

# X-ray Photon Correlation Spectroscopy on Fluctuating Surfaces

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## Introduction

The technique of x-ray photon correlation spectroscopy is a useful tool for probing the dynamics of systems on a submicrometer scale. Because of its sensitivity to fluctuations, it is also a useful tool for diagnosing the stability of a beamline.

X-ray photon correlation spectroscopy relies on the coherence of very narrow x-ray beams. When such a beam is used to illuminate a sample, the resulting scattered pattern contains detailed information about the conformation or configuration of the sample. If the scattered intensity is recorded as a function of time, time constants related to the fluctuation of a sample can be recovered by applying the time autocorrelation function to the intensity data.

## Methods and Materials

Two different types of systems were studied: (1) the interface between a hydrophilic liquid droplet and a hydrophobic surface and (2) a colloidal suspension. The fluctuations in the former result from thermally excited capillary waves at the interface, while the latter are subject to Brownian motion.

The first samples were prepared by coating a Si wafer with octadecyltriethoxysilane (OTE), forming a self-assembled monolayer of hydrocarbon chains. A drop of glycerol was placed on the surface to produce an interface at a well-defined position. Glycerol was chosen because its viscosity changes rapidly with temperature; hence, it is possible to tune fluctuation rates. In order to take advantage of this property, the OTE-coated Si wafer was mounted on the face of a Peltier thermoelectric cooler capable of maintaining a 35°C temperature gradient between its faces. The Peltier cooler was mounted on a water-cooled copper block, yielding sample temperatures as low as -20° C.

This experiment was conducted at sector 34-ID-C operated by the University-National Laboratory-Industry Collaborative Access Team (UNI-CAT) by using a Kappa diffractometer in a reflection geometry. A direct reading charge-coupled device (CCD) with 22.5- $\mu\text{m}^2$  pixels was placed 2.2 m from the sample. Photon energies of 9 and 10 keV were used.

Because the low-angle reflectivity from a surface produces a long streak of intensity on the detector, this experiment was ideally suited to use of the CCD's kinetic mode. In the kinetic mode, most of the detector area is

blocked off so that only a small region is exposed. A short exposure is taken, then all charges are shifted down a set number of pixels. This is repeated until the entire detector is full of images. Then the charge is read out, producing a time series of images as shown in Fig. 1. While in normal mode, the time between points is at least 0.5 s; in the kinetic mode, spacings of 0.03 s were reachable.

Colloidal samples were prepared by suspending 100-nm silica in pure glycerol. Once again, glycerol was used because its viscosity depends strongly on temperature. The colloidal suspension was fed into a 0.5-mm-diameter quartz capillary that was then sealed. Data were taken at sector 34-ID-C by using the same diffractometer and cooling arrangement as described for the OTE samples. Because all scattering from colloids is in the low-angle regime, it is necessary to block out the direct beam, which was done by using lead tape. Because of the expected time constants of the system, and because the scattering pattern is much larger than the reflectivity from a surface, the CCD's normal mode was used for this sample. An example of these data is shown in Fig. 2. This image is log-scaled in order to better show the multiple rings.

## Results

Data from both experiments were analyzed by selecting one point in reciprocal space and recording the intensity as a function of time  $I(t)$ . For the case of the colloids, this simply involved recording the intensity from a single pixel in each frame. For the case of the OTE experiment, where data were read by using the kinetic mode, the same point in each slice was used, yielding approximately 100 data points per frame. In building  $I(t)$ , it was necessary to account for dead time between frames caused by data transfer. Typically, the time between slices was 0.03 s, and the time between frames was 1.5 s. A portion of one such intensity function is shown in Fig. 3.

It is immediately evident that the stability of the beamline needs to be addressed. The intensity is subject to random fluctuations that should be related to fluctuations at the glycerol-OTE interface. The periods of zero intensity are the dead time. The problematic feature is the movement of the streak with a period of 37 s. This change is far too drastic to be a change in the sample; therefore, it must be a feature of the new beamline, which is at the beginning of its commissioning phase.

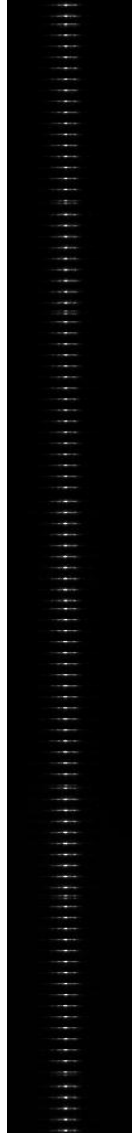


FIG. 1. Reflectivity measurement captured in kinetic mode.

Even more features appear when the autocorrelation function is calculated. This function is defined as

$$g(\tau) = \frac{\langle I(t) \times I(t + \tau) \rangle_t}{\langle I(t) \rangle_t^2},$$

where the brackets denote averaging over time. In calculating this function, it was necessary to write a program that would avoid using points from the dead times. The beamline fluctuations are extremely prominent in the calculated autocorrelation function (Fig. 4). Similar results are found in the data from the colloidal sample.

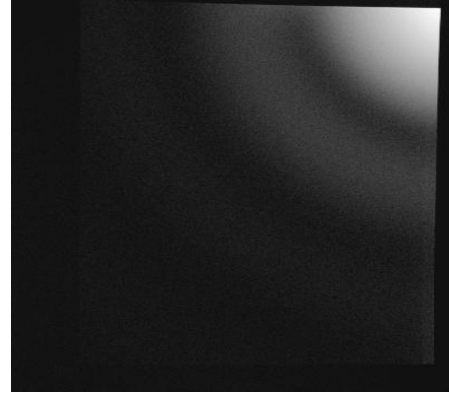


FIG. 2. Diffraction from colloidal silica.

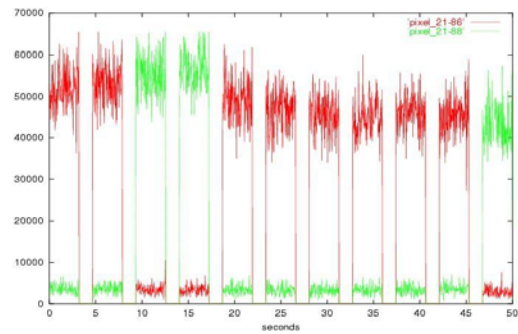


FIG. 3. Intensity vs. time for two positions on the detector.

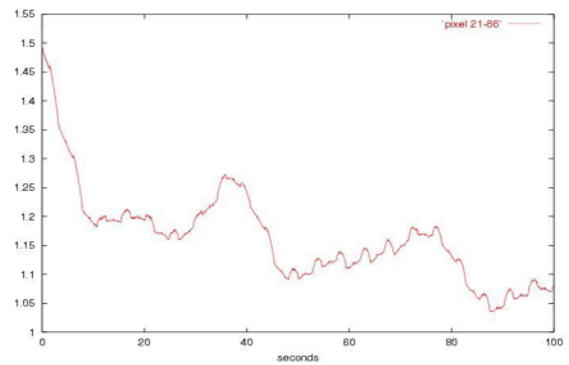


FIG. 4. Time autocorrelation function.

## Discussion

This beamline has the capacity to provide valuable information about small-scale fluctuations on surfaces and in fluids. Continued development is necessary before the full potential can be realized.

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