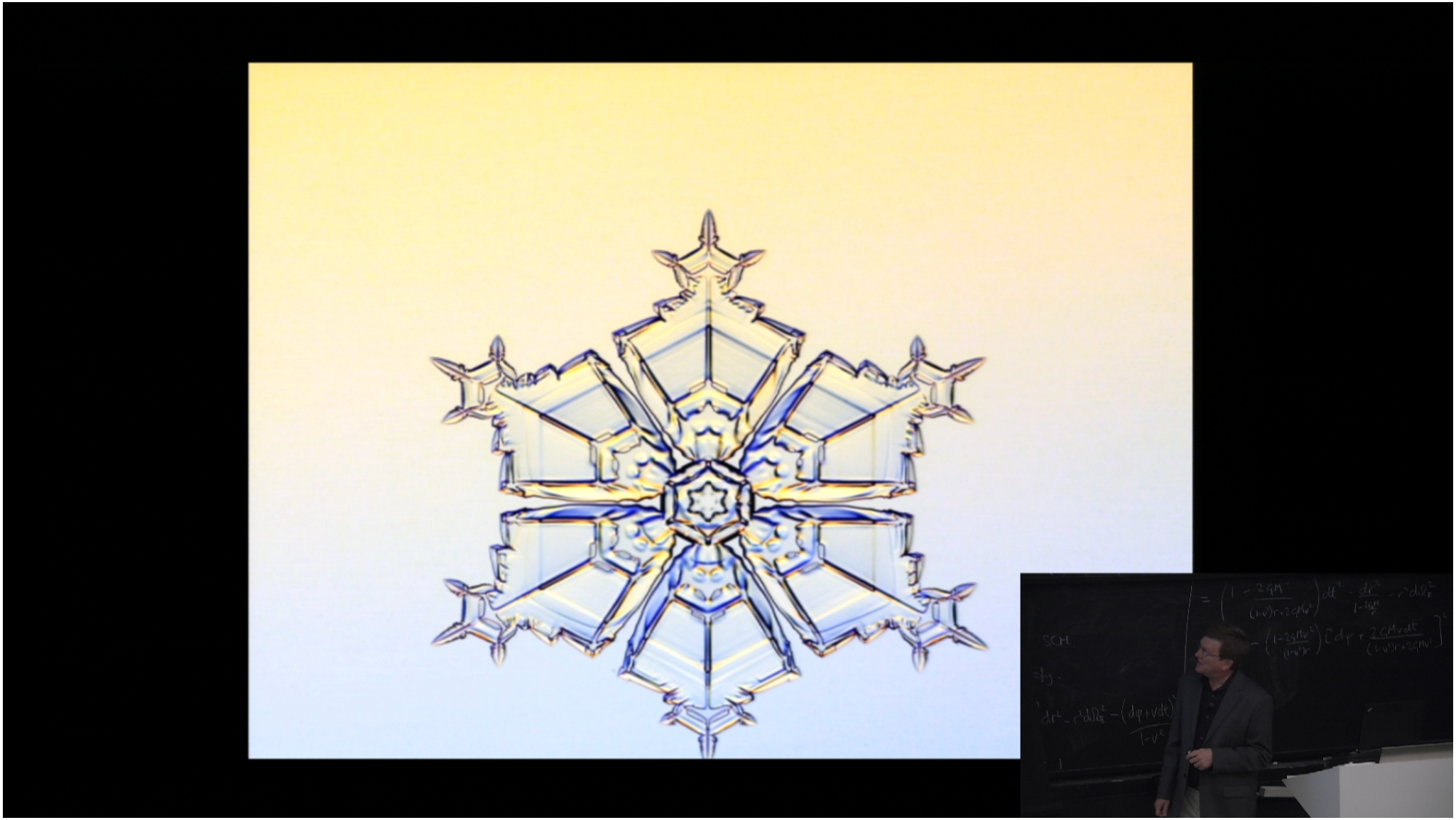
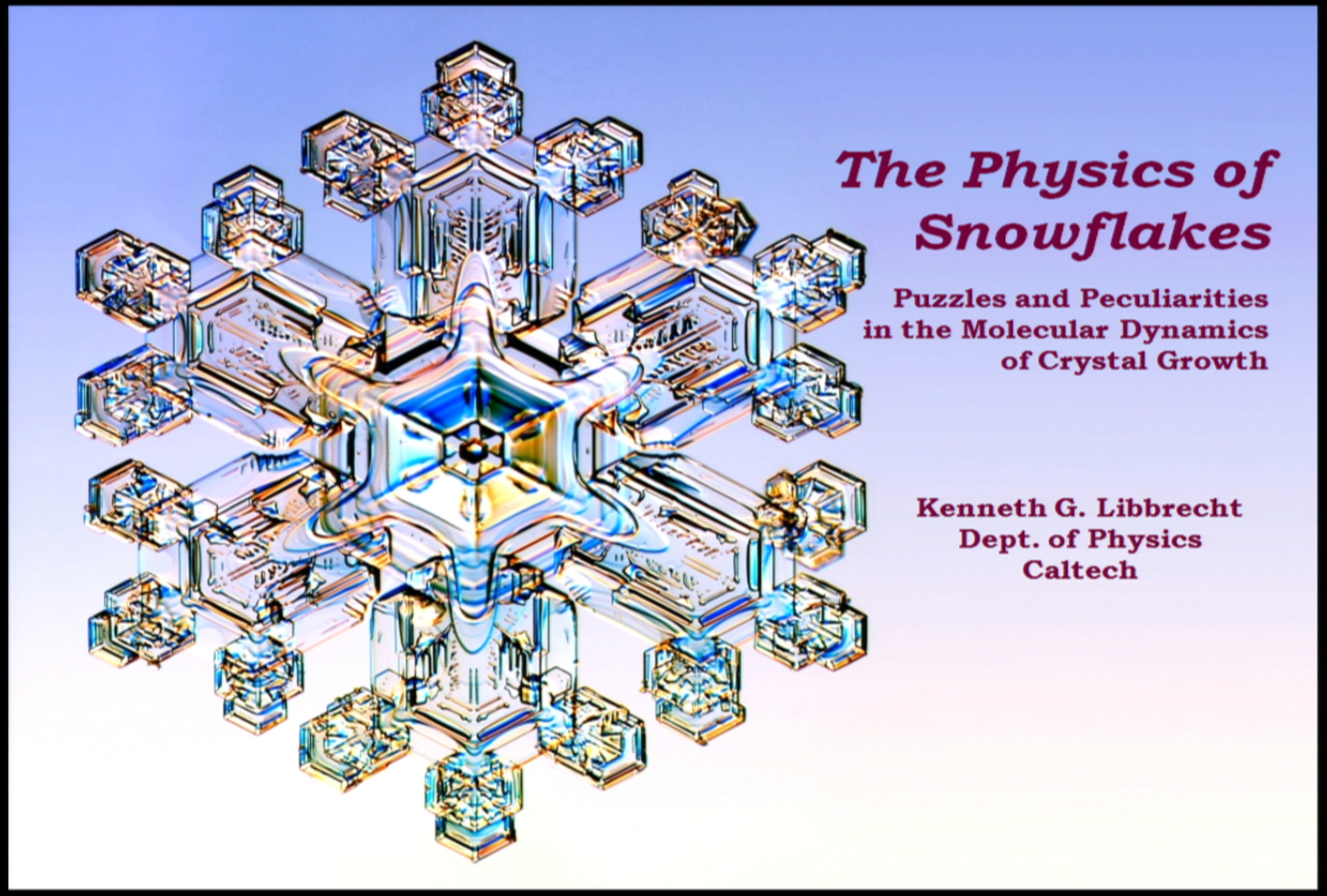
Title: The Secret Life of a Snowflake: An Up-Close Look at the Science and the Splendor of Nature's Frozen Art

Date: Feb 01, 2012 02:00 PM

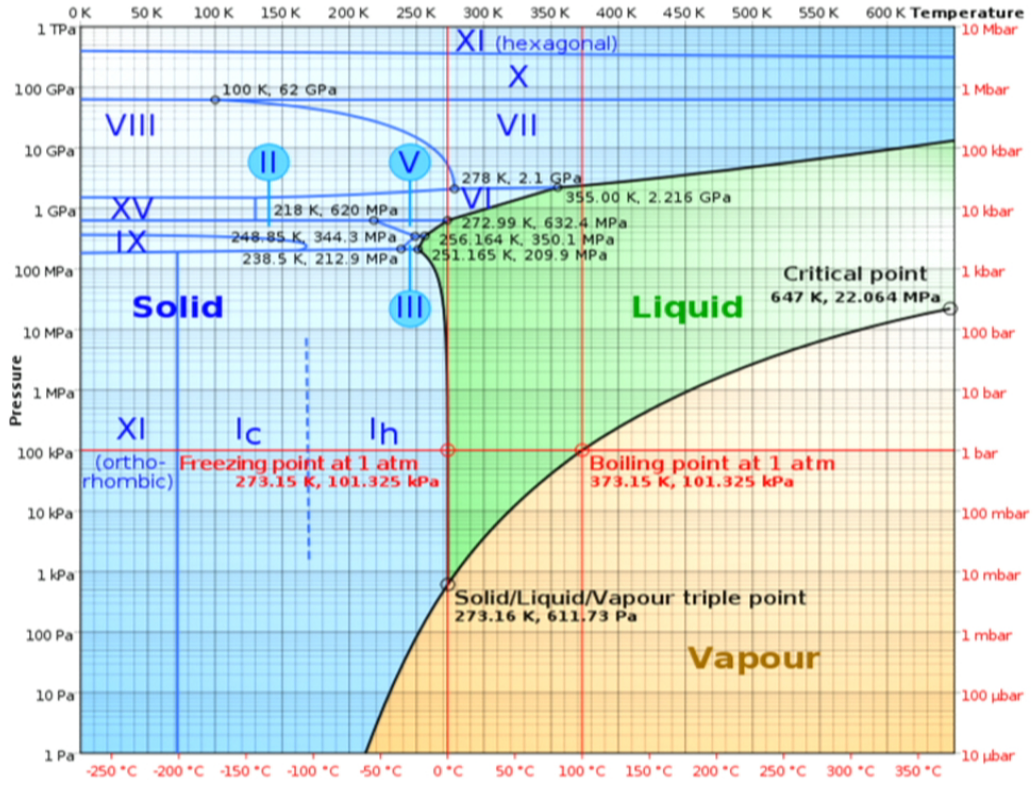
URL: http://pirsa.org/12020090

Abstract: How do snowflakes form?




The Physics of Snowflakes
Puzzles and Peculiarities in the Molecular Dynamics of Crystal Growth
Kenneth G. Libbrecht
Dept. of Physics
Caltech

The Water Phase Diagram



Phase Diagram = Statics (easier)

Phase Transitions = Dynamics (harder)

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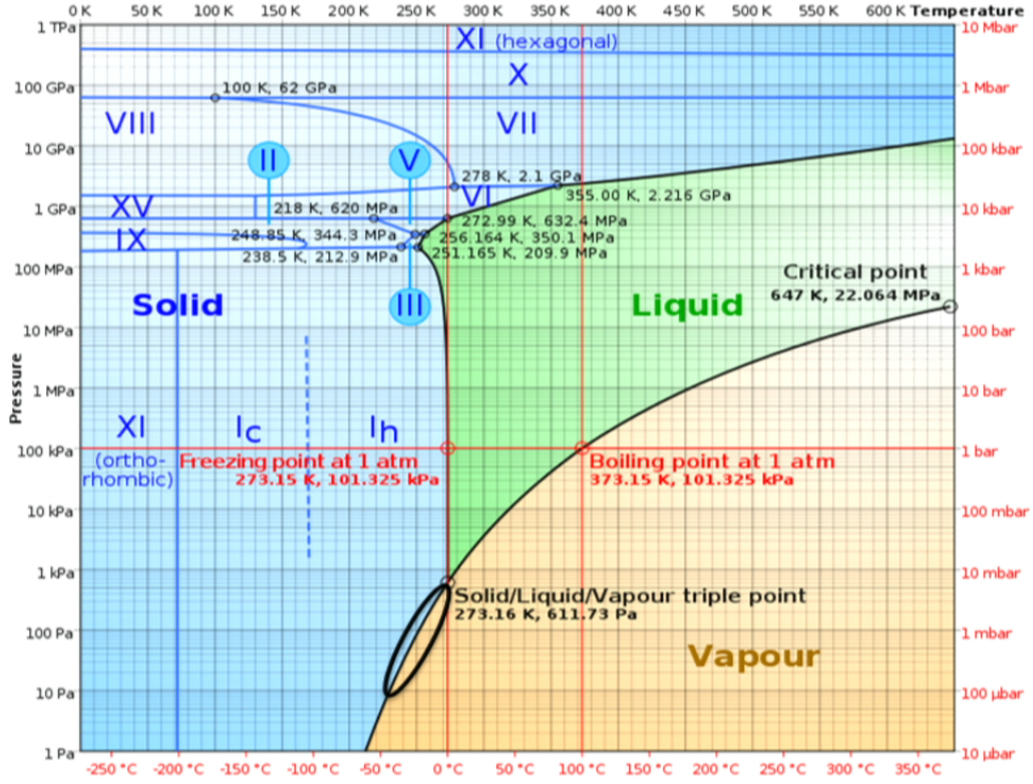

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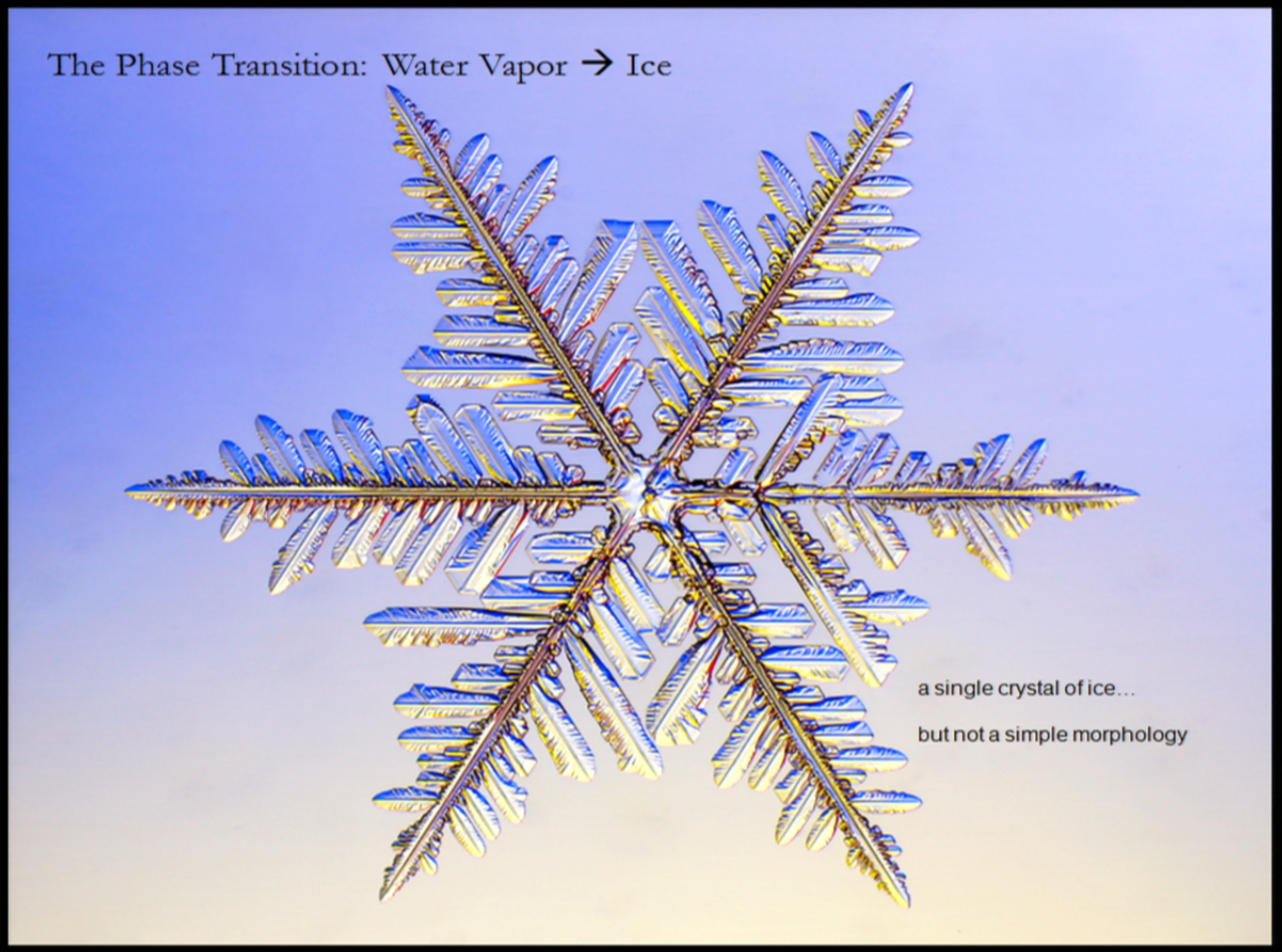
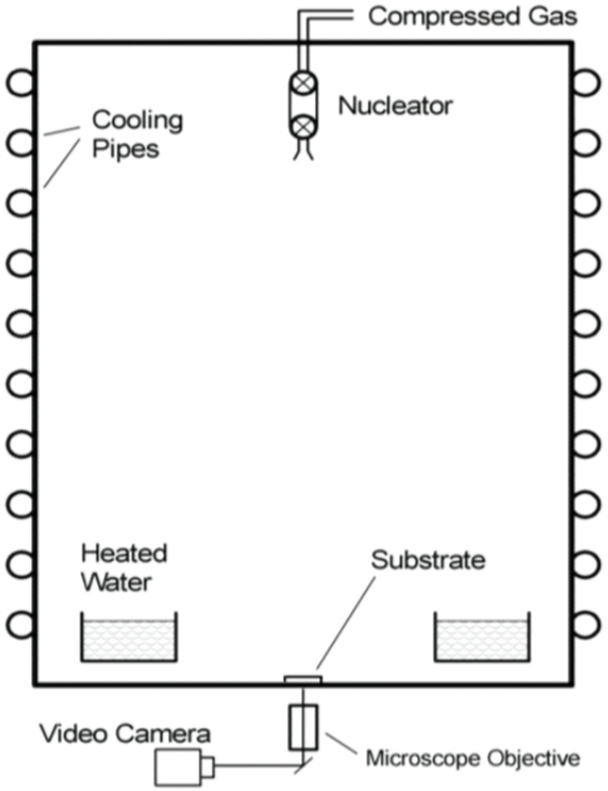

The Phase Transition: Water Vapor → Ice
a single crystal of ice…
but not a simple morphology

A Simple Ice Crystal Growth Experiment



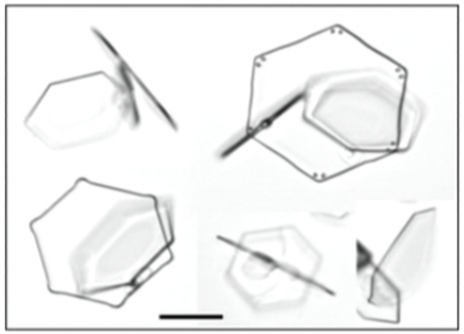
Tank chilled to desired temperature

Heated water provides water vapor; mixed by convection

Nucleator creates pulses of cold gas to produce crystals

Crystals fall and are viewed on substrate

Grow crystals at different air temperatures (supersaturation ~1-10%)



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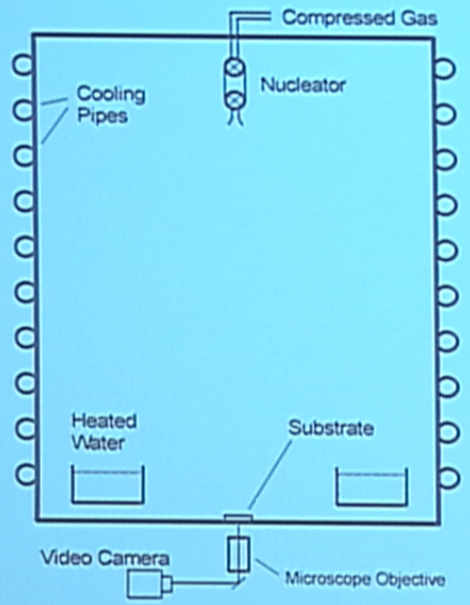

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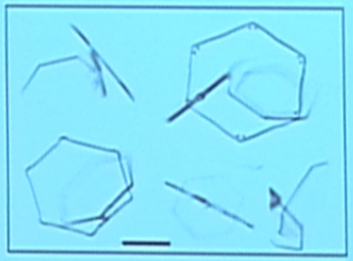
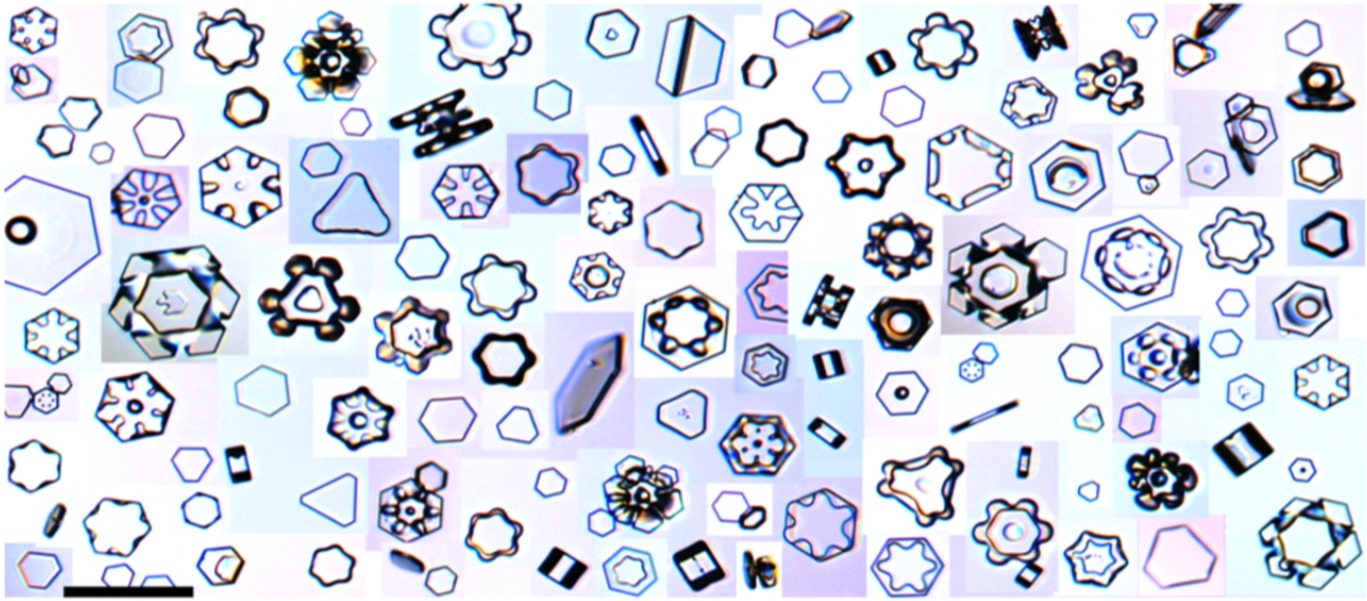


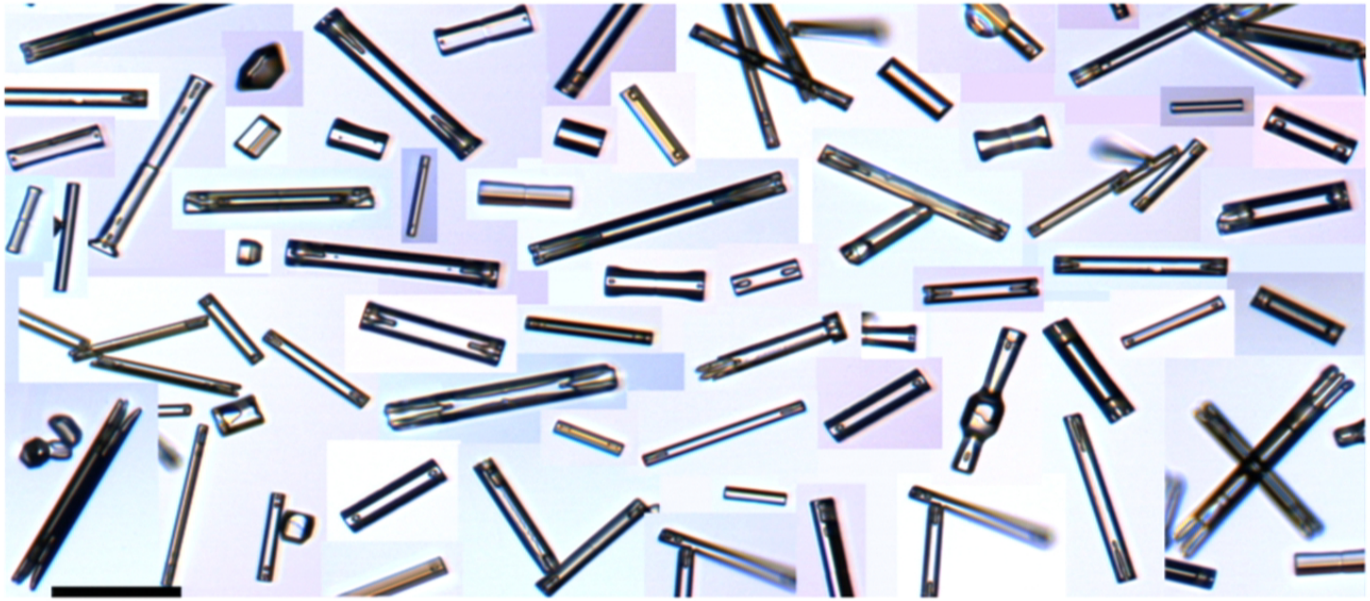
Laboratory Grown Snow Crystals: At -2 C



50 micron
scale bar

Mostly small, thin plates (some seen edge-on)
Some columns, odd-looking crystals, etc.

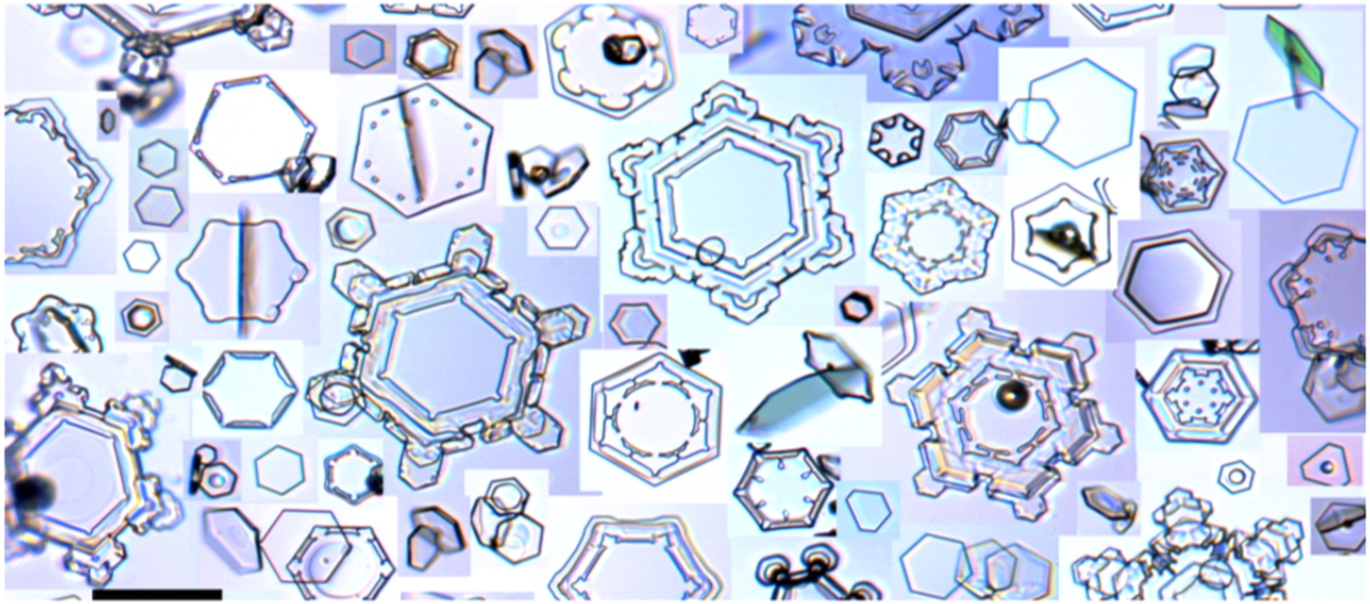
Laboratory Grown Snow Crystals: At -5 C



50 micron
scale bar

Mostly hexagonal columns (some with hollows)

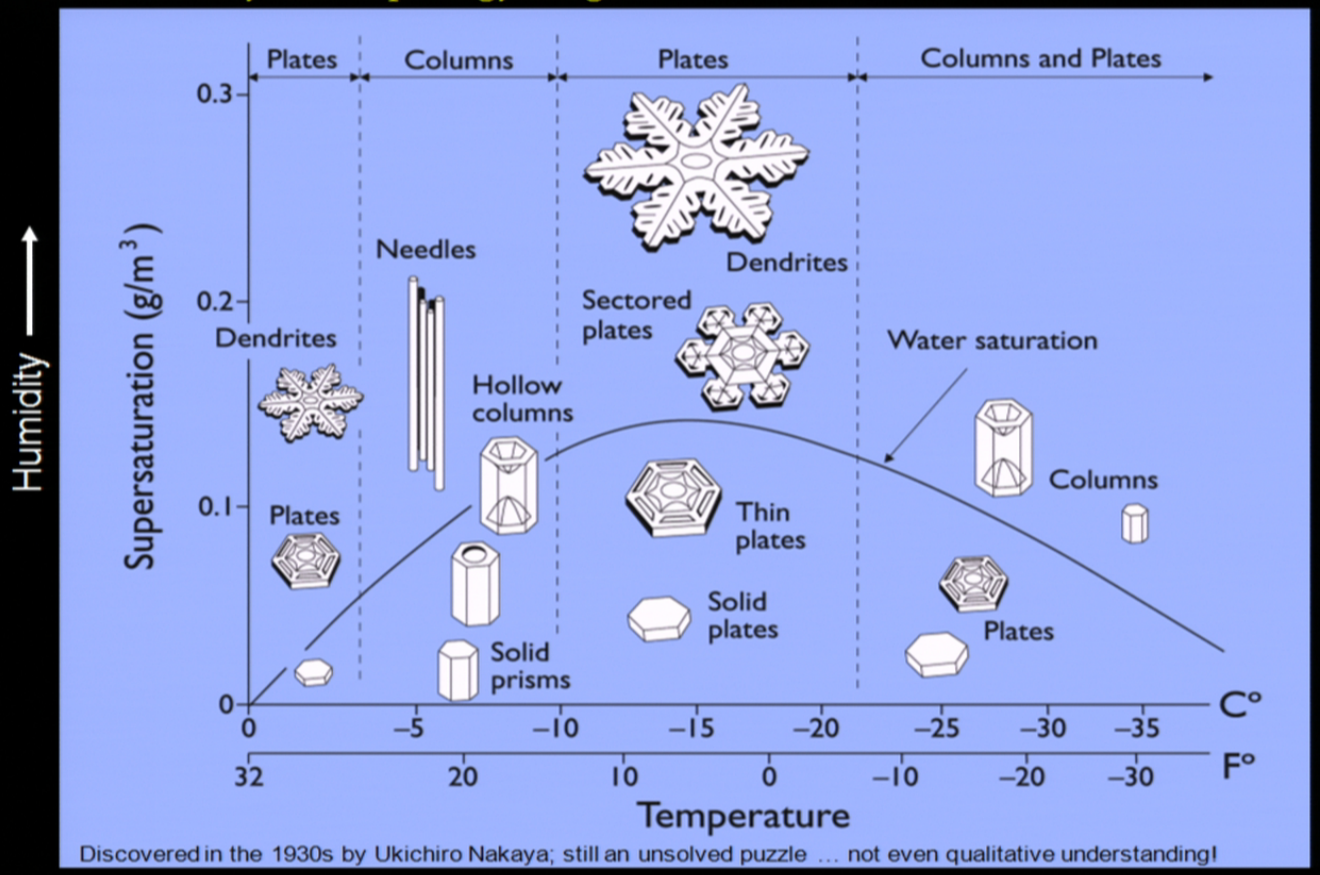
Laboratory Grown Snow Crystals: At -15 C



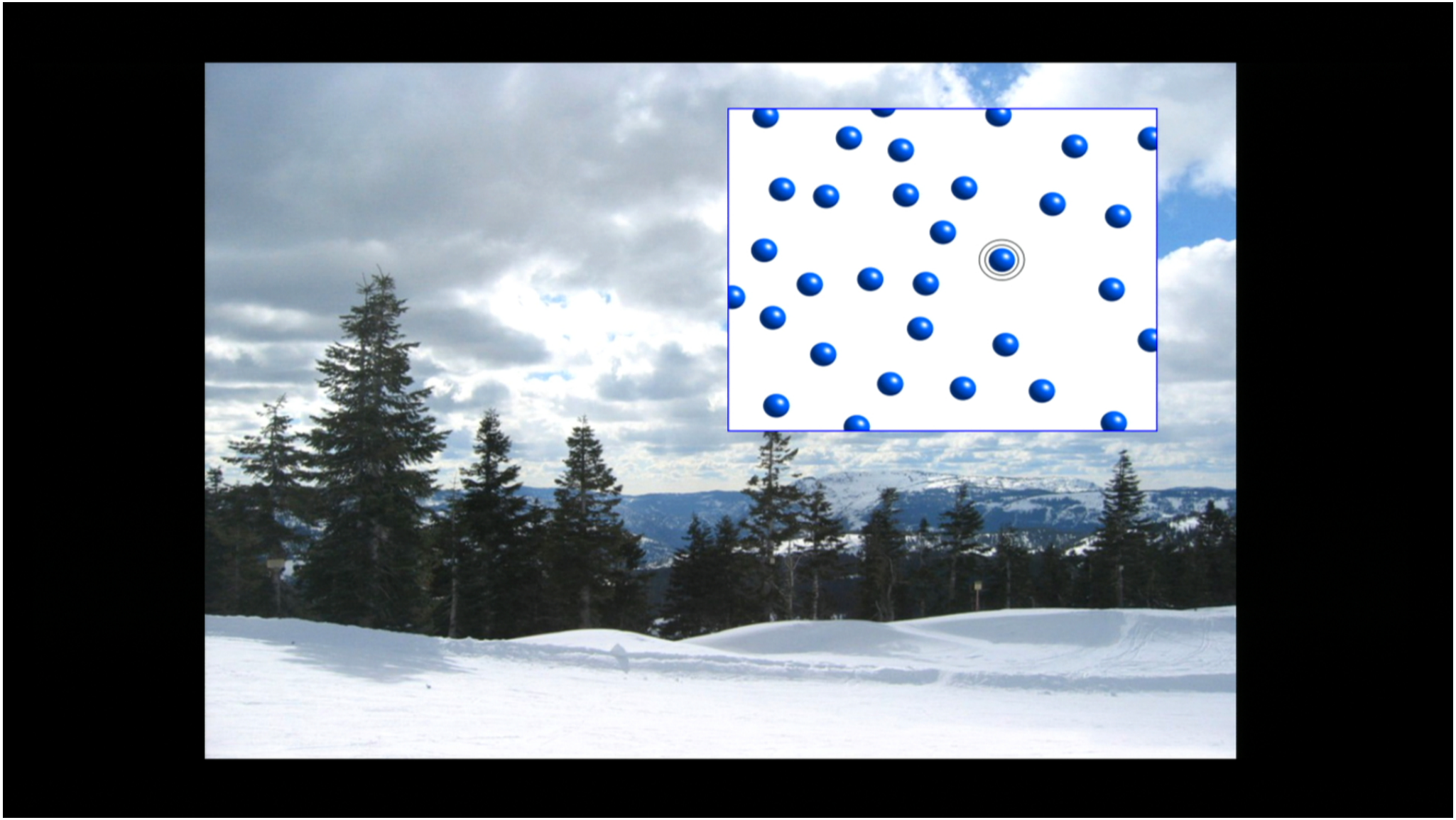
50 micron
scale bar

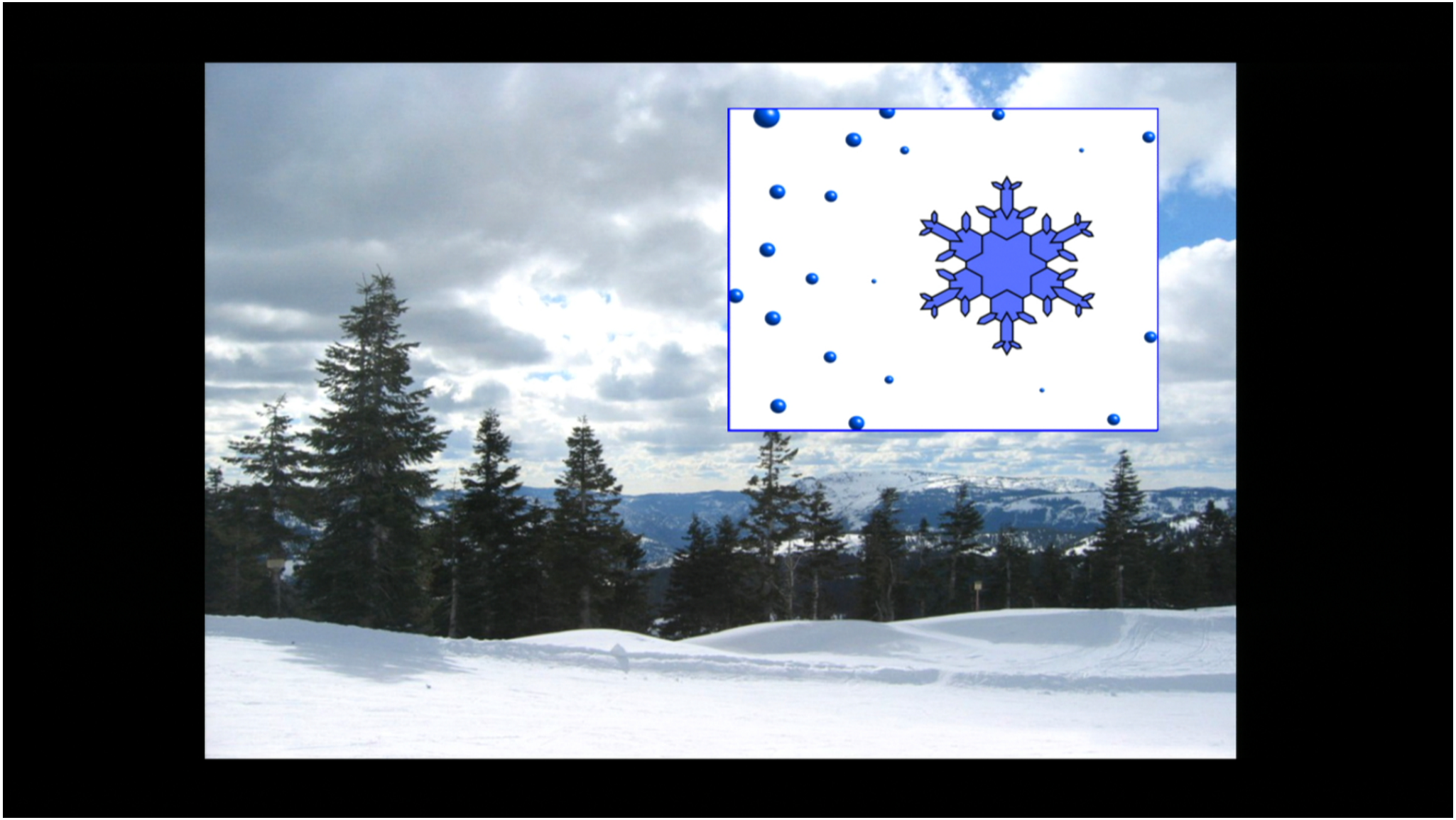
Mostly large, very thin plates
Some hexagonal, some branched

The Snow Crystal Morphology Diagram



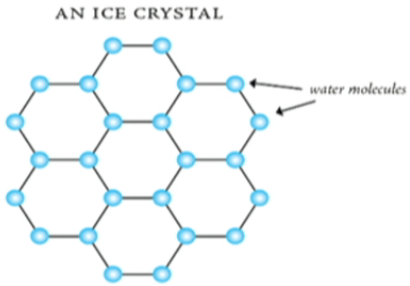
Discovered in the 1930s by Ukichiro Nakaya; still an unsolved puzzle … not even qualitative understanding!

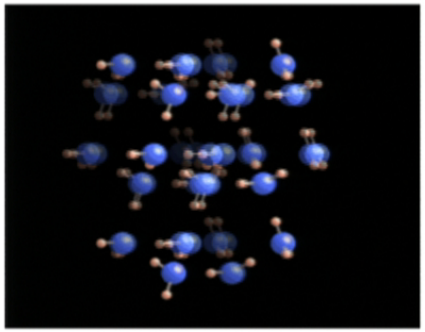


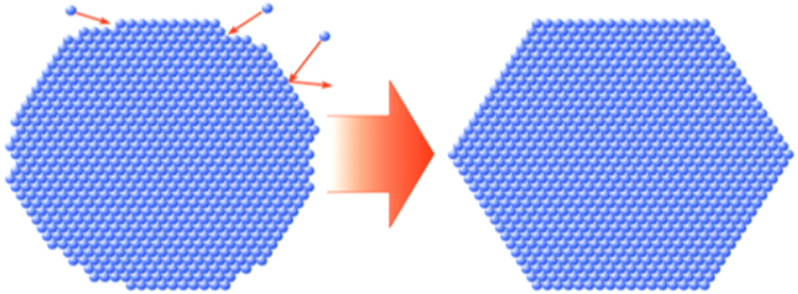


Snowflake Basics I - Faceting

Structure of the Ice Crystal → Facets

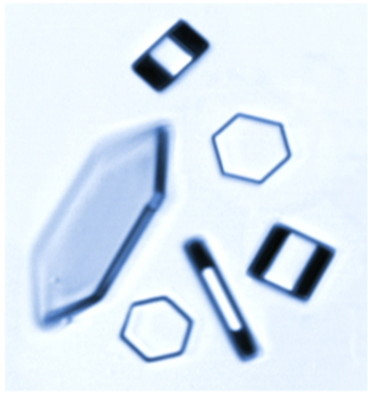






Molecules cannot readily attach to smooth surfaces
→ facets form as crystal grows

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



Tiny, laboratory grown snow crystals ~0.1 mm

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

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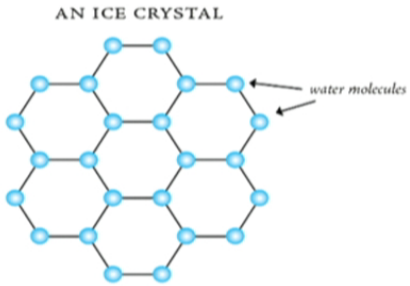

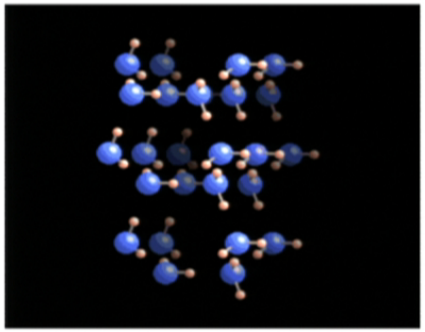

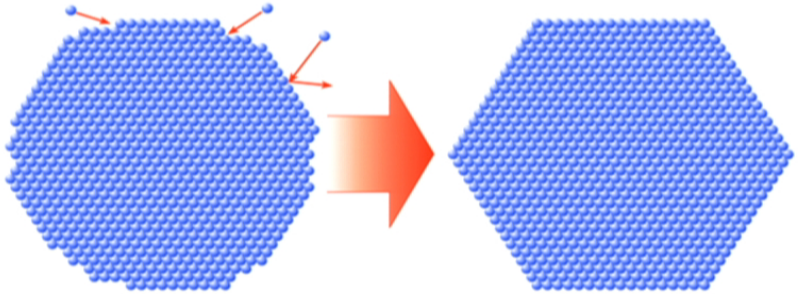

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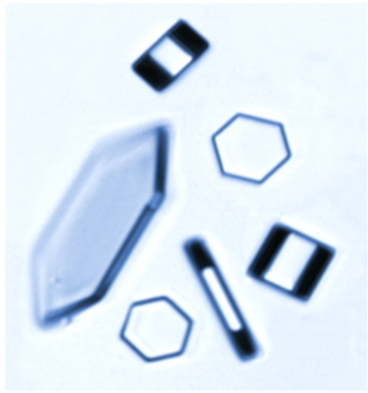

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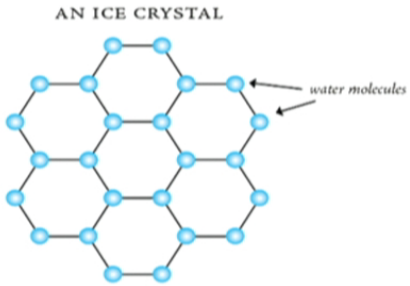

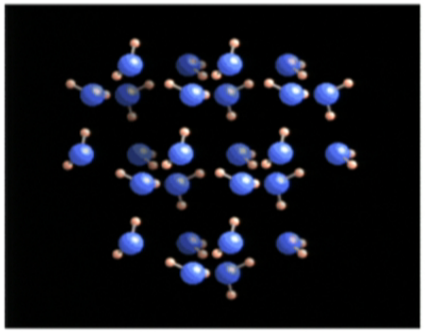

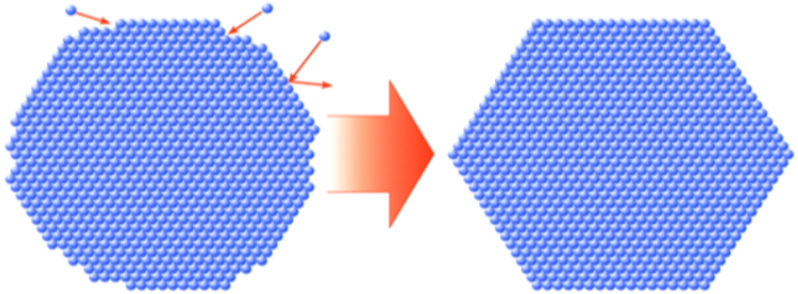

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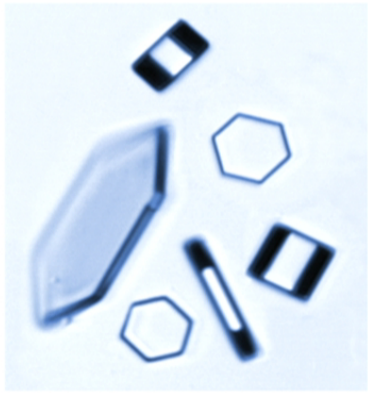

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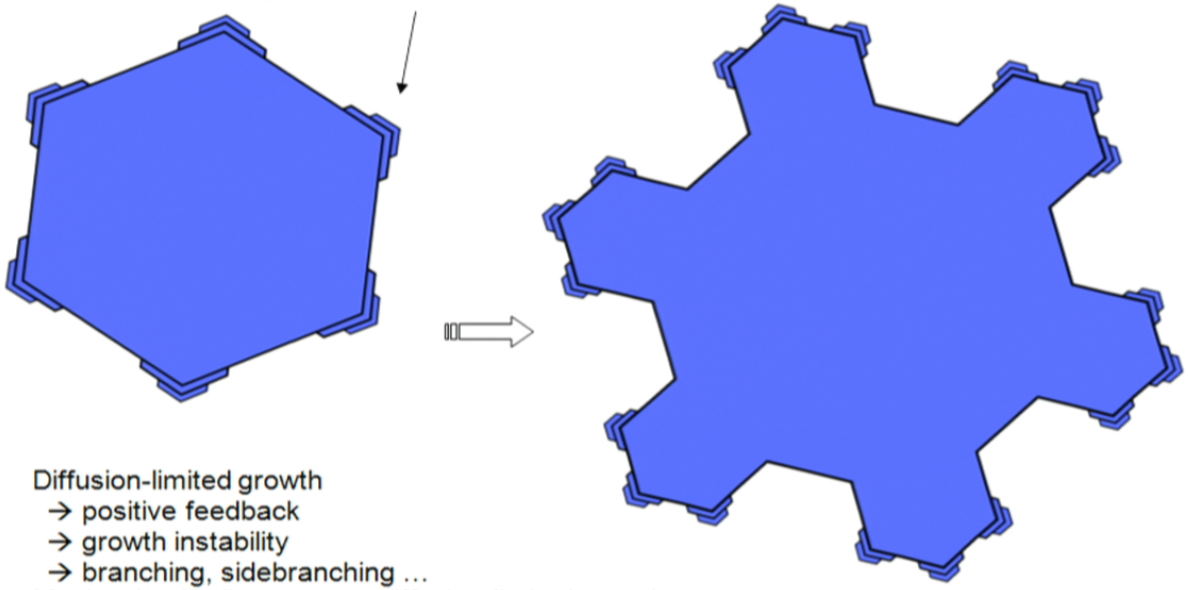
Snowflake Basics II – The Branching Instability

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

Branches form as snowflakes grow larger

A *Growth Instability* – responsible for most complex structure in snow crystals

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

Snowflake Basics III - Complexity and Symmetry

(an explanation of the "No-Two-Alike" conjecture)

- Nucleation of ice particle

Grows to hexagonal prism, since smooth facets grow most slowly

Simple plate unstable as crystal grows larger … corners sprout arms

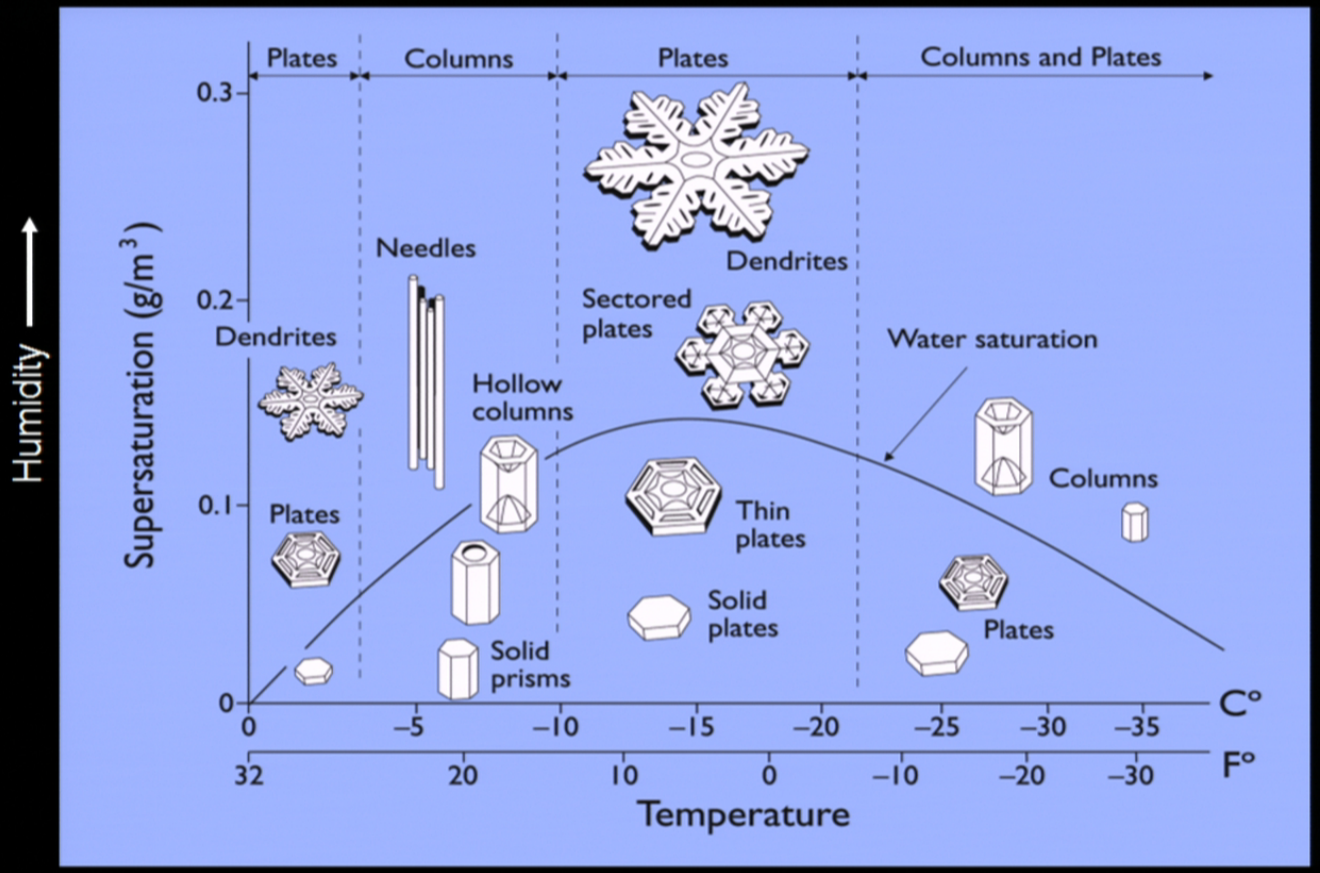
Crystal moves to different temperature … plates grow on arms

Crystal moves through *many different temperatures* … each change causes new growth behavior on arms

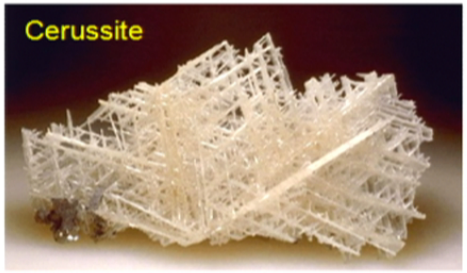
Complex history → Complex crystal shape
Each arm experiences same history → Symmetry
No two paths are the same → No two alike
All because growth sensitive to temperature, humidity

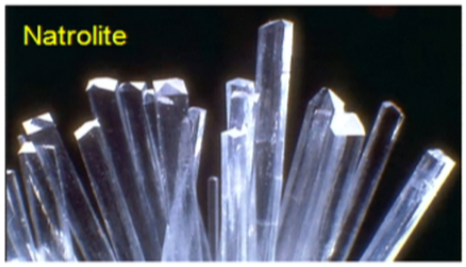

basic features: faceting, branching, side-branching, parallel branches

The Snow Crystal Morphology Diagram



Mineral crystals also show diverse morphologies

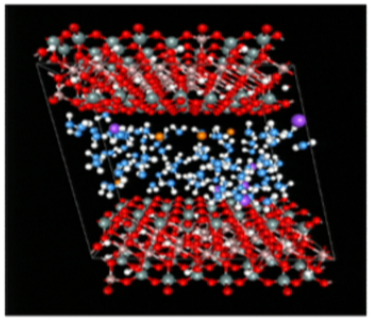




~5000 different minerals known (including ice)
molecular structures determined by X-ray crystallography
growth morphologies cataloged for some
growth often complex (as with ice)

Crystallography = statics problem → symmetry
Crystal growth = dynamics problem → morphology

Model growth from molecular dynamics simulations?
No, simulations cannot deal
with range of lengths, times



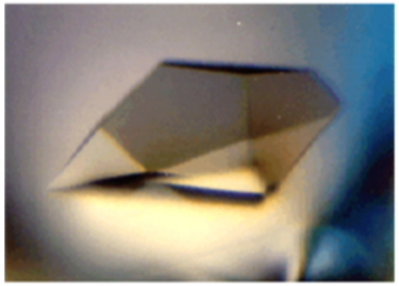
→ morphologies, growth rates cannot yet be explained (for essentially all crystals)

Growth dynamics is important for industrial crystals

(but trial-and-error is still the most successful engineering strategy)

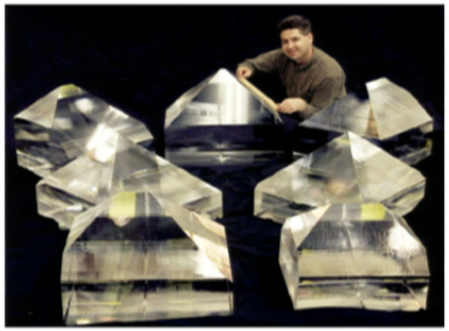
Synthetic gemstones

Protein crystals

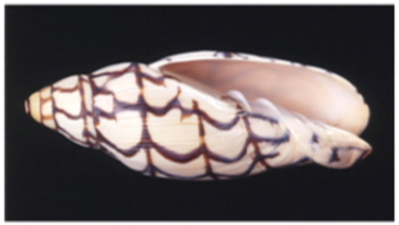


Semiconductor crystals

Optical crystals



Biomineralization



The fundamental molecular dynamics of crystal growth is not well understood... even in silicon and other industrial crystals.
Engineering → recipes → desired final products

→ *morphologies, growth rates not well understood*
...technology advances if understand basic science better

A case study in crystal growth...

Why Ice?

- Monomolecular System
- Well Characterized Material
- Growth from Vapor
- Rich Phenomenology
- No Safety Issues
- Inexpensive
- Seemingly Simple Problems (but unsolved nevertheless)

→ Molecular Dynamics of Crystal Growth

Ice growth from vapor
is a fascinating physical system
Many unsolved puzzles …
(e.g. morphology diagram)
Not at all well studied …

Why so poorly studied?
Materials science without applications

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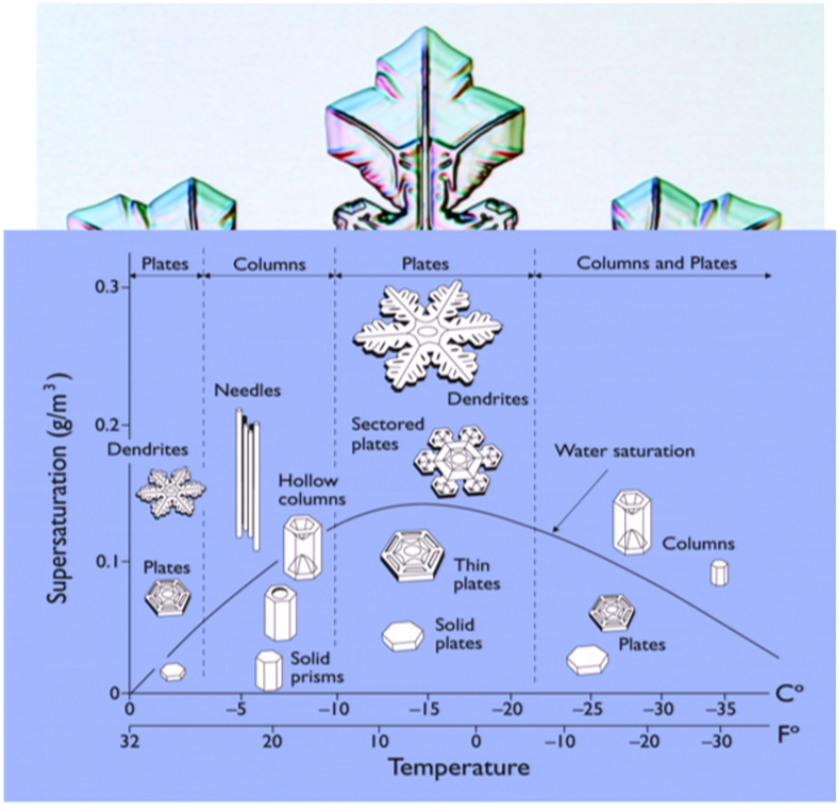

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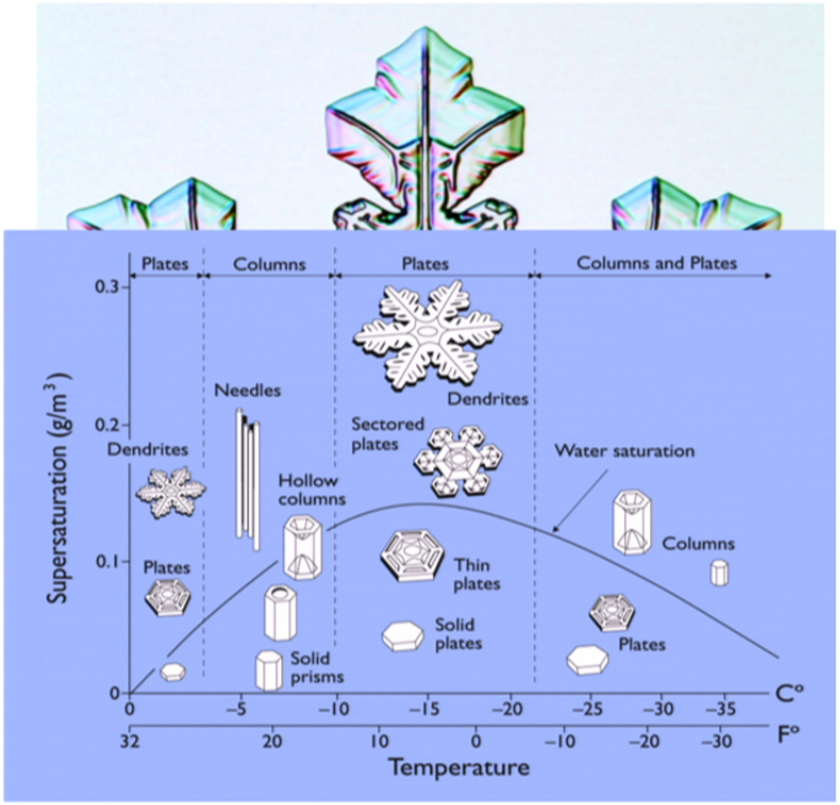

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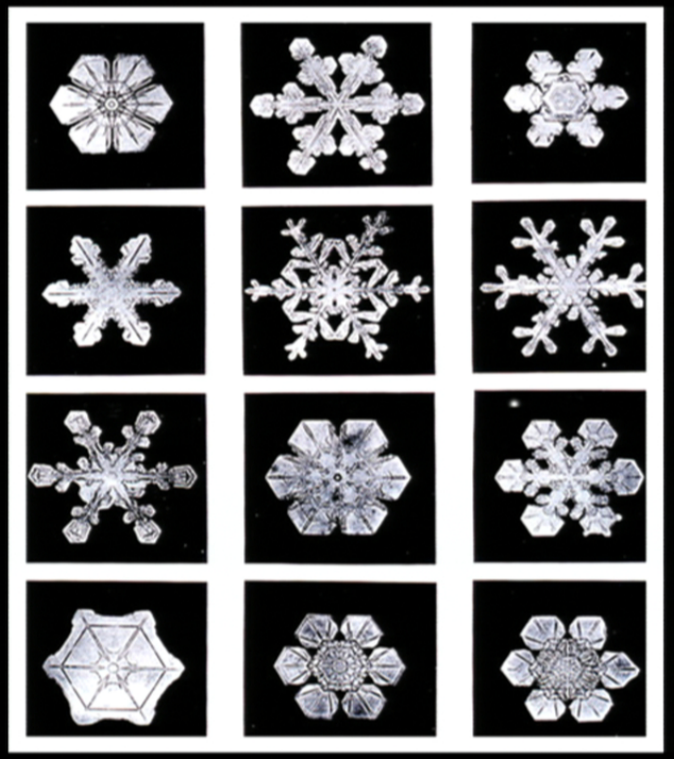
→ zero funding…

Snowflake Photography

Wilson Bentley (1865 –1931)

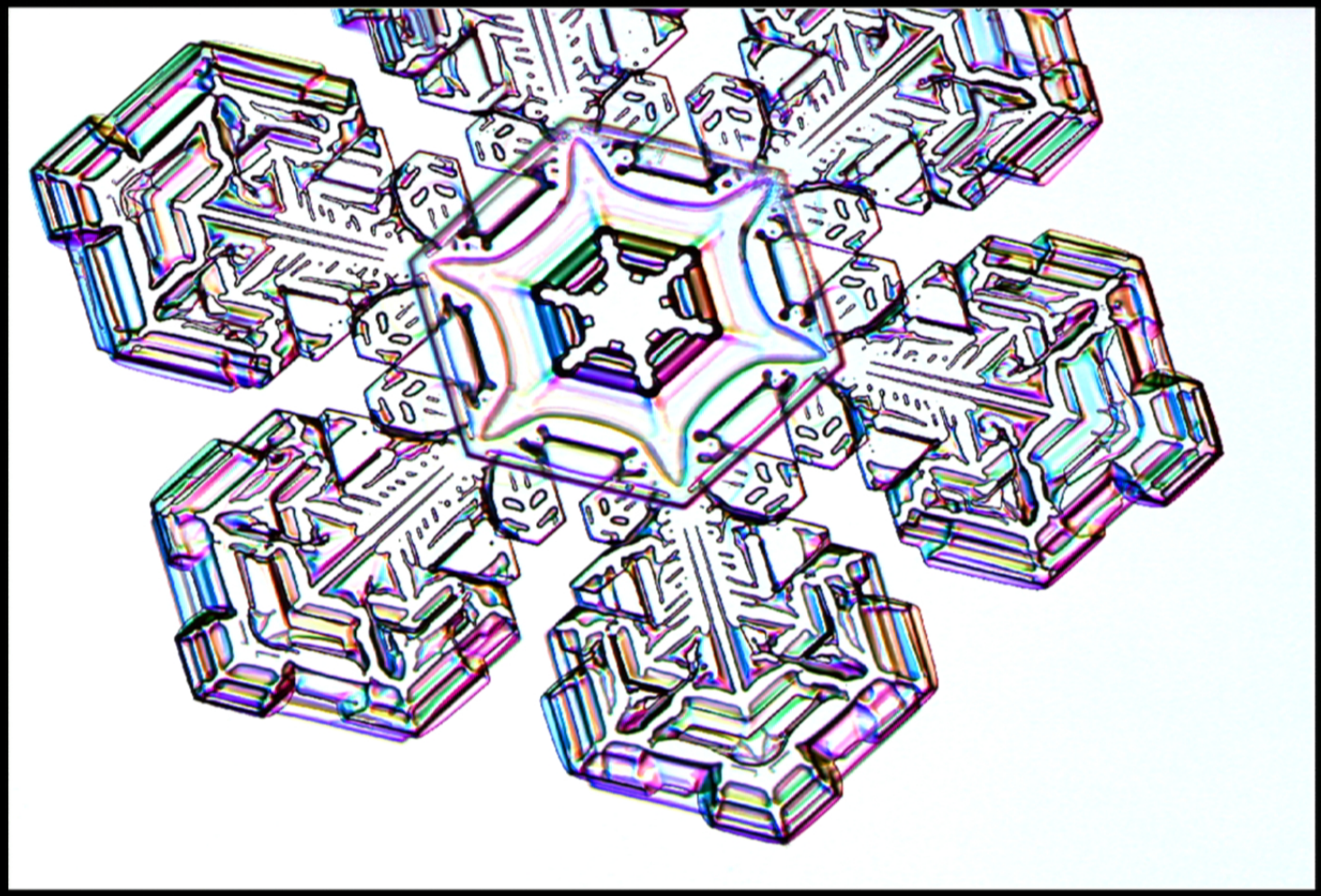


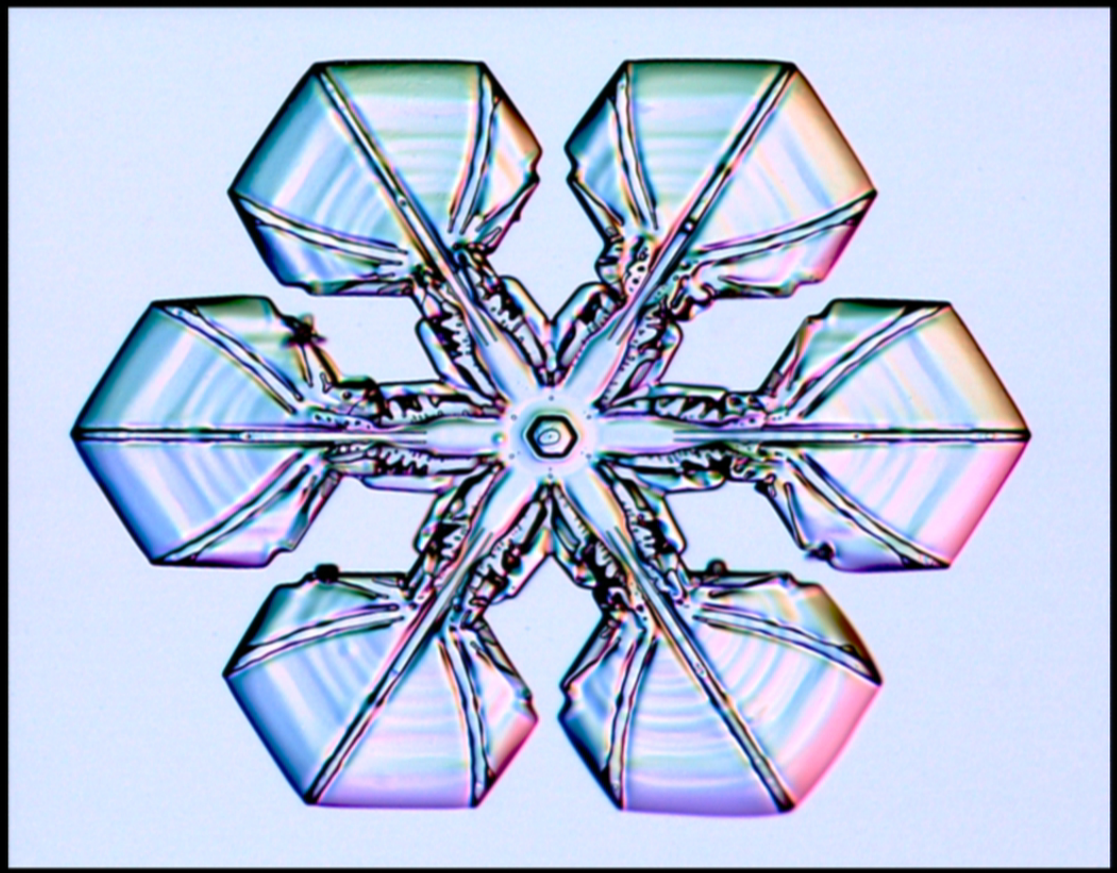
Photographing Snowflakes

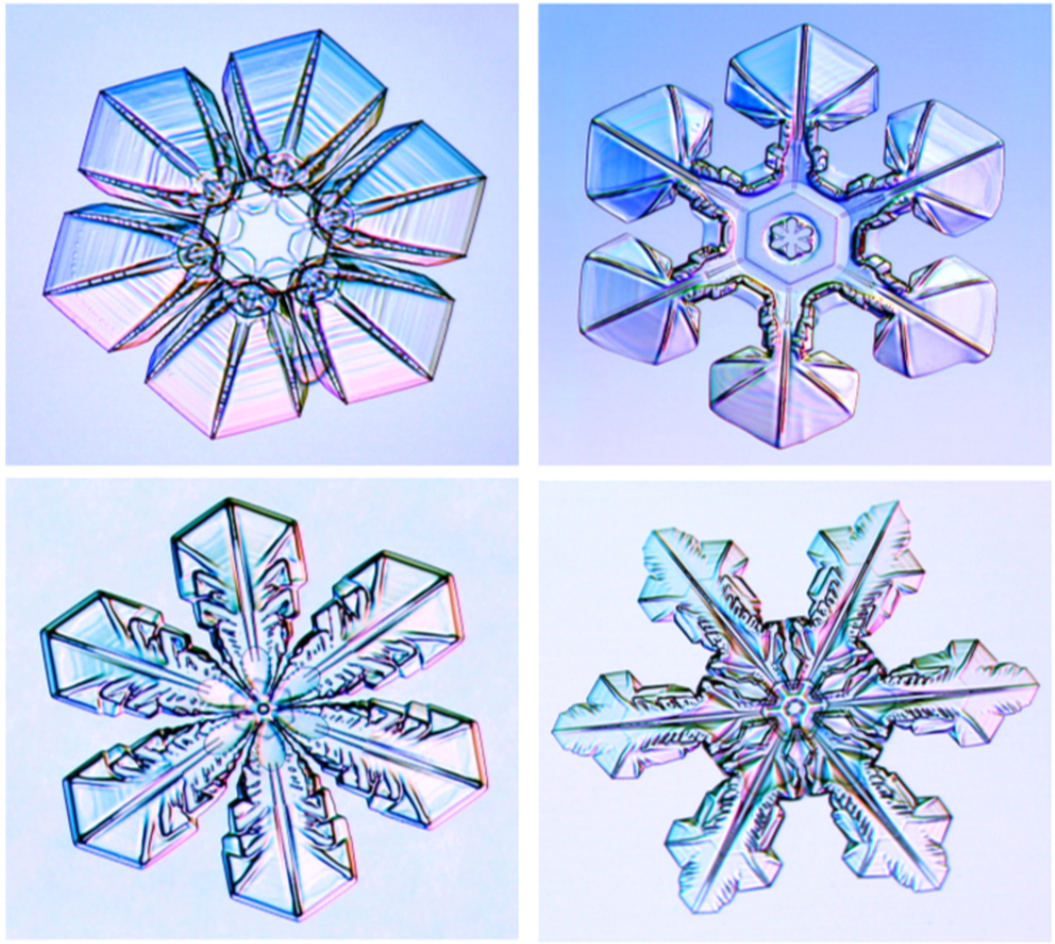
Pictures taken with a traveling snowflake photo-microscope
Best when T ~ -15 C (5 F)

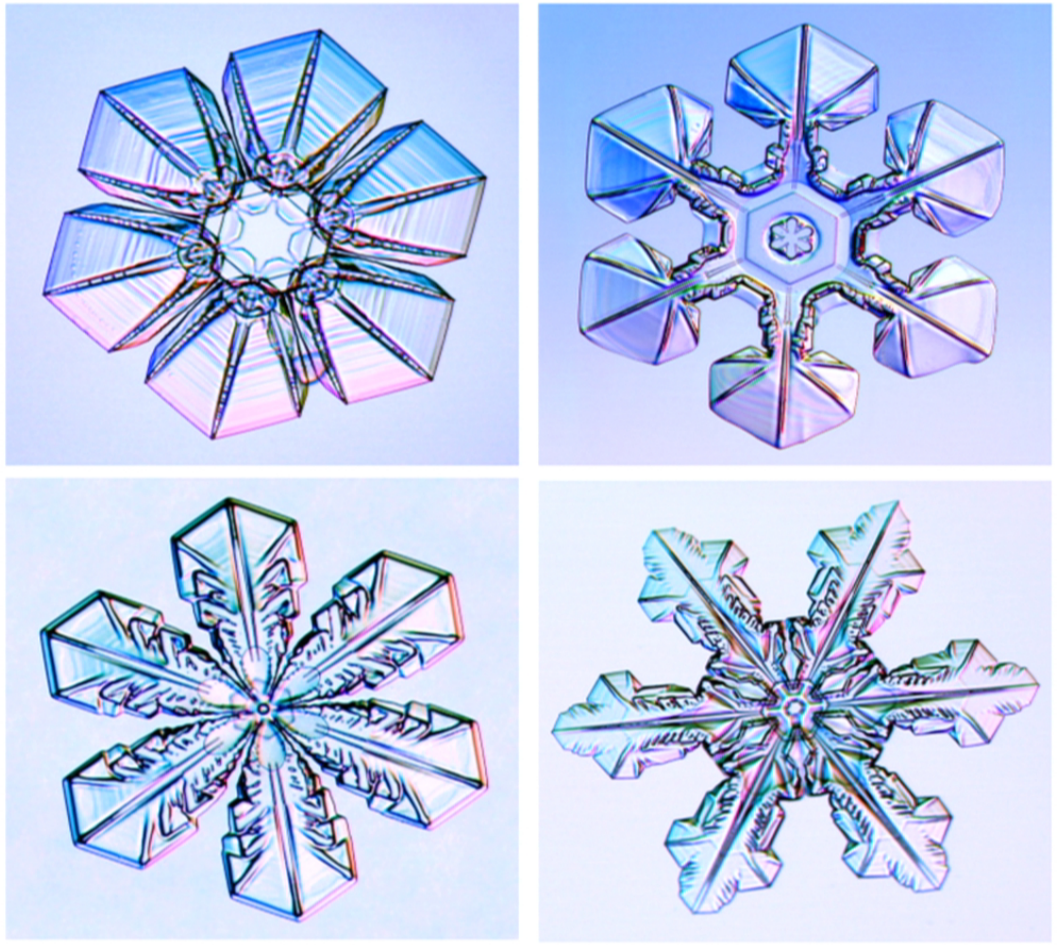
Locations: Northern Ontario, Alaska, Vermont, Michigan, Northern Sweden ...

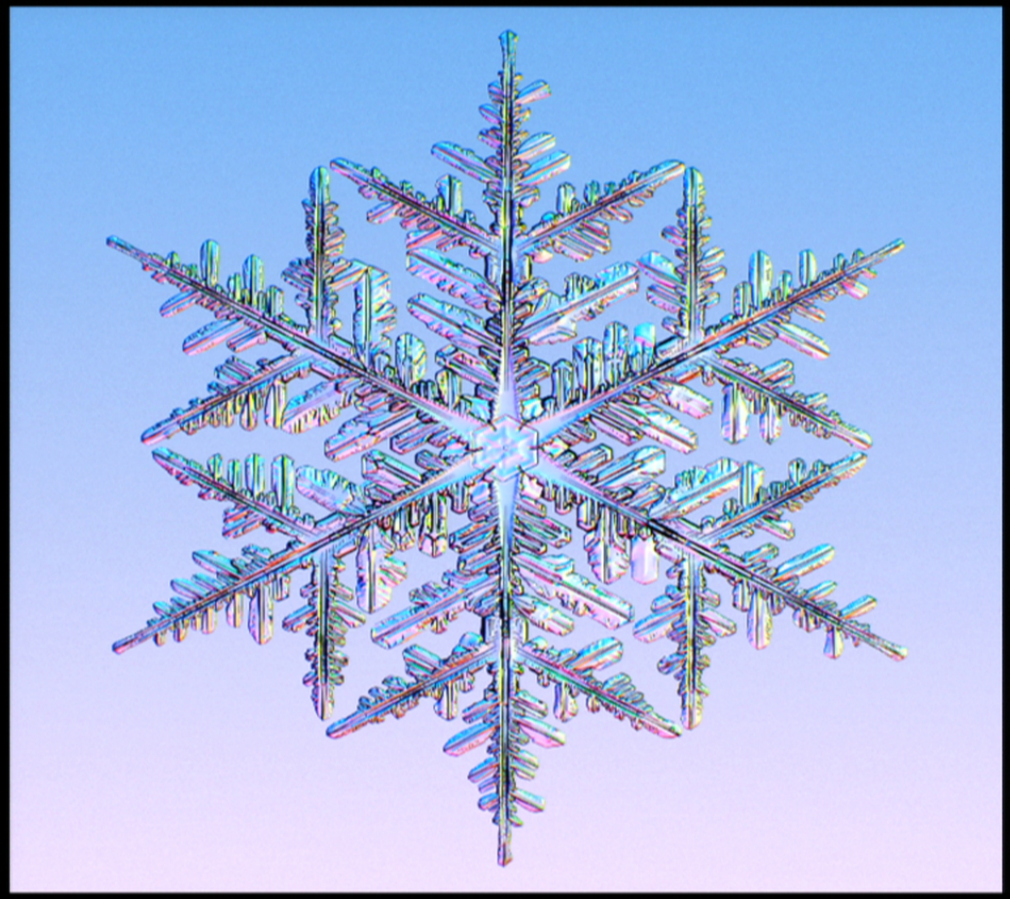
In the Field...

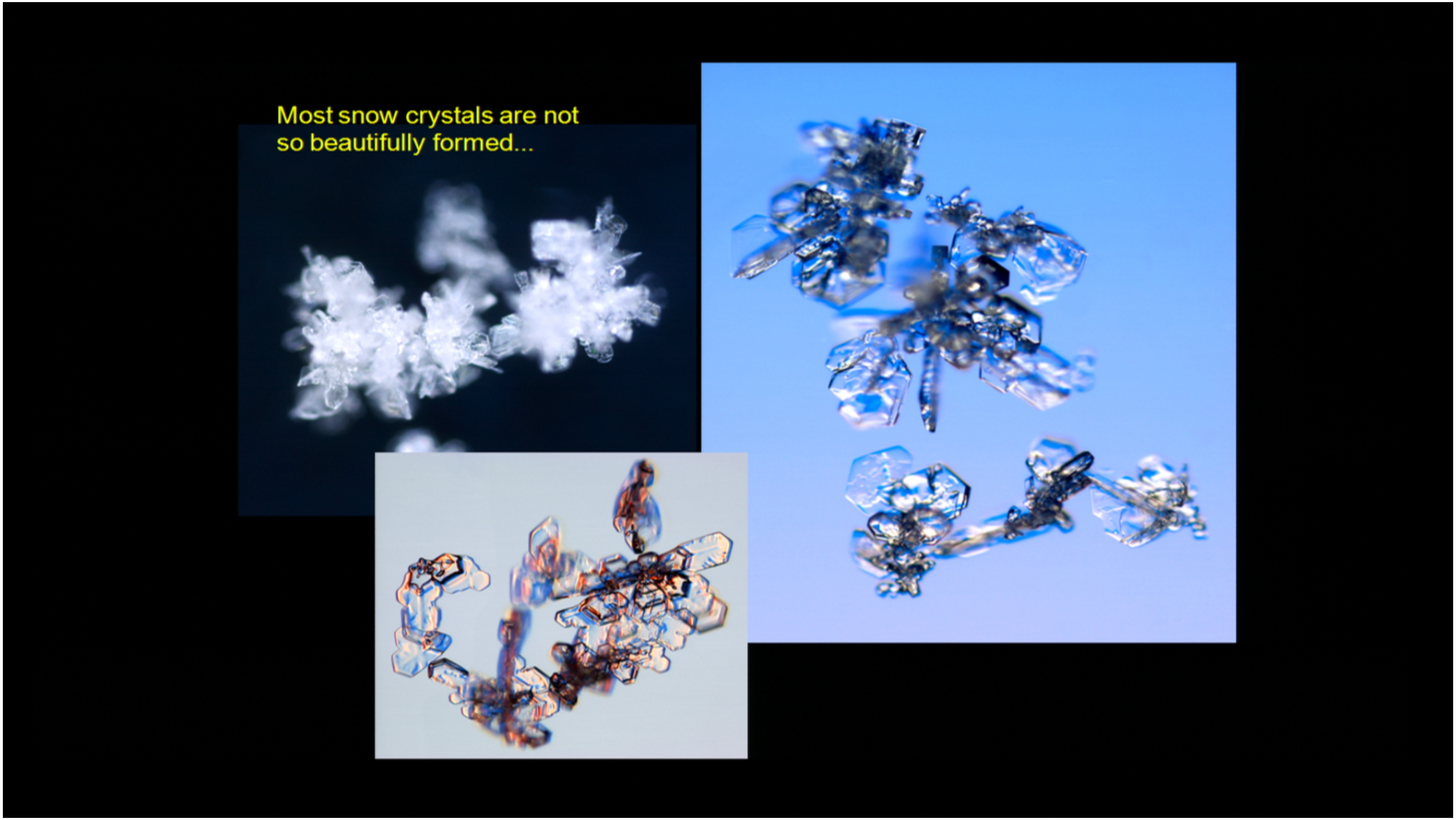


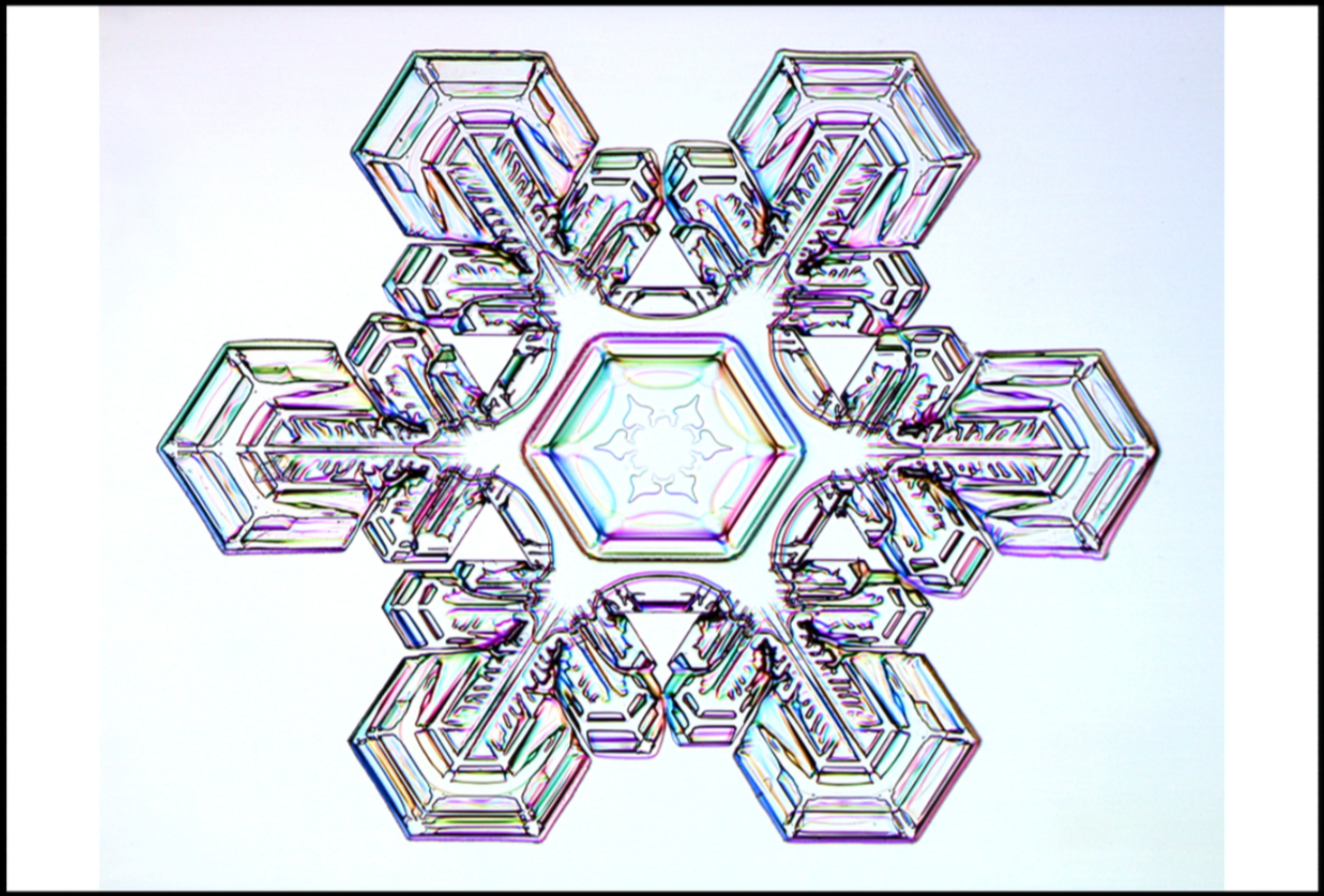


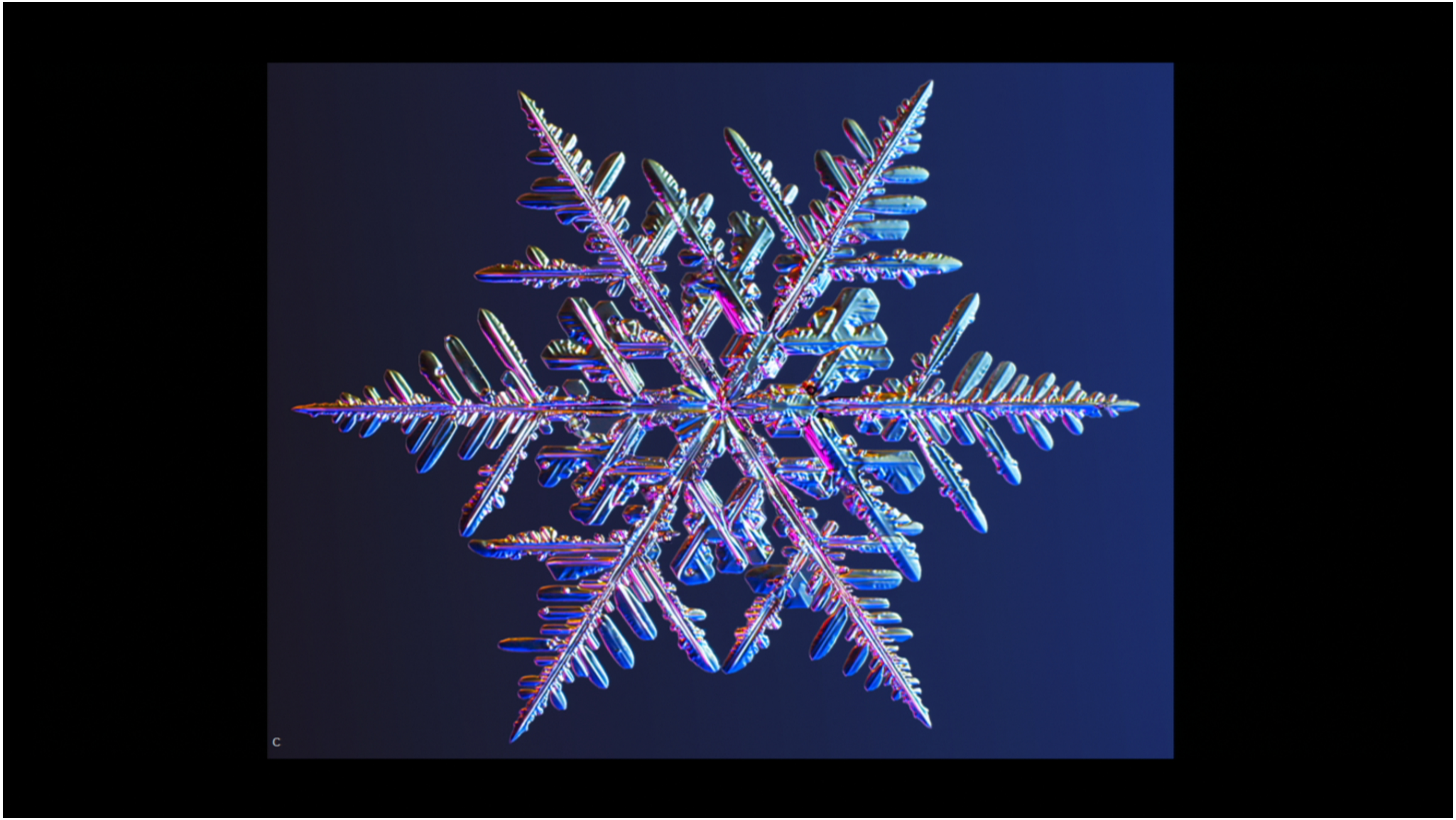




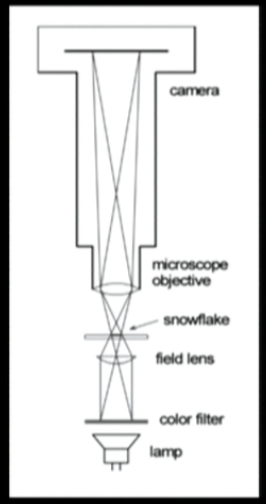


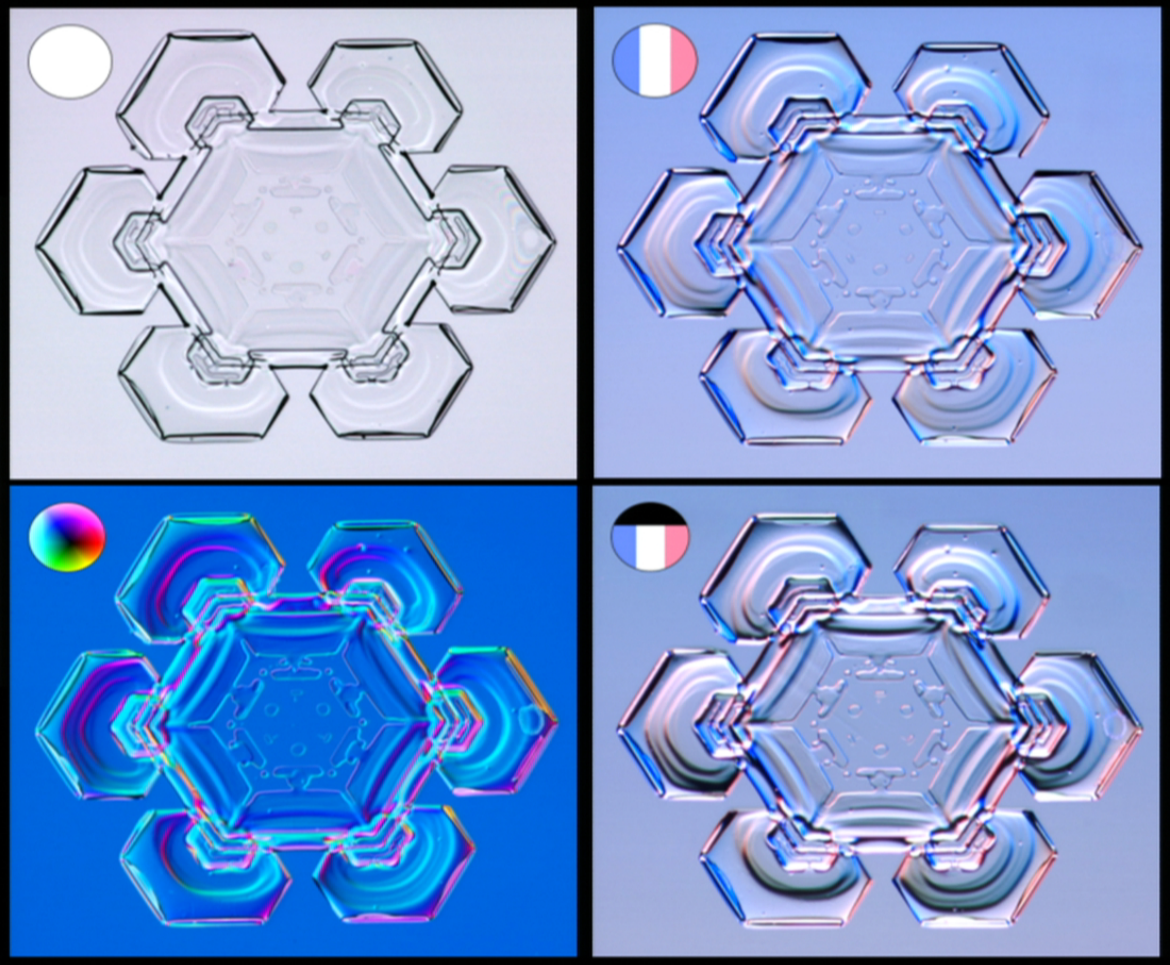

Most snow crystals are not
so beautifully formed...

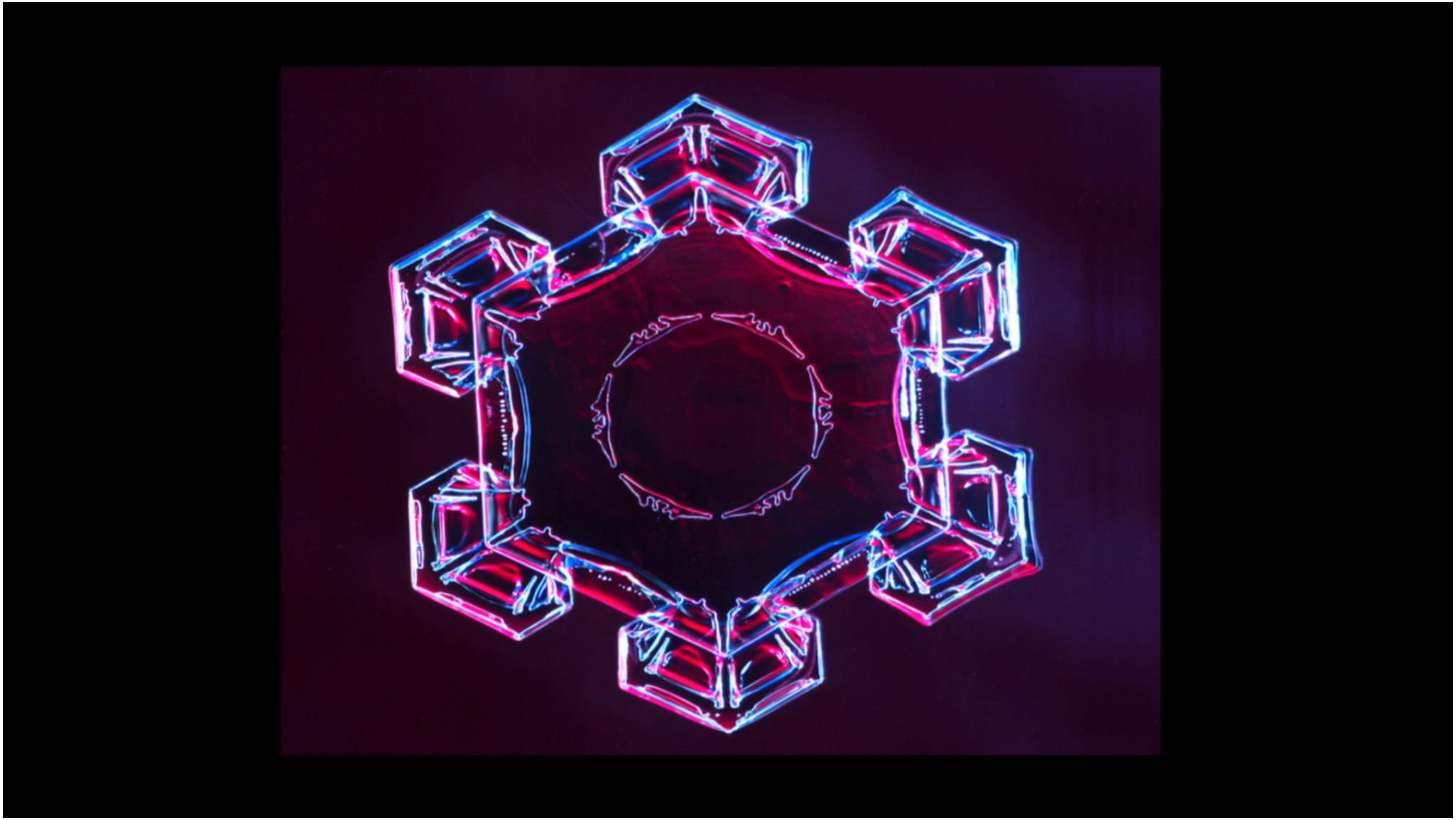


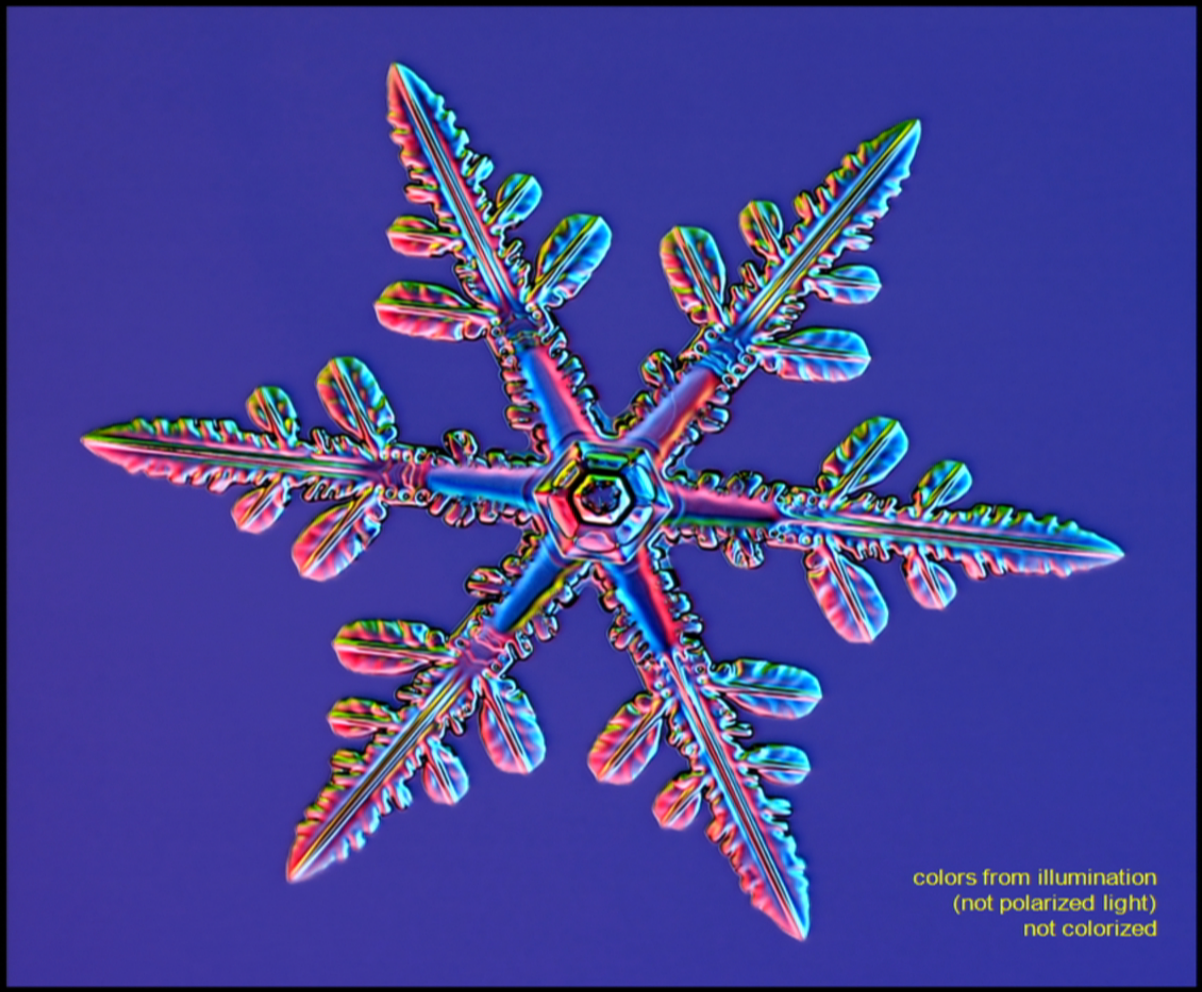


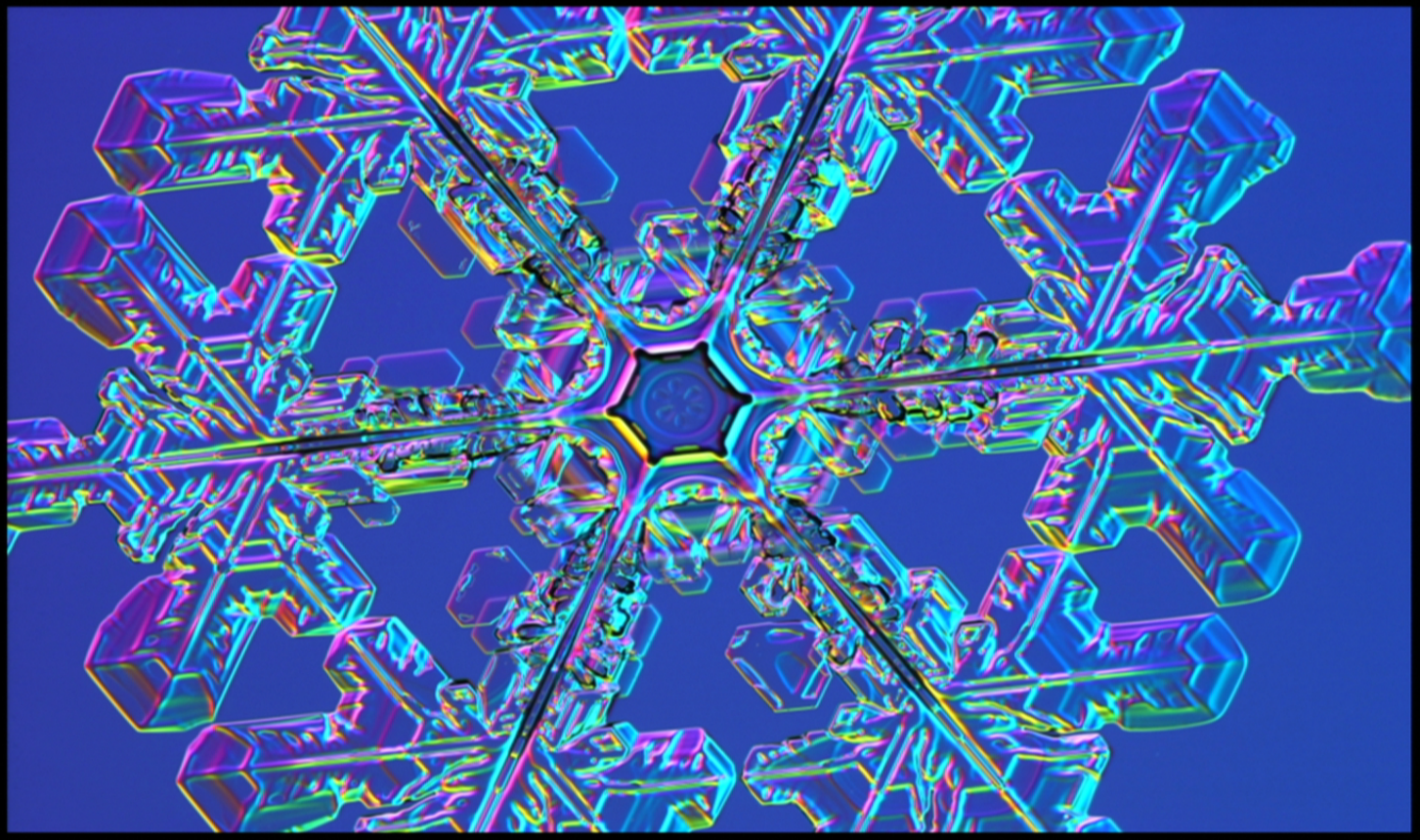
Changing color filters…

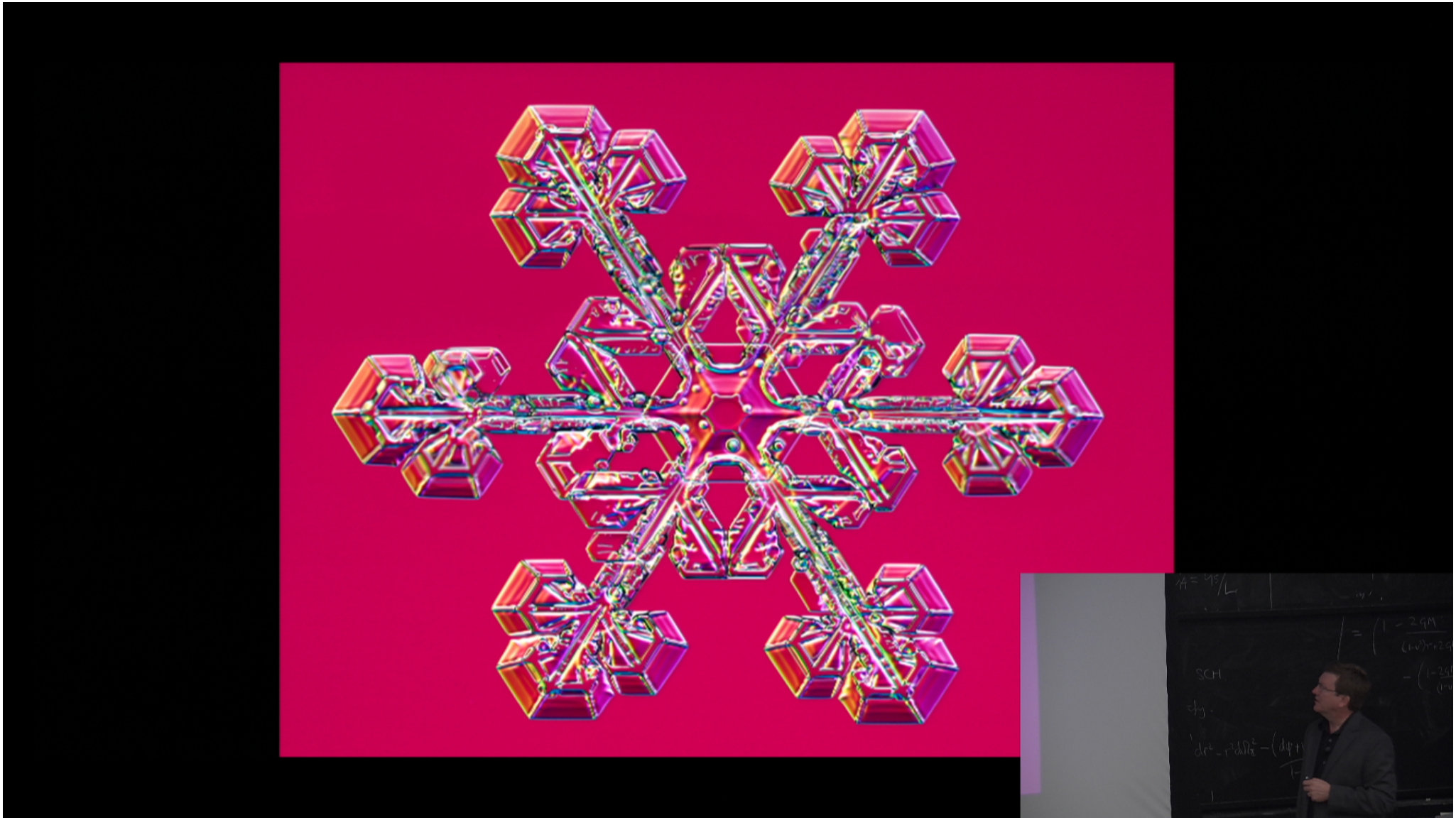


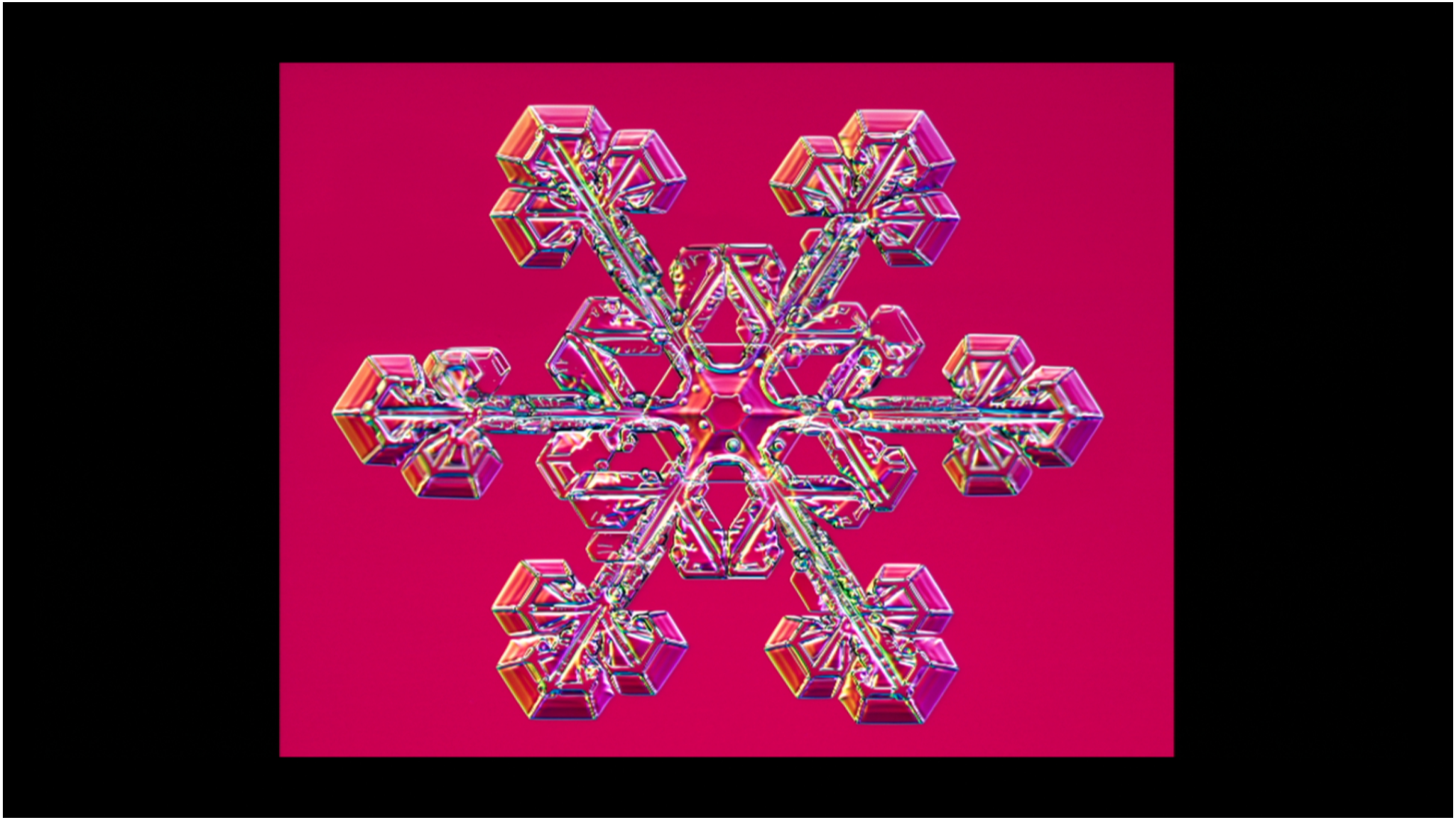





colors from illumination
(not polarized light)
not colorized








The Art of the Snowflake
The Snowflake:
Winter's Secret Beauty
The Secret Life
of a Snowflake
The Little Book
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Ken Libbrecht's
Field Guide to Snowflakes
SNOWFLAKES
The Magic
of Snowflakes


The
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MARTHA
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SNOWFLAKE
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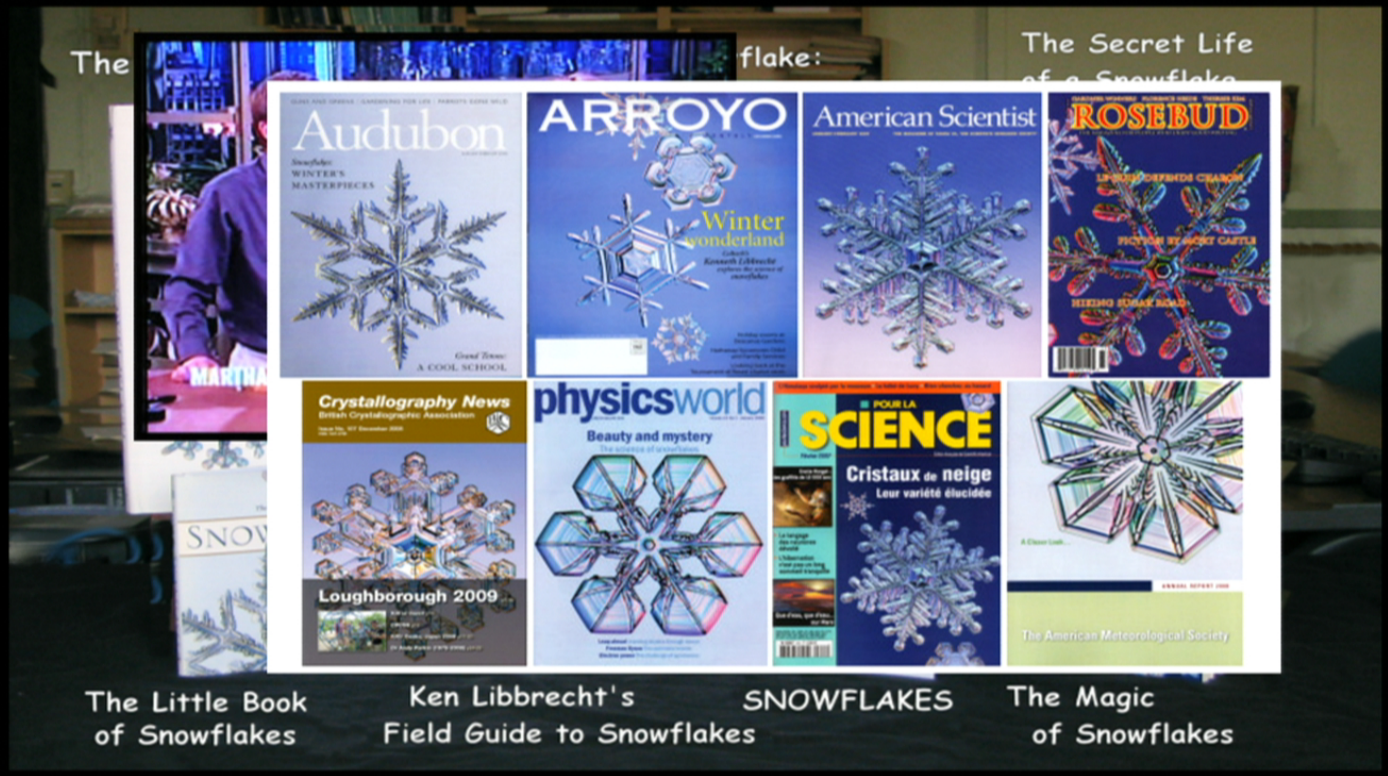
The
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Crystallography News
British Crystallographic Association
Loughborough 2009
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SnowCrystals.com

... Your online guide to snowflakes, snow crystals, and other ice phenomena ...

"How full of the creative genius is the air in which these are generated! I should hardly admire more if real stars fell and lodged on my coat."
--Henry David Thoreau, 1856 [1]

Welcome to ***SnowCrystals.com!*** This site is all about snow crystals and snowflakes -- what they are, where they come from, and just how these remarkably complex and beautiful structures are created, quite literally, out of thin air.

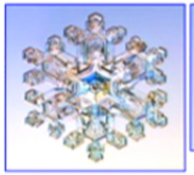
Snowflake News

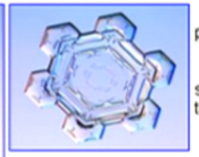
NEW BOOK! SNOWFLAKES
Snowflakes is a chunky book book of terrific snowflake photographs and literary quotations. Fun to flip through! See more at Snowflake Books.

Or purchase snowflake cards, prints, and posters at the Snowflake Store.

FREE! Snowflake Wallpaper. Put an awesome snowflake on your desktop -- guaranteed to make your computer run cooler! Click on the size appropriate for your computer screen: 640x480, 800x600, 1024x768, 1152x864, 1280x1024, 1400x1050, 1600x1200, 1680x1050.

Natural Snowflakes



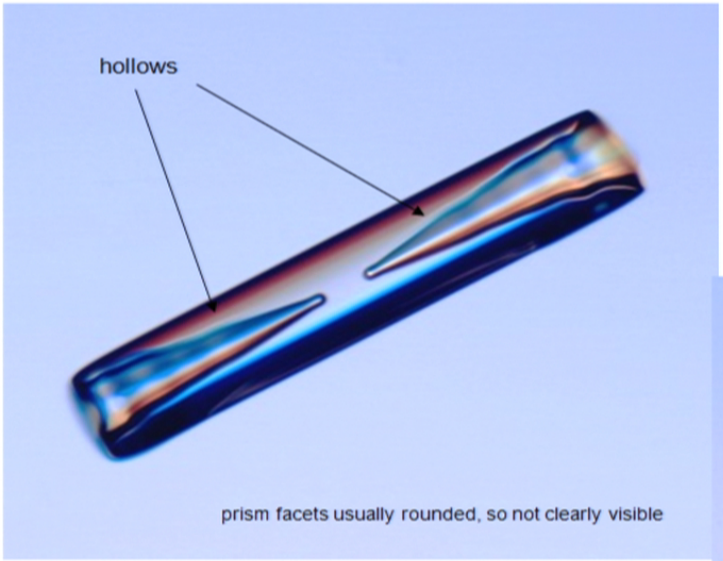


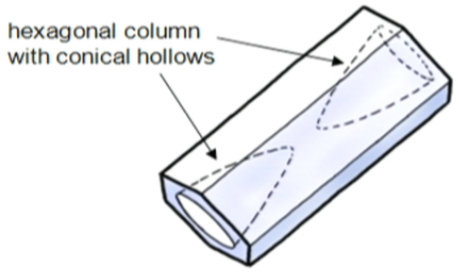
Pictures, pictures, pictures. Visit the three Photo Galleries to see some spectacular photographs of snow crystals.

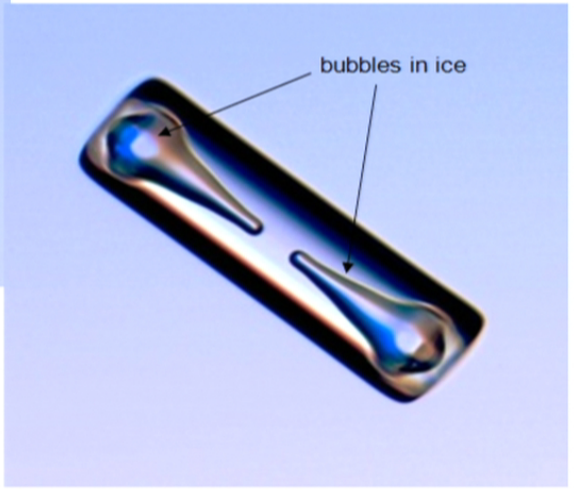
Don't know a stellar dendrite from a capped column? The Guide to Snowflakes shows different kinds of snow crystals that fall from the sky. Browse the other links at the far left to find out more about natural snowflakes.

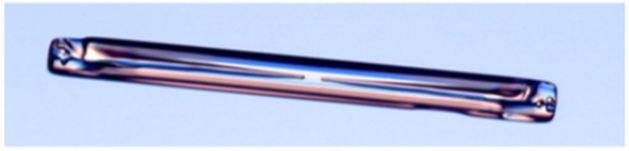
What Else Falls from the Sky...

Hollow Columns



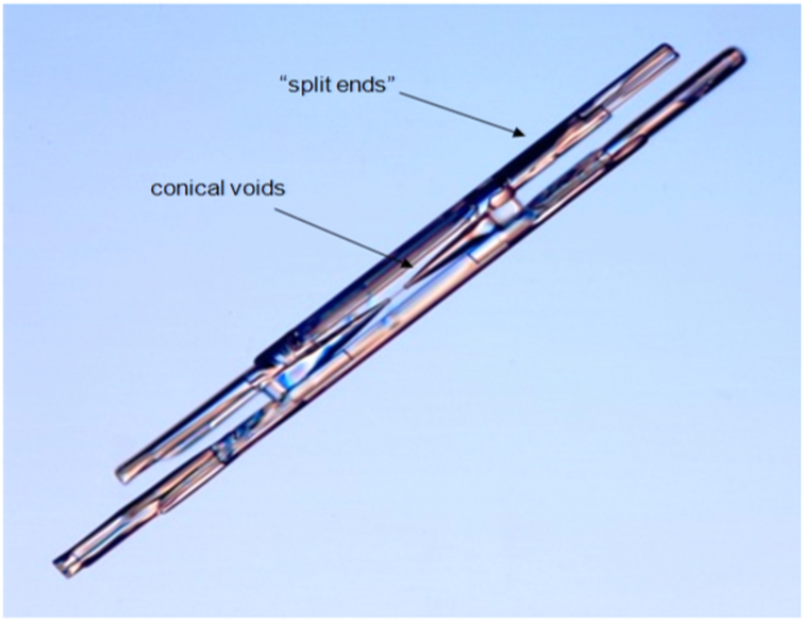


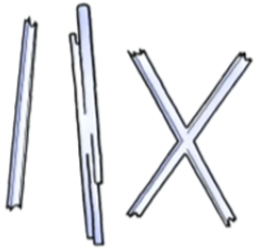




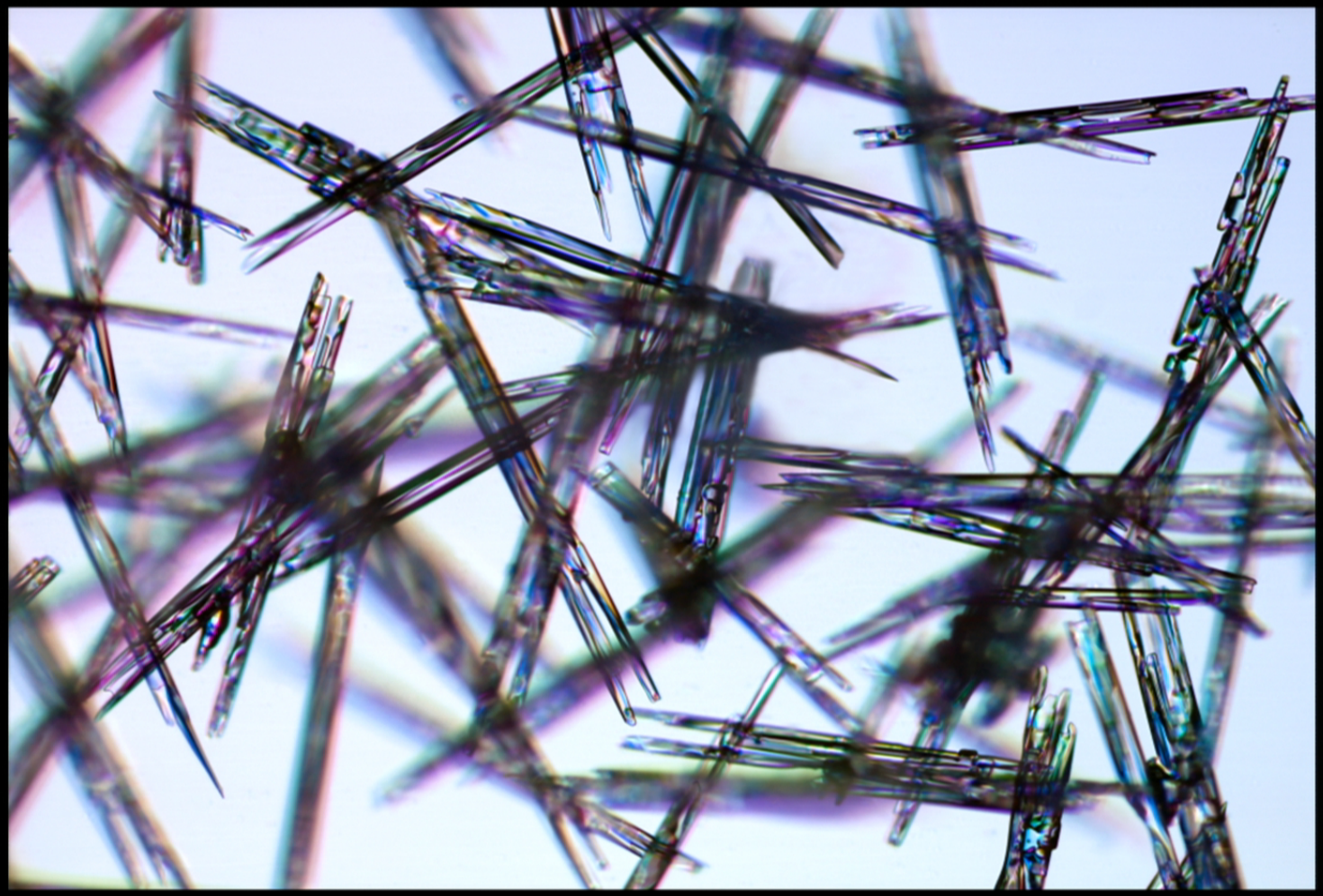
What Falls from the Sky...

Needles



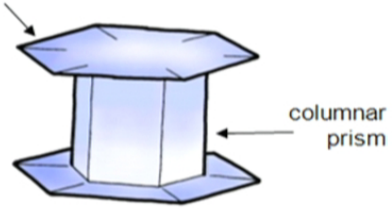


longest of the columnar crystals, up to 2-3 mm long
often find in clusters

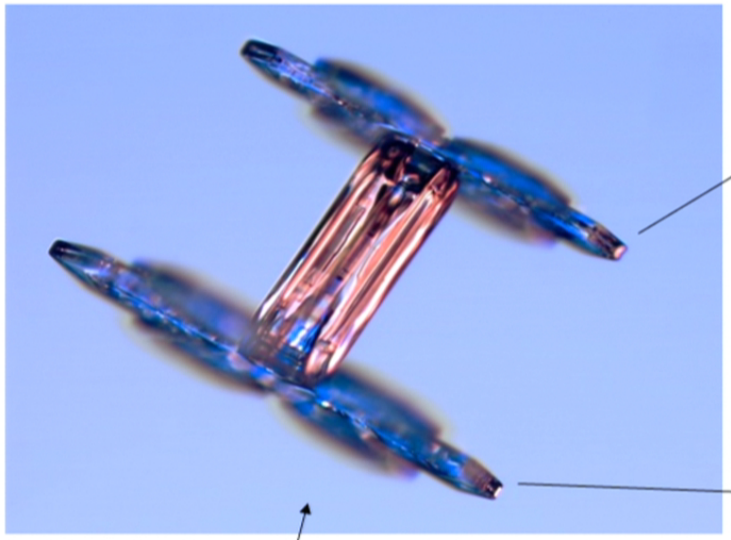


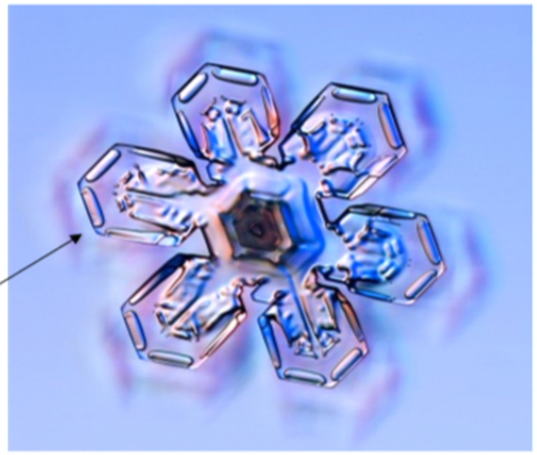
What Falls from the Sky...

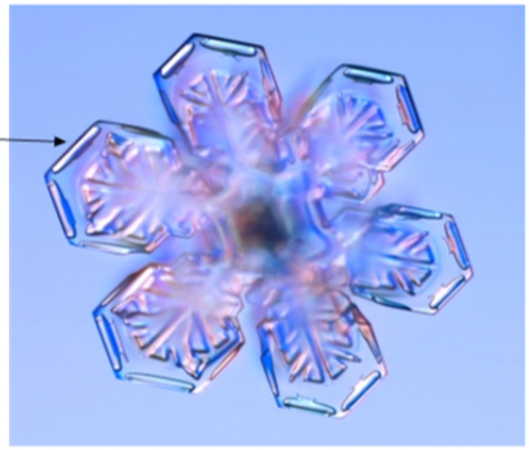
Capped Columns



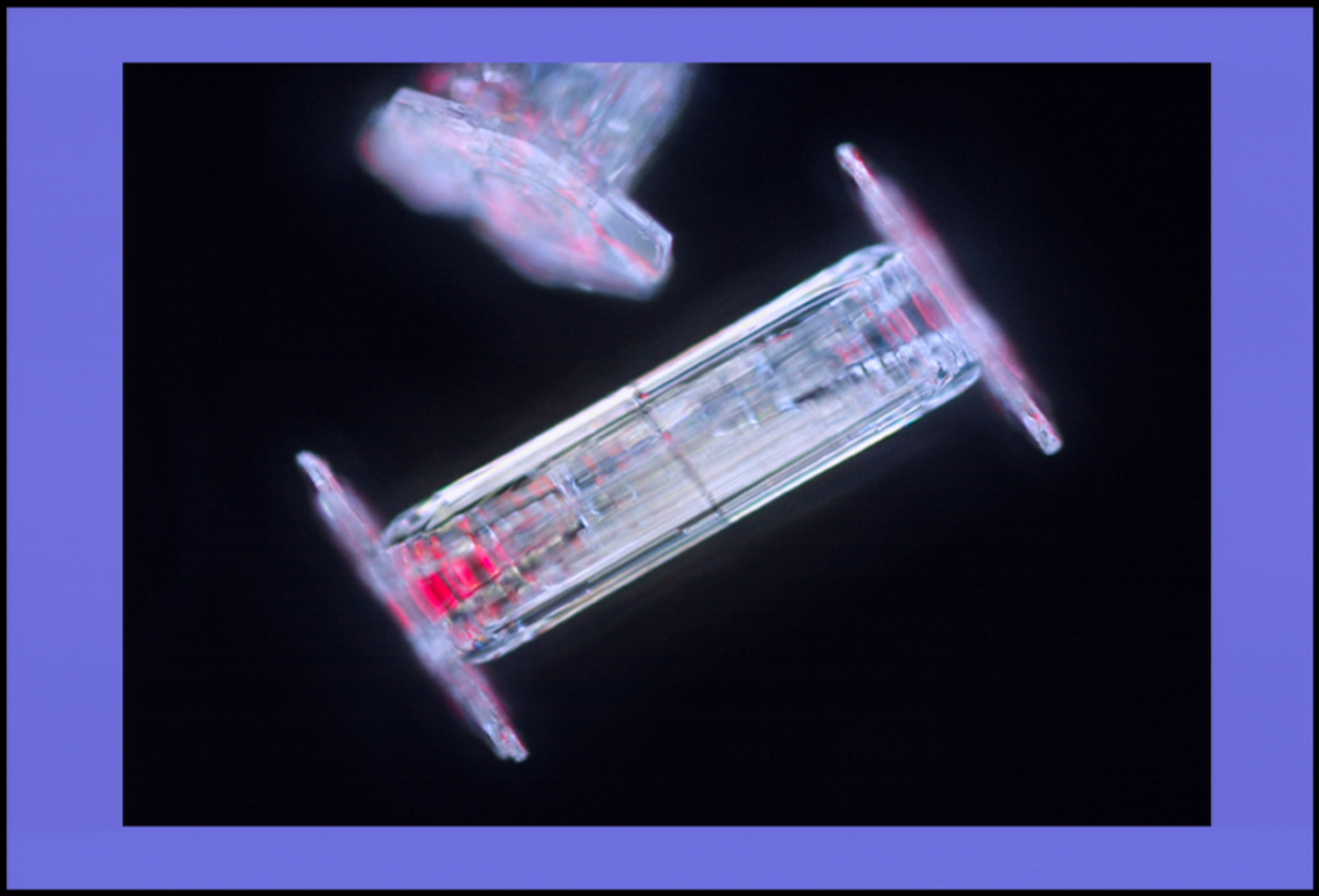
Another Capped Column



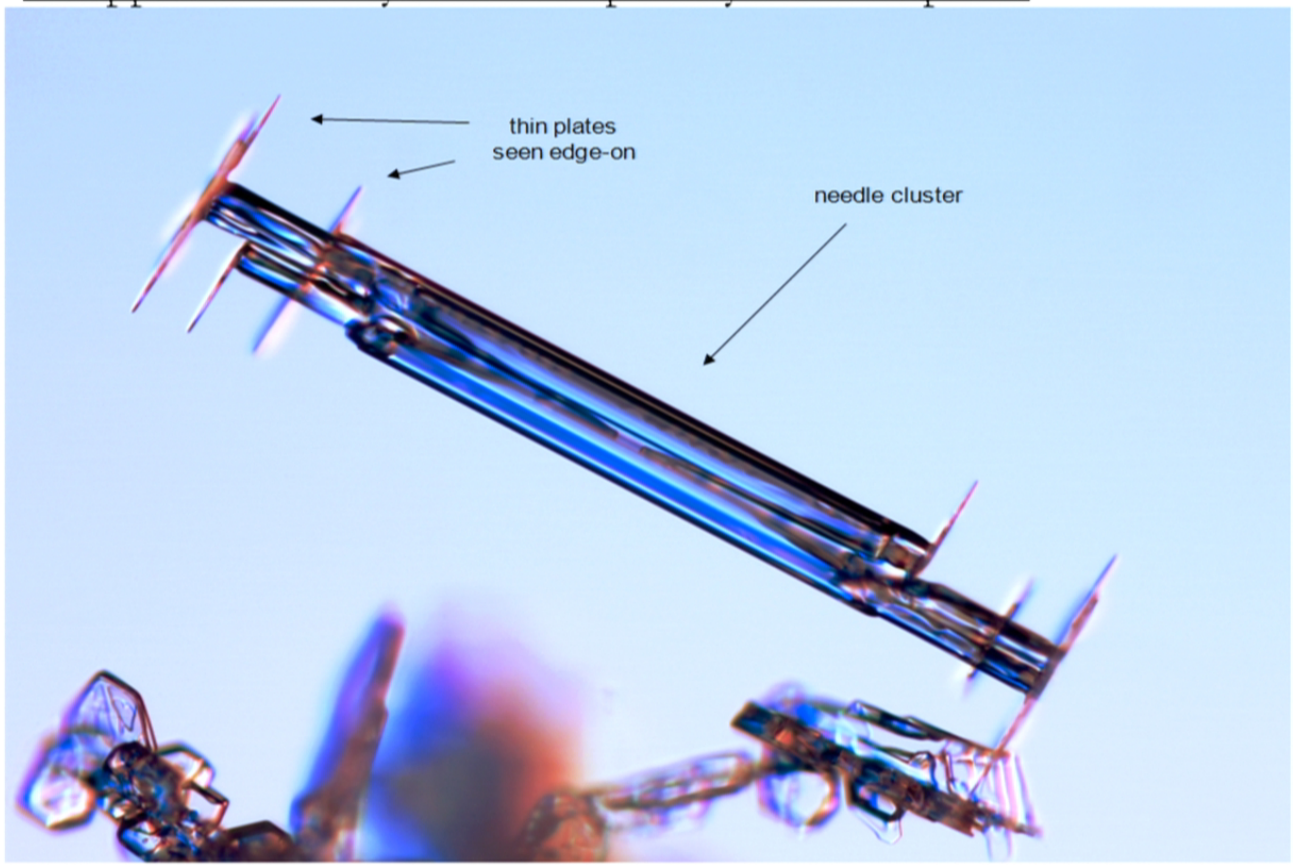


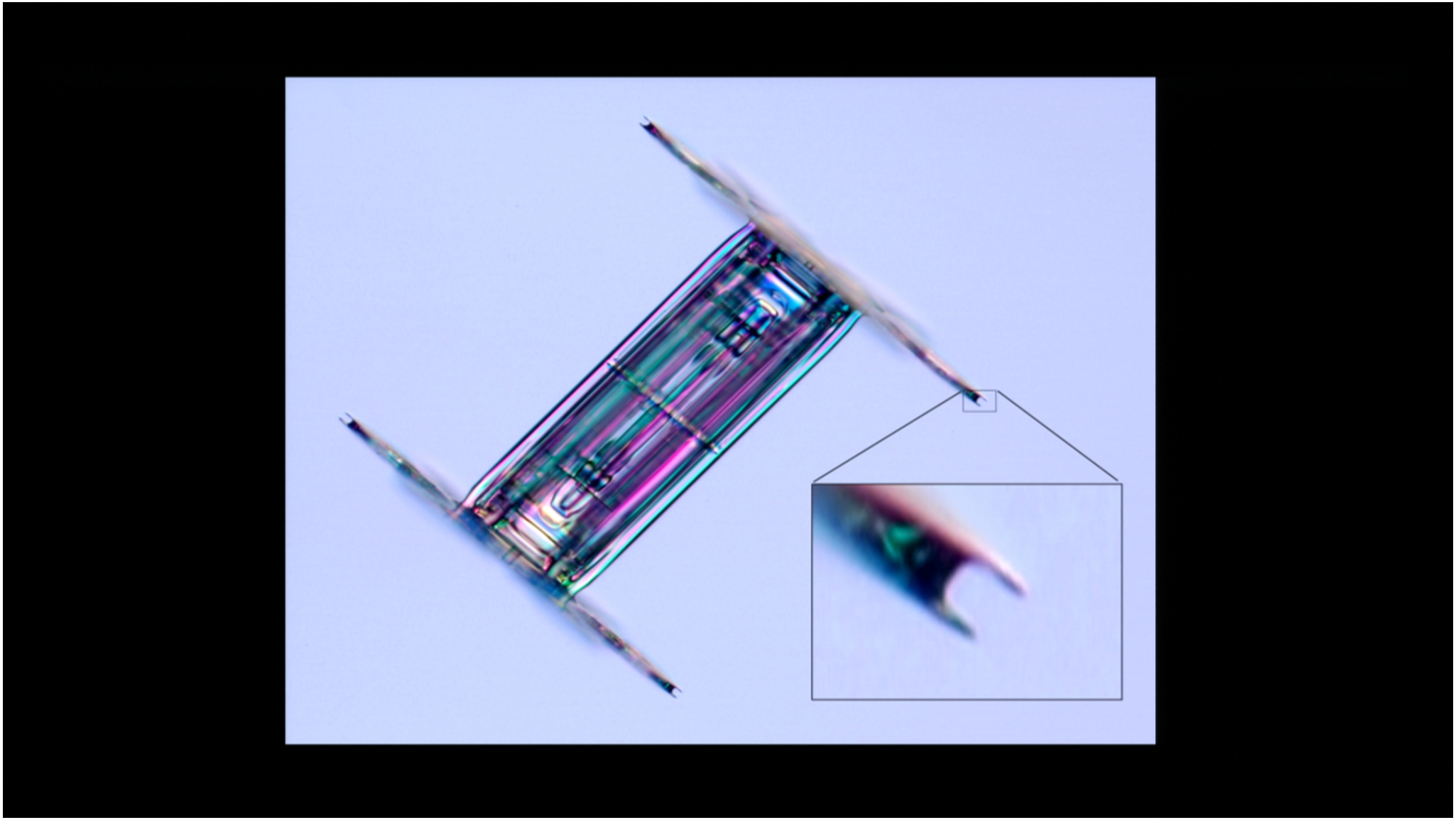


First took picture above
Then flipped crystal on end, focused on top plate
... and then focused on bottom plate



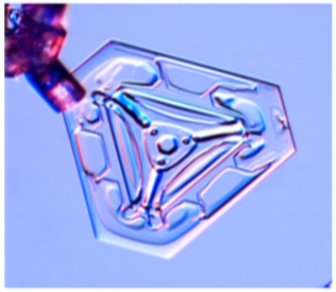
A capped needle crystal with especially thin end plates

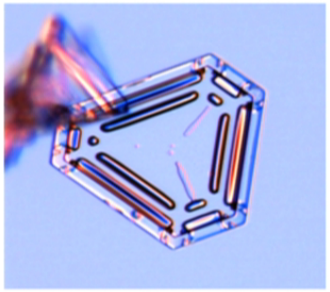


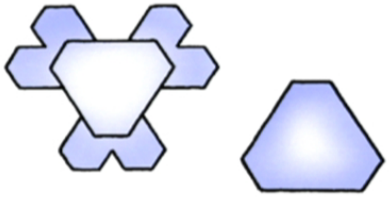


What Falls from the Sky...

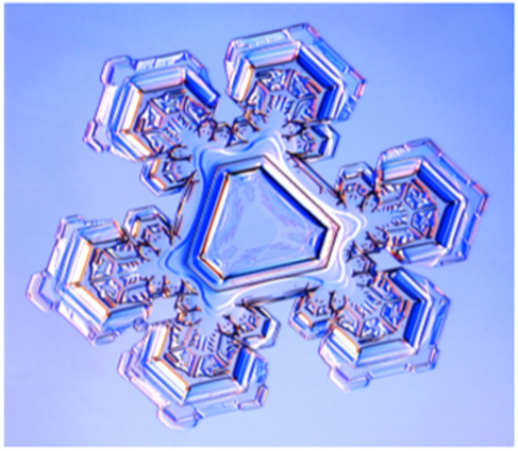
Triangular Crystals

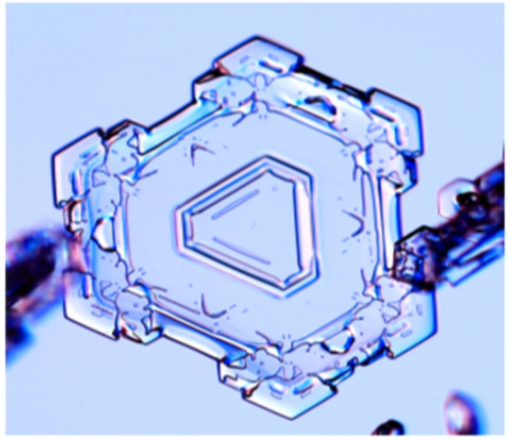


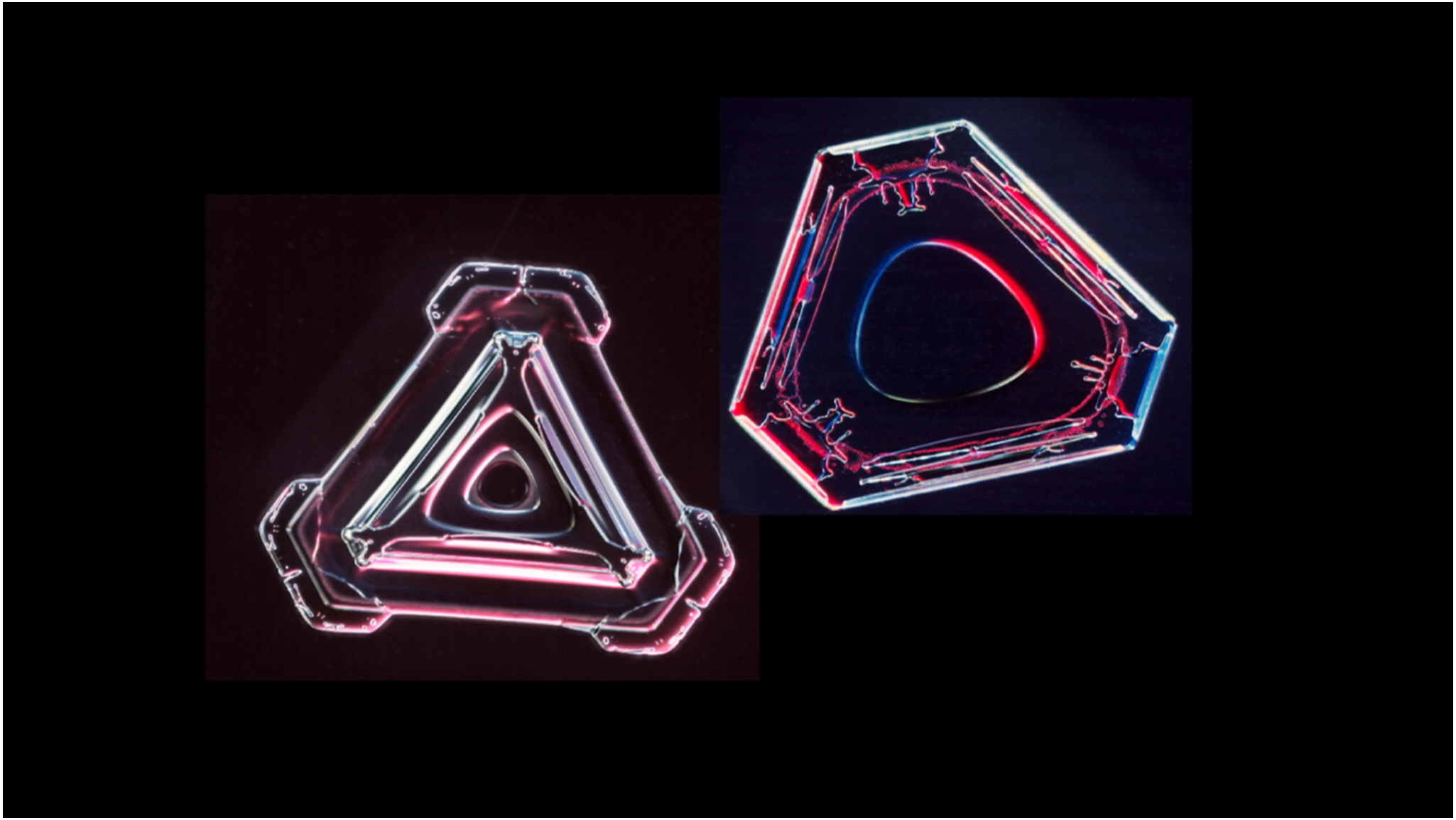


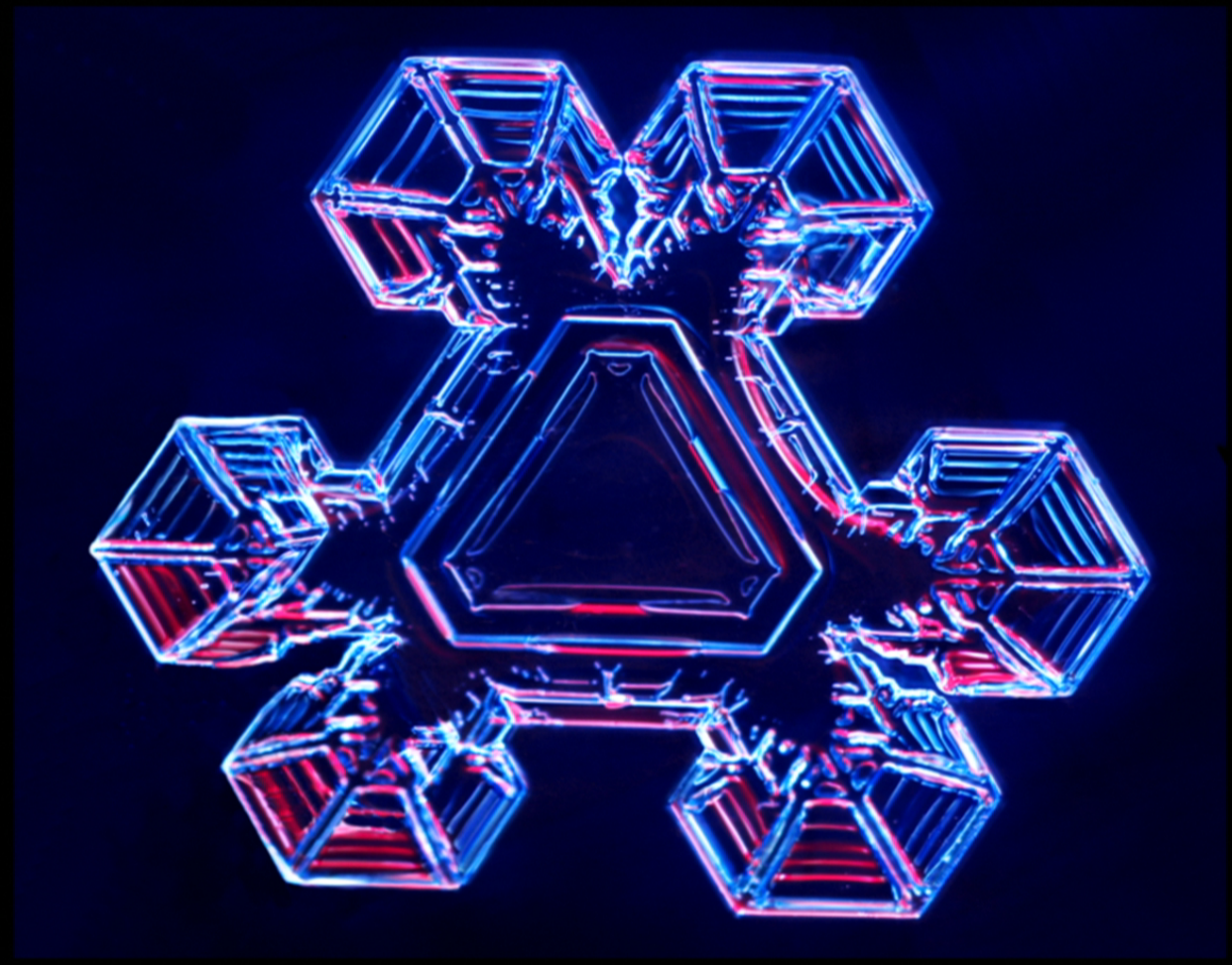


Uncommon, but there if you look…



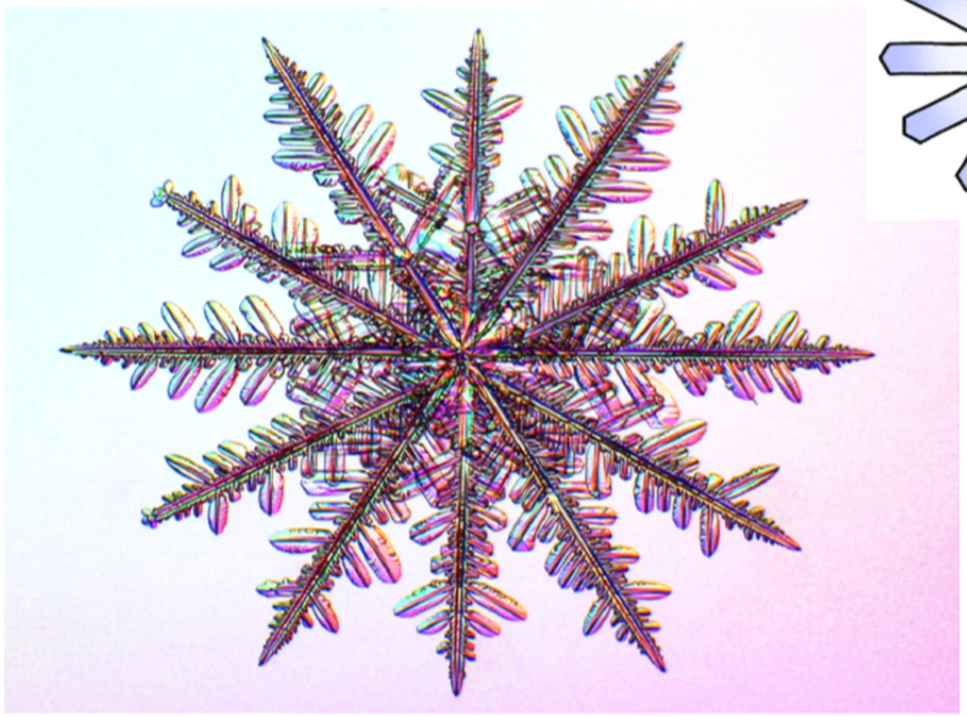


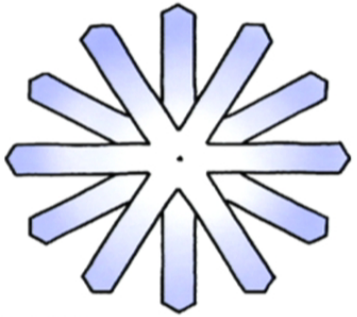


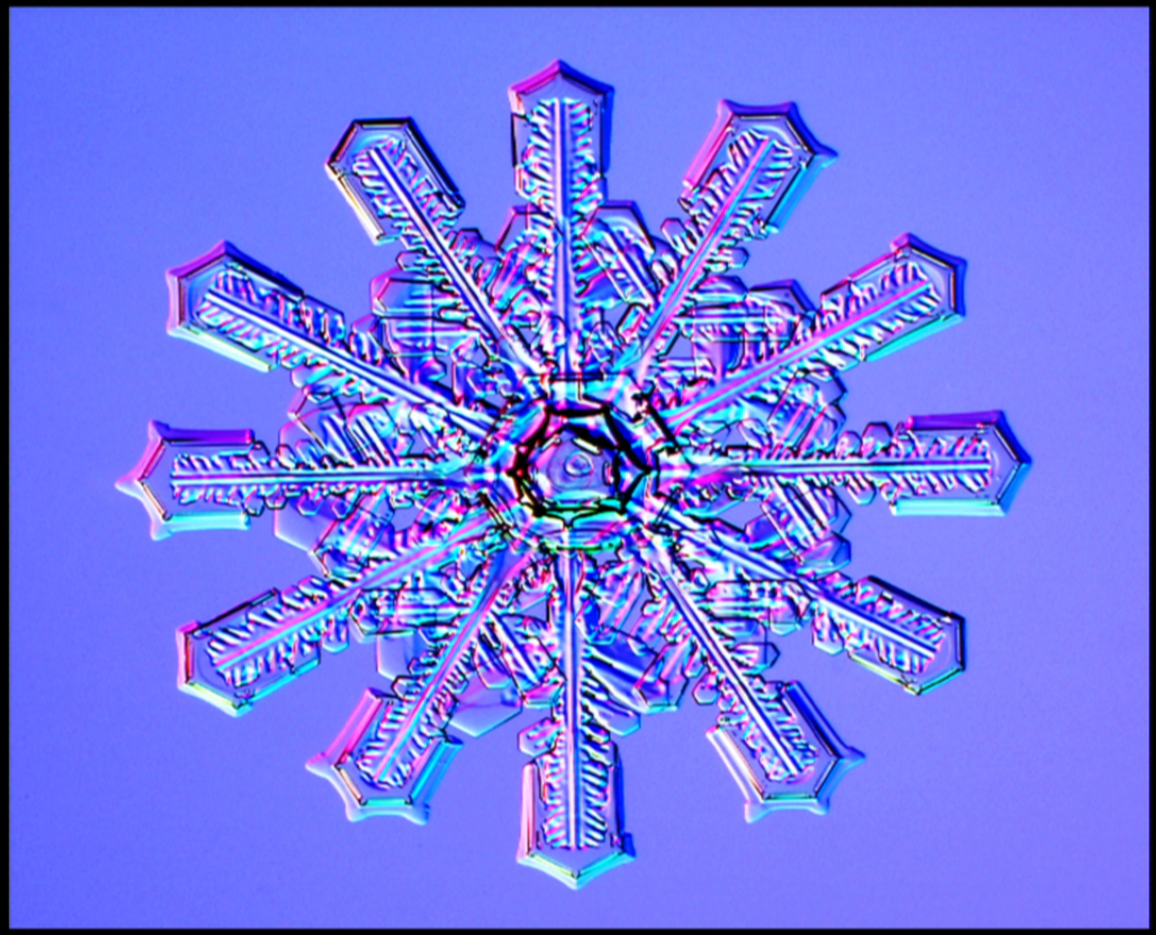


What Falls from the Sky...

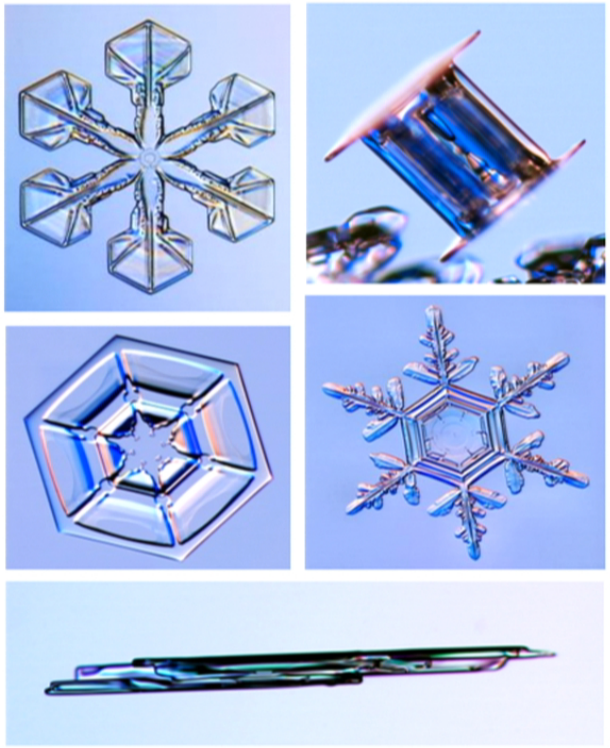
Twelve-branched crystals







The Menagerie of Snow Crystal Types



Why such diversity of shapes?
How do structures arise during crystal growth?
What is the underlying physics?

from *Ken Libbrecht's Field Guide to Snowflakes*

The Essential Physics of Snow Crystal Growth

Crystalline Structure of Ice
- → six-fold symmetry
- → faceting
- dislocations negligible (usually)

Particle Transport (water molecules in air)
- → diffusion-limited growth
- → branching

Statistical Mechanics
- → rate water molecules hit surface
- → equilibrium vapor pressure

Attachment Kinetics
(surface molecular dynamics of condensation)
- → growth rates
- → dynamics of faceting and branching

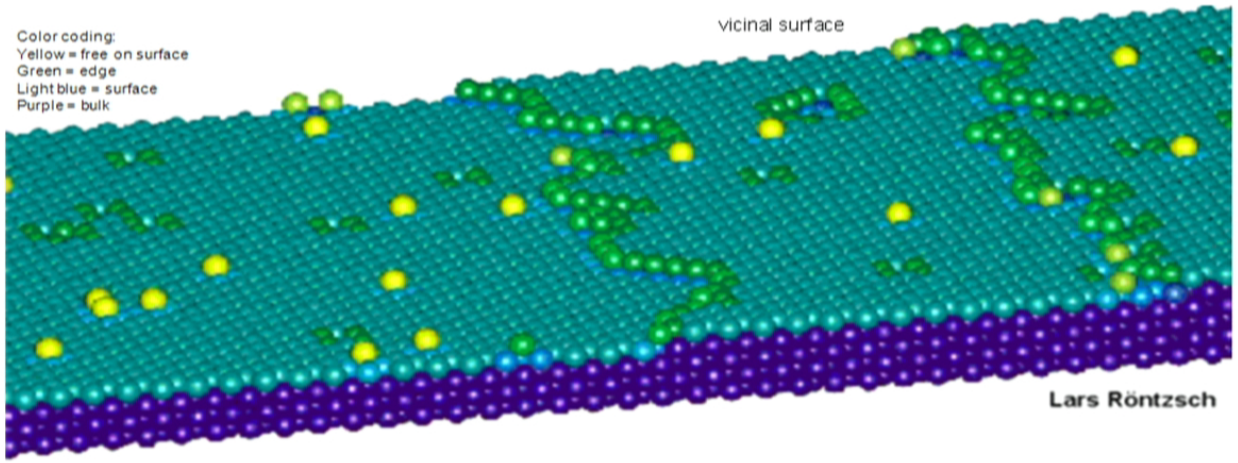
Surface Tension Effects
- negligible compared to attachment kinetics

Heat Transport (from latent heat generation)
- heat transport faster than particle transport
- usually negligible (not always)

Aerodynamics
- airflow changes diffusion field
- usually negligible (not always)

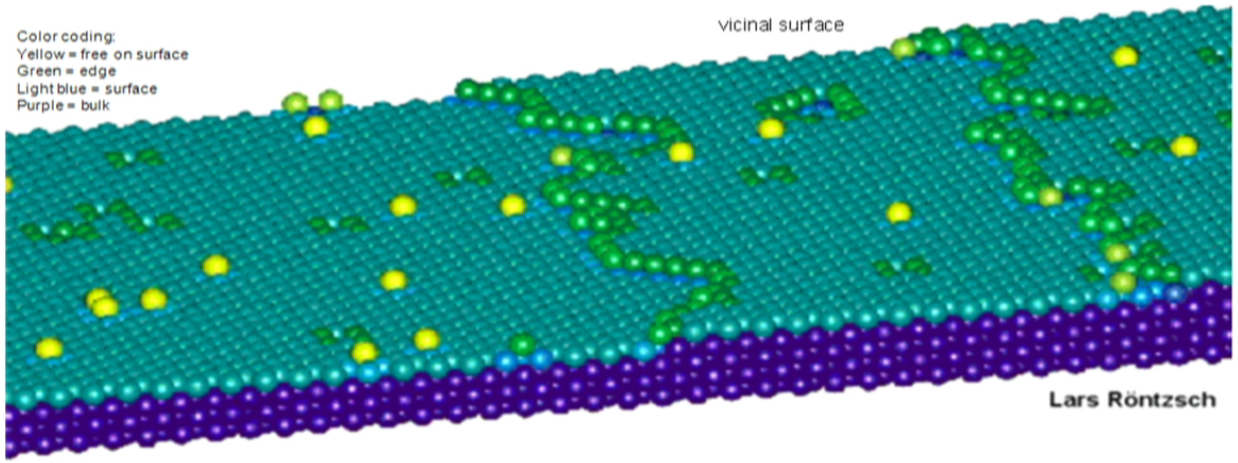
Surface Chemistry (if chemical impurities)
- chemical catalysts affect crystal growth
- ignore for clean environment

Attachment Kinetics: The Molecular Dynamics of Crystal Growth



Things to consider:
> Rate molecules hit surface (statistical mechanics)
> Initial sticking probability
> Residence time
> Diffusion of molecules on surface
> Attachment to terrace edge
> Nucleation of 2D islands
> Evaporation
> Surface structure

Attachment Kinetics: The Molecular Dynamics of Crystal Growth



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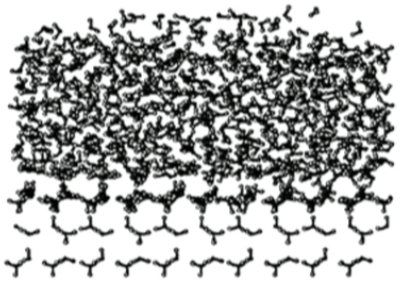
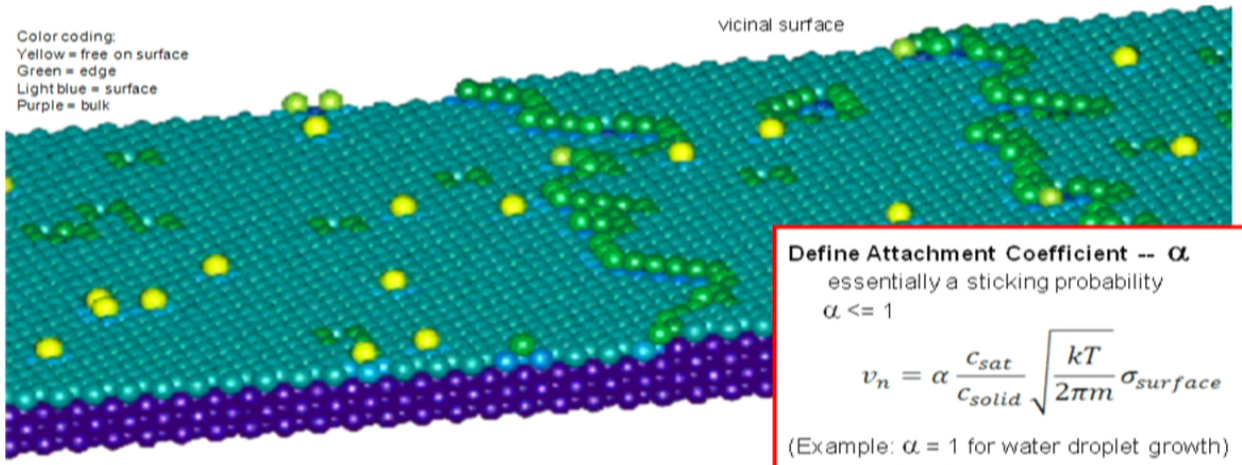


Attachment Kinetics: The Molecular Dynamics of Crystal Growth



Define Attachment Coefficient -- α

essentially a sticking probability

$\alpha <= 1$

$$v_n = \alpha \frac{c_{sat}}{c_{solid}} \sqrt{\frac{kT}{2\pi m}} \sigma_{surface}$$

(Example: α = 1 for water droplet growth)

For a solid surface, α depends on temperature, supersaturation, surface structure, nucleation dynamics, surface diffusion, ...

Things to consider:

> Rate molecules hit surface (statistical mechanics)
> Initial sticking probability
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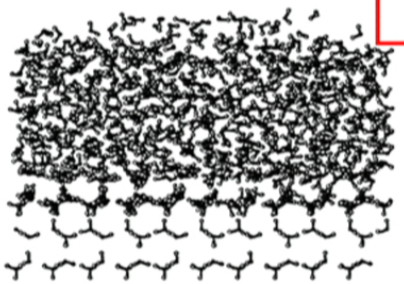
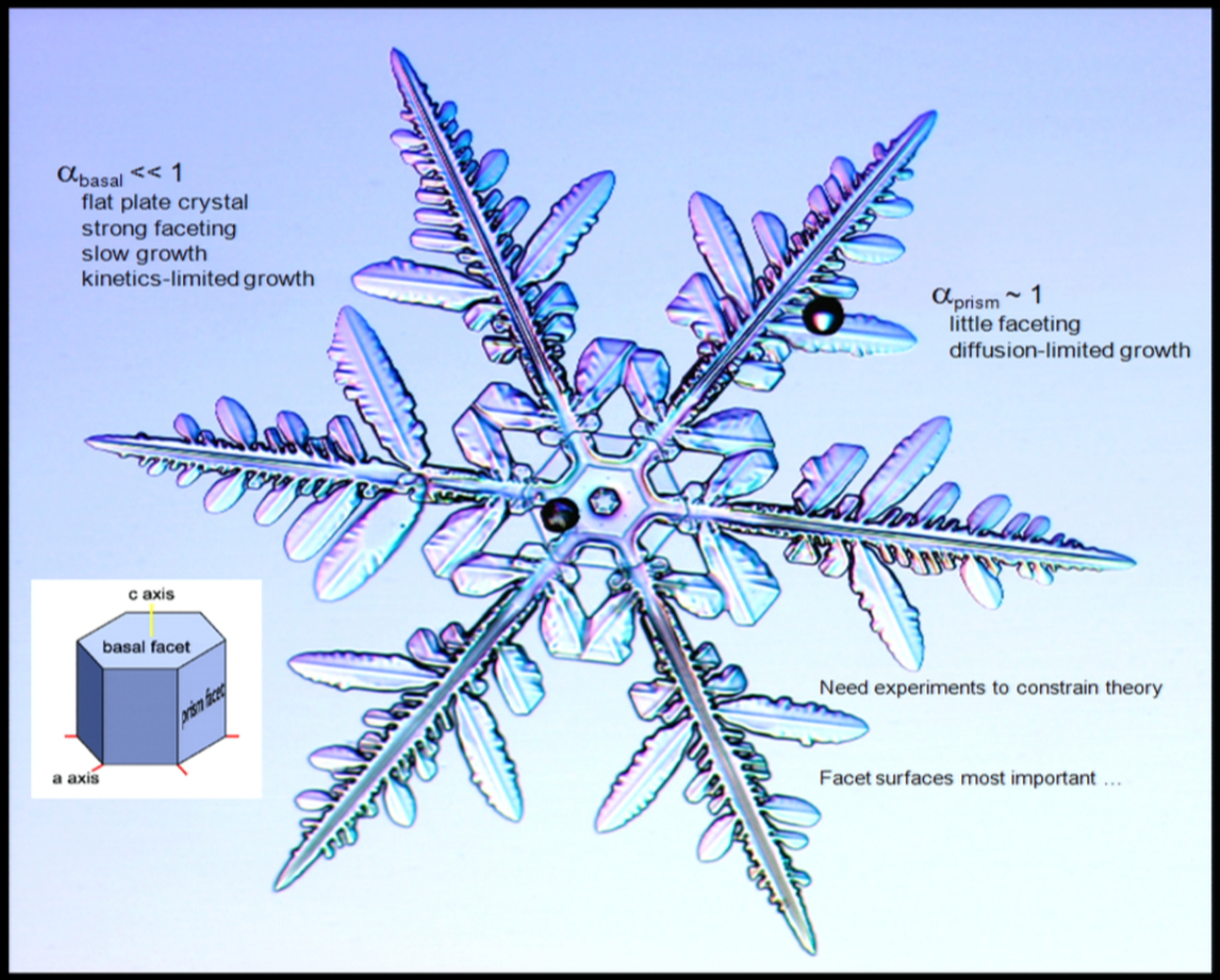
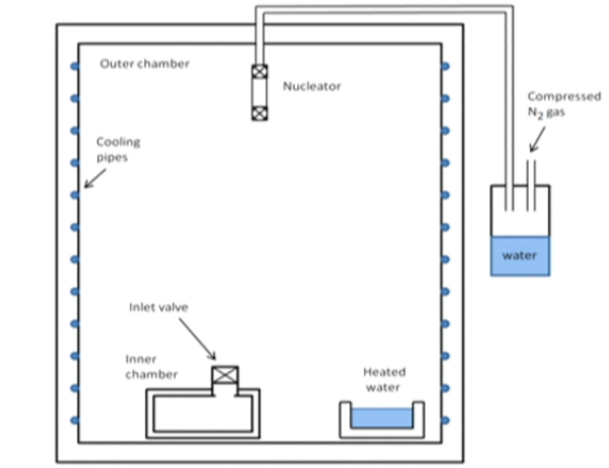
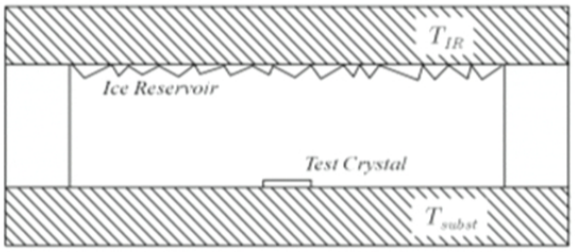
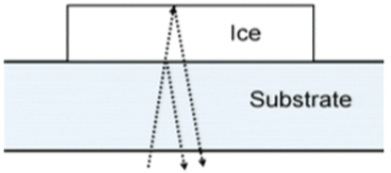


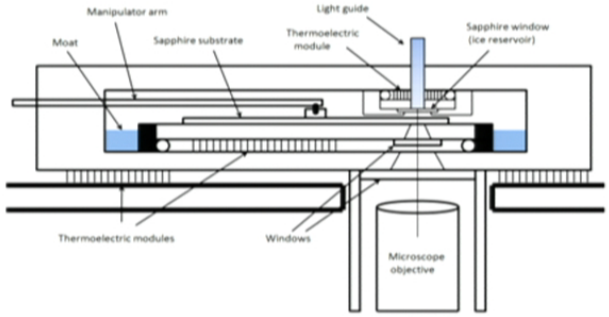

α_{basal} << 1
flat plate crystal
strong faceting
slow growth
kinetics-limited growth
α_{prism} ~ 1
little faceting
diffusion-limited growth
c axis
basal facet
prism facet
a axis
Need experiments to constrain theory
Facet surfaces most important …

Controlled Ice Growth Experiments in a low-pressure environment



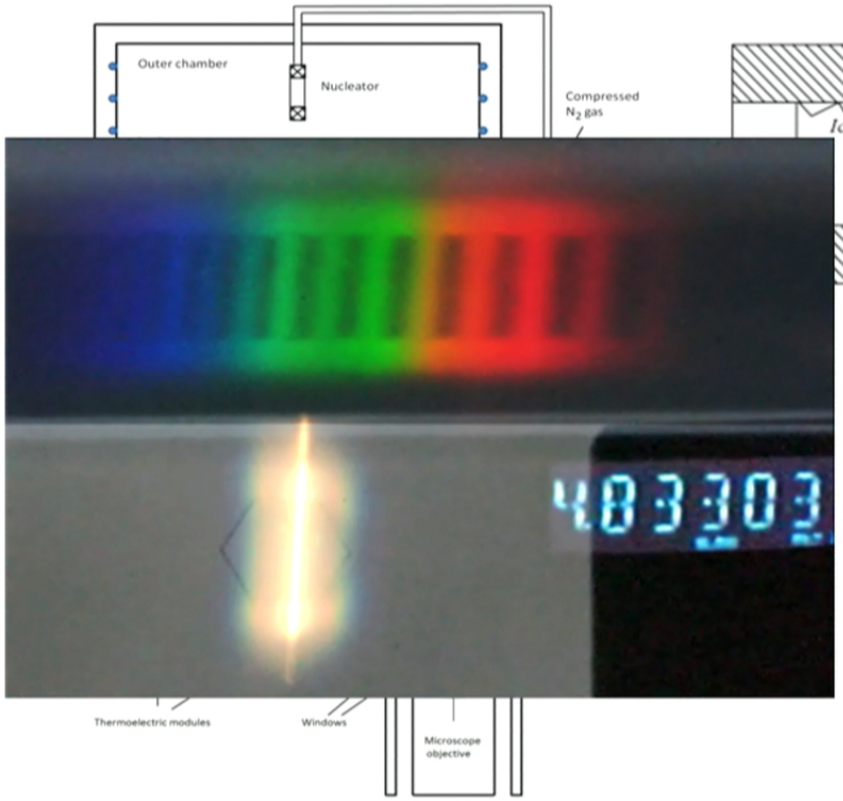


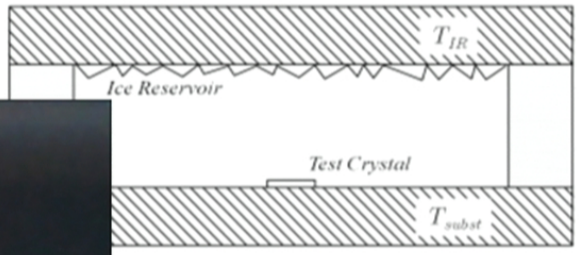


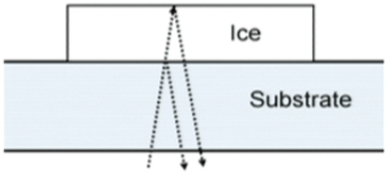


> Make crystals in main chamber
> Transfer some to smaller chamber
> Isolate single crystal on substrate
> Pump out small chamber
(fast particle diffusion → kinetics limited)
> Use optical interferometry to measure thickness vs time → growth velocity
> Supersaturation determined by T_{IR}, T_{subst}

Controlled Ice Growth Experiments in a low-pressure environment







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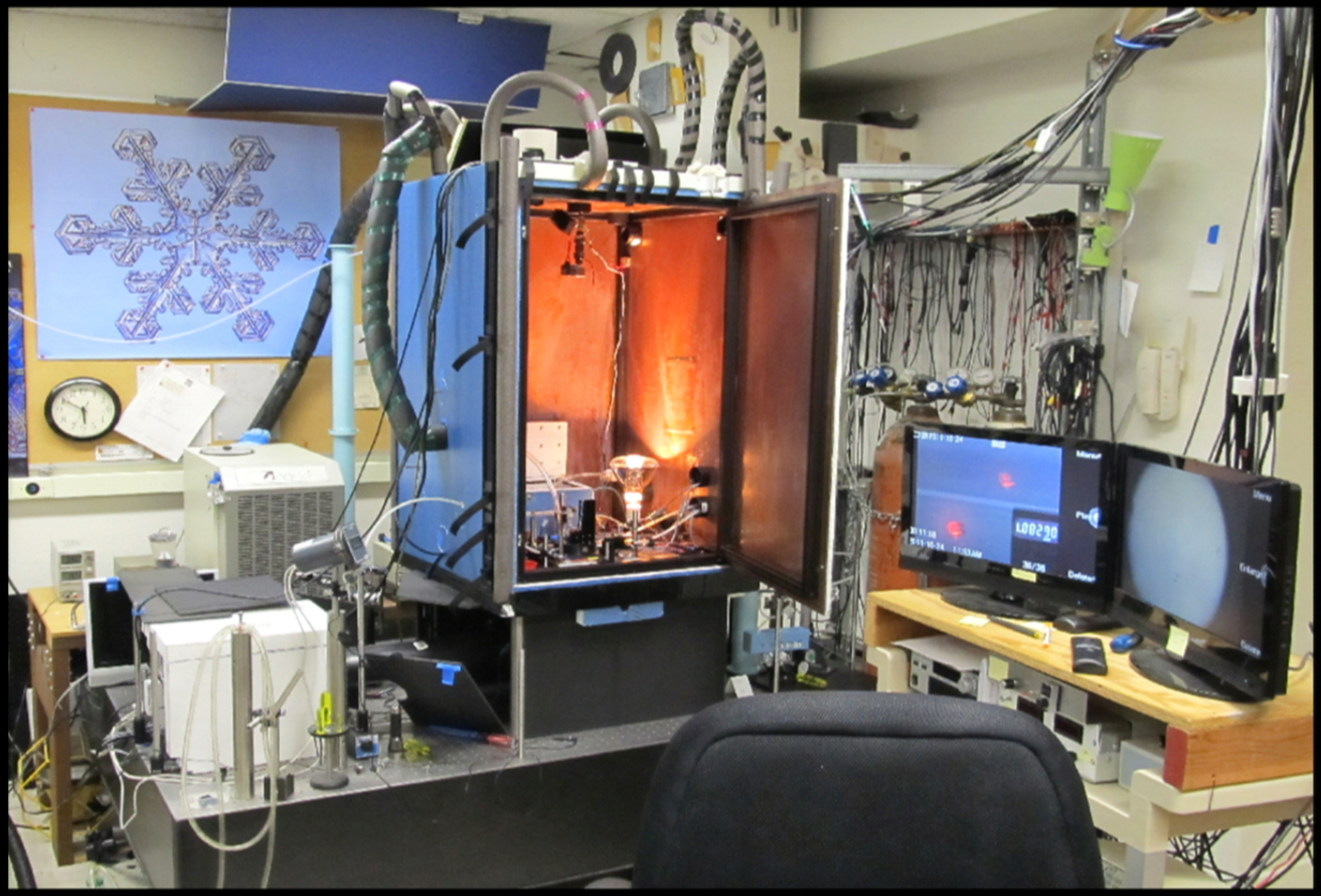
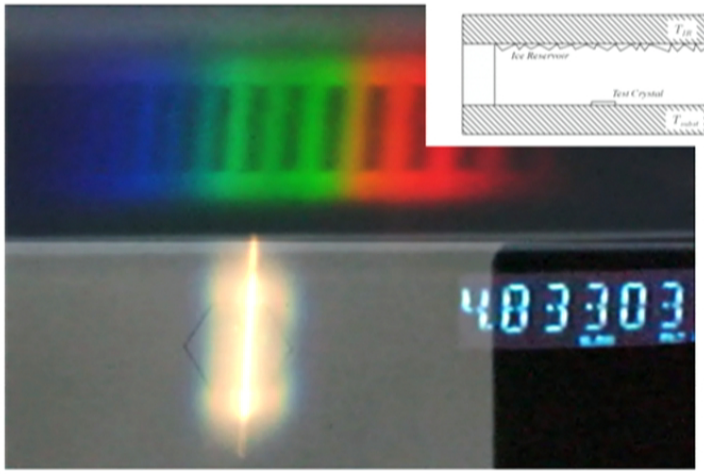
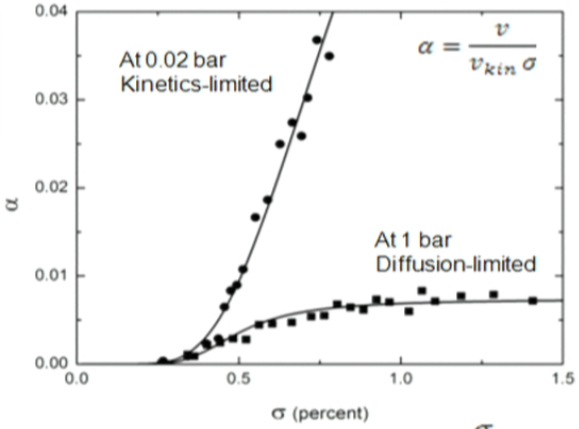
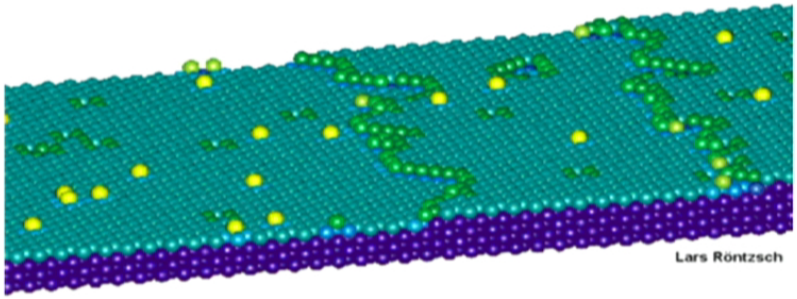


Controlled Ice Growth Experiments in a low-pressure environment





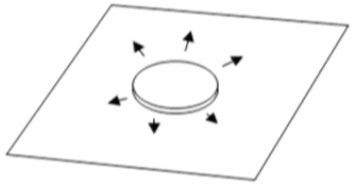
$$\alpha = A exp(-\frac{\sigma_0}{\sigma})$$



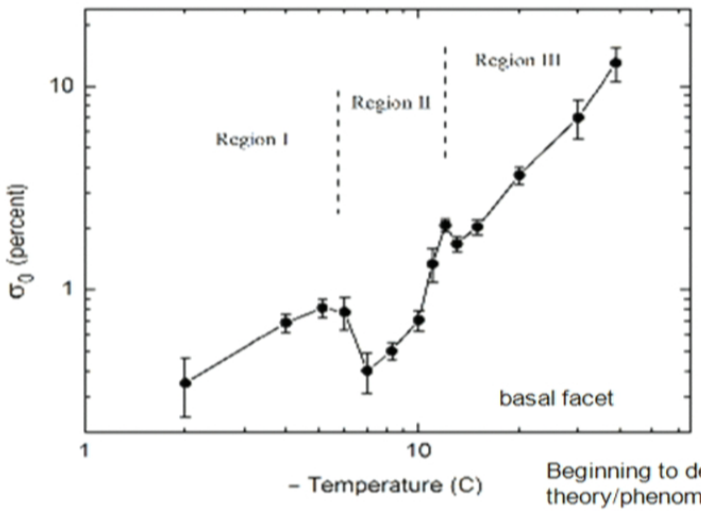
→Attachment Kinetics on faceted surfaces limited by 2D nucleation of islands

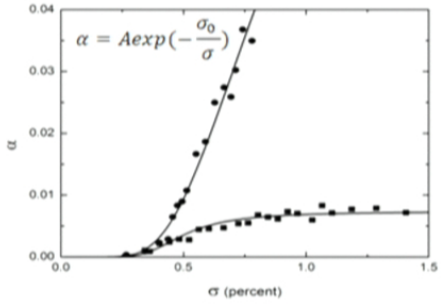
Functional form from classical nucleation theory

σ_0 determined by step energy



2D Nucleation and Surface Melting



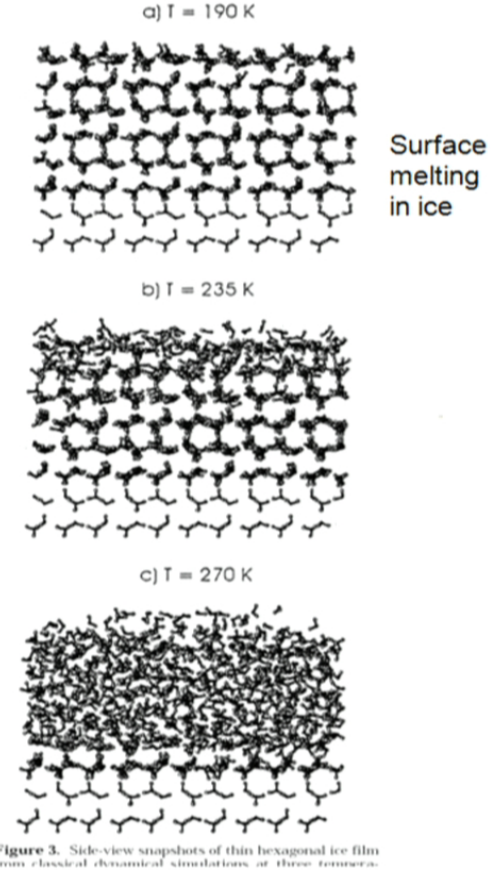


Beginning to develop theory/phenomenology for attachment kinetics on facet surfaces. Not quite there yet…

Possibly calculate σ_0 (step energy) using MD simulations? (static quantity)

Determine α empirically
→ know B.C.
→ solve D.E.

Chemical Reviews, 2003, Vol. 103, No. 12 4785



Surface melting in ice

Figure 3. Side-view snapshots of thin hexagonal ice film from classical dynamical simulations at three tempera-

Numerical Modeling of Diffusion-limited Growth

Basic idea:

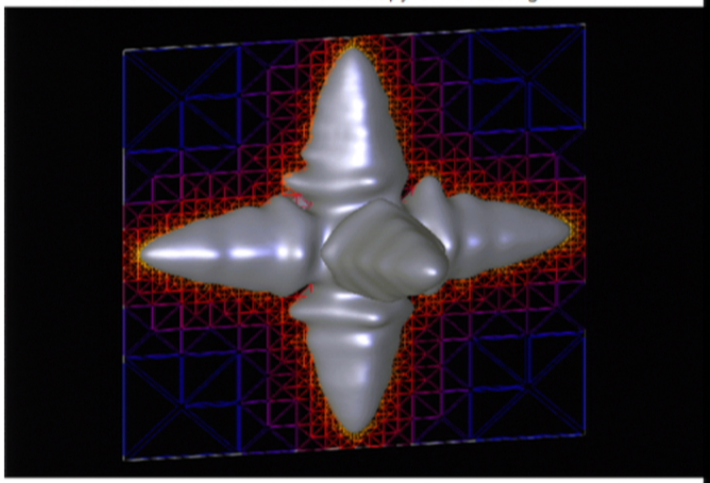
Start with small seed crystal, then

1) numerically solve the diffusion equation around the crystal → $\sigma(x)$
   [need B.C. → need $\alpha(\sigma)$]
2) "grow" crystal outward a small amount
3) repeat

Various methods for finding solution to D.E.
Propagating growth more difficult...
...errors propagate also
Lots or work done in 1980s
Techniques in literature:

1) "Front-tracking" – keep track of solid interface
   lots of bookkeeping
2) "Phase-field" – smear out interface
   less bookkeeping, easier to write code
3) Cellular automata
   fixed grid, nearest-neighbor rules

D.E. solvers work well if weak anisotropy → no faceting...



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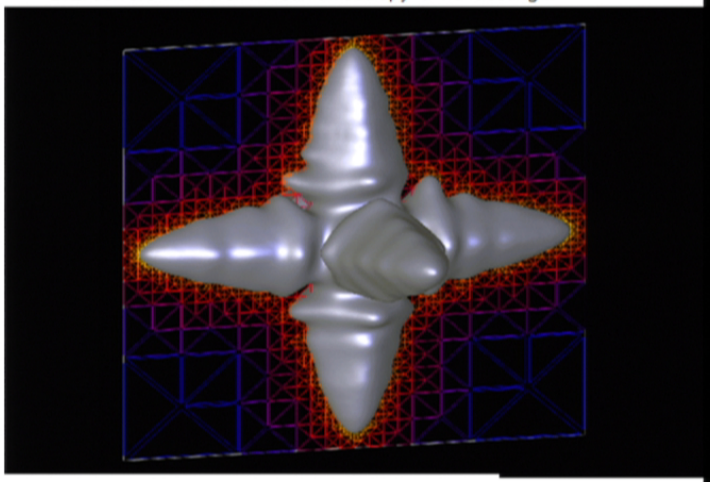
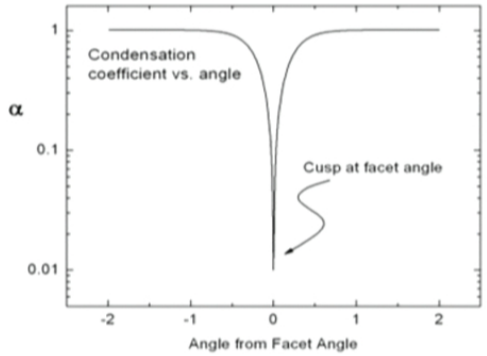
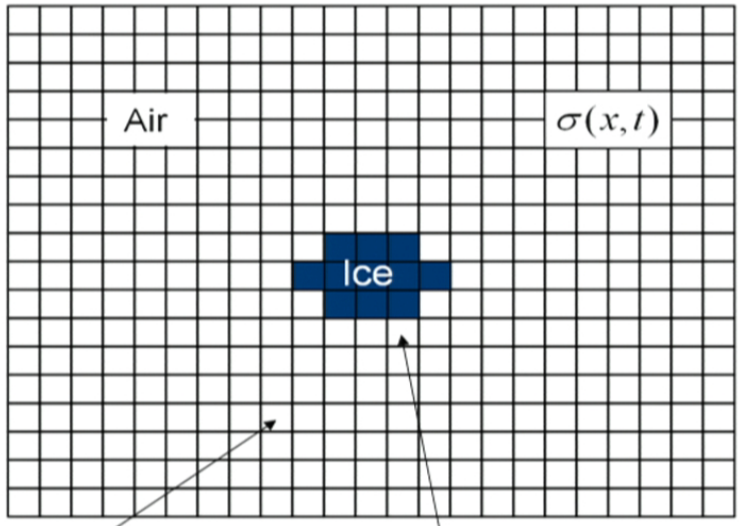




Modeling Crystal Growth using Cellular Automata



Air pixels contain supersaturation field

Propagate by replacing with neighbor average (solves Laplace's equation)

Boundary pixels contain supersaturation and "accumulated mass"

Change to ice pixel when accumulated mass reaches ice mass

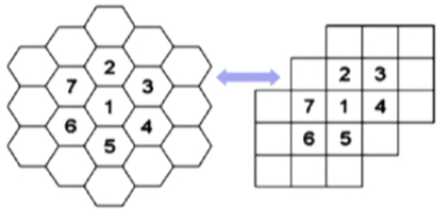
1. Set up grid with appropriate crystal symmetry
2. Define nearest-neighbor rules for evolving supersaturation, growth
3. Go...

Easy to code in 2D, 3D

Works well for strong anisotropy

First computer simulations to produce physically reasonable structures resembling snow crystals (in 2006, by David Griffeath and Janko Gravner)

Can grow hexagonal crystals on a rectangular grid:



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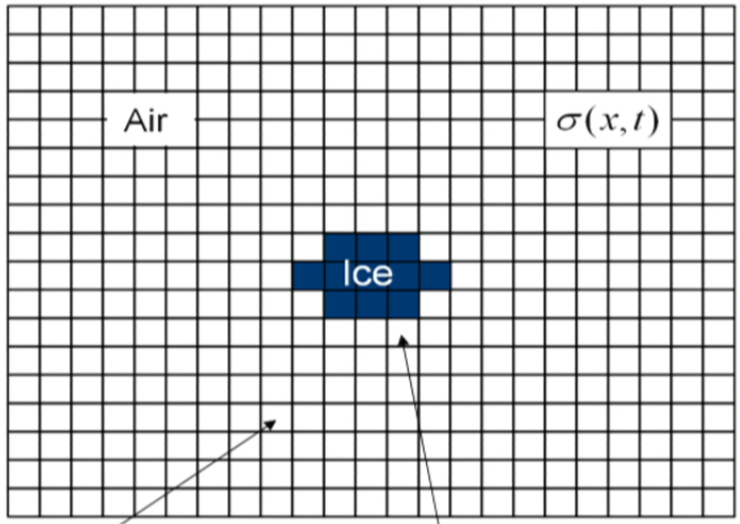

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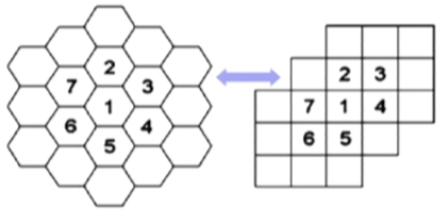
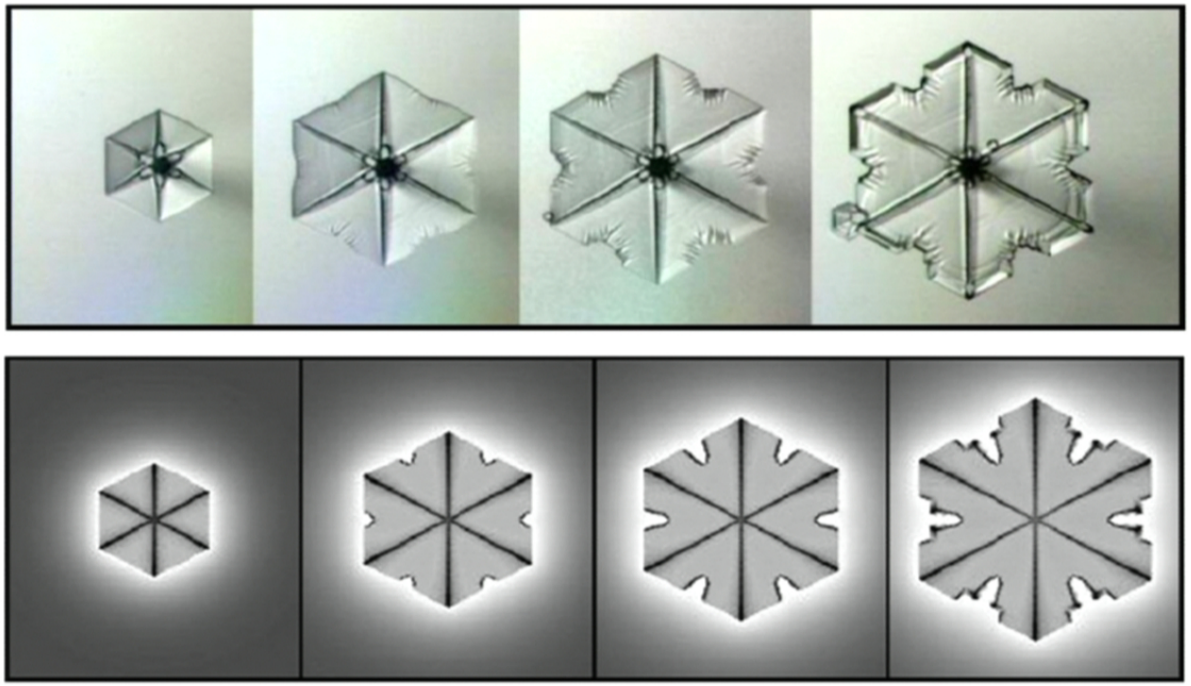
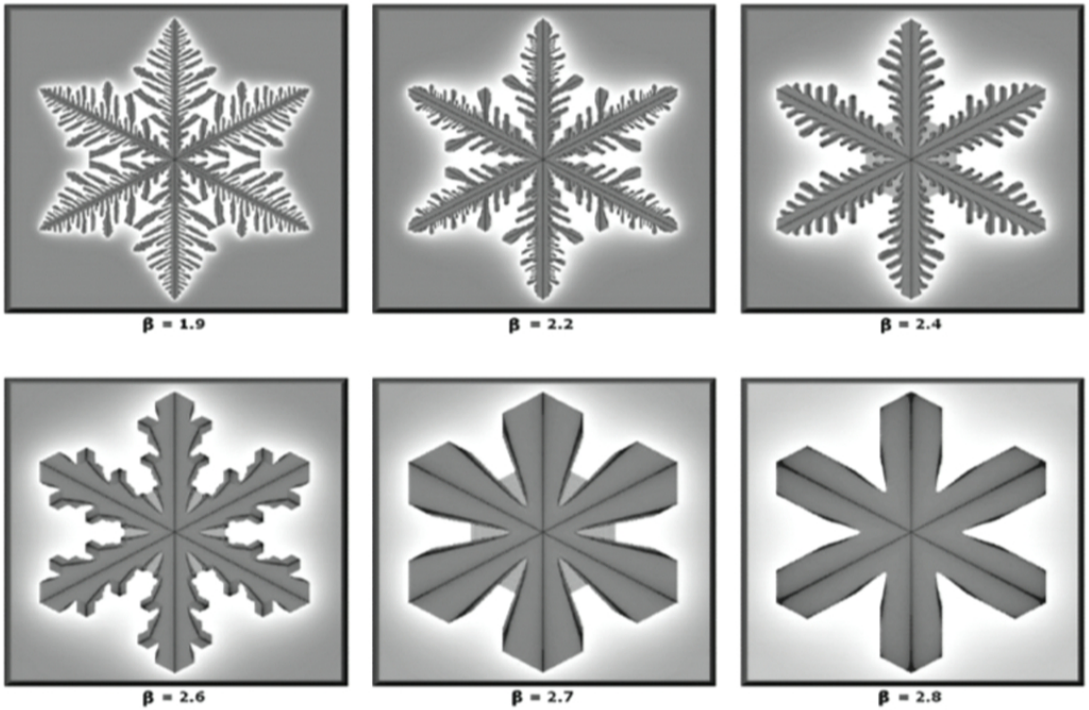


Snow Crystal Modeling using Cellular Automata



Model by J. Gravner & D. Griffeath

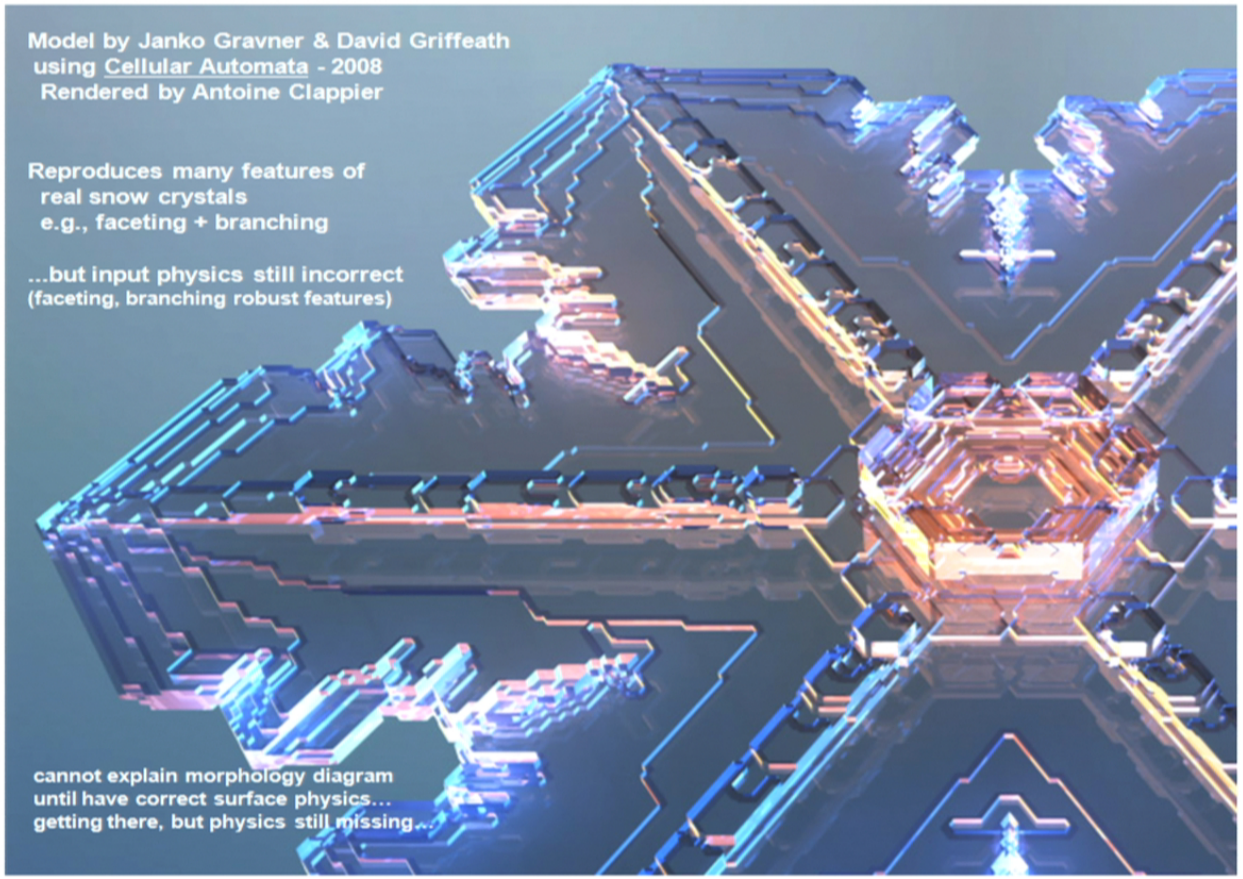
Snow Crystal Modeling using Cellular Automata



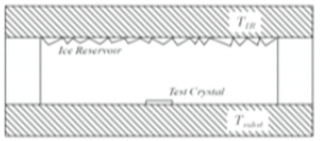
by J. Gravner & D. Griffeath

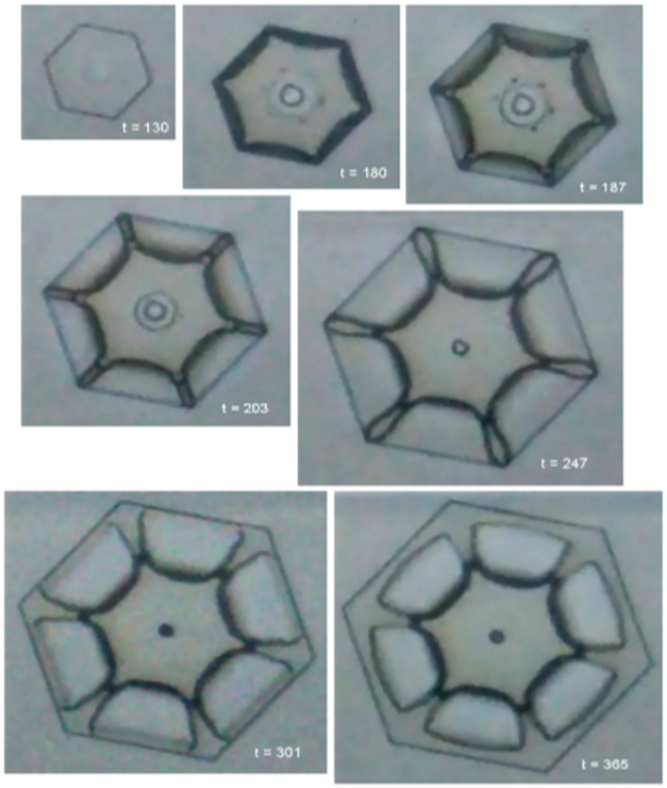
Crystals generated from single-pixel seeds
First time diffusion-limited growth solved to produce ***faceted + branched*** structures
But used non-physical parameterization of B.C.

Computer Modeling of Snowflakes

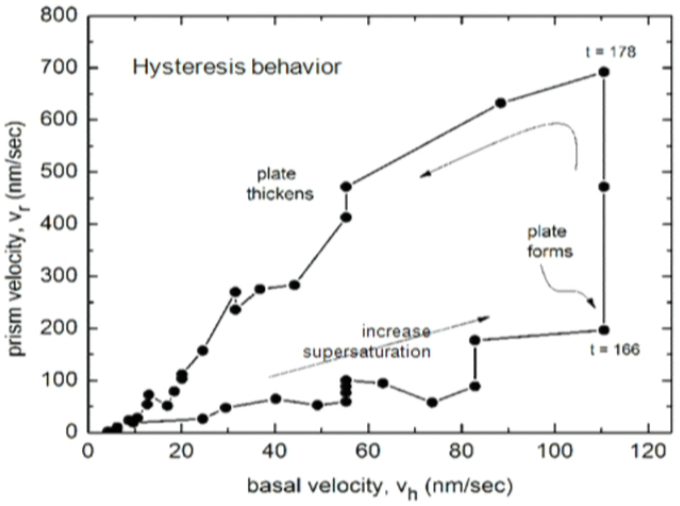


An Edge-Enhancing Growth Instability





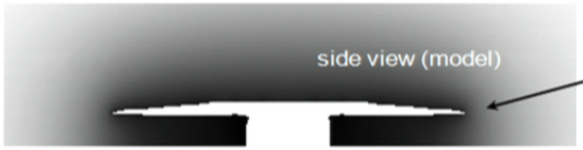
> Start with small ice prism on substrate
> Air pressure = 1 bar
> Increase supersaturation
→ "plate on pedestal" growth



Structure Dependent Attachment Kinetics

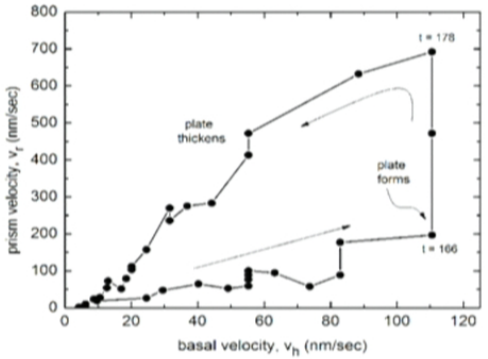
$$\alpha = Aexp(-\frac{\sigma_0}{\sigma})$$

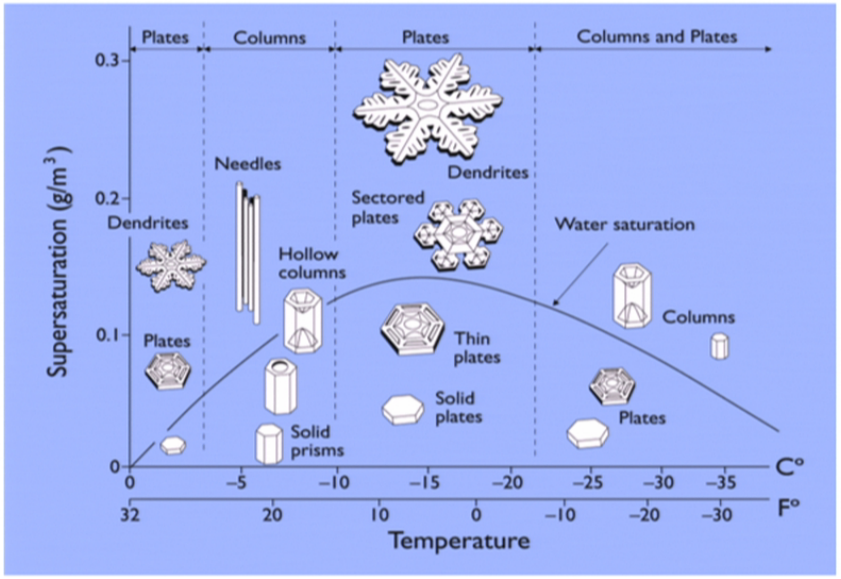
Hysteresis in plate-on-pedestal growth
→ α not single valued function of σ



σ_0 *lower on sharp edge (compared to facet surface)*
→ *nucleation faster on narrow facet*

→ *Edge-enhancing growth instability*
explains why snow crystals to thin and flat
explains rapid transitions between columns and plates
A big player in the morphology diagram





m

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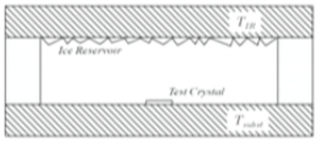

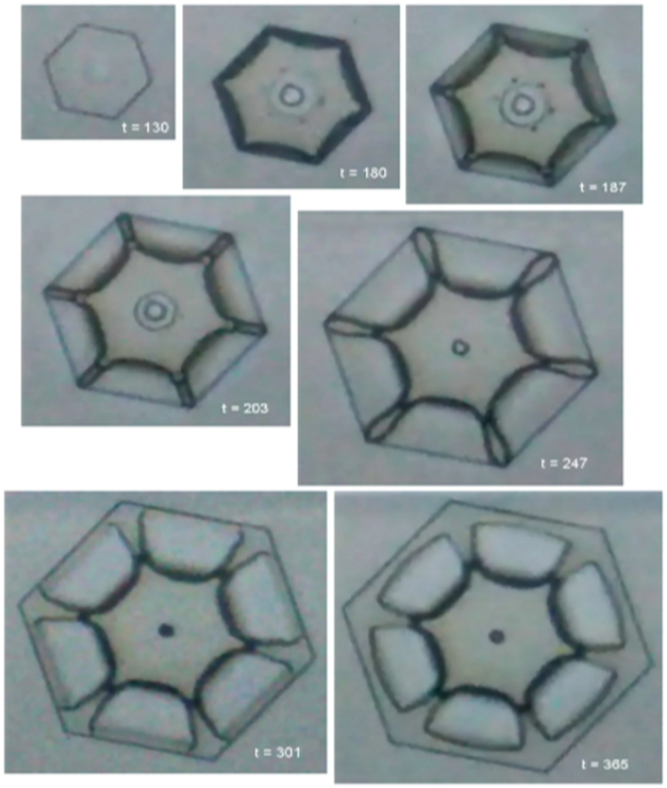

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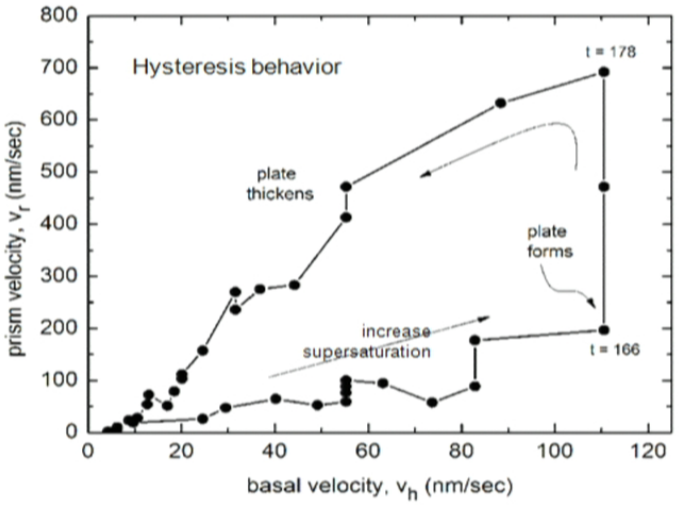

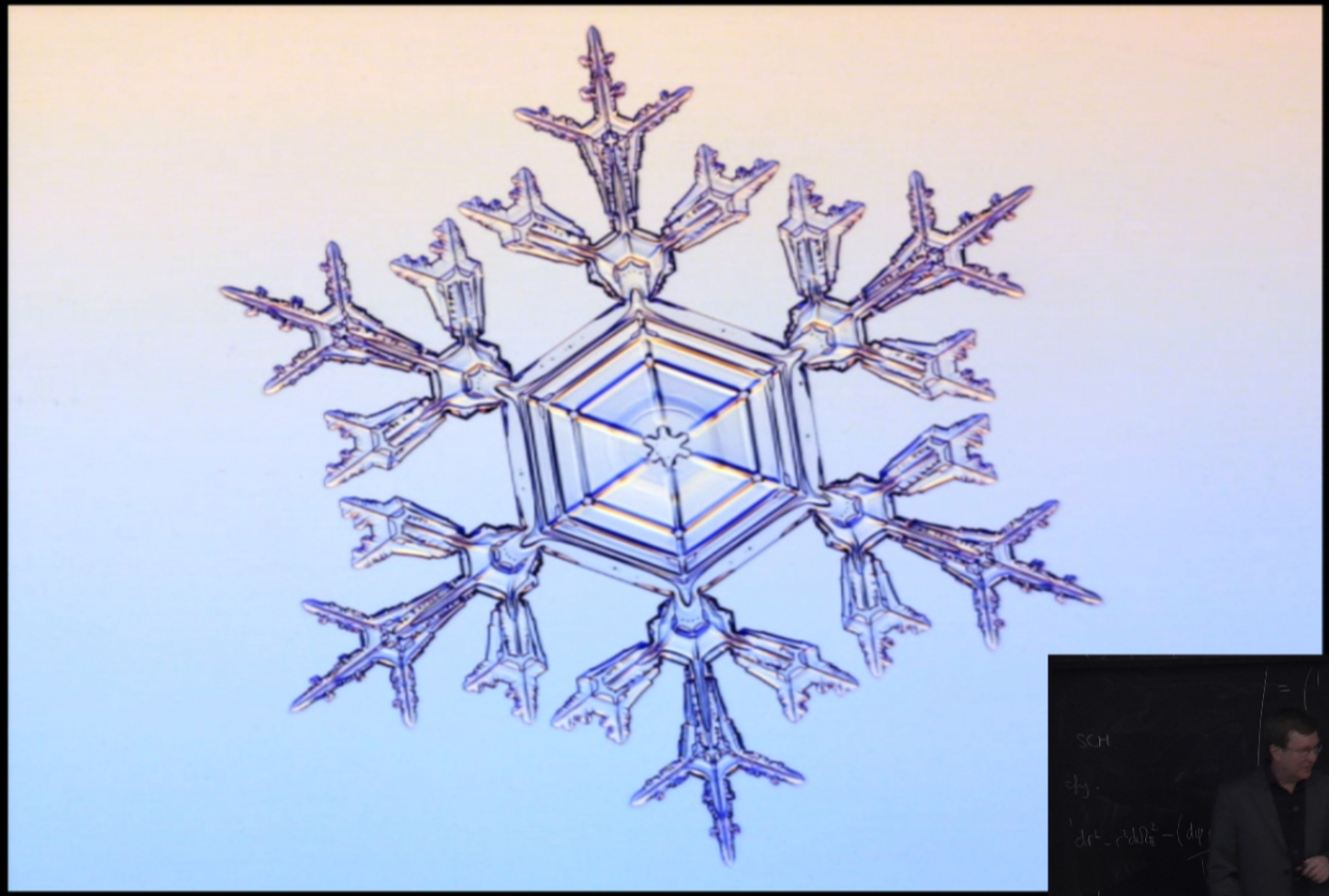

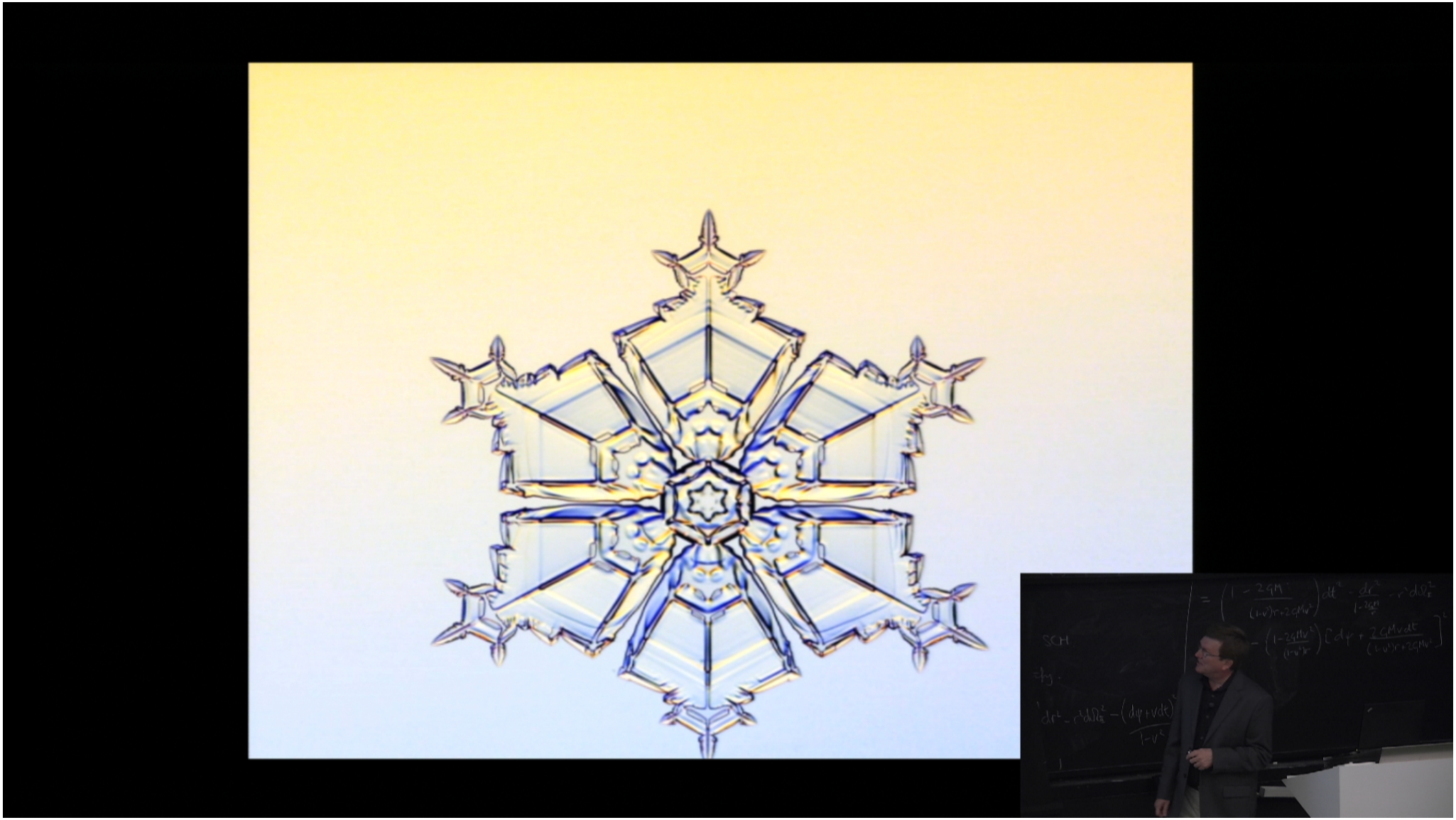

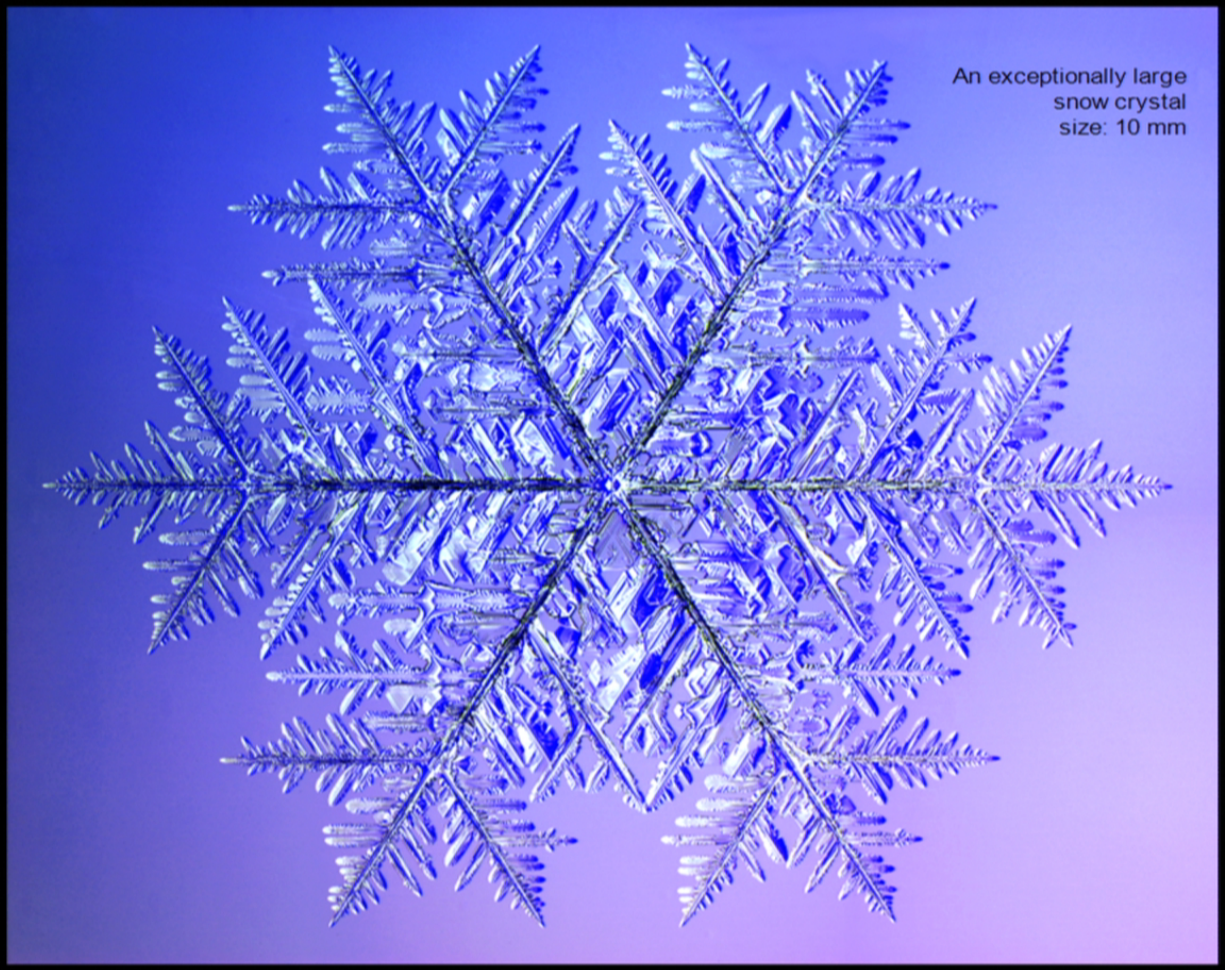
An exceptionally large
snow crystal
size: 10 mm