

# Heterodyne Measurements with Coherent X-rays

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## Introduction

Recently there has been growing interest in x-ray intensity fluctuation spectroscopy (XIFS) [1] as a means of obtaining information on the dynamics of systems at a shorter length scale than is accessible with visible light [2]. X-rays also have another advantage over light: most things are transparent to x-rays.

The normalized autocorrelations of the intensity measurements  $g^{(2)}(q, \tau)$  are related to the normalized autocorrelations of the density  $g^{(1)}(q, \tau)$  by the Siegert relation:

$$g^{(2)}(q, \tau) = 1 + \beta \left| g^{(1)}(q, \tau) \right|^2.$$

This relation indicates that the phase information contained in  $g^{(1)}(q, \tau)$  is lost. Getting information about the phase is important in many systems, particularly when local density fluctuations are superimposed on a slow macroscopic motion. To this end, heterodyne detection, which is routinely used with light [3], could be applied to XIFS by using a high-intensity reference beam. In such conditions, the signal of  $g^{(1)}$  could be enhanced considerably, leading to a mixture of  $g^{(2)}$  and the real part of  $g^{(1)}$  in the measured intensity-intensity autocorrelation function  $\langle I(q, t)I(q, t + \tau) \rangle_t$ . Unexpected heterodyning effects have been recently reported [4] in grazing incidence scattering measurements. The goal of this study is to apply heterodyne detection in small-angle x-ray scattering (SAXS) measurements for investigating the relaxation of nanoparticle aggregates dispersed in rubber after the composite has been stretched.

## Methods and Materials

Our samples were prepared by dispersing nanoparticle aggregates (carbon black or fumed silica) into synthetic rubber. Two different volume fractions were investigated (one below and one above the percolation threshold). Each sample was either un-cross-linked or cross-linked with dicumyl peroxide. The sample thickness was about 0.5 mm, and elongation was 50%. XIFS measurements were performed at beamline 8-ID at the APS. X-ray energy was 7.6 keV, and the sample-to-detector distance was 2.8 m. A square beam ( $15 \times 15 \mu\text{m}$ ) was used, yielding a contrast factor  $\beta$  of 30%. The domain of  $q$ -values investigated

ranged between  $5 \times 10^{-3}$  and  $4 \times 10^{-2} \text{ \AA}^{-1}$ . In order to alternatively use homodyne and heterodyne detection modes, we made a rectangular sample holder (thickness of 1.1 mm) with two holes (diameter of 2 mm). One hole was filled with compacted Aerosil® 200, which served to create the reference beam, while the second one was left empty. The upper end of the filled rubber ribbon being investigated was fixed behind the metallic piece, and the lower end was free. The width of the sample was large enough to cover the two holes. The straight-through beam, the sample alone (homodyne mode), and the sample illuminated by the beam scattered by the Aerosil 200 (heterodyne detection) could be measured by horizontal displacement of the sample holder. For heterodyne detection, both the rubber and the Aerosil were in the coherence volume. Typical measuring time per frame was 250 ms, and the number of frames varied between 200 and 500. The detector was a direct illumination charge-coupled device (CCD) camera (Princeton).

## Results and Discussion

### Preliminary Tests

To check for correctness of this new type of measurement, several tests were made.

The first test was to find the most suitable material to be used to create the high-intensity reference beam. The slightly compacted fumed silica Aerosil 200 worked well;  $g^{(2)}$  remained constant with time and with  $q$ . This also demonstrated the required stability of the experimental setup. The second test was to check the validity of the homodyne-heterodyne measurements. We used a dilute suspension of latex spheres (diameter of 98 nm) in glycerol at 10°C. We verified, as expected, that there is a factor of two between the time constants measured in the homodyne and heterodyne modes.

### Experimental Results

Figure 1 shows the variation in the intensity scattered (expressed as the number of photons per pixel per second) as a function of  $q$  in the homodyne (filled circles) and heterodyne (open squares) modes. The sample under study (T5) is cross-linked rubber filled with 20 vol% of carbon black. The heterodyne curve results from the addition of scattering of T5 and the

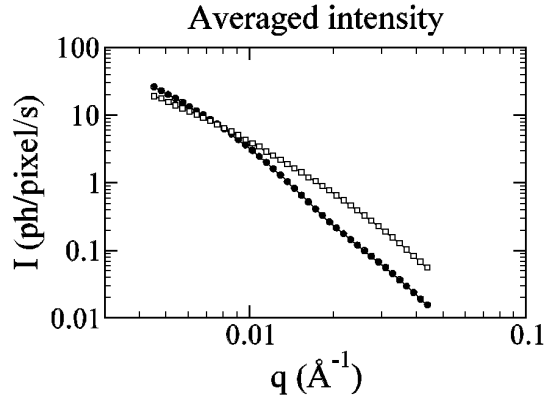


FIG. 1. SAXS intensity curves from sample T5 (homodyne detection, closed symbols) and Aerosil 200 + T5 (heterodyne mode, open symbols).

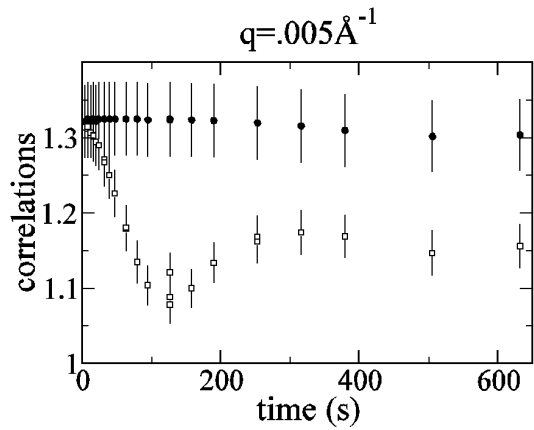


FIG. 2. Homodyne (filled circles) and heterodyne (open squares) correlations at  $q = 0.005 \text{ \AA}^{-1}$  for sample T5.

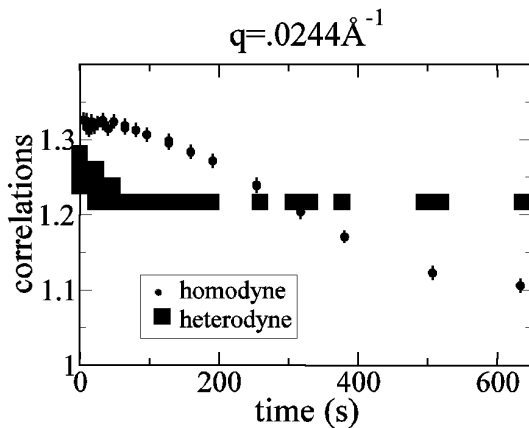


FIG. 3. Homodyne and heterodyne correlations measured at  $q = 0.0244 \text{ \AA}^{-1}$  for sample T5

Aerosil 200 located upstream.

This figure shows that the scattered intensity is large enough to provide accurate results. Note that the Aerosil 200 attenuates the incident beam by a factor of three, so its scattering dominates the total scattering.

The homodyne and heterodyne correlations  $g^{(2)}$  determined for T5 at  $q = 0.005 \text{ \AA}^{-1}$  and  $0.0244 \text{ \AA}^{-1}$  are shown in Figs. 2 and 3, respectively. At small  $q$  (Fig. 2), the curve corresponding to  $g^{(2)}_{\text{homo}}$  displays a very slow decrease.

The shape of the curve  $g^{(2)}_{\text{hetero}}$  shows oscillations that are characteristic of heterodyning and result from the leading term  $\cos(qvt)$  in the real part of  $g^{(1)}$ . From the position of the first minimum at a time  $t$  of about 120 seconds, one can get a first rough estimate of the speed of displacement  $v$  of the sample. It is close to  $2.6 \text{ \AA/s}$ . A precise analysis of the curve will separate the contribution from this macroscopic displacement (as the stretched sample tends to recover its original shape) and the contribution from the local microscopic relaxation of aggregates tending to rebuild a network (the mechanism of interest). Understanding the effect of the macroscopic motion on the relaxation is one goal of this study. At larger  $q$  values (Fig. 3) (i.e., at a smaller length scale),  $g^{(2)}_{\text{homo}}$  starts to decrease for  $t$  larger than about 50 seconds without reaching 1. At shorter times ( $t < 50$  seconds),  $g^{(2)}_{\text{homo}}$  remains constant, while  $g^{(2)}_{\text{hetero}}$  exhibits short time fluctuations. The plateau reached by  $g^{(2)}_{\text{hetero}}$  results from the static contribution of the Aerosil. A complete analysis of the data obtained during this experiment is currently in progress. These results demonstrate the feasibility of the technique. It should become a promising method for investigating the dynamical behavior of complex soft materials.

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