The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific and
Cultural Organization

IAEA
International Atomic Energy Agency

1959-4

Workshop on Supersolid 2008

18 - 22 August 2008

Optical investigations of disorder in solid Helium-4

F. Caupin
ENS Paris

Strada Costiera 11, 34014 Trieste, Italy - Tel. +39 040 2240 111; Fax +39 040 224 163 - sci_info@ictp.it, www.ictp.it

Optical investigations of disorder in solid helium 4

S. Sasaki*, F. Caupin, and S. Balibar

Laboratoire de Physique Statistique

Ecole Normale Supérieure, Paris

* now at Northwestern University

Supersolids, Trieste, August 19th, 2008

Yet another mystery…

Adriatico Guest House, Trieste, Italy, August 18th 2008

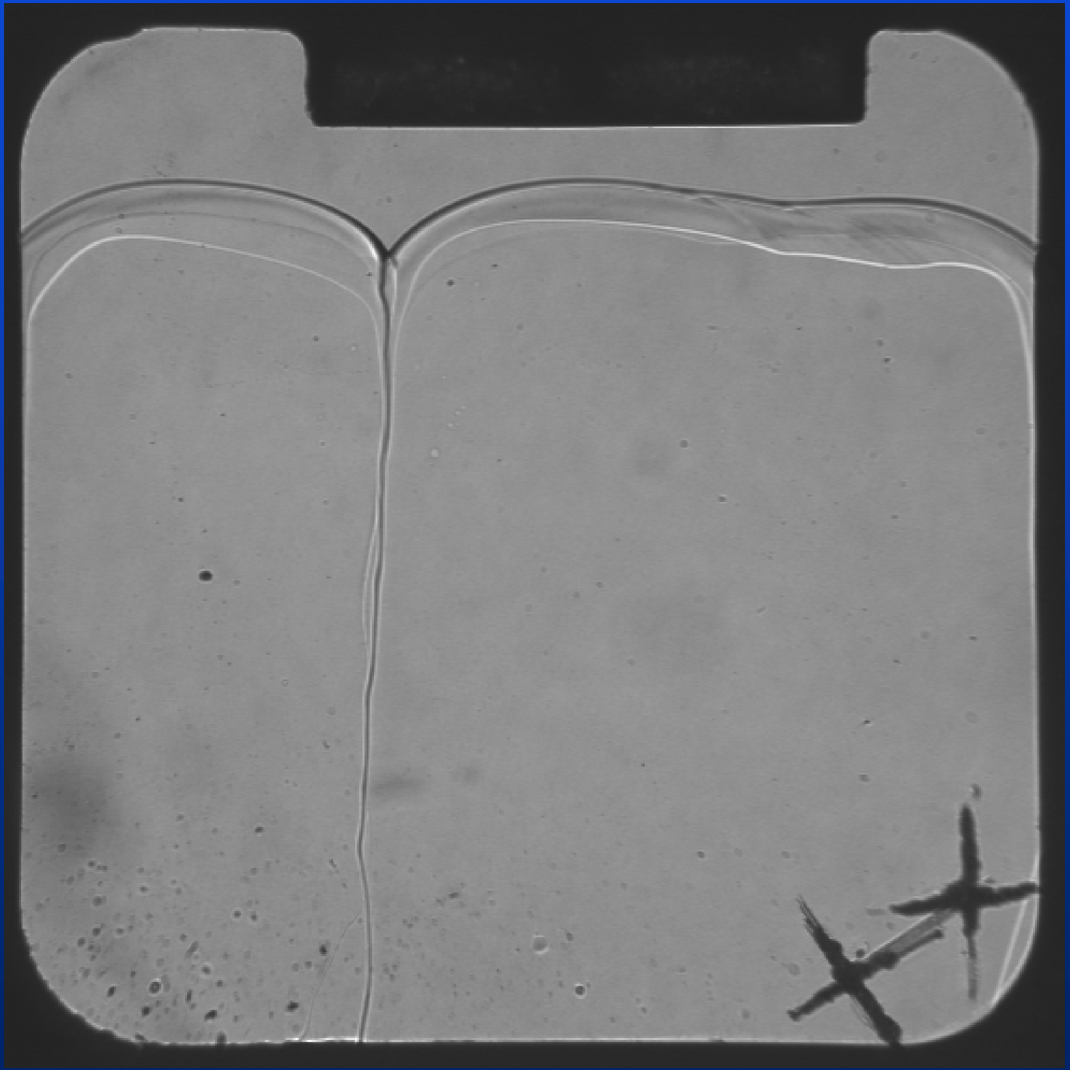
2.17 K

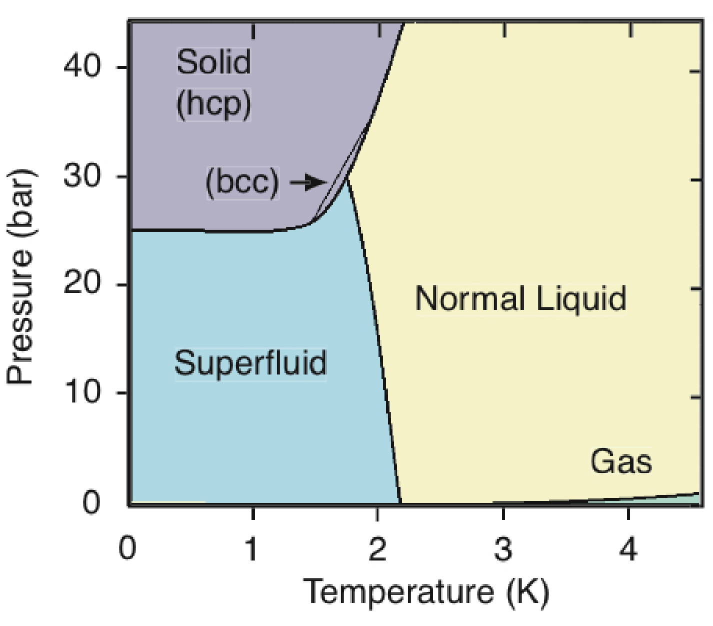
T_λ ???

Outline

- why grain boundaries???
- one grain boundary (GB) between two grains
- GB melting: connection with classical systems
- liquid channels
- consequences for mass flow
- crystals grown by different methods

A grain boundary

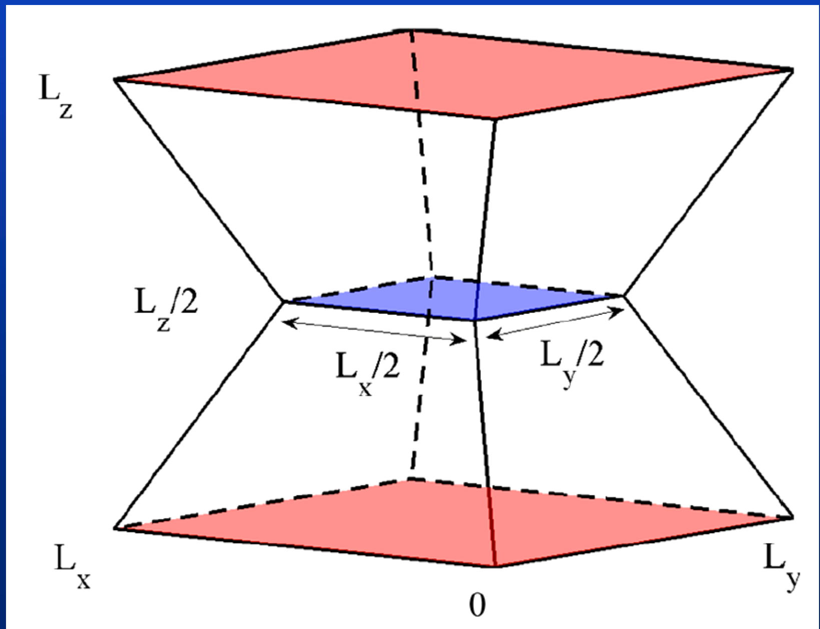




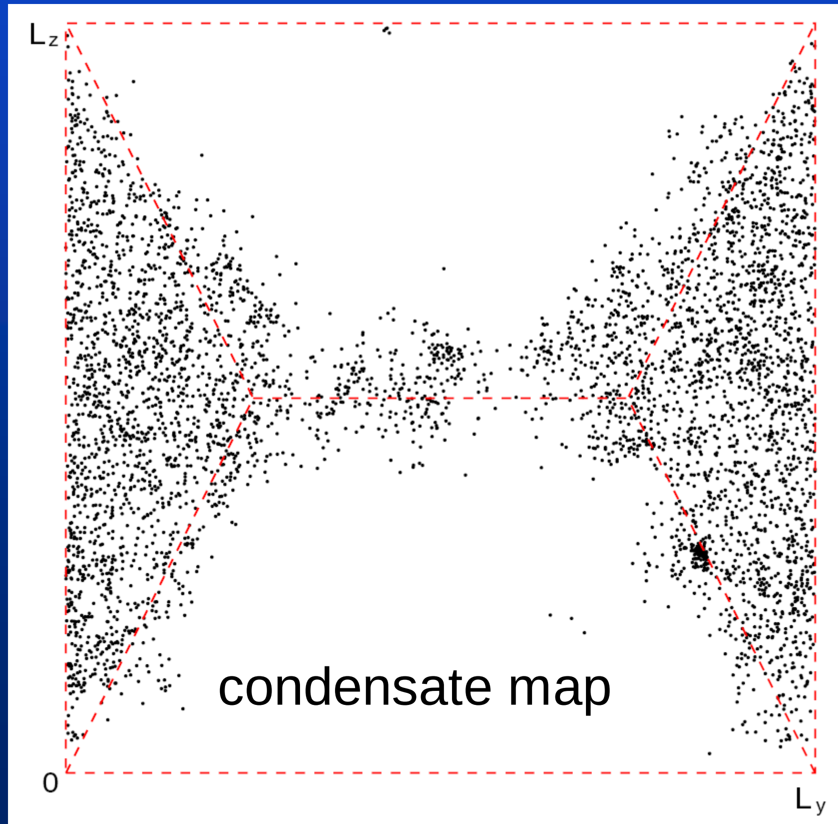
Monte-Carlo simulations of grain boundaries

Pollet et al. *PRL* '06

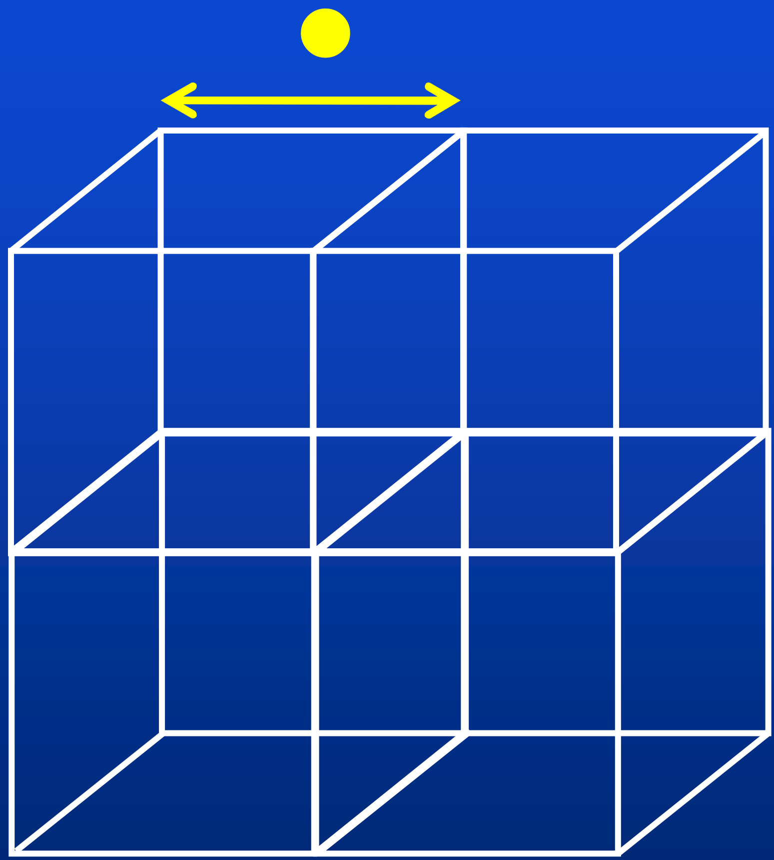
2 crystals truncated pyramidal shape with different orientations



generic GBs are superfluids below ≈0.5 K and ≈3 atoms thick



Grain boundaries cannot explain everything…



cubic network of GB

lattice parameter ●

effective superfluid thickness
= 1 atomic layer a = 0.3 nm

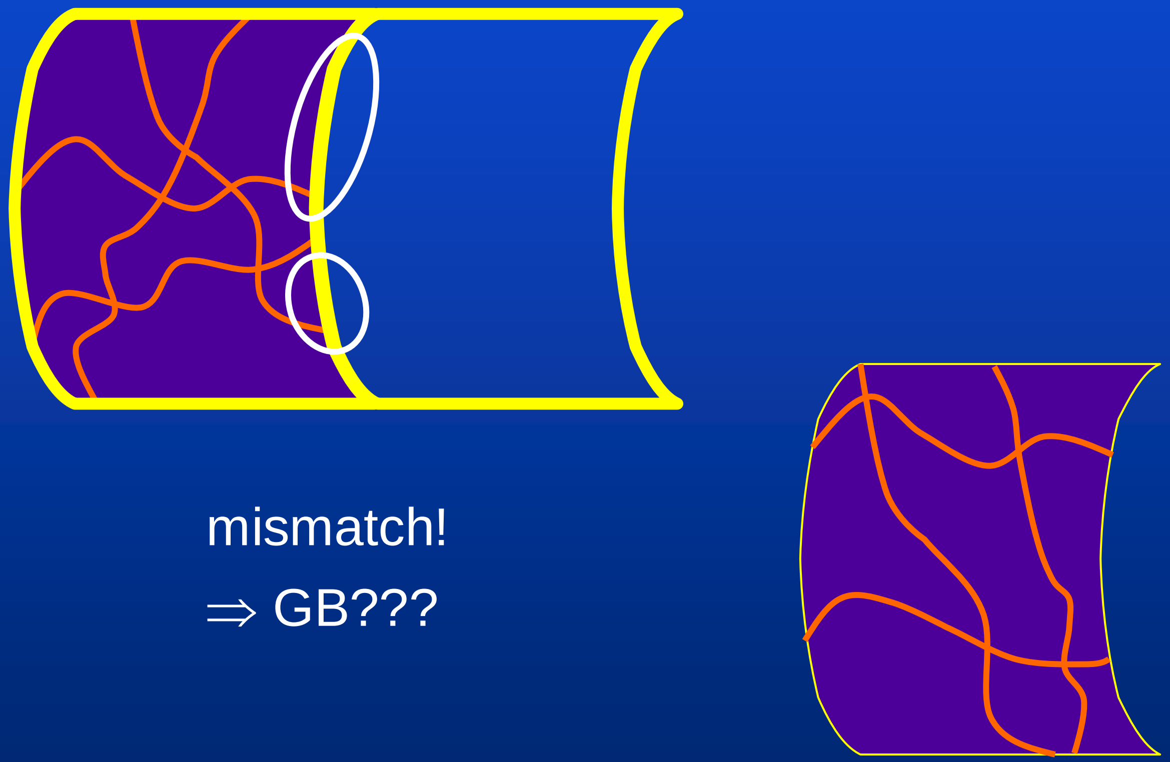
$\Rightarrow$ ● $= 3a\ \rho/\rho_s$

if NCRIF = 0.1 %, ● = 1 µm

if NCRIF = 10 %, ● = 10 nm

… but they might be involved!

how to connect two supersolid grains?

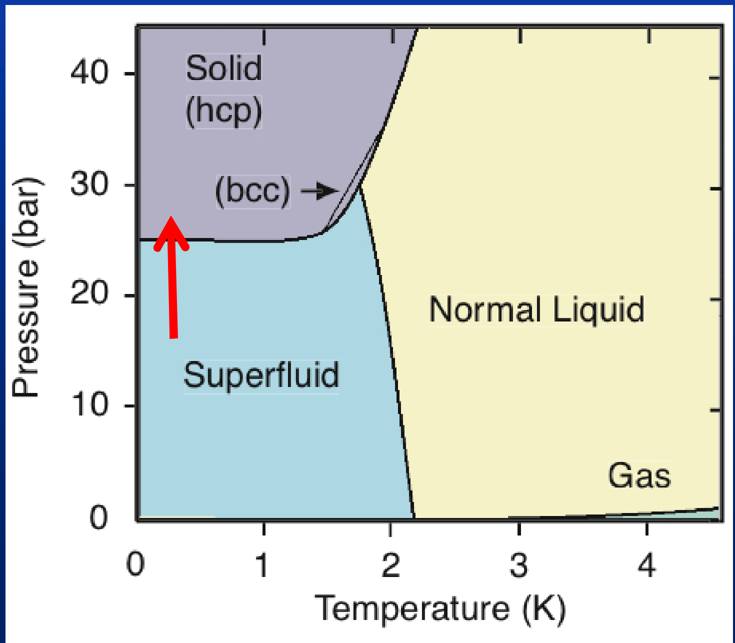


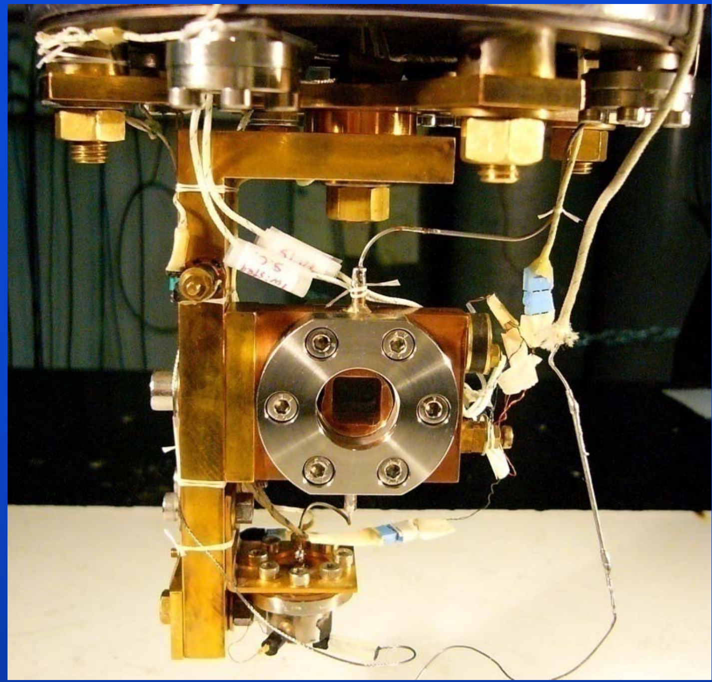
mismatch!

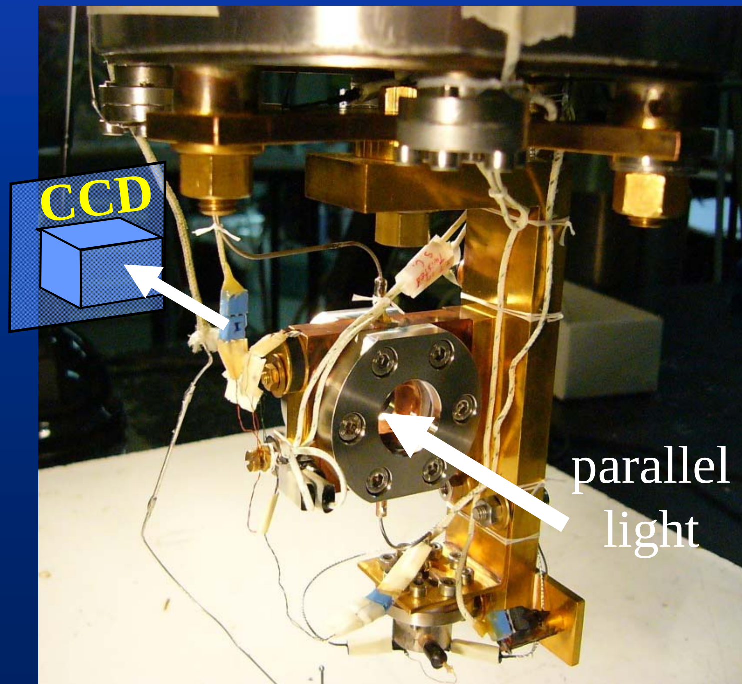
$\Longrightarrow$ GB???

Observation of helium crystals

cubic cell : 11 x 11 x 3 mm^3
10 mm thick copper walls
2 glass windows (thickness 4 mm)
indium seals
stands 65 bar at 300K
Straty-Adams pressure gauge (0 to 37 bar) connected through a CuNi capillary
50 mm long (int. diam. 0.6 mm)







Fast injection of superfluid at 100 mK

Sasaki, Caupin and Balibar *PRL* ’07

45 bar in a bottle – fast opening of a valve on the fill line

inject_160507.mov

inject_160507_sample2.mov

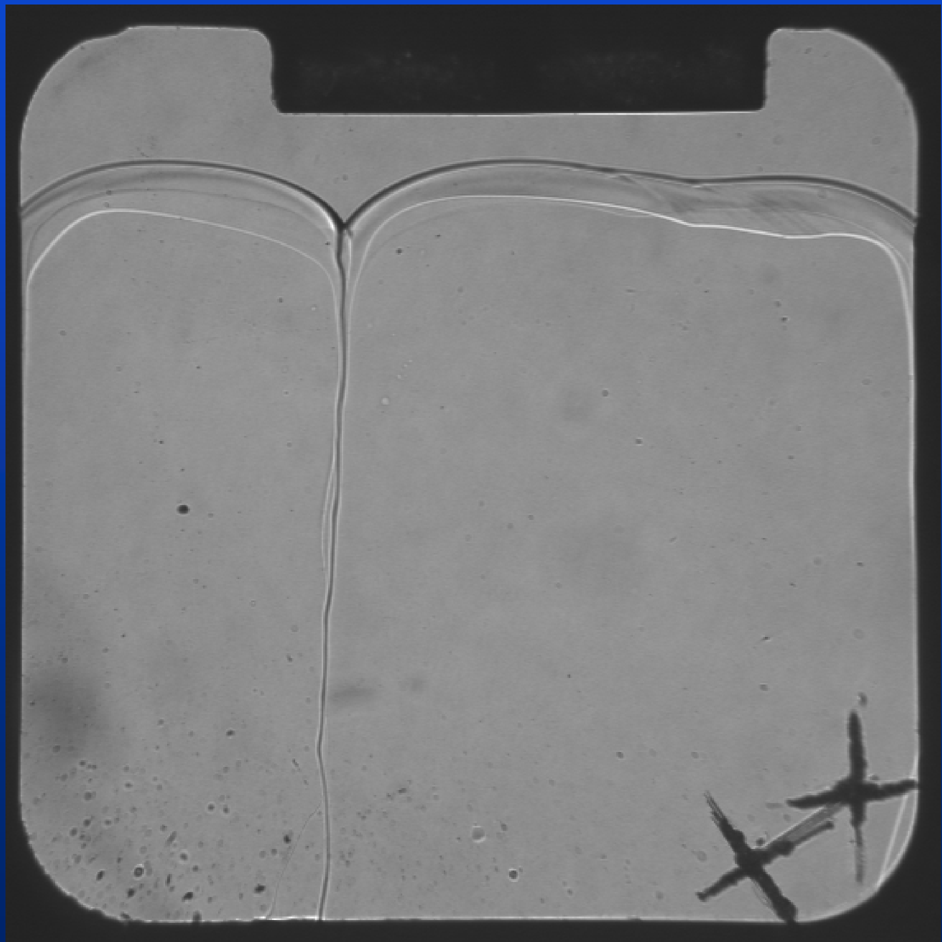
Melting after fast injection

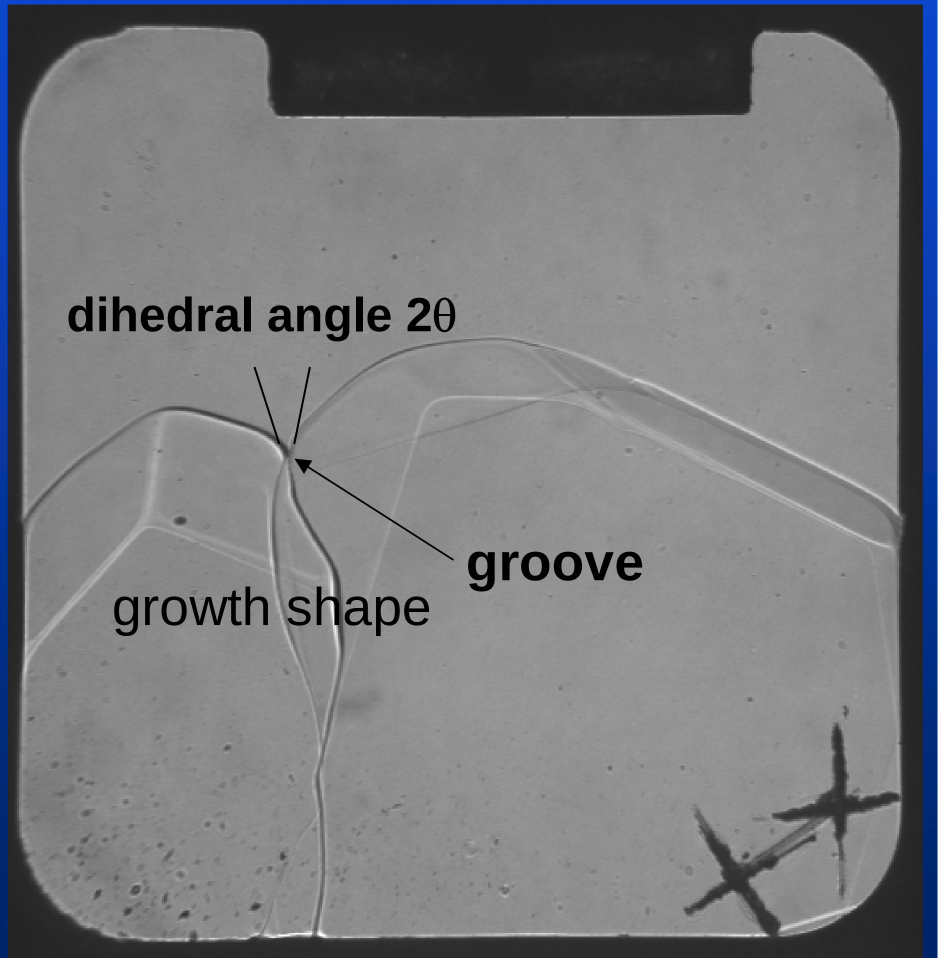
remove helium by opening slowly on a 25 bar reservoir

melt_160507_sample2.mov

Wetting properties of grain boundaries

growing-melting cycles to keep only 2 grains with different orientations





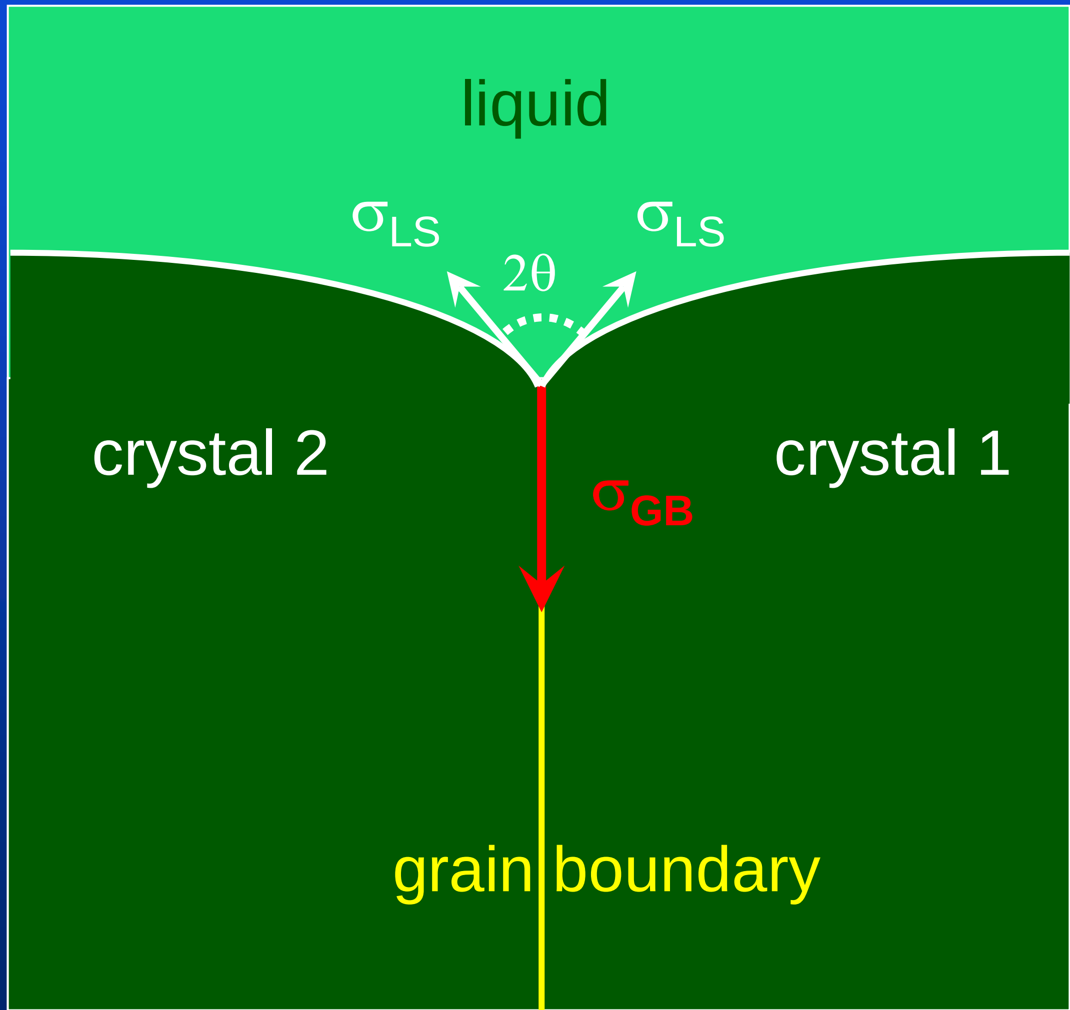
Dihedral angle

fit with Laplace equation near the cusp $\Rightarrow \theta = 14.5 \pm 4°$

force balance (Young)
$\sigma_{GB} = (1.93 \pm 0.04)\, \sigma_{LS}$

other crystals:
$\theta = 11 \pm 3°$
$\theta = 16 \pm 3°$

agrees with values deduced from the groove depth

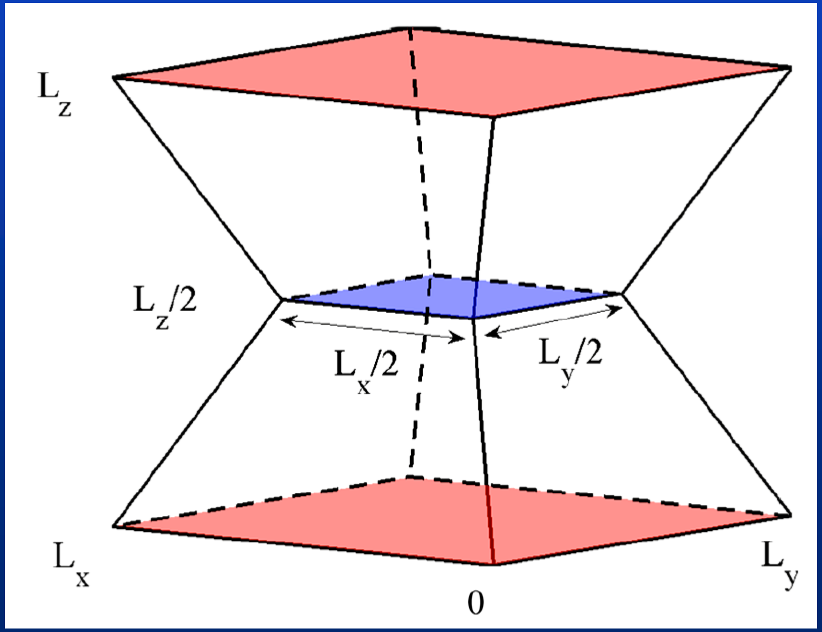


$$(\rho_S - \rho_L)\, g\, (\Delta z)^2 = 2\, \sigma_{LS}\, (1 - \sin\theta)$$

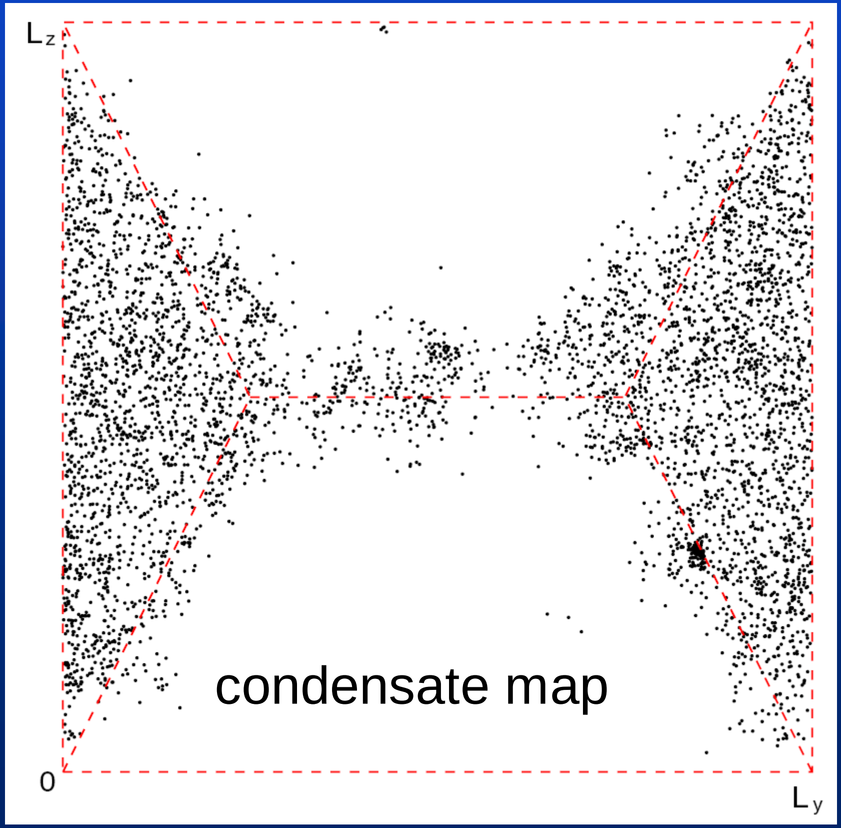
Monte-Carlo simulations of grain boundaries

Pollet et al. *PRL* ’06

2 crystals truncated pyramidal shape with different orientations



generic GBs are superfluids below ≈0.5 K and ≈3 atoms thick



Surface and interface melting

- melting of a classical crystal often starts at its free surface in contact with the vapour
- even premelting (existence of liquid layers) at T below the bulk melting temperature T_m
- and what if no free surface, but grain boundaries?

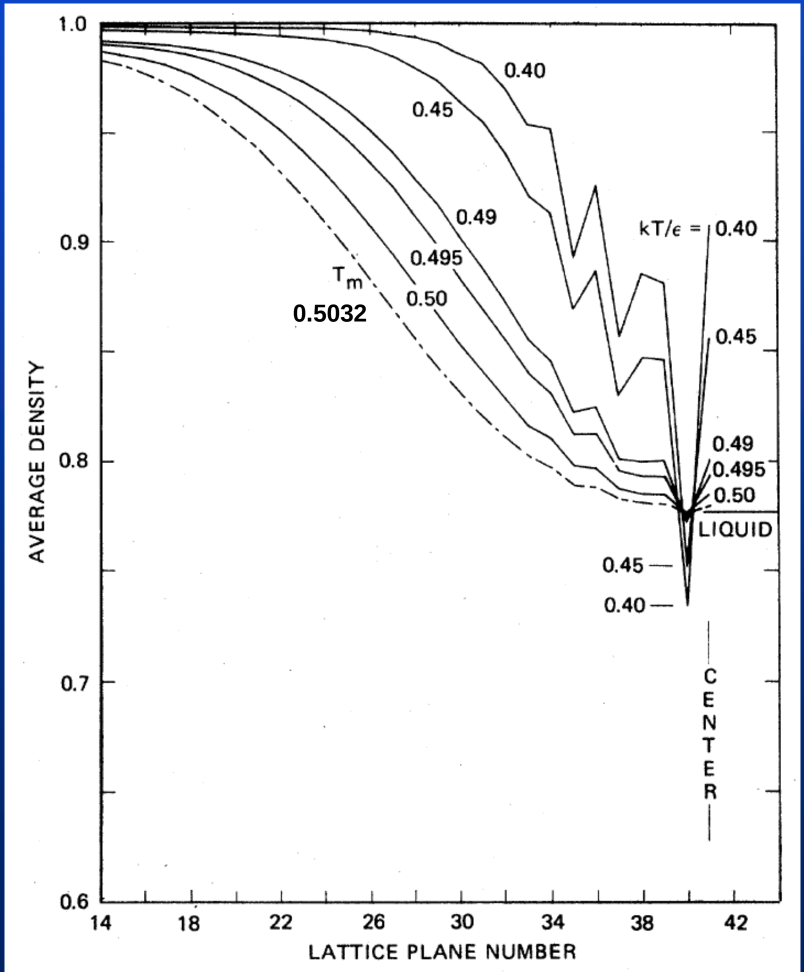
complete wetting of the GB by the liquid seems possible if $\sigma_{GB} = 2\sigma_{LS}$

premelting?

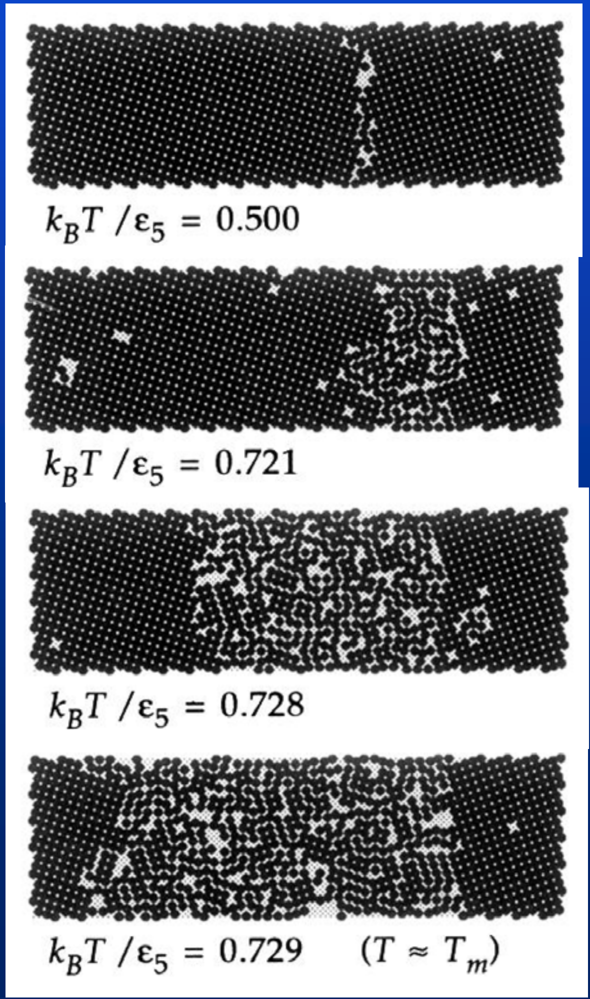
Grain boundary premelting

2D lattice gaz model: complete wetting at T_m and premelting

Kikuchi and Cahn '80 mean field

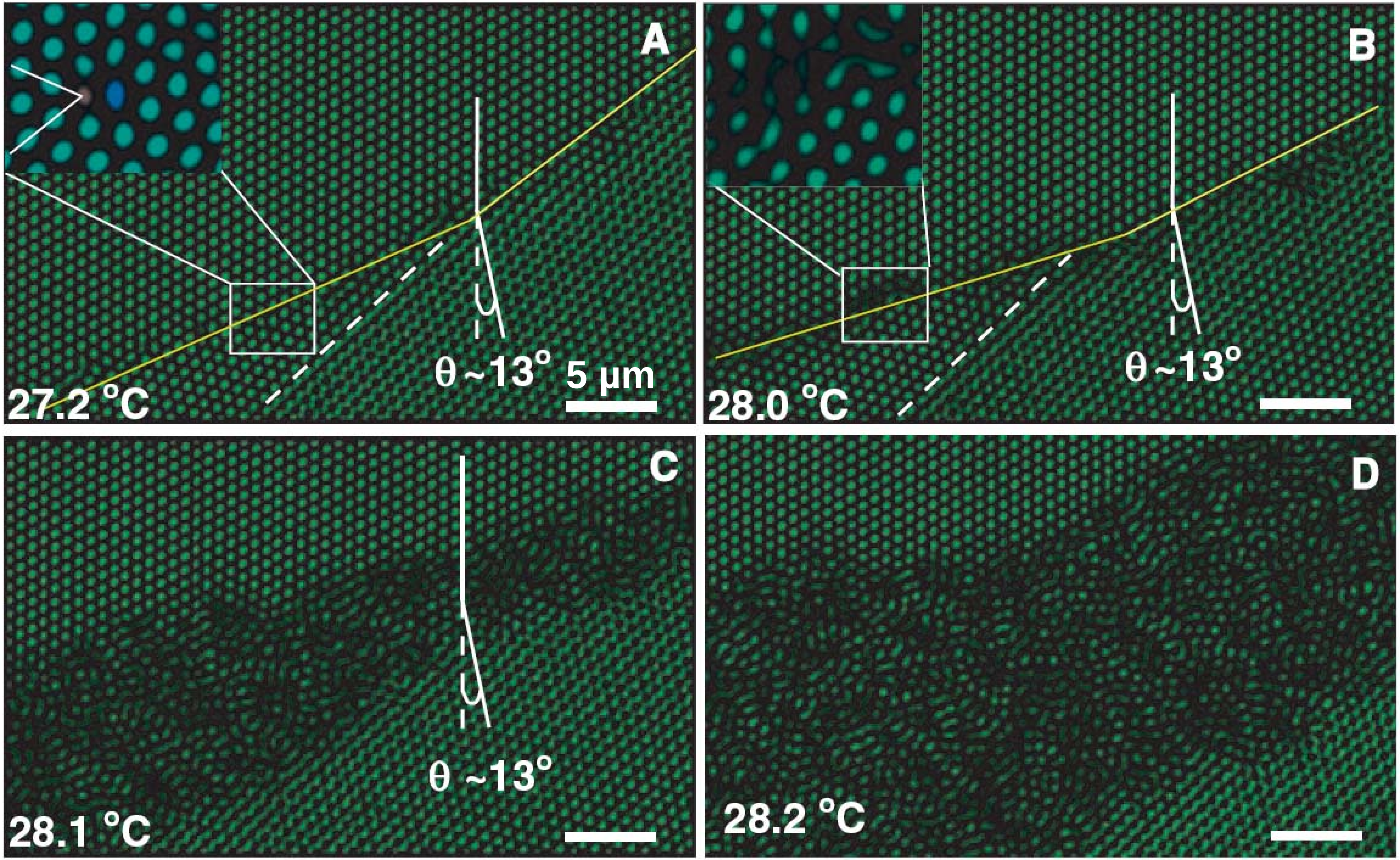


Besold and Mouritsen '94 Monte-Carlo



Grain boundary premelting

colloidal crystals Alsayed et al. *Science* '05 T_m=28.3°C

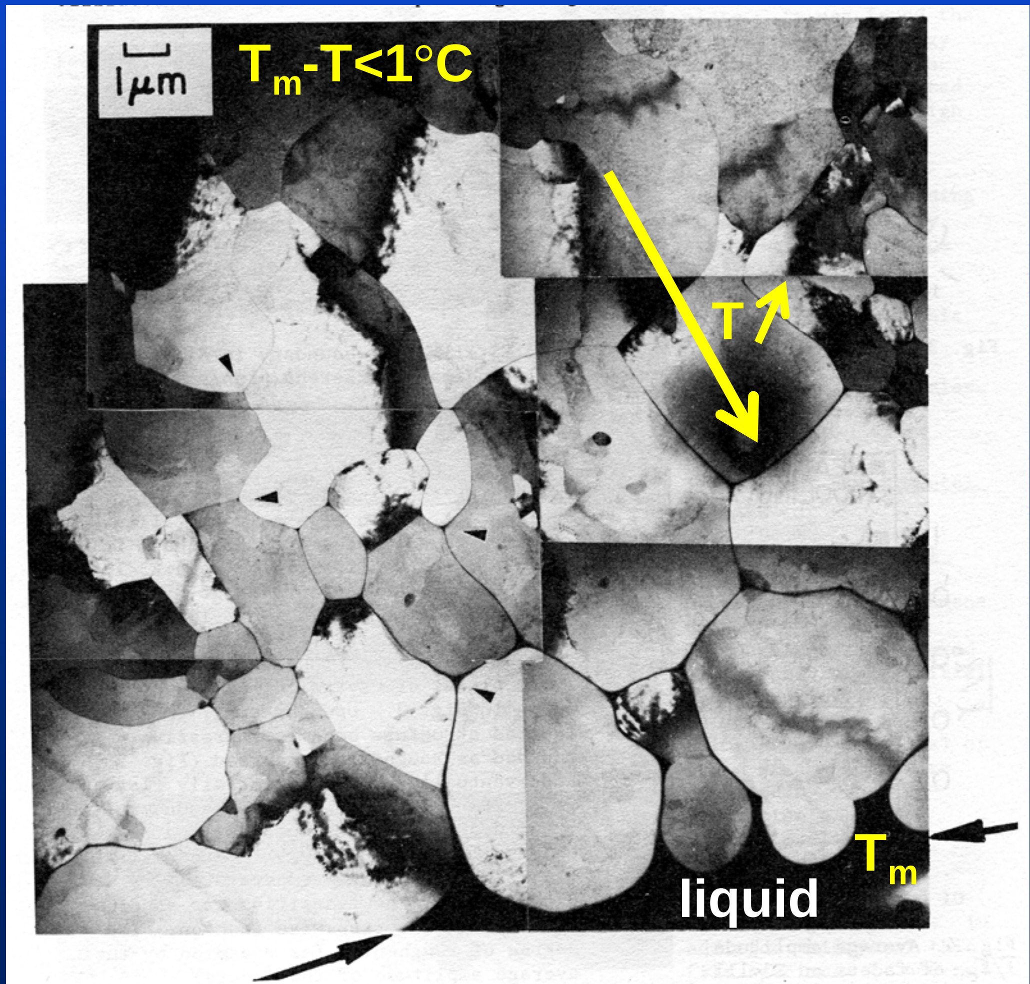


Grain boundary melting

bismuth films 50-100 nm thick Glicksman and Vold *Acta Metall.* '67

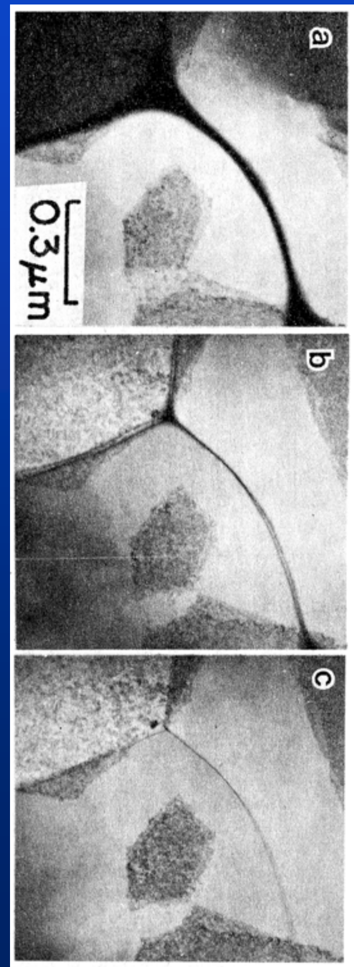
aluminum films 400 nm thick Balluffi and Hsieh *J. de Physique C* '88

GB thickness < 0.7 nm for $T<T_m$-1°C



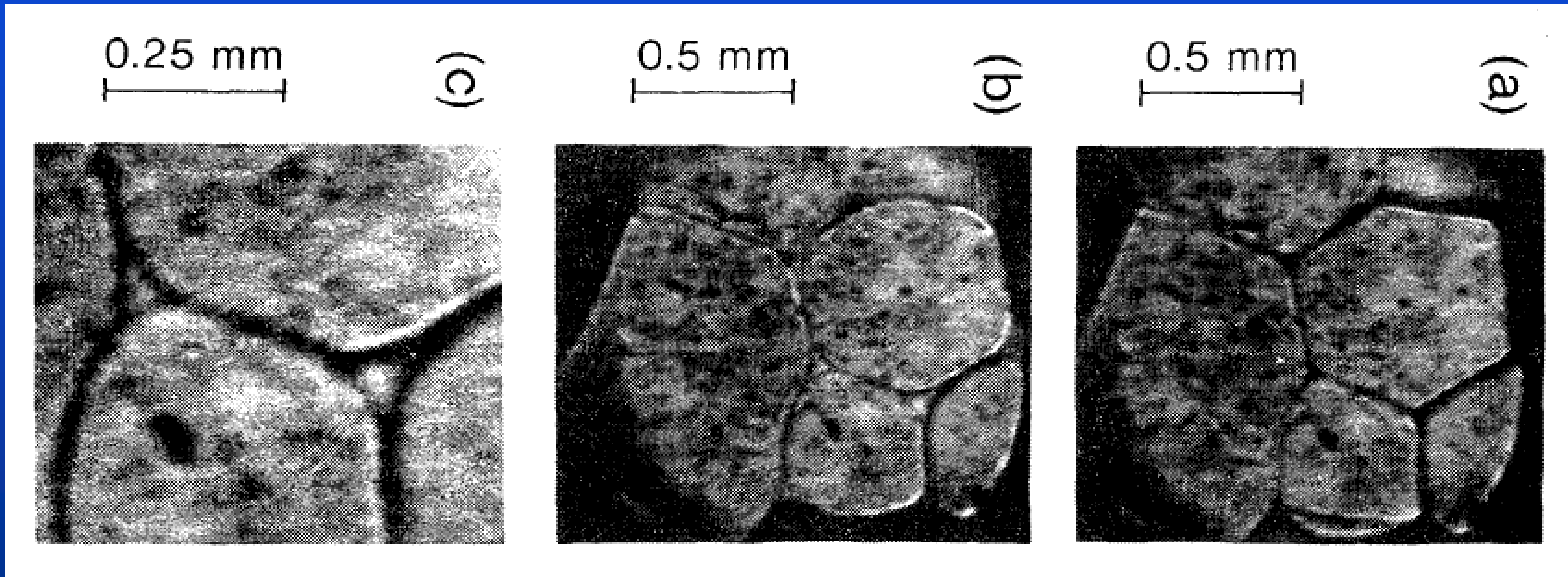
$T=T_m$

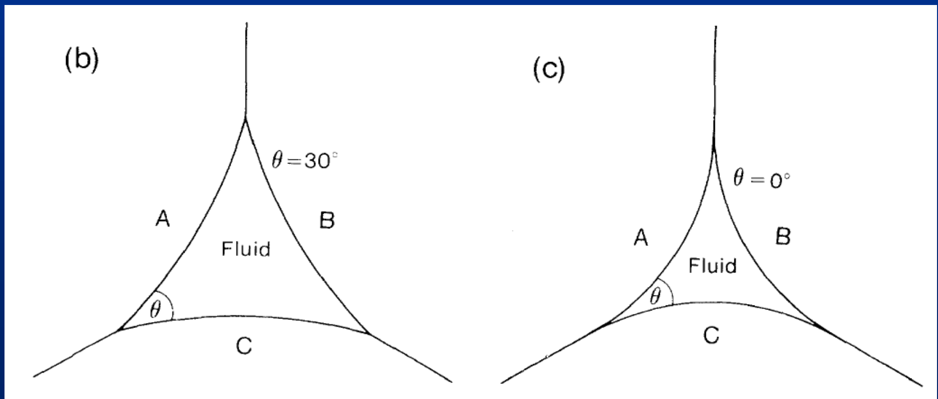
T ↓



Grain boundary melting

Franck et al. *PRL* ’83 helium films, 50µm, fcc, high T – high P





280 MPa
26.3 K

← warming up
by a few mK/min

$0 \leq \theta \leq 30°$

“almost” complete wetting

BUT the interpretation of experiments on films needs to be reconsidered:

- the GB makes a groove at the LS interface
- the GB can open into a liquid channel on a wall

$\Rightarrow$ for thin films, the grains can detach

$\Rightarrow$ whereas in our experiment on helium, the grains are 3 mm thick

And now some theory

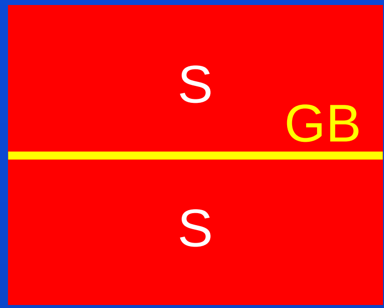
Lipowsky *PRL* '86

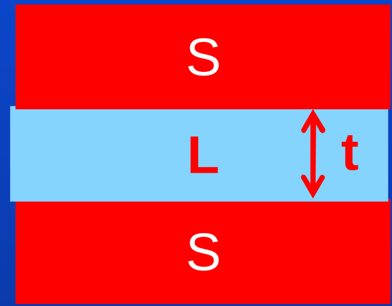
definition: $\Delta\sigma^0(T) = 2\sigma_{LS} - \sigma_{GB}{}^0$

liquid layer between two grains at $T < T_m$

free energy per unit area: $\Delta G(t) = L\,(1-T/T_m)\,t + \Delta\sigma^0 + V(t)$

minimize $\Delta G(t) \Rightarrow$ equilibrium thickness t





short range forces:

$V(t) = K \exp(-t/\xi)$ for large t

if $K>0$

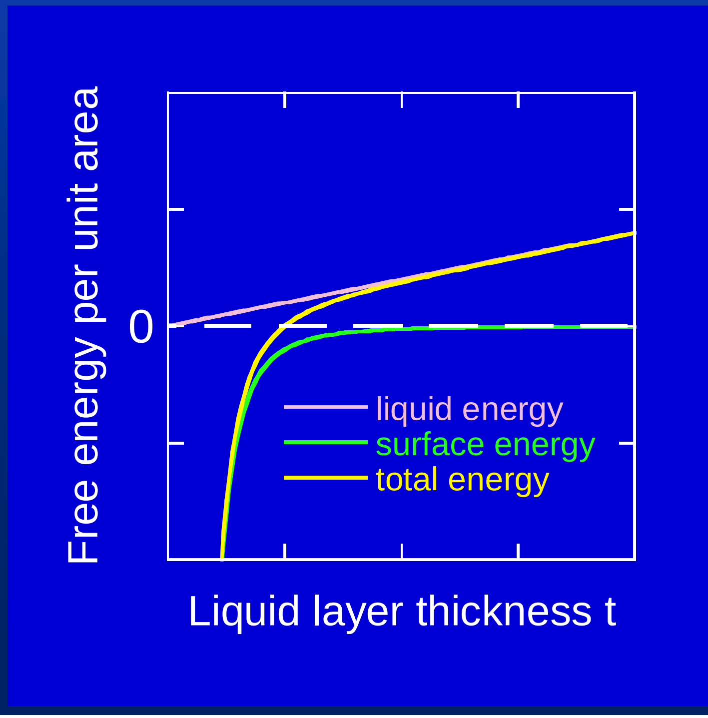
$\Rightarrow$ divergence $t(T) = \xi \ln[K/(T_m - T)]$

$\Rightarrow$ $\Delta G < 0$ if $\Delta\sigma^0$ sufficiently negative

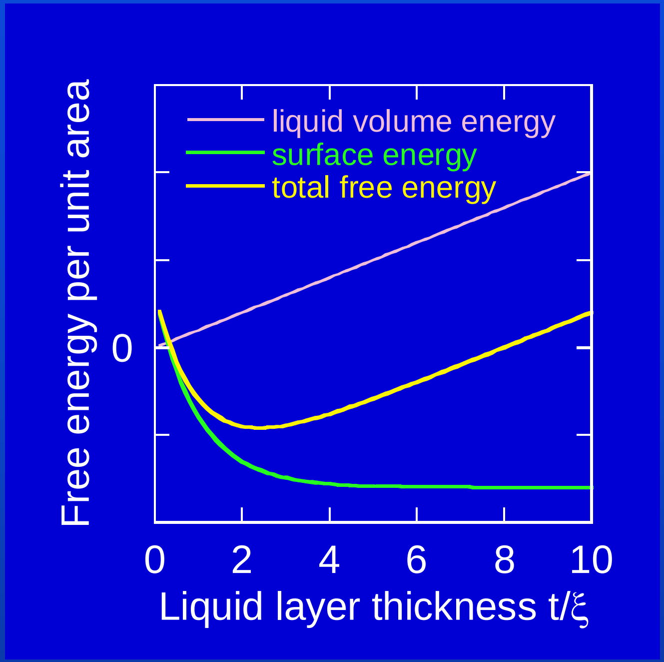
$\Rightarrow$ seen in simulations with

finite range lattice gas model or

truncated L-J potential



And now some theory



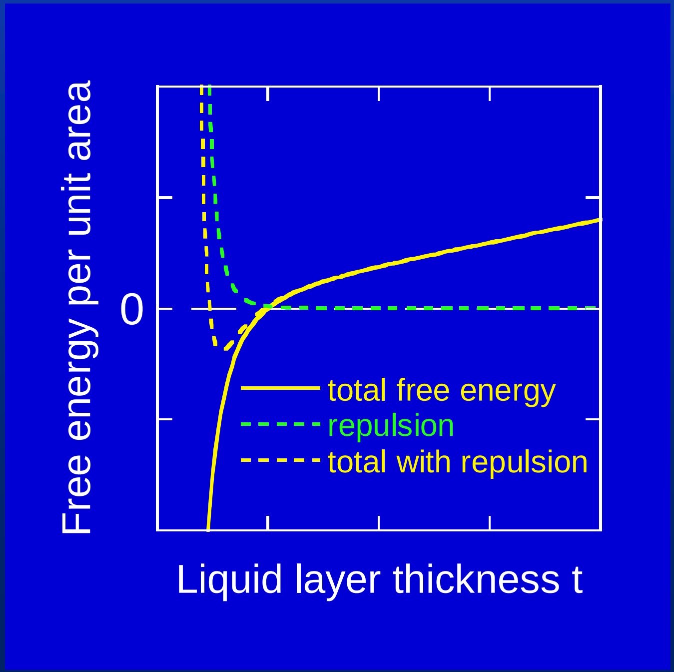
long range forces (VdW):

as both sides have same density:

• large t: V(t) always attractive = $-K/t^n$ with K>0

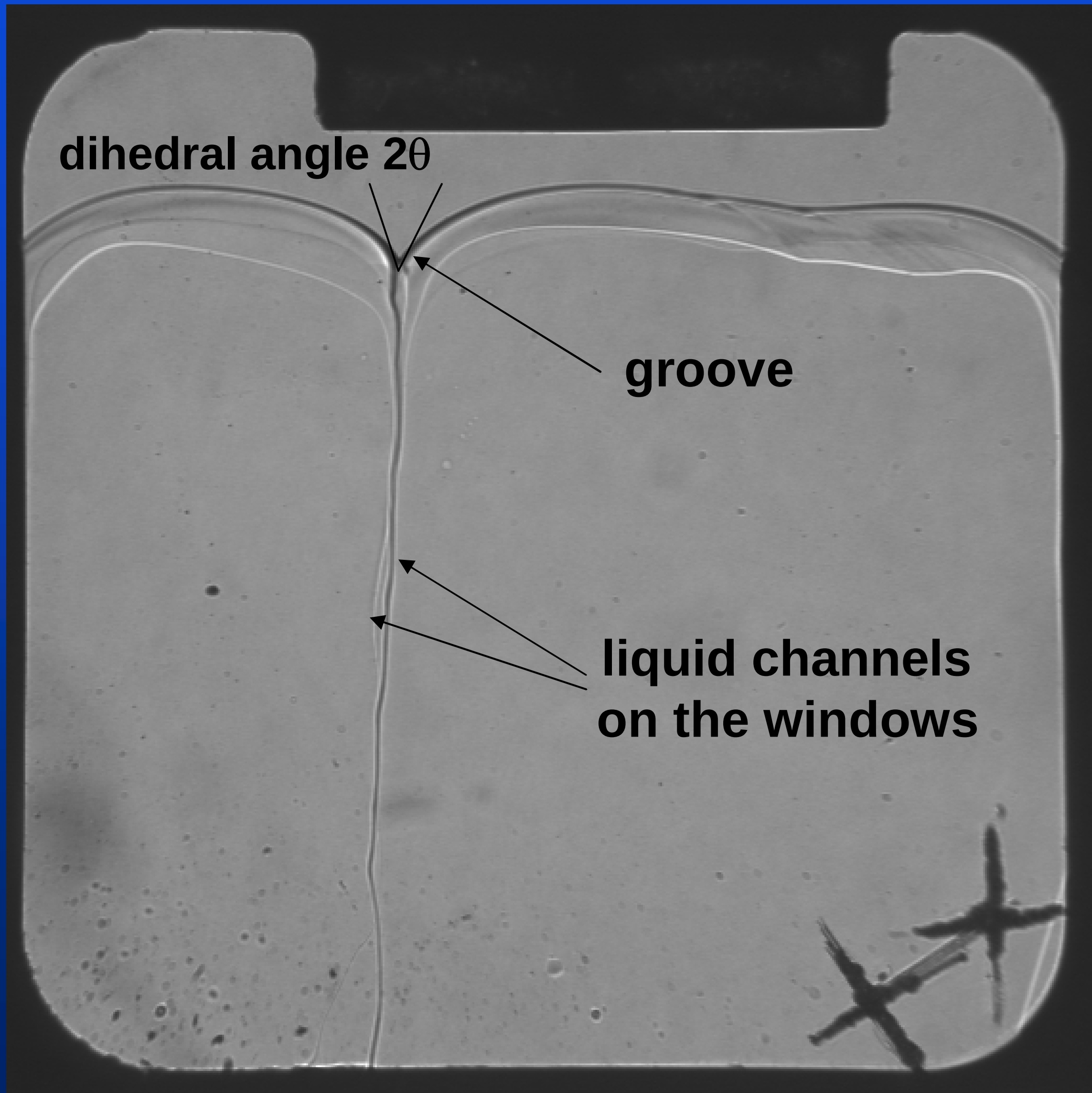
• small t: repulsion can occur (repulsive cores, fluctuations…)

but t remains an atomic scale

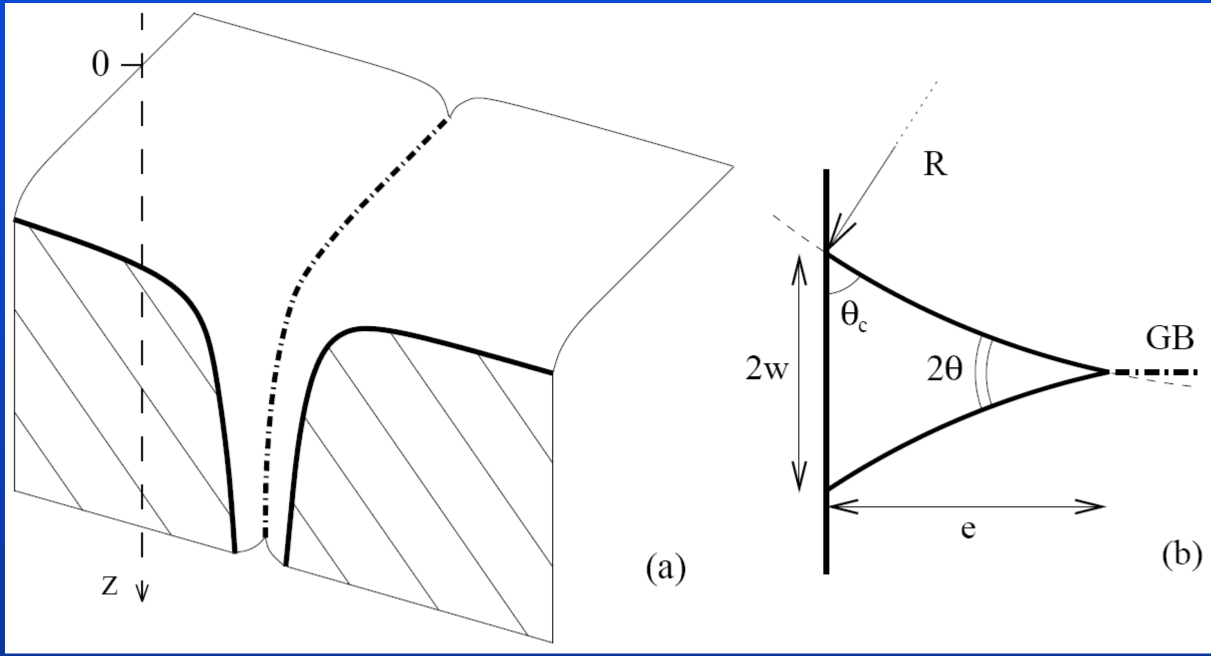


Schick and Shih *PRB* '87

Wetting properties of grain boundaries



Liquid channel on the window



$$l_c = \sqrt{\frac{\sigma_{LS}}{\Delta\rho\, g}}$$

capillary length

contact angle θ_c between the LS interface and the wall

neglecting elasticity ⇒ hydrostatic equilibrium

$$P_L(z) = P_{eq} + \rho_L g z$$

$$P_S(z) = P_{eq} + \rho_S g z$$

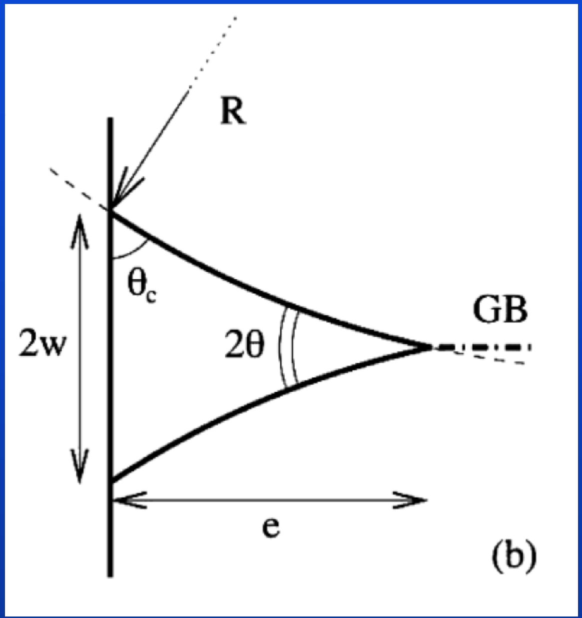
⇒ pressure difference

⇒ curved interface, liquid on the convex side

$$R = \sigma_{LS}/[P_S(z) - P_L(z)] = {l_c}^2/z \quad \text{for} \quad z/l_c > 1.7$$

⇒ requires $\theta + \theta_c < \pi/2$

Liquid channel under pressure



LS equilibrium possible above P_{eq}
for a curved interface:

$$\mu_L(P_L) = \mu_L(P_{eq}) + \frac{P_L - P_{eq}}{\rho_L}$$

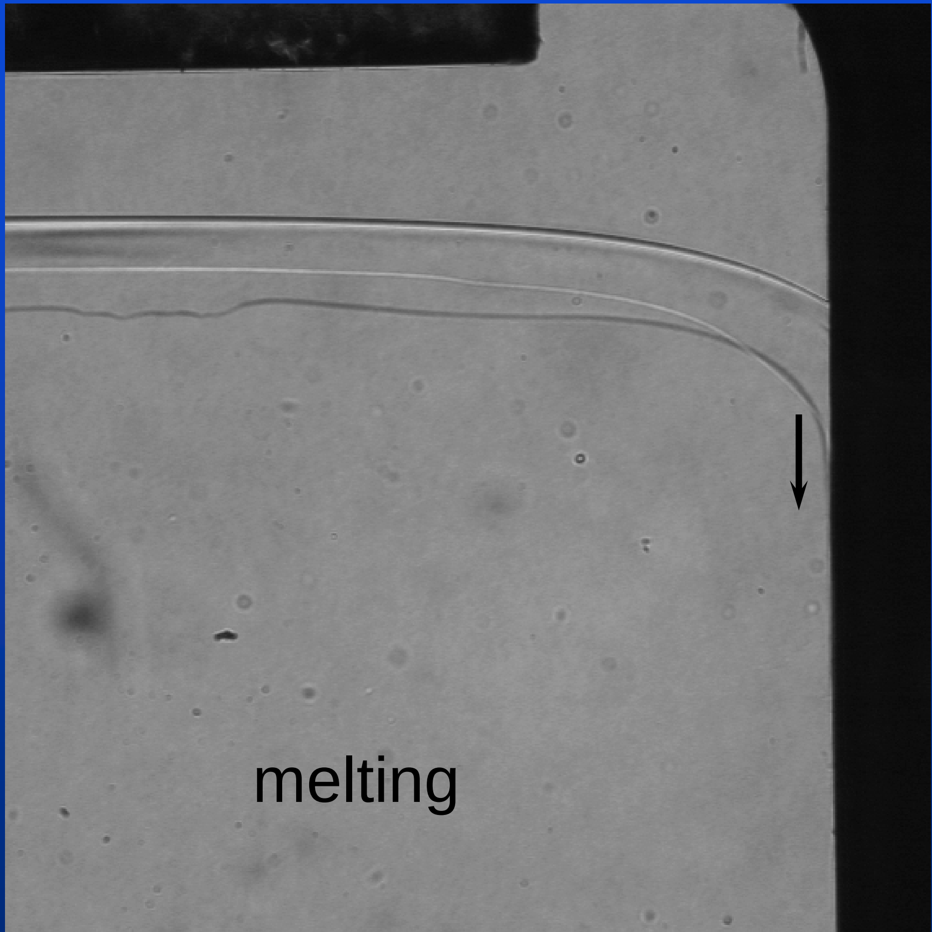
$$\mu_S(P_S) = \mu_S(P_{eq}) + \frac{P_S - P_{eq}}{\rho_S}$$

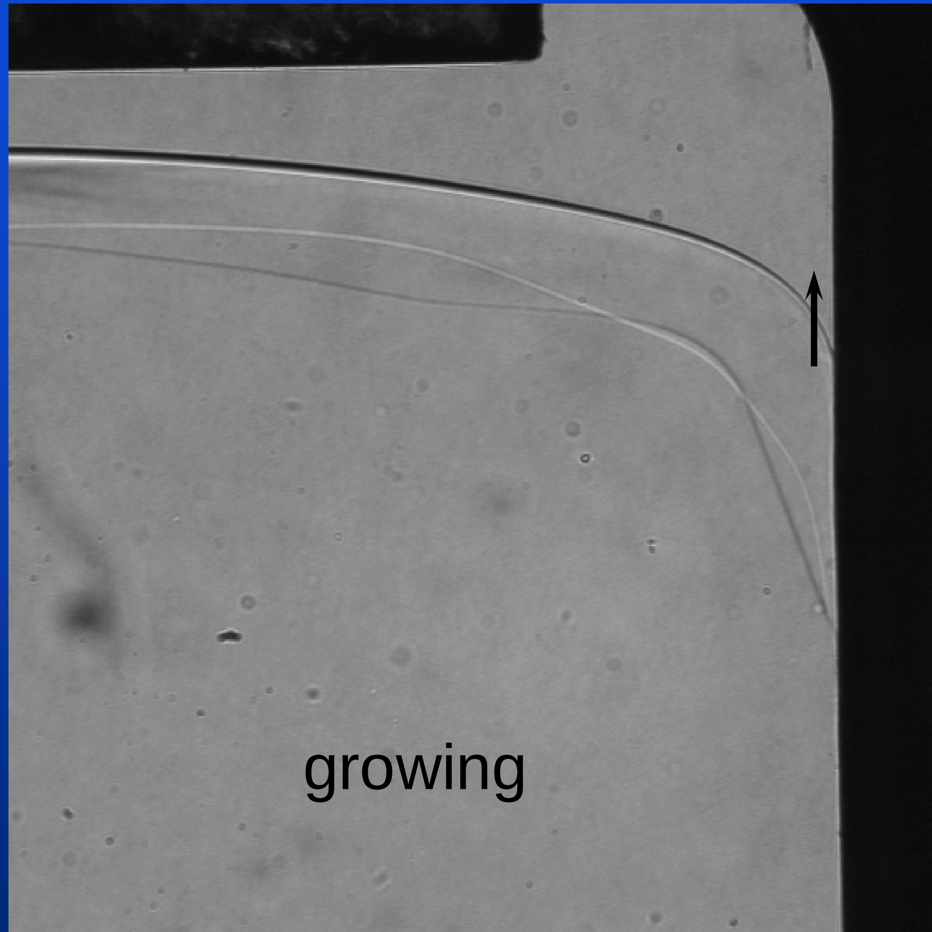
$$\Rightarrow P_L = \frac{\rho_L}{\rho_S} P_S + \left(1 - \frac{\rho_L}{\rho_S}\right) P_{eq}$$

$$R = \frac{\sigma_{LS}}{P_S - P_L} = \frac{\sigma_{LS}}{\left(1 - \frac{\rho_L}{\rho_S}\right)(P_S - P_{eq})}$$

$$S = R^2 \left[(\cos\theta_c - \sin\theta)(\cos\theta - \sin\theta_c) + \cos(\theta + \theta_c) + \theta + \theta_c - \frac{\pi}{2} \right]$$

Contact angle hysteresis





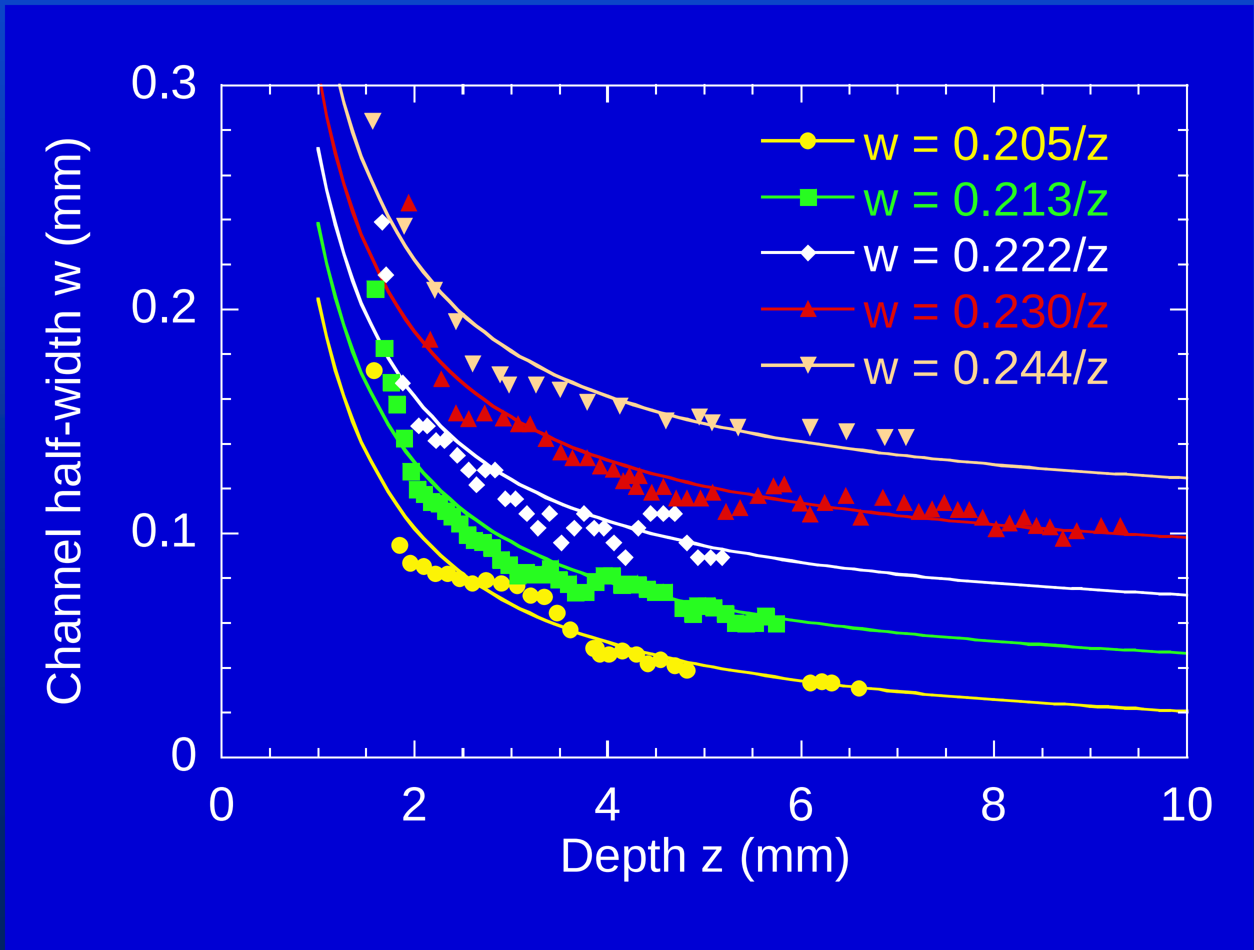
liquid advancing: 55 ± 6 ° (copper) 51 ± 5 ° (glass) 53 ± 9° (graphite)
liquid receeding: 22 ± 6 ° (copper) 26 ± 7 ° (glass) 37 ± 6 ° (graphite)
larger hysteresis on rough copper than on a smooth glass wall

Liquid channel on the window

$$\theta + \theta_c < \pi/2$$

$\theta \approx 15°$, $\theta_c \approx 45°$ ⇒ channel

$$w(z) = \frac{{l_c}^2}{z}(\cos\theta - \sin\theta_c)$$



using $\theta = 15°$, $\theta_c = 45°$

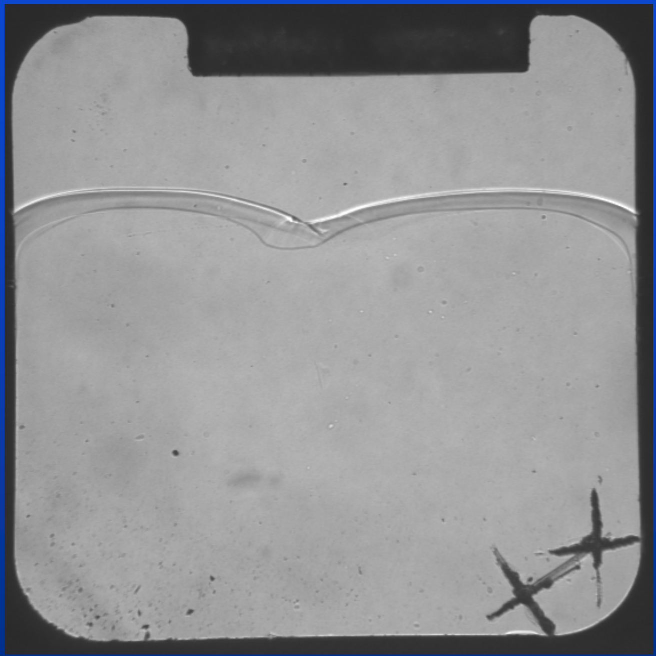
⇒ $l_c \approx$ 0.89 to 0.97 mm

a calculation with σ_{LS}=0.17 mJ/m^2 gives l_c = 0.98 mm

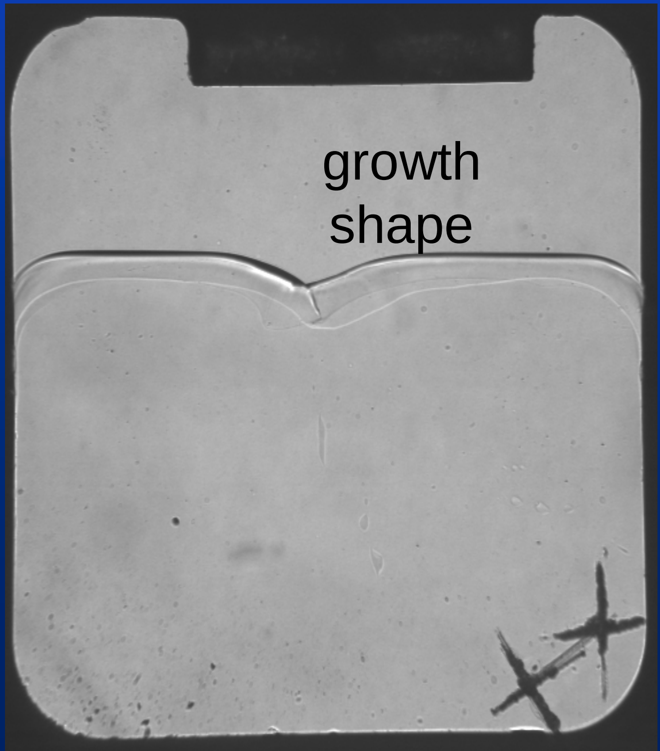
the channel closes for large z (or under pressure)

Direct nucleation of two grains

quick closing of a valve on the fill line
sometimes allows to make two grains with similar orientations



nucleation.mov



small σ_{GB}

$\Rightarrow$ large θ

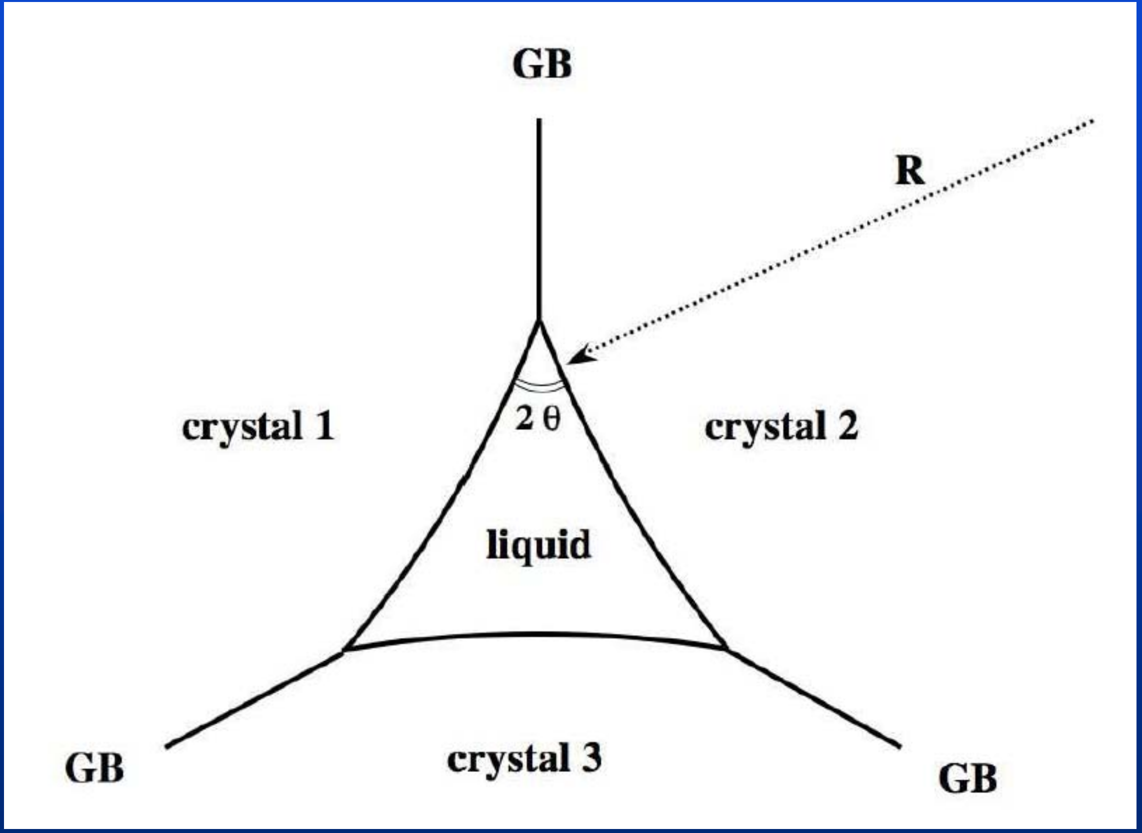
$\Rightarrow \theta + \theta_c > \pi/2$

$\Rightarrow$ no channel

Liquid channel between three grains

$\Rightarrow$ requires $\theta < \pi/6$

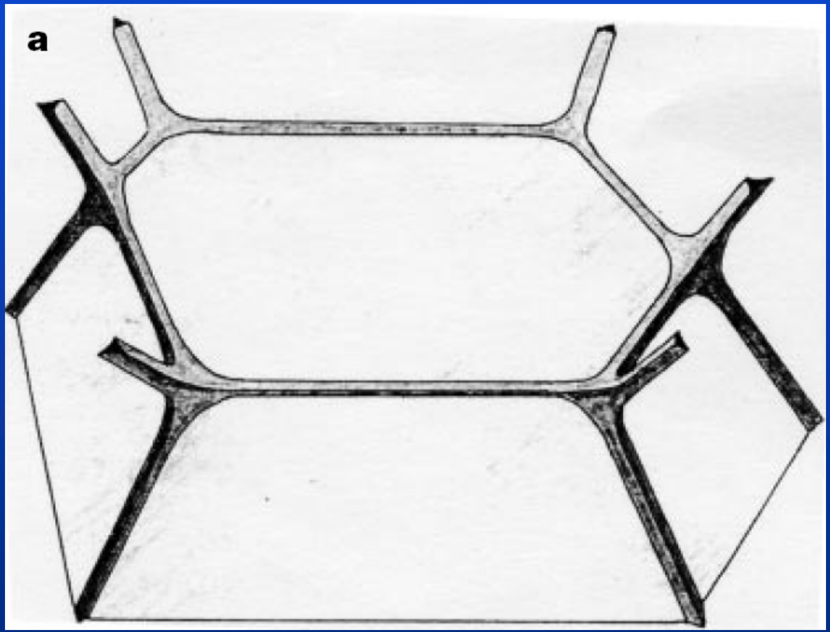
Miller and Chadwick *Acta metall.* '67
Raj *Acta metall. mater.* '90

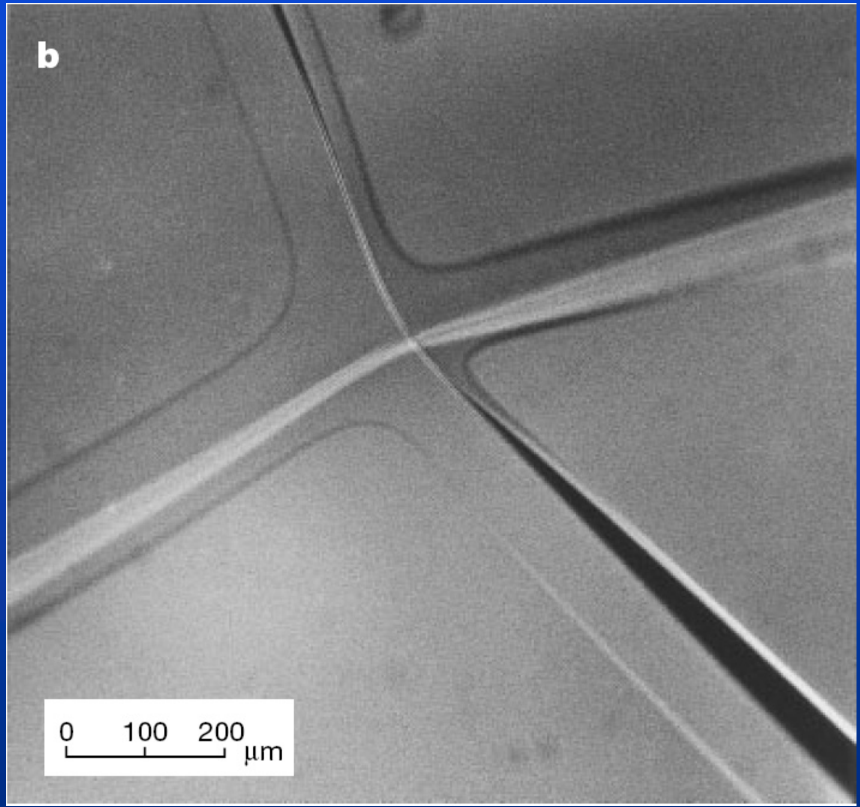


$$S = R^2 \left[2\sqrt{3}\, \sin\phi \,\; \sin\left(\phi + \frac{\pi}{3}\right) - 3\phi \right] \;\text{with}\; \phi = \frac{\pi}{6} - \theta$$

Liquid channels in ice

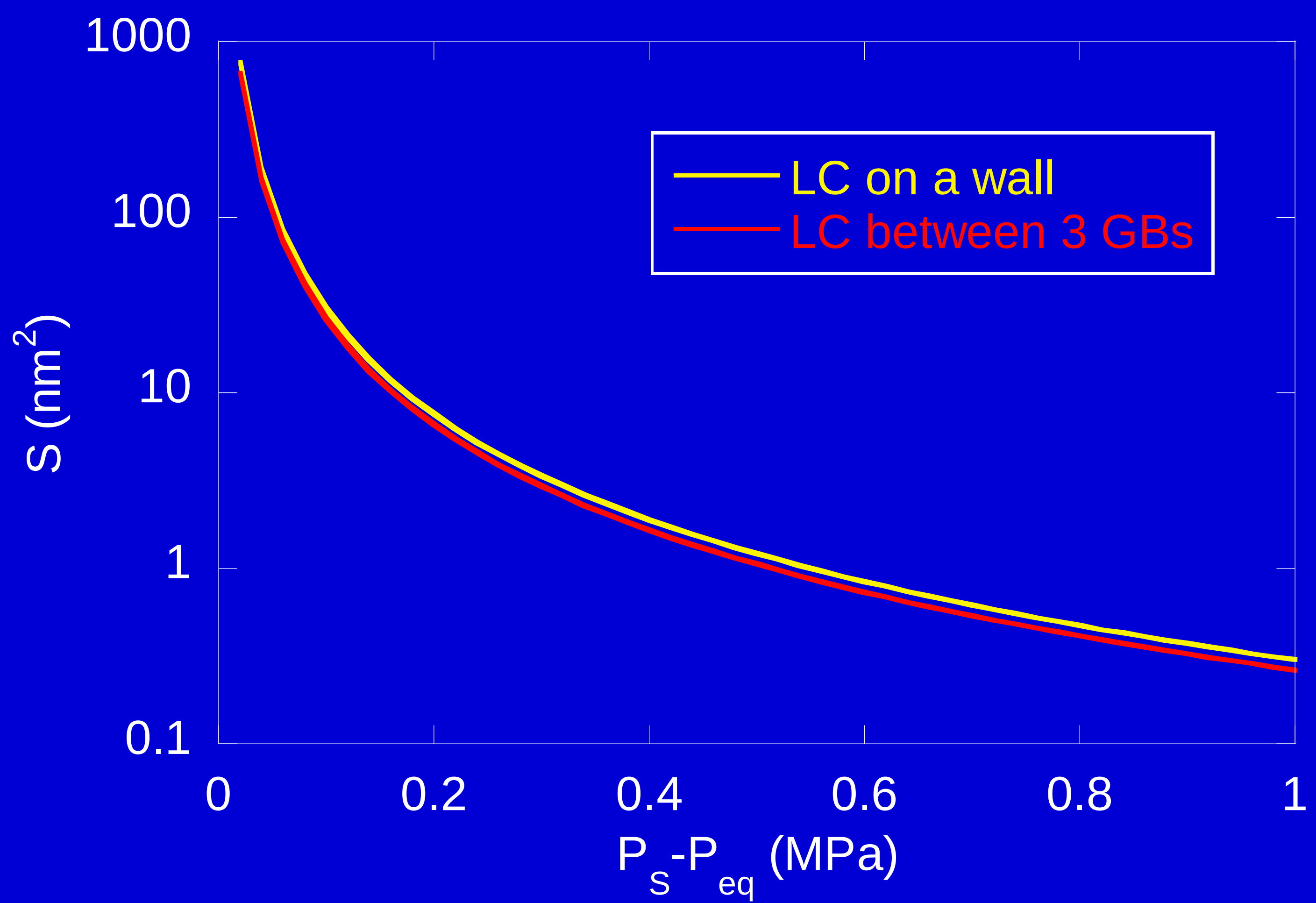
Nye *J. Glac.* ’89
Mader *J. Glac.* ’92





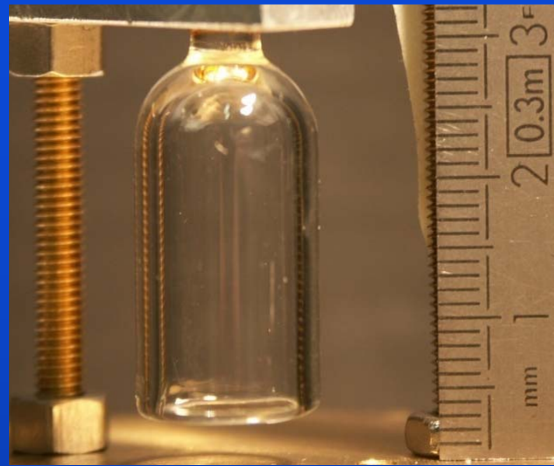
diffusion of impurities (dissolved gases) along the channels
⇒ possible bias in climate reconstruction Rempel et al. *Nature* ’01

Liquid channels under pressure

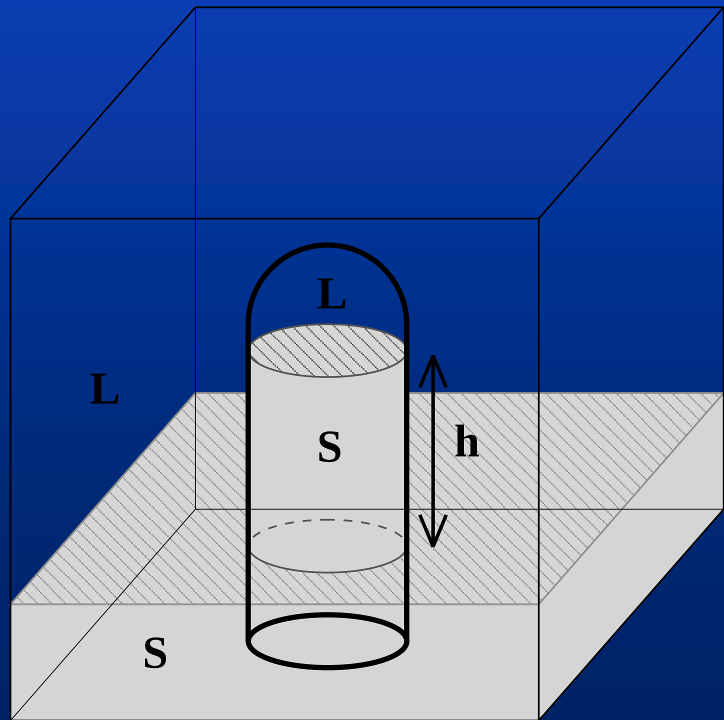


Torricellian experiment

Sasaki et al. *Science* '06



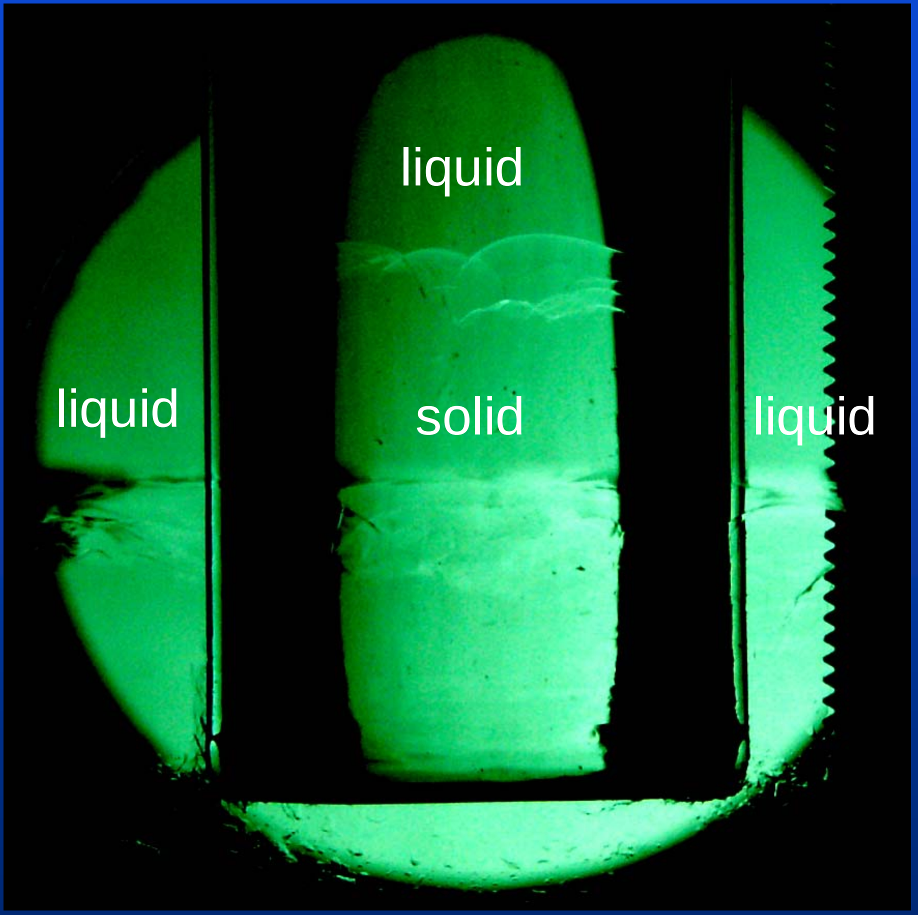
Inverted test tube (diam.10 mm)
solide grown at 1.3 K
cooled to 50 mK
height difference



$\rho_S = 1.1\ \rho_L$
$\Rightarrow$ a change of the solid level
inside the tube requires mass flow

Torricellian experiment

stress applied to crystallize the inside:
outside at 1.4K et
inside at 1.3K
during a few seconds



$P_f(1.4\ K) - P_f(1.3\ K) = 0.3$ bar
fast growth under inhomogeneous stress
$\Rightarrow$ defects

grain boundaries make grooves at the LS interface
many move and disappear, some remain pinned

No flow in good quality crystals

for 10 crystals with no or few grooves:
no flow
no leak along the tube walls

using numbers from the TO experiments :
1% superfluid density with $v_c = 10\ \mu m/s$
$\Rightarrow$ relaxation at $V = [\rho_S/(\rho_C - \rho_L)]v_c = 1\ \mu m/s = 3.6\ mm/h$

0.01% superfluid density with $v_c = 10\ \mu m/s$
$\Rightarrow$ relaxation at $V = [\rho_S/(\rho_C - \rho_L)]v_c = 1\ \mu m/s = 36\ \mu m/h$

Instead, experimental flow is less than 50 µm in 4 hours
$\Rightarrow$ $V < 12.5\ \mu m/h$

Flow in the presence of grain boundaries

flow at 50 mK for two crystals with groove in the tube

Torricelli1_480x.mov

480x real time

1s = 8 min

Torricelli2_480x.mov

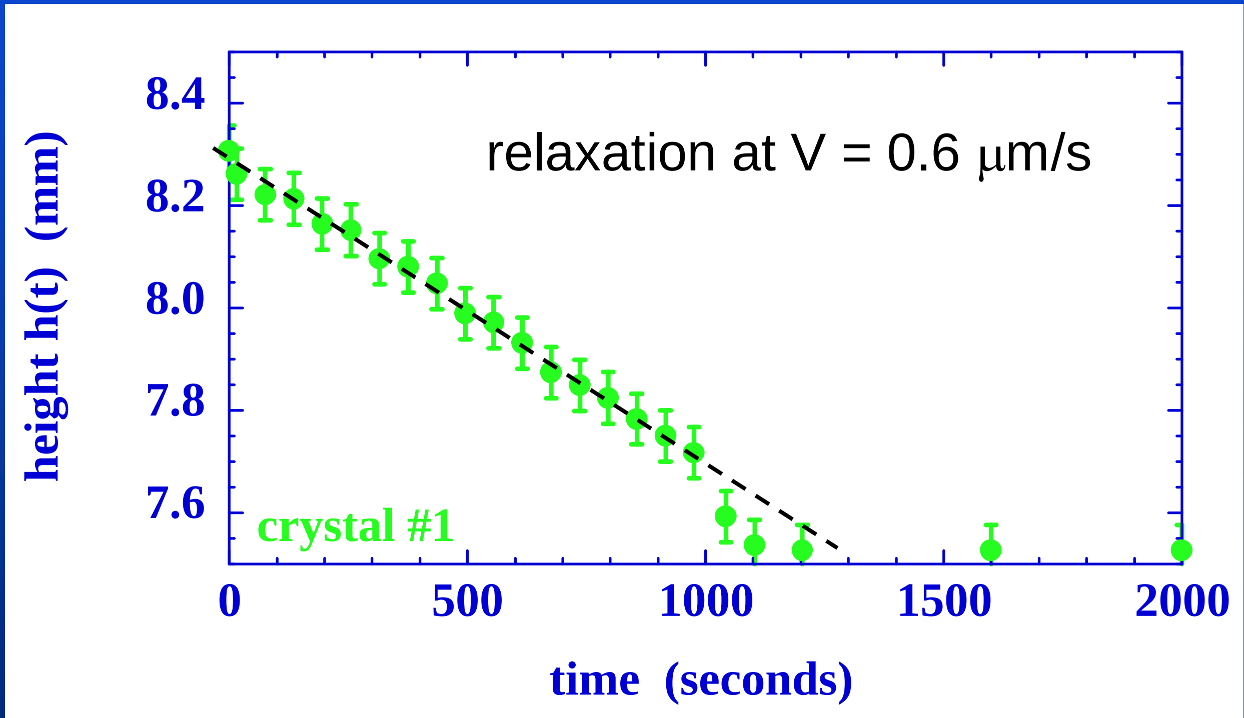
480x real time

1s = 8 min

crystal 1: the flow stops when the groove disappears

crystal 2: the flow continues until equilibrium is reached

Cristal 1: only one grain boundary



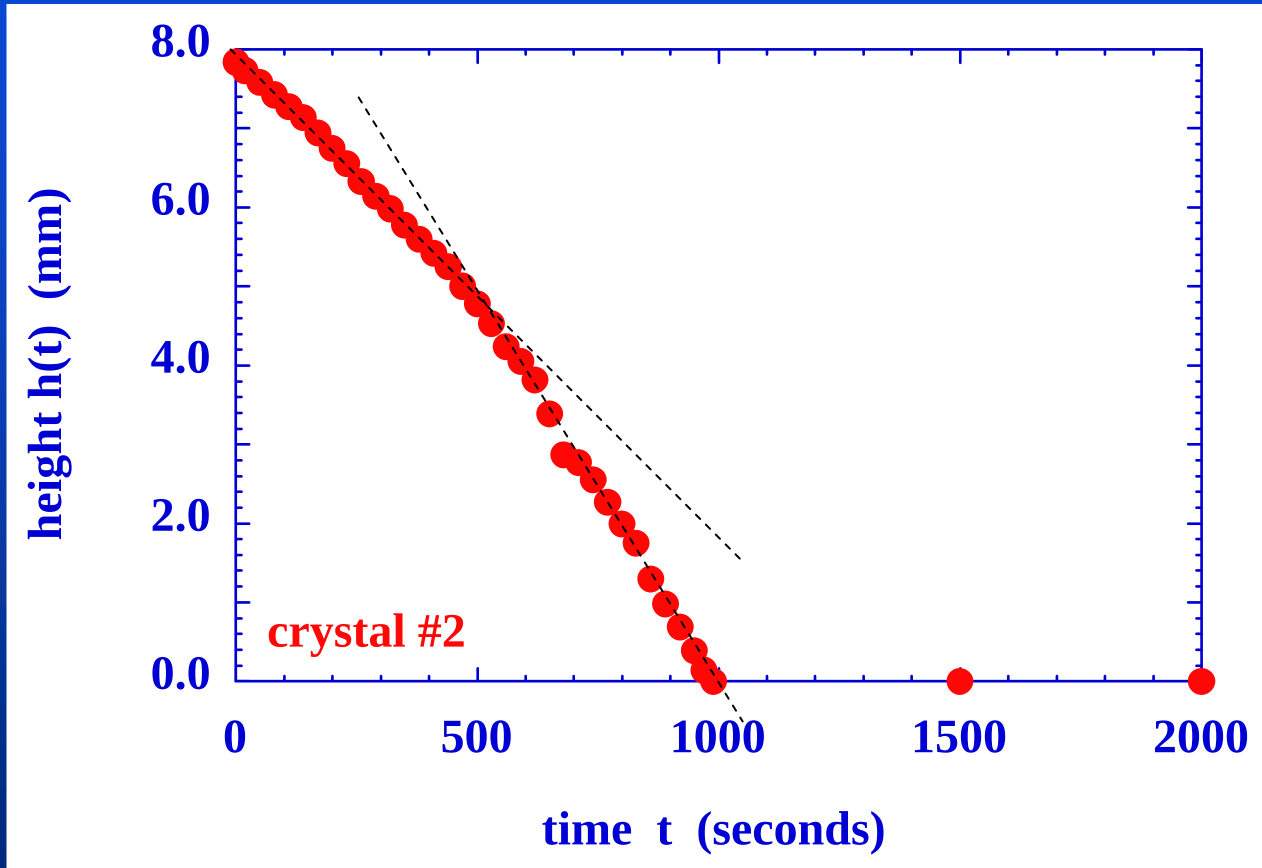
constant V : characteristic of superfluid flow

stops when the groove disappears (unpinning of the grain boundary)

Cristal 2: more defects

linear relaxation
(not exponential)

two regimes:
t < 500 s: 6 μm/s
t > 500 s: 11 μm/s



the velocity increases when the LS interface reaches
a region with more defects at the bottom of crystal 2?

Torricellian experiment revisited

mass flow in the tube (cristal 1):

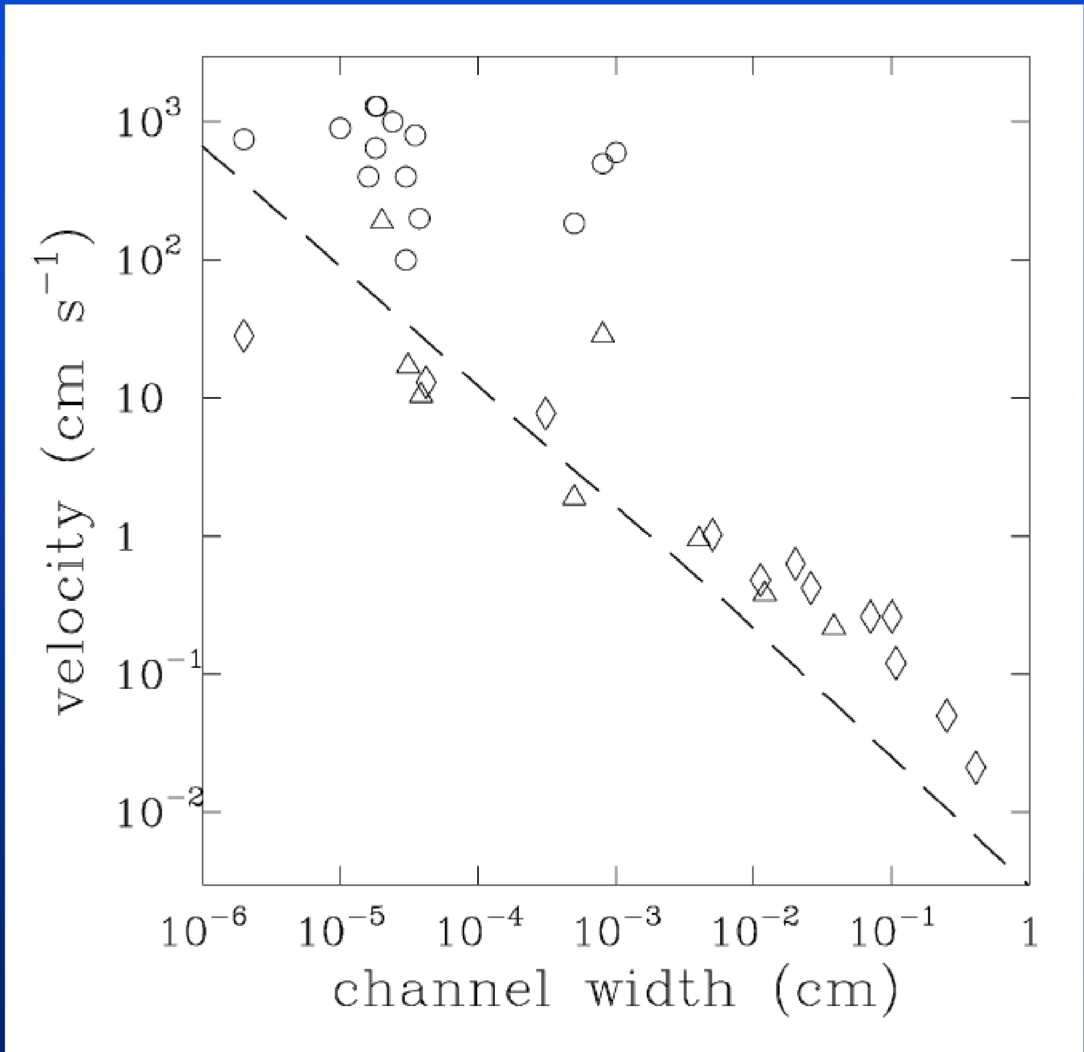
along a GB	along the 2 liquid channels created on the wall
section w e w ≈ tube diameter = 10 mm e ≈ (1/3) x 3 a = 0.3 nm	section = f(w,e) at a depth of 10mm : 870 μm^2

the measure interface velocity implies

v_c = 1.5 m/s comparible to 2 m/s in atomic thick liquid films Telschow et al. *PRL* '74	v_c = 3 mm/s

one sample did flow at 1.13 K ⇒ liquid channels more likely

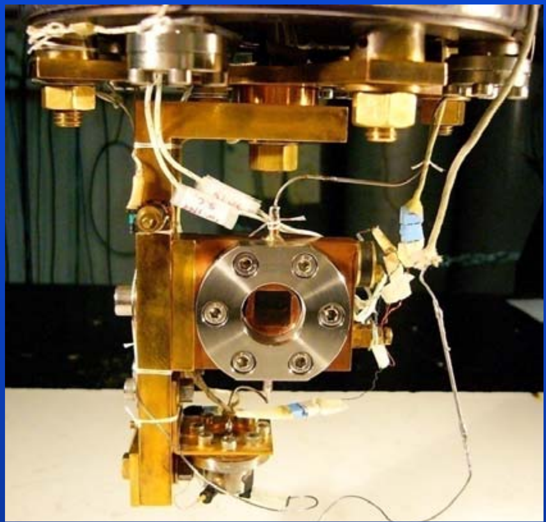
Torricellian experiment revisited



Varoquaux
C.R. Phys. '06

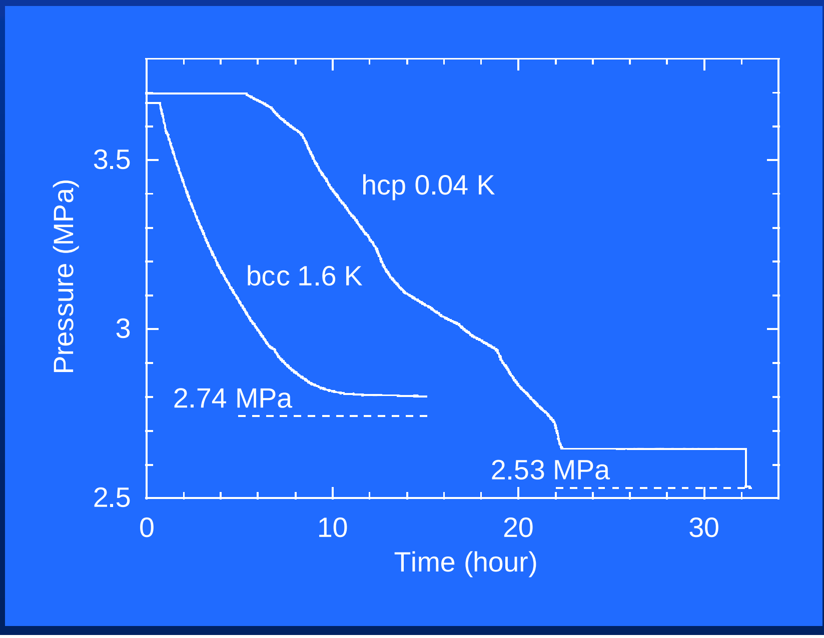
Elastic stress gradients

Rittner and Reppy *PRL* '07



P measured with a capacitive gauge
P increases from 41 to 51bar
after melting by heat pulse and quench cooling

capacitive gauge connected with a capillary (i.d. 0.6 mm, length 50 mm) to the main cell



sample grown with the blocked capillary method, then cooled

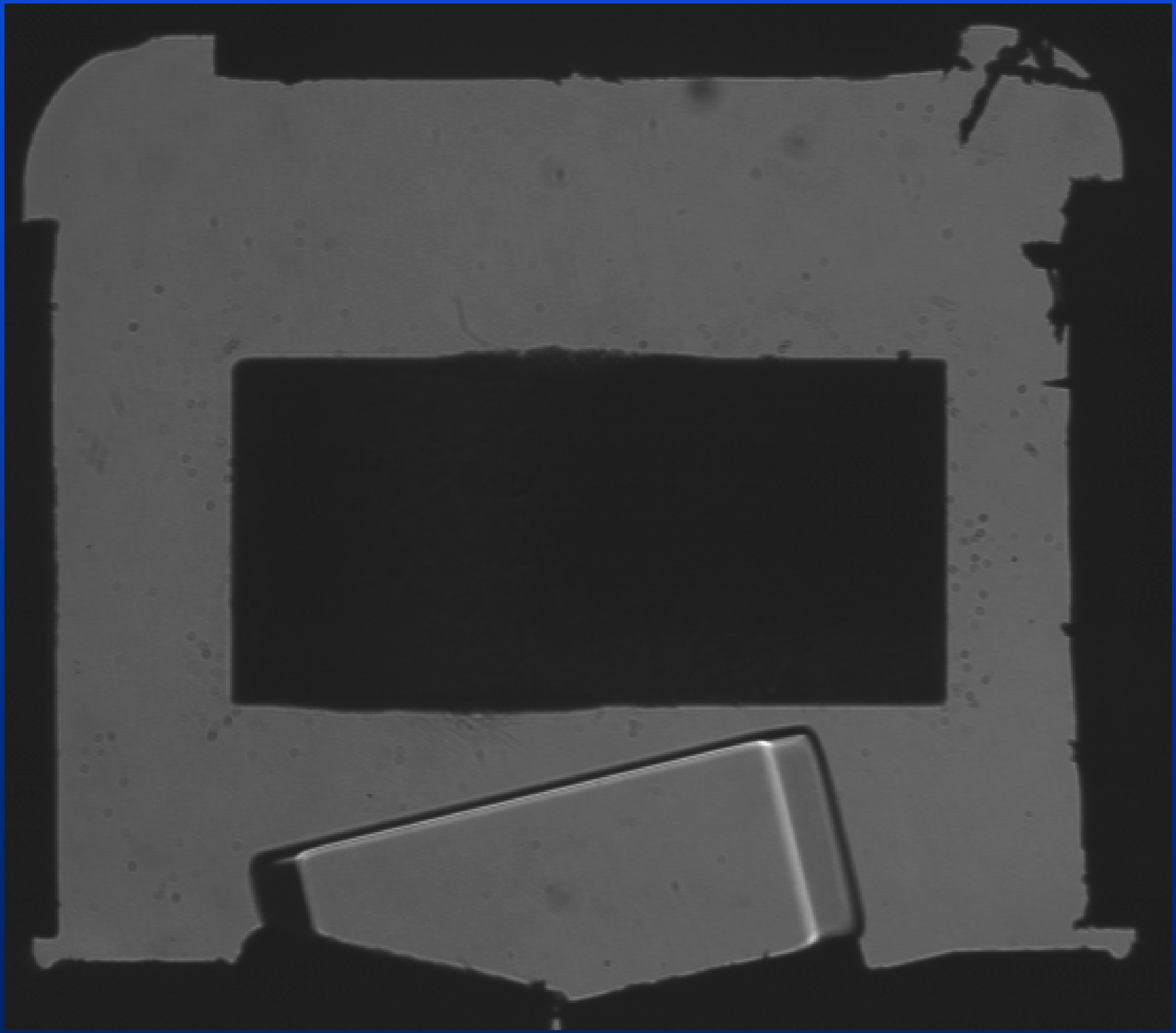
t=0: melted to see the LS interface in the main cell

pressure relaxes, but not to $P_m(T)$

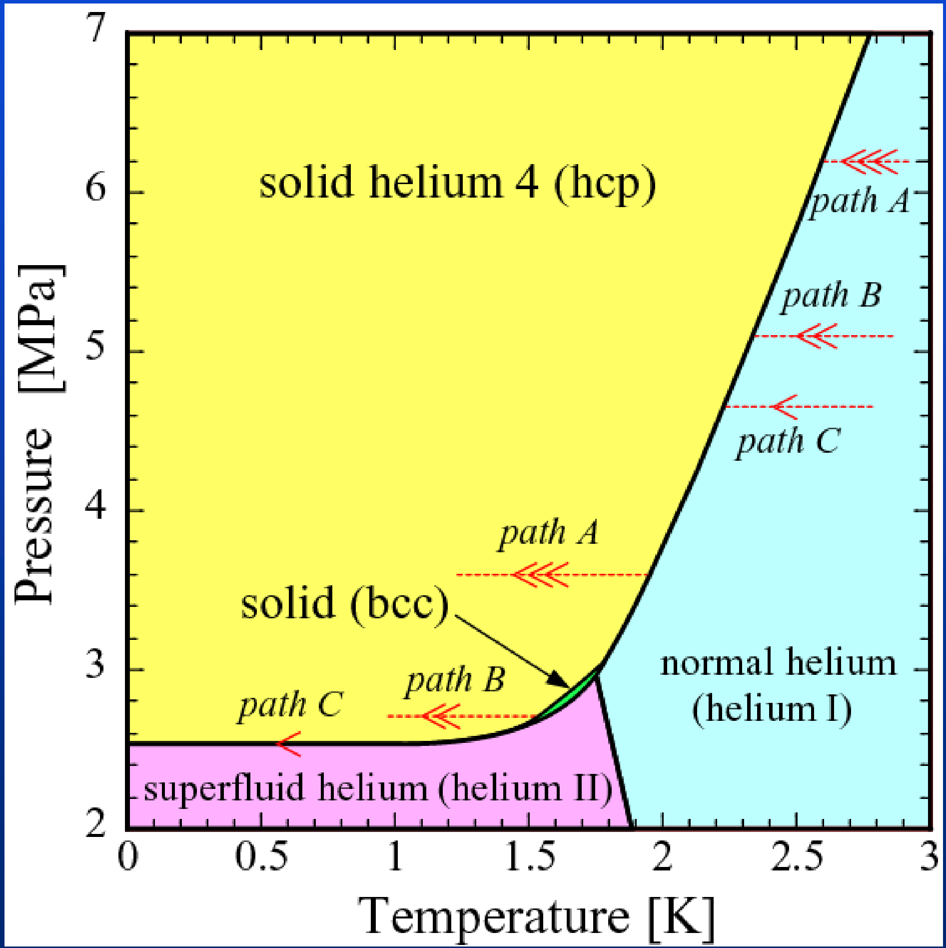
Trying to suppress the liquid channels

HOPG graphite

after pumping the cell 3 days:
able to nucleate an oriented crystal



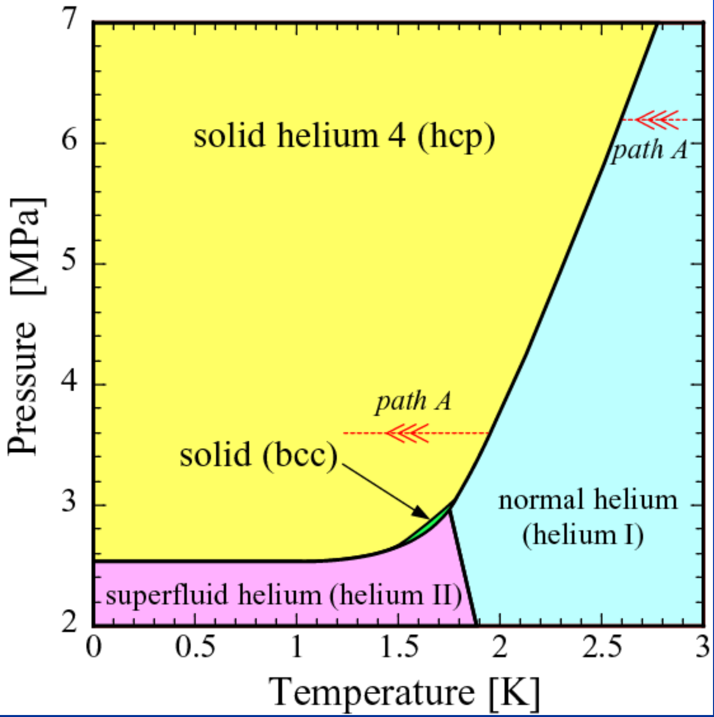
Crystals grown by the blocked capillary method



- start from normal liquid at high pressure and cool down: *path A*, *B* and *C*
- solid plug at a cold spot in the fill line ⇒ constant volume, if the plug does not allow flow…
- requires $P_{ini} > 4.9$ MPa otherwise liquid remains at the end (*path C*).

⇒ leads to polycrystals

Slow crystallization at high pressure: *path A*

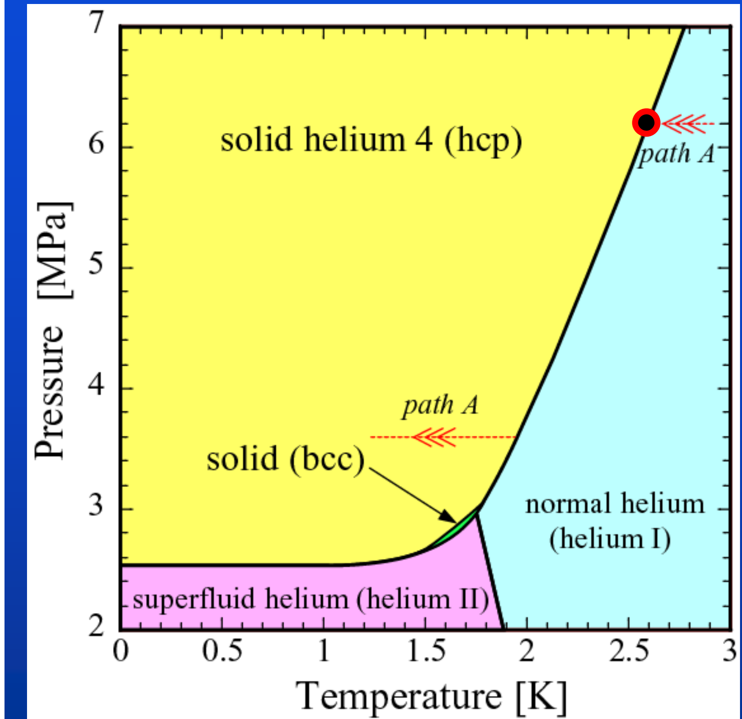


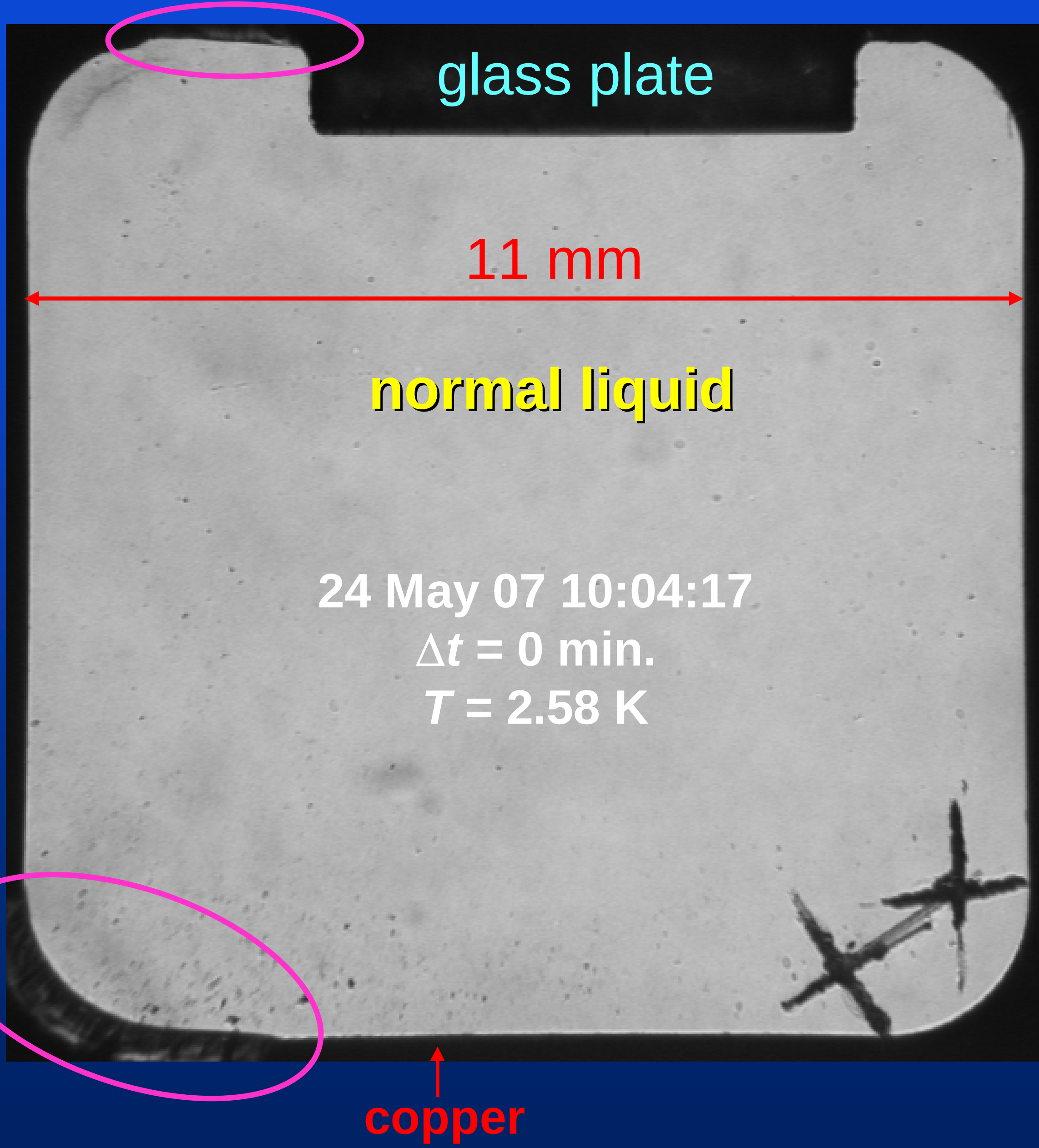
P_{ini} = 6.2 MPa T_{ini} = 2.58 K

hcp grows from the wall

accelerated 740 x
13 s = 160 min

Slow crystallization at high pressure: *path A*

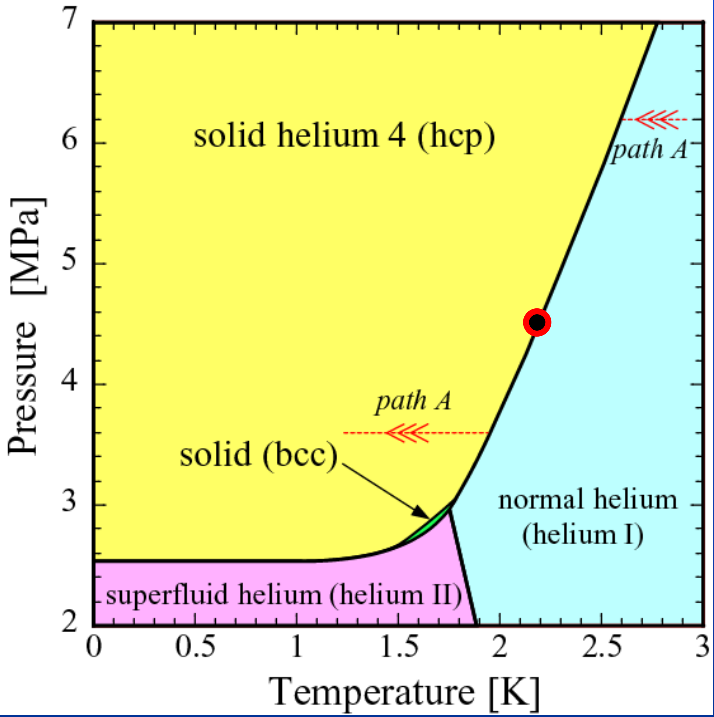




hcp appears at multiple locations in the cell a few minutes after starting to pump the 1 K pot.

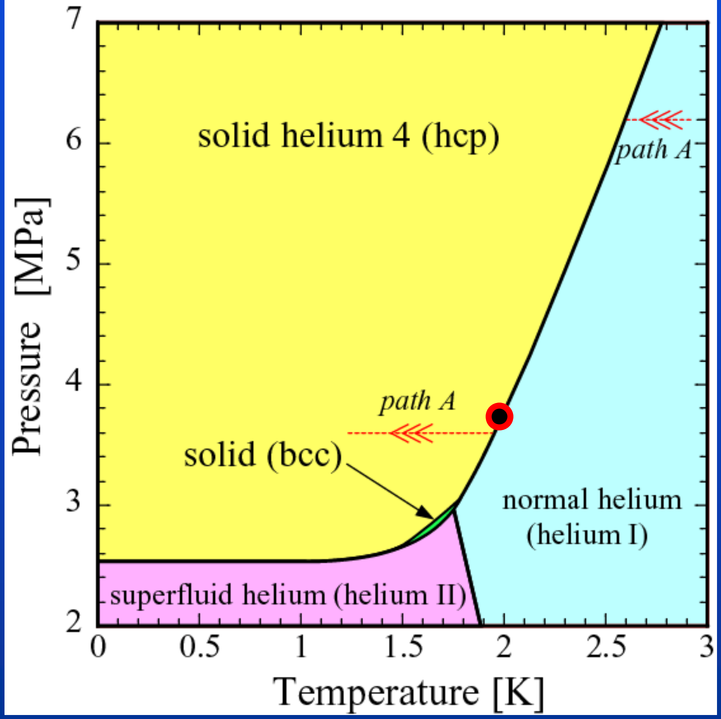
cell volume $V = 0.35$ cm^3.

Slow crystallization at high pressure: *path A*

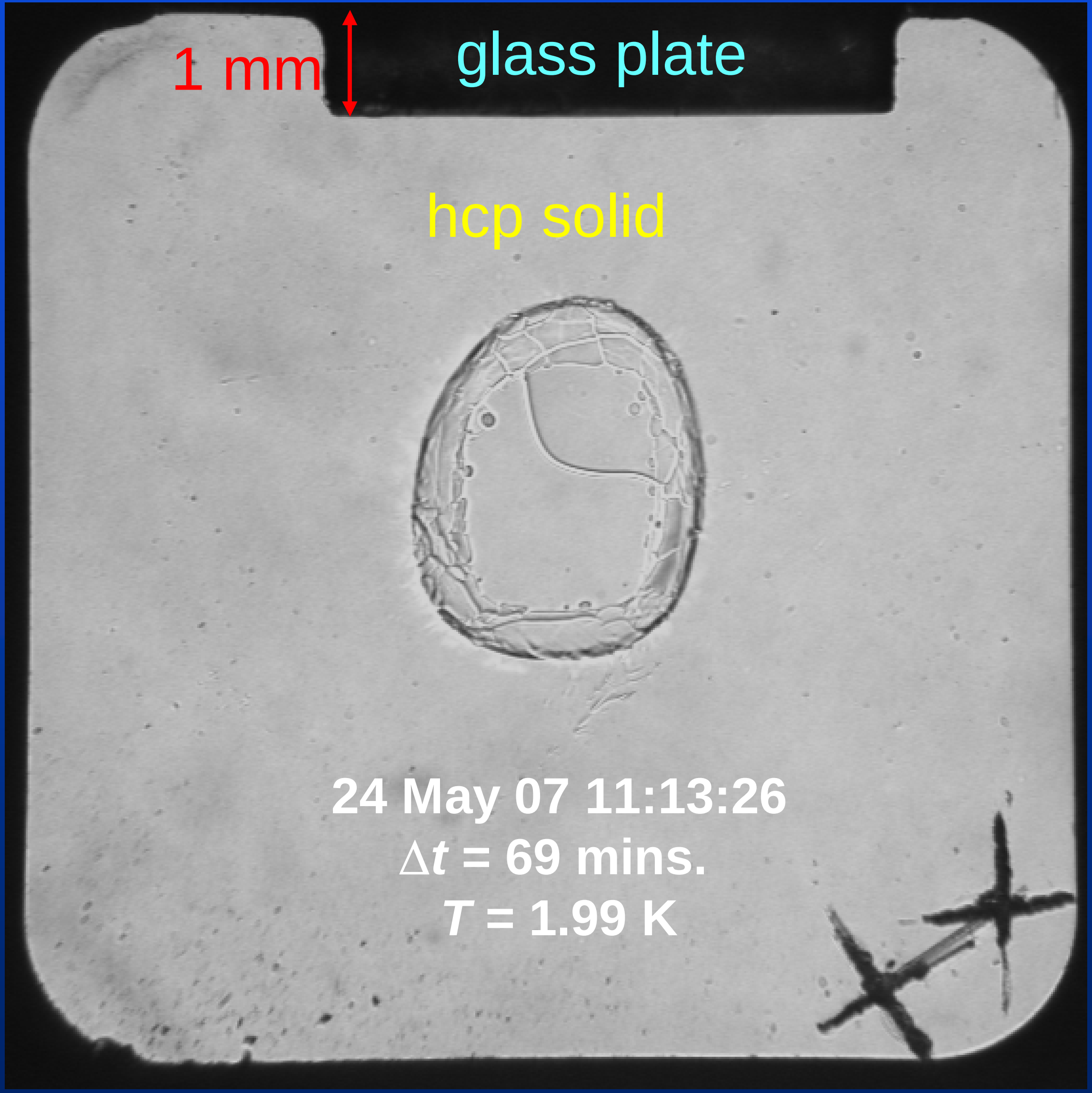


The copper wall is colder than the liquid at the center of the cell.

Slow crystallization at high pressure: *path A*



polycrystalline film ahead of
the growing interface



Melting a crystal slowly grown by BCM

accelerated 4 x

15 s = 53 s

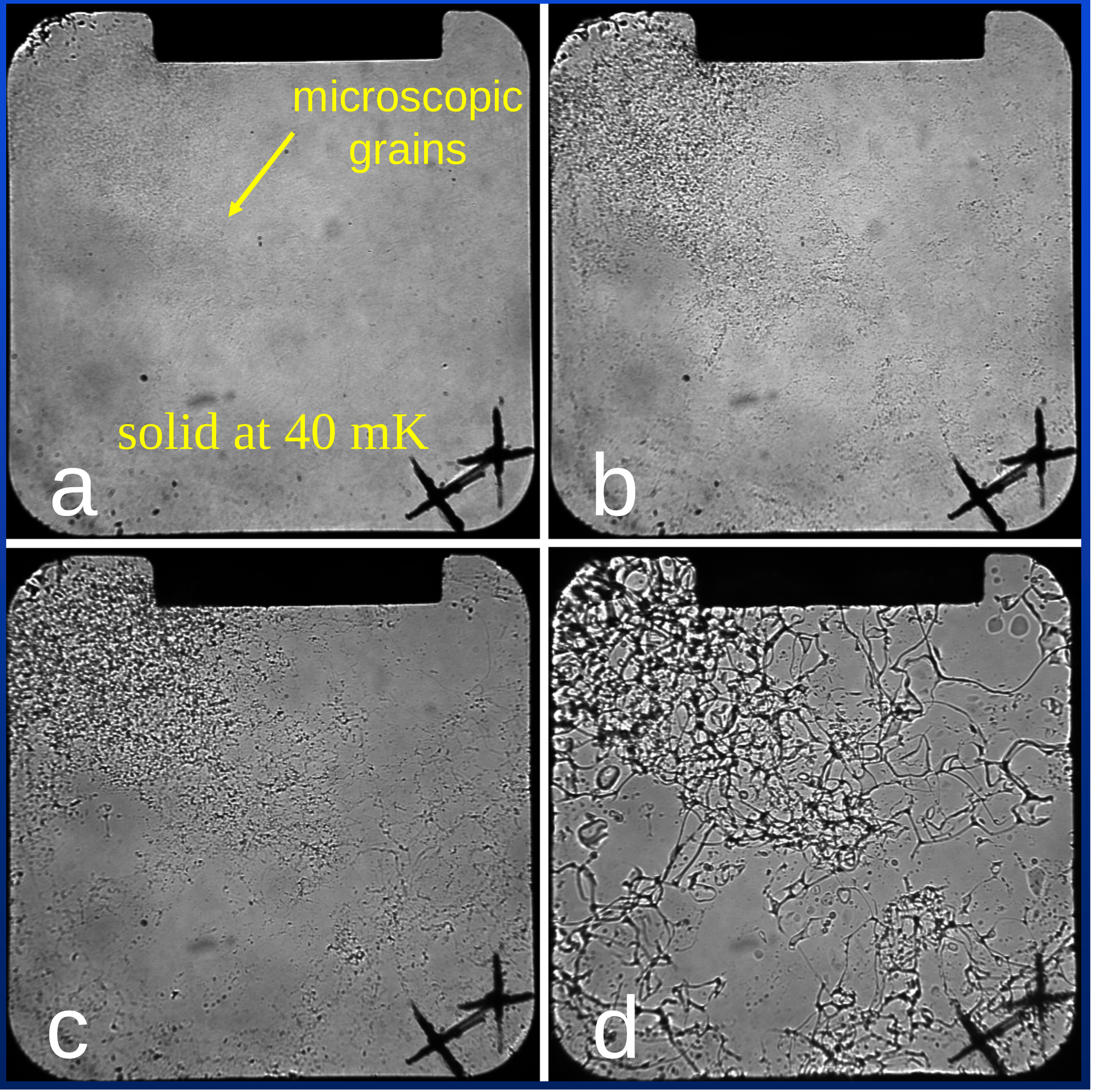
Melting a crystal slowly grown by BCM

removing mass slowly
through the fill line

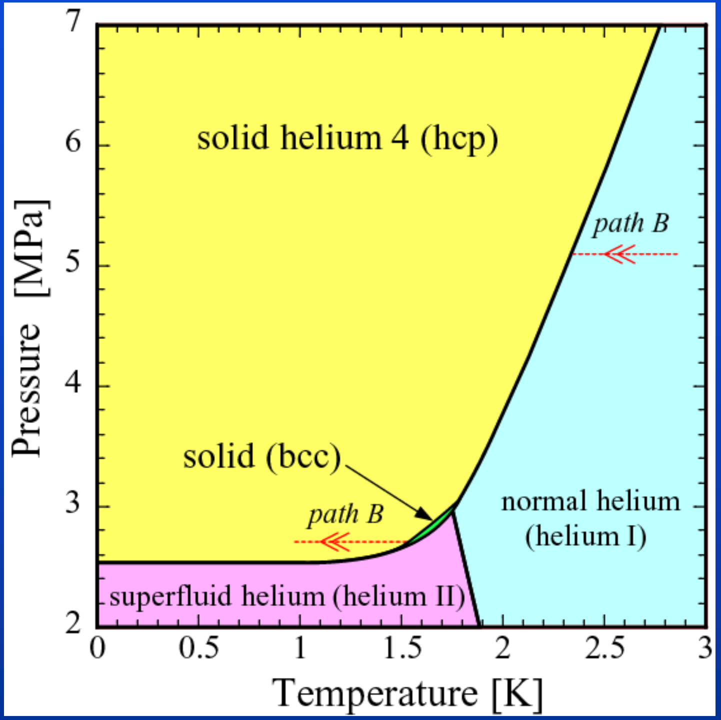
liquid channels
between grains
and on the windows

smallest visible grains
< 20 μm (1 pixel)

the grain size
increases in a few
seconds (ripening)

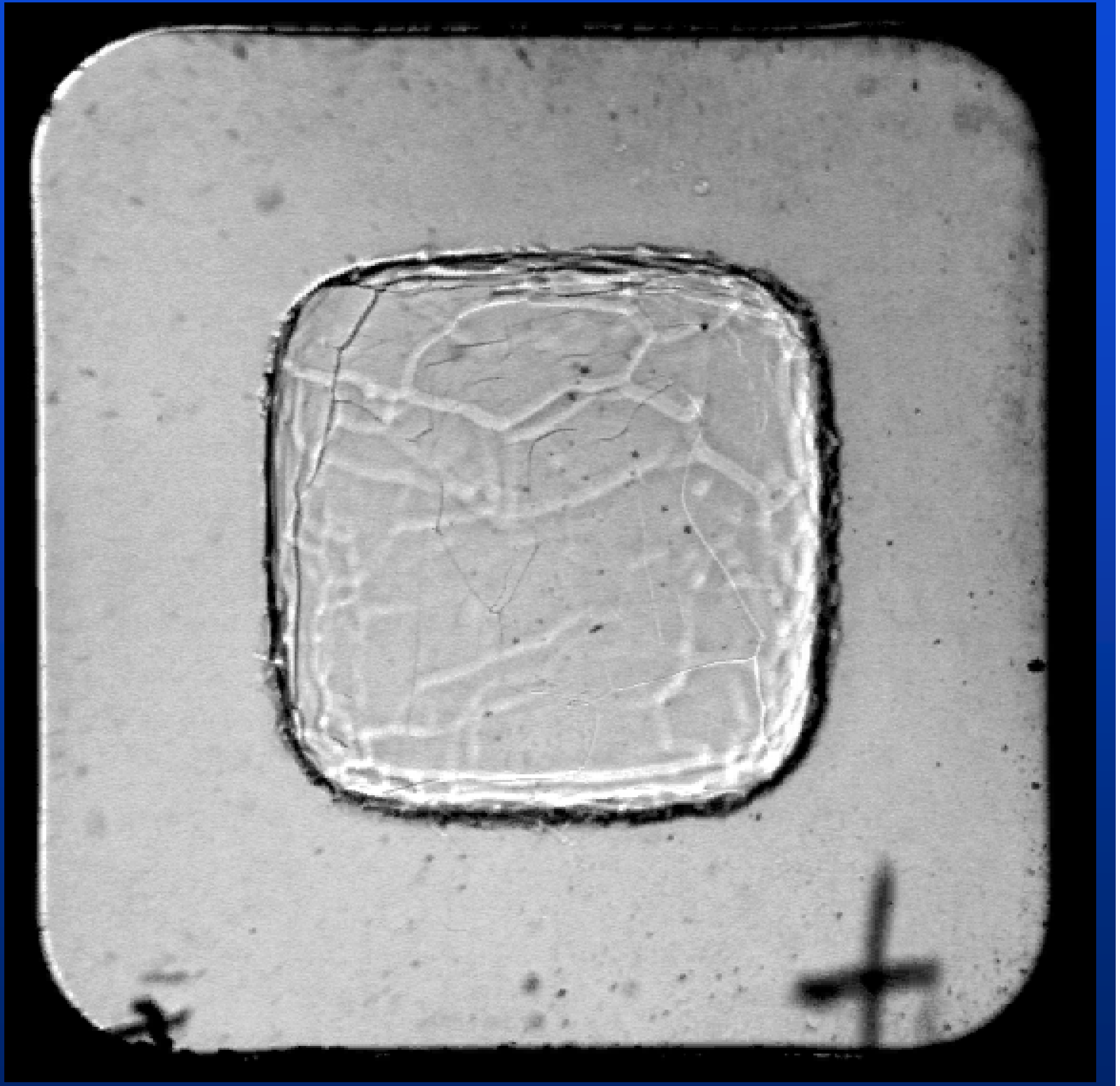


Going through the hcp-bcc transition: *path B*

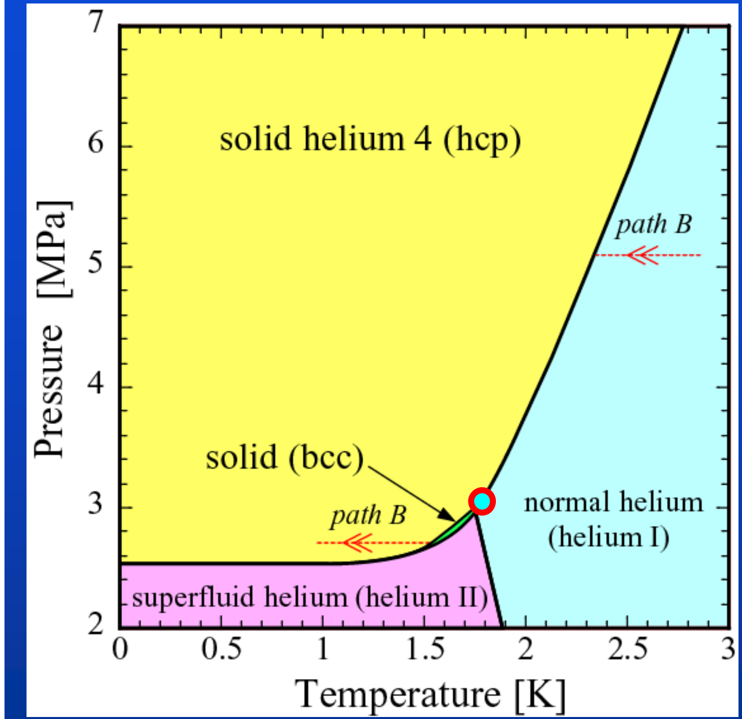


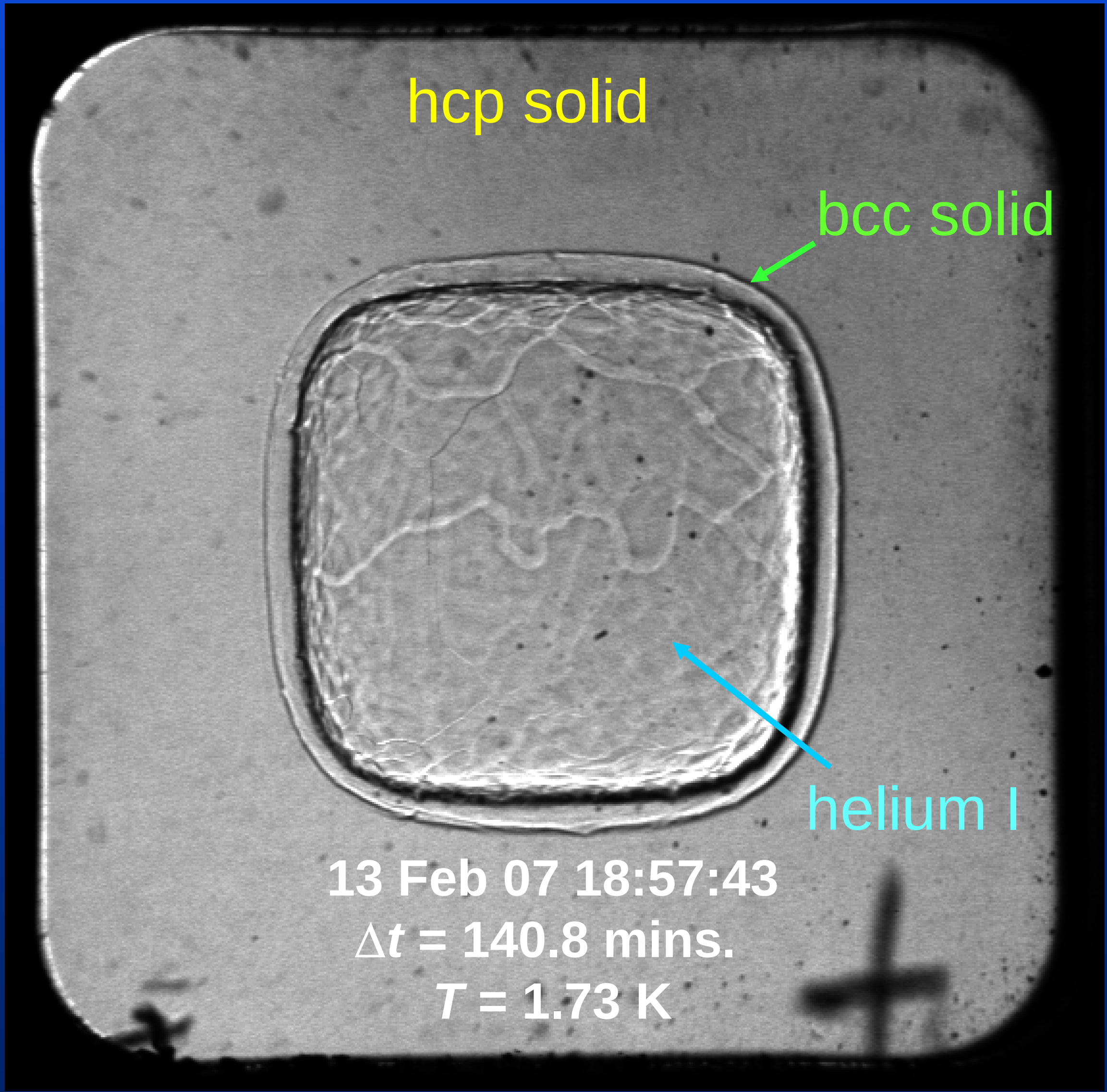
P_{ini} = 5.1 Mpa T_{ini} = 2.36 K

accelerated 100 x
8 s = 13 min



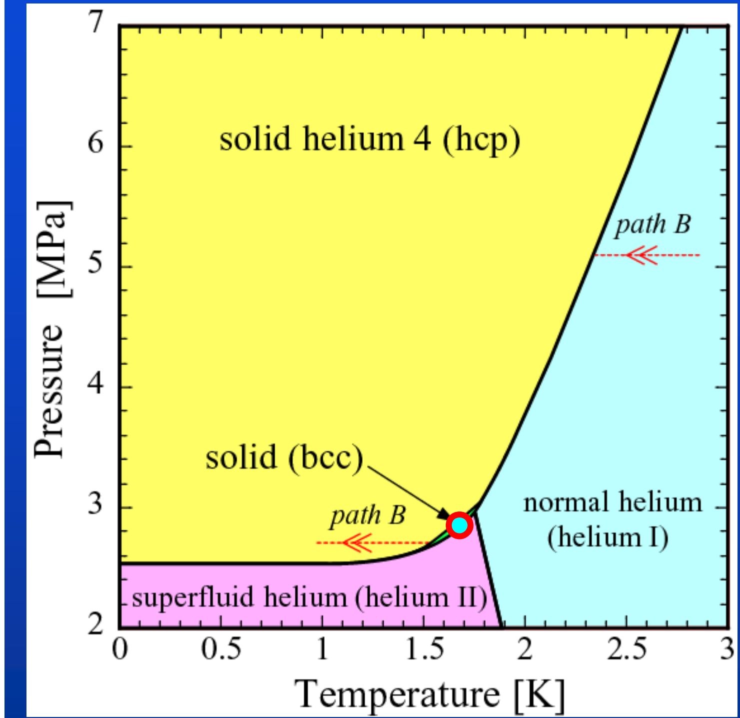
Going through the hcp-bcc transition: *path B*

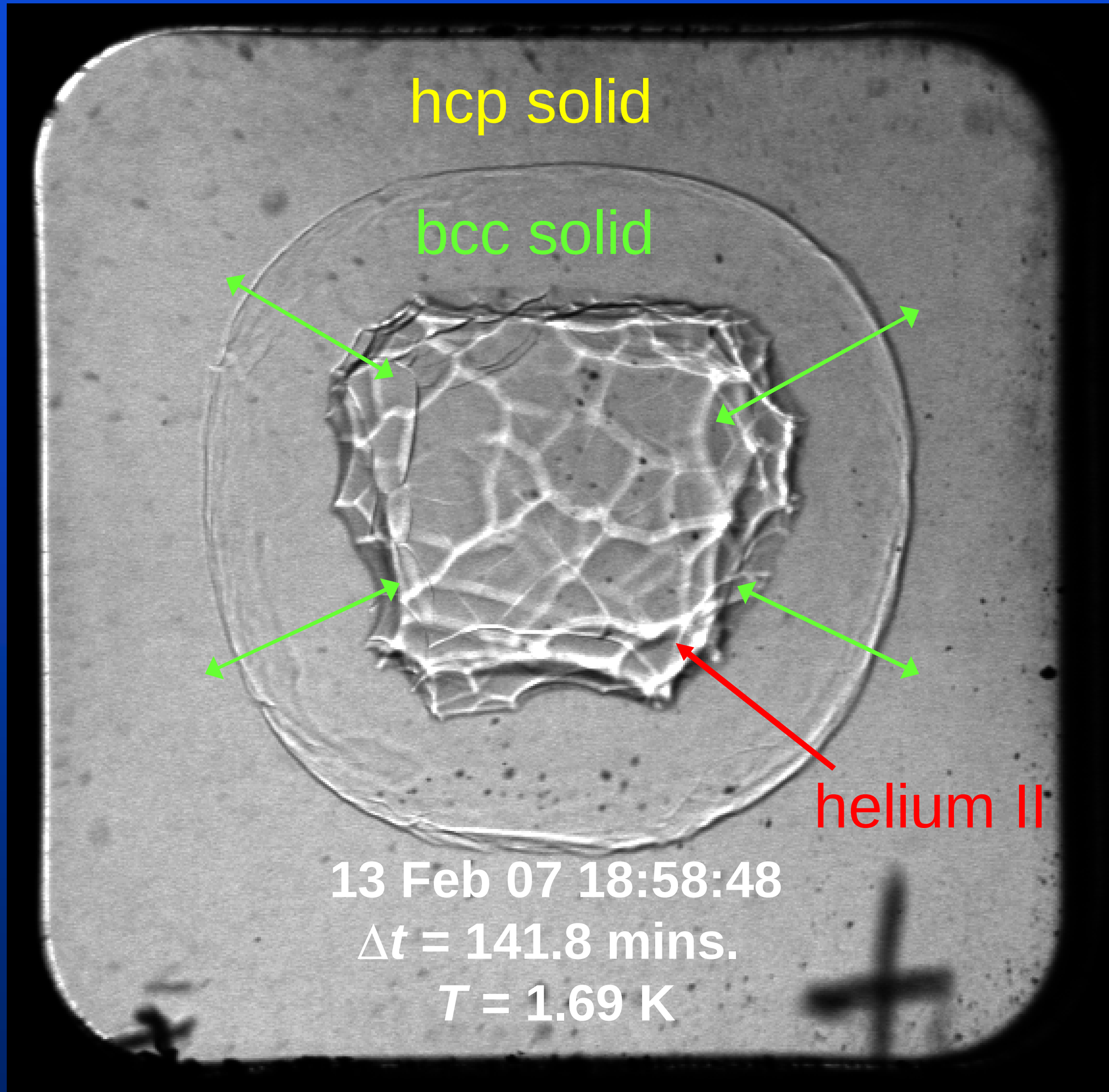




temperature gradient in the cell: 3 phases at $T < T_u$.

Going through the hcp-bcc transition: *path B*





superfluid at T < 1.76 K: small temperature gradient

↓

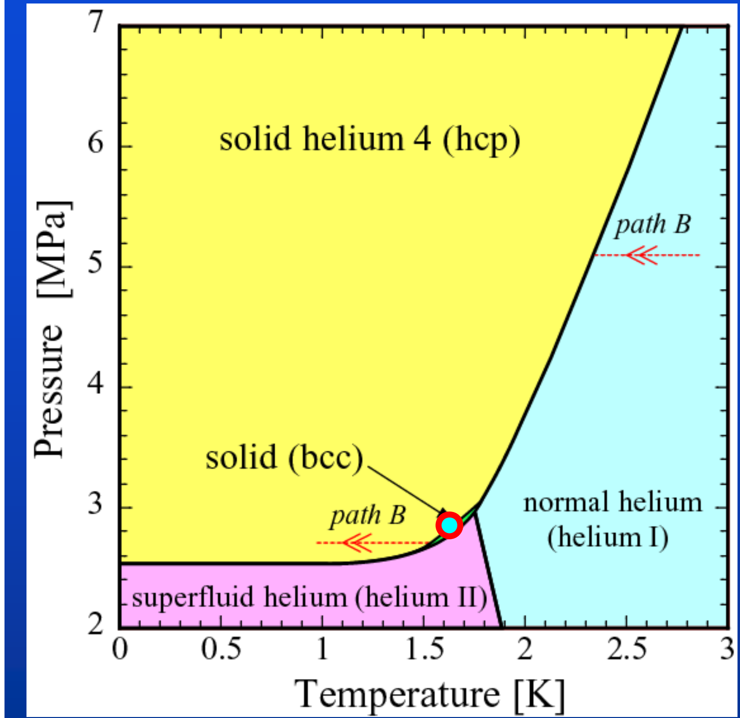
surface tension becomes relevant

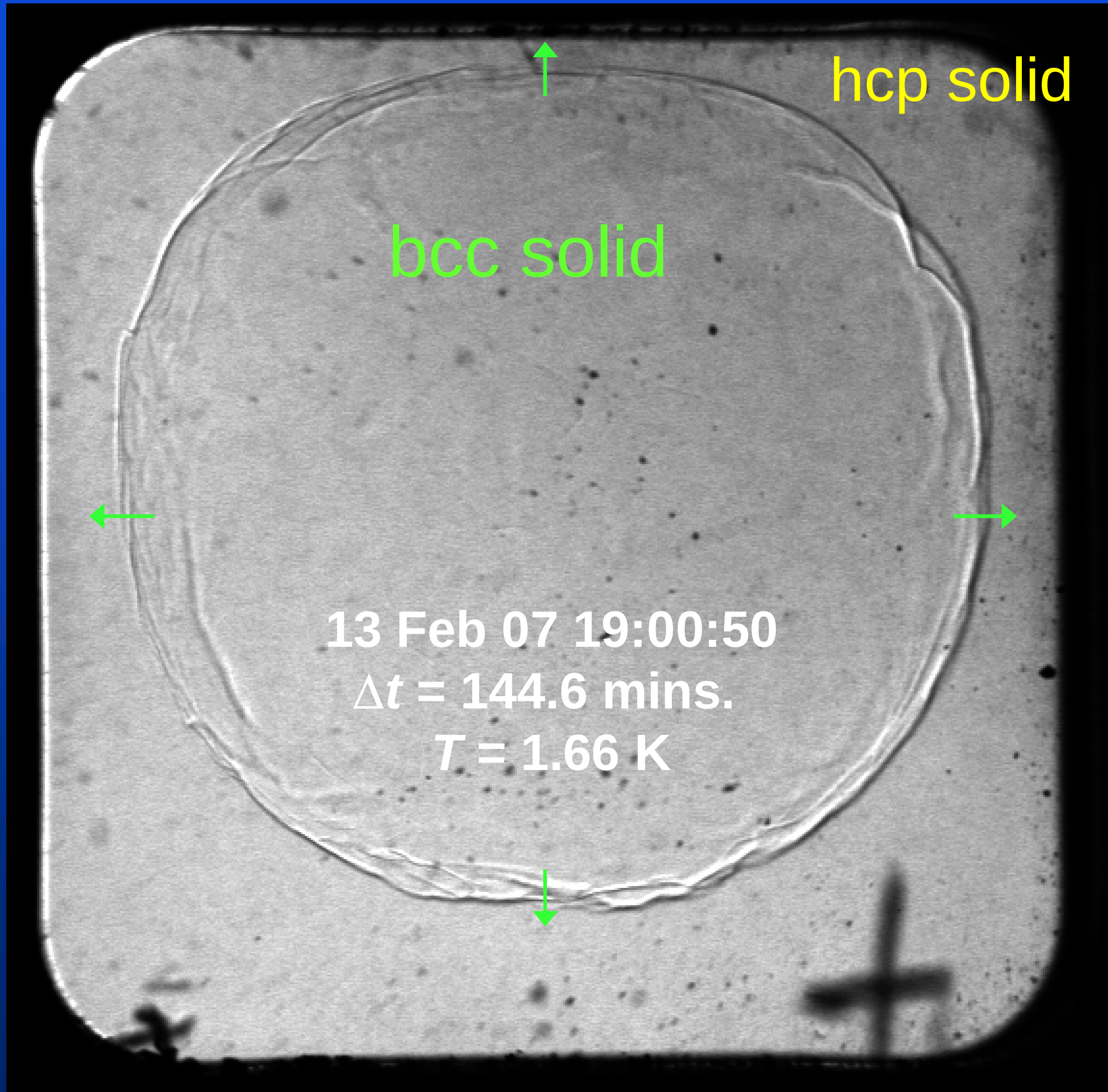
↓

more irregular liquid-solid (bcc) interface

⇒ larger grain sizes

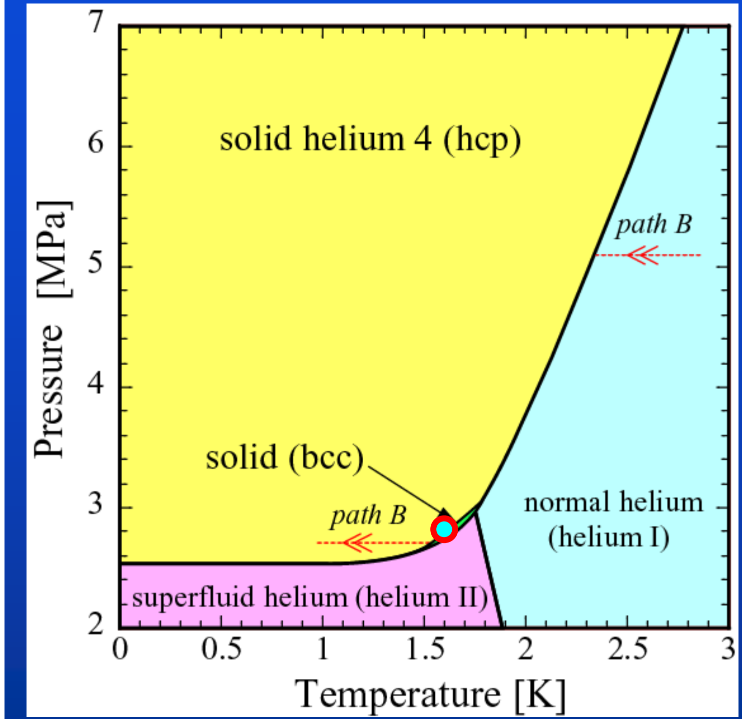
Going through the hcp-bcc transition: *path B*



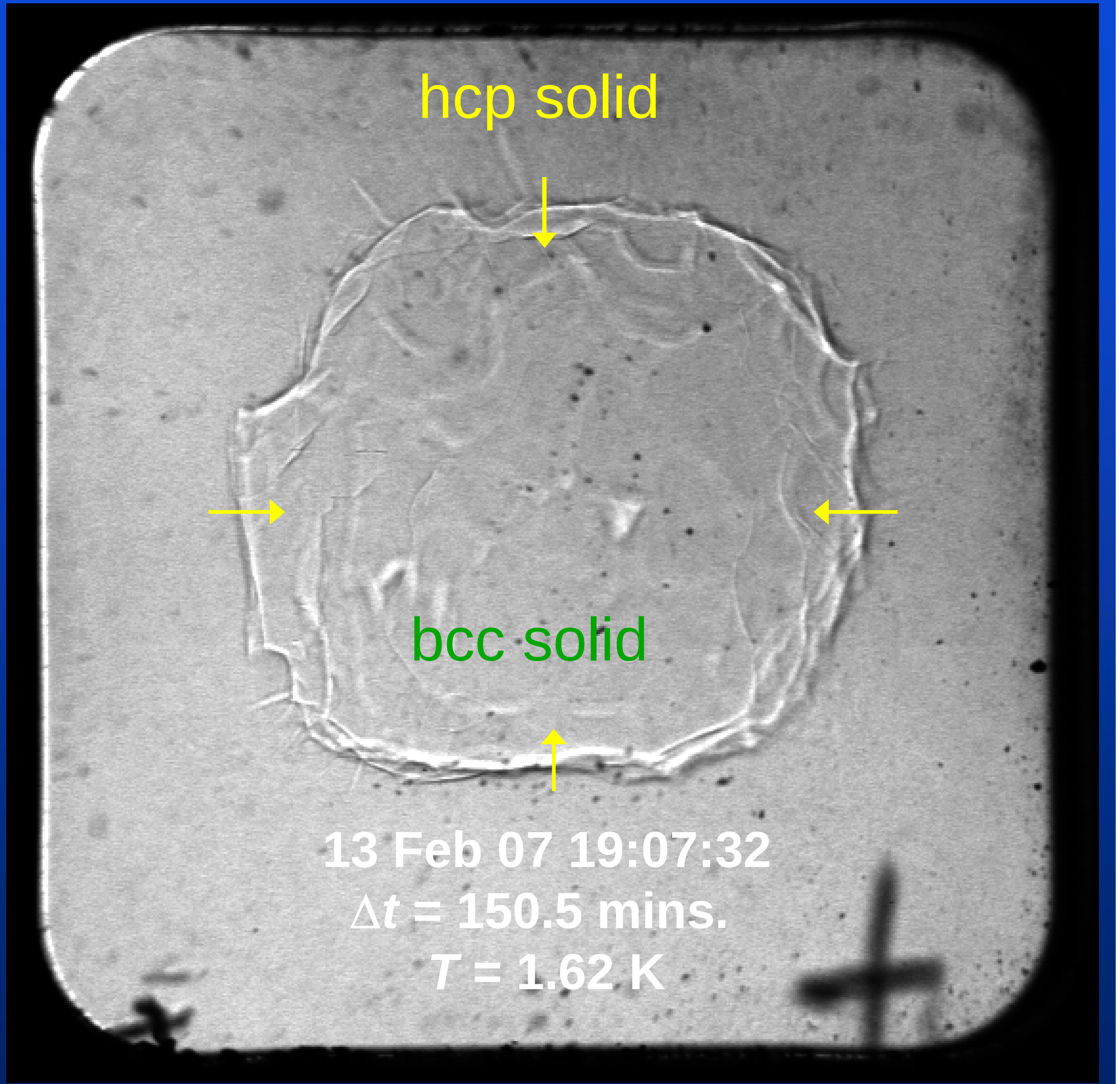


At 1.66 K, all liquid is frozen
only bcc and hcp remain

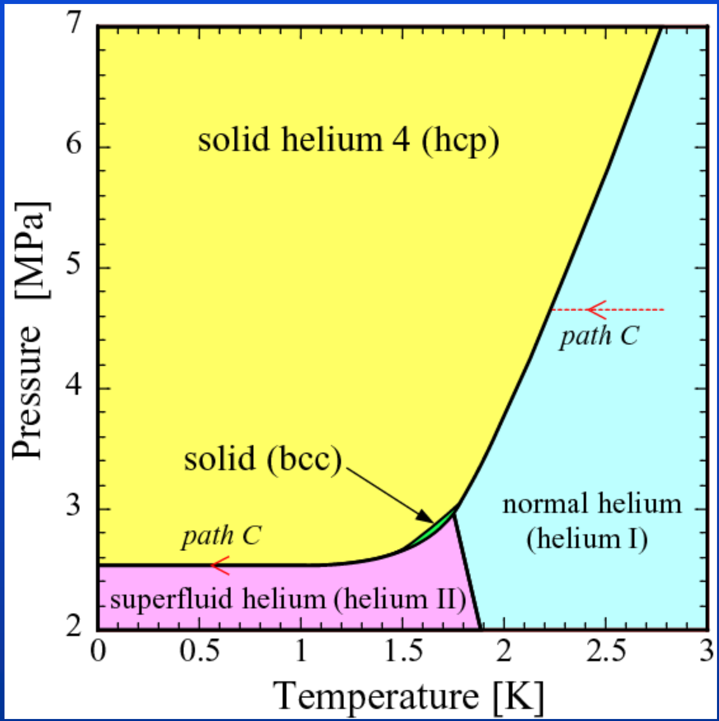
Going through the hcp-bcc transition: *path B*



bcc disappears at 1.59 K



Slow crystallization at low pressure: *path C*

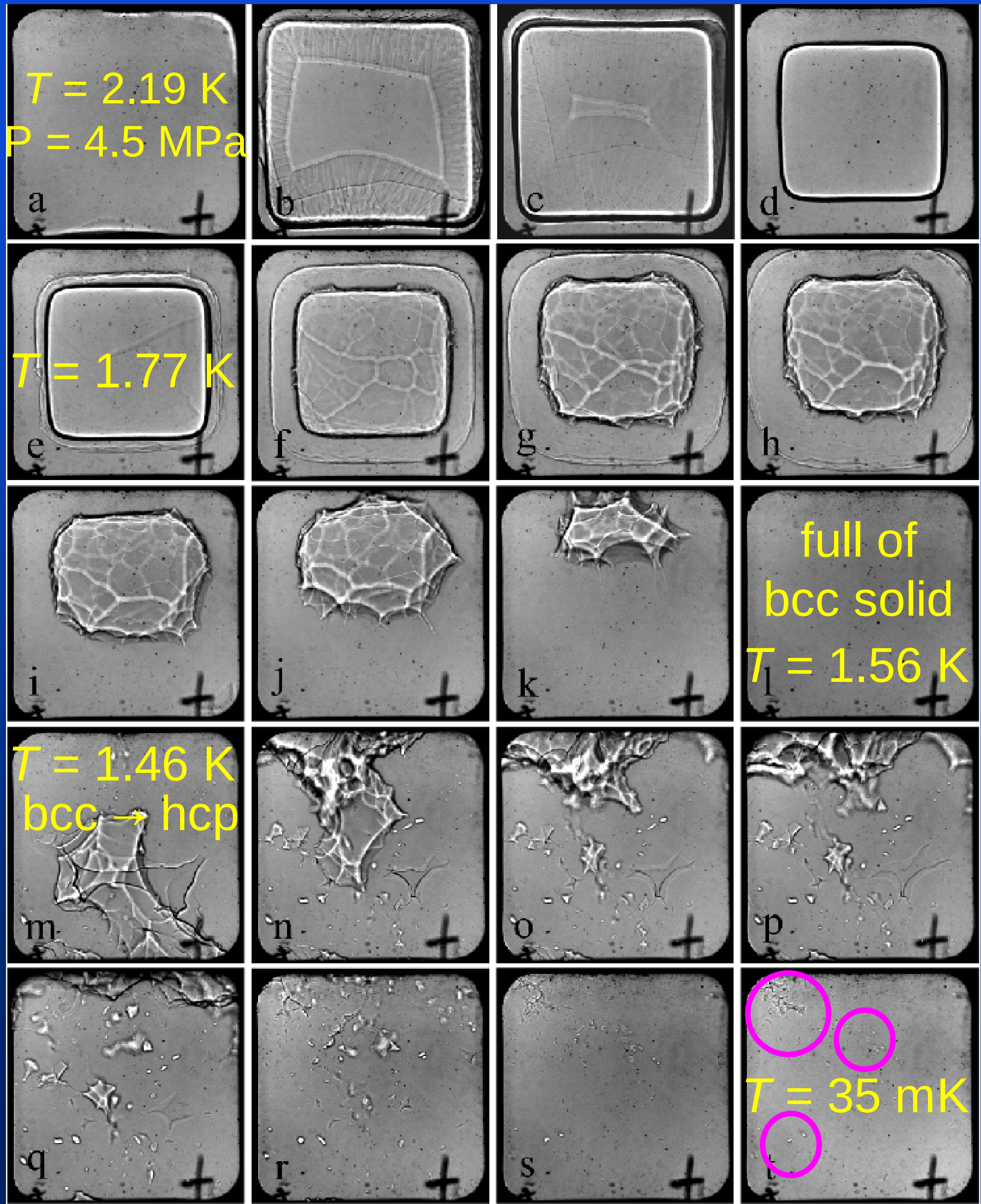


P_{ini} = 4.5 Mpa T_{ini} = 2.19 K

full of bcc at 1.56 K

at 1.46 K (lower bcc-hcp transition)
the superfluid reappears

some of the liquid pockets
never freeze.

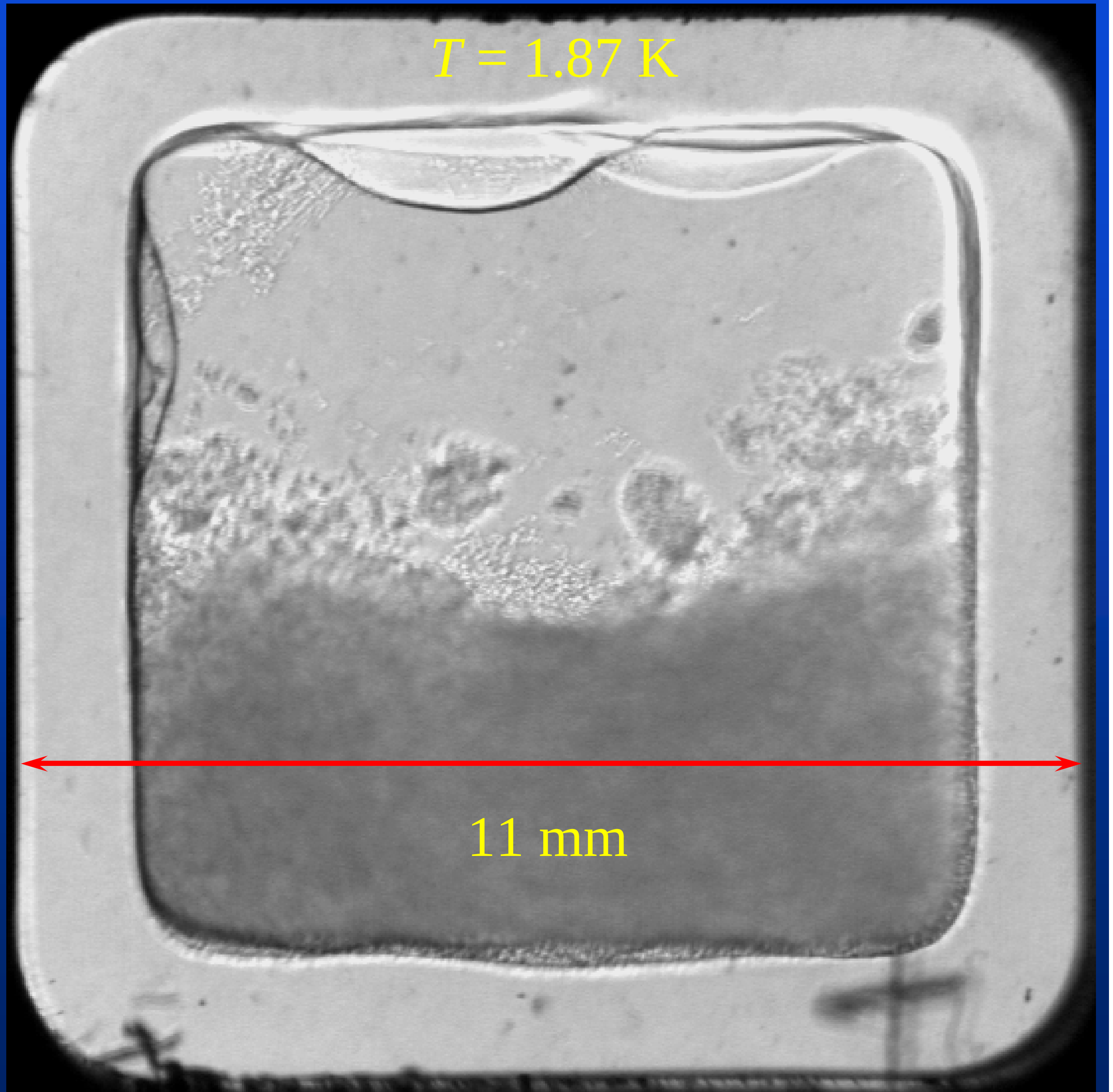


Fast crystallization from the normal liquid T>1.8 K

fast injection
in the normal liquid
⇒ dendritic growth of solid*

dense tangle of dendrites
with liquid regions

quench freezing the
normal liquid may produce
a similar tangle

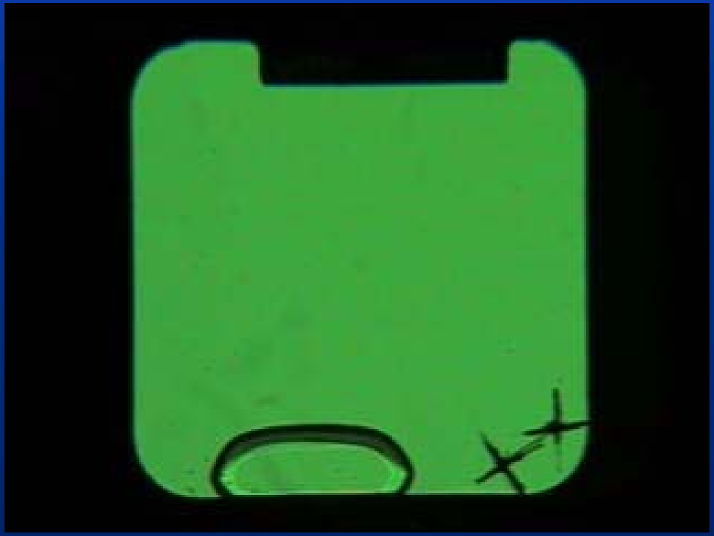


* M. Maekawa et al. *PRB* '02
N.C. Ford et al. *JLTP* '07

Conclusion

- no GB melting in systems with long range interactions, like helium
- the Torricellian experiment is ambiguous: GB or liquid channels?
- the solids grown by the blocked capillary method may have a small grain size (<1μm)

THANK YOU!!!



THANK YOU!!!