Snow Crystals: I

A Case Study in Spontaneous Structure Formation

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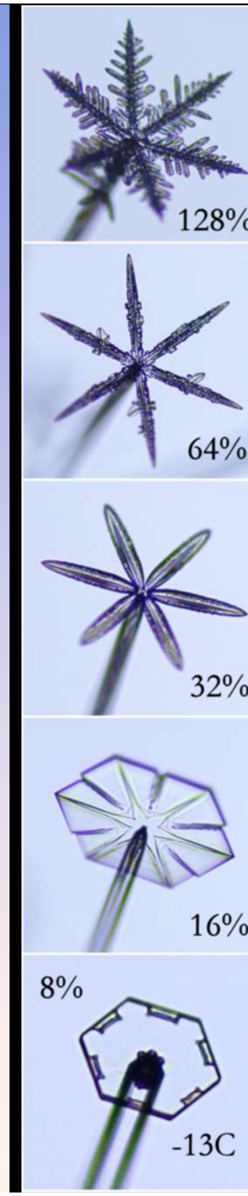



Don Komarechka

Nature makes things using self-assembly

(…not like this)

An archetypal example of large-scale structural self-assembly

Christopher Buchholz

Can we "fully" understand even a simple system?

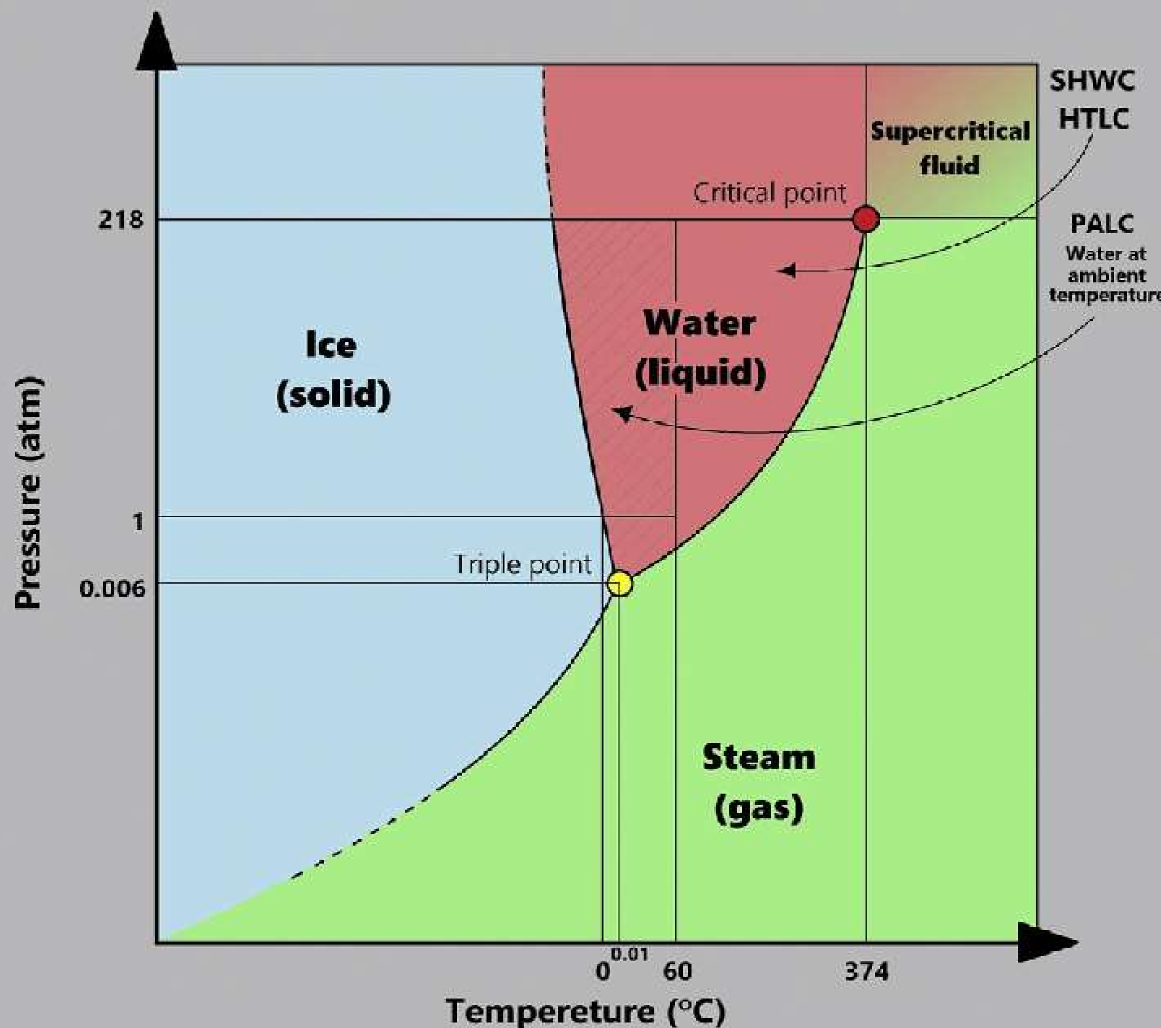
= Make a computational model that reasonably reproduces known growth behaviors, agrees with experiments.

→ Model relevant physical processes

Ice/vapor: An interesting phase transition

Ice/vapor
(T, σ)

Ice/water
(P, ΔT)
→ (P_0, ΔT)



A laboratory "Snowflake on a Stick"

Environment:

Fixed temperature – T < 0 C

Fixed supersaturation – σ > 0

(RH > 100%)

In air at 1 atm

Add seed crystal

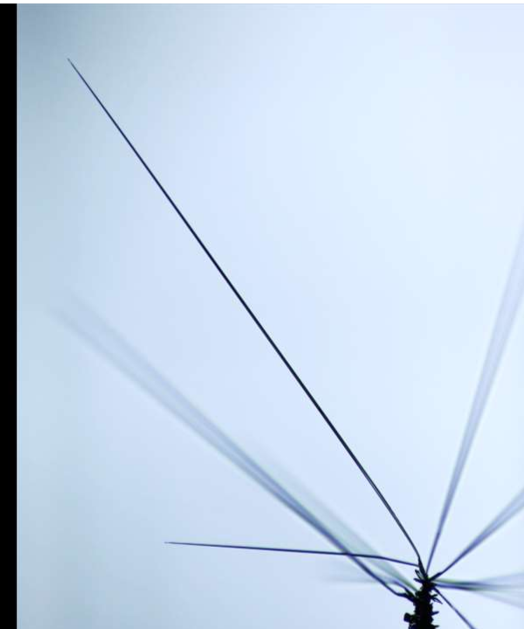
Thin c-axis ice needle

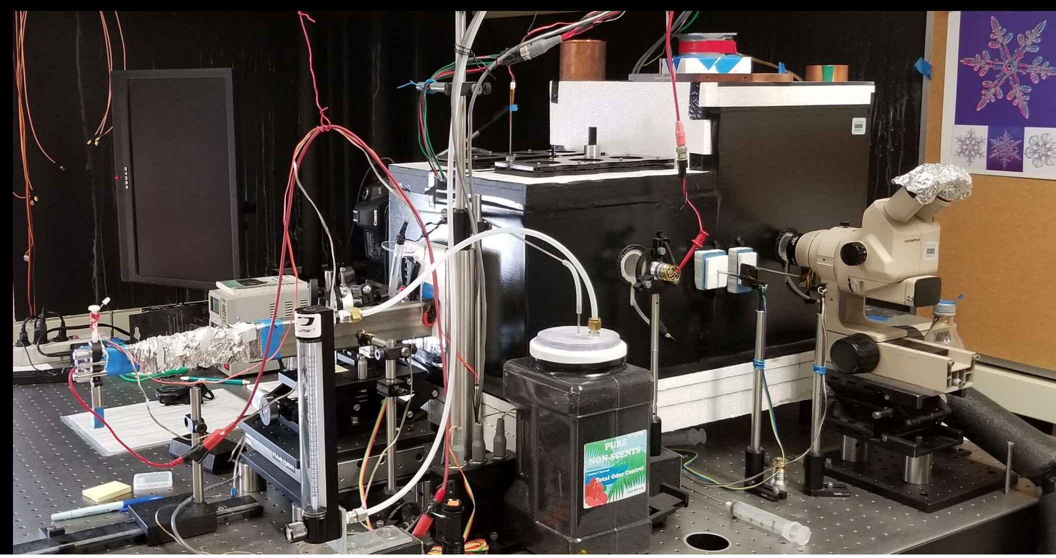
~ 2 mm long, ~2 μm tip

This example:

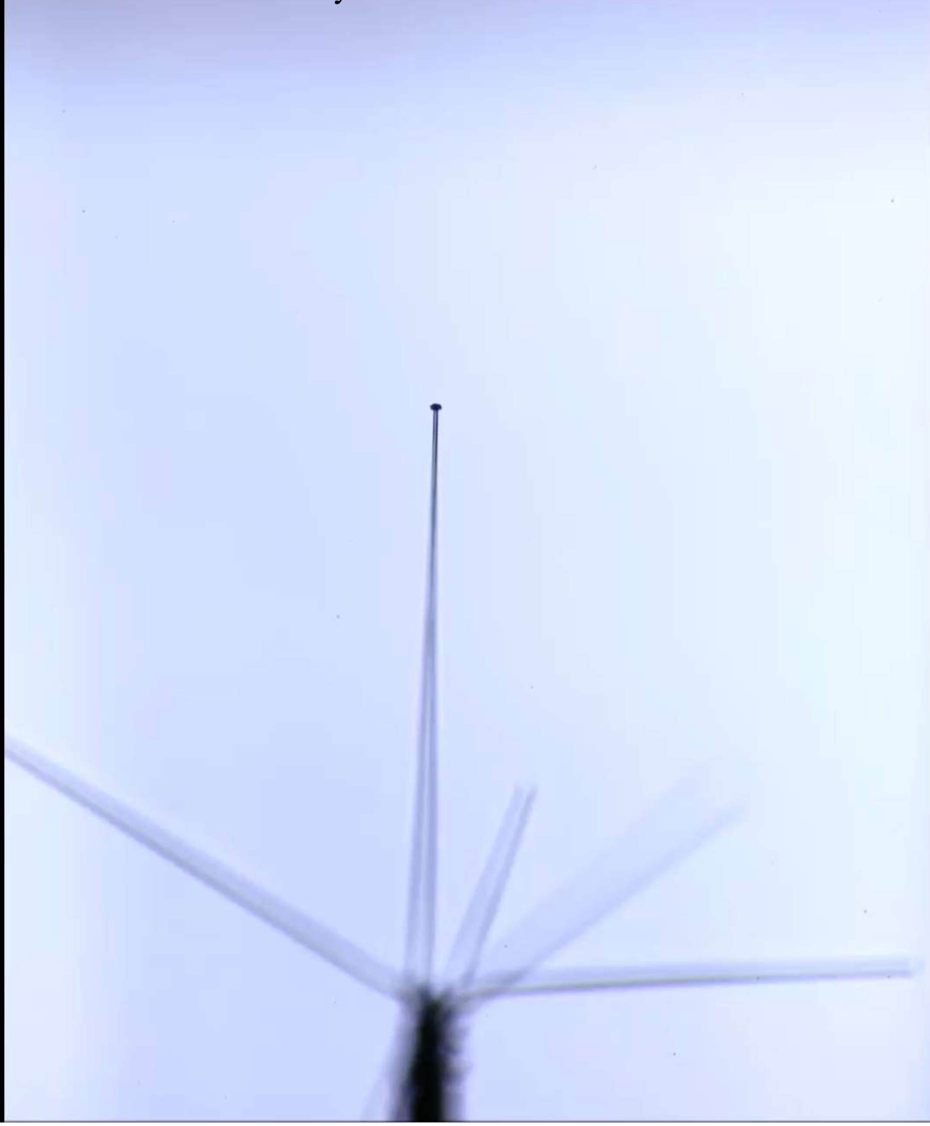
T = -15 C, σ = 16 %

then 64%





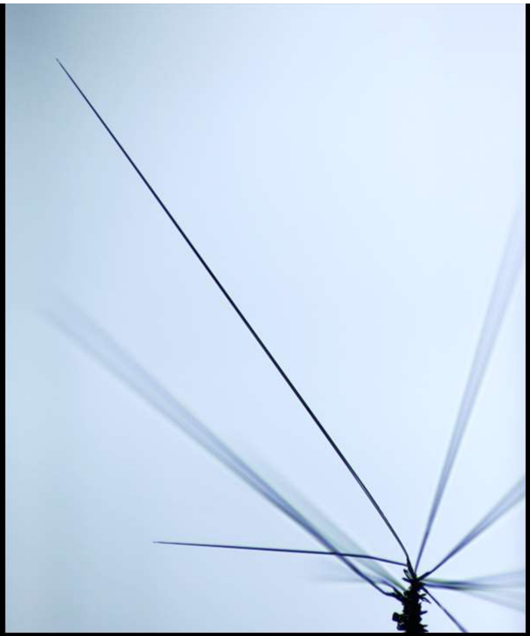
A laboratory “Snowflake on a Stick”

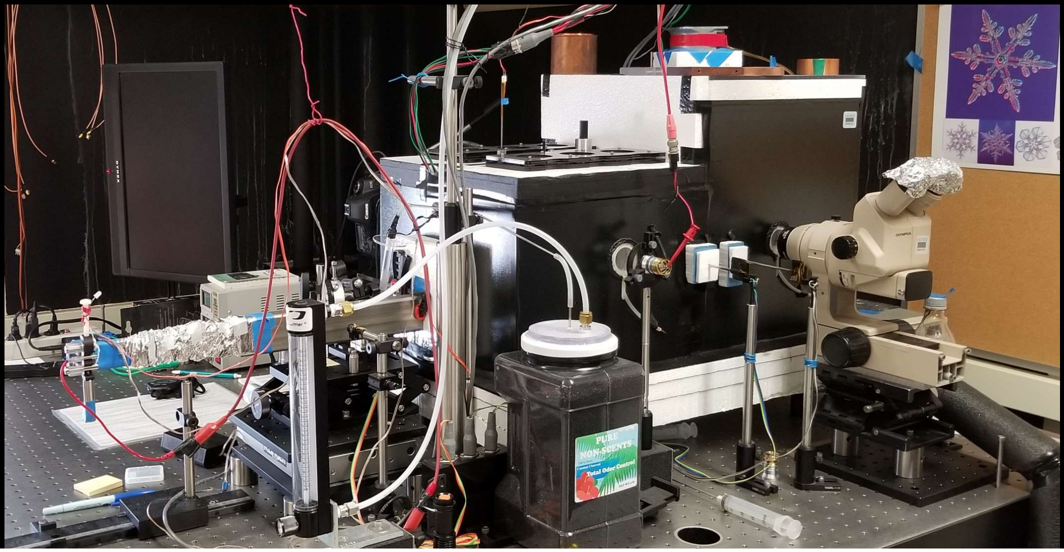


Environment:
Fixed temperature – T < 0 C
Fixed supersaturation – $\sigma > 0$
(RH > 100%)
In air at 1 atm

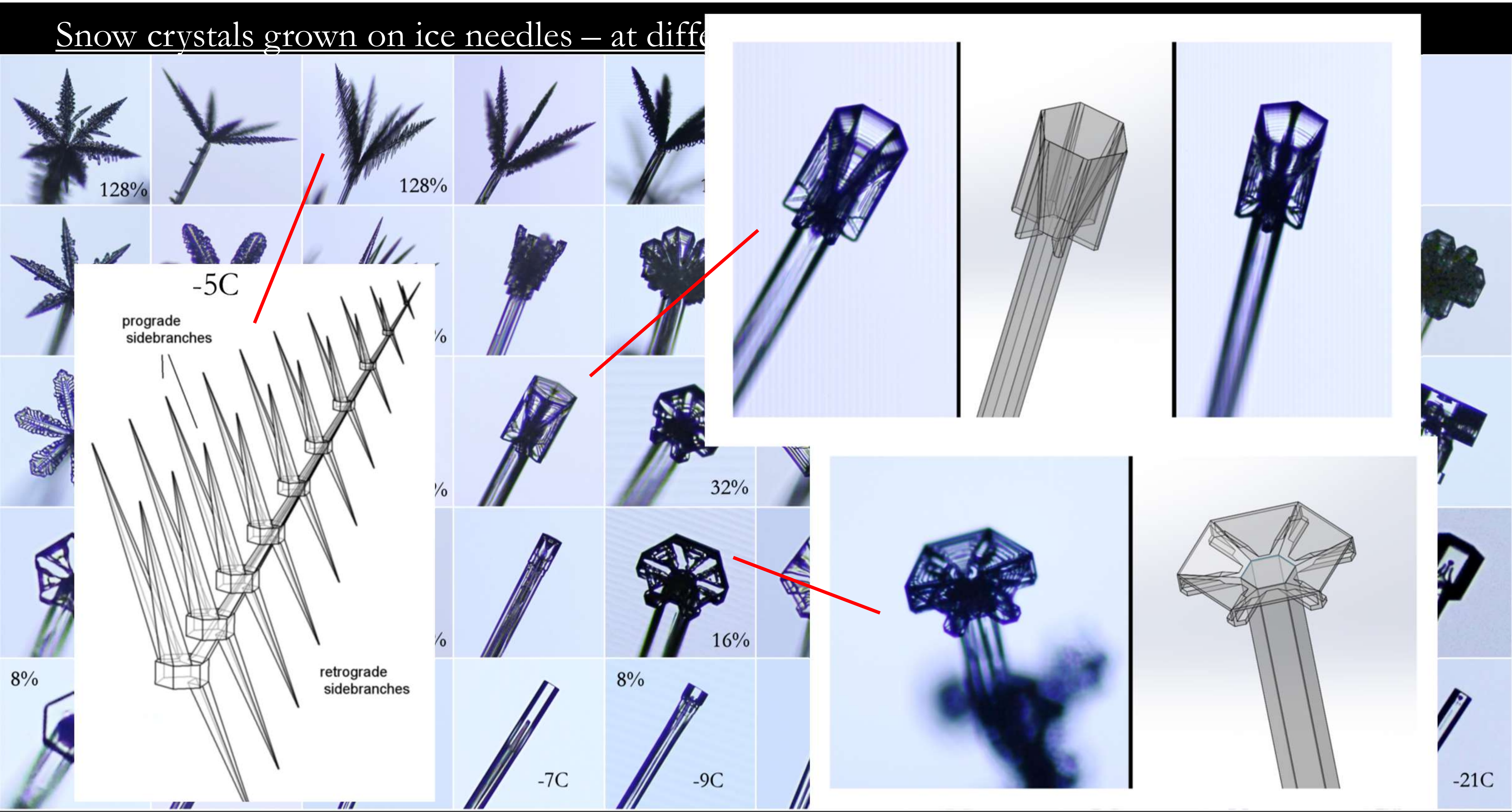
Add seed crystal
Thin ice needle
~ 2 mm long, ~2 μm tip

This example:
T = -15 C, σ = 16 %
then 64%
Growth time ~20 minutes





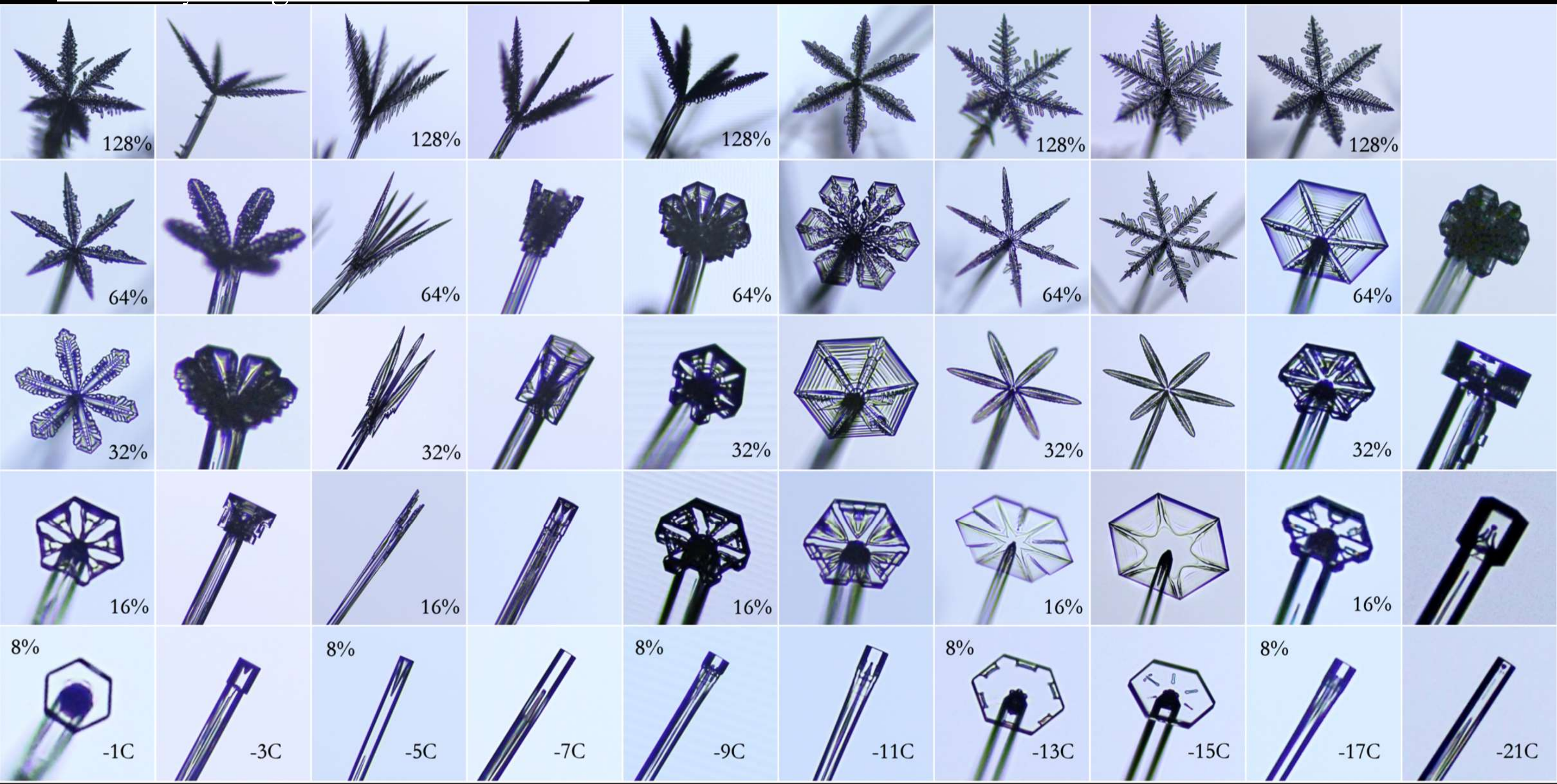
Snow crystals grown on ice needles – at diffe



All single crystals; all grown at constant conditions

A complex physical phenomenon → complex physics

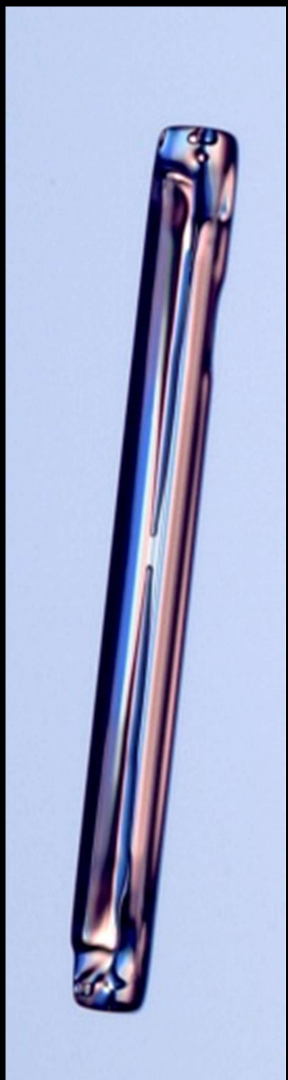
Snow crystals grown on ice needles

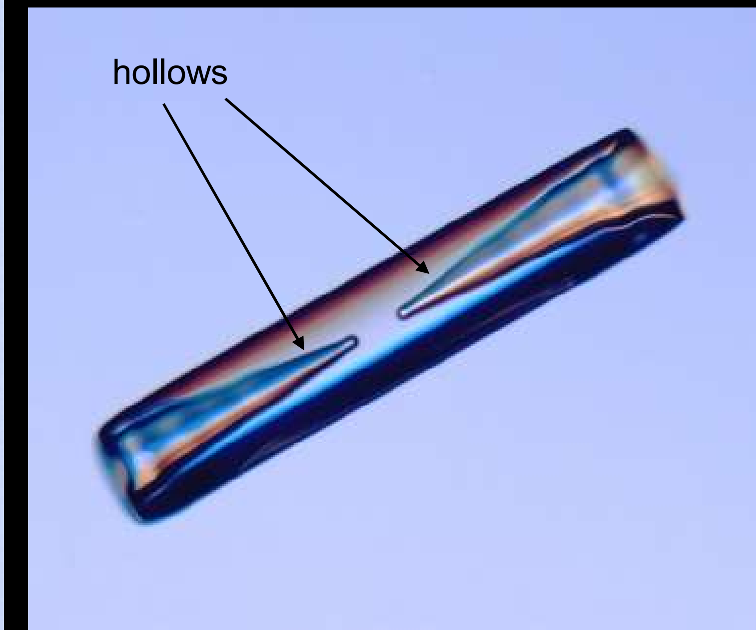


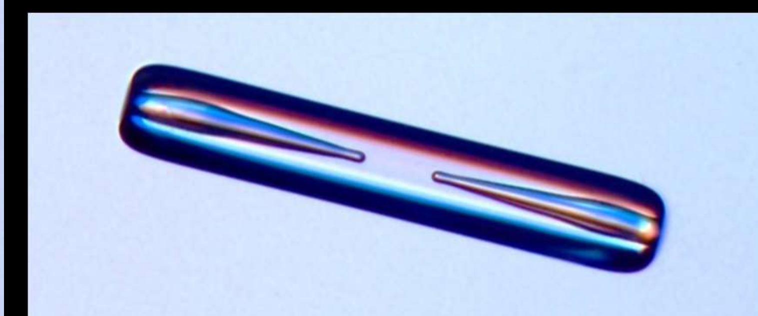
All single crystals; all grown at constant conditions. Possible to make numerical models? What is underlying physics?

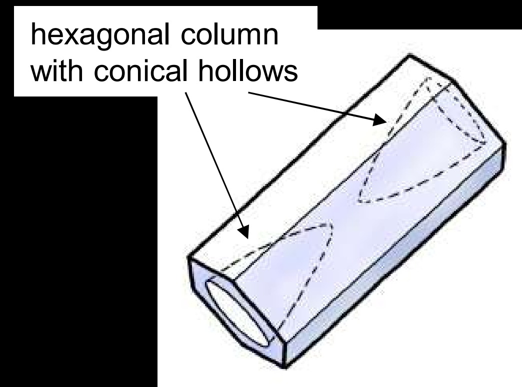
Natural Snow Crystals...

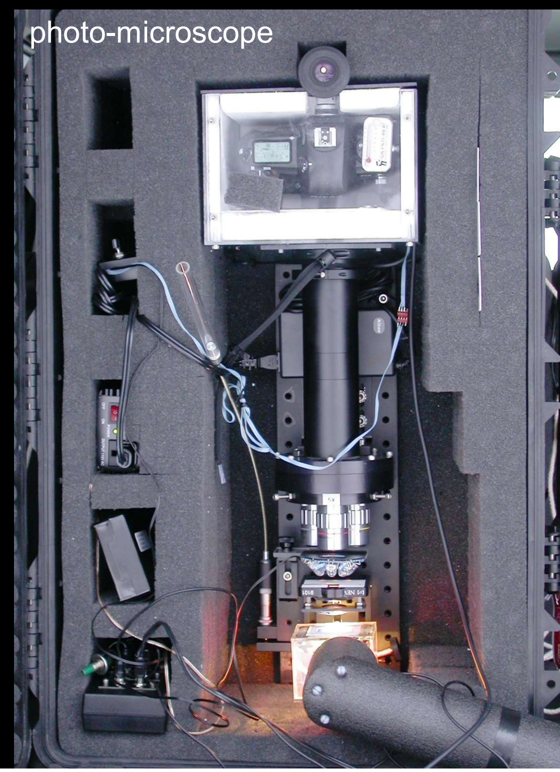
Hollow Columns, form at -5C

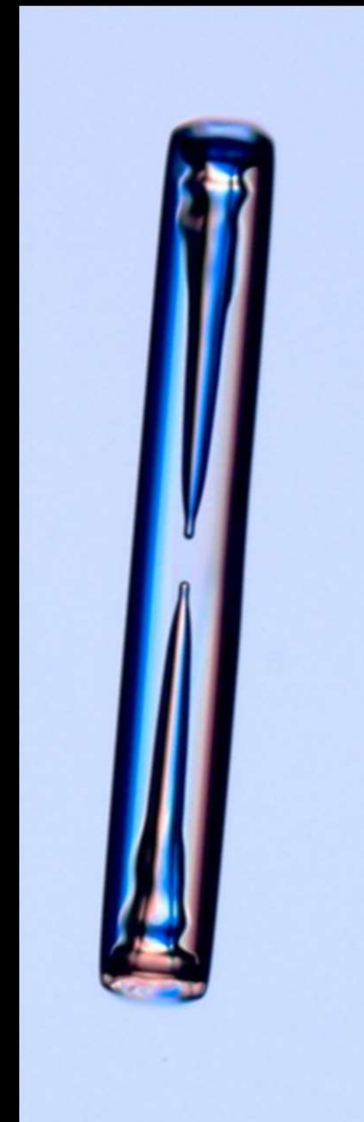






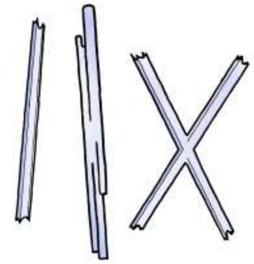


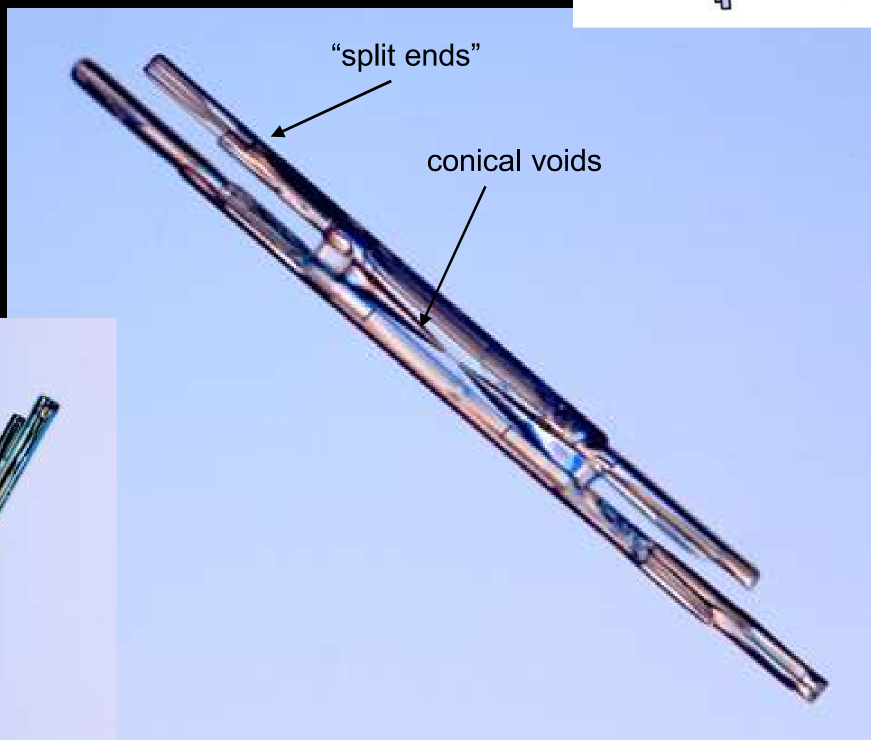


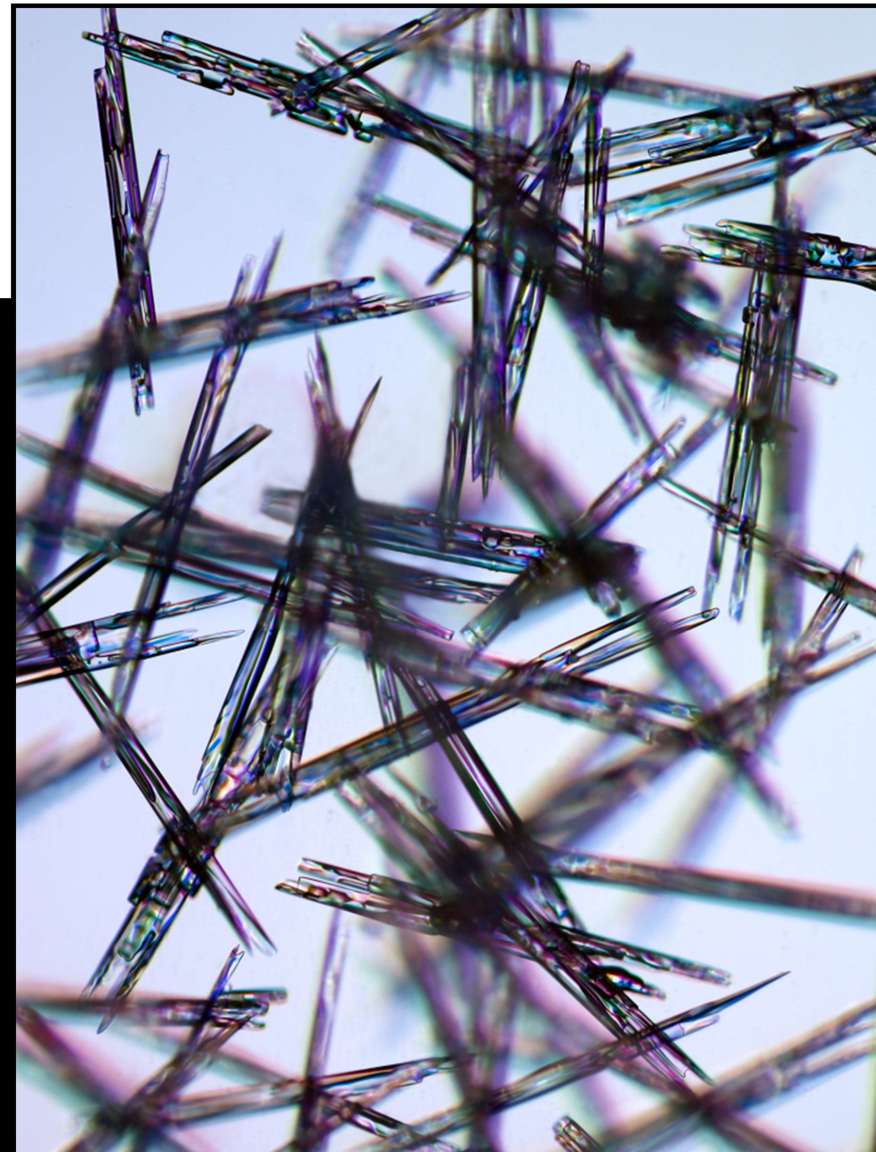


Natural Snow Crystals...

Needle Crystals, form at -5C



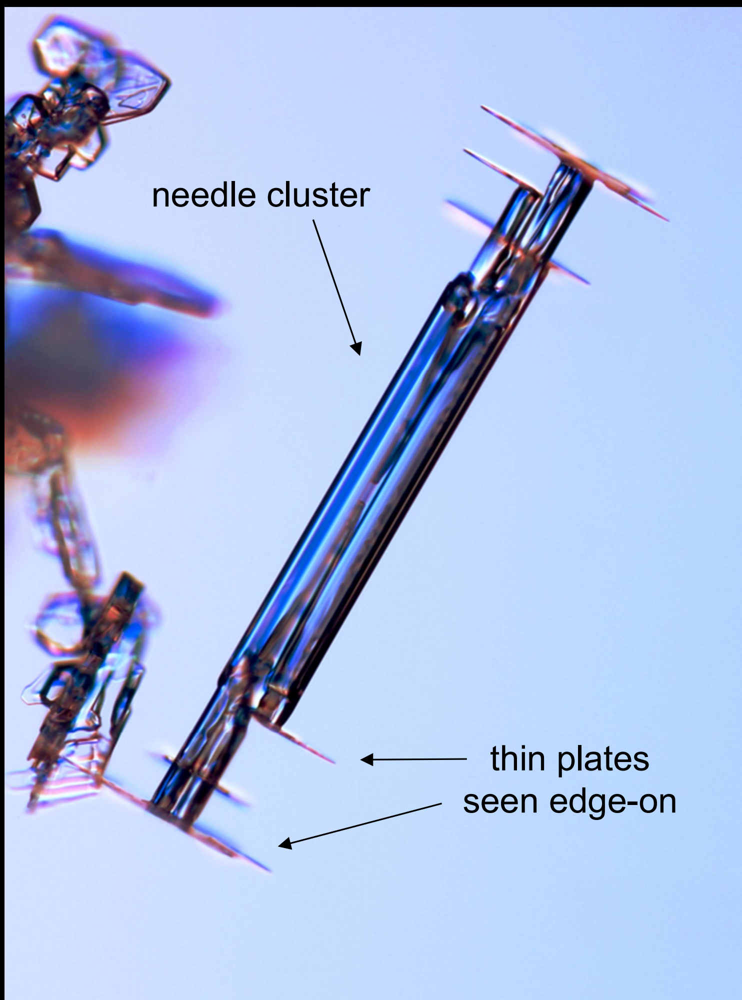


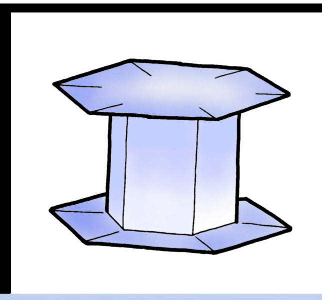


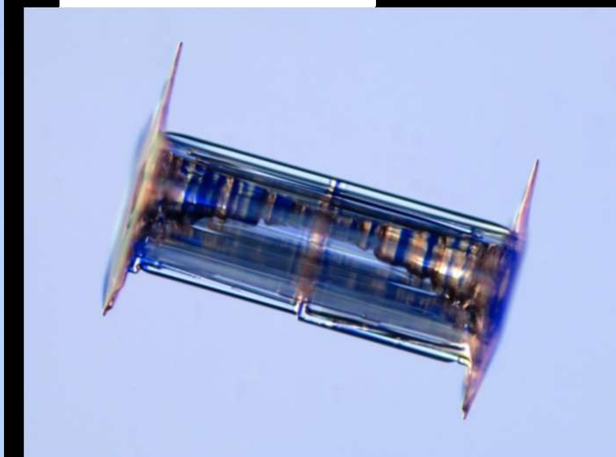
longest columnar crystals 2-3 mm
often find in clusters

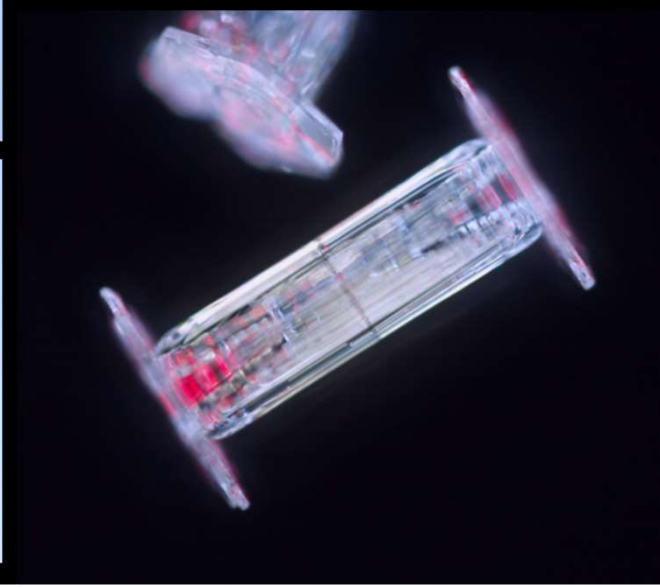
Natural Snow Crystals...

Capped Columns, -6C → -13C



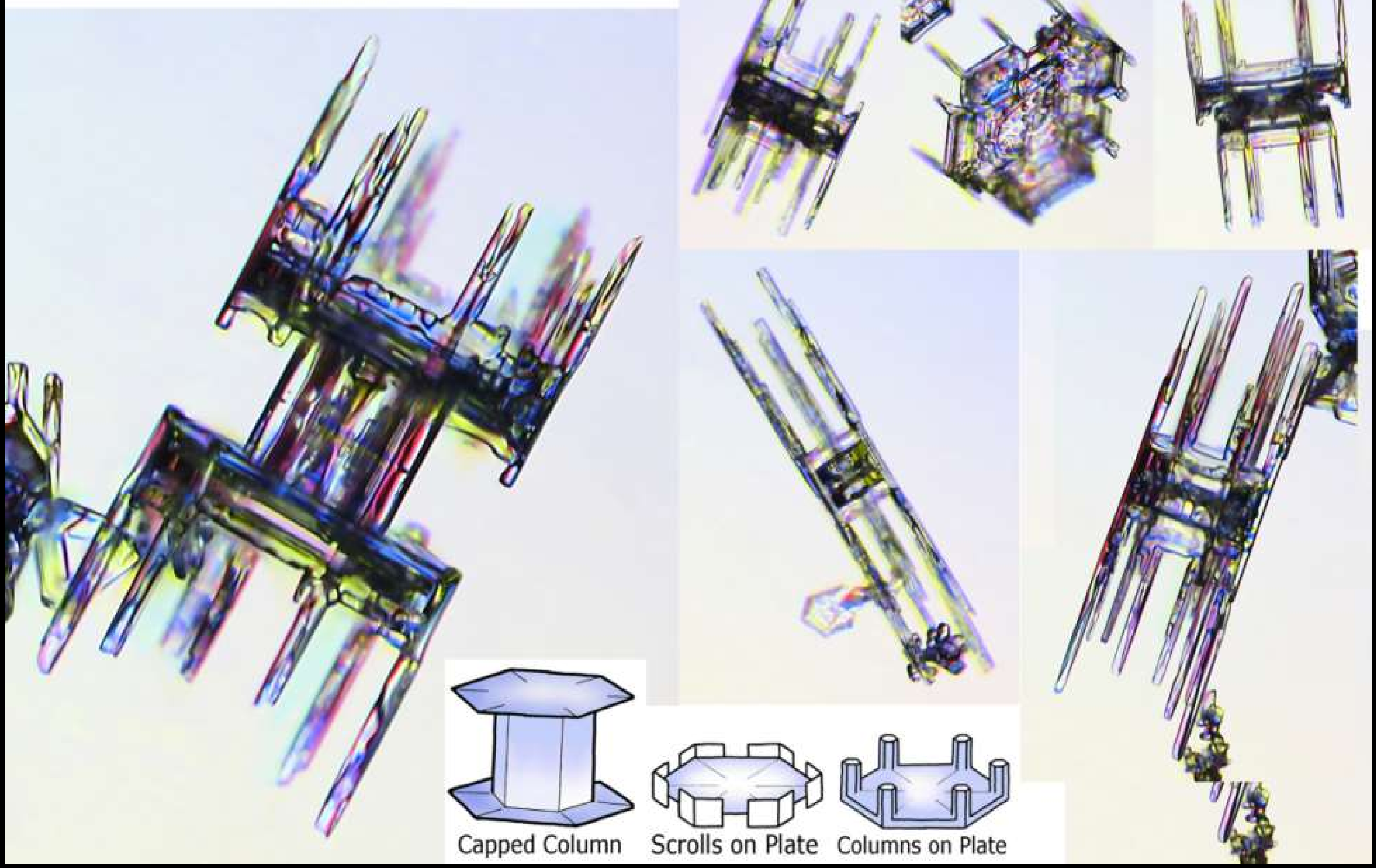






Some especially odd examples: Capped columns with scrolls and columns

Photographed in Fairbanks, Alaska, ~ -10C

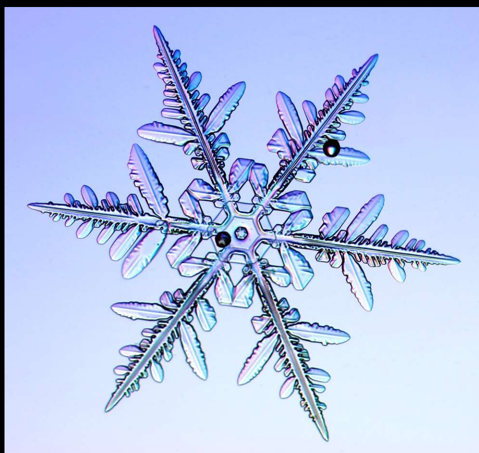


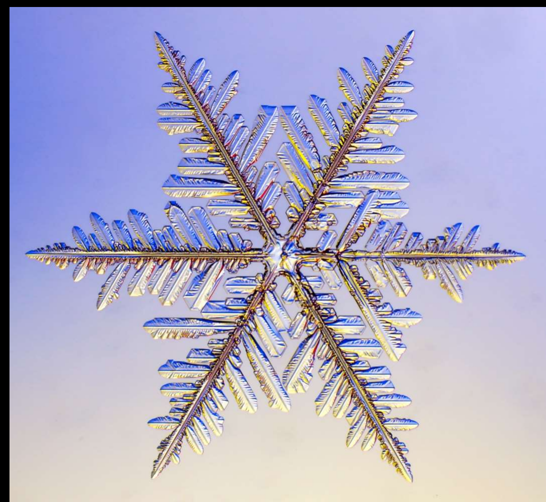
Where to start?....

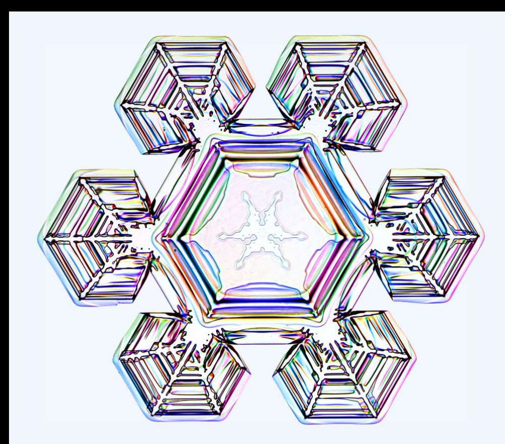
Natural Snow Crystals...

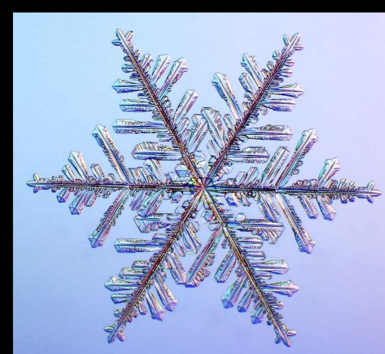
Stellar Crystals, form at -15 C

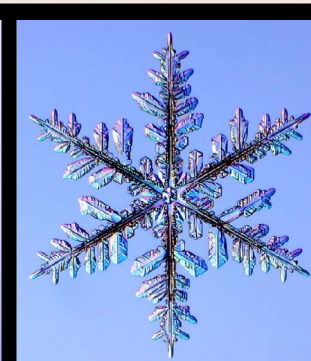
(branched, faceted, thin and flat)

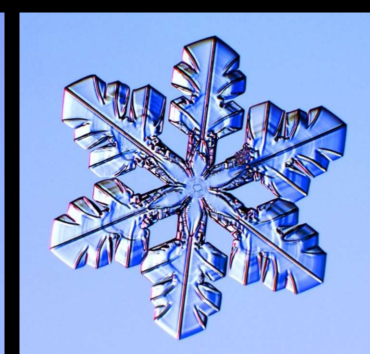




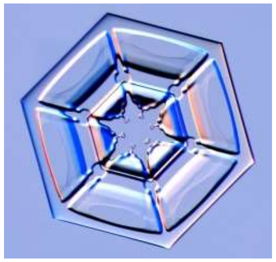


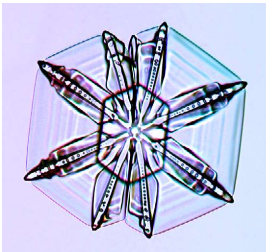


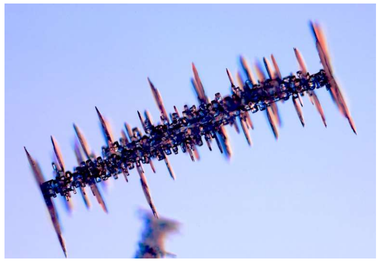


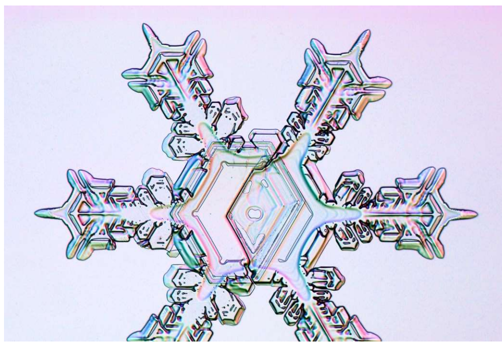


A Menagerie of Natural Snow Crystals...

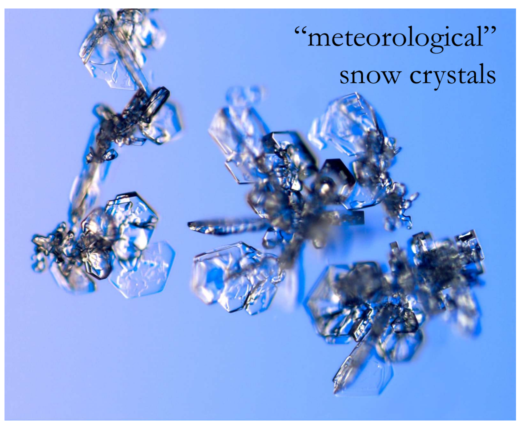


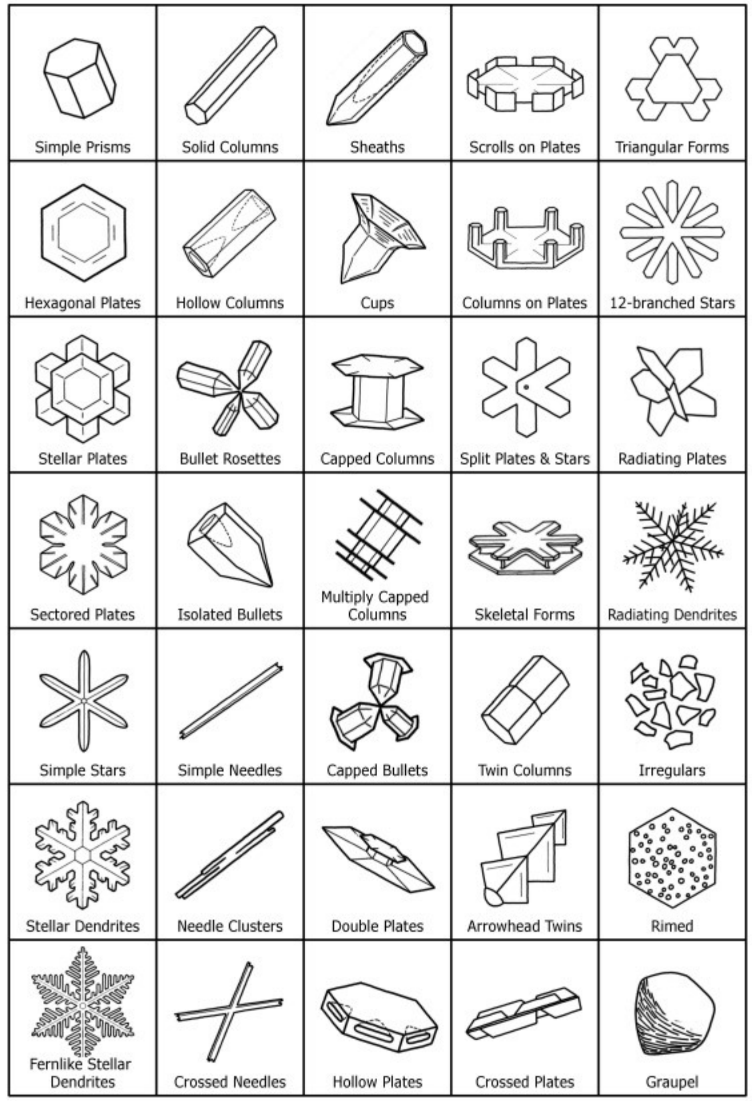




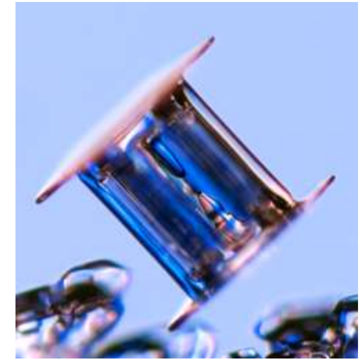


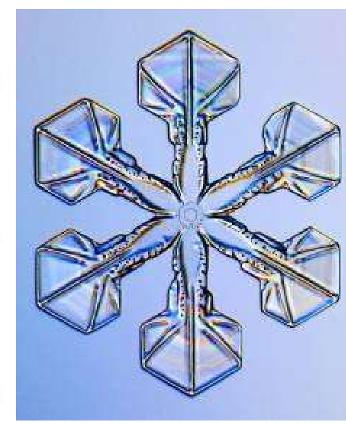
What is the underlying physics?

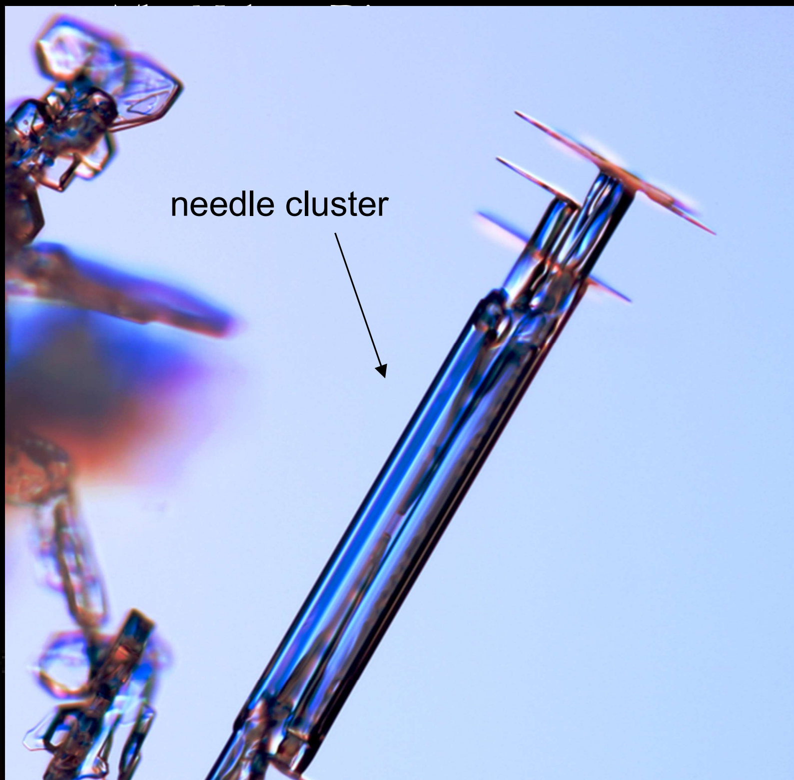


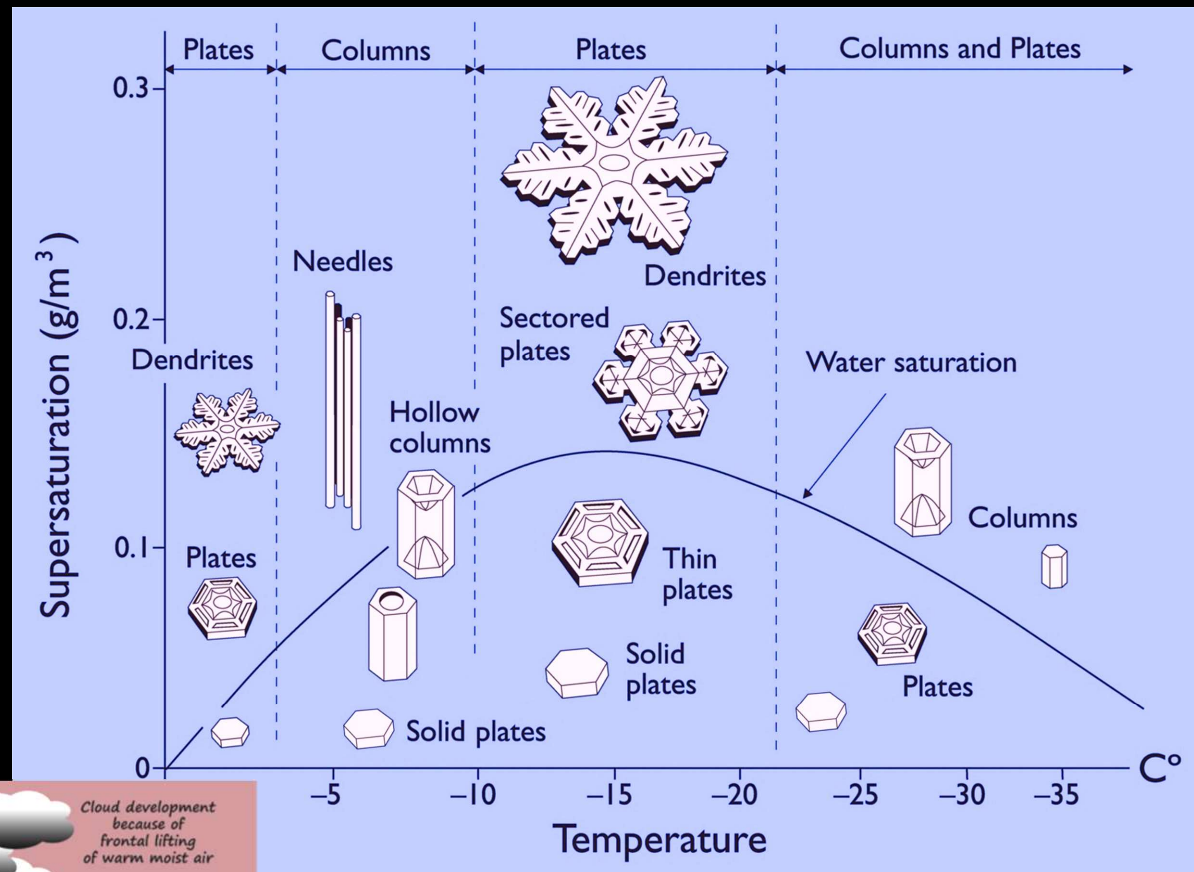


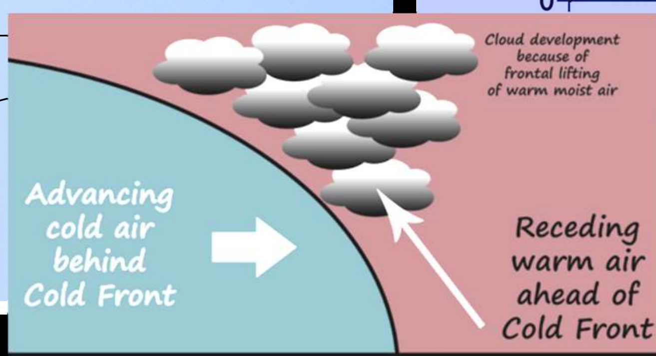
from *Ken Libbrecht’s Field Guide to Snowflakes*







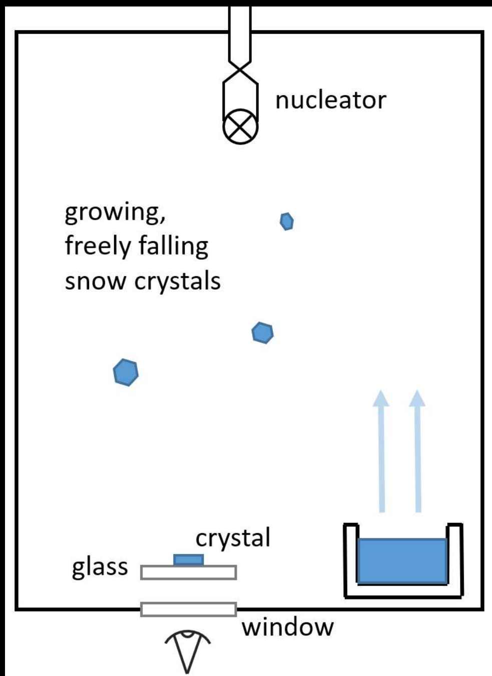




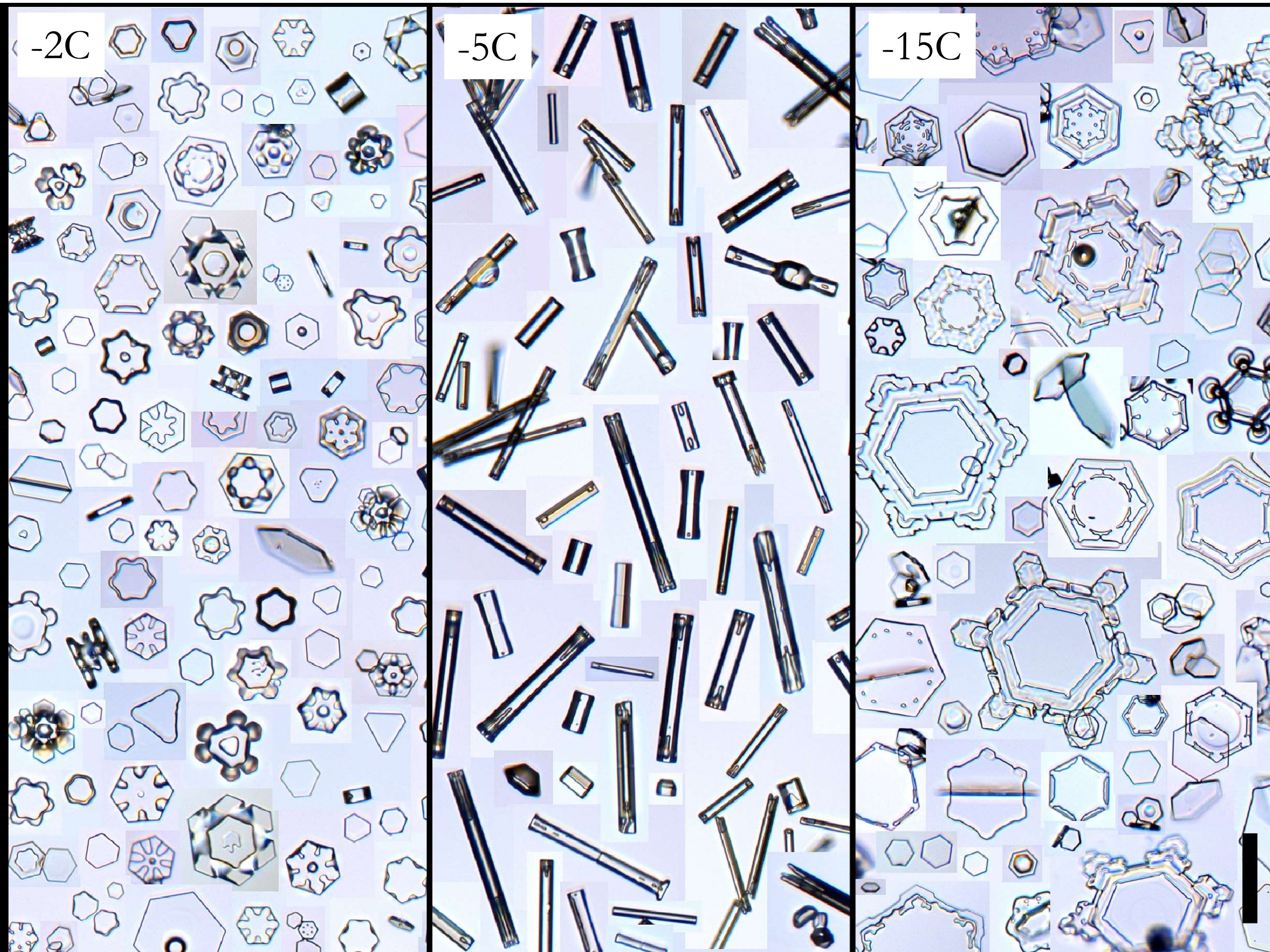
The *Rosetta Stone* for snow crystals…

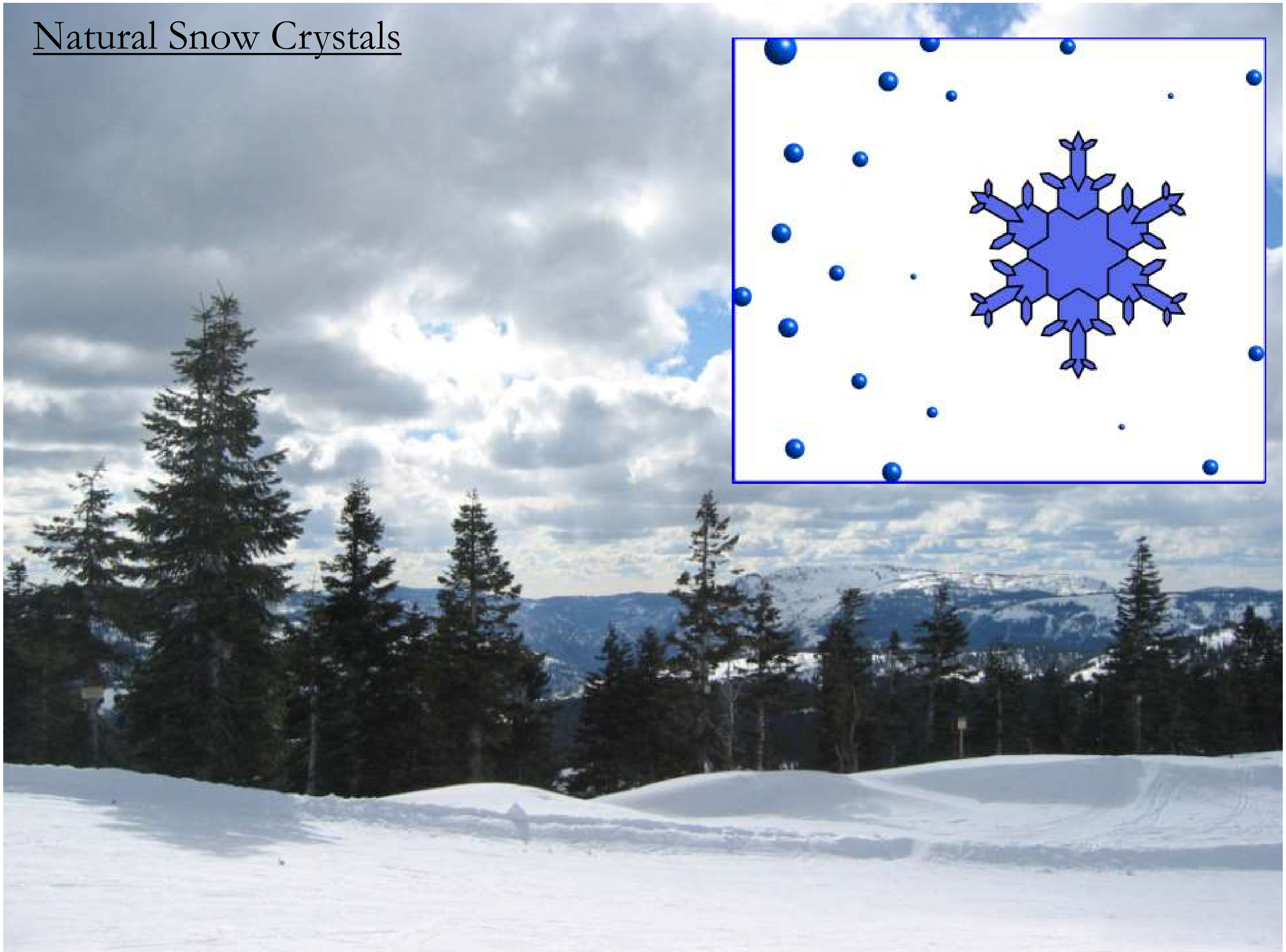
Based on empirical observations…

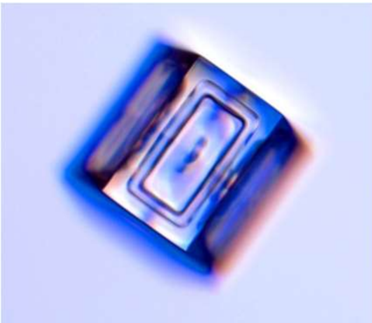
Valid in normal air only…

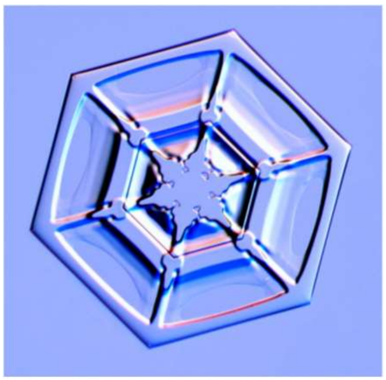


Especially puzzling:
Overall morphology
depends strongly on
temperature




Natural Snow Crystals



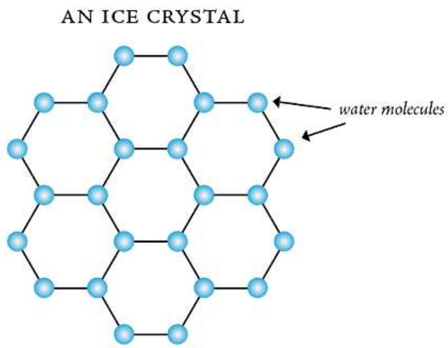


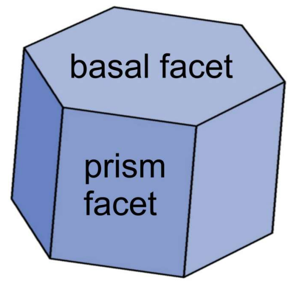
Highly Anisotropic Attachment Kinetics

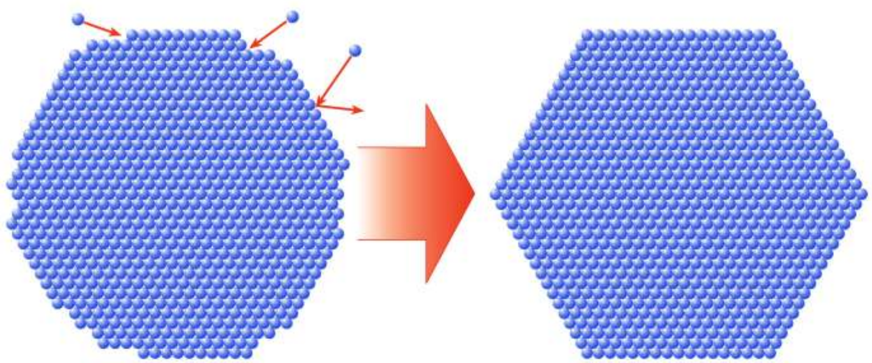
(Surface energy not so important; nearly isotropic)

Snowflake Physics I – Attachment Kinetics

Anisotropic attachment kinetics → Facets



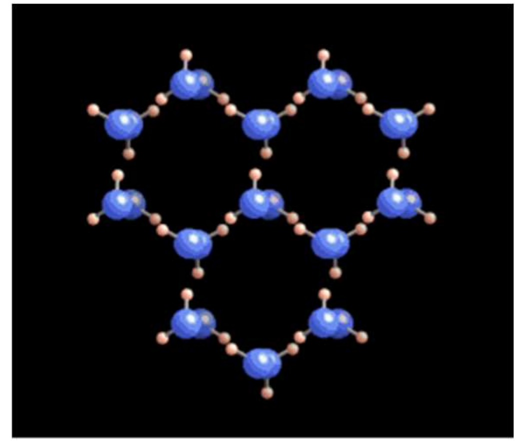


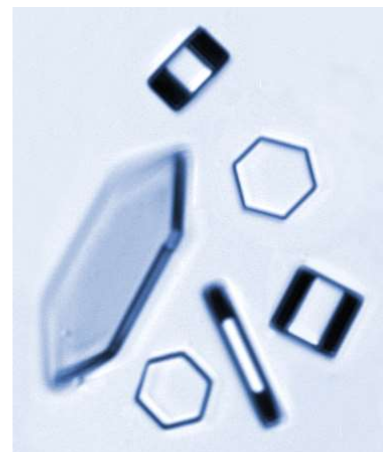


Molecules cannot readily attach to smooth surfaces

→ facets form as crystal grows

A non-equilibrium dynamical process

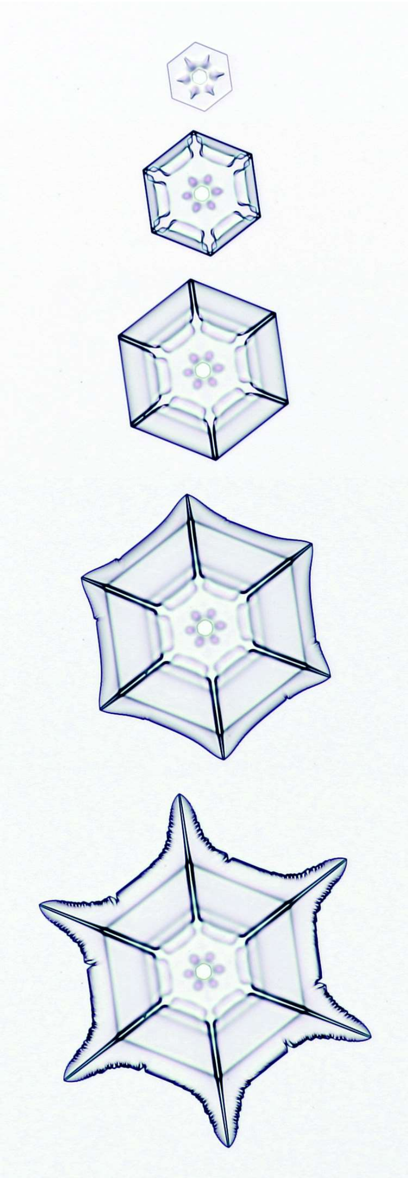




Tiny, laboratory grown snow crystals ~0.1 mm

→ no 4-, 5-, 7-, 8-sided snow crystals

Faceting is how the geometry of the water molecule is transferred to the geometry of a crystal.

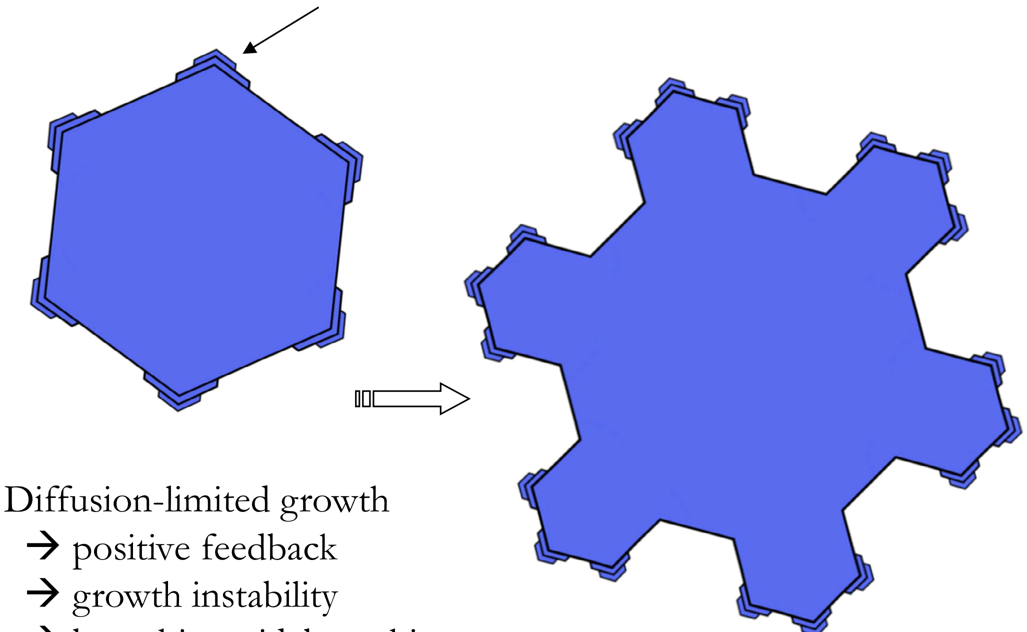


Snowflake Physics II – Diffusion Limited Growth

Particle diffusion → Branching Instability

(a.k.a. the Mullins-Sekerka instability; 1963)

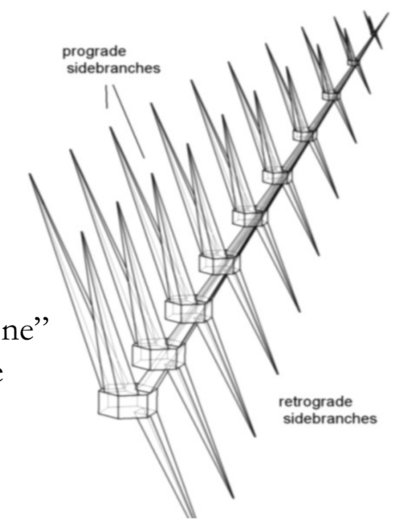
The six corners stick out farther into the humid air
So the corners grow faster... branches sprout



Diffusion-limited growth
- → positive feedback
- → growth instability
- → branching, sidebranching …

Much scientific literature on diffusion-limited growth

Platelike
dendrite
thin & flat
-15C

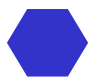


"Fishbone"
dendrite
-5C

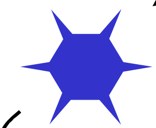
Snowflake Physics III - Complexity and Symmetry

(Why snowflakes are symmetrical, and why "no two are alike")

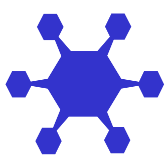
- Nucleation of ice particle



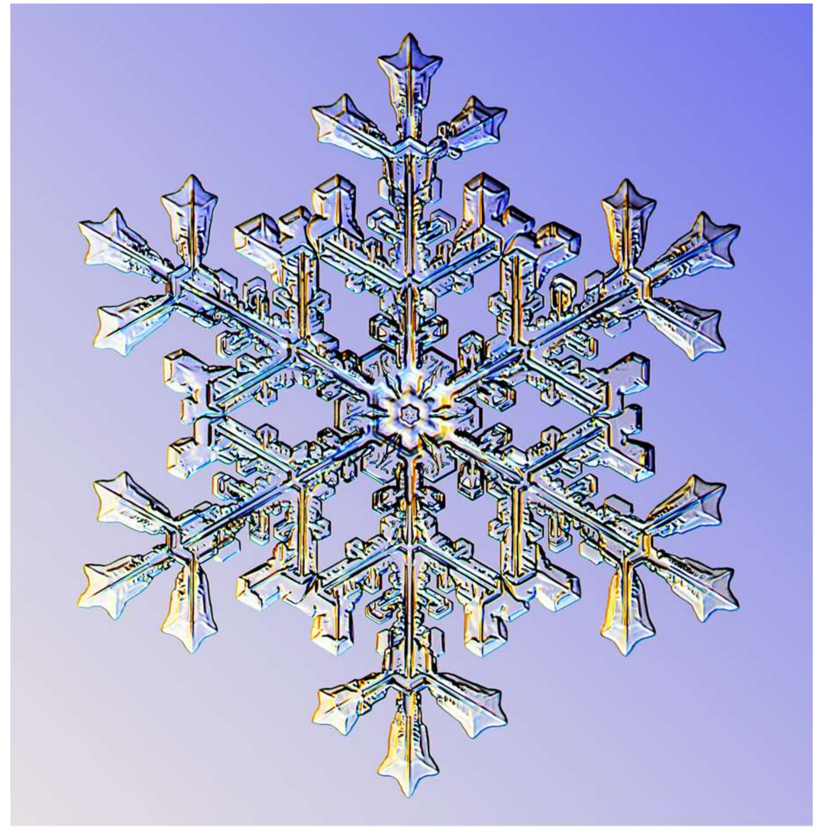
Grows to hexagonal prism, since smooth facets grow most slowly (stellar snow crystal)



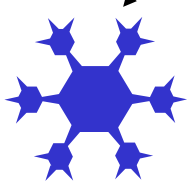
Simple plate unstable as crystal grows larger ... corners sprout arms



Crystal moves to lower supersaturation ... plates grow on arms

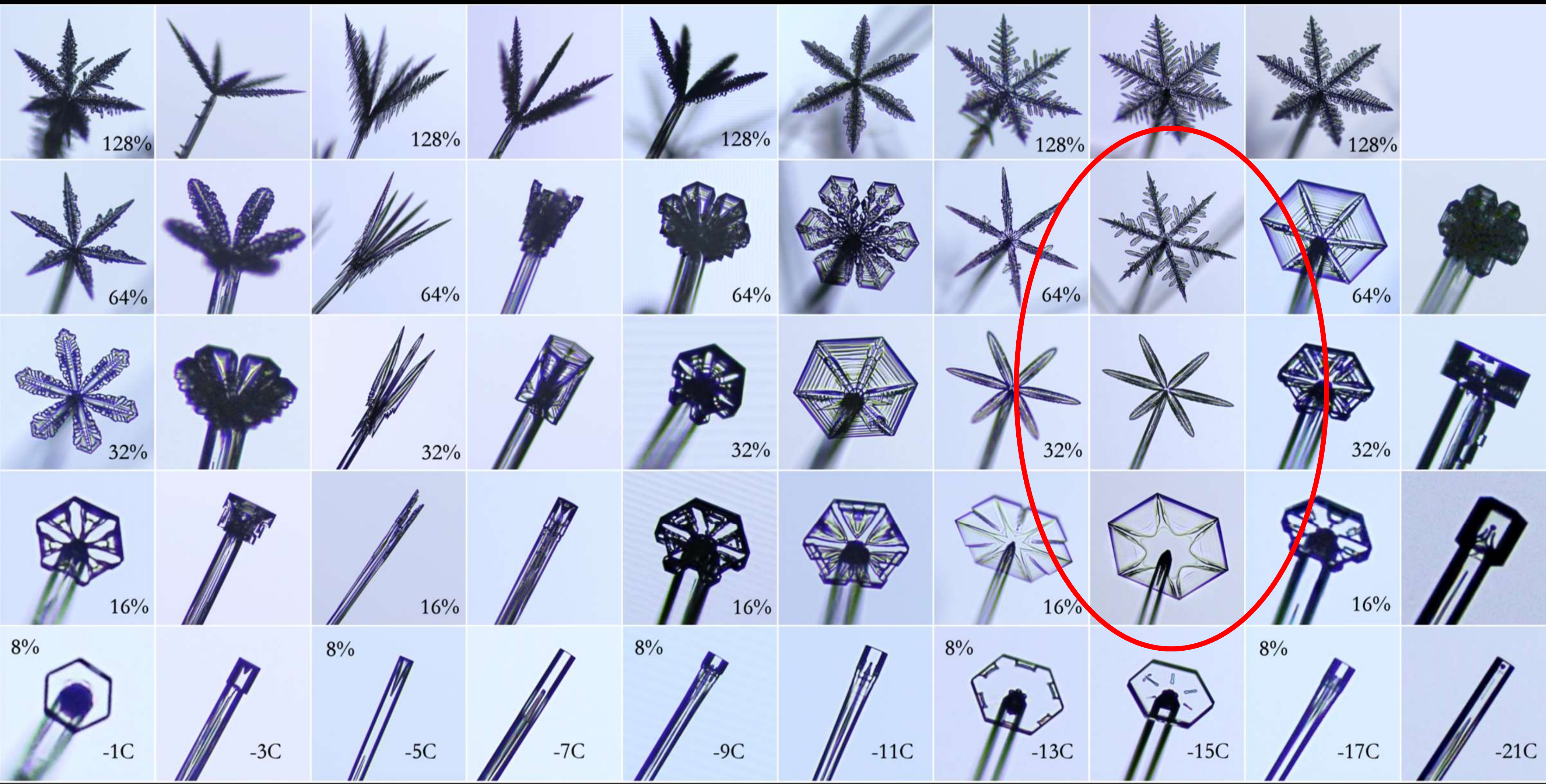


Crystal moves through *many different temperatures, humidities ...* each change causes new growth behavior on arms



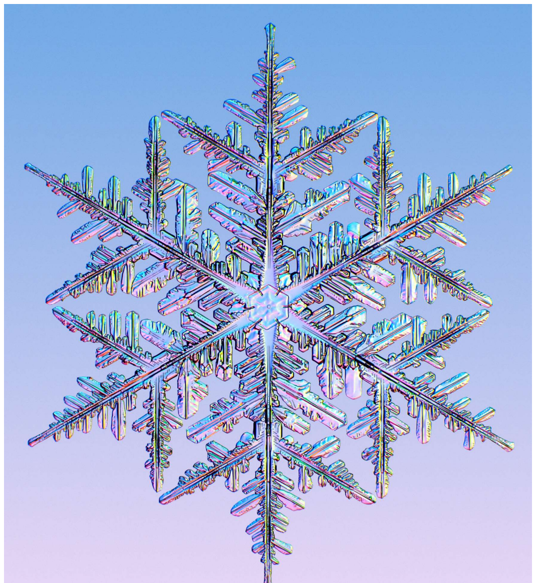
Complex history → Complex crystal shape, faceted & branched
Each arm experiences same history → Symmetry
No two paths are the same → No two alike
All because growth sensitive to temperature, humidity

T~ -1 C → Platelike T~ -5 C → Columnar T~ -15 C → Platelike



Growth slow → faceting dominates; Fast → branching dominates … Attachment kinetics on faceted surfaces key factor

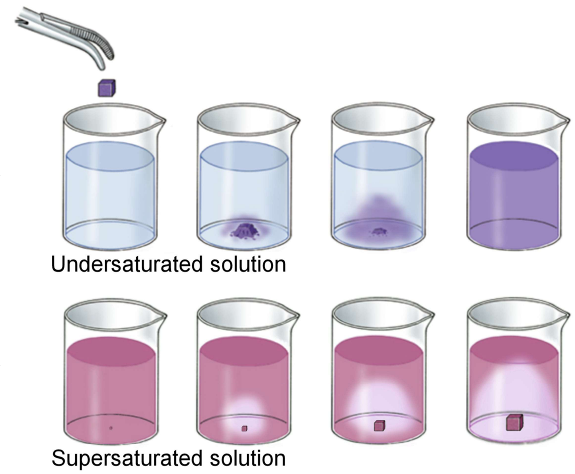
Diffusion-Limited Growth of Snow Crystals



Largely responsible for structure formation, especially branching

Outward diffusion →

Inward diffusion →

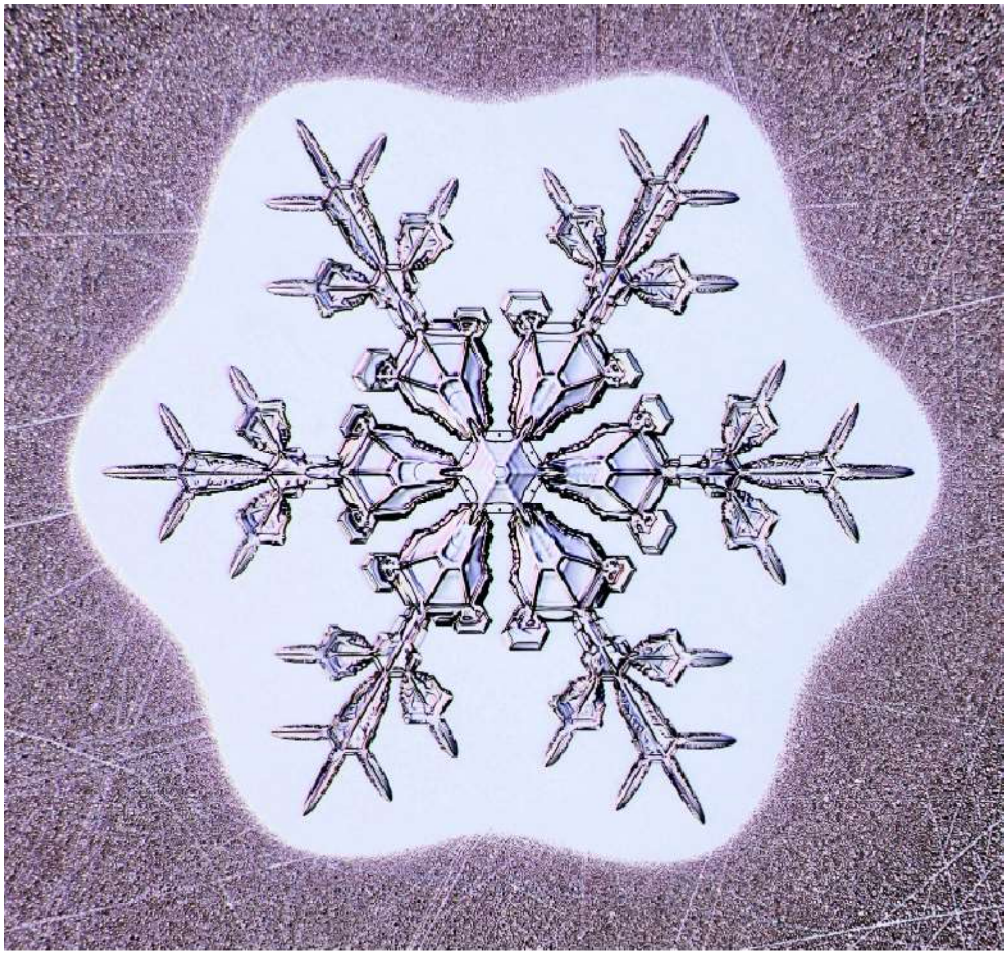


Supersaturation depleted around growing crystal → diffusion-limited growth

← See effect in numerical models

Here 2D model; outer shading shows water vapor supersaturation

Janko Gravner and David Griffeath, Modeling snow crystal growth II: A mesoscopic lattice map with plausible dynamics, Physica D 237, 385-404, 2008.



← **Laboratory example of water vapor depletion around growing crystal**

>> Snow crystal growing on glass substrate

>> Moist air blows down onto crystal to create supersaturated environment

>> Water droplets condense on glass, except where supersaturation depleted by growing crystal

Diffusion-Limited Growth: The Spherical Solution

Diffusion equation: $\nabla^2\sigma = 0$; $\sigma(r) = \text{supersaturation field (Laplace approx.)}$

Attachment kinetics: $v_n = \alpha v_{kin}\sigma_{surf}$; $0 \leq \alpha \leq 1$ ... attachment coefficient

(Hertz-Knudsen relation – 1882)

Can add: Latent heating + Heat diffusion (double diffusion problem)
Surface energy effects (Gibbs-Thomson effect)
On substrate: Hemispherical solution useful

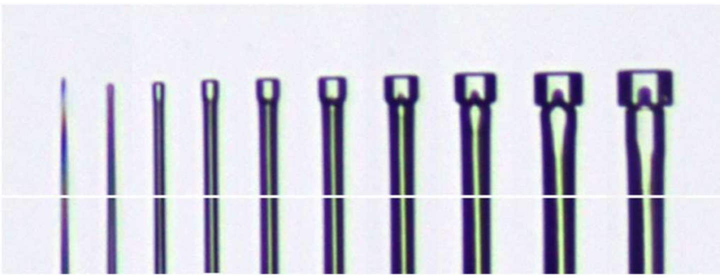
→ In air:
Mainly **attachment kinetics** + **particle diffusion**
Thermal effects from latent heating … minor (not zero)
Surface energy effects … minor (mostly ignore if r > 1μm)

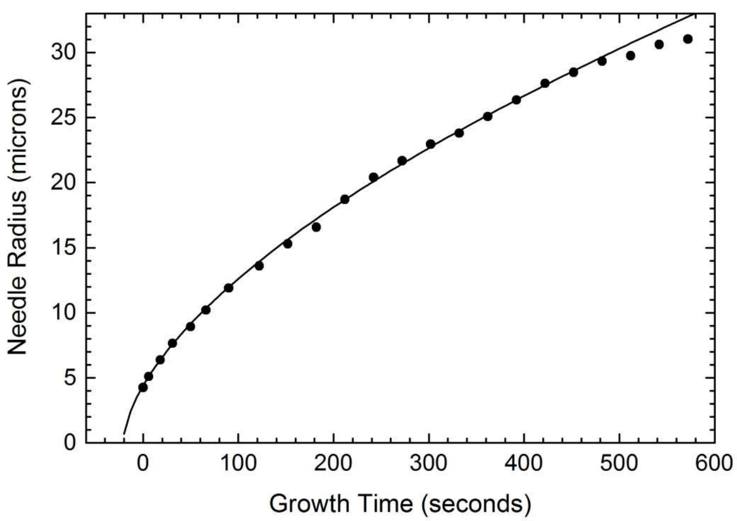
→ In near vacuum:
Mainly attachment kinetics + heat diffusion

Spherical solution extremely useful for understanding the relative important of different physical processes...

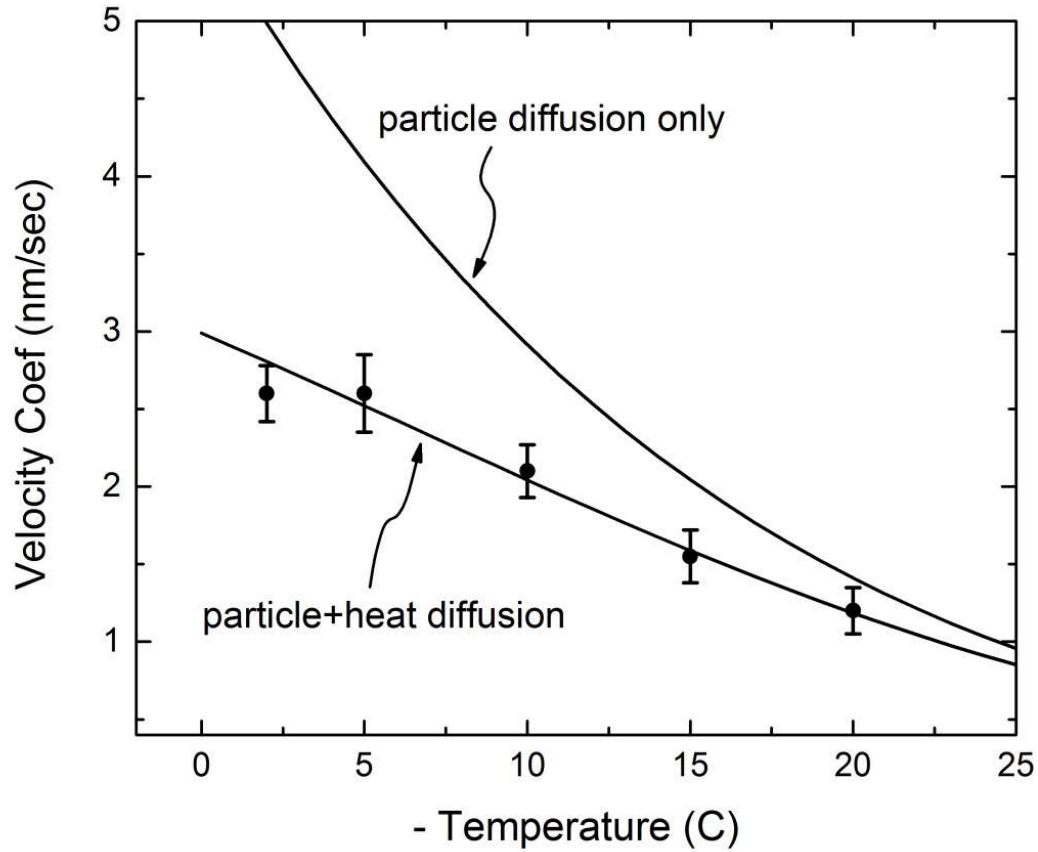
Diffusion-Limited Growth: Cylindrical Growth

Can solve double-diffusion problem analytically: heat and particle diffusion

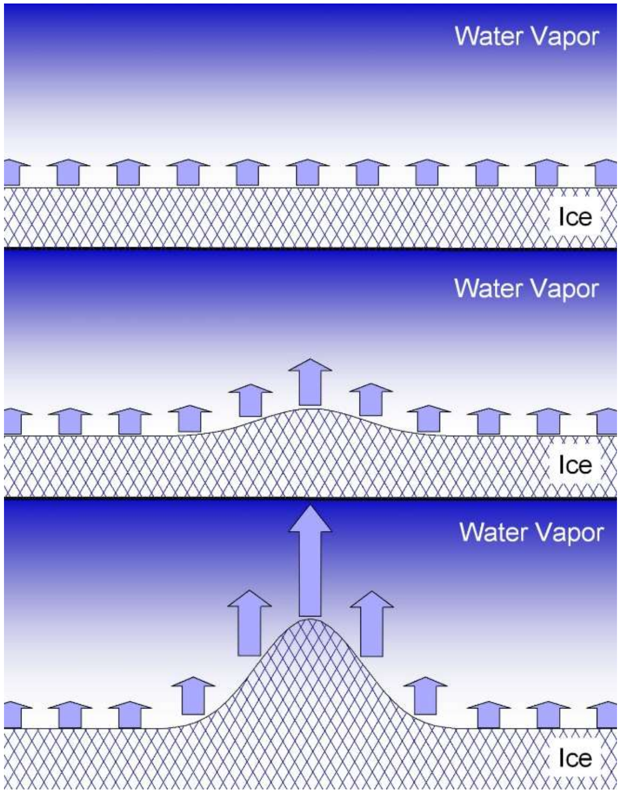




Measure as function of (T, σ)



THE MULLINS-SEKERKA INSTABILITY



← Planer (1D) solution of diffusion equation

Crystal grows upward at uniform rate, $v = const$

Simple 1D supersaturation gradient

← But … simple 1D solution is not a **stable** solution…

Spherical growth →

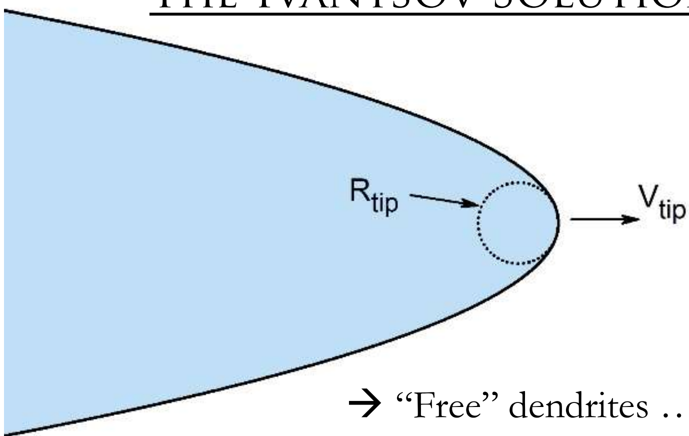
Another 1D solution of the diffusion equation → $v \sim 1/R$

… but, sphere also **unstable** to the Mullins-Sekerka instability

W. W. Mullins and R. F. Sekerka, Stability of a planar interface during solidification of dilute binary alloy, J. Appl. Phys 35, 444-451, 1964.

The Ivantsov Solution

G. P. Ivantsov, Dokl. Akad. Nank USSR 58, 1113, 1947.



← 2D solution in parabolic coordinates

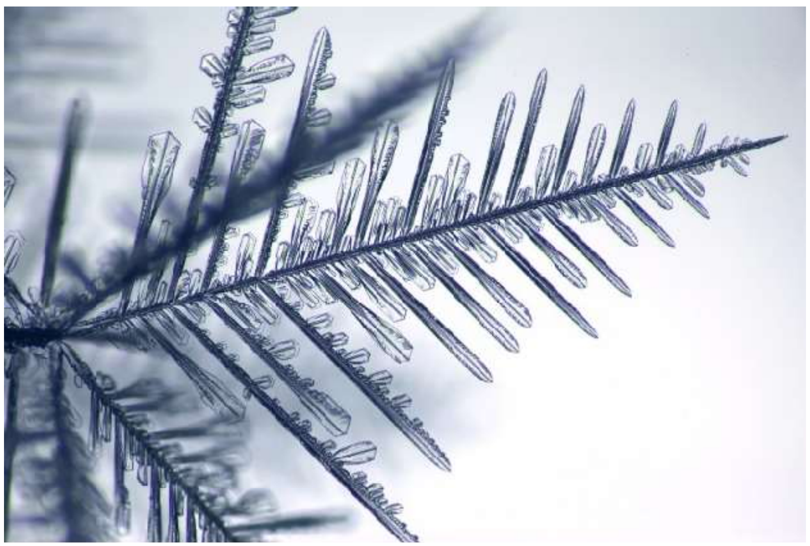
Paraboloid of revolution

$v_{tip} = const \sim 1/R_{tip} \quad (R_{tip} = const)$

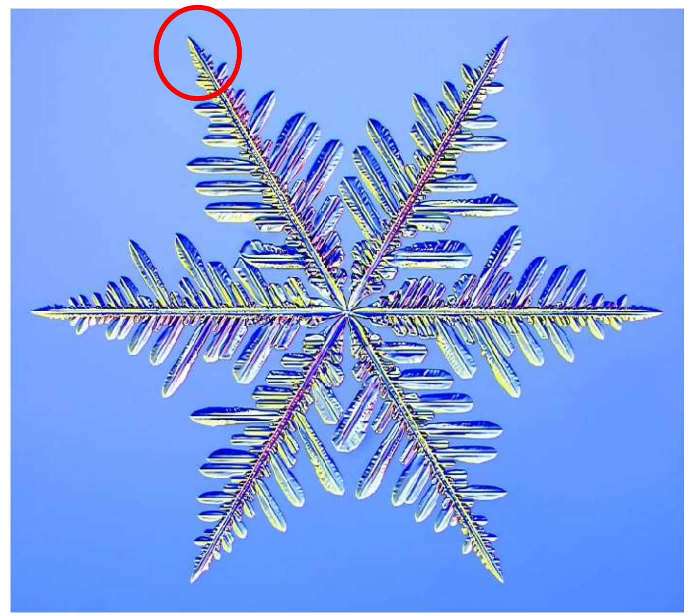
Also **unstable** to the Mullins-Sekerka instability

→ "Free" dendrites … widely studied in 1980s

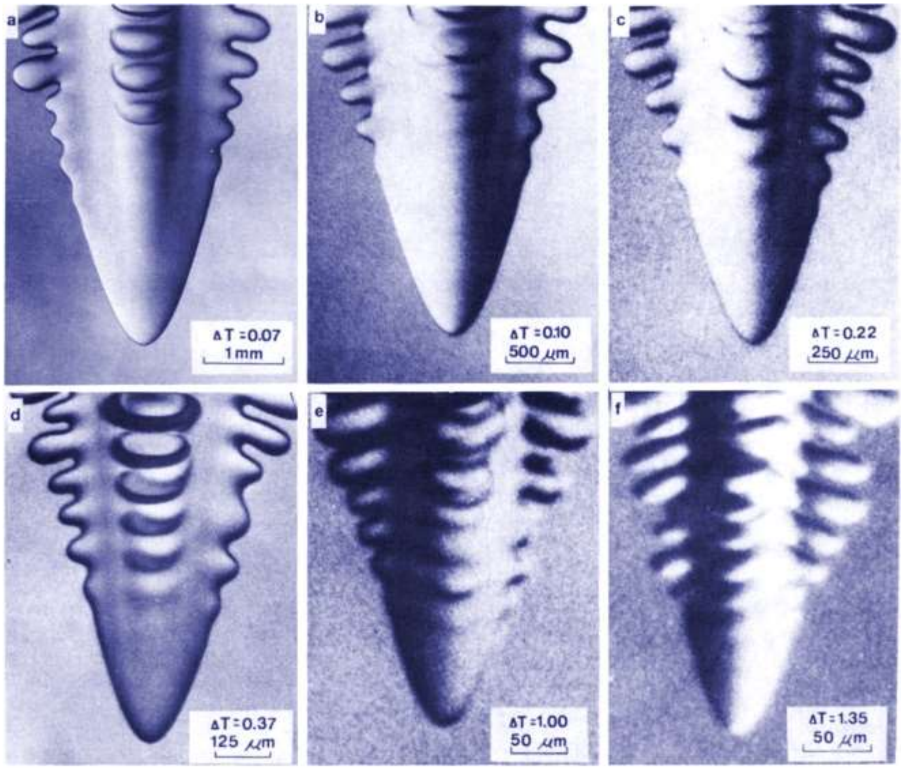
→ "Solvability" theory of free-dendrite growth



Focus on tip → ignore sidebranching



THE SELECTION PROBLEM



S.-C. Huang and M. E. Glicksman, Overview 12: Fundamentals of dendritic solidification – II Development of sidebranch structure, Acta Metall. 29, 717-734, 1981.

← Free dendrites growing during the solidification of liquid succinonitrile (a clear, waxy material that melts at 57 C)

Parabolic tip stable in moving frame….

Low supercooling → low v_{tip}, large R_{tip}
High supercooling → high v_{tip}, small R_{tip}

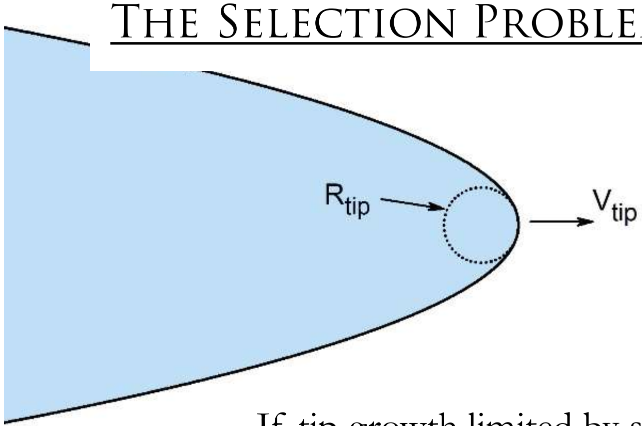
Ivantsov solution says

$$v_{tip} = const \sim 1/R_{tip} \quad (R_{tip} = const)$$

… a *family* of solutions

What "selects" the experimental solution?
Diffusion equation alone is not enough….

The Selection Problem – growth from liquid and vapor



Spherical solution of diffusion equation
with attachment kinetics &
with surface energy (Gibbs-Thomson)…

$$v \approx \frac{X_0}{R}\left(1 - \frac{X_0}{\alpha R}\right)\left(1 - \frac{d}{\sigma_\infty R}\right)$$

Pond ice, Bathsheba Grossman

If tip growth limited by surface energy, then solvability theory gives:

$$v_{tip} \sim \sigma_\infty^2; \quad R \sim \frac{1}{\sigma_\infty}$$

Holds for growth from liquid (mostly) →
(as function of supercooling)

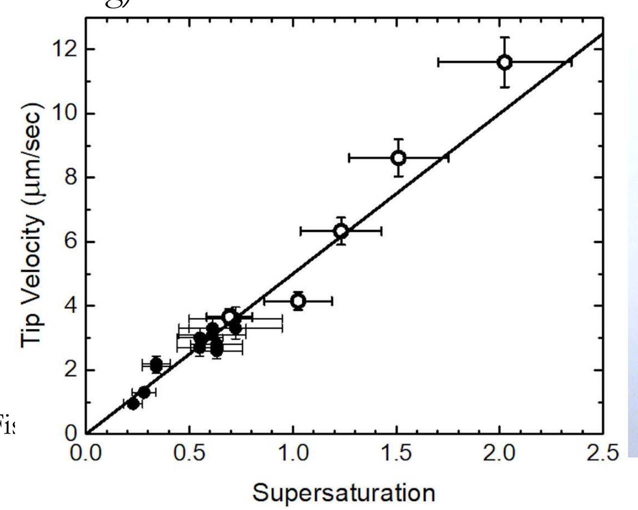
If tip growth limited by attachment kinetics, then

$$v_{tip} \sim \sigma_\infty; \quad R \sim const$$

Holds for growth from vapor (mostly) →
(as function of vapor supersaturation)

$0 \le \alpha \le 1$ … attachment coefficient
d … Gibbs-Thomson length = 1 nm

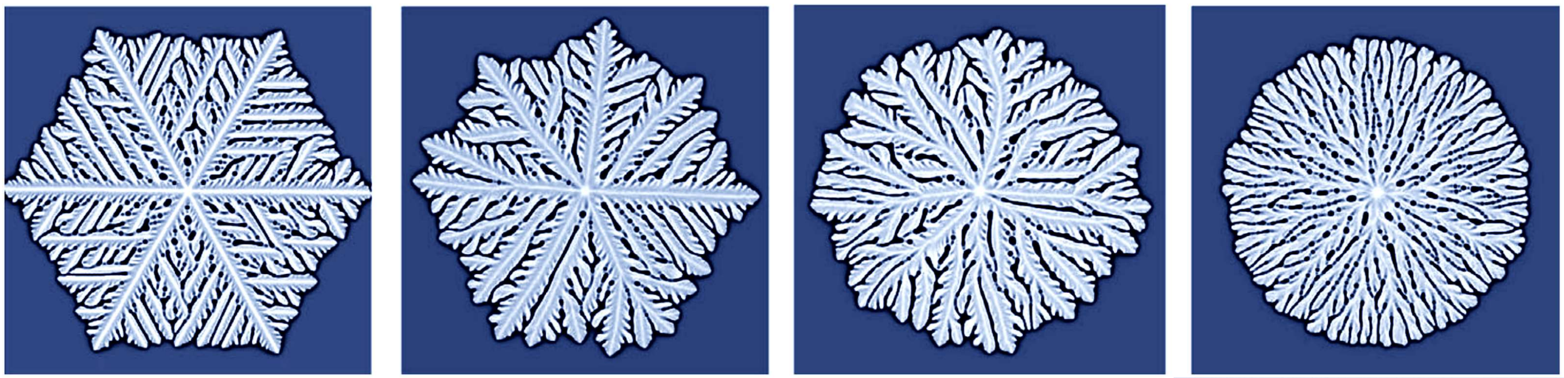
“Fi



The Selection Problem – anisotropy needed

Computer simulations showed Ivantsov solutions **unstable** to "tip splitting" !

← Greater anisotropy   Less anisotropy →



Overarching conclusions from solvability theory:

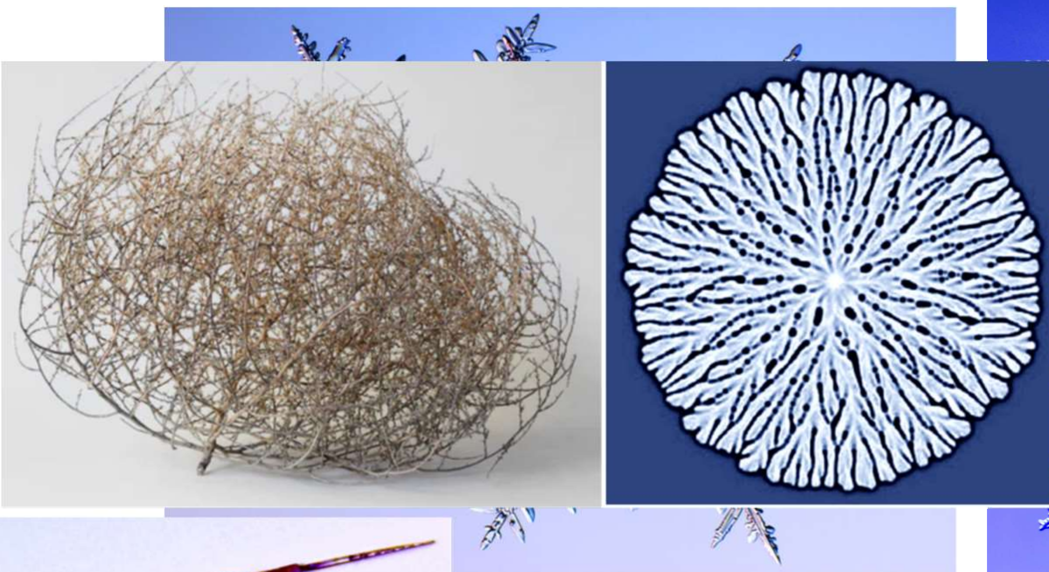
- Stable parabolic tip requires crystal anisotropy
- Surface energy usually dominates in growth from melt
- Attachment kinetics usually dominates in growth from vapor
- Need full 3D computer simulations to make further progress…

Facets → Anisotropic attachment kinetics (not surface energy)

Tip splitting in stellar dendrite growth at high σ_∞ →

Examples of Diffusion-Limited Snow Crystal Growth

1. Fernlike Stellar Dendrites



Rapid growth, erratic sidebranching

Platelike form **not** explained by Mullins-Sekerka instability…
Large-scale morphological asymmetry indicates **anisotropic attachment kinetics**.

(Isotropic → "tumbleweed" growth)

10mm from tip to tip, self-similar

Order and Chaos

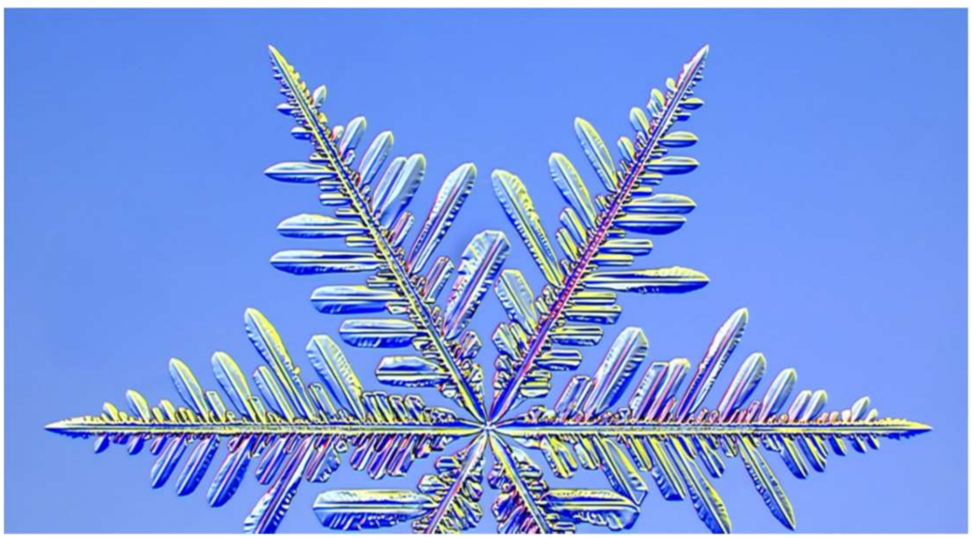
Large-scale morphology determined by attachment kinetics
Slow growth → faceting -- order

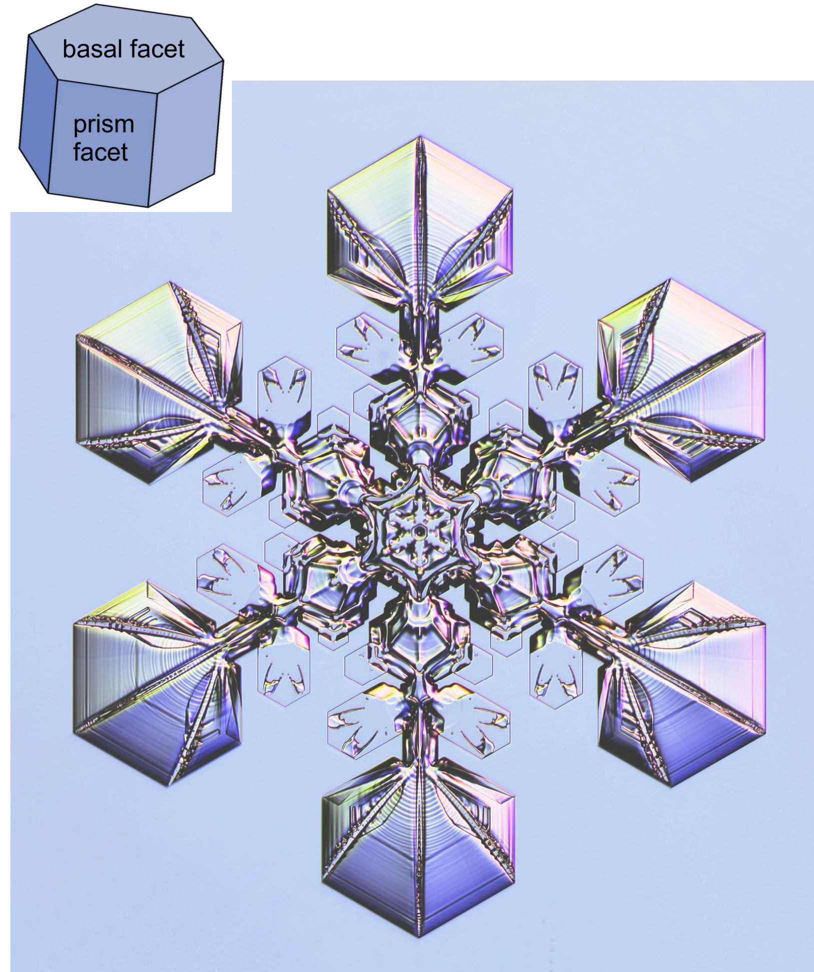
Complexity arises from diffusion-limited growth
Fast growth → branching -- chaos

>> Must have **large-scale anisotropy in attachment kinetics** to make thin plates or slender needles

>> Surface energy nearly isotropic (ice does not cleave in facets)

>> In crystal growth, facets ⟺ anisotropic attachment kinetics

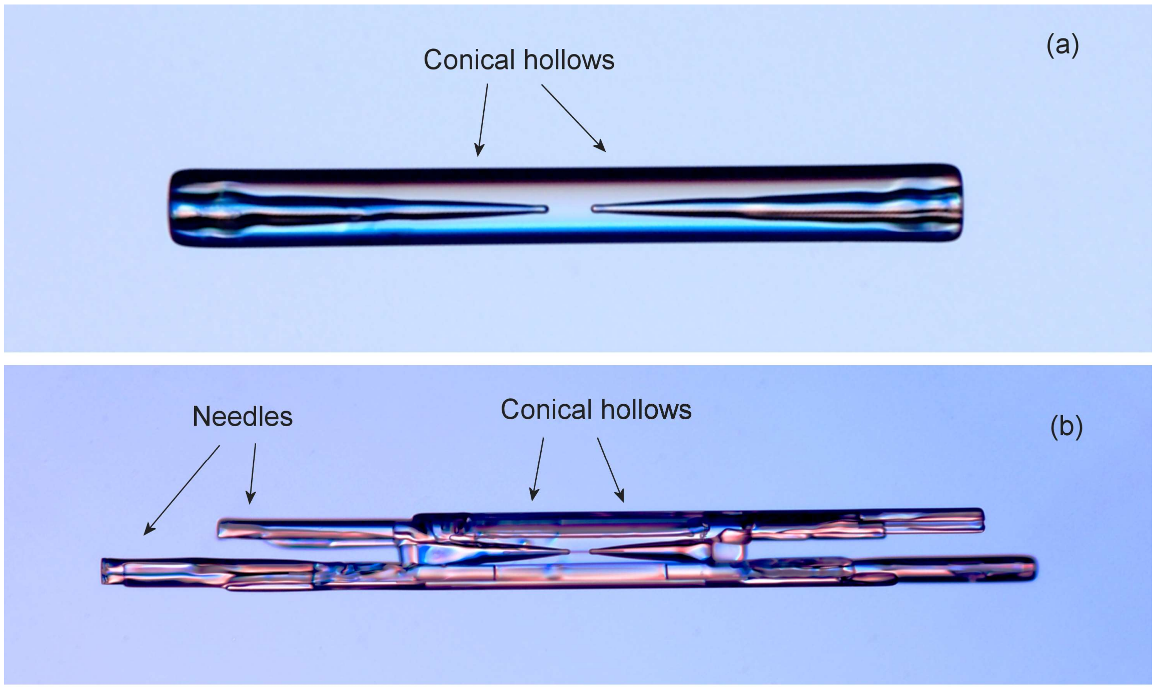




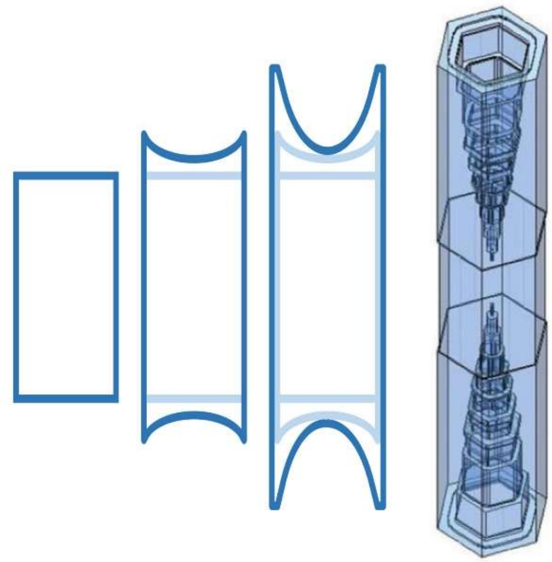
Interplay of faceting and branching
Not grown under constant conditions

Examples of Diffusion-Limited Snow Crystal Growth

2. Hollow Columns and Needle Clusters



Basal faces unstable to hollowing:



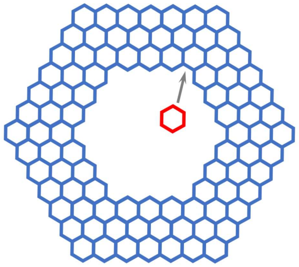
Columnar form **not** explained by Mullins-Sekerka instability…
Large-scale asymmetry indicates anisotropic attachment kinetics.

Model from: Janko Gravner and David Griffeath, Modeling snow-crystal growth: A three-dimensional mesoscopic approach, Phys. Rev. E79, 011601, 2009.

Examples of Diffusion-Limited Snow Crystal Growth

3. Ice bubbles

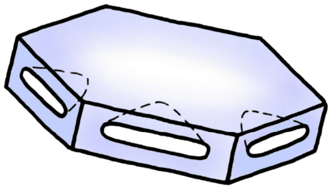
In columns:

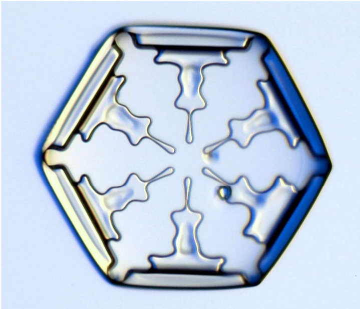


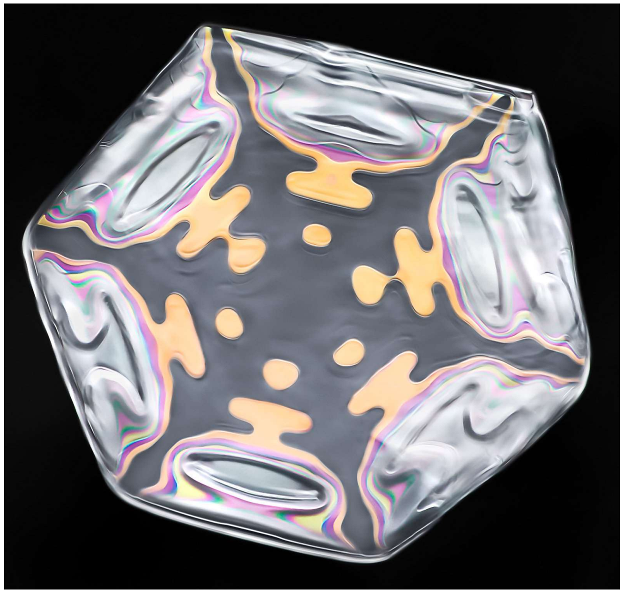
Exterior growth slow
Interior growth fast…
Fast → Hollow column
Then slow → Bubble

In plates:

Hollow plate forms...







Hollows → bubbles

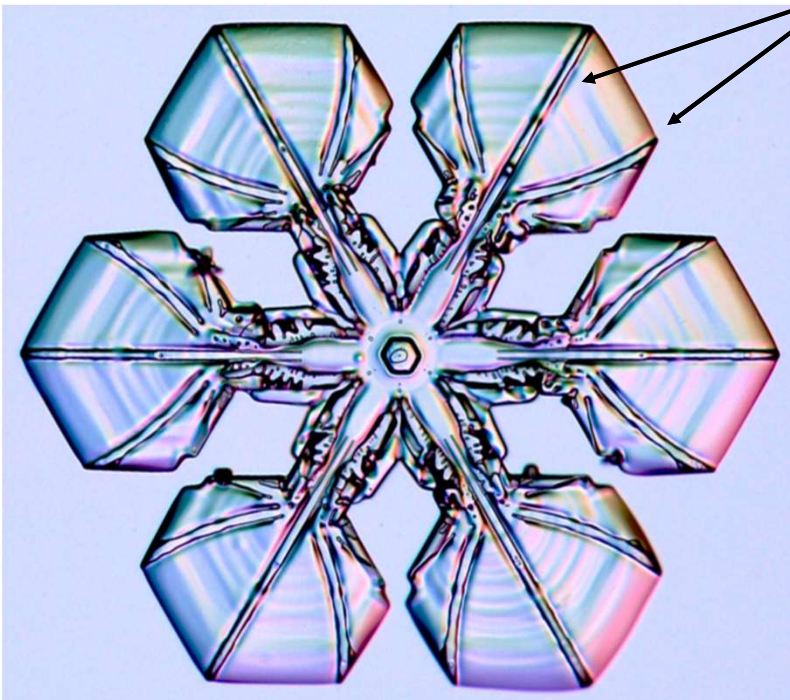
Interference colors
→ Flat bubbles
… just a few μm thick
… interior faceted

Don Komarechka

Examples of Diffusion-Limited Snow Crystal Growth

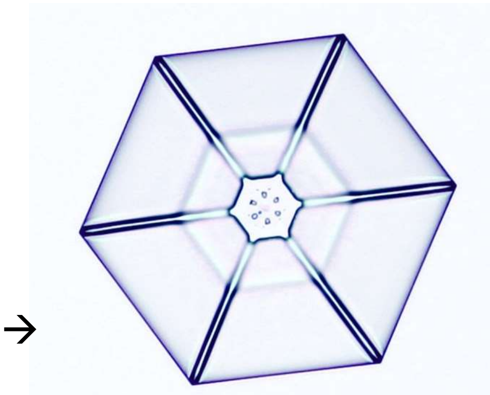
4. Ridge structures

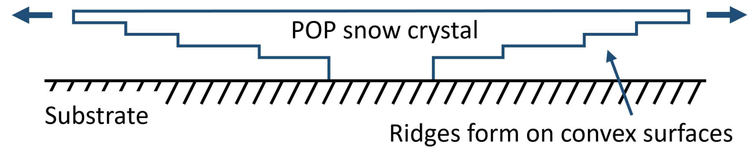
Ridges

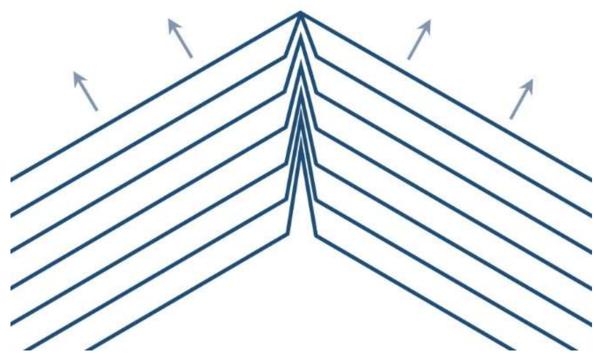


← natural

lab-grown →







A 2D Mullins-Sekerka instability…
Step growth unstable to branching…

“Electric” Ice Needles (an application of solvability theory)

Vapor diffusion chamber
→ High supersaturation
(in air at 1 atm)

Insert wire (bottom)
→ Covers with frost

Apply +2000 volts DC
→ “Electric” needles grow

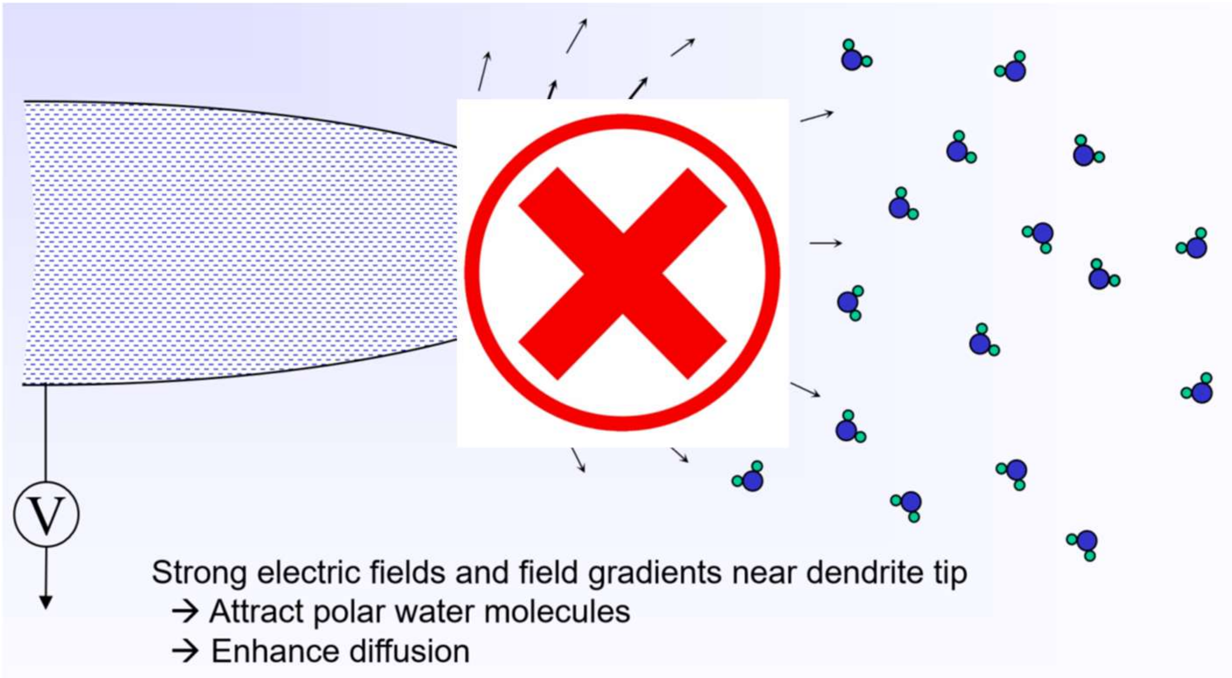
Chemical coaxing
→ c-axis needles

Remove high voltage
Move to 2nd diffusion chamber
→ Normal growth

First e-needles: J. T. Bartlett, A. P. van den Heuvel, and B. J. Mason, Growth of ice crystals in an electric field, Zeit. Fur Ange. Math. Phys. 14, 599-610, 1963.
Theory, c-axis e-needles: K. G. Libbrecht and T. Crosby and M. Swanson, Electrically enhanced free dendrite growth in polar and non-polar systems, J. Cryst. Growth 240, 241-254, 2002.

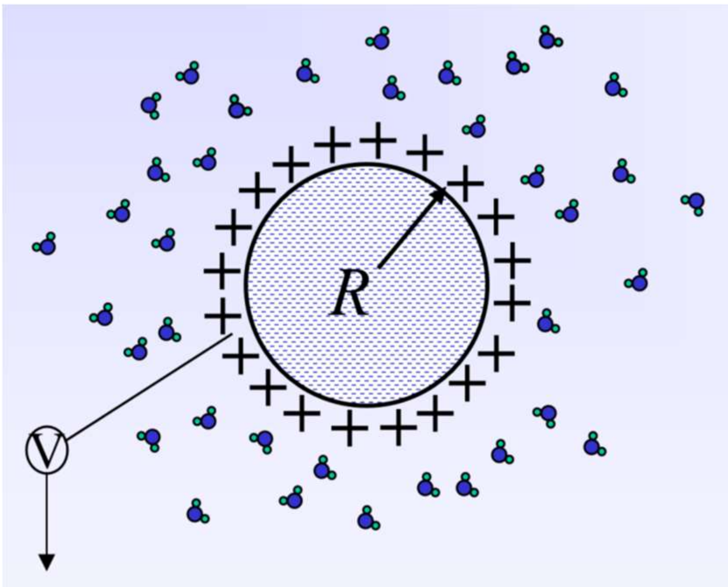
<u>"Electric" Ice Needles - Theory</u>

The obvious (but wrong) explanation:
electrically enhanced diffusion of polar molecules



Why wrong?
Polar water molecules have lower energy in strong E fields
→ Tip vapor pressure higher than normal (E = 0 or P = 0)
→ Effects cancel!

“Electric” Ice Needles - Theory

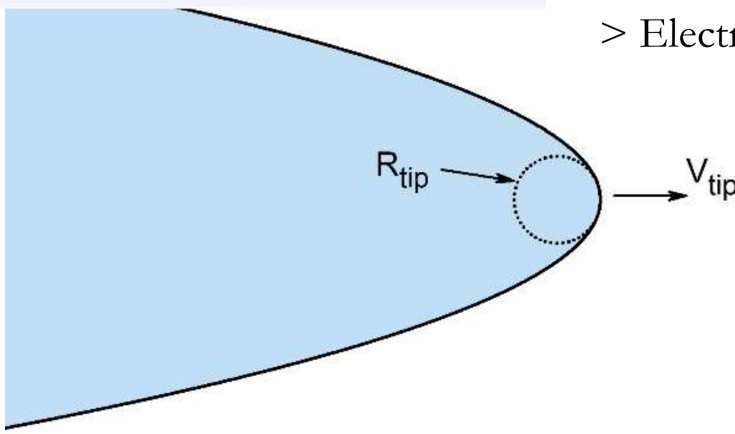


The correct explanation:
Electrostatic effect **decreases** vapor pressure of charged sphere (independent of polarization)

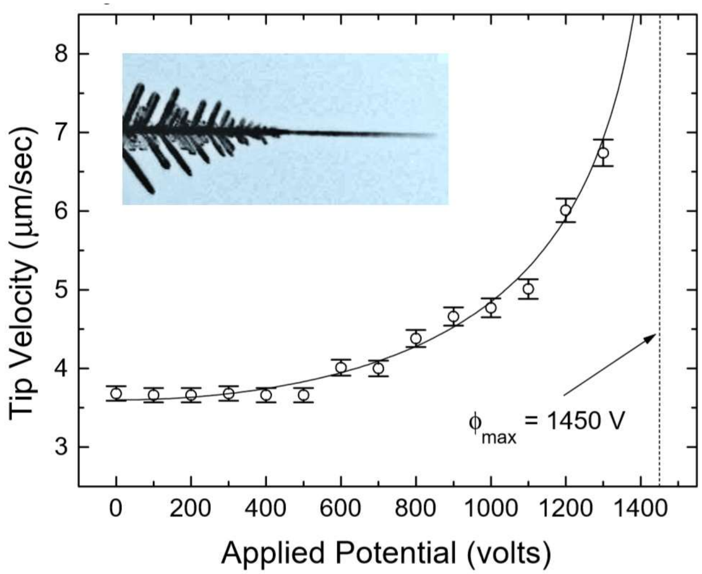
Vapor pressure of tip changed by:
- Gibbs-Thomson effect (surface energy)
- Polarizability effect (for polar molecules)
- Electrostatics (for polar or nonpolar molecule)

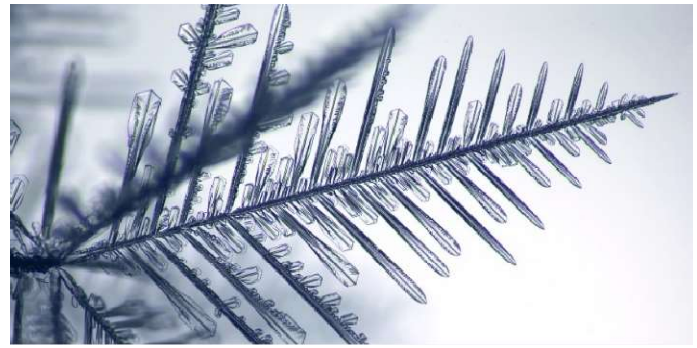
Combine with:
- Solvability theory
- Electrically driven diffusion (for polar molecules)

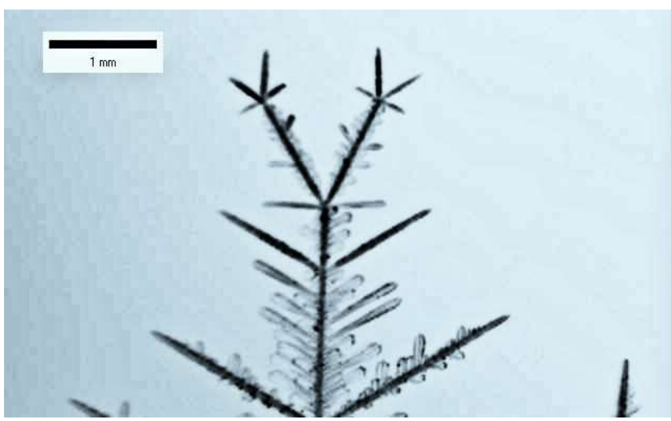
… Messy, but doable with sufficient approximations



"Electric" Ice Needles – An electrically driven tip-growth instability







> Start with a normal snow-crystal dendrite growing on wire

> Apply +V to wire base
can assume ice ~conductor, because no current flow

> At low V, solvability theory → enhanced growth

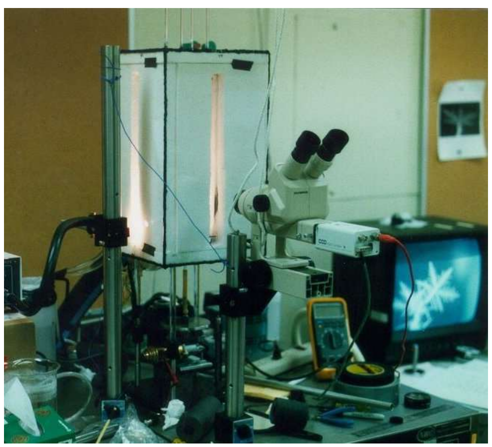
> When $v_{tip} \approx 2v_{tip,0}$ → theory predicts instability
→ $v_{tip} \rightarrow \infty$

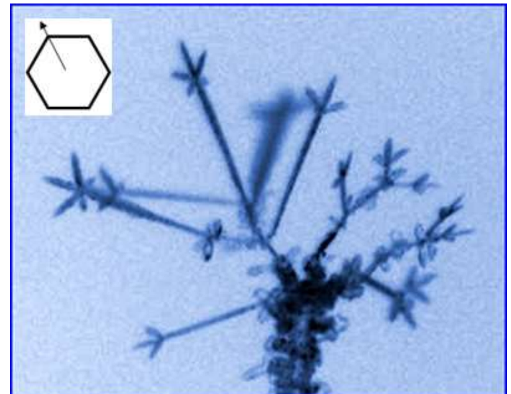
> Consistent with observations (curve through data above)

> $V_{applied} > V_{threshold}$ → e-needle or other phenomena

A serendipitous discovery…

Victoria Tanusheva in the lab, 1997





E-needle growth axis unpredictable

is…

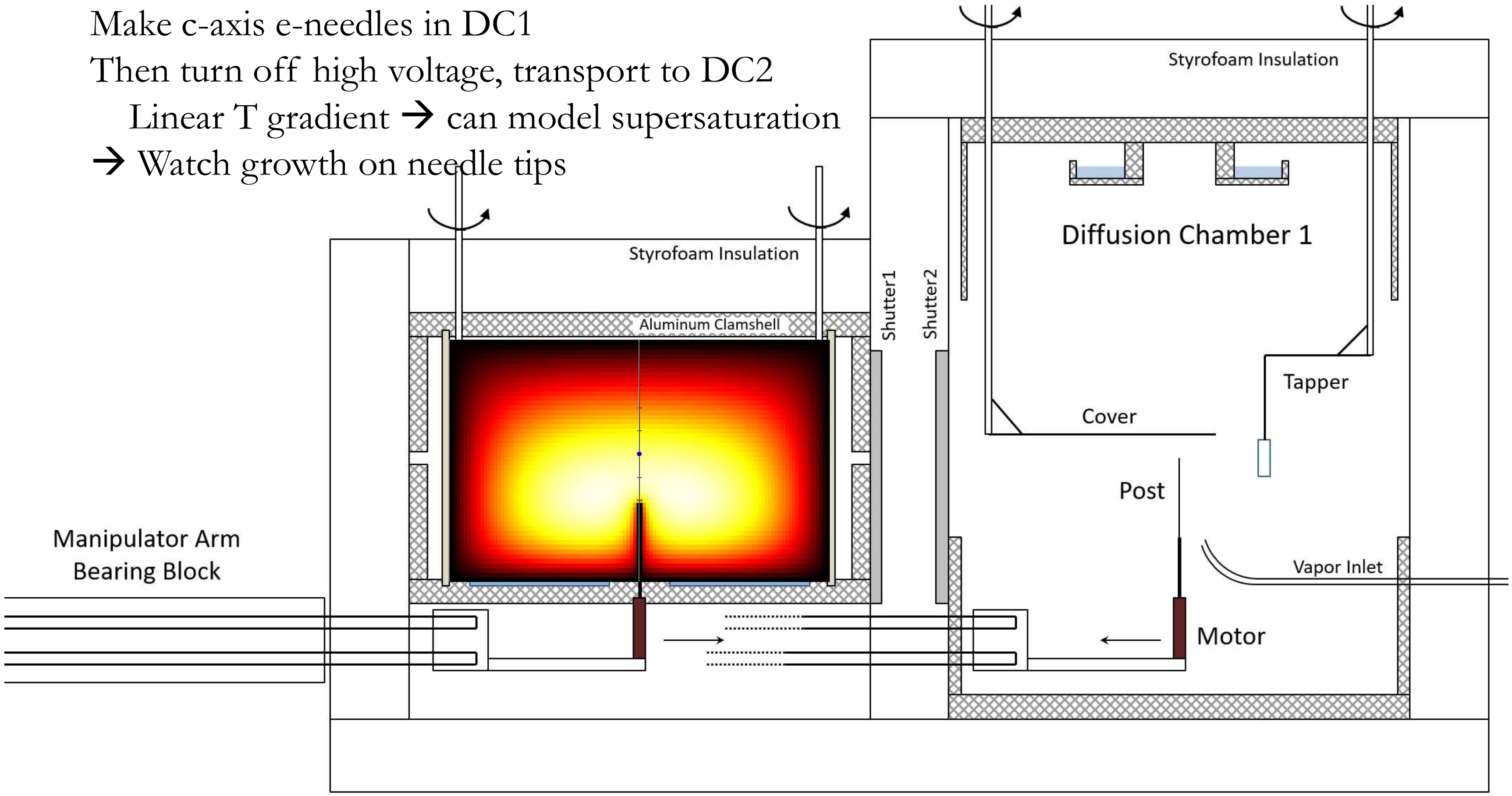
"Electric" Ice Needles as a research tool

Make c-axis e-needles in DC1

Then turn off high voltage, transport to DC2

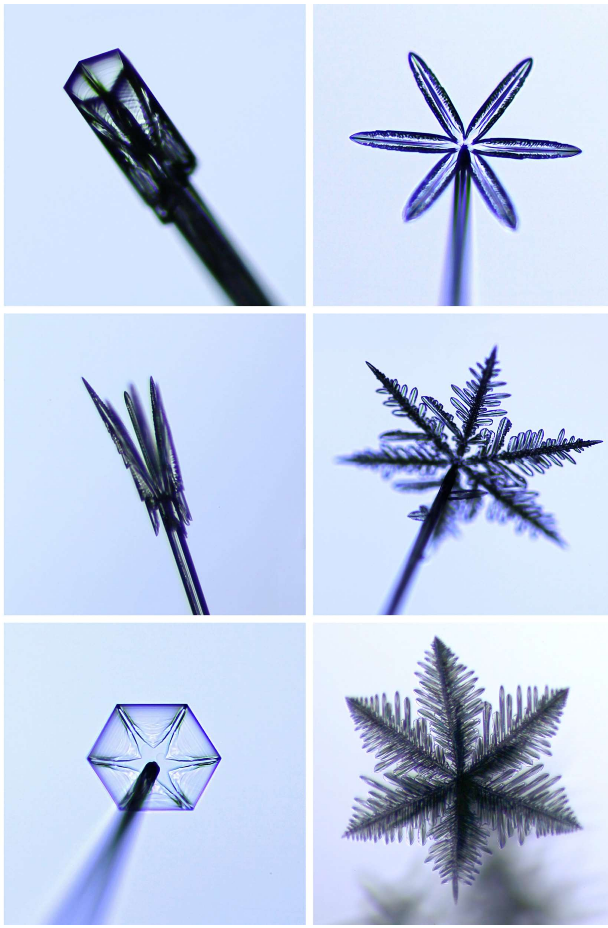
Linear T gradient → can model supersaturation

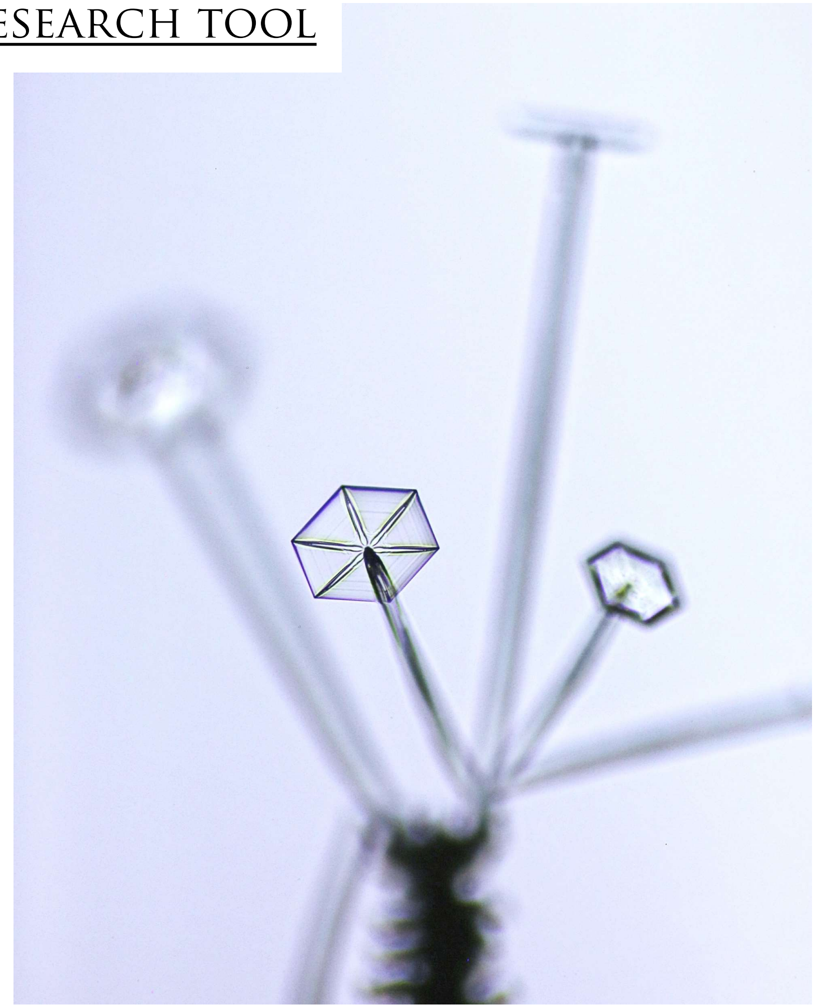
→ Watch growth on needle tips



“Electric” Ice Needles as a research tool

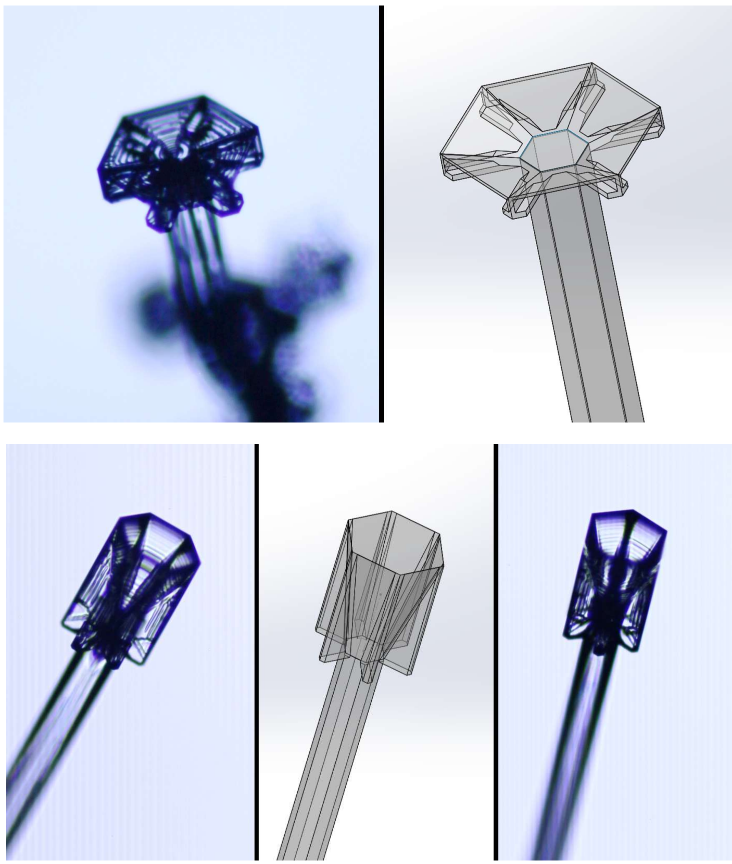
Observe a variety of structures



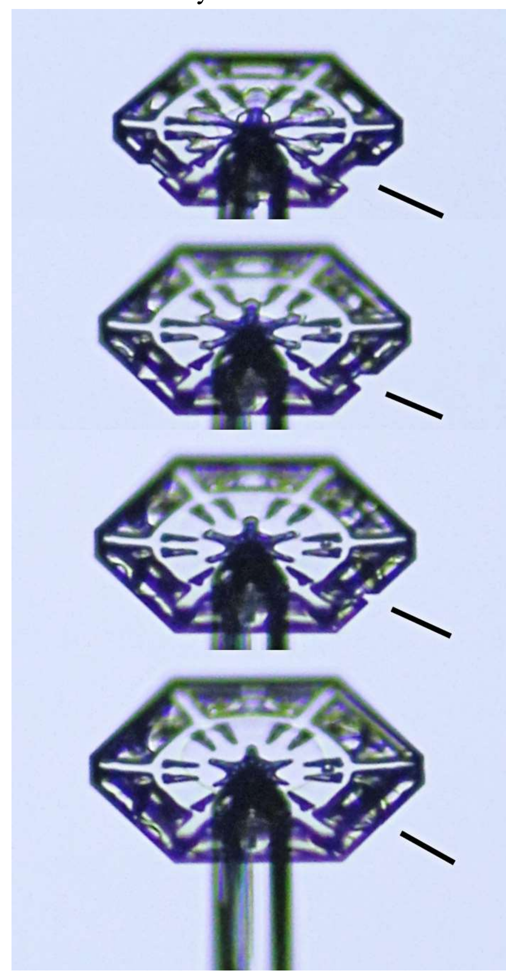


“Electric” Ice Needles as a research tool

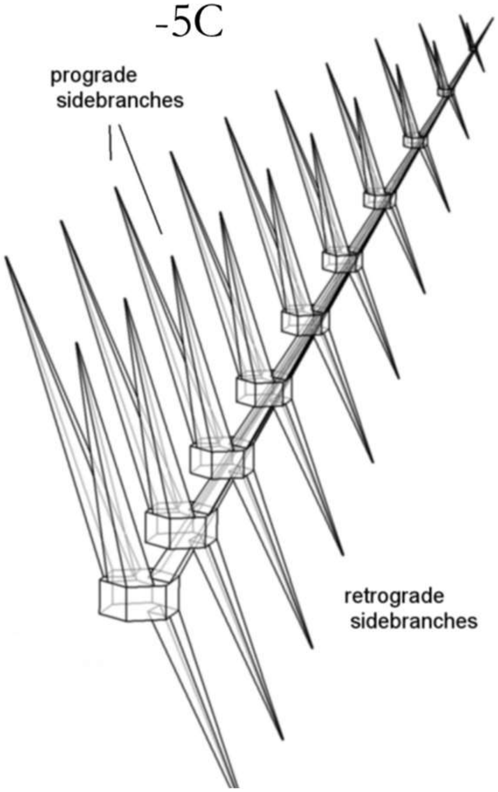
3D Morphology models

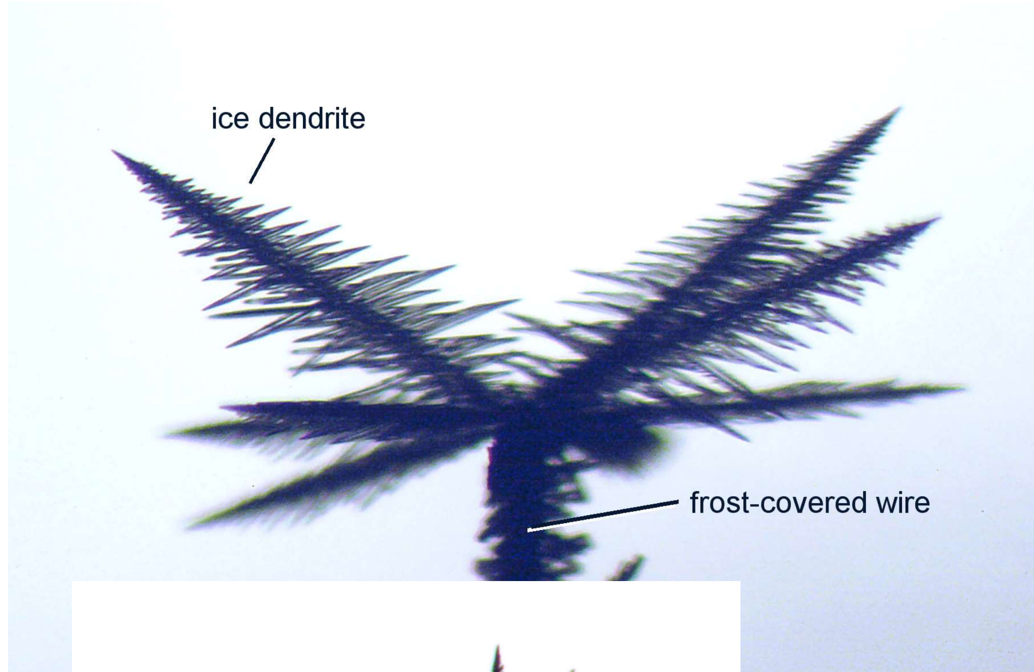


Growth dynamics

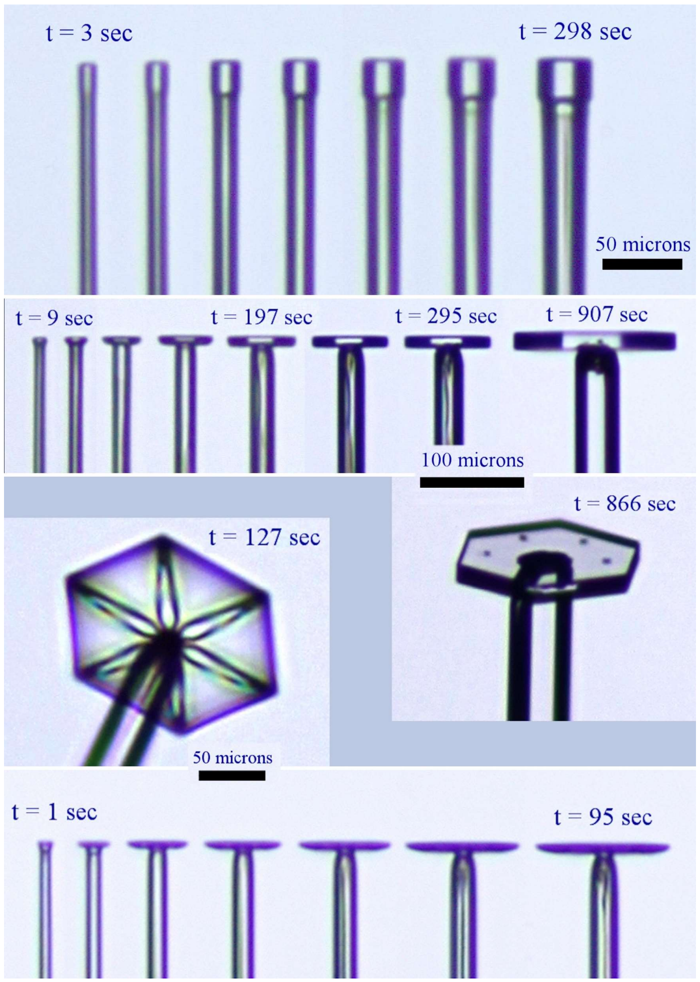


"Fishbone" dendrites

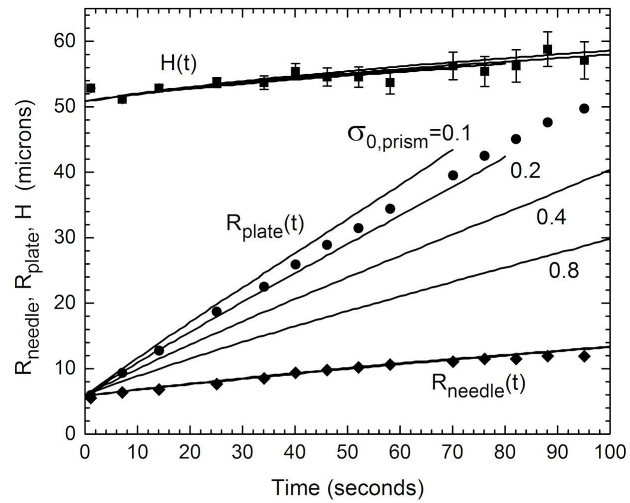


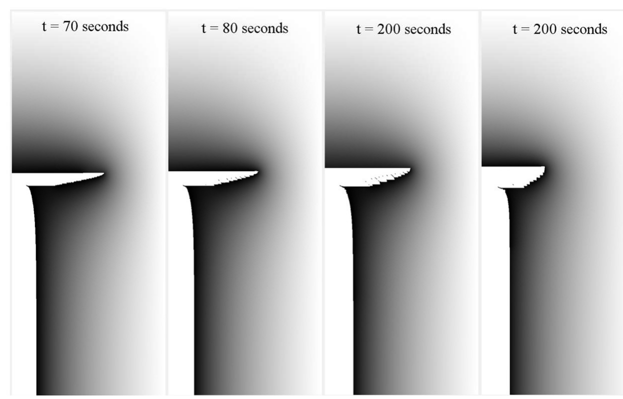


“Electric” Ice Needles as a research tool

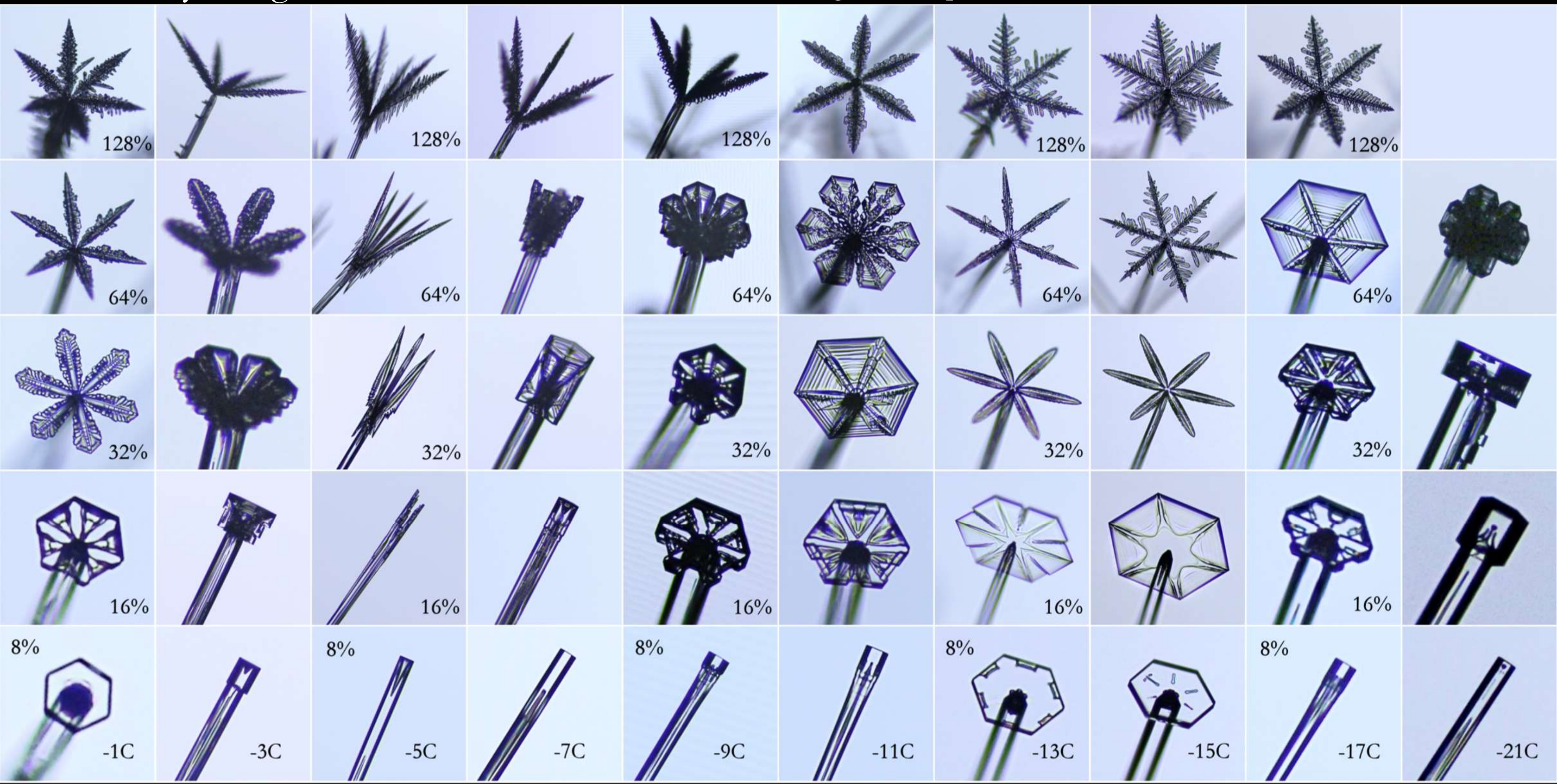


Quantitative 2D cylindrically symmetric models





Snow crystals grown on ice needles – Diffusion-limited growth explains vertical axis, order → chaos



All single crystals; all grown at constant conditions What is underlying physics? Possible to make numerical models?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"How full of the creative genius is the air
I should hardly admire more if real sta
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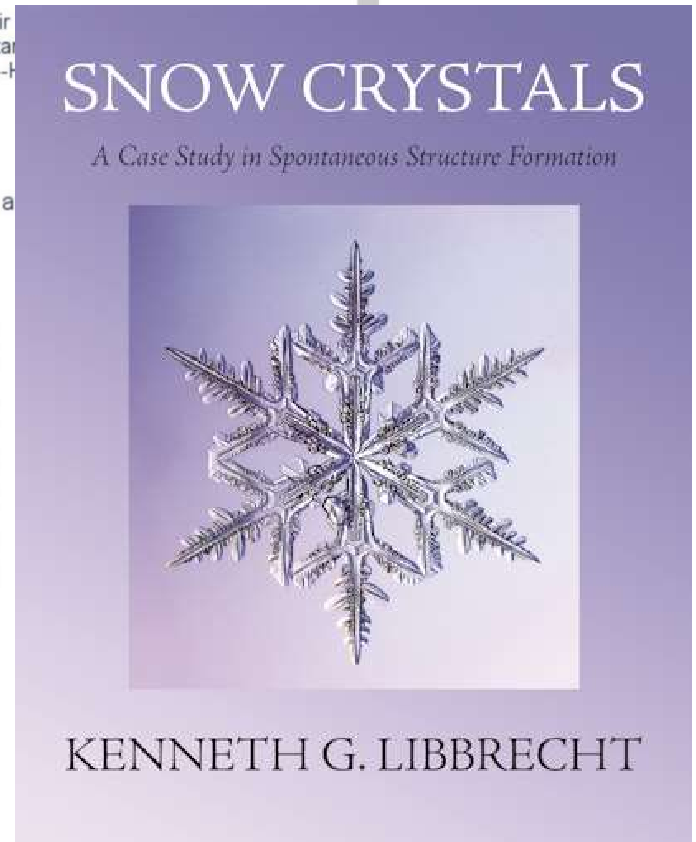
-15°C
???
<< Check out this entertaining YouTube video about snow-crystal science, made by the good folks at Veritasium.
>> You can find the FULL story about the science of snow crystal formation in my magnum opus at right (weighting in at 456 pages)


SNOW CRYSTALS
A Case Study in Spontaneous Structure Formation
KENNETH G. LIBBRECHT