X-ray reflection measurement of a water surface was demonstrated using recently developed liquid interface reflectometer at SPring-8. The reflectometer equipped with two-dimensional hybrid pixel array detector, PILATUS, achieved x-ray reflectivity towards $10^{-9}$ with the integration time at each angle of only 1 sec, having enormous potential for quick measurements.

1. Introduction
X-ray reflection method is a powerful tool to investigate the structure of buried interfaces. Recently, it is widely used for characterization of thin films on solid surfaces. This technique can be also applied for characterization of liquid interfaces, such as the water/air or oil/water interfaces, which are more familiar in our daily life. Free liquid surfaces, of course, cannot be tilted and therefore specialized instrumentation – tilt the beam down on the liquid surface – has to be developed for investigation.

Since Als-Nielsen and Pershan developed such surface-horizontal spectrometer for the first time at HASYLAB in the early 1980s [1], seven spectrometers are currently available at synchrotron facilities around the world. By the early 1990s, specular and off-specular reflection revealed that liquid surfaces are generally described by the capillary wave model. And subsequently, some order structures, e.g. surface layering in liquid metals, surface freezing in chain molecules, were discovered. Also, these spectrometers have shown the abilities to study the structure of Langumuir monolayers, surfactants, polymers, biomembranes on a water surface [2].

In Japan, although there was no surface-horizontal spectrometer at Synchrotron facilities so far, the brilliant x-ray source at SPring-8 has great possibilities to achieve some extensive measurements. In the present paper, we carried out x-ray reflection measurement of a water surface to demonstrate the performance of recently developed liquid interface reflectometer at SPring-8. We also challenged a quick measurement for a protein on the water surface.

2. Experimental methods
X-ray reflection measurements were carried out at BL37XU beamline of the SPring-8. The liquid interface reflectometer is schematically illustrated in Fig. 1. A brilliant undulator radiation of 15keV
with the width of 50 μm in the vertical direction was used as an x-ray source. A two-dimensional hybrid pixel array detector, PILATUS [3], covering an area of 487×195 pixels with 172μm / pixel was located 538 mm away from the center of the sample. The purified water sample was contained in a temperature-controlled Langmuir trough [4] covered with an acrylic hood to suppress water evaporation. A set of aluminum sheets was employed as attenuator as listed in Table 1. The integration time at each incident angle was 1 sec. Observed intensities were integrated horizontally and normalized to the intensity of the incident beam, which was monitored using an ionization chamber.

![Schematic diagram of the liquid interface reflectometer at SPring-8.](image)

**Table 1. Experimental conditions of x-ray reflection measurements**

| Incident angle α / deg | Thickness of Al / mm | Transmittance |
|-----------------------|----------------------|---------------|
| From 0.005 To 0.075   | 6                    | 5.77×10⁻⁶     |
| 0.080                 | 0.105                | 4.31×10⁻⁵     |
| 0.110                 | 0.150                | 3.22×10⁻⁴     |
| 0.160                 | 0.290                | 2.40×10⁻³     |
| 0.300                 | 0.575                | 1.79×10⁻²     |
| 0.600                 | 0.850                | 1.34×10⁻¹     |
| 0.900                 | 2.300                | 1             |

### 3. Reflection profiles of a water surface

Figure 2 demonstrates several examples of the reflected intensity profiles of water at 27.0 °C ± 0.1°C. They are normalized to the direct beam intensity without background subtraction.

For liquid-vapor interfaces, the surface morphology is dominated by thermally fluctuated capillary waves. The amplitudes of the capillary waves controlled by the surface tension are typically about the molecular length, and they are observed as a surface roughness by x-ray reflection. On the other hands, the wavelengths of micrometer order causes large diffuse scattering close to the specular reflection. Therefore, the observed reflection intensity including the diffuse scattering crucially depends on the angular resolution of the detector. We analyzed the reflection profiles in accordance with a previous theoretical formulation for the static structure factor of liquid surface including the effect of instrumental resolution [5].

When the detector has the angular resolution Δβ, the wavevector resolution in the \( q_y \) direction corresponds to

\[
\Delta q_y = \frac{1}{2} q_z \frac{\Delta \beta}{2}.
\]
The measured reflection intensity consists of a sharp reflectivity peak with this resolution limited width, superposed on top of the diffuse scattering intensity. As the result, the measured reflectivity always becomes larger than the theoretical prediction and it gives smaller surface roughness. The specular reflectivity of liquid surfaces can be represented using such “effective” mean-square surface roughness \( \sigma_{\text{eff}} \) by,

\[
R(q_z) = R_F \exp(-\sigma_{\text{eff}}^2 q_z^2),
\]

where \( R_F \) is the Fresnel reflectivity. The effective mean-square surface roughness \( \sigma_{\text{eff}} \) depended on the surface tension \( \gamma \) and the wavevector resolution \( \Delta q_y \) is given by [5]

\[
\sigma_{\text{eff}}^2 = \frac{k_B T}{2 \pi \gamma} \ln \left( \frac{q_{\text{max}}}{2.12 \Delta q_y} \right),
\]

where the minimum wavelength of the capillary wave, \( \pi / q_{\text{max}} \) is 1.4 Å for water. In the present work, the resolution function of the PILATUS can be treated similar to IP, which was characterized by a pseudo-Voight function represented by the summation of Gaussian and Lorenzian functions. Since the peak region of the resolution function is mainly determined by the Gaussian component with the standard deviation \( \sigma_{\text{PILATUS}} \), \( \Delta \beta \) is given by

\[
\Delta \beta = 2 \frac{\sigma_{\text{PILATUS}}}{L},
\]

where \( L \) is the distance between the center of the sample and the detector, 538 mm, and the standard deviation of PILATUS resolution \( \sigma_{\text{PILATUS}} \) corresponds to the pixel size of 0.172 mm. The calculated reflectivity using Eq. (2) is shown as the solid curve in Fig. 2. The observed peak intensities show good agreement with the curve.

![Reflection profiles for water. The circles are the observed reflection intensities and the solid curves are the simulated reflection intensities with capillary wave theory.](image)

The reflection profiles including the diffuse scattering can be calculated in accordance with the theoretical formula [6, see Appendix]. They have Gaussian peaks with power-law tails as shown in Fig.
2. The standard deviation of each Gaussian peak is equal to $\Delta q_y$ and the exponent of the power-law tail is determined by $q_z$ and the surface tension. The observed reflection intensities denoted by the circles are well described by the calculation without any adjustable parameters. In particular, the exponent of the power-law tails and the ratios of observed intensities between the "peak" and "tail" region are correctly obtained. This gives confidence that the estimated instrumental resolution is appropriate and furthermore the background scattering intensities are very low.

4. **X-ray reflectivity of a water surface**

Figure 3 demonstrates x-ray reflectivities of a water surface calculated by integration of the reflection profiles around the Gaussian peak region. The solid curve is the reflectivity calculated using Eq. (2) with instrumental resolution of PILATUS of $4\sigma_{\text{PILATUS}}$. The calculated $\sigma_{\text{eff}}$ is typically 3.02 Å at $q_z = 0.1$ Å$^{-1}$ and 2.76 Å at $q_z = 0.5$ Å$^{-1}$. The observed reflectivity using a conventional x-ray tube [5] and CMC-CAT spectrometer at Advanced Photon Source (APS) [7] are also shown for comparison. In the present work, we obtained the reflectivity data $10^{-3}$ lower than that by an x-ray tube. Furthermore, taking a longer integration time of PILATUS, it is not difficult to compete with APS, even the time required the entire measurement is still much shorter.

![Fig. 3 X-ray reflectivity of water surface.](image_url)

5. **Other example: a protein on the water surface**

Here we show other example measured using the present reflectometer. A globular protein, Lysozyme (LSZ) was spread onto a phosphate buffer solution. The reflectivity shown in Fig.4 was measured under non-equilibrium condition, 2 min after the protein injection. The integration time at each angle was 1 sec and the time required entire measurement was 220 sec. Although the reflectivity of LSZ decreases with $q_z$ monotonically without showing any Kiessig fringes, it clearly deviates from that of the buffer solution.

For a liquid having non-uniform density profile except for the capillary waves, the specular reflection represented by Eq. (2) should be modified as [8],
\[ R(q_z) = R_F |\Phi(q_z)|^2 \exp(-\sigma_{\text{eff}}^2 q_z^2), \]  
(5) 

where \( |\Phi(q_z)|^2 \) is the structure factor along to the surface normal expressed as 
\[ |\Phi(q_z)|^2 = \frac{1}{\rho_{\text{bulk}}} \int dz \left| \frac{\partial (\rho(z))}{\partial z} \right|^2 e^{i q_z z}. \]  
(6) 

The structure factor of a two layers model with uniform electron densities, \( \rho_1, \rho_2 \) and layer thicknesses, \( L_1, L_2 \) becomes \cite{9}:
\[ |\Phi(q_z)|^2 = \frac{1}{\rho_{\text{bulk}}} \left[ \rho_1 + (\rho_2 - \rho_1) e^{i q_z L_1} + (\rho_{\text{bulk}} - \rho_2) e^{i q_z L_2} \right]^2. \]  
(7)

We fixed the roughness between each layer 3Å and obtained a density profile as shown in Fig. 4(c). The corresponding reflectivities are also shown in Figs. 4(a) and (b). Since the reflectivity curve did not change for the first 30 min, the configuration of LSZ at the air-water interface remained during the measurement shown in Fig. 4. However, a careful treatment will be necessary for angular scanning reflectometers to measure a quicker structural transition.

![Fig. 4 X-ray reflectivity of Lysozyme spread on a water surface.](image)

### 6. Conclusion

We measured x-ray reflection from a water surface to demonstrate the performance of recently developed liquid interface reflectometer at SPring-8. The reflectometer equipped with a two-dimensional hybrid pixel array detector, PILATUS, achieved x-ray reflectivity towards \( 10^{-9} \) with the integration time at each angle of only 1 sec. The obtained reflection profiles showed good agreement with theory, indicating background intensities (scattering from surrounding air, bulk water or kapton windows and parasitic scattering from slits) are very low. This reflectometer can surely compete with other liquid reflectometers at third-generation synchrotron facilities.
The synchrotron radiation experiments were performed at the BL37XU in the SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2007A1197).

Appendix: Diffuse scattering from capillary waves on a liquid surface

For a liquid having uniform density profile, the reflection intensity including the diffuse scattering can be exactly predicted by the capillary wave theory. For finite instrumental resolution, the reflection intensity originally calculated by Sanyal et al. [6] and modified by Yano et al. [5] is given by,

\[
R(q_y, q_z) = \frac{q_z^4}{16 q_y^4} |T(\alpha)|^2 |T(\beta)|^2 \exp(-\sigma_{\text{eff}}^2 q_y^2) \cdot F_1(\frac{1-\eta}{2}; \frac{1}{2}, -\frac{q_y^2}{2\Delta q_y^2}), \tag{A1}
\]

where \( q_y = k_0(\sin \beta - \sin \alpha), q_z = k_0(\sin \alpha + \sin \beta) \) with \( k_0 = 2\pi/\lambda, \lambda = 0.8265 \text{ Å} \) and \( \alpha = \beta \) for the specular conditions, and \( q_z \) is the wave vector corresponding to the critical angle \( \alpha_c \). \( \Delta q_y \) is the wavevector resolution in the \( q_y \) direction defined as Eq. (1). \( \eta \) is the coefficient \( C_{q_y} \) for fixed \( q_z \), whereas \( \frac{q_y}{\Delta q_y} \gg 1 \) with fixed \( q_z \), where the coefficient \( C \) is related with \( \eta = k_0 \alpha_c \gamma / (2\pi \alpha_c) \).

The factors \( |T(\alpha)|^2 |T(\beta)|^2 \) arise from the distorted-wave Born approximation [10], since the Born approximation breaks down when either the incident or scattered grazing angle of incidence is close to the critical angle. \( T(\alpha) \) and \( T(\beta) \) are the Fresnel transmission coefficients for a smooth surface given by

\[
T(\alpha) = \frac{2 \sin \alpha}{\sin \alpha + (\sin^2 \alpha - \sin^2 \alpha_c)^2}, \tag{A2}
\]

which implies that the intensity of diffuse scattering has a maximum called “Yoneda peak” at \( \beta = \alpha_c \). These equations indicate that the smaller \( \gamma \) and the larger \( q_z \) give the larger intensity of diffuse scattering.

At \( q_y = 0 \), \( R(q_y, q_z) \) must be represented as the specular reflection

\[
R(0, q_z) = R_f \exp(-\sigma_{\text{eff}}^2 q_z^2), \tag{A3}
\]

with the Fresnel reflectivity represented as

\[
R_f = \frac{q_z^4}{16 q_y^4} |T(\alpha)|^2 |T(\beta)|^2.
\]

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