9

X-RAY INTENSITY FLUCTUATION SPECTROSCOPY

M. SUTTON
Centre for the Physics of Materials, McGill University, Montreal, Quebec, Canada

1. INTRODUCTION

At the outset let me stress that X-ray intensity fluctuation spectroscopy (XIFS) is a diffraction technique. As such, the intuition and expertise that you have developed for diffraction carries over to this new technique. The tendency in this chapter is to emphasize the aspects that are different from conventional diffraction but results learned from conventional diffraction will be called upon as needed.

Wave phenomena are very prevalent in nature. Essential features of wave behaviour are the effects of interference and diffraction. For example, most textbooks on X-rays derive the X-ray diffraction by considering X-rays as planes waves and calculating the constructive and destructive interferences of these waves diffracting from atoms. In spite of the predominance of interference phenomena fundamental to wave phenomena, we are accustomed to the lack of such phenomena when dealing with conventional light. In order to describe whether or not one needs to consider these effects one should discuss the coherence of wave sources. Just the mention of coherence almost universally brings to mind lasers. Although lasers are intrinsically coherent sources of light, coherence effects can be seen from any source of waves.

As an introduction to intensity fluctuation spectroscopy (IFS), let me first describe "speckle". Speckle is an effect, often seen in laser light, that results when coherent light reflects or scatters diffusely off disordered material. The intensity at each spot in the "image" is the result of light from many different points in the disordered materials. The essentially random path lengths of the light from these points to the given spot in the image leads to the light being the sum of rays with a random set

F. Hippert et al. (eds.), Neutron and X-ray Spectroscopy, 297–318.

of phases. However, since the light is coherent, the phase of the resulting light, even though it is randomly distributed from point to point, has a definite value at each point. Where the phases add destructively, it results in a dark spot and where they add constructively a bright spot. This is the origin of the speckled appearance of the image. It is a good thing for us that conventional light sources are incoherent, since speckle could be quite annoying in everyday life.

As an introduction to the mathematics needed to deal with speckle and coherence, I would like to give an alternative derivation[1]. Assume we have a set of N particles, randomly distributed throughout some volume. The scattering $I(\boldsymbol{q})$ at wavevector $\boldsymbol{q}$ from this system is (ignoring constants)

$$
\begin{aligned}
I(\boldsymbol{q}) &= \left| \sum_{j=1}^{N} f_j \, \mathrm{e}^{i\boldsymbol{q}\cdot \boldsymbol{r}_j} \right|^2 \\
&= \sum_{j=1}^{N} \left| f_j \right|^2 + \sum_{k \neq l}^{N} f_k^{\dagger} f_l \, \mathrm{e}^{i\boldsymbol{q}\cdot(\boldsymbol{r}_l - \boldsymbol{r}_k)} \\
&= \sum_{j=1}^{N} \left| f_0 \right|^2 + 2 \sum_{k<l}^{N} \left| f_0 \right|^2 \cos\left(\boldsymbol{q}\cdot(\boldsymbol{r}_l - \boldsymbol{r}_k) \right)
\end{aligned}
\qquad \{1\}
$$

where f_j is the scattering factor for each particle. The last equation has been specialized to identical particles, f_0. From this equation it is easy to see that the average intensity (averaged over particle positions) is N times the scattering of each particle

$$
\left\langle I(\boldsymbol{q}) \right\rangle = N \left| f_0 \right|^2 \qquad \{2\}
$$

To see why there is "speckle", one looks at the standard deviation of the intensity. First, calculate the variance. For identically distributed values, this will be the number of objects times the variance of each object. Since the phase factor above varies between plus and minus one we can estimate the variance of each object as

$$
\begin{aligned}
\sigma_{I(\boldsymbol{q})} &= \left\langle I(\boldsymbol{q})^2 \right\rangle - \left\langle I(\boldsymbol{q}) \right\rangle^2 \\
&= N(N-1) \left| f_0 \right|^4 \\
&\approx \left(N \left| f_0 \right|^2 \right)^2
\end{aligned}
\qquad \{3\}
$$

We can now conclude that the scattering from N randomly placed identical particles is $\left\langle I(\boldsymbol{q}) \right\rangle \pm \left\langle I(\boldsymbol{q}) \right\rangle$ and this varies from zero to about twice the average. A detailed calculation of the distribution of intensities shows, for perfectly coherent

1. This is a variation of an argument I heard in a colloquium by Paul CHAIKIN.