# Surfaces of disordered materials

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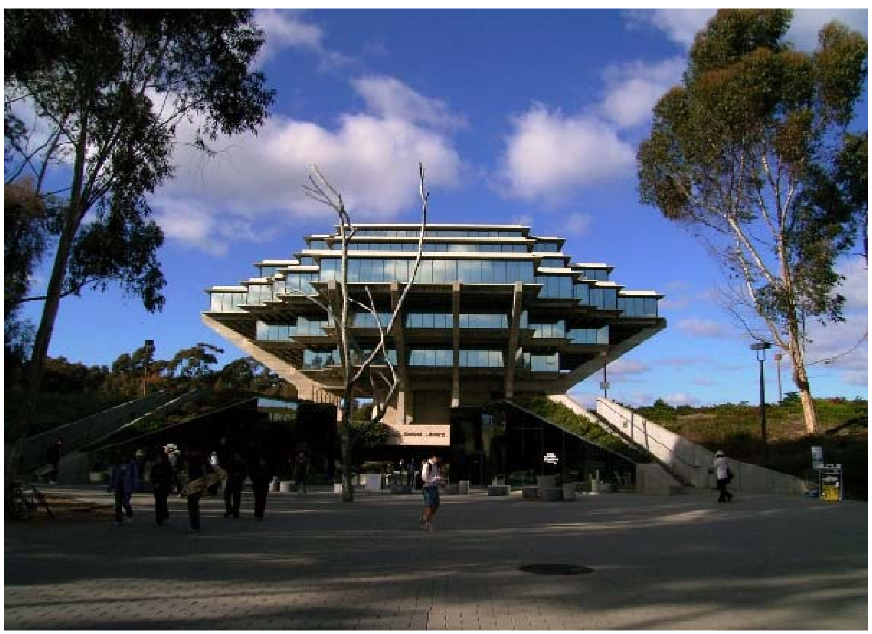
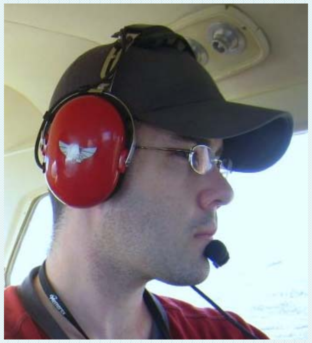


# Shpyrko Group:

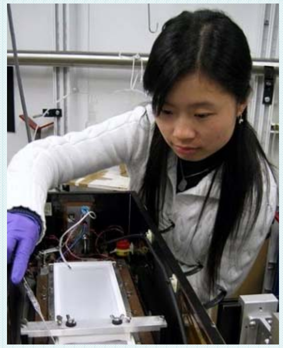
## Postdoc:

Jyoti Mohanty
now @Berlin TU

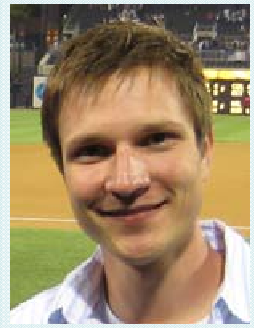
## Grad Students:



Ash Tripathi

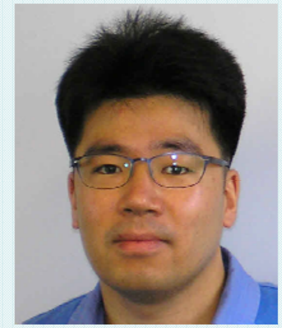


Yeling Dai

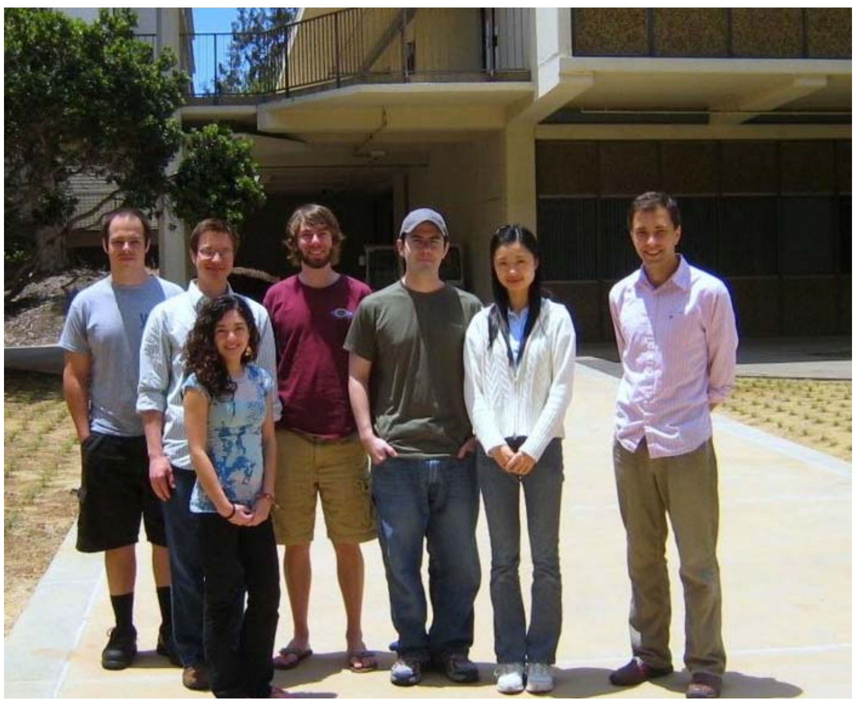


Sebastian Dietze

Moses Marsh



Jong Woo Kim



## Undergrad Students:

Mike Folkerts

Sam Stanwyck

Lluvia Rodriguez

Magnus Heinz

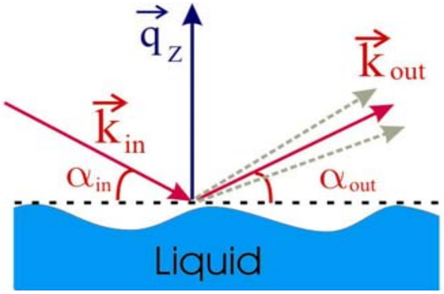
Veronica Burnett

Anashe Bandari

# Surface Scattering:

Specular:

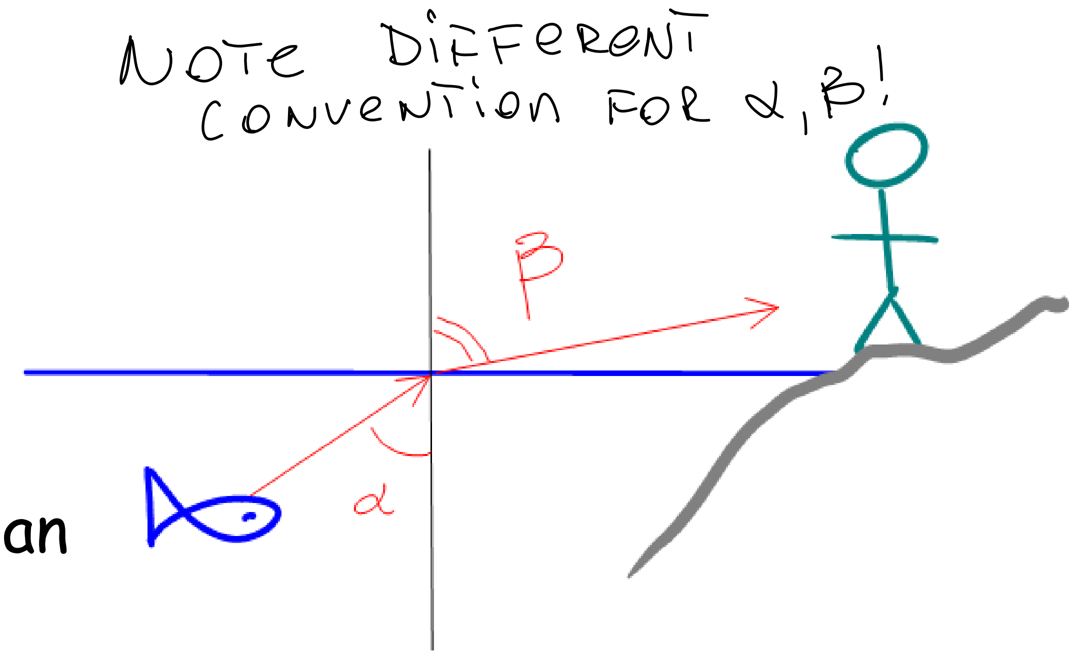
Diffuse:



# Total Internal reflection:

## Snell's Law:

$$n\sin(\alpha) = \sin(\beta)$$




Total Internal Reflection observed for $\alpha$ greater than critical angle $\alpha_c$

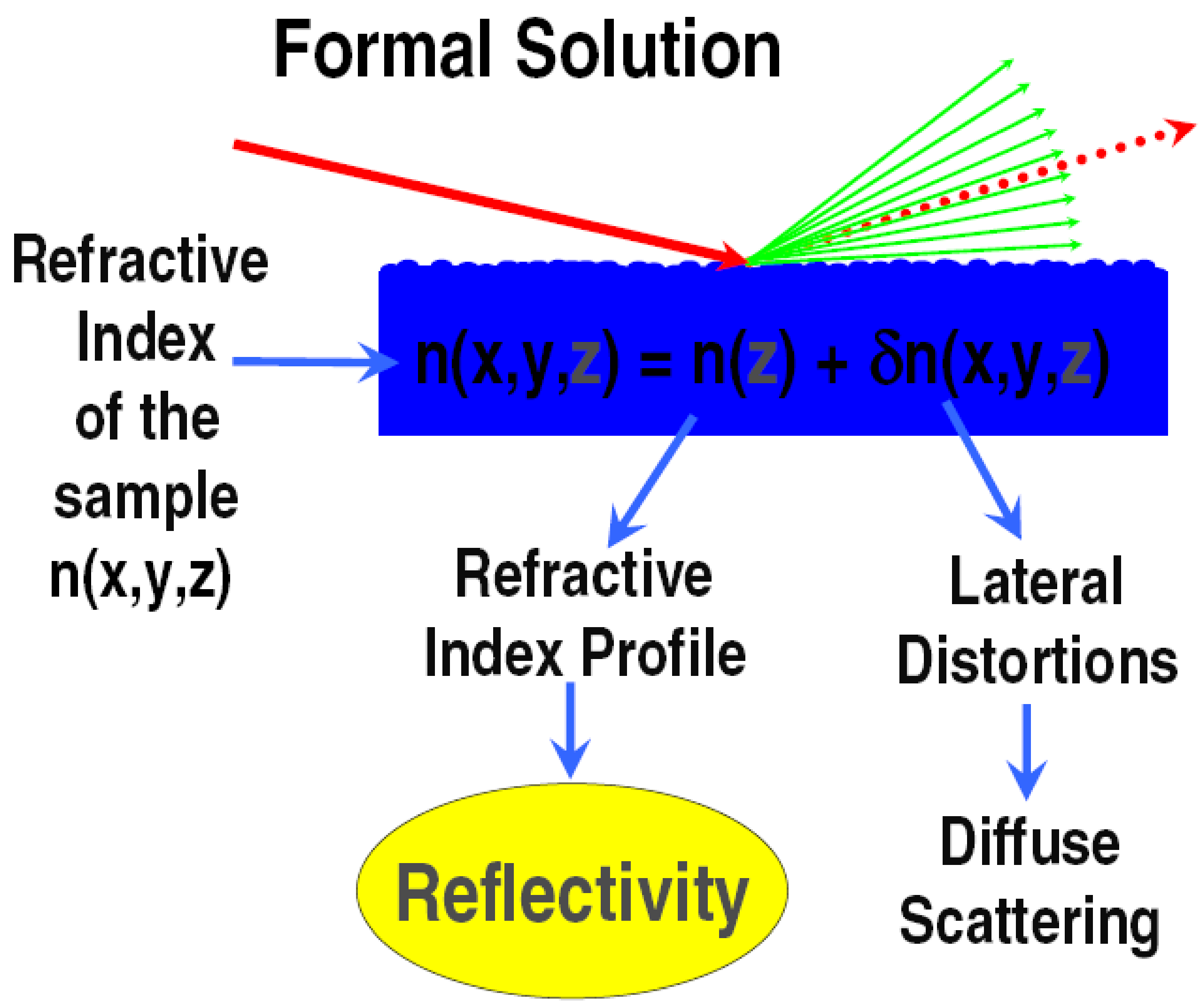
$$n\sin(\alpha_c) = \sin(\frac{\pi}{2}) = 1$$

## For x-rays:

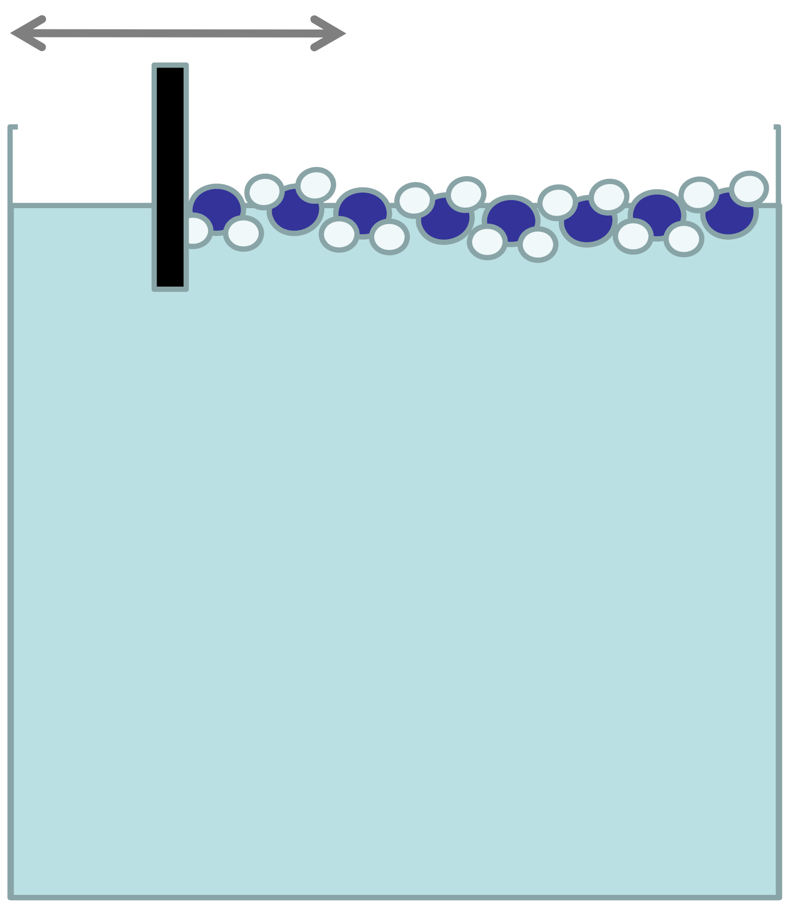
$n = 1 - \delta$ where $\delta \approx 10^{-6}$ (including adsorption $n=1-\delta+i\beta$)

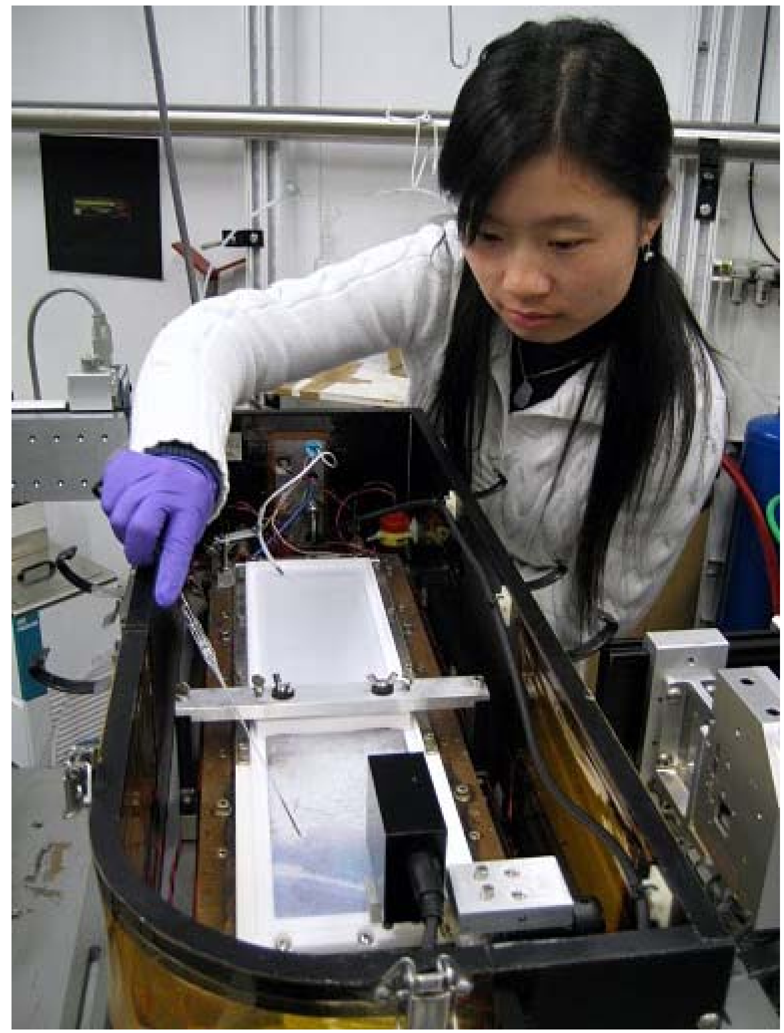
Critical angle $\approx \sqrt{2\delta}$ or ~ $10^{-3}$ a few mrad

# X-ray Reflectivity and Diffuse Scattering

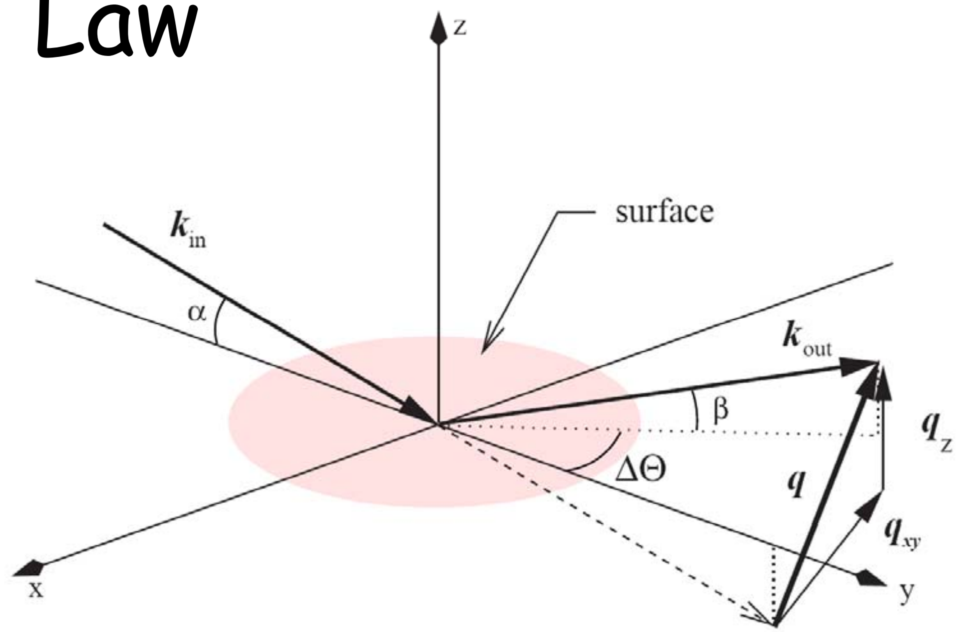


# Self-assembled monolayers (chemistry, biology, physics)





# Fresnel Law




$$R_F(\alpha) = I_r(\alpha)/I_0$$

"Ideal" Interface:
Static, Flat,
Sharply terminated

for $\alpha = \beta$ (specular reflection)

$$R_F(q_z) = \left| \frac{q_z - \sqrt{{q_z}^2 - {q_c}^2}}{q_z + \sqrt{{q_z}^2 - {q_c}^2}} \right|^2 \sim \left( \frac{q_c}{2q_z} \right)^4$$

Where $q_c \approx 4\sqrt{\pi r_e \rho}$

$$q_z = \frac{2\pi}{\lambda}(\sin\alpha + \sin\beta) = \frac{4\pi}{\lambda}\sin\alpha \quad \text{for } \alpha = \beta$$

★ Q: How come reflectivity does not depend on angles & wavelength, but only on combination of the two ($q_z$, $q_c$)

# The Liquid Surface Reflectometer

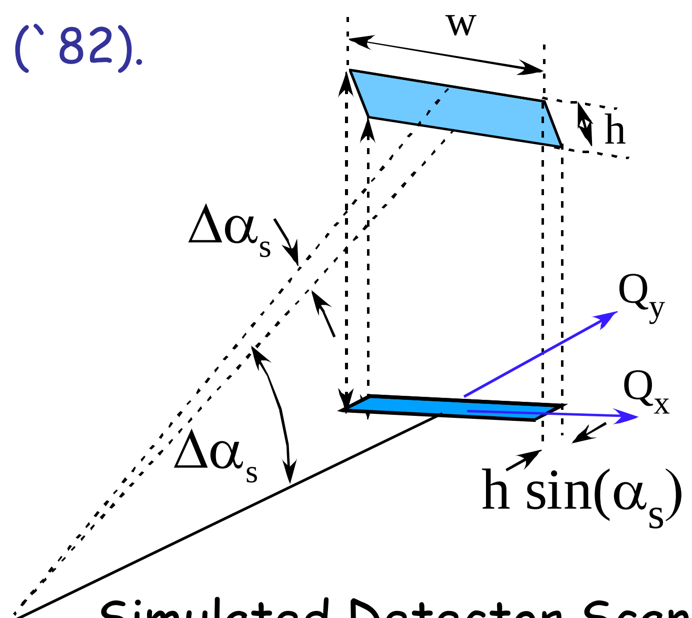
HasyLab: Als-Nielsen, Christensen, Pershan, PRL (`82).

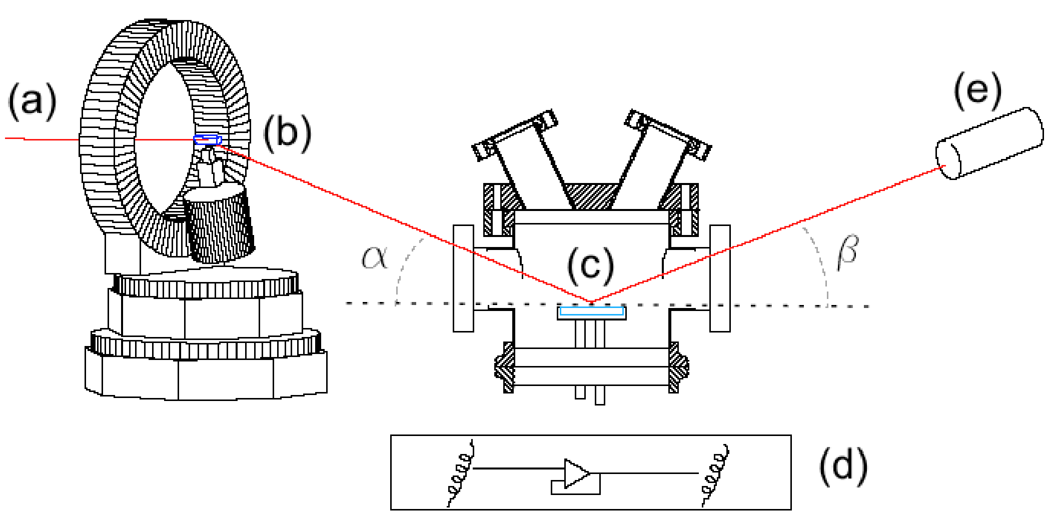
NSLS: X22B, X19C

APS: CHEMMATCARS, CMC, μ–CAT

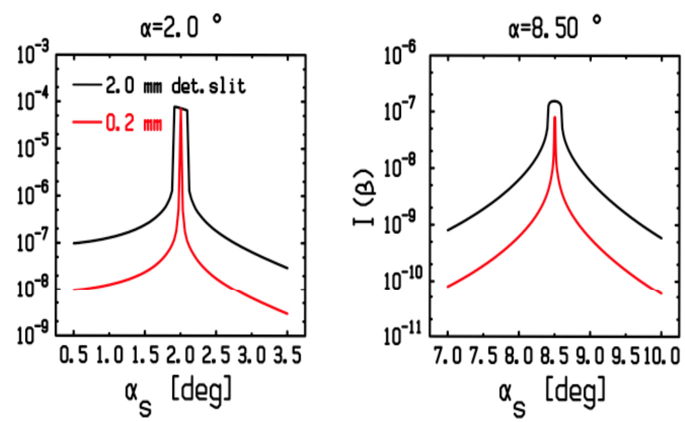
ESRF: ID15A **(Alternate Design)** H. Reichert '03

PETRA-3: Sector P8

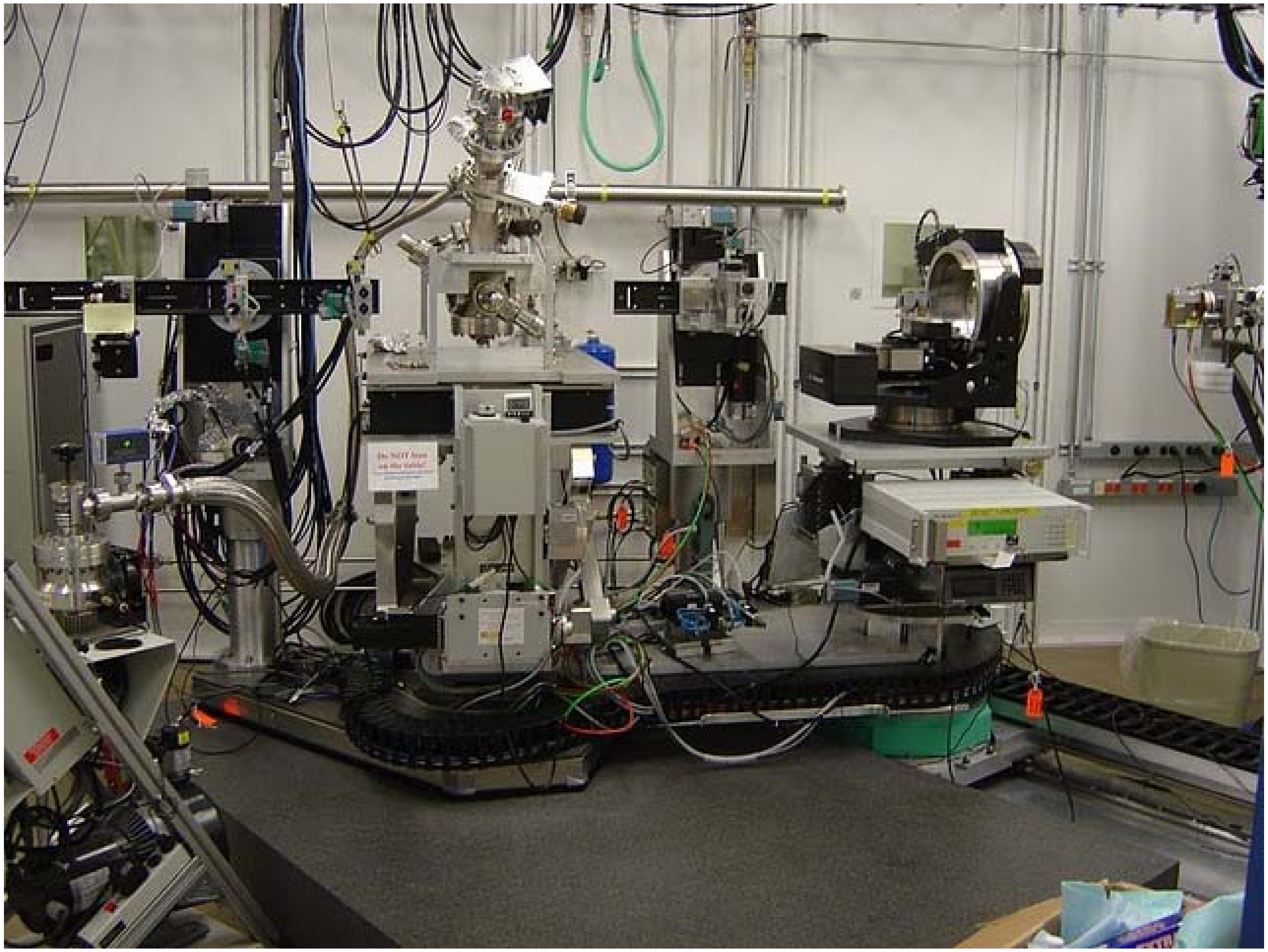


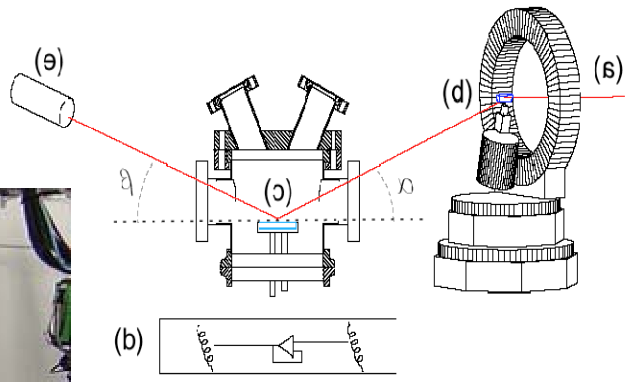




Simulated Detector Scan

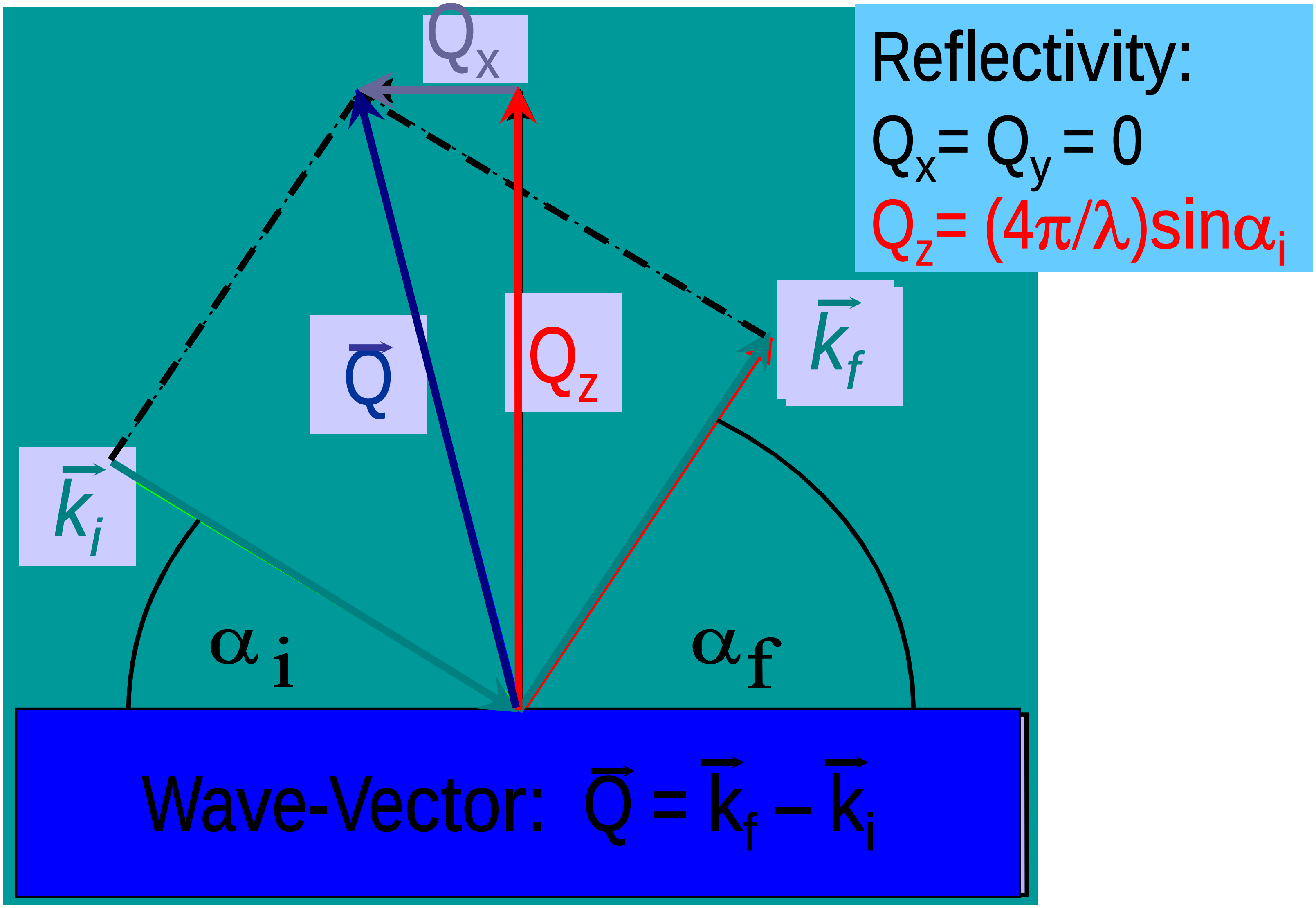


# Liquid Surface Reflectometer





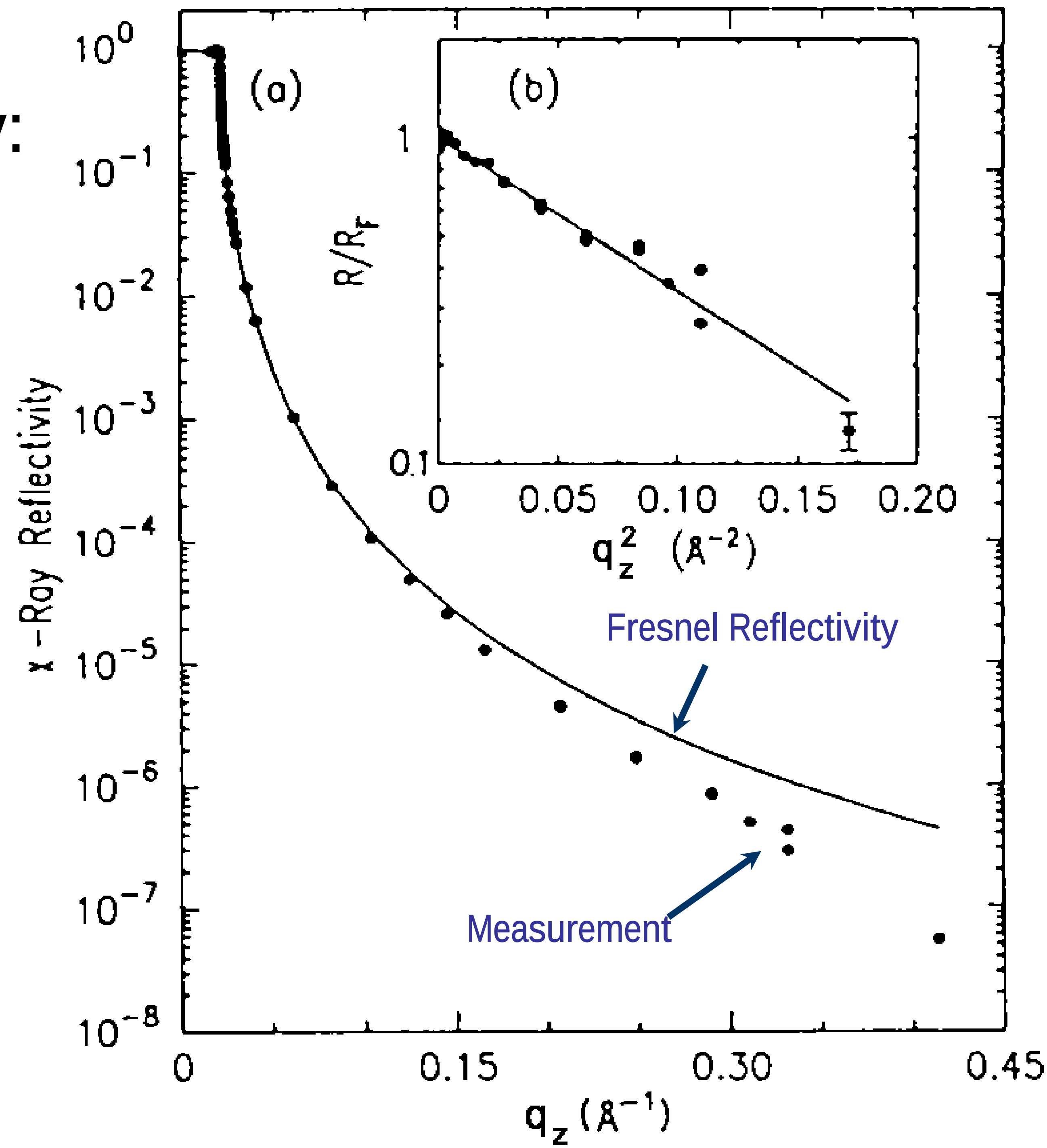
# Scattering Geometry & Notation



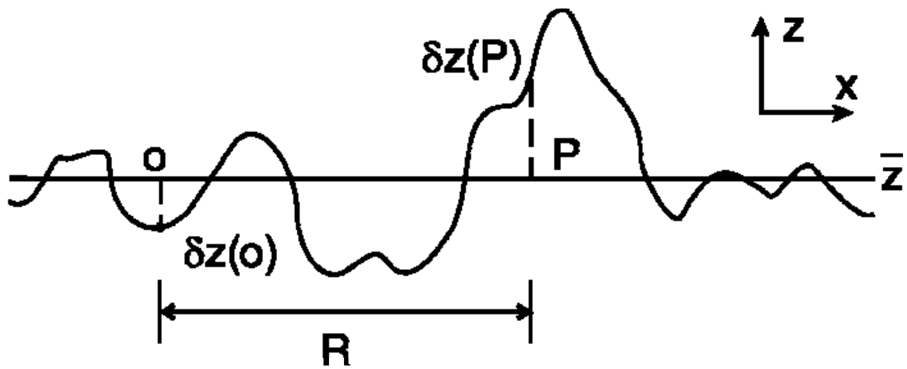
# X-Ray Reflectivity: Water Surface

Difference Experiment-Theory: *Roughness !!*

Braslau et al.
PRL <u>*54*</u>, 114 (1985)



# Rough interfaces (statistical description)




- Surface profile

$$z(\vec{r}_{\|}) = \bar{z} + \delta z(\vec{r}_{\|})$$

- Height-height correlation function for a homogeneous, isotropic and ergodic surface

$$C(R) = \langle \delta z(0)\delta z(R) \rangle$$

- FT[C(R)] measured in a surface scattering experiment

# The „Master Formula“

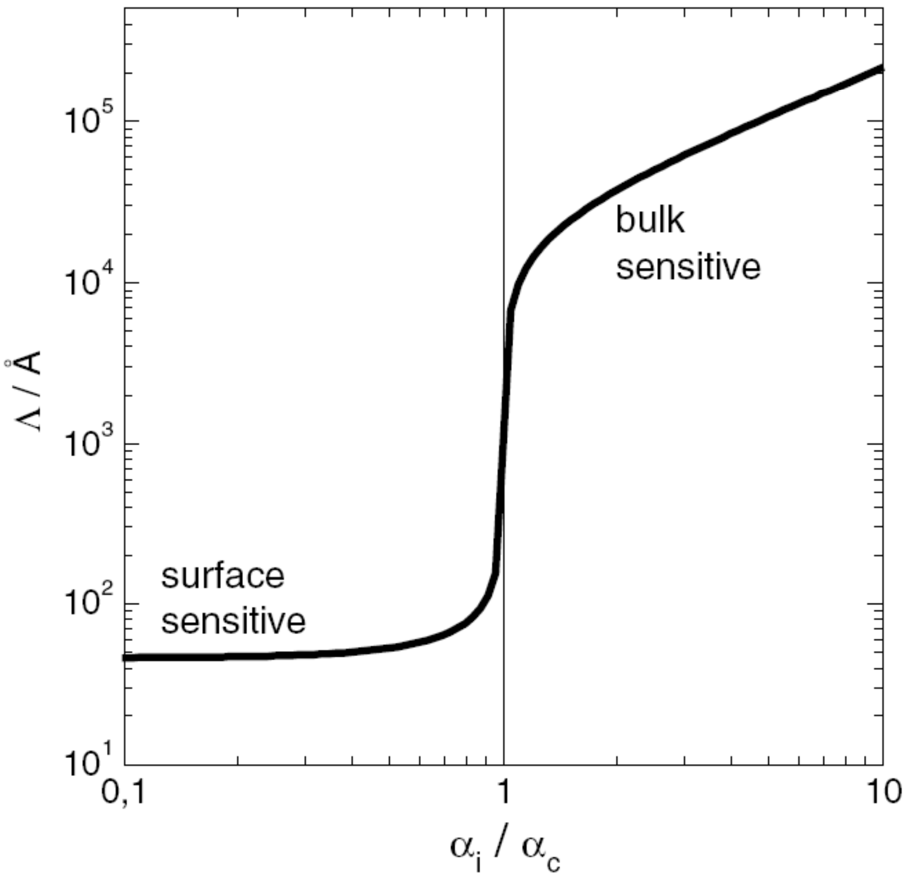
## Reformulation for Interfaces

$$R(q_z) = R_{\mathrm{F}}(q_z) \left| \frac{1}{\varrho_\infty} \int \frac{\mathrm{d}\varrho(z)}{\mathrm{d}z} \exp(\mathrm{i}\, q_z z)\, \mathrm{d}z \right|^2$$

Fresnel-Reflectivity of the Substrate

Electron Density Profile

# Penetration depth:



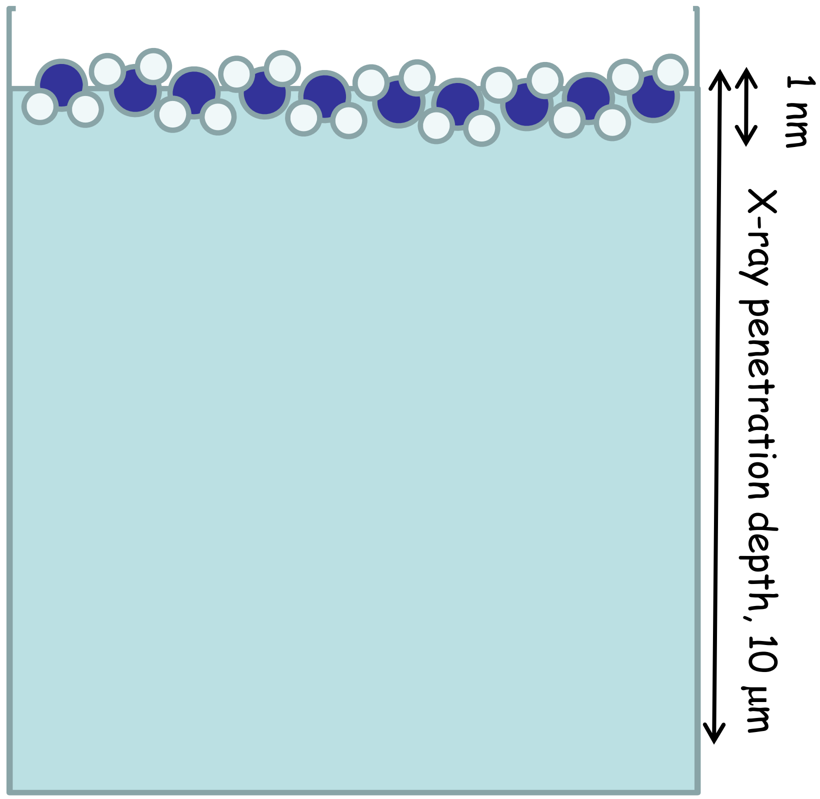

Below critical angle
(grazing incidence geometry):
Enhanced surface sensitivity

Penetration depth for $q<q_c$

$$\Lambda \approx 1/q_c \sim 15 - 100\mathring{A}$$

Problems w/ Grazing incidence:
Multiple scattering effects
(Born approximation breaks
down)

# Puzzle of Surface Scattering

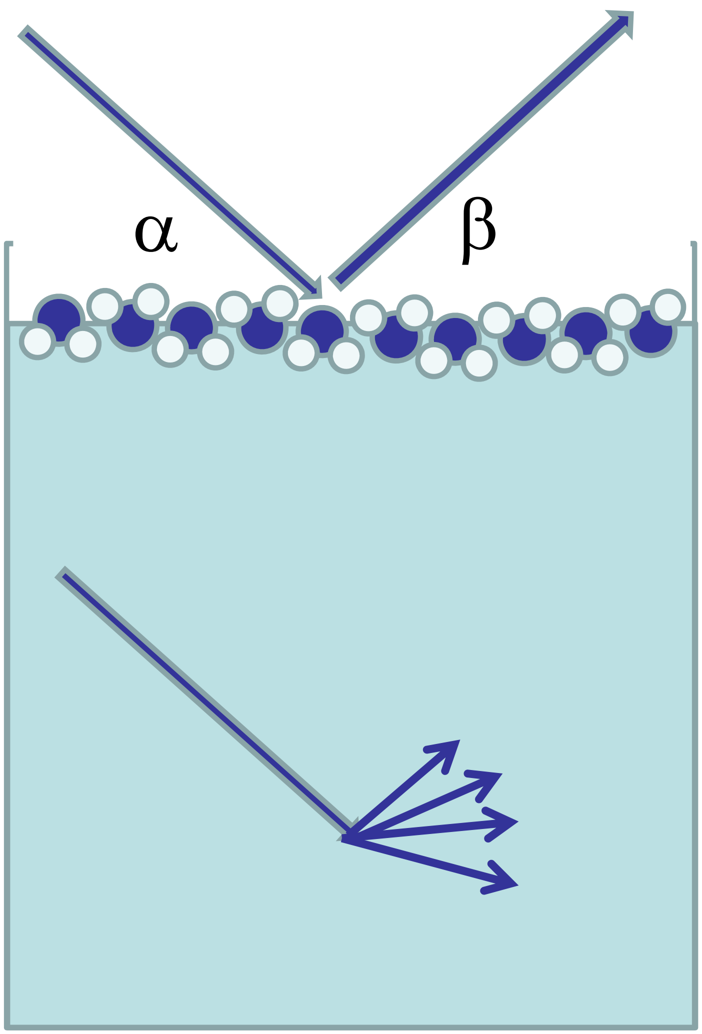



Above $q_c$ x-rays penetrate the liquid over depths ~ many microns, or many thousands of molecules per unit area.

Can we learn about atomic structure of nanoscale-deep near-surface region while ignoring "bulk"?

Yes, with the help of Specular Reflectivity !

# Puzzle of Surface Scattering

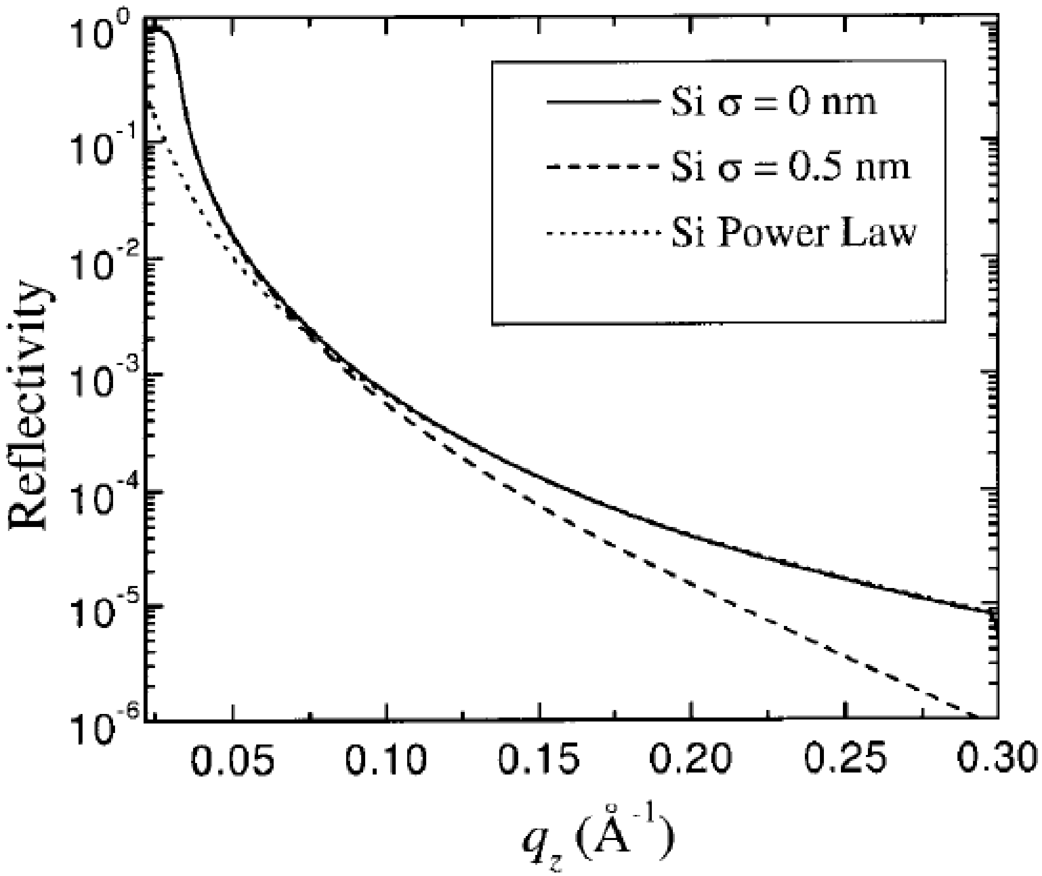



Specular reflection $\alpha=\beta$,
solid angle of acceptance ~$10^{-6}$ sterad.
(can be even smaller, in principle)

Bulk scattering –
spread over entire $4\pi$
Also: can be easily subtracted
(off-specular and on-specular)

# Reflectivity Curve Example

$$R_F(q_z) = \left| \frac{q_z - \sqrt{{q_z}^2 - {q_c}^2}}{q_z + \sqrt{{q_z}^2 - {q_c}^2}} \right|^2 \sim \left( \frac{q_c}{2q_z} \right)^4$$

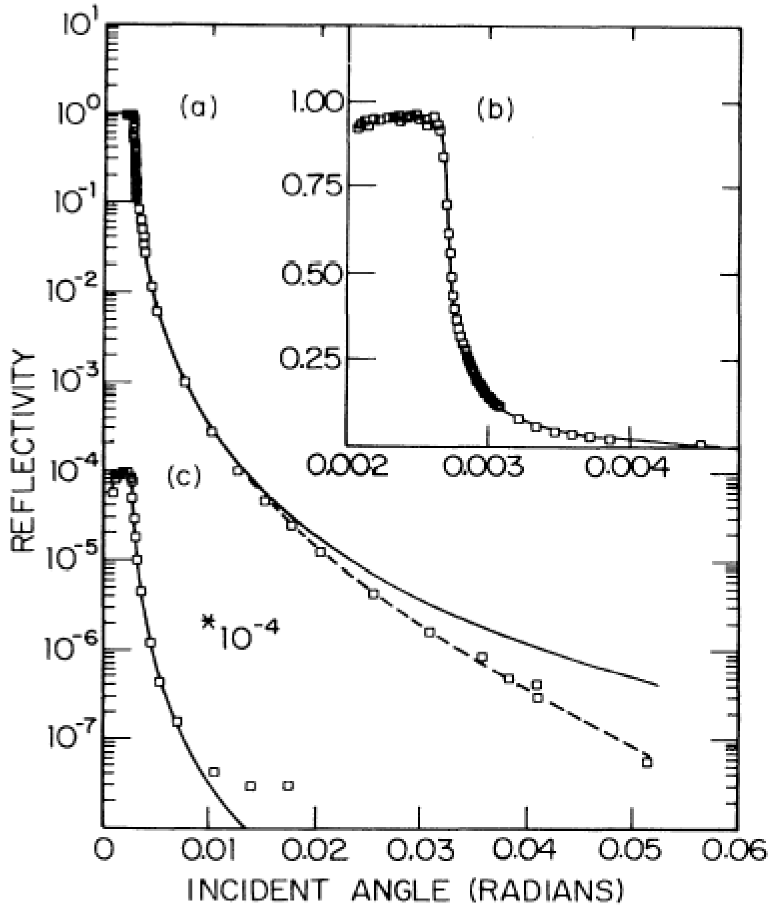


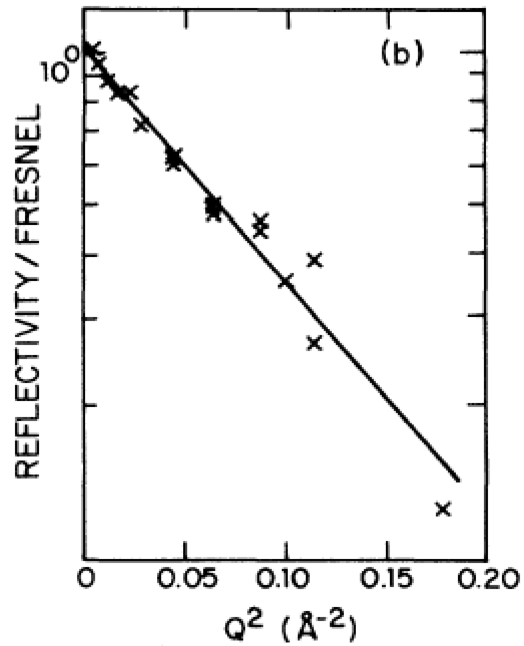

Roughness lowers reflectivity
Scales as $\exp(-\sigma^2 q^2)$

Similar to Debye-Waller factor

Q: Where does the signal "go"?
A: Diffuse scattering

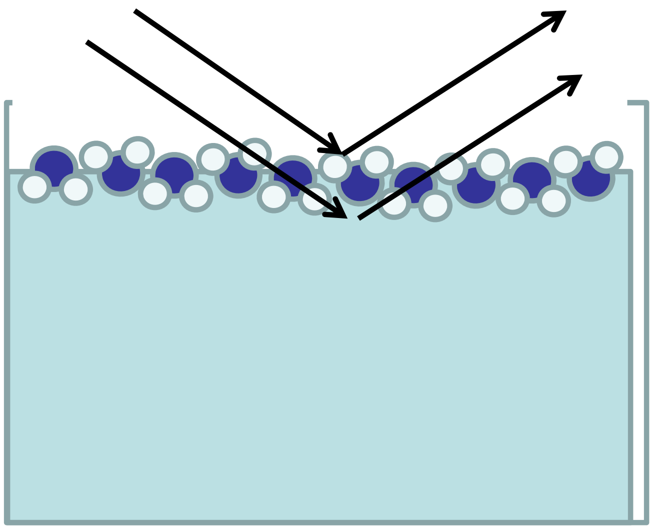
# First Reflectivity measurements from simple liquid (water)

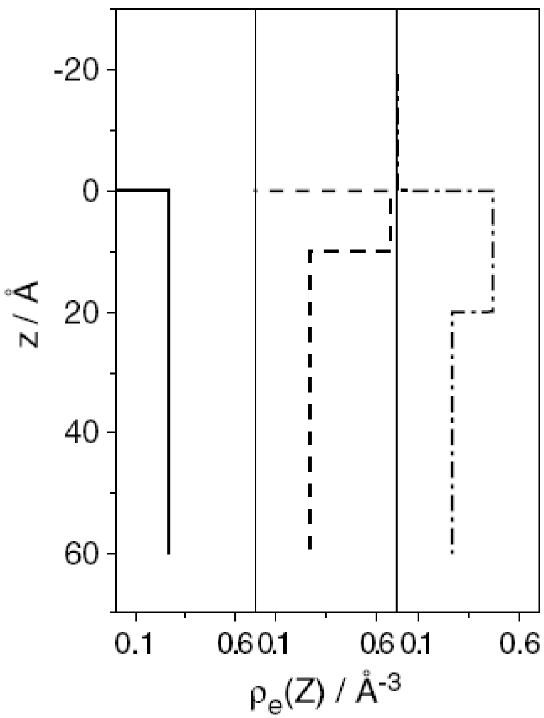


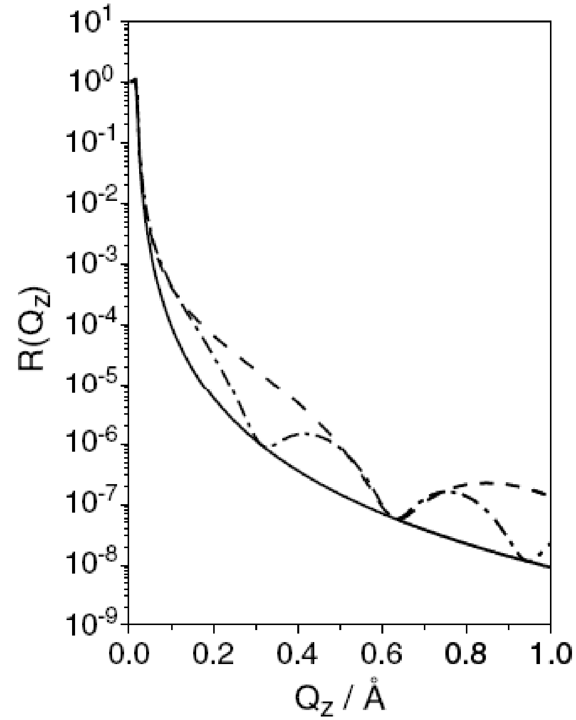




A. Braslau et al., Phys. Rev. Lett. 54, 114 (1985)

# High-angle Specular Reflectivity:



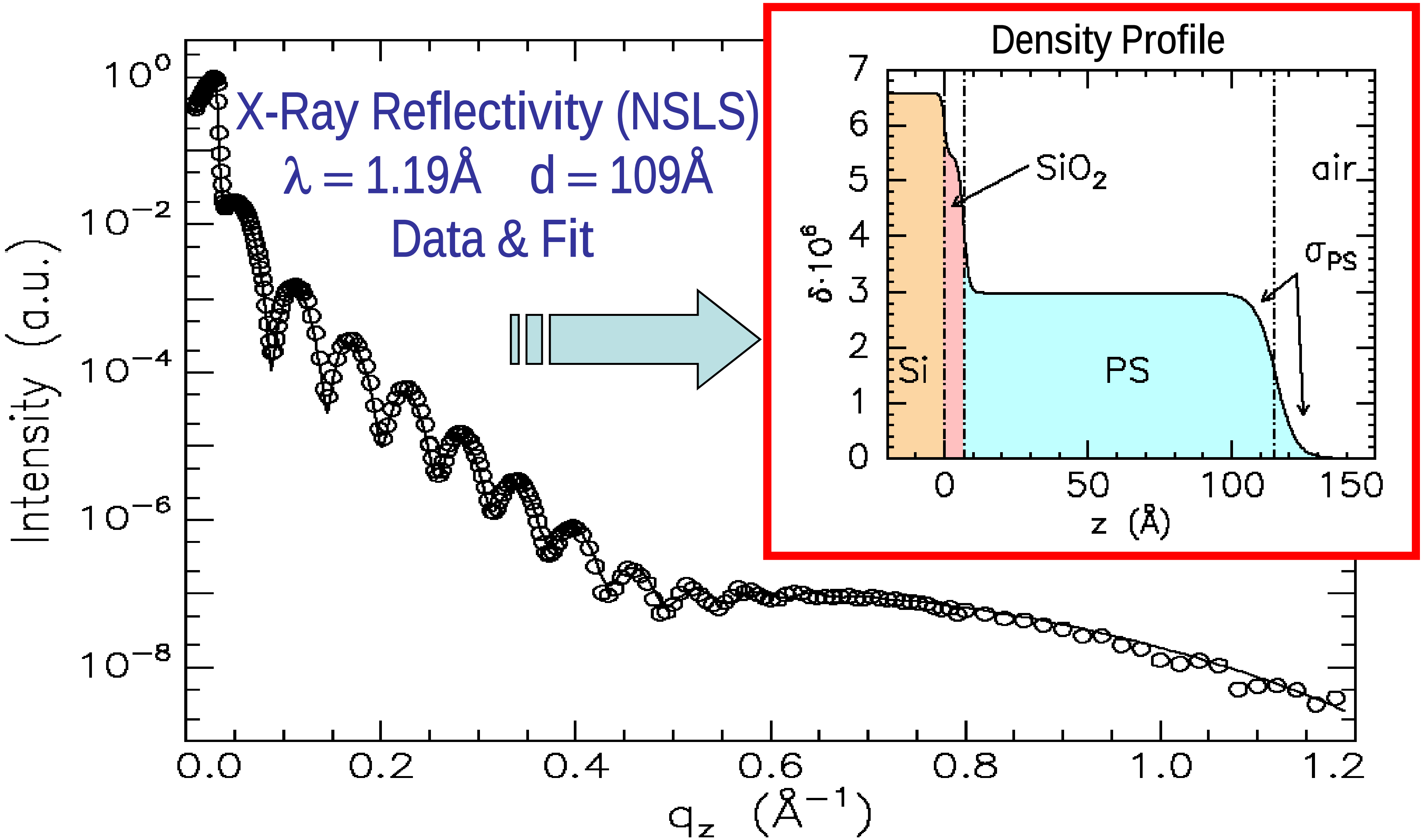



Interference from structure of size *a* with first maximum at $q_z = \pi/a$ & minimum at $q_z = 2\pi/a$

General rule of scattering: to resolve features with size X one needs to measure out to $Q \sim \pi/X$ (at least!)

# Example: PS Film on Si/$SiO_2$



# The need for synchrotrons in liquid surface scattering:

Reflectivity falls off as R ~ $\left(\frac{q_c}{2q_z}\right)^4$

To measure structure with atomic (a ~ 2Å) resolution need to measure reflectivity out to $q_z = 2\pi/a \sim 3$Å$^{-1}$

For typical $q_c \sim 0.03$Å$^{-1}$ this implies reflectivity signal R ~ $10^{-8}$

Including capillary roughness effects can often result in R < $10^{-10}$

This demands for sources with $10^{10}$ ph/sec

# Reflectivity from "Non-Ideal" Interfaces

Two main complications:

1. Structure
2. Dynamics

*Real-life* liquid surfaces are <u>not</u> structureless & <u>not</u> static!

Reflectivity deviates from Fresnel by structure factor $\Phi(q_z)$ and the capillary wave term CW (q, T, $\gamma$)

$$R(q_z) = \underbrace{R_F(q_z)}_{\text{Fresnel (ideal surface)}} \cdot \underbrace{\left|\Phi(q_z)\right|^2}_{\text{structure}} \cdot \underbrace{CW(q,T,\gamma)}_{\text{Dynamics (capillary wave term)}}$$

# Surface Structure Factor:

$$\Phi(q_z) = \frac{1}{\rho_\infty} \int \mathrm{d}z \frac{\mathrm{d}\langle \rho(z) \rangle}{\mathrm{d}z} \exp(\imath q_z z)$$

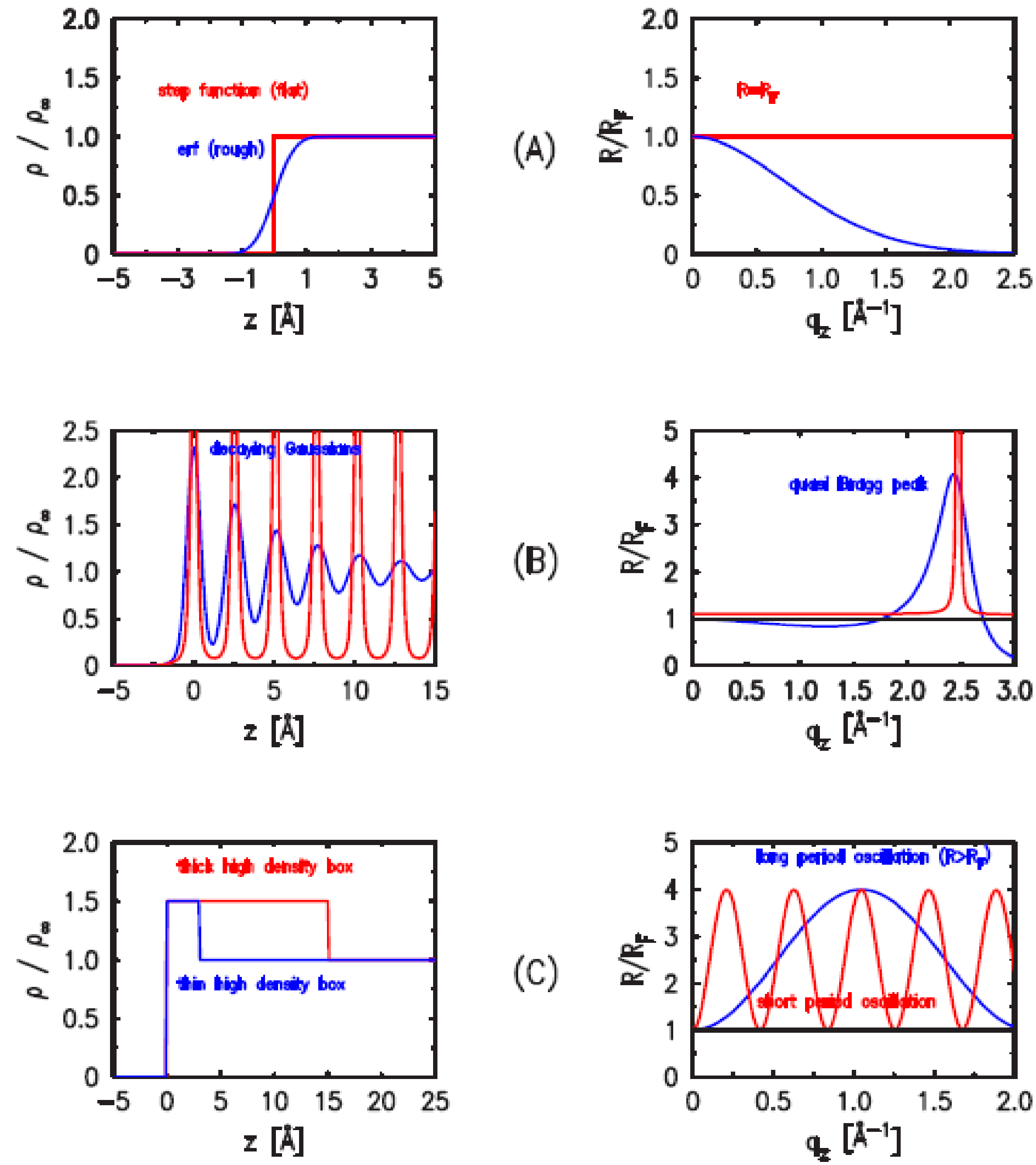
If one measures Surface Structure Factor $\Phi(q_z)$, one can in principle model density profile $\rho(z)$ – inverse solution is difficult due to phase problem.

But first we have to separate dynamics of Capillary Wave contributions (CW) from structure factor $\Phi(q_z)$

$$\underbrace{R(q_z)}_{\substack{\text{measured} \\ \text{(reflectivity)}}} = \underbrace{R_F(q_z)}_{\text{known}} \cdot \left| \underbrace{\Phi(q_z)}_{\substack{\text{want to know} \\ \text{(related to density)}}} \right|^2 \cdot CW(\underbrace{q}_{\substack{\text{measured by diffuse} \\ \text{scattering}}}, T, \gamma)$$

# Real Space    Reciprocal Space

$$\frac{\langle \rho(z) \rangle}{\rho(\infty)}$$




$$\left| \Phi(q_z) \right|$$

# Capillary Waves

Reminder:

gravity waves
(long-wavelengths)

capillary waves
(short-wavelengths)

Crossover at lengthscale $\xi \sim \sqrt{\dfrac{\gamma}{\rho g}}$ (or ~ 3 mm for water)

# Thermally Excited Capillary Waves

Balance between thermal excitation modes ($k_B T$) and the restoring force of surface tension

More dimensional analysis:

Surface tension $\gamma$ [Energy/$L^2$]
vs. Thermal Energy $k_B T$ [Energy]

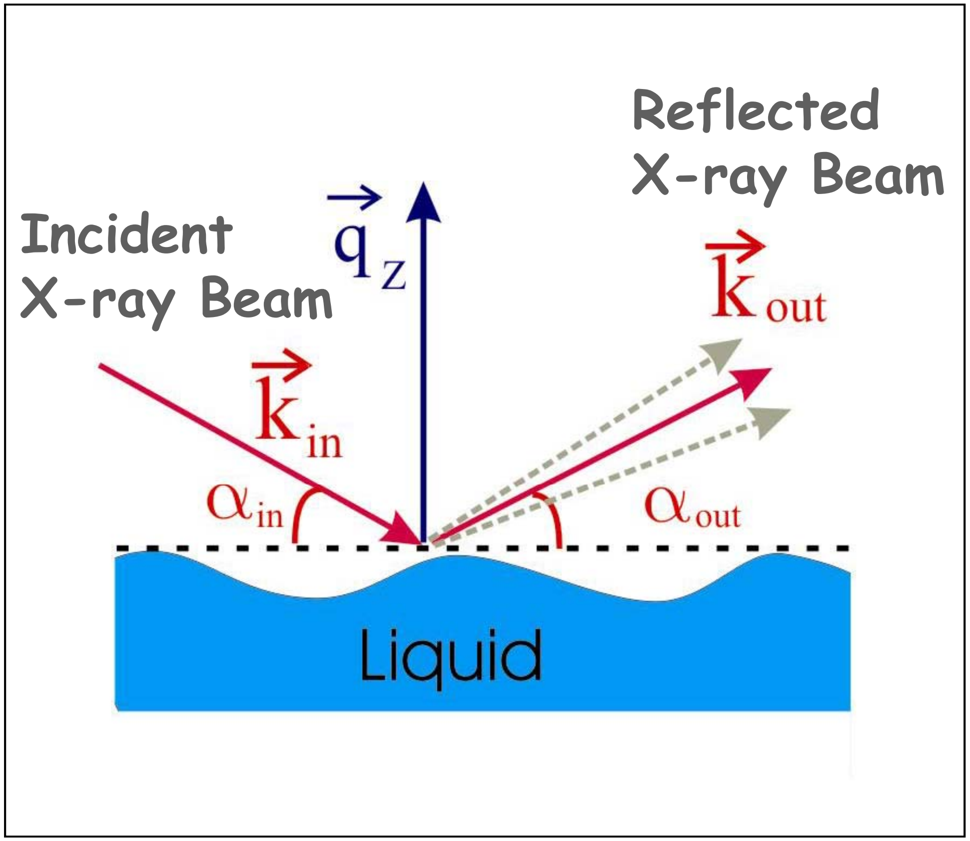
Characteristic length scale (roughness): $\sigma \sim \sqrt{\dfrac{k_B T}{\gamma}}$

For water at room T this roughness estimate is ~ 2.4 Å

Actual (correct) expression includes resolution effects:

$$\sigma_{\mathrm{cw}}^2 = \frac{k_B T}{2\pi\gamma} \ln\left(\frac{k_{\max}}{k_{\min}}\right)$$

# X-ray Reflectivity: a probe of near-surface structure on atomic scale



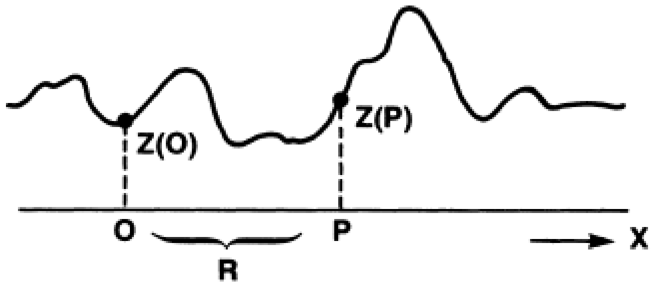

**Reflectivity from solid surfaces:**
Surface profiles are static:

Low thermal diffuse scattering surrounding strong truncation rods/Bragg peaks

**Reflectivity from liquid surfaces:**
Thermal capillary fluctuations: height-height correlation function diverges logarithmically, roughness scales as ~ $T/\gamma$

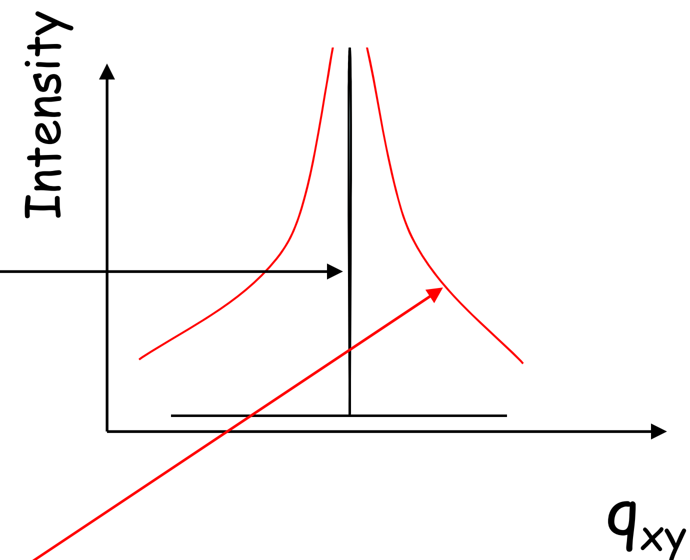
Capillary fluctuations contribute to significant diffuse scattering

# Scattering from rough surfaces: height-height correlation function




$$\langle [z(x',y') - z(x,y)]^2 \rangle = g(R)$$

$$R \equiv (x'-x, y'-y)$$




**Smooth surfaces (atomically flat solids):**

$$\mathrm{g(R)} = 0 \text{ and } \frac{d\sigma}{d\Omega} \approx \frac{1}{q_z^4}\delta(q_x)\delta(q_y)$$

**Liquid Surfaces:** height-height correlations diverge logarithmically

$g(R) \sim k_B T/\gamma \;\; \ln(R)$

$$\frac{d\sigma}{d\Omega} \approx \frac{1}{q_z^4}\frac{1}{q_{xy}^{2-\eta}}$$

where $\eta = \dfrac{k_B T}{2\pi\gamma} q_z^2$

**Sinha et al., Phys. Rev. B 38, 2297 (1988)** "capillary exponent"

# SIDE NOTE:

$$g(R) \sim k_B T/\gamma \ \ln(R)$$

Logarithmic divergence of correlations due to thermal fluctuations is more general in condensed matter physics:
Same underlying reason for lack of 2D crystals
Mermin-Wagner Theorem

$$\langle \sigma_\alpha(r)\sigma_\alpha(0)\rangle = \frac{1}{\beta J}\int^{1/a} \frac{d^d k}{(2\pi)^d}\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{k^2}$$

The integral diverges as ln(r) for $d \leqslant 2$
Thermal fluctuations destroy long range order in 1D, 2D
N.D. Mermin and H. Wagner PRL 17, 1133 (1966)

Also see (Berezinskii-)Kosterlitz-Thouless theory and 2D dislocation-mediated melting by Nelson and Halperin,

Examples: ripples in graphene, 2D atomic gas lattices, Xe on graphite, etc.

# Scattering from liquid surfaces

Scattering cross-section:

$$\frac{d\sigma}{d\Omega} = \frac{A_0}{\sin^2\alpha}\left(\frac{q_c}{2}\right)^4 \frac{1}{8\pi q_z^2}\left|\Phi(q_z)\right|^2\left(\frac{1}{q_{\max}}\right)^{\eta}\frac{\eta}{q_{xy}^{2-\eta}}$$

Experimentally measured reflectivity:

$$R(q_z) = R_F(q_z)\left|\Phi(q_z)\right|^2 \int_{res}\left(\frac{1}{q_{\max}}\right)^{\eta}\frac{\eta}{q_{xy}^{2-\eta}}\,dq_x dq_y$$

Fresnel Reflectivity

$$R(q_z) \sim \left(\frac{q_c}{2q_z}\right)^4$$

Surface Structure Factor

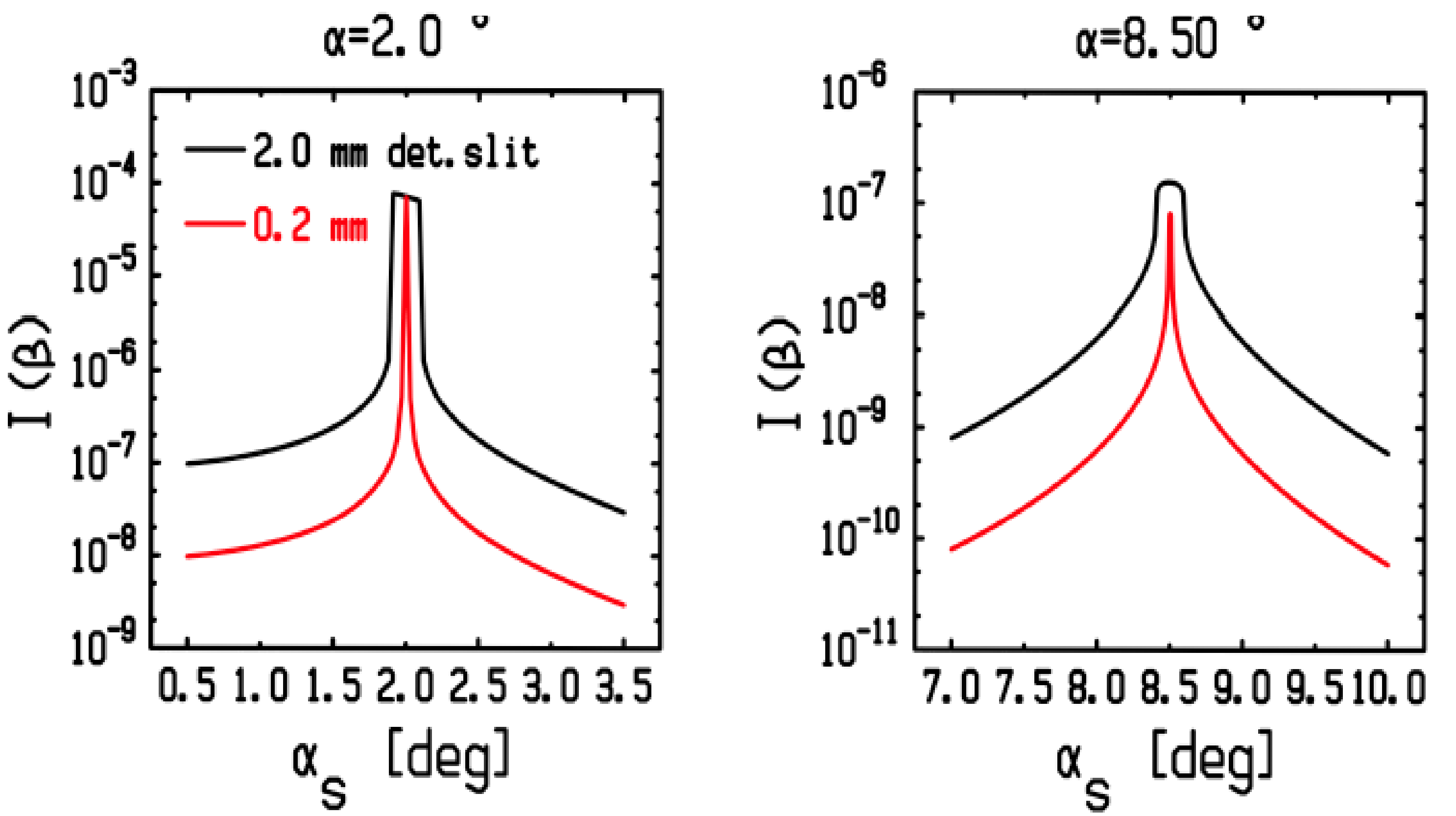
$$\Phi(q_z) = \frac{1}{\rho_\infty}\int dz \frac{\langle d\rho(z)\rangle}{dz}\exp(\imath q_z z)$$

Capillary exitations * Resolution function

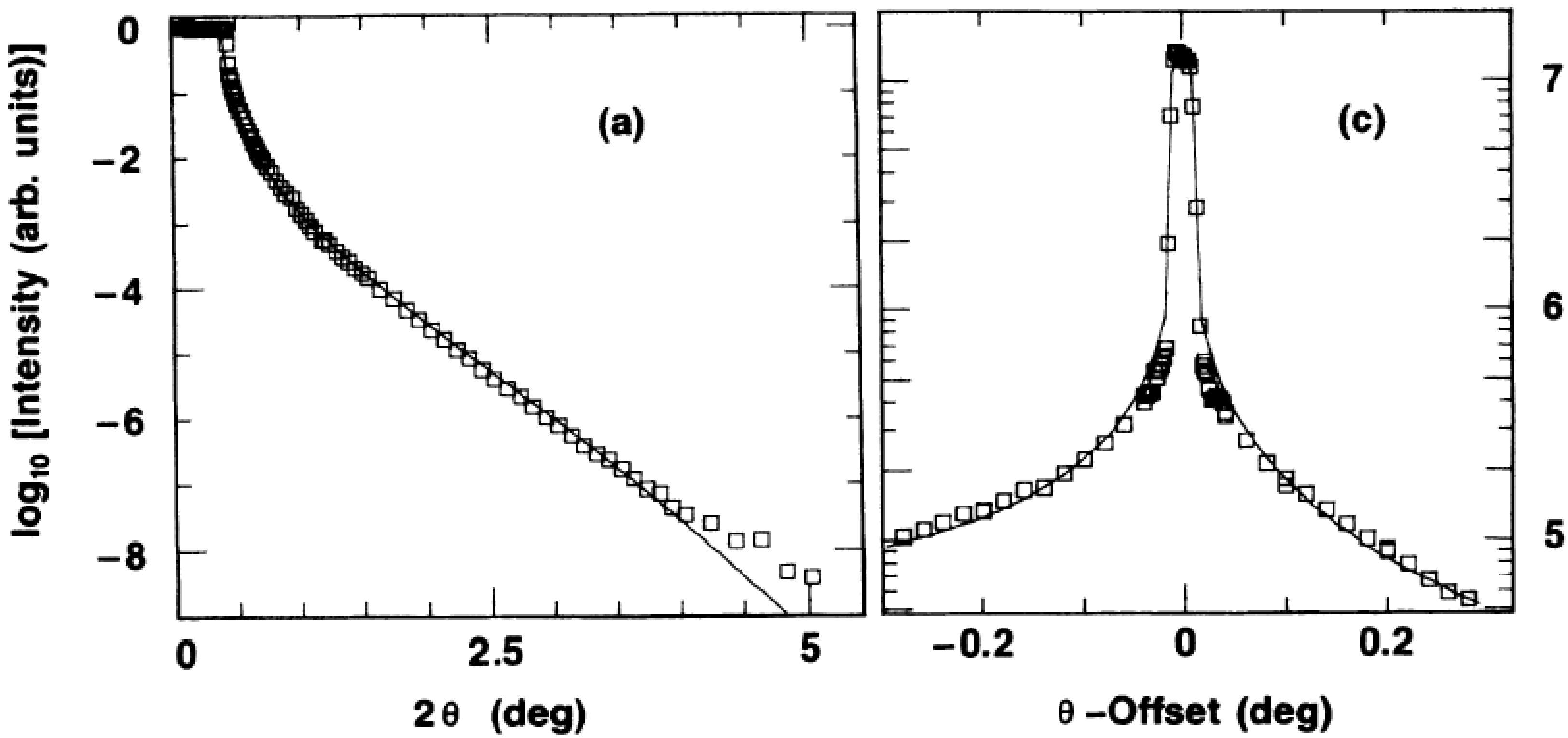
# Know Thy Experimental Resolution!

(Crucially important for diffuse scattering - less so for reflectivity)

Simulated Detector Scan

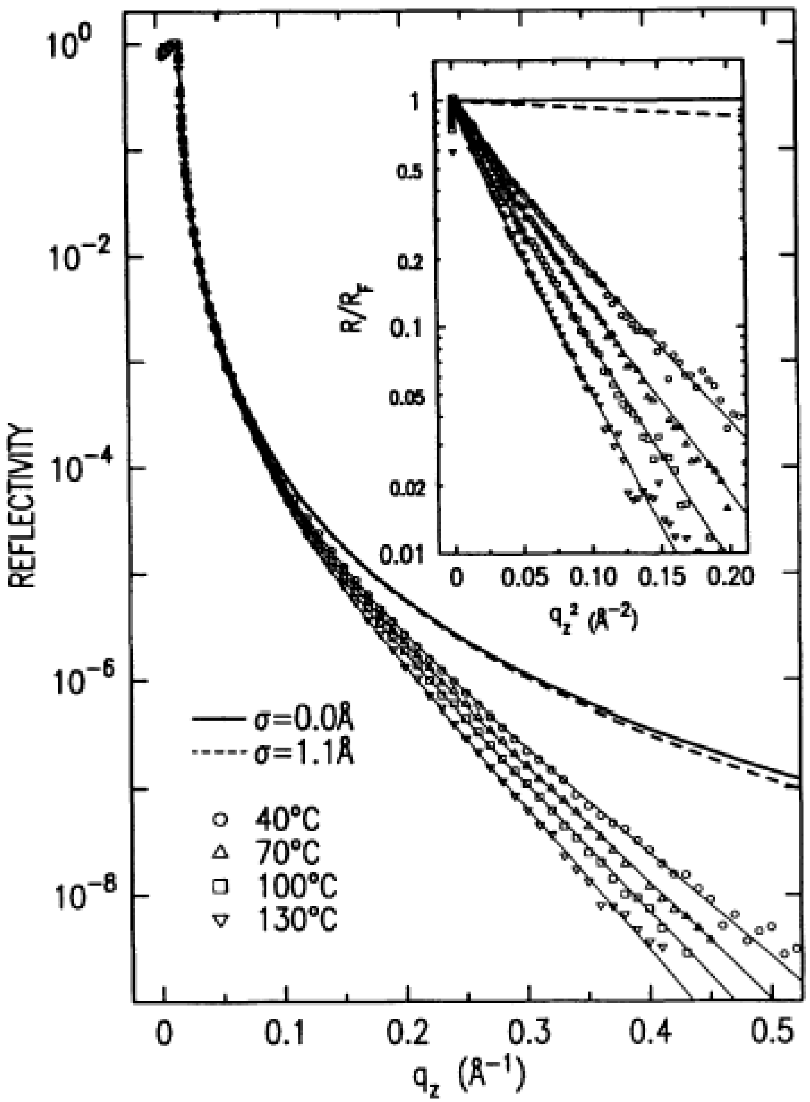


# First measurements of diffuse scattering for water




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

# Temperature dependent capillary wave roughness

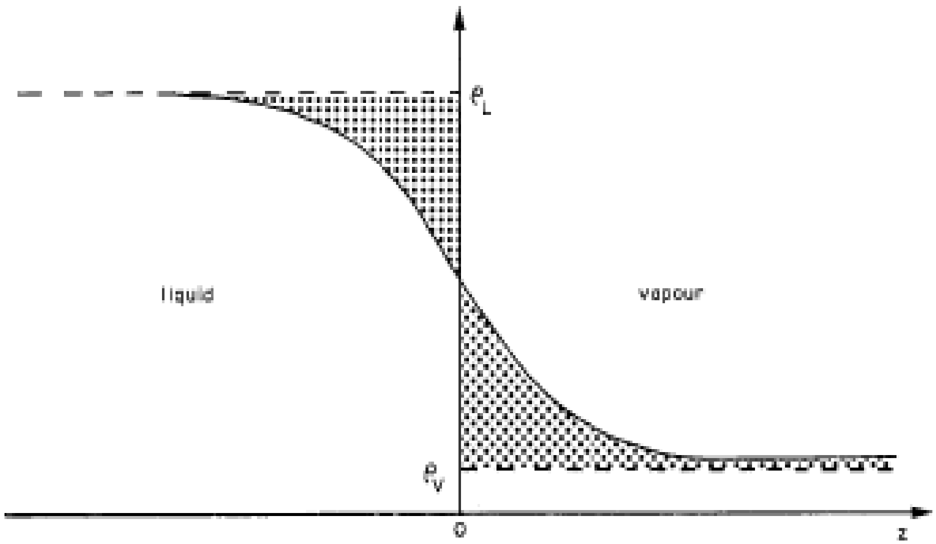


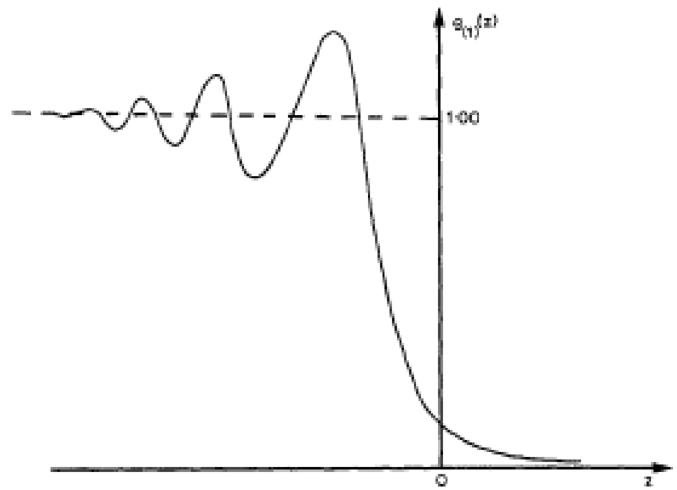

Thermal roughness of C20 alkanes follows thermal scaling predicted by capillary wave theory

$$\sigma^2 = \sigma_0^2 + \sigma_{\mathrm{cw}}^2 = \sigma_0^2 + \frac{k_b T}{2\pi\gamma_{\mathrm{cw}}} \ln\left(\frac{q_{\mathrm{max}}}{q_{\mathrm{min}}}\right)$$

B. Ocko et al., Phys. Rev. Lett. 72, 242 (1994)

# Liquid-Vapor Density profile



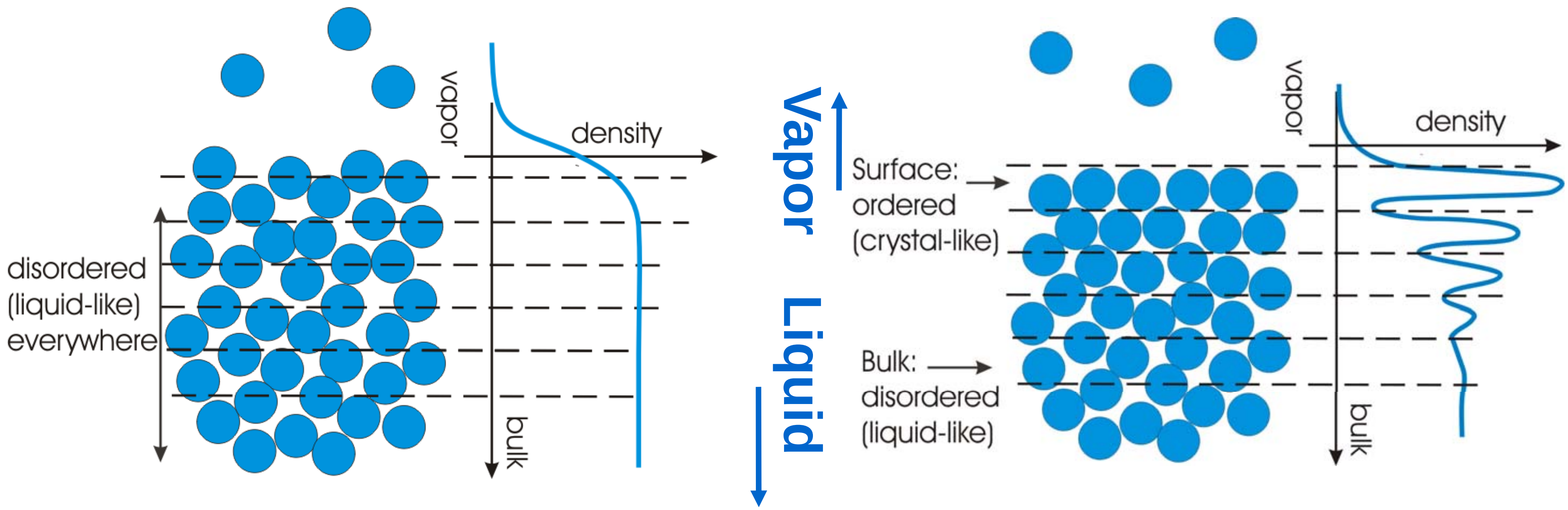




Schematic form of the transition profile for certain liquid metals exhibiting stable density oscillations.

Difference between non-layered and layered liquid-vapor profile
(C. A. Croxton, Adv. Phys., 1971)

"God made solids, but surfaces were the work of the devil"

-- Wolfgang Pauli



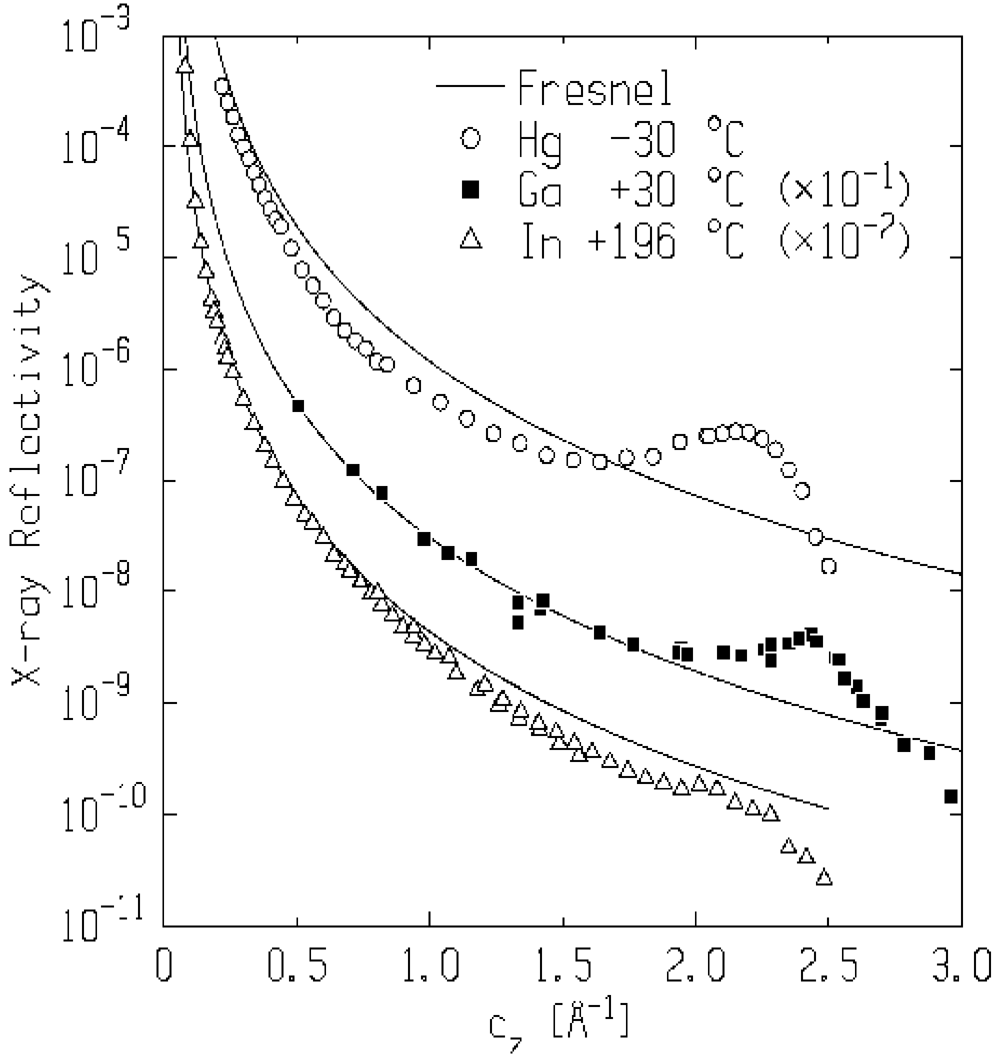

Disordered Interface
(Van-der-Vaals approach)

Surface-Induced Layering

Theory: Croxton (1971), Stuart Rice (1981+)

First Experiments: O. M. Magnussen *et al.*, Phys. Rev. Lett. **74**, 4444 (1995).
M. J. Regan *et al.*, Phys. Rev. Lett. **75**, 2498 (1995).

# Is layering in In weaker than in Ga and Hg?

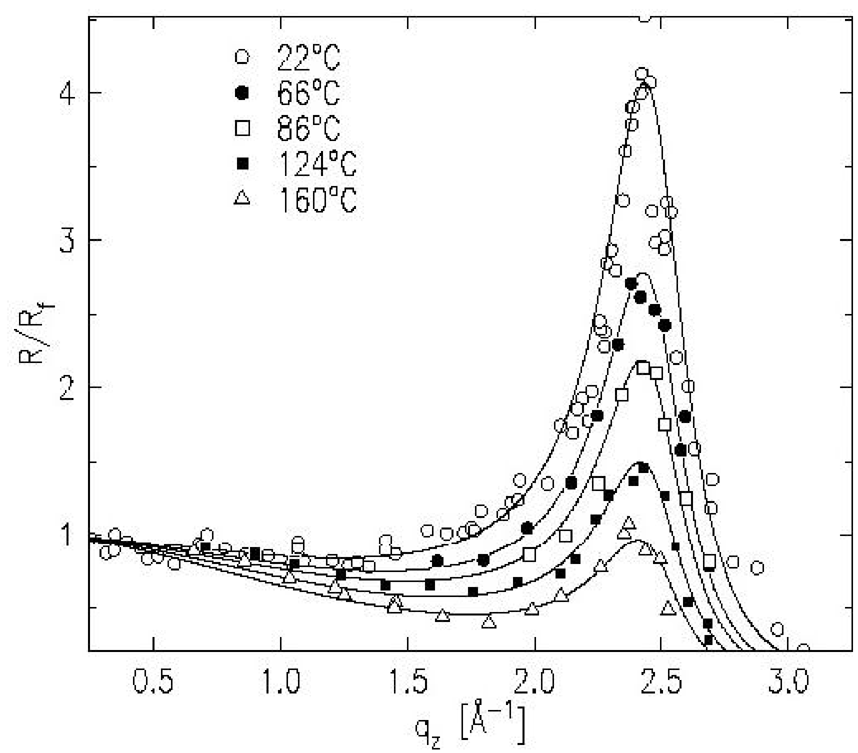



- Quasi-Bragg peak is evidence of layering
- Layering for In appears to be weaker than for Hg and Ga
- After thermal effects are removed, surface structure factor is the same for all three metals!

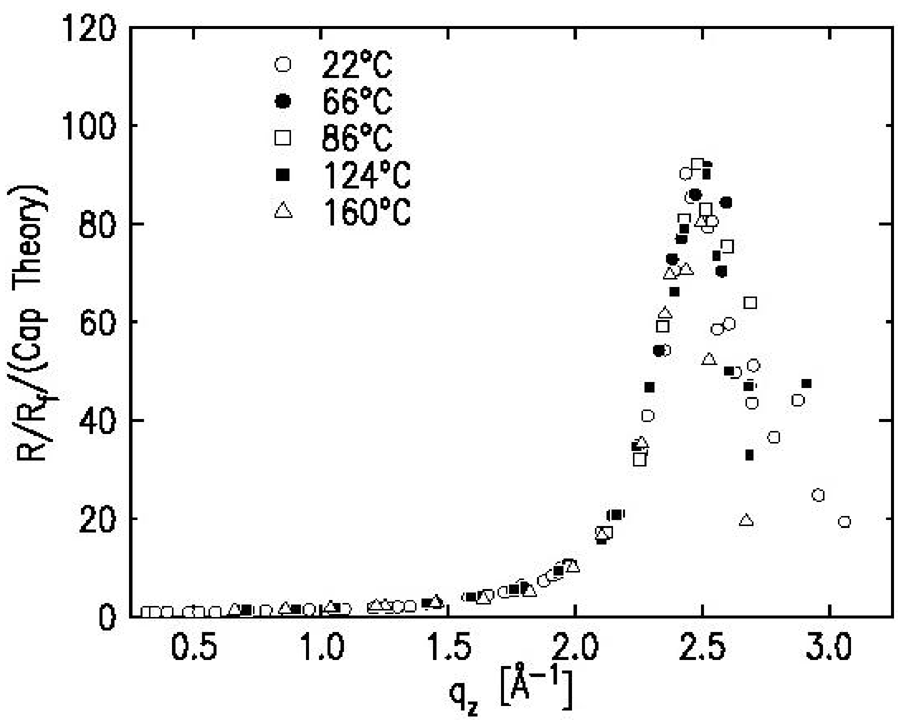
Tostmann et al., Phys. Rev. B **59**, 783 (1999)

# Capillary excitations are T-dependent, intrinsic surface structure is NOT!

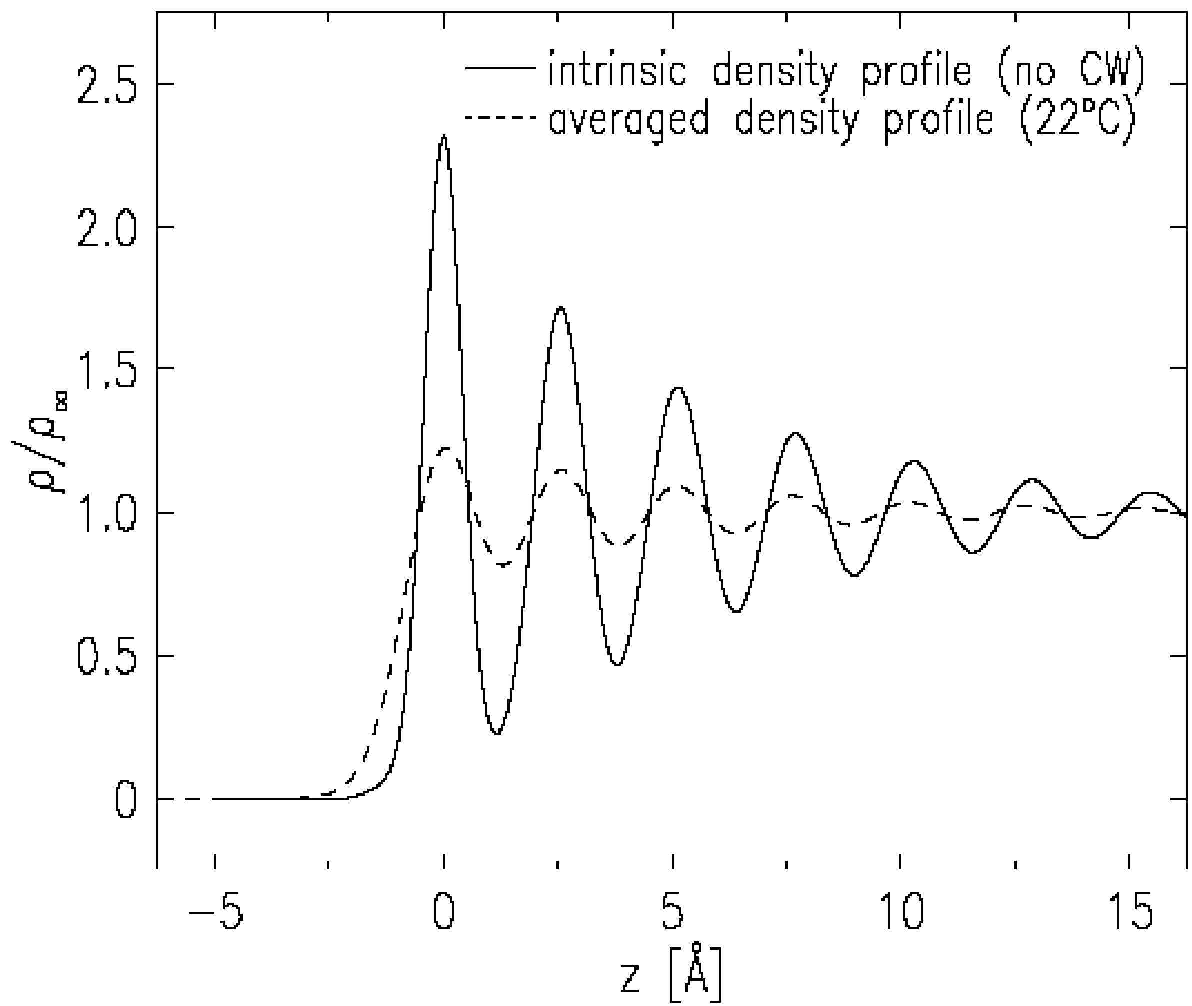
Fresnel-normalized Reflectivity (Ga):



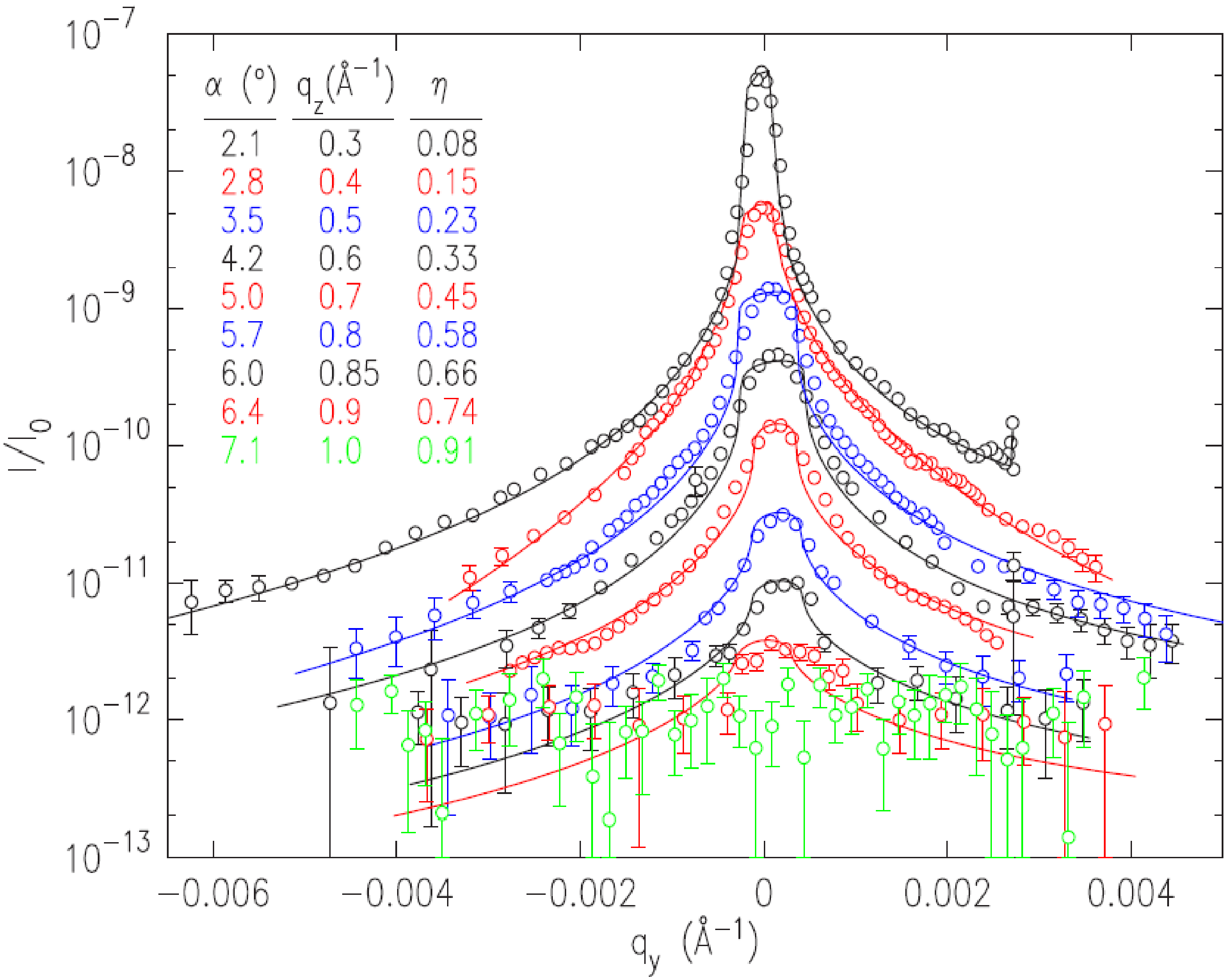

Surface-Structure Factor:
(thermal fluctuations removed)



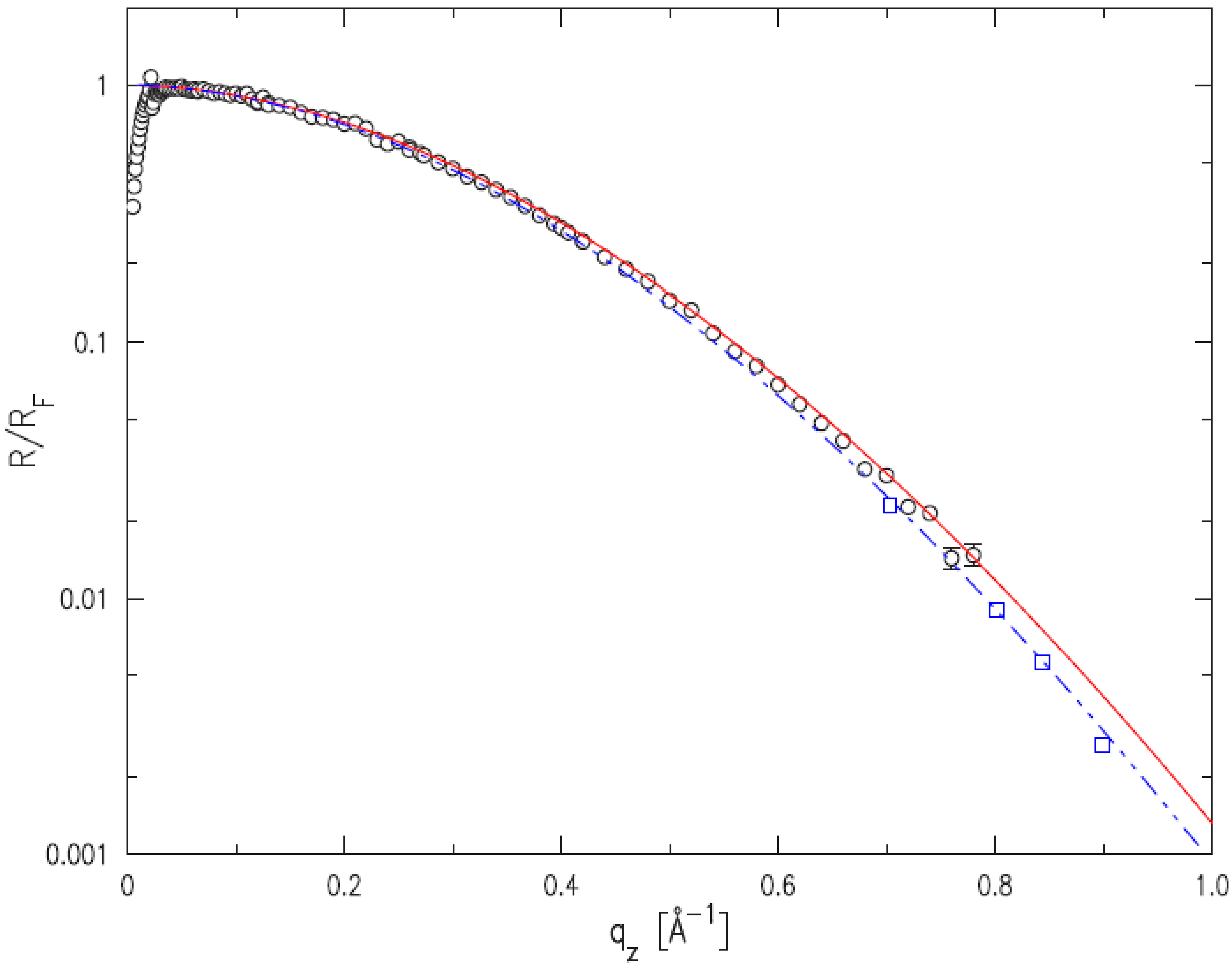
Fluctuation-averaged density profile is not a meaningful way of describing liquid surfaces



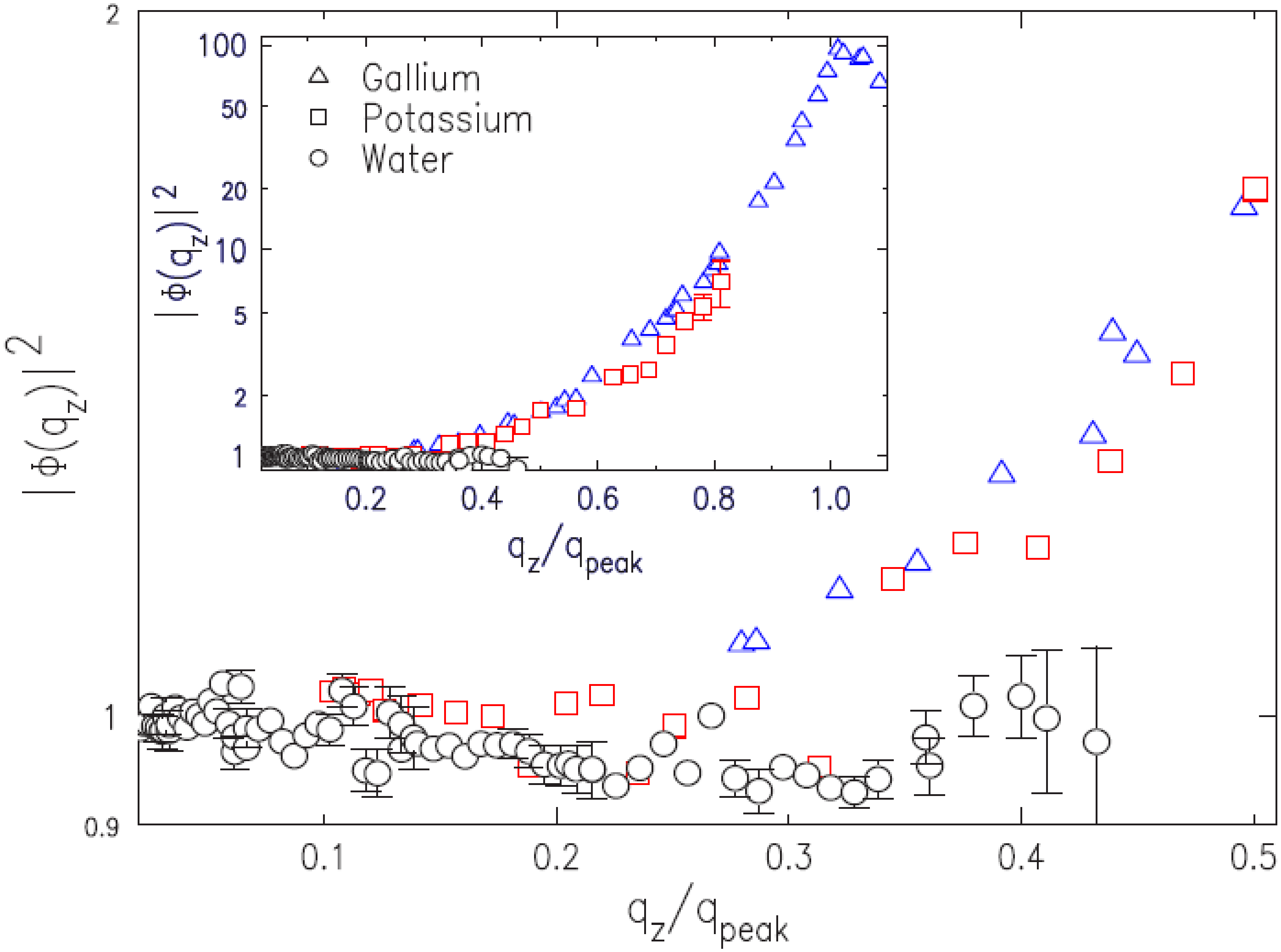
# Diffuse scattering scans for water note decreasing peak-to-wings ratio



# Fresnel-normalized reflectivity for water



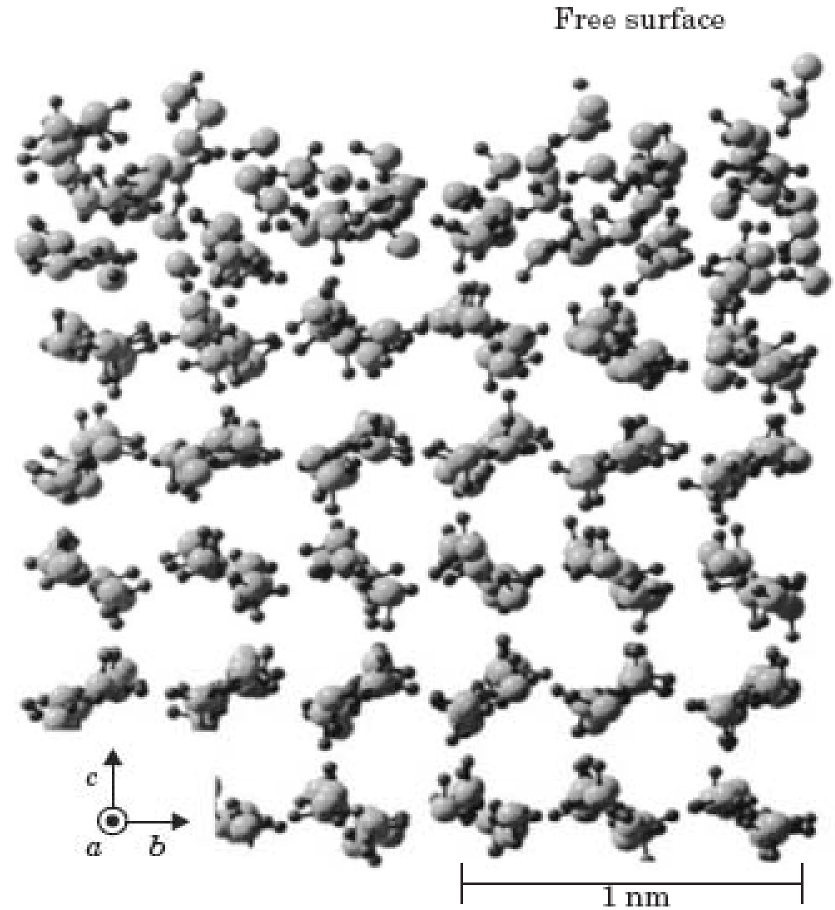
# Structure factor for water



# Surface Freezing and Surface Melting

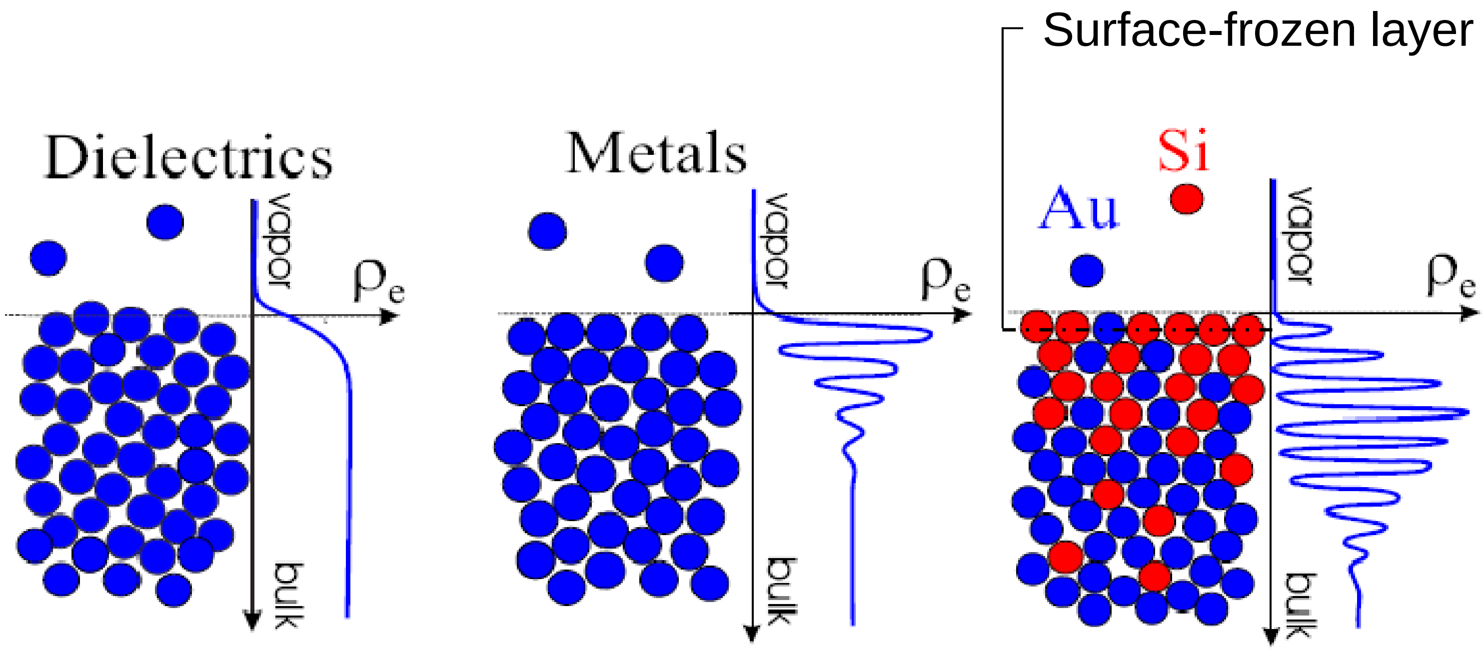
"Why is Ice Slippery?" Cover Story
Physics Today, December 2005

Can the reverse be true?
Yes, but in exotic/rare systems:
- Alkane chains
- Liquid Crystals
- Dilute alloys
- (GaPb, GaTl - S. Rice)



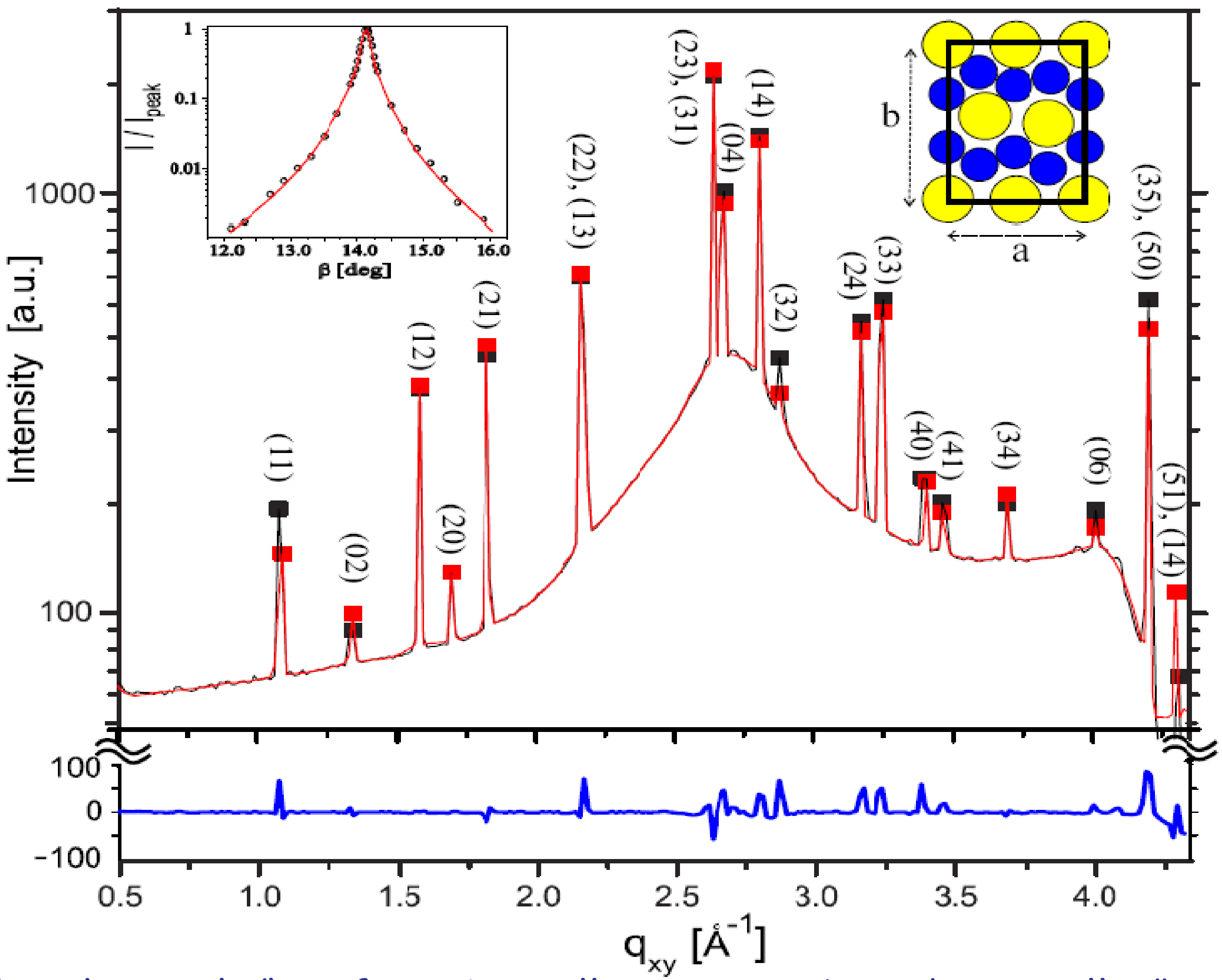

Generally not expected for non-dilute alloys, like AuSi

# Surface Freezing in AuSi

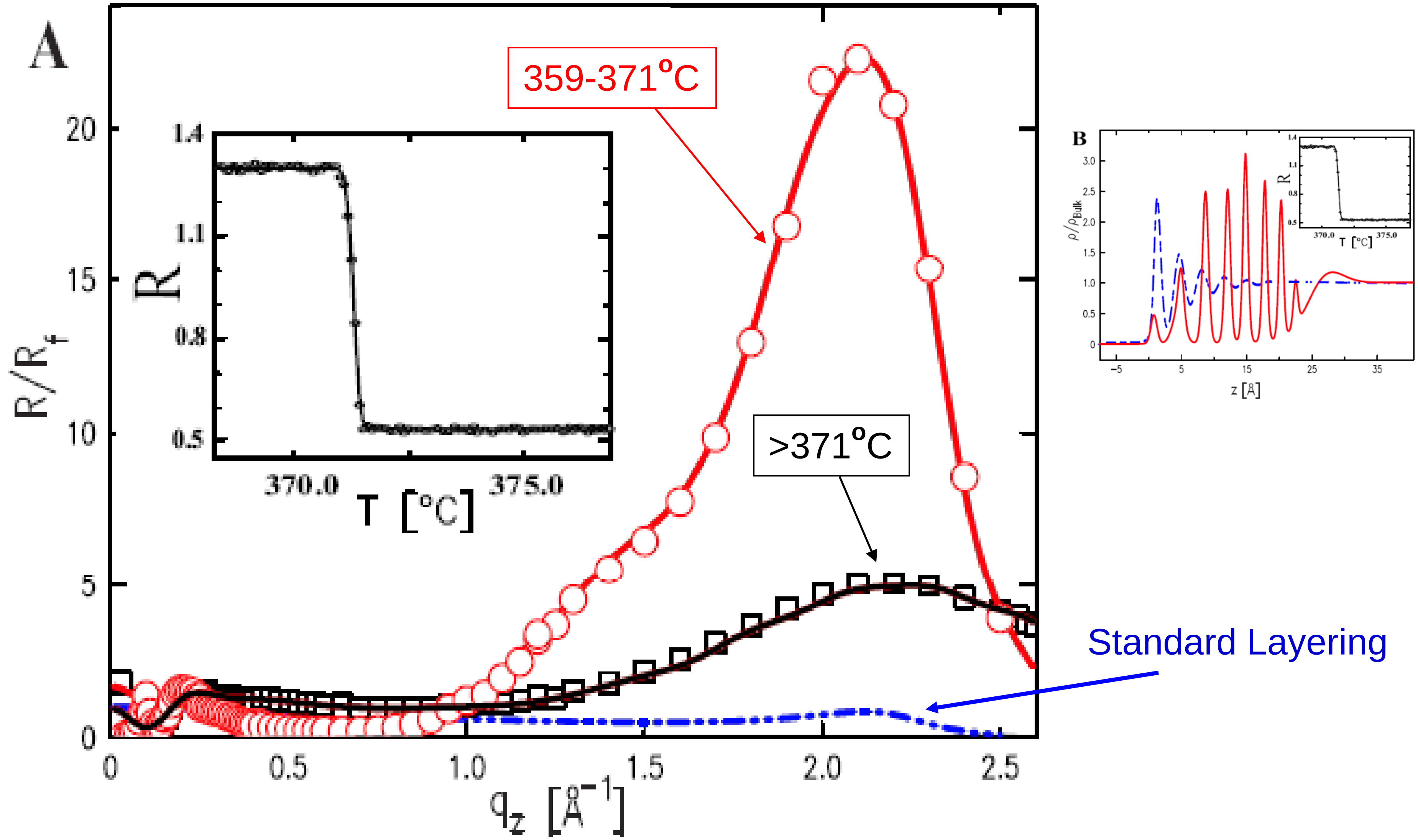



O. G. Shpyrko et al., "Surface Crystallization in a Liquid AuSi Alloy"
Science 313, 77 (2006)

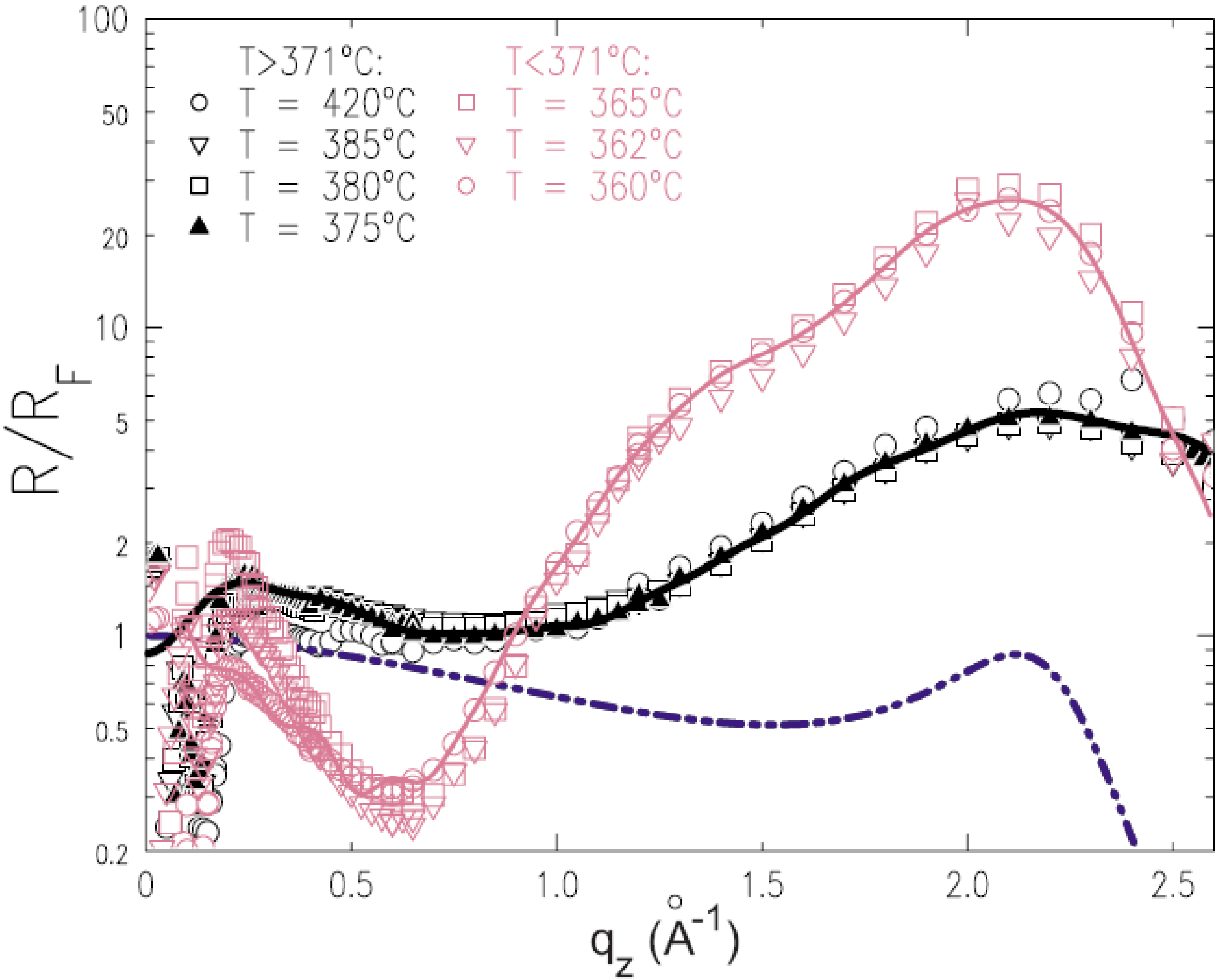
Grazing Incidence Diffraction (penetration depth ~1.4nm, 5 atomic layers)



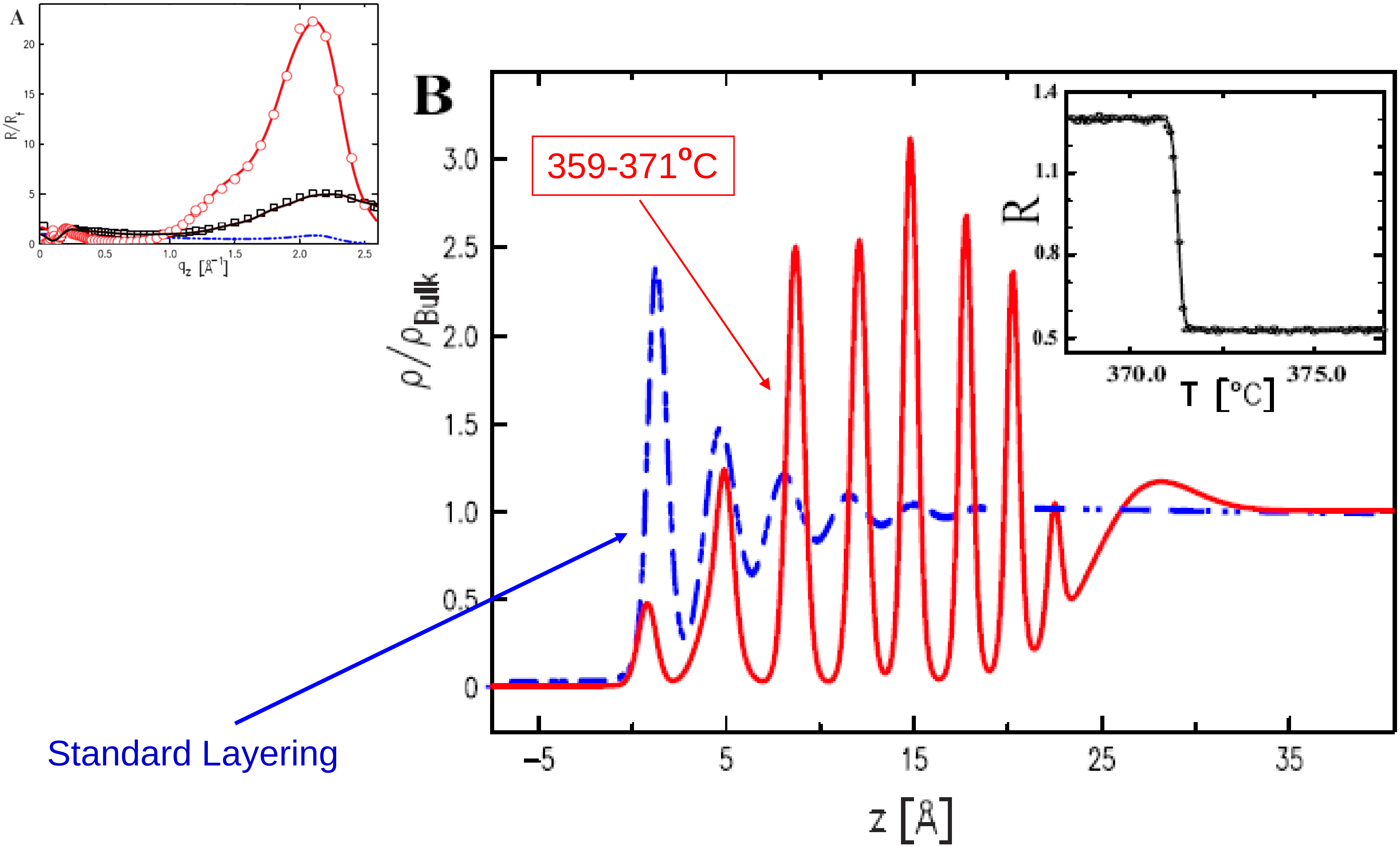

O. G. Shpyrko et al., "Surface Crystallization in a Liquid AuSi Alloy"
Science 313, 77 (2006)




O. G. Shpyrko et al., "Surface Crystallization in a Liquid AuSi Alloy"
Science 313, 77 (2006)



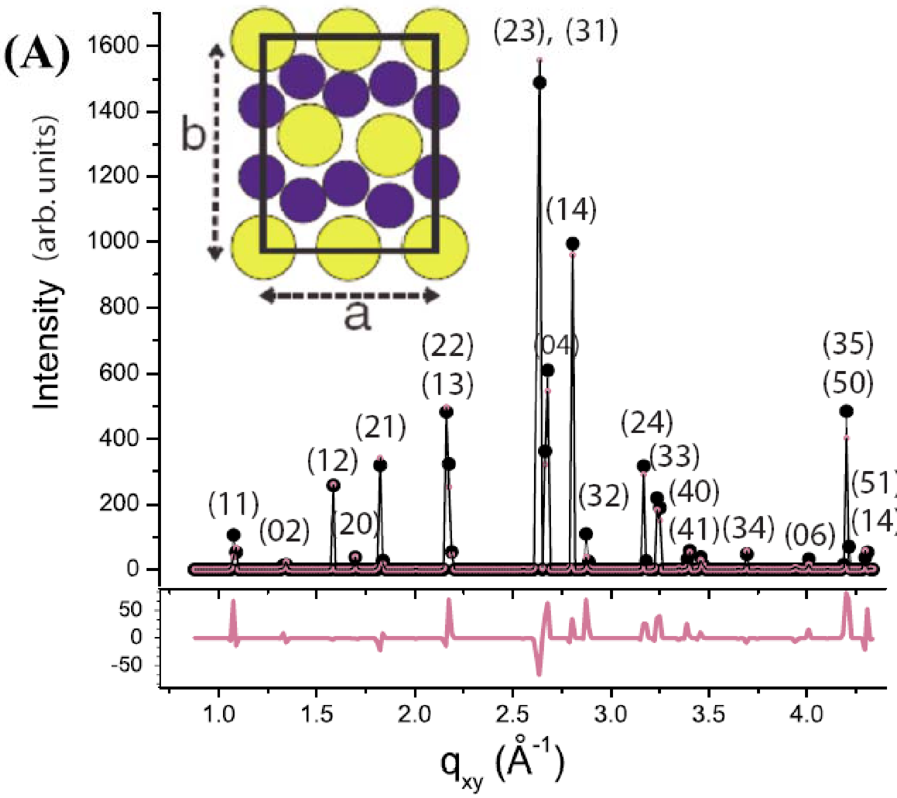

O. G. Shpyrko et al., "Crystalline surface phases of the liquid Au-Si eutectic alloy" Phys. Rev. B 76, 245436 (2007)

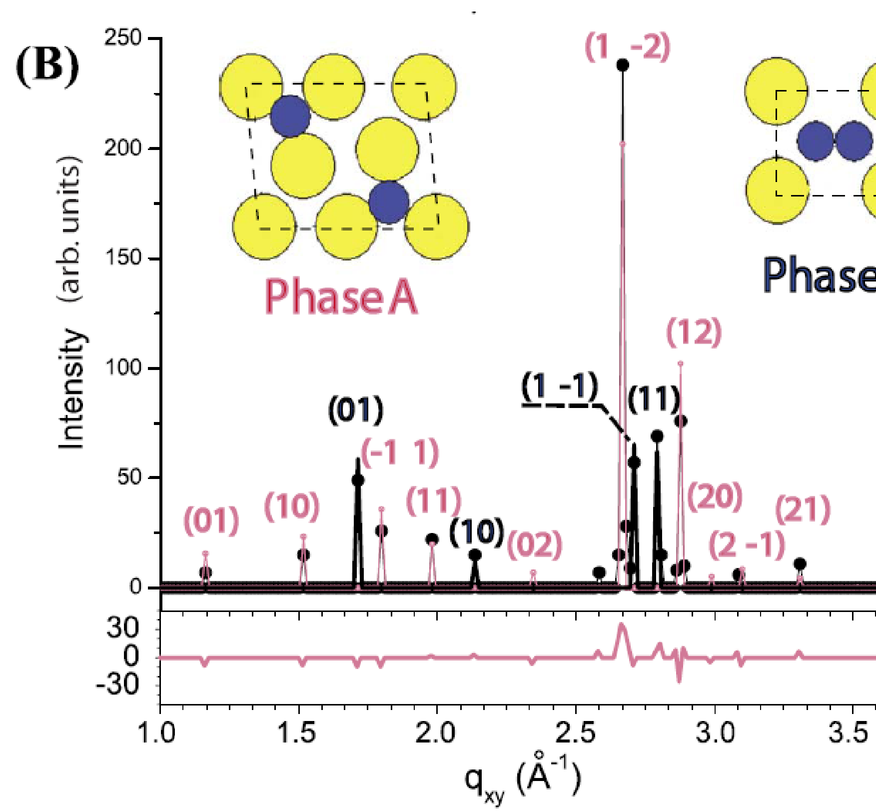



O. G. Shpyrko et al., "Surface Crystallization in a Liquid AuSi Alloy"
Science 313, 77 (2006)

Low-T Phase:
T<371 C

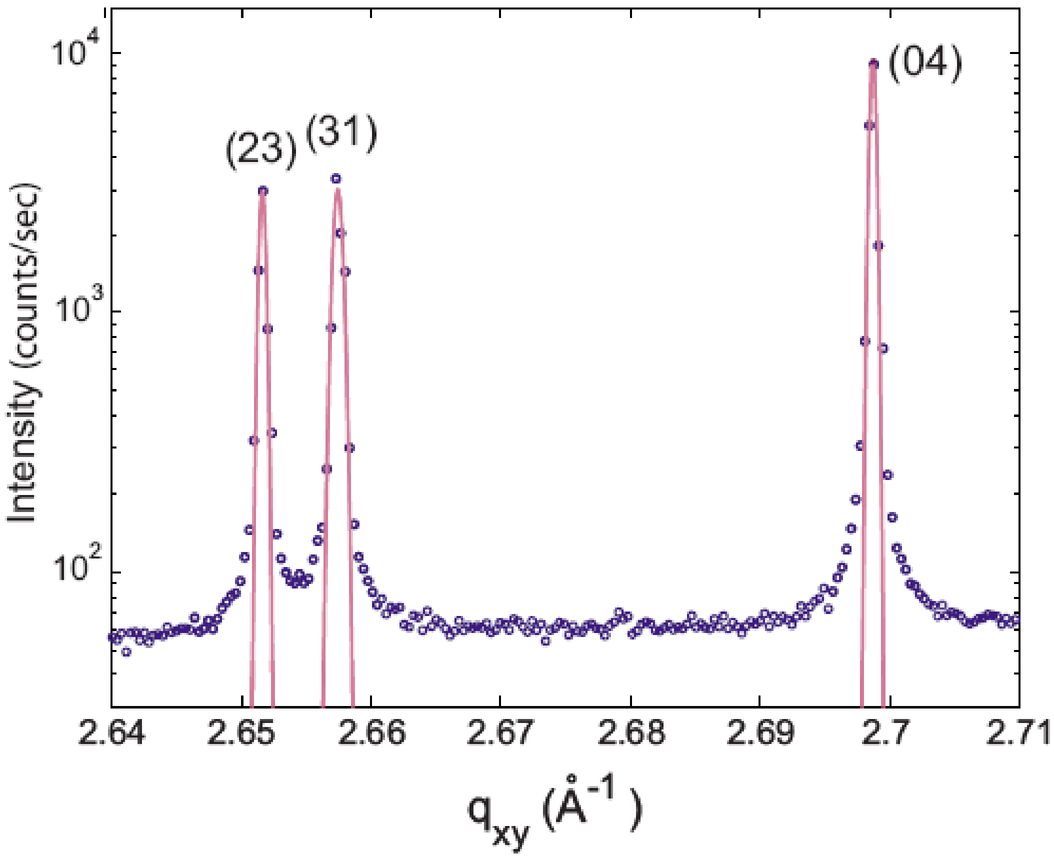
High-T Phase:
T>371 C

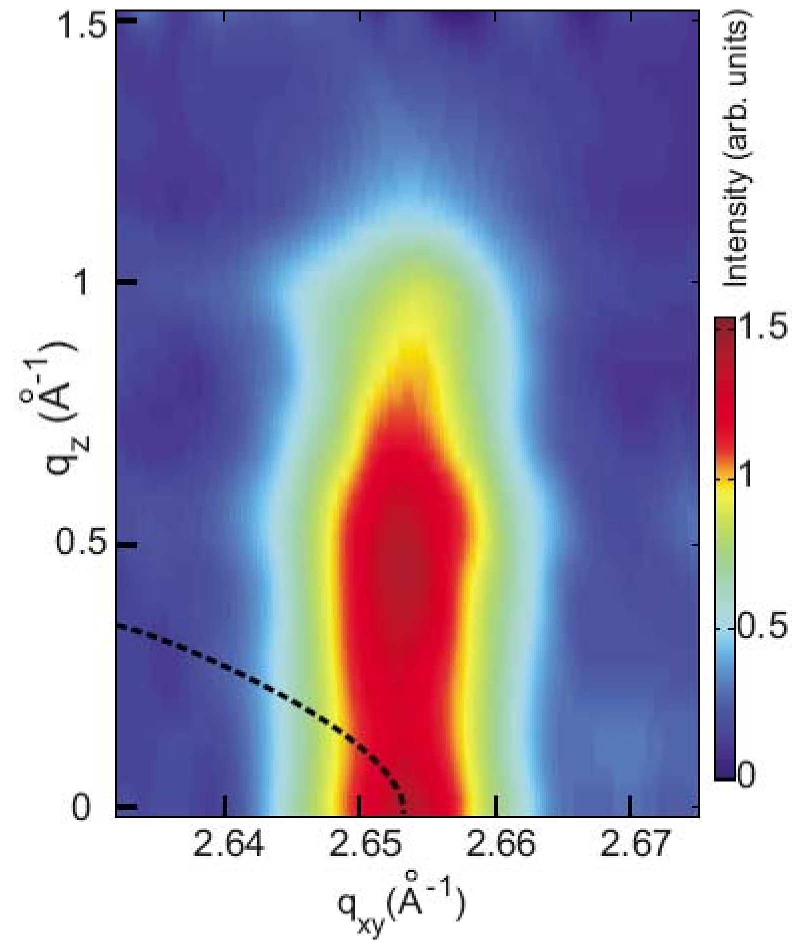



O. G. Shpyrko et al., "Surface Crystallization in a Liquid AuSi Alloy"
Science 313, 77 (2006)

O. G. Shpyrko et al., "Crystalline surface phases of the liquid Au-Si eutectic alloy"
Phys. Rev. B 76, 245436 (2007)

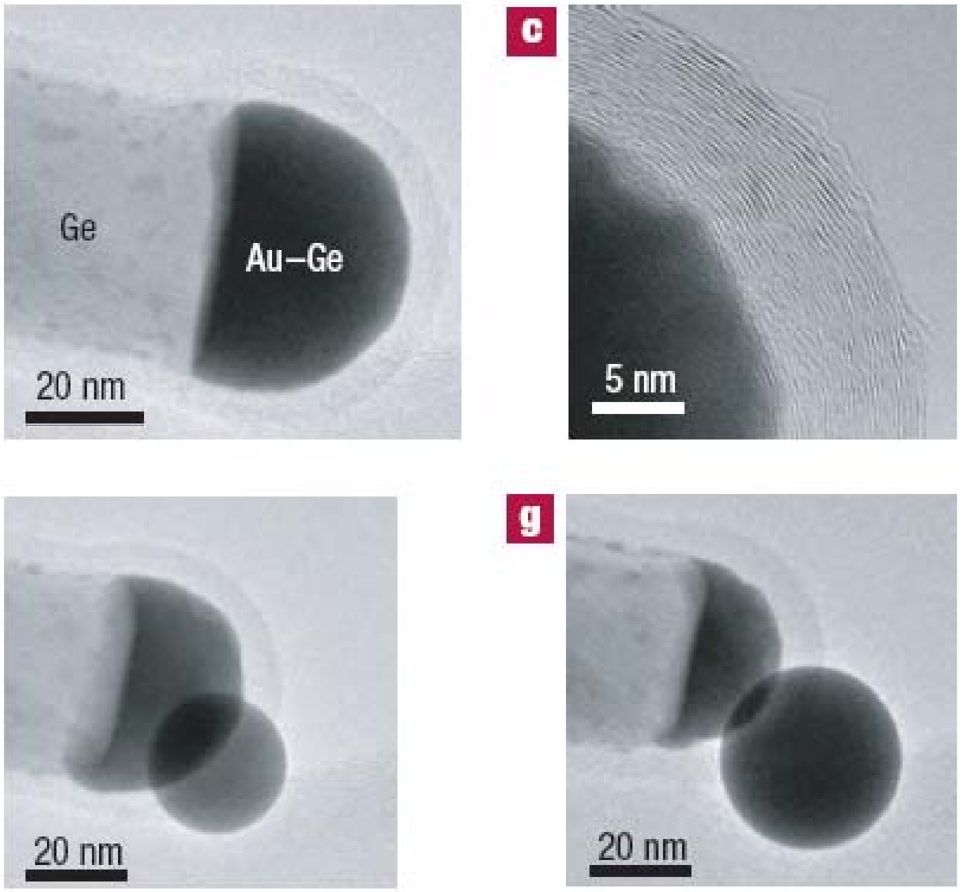



O. G. Shpyrko et al., “Surface Crystallization in a Liquid AuSi Alloy”
Science 313, 77 (2006)

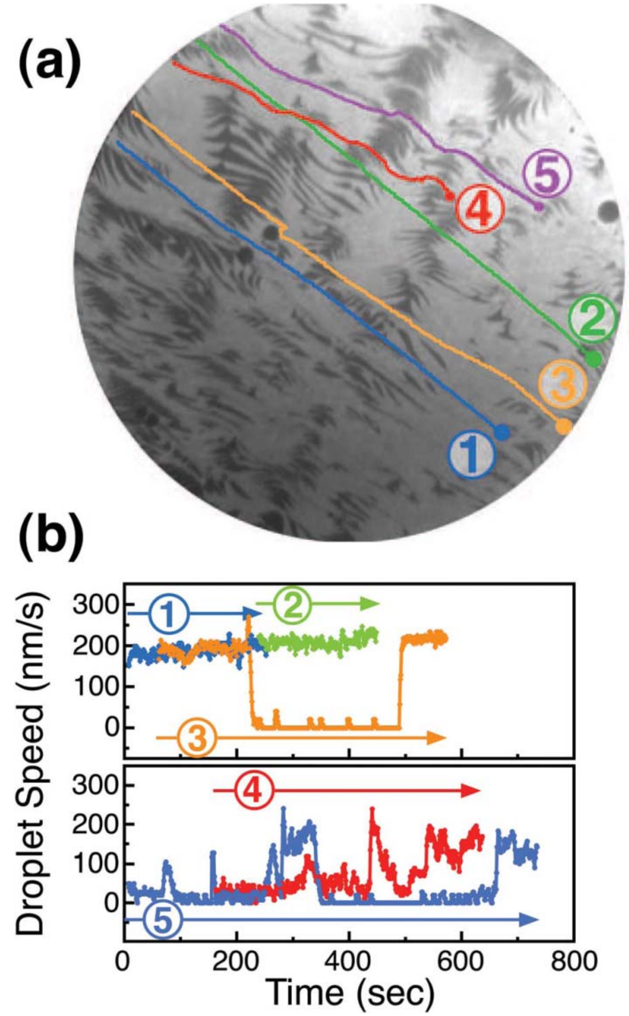
O. G. Shpyrko et al., “Crystalline surface phases of the liquid Au-Si eutectic alloy”
Phys. Rev. B 76, 245436 (2007)

# Examples of related Nanoscience Research:



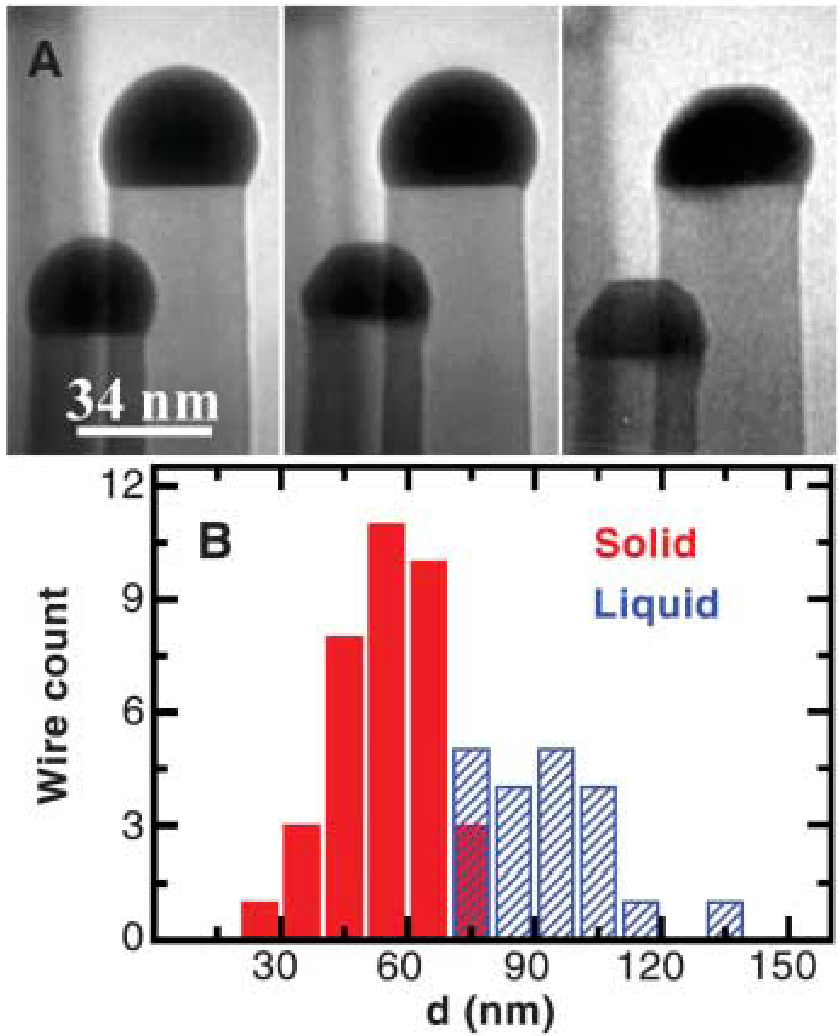

P. Sutter, Nature Materials 6, 363 (2007)
"Dispensing and surface-induced crystallization of zeptolitre liquid metal-alloy drops"

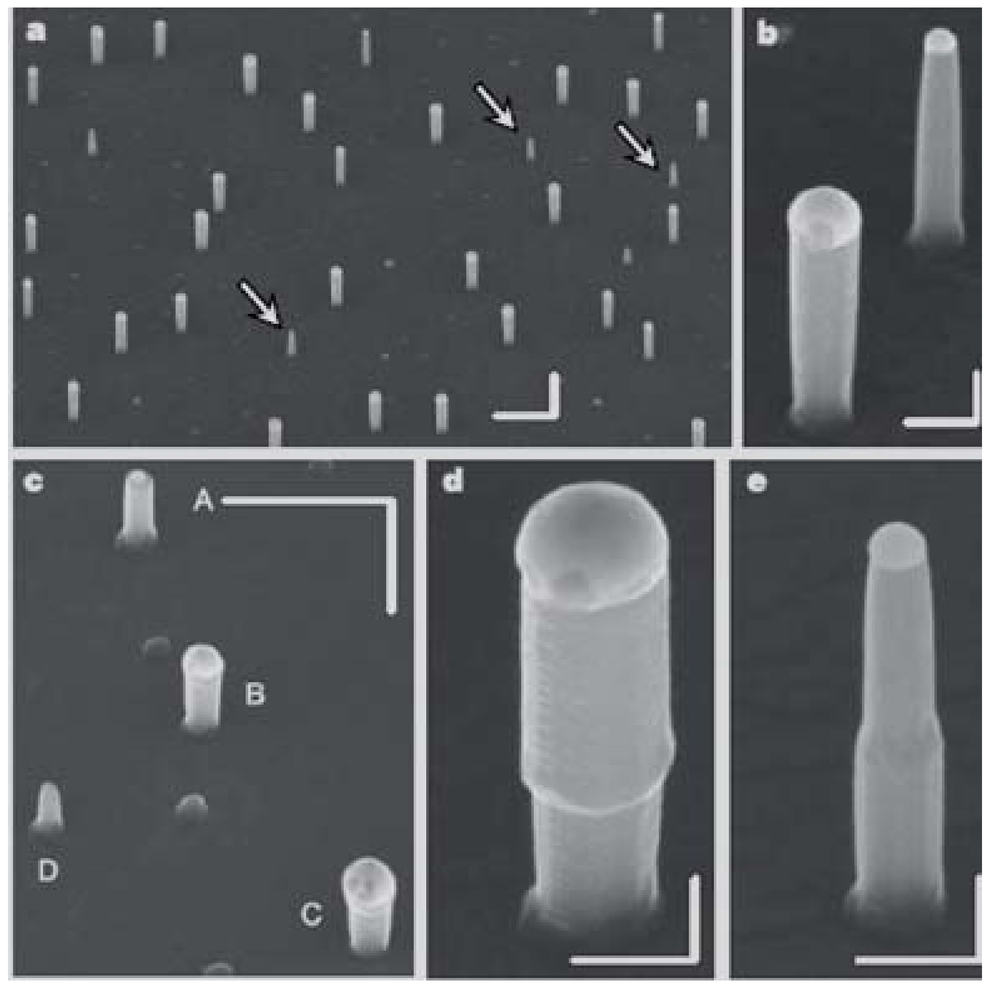
Also discussed, along with our AuSi paper:
M. Wilson, Physics Today, July (2007)




P. Sutter et al., Phys. Rev. Lett. 99, 125504 (2007), "Steering Liquid Pt-Si Nanodroplets on Si(100) by Interactions with Surface Steps"

# Examples of related Nanoscience Research:

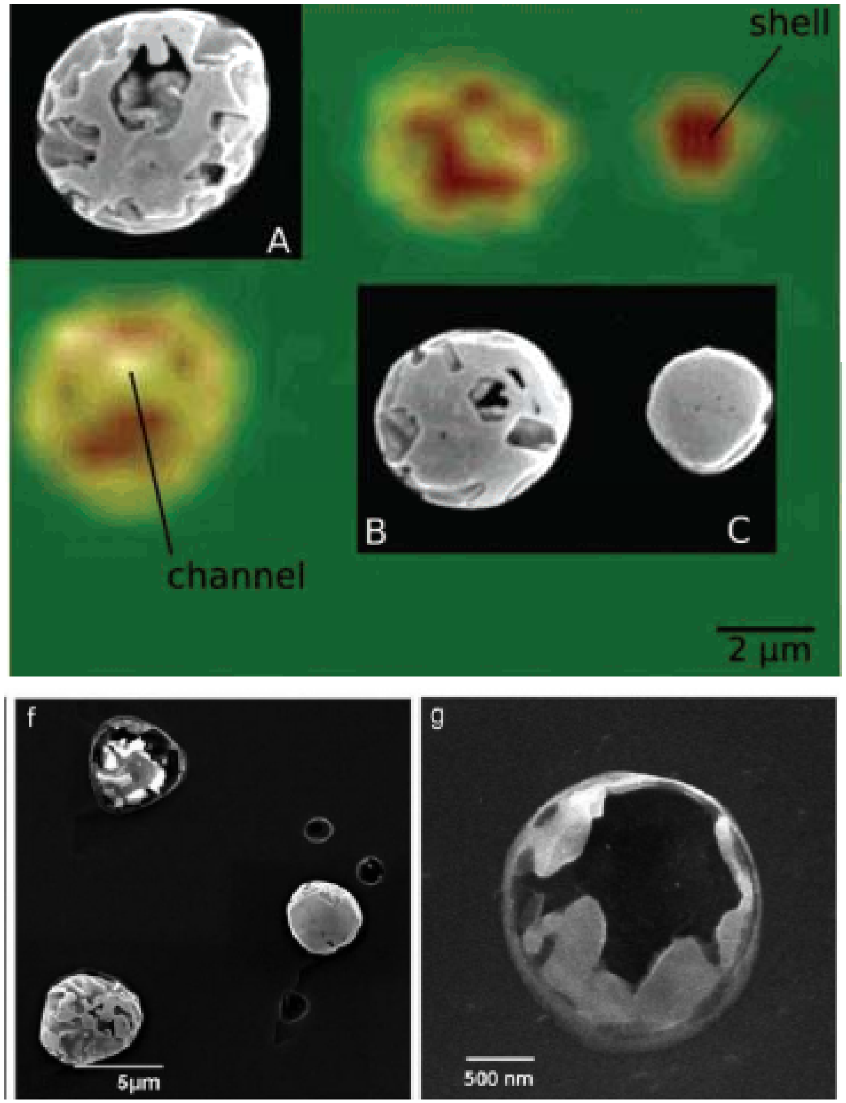


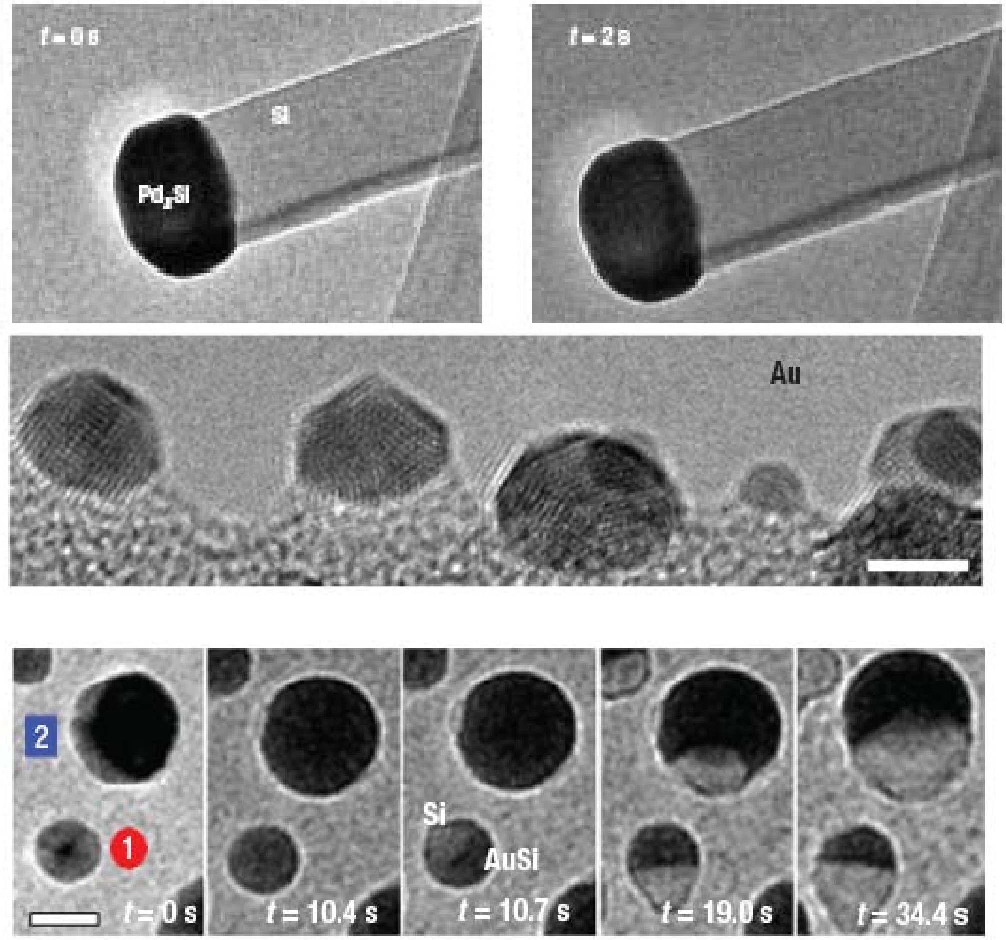




S. Kodambaka et al., Science 316, 729 (2007)
"Germanium Nanowire Growth Below the Eutectic Temperature"

J. Hannon et al., Science, 313, 1266 (2006)
"The influence of the surface migration of gold on the growth of silicon nanowires"

# Examples of related Nanoscience Research:




S. Hofmann et al., Nature Materials, 7 (2008)
"Ledge-flow-controlled catalyst interface dynamics during Si nanowire growth"

N. Ferralis et al., J. Am. Chem. Soc. 130, 2681 (2008)
"Temperature-induced self-pinning and nanolayering of AuSi eutectic droplets"

# Useful References:

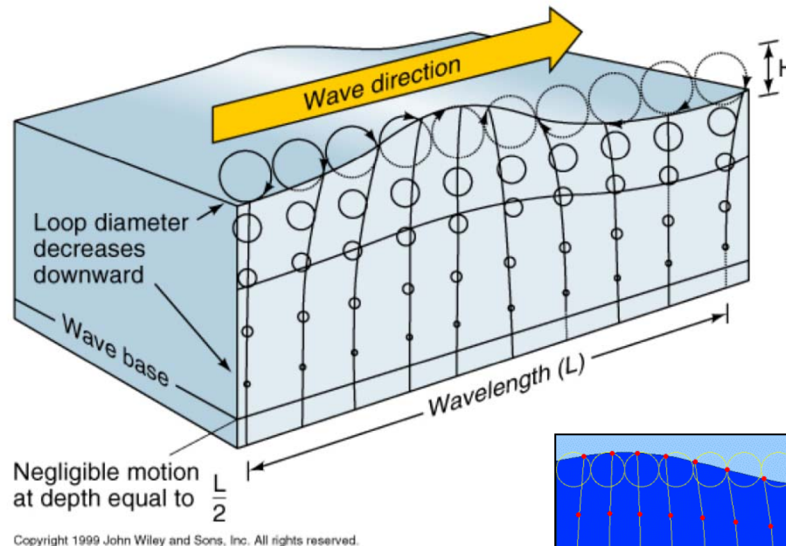
**Books:**
J. Als-Nielsen and D. McMorrow “Elements of Modern X-ray Physics”
M. Tolan “X-Ray Scattering from Soft-Matter Thin Films”
Jean Daillant, Alain Gibaud “X-Ray and Neutron Reflectivity”

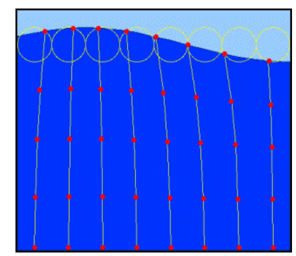
**Theory:**
L. G. Parratt, Phys. Rev. 95, 359 (1954)
S. K. Sinha et al., Phys. Rev. B 38, 2297 (1988)

**Experiment:**
A. Braslau et al., Phys. Rev. Lett. 54, 114 (1985)
D. K. Schwarz et al., Phys. Rev. A 41, 5687 (1990)
H. Tostmann et al., Phys. Rev. B 59, 783 (1999)
O. Shpyrko et al., Phys. Rev. B 69, 245423 (2004)

**Reviews:**
J. Penfold, Rep. Prog. Phys. 64 777 (2001)
J Daillant and M. Alba, Rep. Prog. Phys. **63** 1725 (2000)
P. S. Pershan, J. Phys. Cond. Mat. 6 A37 (1994)

# Capillary Waves on Liquid Surfaces

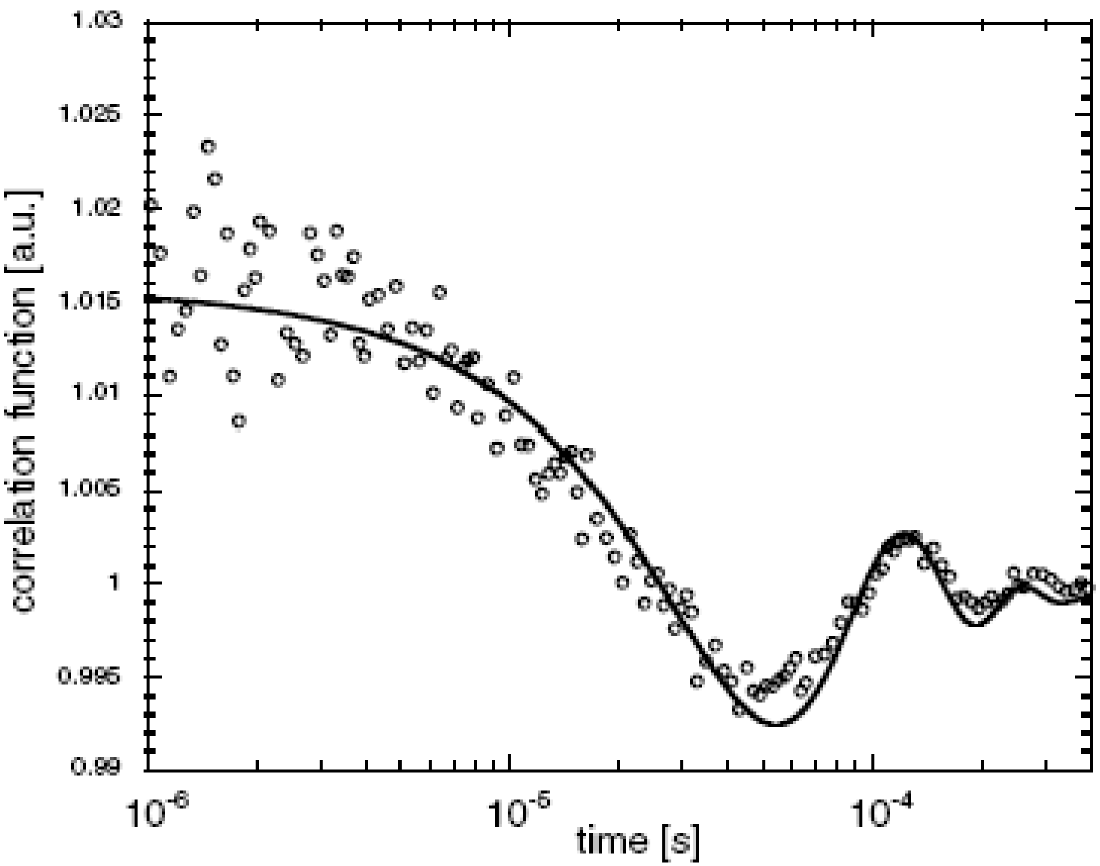



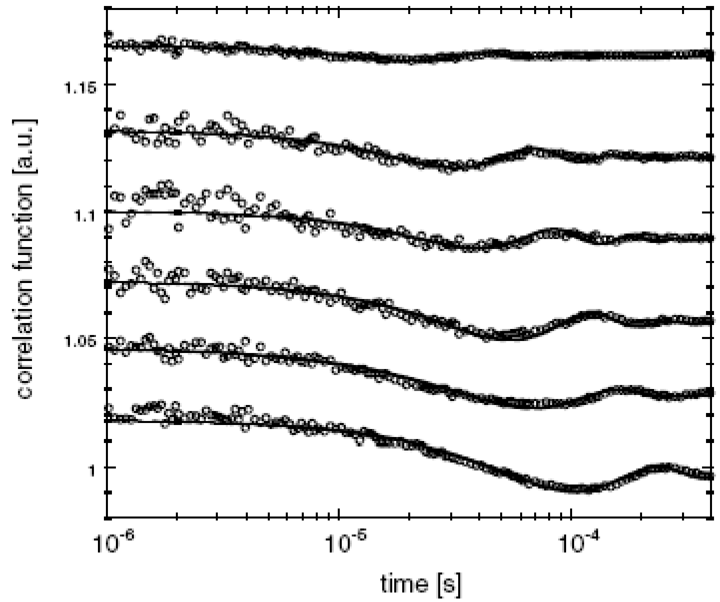
Capillary wave model —— sharp step-like profile decorated with height variations due to thermal excitations.

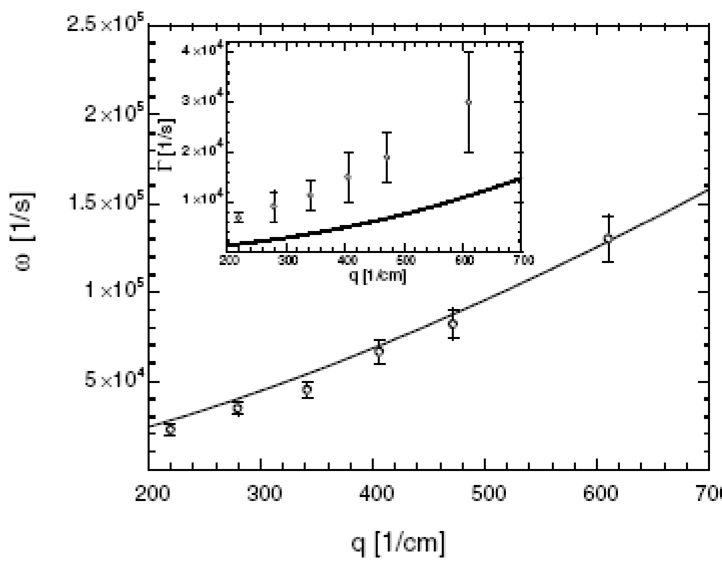
See, for example:

Buff, Lovett, and Stillinger. Phys. Rev. Lett. 15, 621 (1965)

# Real-time observations of propagating capillary waves:

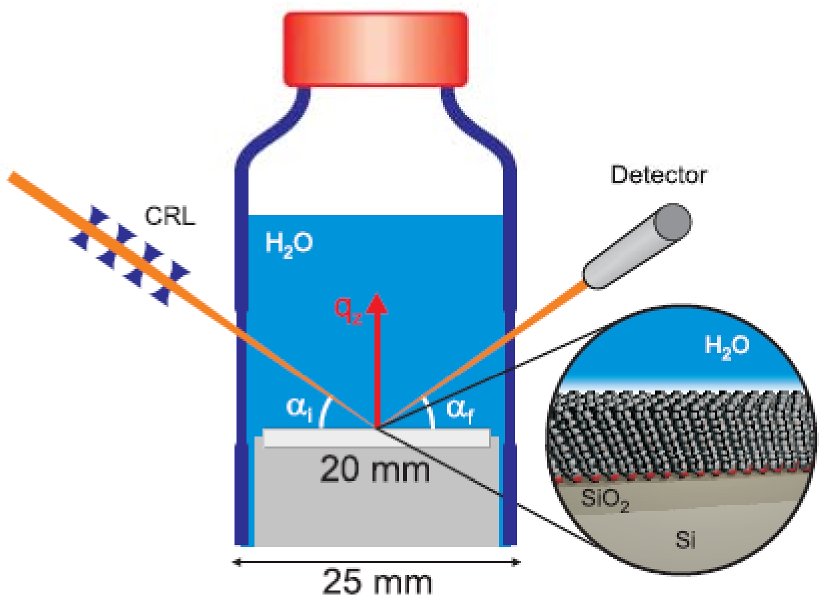


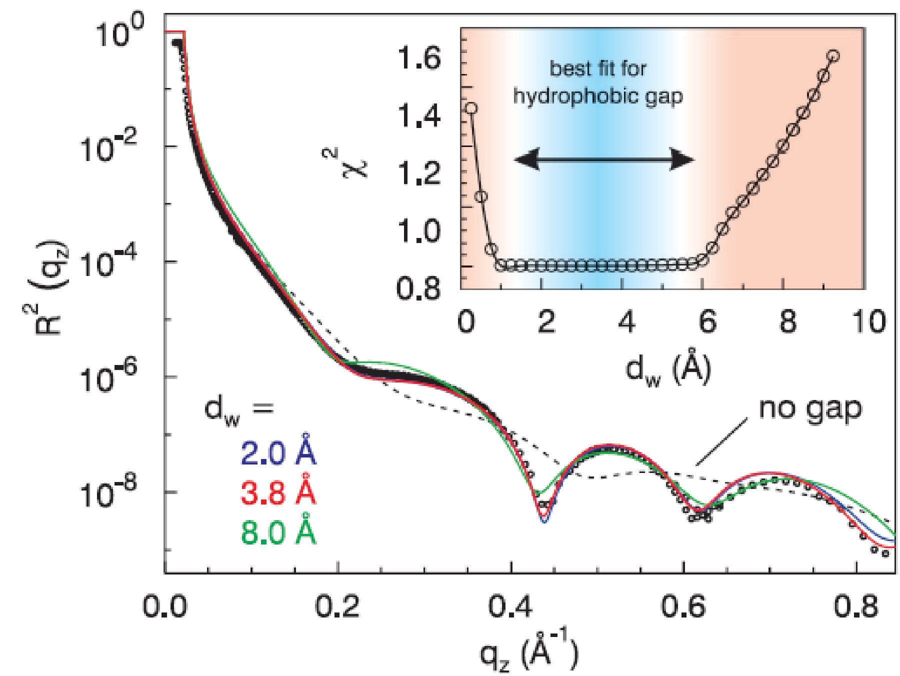



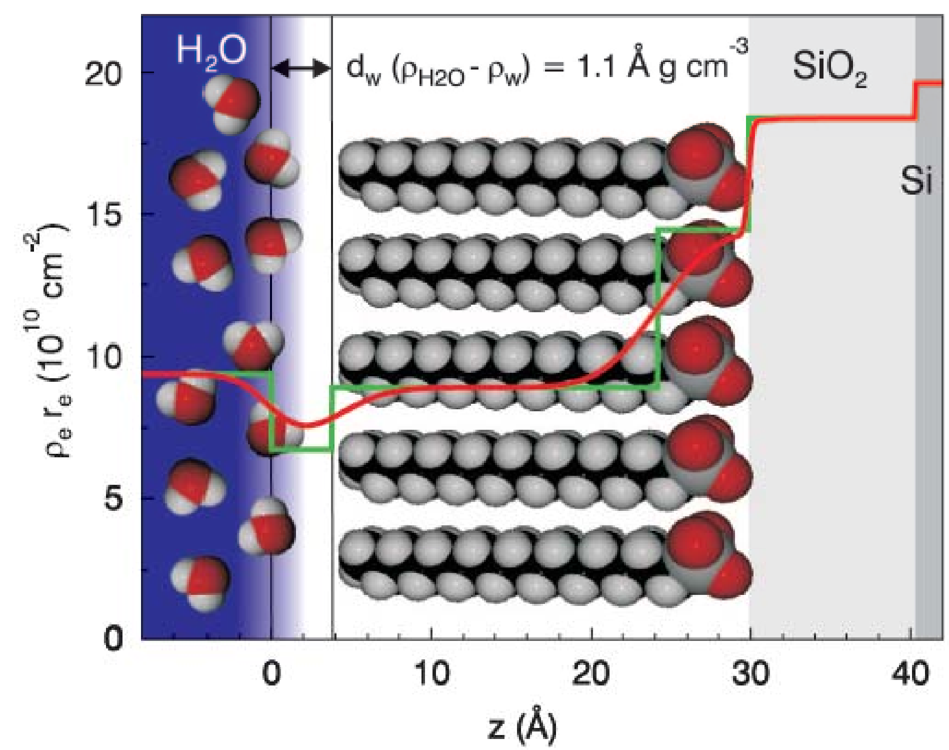




C. Gutt et al., **PRL** 91, 76104 (2003)

# Depletion layer at Solid-Liquid interface:



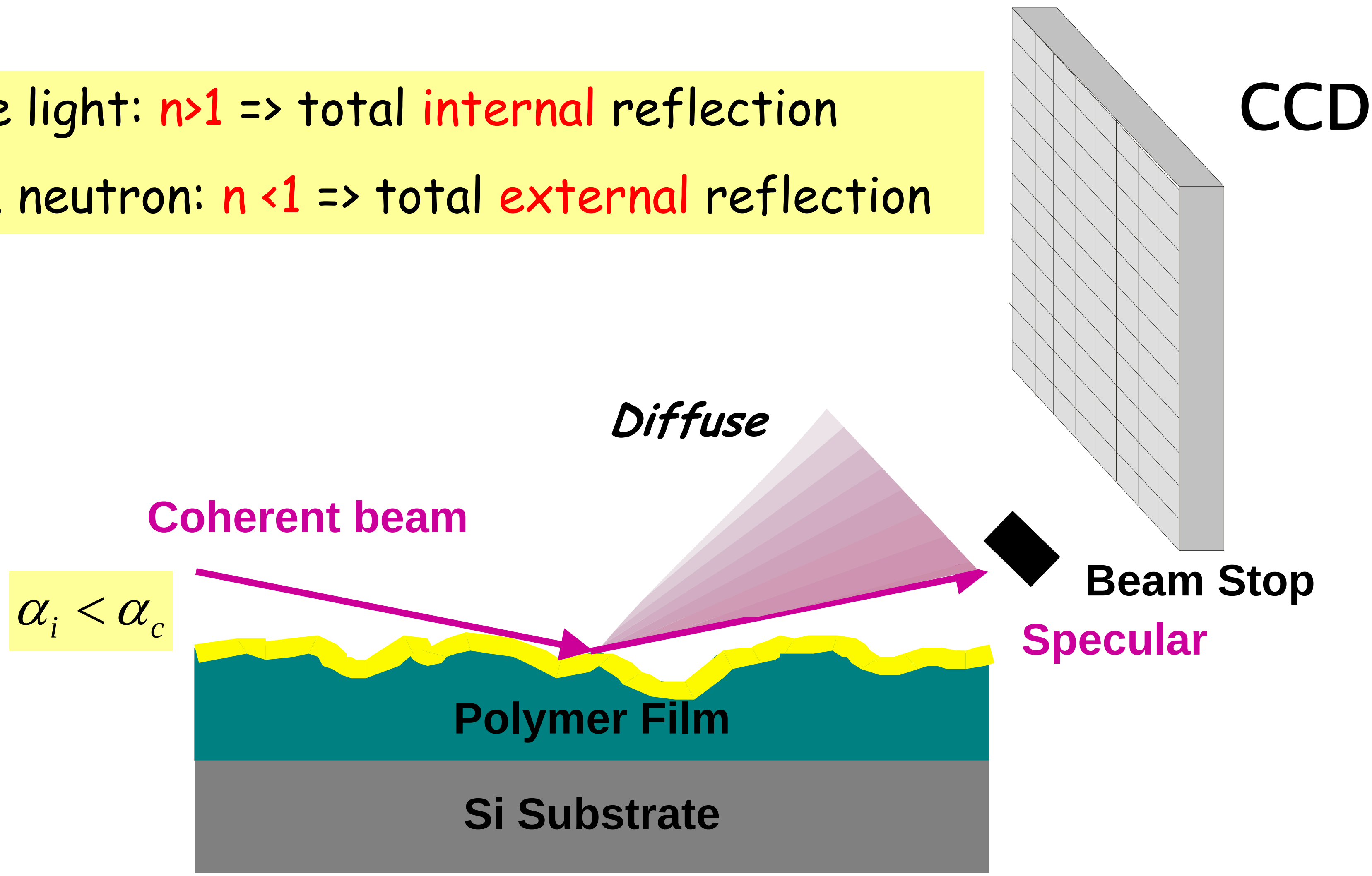




Mezger, Reichert, Dosch et al.
PNAS 103, (2006)

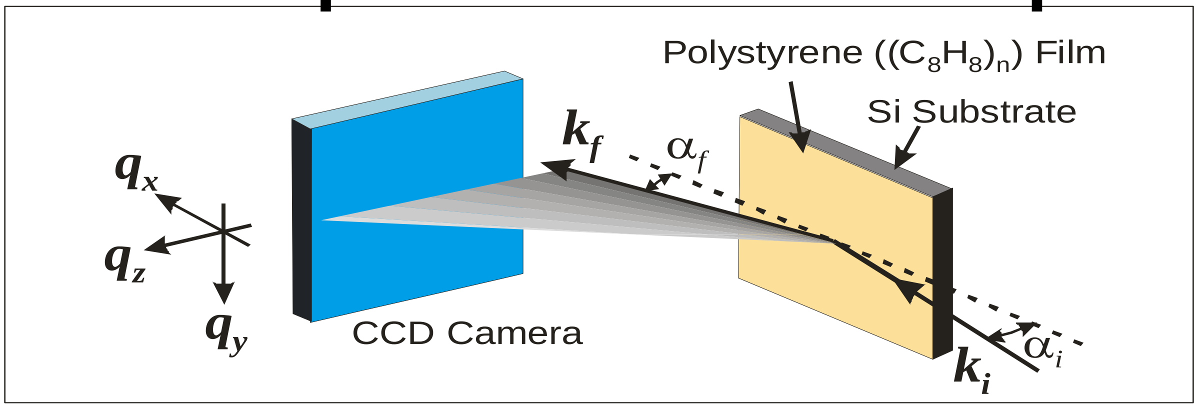
# Surface Sensitive X-ray Photon Correlation Spectroscopy (XPCS)

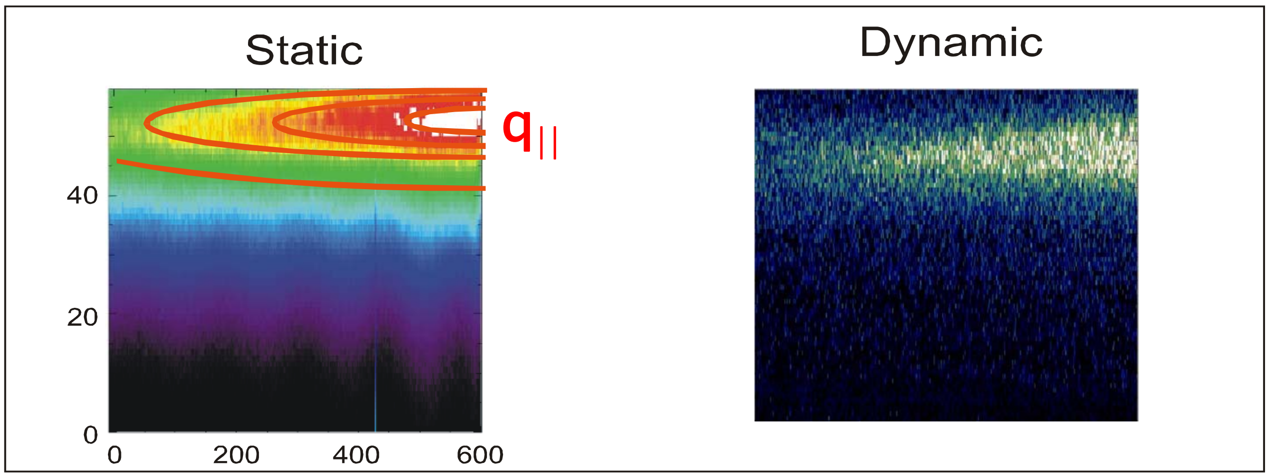
Visible light: n>1 => total internal reflection

X-ray, neutron: n <1 => total external reflection



# Experiment setup




$$\frac{d\sigma}{d\Omega} \cong \frac{k_B T}{\gamma q_{\|}^2} \left|E(\alpha_i)\right|^2 \left|E(\alpha_f)\right|^2$$

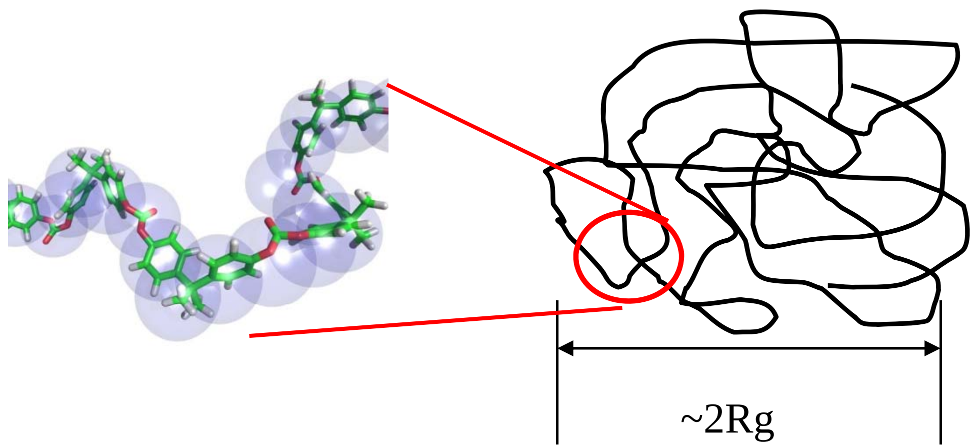
Distorted-wave Born Approximation (DWBA)

Sunil K. Sinha, et.al., PRB, 38 2297 (1988)

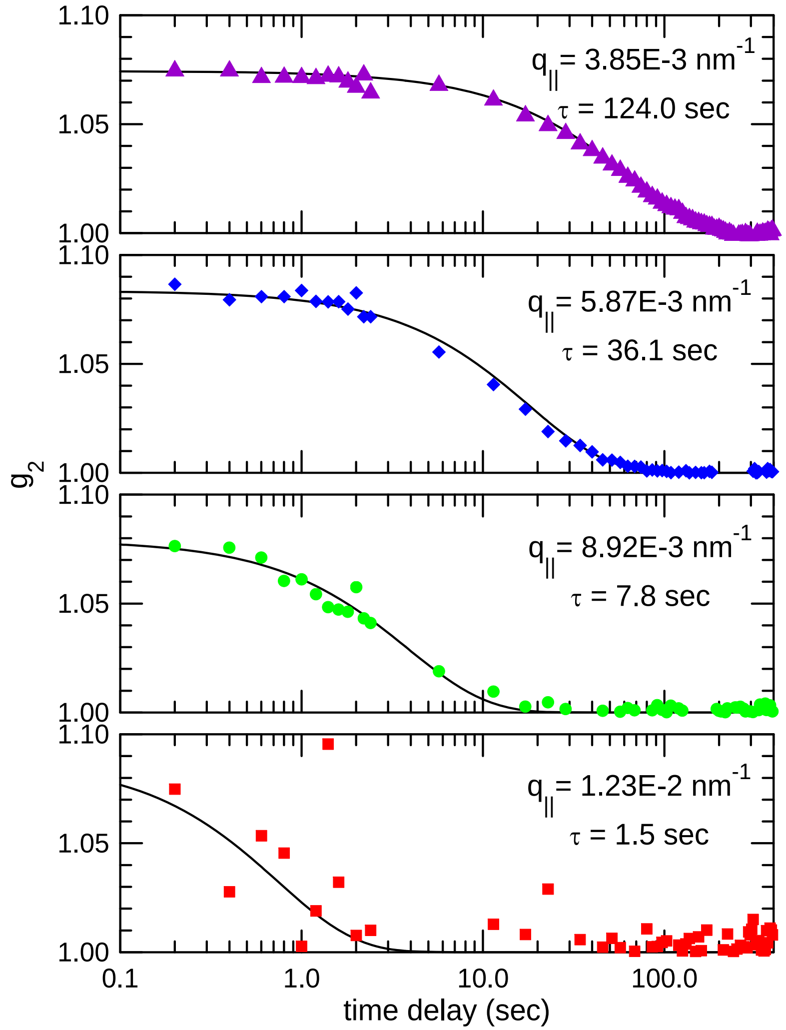
# Surface Dynamics of Si-supported, Thick Polystyrene Films at T>>Tg (~95-100 $^{o}$C)

h>>Rg=9 nm, Mw=123k g/mol

A polymer is a high-molecular-weight organic compound, natural or man-made, consisting of many repeating simpler chemical units or molecules called monomers.



# Auto-correlation Function



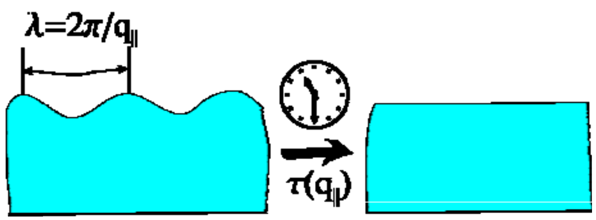

- h=84 nm, T=160 °C (>>Tg)
- Autocorrelation function

$$g_2(q_{||},t) = 1 + \beta \left| f(q_{||},t) \right|^2$$

- Intermediate scattering function

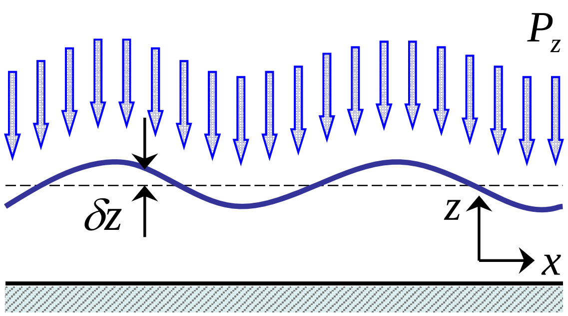
$$f(q_{||},t) = \exp[-(t/\tau)^{\alpha}]$$

- β: speckle contrast
- α: stretching exponent; α≅1
- τ: over-damped relaxation time constant

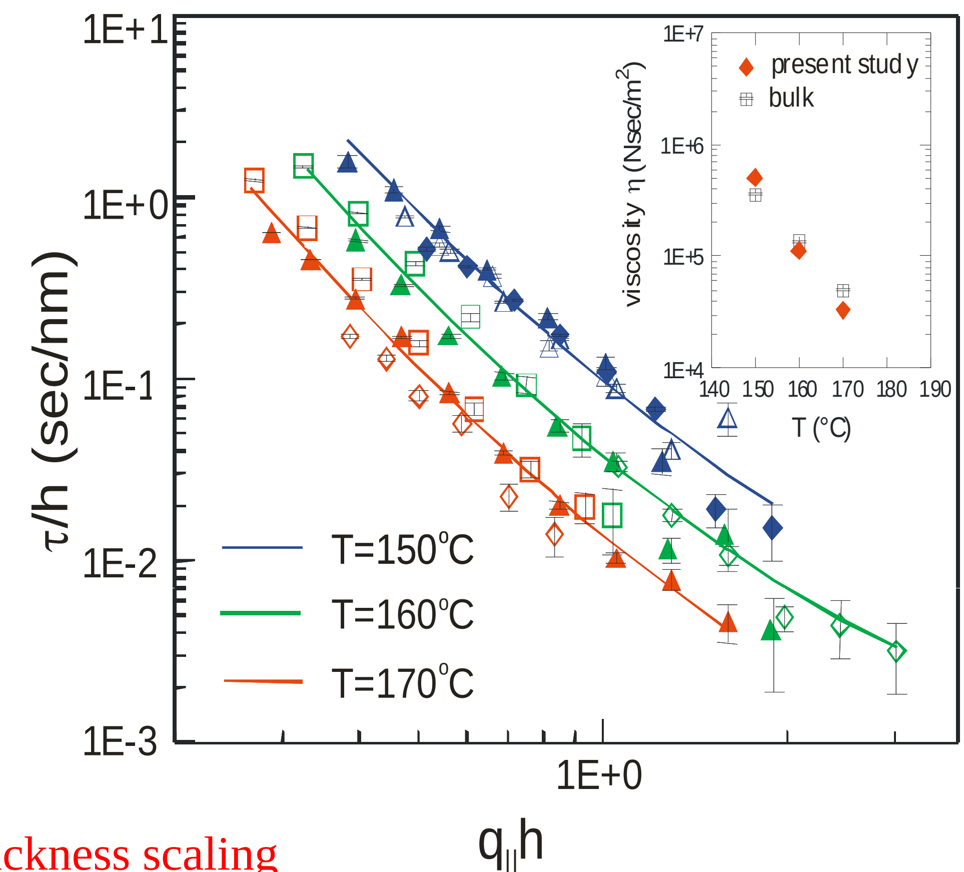



➢ Hyunjung Kim, et al., Phys. Rev. Lett. 90, 68302 (2003)

# Relaxation of Over-damped Capillary Waves




- Linearized Navier-Stokes equation
- Equation of continuity
- Non-slip boundary condition
- High viscosity (over-damped waves)




Over-damped relaxation time constants

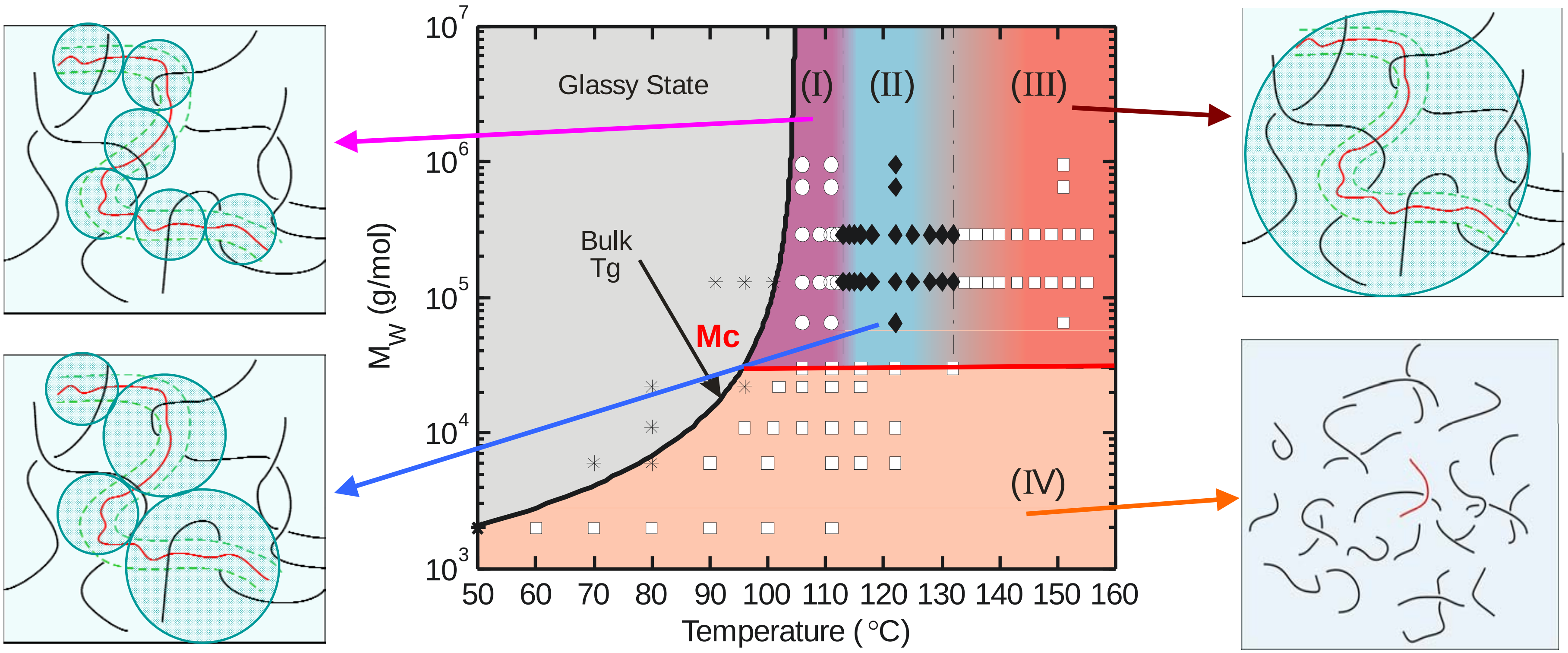
Thickness scaling

$$\tau(q_{\|}) \cong 2\left(\frac{\eta}{\gamma}\right)\left(\frac{1}{q_{\|}}\right)\frac{[\cos(q_{\|}h)^2 + (q_{\|}h)^2]}{[\sinh(q_{\|}h)\cosh(q_{\|}h) - q_{\|}h]} \quad \Rightarrow \quad \frac{\tau}{h} = f(q_{\|}h)$$

η: dynamic viscosity
γ: surface tension
h: film thickness

- J. Jäckle, J. Phys: Condense. Matter 10, 7121 (1998)
- H. Kim, et al., Phys. Rev. Lett. 90, 68302 (2003)
- Z. Jiang, et al., Phys. Rev. E 74, 11603 (2006)

# Mw-T Pseudo "Phase" Diagram of Surface Dynamics




Surface dynamics arise mainly from the collective motion of

- Region I: segments of length equal to critical entanglement length;
- Region II : segments of lengths from critical entanglement length to full chain length;
- Region III and IV : full chains.

# Summary

Synchrotron x-ray scattering is rather unique in being able to access liquid-vapor, liquid-liquid and solid-liquid interfaces with atomic-scale resolution

Diffuse scattering arising from capillary wave fluctuations – seen as “nuisance” in the past, is becoming a source of important information about dynamical properties of liquids, thin films and interfaces