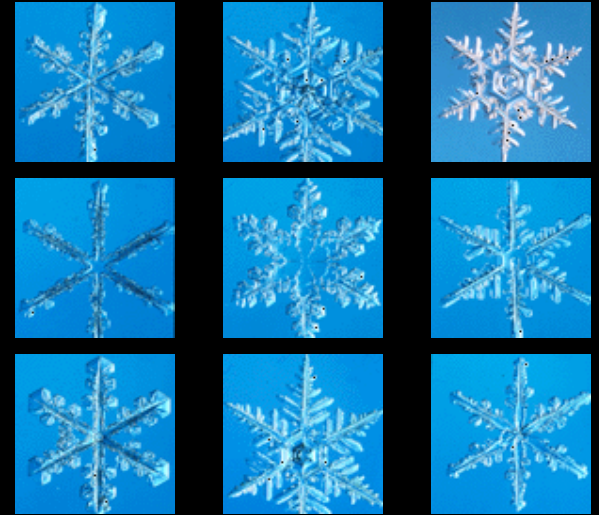
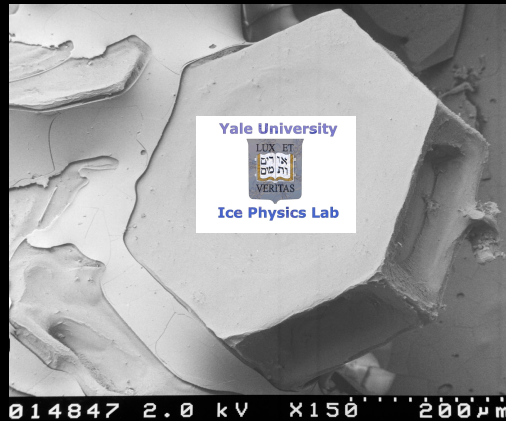
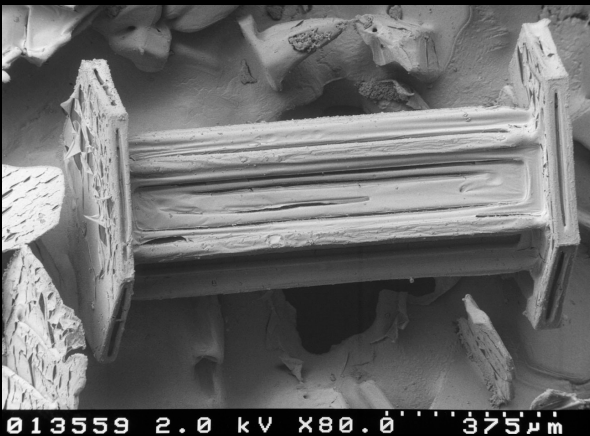


# THE QUANTUM ELECTRODYNAMICS OF SNOWFLAKES, ICE SKATING, EXOBIولوجY & OTHER SUCH MATTERS



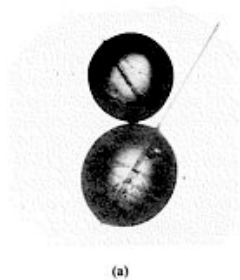
Y. Furukawa



J.S. Wettlaufer  
Yale University  
& Nordita



*September 8, 1842: Michael Faraday (1791-1867) initiates scientific investigation into what we now know as surface melting.*



(a)



(b)

- *“When wet snow is squeezed together, it freezes into a lump (with water between) and does not fall asunder as so much wetted sand or other kind of matter would do.”*
- *“All this seems to indicate that water at 32°F will not continue as water, if it be between two surfaces of ice touching or very near to each other.”*
- *“The ice probably acts as a nucleus, but it appears that the effect of one surface of ice on water is not equal to the joint effect of two.”*

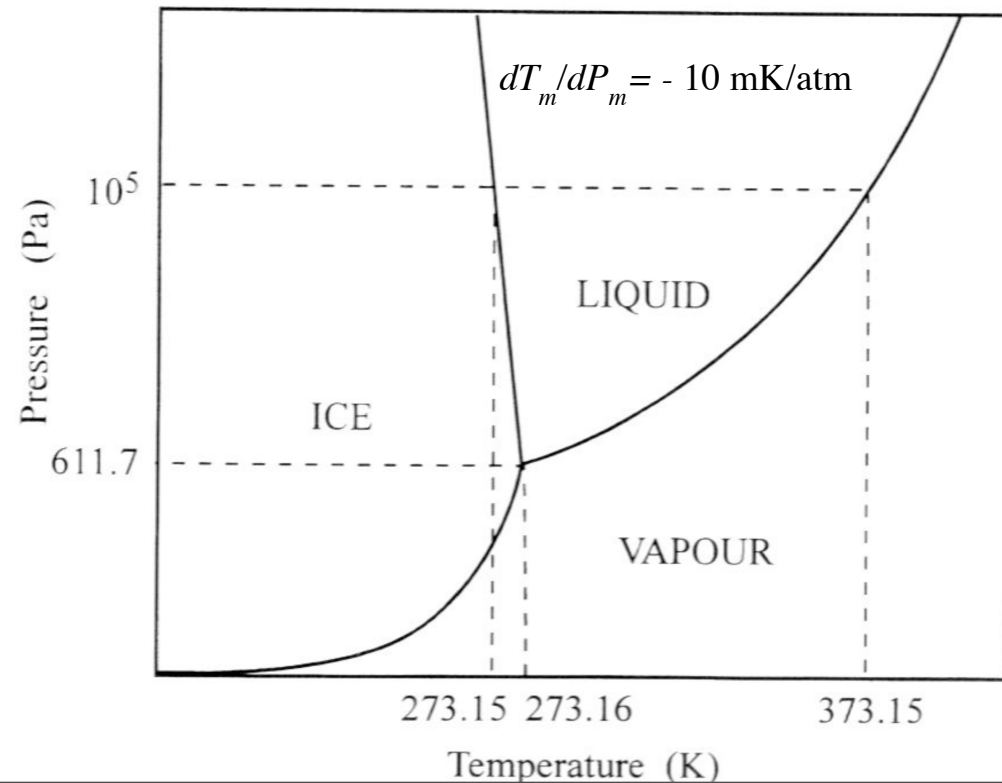
1822–1892

*James Thomson predicted (1849) and showed that ice melts under pressure.*

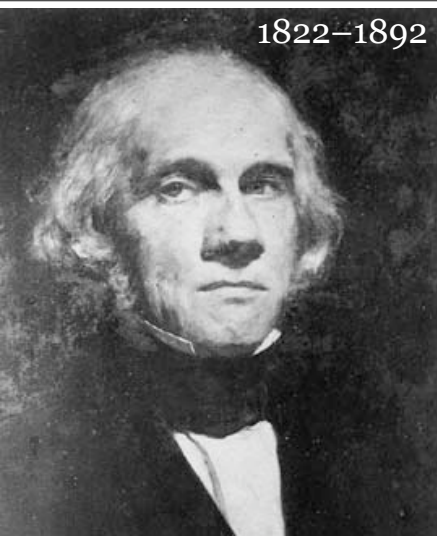
*William Thomson (later Lord Kelvin) communicated his brother's interpretation of Faraday's experiments to the Royal Society on 25 April, 1861*

*“I think the experiments are in perfect accordance with my own theory, and tend to its confirmation.”*

1824 – 1907



1822–1892



*James Thomson predicted (1849) and showed that ice melts under pressure.*

*William Thomson (later Lord Kelvin) communicated his brother's interpretation of Faraday's experiments to the Royal Society on 25 April, 1861*

1824 – 1907

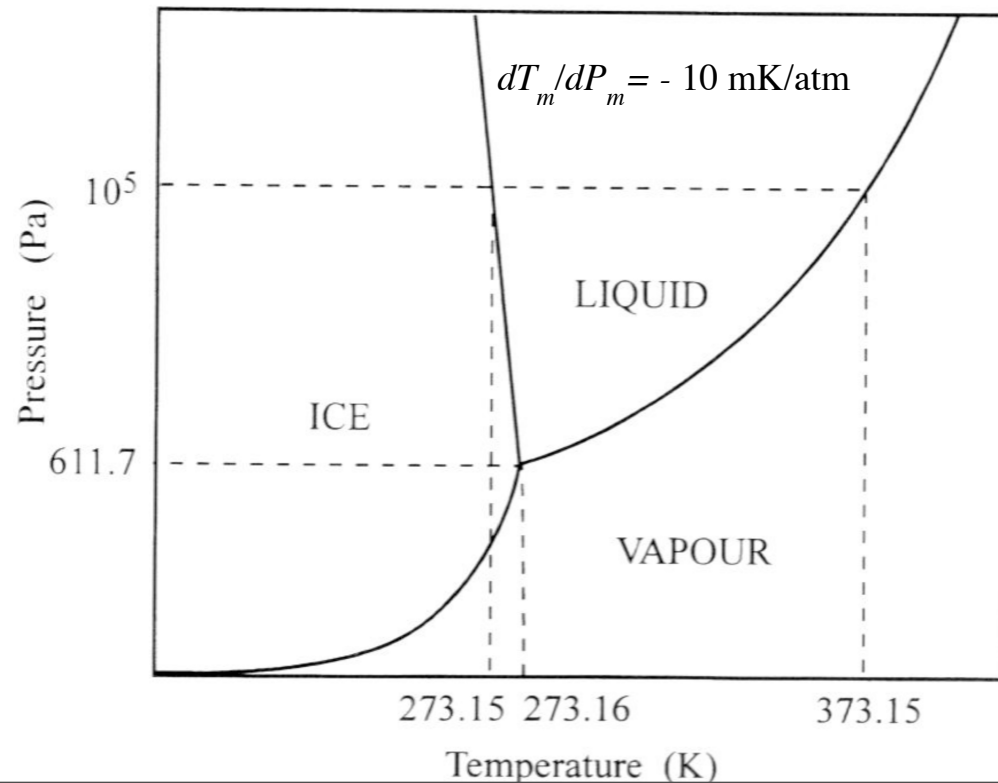


*“I think the experiments are in perfect accordance with my own theory, and tend to its confirmation.”*

In 1900 Kelvin proclaimed:

"There is nothing new to be discovered in physics now. All that remains is more and more precise measurement."

& “X rays are a hoax.”



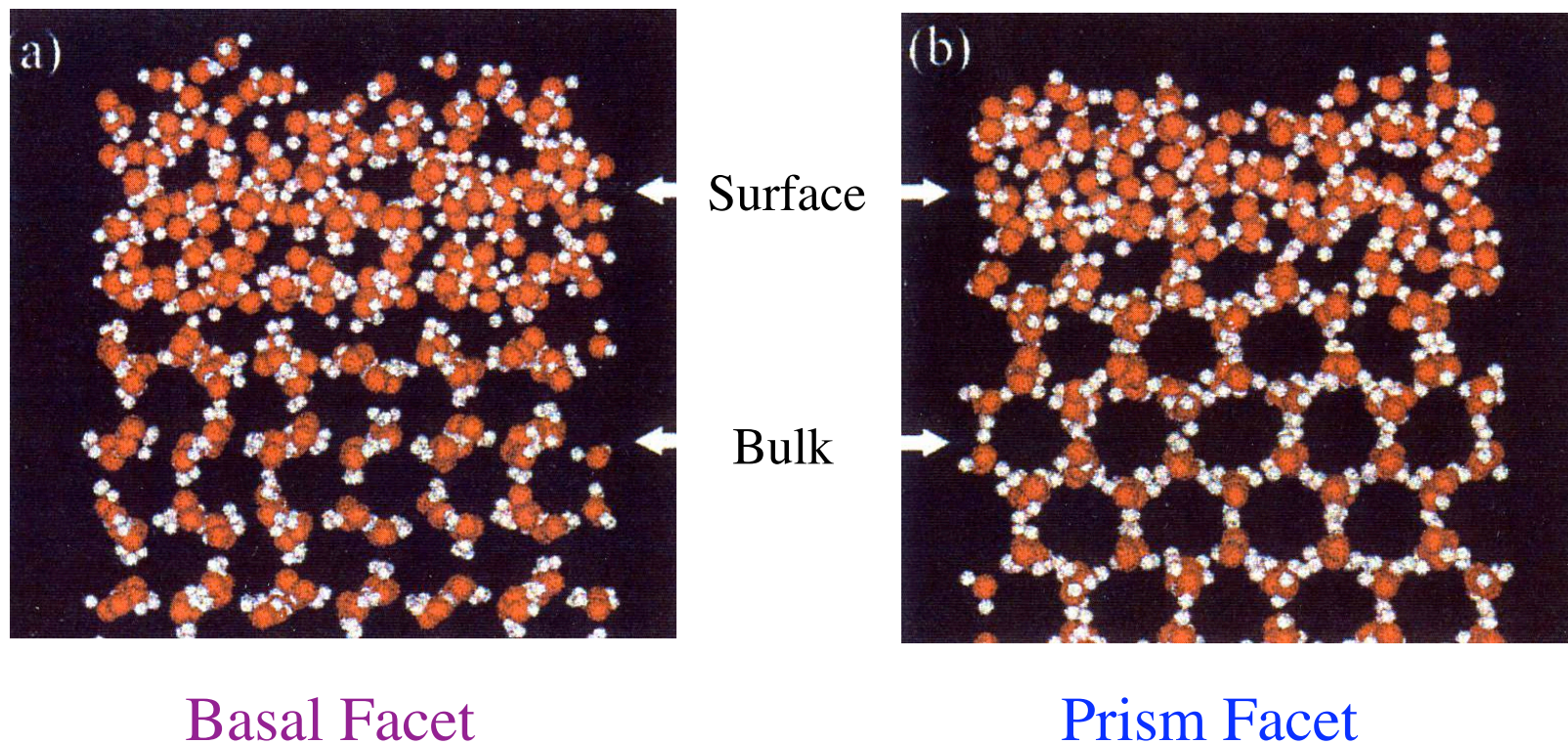


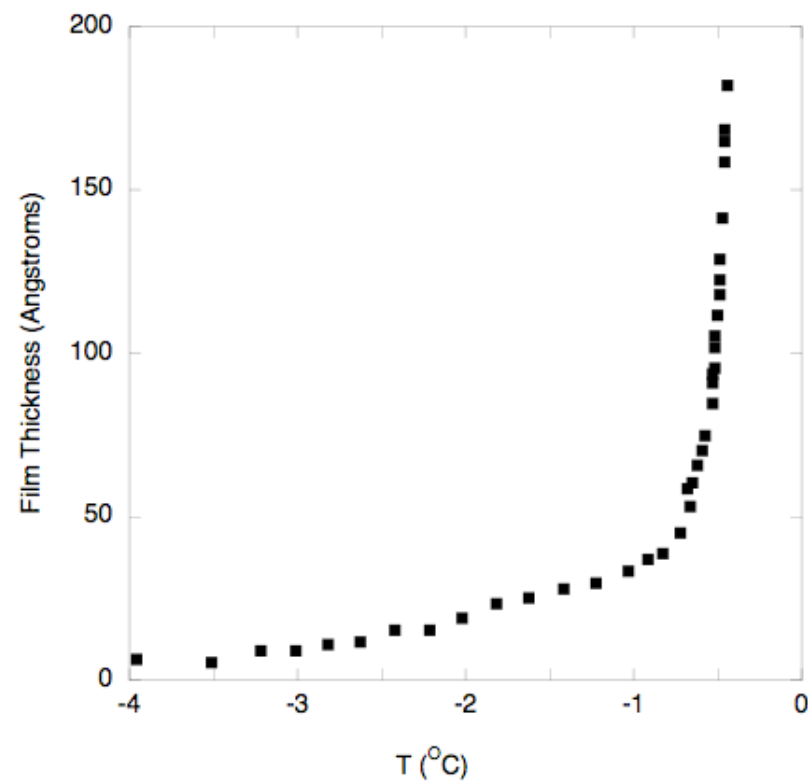
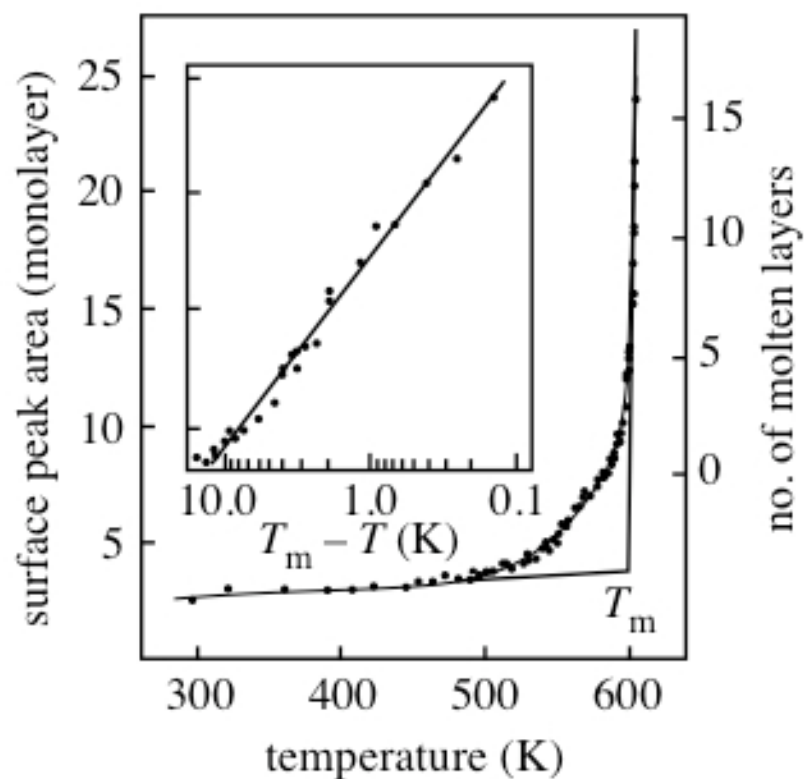
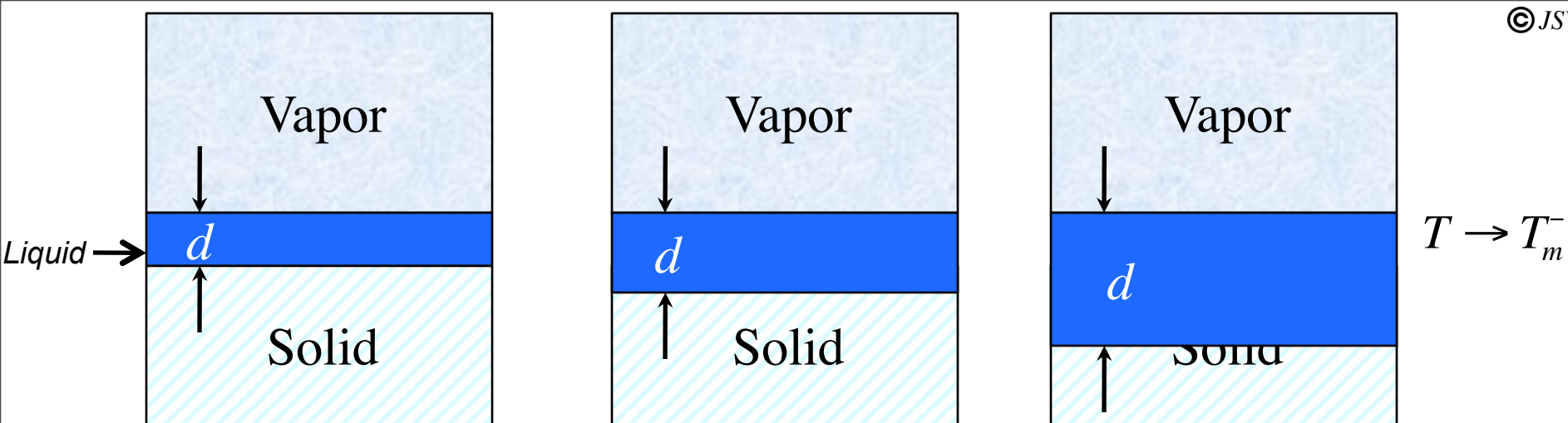
# MELTING BELOW ZERO

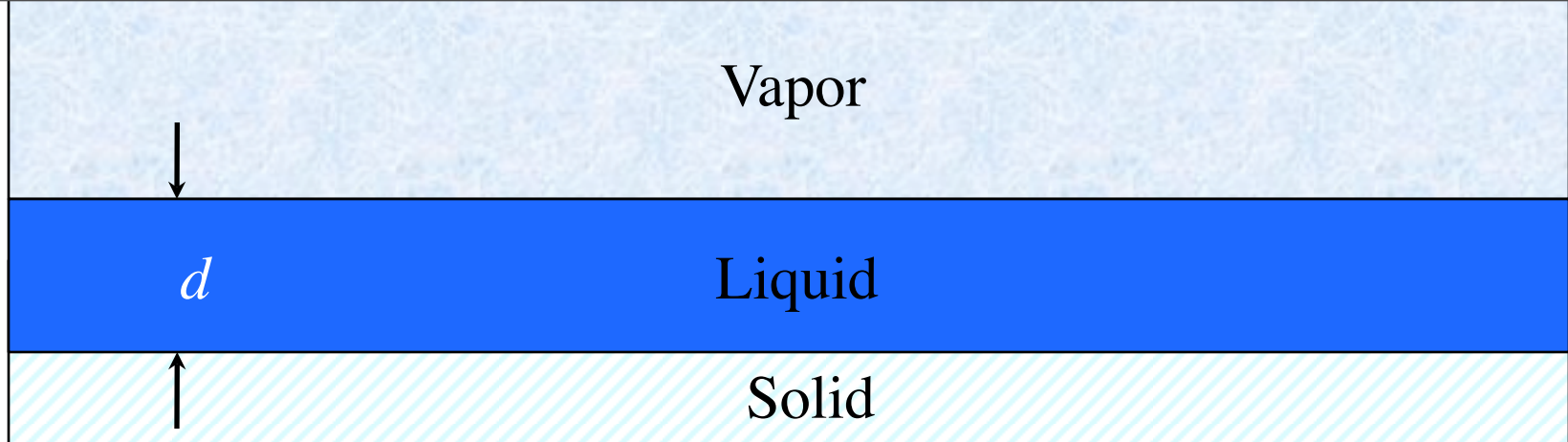
*New research shows how a layer of water on the surface of ice— even at temperatures well below freezing—can account for everything from the slipperiness of a skating rink to the electrification of thunderclouds*

by John S. Wettlaufer and J. Greg Dash

*Missing Bonds at the Surface: Greater Vibrational Anharmonicity than in the bulk...*

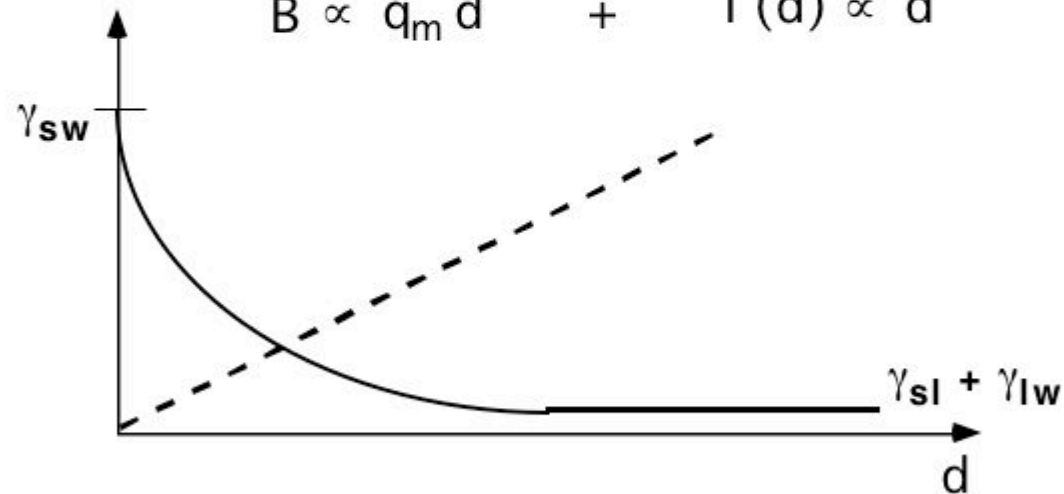






$$\Omega = \text{BULK} + \text{INTERFACIAL}$$

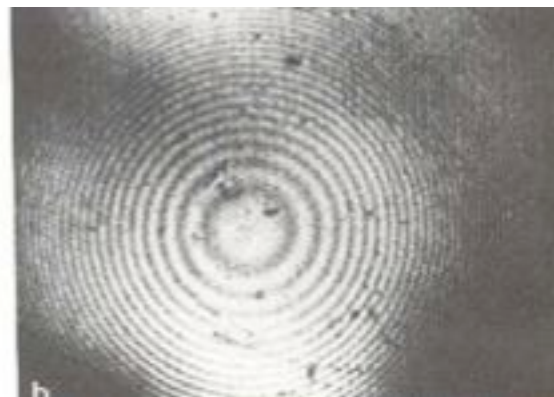
$$B \propto q_m d + I(d) \propto d^{-n}$$



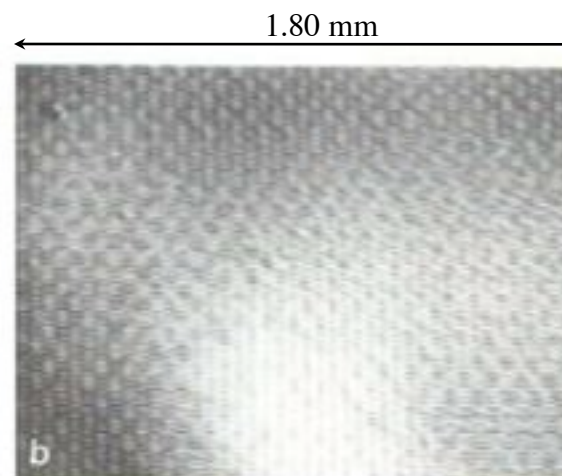
Minimizing  $\Omega$

$$\Rightarrow (1) \quad P_l - P_s = I'(d)$$

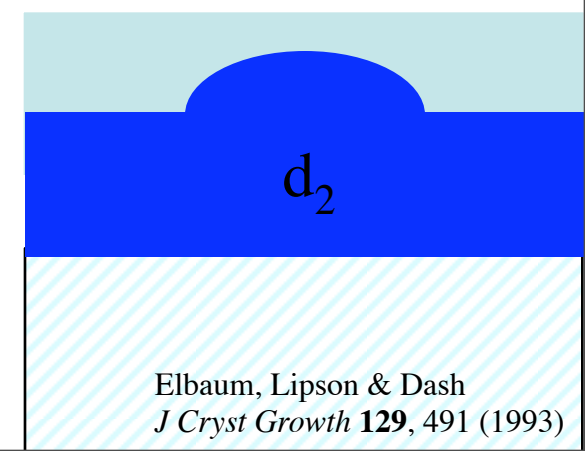
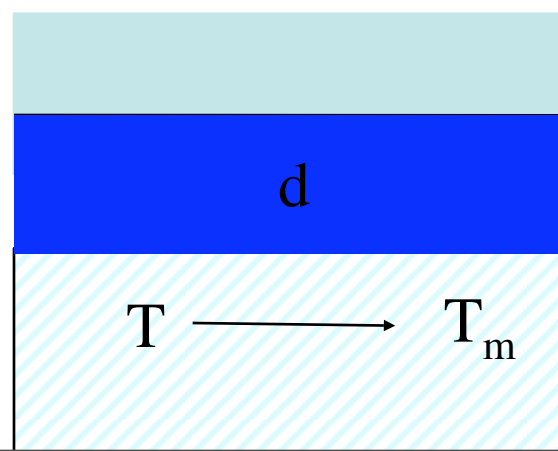
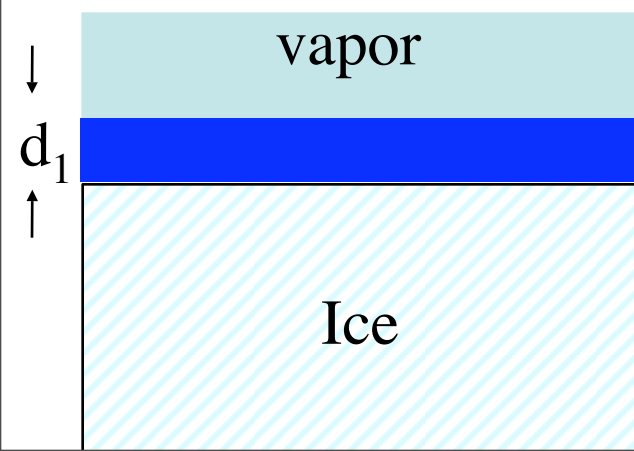
$$(2) \quad d = \lambda (1 - T/T_m)^{\frac{-1}{n+1}}$$



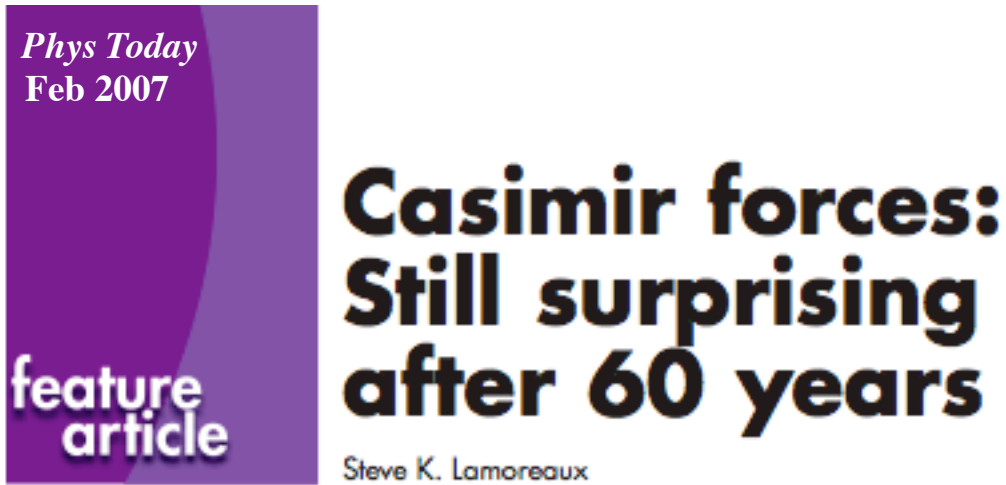
Basal



Vicinal



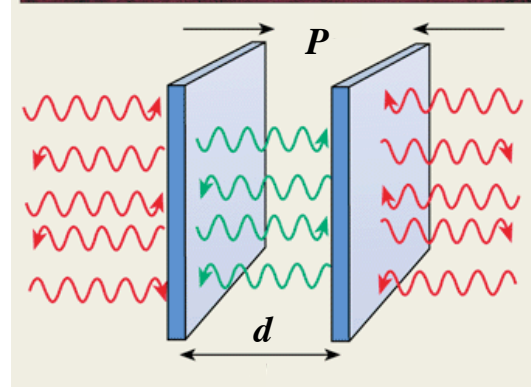
# Mayonnaise, Paint, Gecko's and Vacuum Fluctuations: Casimir, London, Overbeek & Polder (1948)



The once startling idea of a connection between quantum fluctuations and forces has by now been applied throughout physics. Nonetheless, experimentalists and theorists alike still find challenges in the Casimir force.

$$V(r) = -\frac{23\alpha_1\alpha_2\hbar c}{4\pi} \frac{1}{r^7}$$

$$\Rightarrow P(d) = \frac{C}{d^4}$$



$$C = 0.16\mu N(cm^4)cm^{-2}$$

$$d = \text{mm}, A = 1 \text{ cm}^2: F = 10^{-7} \text{ N}$$

Dzyaloshinskii, Lifshitz and Pitaevski, *Adv. Phys.* **10**, 165 (1961).

make precise the intuition that a  
 fluid less polarizable than its solid  
 will be **attracted** to it

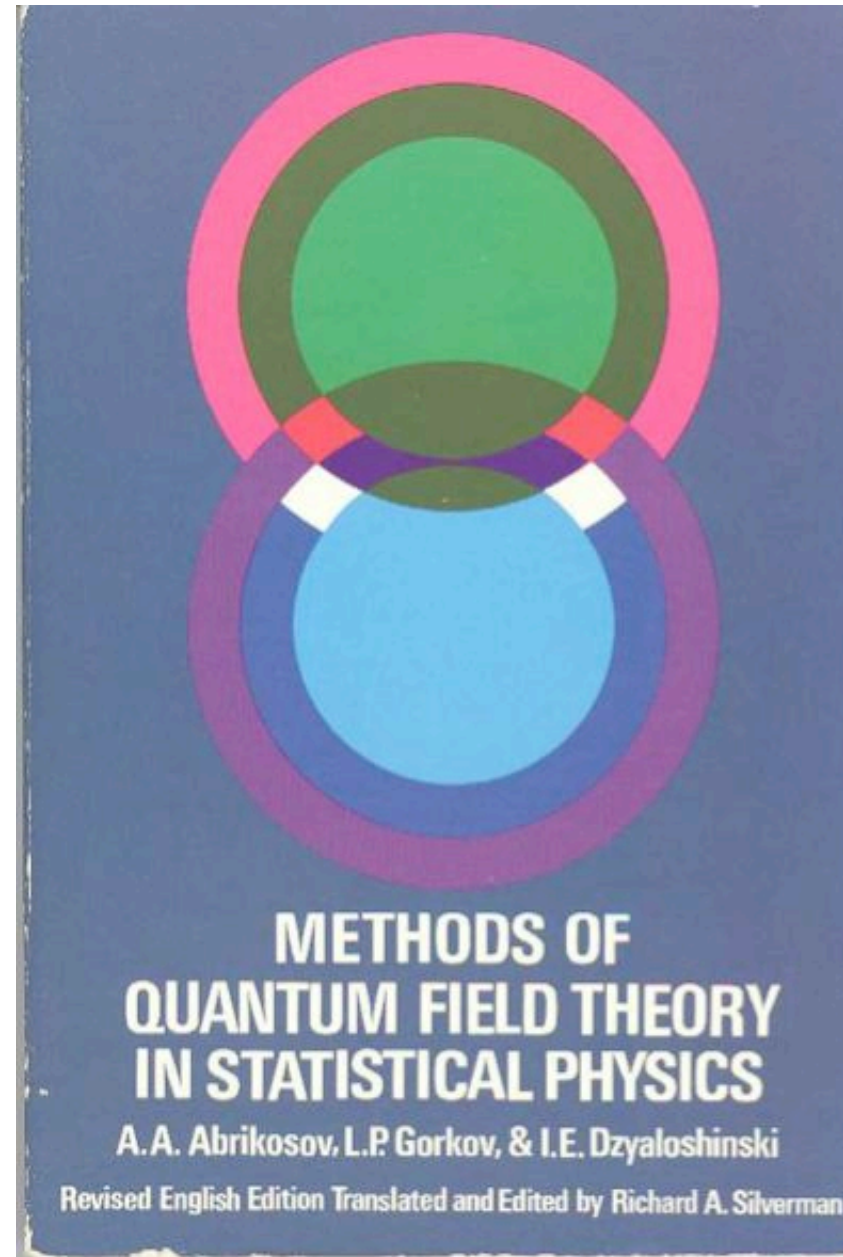
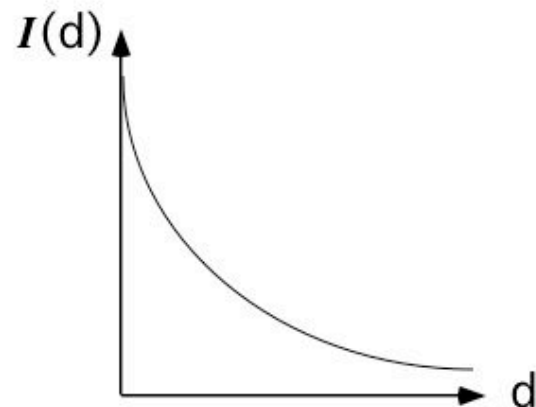


Film growth favored:

$$\epsilon_1 < \epsilon_2 < \epsilon_3$$

$$\epsilon_1 > \epsilon_2 > \epsilon_3$$

Embodied in Interfacial Free Energy  $I(d)$



$$I(d) = \frac{k_b T}{8\pi d^2} \sum_{n=0}^{\infty} \int_{r_n}^{\infty} \left[ \ln \left( 1 - \frac{(x - x_i)(x - x_s)}{(x + x_i)(x + x_s)} e^{-x} \right) \right.$$

$$\left. + \ln \left( 1 - \frac{(\epsilon_s x - \epsilon_w x_s)(\epsilon_i x - \epsilon_w x_i)}{(\epsilon_s x + \epsilon_w x_s)(\epsilon_i x + \epsilon_w x_i)} e^{-x} \right) \right] dx, \quad \text{where}$$

$$r_n = 2d\sqrt{\epsilon_w} \xi_n / c, \quad i\xi_n = i(2\pi kT / \hbar)n$$

$$x_j = \left[ x^2 - r_n^2 \left( 1 - \frac{\epsilon_j}{\epsilon_w} \right) \right]^{1/2} \quad \text{with} \quad j = i, s$$

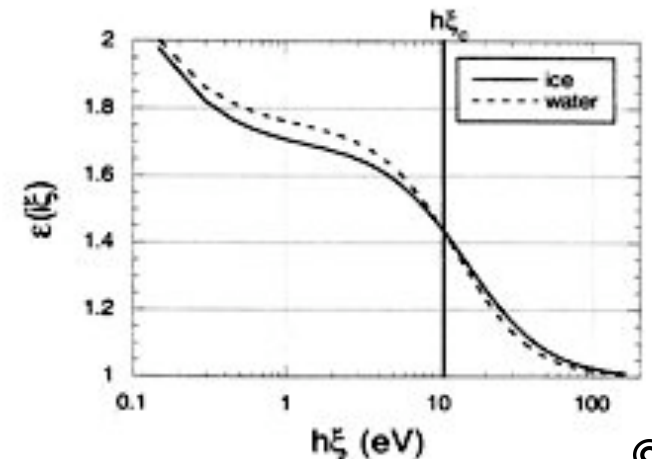
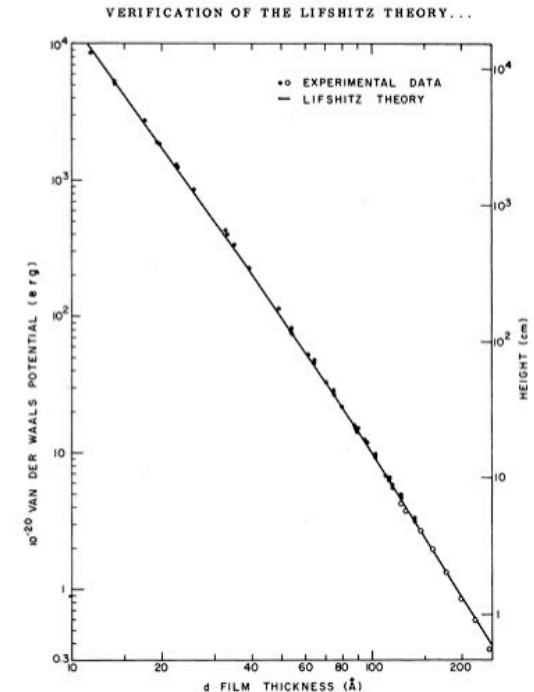
Dielectric functions : damped oscillator model

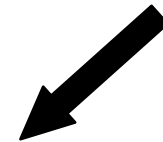
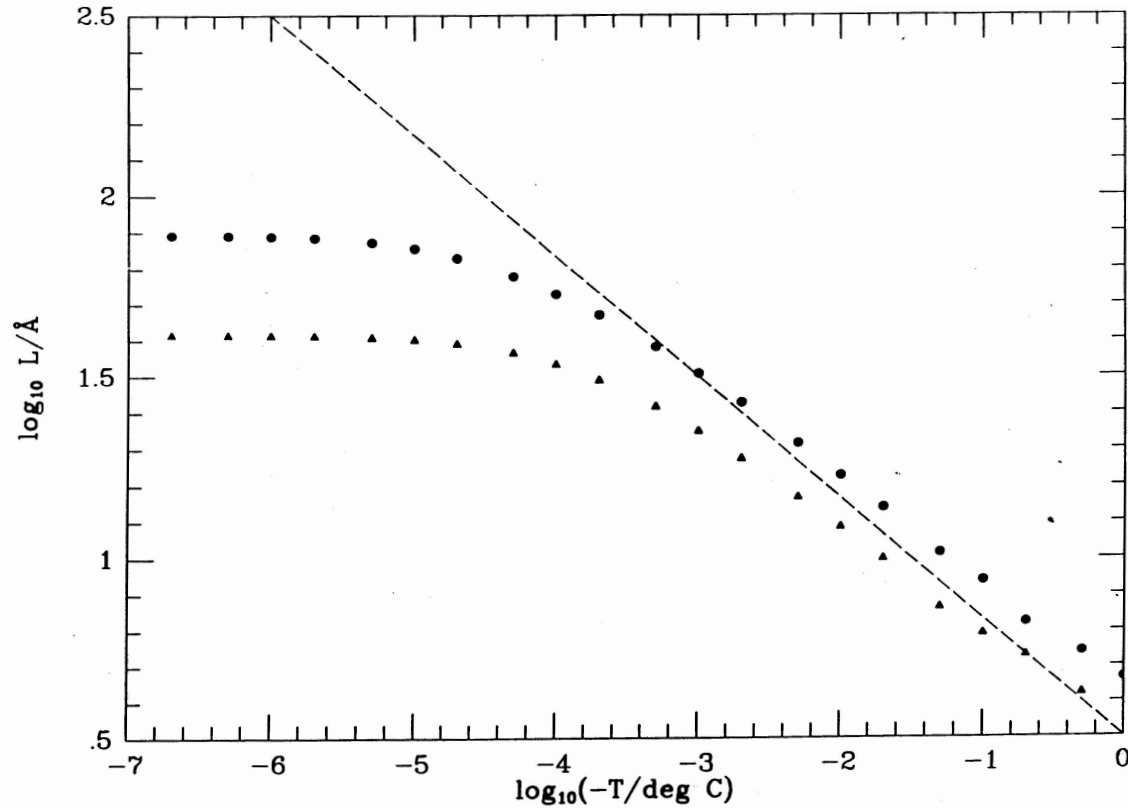
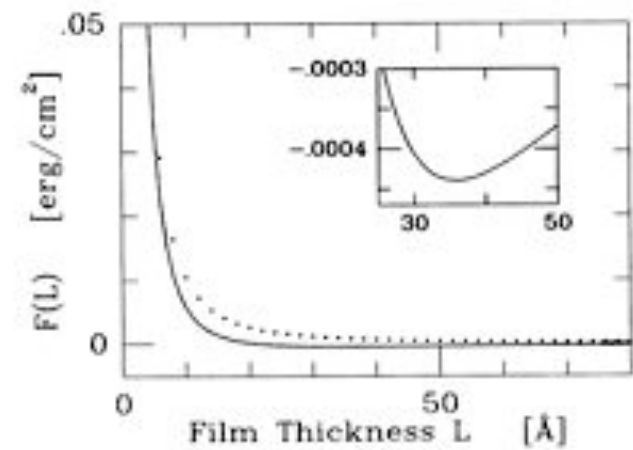
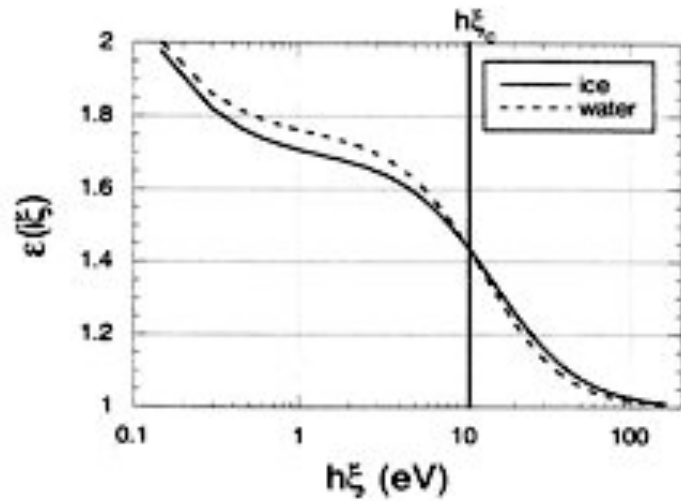
$$\epsilon(\omega) = 1 + \sum_j \frac{f_j}{e_j^2 - i\hbar\omega g_j - (\hbar\omega)^2}$$

$$\text{for} \quad \epsilon_w \approx \epsilon_i \approx \epsilon_s \approx 1$$

$$I(d) = \frac{k_b T}{8\pi d^2} \sum_{n=0}^{\infty} \left( \frac{\epsilon_i - \epsilon_w}{\epsilon_i + \epsilon_w} \right) \left( \frac{\epsilon_w - \epsilon_s}{\epsilon_w + \epsilon_s} \right) (1 + r_n) e^{-r_n}$$

Sabisky & Anderson  
*Phys Rev Lett* **24**, 1049 (1970),  
*Phys Rev A* **7**, 790 (1973).





*Phys Rev Lett* **66** 1713 (1991)  
*Phys Rev B* **52** 12426 (1995)

*Grain*

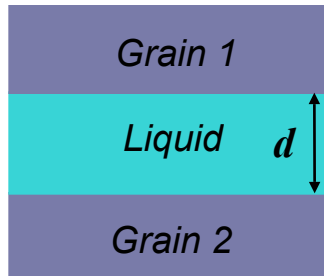
*Boundary*

*Premelting*

## *The Solid-Solid Interface; Incomplete Interfacial (Grain Boundary) Premelting*

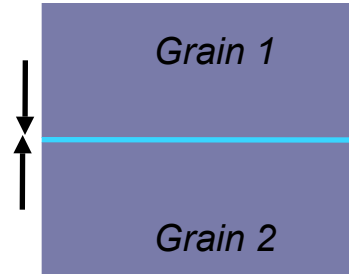
$$T \rightarrow T_m^-$$

?



No

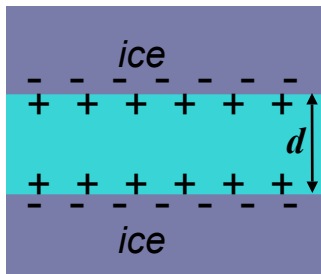
$$d \rightarrow \delta_o$$



$$F_{vdw}(d) = \frac{-A_H}{12\pi d^2}$$

$$A_H > 0$$

System Specificity to impurities...<sup>4</sup>He has superfluid film influenced by <sup>3</sup>He...Olivine by H<sub>2</sub>O



... Ice is *sensitive to ionic impurities*.

**Repulsive screened Coulomb interactions and attractive dispersion forces compete**



# Expectations from Theory

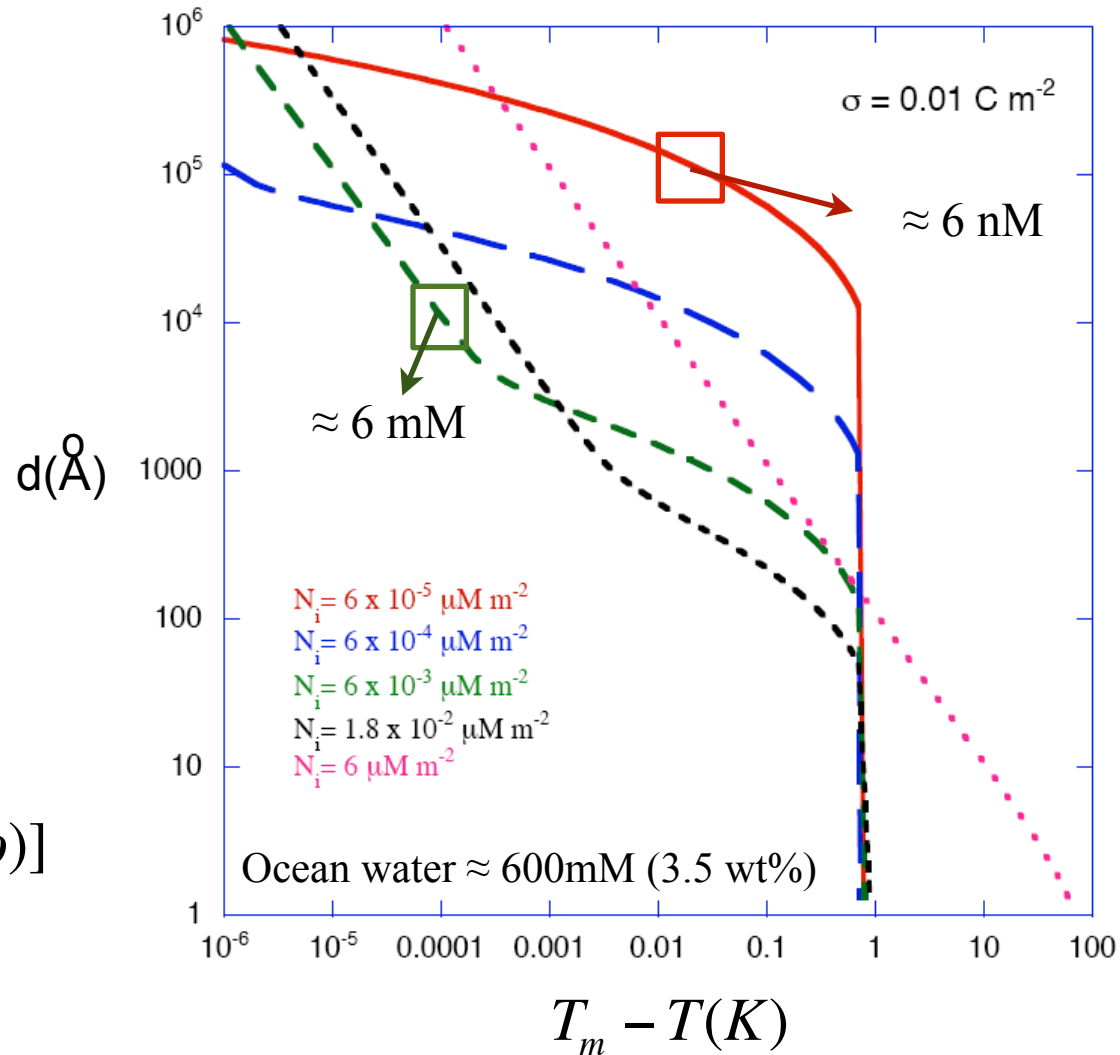
## Impurity Stimulated Grain Boundary Melting

$$F_{total}(d) =$$

$$2\gamma_{sl} +$$

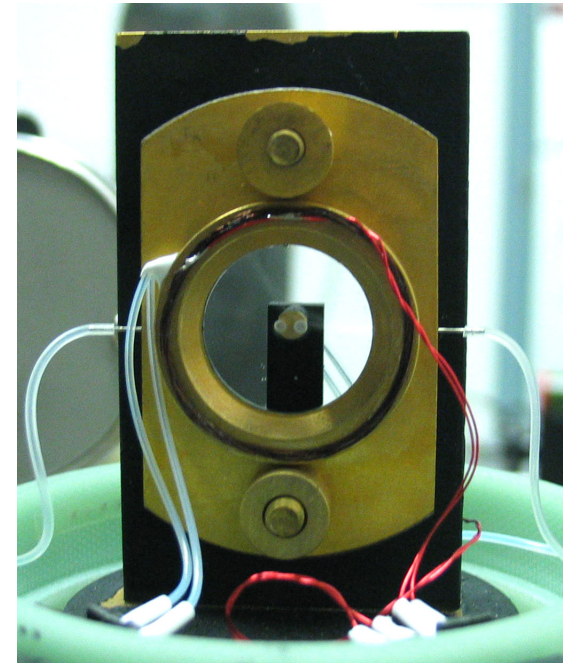
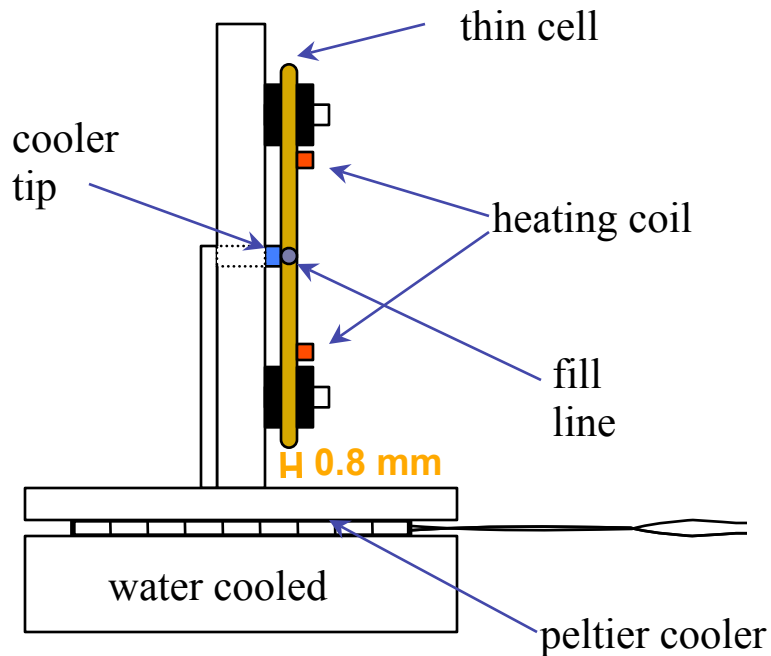
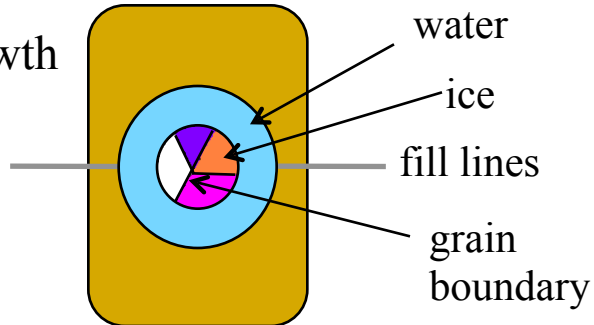
$$\frac{2\sigma^2}{\kappa\epsilon\epsilon_0}\exp(-\kappa d) +$$

$$\frac{kT}{8\pi d^2} \int d\omega K[\epsilon_s(\hbar\omega), \epsilon_l(\hbar\omega)]$$



# Experimental Search for grain boundary melting

Ice Growth  
Cell :



$$(1) \quad P_l - P_s = -A d^{-3}$$

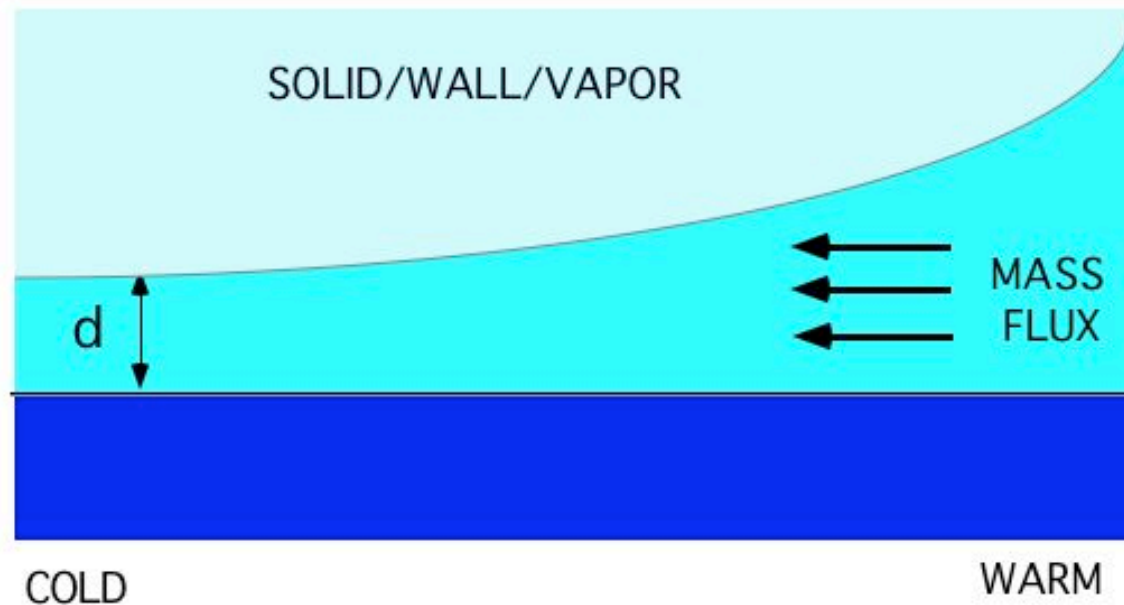
## Dynamics of Unfrozen Films

$$(2) \quad d = \lambda \, t_r^{-\frac{1}{3}}$$

$$t_r = (T_m - T)/T_m$$

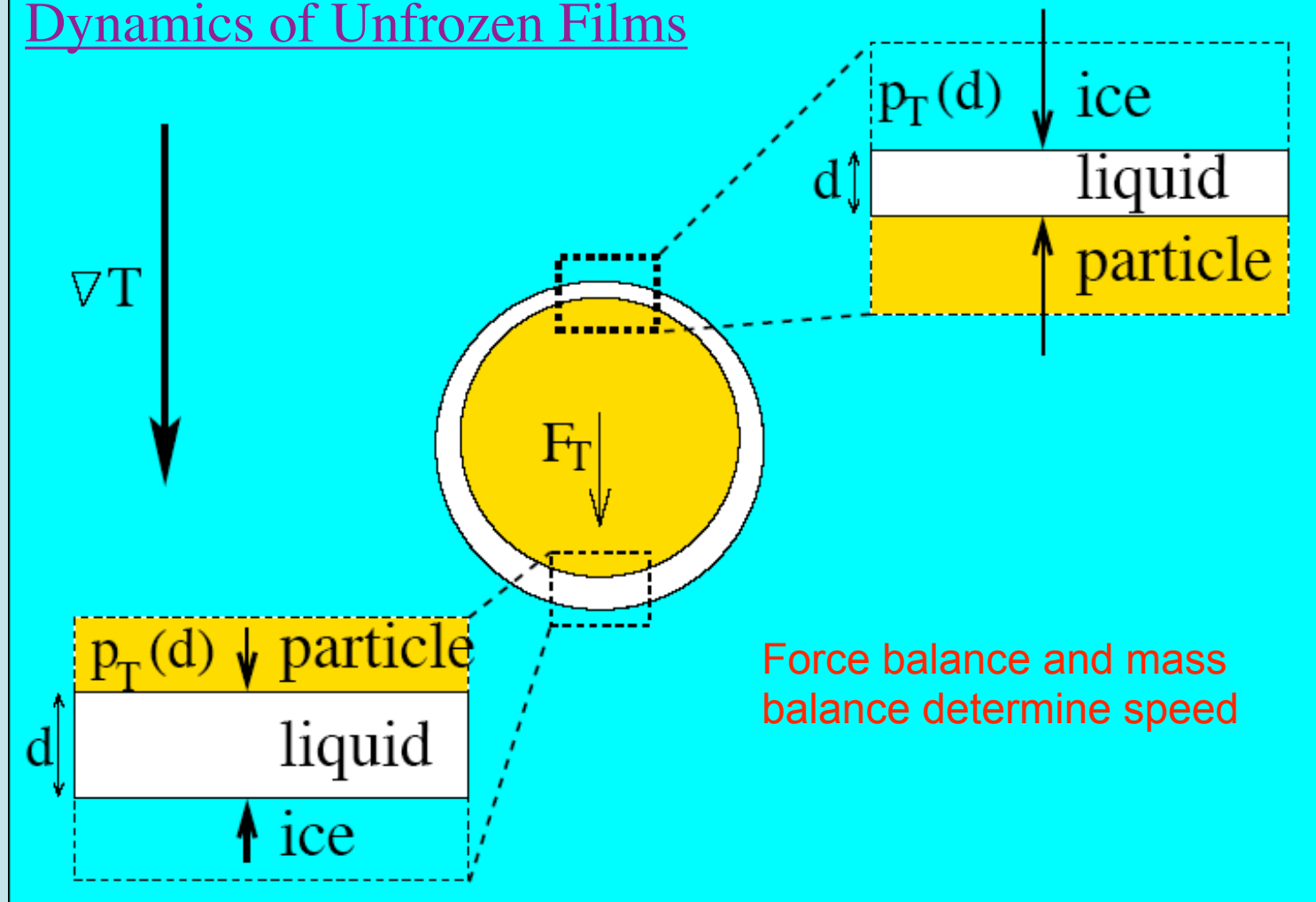
$$\Rightarrow \quad P_l = P_s - \rho_s \, q_m \, t_r$$

$$\left( \frac{dP_l}{dT} = \frac{\rho_s q_m}{T_m} = 11 \text{ atm/K} \right)$$



$$Q(x) = -\frac{d^3}{12\mu} \nabla P_l$$

## Dynamics of Unfrozen Films



*Thermodynamic buoyancy:*  $F_T = m_s G, \quad G = \frac{q_m}{T_m} \nabla T$



The surface of ice is wet by a thin film of water below 0 deg C



The surface of ice is wet by a thin film of water below 0 deg C  
The unfrozen water moves in temperature gradients



The surface of ice is wet by a thin film of water below 0 deg C  
The unfrozen water moves in temperature gradients



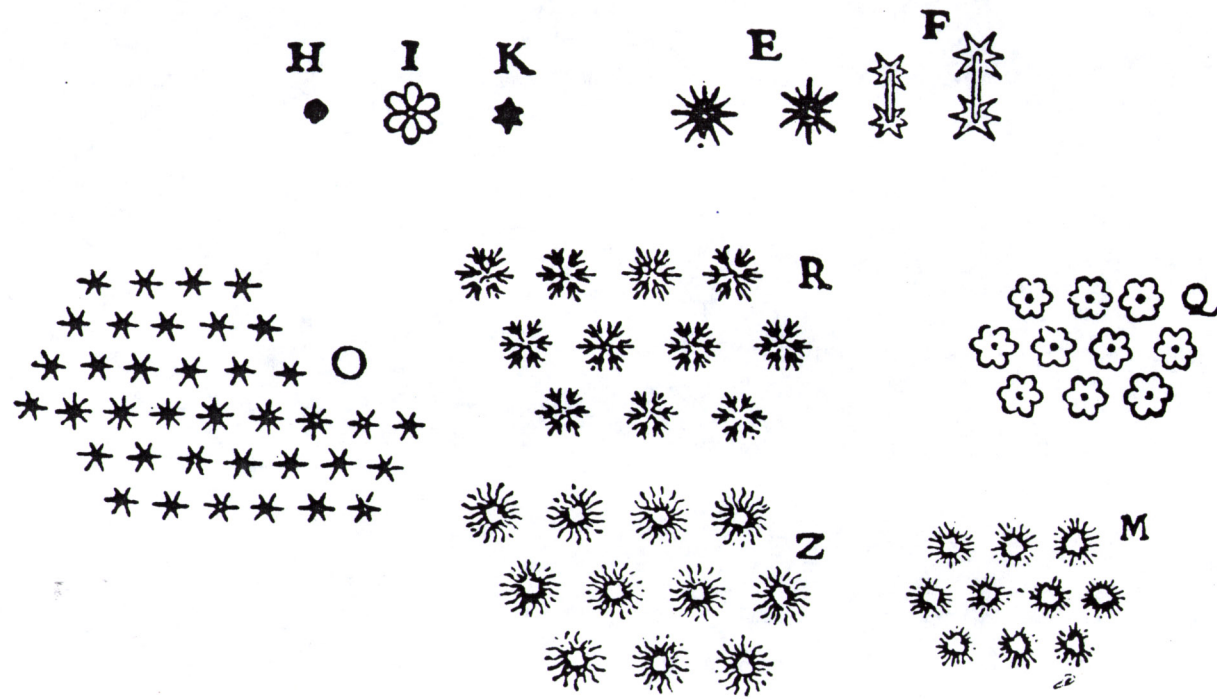
There is a large thermomolecular pressure associated with it

The surface of ice is wet by a thin film of water below 0 deg C  
The unfrozen water moves in temperature gradients



There is a large thermomolecular pressure associated with it  
There are many consequences...

“What astonished me the most was that among the grains which fell last I noticed some which had around them six little teeth, like clock-makers’ wheels such as you see at *I*.”



“I only had difficulty to imagine what could have formed and made so exactly symmetrical these six teeth around each grain in the midst of free air and during the agitation of a very strong wind... it is impossible for men to make anything so exact.”

R. Descartes, 1637. *Les Météores* (published with)  
*Discours de la méthode*, Leiden.



# Faszination der Schneekristalle – wie ihre bezaubernden Formen entstehen

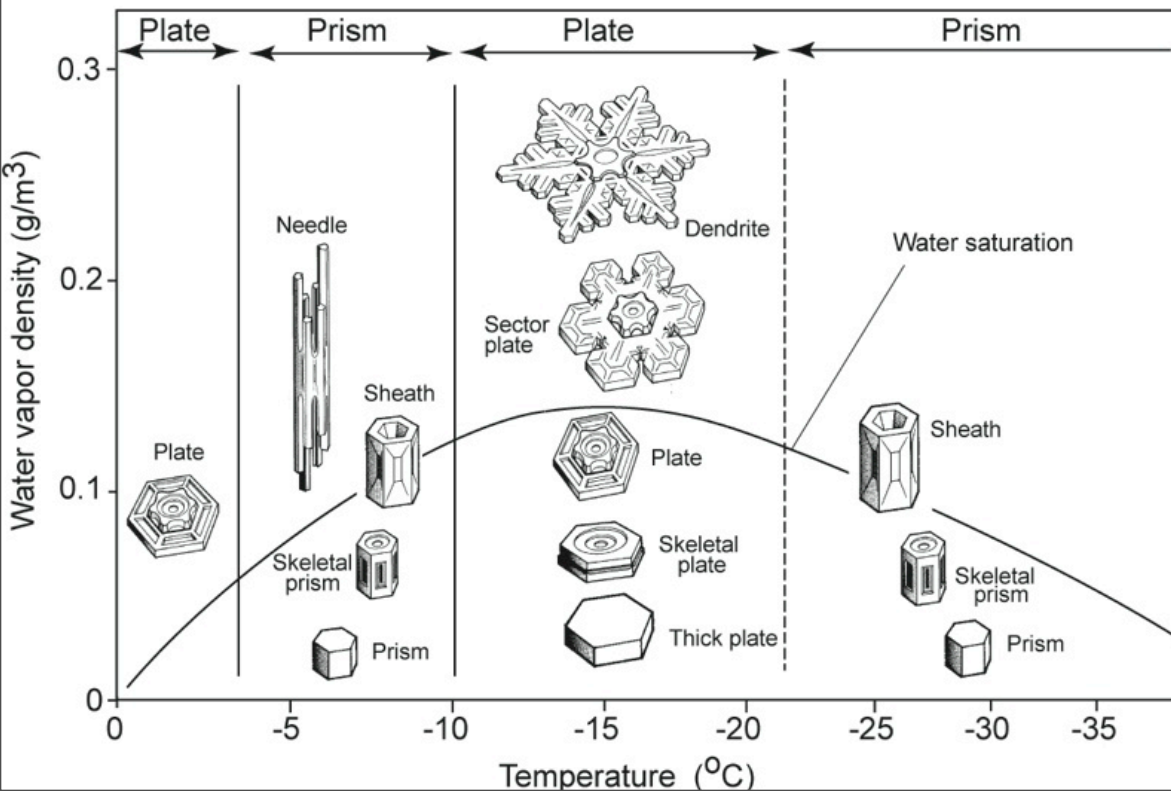


*Yoshinori Furukawa*



...ner Mikroskop-  
...ent Y. Furukawa  
...ntersuchung von  
...ch die in Abbil-  
...t.

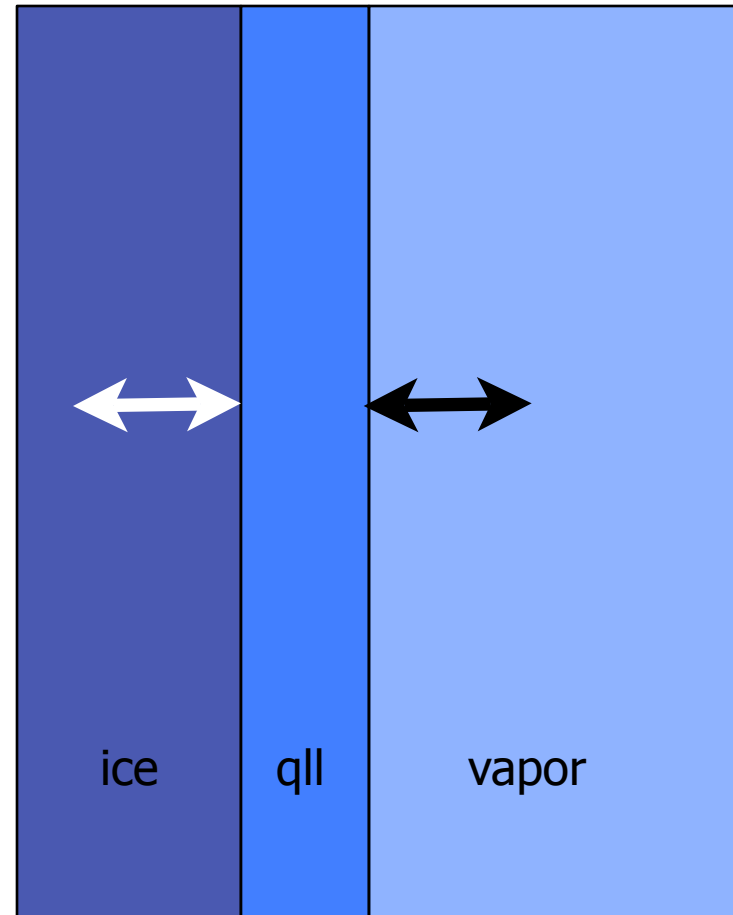
## The Nakaya Diagram

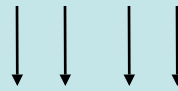


Letters from the Sky

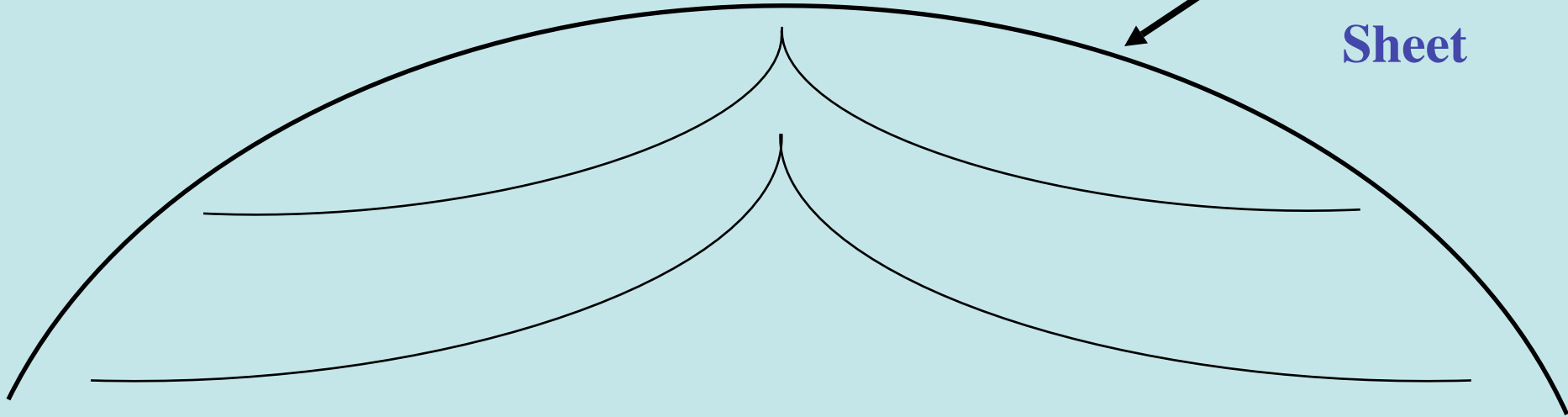
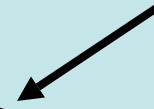
# Disequilibrium Surface Melting

- Growth into liquid phase plays a role in disequilibrium surface melting
- Solid-vapor interface near the triple point is complicated by quasi-liquid layer (qll)
- One prediction in the literature: film *decreases* thickness during growth
- Issues with proper thermodynamic description and dynamics
- Surface melting suspected to play a key role in the habit change of atmospheric ice crystals





**Greenland  
Ice  
Sheet**



Soluble Impurities

Stable Isotopes

Air Bubbles

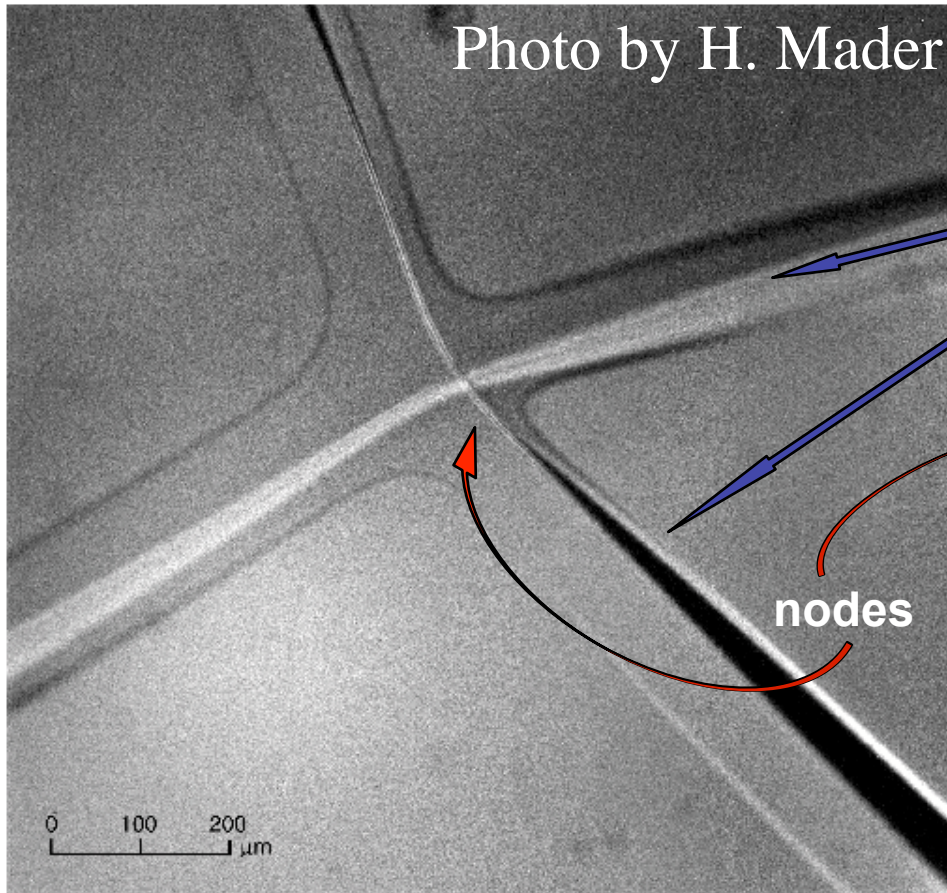
Dust Particles







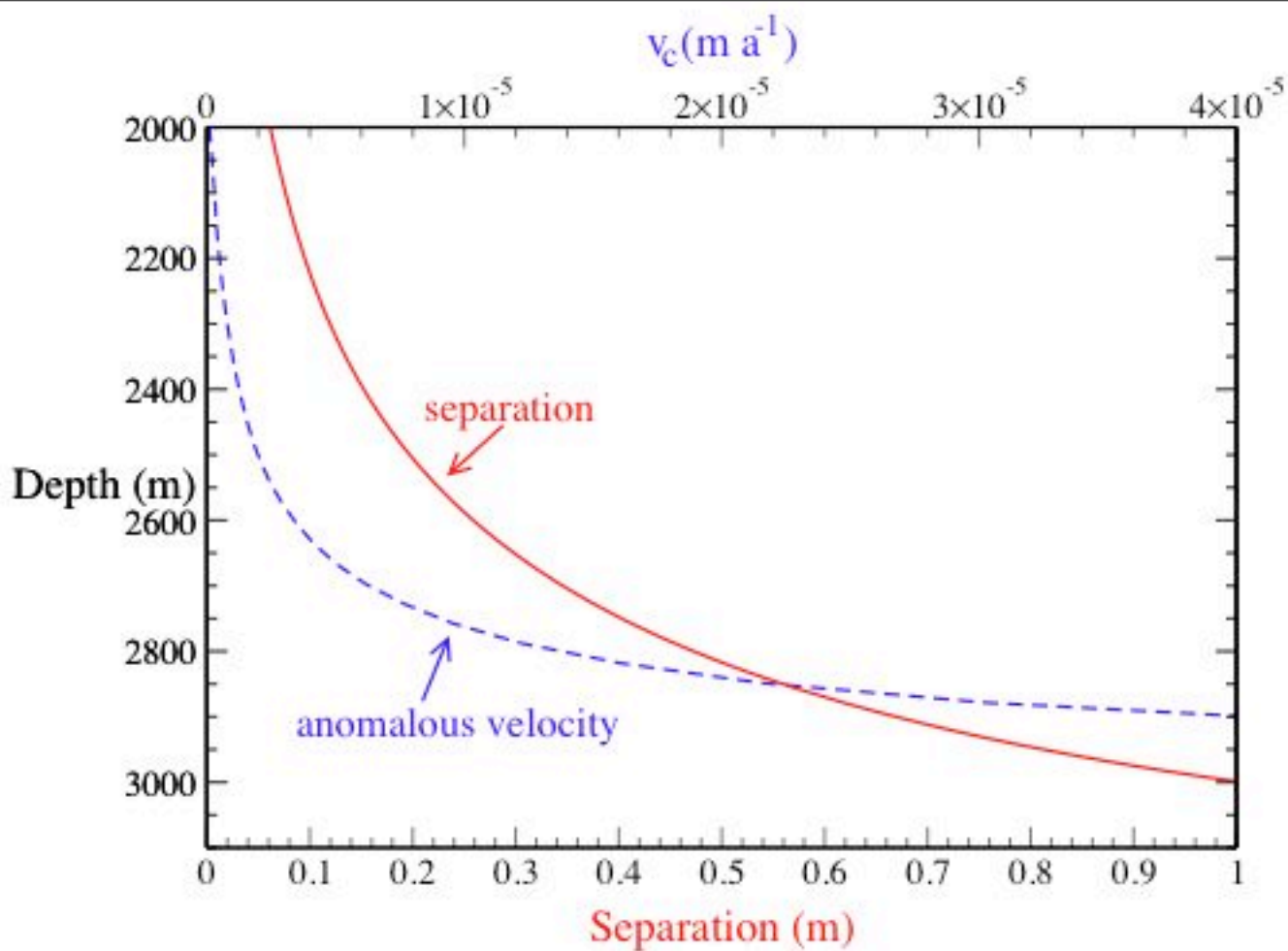
# The phase architecture of polycrystalline ice



veins

nodes

Defined by the presence of liquid water in thermodynamic equilibrium, below the bulk melting temperature,  $T_m$ .



Quantifiable Signal Displacement

Displacement negligible until great depth/age

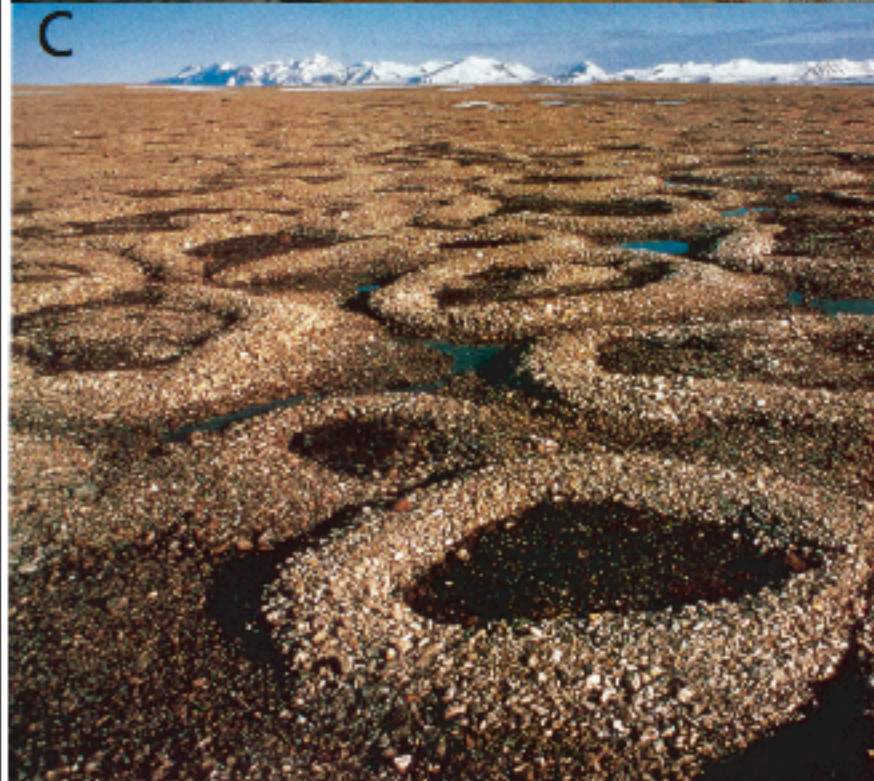
Important for relative timing of old events

A



The Cold “Hard” Ground...

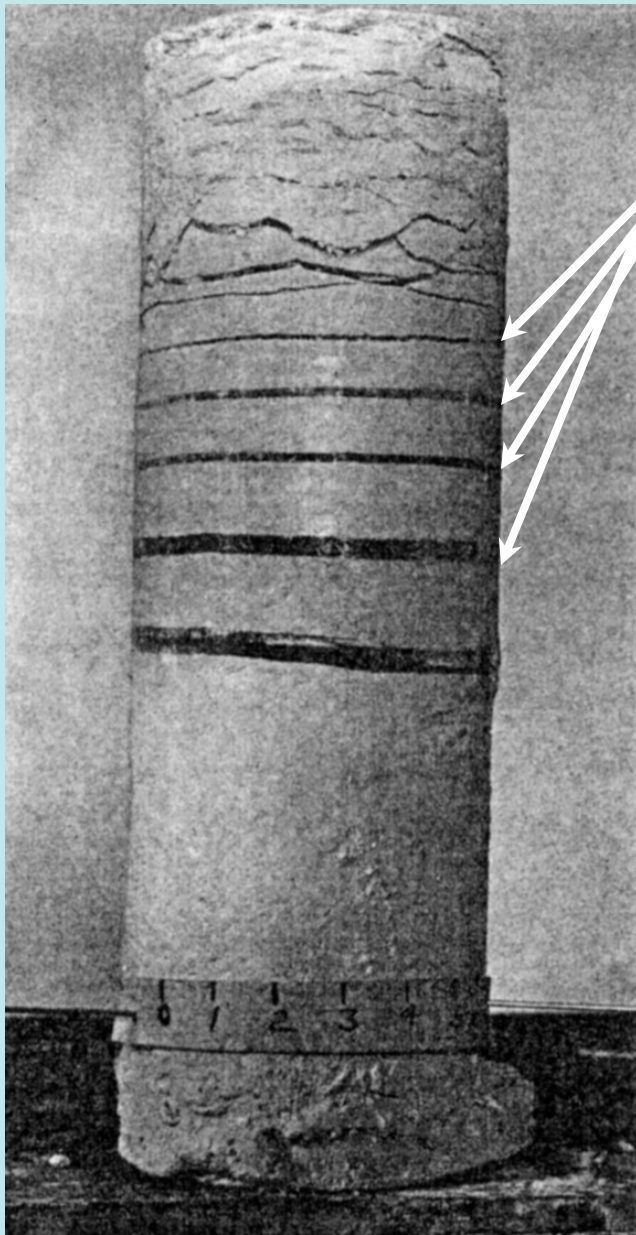
C



# Frost Heave

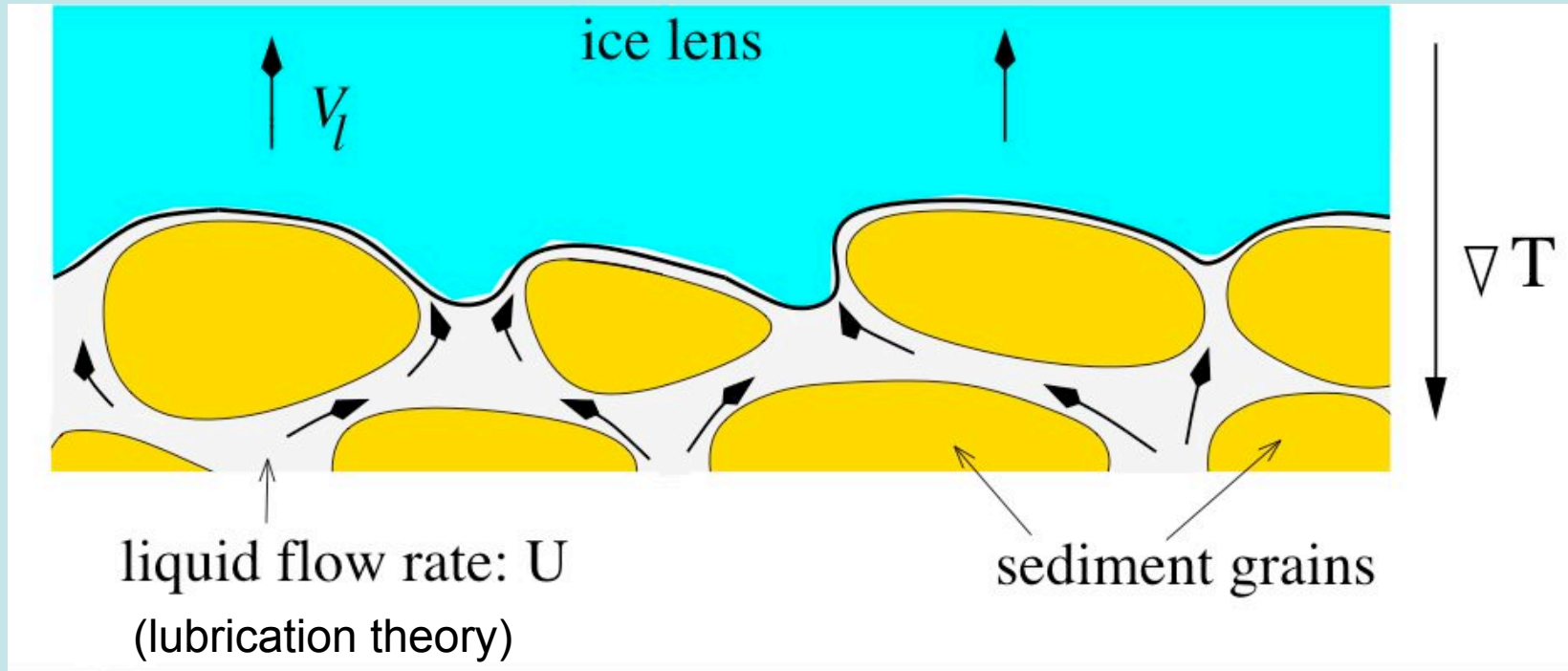
- prolonged ice growth (days/weeks/months)
- fine-grained materials
- capable of lifting large loads

$$\left( \frac{dP_i}{dT} = \frac{\rho_s q_m}{T_m} = 11 \text{ atm/K} \right)$$



Water expands when freezing, but Argon heaves too...*Phys. Rev. Lett.* **85**, 4908 (2000).

# A Growing lens

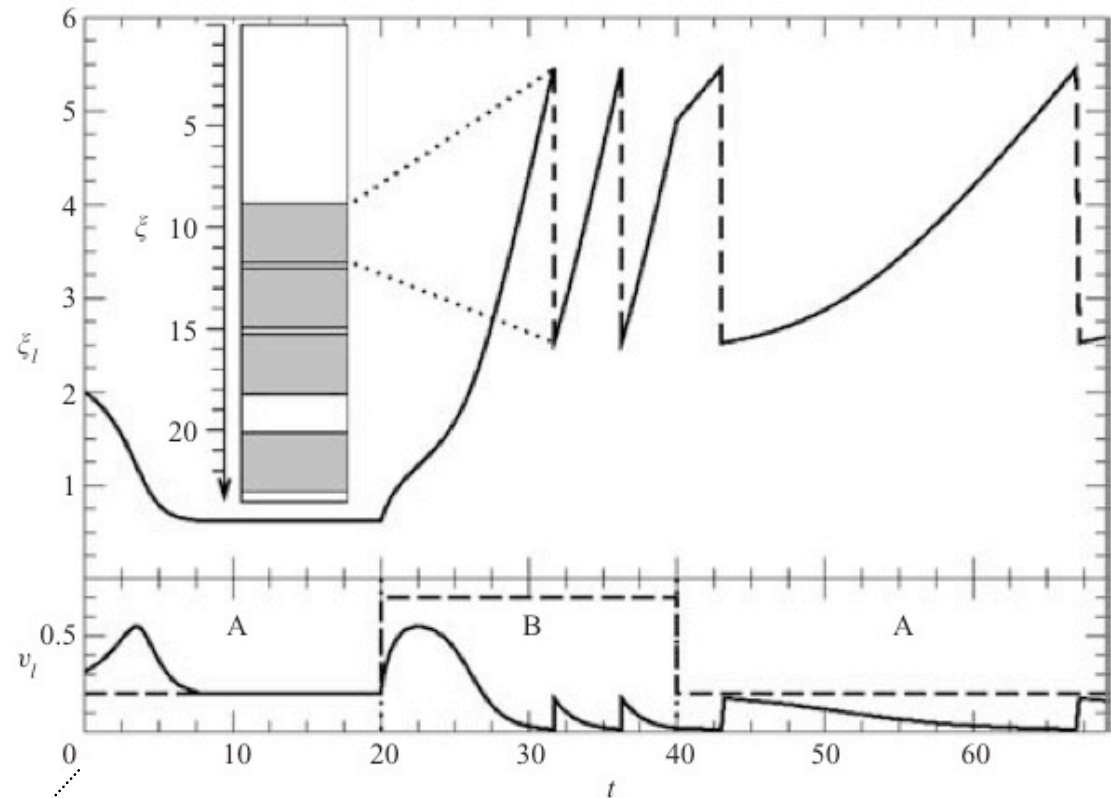
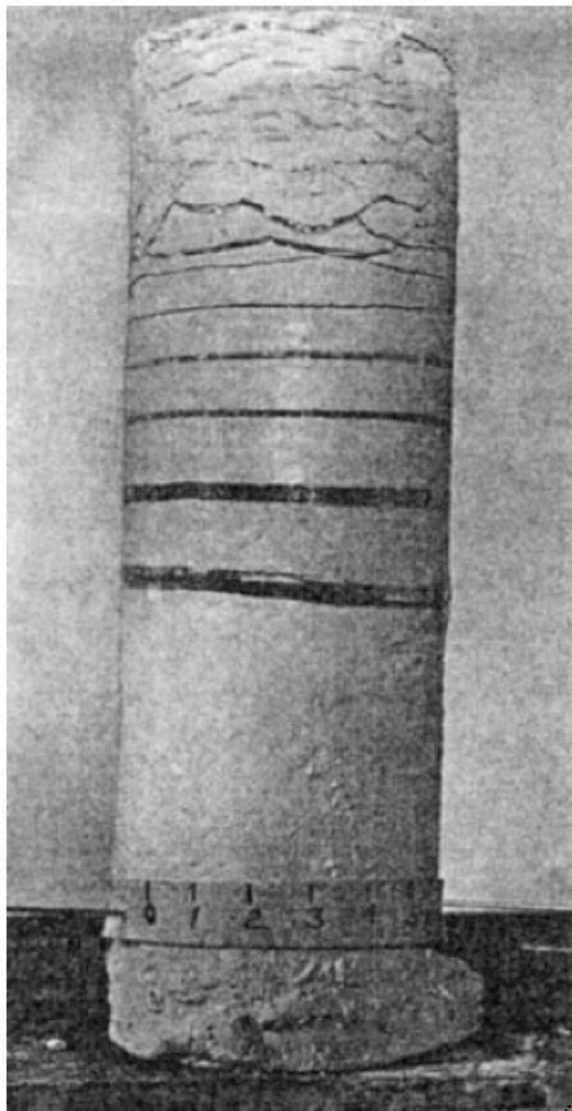


Interface shape satisfies:

$$\rho \frac{q_m}{T_m} (T_m - T) = p_T + \gamma_{sl} \kappa$$

Balance of forces, mass and energy control growth rate

# Periodicity Predicted

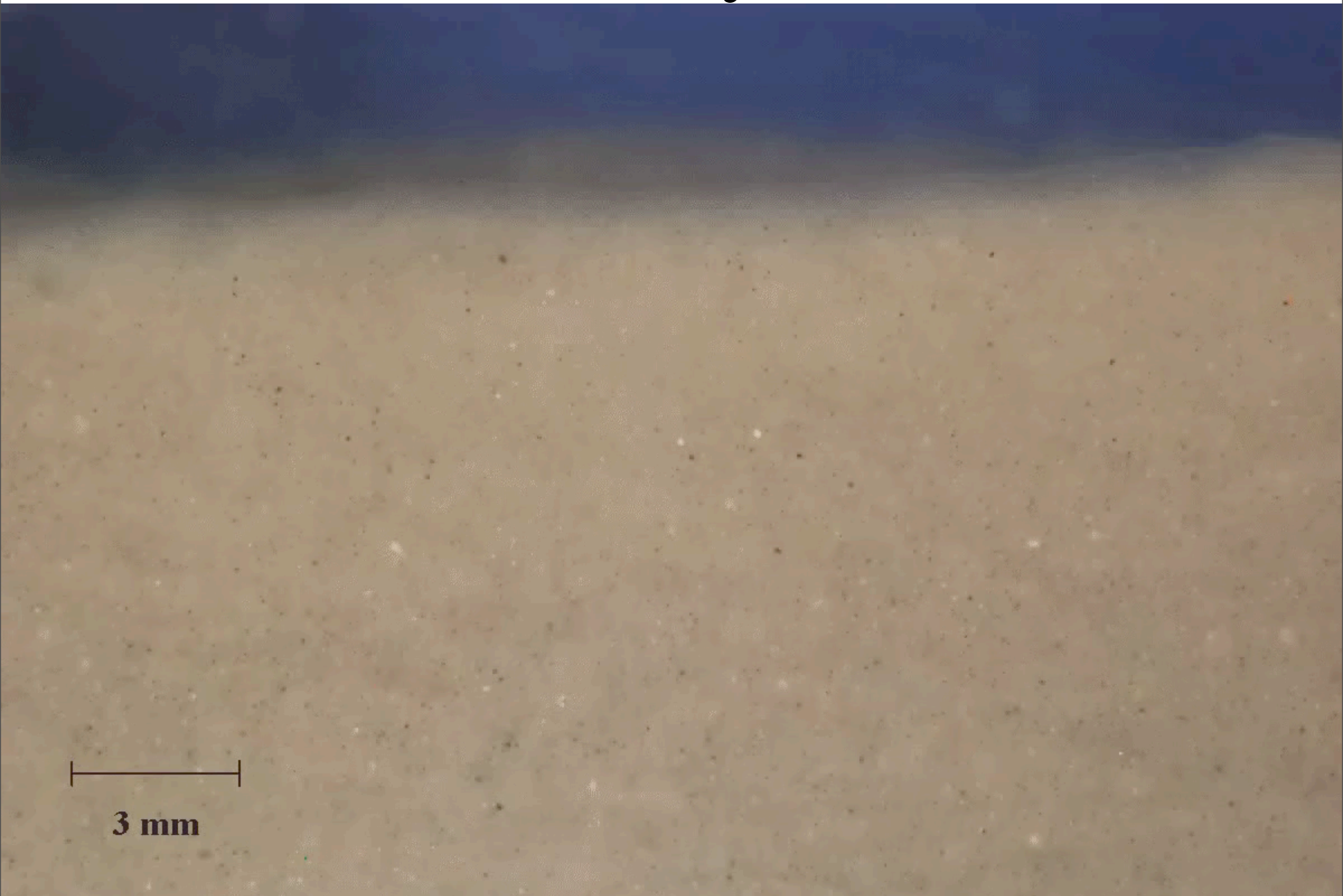


# Not so fast...

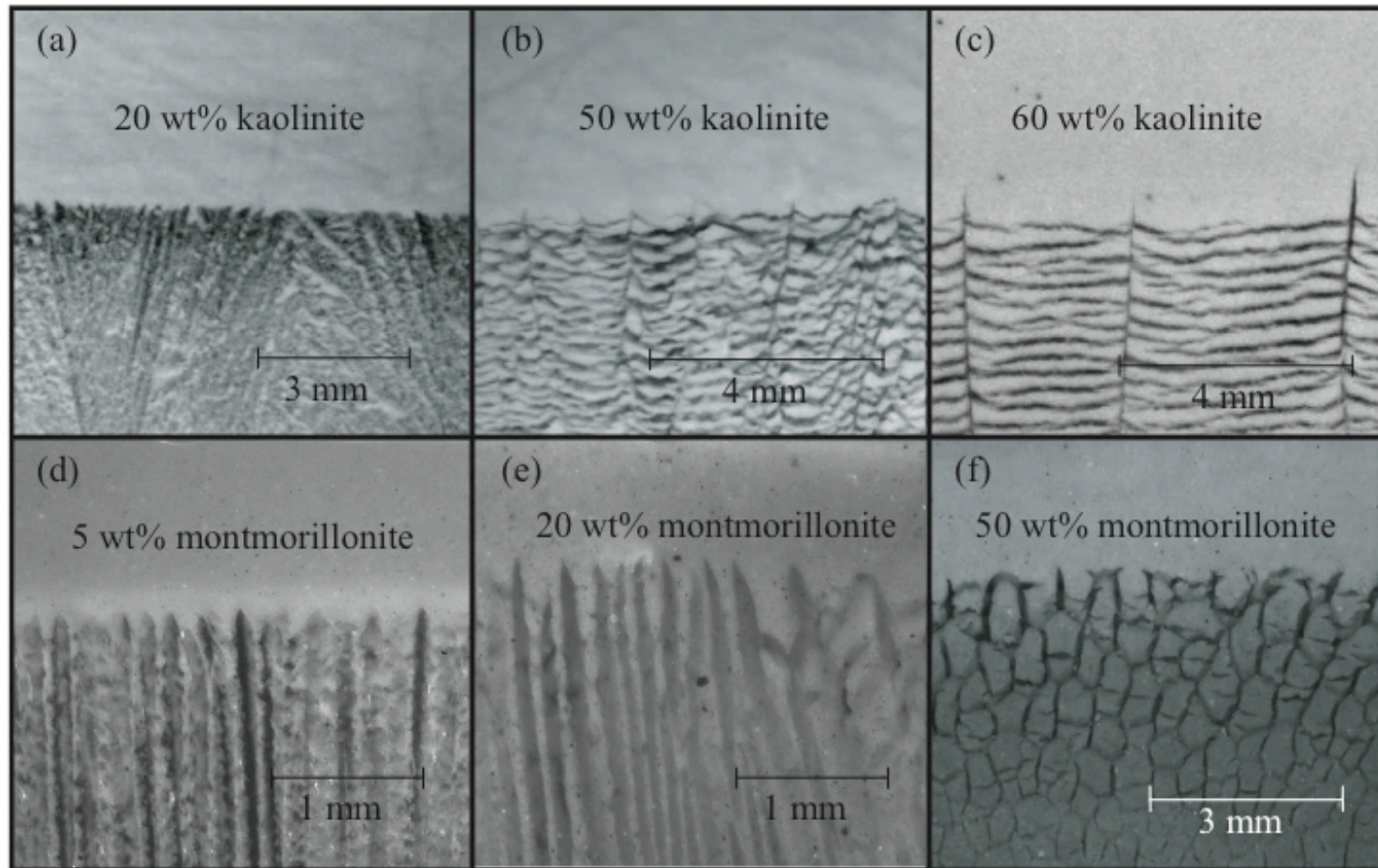


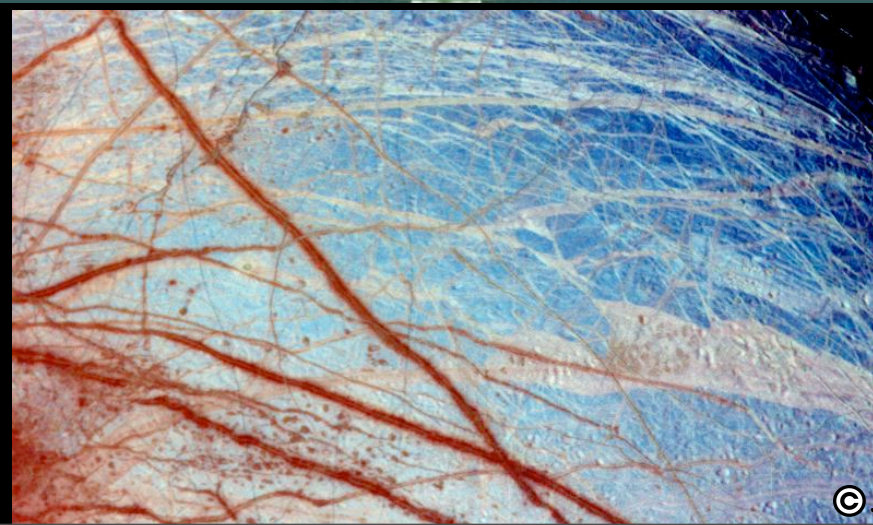
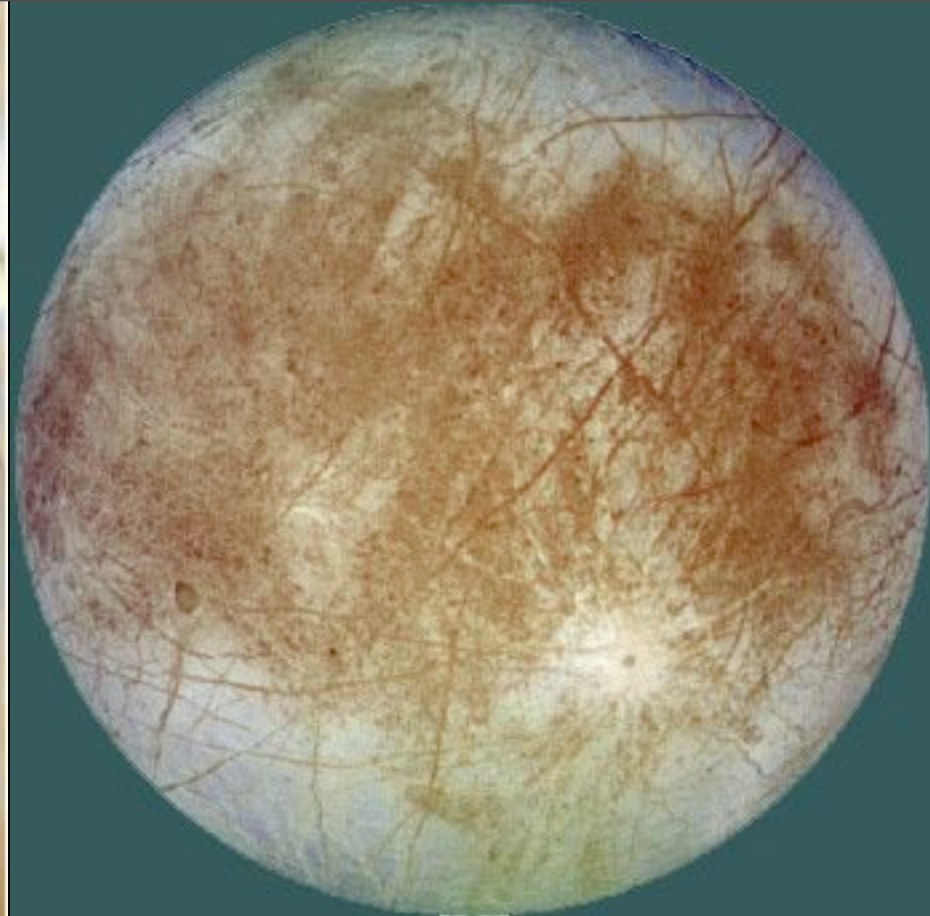
1 mm

# ...in reality...

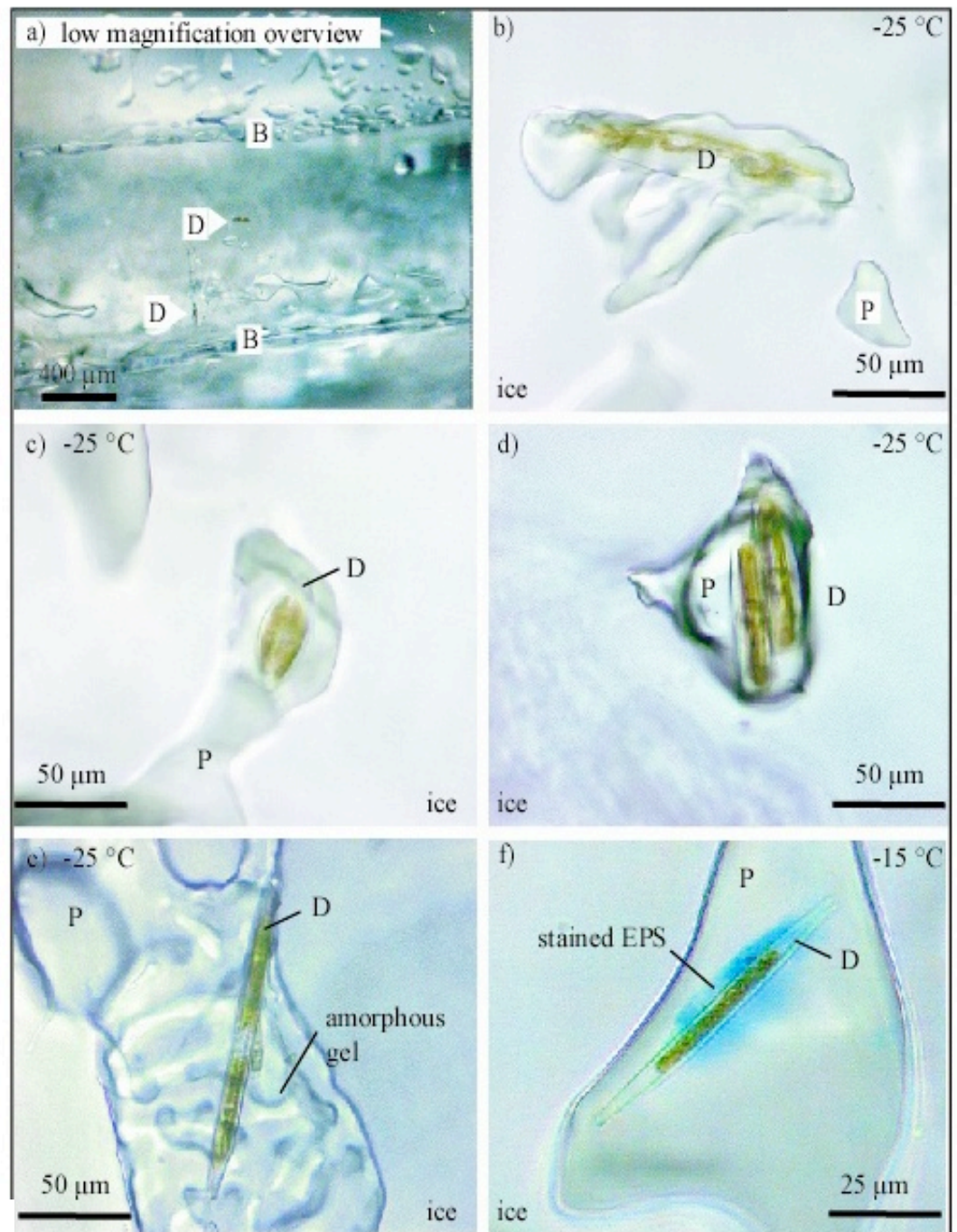


... it's a zoo out there.





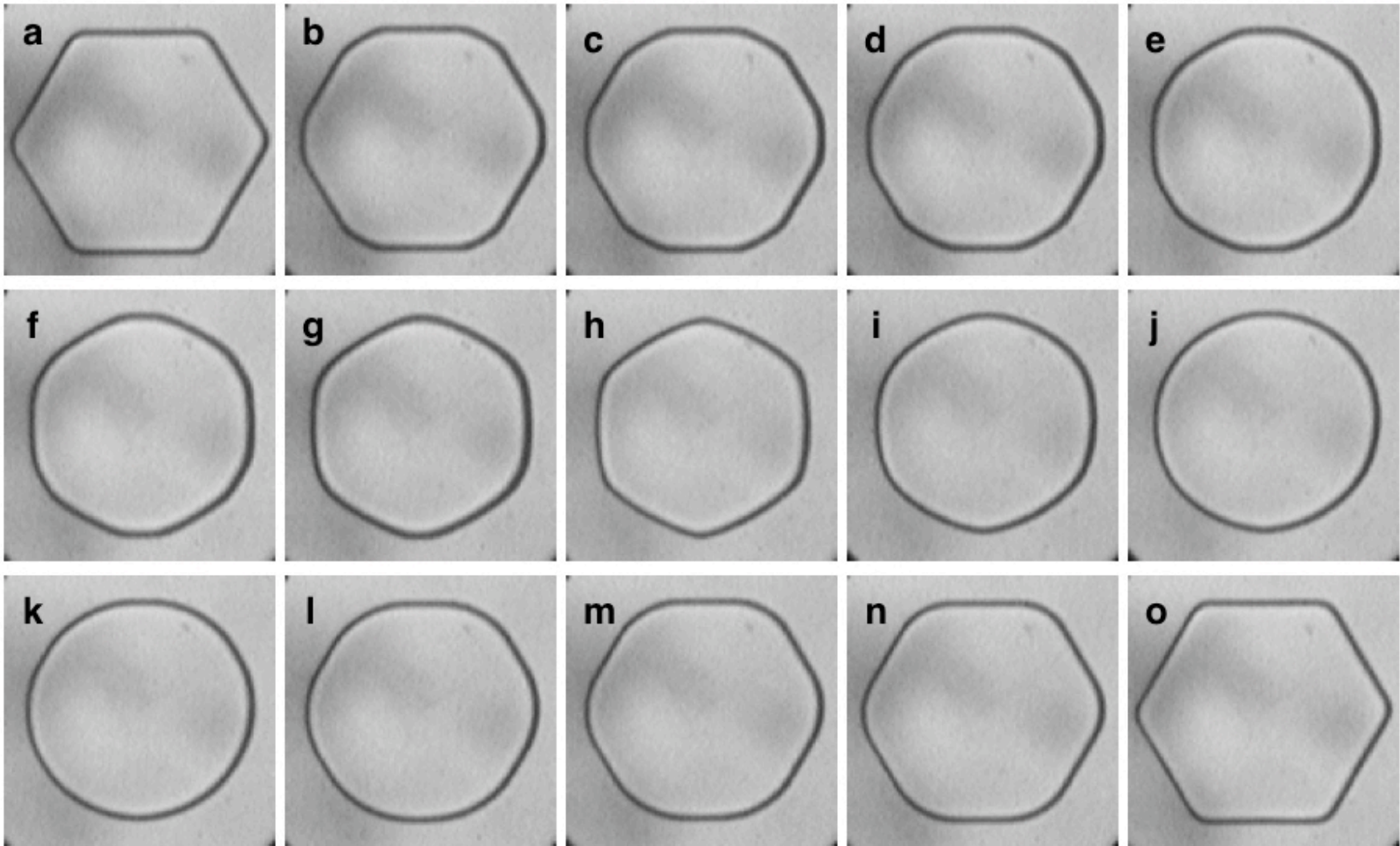
# Whither Life?



C. Krembs

# Pristine Ice Crystal Growth

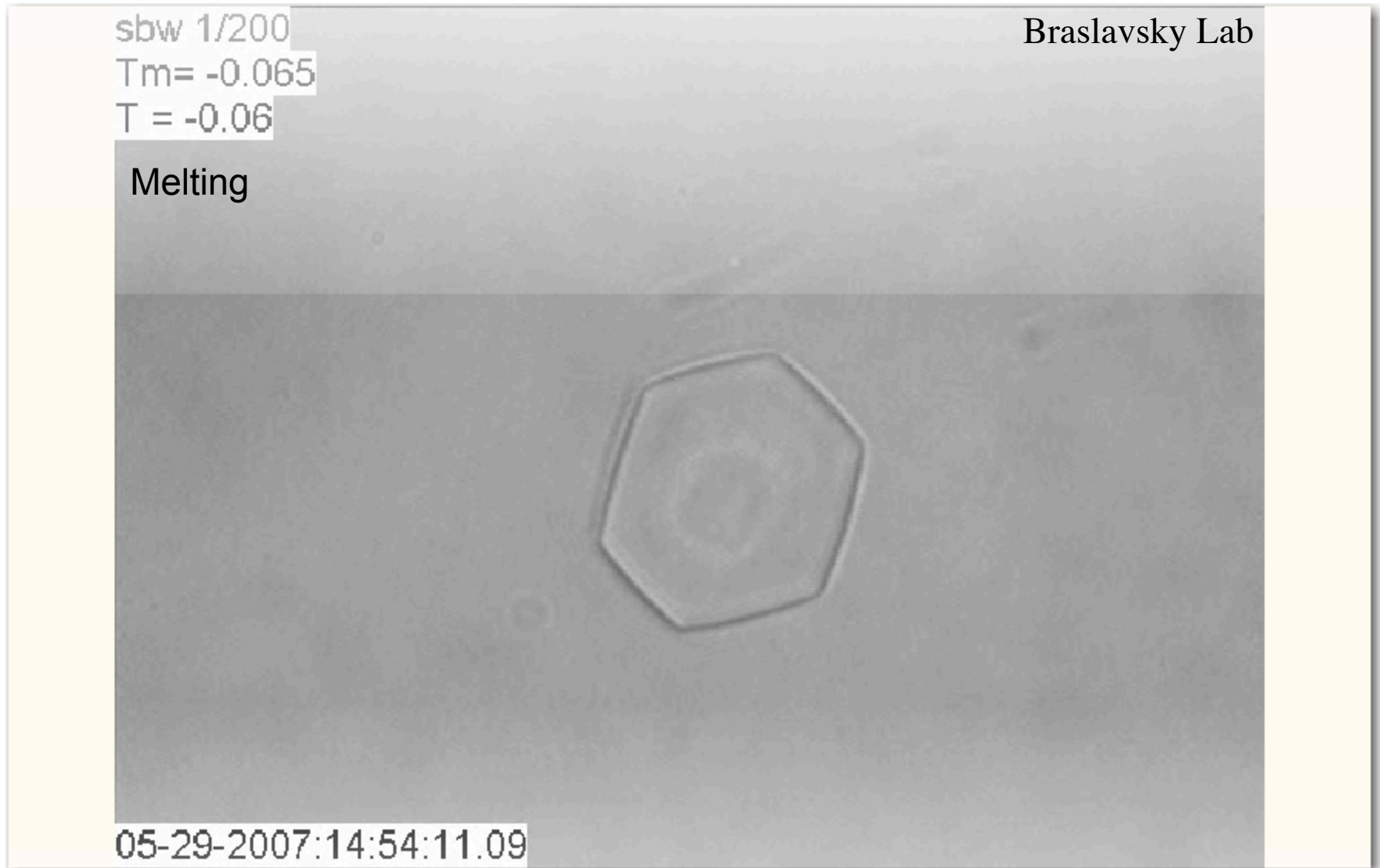
$T = -22\text{ }^{\circ}\text{C}$ ,  $P = 2000\text{ bar}$



0.5mm

*Phys. Rev. Lett.* **96**, 255502 (2006).

# Ice Crystal Growth from sbwAFGP Solution



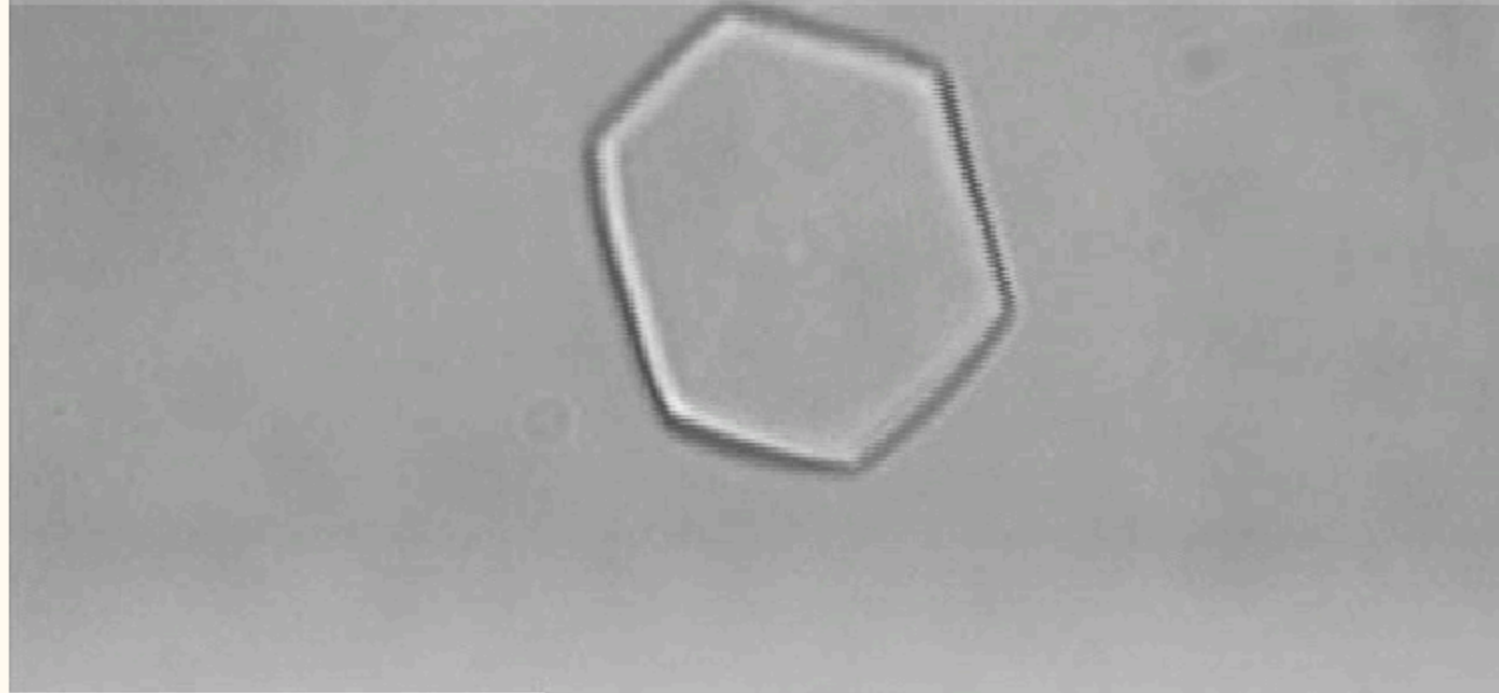
sbwAFP: C=0.01 mg/mL (1.1  $\mu$ M, TH= 0.02K) to 2 mg/mL (220  $\mu$ M, TH= 5K)  
Buffer 10 mM Tris-HCl, 1mM EDTA, 5 mM Ammonium bicarbonate, pH 8.0

sbw 1/200

$T_m = -0.065$

$T = -0.22$

Growing



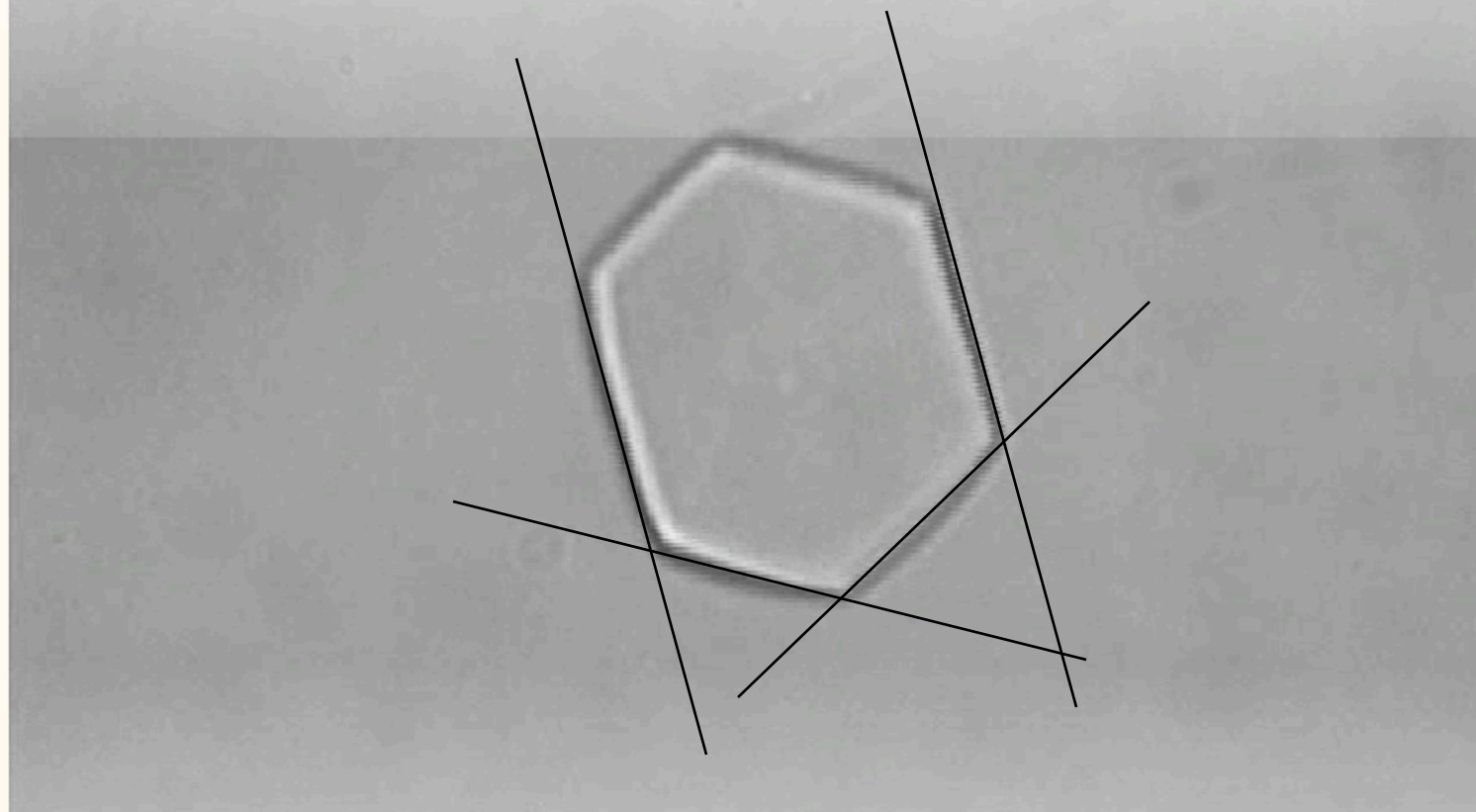
05-29-2007:14:54:48.95

sbw 1/200

$T_m = -0.065$

$T = -0.22$

Growing



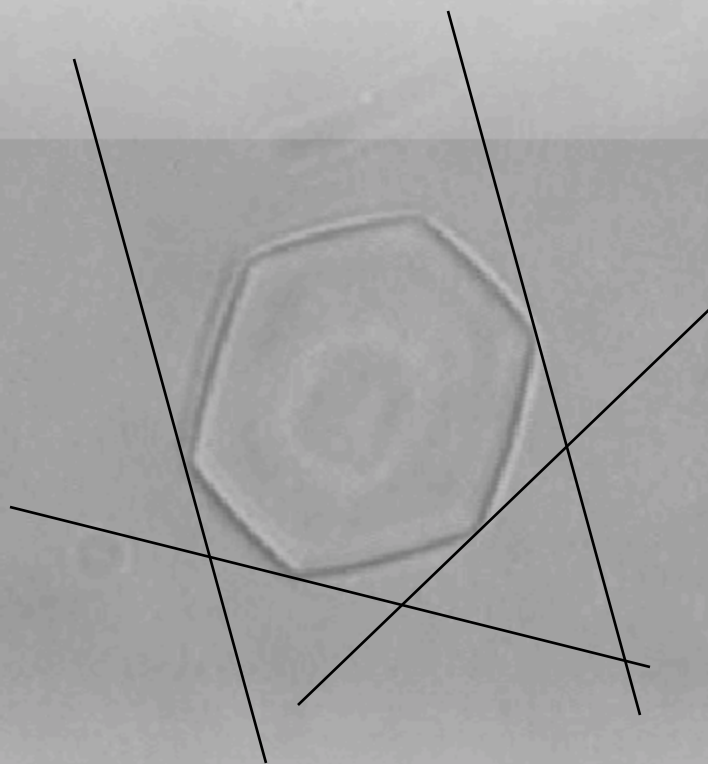
05-29-2007:14:54:48.95

sbw 1/200

$T_m = -0.065$

$T = -0.06$

Melting



05-29-2007:14:54:11.09

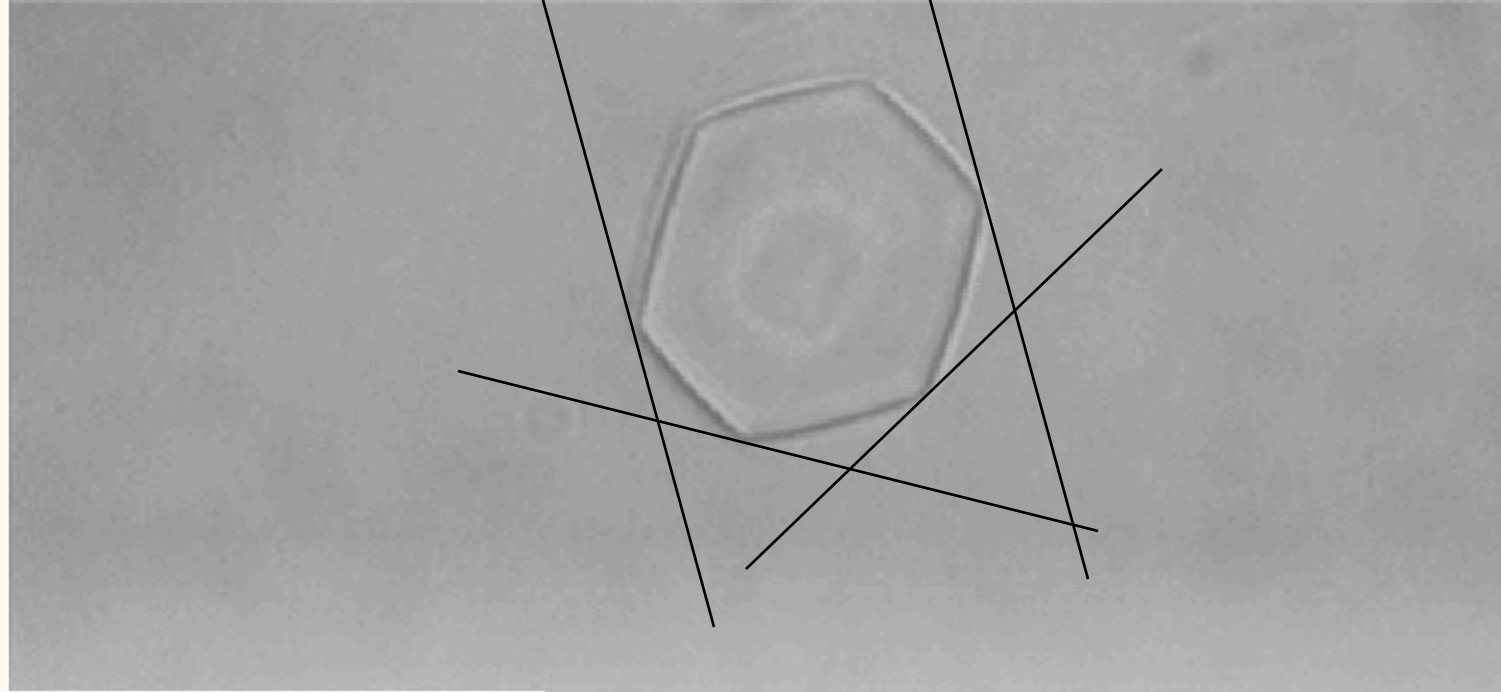
sbw 1/200

$T_m = -0.065$

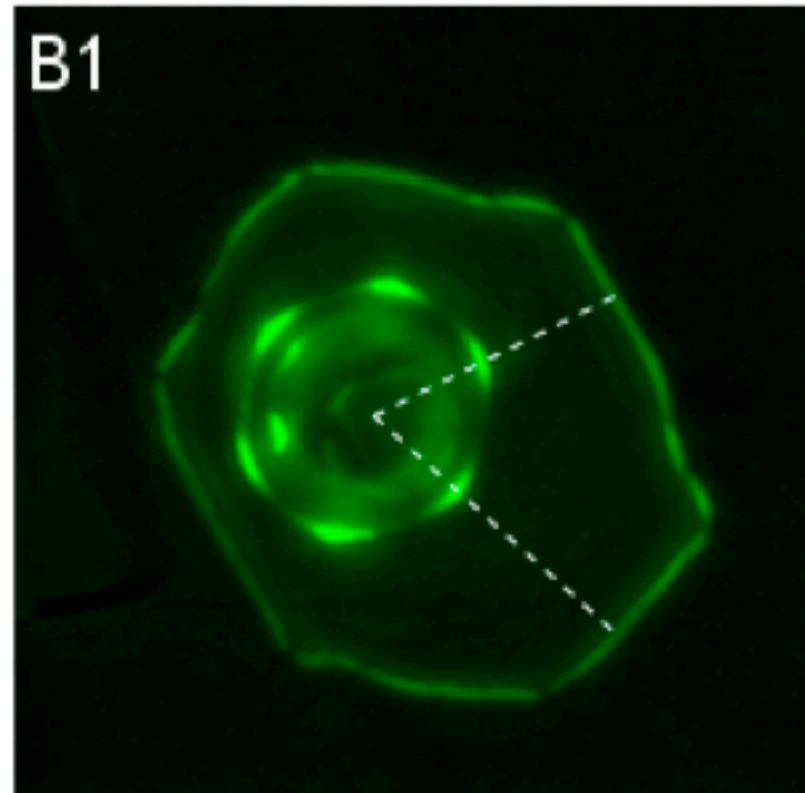
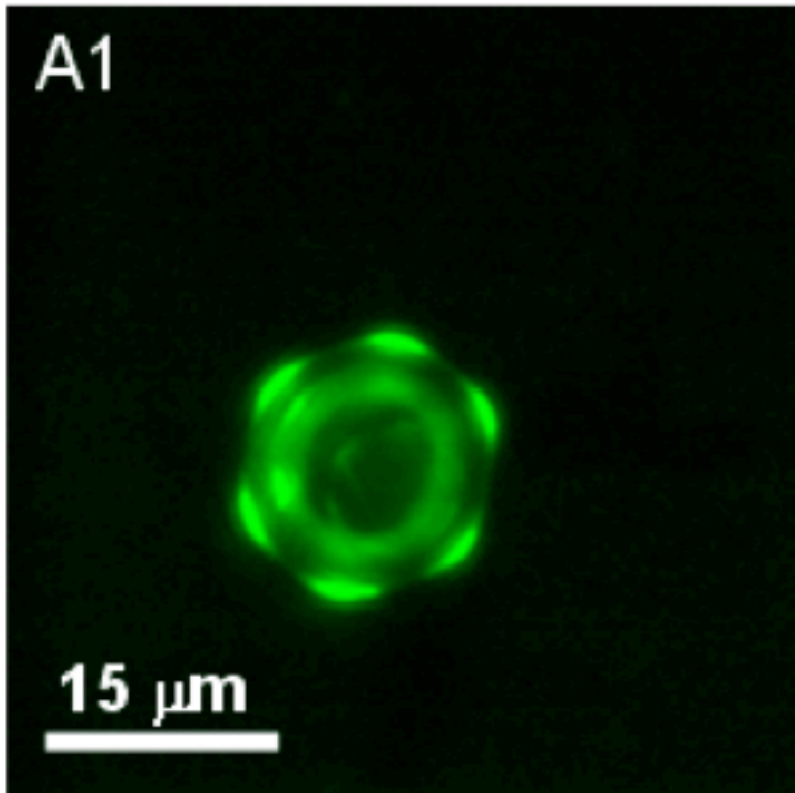
$T = -0.06$



Melting



05-29-2007:14:54:11.09



# Problems & Challenges

Access to Interfaces in Thermodynamic Equilibrium

Nature of Structural Information Provided by Probe of Choice

Nature of Disorder

Definition of Melting (from Peierls to KTHNY)

Onset of Premelting...GULF in ignorance across scales

Systematic Study of Impurity Effects

Nature of Phenomena

Major Experimental Hurdles

Manipulation of amplitude and range of interactions

Applicability across materials systems and disciplines

Emergent Phenomena (Think Natural Phenomena & Manipulation)

Premelting Dynamics (particle trapping & redistribution)

Disequilibrium, pattern formation, ...

Biophysical, Geophysical & Materials Processing

## Acknowledgments

J.G. Dash  
I. Braslavsky  
M. Elbaum  
Y. Furukawa  
M. Maruyama  
J.A. Neufeld  
A.W. Rempel  
M. Schick  
L.A. Wilen  
M.G. Worster

University of Washington  
Ohio University  
Weizmann Institute  
Hokkaido University  
Osaka City University  
Cambridge University  
University of Oregon  
University of Washington  
Ohio University  
Cambridge University

## Yale Postdocs and Students

L. Benatov  
A. Cahoon  
S. Peppin  
M. Spannuth  
E. Thomson

*Rev. Mod. Phys.* **78**, 695 (2006)

*Ann. Rev. Fl. Mech* **38**, 427 (2006)

*Phys. Today* **60**, 70 (2007)

Support  
Bosack & Kruger Foundation  
NSF, DoE and Yale

"Physics is not just Concerning  
the Nature of Things,  
But Concerning the  
Interconnectedness of all the  
Natures of Things".

Sir Charles Frank, FRS, upon retirement from  
Univ. Bristol's Physics Department in 1976.