

Time-Dependent Statistical Mechanics

16. Scattering of particles and radiation by macroscopic systems

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November 27, 2009

1 Review of generic scattering theory

Many scattering experiments in which a beam radiation or particles are sent into a material that scatters them have a number of features in common. (We shall use the word radiation to refer to the thing that is scattered.)

- The radiation is a wave that satisfies a wave equation.
- The incident beam is collimated (moving in one particular direction).
- The incident beam is monochromatic (a narrow range of frequencies and energies).
- The radiation interacts weakly with the sample and only a small fraction of the radiation is scattered. Most of the scattered radiation leaves the sample without being scattered again.
- The detector is shielded so that it detects only that radiation coming out in a narrow range of directions.

This applies to

- scattering of electromagnetic radiation, including
 - visible light

- * Rayleigh light scattering
- * Raman scattering
- x-rays
- scattering of particles
 - electrons
 - neutrons
 - α particles

Other features of the experiments that are common but not as universal are:

- There may be a frequency or energy filter in front of the detector so that the detector responds only to a narrow range of frequencies in the scattered radiation. The frequency that is detected can be tuned.
- There may be polarization or spin filters between the source and the sample so that the incident beam is polarized.
- There may be polarization or spin filters between the scattered beam and the detector so that the measurement can be performed as a function of the polarization of the scattered radiation.

The theory of all these experiments is very similar provided:

- electromagnetic radiation is described classically,¹ using Maxwell's equations;
- particles are described using Schrodinger's equation.

The matter of the sample can be described using either classical or quantum mechanics, and the similarity still survives.

There are several details that vary from one type of scattering to another:

- the form of the wave equation

¹The classical theory of Raman scattering describes some features of Raman scattering but not all. A completely satisfactory theory requires a quantum description of the radiation as well as of the matter. In particular, the classical theory is not very useful for resonant Raman scattering and resonant fluorescence.

- second order in time for Maxwell’s equations;
- first order in time for Schrodinger’s equation;
- the number and type of components to the wave function
 - polarization components, in the case of electromagnetic radiation;
 - spin components, in the case of particles;
 - real and imaginary components, in the case of particles

The generic wave equation is of the form:

$$\left(\frac{i}{\mu} \frac{\partial}{\partial t}\right)^n \phi(\mathbf{r}, t) = -\nabla^2 \phi(\mathbf{r}, t) - \rho(\mathbf{r}, t) \phi(\mathbf{r}, t)$$

where $n = 1$ or $n = 2$. The term on the left and the first term on the right describe the unperturbed propagation of the waves. The second term on the right describes the coupling of the waves to the sample. In the case that there is more than one component to the wave, the equations are similar to this except that the time derivative of one component is related to the other components as well.

The system variable, $\rho(\mathbf{r}, t)$, is the important property of the system as far as the wave is concerned. Nothing else about the system really matters. It is the ‘hook’ by which the scattering probe grabs onto the matter and it is the hook by which the matter scatters the wave. To understand any scattering experiment, it is important to identify that variable and then to recognize that the the experiment is telling us primarily about the behavior of that variable. We shall refer ρ as the ‘density’, but for different experiments it corresponds to different densities. In the case of the wave being particles, $\rho(\mathbf{r}, t)$ is, except for constant factors, equal to the potential energy of interaction of the sample with a particle at \mathbf{r} . ρ depends on the instantaneous state of the sample.

The differential equation can be converted into an exact integral equation of the form

$$\phi(\mathbf{r}, t) = \phi_0(\mathbf{r}, t) + \int d\mathbf{r}' \int_{-\infty}^{\infty} dt' G(\mathbf{r} - \mathbf{r}', t - t') \rho(\mathbf{r}', t') \phi(\mathbf{r}', t')$$

where $G(\mathbf{r}, t)$ is the Green’s function for the combination of differential operators that appear in the wave equation. The form of G depends on n of course.

The first term on the right represents the unperturbed incident beam, and the second term represents the scattered wave. Physically, G corresponds to waves emanating from the places where $\rho\phi$ is nonzero. When the scattering is weak, we can replace ϕ by ϕ_0 in the second term on the right.

Now we deal with the special case of $n = 2$ but the considerations are similar for the other case. Let us put the origin of our coordinate system in the sample in the illuminated region. Then the detector is at \mathbf{R} . Suppose that in the region of illumination the incident wave is of the form

$$\phi_0(\mathbf{r}, t) = A_i(\mathbf{r})e^{i(\mathbf{k}_i \cdot \mathbf{r} - \omega_i t)}$$

then at the detector, the scattered wave is of the form

$$\phi(\mathbf{R}, t) \approx \frac{A_i}{4\pi R} \int_{\mathcal{R}} d\mathbf{r}' \rho(\mathbf{r}', t - R/v) e^{i((\mathbf{k}_i - \mathbf{k}_f) \cdot \mathbf{r}' - \omega_i(t - R/v))}$$

Here $\mathbf{k}_f = |\mathbf{k}_i| \mathbf{R}/R$. I.e. it is a wave vector whose magnitude is that of the incident radiation but whose direction is that of the scattered radiation that is being detected.

This result has a simple interpretation. The wave at the detector at time t must have been scattered off the sample at an earlier time $t - R/v$, and the amplitude of the scattering depends on what the values of ρ were for various points in the illuminated region at that earlier time. Different parts of the illuminated region contribute to the scattered amplitude, but there is the possibility of constructive and destructive interference among waves scattered at different points in the sample.

Notice that the time dependent amplitude of the scattered wave involves the spatial Fourier transform of the $\rho(\mathbf{r}, t)$ at a wave vector equal to the difference in the wave vectors of the outgoing and incoming waves.

There are two distinct types of detection that could take place.

- Total intensity measurement. The detector measures the absolute square of the wave function at its location and averages this over time, and we must do the same thing and average over the ensemble of systems to calculate the measured quantity. We get

$$I_{total}(\hat{\mathbf{k}}_f) = \left| \frac{A_i}{4\pi R} \right|^2 \int_{\mathcal{R}} d\mathbf{r} \int_{\mathcal{R}} d\mathbf{r}' e^{-i(\mathbf{k}_f - \mathbf{k}_i) \cdot (\mathbf{r} - \mathbf{r}')} \langle \rho(\mathbf{r}) \rho^*(\mathbf{r}') \rangle$$

Without any loss of generality, we can write

$$\langle \rho(\mathbf{r})\rho^*(\mathbf{r}') \rangle = \langle \rho(\mathbf{r}) \rangle \langle \rho^*(\mathbf{r}') \rangle + \langle \delta\rho(\mathbf{r})\delta\rho^*(\mathbf{r}') \rangle$$

There are thus two possible terms in the total intensity.

- The first term is

$$\left| \frac{A_i}{4\pi R} \right|^2 \left| \int_{\mathcal{R}} d\mathbf{r} e^{-i(\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{r}} \langle \rho(\mathbf{r}) \rangle \right|^2$$

This is the most important contribution when the material is a crystal. The integral is then nonzero for values of $\mathbf{k}_f - \mathbf{k}_i$ that correspond to the periodicity of the crystal. For x-ray or neutron scattering the integral is proportional to the volume of the illuminated region and hence the contribution is proportional to the square of the volume. Only very specific directions of scattering have this large intensity. This gives the characteristic spot patterns of crystal diffraction. This result is the basis for the use of x-rays and neutrons for crystal structure determination.

- The second term is

$$\left| \frac{A_i}{4\pi R} \right|^2 \mathcal{R} \int d\mathbf{r} e^{-i(\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{r}} \langle \delta\rho(\mathbf{r})\delta\rho^*(0) \rangle$$

It is typically of interest only if the material is not a crystal, in which case this is the entire result. Note that as long as we restrict our attention to the nonzero values of $\mathbf{k}_i - \mathbf{k}_f$ that correspond to a scattering experiment, we could just as well write this in terms of the $\rho\rho$ correlation function.

$$\left| \frac{A_i}{4\pi R} \right|^2 \mathcal{R} \int d\mathbf{r} e^{-i(\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{r}} \langle \rho(\mathbf{r})\rho^*(0) \rangle$$

Thus one term is proportional to the square of the Fourier transform of the average density ρ , and the other is proportional to the Fourier transform of the correlation function of the density fluctuation. Note that both of these averages are static averages. This is characteristic of total intensity measurements.

- Frequency resolved measurement. We will consider only the case of materials that are not crystals. Then

$$I(\hat{\mathbf{k}}_f, \omega) = \frac{1}{2\pi} \left| \frac{A_i}{4\pi R} \right|^2 \mathcal{R} \int d\mathbf{r} \int_{-\infty}^{\infty} dt e^{-i(\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{r}} e^{i(\omega - \omega_i)t} \langle \rho(\mathbf{r}, t) \rho^*(0, 0) \rangle$$

A frequency resolved experiment has the possibility of observing dynamic correlations. In this case, it is the space-time Fourier transform of the density-density autocorrelation function that is measured. The wave vector for the Fourier transform is $\mathbf{k}_f - \mathbf{k}_i$, the difference between the wave vector of the scattered and incident waves. The frequency for the Fourier transform is $\omega - \omega_i$, the frequency observed scattered wave minus the frequency of the incident wave.

- These results for the total intensity measurement and the frequency resolved experiment are consistent in that

$$\int_{-\infty}^{\infty} d\omega I(\hat{\mathbf{k}}_f, \omega) = I(\hat{\mathbf{k}}_f)$$

2 Neutron scattering

Neutron scattering is much less familiar to chemists than light scattering and x-ray scattering, but it has historically been very important in understanding the dynamics of liquids. We start with it because in some sense it is one of the simplest to discuss and some of the results are analogous to those of the other light scattering techniques.

Neutrons have no charge, but they have spin (and hence a magnetic moment) and they have exert nuclear forces. Neutrons thus have three interactions with matter:

- They interact with nuclei at short distances (i.e. distances of the order of the nuclear diameter, about 10^{-13} cm.)
- Their spin can interact with nuclear spins at short distances.
- Their magnetic moment can interact with net magnetic moments of the matter.

Let's focus on the first two. The last is important for scattering from magnetic crystals and other magnetic materials.

Since the neutron spin is $1/2$, there are two components to the wave function. A simple model for the very short range interaction of a neutron with a nucleus is

$$V(\mathbf{r}, \sigma, \mathbf{R}_i, \sigma_i) = (a_{1i} + a_{2i} \hat{\sigma} \cdot \hat{\sigma}_i) \delta(\mathbf{r} - \mathbf{R}_i)$$

Here \mathbf{R}_i and $\hat{\sigma}_i$ are the position and spin operator of atom i , and \mathbf{r} and $\hat{\sigma}$ are the position and spin of the neutron. The interaction is of such a short range that its position dependence is represented as a delta function. There are two numbers, a_{1i} and a_{2i} that represent the strength of the interactions. The first interaction is spin independent and the second is spin dependent. The two numbers depend on the atomic number and atomic mass of the nucleus, thus they are in general different for different isotopes of the same element. These numbers are related to what nuclear scattering people called 'scattering lengths'.

The total interaction of a neutron with a sample containing a large number of atoms is

$$\sum_i V(\mathbf{r}, \sigma, \mathbf{R}_i, \sigma_i) = \sum_i (a_{1i} + a_{2i} \sigma \cdot \sigma_i) \delta(\mathbf{r} - \mathbf{R}_i)$$

It is this potential that, except for constant factors, is the ρ in the Schrodinger equation for the neutrons.

The ρ has two spin components, and it appears in an equation for a two-component wave function. The general structure of the result for the scattered intensity is clear from the above discussion. We end up with the Fourier transform of the space time correlation function of this function with itself. Each component of ρ contains a spin-independent and spin-dependent term. You have to do detailed bookkeeping on the various terms and on the various components.

Let's consider the total scattered intensity for the case of an unpolarized incident beam and no polarization detection. Let's skip the details, but merely note the following. Cross terms involving the correlation of the spin dependent part of ρ with the spin independent part of ρ vanish exactly, basically because the average spin of a nucleus is zero. The two separate

densities that are of importance are

$$\begin{aligned}\rho_1(\mathbf{r}) &= \sum_i a_{1i} \delta(\mathbf{r} - \mathbf{R}_i) \\ \rho_2(\mathbf{r}) &= \sum_i a_{2i} \hat{\sigma}_i \delta(\mathbf{r} - \mathbf{R}_i)\end{aligned}$$

ρ_1 is a density of nuclei, as a function of position, with each nucleus being weighed according to the strength of its interaction with the incoming neutrons. ρ_2 is a similar weighted density of nuclear spin. The total scattered intensity is the sum of two contributions, each of which is the Fourier transform of the autocorrelation function of a ρ_i with itself.

For simplicity, let's consider the case of a system with only one kind of nucleus. Then the a constants can come out of the sum.

$$\begin{aligned}\rho_1(\mathbf{r}) &= a_1 \sum_i \delta(\mathbf{r} - \mathbf{R}_i) = a_1 f(\mathbf{r}) \\ \rho_2(\mathbf{r}) &= a_2 \sum_i \hat{\sigma}_i \delta(\mathbf{r} - \mathbf{R}_i)\end{aligned}$$

The first equation defines a basic atomic density of the material as a function of position.

The space time autocorrelation function of ρ_1 is

$$\langle \rho_1(\mathbf{r}, t) \rho_1(\mathbf{r}', t') \rangle = a_1^2 \langle f(\mathbf{r}, t) f(\mathbf{r}', t') \rangle = a_1^2 \sum_{ij} \langle \delta(\mathbf{r} - \mathbf{R}_i(t)) \delta(\mathbf{r}' - \mathbf{R}_j(t')) \rangle$$

It gives rise to what is called “coherent scattering”.

$$I_{coh}(\hat{\mathbf{k}}, \omega) \propto \int d\mathbf{r} \int_{-\infty}^{\infty} dt e^{-i((\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{r} - (\omega - \omega_i)t)} a_1^2 \langle f(\mathbf{r}, t) f(\mathbf{0}, 0) \rangle$$

The Fourier transform that appears here is proportional to

$$\sum_{ij} e^{-i\mathbf{k} \cdot (\mathbf{R}_i(t) - \mathbf{R}_j(t'))}$$

Fluctuations in the atomic density at different points and times determine the scattering intensity. This is called coherent scattering because scattering from different atoms contribute to the amplitude and the amplitude is squared to get the total intensity. Thus there can be constructive or destructive interference between the scattering from different atoms.

The space time autocorrelation function of ρ_2 is distinctly different.

$$\begin{aligned}
\langle \rho_2(\mathbf{r}, t) \rho_2(\mathbf{r}', t') \rangle &= a_2^2 \sum_{ij} \langle \sigma_i(t) \sigma_j(t') \delta(\mathbf{r} - \mathbf{R}_i(t)) \delta(\mathbf{r}' - \mathbf{R}_j(t')) \rangle \\
&= a_2^2 \sum_{ij} \langle \sigma_i(t) \sigma_j(t') \rangle \langle \delta(\mathbf{r} - \mathbf{R}_i(t)) \delta(\mathbf{r}' - \mathbf{R}_j(t')) \rangle \\
&= a_2^2 \sum_i \langle \sigma_i(t) \sigma_i(t') \rangle \langle \delta(\mathbf{r} - \mathbf{R}_i(t)) \delta(\mathbf{r}' - \mathbf{R}_i(t')) \rangle \\
&= a_2^2 \langle \sigma^2 \rangle \sum_i \langle \delta(\mathbf{r} - \mathbf{R}_i(t)) \delta(\mathbf{r}' - \mathbf{R}_i(t')) \rangle
\end{aligned}$$

Then we have

$$I_{inc}(\hat{\mathbf{k}}, \omega) \propto a_2^2 \langle \sigma^2 \rangle \sum_i e^{i\mathbf{k} \cdot (\mathbf{R}_i(t) - \mathbf{R}_i(0))}$$

In getting the second equality, we used the fact that the nuclear spins interact with the other degrees of freedom so weakly that they are uncorrelated with the positions. In getting the third equality we used the fact that nuclear spins on different atoms interact so weakly that they are not correlated. In getting the fourth equality we used the fact that the nuclear spins do not change with time because there is the interactions of the spins with the other degrees of freedom are so weak. Notice that there are no cross terms between different particles. Each particle contributes independently to the scattering. There is no interference between the scattering of different particles. This is called incoherent scattering.

Coherent and incoherent scattering measure two different aspects of the time and space dependent density fluctuations in a fluid. Coherent scattering gives information about the collective behavior of the atoms. Incoherent scattering gives information about correlations involving a single atom. (Incidentally, it is the incoherent scattering that is related to the same correlation function that is needed to calculate the mean square distance moved by a particle in time t , which is related to the self diffusion coefficient.) The frequencies $\omega - \omega_i$ and wave vectors $\mathbf{k}_f - \mathbf{k}_i$ that can be used in neutron scattering are such that it can be used to probe a material on the time scale of picoseconds and the distance scale of Angstroms. Thus, it is ideal for studying short time dynamics of atomic motion in fluids.

The information obtainable from a neutron experiment depends crucially on the values of the a_1 and a_2 parameters of the interaction of the neutrons with the nuclei.

- Atoms differ in the amounts of coherent vs. incoherent scattering.
 - Argon-36 has primarily coherent scattering.
 - Protons have much larger incoherent scattering intensities than coherent intensities.
- In a sample, with two or more types of nuclei, the two types may make very different contributions to the total intensity.
- The interaction parameters can be positive or negative. For some elements there are some isotopes with positive values and some with negative. In some cases it is possible to prepare isotopic mixtures of an element in which the average a_1 of all the atoms is zero. If you make an alloy containing this, these atoms will not contribute to the coherent scattering. Only the other types of atoms will be seen.
- More generally, the results of an experiment are a superposition of the coherent correlation functions and the incoherent correlations, with weights that depend on the scattering parameters.

slides

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Focus on the first two.

The neutron spin has 1/2; there are two components to the wave function. A simple model for the very short range interaction of a neutron with a nucleus i is

$$V(\mathbf{r}, \sigma, \mathbf{R}_i, \sigma_i) = (a_{1i} + a_{2i} \hat{\sigma} \cdot \hat{\sigma}_i) \delta(\mathbf{r} - \mathbf{R}_i)$$

\mathbf{R}_i and $\hat{\sigma}_i$ are the position and spin operator of atom i

\mathbf{r} and $\hat{\sigma}$ are the position and spin of the neutron.

The first interaction is spin independent.

The second is spin dependent.

$$V(\mathbf{r}, \sigma, \mathbf{R}_i, \sigma_i) = (a_{1i} + a_{2i} \hat{\sigma} \cdot \hat{\sigma}_i) \delta(\mathbf{r} - \mathbf{R}_i)$$

The two numbers, a_{1i} and a_{2i} , represent the strength of the interactions.

a_{1i} and a_{2i} depend on the atomic number and atomic mass of the nucleus.

They are in general different for different isotopes of the same element.

They are related to what nuclear scattering people called ‘scattering lengths’.

The total interaction of a neutron with a sample containing a large number of atoms is

$$\sum_i V(\mathbf{r}, \sigma, \mathbf{R}_i, \sigma_i) = \sum_i (a_{1i} + a_{2i} \sigma \cdot \sigma_i) \delta(\mathbf{r} - \mathbf{R}_i)$$

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Consider the frequency resolved experiment for the case of an unpolarized incident beam and no polarization detection.

Let’s skip the details, but merely note the following.

Cross terms involving the correlation of the spin dependent part of ρ with the spin independent part of ρ vanish exactly, basically because the average spin of a nucleus is zero.

The two separate densities that are of importance are

$$\begin{aligned}\rho_1(\mathbf{r}) &= \sum_i a_{1i} \delta(\mathbf{r} - \mathbf{R}_i) \\ \rho_2(\mathbf{r}) &= \sum_i a_{2i} \hat{\sigma}_i \delta(\mathbf{r} - \mathbf{R}_i)\end{aligned}$$

ρ_1 is a density of nuclei, as a function of position, with each nucleus being weighed according to the strength of its interaction with the incoming neutrons.

ρ_2 is a weighted density of nuclear spin.

The total scattered intensity is the sum of two contributions, each of which is the Fourier transform of the autocorrelation function of a ρ_i with itself.

For simplicity, consider the case of a system with only one kind of nucleus. Then the a constants can come out of the sum.

$$\begin{aligned}\rho_1(\mathbf{r}) &= a_1 \sum_i \delta(\mathbf{r} - \mathbf{R}_i) = a_1 f(\mathbf{r}) \\ \rho_2(\mathbf{r}) &= a_2 \sum_i \hat{\sigma}_i \delta(\mathbf{r} - \mathbf{R}_i)\end{aligned}$$

The first equation defines a basic atomic density of the material as a function of position.

The space time autocorrelation function of ρ_1 is

$$\langle \rho_1(\mathbf{r}, t) \rho_1(\mathbf{r}', t') \rangle = a_1^2 \langle f(\mathbf{r}, t) f(\mathbf{r}', t') \rangle = a_1^2 \sum_{ij} \langle \delta(\mathbf{r} - \mathbf{R}_i(t)) \delta(\mathbf{r}' - \mathbf{R}_j(t')) \rangle$$

It gives rise to what is called “coherent scattering”.

$$I_{coh}(\hat{\mathbf{k}}, \omega) \propto \int d\mathbf{r} \int_{-\infty}^{\infty} dt e^{-i((\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{r} - (\omega - \omega_i)t)} a_1^2 \langle f(\mathbf{r}, t) f(\mathbf{0}, 0) \rangle$$

The Fourier transform that appears here is proportional to

$$\sum_{ij} e^{-i\mathbf{k} \cdot (\mathbf{R}_i(t) - \mathbf{R}_j(t'))}$$

The space time autocorrelation function of ρ_2 is distinctly different.

$$\begin{aligned}
\langle \rho_2(\mathbf{r}, t) \rho_2(\mathbf{r}', t') \rangle &= a_2^2 \sum_{ij} \langle \sigma_i(t) \sigma_j(t') \delta(\mathbf{r} - \mathbf{R}_i(t)) \delta(\mathbf{r}' - \mathbf{R}_j(t')) \rangle \\
&= a_2^2 \sum_{ij} \langle \sigma_i(t) \sigma_j(t') \rangle \langle \delta(\mathbf{r} - \mathbf{R}_i(t)) \delta(\mathbf{r}' - \mathbf{R}_j(t')) \rangle \\
&= a_2^2 \sum_i \langle \sigma_i(t) \sigma_i(t') \rangle \langle \delta(\mathbf{r} - \mathbf{R}_i(t)) \delta(\mathbf{r}' - \mathbf{R}_i(t')) \rangle \\
&= a_2^2 \langle \sigma^2 \rangle \sum_i \langle \delta(\mathbf{r} - \mathbf{R}_i(t)) \delta(\mathbf{r}' - \mathbf{R}_i(t')) \rangle
\end{aligned}$$

It gives rise to ‘incoherent scattering’. Then we have

$$I_{inc}(\hat{\mathbf{k}}, \omega) \propto a_2^2 \langle \sigma^2 \rangle \sum_i e^{i\mathbf{k} \cdot (\mathbf{R}_i(t) - \mathbf{R}_i(0))}$$

In a typical experiment, there is more than one type of nucleus in the sample.

The information obtainable from an experiment depends crucially on the values of the a_1 and a_2 parameters of the various nuclei.

- Atoms differ in the amounts of coherent vs. incoherent scattering.
 - Argon-36 has primarily coherent scattering.
 - Protons have much larger incoherent scattering intensities than coherent intensities.
- In a sample, with two or more types of nuclei, the two types may make very different contributions to the total intensity.
- The interaction parameters can be positive or negative. For some elements there are some isotopes with positive values and some with negative.
- More generally, the results of an experiment are a superposition of the coherent correlation functions and the incoherent correlations, with weights that depend on the scattering parameters.

end of slides

3 Electron scattering

Electron scattering is even simpler in principle than neutron scattering.

Electrons have charge and spin. The dominant interactions of electrons with a sample is the electrostatic interaction with the charge density of the sample. Even if the sample is electrically neutral, the charge density is positive at the nuclei and negative elsewhere.

The potential energy of an electron as a function of position \mathbf{r} is the relevant ρ . We get

$$\rho(\mathbf{r}) = \int d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} q(\mathbf{r}')$$

where $q(\mathbf{r}')$ is the charge density in the material. Unlike the case of neutrons, we have no spin dependent part of the interaction.

Thus, the scattering is coherent, and it is related to the Fourier transform of the correlation function of this ρ . Since the q is in some sense more fundamental and simple, we want to express the correlation function of ρ in terms of the correlation function of q . There is a relationship between the two of them, but rather than derive it directly, let's discuss it more generally.

Lemma on Fourier transforms of correlation functions. Suppose we have a density of some sort, call it $\rho(\mathbf{r})$. Suppose its correlation function is $\langle \rho(\mathbf{r}, t) \rho(\mathbf{r}', t') \rangle$. For a homogeneous equilibrium material, this is a function of $\mathbf{r} - \mathbf{r}'$ and $t - t'$.

Consider calculating

$$Integral = \int_V d\mathbf{r}_1 \int_0^T dt_1 \int_V d\mathbf{r}_2 \int_0^T dt_2 e^{-i(\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2) - \omega(t_1 - t_2))} \langle \rho(\mathbf{r}_1, t_1) \rho(\mathbf{r}_2, t_2) \rangle$$

where V is some very large volume and T is some very large time. We could introduce the average coordinate and the relative coordinate, as well as the average time and the relative time and get a result of the form

$$Integral = \int_V d\mathbf{R} \int_0^T dt \int d\mathbf{x} \int d\tau e^{-i(\mathbf{k} \cdot \mathbf{r} - \omega\tau)} \langle \rho(\mathbf{r}, \tau) \rho(\mathbf{0}, 0) \rangle$$

The limits on the \mathbf{r} and τ integrals are somewhat complicated and depend on the value of \mathbf{R} and t . However, if V and T are very large and if the correlation function decays to zero for large $|\mathbf{r}|$ and for large τ , we can remove the limits on the \mathbf{r}, τ integrals. Then the remaining integrals give a factor of VT , and we get

$$Integral = VT \int d\mathbf{r} \int d\tau e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega\tau)} \langle \rho(\mathbf{r}, \tau) \rho(\mathbf{0}, 0) \rangle$$

The integral is just the typical space time correlation function that we want.

But going back to the original form of the integral, we see that there is another way of doing it.

$$Integral = \int_0^T dt_1 \int_0^T dt_2 e^{i\omega(t_1-t_2)} \left\langle \int_V d\mathbf{r}_1 e^{-i\mathbf{k}\cdot\mathbf{r}_1} \rho(\mathbf{r}_1, t_1) \int_V d\mathbf{r}_2 e^{i\mathbf{k}\cdot\mathbf{r}_2} \rho(\mathbf{r}_2, t_2) \right\rangle$$

If we define

$$\hat{\rho}(\mathbf{k}) = \int_V d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \rho(\mathbf{r})$$

Then we have

$$\begin{aligned} Integral &= \int_0^T dt_1 \int_0^T dt_2 e^{i\omega(t_1-t_2)} \langle \hat{\rho}(\mathbf{k}, t_1) \hat{\rho}(\mathbf{k}, t_2)^* \rangle \\ &= T \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \langle \hat{\rho}(\mathbf{k}, \tau) \hat{\rho}(\mathbf{k}, 0)^* \rangle \end{aligned}$$

In getting the last equality, we used the same type of trick about changing the variable of integration as we did above, and we used the fact that the correlation function decays to zero for large time intervals.

Comparing the two results for the same integral, we get

$$\int d\mathbf{r} \int d\tau e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega\tau)} \langle \rho(\mathbf{r}, \tau) \rho(\mathbf{0}, 0) \rangle = \frac{1}{V} \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \langle \hat{\rho}(\mathbf{k}, \tau) \hat{\rho}(\mathbf{k}, 0)^* \rangle$$

In words, this says that if we want the space time Fourier transform of a correlation function of a density, we can get the answer by first performing the space Fourier transform of the density, then taking the time correlation function of the Fourier transform with the complex conjugate of itself, and then Fourier transforming with regard to time. The two results differ by a mere factor of $1/V$.

Lemma on the Fourier transform of a convolution. Suppose we have the following convolution.

$$f(\mathbf{r}) = \int d\mathbf{r}' g(\mathbf{r} - \mathbf{r}')h(\mathbf{r}')$$

Then

$$\hat{f}(\mathbf{k}) = \hat{g}(\mathbf{k})\hat{h}(\mathbf{k})$$

The proof is elementary, and we won't give it here.◊

Let's put the two lemmas together to continue the discussion of electron scattering. We want the space time Fourier transform of the correlation function of $\rho(\mathbf{r})$. So we use the first lemma and decide to focus instead on $\hat{\rho}(\mathbf{k})$. But $\rho(\mathbf{r})$ is of the form of a convolution.

$$\hat{\rho}(\mathbf{k}) = \frac{4\pi}{k^2}\hat{q}(\mathbf{k})$$

where $4\pi/k^2$ is the Fourier transform of $1/r$.

Then we get

$$\begin{aligned} I(\hat{\mathbf{k}}, \omega) &\propto \int d\mathbf{r} \int d\tau e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega\tau)} \langle \rho(\mathbf{r}, \tau) \rho(\mathbf{0}, 0) \rangle \\ &= \frac{1}{V} \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \langle \hat{\rho}(\mathbf{k}, \tau) \hat{\rho}(\mathbf{k}, 0)^* \rangle \\ &= \frac{1}{V} \left(\frac{4\pi}{k^2} \right)^2 \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \langle \hat{q}(\mathbf{k}, \tau) \hat{q}(\mathbf{k}, 0)^* \rangle \\ &= \frac{1}{V} \left(\frac{4\pi}{k^2} \right)^2 \int d\mathbf{r} \int d\tau e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega\tau)} \langle q(\mathbf{r}, \tau) q(\mathbf{0}, 0) \rangle \end{aligned}$$

Thus, we get the basic result that the intensity of electron scattering is proportional to the space-time correlation function of the charge density of the material. Notice the factor of $(4\pi/k^2)^2$ out front. This is a characteristic of the Coulomb interaction and is a reminder that the original 'hook' by which the matter influences the electrons is the potential created by the matter. In the end, however, we have expressed everything in terms of the charge density of the matter.

Let's proceed to express the charge density in a more fundamental form. To a good approximation, charge density of a sample is the sum of the charge

densities of the individual atoms in the sample. Suppose we consider an atom and construct a coordinate system centered on the nucleus. To a good approximation, the charge density of the atom is some function of the distance from the nucleus; call it $Q_i(\mathbf{r})$. It has one piece that is of the form $Z_i\delta(\mathbf{r})$ and another continuous contribution representing the electron density. If the atom is at \mathbf{R}_i , then in the laboratory frame of reference the charge density of the atom is $Q_i(\mathbf{r} - \mathbf{R}_i)$. But this can be written as

$$\int d\mathbf{r}' Q_i(\mathbf{r} - \mathbf{r}')\delta(\mathbf{r}' - \mathbf{R}_i)$$

The total charge density of all the atoms is

$$q(\mathbf{r}) = \sum_i \int d\mathbf{r}' Q_i(\mathbf{r} - \mathbf{r}')\delta(\mathbf{r}' - \mathbf{R}_i)$$

To get some insight into the structure of this, let's consider the case in which all atoms have the same atomic number. Then this is

$$q(\mathbf{r}) = \int d\mathbf{r}' Q_i(\mathbf{r} - \mathbf{r}') \sum_i \delta(\mathbf{r}' - \mathbf{R}_i) = \int d\mathbf{r}' Q_i(\mathbf{r} - \mathbf{r}')f(\mathbf{r}')$$

Two things to notice.

- The same atomic density function is appearing here as appears in neutron scattering.
- This is of the form of a convolution. So

$$\hat{q}(\mathbf{k}) = \hat{Q}_i(\mathbf{k})\hat{f}(\mathbf{k})$$

Using the same set of tricks as we did before, we get

$$I(\hat{\mathbf{k}}, \omega) \propto \frac{1}{V} \left(\frac{4\pi}{k^2}\right)^2 |\hat{Q}_i(\mathbf{k})|^2 \int d\mathbf{r} \int d\tau e^{-i(\mathbf{k}\cdot\mathbf{r} - \omega\tau)} \langle f(\mathbf{r}, \tau) f(\mathbf{0}, 0) \rangle$$

This is basically the same result as for coherent neutron scattering from a system with only one type of atom. The same fundamental correlation appears. But here we have two additional prefactors. The first recalls the fact that the basis of the interaction was Coulomb's law. The second factor is the absolute square of the charge density of an atom.

Comments:

- Electron scattering is strongest for systems with high electron density, which in general means atoms with large atomic number.
- If you have a system that contains more than one type of atom, in general the atoms with the larger atomic number will dominate the scattering.

slides

Electrons have charge and spin.

The dominant interactions of electrons with a sample is the electrostatic interaction with the charge density of the sample.

Even if the sample is electrically neutral, the charge density is positive at the nuclei and negative elsewhere.

The potential energy of an electron as a function of position \mathbf{r} is the relevant ρ . We get

$$\rho(\mathbf{r}) = \int d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} q(\mathbf{r}')$$

where $q(\mathbf{r}')$ is the charge density in the material.

Unlike the case of neutrons, we have no spin dependent part of the interaction.

Thus, the scattering is coherent, and it is related to the Fourier transform of the correlation function of this ρ .

Lemma on Fourier transforms of correlation functions

Suppose we have a density of some sort, call it $\rho(\mathbf{r})$.

Suppose its correlation function is $\langle \rho(\mathbf{r}, t) \rho(\mathbf{r}', t') \rangle$.

For a homogeneous equilibrium material, this is a function of $\mathbf{r} - \mathbf{r}'$ and $t - t'$.

Consider calculating

$$Integral = \int_V d\mathbf{r}_1 \int_0^T dt_1 \int_V d\mathbf{r}_2 \int_0^T dt_2 e^{-i(\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2) - \omega(t_1 - t_2))} \langle \rho(\mathbf{r}_1, t_1) \rho(\mathbf{r}_2, t_2) \rangle$$

where V is some very large volume and T is some very large time.

We could do it in two ways.

First way. We could introduce the average coordinate and the relative coordinate, as well as the average time and the relative time and get a result of the form

$$\begin{aligned} Integral &= \int_V d\mathbf{r}_1 \int_0^T dt_1 \int_V d\mathbf{r}_2 \int_0^T dt_2 e^{-i(\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2) - \omega(t_1 - t_2))} \langle \rho(\mathbf{r}_1, t_1) \rho(\mathbf{r}_2, t_2) \rangle \\ &= \int_V d\mathbf{R} \int_0^T dt \int d\mathbf{r} \int d\tau e^{-i(\mathbf{k} \cdot \mathbf{r} - \omega\tau)} \langle \rho(\mathbf{r}, \tau) \rho(\mathbf{0}, 0) \rangle \end{aligned}$$

The limits on the \mathbf{r} and τ integrals are somewhat complicated and depend on the value of \mathbf{R} and t .

However, if V and T are very large and if the correlation function decays to zero for large $|\mathbf{r}|$ and for large τ , we can remove the limits on the \mathbf{r}, τ integrals. Then the remaining integrals give a factor of VT , and we get

$$Integral = VT \int d\mathbf{r} \int d\tau e^{-i(\mathbf{k} \cdot \mathbf{r} - \omega\tau)} \langle \rho(\mathbf{r}, \tau) \rho(\mathbf{0}, 0) \rangle$$

The integral is just the typical space time correlation function that we want.

Second way. There is another way of doing it.

$$\begin{aligned} \text{Integral} &= \int_V d\mathbf{r}_1 \int_0^T dt_1 \int_V d\mathbf{r}_2 \int_0^T dt_2 e^{-i(\mathbf{k}\cdot(\mathbf{r}_1-\mathbf{r}_2)-\omega(t_1-t_2))} \langle \rho(\mathbf{r}_1, t_1) \rho(\mathbf{r}_2, t_2) \rangle \\ &= \int_0^T dt_1 \int_0^T dt_2 e^{i\omega(t_1-t_2)} \left\langle \int_V d\mathbf{r}_1 e^{-i\mathbf{k}\cdot\mathbf{r}_1} \rho(\mathbf{r}_1, t_1) \int_V d\mathbf{r}_2 e^{i\mathbf{k}\cdot\mathbf{r}_2} \rho(\mathbf{r}_2, t_2) \right\rangle \end{aligned}$$

If we define

$$\hat{\rho}(\mathbf{k}) = \int_V d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \rho(\mathbf{r})$$

Then we have

$$\begin{aligned} \text{Integral} &= \int_0^T dt_1 \int_0^T dt_2 e^{i\omega(t_1-t_2)} \langle \hat{\rho}(\mathbf{k}, t_1) \hat{\rho}(\mathbf{k}, t_2)^* \rangle \\ &= T \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \langle \hat{\rho}(\mathbf{k}, \tau) \hat{\rho}(\mathbf{k}, 0)^* \rangle \end{aligned}$$

In getting the last equality, we used the same type of trick about changing the variable of integration as we did above, and we used the fact that the correlation function decays to zero for large time intervals.

Comparing the two results for the same integral, we get

$$\int d\mathbf{r} \int d\tau e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega\tau)} \langle \rho(\mathbf{r}, \tau) \rho(\mathbf{0}, 0) \rangle = \frac{1}{V} \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \langle \hat{\rho}(\mathbf{k}, \tau) \hat{\rho}(\mathbf{k}, 0)^* \rangle$$

If we want the space time Fourier transform of a correlation function of a density,

we can get the answer by

1. performing the space Fourier transform of the density,
2. taking the time correlation function of the Fourier transform with the complex conjugate of itself,
3. Fourier transforming with regard to time.
4. Dividing by $1/V$.

Lemma on the Fourier transform of a convolution

Consider the following convolution.

$$f(\mathbf{r}) = \int d\mathbf{r}' g(\mathbf{r} - \mathbf{r}')h(\mathbf{r}')$$

Then

$$\hat{f}(\mathbf{k}) = \hat{g}(\mathbf{k})\hat{h}(\mathbf{k})$$

The proof is elementary.

Now continue the discussion of electron scattering. We want the space time Fourier transform of the correlation function of $\rho(\mathbf{r})$.

$$\rho(\mathbf{r}) = \int d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} q(\mathbf{r}')$$

So we use the first lemma and decide to focus instead on $\hat{\rho}(\mathbf{k})$. But $\rho(\mathbf{r})$ is of the form of a convolution. Hence

$$\hat{\rho}(\mathbf{k}) = \frac{4\pi}{k^2} \hat{q}(\mathbf{k})$$

where $4\pi/k^2$ is the Fourier transform of $1/r$.

Then we get

$$\begin{aligned} I(\hat{\mathbf{k}}, \omega) &\propto \int d\mathbf{r} \int d\tau e^{-i(\mathbf{k}\cdot\mathbf{r} - \omega\tau)} \langle \rho(\mathbf{r}, \tau) \rho(\mathbf{0}, 0) \rangle \\ &= \frac{1}{V} \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \langle \hat{\rho}(\mathbf{k}, \tau) \hat{\rho}(\mathbf{k}, 0)^* \rangle \\ &= \frac{1}{V} \left(\frac{4\pi}{k^2} \right)^2 \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \langle \hat{q}(\mathbf{k}, \tau) \hat{q}(\mathbf{k}, 0)^* \rangle \\ &= \frac{1}{V} \left(\frac{4\pi}{k^2} \right)^2 \int d\mathbf{r} \int d\tau e^{-i(\mathbf{k}\cdot\mathbf{r} - \omega\tau)} \langle q(\mathbf{r}, \tau) q(\mathbf{0}, 0) \rangle \end{aligned}$$

Thus, the intensity of electron scattering is proportional to the space-time correlation function of the charge density of the material.

Notice the factor of $(4\pi/k^2)^2$ out front. This is a characteristic of the Coulomb interaction.

It is a reminder that the matter influences the electrons because of the electrostatic potential created by the matter.

In the end, however, we have expressed everything in terms of the charge density of the matter.

Let's express the charge density in a more fundamental form.

To a good approximation, charge density of a sample is the sum of the charge densities of the individual atoms in the sample.

Suppose we consider an atom and construct a coordinate system centered on the nucleus. To a good approximation, the charge density of the atom is some function of the distance from the nucleus; call it $Q_i(\mathbf{r})$.

It has one piece that is of the form $Z_i\delta(\mathbf{r})$ and another continuous contribution representing the electron density.

If the atom is at \mathbf{R}_i , then in the laboratory frame of reference the charge density of the atom is $Q_i(\mathbf{r} - \mathbf{R}_i)$. But this can be written as

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The total charge density of all the atoms is

$$q(\mathbf{r}) = \sum_i \int d\mathbf{r}' Q_i(\mathbf{r} - \mathbf{r}')\delta(\mathbf{r}' - \mathbf{R}_i)$$

To get some insight into the structure of this, consider the case in which all atoms have the same atomic number. Then

$$q(\mathbf{r}) = \int d\mathbf{r}' Q_i(\mathbf{r} - \mathbf{r}') \sum_i \delta(\mathbf{r}' - \mathbf{R}_i) = \int d\mathbf{r}' Q_i(\mathbf{r} - \mathbf{r}')f(\mathbf{r}')$$

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- The same atomic density function is appearing here as appears in neutron scattering.
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$$\hat{q}(\mathbf{k}) = \hat{Q}_i(\mathbf{k})\hat{f}(\mathbf{k})$$

Using the same set of tricks as we did before, we get

$$I(\hat{\mathbf{k}}, \omega) \propto \frac{1}{V} \left(\frac{4\pi}{k^2} \right)^2 |\hat{Q}_i(\mathbf{k})|^2 \int d\mathbf{r} \int d\tau e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega\tau)} \langle f(\mathbf{r}, \tau) f(\mathbf{0}, 0) \rangle$$

This is basically the same result as for coherent neutron scattering from a system with only one type of atom.

The same fundamental correlation function appears.

But here we have two additional prefactors.

The first recalls the fact that the basis of the interaction was Coulomb's law.

The second factor is the absolute square of the charge density of an atom.

Comments:

- Electron scattering is strongest for systems with high electron density, which in general means atoms with large atomic number.
- If you have a system that contains more than one type of atom, in general the atoms with the larger atomic number will dominate the scattering.

end of slides

4 X-ray scattering

X-rays are electromagnetic radiation, not particles, so we must deal with the $n = 2$ equation above.

There are at least two types of scattering. The first is an incoherent scattering, analogous to the neutron case. It arises when the scattering of the x-ray is accompanied by a change of the electronic state of the system. It is basically an annoyance; its magnitude must be estimated and subtracted from the experimental data before interpreting the coherent scattering.

The coherent scattering is due to electrons. In fact, to a good approximation the ρ that is important for electron scattering is the electron density. The

result for the scattering is much like the case of electron scattering.

$$I(\hat{\mathbf{k}}, \omega) \propto \frac{1}{V} |\hat{Q}_i^{(e)}(\mathbf{k})|^2 \int d\mathbf{r} \int d\tau e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega\tau)} \langle f(\mathbf{r}, \tau) f(\mathbf{0}, 0) \rangle$$

Here $\hat{Q}_i^{(e)}(\mathbf{k})$ is basically the Fourier transform of the electron density of an atom. (I think it is technically called the ‘atomic form factor’ by x-ray people.)

For x-rays experiments, the frequency resolved experiment is not performed, only the total intensity experiment. We can get the result for this by integrating over all frequency. We get

$$I(\hat{\mathbf{k}}) \propto \frac{1}{V} |\hat{Q}_i^{(e)}(\mathbf{k})|^2 \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \langle f(\mathbf{r}) f(\mathbf{0}) \rangle$$

a static, zero time average.

Above we are assume we don’t have a crystal. For a crystal, we would have the other term, discussed above, that gives diffraction spots.

slides

X-rays are electromagnetic radiation, not particles.

We must deal with the wave equation that is second order in time.

The results are essentially the same as for the first equation, at the level of detail that we have been discussing.

There are at least two types of x-ray scattering.

- Incoherent scattering, analogous to the neutron case.

Scattering of the x-ray is accompanied by a change of the electronic state of the system.

Basically an annoyance to users of x-rays to study structure of solids and liquids.

Its magnitude must be estimated and subtracted from the experimental data before interpreting the coherent scattering.

- Coherent scattering due to electrons

To a good approximation the ρ that is important for electron scattering is the electron density. For a system containing one type of atom

$$I(\hat{\mathbf{k}}, \omega) \propto \left| \hat{Q}_i^{(e)}(\mathbf{k}) \right|^2 \int d\mathbf{r} \int d\tau e^{-i(\mathbf{k}\cdot\mathbf{r} - \omega\tau)} \langle f(\mathbf{r}, \tau) f(\mathbf{0}, 0) \rangle$$

$\hat{Q}_i^{(e)}(\mathbf{k})$ is basically the Fourier transform of the electron density of an atom.

For x-rays scattering, only the total intensity experiment is performed.

$$I(\hat{\mathbf{k}}) \propto \left| \hat{Q}_i^{(e)}(\mathbf{k}) \right|^2 \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \langle f(\mathbf{r}) f(\mathbf{0}) \rangle$$

a static, zero time average.

For a typical sample with more than one type of atom, would have multiple terms, including cross terms between species.

For a crystal, we would have another term that gives diffraction spots.

end of slides

5 Summary of neutron, electron, and x-ray scattering

All three scattering methods probe fluctuations of the density of atoms.

Define a density for each species α .

$$f_\alpha(\mathbf{r}) = \sum_{i=1}^{N_\alpha} \delta(\mathbf{r} - \mathbf{r}_{i\alpha}) = \sum_{i=1}^{N_\alpha} f_{i\alpha}(\mathbf{r})$$

The time dependent version is

$$f_\alpha(\mathbf{r}, t) = \sum_{i=1}^{N_\alpha} \delta(\mathbf{r} - \mathbf{r}_{i\alpha}(t)) = \sum_{i=1}^{N_\alpha} f_{i\alpha}(\mathbf{r}, t)$$

Then we have several dynamic correlation functions of the form

$$S_{\alpha\beta}^{coh}(\mathbf{r}, t) \equiv \langle f_{\alpha}(\mathbf{r}, t) f_{\beta}(\mathbf{0}, 0) \rangle = \sum_{i=1}^{N_{\alpha}} \sum_{j=1}^{N_{\beta}} \langle f_{i\alpha}(\mathbf{r}, t) f_{j\beta}(\mathbf{0}, 0) \rangle$$

$$S_{\alpha}^{inc}(\mathbf{r}, t) \equiv \sum_{i=1}^{N_{\alpha}} \langle f_{i\alpha}(\mathbf{r}, t) f_{i\alpha}(\mathbf{0}, 0) \rangle$$

The static versions are

$$S_{\alpha\beta}^{coh}(\mathbf{r}) \equiv \langle f_{\alpha}(\mathbf{r}) f_{\beta}(\mathbf{0}) \rangle = \sum_{i=1}^{N_{\alpha}} \sum_{j=1}^{N_{\beta}} \langle f_{i\alpha}(\mathbf{r}) f_{j\beta}(\mathbf{0}) \rangle$$

$$S_{\alpha}^{inc}(\mathbf{r}) \equiv \sum_{i=1}^{N_{\alpha}} \langle f_{i\alpha}(\mathbf{r}) f_{i\alpha}(\mathbf{0}) \rangle$$

For oriented crystals, there is an additional static function.

$$F_{\alpha}(\mathbf{r}) = \langle f_{\alpha}(\mathbf{r}) \rangle = \sum_{i=1}^{N_{\alpha}} \langle f_{i\alpha}(\mathbf{r}) \rangle$$

The dynamic versions are relevant for experiments in which the scattered wave intensity is measured as a function of frequency. This is the case for neutron scattering.

The static versions are relevant for experiments in which only the total intensity is measured. This is the usual case for x-rays and electrons.

The intensity measured in an experiment is the sum of the coherent intensity (if any) and the incoherent intensity (if any).

For dynamic experiments

$$\begin{aligned} & \text{measured intensity} \\ & \propto V \left(\sum_{\alpha\beta} A_\alpha(\mathbf{k}) A_\beta^*(\mathbf{k}) \hat{S}_{\alpha\beta}^{coh}(\mathbf{k}, \omega) + \sum_{\alpha} |A_\alpha(\mathbf{k})|^2 \hat{S}_\alpha^{inc}(\mathbf{k}, \omega) \right) \end{aligned}$$

For static experiments

$$\begin{aligned} & \text{measured intensity} \\ & \propto V \left(\sum_{\alpha\beta} A_\alpha(\mathbf{k}) A_\beta^*(\mathbf{k}) \hat{S}_{\alpha\beta}^{coh}(\mathbf{k}) + \sum_{\alpha} |A_\alpha(\mathbf{k})|^2 \hat{S}_\alpha^{inc}(\mathbf{k}) \right) \end{aligned}$$

For static experiments on oriented crystals, we have these terms plus

$$+V^2 \left| \sum_{\alpha} A_\alpha(\mathbf{k}) F_\alpha(\mathbf{k}) \right|^2$$

The A quantities are:

- For x-rays: $A_\alpha(\mathbf{k})$ = the Fourier transform of the electron density of an atom of type α .
- For electrons: $A_\alpha(\mathbf{k})$ = the Fourier transform of the charge density of an atom.
- For neutrons: $A_\alpha(\mathbf{k})$ = the scattering length of a nucleus of type α .
(It is independent of \mathbf{k}).

The \mathbf{k} value is $\mathbf{k}_f - \mathbf{k}_i$. Its magnitude is

$$2|\mathbf{k}_i| \sin(\theta/2)$$

This is equal to

$$\frac{4\pi}{\lambda_i} \sin(\theta/2)$$

where λ_i is the wave length of the incident radiation. If we set this equal to $2\pi/\ell$, then we get

$$2\pi/\ell = \frac{4\pi}{\lambda_i} \sin(\theta/2)$$

$$\ell = \frac{\lambda_i}{2 \sin(\theta/2)}$$

This is the length scale of the fluctuations that are observed.

Similar wave vector ranges for all three experiments. Capable of probing the Angstrom distance scale, which is needed for understanding the most basic features of atomic motion.

Note that for any one particular incident wave vector, there is a limited range of length scales that can be studied.

- Smallest corresponds to $\theta = \pi$ or back scattering. $\ell = \lambda/2$.
- Largest lengths scale is seen for smallest scattering angles. $\ell \approx \lambda_i/\theta$. The smallest angles that can be studied is limited by the collimation of the incident beam and the width of the detector.

The ω value is $\omega_f - \omega_i$. For neutron scattering, this typically corresponds to time scales of picoseconds.

X-ray gives just static information because it is usually a total intensity measurement.

- For crystals that are oriented, it gives sharp diffraction spots, whose values can be used to deduce the crystal structure.
- For liquids, it gives the radial distribution function

Electrons can give both static and dynamic information, but traditionally electron scattering is primarily performed as a total intensity measurement when done on condensed phases.

All three measure correlation functions (static or dynamic) of the atom density, but they give different weights to different atoms, based on

- scattering length - for neutrons (can be different for different isotopes of the same element)
- charge density - for electrons
- electron density - for x-rays.

Light scattering. Measures the same correlation functions under many conditions.

The wavelength of light is much longer, and so the values of $\mathbf{k}_f - \mathbf{k}_i$ are much smaller.

The frequency shifts measured in light scattering are much smaller.

As a result, entirely different phenomena (with longer distance scales and time scales) are observed in light scattering.

Correlation functions based on atomic densities are less useful for their interpretation.