Synchrotron X-ray Scattering from Liquid Surfaces and Interfaces

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Abstract: Synchrotron X-ray scattering studies have transformed our understanding of liquid surfaces and interfaces, which play an important role in many biological, environmental, and technological processes. During the past several decades these studies have begun to explore the relationship between the nanoscale interfacial structure and interfacial properties and function. Recent work has explored the advantages of energy-dependent surface probes and, in some cases, combined them with more traditional surface scattering techniques. This chapter presents the capabilities and applications of traditional and developing surface X-ray scattering techniques used in the study of liquid surfaces and interfaces.
# Table of Contents

Abbreviations .................................................................................................................. 3

Introduction to Scattering from Liquid Surfaces and Interfaces ........................................ 4

X-ray Reflectivity (XR) ....................................................................................................... 6

X-ray Diffuse Scattering (XDS) .......................................................................................... 19

Grazing Incidence X-ray Diffraction (GIXD) .................................................................. 24

Grazing Incidence Small Angle X-ray Scattering (GISAXS) ............................................ 28

Spectroscopy at Liquid Interfaces ....................................................................................... 31

Anomalous X-ray Reflectivity. ............................................................................................ 32

X-ray Fluorescence Near Total Reflection (XFNTR). ......................................................... 33

X-ray Absorption Fine Structure (XAFS) ......................................................................... 38

Time Resolved Measurements ........................................................................................... 39

1D Pinhole GIXD. .............................................................................................................. 39

Grazing Incidence X-ray Off-Specular Scattering (GIXOS). .............................................. 41

Energy Dispersive Reflectivity. .......................................................................................... 42

Surface X-ray Photon Correlation Spectroscopy (XPCS) .................................................. 44

References ......................................................................................................................... 46
## Abbreviations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>DHDP</td>
<td>Di-hexadecyl phosphate</td>
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<td>DWA</td>
<td>Distorted-wave approximation</td>
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<tr>
<td>EXAFS</td>
<td>Extended X-ray absorption fine structure</td>
</tr>
<tr>
<td>GISAXS</td>
<td>Grazing incidence small angle X-ray scattering</td>
</tr>
<tr>
<td>GIXD</td>
<td>Grazing incidence X-ray diffraction</td>
</tr>
<tr>
<td>GIXOS</td>
<td>Grazing incidence X-ray off-specular scattering</td>
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<tr>
<td>XAFS</td>
<td>X-ray absorption fine structure</td>
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<td>XANES</td>
<td>X-ray absorption near edge structure</td>
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<tr>
<td>XAS</td>
<td>X-ray absorption spectroscopy</td>
</tr>
<tr>
<td>XDS</td>
<td>X-ray diffuse scattering</td>
</tr>
<tr>
<td>XFNTR</td>
<td>X-ray fluorescence near total reflection</td>
</tr>
<tr>
<td>XPCS</td>
<td>X-ray Photon Correlation Spectroscopy</td>
</tr>
<tr>
<td>XR</td>
<td>X-ray reflectivity</td>
</tr>
</tbody>
</table>
Introduction to Scattering from Liquid Surfaces and Interfaces

Synchrotron X-ray scattering from liquid surfaces and interfaces has been indispensable in the investigation of the fundamental science of soft interfaces and in the study of controlled model systems for natural processes important in physical, chemical, biological, and technological systems. X-ray surface scattering is the most powerful probe of near-atomic level structure at liquid-vapor and liquid-liquid interfaces, though neutron reflectivity provides complementary structural information. Over the past twenty years surface-sensitive X-ray techniques have led to many key discoveries, which include the role of fluctuations at soft interfaces (Schwartz et al. 1990; Sanyal et al. 1991), the structures of two-dimensional molecular and biomolecular films supported on liquid surfaces and interfaces (Dutta et al. 1987; Wolf et al. 1987; Kjaer et al. 1987), surface ordering of organic and metallic liquids (Pershan et al. 1987; Wu et al. 1993; Regan et al. 1995), and the distribution of ions at charged and electrified interfaces (Bloch et al. 1988; Luo et al. 2006). Such studies provide information that is unobtainable by any other technique and have led to a fundamentally new scientific understanding of these systems (Pershman and Schlossman 2012).

Liquid interfaces are relevant to scientific and technological processes in the areas of energy and the environment. To address these vital needs there is currently much interest in understanding complex phenomena at liquid interfaces. These include the separation of toxic or radioactive metals from polluted environments and nuclear waste, as well as the production of industrially relevant metals (Rydberg et al. 1992; Guyon et al. 2000; Stevens et al. 1997). A range of scientific investigations into interfacial structure and kinetics supports applications in these areas, including studies of interfacial distributions of metal ions, the organization of amphiphilic extractants, ion/amphiphile interactions, and the role of electrostatics at interfaces. Another example of complex phenomena at liquid interfaces is

\[ \Delta \]
the heterogeneous chemistry at the liquid surface of sea salt aerosols, which influences many reactions including those believed responsible for depletion of ozone in the lower troposphere at high latitudes in the spring (Jungwirth and Tobias 2001; Rossi 2003). More generally, liquid interfaces provide model systems to study the self-assembly, interfacial orientation and forces, molecular interactions, and chemical reactivity of a wide range of materials. Understanding these complex processes requires X-ray surface scattering techniques because they probe molecular adsorption and ordering at the interface.

An area of increasing interest is the use of directed assembly on the nanoscale to fabricate functional biomolecular materials. Studies in these areas take advantage of chemically and biologically inspired pathways to harness nanoscale ordering for specific functionalities such as switches, charge transport, molecular recognition and synthesis. Monolayers of biomolecules on the surface of aqueous solutions are used to model processes such as signaling, electron transfer, and optical responses that are important for the development of biomolecular materials with novel properties. X-ray scattering from liquid interfaces has a unique role in monitoring the assembly of these materials on atomic and molecular length scales.

The investigation of such complex interfacial structures will require the high spatial resolution, element sensitivity, and time resolution that can be provided by the ongoing development of synchrotron X-ray sources and surface scattering techniques. Multiple surface scattering techniques are required to investigate these systems in order to span the relevant length scales (Ångstroms to micrometers) and to probe the varied structures of these materials, which range from crystalline to weakly ordered to amorphous. New scientific opportunities have emerged from recent advances in techniques to provide element sensitivity within complex liquid interfaces. The development of both element-specific and time-resolved techniques applicable to liquid interfaces has the potential to enable a broad class of new research. Nearly the full range of X-ray surface scattering techniques that have
been applied to the study of liquid surfaces and interfaces is reviewed in this article, along with selected examples of applications of these techniques.

**X-ray Reflectivity (XR)**

X-rays reflect from an interface separating two materials with different refractive indices, where the X-ray refractive index $n$ of a material varies with its electron density $\rho$ (electrons per unit volume), according to

$$ n = 1 - \zeta + i\beta, $$

with

$$ \zeta = 2\pi\rho r_e (1 + f' / Z) / k_0^2 $$

and

$$ \beta = 2\pi\rho r_e (f'' / Z) / k_0^2 = \mu / 2k_0, $$

where $r_e \approx 2.818 \times 10^{-15}$ m is the classical radius of the electron, $f'$ and $f''$ are the real and imaginary parts of the anomalous dispersion correction to the atomic scattering factor, $Z$ is the atomic number, $k_0 = 2\pi/\lambda$ is the wave vector where $\lambda$ is the X-ray wavelength, and $\mu$ is the linear absorption coefficient. The expressions for $\zeta$ and $\beta$ are accurate near the forward scattering direction, though corrections are negligible for most X-ray scattering from liquid interfaces. The factors $\zeta$ and $\beta$ are wavelength dependent, and typically of the order of $10^{-6}$ and $10^{-8}$, respectively, for low $Z$ liquids and X-ray wavelengths near 1 Å. The real part of the index of refraction is slightly less than unity and decreases with increasing electron density of the material. Here, we have assumed that the material consists of one type of atom, but Eq. (1) can be applied to materials with multiple types of atoms by weighting their contributions appropriately, as described later.

X-rays are reflected by a sufficiently smooth surface into the specular direction defined by $\alpha_i = \alpha_d$ and $\theta_d = 0$, where the angles are defined in Fig. 1. X-rays are totally externally reflected from
a liquid-vapor interface when the incident angle $\alpha_i$, measured from the interfacial plane, is below a small angle $\alpha_c \approx \sqrt{2\zeta}$, known as the critical angle for total reflection. The reflected beam intensity varies with larger values of $\alpha_i$. X-ray reflectivity (XR) measurements record the intensity of the reflected beam normalized by the intensity of the incident beam as a function of the incident angle to yield $R(Q_z)$, the reflectivity as a function of wave vector transfer $Q_z = 2k_0 \sin \alpha_i$. XR probes the variation of electron density $\langle \rho(z) \rangle$ along the direction $z$ perpendicular to the interface, but averaged over the $x-y$ region of the X-ray footprint on the interface. The electron density profile $\langle \rho(z) \rangle$ can be subsequently interpreted to reveal the arrangement of molecules at the interface.

![Figure 1. Kinematics for surface X-ray scattering techniques. An incident X-ray beam propagating in the $x-z$ plane strikes the surface at an angle of incidence $\alpha_i$ with respect to the interface, and the scattered beam is detected at an angle $\alpha_d$ with respect to the interface and at an azimuthal angle $\theta_d$ measured from the $x$ axis. Angular constraints or ranges for various techniques are given as follows: (a) $\alpha_i = \alpha_d$ and $\theta_d = 0$ define the specular condition for X-ray reflectivity (XR); (b) $\alpha_i < \alpha_c$ and $\theta_d \neq 0$ is used for grazing incidence X-ray diffraction (GIXD); (c) $\alpha_i < \alpha_c$ and $\theta_d \approx 0$ is used for grazing incidence small angle X-ray scattering (GISAXS); (d) $\alpha_i \neq \alpha_d$ and $\theta_d = 0$ can be used for off-specular surface]
diffuse scattering, though it is also possible to measure this scattering by scanning away from $\theta_d = 0$;

(e) $\alpha_i \approx \alpha_c$ and $\theta_d \approx 90^\circ$ or $\alpha_d \approx 90^\circ$ is often used to measure X-ray fluorescence near total reflection (XFNTR).

Theoretical calculations of XR vary with the complexity of the interface. The simplest example is the Fresnel reflectivity, $R_F(Q_z)$, that is the result of X-rays reflecting from an ideal interface, which is mathematically flat with an abrupt step-function variation of electron densities from the value $\rho_i$ of the top phase to the value $\rho_b$ of the bottom phase. Taking into account the electromagnetic wave properties and the boundary conditions at the interface (Born and Wolf 1980), the Fresnel reflection coefficient $R_F$ and transmission coefficient $T$ are given by

\[
R_F(Q_z) = \frac{Q_z - \sqrt{Q_z - Q_c}}{Q_z + \sqrt{Q_z - Q_c}}^2
\]

\[
T(Q_z) = \frac{2Q_z}{Q_z + \sqrt{Q_z - Q_c}}^2
\]

Total external reflection, $R_F(Q_z) = 1$, occurs when $Q_z \leq Q_c = 4\pi\Delta\rho r_0$ (with $\Delta\rho = \rho_b - \rho_i$), where $Q_c$ is the critical wave vector transfer for total reflection.

The arrangement of molecules and nanoparticles at liquid surfaces and interfaces leads to a variation of $\langle \rho(z) \rangle$ through the interface, typically on the scale of angstroms to nanometers. In addition, thermal fluctuations roughen the interface with capillary waves. Under the approximation that $x-y$ variations in $\rho(x,y,z)$ can be neglected, the exact solution of reflectivity from $\langle \rho(z) \rangle$ can be calculated using the Parratt formalism for which a continuously varying electron density function $\langle \rho(z) \rangle$ is approximated by a discretized multi-step function (Parratt 1954). Each step represents a
single layer of constant electron density whose thickness can be adjusted to model \( \rho(z) \) with arbitrary precision. The amplitude of the Fresnel reflected and transmitted waves are calculated for each interface between adjacent layers. Successively combining the reflection and transmission from the internal interfaces between layers yields the reflectivity for the entire interfacial structure.

The reflectivity from a general density profile can also be calculated from the Born approximation to yield the so-called master formula (Pershan and Als-Nielsen 1984), given by

\[
\frac{R(Q_z)}{R_F(Q_z)} \approx \left| \Phi_{\text{eff}}(Q_z) \right|^2 \quad \text{with} \quad \Phi_{\text{eff}}(Q_z) = \frac{1}{\Delta \rho} \int d\left\langle \rho(z) \right\rangle \exp(-iQ_z z) dz,
\]

where \( \Phi_{\text{eff}}(Q_z) \) is the effective surface structure factor, which includes the effect of capillary roughness as well as the arrangement of molecules or particles at the interface. Equation (3) demonstrates that the reflectivity normalized to the Fresnel reflectivity is given by the Fourier transform of the electron density gradient in the direction perpendicular to the interface. The master formula is accurate when refraction effects can be neglected, typically in the range \( Q_z > 4Q_c \). Its analytic simplicity is also useful as a guide to understanding qualitative structural features independent of a numerical analysis of reflectivity data. An example of this is provided later.

Since the introduction of the first liquid surface reflectometer (Als-Nielsen and Pershan 1983), XR has become a powerful tool to measure the electron density profile \( \left\langle \rho(z) \right\rangle \) of liquid interfaces with sub-nanometer spatial resolution. It has been applied to study a wide range of molecular and nanoparticle ordering phenomena at liquid surfaces and interfaces, where we use the term surface to refer to the liquid-vapor or liquid-vacuum interface, whereas the term interface refers to the region
between any two media. Examples of phenomena at liquid surfaces and interfaces include phases and phase transitions of single layers of molecules and nanoparticles at water-vapor and water-oil interfaces (Langmuir and Gibbs monolayers), atomic ordering at liquid metal surfaces, the surface ordering of liquid crystals, ultrathin wetting films, the distribution of ions near liquid interfaces, and biomolecular processes such as lipid/protein binding that occur at the interface formed by a biomembrane.

One example that illustrates the capabilities of XR is the appearance of molecular order at the surface of a single component $n$-alkane ($\text{CH}_3(\text{CH}_2)_n\text{CH}_3$) liquid, and also observed at the surfaces of liquids consisting of other types of linear long-chain organic molecules. The original experiments observed the formation of a single ordered layer of alkanes at the liquid alkane-vapor interface within a few degrees above the bulk melting temperature (Wu et al. 1993). Far above the bulk melting temperature, the surface molecules are disordered and do not form a surface layer. The XR data shown in Fig. 2 that do not exhibit oscillations are taken from samples whose temperature is far above ($>> 3^\circ$ above) the bulk melting transition. The form of this data is typical of XR measurements from simple liquids without any surface order. At very low values of $Q_z$ below the critical wave vector transfer for total reflection, $Q_z \leq Q_c$, the XR saturates at 100% reflection. The XR data decreases rapidly in intensity at larger values of $Q_z$ as a result of essentially two factors: the variation in Fresnel reflectivity with $Q_z$,

$$R_F(Q_z) = \left(Q_z/Q_c\right)^4,$$  

and the additional decrease in XR due to thermally-induced capillary waves on the liquid surface,

$$R(Q_z) \approx R_F(Q_z) \exp\left(-Q_z^2\sigma^2\right),$$  

where $\sigma$ is the interfacial width that originates from averaging the fluctuating interface over the $x-y$ plane of the interface. As explained elsewhere, the width $\sigma$ may contain a contribution from the
intrinsic profile that represents the arrangement of interfacial molecules, even if disordered (Pershans and Schlossman 2012). The roughness due to capillary waves reduces the XR by scattering X-rays into a direction away from the specular direction, and depending upon the angular acceptance of the X-ray detector, some of these X-rays will not be recorded by the detector (Schwartz et al. 1990).

Figure 2. XR from the liquid-vapor interface of C20, C30, and C44 n-alkane liquids at temperatures far above the bulk melting transition. Circles represent XR data that decay monotonically with $Q_z$ (labeled $q_z$ in the figure) and squares represent XR data measured within a few degrees of the transitions that exhibit oscillations with $Q_z$. The corresponding electron density profiles in the frozen (solid lines) and liquid (dashed line) surface phases are shown in the inset (Ocko et al. 1997).
XR measurements from samples within a few degrees of the bulk melting transition illustrate the surface freezing of liquids containing long $n$-alkanes, shown in Fig. 2. Oscillations in the XR data, sometimes referred to as Kiessig fringes, indicate the presence of a surface layer whose electron density is different from that of the bulk liquid. Numerical fitting of the XR data to a model for the electron density profile $\rho(z)$, which contains a single surface layer of electron density distinct from the electron density of the bulk liquid, demonstrates that the surface electron density is similar to previously known electron densities of solid crystalline or rotator bulk phases of $n$-alkanes (Ocko et al. 1997). This leads to the interpretation that the surface $n$-alkane molecules form a single frozen layer on the surface of the bulk liquid. Grazing incidence X-ray diffraction, a technique to be discussed later which probes in-plane molecular order, has confirmed this interpretation (Wu et al. 1993).

The period of oscillations in Fig. 2 can be simply related to the thickness of the surface layer by use of the master formula (Eq. 3). With the assumption of a single surface layer of uniform electron density $\rho_j$ and thickness $d$ residing at the interface, the master formula yields the reflectivity

$$R(Q_z) = \frac{R_F(Q_z)}{\rho_b^2} \left| \rho_j^2 + (\rho_b - \rho_j)^2 + 2\rho_j(\rho_b - \rho_j)\cos(Q_z d) \right|$$

(6)

Here, for pedagogical purposes, the surface roughness has been taken to be zero, though a non-zero roughness is required to fit the data in Fig. 2. This analytic approach shows that a single layer of thickness $d$ produces oscillations in XR data, whose modulation period is $\Delta Q_z = 2\pi/d$ and whose amplitude is determined by the electron density contrast $\rho_b - \rho_j$ between the bulk material and the surface layer. The master formula shows that XR can be thought of as a form of interferometry, where the sample interface forms the interferometer. X-rays are reflected from regions of the interface that contain gradients $d(\rho(z))/dz$. In this case, the electron density gradients are located primarily at the
top and bottom of the layer of surface frozen molecules. The interference pattern that consists of oscillations in XR is due to the coherent interference of reflections from the top and bottom of the layer.

Equation 6 indicates that the measured range of $Q_z$ and layer thickness determines the number of oscillations observed in an XR measurement. Thinner layers, in this case due to shorter molecules, produce fewer oscillations within a given range of $Q_z$ (Fig. 2). This limitation, together with low electron density contrast (i.e., small $\rho_b - \rho_i$ in Eq. 6), can reduce the distinguishing features in XR data, thereby increasing uncertainty in the determination of the interfacial structure. Blasie and co-authors addressed this difficulty in a study of Langmuir monolayers of peptide bundles by positioning a silicon wafer in the water whose top surface was within nanometers of the peptide layer (Fig. 3). A synthetic inorganic monolayer coating the silicon was designed to enhance interference between X-rays reflected from the multilayer and the peptide monolayer. XR measurements from this reflection configuration yielded an electron density profile of the Langmuir monolayer that had much better spatial resolution than obtained by conventional methods that did not include the coated silicon (Krishnan et al. 2010).

![Figure 3](image3.png)

Figure 3. Schematic representation of the substrate interferometric approach to determine the electron density profile of a Langmuir monolayer at the liquid-vapor interface (Krishnan et al. 2010).
XR has been applied to the study of ion distributions near interfaces, which underlie the electrostatic interactions between charged molecules, particles, and surfaces in electrolyte solutions (Luo et al. 2006; Duval et al. 2012; Elsen et al. 2013). X-ray studies include measurements of ions adsorbed to charged organic monolayers or other charged surfaces, which will be discussed further in the section on fluorescence spectroscopy. An example of a recent study that explored the diffuse distribution of ions that extend from an interface into the bulk electrolyte solution is illustrated by the XR measurements in Fig. 4 from an interface between two immiscible electrolyte solutions (Hou et al. 2013). Electrodes inserted into the two electrolyte phases were used to establish a tunable electric potential difference between the two phases.

In this case, the electron density profile that was used to fit the XR measurements was based upon a theory for the interfacial distribution of ions that utilized an analytic model of the potentials of mean force for the different types of ions in the sample. The potential of mean force is essentially an excess chemical potential due to repositioning an ion at different distances from the interface. Analysis of the XR data led to extracting the potentials of mean force for several different ions, based upon an assumed analytic form of the potential of mean force. The advantage of this approach is that once the potential of mean force is known, the dependence of ion distribution on the electric potential difference can be predicted. This dependence is found to be in good agreement with the measurements, though in practice very small variations in the interfacial roughness from the predicted capillary wave values were fit to the XR data. Figure 4A illustrates an example of this, for which the XR data at the highest value of electric potential difference, $\Delta \phi^\text{w-o} = 0.355$ V, were fit to determine the potential of mean force for Li$^+$. The solid lines for the other values of $\Delta \phi^\text{w-o}$ represent predictions based upon the experimentally derived potentials of mean force (Hou et al. 2013). Figure 4B shows experimentally-derived potentials of mean force for Li$^+$, Rb$^+$, and Cs$^+$, which illustrate a trend in the crossover that is consistent with the
decreasing hydration energy of the ions, in the order Li\(^+\) > Rb\(^+\) > Cs\(^+\). The most strongly hydrated ion, Li\(^+\), is surrounded by strongly bound water molecules and is, therefore, positioned furthest from the DCE-water interface. Subsequent measurements have explored the role of ion-ion correlations on interfacial ions (Laanait et al. 2012).

Figure 4. XR data that determines ion potentials of mean force. (A) X-ray reflectivity normalized to the Fresnel reflectivity \(R(Q_z) / R_F(Q_z)\) for various electric potential differences \(\Delta \phi_{w-o}\) as a function of wave vector transfer \(Q_z\) from liquid-liquid interfaces between a 10 mM LiCl aqueous solution and a 5 mM organic solution of BTPPATPFB (bis(triphenylphosphoranylidene)ammonium tetrakis(pentafluoro phenyl)borate) in DCE (1,2-dichloroethane). Curves are ordered from bottom to top according to increasing \(\Delta \phi_{w-o}\), as marked, and are successively displaced upwards by +0.1 for clarity (note that
\( R(Q_z)/R_F(Q_z) \rightarrow 1 \) as \( Q_z \rightarrow 0 \) for all measurements. Values at \( Q_z = 0 \) are measurements of the direct beam that passes, without reflection, through the aqueous phase just slightly above the interface.

(B) Potentials of mean force for aqueous ions, as marked (the water phase is at \( z > 0 \) and the DCE phase is at \( z < 0 \)) (Hou et al. 2013).

Interactions between lipids or other amphiphiles at interfaces and metal ions occurs in a range of biological, environmental, and industrial processes. For example, the solvent extraction of metal ions often involves the amphiphile-assisted transport of metal ions across the interface between an aqueous phase and an immiscible organic liquid phase. The assisting amphiphile, referred to as an extractant, is chosen to selectively extract a particular type of ion from what is in practice a complex aqueous mixture of ions. As a result, solvent extraction is useful for separating and purifying metal ions, and has found applications in environmental remediation, nuclear fuel reprocessing, and the production of precious and base metals.

Recently, X-ray surface studies have investigated the ordering of extractant molecules at the aqueous-organic liquid-liquid interface in a system that allowed the extraction process to be switched on and off, thereby enabling the investigation of the interface at different stages in the extraction process. XR measurements of an interface between pure water and the extractant di-hexadecyl phosphate (DHDP) dissolved in dodecane revealed the presence of a conventionally ordered monolayer at the interface, for which the DHDP phosphate headgroups were in contact with water and the hexadecyl chains were on the dodecane oil side of the interface (Bu et al. 2014b). Subsequent addition of \( \text{ErBr}_3 \) to the water as well as thermally switching off the extraction process before all \( \text{Er}^{3+} \) ions were extracted into the bulk dodecane led to XR observations of the inverted bilayer structure illustrated in Fig. 5. XR data from samples under these conditions exhibit oscillations with about one-half the wavelength of those from samples without \( \text{Er}^{3+} \) (Fig. 5A). This suggests the presence of a bilayer, i.e., an interfacial film about twice as thick as a conventional DHDP monolayer. A full analysis of these data,
that led to the interfacial structure illustrated in Fig. 5C, requires fitting the XR data to a model for the electron density, subsequent comparison with known values of electron densities for relevant structures and, importantly, complementary information on the interfacial density of erbium ions that was obtained from interfacial X-ray fluorescence studies, a technique that will be described later in this article. Nevertheless, the overall features of the interfacial structure shown in Fig. 5C are unintuitive, as they involve DHDP tailgroups in contact with water instead of the expected arrangement of headgroups at the interface with water. Interestingly, the master formula can provide justification for this arrangement of DHDP molecules at the interface, which is independent of detailed, numerical fitting of the XR data. This analysis is now discussed in more detail in order to provide the reader with an example of a type of simple analysis that provides qualitative insight, which can form the basis for subsequent numerical analysis.

Figure 5. (A) Normalized X-ray reflectivity, $R(Q_z) / R_F(Q_z)$, from the interface between $5 \times 10^{-7}$ M ErBr$_3$ in water (pH=2.5) and $10^{-4}$ M dihexadecyl phosphate (DHDP) in dodecane (dots with blue line fit; inverted bilayer), and the interface between pure water and $10^{-4}$ M DHDP in dodecane (solid squares with red line fit; monolayer). (B) The electron density profile of the inverted bilayer, which generates the best fit (blue line) in (A). (C) Sketch of the inverted bilayer structure. The dashed box encloses the ion-
extractant complex that is observed both at the interface when the extraction process is arrested and in the bulk dodecane phase upon letting the extraction proceed to completion (Bu et al. 2014b).

The appearance of a minimum in the XR data at low $Q_z$ ($\approx 0.006$ Å$^{-1}$; see the blue line in Fig. 5A) is a signature of the inverted bilayer that would not be observed for a conventional monolayer, bilayer, or trilayer for which headgroups would be in contact with the water phase. To see this, we construct the electron density profile from a sum of error functions:

$$\rho(z) = \frac{1}{2} \sum_{i=0}^{N-1} \text{erf} \left( \frac{z - z_n}{\sqrt{2} \sigma} \right) (\rho_{i+1} - \rho_i) + \frac{\rho_0 + \rho_N}{2},$$

(7)

where $\text{erf}(z) = \left( \frac{2}{\sqrt{\pi}} \right) \int_0^z e^{-t^2} dt$ describes a smooth monotonic crossover, $N$ is the number of internal interfaces within the surface film, $\sigma$ is the interfacial roughness of the entire interfacial film, and $\rho_i$ and $z_i$ are the electron density and position of the $i$th slab and interface, respectively, where $\rho_0$ is the electron density of the bulk aqueous phase and $\rho_N$ that of the bulk dodecane phase. Substitution of $\rho(z)$ into the master formula (Eq. 3) yields

$$\frac{R(Q_z)}{R_F(Q_z)} = \frac{e^{-Q_z^2 \sigma^2}}{(\rho_0 - \rho_N)^2} \left( \sum_{i=0}^{N-1} (\rho_{i+1} - \rho_i)^2 + 2 \sum_{i=0}^{N-1} \sum_{j>i} (\rho_{i+1} - \rho_i)(\rho_{j+1} - \rho_j) \cos(Q_z(z_j - z_i)) \right).$$

(8)

At the smallest values of $Q_z$, the behavior of XR is sensitive to the interference of X-rays reflected from internal interfaces that are separated furthest from each other. The term in Eq. (8) that represents this interference contains the electron density contrast at the top and bottom of the interfacial layer,

$$\frac{R}{R_F} \propto (\rho_1 - \rho_0)(\rho_N - \rho_{N-1})\cos(Q_zd),$$

where $d = (z_{N-1} - z_0)$ is the total thickness of the interfacial film. Figure 5B shows that the quantities $\rho_1 - \rho_0$ and $\rho_N - \rho_{N-1}$ have the same sign for the inverted bilayer, therefore $\frac{R}{R_F} \propto +\cos(Q_zd)$ and $\frac{R}{R_F}$ is expected to decrease as $Q_z$ increases from zero.
In contrast to this, it can be shown that \( R/R_F \approx -\cos(Q_z d) \) for conventional mono-, bi-, and tri-layers of DHDP at the interface (Bu et al. 2014b).

**X-ray Diffuse Scattering (XDS)**

X-ray scattering is sensitive to the correlations between thermally induced capillary height fluctuations at different positions on the surface or interface. These correlations are expressed in terms of the height-height correlation function \( g(\vec{r}_{xy}) = \left\langle h^2(0) - h(\vec{r}_{xy})h(0) \right\rangle \), where \( h(\vec{r}_{xy}) \) defines a characteristic height along the surface normal for the in-plane displacement \( \vec{r}_{xy} \). Within the context of the Born approximation, the differential scattering cross section with respect to the in-plane wave vector transfer \( \vec{Q}_{xy} \), under conditions for which the angle of reflection \( \alpha_d \) and the azimuthal angle of scattering \( \theta_d \) are small, is given by (Pershan and Schlossman 2012)

\[
\frac{d\sigma}{d^2\vec{Q}_{xy}} \approx A_o \left( \frac{Q_z}{2Q_z} \right)^4 |\Phi(Q_z)|^2 H(\vec{Q}_{xy}, Q_z)
\]

where

\[
H(\vec{Q}_{xy}, Q_z) = \frac{1}{4\pi^2} \int d^2\vec{r}_{xy} \exp[-Q_z^2 g(\vec{r}_{xy})] \exp[-i\vec{Q}_{xy} \cdot \vec{r}_{xy}].
\]

Since the effect of capillary waves on the scattering is included in \( H(\vec{Q}_{xy}, Q_z) \), the intrinsic surface structure factor \( \Phi(Q_z) \) appears in Eq. (9) instead of the effective surface structure factor that appears in Eq. (3). The scattered intensity \( I(\vec{Q}_{xy}, Q_z) \) is obtained from the cross section by integrating over a region in \( \vec{Q} \)-space that is determined by the range in scattered wave vectors measured by the
reflectometer for a given range in incident wave vectors. This region is characterized by the resolution function \( \Gamma_r(\bar{Q}_{xy}, Q_z; \bar{Q}'_{xy}, Q'_z) \) where \( (\bar{Q}'_{xy}, Q'_z) \) represents the detected wave vector transfers about the nominal settings \( (\bar{Q}_{xy}, Q_z) \) of the reflectometer. For circumstances in which the dependence on \( Q'_z \) can be neglected the resolution function \( \Gamma_r(\bar{Q}_{xy}, Q_z; \bar{Q}'_{xy}, Q'_z) \approx \Gamma_r(\bar{Q}_{xy}, Q_z - \bar{Q}'_{xy}) \) and the scattered intensity \( I(\bar{Q}_{xy}, Q_z) \) normalized by the incident intensity \( I_o \) is given by

\[
\frac{I(\bar{Q}_{xy}, Q_z)}{I_o} = \frac{1}{A_o} \int d^2\bar{Q}'_{xy} \Gamma_r(\bar{Q}_{xy}, Q_z - \bar{Q}'_{xy}) \frac{d\sigma(\bar{Q}_{xy}, Q_z)}{d^2\bar{Q}'_{xy}}, \tag{11}
\]

where \( A_o \) is the cross-sectional area of the incident X-ray beam. When the surface is flat, that is, \( h(\bar{r}_{xy}) = h(0) \), the master formula for the reflectivity given by Eq. (3) can be simply derived from Eq. (11) (Pershan and Schlossman 2012). The expression in Eq. (11) can also be used to calculate off-specular diffuse scattering from surface fluctuations. Off-specular diffuse scattering of X-rays outside the finite resolution of the detector, i.e., X-rays that are not scattered into the detector during a reflectivity measurement, provides an explanation for the reduction of the reflectivity by a factor of \( \exp\left(-Q_z^2\sigma^2\right) \) shown in Eq. (5). This implies that the value of the interfacial roughness \( \sigma \) of a liquid surface measured by X-ray reflectivity depends upon the resolution of the measurement (Schwartz et al. 1990).

For most purposes, the height-height correlation function of liquid surfaces can be approximated by

\[
g(\bar{r}_{xy}) = \begin{cases} 
\frac{k_BT}{2\pi\gamma} \ln(r_{xy}q_{max}) & \text{for } 1/q_{max} \leq r_{xy} < \xi_g \\
0 & \text{for } r_{xy} < 1/q_{max} 
\end{cases} \tag{12}
\]
where the value 0 for $r_{xy} < 1/q_{\text{max}}$ expresses the idea that surfaces cannot support fluctuations on length scales smaller than the molecular size, represented by $1/q_{\text{max}}$. The expression in Eq. (12) is derived from the capillary wave dispersion relation (Rowlinson and Widom 1982) and is valid for distances $r_{xy}$ along the surface that are smaller than the macroscopic capillary length $\xi = \sqrt{\gamma / \rho_m g}$, where $\gamma$ is the surface tension, $\rho_m$ is the mass density of the liquid, and $g$ is the gravitational acceleration. This expression illustrates an important difference between liquid and solid surfaces: $g(r_{xy})$ typically approaches a constant value for large $r_{xy}$ on solid surfaces, but increases logarithmically for liquid surfaces. The expression in Eq. (12) leads to the differential cross section for scattering from liquid surfaces (Sinha et al. 1988; Pershan and Schlossman 2012),

$$
\frac{d\sigma}{d^2Q_{xy}} \approx A_0 \left( \frac{Q_z}{2Q_c} \right)^4 |\Phi(Q_c)|^2 \left( \frac{Q_{xy}}{q_{\text{max}}} \right)^\eta \left( \frac{\eta}{2\pi Q_{xy}^2} \right),
$$

(13)

where $\eta = (k_B T / 2\pi \gamma)Q_c^2$. This expression can be substituted into Eq. (11) to calculate off-specular diffuse scattering from liquid surfaces. A detailed discussion of the effect of the resolution function on the scattered intensity can be found in the literature (Pershan and Schlossman 2012).

It has been shown that the Born approximation is sufficiently accurate when the incident and scattering angles, $\alpha_i$ and $\alpha_d$, are greater than approximately 4 times the critical angle for both the bulk and the surface layers. However, for $\alpha_i \leq \alpha_c$, the amplitude of the reflected wave is comparable to that of the incident wave. Since the diffuse scattering from the surface is proportional to the square modulus of the total field at the surface, the scattering can be enhanced by up to a factor of 4 over that calculated by neglecting the reflected wave. The distorted-wave approximation (DWA, (Rodberg and Thaler 1967), sometimes referred to as the distorted-wave Born approximation) addresses this issue by calculating the scattering from surface inhomogeneities of a wave that is the sum of the incident and
reflected waves from a flat, homogeneous surface (Vineyard 1982; Sinha et al. 1988). Detailed discussions of the DWA can be found in recently published books (Pershan and Schlossman 2012; Daillant and Gibaud 2009). The DWA is useful for understanding small angle off-specular diffuse scattering when $\alpha_i$ and/or $\alpha_d$ are similar to $\alpha_c$, as well as grazing-incidence scattering, for example, grazing-incidence diffraction (GIXD) or grazing-incidence small angle scattering (GISAXS).

In the case of small angle off-specular diffuse scattering, for $\alpha_d \approx \alpha_i$, the cross section can be written as (Pershan and Schlossman 2012)

$$\frac{d\sigma}{d^2Q_{xy}} \approx \frac{A_o}{4\pi^2} \left( \frac{Q_c}{2Q_z} \right)^4 \left( 1 + r\left(\vec{k}_{i,xy}\right) \right)^2 \left( 1 + r\left(\vec{k}_{s,xy}\right) \right)^2 Q^2 S_{hh}\left(\vec{k}_{s,xy} - \vec{k}_{i,xy}\right),$$

(14)

with

$$S_{hh}\left(\vec{k}_{s,xy} - \vec{k}_{i,xy}\right) = \int d^2\vec{r}_{xy} \left(h\left(\vec{r}_{xy}\right)h(0)\right) \exp\left[-i\left(\vec{k}_{s,xy} - \vec{k}_{i,xy}\right) \cdot \vec{r}_{xy}\right],$$

(15)

where, for example, $r\left(\vec{k}_{i,xy}\right)$ or $r\left(\vec{k}_{s,xy}\right)$ are the reflection amplitudes for a corresponding flat surface evaluated at a particular value of the in-plane component of the incident or scattered wave vectors, $\vec{k}_{i,xy}$ or $\vec{k}_{s,xy}$. The primary difference between the differential cross section calculated from the Born approximation used in Eq. (9) and the DWA in Eq. (14) is the presence of the factors

$$\left|1 + r\left(\vec{k}_{i,xy}\right)\right|^2 \left|1 + r\left(\vec{k}_{s,xy}\right)\right|^2,$$

which arise because the total electric field at the surface is the sum of the incident and reflected fields. For the case of a fluctuating liquid surface that does not have a distinct surface layer due to, for example, surfactants or other surface molecular ordering, the factor $1 + r(\vec{k}_{i,xy})$
can be replaced by the transmission coefficient \( t(\tilde{k}_{i,xy}) \), where \( |t(\alpha_i)|^2 = \left( \frac{2\alpha_i}{\alpha_c} \right)^2 \sqrt{R_F(\alpha_i)} \) for small angles \( \alpha_i \). A similar effect occurs for the scattered wave vector, which can be replaced by \( |t(\alpha_d)|^2 \).

The differential cross section in Eq. (13) exhibits a dependence on \( Q_{xy}^{-2} \) (which is also implicit in the expression in Eq. (14)). Under the approximation of an infinitely wide slit in front of the detector, for which the scattering is integrated over the full range of \( Q_y \), the diffuse scattered intensity should be proportional to \( Q_x^{-1} \), as illustrated by a measurement of the surface of ethanol shown in Fig. 6. Excellent fits represented by the solid lines verify the quantitative agreement between the experimental data and the distorted-wave approximation, and yield the surface roughness \( \sigma = 6.9 \text{ Å} \).

![Figure 6](image)

Figure 6. Log-log plot of off-specular diffuse scattering data normalized to unity at \( Q_x = 0 \) from the ethanol-air interface for different fixed values of \( Q_z \) (= 0.3, 0.25, 0.2, 0.15, 0.1 Å\(^{-1}\), from top to bottom). Open diamonds represent the instrumental resolution at small \( Q_z \). Note that \( Q_x \) is labeled \( q_x \) in the figure. The solid lines are based upon the distorted-wave approximation (Sanyal et al. 1991).

In addition to investigations of fluctuations at the surfaces of organic liquids and water, X-ray diffuse scattering has been applied to measure fluctuations of the interface between two immiscible liquids, including studies of the large fluctuations (e.g., 200 Å in height) that occur at liquid-liquid
interfaces with ultra-low interfacial tensions (McClain et al. 1994; McClain et al. 1999; Mitrinovic et al. 2001). Thermal fluctuations at these interfaces are an order of magnitude larger than the molecular sizes, in contrast to the much smaller surface fluctuations observed in many other systems.

The dispersion of interfacial fluctuations is determined by the elastic properties of the medium. For example, the capillary wave dispersion relation led to the expression for the height-height correlation function in Eq. (12). Diffuse scattering from thin polymer films has explored the effect of the properties of long-chain melts on surface fluctuations, as well as the influence of a structured substrate that supports the film (Tolan 1999). For example, fluctuations from thin films of polymers whose length exceeds the entanglement length show strong deviations from liquid-like capillary wave behavior (Seo et al. 2005). The dispersion relation can also be altered by the coupling of capillary waves between two nearby fluctuating interfaces, as demonstrated by XDS from very thin liquid films supported by liquid substrates (Li et al. 2001; Paulus et al. 2005; Fukuto et al. 2006). XDS has been used to probe the bending modulus that influences primarily the short wavelength surface fluctuations at, for example, pure liquid surfaces (Mora et al. 2003), organic Langmuir monolayers supported on the surface of water (Mora et al. 2004; Daillant et al. 2009), and surface phases formed at the surface of Au$_{82}$Si$_{18}$ liquid metal alloys (Mechler et al. 2010). In-plane density modulations formed by monolayer domains that form an inhomogeneous coverage of the liquid interface can also be characterized with XDS (Li et al. 2002).

Grazing Incidence X-ray Diffraction (GIXD)

Grazing incidence X-ray diffraction (GIXD) probes the ordering of molecules or particles within the plane of the interface, which is particularly useful for studying the surface crystallization of liquids or molecular monolayers. The kinematics for this technique are shown in Fig. 1, for which the incident beam strikes the surface with an angle $\alpha_i$ smaller than the critical angle for total reflection.
\[ \alpha_c = \arcsin \left( \frac{Q_c}{2k_0} \right) \] and the intensity of the outgoing beam is recorded as a function of \( \alpha_d \) and \( \theta_d \).

The advantage of fixing \( \alpha_i \) to be smaller than \( \alpha_c \) (\( \alpha_i \approx 0.8 \alpha_c \) typically) is two-fold: first, the X-ray penetration depth into the lower phase is on the order of a few nanometers under these conditions, rendering surface sensitivity to the measurement; second, as discussed for the distorted-wave approximation, the scattering of X-rays from the surface is amplified by \( |f(\alpha_j)|^2 \), which can be as large as a factor of 4.

Assuming that the interfacial structure of a Langmuir monolayer of uniformly oriented identical molecules has 2-dimensional (2-D) quasi-long range order (see Fig. 7A), the GIXD pattern is determined by two factors: the structure factor that describes the lattice of ordered molecules within the plane of the interface and the form factor that describes the electron density distribution of an individual molecule. The structure factor of a 2-D planar lattice consists of a set of Bragg rods along the z-direction perpendicular to the plane (see Fig. 7B), unlike the Bragg points observed for a 3-D crystal. The form factor of an idealized cylindrical molecule has its maximum within a reciprocal disk oriented perpendicular to the molecular axis. The intersections of the Bragg rods with the reciprocal disk give rise to diffraction maxima. If the molecular axis is not normal to the surface (e.g., if the molecules are tilted; see Fig. 7C), some or all of the diffraction maxima will be out-of-plane (\( Q_z \neq 0 \)). Figure 7D-G illustrates common GIXD patterns in \( Q_{xy}-Q_z \) space, where

\[
Q_{xy} = k_0 \sqrt{\cos^2 \alpha_i + \cos^2 \alpha_d - 2 \cos \alpha_i \cos \alpha_d \cos \theta_d} \quad \text{and} \quad Q_z = k_0 \left( \sin \alpha_i + \sin \alpha_d \right). \quad (16)
\]
Figure 7. (A) Lattice structures in real space. (B) Lattice structures in reciprocal space, including Bragg rods, and the form factor reciprocal disk of an idealized cylindrical molecule. (C) Tilt angle defined as the angle between the molecular axis and z-direction. (D-G) Real space (first row), reciprocal space (second row), and sketched diffraction pattern (third row) for four common phases, where NN and NNN refer to the molecular tilt in the direction of the nearest neighbor or next nearest neighbor, as given by the arrows in panels (F) and (G).

The earliest GIXD measurements from liquid surfaces were carried out independently on compressed monolayers at the water-vapor interface (Dutta et al. 1987; Kjaer et al. 1987). Since this pioneering work, GIXD has become the primary technique to probe the lateral structure of Langmuir monolayers on the water surface, allowing the determination of unit cell parameters, molecular tilt angles and the azimuth of the tilt direction, which have distinctive values for different phases of Langmuir monolayers. As an example, Fig. 8 shows GIXD measurements on heneicosanoic acid (CH₃(CH₂)₁₉COOH) monolayers at a fixed surface pressure (31 mN/m) that exhibit a smooth transition from two peaks to a single peak with increasing temperature, thereby demonstrating a first-order transition between S and LS phases (Shih et al. 1992). The lower temperature solid S phase possesses
two in-plane diffraction peaks, indicating a centered rectangular packing of untitled molecules, as illustrated in Fig. 7E, whereas the higher temperature superliquid LS phase has only a single peak, implying hexagonal packing (Fig. 7D). However, data for intermediate temperatures (18.5-20 °C) exhibit a single but distinctly asymmetric peak, as a result of an additional phase between the S and LS phases.

Figure 8. GIXD data for heneicosanoic acid monolayers along a 31 mN/m isobar, where \( Q_z = 0 \) and \( k \) refers to \( Q_{xy} \). Left and right column, labeled by A′ and rotator II, represent the S and LS phases mentioned in the text, respectively; while the middle column, labeled by rotator I, represents an additional phase. The solid lines are fits to the data that use one or two Lorentzian functions, as appropriate; the dotted lines are the individual Lorentzians (Shih et al. 1992).

Recent developments in measurement accuracy and in methods of data analysis have demonstrated that GIXD spectra are accurate enough to obtain near-atomic level structural information. The method consists of careful extraction of structure factors from GIXD data followed by fitting with a 3-D crystal structure refinement program (SHELX-97). More recently, simulated annealing, a Monte-Carlo method, has been used to considerably reduce the computation time involved in this analysis (Pignat et al. 2007). This method was applied to model Bragg rods measured from Langmuir monolayers.
of behenic acid (CH₃(CH₂)₂₀COOH) in the $L''_2$ phase. In addition to unit cell dimensions and molecular tilt angle, the refinement method also determined the orientation of chain backbone planes, the orientation of carboxylic acid headgroups, and conformational defects within the long chains (Fig. 9).

Figure 9. Behenic acid in the $L''_2$ phase (0.2 mN/m and $T = -2.5 \, ^\circ\mathrm{C}$). (a) Transverse cell seen from the terminal methyl groups of the chains. (b) Bottom view of the unit cell showing the headgroup organization. (c) and (d) Projection of the super-cell with 18 molecules along two different directions (Pignat et al. 2007).

**Grazing Incidence Small Angle X-ray Scattering (GISAXS)**

Grazing incidence small angle X-ray scattering (GISAXS) combines the measurement of the longer length scales typical of small angle X-ray scattering with the surface sensitivity of grazing incidence techniques. Its experimental setup is similar to that of GIXD as shown in Fig. 1. However, the scattering pattern of interest appears at small $Q$ close to the specular direction; therefore, GISAXS data are typically measured by an area detector centered near $\theta_d = 0$ with a beam stop to block the direct beam.
A typical application of GISAXS at liquid interfaces is the study of the interfacial ordering of larger macromolecular systems, such as membrane proteins and polymers, or nanoparticles. Recent studies of the 2-D assembly of the protein streptavidin on a biotin-bearing lipid monolayer at the water-vapor interface measured the variation of streptavidin adsorption, 2-D phase behavior, and binding state with biotin surface density (Fukuto et al. 2010). The presence of Bragg rods in the GISAXS pattern (Fig. 10) reveals 2-D streptavidin crystallization at the interface. The diffraction intensity is reduced, and eventually disappears, at low biotin-bearing lipid density, suggesting that high lateral packing density is essential for 2-D crystallization of proteins.

Figure 10. (A) GISAXS pattern measured with $a_b = 0.74$, where $a_b$ is the ratio of the surface area per biotin-bearing lipid to half the surface area per streptavidin protein. (B) Intensity versus $Q_{xy}$ plot for $a_b = 1.61, 1.22, 0.98$, and $0.74$ (shifted vertically for clarity), obtained by integrating the GISAXS patterns over $0.02 < Q_z < 0.06$ Å$^{-1}$ (Fukuto et al. 2010).
Neither GIXD nor GISAXS are often used to study the liquid-liquid interface because bulk scattering generated by X-rays passing through the top phase overwhelms the diffraction intensity from organic monolayers. However, some materials, such as gold nanoparticles, have a larger electron density contrast with the surrounding environment, which produces a measurable diffraction intensity. Recent studies of charged nanoparticles at the electrified water/1,2-dichloroethane interface demonstrated the formation of 2-D hexagonal ordering of 6 nm diameter nanoparticles at the interface (Fig. 11) (Bera et al. 2014). A nearly linear increase of lattice spacing with the electric potential difference between the two immiscible electrolyte phases was observed (Fig. 11c). The in-plane lattice spacing can be adjusted by an electric field perpendicular to the interface because this field re-distributes counter- and co-ions in the vicinity of the nanoparticles, which, in turn, mediate electrostatic interactions between nanoparticles adsorbed to the interface.

Figure 11. (a) Measured GISAXS pattern from charged nanoparticles at the water/1,2-dichloroethane interface with electric potential difference \( \Delta \phi^{\text{water}} = 30 \) mV between the two liquid phases. (b) Scattered intensity versus \( Q_{xy} \) for different values of \( \Delta \phi^{\text{water}} \) indicated in the figure (shifted vertically for clarity), obtained by integrating the GISAXS patterns over \( 0 < Q_z < 0.1 \ \text{Å}^{-1} \). (c) The dependence on
of the variation in nearest neighbor spacing from the value measured at 30 mV (Bera et al. 2014).

**Spectroscopy at Liquid Interfaces**

Synchrotron X-rays can be tuned continuously in energy, providing the opportunity to use interface spectroscopies that highlight the interfacial properties or location of a chosen element. Examples include resonant scattering techniques, such as anomalous XR, which probes the contribution of a particular element to the electron density profile, X-ray fluorescence near total reflection (XFNTR), which records the presence and interfacial density of elements, and surface X-ray absorption spectroscopy (XAS), which can determine the nearest neighbor ordering and oxidation state of specific elements.

In general, the electron density is complex and energy dependent,

\[ \rho(z,E) = \sum_j n_j(z) Z_j f_j(E) \tag{17} \]

where \( n_j \) is the number density of an atomic constituent of type \( j \) with \( Z_j \) electrons. The atomic form factor,

\[ f(E) = f^0(\tilde{Q}) + f'(E) + if''(E) \tag{18} \]

contains a \( \tilde{Q} \) dependent term \( f^0(\tilde{Q}) \), and real and imaginary parts of the anomalous dispersion correction to the atomic scattering factor, \( f'(E) \) and \( f''(E) \). The Thomson scattering atomic form factor, \( f^0(\tilde{Q}) \), is the Fourier transform of the charge distribution normalized by the total number of electrons in an atom. Over the typically small angular range of an XR measurement, \( Q = Q_z \) is small enough that \( f^0(Q_z) = 1 \) is a good approximation. The real part of the dispersion correction, \( f'(E) \),
describes the elastic response of the electron to X-rays, whereas the imaginary part, $f''(E)$, related to $f'(E)$ by Kramers-Kronig relations, characterizes the X-ray absorption. The dispersion corrections vary smoothly when the X-ray energy is on the order of 1 keV away from an atomic X-ray absorption edge. Near an absorption edge, corresponding for example to ionization of an electron from an atom, a sharp step-like increase in $f''(E)$ indicates enhanced absorption of X-rays and $f'(E)$ exhibits a sharp dip over an extended range of energy on the order of 100 eV. Resonant measurements, in which the X-ray energy is tuned through the absorption edge of a chosen element, as well as non-resonant measurements, which compare the response to X-rays measured at energies near and far from the absorption edge, highlight a particular element in the interfacial structure (Park and Fenter 2007).

**Anomalous X-ray Reflectivity.** Conventional XR probes the electron density profile due to all elements without distinguishing one element from another, whereas anomalous XR takes advantage of the energy dependence of $\rho(z, E)$ to distinguish the contribution from a chosen element to the electron density profile $\langle \rho(z, E) \rangle$ averaged over the $x - y$ plane of the interface. If other elements in the sample have absorption energies far from that of the chosen element, the difference between the electron density profiles measured by non-resonant anomalous XR at energies near and far from the absorption edge for the element of interest is proportional to the number density profile of the chosen element.

Non-resonant anomalous XR has been used to determine the enrichment and depletion of a targeted element near liquid surfaces in various systems. For example, Gibbs adsorption theory predicts that the species in a two-component liquid with the lower surface tension segregates preferentially to the surface. This effect was demonstrated in a binary metal alloy, Bi$_{22}$In$_{78}$, using non-resonant anomalous XR measurements near and far from the Bi $L_{III}$ edge shown in Fig. 12 (DiMasi et al. 2001). The two sets of XR data were fit simultaneously by an atomic layer density profile, in which the density
distributions of both components were represented by a sum of Gaussian functions (see Fig. 13c). The data analysis revealed an enrichment of Bi with a molar fraction \( \chi_{0,Bi} \approx 0.35 \) in the first atomic layer adjacent to the vapor, which is larger than the bulk value of \( \chi_{Bi} \approx 0.22 \). This is qualitatively consistent with the enrichment predicted by the Gibbs adsorption equation, but lower than the value of \( \chi_{0,Bi} \approx 0.69 \) predicted for an ideal mixture of non-interacting Bi and In. Attractive Bi-In interactions are necessary to reproduce the experimental result, implying that the surface adsorption is dominated by the increasing number of Bi-In neighbors at the surface.

Figure 12. (a) X-ray intensity transmitted through a Bi foil as a function of X-ray energy, which demonstrates the Bi \( L_{III} \) absorption edge near 13.42 keV. (b) Normalized XR data of Bi\(_{22}\)In\(_{78}\) at X-ray energies of 12.5 (circles) and 13.4 keV (dots; just below the Bi \( L_{III} \) edge) as well as the corresponding best fits. (c) Number density profiles relative to the bulk values shown separately for In and Bi, as well as the total density. (d) Surface energy versus surface Bi concentration \( \chi_{0,Bi} \) with \( w = -10 \ k_B T \) (solid line) and without \( w = 0 \) (dashed line) Bi-In pairing, where \( w \) is the excess interaction energy of Bi-In pairs over the average of the Bi-Bi and In-In interaction energies; for an ideal mixture, \( w = 0 \) (DiMasi et al. 2001).

**X-ray Fluorescence Near Total Reflection (XFNTR).** When an atom is struck by X-rays with an energy greater than its inner shell electron binding energy, inner shell electrons can be ejected, followed by electrons from outer shells falling into their place. The byproduct of this process is the generation of fluorescence X-rays with characteristic energies equal to the energy difference between
inner and outer shells. Since each element has electronic orbitals of characteristic energy, each element has a unique fluorescence spectrum.

X-ray fluorescence near total reflection (XFNTR) consists of measurements of fluorescence spectra over a range of $Q_z$ above and below the value $Q_c$ for total reflection (Bloch and Yun 1990). The XFNTR intensity is proportional to an integration over the product of the incident X-ray intensity at the position of the fluorescing atoms and a factor that describes the attenuation of fluorescent X-rays along their path to the detector, given by

$$I = Cl_0 \int n(z)T(\alpha)\exp\left(-z/\Lambda_i\right)\exp\left(-z/\Lambda_f\right)dV,$$

where the calibration factor $C$ accounts for the effect of the scattering geometry and the physics of the fluorescence process for an individual atom, $I_0$ is the incident beam intensity, $n(z)$ is the ion concentration profile, $T(\alpha) = |t(\alpha)|^2$ is the Fresnel transmission coefficient, $\Lambda_i = \left[\text{Im}\left(\sqrt{Q_z^2 - Q_c^2 + 8i\beta k_0^2}\right)\right]^{-1}$ is the X-ray penetration depth of the incident beam, $\Lambda_f$ is the attenuation length of fluorescent X-rays that travel from the fluorescing atom to the detector, and $V$ is the scattering volume. XFNTR signals at values of $Q_z$ below and above $Q_c$ are dominated by fluorescence from interfacial atoms and bulk atoms, respectively, because the incident X-ray penetration depth $\Lambda_i$ changes rapidly from nanometers for $Q_z < Q_c$ to micrometers for $Q_z > Q_c$, as illustrated in Fig. 13.
Figure 13. X-ray penetration depth $\Lambda_i$ of the incident beam versus $Q_z$ at the pure water-air interface for different incident X-ray energies as indicated. The arrow indicates the location of the critical wave vector transfer for total reflection $Q_c$.

Unlike conventional XR and GIXD, which probe the electron density from all atomic species in the sample, XFNTR can distinguish one element from others. As a result of its high elemental selectivity and interfacial sensitivity, XFNTR is a powerful tool to study metal ions at liquid–vapor (Daillant et al. 1991) and liquid–liquid interfaces (Bu et al. 2011). As one example, XFNTR has been used to study the interactions between negatively charged monolayers (DHDP; dihexadecyl phosphate) and subphase ions (CsI) at the water-vapor interface (Bu and Vaknin 2009). Figure 14 shows XFNTR measured with and without the DHDP monolayer. The fluorescence pattern is relatively simple in the absence of the monolayer. Fluorescence intensity is not observed below total reflection ($Q_z < Q_c = 0.0217 \text{ Å}^{-1}$), revealing that the concentration of Cs$^+$ and I$^-$ within the interfacial region is lower than the detection limit ($\sim$0.1 per DHDP). This is consistent with the low bulk concentration of CsI and the negligible adsorption of Cs$^+$ and I$^-$ to the water-vapor interface. Above total reflection, the X-ray beam penetrates into the bulk aqueous phase, where the bulk concentration of CsI is sufficient to generate fluorescence from this larger scattering volume. When a DHDP monolayer is spread at the liquid-vapor interface of a
CsI solution, the fluorescence spectrum changes significantly, as shown in Fig. 14B. Emission lines from Cs⁺ are present above and below total reflection, but lines from I⁻ are observed only above total reflection. This provides evidence that Cs⁺ adsorbs exclusively to the negatively charged surface. No emission lines from I⁻, including the strongest Lα line, are observed below the critical angle, implying that I⁻ is not enriched at the surface.

Figure 14. Contour plots of fluorescence intensity measured at the air-water (10⁻³M CsI) interface. Spectra measured (A) without and (B) with a monolayer DHDP. Emission lines are labeled on the right (Bu and Vaknin 2009). The colors red, orange, yellow, green, light blue, to dark blue represent the most to least intense fluorescence for a given fluorescence energy measured at 8 keV X-ray illumination for varying angles of incidence that correspond to the $Q_z$ values shown for a reflectivity measurement. The value of $Q_z$ at total reflection is $Q_z = 0.0217 \, \text{Å}^{-1}$. 
In addition to detecting the presence of target metal ions, the preferential binding of one metal ion in favor of another has been measured with XFNTR (Shapovalov et al. 2007). Observation of the raw data alone or simple data analysis is sufficient to yield such conclusions in these and similar measurements (Vaknin and Bu 2010; Bu et al. 2009), thus making XFNTR a truly simple tool for elemental analysis at liquid interfaces.

Notwithstanding these qualitative conclusions from the observation of XFNTR spectra, a quantitative determination of the interfacial coverage of target metal ions requires careful consideration of the scattering volume. Under the assumption that variations of ion concentration near the interface occur within a depth much smaller than $\Lambda_i$, the fluorescence intensity from the bulk ($I_{\text{bulk}}$) and interfacial ($I_{\text{int}}$) regions can be decoupled as follows,

$$
I_{\text{bulk}} = CI_0 n_M T(\alpha) \int \exp(-z/\Lambda_i) \exp(-z/\Lambda_f) \, dV
$$

$$
I_{\text{int}} = CI_0 \Phi_M T(\alpha) A,
$$

where $n_M$ and $\Phi_M$ are the bulk concentration and interfacial coverage (ion number per Å$^2$) of the target metal ion $M$, respectively (Bu et al. 2011). The scattering area $A$ is determined by the overlap of the detector acceptance region and the beam footprint on the interface. The calibration factor $C$ is common for both intensities. A determination of the metal ion interfacial coverage generally consists of XFNTR measurements on both reference and unknown samples. The bare interface or surface of a concentrated metal ion solution is often used as a reference sample, under the assumption that the bare interface has a negligible enrichment or depletion of metal ions at the interface. In other words, the interfacial contribution $I_{\text{int}}$ is negligible for the reference sample. The XFNTR measurement on the reference sample determines the calibration factor $C$, which can be used subsequently to analyze XFNTR data from other samples in order to extract the interfacial coverage of metal ions.
A recent application of the XFNTR technique to the liquid-liquid interface was used to investigate a model solvent extraction system containing DHDP as an extractant molecule dissolved in the organic phase and metal ions, Er$^{3+}$ and Sr$^{2+}$, in the aqueous phase (Bu et al. 2014a; Bu et al. 2014b). These measurements used a custom designed liquid-liquid sample cell, which contained a collimator to define the effective scattering volume. Quantitative data analysis relied upon detailed geometrical calculations which included beam absorption in the oil phase, the background intensity from secondary scattering, and the effect of interfacial curvature. Combining the XFNTR analysis with X-ray reflectivity measurements led to the unexpected inverted bilayer interfacial structure for the Er$^{3+}$ system, previously shown in Fig. 5C, which represents an intermediate state in the process of extracting metal ions from the aqueous into the organic phase. A similar analysis for samples with Sr$^{2+}$ led to the expected interfacial structure of a monolayer of DHDP with headgroups exposed to the water phase and complexed with Sr ions.

**X-ray Absorption Fine Structure (XAFS)** Extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) have been used to characterize metal ion coordination in bulk electrolyte solutions, including the identity and number of coordinating ligands as well as the metal-ligand distances (Filipponi 2001). These techniques are element-specific and characterize the coordination environment for metal-ligand distances out to approximately 5 Å with a precision of ±0.01 Å and measure the number of ligands coordinating to the metal ion within this distance to within ±10%. Application of these techniques to the water-vapor interface since the 1990’s has been primarily concerned with the binding of metal ions, such as Br$^{-}$, Zn$^{2+}$, and Mn$^{2+}$, to cationic surfactants or porphyrins at the interface (Watanabe and Tanida 1995; Bloch et al. 1988; Ruggles et al. 2006; Kashimoto et al. 2008). Surface sensitivity is obtained by confining the X-ray field to a region near the interface under the conditions of total reflection. The XAFS signal is measured as a function of the incident X-ray energy by recording the fluorescence, the electron yield, or He$^{+}$ cations created by the
emitted Auger electrons which pass through a He atmosphere above the liquid surface. In addition to measuring the metal-ligand coordination at the interface, the height of the step-like response at the absorption edge has been used to measure the surface excess of the metal ion (Takiue et al. 2003). Experiments on disk-like porphyrin molecules that can lie flat on the water surface, or may be tilted with respect to it, have taken advantage of varying the incident X-ray polarization from horizontal to vertical to probe directional coordination at the liquid surface (Tanida et al. 2003). Recent studies have applied these techniques to the liquid-liquid interface (Nagatani et al. 2010), including the electrified interface between two immiscible electrolyte solutions (Nagatani et al. 2014).

**Time Resolved Measurements**

Real interfacial processes occur over a wide range in time scales that are only just beginning to be explored by x-ray surface scattering. Re-equilibration of the many degrees of freedom in complex and dense molecular interfaces may take minutes to hours, but conformational changes triggered by applied interfacial electric fields are expected to occur on the sub-second time scale. Nucleation and growth of nanoparticles or nucleated mineralization can take place on a time scale of seconds. Interfacial chelation and transfer of metal ions by extractants occurs on essentially unknown time scales likely to be sub-second. Until fairly recently it has not been possible to probe the dynamics of most of these processes at liquid interfaces with x-ray scattering; however, recent developments have begun to change this. The clever use of area detectors as pioneered at the Advanced Photon Source Sector 15-ID (Uysal et al. 2010; Meron et al. 2009) and Spring-8 (Yano et al. 2009; Yano et al. 2010), in particular, seems promising.

**1D Pinhole GIXD.** A standard setup for grazing-incidence X-ray diffraction (GIXD) measurements with a pixel-array area detector is illustrated in Fig. 15a, in which two pairs of slits in front of the detector define the angular resolution of the measurement. The slits are open wide in the
vertical direction (perpendicular to the plane of the figure), but closed horizontally to a small gap. By exposing only a narrow vertical strip of the detector to X-rays, this setup does not take full advantage of the active area of the detector and requires scanning the in-plane angle to record the diffraction peak intensity as a function of in-plane $Q_{xy}$. An alternative slit geometry, shown in Fig. 15b, has become known as the 1D pinhole GIXD method (Meron et al. 2009). In this setup, the area detector records a wide angular range in a single measurement. Each vertical column of pixels records scattering from a given in-plane angle of scattering. This method significantly improves the photon collection efficiency without sacrificing angular resolution. More importantly, the data over the angular range is measured simultaneously, instead of sequentially, making it feasible to observe and track sample changes that occur over short time intervals, down to a few seconds.

For direct comparison, Fig. 15 shows GIXD data from a 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) lipid monolayer measured with standard and 1D pinhole geometries. The measurement time for the 1D pinhole geometry was 30 s, versus 42 s for the standard GIXD, while the resolution for the pinhole was 0.02°, versus 0.09° for the standard GIXD. In spite of the shorter exposure time and finer resolution, the diffraction intensity collected by the 1D pinhole geometry was nearly 4 times larger than for standard GIXD, yielding a factor of 2 improvement in the signal to noise ratio.
Figure 15. GIXD scattering geometries. From top to bottom: setup, raw data from a compressed DPPC monolayer, and data integrated over $Q_z$ for (a) standard GIXD and (b) 1D pinhole GIXD. The Pilatus is a pixel-array area detector. The units for $Q_{xy}$ and $Q_z$ are in inverse angstroms (Meron et al. 2009).

**Grazing Incidence X-ray Off-Specular Scattering (GIXOS).** XR consists of measuring the intensity of specular reflection over a range of values of $Q_z$. This consists of numerous measurements, which involve mechanical motions at each value of $Q_z$. Off-specular diffuse scattering also contains information on the surface structure factor that is provided by XR (Daillant et al. 2009). A single exposure measurement of the diffuse scattering that contains a wide range of values of $Q_z$ can be made by fixing the incident angle below that for total reflection and using an area detector to record the scattering intensity only slightly off the specular condition at small $\theta_d$ (Fig. 16). The high efficiency of data collection makes GIXOS a faster technique than XR, which may be appropriate to monitor temporal changes in the interfacial structure.
Figure 16. Schematic view of GIXOS. X-rays are incident at grazing incidence, such that $\alpha < \alpha_c$. Off-specular diffuse scattering is recorded by an area detector simultaneously for a wide range of $\beta$ at a specific azimuthal angle $\theta_d \neq 0$ ($\theta$ in the figure). The cartoon in the upper right shows the multilayer evolution of a gold nanoparticle film under lateral compression (Dai et al. 2013).

GIXOS data can be calculated from the diffuse scattering theory previously described, which allows the intrinsic surface structure factor $\Phi(Q_z)$ to be determined. A recent study of a compressed DPPC Langmuir monolayer demonstrated that GIXOS is capable of extracting the intrinsic electron density profile with a spatial resolution comparable to XR (Dai et al. 2011). GIXOS studies of a gold nanoparticle film under lateral compression at the air-water interface monitored a transition from monolayer to bilayer to trilayer films of nanoparticles, as illustrated in Fig. 16, with sub-minute temporal resolution (Dai et al. 2013).

**Energy Dispersive Reflectivity.** Energy dispersive XR measures the intensity of polychromatic X-rays reflected at a fixed angle of incidence (Neissendorfer et al. 1999). The range in $Q_z$ measured during a single exposure is determined by the range in X-ray energies in the polychromatic beam. Sub-second measurements of XR over a substantial range in $Q_z$ (0.2 Å$^{-1}$) have been
demonstrated (Matsushita et al. 2008). A recently developed angle-energy dispersive mode illustrated in Fig. 17 widens the single exposure $Q_z$ range by combining a range of incident angles with the spread in incident energies (Matsushita et al. 2013). A broadband X-ray beam with a rectangular shape penetrates through an inclined slit and strikes a crystal along the curve $A_1C_1$ shown in Fig. 17. The X-ray beam reflected from the bent and twisted crystal strikes the sample with incident angles varying continuously from $\alpha_H$ to $\alpha_L$ that correspond to energies varying from $E_H$ to $E_L$. The crystal is designed to focus the beam horizontally and vertically onto the sample center. X-rays reflected from the sample strike a pixel-array area detector along the line $A_3C_3$. Each pixel in the reflected beam pattern has a one-to-one correlation with incident X-ray energy and angle, and therefore records a reflection for a particular value of $Q_z$. Measurements from a liquid surface of ethylene glycol demonstrated that the XR spectrum up to $Q_z = 0.43$ Å$^{-1}$ is recorded by a single exposure for as short as 100 seconds.

Figure 17. Bird’s eye (a) and side (b) views of the geometry of angle-energy dispersive reflectivity. The incident angles $\alpha_H$ and $\alpha_L$ correspond to the highest ($E_H$) and lowest ($E_L$) energy X-rays (Matsushita et al. 2013).
Surface X-ray Photon Correlation Spectroscopy (XPCS)

Speckle patterns can be observed when coherent beams scatter from samples with spatial inhomogeneities, including liquid surfaces with capillary wave fluctuations. The origin of the speckle pattern is the irregular phase between coherent beams scattered from different parts of a surface, which results in irregular interference and consequently irregular scattered intensity in the plane of the detector. If the spatial disorder of the surface fluctuates with time the corresponding speckle pattern will also fluctuate, therefore the intensity fluctuations of the speckles can provide information on the underlying dynamics. Although this phenomenon was observed with optical lasers about a half-century ago, the observation of X-ray speckles required the availability of synchrotron radiation sources with sufficient coherent flux.

X-ray photon correlation spectroscopy (XPCS) probes the dynamics by analyzing the temporal autocorrelation function of the speckle pattern,

\[ g_2(Q,\tau) = \frac{\langle I(Q,t)I(Q,t+\tau) \rangle}{\langle I(Q,t) \rangle^2}, \]  

(21)

where \( \tau \) is the time delay and \( I(Q,t) \) is the instantaneous scattered intensity at time \( t \). XPCS experiments have studied dynamics on time scales from microseconds to thousands of seconds and over length scales from nanometers to micrometers. Surface dynamics of low viscosity liquids, high viscosity polymer liquids, and nanoparticle films have been studied by XPCS (Sinha et al. 2014). For example, an XPCS study of the surface dynamics of molten polystyrene films of different thickness, temperature, and polymer molecular weight probed capillary wave surface dynamics from 1 to \( 10^3 \) seconds over length scales from 10 to \( 10^3 \) nm (Z. Jiang et al. 2008). Figure 18 shows autocorrelation function data from a 160 nm thick polystyrene film at temperatures varying from well above to near the bulk glass transition temperature. A transition from single exponential relaxation at 151 °C to multiple relaxation times at 122 °C and 116 °C, and back to single exponential relaxation at 111 °C and 106 °C was observed, thus providing insight into the underlying polymer chain dynamics in the film. Surface dynamics was not observed at 101 °C, which is below...
the bulk glass temperature. The surface viscosity was calculated from a combination of the measured relaxation time as a function of $Q$ and the interfacial tension determined by static diffuse scattering. Scaling of the viscosity with tension, film thickness, and $Q$ was shown to be consistent with a hydrodynamic theory of a film with uniform viscosity.

Figure 18. Temporal autocorrelation functions obtained from a polystyrene film at various temperatures for (a) $Q = 7.4 \times 10^{-3} \, \text{nm}^{-1}$ and (b)-(f) $Q = 1.9 \times 10^{-2} \, \text{nm}^{-1}$ (Z. Jiang et al. 2008).
References


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