Chapter 12

Scattering

Figure 12.1:

Scattering experiments evidently involve the change in momentum of some incident particle or radiation by a sample. The momentum transferred to the sample (in units of $\hbar$) is

\[ \vec{q} = \vec{k}_i - \vec{k}_f \quad (12.1) \]

by conservation of momentum. This, along with the intensity of the scattered radiation

\[ I(\vec{q}) \quad (12.2) \]

is measured at the detector. We shall only consider elastic scattering where energy, $w$ in units of $\hbar$, is unchanged. Furthermore, we are implicitly considering the first Born approximation and thereby neglecting multiple scattering.

The intensity of the scattered radiation might be due to an electromagnetic field. That is

\[ I(\vec{q}) \propto |\tilde{E}(q)|^2 \quad (12.3) \]
where $\hat{E}$ is the electric field. Clearly the electric field variations with $\vec{q}$ are due to variations in the dielectric properties of the sample, i.e.,

$$\hat{E}(q) \propto \delta\hat{\epsilon}(q)$$  \hspace{1cm} (12.4)

where $\delta\hat{\epsilon}$ is the dielectric variability. Now, if $\delta\hat{\epsilon}$ is a function of only a small number of local thermodynamic variables, like density and temperature

$$\delta\hat{\epsilon} = \left(\frac{\partial\epsilon}{\partial \rho}\right)\delta\hat{\rho} + \left(\frac{\partial\epsilon}{\partial T}\right)\delta\hat{T}$$  \hspace{1cm} (12.5)

Usually $\partial\epsilon/\partial T$ is exceedingly small, so we have

$$I(q) \propto |\hat{\rho}(q)|^2$$  \hspace{1cm} (12.6)

A similar argument can be constructed if the scattering is not electromagnetic, giving the same result. We’ll not focus on $|\hat{\rho}(q)|^2$ letting

$$S(q) \equiv |\hat{\rho}(q)|^2$$  \hspace{1cm} (12.7)

be the structure factor.

I should note that, although I’ve skimmed this, the details giving Eq. 12.6 are often experimentally important. But that’s their job, ours is to figure out $S(q)$. We will deal with two cases for $\hat{\rho}(q)$

1. $\rho$ corresponds to the order parameter, a local density or local concentration.

2. The order parameter is not the local density, but instead corresponds to a sublattice concentration or magnetization, or to a Bragg peak’s intensity.

The first of these is easier. Consider a system of uniform density (we’ll do interfaces later), then

$$\langle \rho(x) \rho(0) \rangle = \rho^2$$  \hspace{1cm} (12.8)

of course, so the fourier transform gives

$$S(q) \propto \delta(q)$$  \hspace{1cm} (12.9)

A cartoon (fig. 12.2) may make this clear. The second case is more subtle. An example is the sublattice concentration of a binary alloy. Say atoms are A and B in the alloy, and that locally, A wants to be neighbours with B but not with another A. This makes the ordered state look like a checker–board as shown in fig. 12.3.

Assuming the scattering is different from A or B atoms this sort of order can be seen by looking at $S(q)$. However, it must be realized that the ordering of, say, the A atoms is on a sublattice, which has twice the lattice spacing of the original system as shown in fig. 12.4. Hence the density of A atoms is uniform on a sublattice with twice the lattice constant of the original system, and the
Uniform boring system
\[ \langle \rho(x) \rho(0) \rangle = \rho^2 \]

Figure 12.2:
Perfectly ordered
\[ A - B \text{ alloy} \]
\[ \begin{align*}
    = A \\
    = B
\end{align*} \]

Figure 12.3:
Sublattice 1 (Shaded)
(Sublattice 2 is unshaded)
scattering will show peaks not at $\vec{q} = 0$ but at $\vec{q} = \vec{q}_0$ corresponding to that structure

$$S(\vec{q}) \propto \sum_{\vec{q}_0} \delta(\vec{q} - \vec{q}_0)$$  \hspace{1cm} (12.10)

where $q_0 = 2\pi/(2a)$, and $a$ is the original lattice spacing.

The same thing happens in a crystal, where Bragg peaks form at specific positions in $\vec{q}$ space. By monitoring the height and width of such peaks, the degree of order can be determined. A further complication is that usually the sample will not be so well aligned with the incident radiation that one gets spots on the $q_x$ and $q_y$ axes as shown. Instead they appear at some random orientation (fig. 12.6). This might seem trivial (one could just realign the sample), except that often one has many different crystallite orientations scattering simultaneously, so that all the orientations indicated above are smeared into a ring of radius $q_0$. 

$$q_y$$

Figure 12.7: Average of Many Crystallites
12.1 Scattering from a Flat Interface

Consider a flat interface without roughening, as drawn in fig. 12.8. For simplicity we will usually consider an interface embedded in dimension $d = 2$. If the density is uniform, it can be written as

$$\rho(x, y) = A \theta(y) + B$$

(12.11)

where $\theta(y)$ is the Heaviside step function, and $A$ and $B$ are constants. For simplicity, we will let $A = 1$ and $B = 0$ from now on:

$$\rho(x, y) = \theta(y)$$

(12.12)

To get $S(q)$ we need the fourier transform of $\theta$. Let

$$\theta = H + C$$

where $C$ is a to-be-determined constant. Taking a derivative gives

$$\frac{d\theta}{dy} = \frac{dH}{dy} + 0$$

or,

$$\frac{dH}{dy} = \delta(y)$$

Fourier transform gives

$$\hat{H}(k_y) = \frac{1}{ik_y}$$

so that

$$\hat{\theta}(k_y) = \frac{1}{ik_y} + C \delta(k_y)$$

To determine $C$, note that

$$\theta(x) + \theta(-x) = 1$$
so
\[ \hat{\theta}(k_y) + \hat{\theta}(-k_y) = \delta(k_y) \]

Hence \( C = 1/2 \) and,
\[ \hat{\theta}(k_y) = \frac{1}{ik_y} + \frac{1}{2} \delta(k_y) \] (12.13)

The two-dimensional Fourier transform of \( \rho(x, y) = \theta(y) \) is therefore
\[ \hat{\rho}(\vec{k}) = \frac{1}{ik_y} \delta(k_x) + \frac{1}{2} \delta(\vec{k}) \] (12.14)

From this we obtain the scattering from a flat interface \( y = 0 \) as the modulus,
\[ S(k) = |\hat{\rho}(k)|^2 \propto \frac{1}{k_y^2} \delta(k_x) \] (12.15)

where we have neglected the trivial bulk factor delta function. If the unit vector normal to the interface is \( \hat{n} \) and that along the surface is \( \hat{n}_\perp \), then
\[ S(k) \propto \frac{1}{(k \cdot \hat{n})^2} \delta(k \cdot \hat{n}_\perp) \] (12.16)

As a cartoon (fig. 12.10), the scattering appears as a streak pointed in the direction of \( \hat{n} \) (\( \hat{y} \) in fig. 12.10).
12.1. SCATTERING FROM A FLAT INTERFACE

\[ \rho(x, y) = \delta(y) \quad (12.17) \]

Then
\[ \hat{\rho} = \delta(k_x) \quad (12.18) \]

and
\[ S(k) \propto \delta(k_x) \quad (12.19) \]

or if the unit vector normal to the surface is \( \hat{n} \), and that along the surface is \( \hat{n}_\perp \),
\[ S(k) \propto \delta(\vec{k} \cdot \hat{n}_\perp) \quad (12.20) \]

for a line defect. Now, if \( \rho \) is **not** the order parameter (like the second case discussed above) so that the density doesn’t vary across the interface, but an order parameter corresponding to sublattice concentration or crystalline orientation does, we have to incorporate the wavenumber \( \vec{k}_0 \) corresponding to that structure. For simplicity, we will assume that all one has to do is modulate the structure up to that wavenumber. That is, for an interface
\[ S(k) \propto \frac{1}{|\vec{k} - \vec{k}_0|} \delta((\vec{k} - \vec{k}_0) \cdot \hat{n}_\perp) \quad (12.21) \]
while for a line defect
\[ S(k) \propto \delta((\vec{k} - \vec{k}_0) \cdot \hat{n}_\perp) \] (12.22)

### 12.2 Roughness and Diffuseness

So far this is only geometry. And even as geometry, we have not considered a diffuse interface. Before doing roughness, let’s consider a diffuse interface as shown in fig. 12.13. One example of this is

\[ \rho_{\text{diffuse}}(x, y) \sim \tanh(y/\xi) \] (12.23)

So that
\[ S(k) = |\hat{\rho}(k)_{\text{diffuse}}|^2 \sim \frac{\delta(k_x)}{k_y^2}(1 + \mathcal{O}(\xi k_y^2)) \] (12.24)

for an interface at \( y = 0 \). So the diffuseness only effects scattering at \( k_x = 0 \)

and large \( k_y \). On the other hand, let us now consider a rough interface, with no diffuseness, where the interface is given by
\[ y = h(x) \] (12.25)

and
\[ \rho_{\text{Rough}}(x, y) = \theta(y - h(x)) \] (12.26)
If \( h(x) \) involves a small variation, we can accordingly expand to obtain

\[
\rho_{\text{Rough}} \approx \theta(y) + h(x)\delta(y) + ...
\]  

(12.27)

since \( d\theta/dy = \delta(y) \).

Taking the fourier transform and squaring this gives

\[
S(k) = |\hat{\rho}_{\text{Rough}}(k)|^2 \sim \frac{\delta(k_x)}{k_y^2} + |\hat{h}(k_x)|^2
\]

(12.28)

Averaging over thermal fluctuations using

\[
\langle |\hat{h}(k_x)|^2 \rangle \sim \frac{1}{k_x^{2-\eta}}
\]

(12.29)

which defines \( \eta \), gives

\[
S_{\text{Rough}}(\vec{k}) \sim \frac{\delta(k_x)}{k_y^2} + \frac{T}{k_x^{2-\eta}}
\]

(12.30)

where \( T \) is a constant. It would appear, then, that one could deconvolute the geometry \( \frac{\delta(k_x)}{k_x^2} \) from the diffuseness \( \mathcal{O}(\xi k_y)^2 \), from the roughness \( 1/k_x^{2-\eta} \), since they have different signatures in \( k \) space. For excellent samples this is in fact true, but if there are many randomly oriented interfaces present, these signatures are smeared out, and washed away.
12.3 Scattering From Many Flat Randomly–Oriented Surfaces

Evidently the scattering from many randomly–oriented surfaces gives a pinwheel–like cluster of streaks as shown in fig. 12.17. Angularly averaging over all orientations of the interface gives

\[
S = \frac{\int d\hat{n} |\hat{\rho}_k|^2}{\int d\hat{n}}
\]

(12.31)

where \( \hat{n} \) is the unit vector normal to the surface. We will write

\[
\hat{n} = -\sin \theta \hat{x} + \cos \theta \hat{y}
\]

(12.32)

and

\[
\hat{n}_\perp = \cos \theta \hat{x} + \sin \theta \hat{y}
\]

(12.33)

with

\[
\vec{k} = k \cos \beta \hat{x} \pm k \sin \theta \hat{y}
\]

(12.34)

Then, for scattering from a surface where \( |\hat{\rho}_k|^2 = \frac{\delta(\vec{k} \cdot \hat{n}_\perp)}{|\hat{n}_\perp|^2} \) we have (in \( d = 2 \))

\[
S = \frac{1}{2\pi} \int_0^{2\pi} d\theta \frac{\delta[k \cos \beta \cos \theta + k \sin \beta \sin \theta]}{|k \cos \beta \sin \theta + k \sin \beta \cos \theta|^2} \int_0^{2\pi} d\theta \frac{\delta[\cos (\theta - \beta)]}{|\sin (\theta - \beta)|^2}
\]

(12.35)

\[
S_{Surfaces} = \frac{1}{\pi} \frac{1}{k^3}
\]

Similarly, in arbitrary dimension one has

\[
S_{Surfaces} \propto \frac{1}{k^{d+1}}
\]

(12.36)
12.3. SCATTERING FROM MANY FLAT RANDOMLY-ORIENTED SURFACES

for scattering from a surface. For scattering from a line defect which has $|\tilde{\rho}(k)|^2 \propto \delta(k_x)$, one similarly obtains

$$S_{\text{linedefects}} \propto \frac{1}{k^{d-1}}$$

(12.37)

We shall call these results, Porod's Law. They involve only geometry.

The case where $\rho$ is not the order, and a modulated structure exists is more subtle. If the wavenumber of that structure is $k_0$ then this introduces a new angle via

$$k_0 = k_0 \cos \alpha \hat{x} + k_0 \sin \alpha \hat{y}$$

(12.38)

Now there are two possible averages

1. $\alpha$ or $\beta$, average over crystallite orientation, or, angles in a non-angularly resolved detector. These are equivalent (look at the cartoon for a few seconds), and so we only need to do one of these two averages.

2. $\theta$, averages over surface orientation.

If we average over $\alpha$ or $\beta$, for a fixed $\hat{n}$, it is easy to anticipate the answer as shown in fig. 12.19, where in the cartoon the regions around $(k_x = k_0, k_y = 0)$

retain the singularity of the original $\delta(k_x - k_0)/(k_y - k_0)^2$. 
CHAPTER 12. SCATTERING

This is basically a detector problem, so instead we will consider averaging \( \theta \) first. In fact it is obvious what the result of such an average is, it must be the previous result, but shifted from \( \vec{k} = 0 \) to \( \vec{k} = \vec{k}_0 \), that is

\[
S_{\text{surface}}(k) \propto \frac{1}{|\vec{k} - \vec{k}_0|^{d+1}}
\]

\[
S_{\text{line}}(k) \propto \frac{1}{|\vec{k} - \vec{k}_0|^{d-1}}
\]

If a further average is done over crystallite orientation, we can take these expressions and angularly average them over the angle between \( \vec{k} \) and \( \vec{k}_0 \). Clearly after averaging we will have

\[
\bar{S} = S\left( \frac{|k| - |k_0|}{|k_0|} \right) \equiv S(\Delta k)
\]

First, let

\[
\phi = \beta - \alpha
\]

so that

\[
(\vec{k} - \vec{k}_0)^2 = k^2 - 2kk_0 \cos \phi + k_0^2
\]

or, on using

\[
k \equiv k_0(\Delta k + 1)
\]

we have

\[
(\vec{k} - \vec{k}_0)^2 = k_0^2 \{(\Delta k)^2 + 2(1 - \cos \phi)(\Delta k + 1)\}
\]

Hence in two dimensions, for a surface, we have

\[
\bar{S}(\Delta k) = \frac{1}{2\pi k_0^3} \int_0^{2\pi} d\phi \frac{1}{[(\Delta k)^2 + 2(1 - \cos \phi)(\Delta k + 1)]^{3/2}}
\]

which is some weird integral. We will work out its asymptotic limits \( \Delta k \gg 1 \) and \( \Delta k << 1 \).

Firstly, if \( \Delta k \gg 1 \), then

\[
\bar{S}(\Delta k) = \frac{1}{2\pi k_0^3} \frac{1}{(\Delta k)^3} \int_0^{2\pi} d\phi + ...
\]
12.3. SCATTERING FROM MANY FLAT RANDOMLY-ORIENTED SURFACES

or (in arbitrary $d$)

$$ S(\Delta k) \sim \frac{1}{(\Delta k)^{d+1}}, \Delta k >> 1 \quad (12.45) $$

If $\Delta k << 1$, consider

$$ S(\Delta k \to 0) \approx \frac{1}{2\pi k_0^3} \int_0^{2\pi} d\phi \frac{1}{2|1 - \cos \phi|^{3/2}} $$

which diverges due to the $\phi = 0$ (and $\phi = \pi$) contribution. Oops. So we had better keep a little $\Delta k$. For convenience, we will also expand $\phi$ around 0.

$$ S(\Delta k) \approx \frac{1}{2\pi k_0^3} \int_0^{2\pi} d\phi \frac{1}{(\Delta k)^2 + \phi^2}^{3/2} + ... $$

Now let $u = \phi/\Delta k$

$$ S(\Delta k) = \frac{1}{2\pi k_0^3} \frac{1}{(\Delta k)^2} \int_0^{2\pi/\Delta k \to \infty} du \frac{1}{1 + u^2}^{3/2} $$

so,

$$ S(\Delta k) \sim \frac{1}{(\Delta k)^2} \text{ as } \Delta k \to 0 \quad (12.46) $$

for all dimensions $d$.

If one does this in $d$ dimensions with

$$ S = \frac{1}{|k - k_0|^{\gamma}} \quad (12.47) $$

then

$$ \bar{S} = \begin{cases} \frac{1}{(k - k_0)^{\gamma - (d-1)}}, & \frac{k - k_0}{k_0} << 1 \\ \frac{1}{(k - k_0)^{\gamma}}, & \frac{k - k_0}{k_0} >> 1 \end{cases} \quad (12.48) $$

If $\gamma - (d - 1) > 0$. For the case $\gamma = d - 1$, one obtains

$$ \bar{S} \sim \begin{cases} -\ln (k - k_0), & \frac{k - k_0}{k_0} << 1 \\ \frac{1}{(k - k_0)^{d-1}}, & \frac{k - k_0}{k_0} >> 1 \end{cases} \quad (12.49) $$

It should be noted that the actual scattering is given by a weird boring integral.
like Eq. 12.44, which is pretty close to an elliptical integral.

Finally, note the big mess of power laws, and we have not considered diffuseness or roughness! Everything is just geometry.