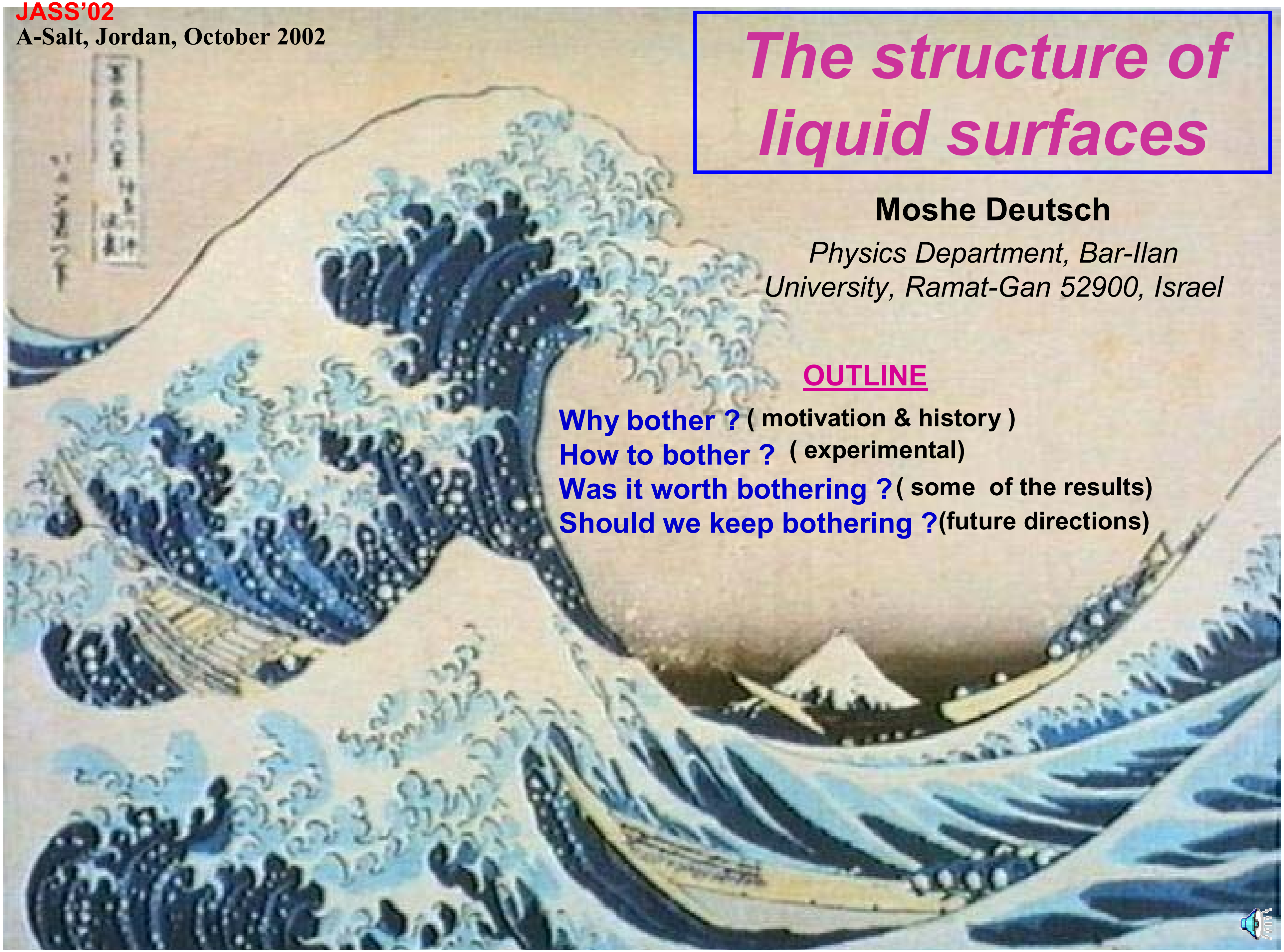
JASS'02
A-Salt, Jordan, October 2002



The structure of liquid surfaces

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OUTLINE

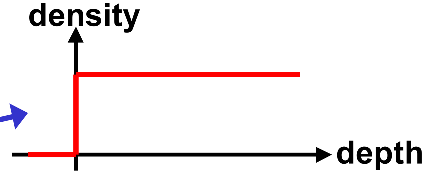
Why bother ? (motivation & history)
How to bother ? (experimental)
Was it worth bothering ? (some of the results)
Should we keep bothering ? (future directions)

Motivation & History

On the one hand:

- **Bulk liquids are boring: no order, no defects, no phases/transitions…**
- **Theory very difficult: No comprehensive theory to date.**

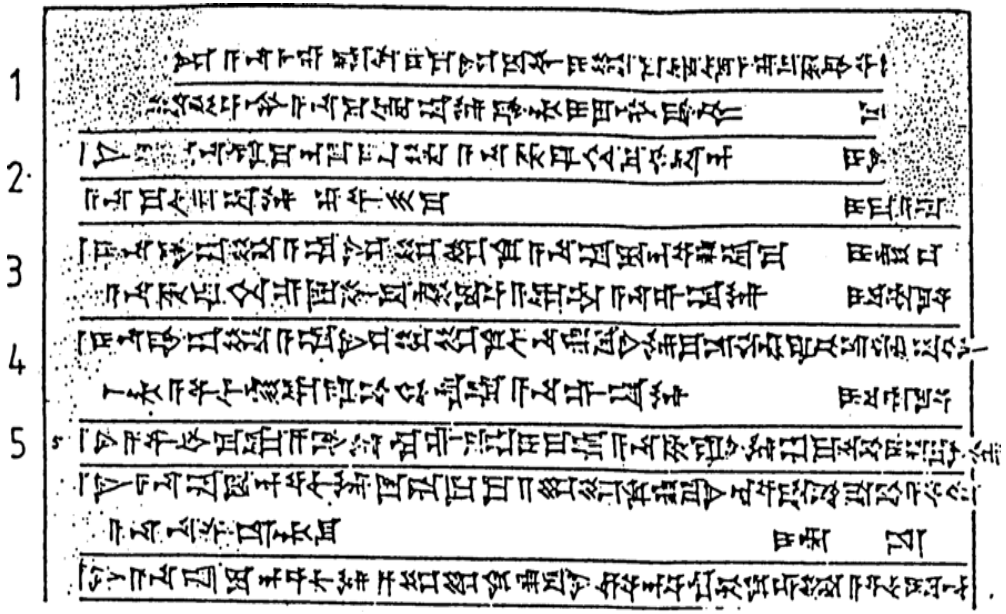
∴ The surface of a boring bulk must be a boring surface :



On the other hand:

- **Liquid surfaces have attracted interest (not always scientific) since ancient times.** (Bible, China, Greece, Ben Franklin ….)
- **X-ray methods developed only in 1982-6.**
- **Increasing number of studies since then.**

Atomic resolution liquid surface studies reveal many new and intriguing effects !

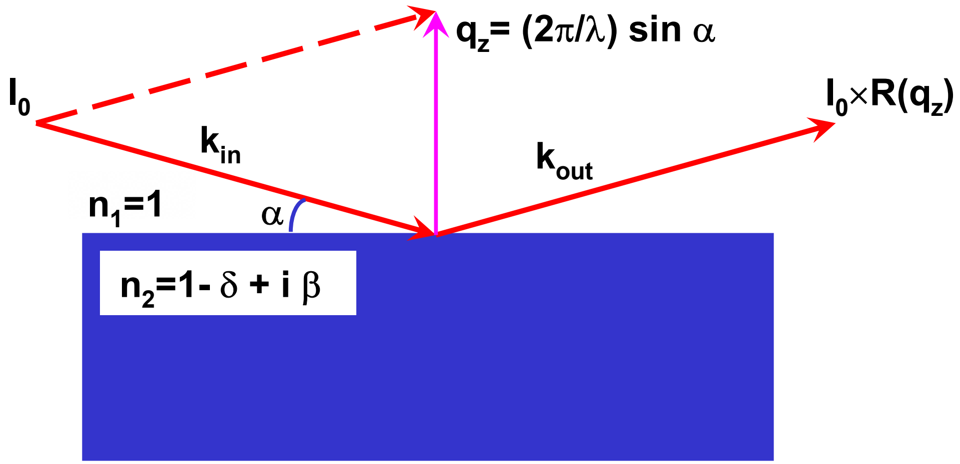


The art of lecanomancy (Hamurabi, 18th century B.C.E.)

The spreading of oil on water in a ceremonial bowl

(1) Oil sinks, rises and spreads: war-lost sick- divine punishment
(2) Oil splits in two: war-both camps march together sick- death
(3) Single oil drop emerges in the east: war-booty sick-recovery
(4) 2 drops (large & small): male child will be born sick- recovery
(5) Oil fills bowl: war-defeat for the leader sick- death

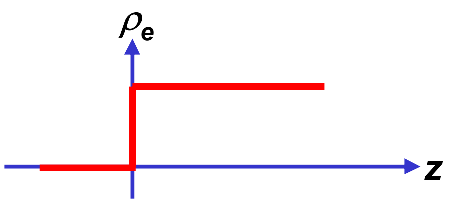
X-Ray Reflectivity (I)

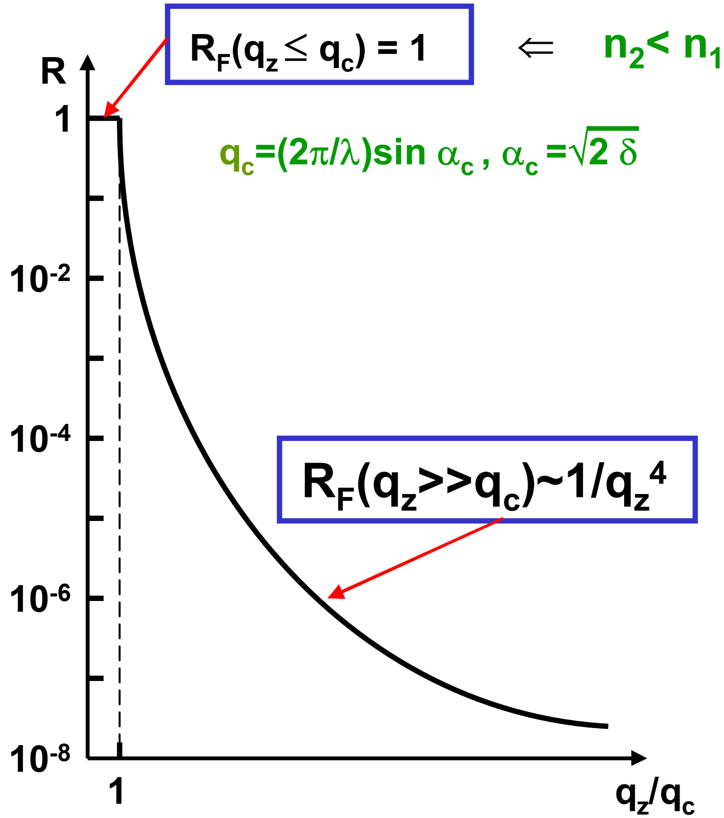


For a surface which is:

(1) flat

(2) abrupt



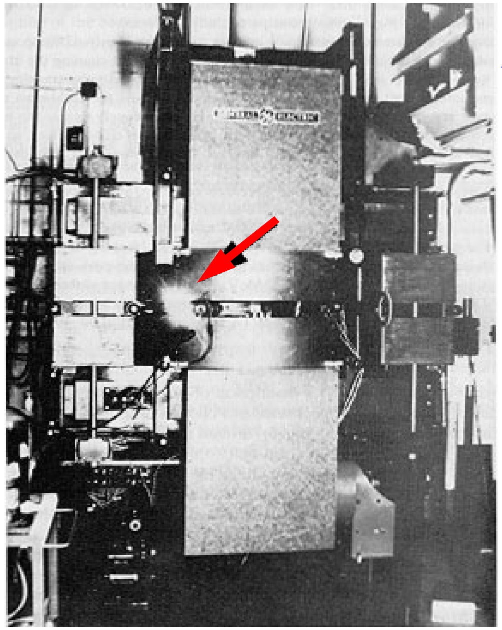


Fresnel reflectivity

$$R_F(q_z)=\left|\frac{q_z-\sqrt{q_z^2+q_c^2}}{q_z+\sqrt{q_z^2+q_c^2}}\right|^2$$

- High resolution ⇔ high q_z.
- $q_z/q_c \approx 50 \Rightarrow R=10^{-8}$, (for $H_2O \Rightarrow$ Res. ~6 Å only.
- High intensity source required ⇒ Synchrotron !

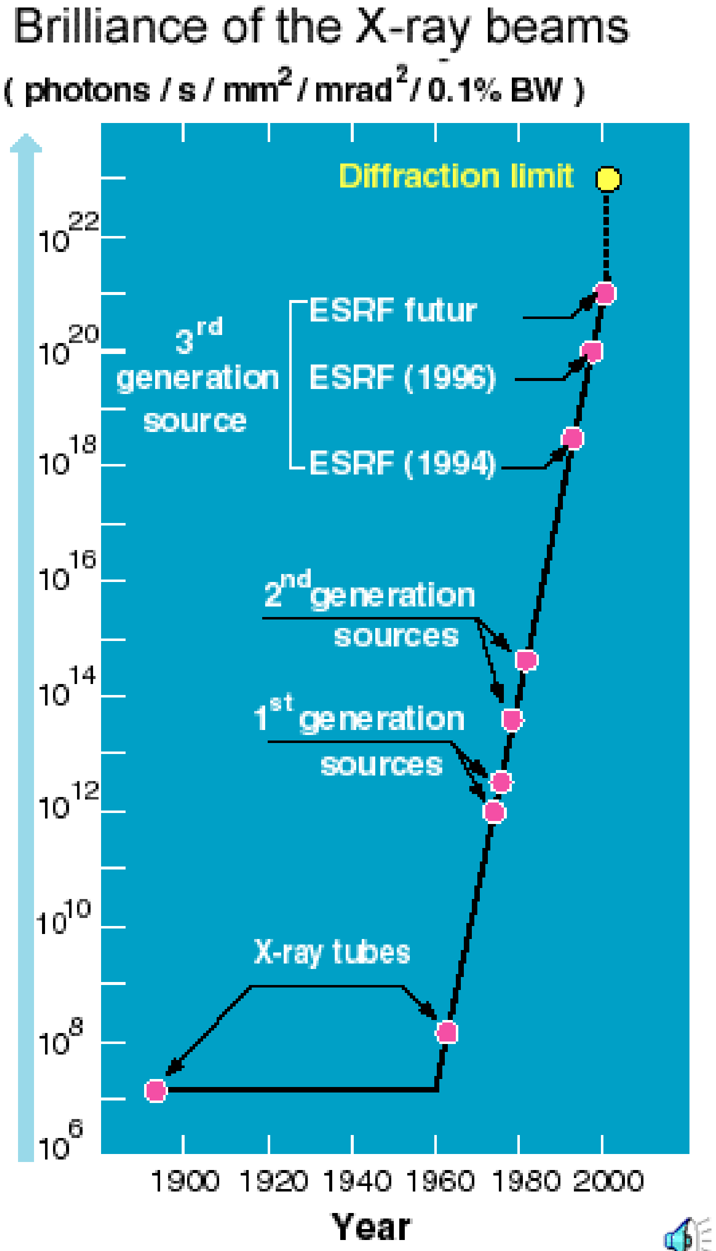
Synchrotron !!



The GE 70 MeV synchrotron, 1947

The ESRF 6GeV Synchrotron, 1994

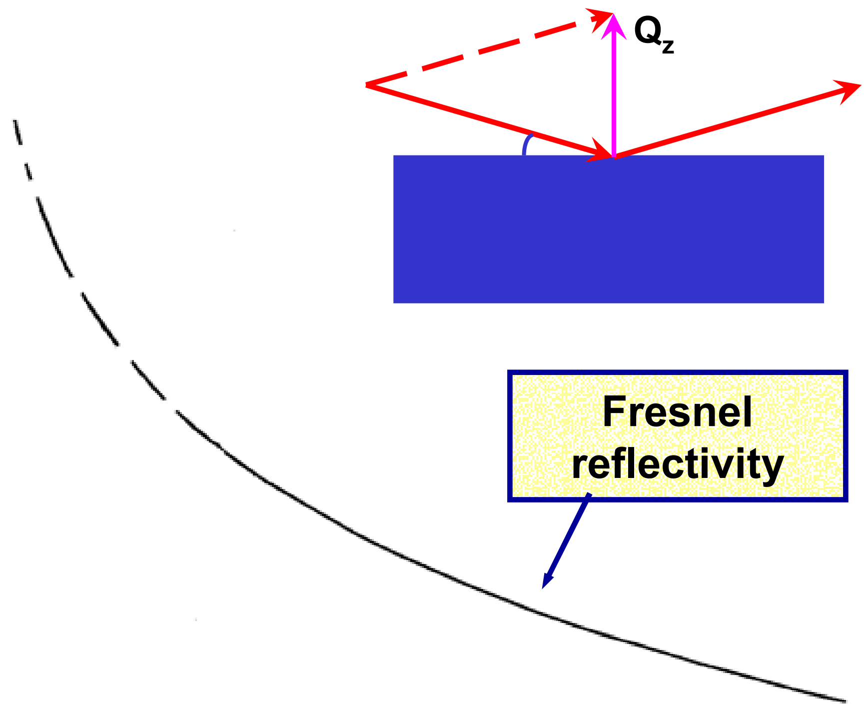
Evolution of x-ray intensity



The surface of liquid water (I)

- Looks like pure Fresne
- Surface must be abrup and flat.

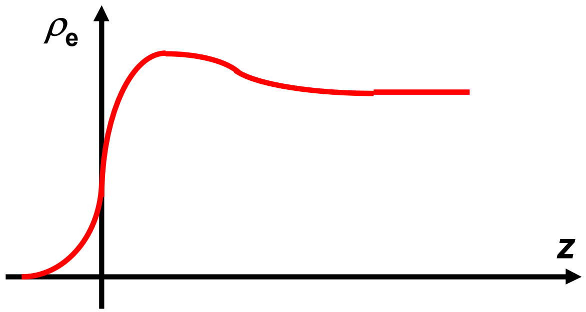
However →



- Why the deviation ?
- How to analyze non-Fresnel reflectivities

X-Ray Reflectivity (II)

Arbitrary density profile:



$$\frac{R(q_z)}{R_F(q_z)} = \frac{1}{\rho_\infty^2}\left|\int_{-\infty}^{+\infty} \frac{d\langle \rho_e(z)\rangle}{dz} \exp(iq_z z)\,dz\right|^2$$

THUS…

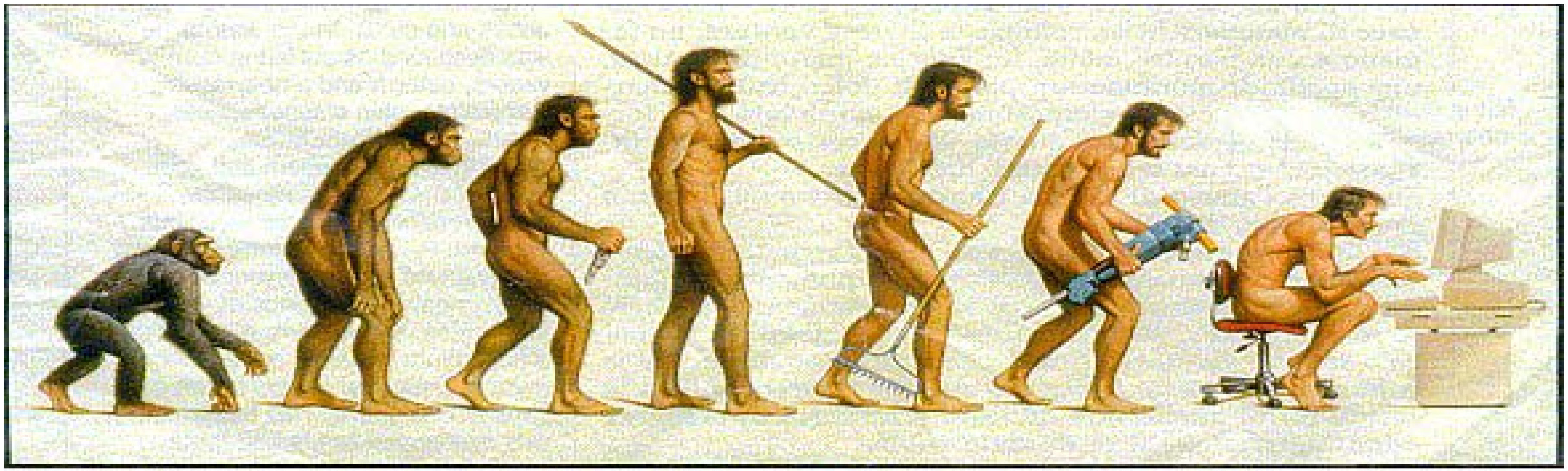
(1) Measure $R(q_z)$.

(2) Divide by $R_F \Rightarrow$ measured $R(q_z)/R_F(q_z)$.

(3) Construct model for $\rho_e(z)$.

(4) Calculate $|.....|^2$ for model.

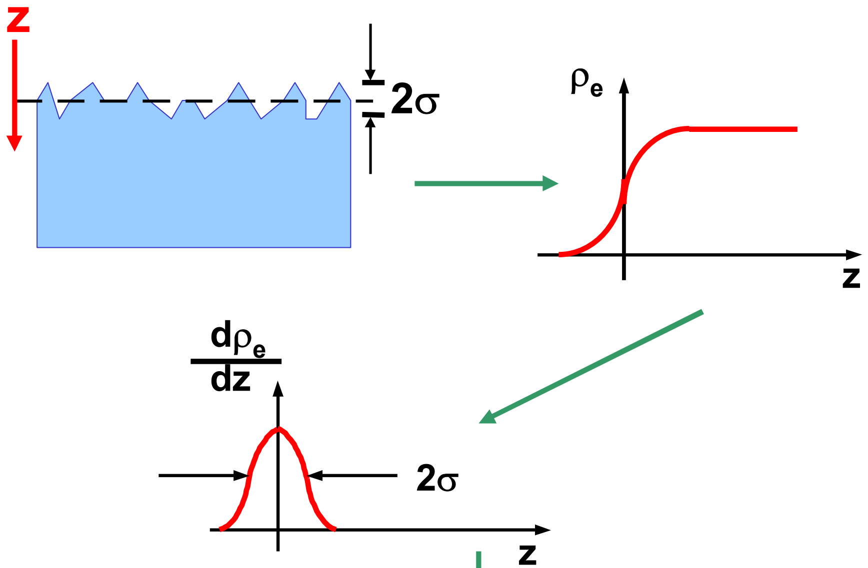
(5) Fit calculated $|.....|^2$ to measured $R(q_z)/R_F(q_z) \Rightarrow$ model parameters.



Somewhere, something went terribly wrong

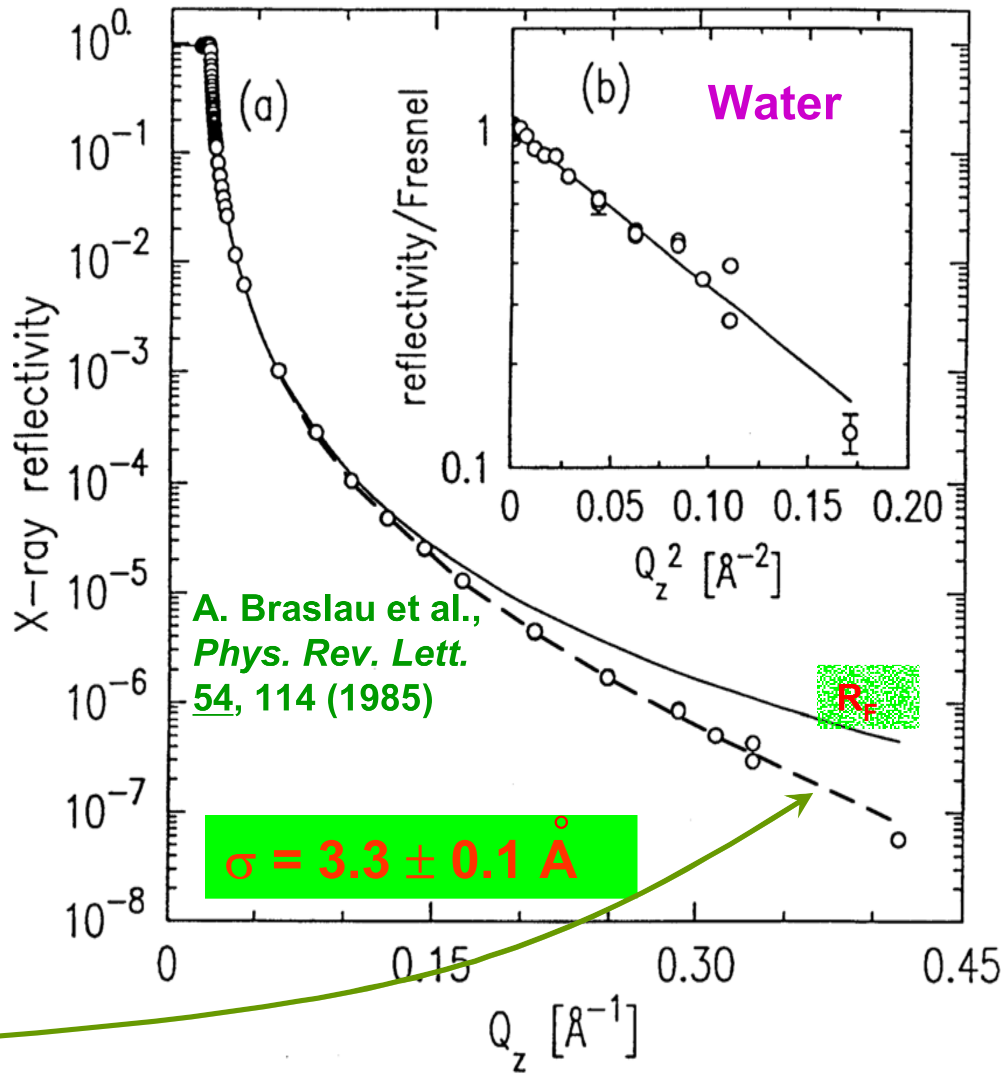
X-Ray Reflectivity (III)

Example: Gaussian surface roughness



$$\frac{R(q_z)}{R_F(q_z)} = \frac{1}{\rho_\infty^2}\left|\int_{-\infty}^{+\infty}\frac{d\langle\rho_e(z)\rangle}{dz}\exp(iq_z z)dz\right|^2$$

$$\frac{R(q_z)}{R_F(q_z)} = \exp(-q_z^2\sigma^2)$$



Where does the roughness come from ?

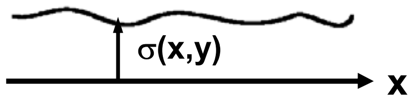
Capillary waves (I)

Where does the roughness come from ?

A. Braslau et al., *Phys. Rev. Lett.* 54, 114 (1985)

Thermally excited capillary waves are common to all liquid surfaces.

Start with:



Equipartition of surface energy and averaging over all modes yields:

$$\langle \sigma^2 \rangle = \frac{k_B T}{2\pi} \int_{q_{min}}^{q_{max}} \frac{q\,dq}{\Delta\rho g + \gamma q^2}$$

Cutoffs are determined by the atomic size (q_{max}) and resolution or gravitation (q_{min}).

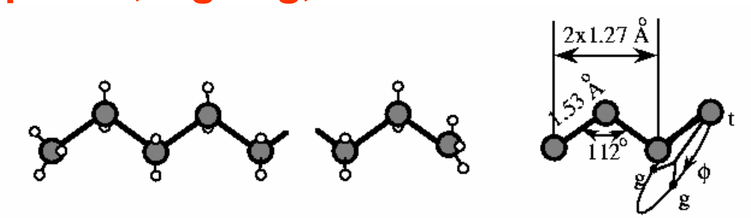
Taking into account non-capillary contributions:

$$\sigma^2 = \sigma_0^2 + \sigma_{cw}^2 = \sigma_0^2 + \frac{k_B T}{4\pi\gamma} \ln\left(\frac{q_{max}^2}{q_{min}^2}\right)$$

Using this for water yields σ = 3.2 Å !

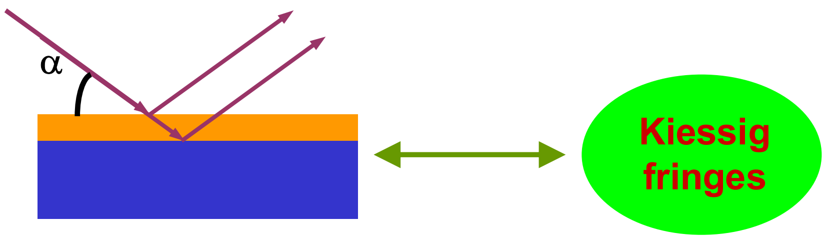
Molten chain molecules

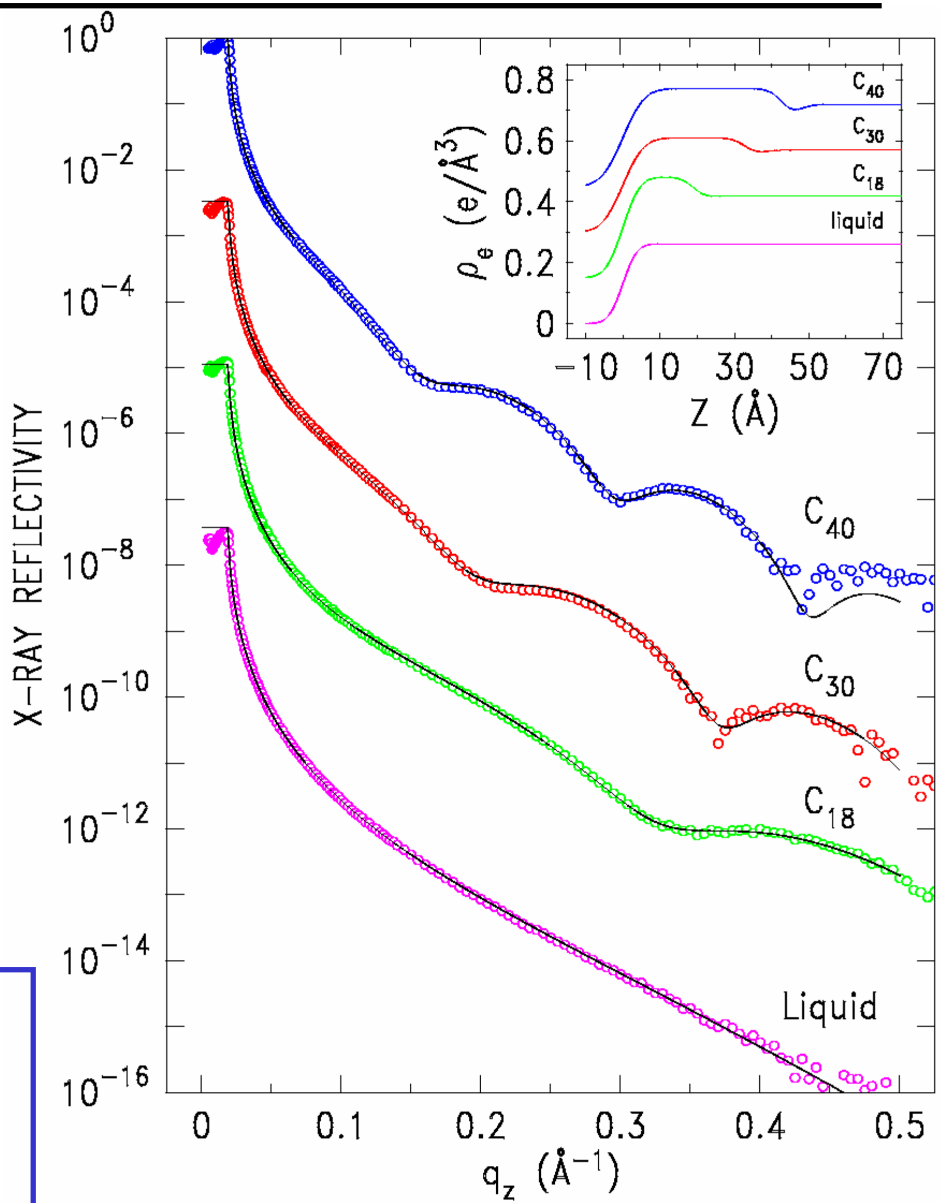
Alkanes (C_n): CH_3-$(CH_2)_{n-2}$-CH_3 :
planar, zig-zag, chain molecule.



- **Basic building block of organic molecules**
- **Determines the molecules' properties**
- **Of great scientific and commercial interest**

What is the structure of the melt's surface ?
How does it change with temperature ?





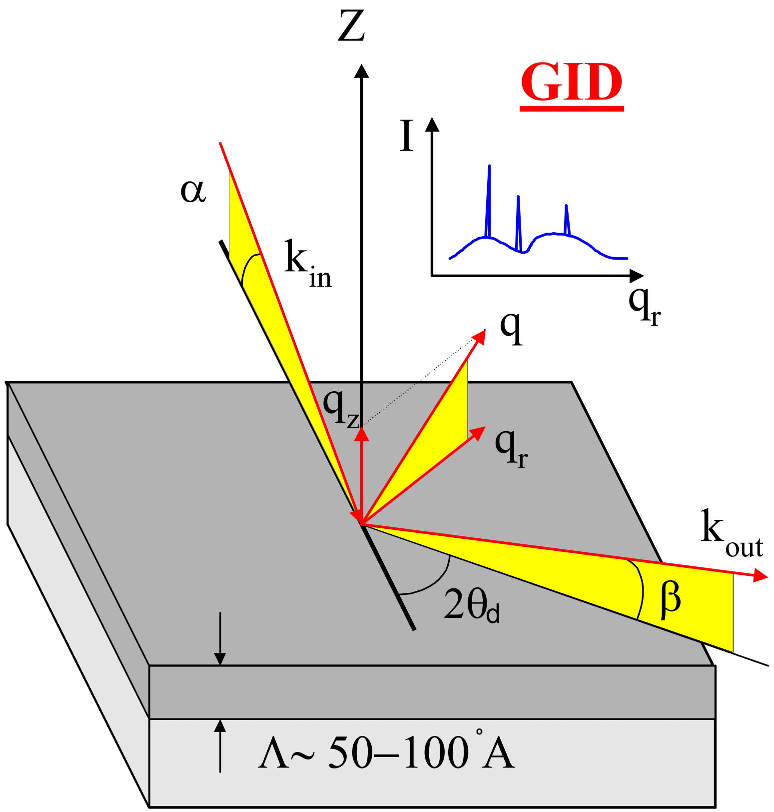
X. Wu et al., *Phys. Rev. Lett.* 70, 958 (1993)

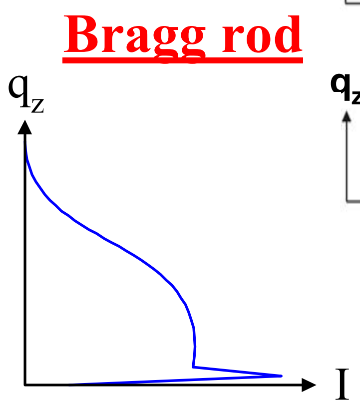
Surface Layer

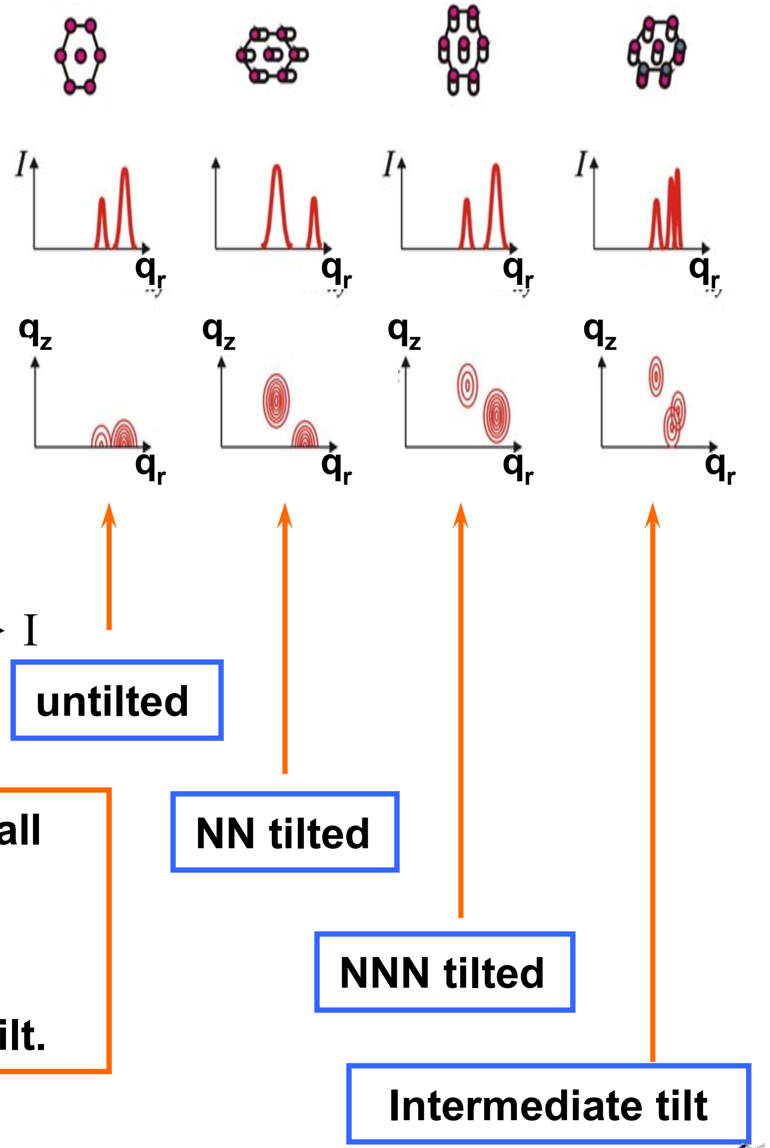
- **Appears at T_s close to, but above T_f.**
- **A single dense monolayer is formed.**

Is it a solid ?

X-ray in plane scattering geometry

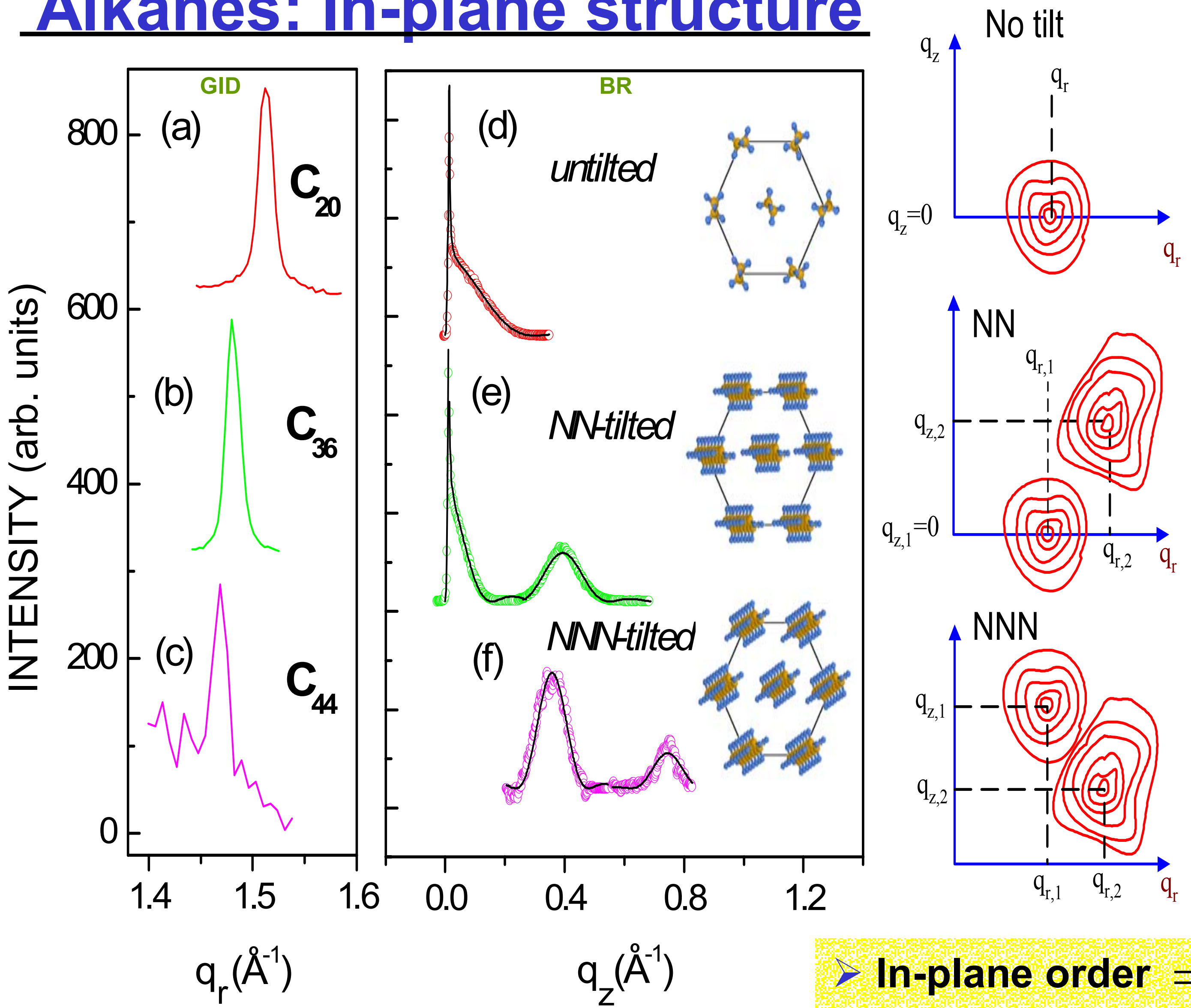






- Incidence at $\alpha < \alpha_c$ $\Rightarrow$ low penetration, ~50 Å, $\Rightarrow$ small bulk contribution.
- GID depends on q_r $\Rightarrow$ probes in-plane order.
- BR depends on q_z at q_r peaks $\Rightarrow$ probes molecular tilt.

Alkanes: In-plane structure



X. Wu et al., *Science* 261, 1018 (1993)

B. Ocko et al., *Phys. Rev. E* 55, 3164 (1997)

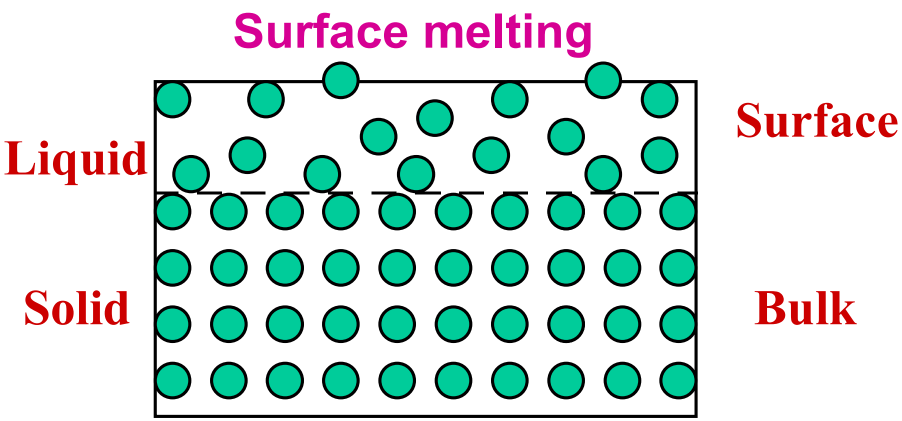
- **In-plane order ⇒ quasi-2D crystal .**
- **Hexagonal packing.**
- **Three types: no tilt, NN tilt, NNN tilt.**

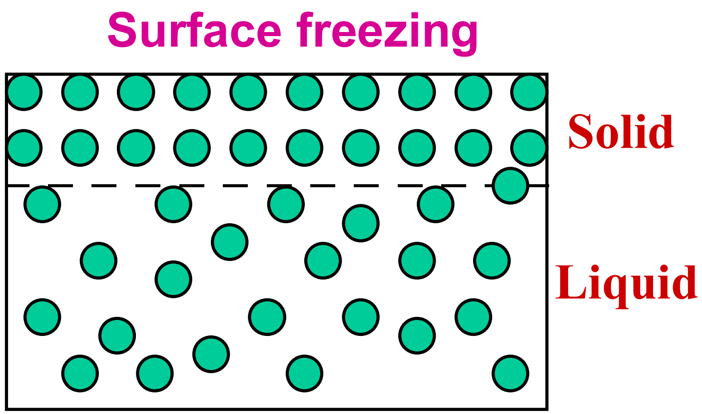
Surface Freezing

Statistical Mechanics

- Phase diagrams and boundaries depend on dimensionality
- For all materials $T_{melt}(2D) < T_{melt}(3D)$

Molecules at the surface are less confined, have higher entropy, and hence melt at a lower temperature than in the bulk.





The general rule

Observed in:
- metals
- semiconductors
- molecular crystals
- ice etc.

Very rare

The only related effect : surface ordering in liquid crystals.
(but order is smectic not crystalline)

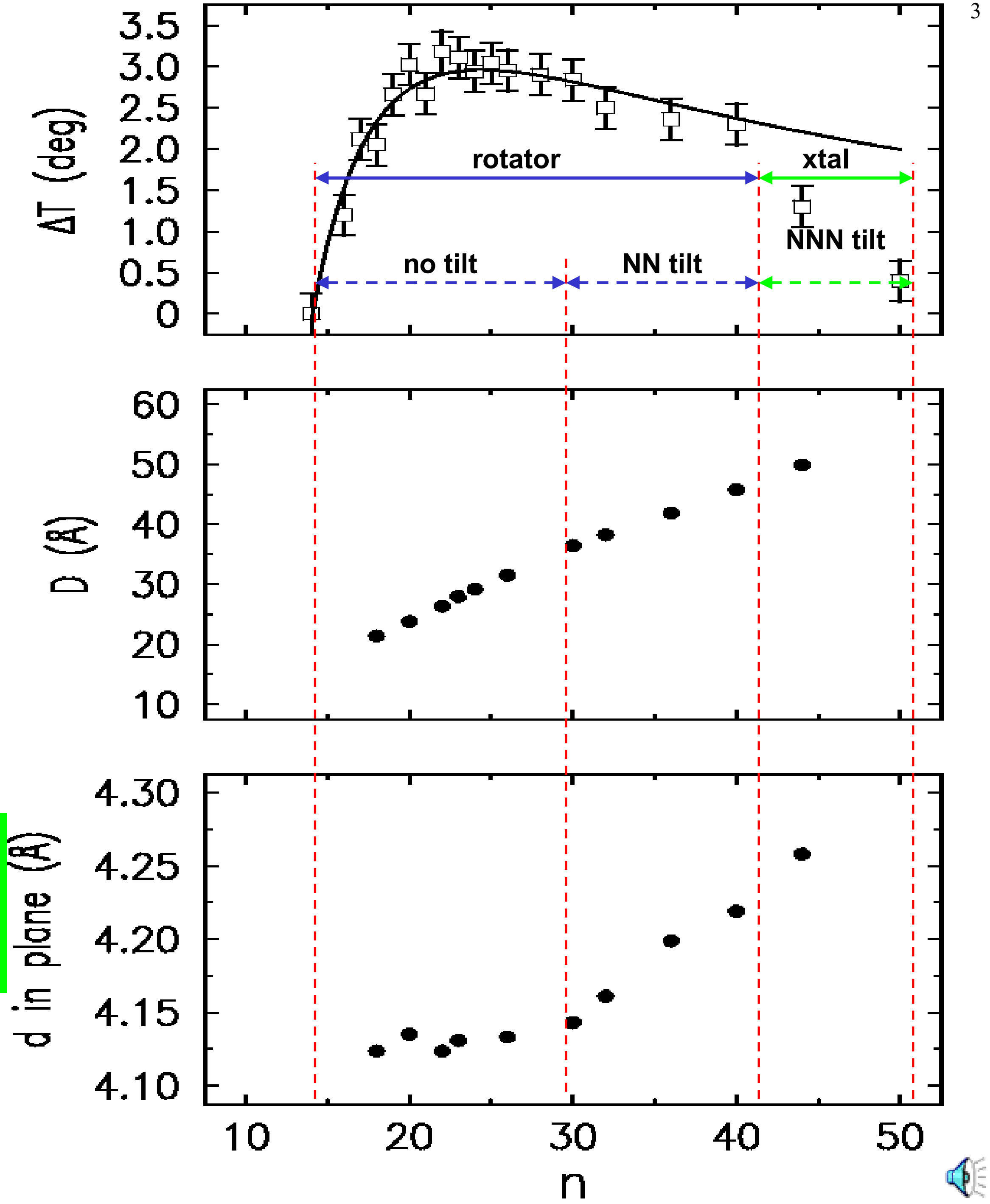
Theory: entropic stabilization by large vertical fluctuations, possible at the surface but not in the bulk.

Tkachenko & Rabin, *Phys. Rev. Lett.* 76, 2527 (1996)

Alkanes:
2D surface phase diagram

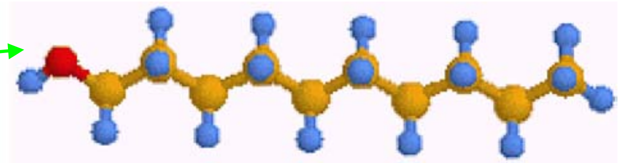
- Always a *monolayer*.
- Packing always hexagonal.
- No structure variations with T.
- Structure varies with n.
- Limited chain length range.
- Limited temperature range.

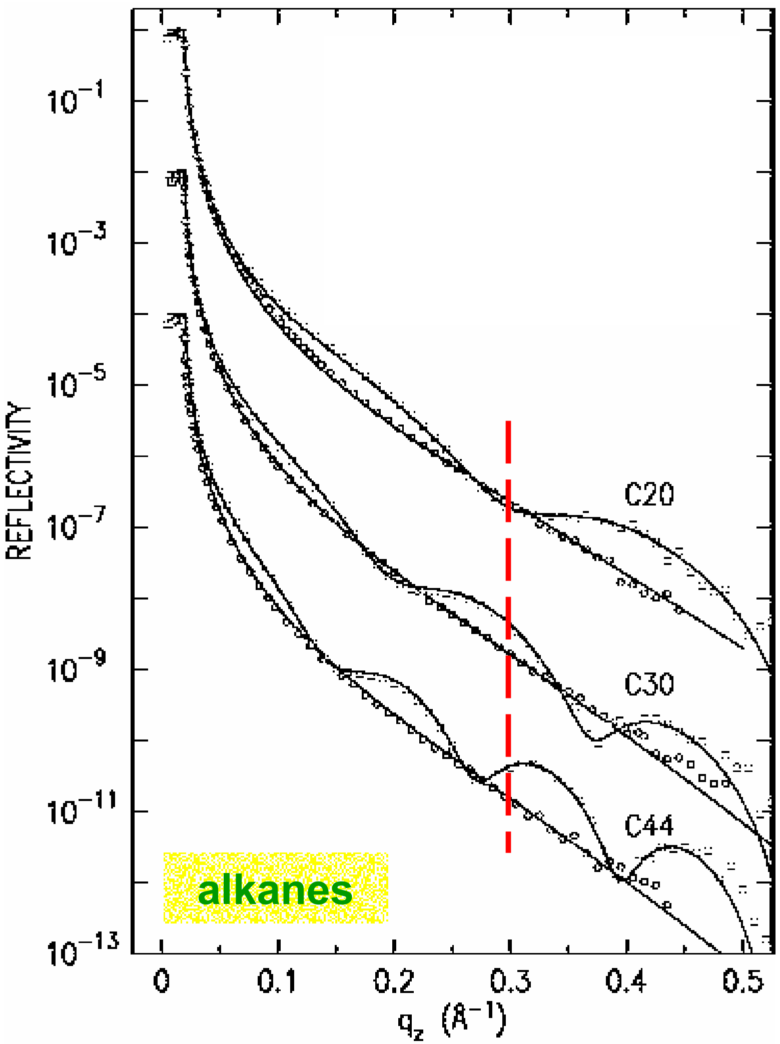
Does surface freezing occur in other molecules, or just in alkanes ?

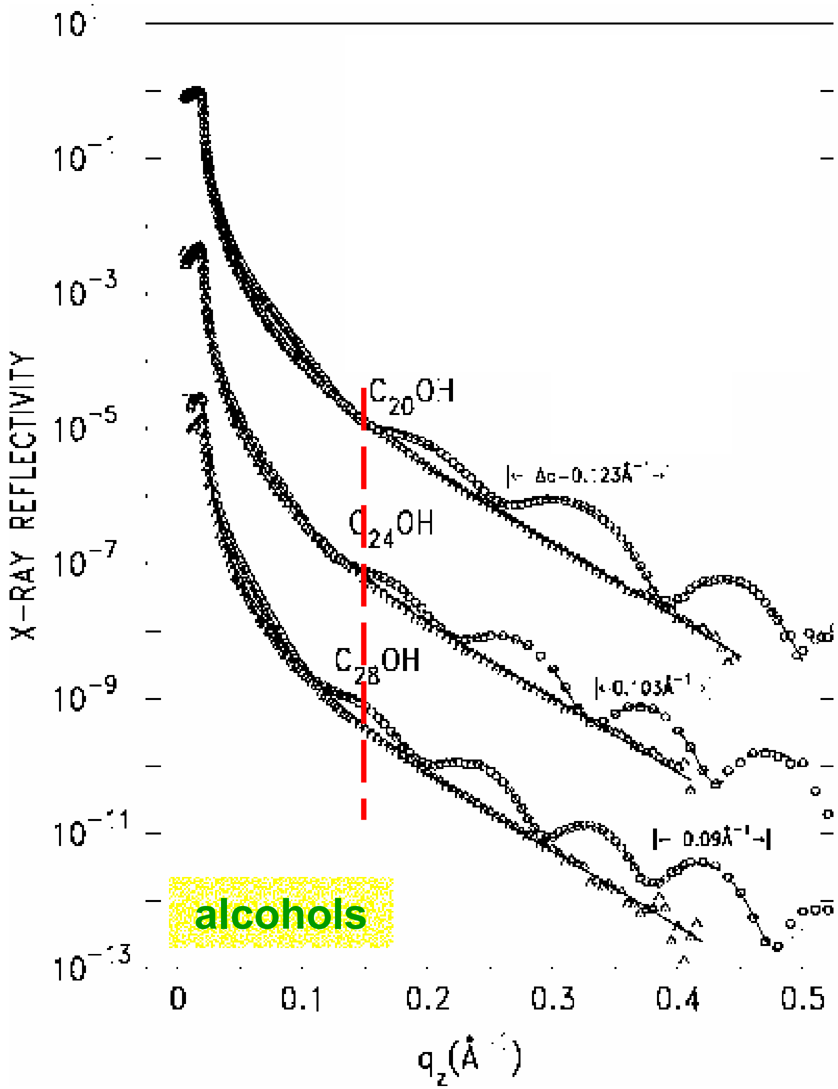


Surface Freezing in Alcohols (I)

OH headgroup, allows hydrogen bonding.

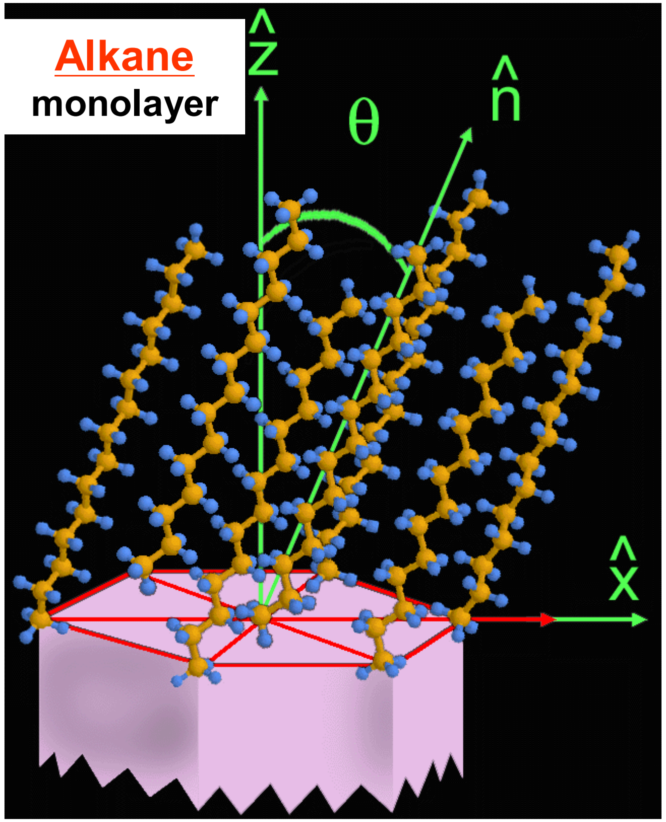


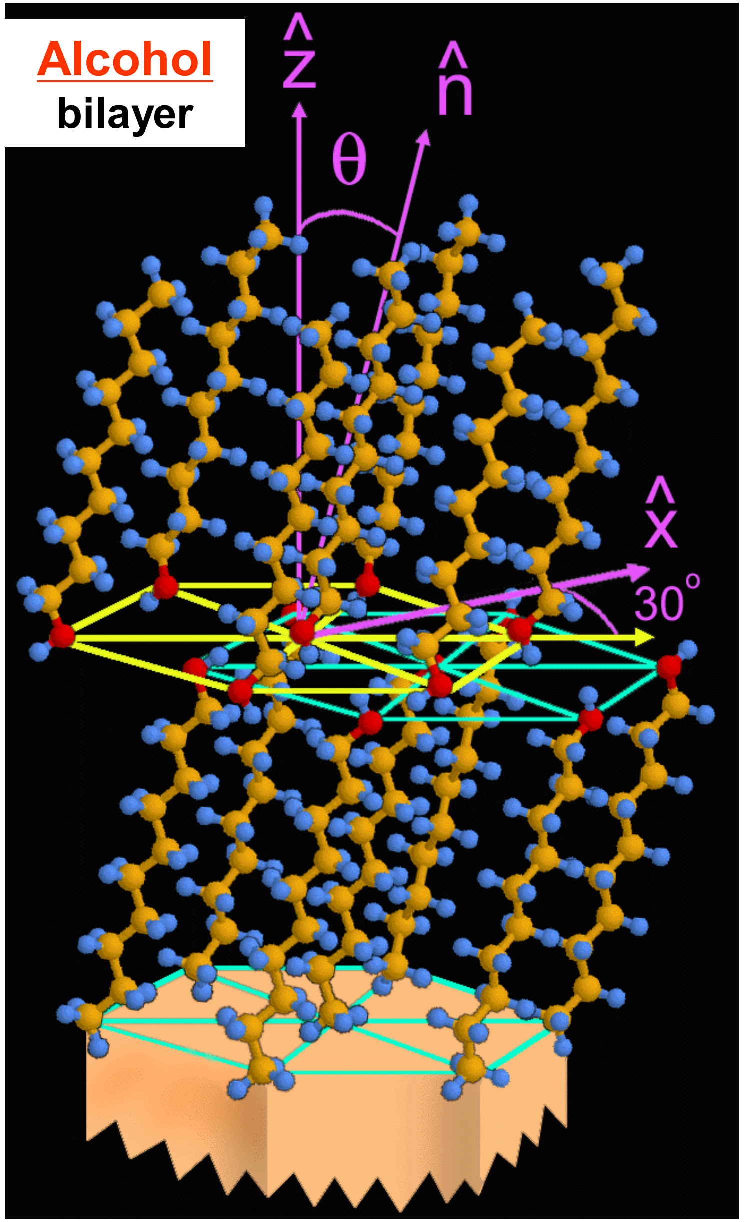




Surface Freezing in Alcohols

O. Gang et al.,
Phys. Rev. E
58, 6068 (1998)



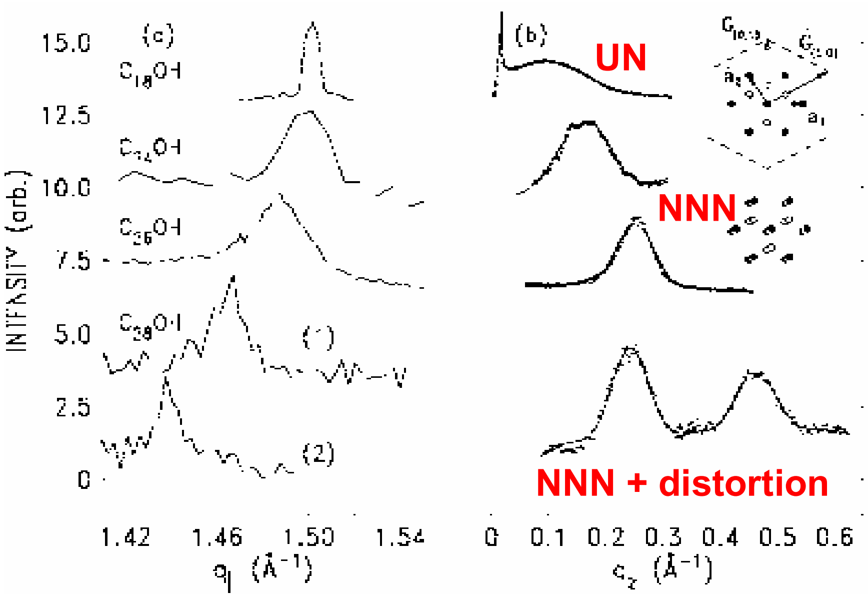


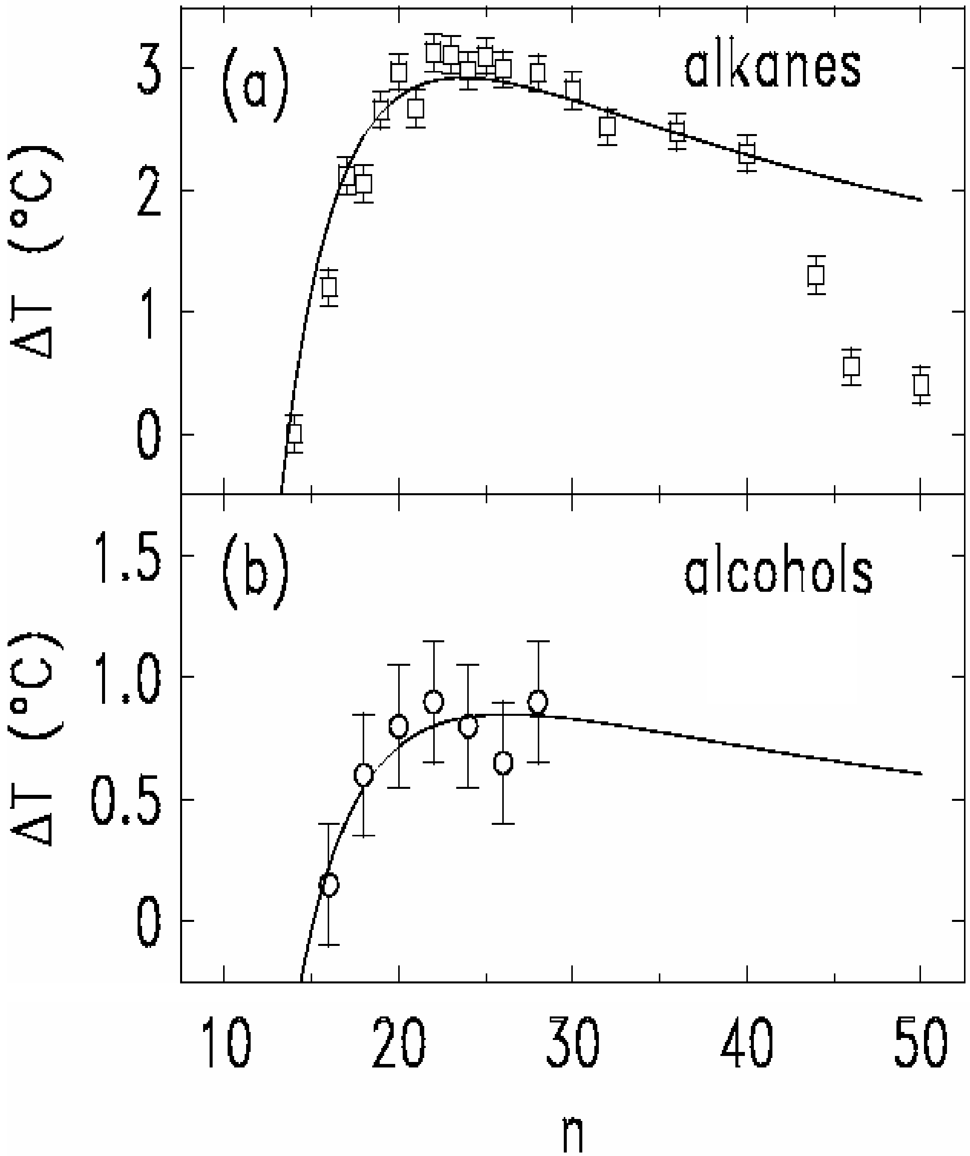
Surface Freezing in Alcohols(III)

- Only even alcohols show SF.
- T-range smaller than alkanes.
- n-range smaller than alkanes.
- Phases: UN→NNN →NNN+dist.
  (alkanes: UN→NN →NNN)

But….

- Max. SF layer thickness larger.
- T_S and T_F much higher.

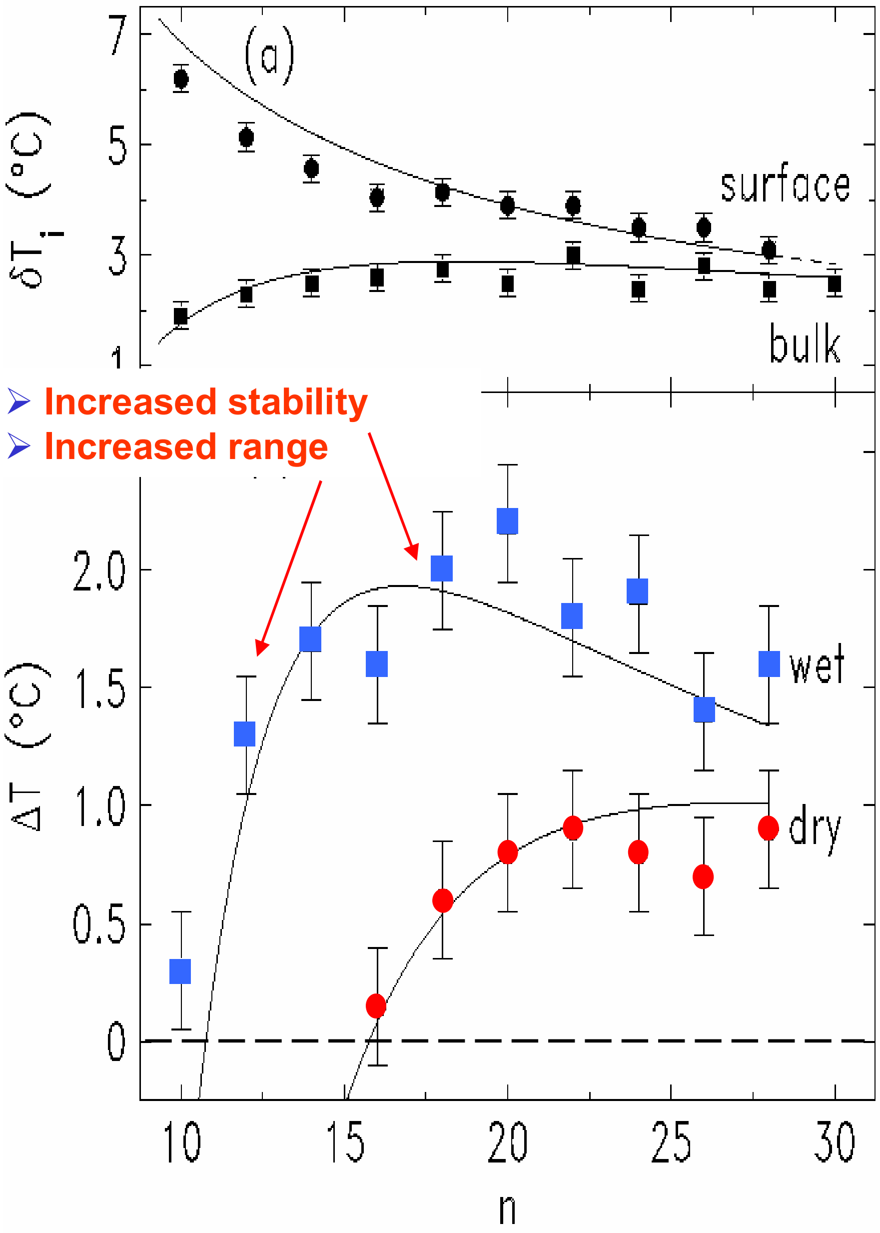


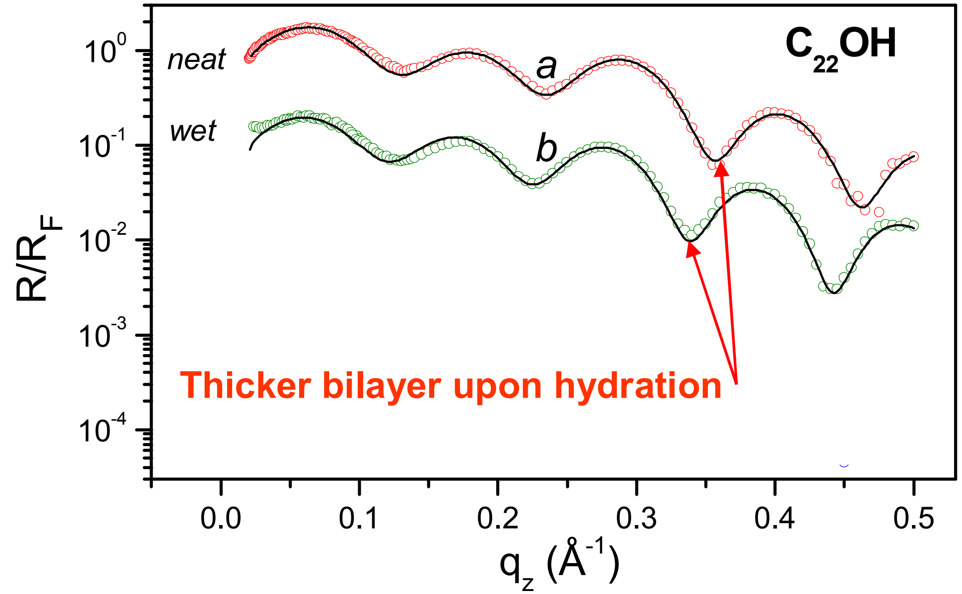


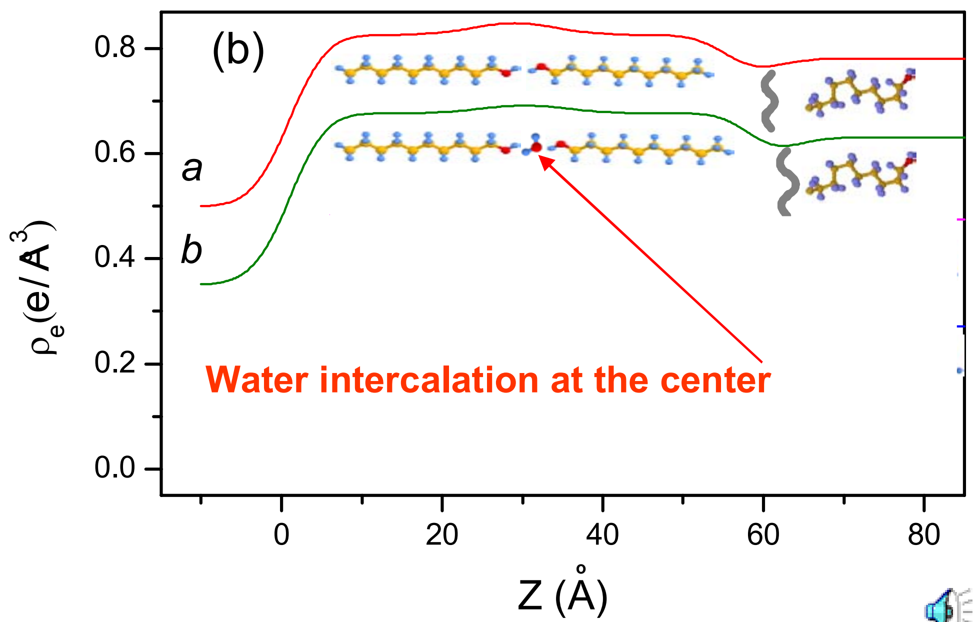
O. Gang et al., *Phys. Rev. E* 58, 6068 (1998)

Alcohols: Straight or On the Rocks

O. Gang et al., *Phys. Rev. Lett.* 80, 1264 (1998)







Liquid metals (I)

Unique properties

- two component fluid (ion jellium + quantum fluid)
- Ga: $0.50\ T_m$ < liquid range < $8.3\ T_m$

  Largest of all liquids
- magnitude of surface tension and variation from metal to metal not explained by theory:

	γ	T_m	γ / T_m
Cs	70	301	0.23
W	2500	3655	0.68
Al	914	933	0.98
Hg	498	234	2.13
Ga	718	302	2.38
I_2	38	380	0.1
NaCl	114	1076	0.11
SiO_2	307	2073	0.15
Ar	13.1	84	0.16
H_2O	72.8	293	0.25

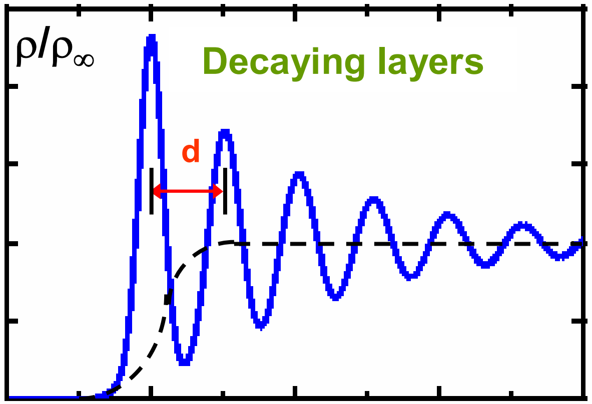
- pronounced supercooling in LM

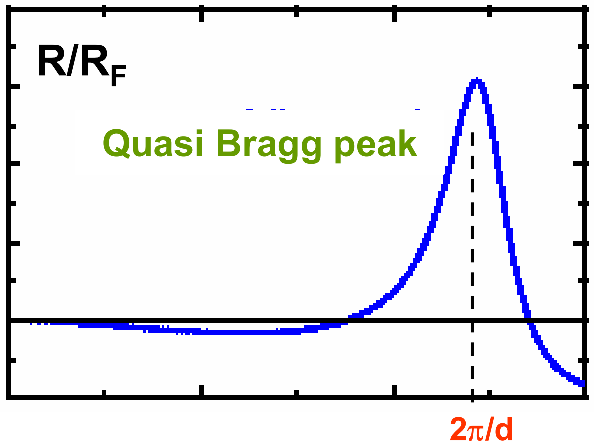
How would these properties be reflected in the structure of the surface ?

Surface layering, similar to atoms at a solid wall

Theory & simulations Rice & others (1960-1985)

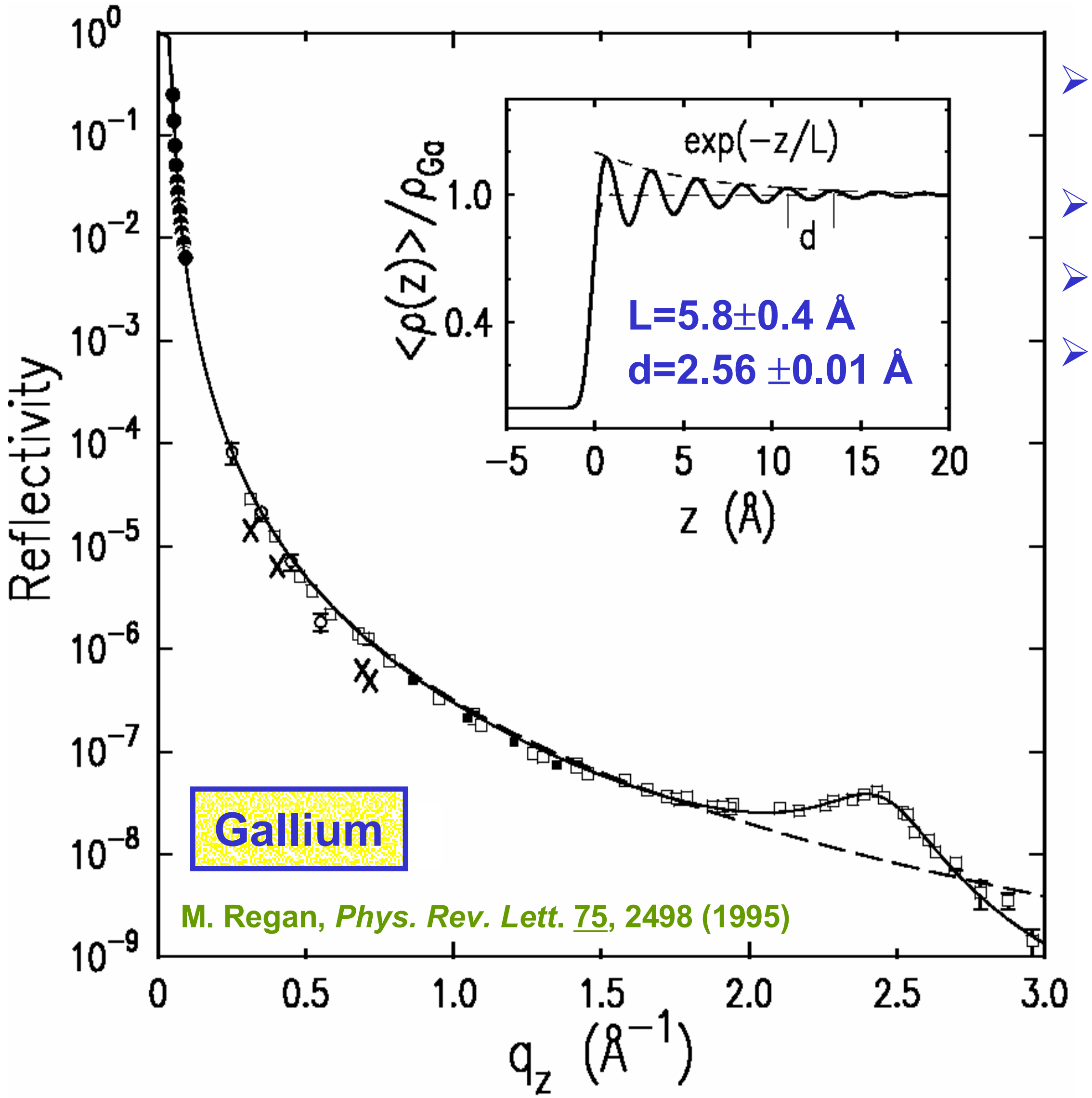
Expected:





Liquid metals (II)

Observed:

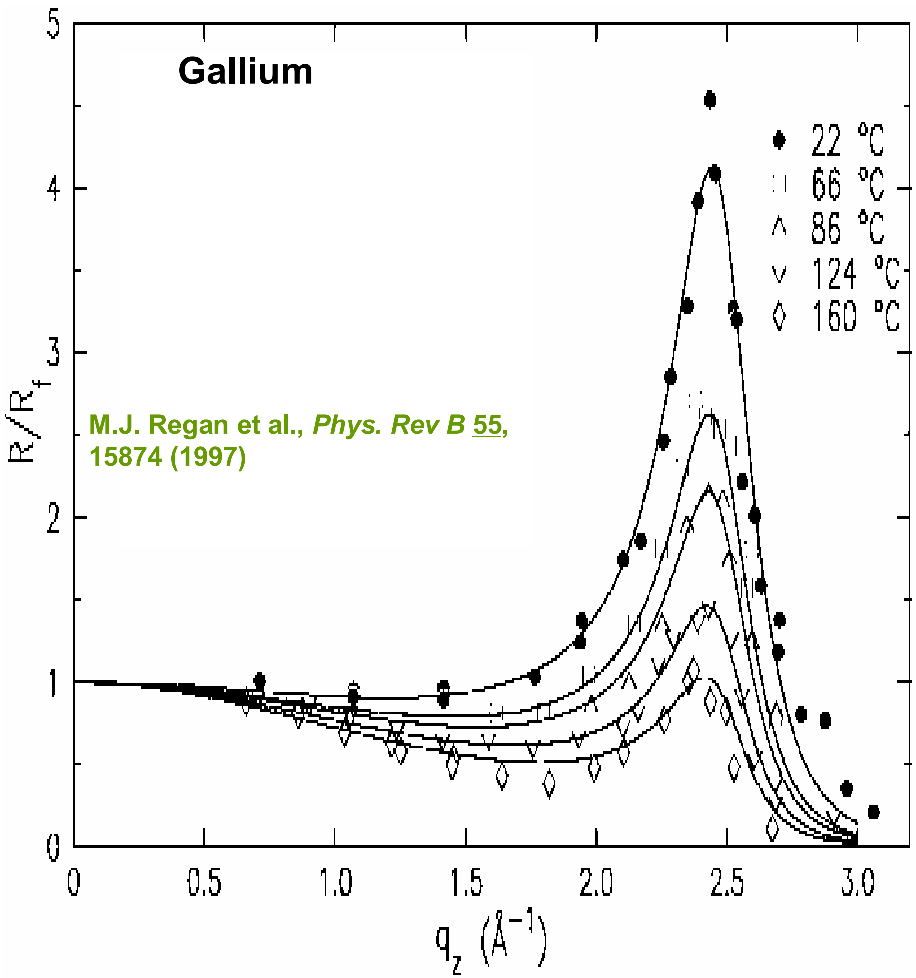


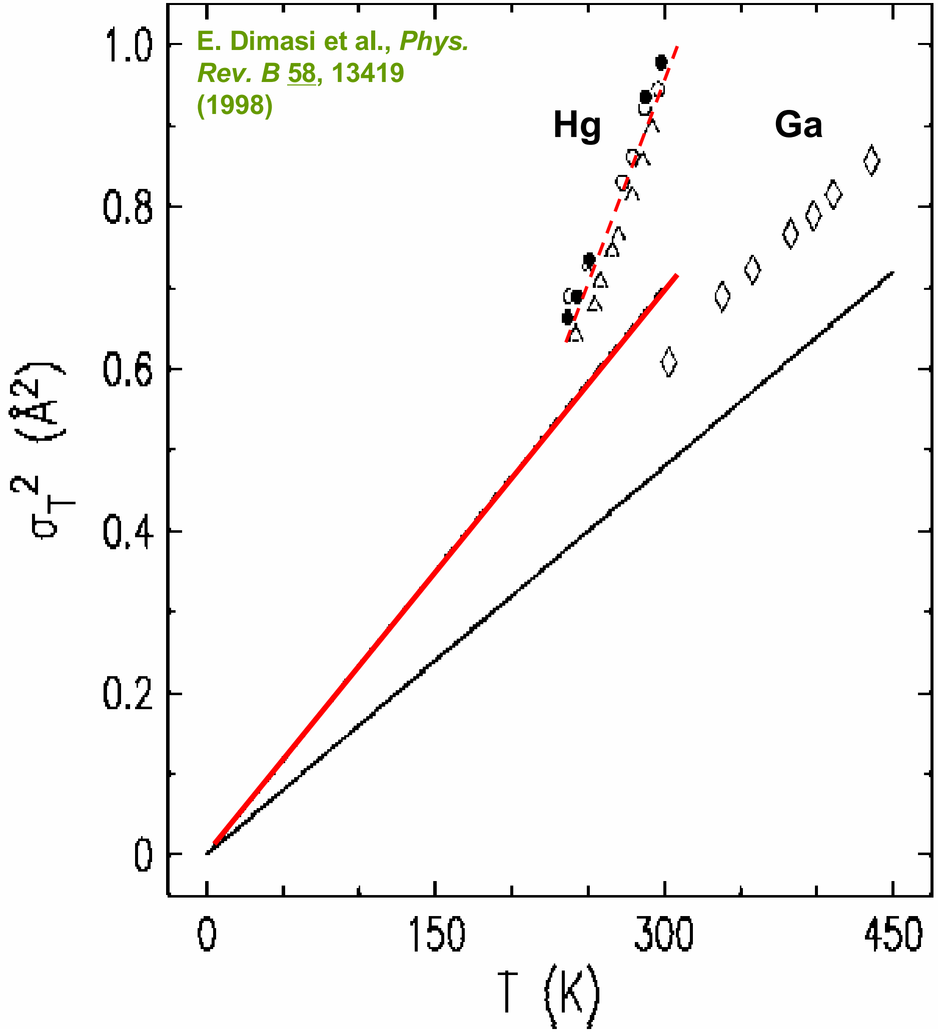
- **First clear observation of layering (now also in Hg, In, Sn, alloys….).**
- **Roughness: 0.8 Å vs. 3.2 Å for water**
- **q_z- range: 3 Å^{-1} vs. 0.7 Å^{-1} for water.**
- **L at surface > L at bulk ! (dimers ?).**

Liquid metals (III)

Does the layering interfere with CW ?

$$\sigma^2 = \sigma_0^2 + \frac{k_B T}{4\pi\gamma} \ln\left(\frac{q_{max}^2}{q_{min}^2}\right)$$





What was left out…………..

Because of time limitaion many current studies were left out:

- **The surface structure of van der Waals liquids (organic liquids etc.).**
- **The structure of liquid alloys.**
- **Wetting in binary liquid mixtures (long range, short range).**
- **Adsorbed Gibbs layers at the liquid surface.**
- **Overlayers on water: Langmuir films.**
- **Overlayers on metals: surface oxidation, organics monolayers on metals.**
- **The structure of the liquid-liquid interface.**
- **The structure of a solid-liquid interface.**

Thanks ......

<u>Water</u>

- A. Braslau, B. Ocko, A. Weiss, P. Pershan (Harvard), J. Als-Nielsen, J. Bohr (Risø)

<u>Liquid metals</u>

- N. Maskil, H. Kraack (Bar-Ilan), M. Regan, H. Tostmann, P. Pershan (Harvard), O.Magnussen, E. DiMasi, B. Ocko (BNL)

<u>Surface Freezing</u>

- O. Gang, H. Kraack, E. Sloutskin (Bar-Ilan), X. Wu, E. Sirota (Exxon), B. Ocko (BNL)

<u>$$$$$$ (actually ¢¢¢)</u>

Israel: U.S.-Israel BSF, ISF, Exxon
U.S. :DOE, NSF

<u>Beamtime:</u>

NSLS, Brookhaven National Laboratory
APS, Argonne National Laboratory
HASYLAB, Hamburg, Germany
ESRF, Grenoble, France

One of my previous talks

at the University of ……