Off-specular Diffuse Scattering

Liquid Scattering X-ray School November 2007

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⭐ “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 \( \alpha_c \)

\[ n \sin(\alpha_c) = \sin\left(\frac{\pi}{2}\right) = 1 \]

For x-rays:

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

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

Q: How can \( n \) be < 1? (Speed of light > c?)
X-ray Reflectivity and Diffuse Scattering

Formal Solution

\[ n(x,y,z) = n(z) + \delta n(x,y,z) \]

- Refractive Index of the sample \( n(x,y,z) \)
- Refractive Index Profile
- Lateral Distortions
- Diffuse Scattering
Fresnel Law

\[ R_F(\alpha) = \frac{I_r(\alpha)}{I_0} \]

"Ideal" Interface:
Static, Flat,
Sharply terminated

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

\[ R_F(q_z) = \left| \frac{q_z - \sqrt{q_z^2 - q_c^2}}{q_z + \sqrt{q_z^2 - q_c^2}} \right|^2 \approx \left( \frac{q_c}{2q_z} \right)^4 \]

Where \( q_c \approx 4\sqrt{\pi \rho} \)

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

\[ \star \star \quad \text{Q: How come reflectivity does not depend on angles & wavelength, but only on combination of the two (q_z, q_c)} \]
Penetration depth:

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

Penetration depth for $q < q_c$

$$\Lambda \approx \frac{1}{q_c} \sim 15 - 100 \text{ Å}$$

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

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

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 $\sim$ 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 $\sim 10^{-6}$ 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)

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

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

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

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

This demands for sources with $10^{10} \text{ph/sec}$
Reflectivity from “Non-Ideal” Interfaces

Two main complications:
1. Structure
2. Dynamics

Real-life liquid surfaces are not structureless & not static!

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

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

- $R_F(q_z)$: Fresnel (ideal surface)
- $\Phi(q_z)$: structure
- $CW(q, T, \gamma)$: Dynamics (capillary wave term)
Surface Structure Factor:

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

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
\[
\frac{\langle \rho(z) \rangle}{\rho(\infty)}
\]
Capillary Waves

Reminder:

- gravity waves (long-wavelengths)
- capillary waves (short-wavelengths)

Crossover at lengthscale $\xi \sim \sqrt{\frac{\gamma}{\rho g}}$ (or $\sim 3$ 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 \(\sim 2.4\ \text{Å}\)

Actual (correct) expression includes resolution effects:

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

★ 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 $\sim T/\gamma$
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
\[ g(R) \sim k_BT/\gamma \ln(R) \]
\[ \frac{d\sigma}{d\Omega} \approx \frac{1}{q_x^4} \frac{1}{q_{xy}^{2-\eta}} \]
where \[ \eta = \frac{k_BT}{2\pi\gamma q_z^2} \]

☆ Read this paper!
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)

\[ \langle \sigma_\alpha(r)\sigma_\alpha(0) \rangle = \frac{1}{\beta J} \int_0^{1/a} \frac{d^d k}{(2\pi)^d} \frac{e^{ik\cdot r}}{k^2} \]

The integral diverges as ln(r) for \( d \leq 2 \)
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:

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

Experimentally measured reflectivity:

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

Fresnel Reflectivity

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

Surface Structure Factor

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

Capillary excitations * Resolution function
Know Thy Experimental Resolution!
(Crucially important for diffuse scattering - less so for reflectivity)

Simulated Detector Scan

![Graphs showing simulated detector scans with different slit widths and scattering angles.](attachment:image.png)
First measurements of diffuse scattering for water

Temperature dependent capillary wave roughness

Thermal roughness of $C_{20}$ alkanes follows thermal scaling predicted by capillary wave theory

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

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 the same for all three metals!

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)

Experiment:

Reviews:
Surface tension at small lengthscales

(deviations at lateral scales < 1nm)

D. Li et al., PRL 92, 136102 (2004)
Hidden Bonus Slide: Diffuse Scattering in Solid State

Diffuse scattering in Si crystals

Look up:
Lindemann criterium for melting
Capillary Wave calculations
(for mathematically inclined)

\[ U = \frac{\gamma}{2} \int d^2r_{xy} \left| \nabla_{xy} h(r_{xy}) \right|^2 + \frac{\rho g}{2} \int d^2r_{xy} h(r_{xy})^2 \]

\[ h(r_{xy}) \equiv \frac{1}{2\pi} \int d^2Q_{xy} \tilde{h}(Q_{xy}) e^{iQ_{xy} \cdot r_{xy}} \]

\[ \frac{k_B T}{2} = \frac{1}{2}(\gamma \left| Q_{xy} \right|^2 + \rho g) 4\pi^2 \langle \tilde{h}(Q_{xy})^2 \rangle \]

\[ \langle h(0)^2 \rangle = \frac{k_B T}{4\pi^2\gamma} \int d^2Q_{xy} \frac{1}{\left| Q_{xy} \right|^2 + k_g^2} \]