite wedge using molecular simulations

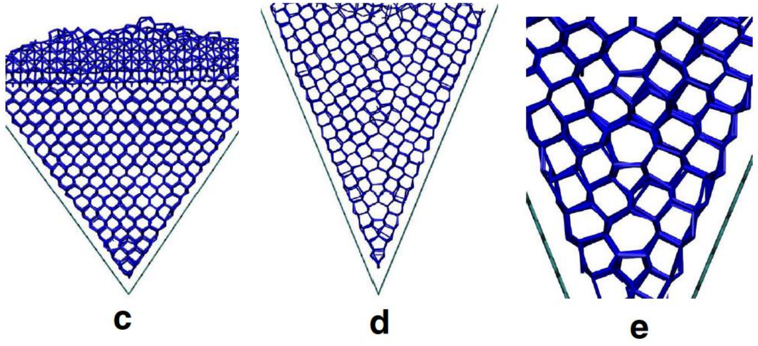
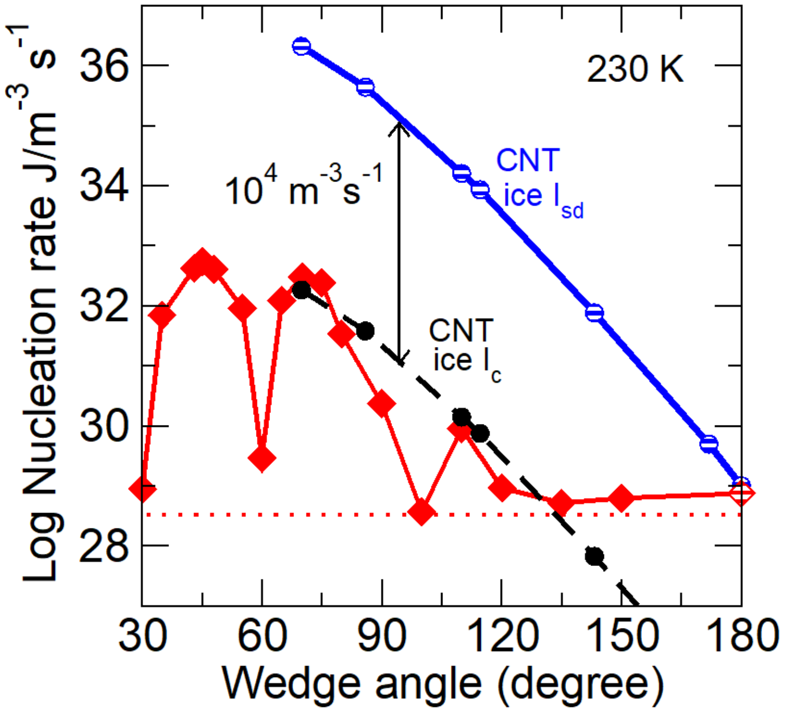


Figure 1 | Crystallization of mW water within atomically sharp wedge.

Bi et al. found non-monotonous nucleation rate vs wedge angle: they proposed that some defects on ice favor nucleation

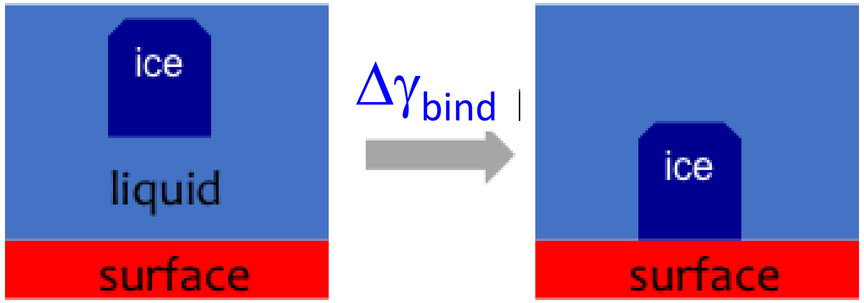
They found these best wedges form cubic ice



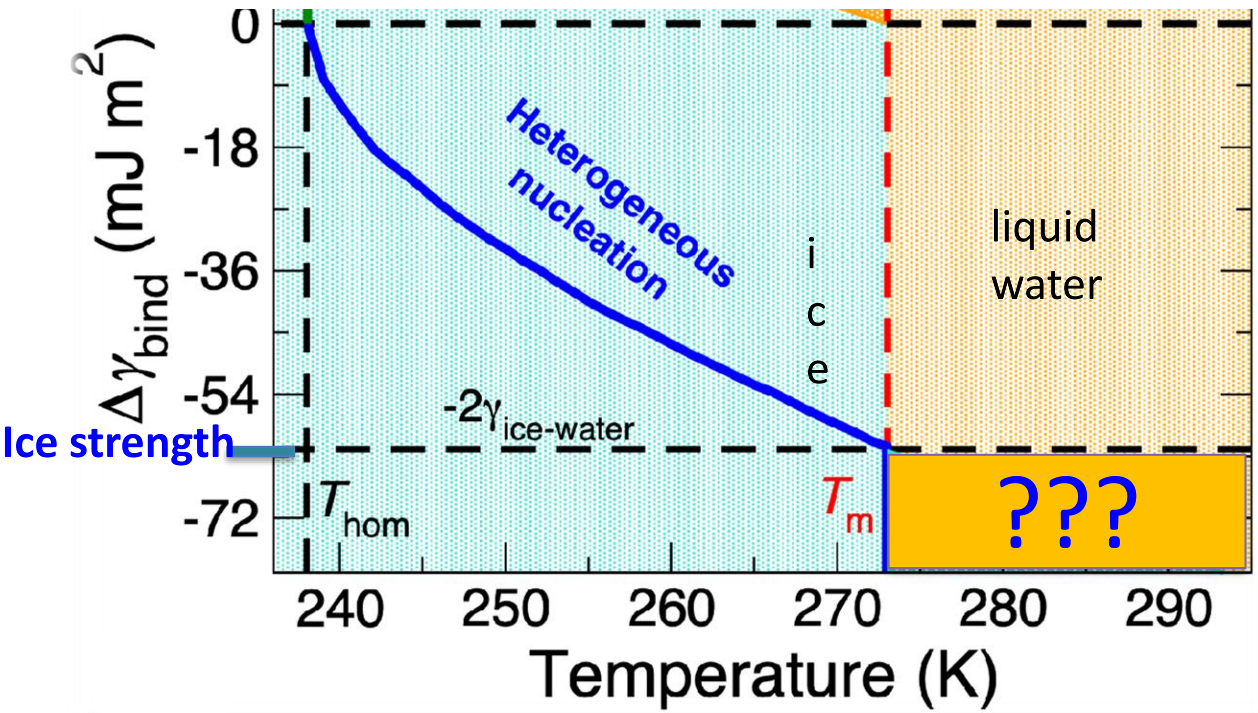
We find that special geometries produce the nucleation rate predicted by CNT for cubic ice
all others angles are worse, because ice is destabilized by strain and/or defects
(akin to the special distances for INP dimers)

Metya, Qiu and Molinero, to be submitted

Bacterial ice nucleating proteins and phloroglucinol dihydrate can bind ice at least as strongly as ice itself



$$\Delta\gamma_{bind} = \gamma_{ice\text{-}surface} - (\gamma_{ice\text{-}liquid} + \gamma_{liquid\text{-}surface})$$

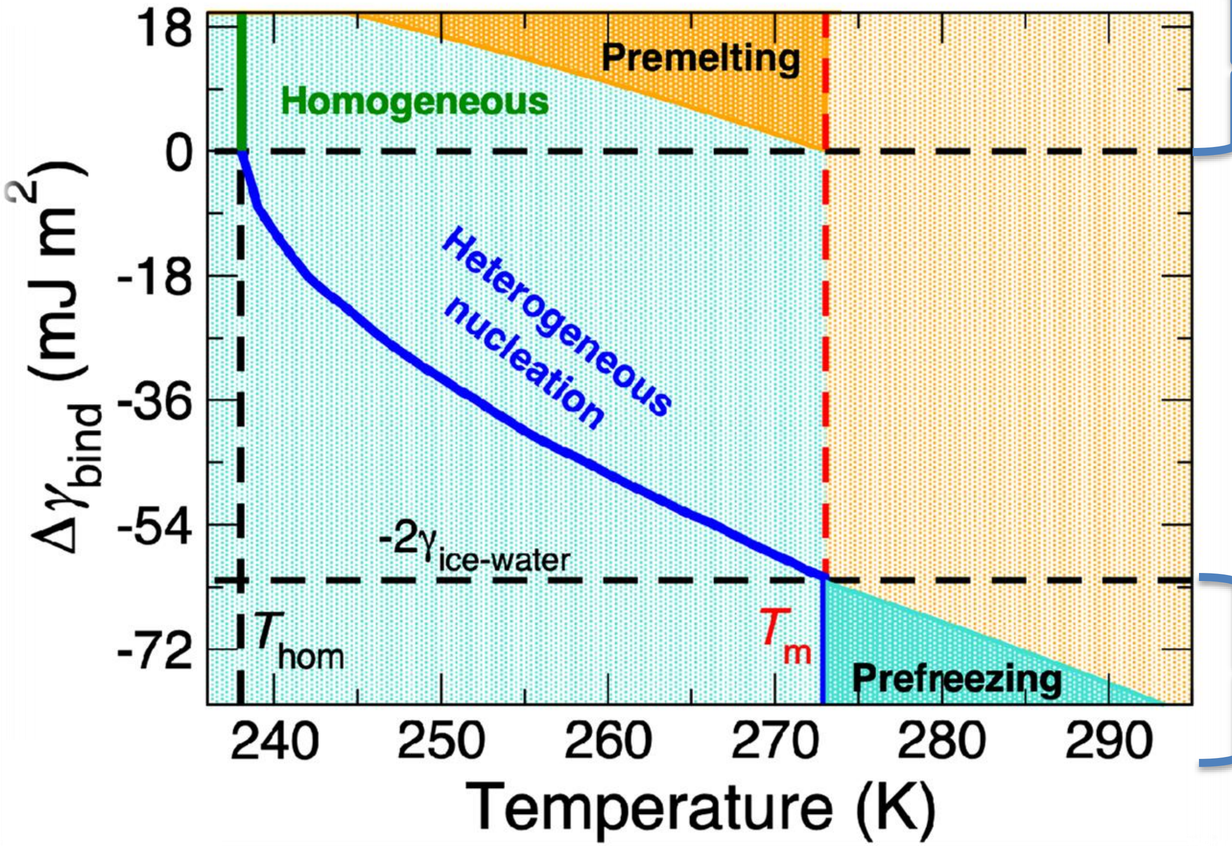


Ice nucleation temperature approaches T_m as binding free energy → $-2\gamma_{ice\text{-}water}$

What happens if the surface binds ice even <u>stronger</u> than ice itself?

We predict a prefreezing regime, mirror image of premelting

Theoretical prediction using experimental data of water



$\Delta\gamma_{bind} > 0$ is condition of premelting:

$\gamma_{ice\text{-}surface} > \gamma_{ice\text{-}liquid} + \gamma_{liquid\text{-}surface}$

Surfaces that induce premelting cannot promote the nucleation of ice

(Qiu and Molinero, *JPC Lett* 2019)

$\Delta\gamma_{bind} < -2\,\gamma_{ice\text{-}liquid}$ is equivalent to:

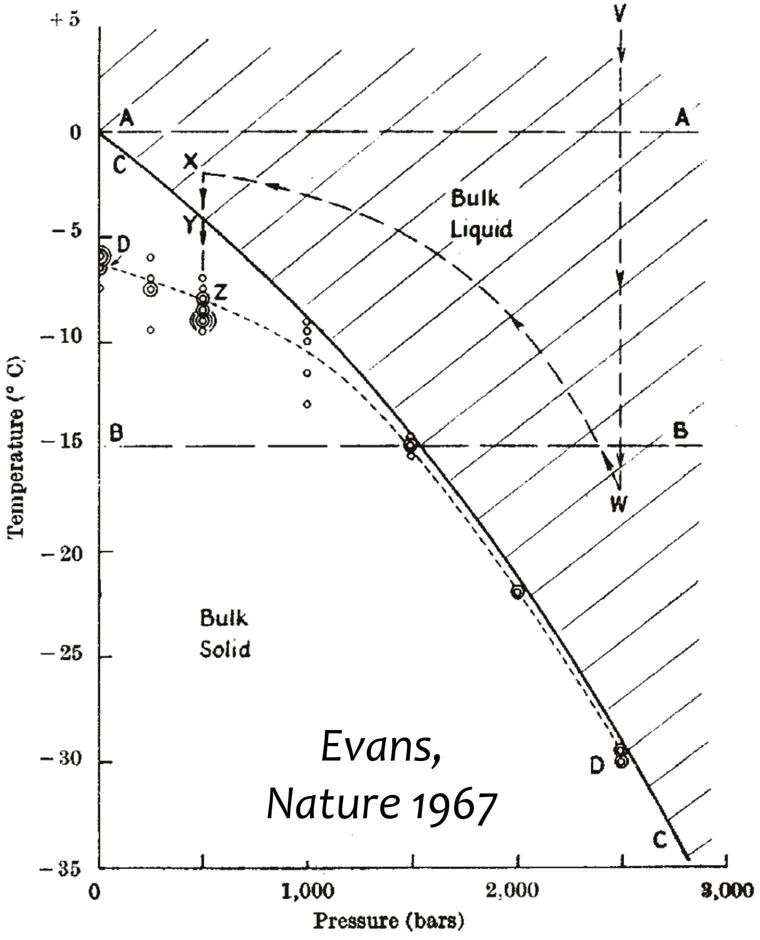
$\gamma_{ice\text{-}surface} + \gamma_{ice\text{-}liquid} < \gamma_{liquid\text{-}surface}$

If surface free energies favor ice very strongly, ice layers would form in equilibrium above the melting temperature

Qiu and Molinero, to be submitted

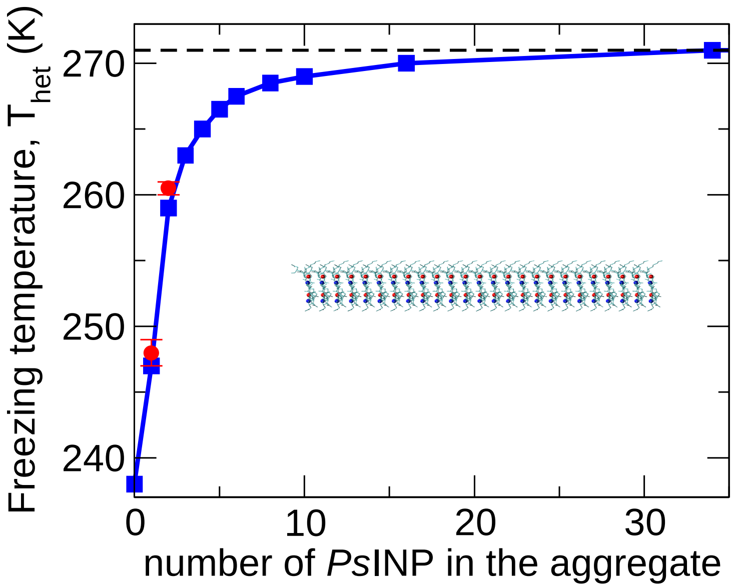
To access water prefreezing we look for exceptional ice nucleants

Potent organic crystal nucleant at high pressure (e.g. phloroglucinol)



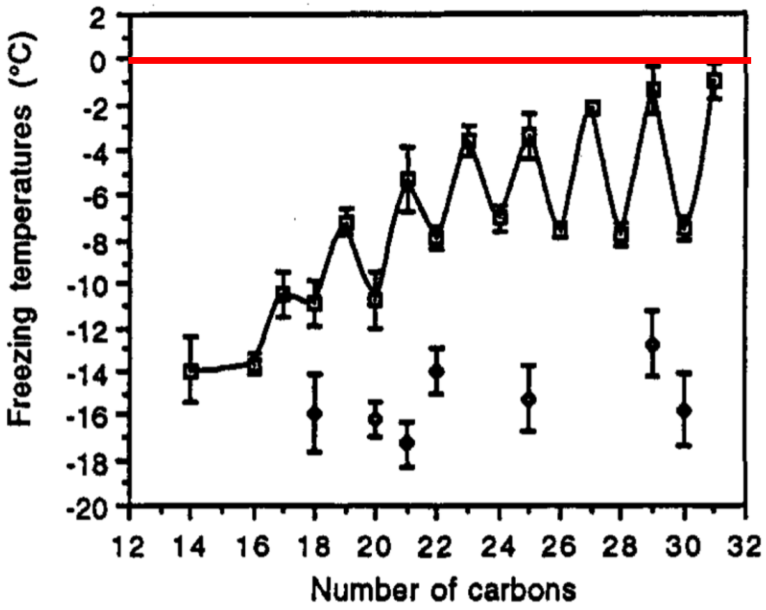
Evans, Nature 1967

Ice nucleating bacteria (probably at boundary)



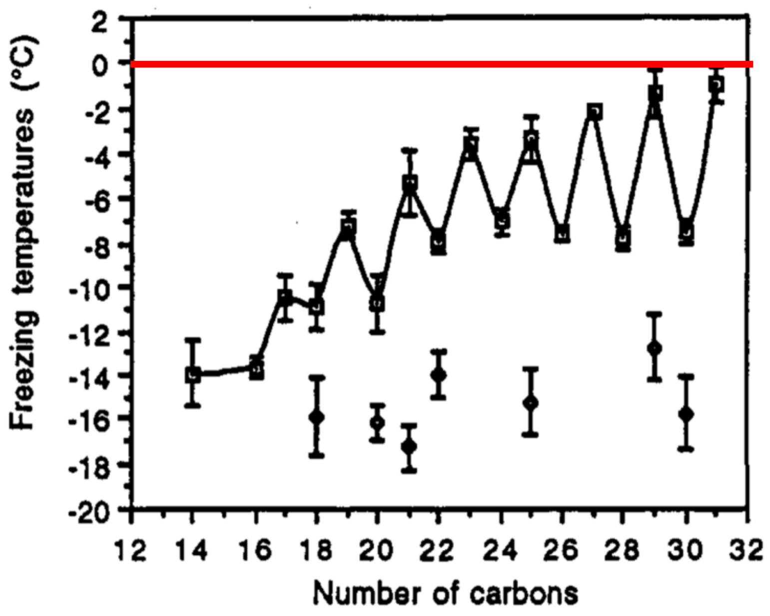
Qiu, Hudait and Molinero, JACS 2019

C31OH alcohol monolayer is extremely close

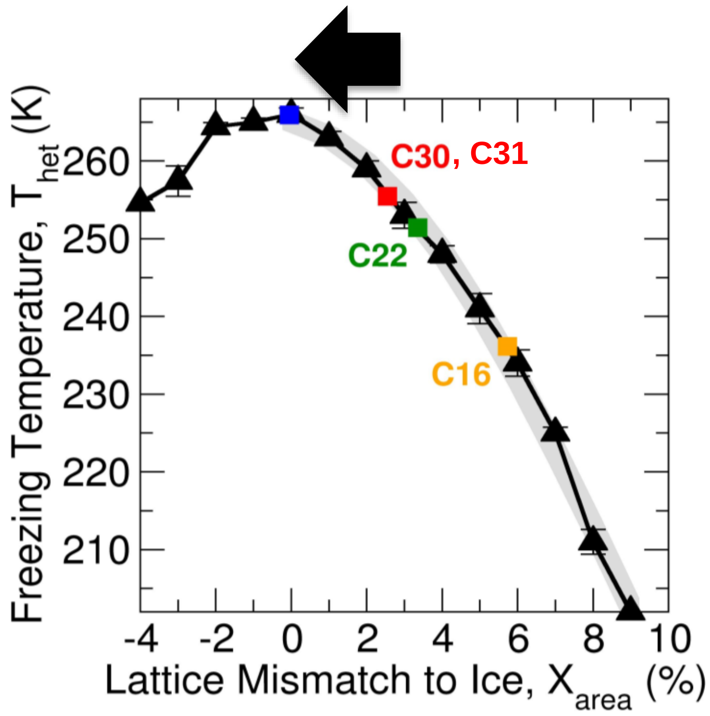


Gavish et al., Science 1990

$C_{31}OH$ alcohol monolayers nucleate ice at -1ºC: they need a very small push to reach the prefreezing region



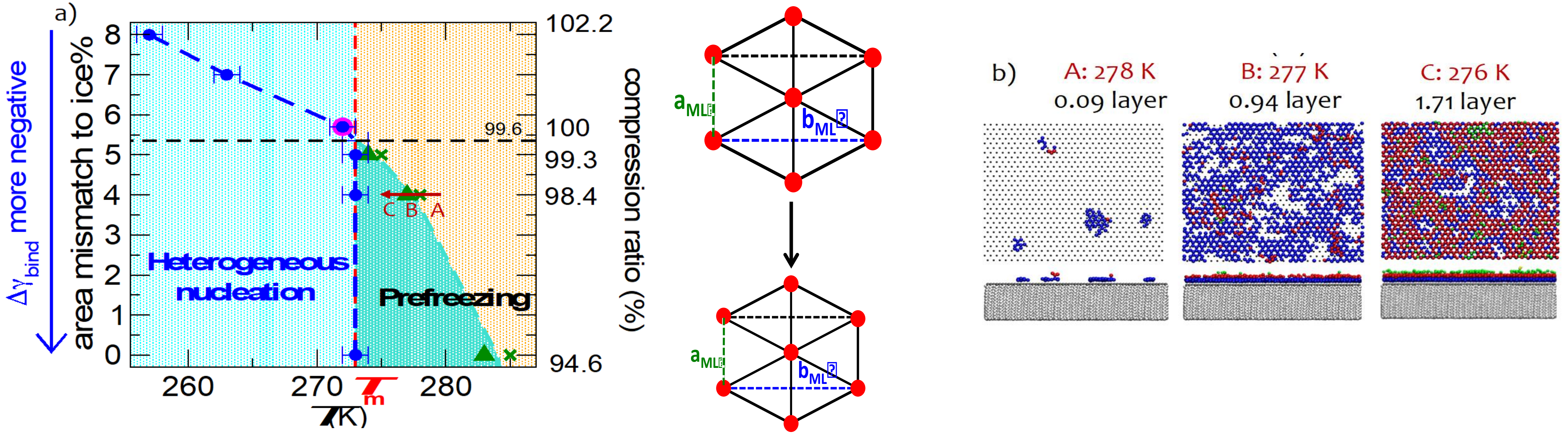
Gavish et al. Science 1990



Qiu, Odendahl, Hudait, Mason, Bertram, Paesani, DeMott & Molinero, JACS 2017

Lattice mismatch to ice controls freezing efficiency of the alcohols: Compression of the monolayer will make it better ice nucleant

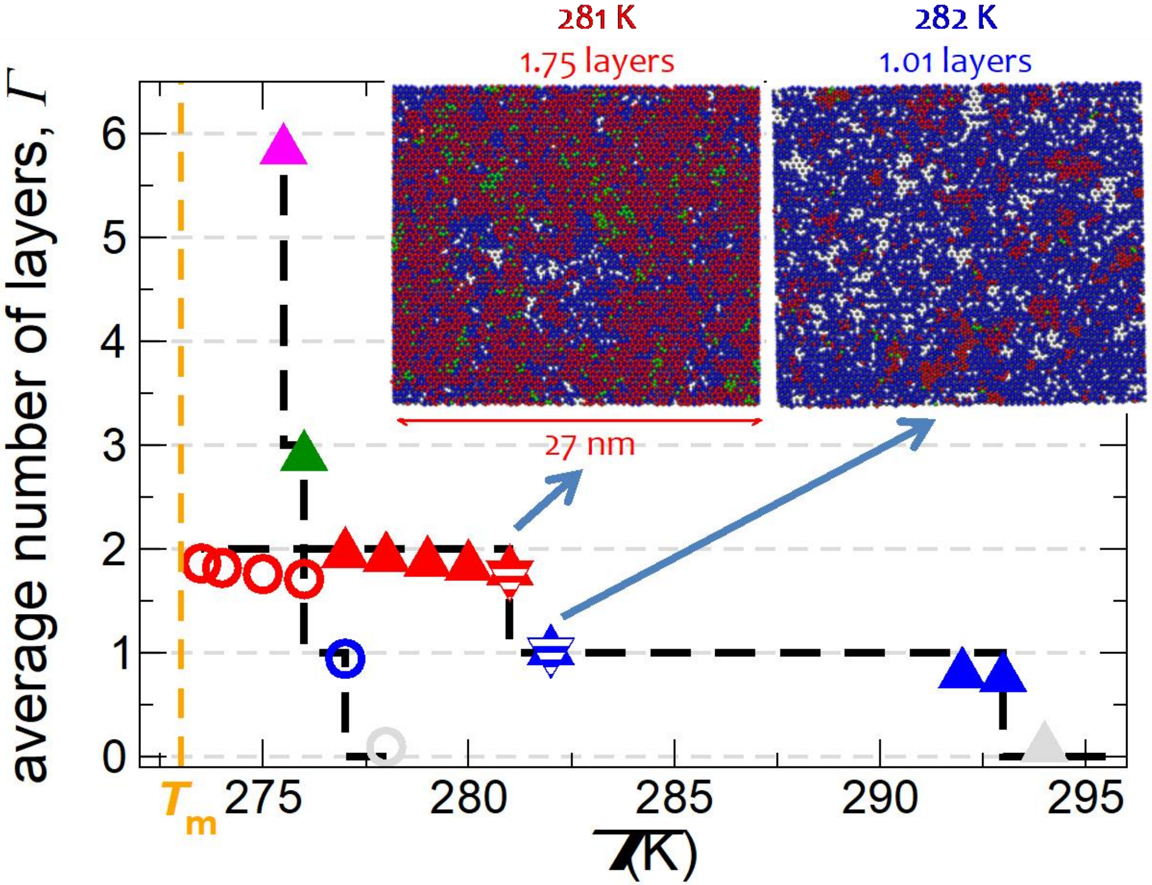
Compression of the $C_{31}OH$ monolayer by as little as 0.3% would suffice to enter the prefreezing regime

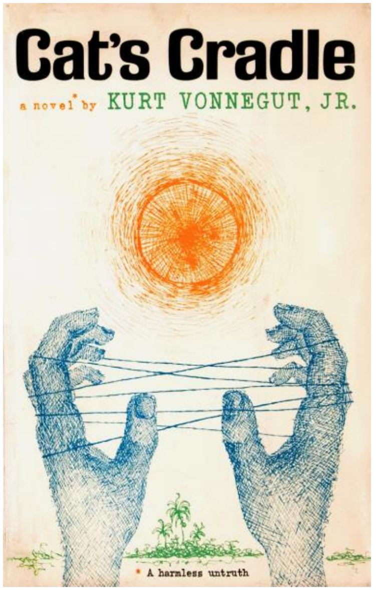


If the surface induces prefreezing, ice is already on the surface at T_{melt} and liquid water cannot be supercooled: the most potent nucleant

Qiu and Molinero, to be submitted

Number of pre-frozen ice layers increases on approaching the melting temperature from above





Is this like "ice nine"?

Will it crystallize all water and destroy our planet???

No: surface freezing cannot grow macroscopic ice

Free energy cost of growing ice at $T > T_m$ compensates the driving force by interfacial free energies… and that sets how many layers of ice form ay any temperature.

Conclusions

Size of ice-binding surfaces and their strength of binding to ice determine the temperature at which they can nucleate ice.

Bacterial ice nucleating proteins are powerful ice-binding: they form aggregates to reach their full potency.

Potent organic crystal nucleants develop ordered water monolayer that facilitates the binding to ice.

Organics constitute 20 to 80% of tropospheric aerosols.

Organic crystals may contribute to the ability of these aerosols of nucleating ice in clouds

Topographical defects can make even mediocre nucleants act as exceptional ones

It is possible to nucleate ice without any supercooling!

Prefreezing of water above the melting temperature can be reached in simulations and is close or already there in high pressure organic crystals, long-chain alcohol monolayers, and ice nucleating bacteria

Synthetic analogues can have potency that rival and surpass bacterial proteins: could be effective for seeding clouds to promote precipitation

Since weather weapons were banned in 1978,

US federal funding for fundamental research on cloud seeding mostly stopped

…but programs for cloud seeding continued

The Salt Lake Tribune

By Zak Podmore | March 28, 2021, 6:00 a.m.

Utah is a leader in cloud seeding. Is it working?

As drought deepens in the Colorado River Basin, the state's program could serve as a model for boosting West's water supplies.

and may intensity as arid regions become even dryer

A modeling examination of cloud seeding conditions under the warmer climate in Utah, USA

Binod Pokharel[a,b,*], S.-Y. Simon Wang[a,b], Hongping Gu[b], Matthew D. LaPlante[a,c], Jake Serago[d], Robert Gillies[a,b], Jonathan Meyer[a,b], Stephanie Beall[e], Kyoko Ikeda[f]

Jan 2o21

How will cloud seeding impact water rights in a warming atmosphere?