Off-specular Diffuse Scattering

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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:

\[ n = 1 - \delta \text{ where } \delta \approx 10^{-6} \]

Critical angle \( \approx \sqrt{2\delta} \) or \( \sim 1\text{mrad} \)

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

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

“Ideal” Interface:
Static, Flat,
Sharply terminated

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

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

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

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

\( \star \) 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 $q < q_c$

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

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)
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 $\sim 10^{-6}$ 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

\[ R_F(q_z) = \left( \frac{q_z - \sqrt{q_z^2 - q_c^2}}{q_z + \sqrt{q_z^2 - q_c^2}} \right)^2 \sim \left( \frac{q_c}{2q_z} \right)^4 \]
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 $10^{10}$ 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 $CW(q, T, \gamma)$

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

- $R_F$ (Fresnel, ideal surface)
- $\Phi(q_z)$ (structure)
- $CW(q, T, \gamma)$ (capillary wave term)
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 \(\gamma\) \([\text{Energy}/\text{L}^2]\)

vs. Thermal Energy \(k_B T\) \([\text{Energy}]\)

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:

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

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

Specular (mostly):

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):

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

Liquid Surfaces:

\[ g(R) \sim k_B T/\gamma \ln(R) \]

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

where

\[ \eta = \frac{k_B T}{2\pi \gamma q_z^2} \]

Scattering from liquid surfaces

Scattering cross-section:

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

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

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

Resolution function

Capillary excitations
Structure Factor:

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

![Graph showing the structure factor for water and other elements like Gallium, Potassium, and Water. The x-axis represents \( q_z/q_{\text{peak}} \), and the y-axis represents \( |\Phi(q_z)|^2 \).]
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: