Using specular X-ray reflectivity to study liquid surfaces & interfaces

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X-ray scattering from surfaces

\[ R(q) = R_F(q) \left| \frac{1}{\rho_o} \int d\rho(z) \exp(i q'z) dz \right|^2 \]

Here \( \rho(z) \) is averaged over the x- and y-directions.

\[ q = k_{out} - k_{in} \]

\[ q = |q| = 2|k| \sin \theta \]

\[ q'^2 = q^2 - q_{crit}^2 \]
\[ R(q) = R_F(q) \left| \frac{1}{\rho_o} \int \frac{d\rho(z)}{dz} \exp(iq'z) dz \right|^2 \]

If interface is sharp: \( d\rho/dz = \rho_o \delta(z) \)

Then \( R = R_F \approx (q_c/2q)^4 \)…very steep (solid lines)

If \( \rho(z) \) is not a step function but something more interesting, the reflectivity deviates from \( q^{-4} \).

(Usually \( R/R_F \) is plotted…ideally flat)

Tostmann et al, PRB (1999)
X-ray reflectivity studies of liquids

Liquid surfaces:
• capillary waves at liquid surfaces
• layering (liquid-crystalline order) at liquid surfaces
• Langmuir monolayers

Liquid interfaces:
• layering (liquid-crystalline order) at liquid-solid interfaces
• monolayer formation (self-assembly) at solution-solid interfaces
• the interface between water and a hydrophobic surface
• liquid-liquid interfaces

(not all these will be discussed here…some have been covered in previous talks)
Strengths of the technique:

can be used to determine **arbitrary density profiles** (not limited to periodic functions or other specific functions)

can go to **much smaller length scales** than e.g. optical methods

X-rays can penetrate materials to reflect from **internal interfaces**

Provides information averaged over the X-ray “footprint”
Weaknesses of the technique:

Sees structure only in **one direction** (averaged over other directions)

**sharp drop in intensity with** \( q \) **makes it harder to get statistically significant data at large** \( q \); **and total external reflection places a low-**\( q \) **limit on the data**

the Fourier transforms of data with limited range and accuracy are not unique…. **postulated density functions (models) must be fitted to the data**

for X-rays, \( \rho \) is the **electron density**…X-rays are not chemically sensitive

**surface roughness** must be small compared to length scales of interest
1. In situ studies of self-assembly from solution

or: how we learned about density contrast the hard way!

octadecyltrichlorosilane SAMs on oxidized silicon

solution

SAM

substrate

Island Growth

Uniform Growth

Vertical, Random Growth
Typical density profiles:
Si/film/air and Si/film/solvent

Calculated reflectivity data with various solvents

Time-resolved X-ray reflectivity data during SAM growth
SAM thickness and density monitored in real time using X-ray reflectivity.

2. Is there a depletion layer between water and a hydrophobic surface?

3. The interface between a solid and a pure liquid

Density Profile vs Depth

Simulation of Lennard-Jones fluid

Surface force measurements

Israelachvili and Gourdon, Science 292, 867 (2001)
X-rays can be used to look at a single interface

Sample: ~5000Å wetting film of liquid on a solid substrate

Too thick to see interference between substrate and interface reflections (which we don’t want to see)

…but thin enough that X-rays can go to the interface and back out without too much absorption.

Sample need not be kept horizontal.
TEHOS film at Si surface

OMCTS, TTMSS

![Graphs showing R vs. q for OMCTS and TTMSS](slide)

- **OMCTS**
  - Graph showing R vs. q with a peak at q ≈ 1 Å⁻¹.
  - Inset graph showing R vs. q with a peak at q ≈ 0.8 Å⁻¹.

- **TTMSS**
  - Graph showing R vs. q with a peak at q ≈ 0.9 Å⁻¹.
Squalane film at Si surface

Structure of squalane as projected onto its carbon backbone plane

Specular (red) and slightly off-specular (blue, black) reflectivity scans from a squalane-silicon interface, showing that there is anisotropic order

Effect of shear on interfacial ordering

- kapton window
- silicon substrate under window
- Sample holder
- housing
- Magnetic seal
- liquid (between window and seal)
Shear thinning of TEHOS films

Normalized x-ray reflectivity data for ~13μm thick TEHOS film: unsheared (top), after rotational shear for one minute at the shear rate of 270 ± 40 s⁻¹ (center) and 800 ± 40 s⁻¹ (bottom).

The height of the TEHOS diffraction peak (A) vs. shear rate (applied for 1 min.) Beyond a threshold rate, the amplitude drops rapidly.

Effect of shear on chain-molecule liquids

Normalized x-ray reflectivity data for a ~1μm thick PDMS film. Scan (a) is from unsheared PDMS. Subsequent scans shown were taken (b) 0.5 hours (c) 1 hour (d) 3 hours after shear was applied for 1.5 minutes at a rate of $10^4$ s$^{-1}$.

4. Why do liquid metals show surface layering while dielectric liquids do not?

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Surface layering near room temp?</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg</td>
<td>yes</td>
<td>Magnussen et al., PRL 74, 4444 (1995)</td>
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<td>In</td>
<td>yes</td>
<td>Regan et al., PRL 75, 2498 (1995)</td>
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<td>Ga</td>
<td>yes</td>
<td>Tostmann et al., PRB 59, 783 (1999)</td>
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<tr>
<td>alkanes</td>
<td>no</td>
<td>Ocko et al., PRL 72, 242 (1994)</td>
</tr>
<tr>
<td>ethanol</td>
<td>no</td>
<td>Sanyal et al., PRL 66, 628 (1991)</td>
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<tr>
<td>toluene</td>
<td>no</td>
<td>Zhao et al., JCP 97, 8536 (1992)</td>
</tr>
<tr>
<td>TEHOS</td>
<td>no</td>
<td>Yu et al., PRE 63, 21205 (2001)</td>
</tr>
<tr>
<td>etc…</td>
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Surface layers seen in Monte Carlo simulations by Chacón et al, PRL 87, 166101 (2001); Li & Rice, JPC B 108, 19640 (2004): *no electrons in simulation, but T must be less than ~0.2 T_c*

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<th>Liquid</th>
<th>Surface layering near room temp?</th>
<th>T/Tc near room temp</th>
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</table>
Unfortunately, most dielectric liquids **freeze well above the predicted $T/T_c$ range.**

Dielectric liquid used in our experiments: **tetrakis(2-ethylhexoxy)silane**

$T_c \sim 950$ K, $T_m < 190$ K, Vapor pressure: $< 0.01$ mm Hg

not liquid crystalline, not viscoelastic

Molecular diameter $\sim 10$ Å

![Silane group is surrounded by four branched alkanes forming a nonreactive protective shell](image-url)
We studied wetting films of TEHOS on oxidized silicon surfaces with roughness $>20\text{Å}$. This eliminates any features due to interfacial ordering.
Reflectivity data from TEHOS film at various temperatures

Features appear as temperature is lowered

At 225K, $T/T_c \sim 0.23$

Modified Distorted Crystal model
[based on DiMasi et al., PRB 58, R13419 (1998)]

\[
\frac{\rho}{\rho_{\text{bulk}}} = r \sum_{n=0}^{1} \frac{d_0}{\sqrt{2\pi}\sigma_n} e^{-\frac{(z+nd_0)^2}{2\sigma_n^2}} + \sum_{n=2}^{\infty} \frac{d_1}{\sqrt{2\pi}\sigma_n} e^{-\frac{[z+(n-2)d_1+2d_0]^2}{2\sigma_n^2}}
\]

where

\[
\sigma_n^2 = \sigma_i^2 + \sigma_{cw}^2 + n\bar{\sigma}^2,
\]

\(\sigma_i\): intrinsic layer width
\(\sigma_{cw}\): capillary width
\(n\sigma^2\): layer-number-dependent term
Red dashed lines: best fit electron density profile (using modified distorted crystal model)

Blue lines: same function with $\sigma_{CW} = 0$, i.e. density profile with capillary broadening removed

Other fitting methods also work, and reveal the same basic features (density oscillations, density increase near surface)

Prior report of density enhancement at layered surface (of liquid Sn):

Shpyrko et al., PRB 70, 224206 (2004)

Surface layering (when not preempted by freezing) is a universal property of liquids.

Fitting parameters appear to vary continuously through the onset of layering (no theoretical work on the ‘transition’ yet)

Layer spacing, first two layers

Intrinsic (non-capillary) layer width

Mean density, first two layers (1.0=bulk density)

Layer spacing, 3rd layer and beyond

Red and blue symbols are from different samples.

SUMMARY

Specular X-ray reflectivity can be used to study a wide variety of problems in the area of liquid surfaces and interfaces.

It has its limitations, requires very smooth surfaces, and some caution is required when interpreting the data…

…but where it works well, no other tool can see what it sees!

Other relevant topics that were not discussed:

- Langmuir (floating) monolayers
- Off-specular scattering, capillary waves
- Liquid-liquid interfaces
\[ \sigma_{cw}^2 = \frac{k_B T}{2 \pi \gamma} \ln \frac{2q_{\text{max}}}{q_z \Delta \beta}, \quad q_{\text{max}} \sim \frac{\pi}{a}, \quad q_z = 0.4 \text{ Å}^{-1} \]
Comparison of bulk diffraction data (red) and grazing-incidence scattering data (blue) at 190K.

(a) no sharp peaks in surface data, i.e. no surface freezing;
(b) no new broad peaks (e.g. from impurities) visible in surface data.
Could the structure be due to impurities segregating to the surface?

Impurities will go to the surface only if this sufficiently decreases the surface energy.

No evidence of surface width increase at lower temperatures.

(The plotted surface width is the distance from $\rho/\rho_{bulk} = 0.9$ to $\rho/\rho_{bulk} = 0.1$.)
Measured TEHOS surface tension vs. temperature, fitted to

\[ \ln(\gamma) = A + n \ln(T_c - T) \]  

(see e.g. Maroto et al., Eur. J. Phys. 25, 297 (2004))

...and extrapolated to estimate the surface capillary width at lower temperatures