8.512 Theory of Solids II
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Lecture Notes: Theory of Solids II

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Contents

Chapter 1

Lecture 2: Scattering and the Correlation Function

We ended the last lecture with a brief discussion of the connection between scattering experiments and measurements of the correlation function $S(\vec{q}, \omega)$. In this lecture we will discuss scattering in more depth in terms of two concrete examples (electron and neutron scattering). After that, we will look at some more general properties of response functions.

1.1 Scattering

The picture we have is of some blob of material, with a plane wave $|\vec{k}_i\rangle$ coming in, and a different plane wave $|\vec{k}_f\rangle$ coming out. We define the momentum and energy transfer *to the sample*

$$\vec{Q} = \vec{k}_i - \vec{k}_f \tag{1.1}$$

$$\omega = E_{\vec{k}_i} - E_{\vec{k}_f} \tag{1.2}$$

Let $\vec{R}$ be the coordinate of the scattering particle. Recall from last time that application of Fermi's Golden Rule and the 1st order Born Approximation leads to the differential rate

$$W_{i\to[f]}\, d^3k_f = 2\pi \sum_n \left| \sum_{\vec{q}} v_{\vec{q}}\, \langle n|\hat{\rho}^\dagger_{\vec{q}}|\phi_0\rangle \int d\vec{R}\; e^{i(\vec{k}_f - \vec{k}_i)\cdot\vec{R}} e^{-i\vec{q}\cdot\vec{R}} \right|^2 \delta\left(\omega - (E_n - E_0)\right) d^3k_f \tag{1.3}$$

$$= |v_{\vec{Q}}|^2\, 2\pi \sum_n |\langle n|\hat{\rho}^\dagger_{\vec{Q}}|\phi_0\rangle|^2\; \delta(E_f - E_i) d^3k_f \tag{1.4}$$

$$= |v_{\vec{Q}}|^2\, S(\vec{Q},\omega)\, d^3k_f \tag{1.5}$$

$$\tag{1.6}$$

$$P(\vec{Q},\omega) = |v_{\vec{Q}}|^2\, S(\vec{Q},\omega) \tag{1.7}$$

for scattering into a final state with momentum somewhere in a volume element d^3k_f of momentum space centered on k_f. Here, $v_{\vec{Q}}$ is the Fourier Transform of the interaction potential. The key result here is that the rate of scattering with momentum transfer $\vec{Q}$ and energy loss ω is directly proportional to the correlation function $S(\vec{Q},\omega)$.

1.2 Application: Electron Energy Loss Spectroscopy (EELS)

The experiment we imagine here is that of shooting high energy electrons (100 keV) at a thin film of material, and collecting them as they emerge with an energy-resolved detector. For this case, the interaction potential is just the Coulomb interaction between the electron and the sample's charge density, so

$$|v_{\vec{q}}| = \frac{4\pi e^2}{q^2} \tag{1.8}$$

Recall the definition

$$\frac{1}{\epsilon(\vec{q}, \omega)} = \frac{U_{Tot}}{U_{Ext}} \tag{1.9}$$

$$= 1 + \frac{U_{scr}}{U_{Ext}} \tag{1.10}$$

Remembering that $U_{scr}(\vec{q}) = \frac{4\pi e^2}{q^2} \delta n(\vec{q})$, where $n(\vec{q})$ are the Fourier components of the density fluctuations,

$$\frac{1}{\epsilon(\vec{q}, \omega)} = 1 + \frac{4\pi e^2}{q^2} \frac{\delta n(\vec{q}, \omega)}{U_{Ext}(\vec{q}, \omega)} \tag{1.11}$$

As defined in the previous lecture, the (linear) density response function $\chi(\vec{q}, \omega)$ is defined by the ratio

$$\chi(\vec{q}, \omega) = \frac{\delta n(\vec{q}, \omega)}{U_{Ext}(\vec{q}, \omega)} \tag{1.12}$$

Substituting this into the relation for $\frac{1}{\epsilon(\vec{q}, \omega)}$, we get

$$\frac{1}{\epsilon(\vec{q}, \omega)} = 1 + \frac{4\pi e^2}{q^2} \chi(\vec{q}, \omega) \tag{1.13}$$

With $\chi''(\vec{q}, \omega)$ defined as the *imaginary* part of χ, the relation

$$S(\vec{q}, \omega) = -2\chi''(\vec{q}, \omega) \tag{1.14}$$

combined with equation (1.7) for the scattering rate into momentum space volume $d^3 k_f$ gives the following relation for the scattering rate in terms of the dielectric function:

$$P(\vec{q}, \omega) = \frac{8\pi e^2}{q^2} \left(-\text{Im} \left[\frac{1}{\epsilon(\vec{q}, \omega)} \right] \right) \tag{1.15}$$

What useful information can we get out of this? For one, we are able to investigate the dielectric constant at *finite* values of $\vec{q}$ (0 to k_F). In optical experiments, the vanishingly small photon momentum in comparison with typical electron/nucleus momenta means that we are only able to investigate the $\vec{q} \approx 0$ regime with photons.

On the downside, the best energy resolution we can achieve today is around 0.1 eV, which is far too coarse to obtain much useful information. This energy resolution is already $1 : 10^6$ when compared with the total electron energy of around 100 keV. To get around this, one might

consider trying lower energy experiments. However, the problem with low energy experiments is that the probability of multiple scattering events within the sample becomes significant, leading to complicated and messy results.

With EELS, we can also look at high energy excitations of the electrons in a metal. Recall that there is a high energy *collective mode* of the sample electrons at a frequency equal to the plasma frequency ω_{pl}. The plasma frequency is defined in terms of the zero of the dielectric function

$$\epsilon(\vec{q}, \omega_{pl}) = 0 \tag{1.16}$$

The situation where the dielectric function becomes zero is interesting, because it represents a singularity in the system's response to an external perturbation:

$$\frac{1}{\epsilon(\vec{q}, \omega_{pl})} = \frac{U_{Tot}}{U_{Ext}} \tag{1.17}$$

Thus even a tiny perturbation at the plasma frequency results in a large response of the system.

1.3   Application: Neutron Scattering

Since neutrons are uncharged, they do not see the electrons as they fly through a piece of material[1]. The dominant scattering mechanism is through a contact potential with the *nuclei* of the sample

$$V(\vec{r}) = \frac{2\pi b}{M_n} \delta(\vec{r}) \tag{1.18}$$

where b is the scattering length and M_n is the mass of the neutron. Since the Fourier transform of a delta function in space has no $\vec{q}$ dependence, the Fourier components of the interaction potential are all simply

$$v_{\vec{q}} = \frac{2\pi b}{M_n} \tag{1.19}$$

Inserting this into equation (1.7) for the scattering rate, we get

$$P(\vec{Q}, \omega) = \left(\frac{2\pi b}{M_n}\right)^2 S(\vec{Q}, \omega) \tag{1.20}$$

Here, $S(\vec{Q}, \omega)$ is the correlation for the nuclear positions (density)

$$S(\vec{Q}, \omega) = \int dt\, e^{i\omega t} \langle \hat{\rho}_{\vec{Q}}(t) \hat{\rho}_{-\vec{Q}}(0) \rangle_T \tag{1.21}$$

with

$$\hat{\rho}_{\vec{Q}} = \sum_i e^{i\vec{Q} \cdot \vec{R}_i(t)} \tag{1.22}$$

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[1] The can interact, however through spin-spin magnetic interactions.

where $\{\vec{R}_i(t)\}$ are the coordinates of the nuclei at time t. Now we can substitute this in to the expression for $S(\vec{Q}, \omega)$:

$$S(\vec{Q}, \omega) = \int dt \, e^{i\omega t} \sum_{j,\ell} \langle \, e^{-i\vec{Q}\cdot\vec{R}_j(t)} e^{i\vec{Q}\cdot\vec{R}_\ell(0)} \, \rangle_T \tag{1.23}$$

To make progress, we must put in a specific form for $\vec{R}_j(t)$. We consider the case of small distortions from a Bravais lattice:

$$\vec{R}_j = \vec{R}_j^0 + \vec{u}_j \tag{1.24}$$

where $\{\vec{R}_j^0\}$ are the Bravais lattice sites, and $\{\vec{u}_j\}$ are small displacements. The $\{\vec{u}_j\}$ can be expanded in phonon coordinates, yielding

$$\vec{u}_j = \sum_\alpha \sum_{\vec{q}} \vec{\lambda}_\alpha \frac{1}{\sqrt{2NM\omega_{\vec{q}}}} \left(\hat{a}_{\vec{q}} e^{i(\vec{q}\cdot\vec{R} - \omega_{\vec{q}}(t))} + \hat{a}_{\vec{q}}^\dagger e^{-i(\vec{q}\cdot\vec{R} - \omega_{\vec{q}}(t))} \right) \tag{1.25}$$

where the sum over α is a sum over all phonon polarizations, $\vec{\lambda}_\alpha$ is the polarization of the αth mode.

After some algebra (see problem set), it can be shown that this decomposition yields

$$S(\vec{Q}, \omega) \propto e^{-2W} \left[\sum_{\vec{Q}} \delta(\vec{Q} - \vec{G})\delta(\omega) + \sum_{\vec{q}} \frac{Q^2}{2NM\omega_{\vec{q}}} \left\{ (n_{\vec{q}} + 1) \sum_{\vec{G}} \delta(\vec{Q} - \vec{q} - \vec{G})\delta(\omega - \omega_{\vec{q}}) \right. \right. \tag{1.26}$$

$$\left. \left. + \, n_{\vec{q}} \sum_{\vec{G}} \delta(\vec{Q} + \vec{q} - \vec{G})\delta(\omega + \omega_{\vec{q}}) \right\} \right]$$

where W is the Debye-Waller factor, and $n_{\vec{q}}$ is the Bose statistical occupation factor.

There are several interesting features about this expression for the correlation function. The first term corresponds to simple elastic Bragg scattering through a momentum transfer $\vec{Q}$. Even in the presence of fluctuations, this term is still a sum of delta function peak. Thus the effect of fluctuations on the Bragg peaks is only to decrease their amplitude via e^{-2W}, and *not* to induce any broadening.

The 2nd and 3rd terms give rise to peaks at $\pm\hbar\omega_{\vec{q}}$ arising from the emission/absorption of a phonon with wave vector $\vec{q}$. Note that each of these terms is multipled by a prefactor Q^2. Because of this prefactor, it is possible to experimentally achieve enhancement of the phonon emission/absorption peaks by looking at large $\vec{Q}$ scattering. Because the crystal momentum is conserved only up to a reciprocal lattice vector $\vec{G}$, $\vec{Q}$ is allowed to run outside of the first Brillouin Zone. Thus very large values of $\vec{Q}$ are possible. However, there is a dependance on $\vec{Q}$ hidden the Debye-Waller factor, which kills this enhancement for large Q^2

$$2W = \frac{1}{3} Q^2 \langle u_j^2 \rangle \tag{1.27}$$

$$= \frac{1}{3} \frac{Q^2}{2NM} \sum_{\alpha,\vec{q}} \frac{2n_{\vec{q}} + 1}{\omega_{\vec{q}}} \tag{1.28}$$

The expectation value $\langle u_j^2 \rangle$ in this expression represents the mean square fluctuations of the nuclei from their ideal Bravais lattice positions. These fluctuations result in the overall

suppression of both *elastic* and *inelastic* scattering peaks. Furthermore, as noted above, the Bragg peak delta functions are *not* smeared out by thermal fluctuations.

In the low temperature limit, we can employ the Debye model[2] to evaluate the sum in equation (1.28). This gives

$$2W \to \frac{3}{4}\frac{Q^2}{M\omega_D} \quad \text{as } T \to 0 \tag{1.29}$$

which is the damping due to *zero-point fluctuations*.

For $k_B T \gg \hbar\omega_D$, the Bose factors $n_{\vec{q}} \to \frac{k_B T}{\hbar\omega_D}$. In this case

$$2W = \frac{Q^2}{2M\omega_D^2}k_B T \quad \text{for } k_B T \gg \hbar\omega_D \tag{1.30}$$

which comes from the fact that at high temperatures, the mean square fluctuations are proportional to $k_B T$ according to the equipartition theorem.

In two dimensions, we get an interesting result. Using the fact that (for an "infinite" sample) there are phonon modes of arbitrarily small frequency, we can approximate the numerator of equation (1.28) with $k_B T$. Using the Debye relation $\omega_{\vec{q}} = v|\vec{q}|$,

$$\sum_{\vec{q}} \frac{2n_{\vec{q}}+1}{\omega_{\vec{q}}} \approx \sum_{\vec{q}} \frac{k_B T}{\omega_{\vec{q}}^2} \tag{1.31}$$

$$\approx k_B T \int_0^{k_B T/\hbar v} d^2 q \frac{1}{v^2 q^2} \to \ln(0) \tag{1.32}$$

which is logarithmically divergent. Thus $2W$ is infinite for a 2D crystal. Although this would seem to imply the complete disappearance of the Bragg peaks, a more careful calculation reveals that the Bragg delta peaks are actually broadened to a power law.

What is the reason for this strange behavior? The answer is that in two dimensions, thermal fluctuations are sufficiently influential that they can destroy the long-range order of a crystal. If you imagine nailing down a single nucleus to be used as the origin of a Bravais lattice, then at large distances the mean positions of the nuclei will *not* be described by lattice vectors for a 2D crystal with thermal fluctuations. Because of this, some authors claim that there is no such thing as a 2D crystal.

However, we may ask a different question about our material to judge its crystallinity. Is orientational order preserved at long distances? Imagine nailing down *two adjacent* nuclei at their equilibrium separation, with the line connecting the two nuclei oriented along a particular direction. Far away from these two nuclei, are similar bonds still parallel to this one? The answer is yes, bond orientation *is* preserved over large distances for a 2D crystal[3]. In this sense, it still does make sense to speak of a two dimensional crystal.

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[2] Recall that in the Debye model, the phonon dispersion relation is assumed to be linear for all $\vec{q}$.
[3] In order to exhibit a change in bond orientation, it is necessary for a dislocation, or *topological defect* to be present.