3.1: Light Scattering

Scattering and Correlation Functions

A particle or light field propagating through space can be described by a wave vector $\vec{k}$. The direction of k indicates the direction of propagation of the wave, and the magnitude of k indicates the wave number, or inverse wavelength, of the wave. Scattering occurs when a propagating wave encounters a medium which alters the magnitude or direction of its wave vector. In this section, we will show that the behavior of light scattered from a medium is related to the density correlation functions of the medium. As a result, light scattering experiments can be used to probe the structure of a material.

Elastic Scattering

Neutron or Light Scattering

In this section, we want to describe the behavior of a particle or light field that undergoes elastic scattering from a medium. This discussion could apply to x-ray, proton, neutron, or electron scattering, among others.

Elastic scattering occurs when there is no transfer of energy from the particle to the scattering medium. The direction of the particle's wave vector changes, but its wave number (or frequency) remains the same. A schematic of the scattering process is depicted in Figure 3.1. The incident particle or light field with wave vector $\overrightarrow{k_o}$ is scattered from the sample at point $\vec{r}$, changing its wave vector to $\overrightarrow{k_f}$. The vector $\overrightarrow{k_f}$ has the same magnitude as $\overrightarrow{k_o}$, but a different direction. The scattered light is detected at point $\overrightarrow{r'}$.

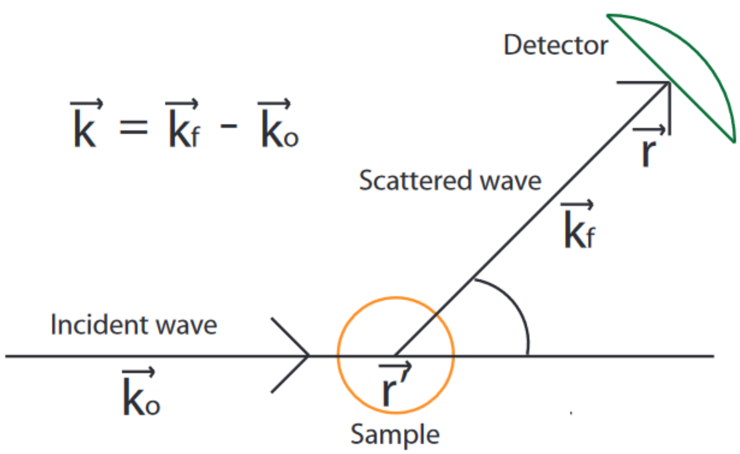

Figure 3.1: Elastic Scattering of a particle or light field from a medium

The scattered particle or light field can be modelled as a spherical wave. The quantum mechanical expression for this wave is

$$\Psi_s = \frac{i}{\hbar}\int \frac{e^{ik\left|\vec{r}-\overrightarrow{r'}\right|}}{\left|\vec{r}-\overrightarrow{r'}\right|} e^{i\overrightarrow{k_o}\cdot\overrightarrow{r'}} \rho\left(\overrightarrow{r'}\right) d\overrightarrow{r'} \tag{3.1.1}$$

where $\rho(\vec{r})$ is the density of scattering agents and the integral is carried out over all scattering agents.

In most light scattering experiments, the distance from the sample to the light detector is significantly larger than the size of the sample itself. In this case it is valid to make the assumption that $r >> r'$. Then

$$e^{ik\left|\vec{r}-\vec{r}'\right|} \rightarrow e^{ikr - i\overrightarrow{k_f}\cdot\overrightarrow{r'}} \tag{3.1.2}$$

and the wavefunction can be written

$$\Psi_s = \frac{i}{\hbar}\frac{e^{ikr}}{r}\int \rho\left(\overrightarrow{r'}\right) e^{-i\left(\overrightarrow{k_f}-\overrightarrow{k_o}\right)\cdot\overrightarrow{r'}} d\overrightarrow{r'} = \frac{i}{\hbar}\frac{e^{ikr}}{r}\int \rho\left(\overrightarrow{r'}\right) e^{-i\vec{k}\cdot\vec{r}'} d\overrightarrow{r'} \tag{3.1.3}$$

where $\vec{k}=\overrightarrow{k_f}-\overrightarrow{k_o}$ is the difference between the initial and scattered wave vector.

We can also assume that the medium is composed of point particles, so the density is the sum over all points

$$\rho(\vec{r})=\sum_{i=1}^{N} a_i \delta\left(\vec{r}-\vec{r}_i\right)=a \sum_{i=1}^{N} \delta\left(\vec{r}-\vec{r}_i\right) \tag{3.1.4}$$

Then the wavefunction simplifies to

$$\Psi_s=\frac{i}{\hbar} \frac{e^{ikr}}{r} a \sum_{i=1}^{N} e^{-i\vec{k}\cdot\overrightarrow{r_i}} \propto a \sum_{i=1}^{N} e^{-i\vec{k}\cdot\overrightarrow{r_i}} \tag{3.1.5}$$

In light scattering experiments the measured quantity is the intensity of scattered light over the angle spanned by the detector. This quantity is called the scattering cross section $\frac{d\sigma}{d\Omega}$, and it is proportional to the square of the wavefunction:

$$I(\vec{k})=\left|\Psi_s\right|^2 \propto \frac{1}{r^2} \frac{d\sigma}{d\Omega}=\frac{a^2}{r^2}\left\langle\sum_{i=1}^{N} e^{-i\vec{k}\cdot\vec{r}_i}\right|^2\left.\right\rangle=\frac{a^2}{r^2} N S(\vec{k}) \tag{3.1.6}$$

where $S(\vec{k})$ is called the static structure factor, and is defined as:

$$S(\vec{k})=\frac{1}{N}\left\langle\left|\sum_{i=1}^{N} e^{-i\vec{k}\cdot\vec{r}_i}\right|^2\right\rangle \tag{3.1.7}$$

In order to find the scattering intensity, we must evaluate this term.

The Static Structure Factor

The static structure factor can be rewritten as:

$$S(k)=\frac{1}{N}\left\langle\rho_k \rho_{-k}\right\rangle \tag{3.1.8}$$

where

$$\rho_k=\int e^{-i\vec{k}\cdot\vec{r}} \rho(\vec{r}) d\vec{r} \tag{3.1.9}$$

and $\rho(r)$ is the local number density. For a homogeneous liquid, $\langle\rho(r)\rangle=\rho_o$.

To model real systems, we can simplify the calculations by expressing the density correlations as a sum of the homogeneous density ρ_o and local fluctuations $\delta\rho$.

$$\rho(r)=\rho_o+\delta\rho \tag{3.1.10}$$

Using this separation, the scattering function can be written in two pieces:

$$S(k)=\frac{1}{N}\left\langle\rho_k \rho_{-k}\right\rangle=\rho_0(2\pi)^3 \delta(\vec{k})+\frac{1}{N}\left\langle\delta\rho_k \delta\rho_{-k} \mid\right\rangle \tag{3.1.11}$$

The first term arises from the homogeneous background and is called the forward scattering. The second term gives the scattering from the density fluctuations. In an ideal gas, there is no interaction between the particles $\delta\rho=0$, and so there is only forward scattering.

The Density Correlation function It is also helpful to think about the scattering in real space. Define the density correlation function $G(\vec{r})$ as the Fourier transform of $S(k)$ into coordinate space.

$$G(\vec{r}) = \frac{1}{(2\pi)^3}\int S(\vec{k})e^{-i\vec{k}\cdot\vec{r}}d\vec{k}$$

$$= \frac{1}{N}\frac{1}{(2\pi)^3}\int e^{-i\vec{k}\cdot\vec{r}}\left\langle \sum_i e^{i\vec{k}\cdot\vec{r}_i}\sum_j e^{-i\vec{k}\cdot\vec{r}_j}\right\rangle d\vec{k}$$

$$= \frac{1}{N}\sum_{i,j}\langle\delta\left(\vec{r}-\vec{r}_{i,j}\right)\rangle$$

From this, we can see that the Fourier transform of the structure factor gives probability of finding two particles separated by a vector $\vec{r}$.

We can also write the density correlation function in a slightly different form:

$$G(\vec{r}) = \frac{1}{N}\sum_{i,j}\int d\overrightarrow{r_o}\left\langle\delta\left(\overrightarrow{r_i}-\overrightarrow{r_o}-\vec{r}\right)\delta\left(\overrightarrow{r_j}-\overrightarrow{r_o}\right)\right\rangle$$

$$= \frac{1}{N}\int d\overrightarrow{r_o}\left\langle\rho\left(\overrightarrow{r_o}+\vec{r}\right)\rho\left(\overrightarrow{r_o}\right)\right\rangle = \frac{V}{N}\langle\rho(\vec{r})\rho(0)\rangle = \frac{1}{\rho_o}\langle\rho(\vec{r})\rho(0)\rangle$$

The Pair Distribution Function

To better understand the physical interpretation of the structure factor and the density correlation function, we can rewrite them in terms of the pair distribution function $g(r)$. The pair distribution function is given by:

$$g(r) = \frac{1}{N^2}\sum_{i\neq j}\langle\delta\left(\vec{r}-\vec{r}_{i,j}\right)\rangle \tag{3.1.12}$$

This gives the probability that, if I have a single particle i, I will be able to find another particle j at a distance $\vec{r}$ away. It is defined only for terms with $i\neq j$. We can write $g(r)$ as:

$$g(r) = h(r)+1 \tag{3.1.13}$$

where $h(r)$ is the pair correlation function. The Fourier transform of the pair distribution function can be written:

$$\tilde{g}(\vec{k}) = \tilde{h}(\vec{k})+(2\pi)^3\delta(\vec{k}) \tag{3.1.14}$$

This allows us to rewrite the structure factor and the density correlation function in terms of the interactions between individual pairs of particles.

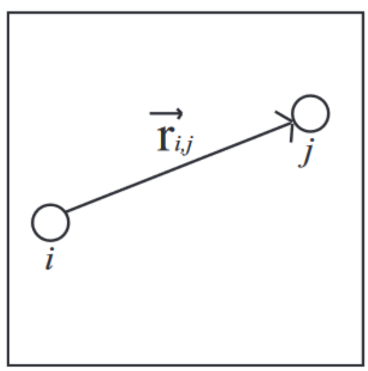

Figure 3.2: The pair distribution function

To write the structure factor $S(k)$ and the density correlation function $G(r)$ in terms of the pair distribution function, separate the summations into terms with $i=j$ and terms with $i\neq j$. The structure factor is written:

$$S(k) = \frac{1}{N}\sum_{i,j}\left\langle e^{-ikr_i}e^{ikr_j}\right\rangle \tag{3.1.15}$$

The terms with $i=j$ each contribute a value of $\frac{1}{N}$. After taking the summation over all N particles, this gives a value of 1 .

$$S(k)=1+\sum_{i\neq j}\left\langle e^{-ik(r_i-r_j)}\right\rangle=1+\rho\tilde{g}(k)=1+\rho\tilde{h}(\vec{k})+(2\pi)^3\delta(\vec{k})\rho \tag{3.1.16}$$

Now, the first two terms $1+\rho\tilde{h}(\vec{k})$ give the scattering due to the molecular structure, or fluctuations. The third term gives the forward scattering, which as we discussed earlier is the scattering that we would expect in a system with no fluctuations (an ideal gas).

The density correlation function is written:

$$G(\vec{r})=\frac{1}{N}\left\langle\sum_{i,j}\delta\left(r_{i,j}-r\right)\right\rangle \tag{3.1.17}$$

when $i=j$, we are discussing a single particle. Therefore, $r_{i,j}=0$ and each term contributes $\frac{1}{N}\delta(\vec{r})$. After taking the summation over all N particles, the N cancels and we are left with $\delta(\vec{r})$.

$$\begin{aligned}G(\vec{r})&=\delta(\vec{r})+\frac{1}{N}\left\langle\sum_{i\neq j}\delta\left(r_{i,j}-r\right)\right\rangle\\&=\delta(\vec{r})+\rho g(\vec{r})=\delta(\vec{r})+\rho(h(\vec{r})+1)\end{aligned}$$

By writing the expressions for $S(\vec{k})$ and $G(\vec{r})$ in terms of $g(\vec{r})$, their physical interpretation becomes more clear. The pair distribution function for a typical liquid and a typical solid are shown in Figure 3.3 and Figure 3.4. If a particle has a radius d, then clearly no other particle can be closer than distance d. Therefore, for both the solid and the liquid, $g(\vec{r})$ has a value of 0 from a distance 0 to a distance d. At this point, the probability rapidly increases and begins oscillating around a value of 1 . In a liquid, there is short range structure as weak intermolecular interactions form a series of solvation shells around a particle. However, these forces only act at short range, and as the distance increases the correlation decays to zero. In a solid, the structure persists throughout the sample, and therefore the oscillations do not decay.

Inelastic Scattering

The previous section described the behavior of a particle as it undergoes an elastic scattering event. In this section, we will address the phenomenon of inelastic scattering, which applies primarily to light fields. Inelastic scattering occurs when scattered light transfers some energy to the scattering material. While an elastic scattering event causes only a change in the direction of the wave vector, an inelastic scattering event causes both a change in the direction and the wavenumber of the scattered light. In other words, the scattered wave becomes frequency dispersed. Figure 3.5 gives a schematic of an inelastic scattering event.

Scattered Intensity

To calculate the intensity of scattered light from an inelastic scattering event, we can follow a very similar process to that which we used for elastic scattering: model the scattered light as a spherical wave, and simplify it by assuming that the distance from the sample to the light detector is large compared with the size of the sample, and that the medium is composed of point particles. However, there is one major difference. Since the scattered light can transfer energy to the material, the position of the particles now depends on time. The scattered wavefunction is then:

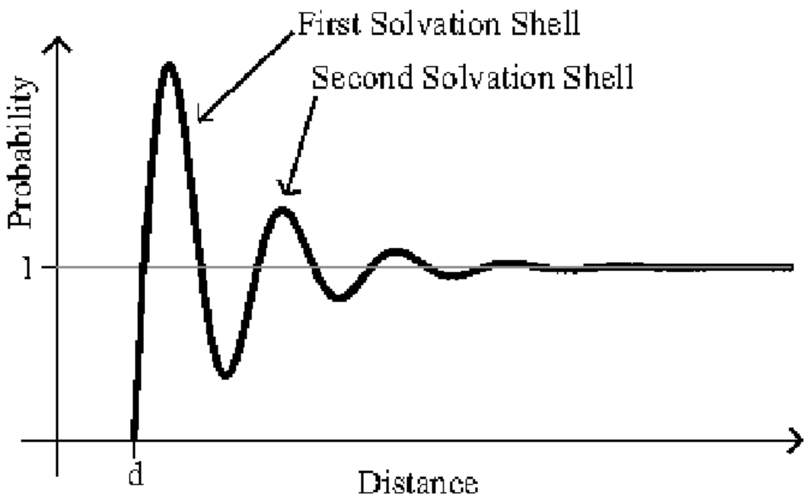

Figure 3.3: Pair Distribution Function for a Liquid

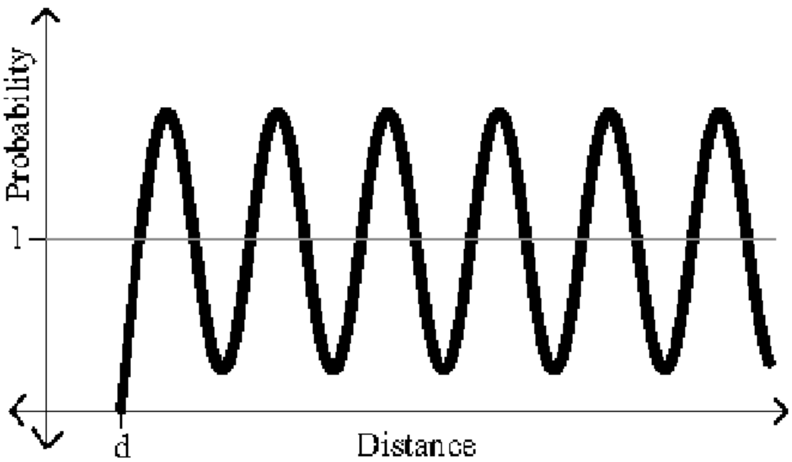

Figure 3.4: Pair Distribution Function for a Solid

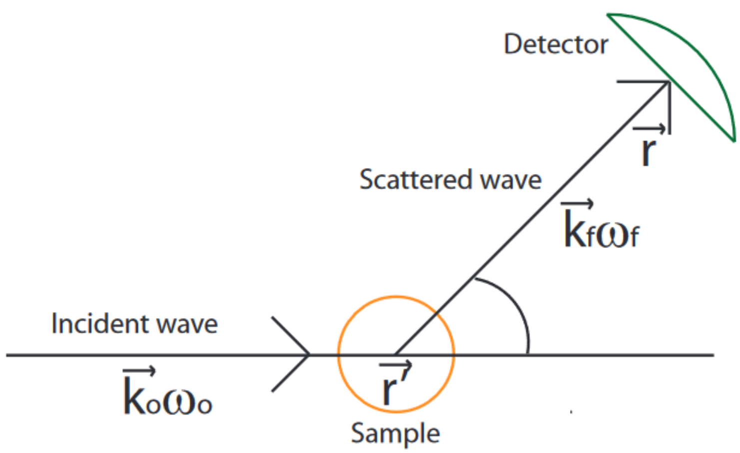

Figure 3.5: Schematic of an Inelastic Scattering Event

$$\Psi_s \propto \frac{a}{r} \sum_{i=1}^{N} e^{-i\vec{k}\cdot\vec{r}_i(t)} \tag{3.1.18}$$

which gives a differential cross-section of:

$$\frac{d\sigma}{d\Omega d\omega} = a^2 \left\langle \sum_i e^{-i\vec{k}\cdot\vec{r_i}(t)} \sum_j e^{-i\vec{k}\cdot\vec{r_j}(t)} \right\rangle \tag{3.1.19}$$

By taking the temporal Fourier transform, we can find the structure factor:

$$\begin{aligned} \frac{d\sigma}{d\Omega d\omega} &= a^2 \int e^{iwt} \left\langle \sum_i e^{-i\vec{k}\cdot\vec{r}_i(t)} \sum_j e^{-i\vec{k}\cdot\vec{r}_j(t)} dt \right\rangle \\ &= a^2 N S(\vec{k},\omega) \end{aligned}$$

Note that the structure factor S is now dependent on both the wave vector $\vec{k}$ and the frequency ω. Therefore, it is called the Dynamic Structure Factor.

The Intermediate Scattering Function

The intermediate scattering function is defined as the Fourier transform of the dynamic structure factor into real time.

$$\begin{aligned} F(\vec{k},t) &= \frac{1}{2\pi}\int S(\vec{k},\omega)e^{i\omega t}d\omega \\ S(\vec{k},\omega) &= \int F(\vec{k},t)e^{-i\omega t}dt \end{aligned}$$

It is called the **Intermediate scattering function** is because it has one variable, the spatial dimension k, expressed in Fourier space, and the other variable, the time dimension t, expressed in real space. It can be expressed explicitly as:

$$F(\vec{k},t) = \frac{1}{N}\langle \rho_k(t)\rho_{-k}(0)\rangle \tag{3.1.20}$$

where:

$$\rho_k(t) = \sum_i e^{-i\vec{k}\cdot\vec{r_i}(t)} \tag{3.1.21}$$

Note that this function looks identical to the static structural factor from section 1, except that now the density is a function of time.

The Van Hove Function

The Van Hove Function is defined as the Fourier transform of the intermediate scattering function into real space.

$$G(\vec{r},t) = \frac{1}{(2\pi)^3}\int F(\vec{k},t)e^{i\vec{k}\cdot\vec{r}}d\vec{k} = \frac{1}{N}\sum_{i,j}\left\langle \delta\left(\vec{r}_i(t) - \vec{r_j}(0) - \vec{r}\right)\right\rangle \tag{3.1.22}$$

The Van Hove Function can also be expressed as

$$\begin{aligned} G(\vec{r},t) = \frac{1}{N}\int d\vec{r_o}\left\langle \sum_i \delta\left(\vec{r_i}(t) - \vec{r} - \vec{r_o}\right) \sum_j \delta\left(\vec{r_j}(0) - \vec{r_o}\right)\right\rangle \\ = \frac{1}{N}\int d\vec{r_o}\left\langle \rho\left(\vec{r} + \vec{r_o}, t\right)\rho\left(\vec{r_o}, 0\right)\right\rangle \\ = \frac{V}{N}\langle \rho(\vec{r},t)\rho(0,0)\rangle \end{aligned}$$

where $\frac{V}{N} = \rho_o^{-1}$. The Van Hove function describes the fluctuation of densities at different times and positions.

It can be difficult to keep track of the many functions used to describe inelastic scattering. The following table summarizes these functions and their different spatial and temporal variables.

Name	Symbol	Spatial Dimension	Temporal Dimension
Dynamic Structure Factor	$S(\vec{k},\omega)$	Fourier, $\vec{k}$	Fourier, ω
Intermediate Scattering Function	$F(\vec{k},t)$	Fourier, $\vec{k}$	Real, t

Name	Symbol	Spatial Dimension	Temporal Dimension
Van Hove Function	$G(\vec{r}, t)$	Real, $\vec{r}$	Real, t

5. If we are only interested in the spatial structure, we can perform a sum over the temporal dimension:

$$S(\vec{k}) = \frac{1}{2\pi}\int S(\vec{k},\omega)d\omega = F(\vec{k},0) \tag{3.1.23}$$

This gives the spatial structure.

6. The density can again be expressed as the sum of a constant background ρ_o and fluctuations $\delta\rho$:

$$\rho = \rho_o + \delta\rho \tag{3.1.24}$$

Then the dynamic structure factor can be expressed as

$$S(\vec{k},w) = (2\pi)^4\delta(\vec{k})\delta(\omega)\rho_o + \int e^{i\omega t}\frac{1}{N}\langle\delta\rho_k(t)\delta\rho_{-k}(0)\rangle\, dt \tag{3.1.25}$$

In the first term, $\vec{k} = 0$ and $\omega = 0$. This is the forward, elastic, not scattered wave for an ideal gas. The second term gives the spectrum of density fluctuations in the fluid.