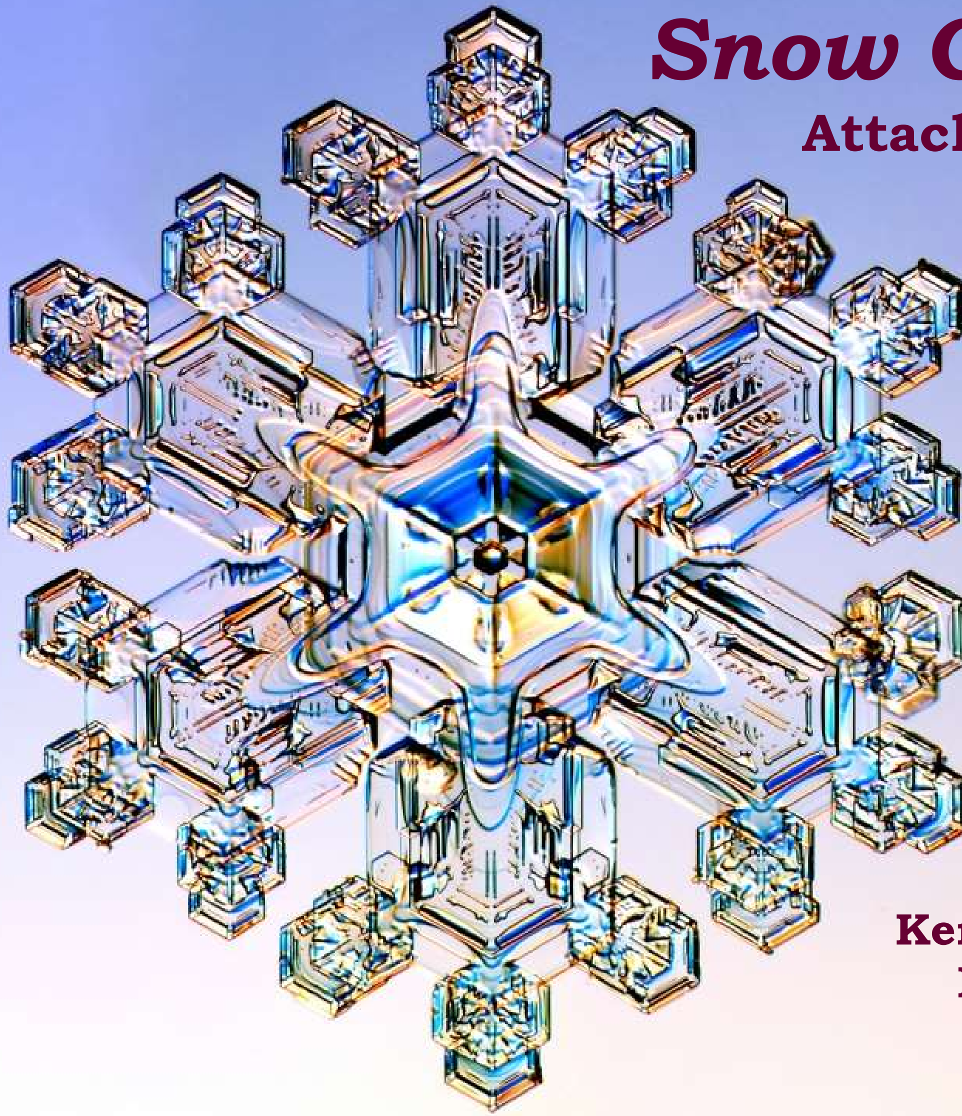
Snow Crystals: II

Attachment Kinetics & Explaining the Nakaya Diagram



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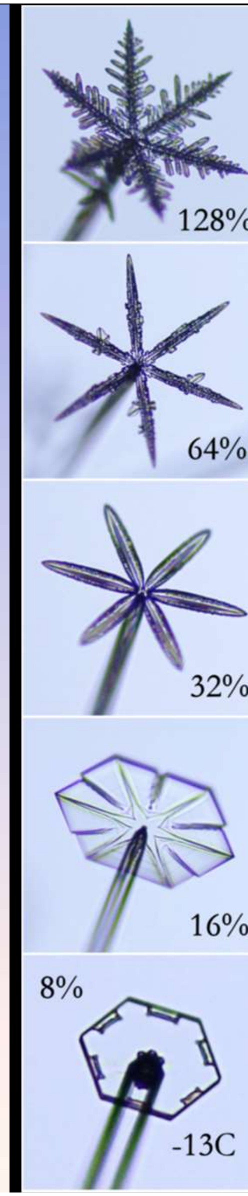
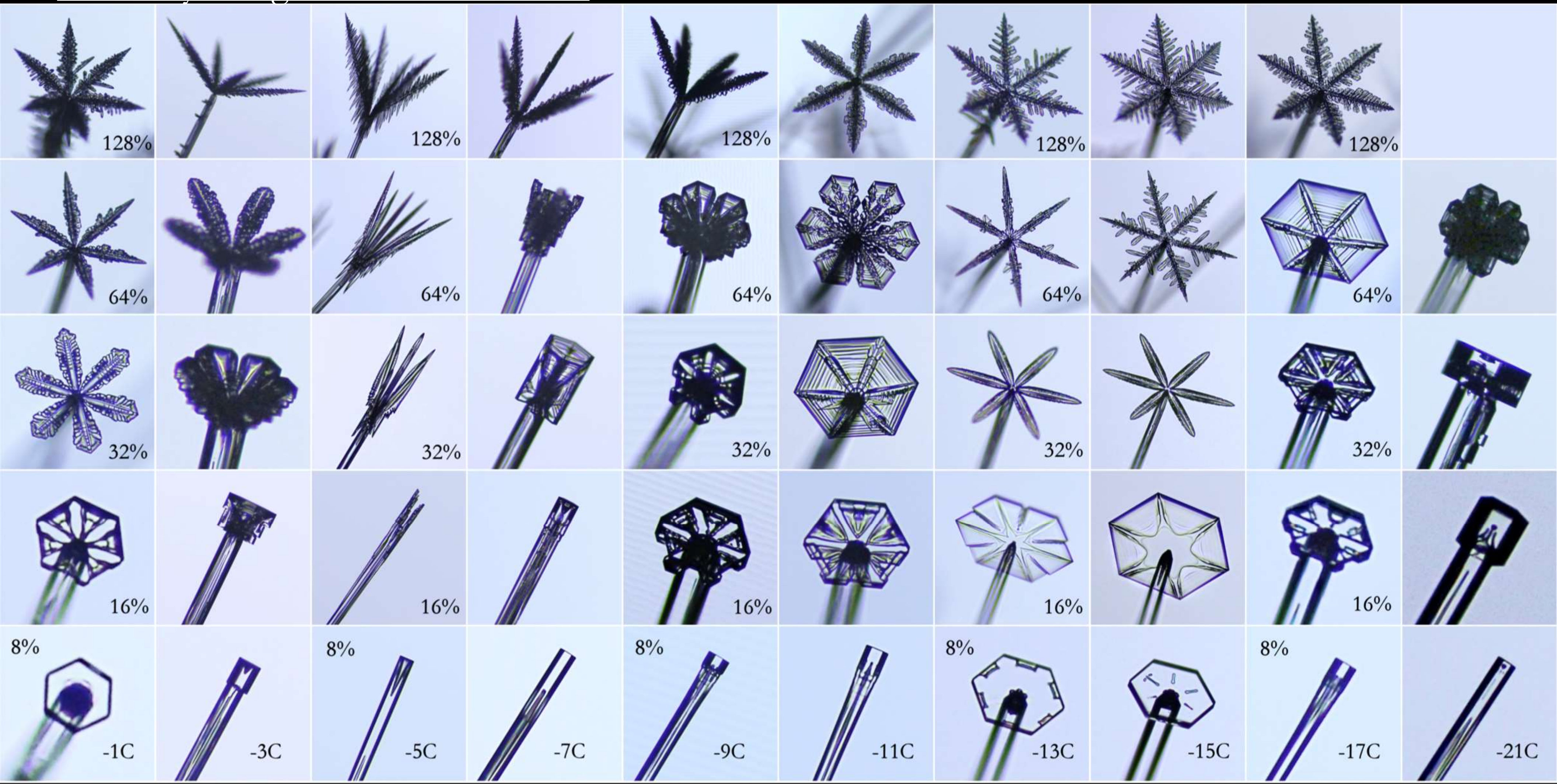


Snow crystals grown on ice needles



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

Explaining the Nakaya Diagram

150%

-0.5 C 7% -24 C

Goal: A comprehensive physical model → Quantitative computational modeling

→ Reproduce robust growth morphologies and growth rates … a challenging task!

Explaining the Nakaya Diagram

150%

-0.5 C

Step 1: Diffusion-limited growth (particle diffusion; heat diffusion less important in air)

Underlying physics well understood, easy to develop algorithms … $\nabla^2\sigma = 0$

Can be difficult to solve for complex structures (see Lecture 3)

7%

-24 C

→ vertical axis

Explaining the Nakaya Diagram

150%

-0.5 C

-24 C

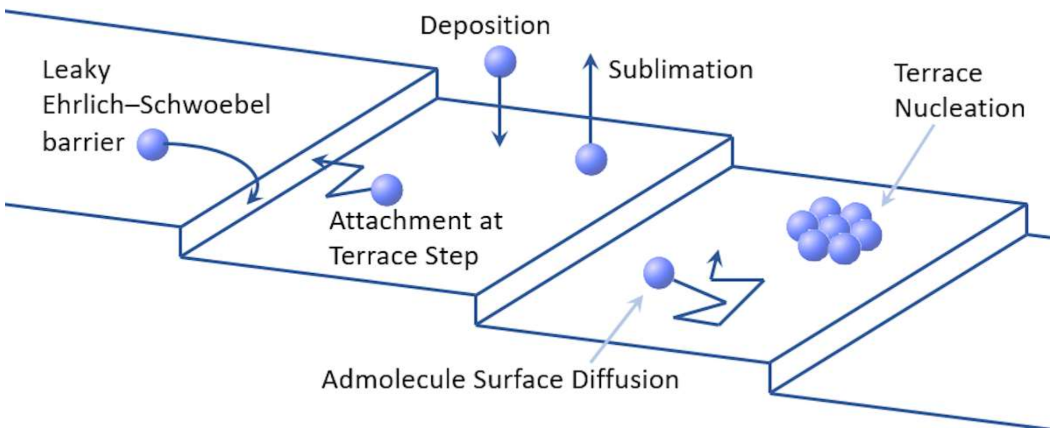
Step 2: Attachment kinetics … $v_n = \alpha v_{kin}\sigma_{surf}$; $0 \leq \alpha \leq 1$ … **attachment coefficient**

Underlying physics poorly understood, molecular dynamics of crystal growth

Large anisotropy → faceting

→ horizontal axis

The molecular dynamics of crystal growth



Condensed-matter physics:
Reduce complex
many-body problem to
essential processes…

Attachment Kinetics

A collection of physical processes describing crystal growth.
Hertz-Knudsen relation (1882) (here for ice growth from water vapor):

$$v_n = \alpha v_{kin} \sigma_{surf}$$

Surface supersaturation
($\sigma_{surf} \ll \sigma_\infty$)

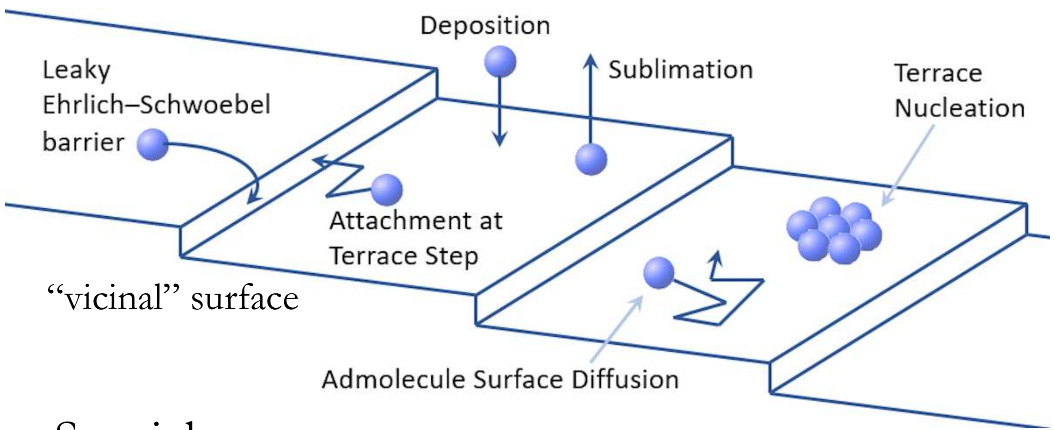
Growth velocity
(normal to surface)

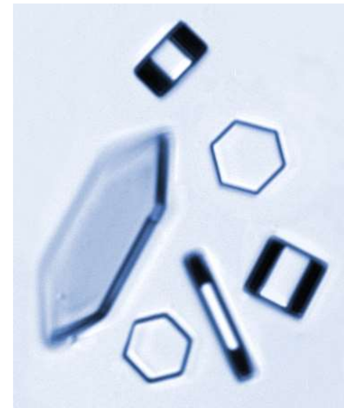
Attachment coefficient
$\mathbf{0 \leq \alpha \leq 1}$

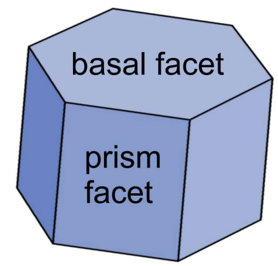
Stat mech:

$$v_{kin} = \frac{c_{sat}}{c_{ice}} \sqrt{\frac{kT}{2\pi m_{mol}}}$$

THE MOLECULAR DYNAMICS OF CRYSTAL GROWTH







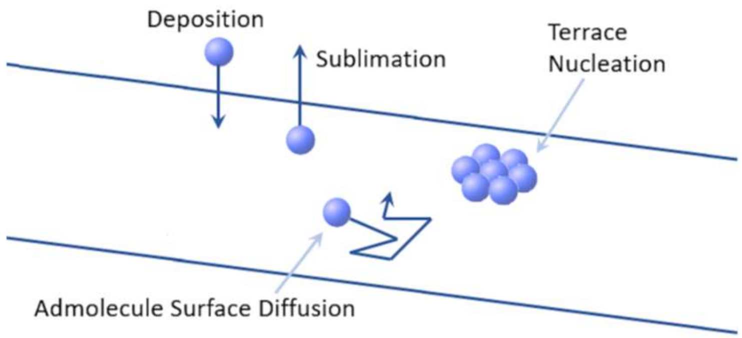
Special cases

$$v_n = \alpha v_{kin} \sigma_{surf}$$

- Liquid water surface: $\alpha \approx 1$ … impinging water vapor molecules immediately incorporate into surface
- "Rough" ice surface: $\alpha \approx 1$ … fast surface diffusion + fast attachment at terrace steps
- Faceted ice surfaces (basal and prism): $\alpha(\sigma) \ll 1$

→ Essential to understand α_{basal} and α_{prism}

TERRACE NUCLEATION THEORY



Crystal Energetics

3D – latent heat (solid/vapor) *(energy/volume)*

… energy to vaporize crystal

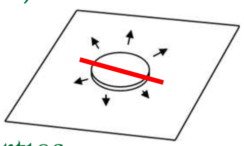
2D – surface energy (tension) *(energy/area)*

… energy to break bonds & create surface

1D – terrace step energy *(energy/length)*

… energy to split island terrace

(on faceted surface)



All three are ***equilibrium*** material properties

2D Gibbs-Thomson effect for molecular island terrace:

$$c_{eq} \approx c_{sat}\left(1 + \frac{a^2}{kT}\frac{\beta}{R}\right) \qquad \beta = \text{ terrace “step energy”}$$

$a =$ size of molecule

$R =$ radius of terrace

Small islands unstable to sublimation → a 2D nucleation problem

Stat mech of island dynamics →

$$\alpha(\sigma_{surf}) = Ae^{-\sigma_0/\sigma_{surf}}$$

$$\sigma_0(T) \approx \frac{a^2}{k^2T^2}\beta^2 \qquad \sigma_0 = \text{ nucleation barrier}$$

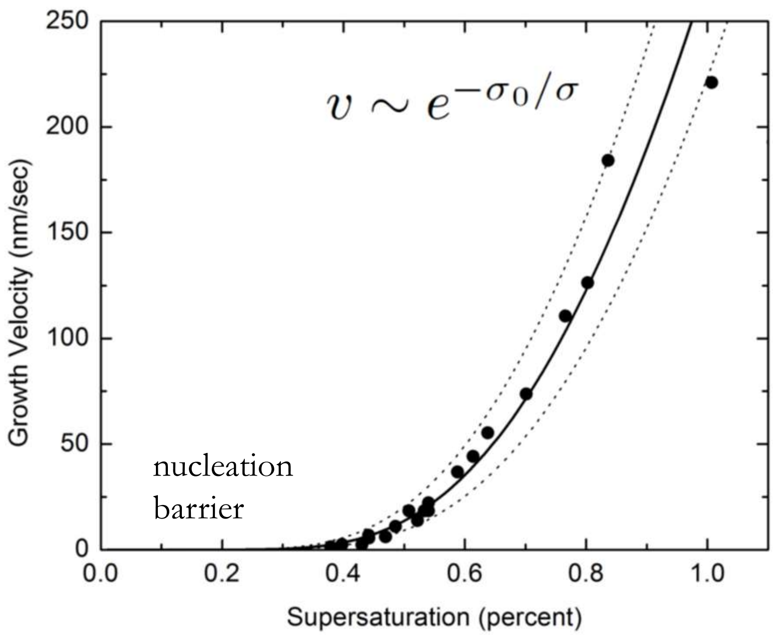
Theory → σ_0 *robust* feature, A model dependent (ignore weak dependence on σ_{surf})

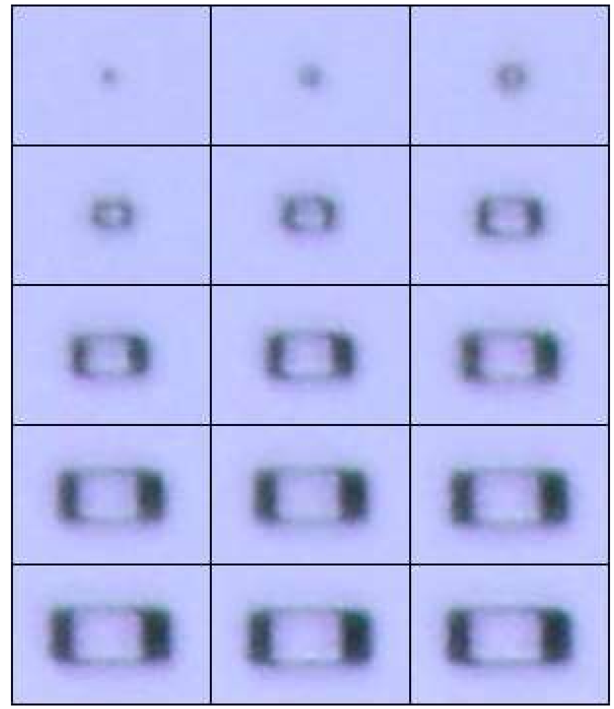
Result from ~1950s, responsible for most faceting phenomena (if no dislocations)

Terrace nucleation – Application to ice

Watch ice crystals grow as a function of σ_{surf}

Usually in near vacuum, so uniform $\sigma \approx \sigma_{surf}$





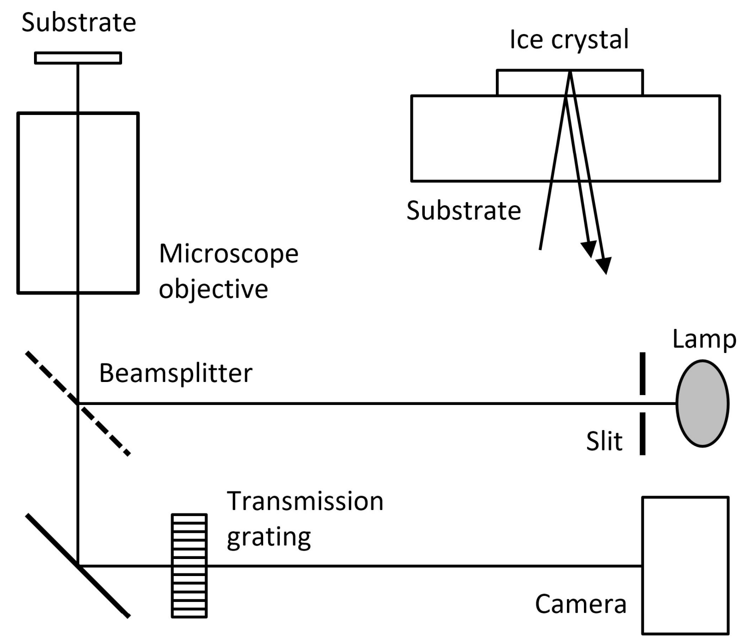
$\sigma_0 =$ adjustable parameter in fit

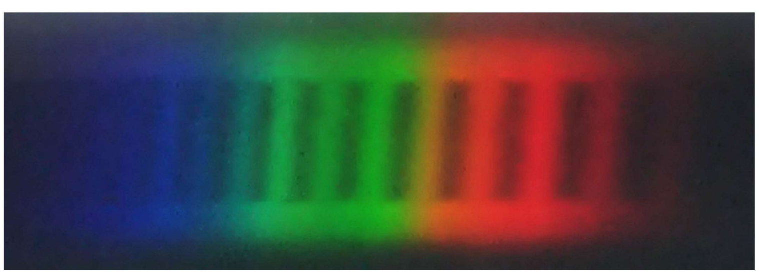
→ use growth to measure σ_0 → measure β

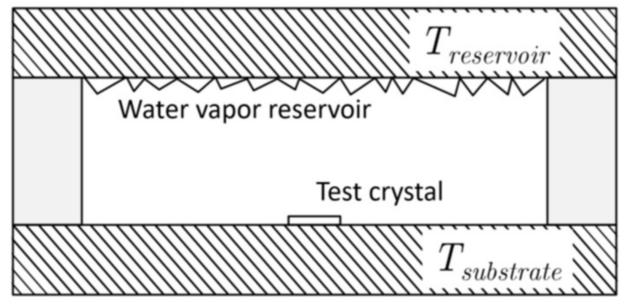
Ice growth usually acts as if dislocation-free

Kenneth G. Libbrecht and Mark E. Rickerby, Measurements of surface attachment kinetics for faceted ice crystal growth, J. Crystal Growth 377, 1-8, 2013. Preprint at arXiv:1208.5982.

Terrace nucleation – Laboratory measurements







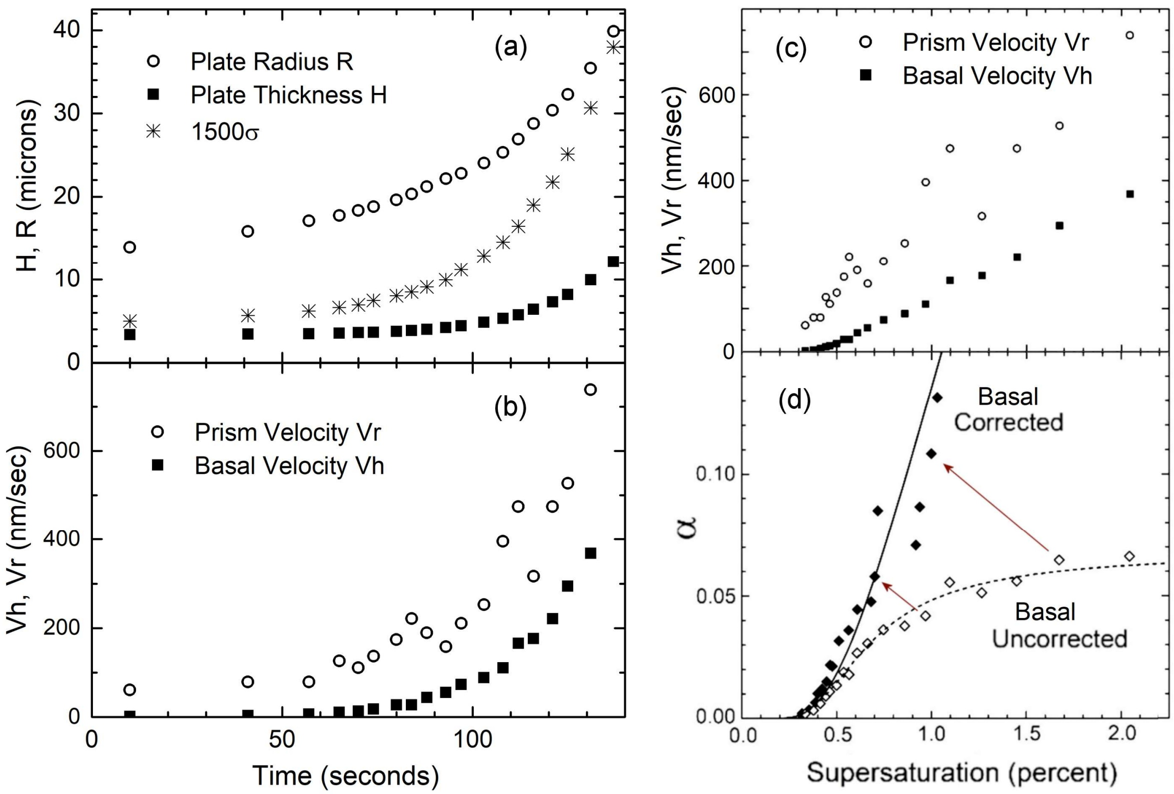
Ideal experimental geometry

Measuring the basal growth rate
using white-light interferometry

- Drop thin hexagonal plate on substrate (~50 μm diameter)
- White light reflects from ice/air and ice/substrate interfaces → interference
- Measure absolute thickness from fringes
- Supersaturation from $(T_{reservoir} - T_{substrate})$

Terrace nucleation – Laboratory measurements

Example: Data from a single crystal growing at -12C, 0.005 Atm pressure



Many possible systematic errors to think about …

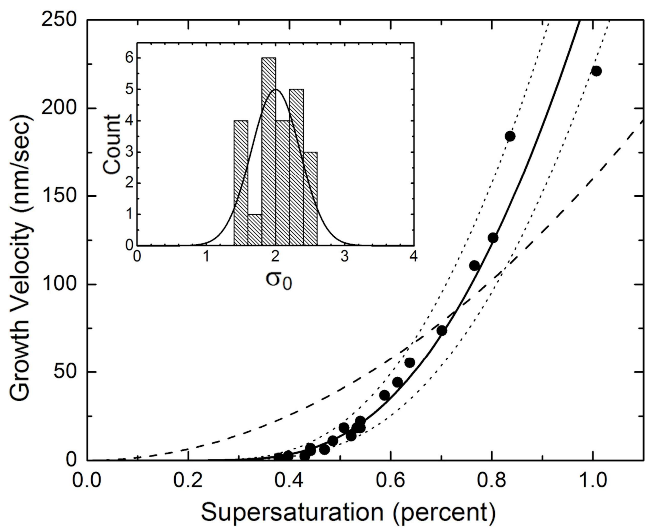
- Diffusion
  (even in near vacuum)
- Substrate interactions
- Model σ
- Chemical impurities
  (use fresh crystals, once)
- Finding $\sigma = 0$
- Crystal imperfections
- …

Finally got it right after 10+ years!

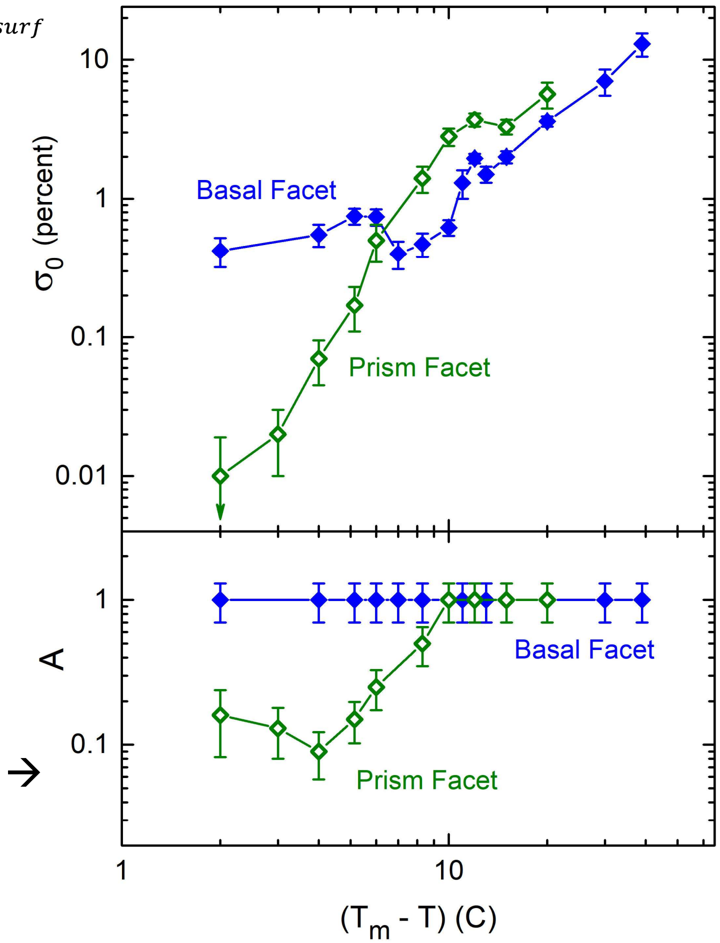
$$v_n = \alpha v_{kin} \sigma_{surf}$$

Terrace nucleation – Laboratory measurements

$$\alpha(\sigma_{surf}) = Ae^{-\sigma_0/\sigma_{surf}}$$



A measurement of σ_0 at a single T from 23 crystals

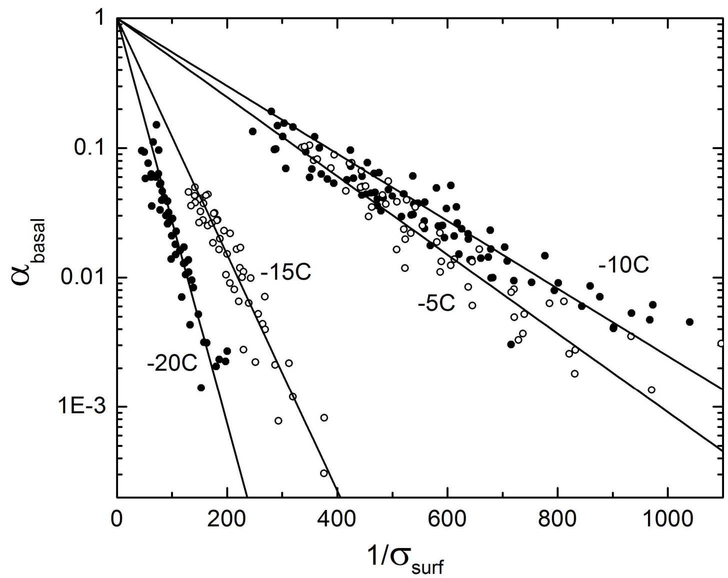


Results as a function of temperature →

Fully defines large-facet growth…

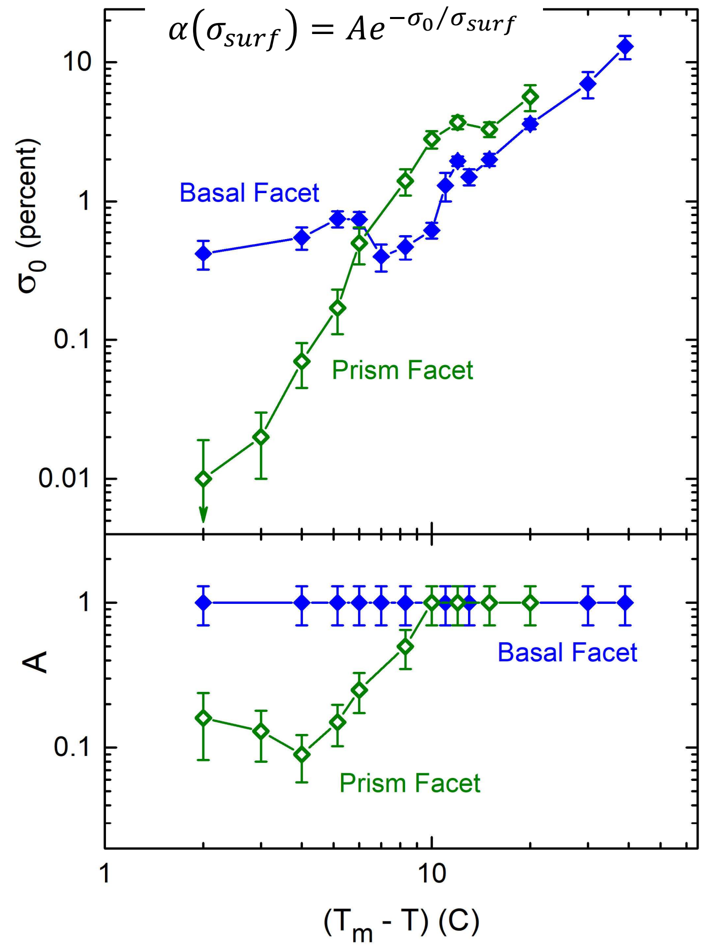
Terrace nucleation – Laboratory measurements

Reality check: $\alpha(\sigma)$ convergence

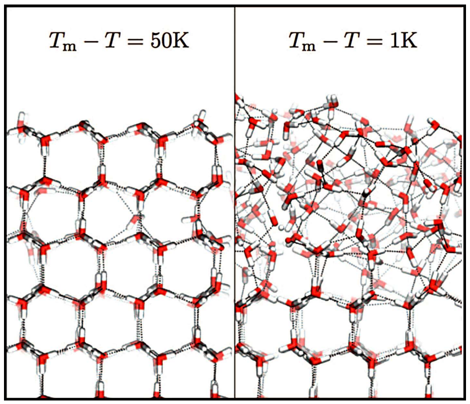


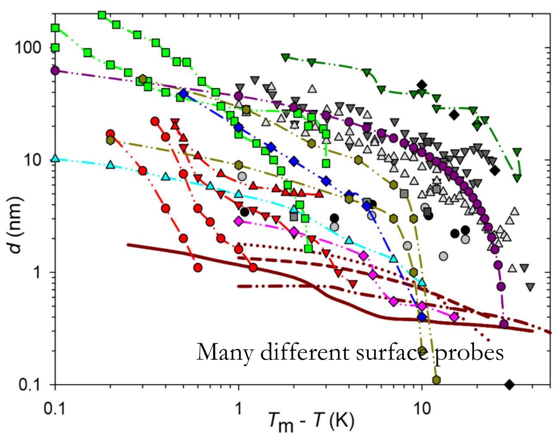
Data not constrained to yield $\alpha \to 1$ at high supersaturation

Makes physical sense far above the nucleation barrier…
But prism facet behaves differently (???)

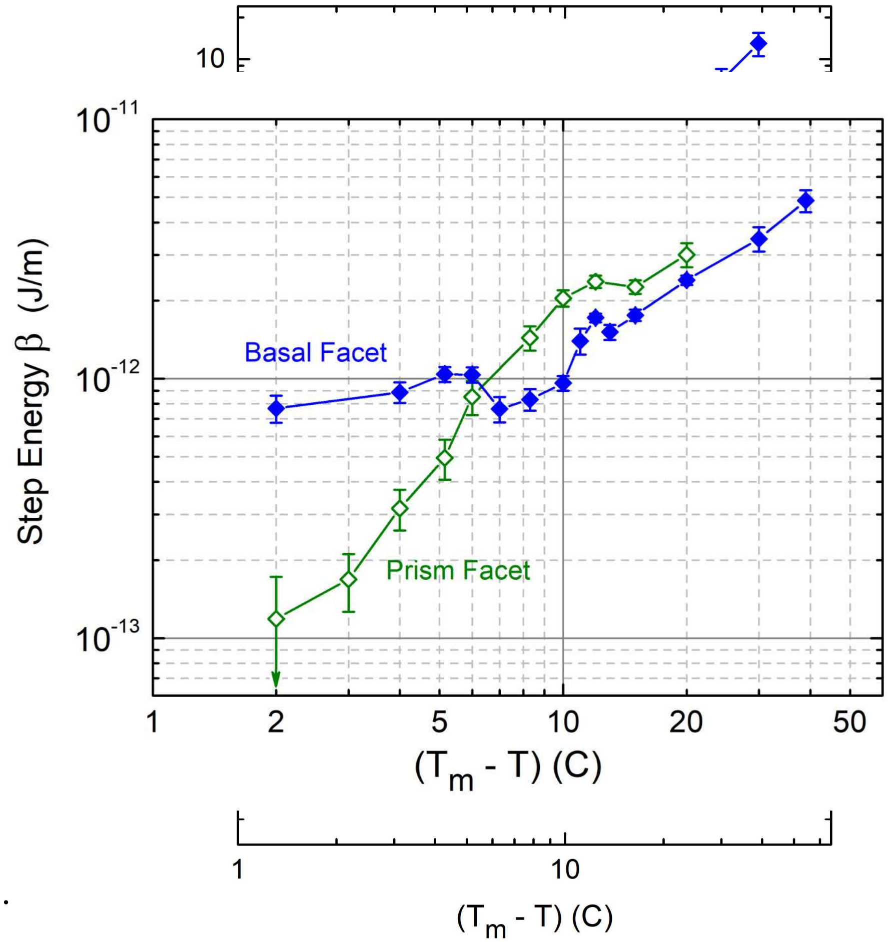


Terrace nucleation & Surface premelting

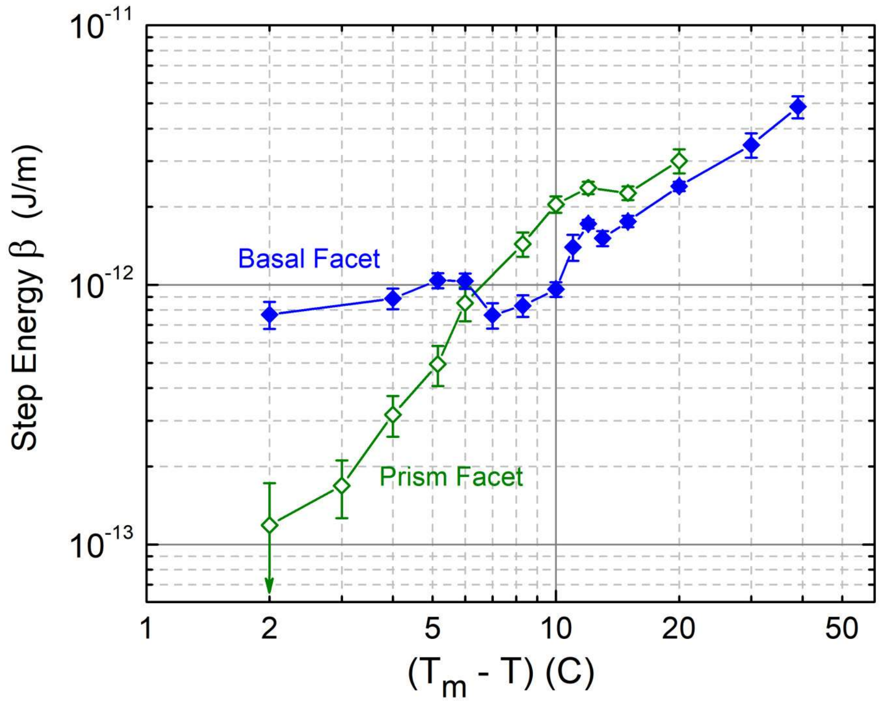




Phenomenon not well understood…
but could explain $\sigma_0(T)$

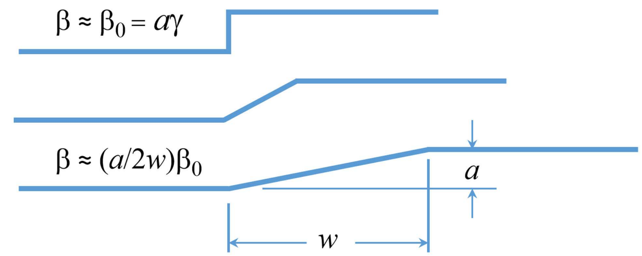


Step energies & Surface premelting – The low-T limit



Step energy is *equilibrium* material property
Should be able to calculate from MD simulations…

← Convert $\sigma_0(T)$ to $\beta(T)$
Then consider step geometry…

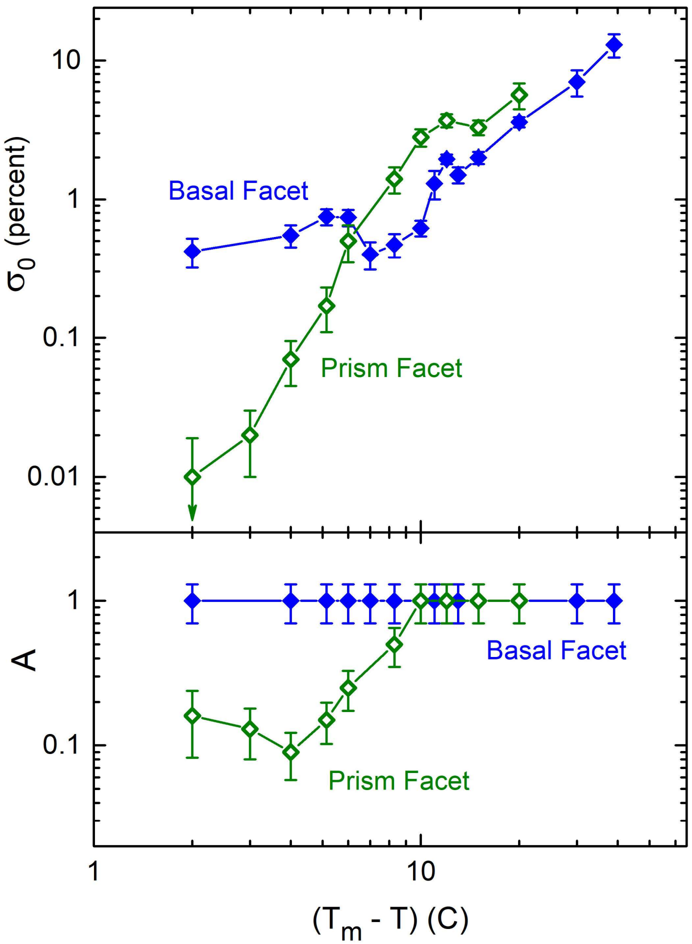


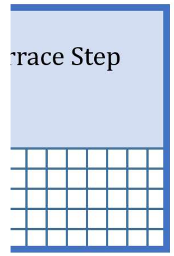
$\beta_0 \approx 3 \times 10^{-1}$ J/m

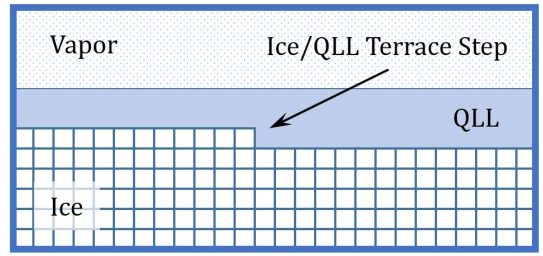
Physical picture (qualitative):

- At low temperature, no surface premelting → simple molecular step → $\beta \approx \beta_0$
- At higher temps, surface premelting "smooths" step, lowers step energy

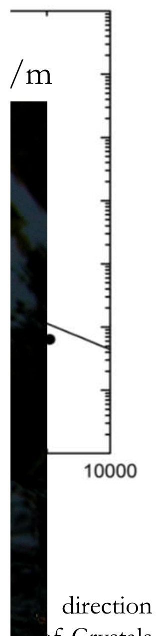
A Correspondence between ice/vapor & ice/liquid growth

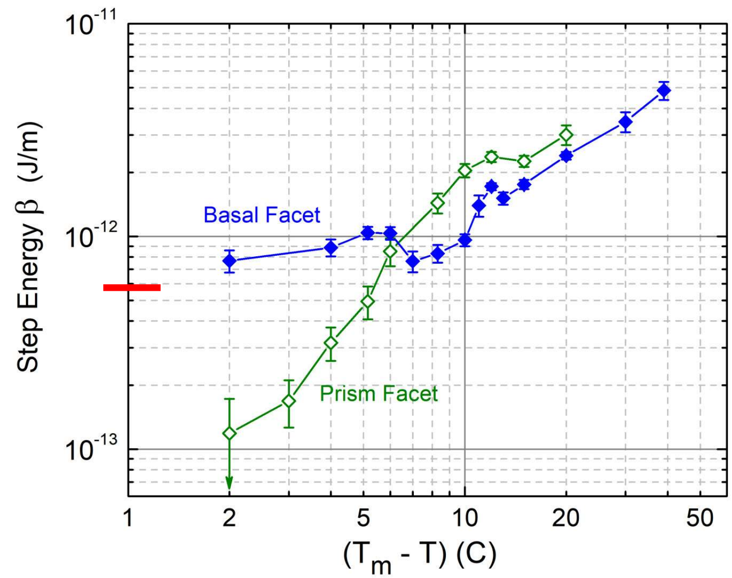






Basal facets



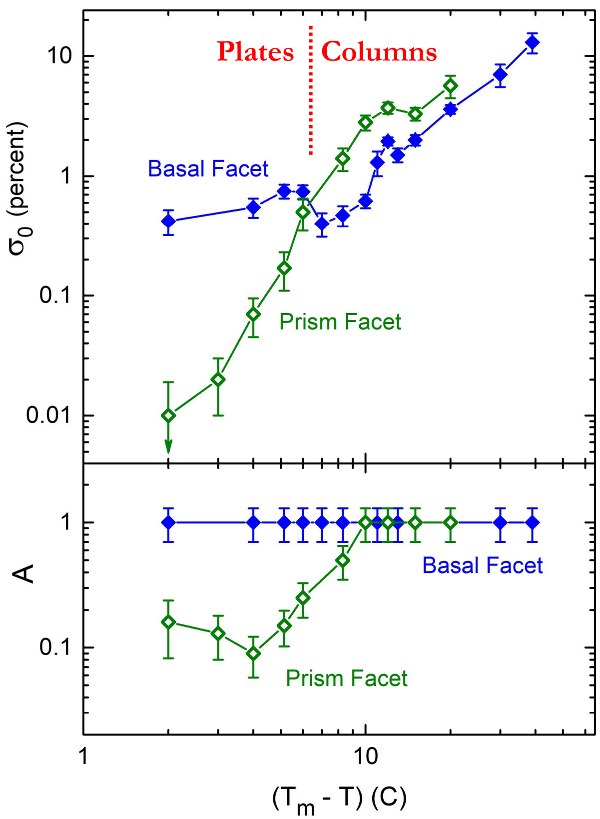


direction
of Crystals
0-360, 1958.

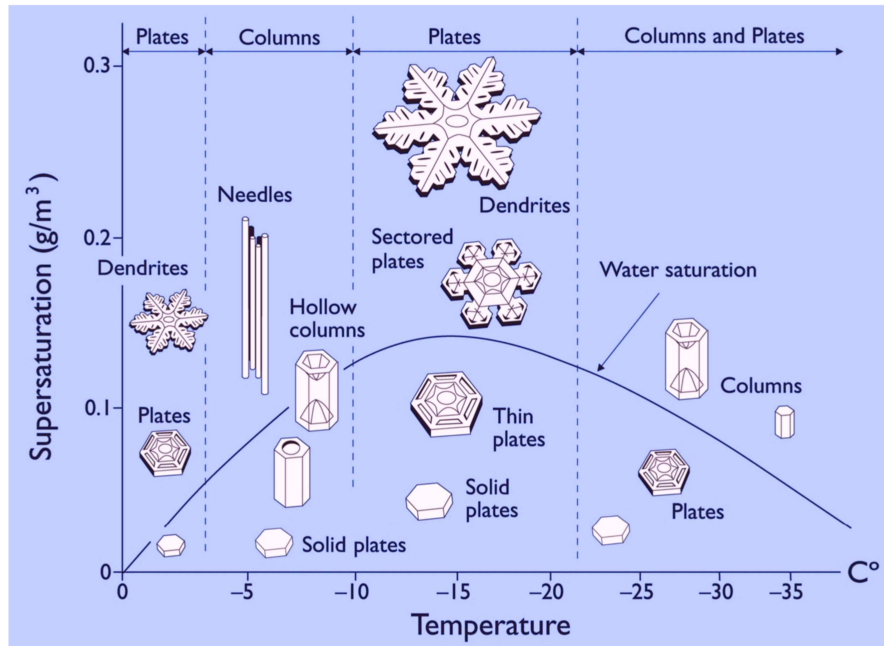
KGL, Toward a comprehensive model of snow crystal growth dynamics: 3. The correspondence between ice growth from water vapor and ice growth from liquid water, arXiv:1407.0740, 2014.

Ice facet growth & the Nakaya diagram

Ice growth in near vacuum



Snow crystal growth in air

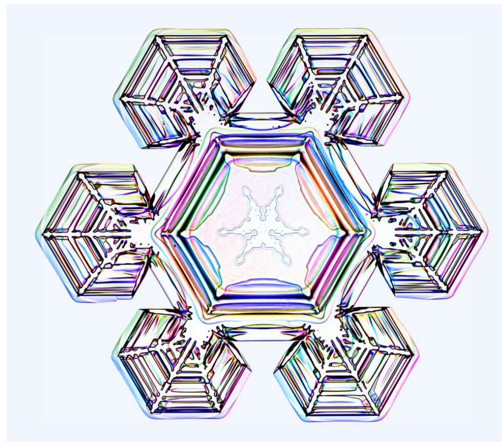


Measurements of facet growth in near-vacuum conditions **cannot** explain essential features of Nakaya diagram…

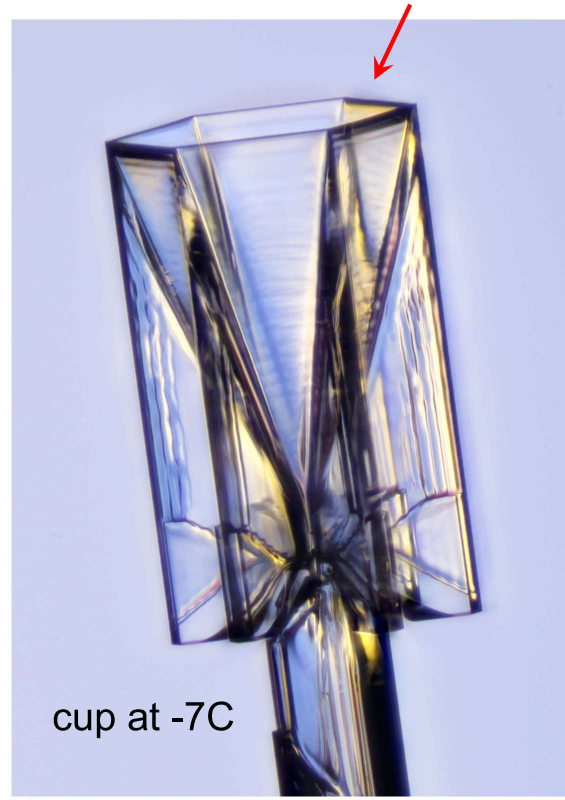
Not diffusion-limited growth; **need new physics in the attachment kinetics**…

A KEY OBSERVATION: Sharp edges exhibit anomalously high attachment kinetics

[1. Rough = fast kinetics] [2. Facets = terrace nucleation] [3. Narrow facets = ???]



sharp edges



plates at -15C

sharp edges

Narrow edge facets; last terrace ~1000 molecules wide

No narrow facets in vacuum

<u>SDAK: Structure Dependent Attachment Kinetics</u>

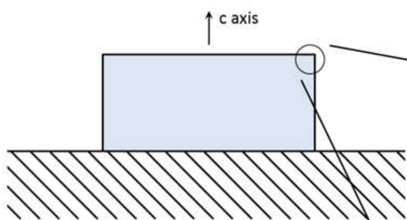
Hypothesis:

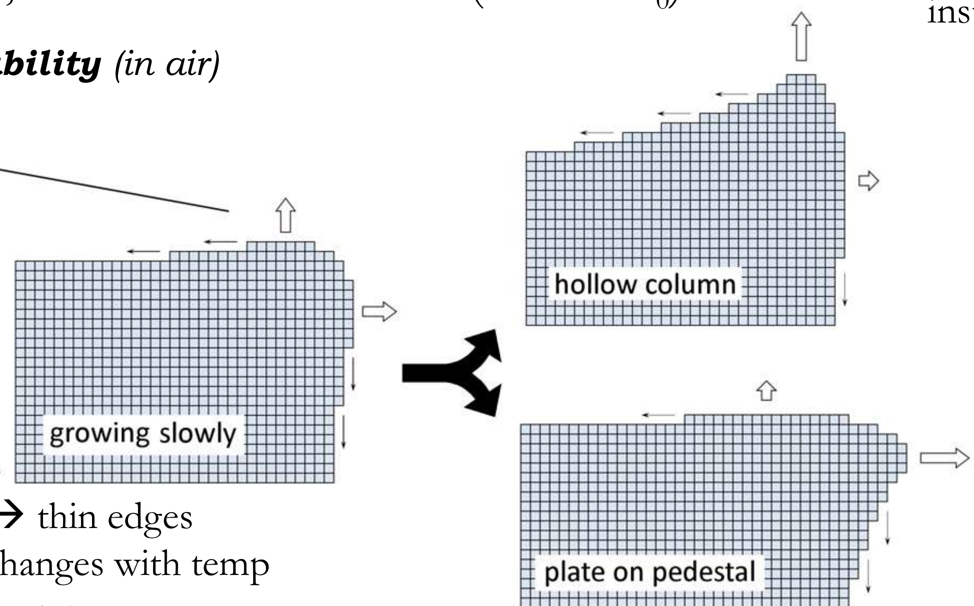
Large facet → normal terrace nucleation model (measured σ_0) … done

Narrow facet (edge) → higher α, smaller nucleation barrier (reduced σ_0)

→ an ***edge-sharpening instability*** *(in air)*

Not the Mullins-Sekerka instability!





Assume SDAK hypothesis…

→ Abrupt changes in *anisotropy* of the attachment kinetics → thin edges

→ Can have abrupt morphological changes with temp

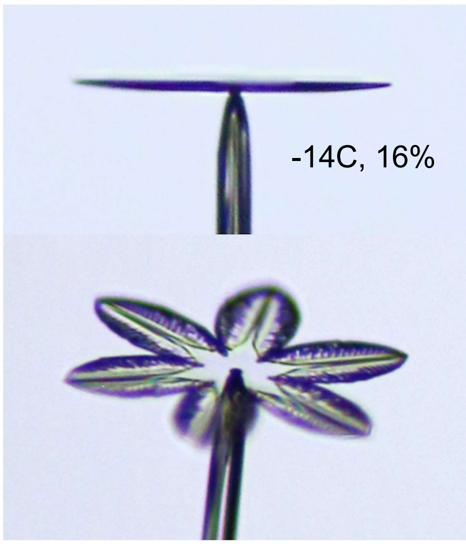
→ Explains this aspect of Nakaya diagram

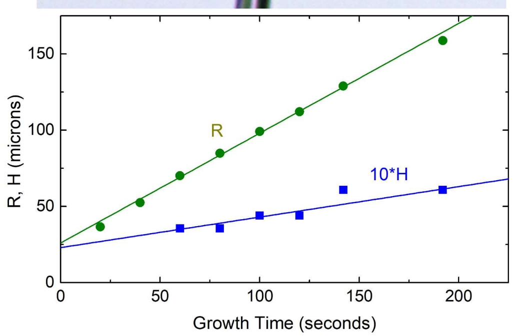
→ Explains why no narrow facets in vacuum

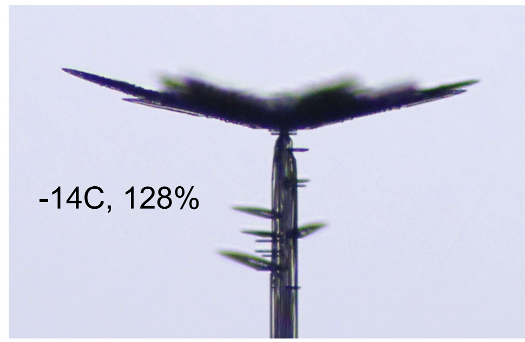
KGL, Explaining the formation of thin ice-crystal plates with structure-dependent attachment kinetics, J. Cryst. Growth 258, 168-175, 2003.

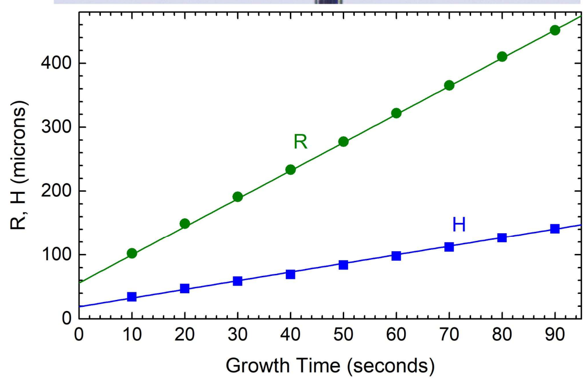
SDAK: Test hypothesis using measurements

Plates on e-needles as function of T and σ_∞









SDAK model predicts:

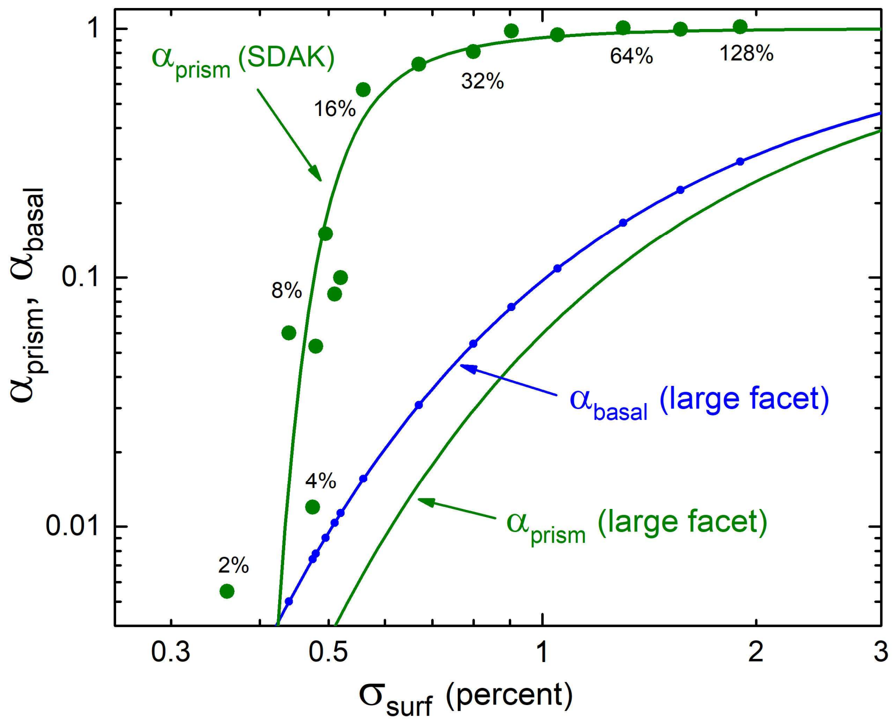
- Basal growth follows terrace nucleation model with known σ_0
- Prism growth has reduced σ_0, $\alpha_{prism} \rightarrow 1$ at high growth rates

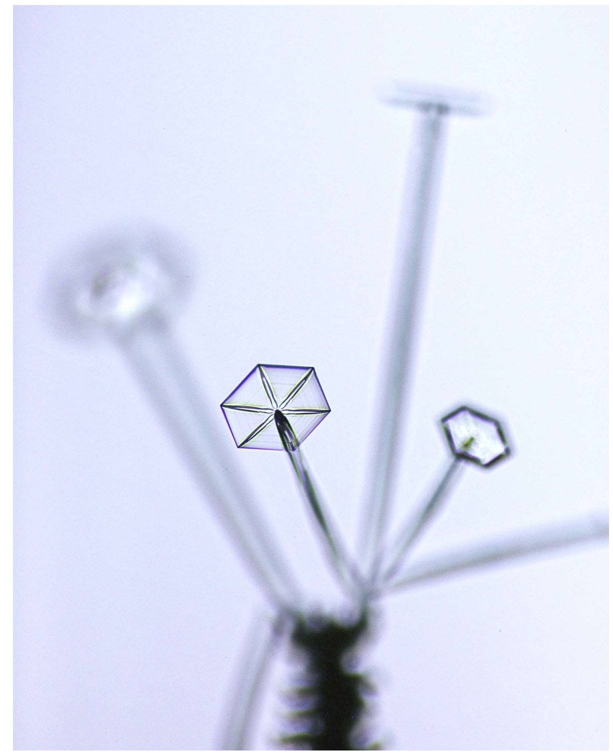
Cannot solve diffusion-limited growth fully…

But can measure ratios using "witness surfaces"

SDAK: Test hypothesis using measurements

Plates on e-needles at $T = -14\,C$ …





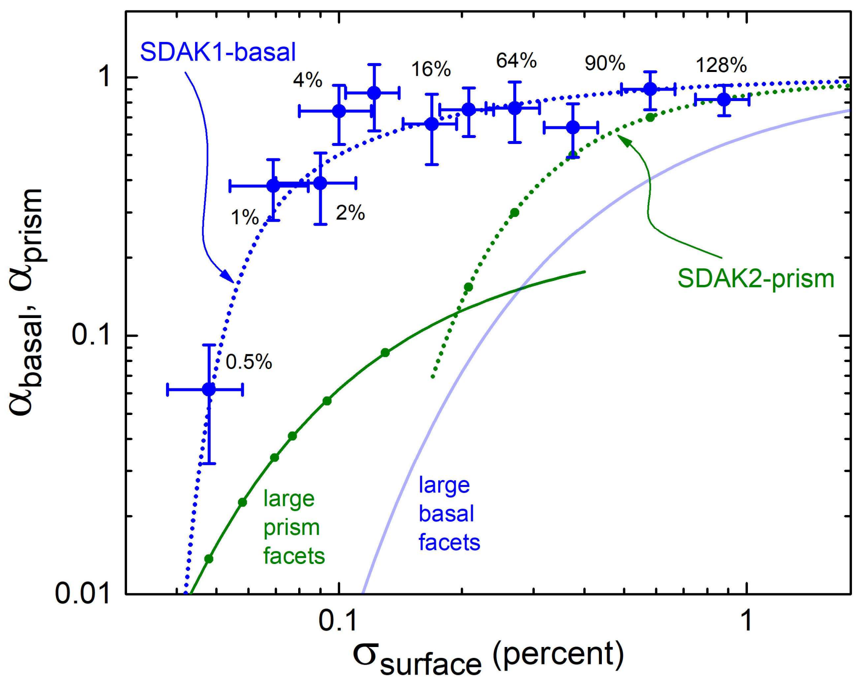
→ Data support SDAK model …

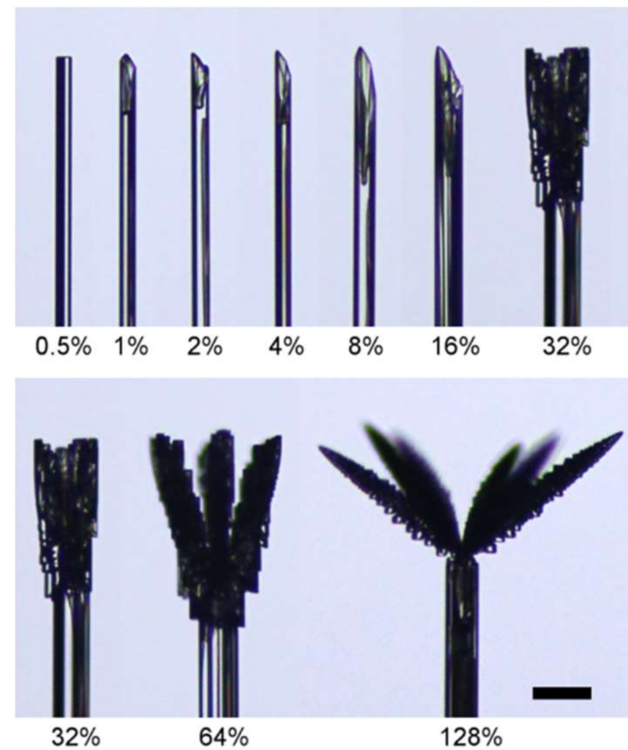
$\alpha_{prism} \to 1$ while α_{basal} fits terrace nucleation model

KGL, Toward a comprehensive model of snow crystal growth: 8. Characterizing structure-dependent attachment kinetics near -14 C, arXiv:2009.08404, 2020.

SDAK: Test hypothesis using measurements

Columns on e-needles at $T = -4\ C$ …





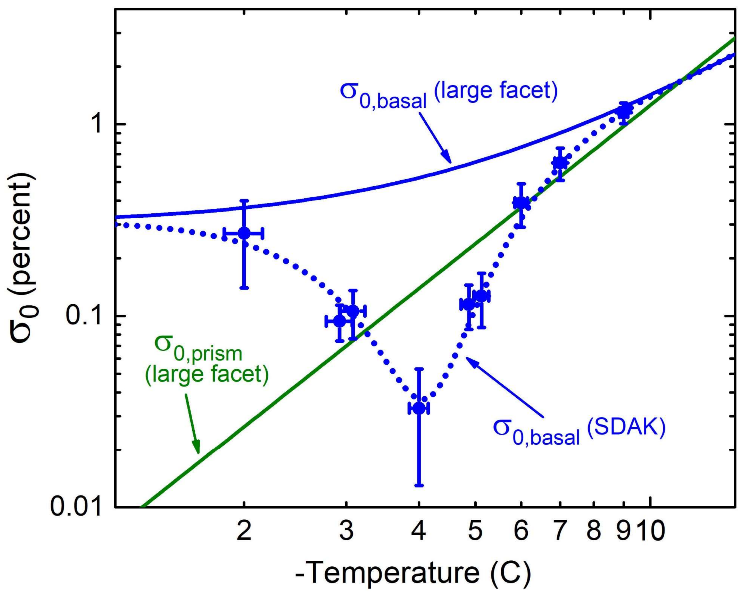
→ Data support SDAK model …

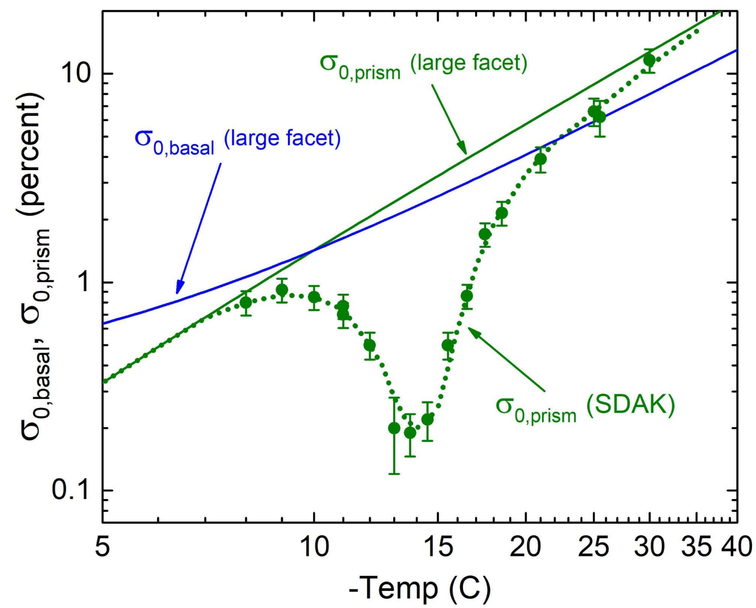
$\alpha_{basal} \rightarrow 1$ while α_{prism} fits terrace nucleation model

KGL, Toward a comprehensive model of snow crystal growth: 9. Characterizing structure-dependent attachment kinetics near -4 C, arXiv:2011.02353, 2020.

SDAK: Test hypothesis using measurements

Putting all the data together → a pair of "SDAK dips"





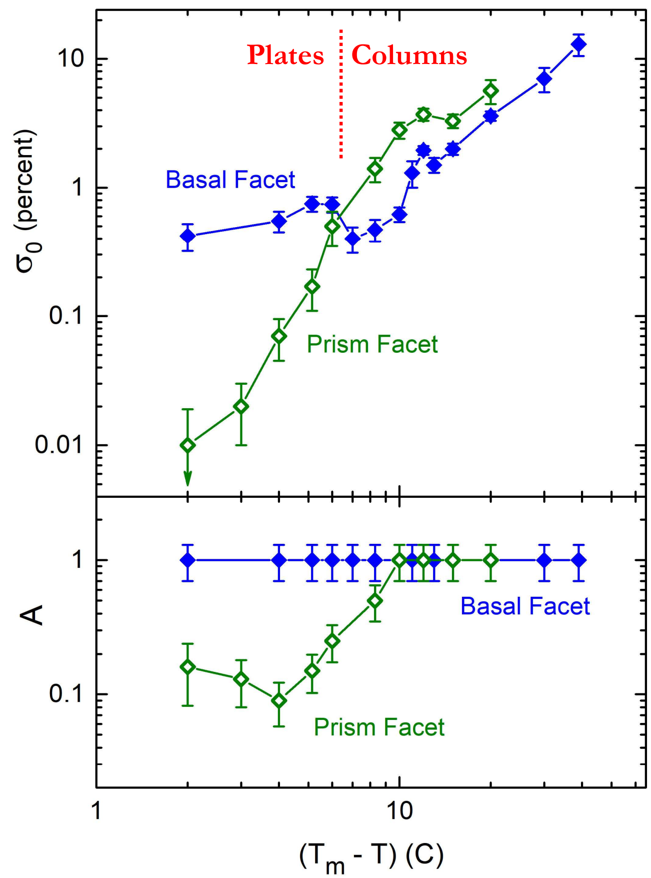
→ Data support fundamental tenet of SDAK model:

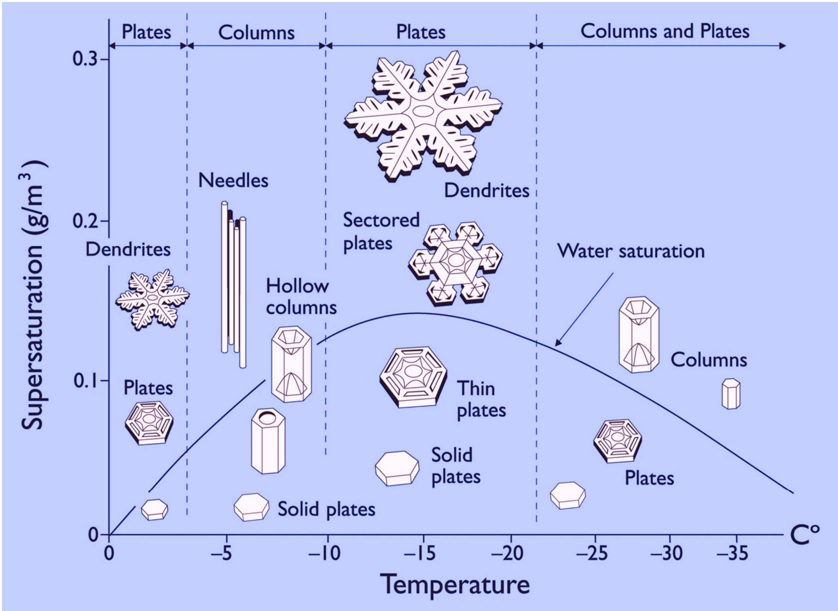
Narrow basal facets grow anomalously fast near -4C (model with small nucleation barrier $\sigma_{0,basal}$)

Narrow prism facets growth anomalously fast near -14C (model with small nucleation barrier $\sigma_{0,prism}$)

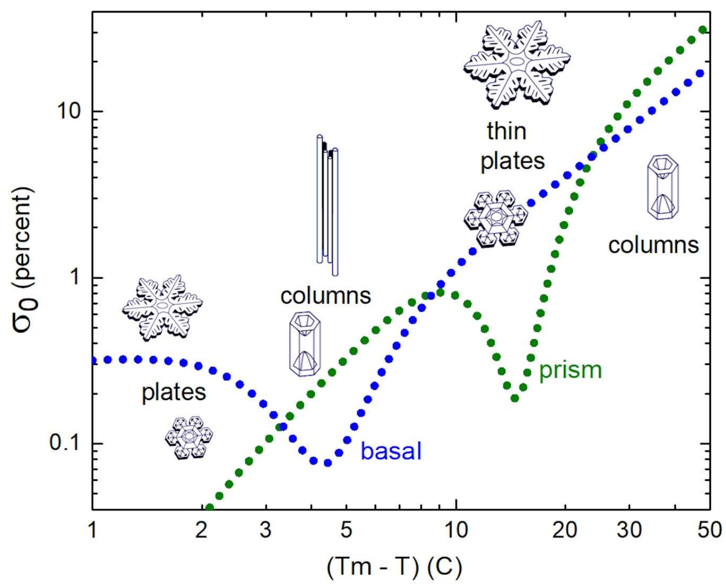
The SDAK model & the Nakaya diagram

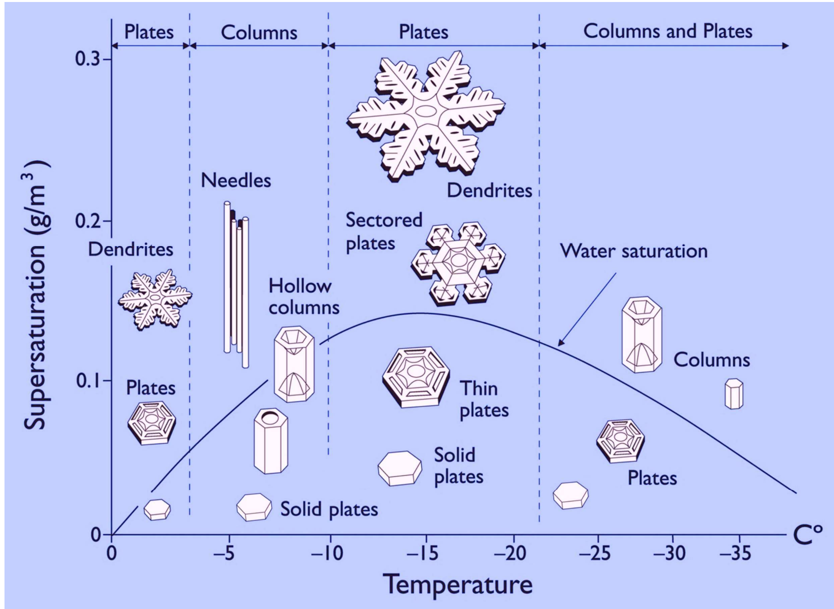
Large facets only: not enough:





THE SDAK MODEL & THE NAKAYA DIAGRAM

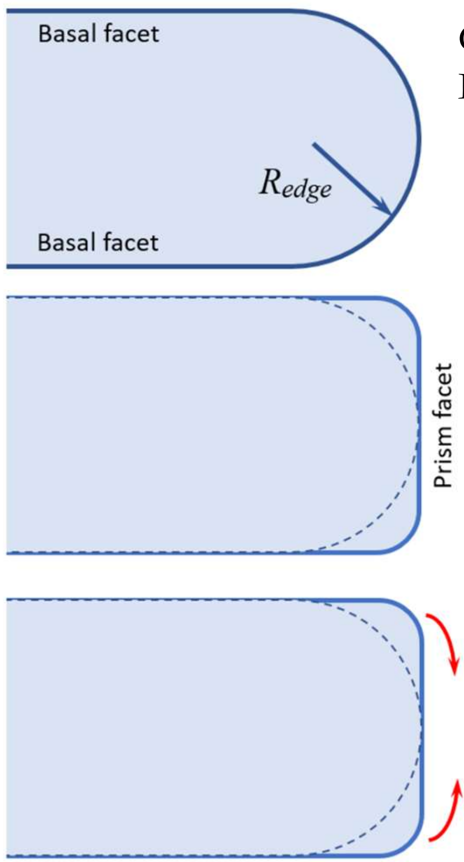




Add the SDAK dips → Can explain the full Nakaya diagram
… and broad facet growth, and air-pressure dependence …
Best model we have so far…

At this point, still a *semi-quantitative* model, based solely on observations …
What is physical mechanism responsible for the SDAK effect?

SDAK: A physical model



Consider the edge of a platelike snow crystal

Low supersaturation → basal surfaces do not grow appreciably

→ rounded prism edge ~stable equilibrium

Increase supersaturation slightly

→ corners become less rounded

→ surface energy out of equilibrium

Allow surface admolecule diffusion (to prism surface only)

→ energetically favorable to move molecules to prism facet

→ prism admolecule density anomalously high (if narrow facet)

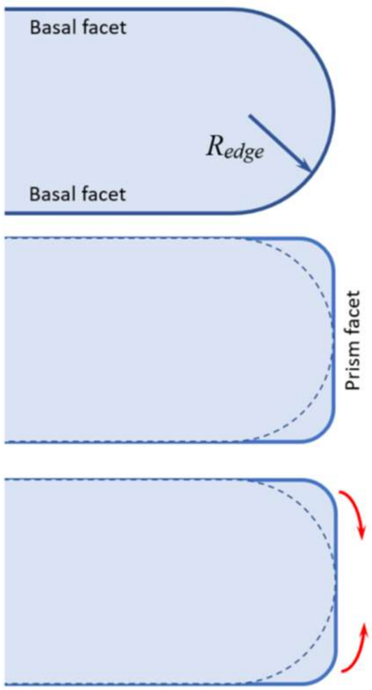
→ enhances terrace nucleation

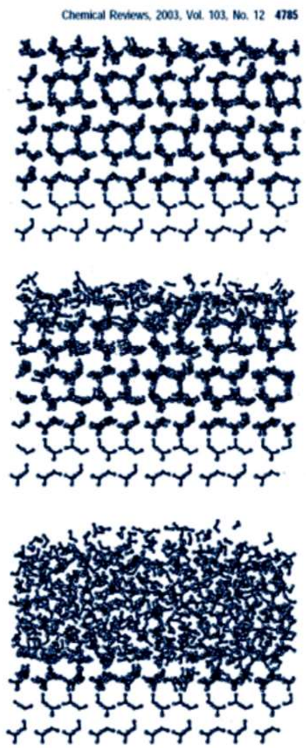
→ lowers effective $\sigma_{0,prism}$ (but only on narrow prism facets)

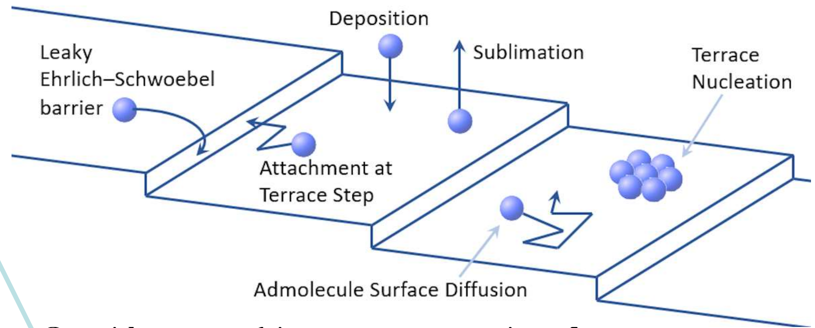
→ SDAK effect!

KGL, A quantitative physical model of the snow crystal morphology diagram, arXiv:1910.09067, 2019.

SDAK, surface premelting, & the Ehrlich-Schwoebel barrier







Consider premelting on narrow prism facet
No premelting → solid surface → no E-S jumps
→ little surface diffusion

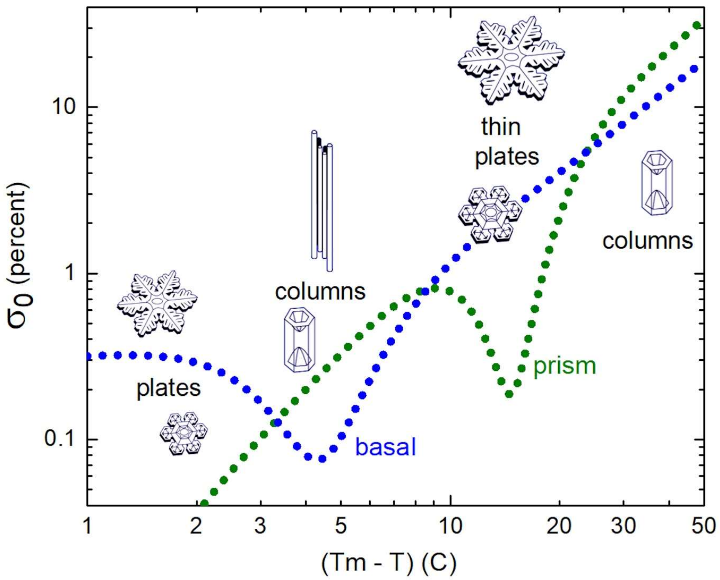
Strong premelting → lots of surface diffusion
But has little effect on terrace nucleation at QLL/ice

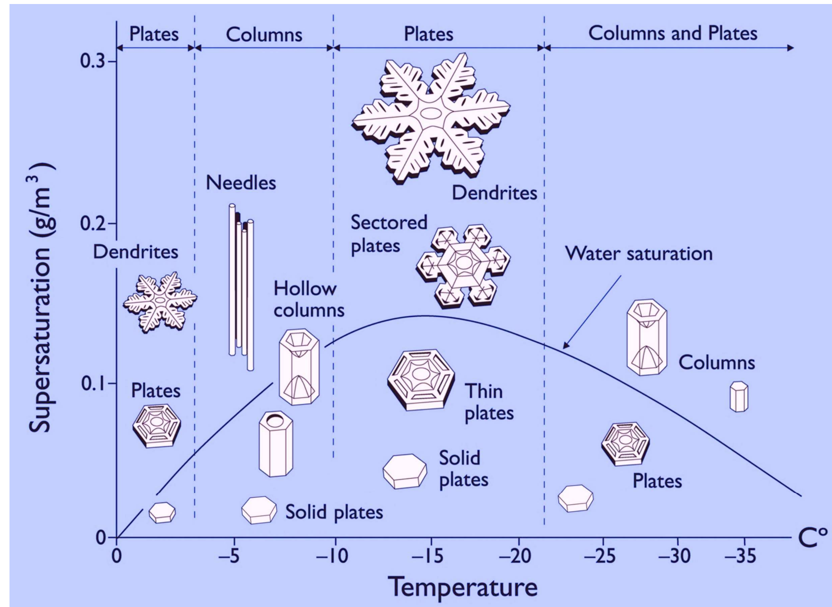
***Onset* of premelting** → low E-S barrier
→ surface diffusion
→ and decreases effective nucleation barrier

Final Result: a *plausible* physical mechanism for the SDAK phenomenon
To complete the picture: ***Postulate* onset of prism premelting at -14C, onset of basal premelting at -4C**

KGL, A quantitative physical model of the snow crystal morphology diagram, arXiv:1910.09067, 2019.

The SDAK model & the Nakaya diagram



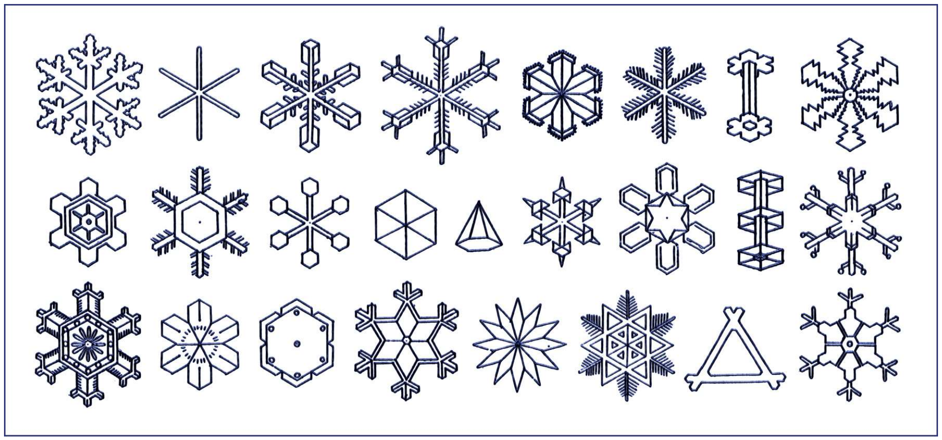


SDAK dips → Can explain the full Nakaya diagram
Plausible physical mechanism based on generally well-accepted physical assumptions
Explains why high anisotropy not seen in low-pressure growth

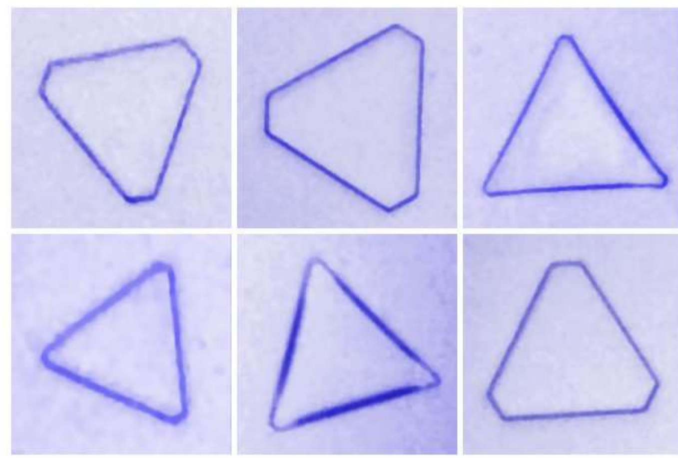
SDAK model makes lots of predictions … suggests targeted experiments
Other explanations of the Nakaya diagram? None that fit the existing quantitative data ….
"Something else" makes no useful predictions…

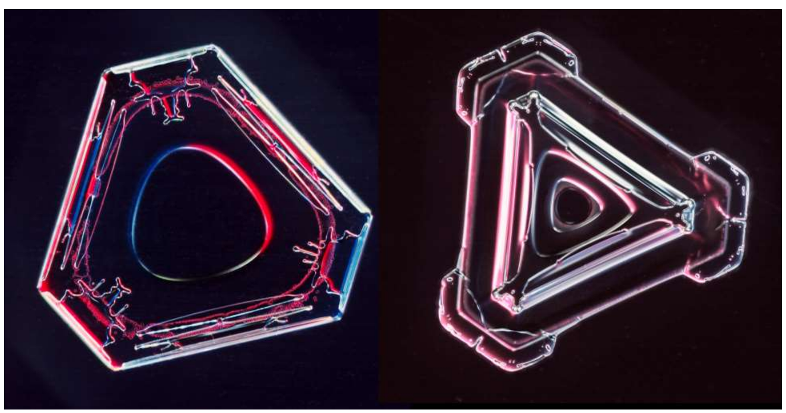
EXPLAINING TRIANGULAR SNOW CRYSTALS

Another old puzzle…



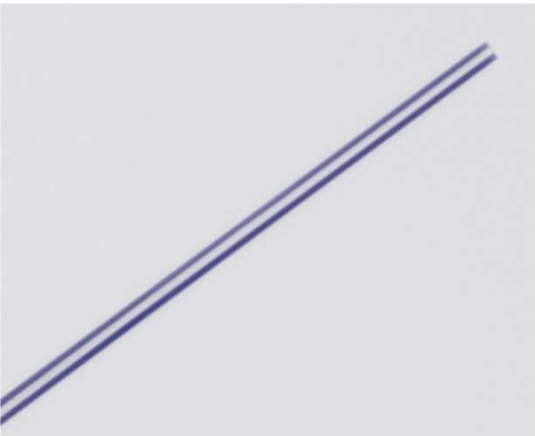
William Scoresby, An Account of the Arctic Regions with a History and Description of the Northern Whale-Fishery, Edinburgh, 1820.

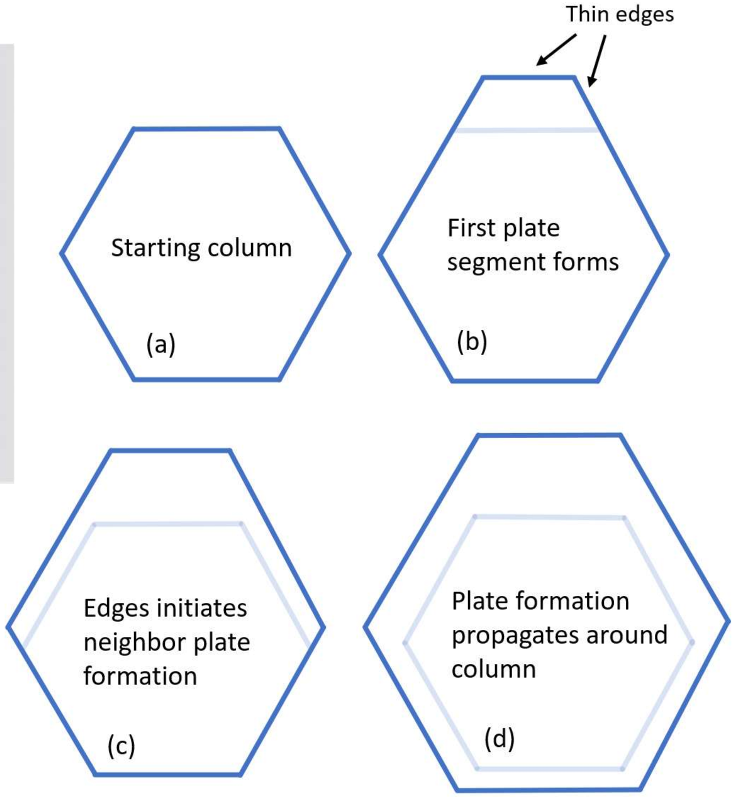




Explaining triangular snow crystals

Consider the formation of plates on electric needles…

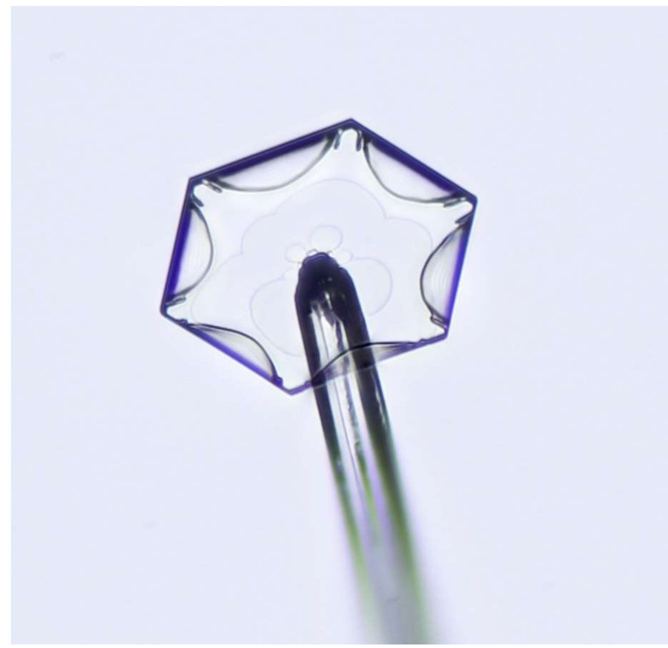




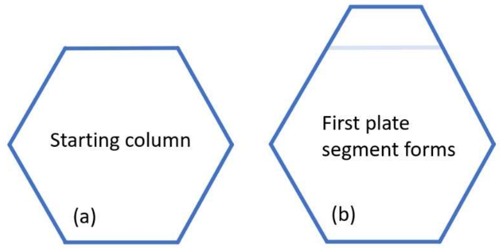
Fast growth

Edge-Sharpening Instability***
propagates around column…

→ Full hexagonal plate grows from columnar tip



Explaining triangular snow crystals – Validates SDAK model

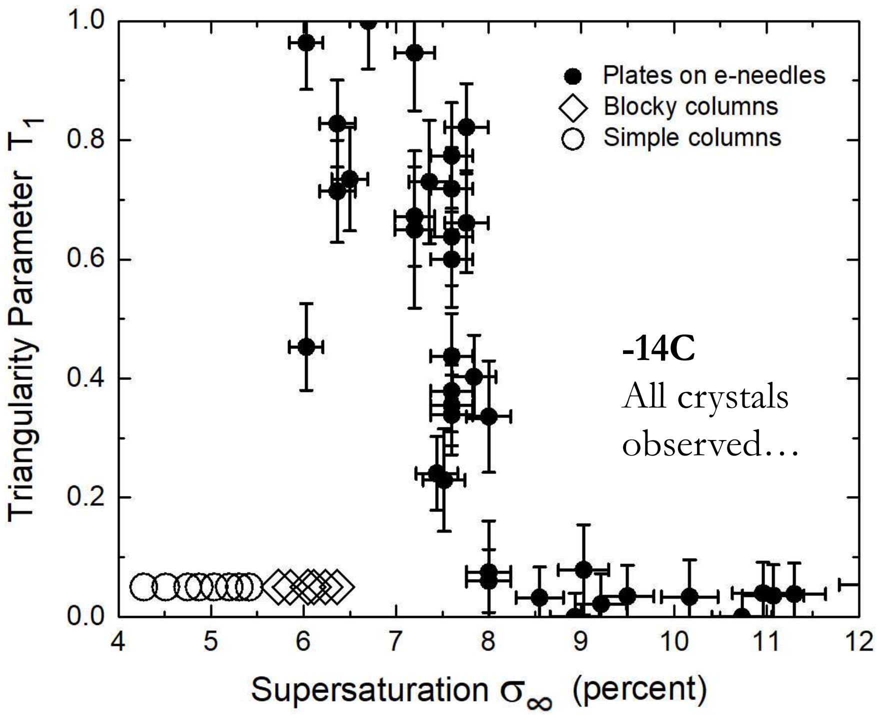


Slow growth

Edge-Sharpening Instability barely functions

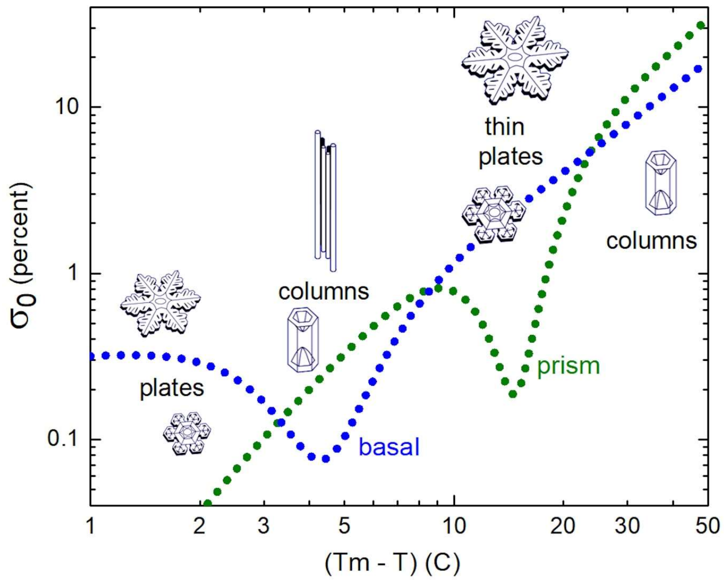
→ propagates ***slowly*** around column…

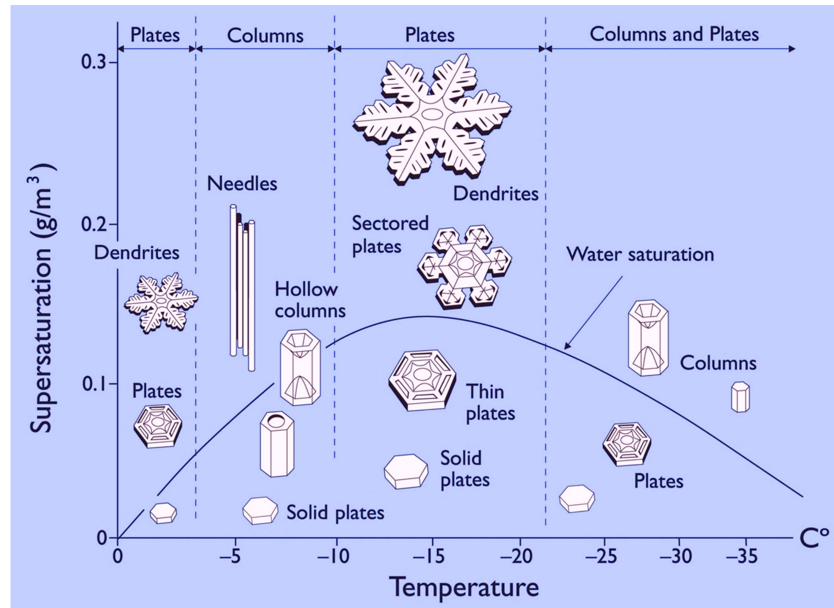
→ Triangular plate



First on-demand triangular snow crystals!

The SDAK model & the Nakaya diagram





SDAK dips → Can explain the full Nakaya diagram
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Explains why high anisotropy not seen in low-pressure growth

SDAK model makes lots of predictions … suggests more targeted experiments
Other explanations of the Nakaya diagram? None that fit the existing quantitative data ….

Not the last word … but the start of an interesting dialog! (see Lecture 3)

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I should hardly admire more if real sta
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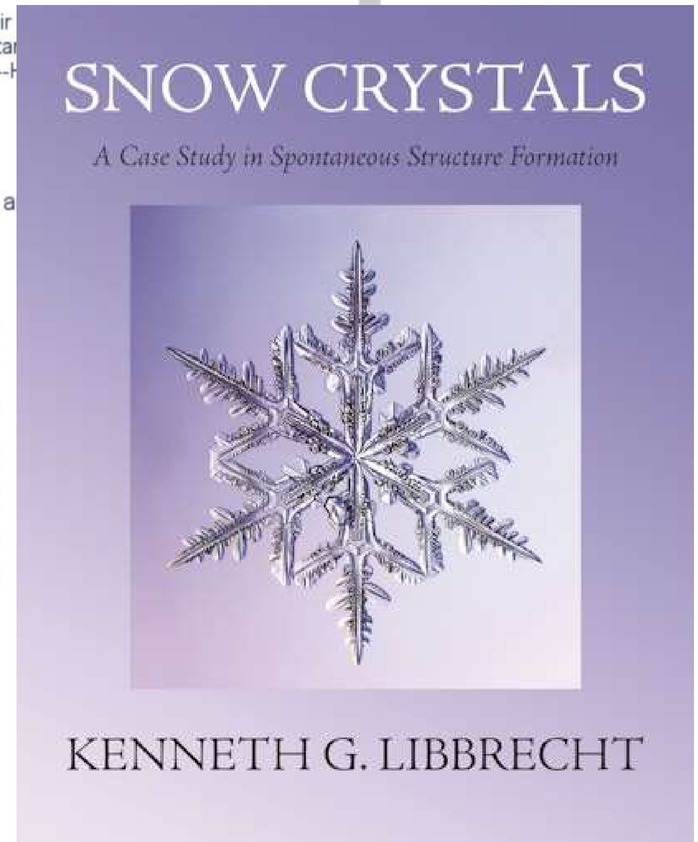
-15°C
???
<< Check out this entertaining YouTube video about snow-crystal science, made by the good folks at Veritasium.
>> You can find the FULL story about the science of snow crystal formation in my magnum opus at right (weighting in at 456 pages)



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