Workshop on Supersolid 2008

18 - 22 August 2008

Optical investigations of disorder in solid Helium-4

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Optical investigations of disorder in solid helium 4

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Supersolids, Trieste, August 19th, 2008
Yet another mystery...

Adriatico Guest House, Trieste, Italy, August 18th 2008
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 \( \approx 0.5 \) K and \( \approx 3 \) atoms thick
Grain boundaries cannot explain everything…

![Cubic network of GB](image)

- Cubic network of GB
- Lattice parameter $a = 0.3$ nm
- Effective superfluid thickness $= 1$ atomic layer

$\Rightarrow \bullet = 3a \frac{\rho}{\rho_s}$

- If NCRIF = 0.1 %, $\bullet = 1$ µm
- If NCRIF = 10 %, $\bullet = 10$ nm
… but they might be involved!

how to connect two supersolid grains?

mismatch!
⇒ 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](#)  [infect_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 $\Rightarrow \theta = 14.5 \pm 4^\circ$

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

other crystals:
$\theta = 11 \pm 3^\circ$
$\theta = 16 \pm 3^\circ$

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 $\approx 0.5$ K and $\approx 3$ atoms thick

condensate map
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

$k_B T / \epsilon_5 = 0.500$

$k_B T / \epsilon_5 = 0.721$

$k_B T / \epsilon_5 = 0.728$

$k_B T / \epsilon_5 = 0.729 \quad (T \approx T_m)$
Grain boundary premelting

colloidal crystals Alsayed et al. Science ’05 $T_m = 28.3^\circ$C

27.2°C  $\theta \sim 13^\circ$  5 µm

28.0°C  $\theta \sim 13^\circ$

28.1°C  $\theta \sim 13^\circ$

28.2°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
Grain boundary melting

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

- Warming up by a few mK/min
- 280 MPa
- 26.3 K
- \(0 \leq \theta \leq 30^\circ\)

“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

⇒ for thin films, the grains can detach

⇒ 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

dihedral angle $2\theta$

groove

liquid channels on the windows
Liquid channel on the window

contact angle $\theta_c$ between the LS interface and the wall
neglecting elasticity \(\Rightarrow\) hydrostatic equilibrium
\(\Rightarrow\) pressure difference
\(\Rightarrow\) curved interface, liquid on the convex side

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

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

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

\(\Rightarrow\) 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 receding: 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

\[ \theta + \theta_c < \frac{\pi}{2} \]

\[ \theta \approx 15^\circ, \ \theta_c \approx 45^\circ \Rightarrow \text{channel} \]

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

using \( \theta = 15^\circ, \ \theta_c = 45^\circ \)

\[ \Rightarrow l_c \approx 0.89 \text{ to } 0.97 \text{ mm} \]

a calculation with \( \sigma_{LS}=0.17 \text{ mJ/m}^2 \) gives

\[ l_c = 0.98 \text{ mm} \]

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

growth shape

small $\sigma_{GB}$
$\Rightarrow$ large $\theta$
$\Rightarrow \theta + \theta_c > \pi/2$
$\Rightarrow$ no channel
Liquid channel between three grains

\[ \Rightarrow \text{requires } \theta < \frac{\pi}{6} \]

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

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

- LC on a wall
- LC between 3 GBs

$S$ (nm$^2$) vs. $P_s - P_{eq}$ (MPa)
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

Sasaki et al. *Science* ‘06
stress applied to crystallize the inside:
outside at 1.4K and inside at 1.3K
during a few seconds

\[ P_f(1.4 \text{ K}) - P_f(1.3 \text{ K}) = 0.3 \text{ bar} \]

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 $v_c = 10 \ \mu m/s$
⇒ relaxation at $V = [\rho_s/(\rho_C - \rho_L)]v_c = 1 \ \mu m/s = 3.6 \ mm/h$

0.01% superfluid density with $v_c = 10 \ \mu m/s$
⇒ 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 \ \mu m in 4 hours
⇒ $V < 12.5 \ \mu m/h$
Flow in the presence of grain boundaries

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

crystal 1: the flow stops when the groove disappears

crystal 2: the flow continues until equilibrium is reached

Torricelli1_480x.mov
480x real time
1s = 8 min

Torricelli2_480x.mov
480x real time
1s = 8 min
Cristal 1: only one grain boundary

Constant $V = 0.6 \ \mu\text{m/s}$: characteristic of superfluid flow stops when the groove disappears (unpinning of the grain boundary)
the velocity increases when the LS interface reaches a region with more defects at the bottom of crystal 2?

Cristal 2: more defects

linear relaxation (not exponential)

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

mass flow in the tube (crystal 1):

along a GB

section \( w e \)

\( w \approx \text{tube diameter} = 10 \text{ mm} \)

\( e \approx (1/3) \times 3a = 0.3 \text{ nm} \)

along the 2 liquid channels created on the wall

section = \( f(w,e) \)

at a depth of 10 mm: \( 870 \mu m^2 \)

the measure interface velocity implies

\( v_c = 1.5 \text{ m/s} \)

comparable to 2 m/s

in atomic thick liquid films

Telschow et al. *PRL* '74

\( v_c = 3 \text{ mm/s} \)

one sample did flow at 1.13 K \( \Rightarrow \) 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 51 bar
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 $P_{\text{ini}} > 4.9$ MPa otherwise liquid remains at the end (*path C*).

⇒ leads to polycrystals
$P_{\text{ini}} = 6.2 \text{ MPa} \quad T_{\text{ini}} = 2.58 \text{ K}$

hcp grows from the wall

accelerated 740 x

$13 \text{ s} = 160 \text{ min}$
hcp appears at multiple locations in the cell a few minutes after starting to pump the 1 K pot. Cell volume \( V = 0.35 \text{ cm}^3 \).
The copper wall is colder than the liquid at the center of the cell.

The diagram shows a phase diagram with the following points:
- Superfluid helium (helium II)
- Solid (bcc)
- Solid helium 4 (hcp)
- Normal helium (helium I)

The path labeled $\Delta t = 23$ mins. is marked on the diagram, indicating a transition from a liquid to a solid phase. The temperature $T = 2.18$ K is also indicated in the diagram.
Slow crystallization at high pressure: path A

polycrystalline film ahead of the growing interface

Δt = 69 mins.
T = 1.99 K
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*

\[ P_{\text{ini}} = 5.1 \text{ Mpa} \quad T_{\text{ini}} = 2.36 \text{ K} \]

- accelerated 100 x
- 8 s = 13 min
Going through the hcp-bcc transition: *path B*

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

$hcp$ solid

$bcc$ solid

helium I

13 Feb 07 18:57:43

$\Delta t = 140.8$ mins.

$T = 1.73$ K
Going through the hcp-bcc transition: *path B*

- **superfluid** at $T < 1.76 \text{ K}$: small temperature gradient
  - ↓ surface tension becomes relevant
  - ↓ more irregular liquid-solid (bcc) interface

- \[ \Delta t = 141.8 \text{ mins.} \]
  - $T = 1.69 \text{ K}$

\[ \Rightarrow \text{larger grain sizes} \]
At 1.66 K, all liquid is frozen only bcc and hcp remain

Going through the hcp-bcc transition: path B

13 Feb 07 19:00:50
Δt = 144.6 mins.
T = 1.66 K
Going through the hcp-bcc transition: *path B*

- hcp solid
- bcc solid

bcc disappears at 1.59 K

\[ \Delta t = 150.5 \text{ mins.} \]

\[ T = 1.62 \text{ K} \]
Slow crystallization at low pressure: path C

$P_{\text{ini}} = 4.5 \text{ Mpa}$ $T_{\text{ini}} = 2.19 \text{ K}$

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.

$T = 1.77 \text{ K}$

$T = 1.46 \text{ K}$

$P = 4.5 \text{ MPa}$

$T = 2.19 \text{ K}$

full of bcc solid

$T = 1.56 \text{ K}$

$T = 35 \text{ mK}$
Fast crystallization from the normal liquid $T > 1.8$ K

fast injection in the normal liquid $\Rightarrow$ 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!!!

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