# Off-specular Diffuse Scattering

Liquid Scattering X-ray School November 2007

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# These notes are available on the web

Visit http://oleg.ucsd.edu

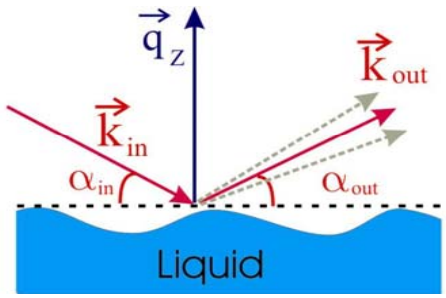
Or email me at oshpyrko@ucsd.edu

★ "Extra Credit" Homework
(think about it later, look up references)

# What is Diffuse Scattering?

Specular:

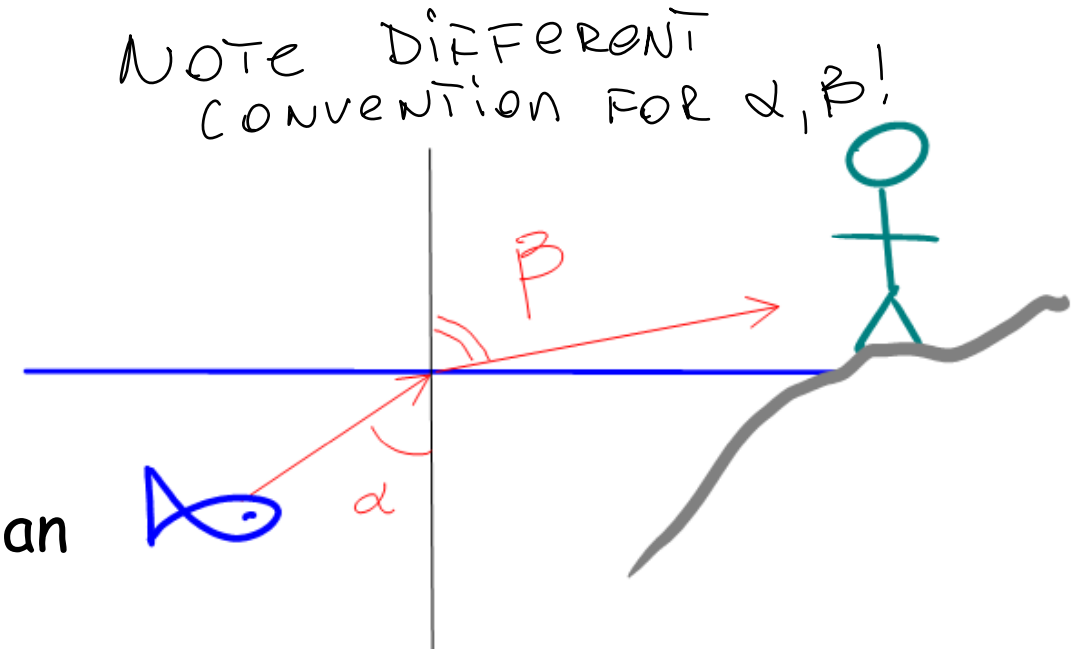
Diffuse:



# Total Internal reflection:

## Snell's Law:

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




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

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

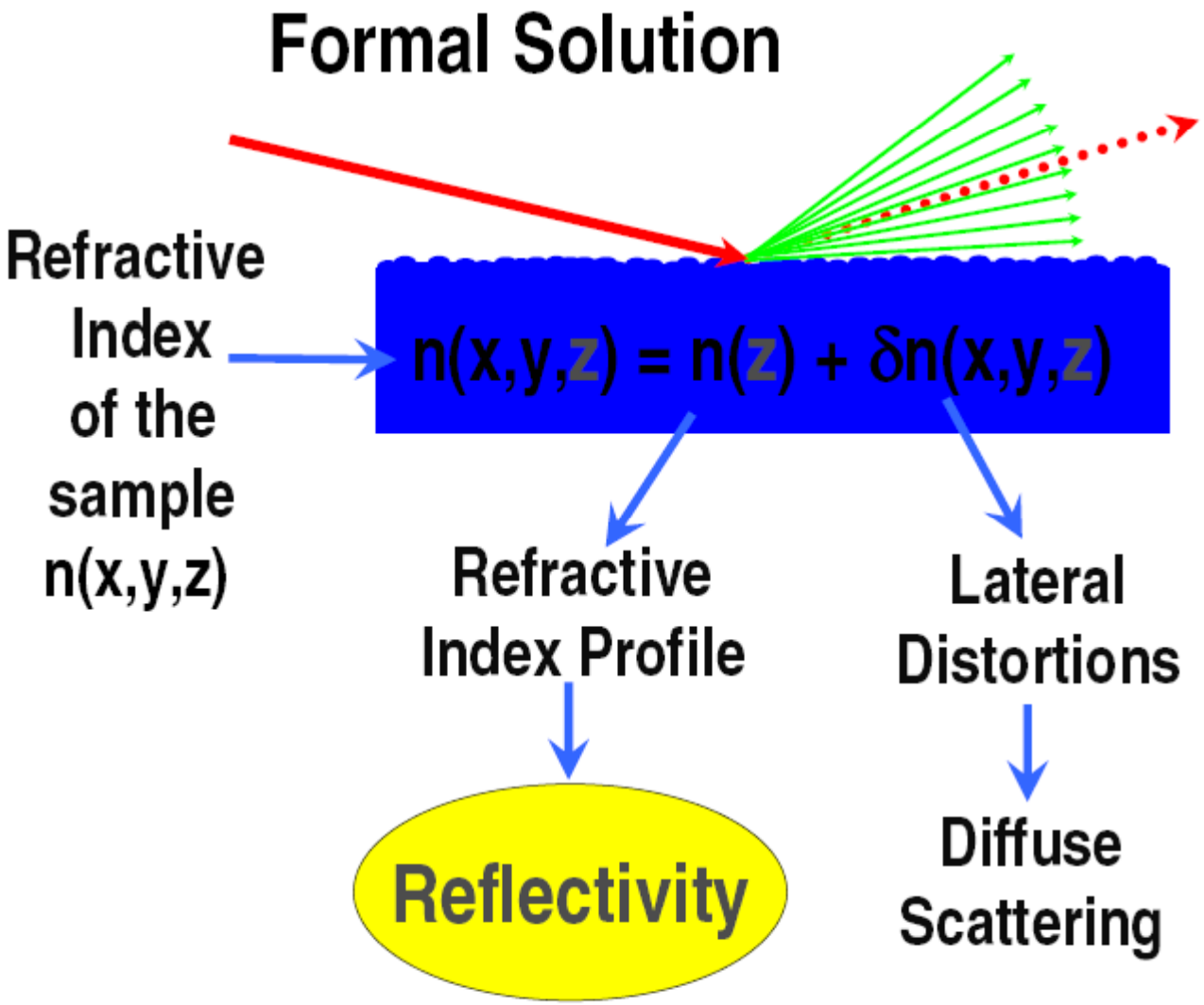
★ Q: How can n be < 1? (Speed of light > c?)

## For x-rays:

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

Critical angle $\approx \sqrt{2\delta}$ or ~ a few mrad

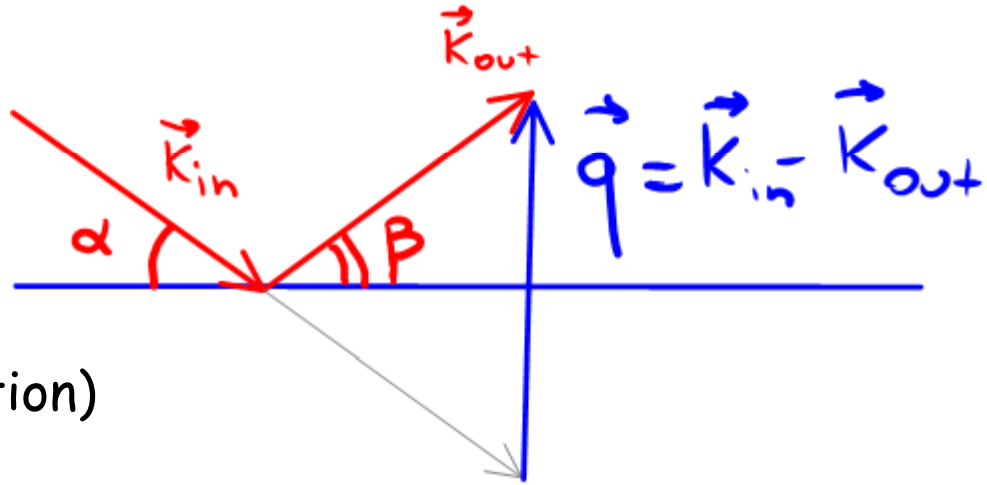
# X-ray Reflectivity and Diffuse Scattering



# Fresnel Law

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

"Ideal" Interface:
Static, Flat,
Sharply terminated




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

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

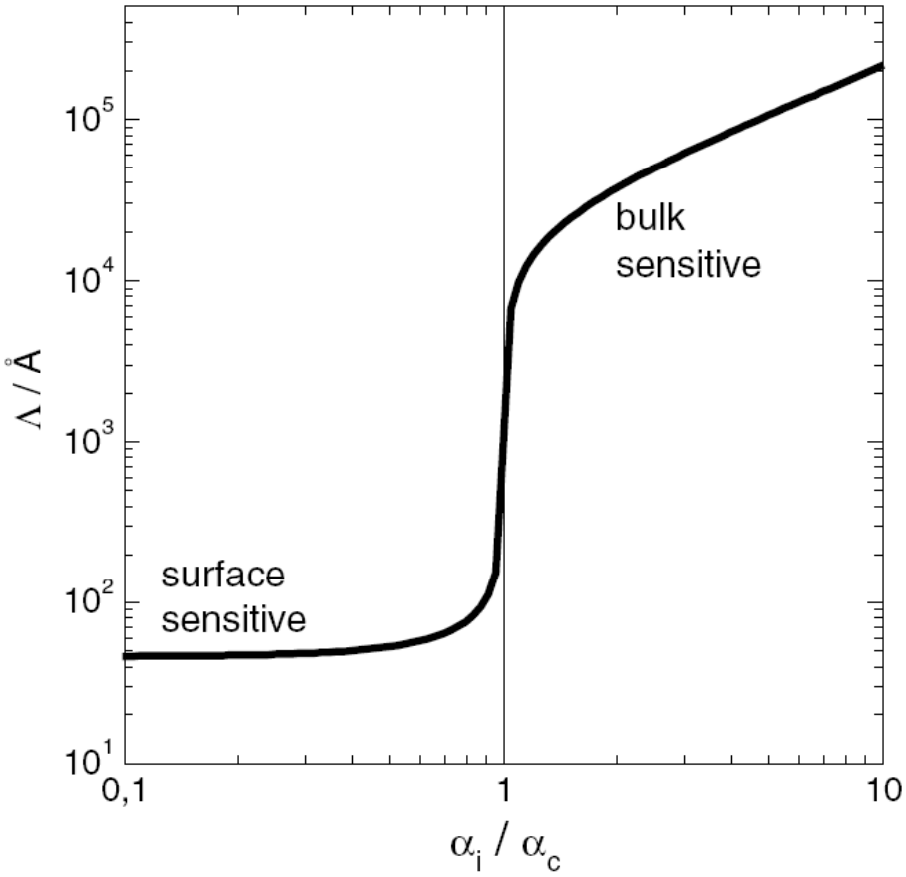
★ Derive

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

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

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

# Penetration depth:




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

Penetration depth for $q<q_c$

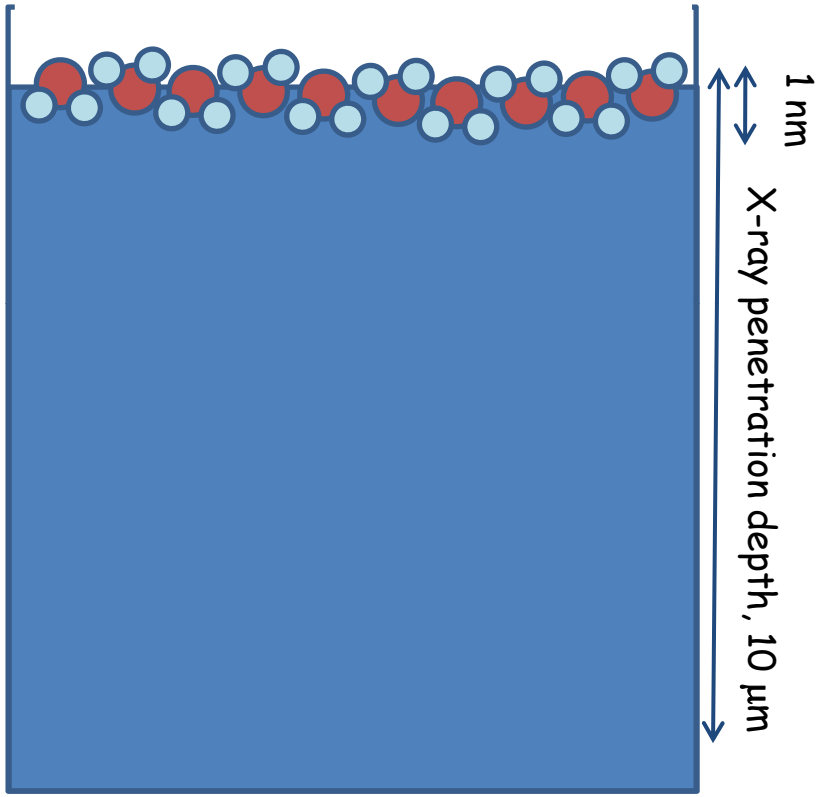
$$\Lambda \approx 1/q_c \sim 15 - 100\mathring{A}$$

★ Derive. Q: What is $\Lambda$ for water?

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

★ Q: What is Born approximation (kinematical theory)?
Also look up: dynamic (Parratt) formalism

# Puzzle of Surface Scattering

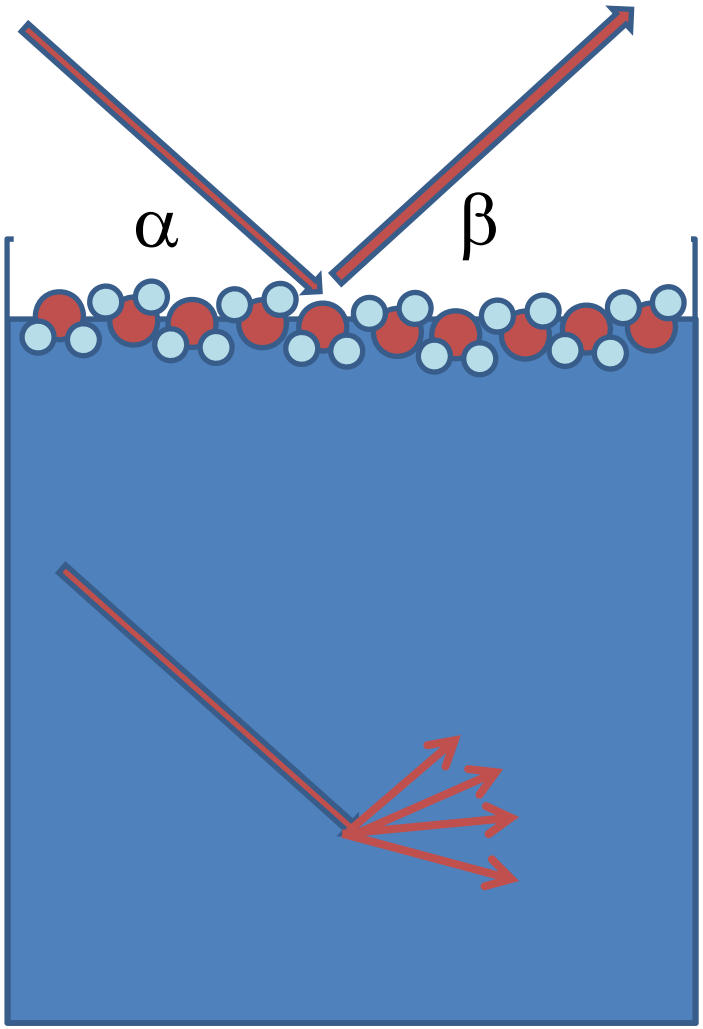



Above $q_c$ x-rays penetrate the liquid over depths ~ many microns, or many thousands of molecules per unit area.

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

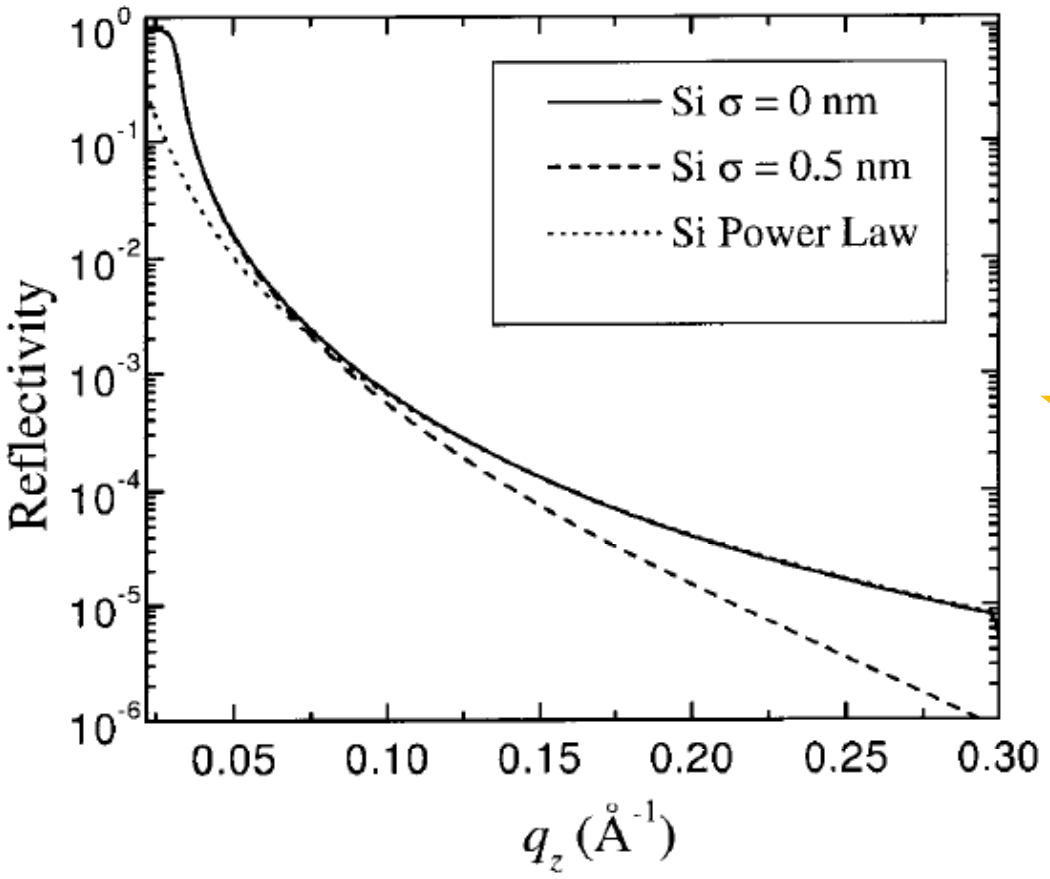



Specular reflection $\alpha=\beta$,
solid angle of acceptance ~$10^{-6}$ sterad.
(can be even smaller, in principle)

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

# Reflectivity Curve Example

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



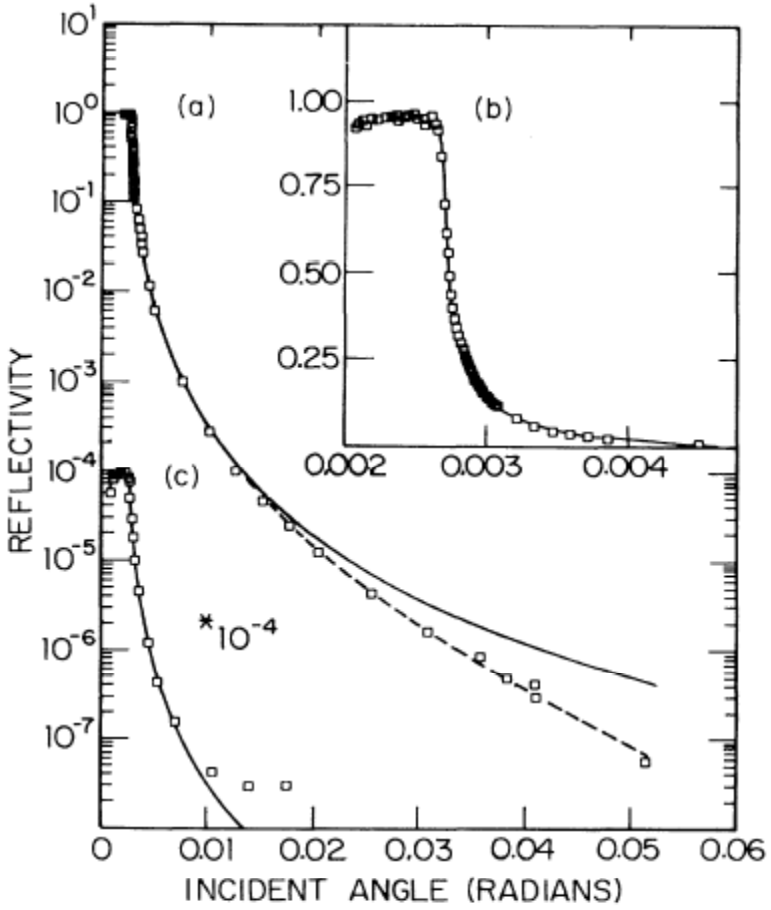

Roughness lowers reflectivity
Scales as $\exp(-\sigma^2 q^2)$

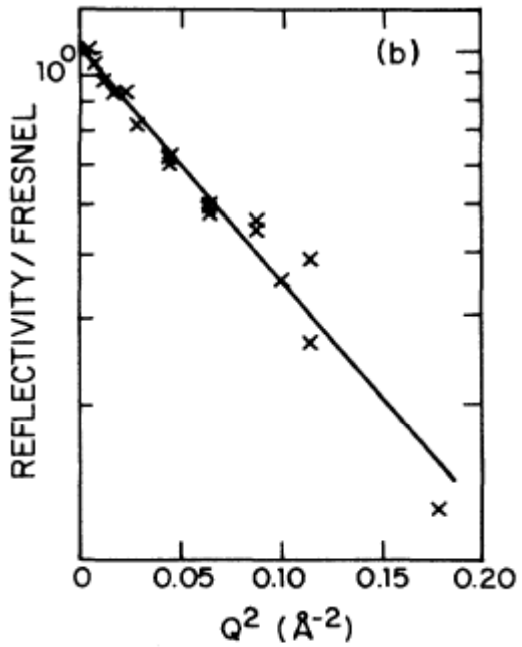
Similar to Debye-Waller factor

★ What is Debye-Waller?
(look up in Solid State text:
Kittel, Ashcroft&Mermin, etc.)

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

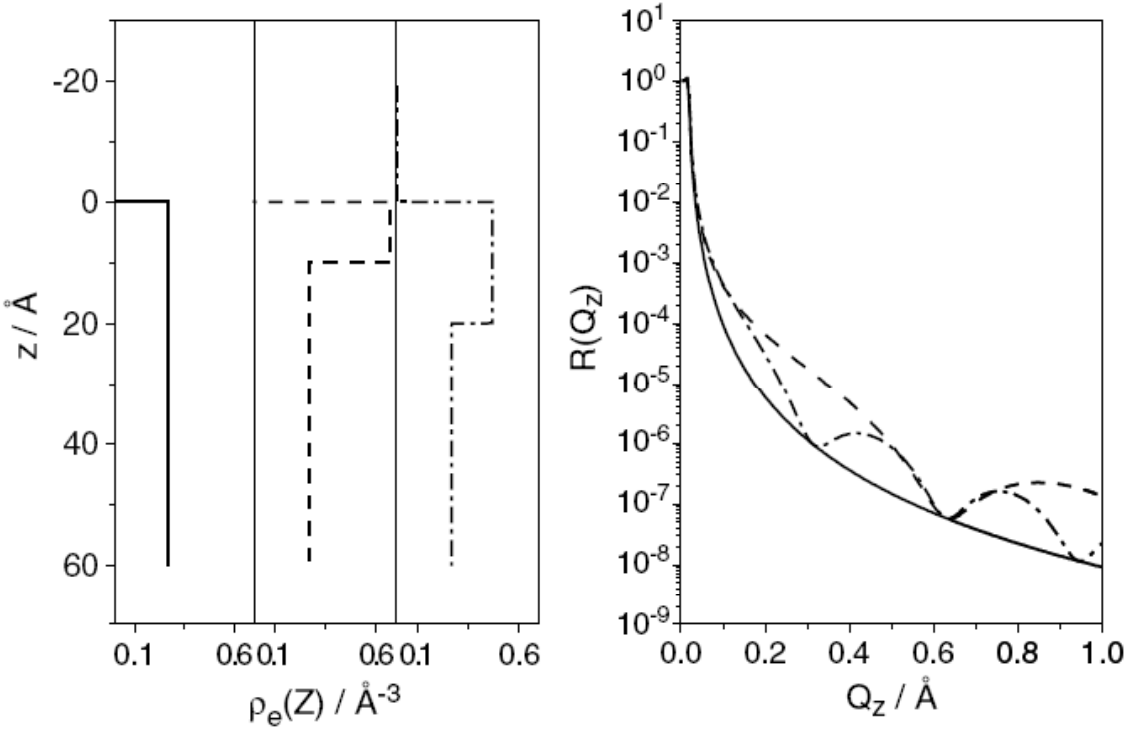
# First Reflectivity measurements from simple liquid (water)




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!)

# 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 $q_z = 2\pi/a \sim 3Å^{-1}$

For typical $q_c \sim 0.03Å^{-1}$ 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, $\gamma$)

$$R(q_z) = R_F(q_z) \cdot \left|\Phi(q_z)\right|^2 \cdot CW(q, T, \gamma)$$

Fresnel (ideal surface)

structure

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.

★ Why can't we do inverse FT of $\Phi(q_z)$ to get $\rho(z)$ directly?

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

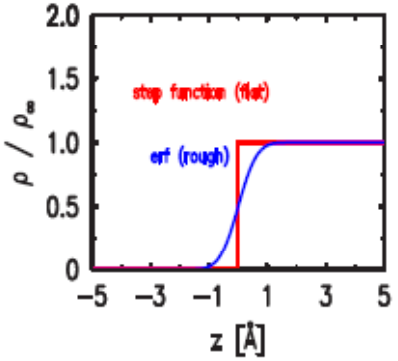
$$R(q_z) = R_F(q_z) \cdot \left|\Phi(q_z)\right|^2 \cdot CW(q, T, \gamma)$$

measured (reflectivity) — known — want to know (related to density) — measured by diffuse scattering

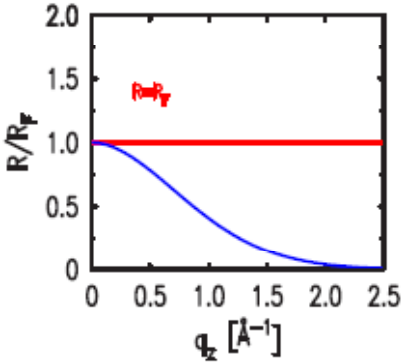
Real Space

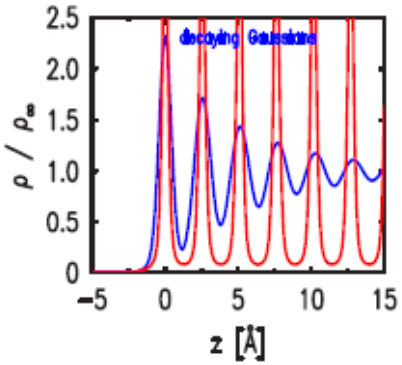
Reciprocal Space

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

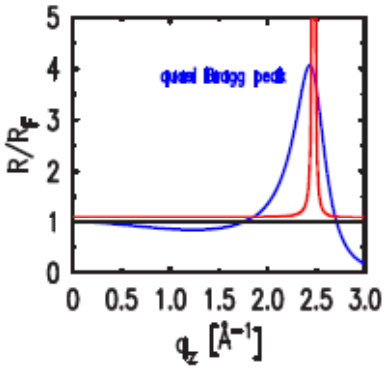



(A)

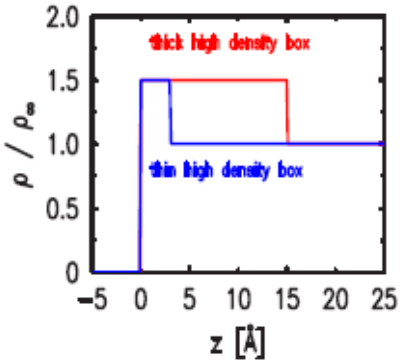


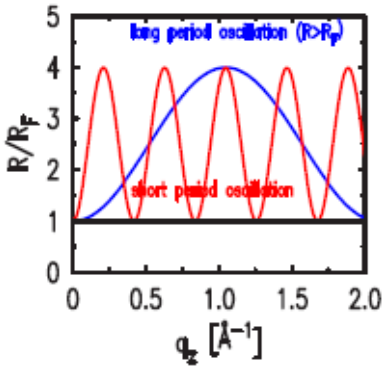

(B)




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




(C)



# Capillary Waves

Reminder:

gravity waves
(long-wavelengths)

capillary waves
(short-wavelengths)

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

★ Derive from dimensional considerations

# 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): $\sigma \sim \sqrt{\frac{k_B T}{\gamma}}$

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

Actual (correct) expression includes resolution effects:

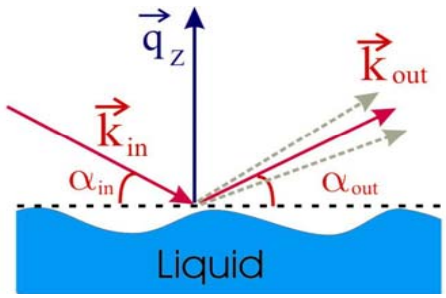
$$\sigma_{\mathrm{cw}}^2 = \frac{k_B T}{2\pi\gamma} \ln\left(\frac{k_{\max}}{k_{\min}}\right)$$

★ Q: What is the roughness for helium at 4K? Liquid mercury at room T?

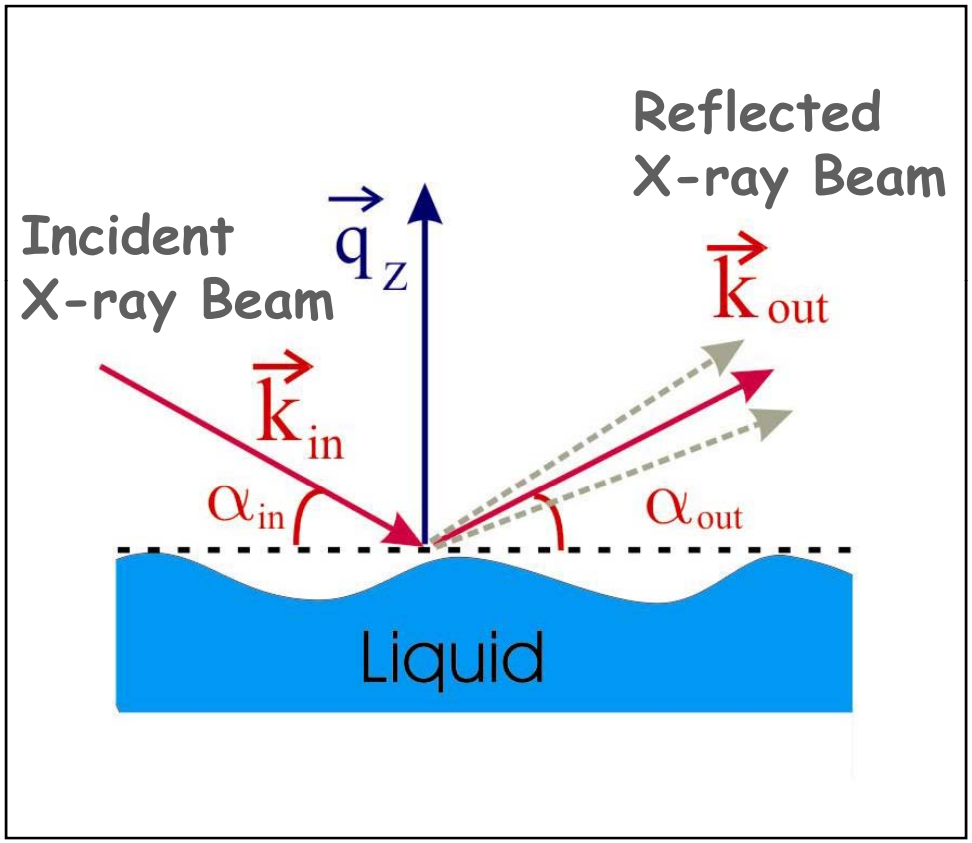
# What is Diffuse Scattering?

Specular:

Diffuse:



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



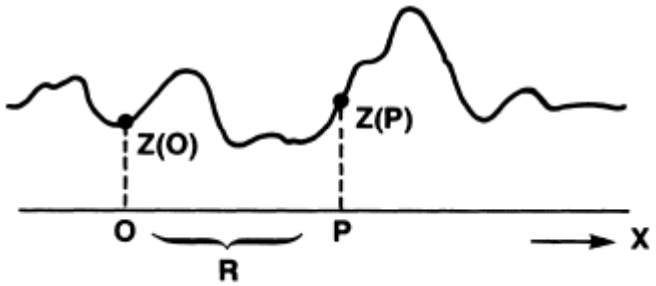

**Reflectivity from solid surfaces:**
Surface profiles are static:

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

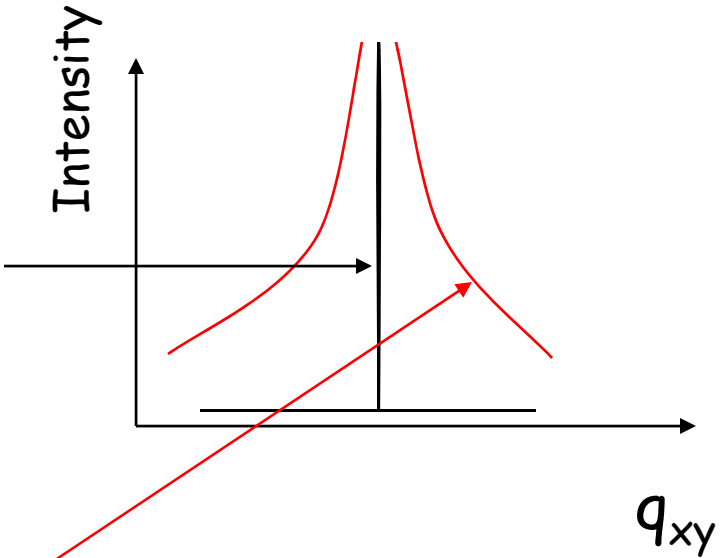



$$\langle [z(x',y') - z(x,y)]^2 \rangle = g(R)$$

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

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

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




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

★ Read this paper!

**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 (+Landau +Peierls +Hohenberg)

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

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

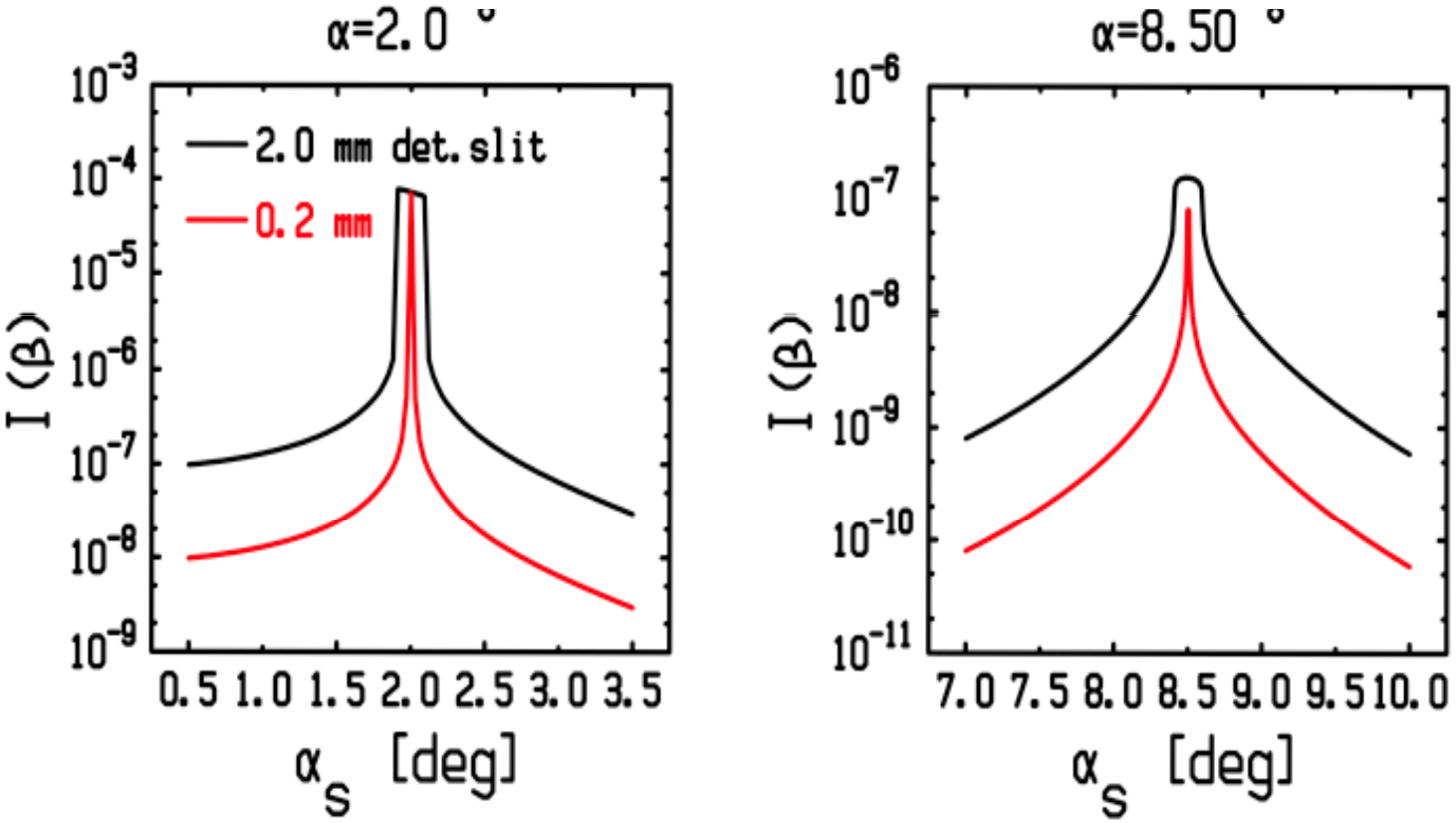
$$\Phi(q_z) = \frac{1}{\rho_\infty}\int dz \frac{\langle d\rho(z)\rangle}{dz}\exp(\imath q_z z)$$

Capillary exitations * Resolution function

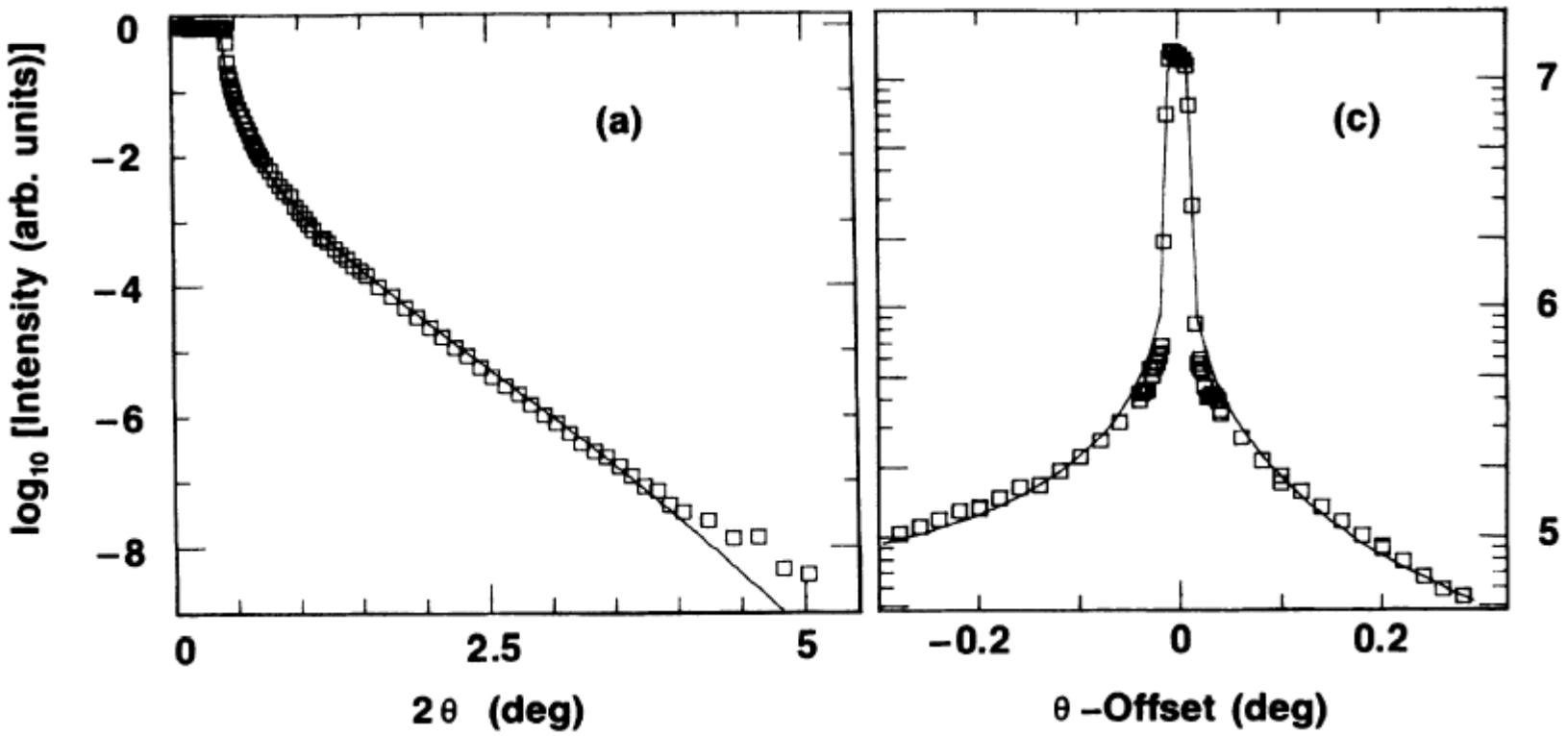
# Know Thy Experimental Resolution!

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

Simulated Detector Scan

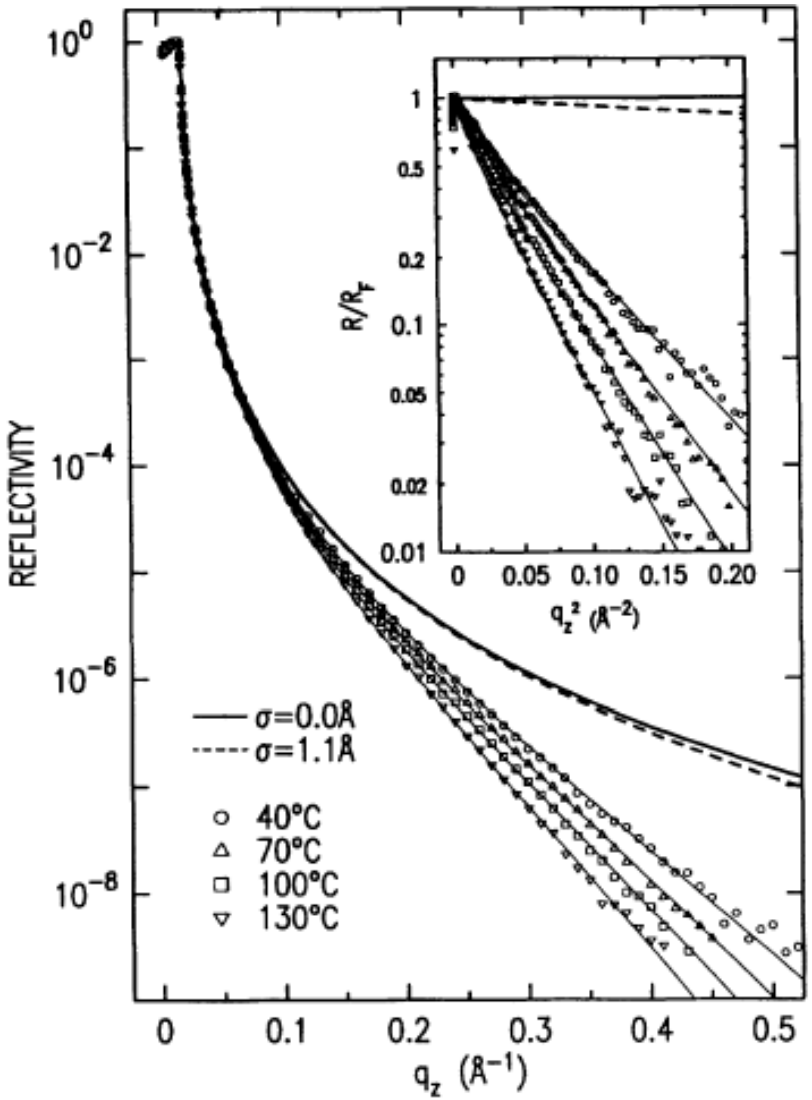


# First measurements of diffuse scattering for water




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

# Temperature dependent capillary wave roughness

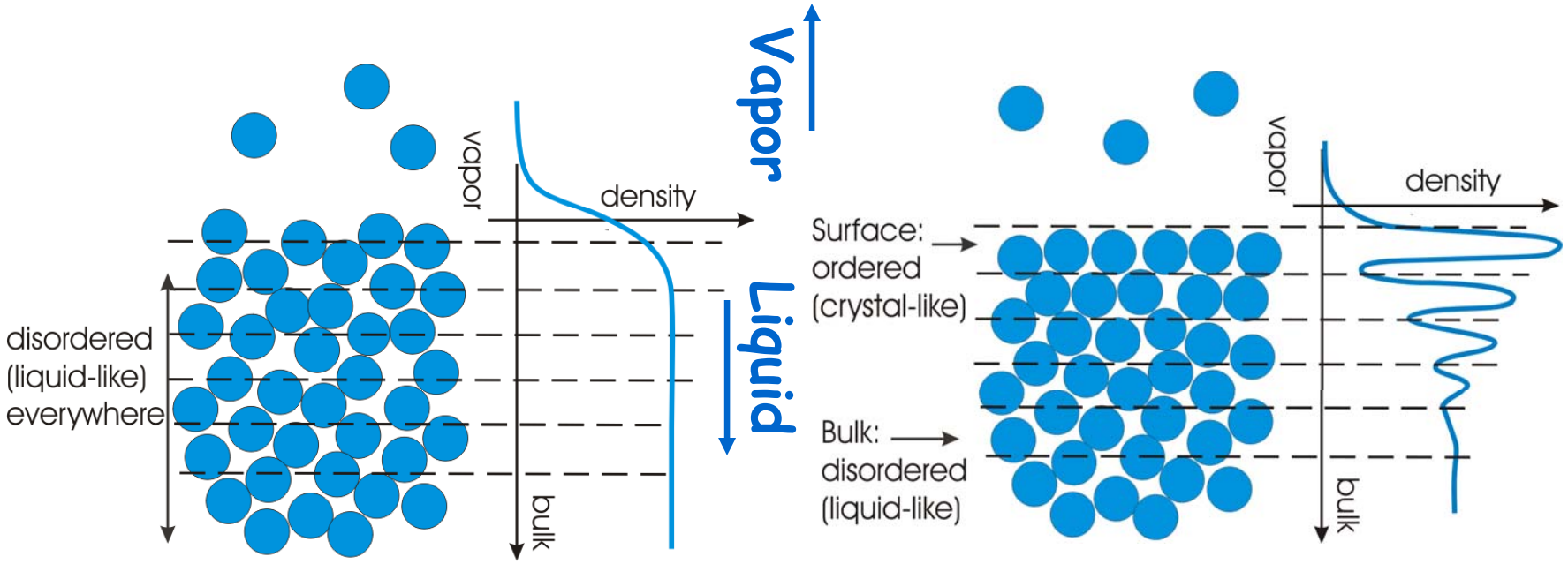



Thermal roughness of C20 alkanes follows thermal scaling predicted by capillary wave theory

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

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

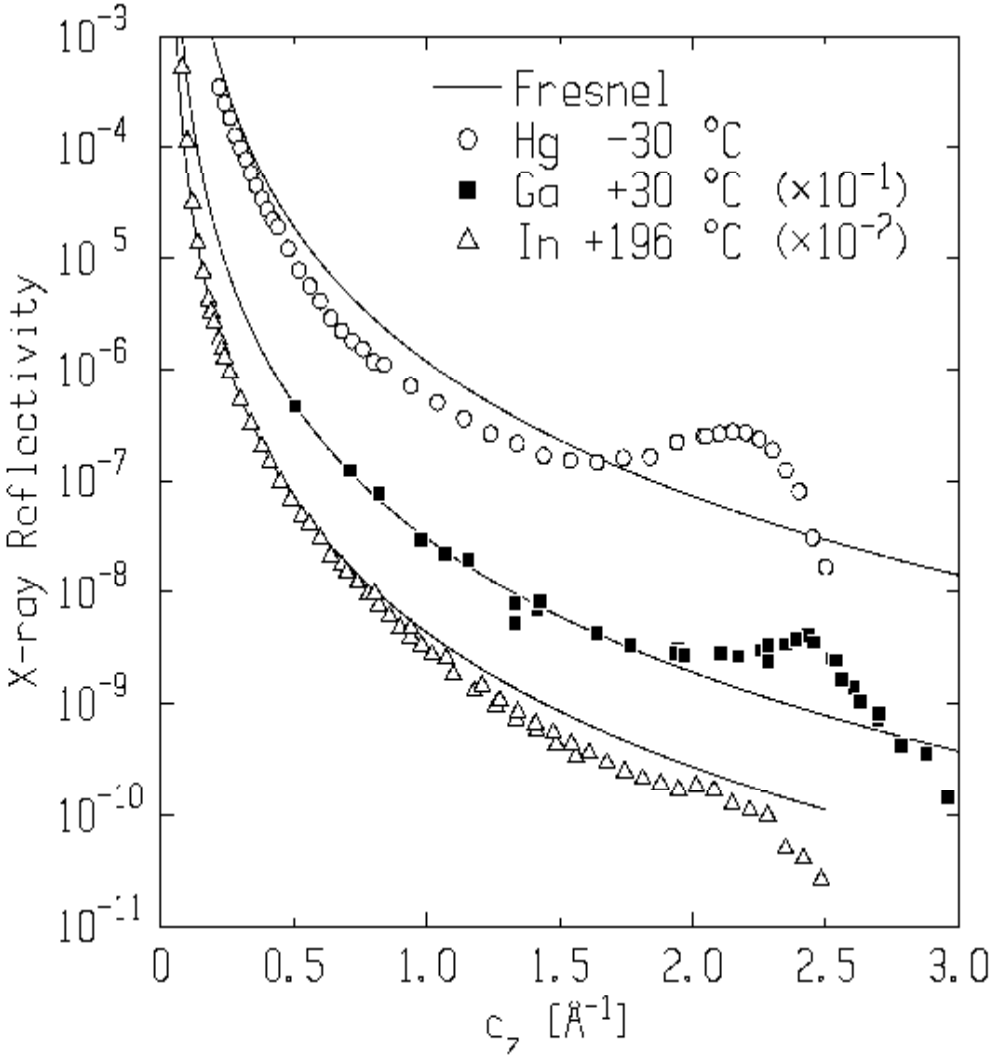
# Examples: surface-induced layering




Disordered Interface
(classical Van-der-Vaals treatment)

Ordered Interface:
Surface-Induced Layering

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

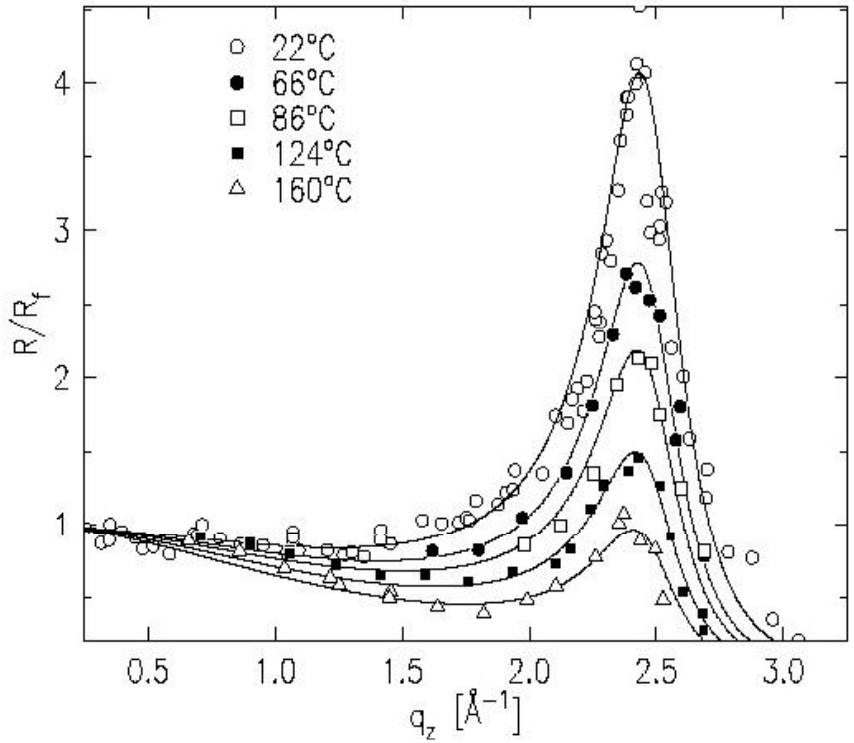



- Quasi-Bragg peak is evidence of layering
- Layering for In appears to be weaker than for Hg and Ga
- After thermal effects are removed, surface structure factor is <u>the same</u> for all three metals!

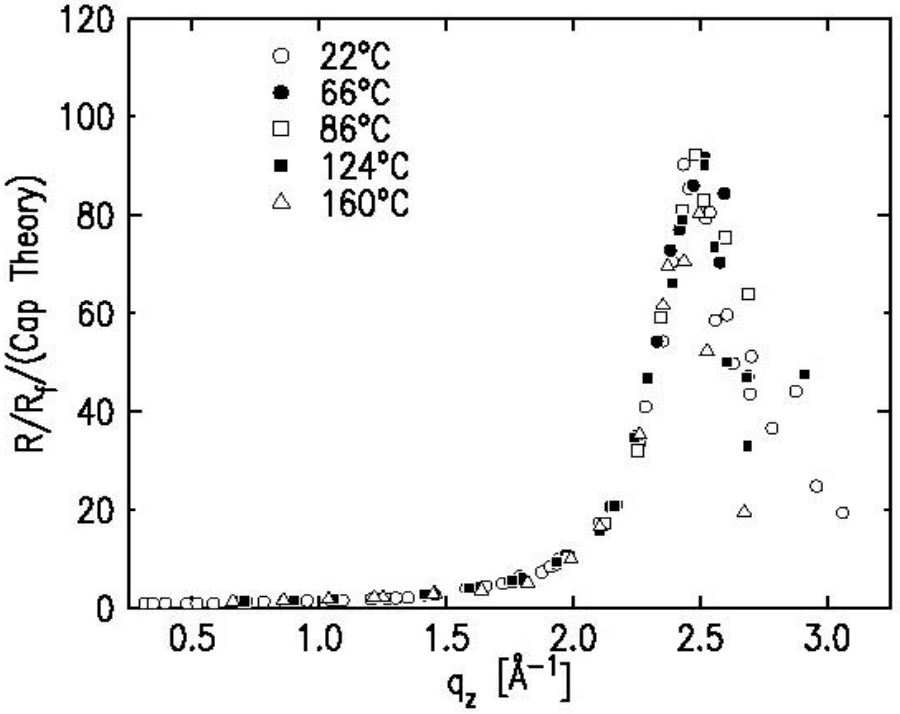
Tostmann et al., Phys. Rev. B **59**, 783 (1999)

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

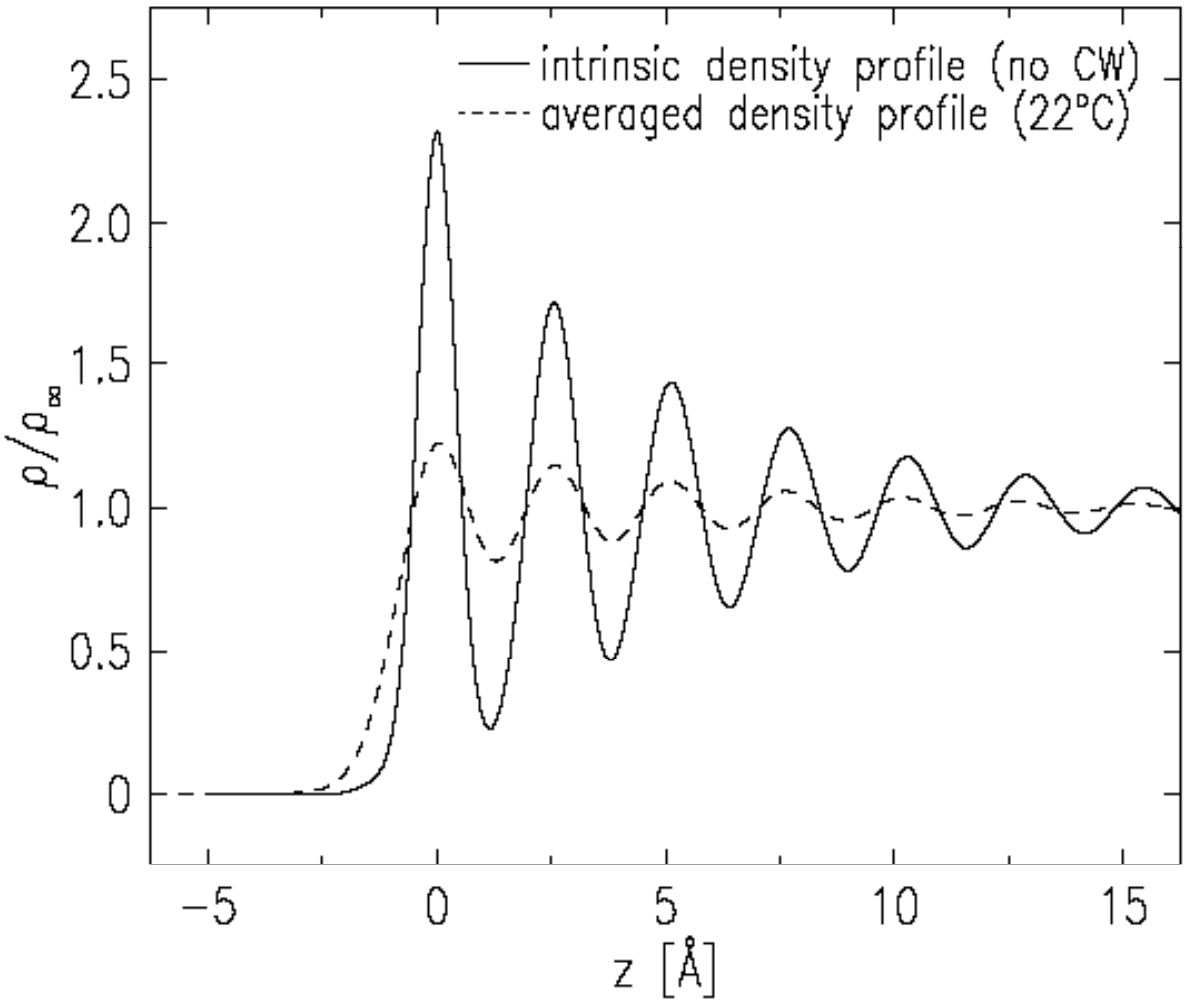
Fresnel-normalized Reflectivity (Ga):



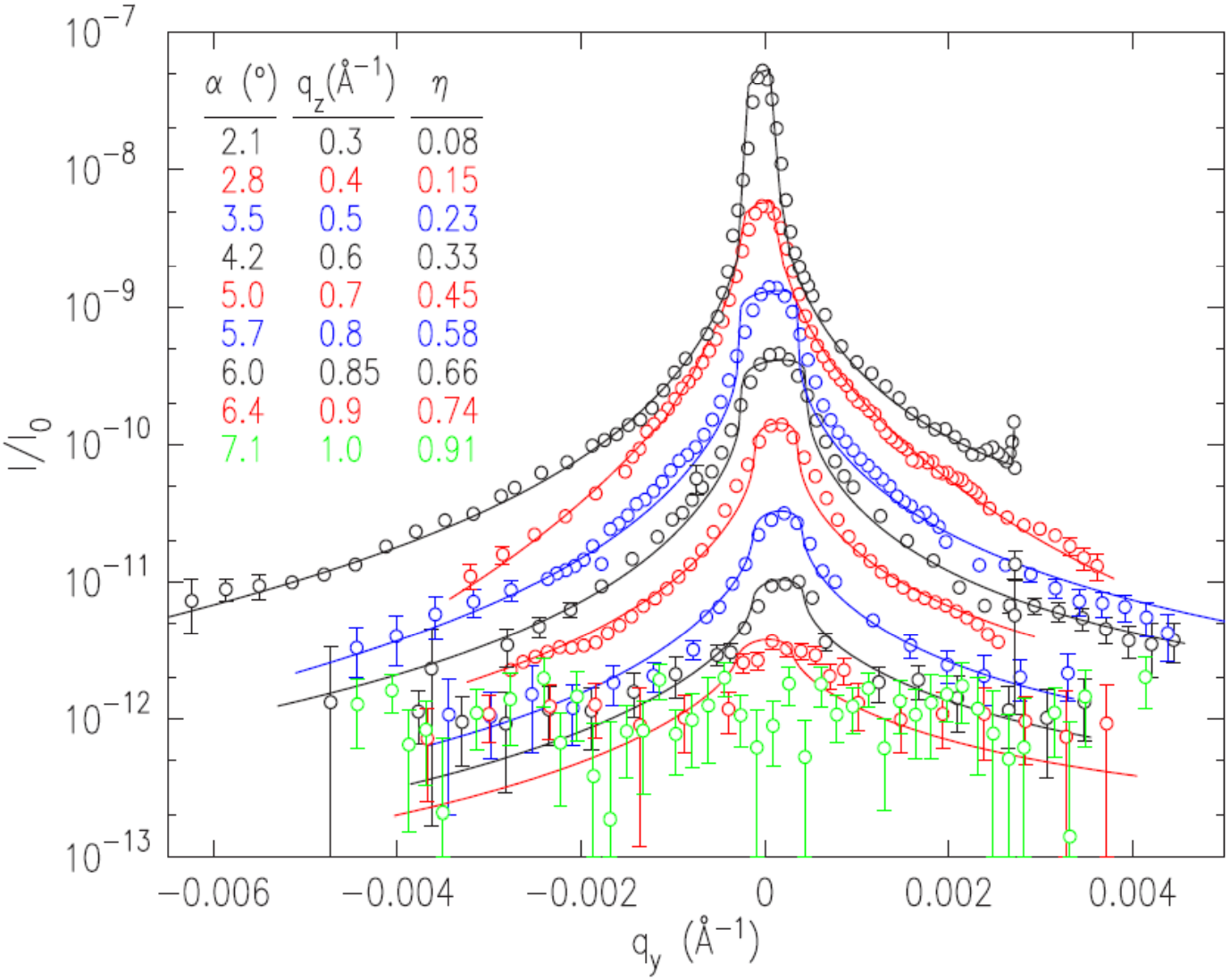

Surface-Structure Factor:
(thermal fluctuations removed)



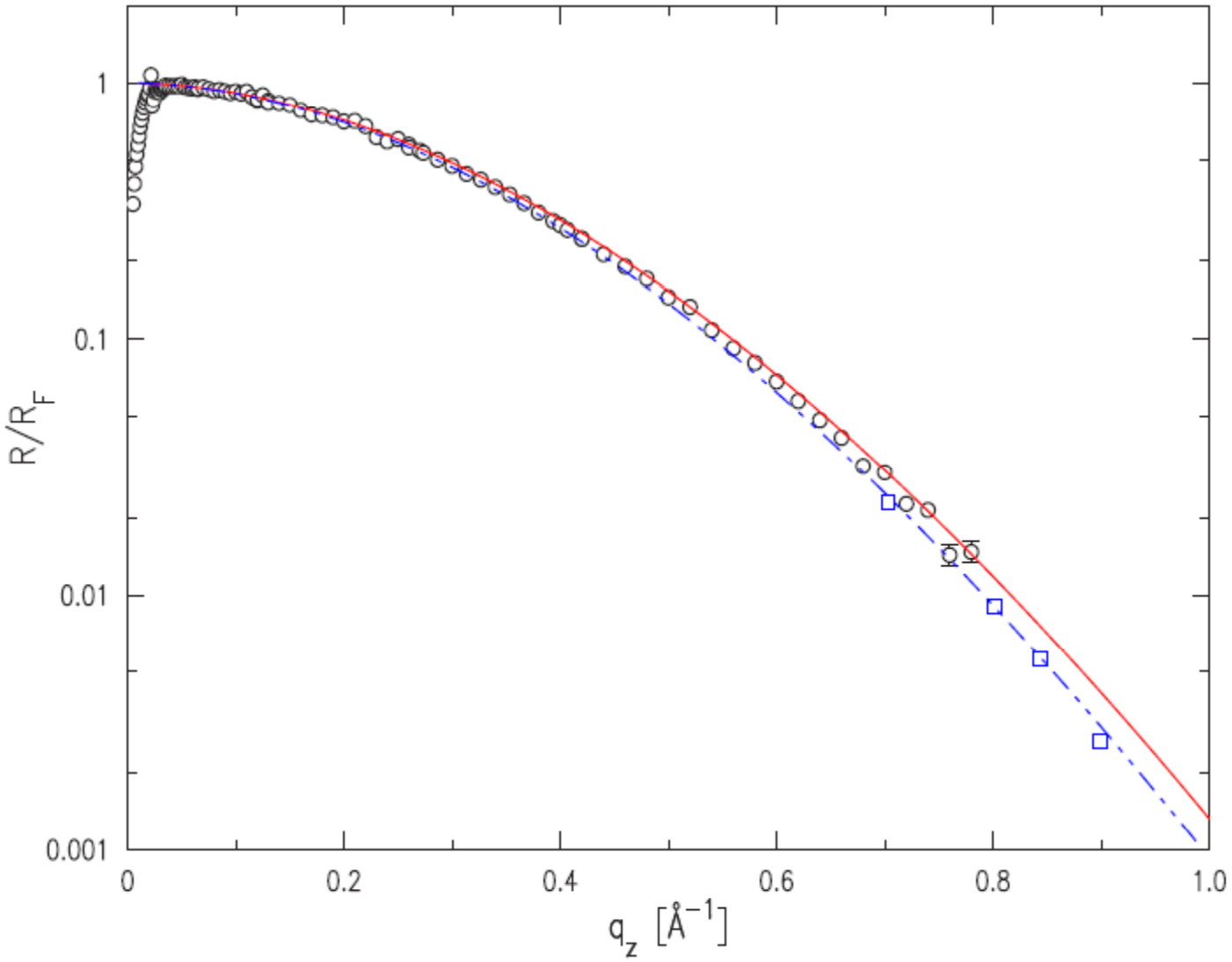
# Fluctuation-averaged density profile is not a meaningful way of describing liquid surfaces



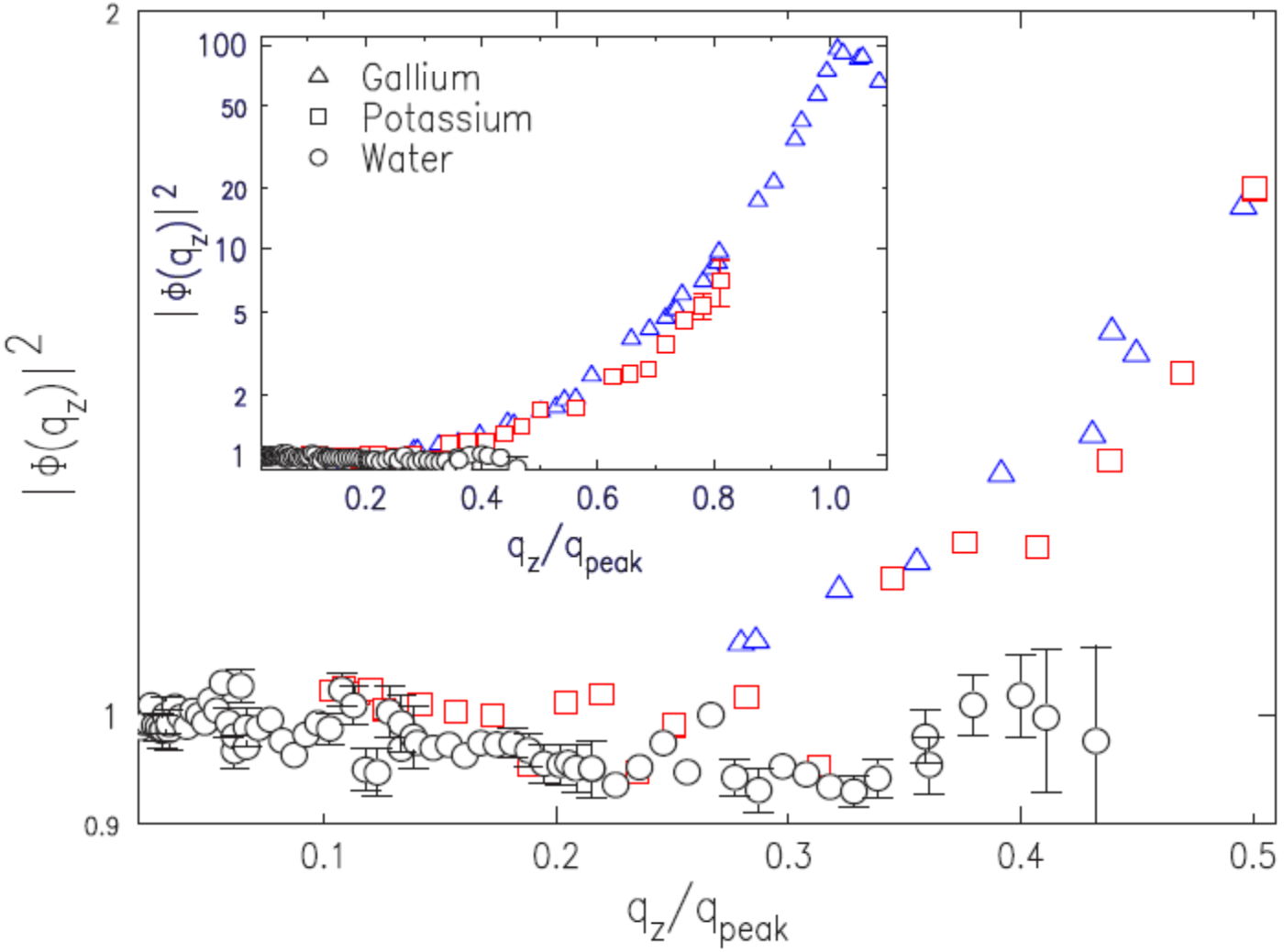
# Diffuse scattering scans for water note decreasing peak-to-wings ratio



# Fresnel-normalized reflectivity for water



# Structure factor for water



# 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)

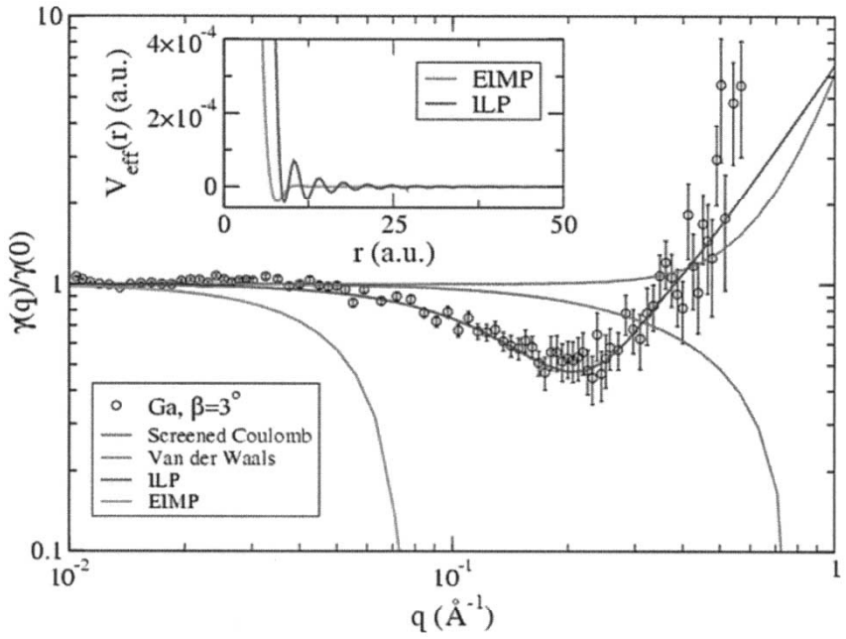
**Reviews:**

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)

# Surface tension at small lengthscales

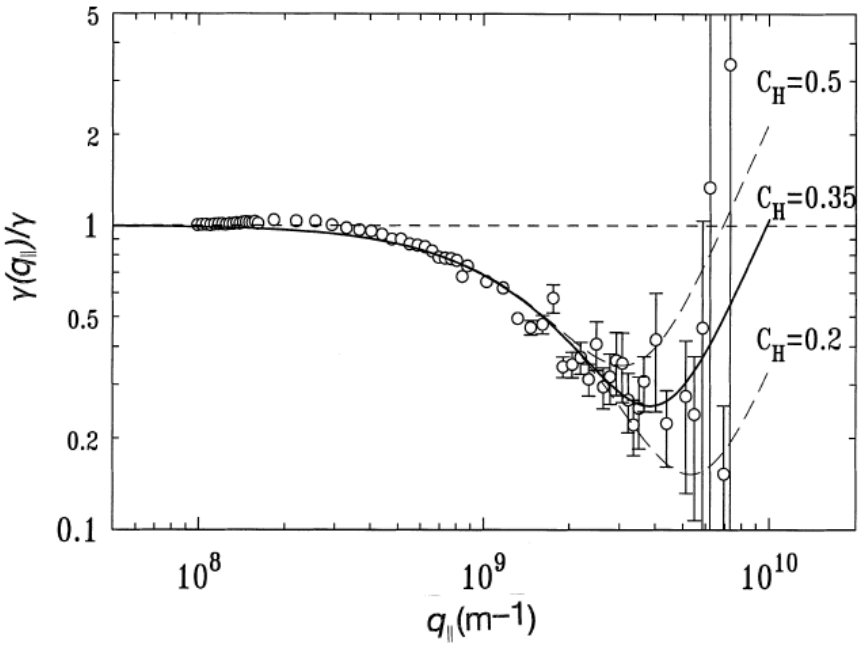
## (deviations at lateral scales < 1nm)

Liquid Ga



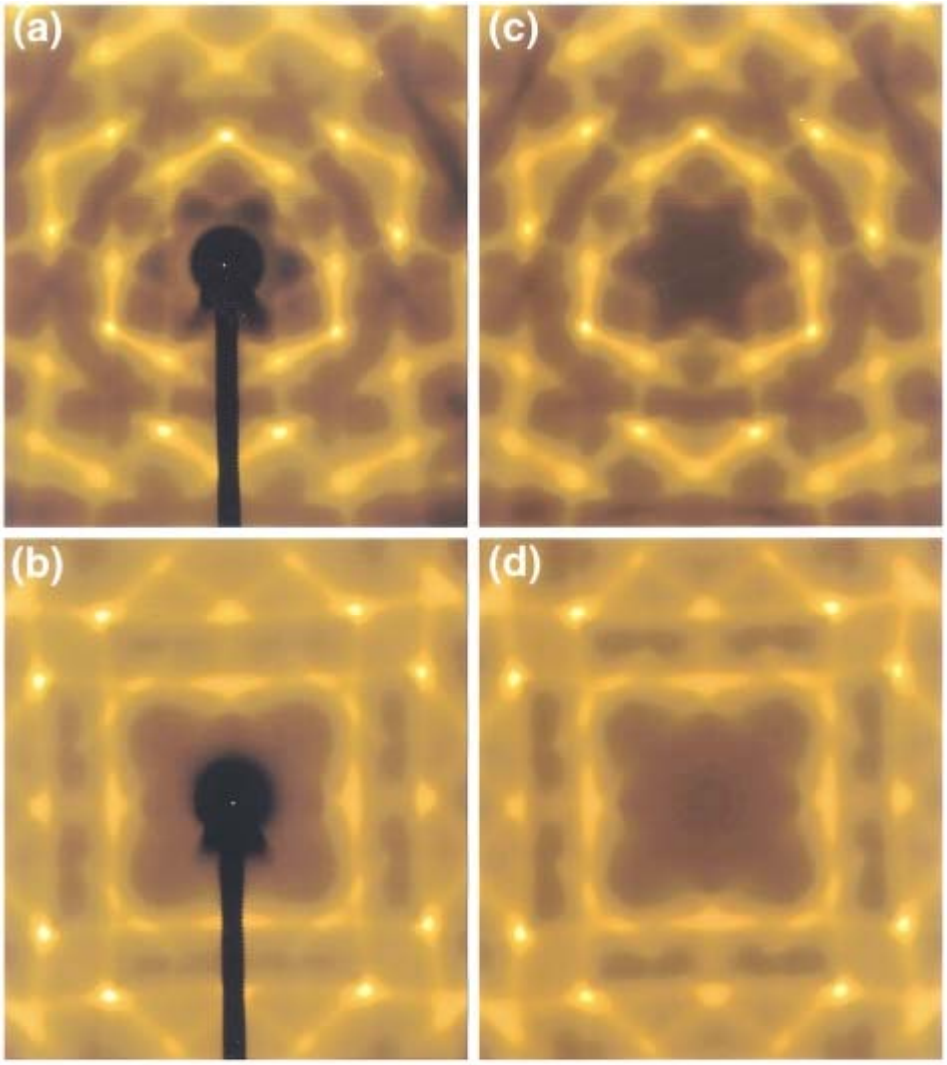

D. Li et al., PRL **92**, 136102 (2004)

Liquid water

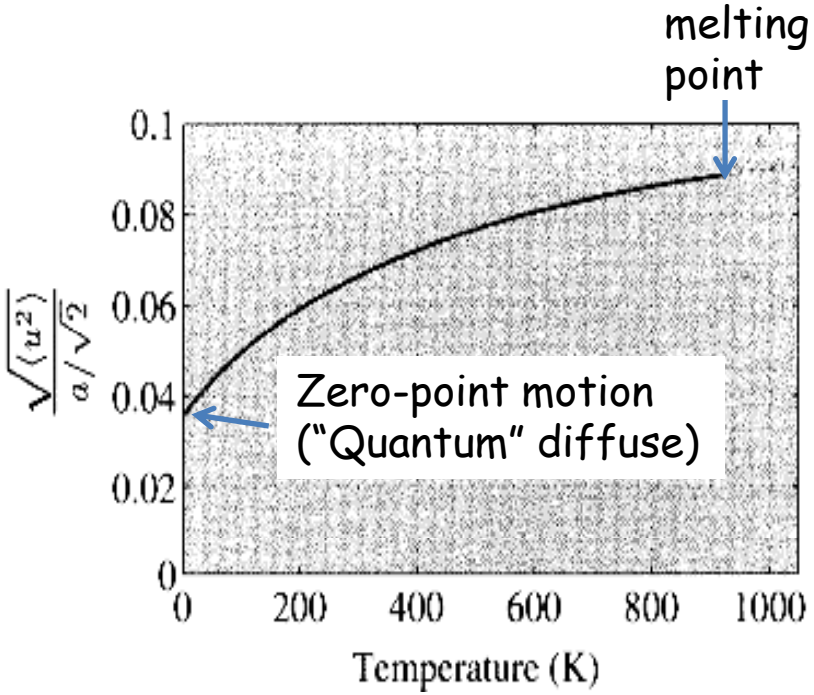



C. Fradin et al., *Nature* **403**, 871 (2000)

# Hidden Bonus Slide: Diffuse Scattering in Solid State




Diffuse scattering in Si crystals
M. V. Holt et al., Phys. Rev. Lett. 83, 3317 (1999)




Average atomic displacement for Al

★ Look up:
Lindemann criterium for melting

# Capillary Wave calculations

(for mathematically inclined)

$$U = \frac{\gamma}{2} \int d^2\mathbf{r}_{xy} \mid \nabla_{xy} h(\mathbf{r}_{xy}) \mid^2 + \frac{\rho g}{2} \int d^2\mathbf{r}_{xy} h(\mathbf{r}_{xy})^2$$

$$h(\mathbf{r}_{xy}) \equiv \frac{1}{2\pi} \int d^2\mathbf{Q}_{xy} \tilde{h}(\mathbf{Q}_{xy}) e^{i\mathbf{Q}_{xy} \cdot \mathbf{r}_{xy}}$$

$$\frac{k_B T}{2} = \tfrac{1}{2}(\gamma \mid \mathbf{Q}_{xy} \mid^2 + \rho g) 4\pi^2 \langle \tilde{h}(\mathbf{Q}_{xy})^2 \rangle$$

$$\langle h(0)^2 \rangle = \frac{k_B T}{4\pi^2 \gamma} \int d^2\mathbf{Q}_{xy} \frac{1}{\mid \mathbf{Q}_{xy} \mid^2 + k_g^2}$$