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SPATIAL STRUCTURE

READ CH 2. SG & KY

How to probe matter?

The most difficult questions?

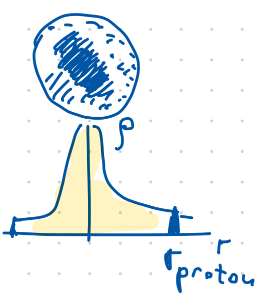
1. Why atoms condens?
2. Condensed matter breaks Galilean invarience. Does it matter?

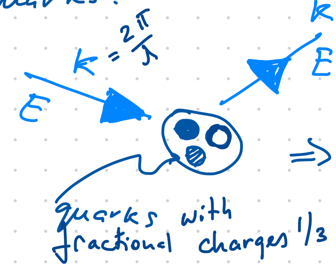
Apart from that how can we understand the organization of matter?

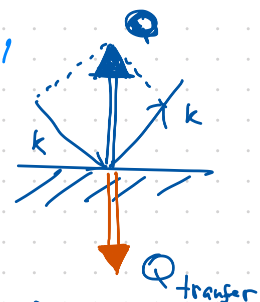
We need a probe which will do some quantum mechanics for us.

Think e.g. how do we test matter for the presence of quarks?

$\bar{Q} = \bar{k} - \bar{k}'$



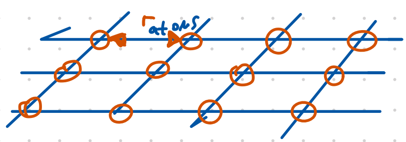




$Q = \frac{2\pi}{r}$

So for $r < r_p$ $\quad Q > Q_c = \frac{2\pi}{r_p}$

Back to condensed matter.



we need a probe with $\lambda \sim r_{atoms}$

if energy of the probe E $\quad \lambda = \frac{\hbar c}{E}$

if we change the units into Å and eV

$$\begin{cases} \lambda = \dfrac{12.4}{E\,(keV)}\ (Å) & (\text{photons}) \\ \lambda \approx \dfrac{0.28}{E\,(eV)^{1/2}}\ (Å) & \left(\text{nuetrons with } \lambda = \dfrac{h}{\sqrt{2ME}}\right) \\ \lambda \cong \dfrac{12}{E\,(eV)^{1/2}}\ (Å) & (\text{electrons}) \end{cases}$$

Q: if the distance between atoms ~ 1Å Calculate E for each probe.

Lets work out in some detail X-ray scattering

We will use semiclassical approximation

assume e^- has speed $v/c \ll 1$ so it couples only to $\mathcal{E}$ field and not magnetic.

↓ no Lorentz force

$$m\,\delta \ddot{\vec{r}} = -e\,\bar{\mathcal{E}}$$

we consider the case of a plane wave

$$\bar{\mathcal{E}} = \bar{E}_{in}\, e^{i(k\cdot r - \omega t)}$$

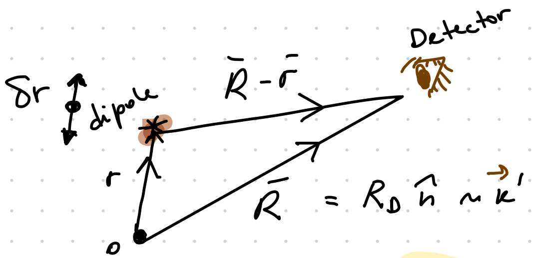
which induces an electric dipole

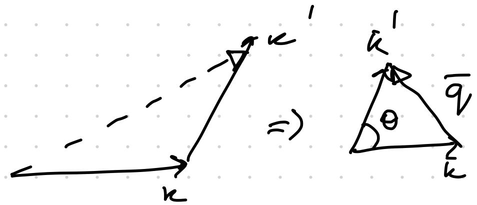
$$\bar{P}(t) = -e\,\delta r(t)$$

$$m\,\delta \ddot{\vec{r}} = -e\,E_{in}\,e^{i(kr - \omega t)} \Rightarrow \delta r = \frac{e\bar{E}_{in}}{m\omega^2}\,e^{i(kr-\omega t)}$$

$$\bar{P}(t) = -\frac{e^2}{m\omega^2}\,\bar{E}_{in}\,e^{i(kr-\omega t)}$$

From your E & M class you should remember that
this electric dipole will radiate the electric field at the position $\bar{R}$





a radius of electron

$$\vec{E}_a = \frac{e^2}{m_e c^2}\left[\hat{n} \times (\hat{n} \times \bar{E}_{in}\right) e^{i(kr - \omega t)} \cdot$$

$$\cdot \underbrace{\frac{e^{ik|R-r|}}{|R-r|}}_{\text{spherical wave}}$$

where $\hat{n} = \dfrac{\bar{R} - \bar{r}}{|R-r|}$

and since $|R| \gg |r|$ (far field approx.)

we get $\hat{n} \sim \dfrac{\bar{R}}{|R|}$

here $\dfrac{e^2}{m_e c^2} \equiv r_c = \underset{\frac{1}{137}}{\alpha^2} \cdot a_B$ = classical radius of the electron

$k = \dfrac{\omega}{c}$

Now since inside the atom we have more than 1 electron; All the electrons will <u>interfere</u>.

if the detector is in the position $R_D \approx |\bar{R} - \bar{r}|$ we can make the replacement like this term in the amplitude ✓ but not in the phase ✓!

term

we have to be very careful as phase is very sensetive.

Instead in:

$$\boxed{\frac{e^{ik(R-r)}}{R-r}} \qquad k\,\underbrace{|R-r|}_{\approx R_D} = k\sqrt{R_D^2 - 2\bar{r}\cdot\bar{R}_D + r^2} \approx$$

Taylor exp

$$\approx kR_D\left[1 - \frac{\bar{r}\cdot\bar{R}_D}{R_D^2} + \dots\right] \qquad -\bar{r}\,\frac{\bar{R}_D}{|R_D|}$$

$$K'\hat{n} = k + q$$

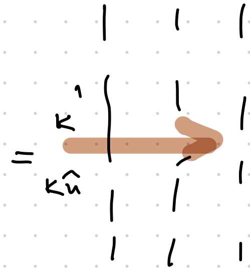
and since $k' = k + q = k\,\underbrace{\frac{\bar{R}_D}{|R_D|}}_{=\vec{n}} = k\vec{n}$

the direction to the detector determines the final state k'

now recall from Q.M. :

but far away

$=$



or

the phase term $\dfrac{e^{ik|R-r|}}{|R-r|} \approx \dfrac{e^{ikR_D}}{R_D} \cdot e^{-i(k+q)\cdot r}$

Here $\hbar \vec{q}$ = momentum taken from xtal and transfered to xrays beam

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And going back (see page 3)

$$\mathcal{E}_a \sim \frac{e^2}{m_e c^2} \frac{e^{ikR_D}}{R_D} [n \times (n \times \mathcal{E}_{in})]$$
$$\cdot\, e^{i\omega t} e^{-iqr}$$

[The factor e^{iqr} comes from the fact that when e^- moves from the origin to $\bar{r}$ the phase of the driving force of an Xray changes, as does the phase of the scattered wave since the distance to the detector changes.
($\bar{R}_D = \bar{R} - \bar{r}$)]

It is the sensitivity to this phase of the scattered wave to the position $\vec{r}$ of the electron that enables the <u>spatial structure of atoms</u> to be resolved by X-rays

Now if we have Z electrons

in the atom, we should replace e^{-iqr} by

$$\boxed{\sum_{j=1}^{Z} e^{-i\bar{q}\cdot\bar{r}_j} \equiv f(q)}$$

it is called → the atomic form factor (see e.g. NIST web site for tables)

It can be also written as:

$$f(q) = \int d^3r \, e^{-iqr} \rho(r)$$

where $\rho \equiv \sum_{j=1}^{Z} \delta^3(r - r_j)$

i.e., $f(q) = \sum_{j=1}^{Z} \int d^3r \, e^{-iqr} \delta^3(r - r_j)$

$$= \sum_{j=1}^{Z} e^{-iqr_j}$$

in quantum mech. we just replace $\rho(r)$ by $\langle \rho(r) \rangle$ ← quantum expectation

Thus we can see that $f(q)$ directly measures the F.T. charge density

in experiment we can only measure $|f(q)|^2$ via $d\sigma/d\Omega \sim |f(q)|^2$

Note if $q \to 0$ $f(0) = Z$

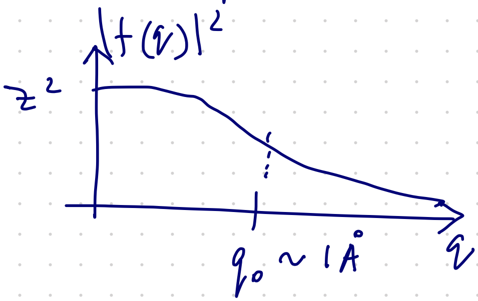
or if the resolution is poor $\sim \frac{2\pi}{q}$

the atom looks like a single $-Ze$ oscillating charge coherently with an applied field.

On the other hand if

$q \to \infty$ (high res.)

we expect $f(q) \to 0$ (we see fine grained atoms, e^-, ions and more)



multielectron atoms

This was about a multielectron atom

but what about a solid state material?

If we assume that all atoms inside a solid at the position R_i:

$$\rho(r) = \sum_{i=1}^{N} \rho_a(\bar{r} - \bar{R}_i)$$

atomic electron density

Let's calulate the form factor $F(q)$ ⑧⓪

$$F(q) = \int d^3r \; e^{-iqr} \sum_{i=1}^{N} \rho_a(\bar{r}-\bar{R}_i) =$$

$$\overset{|r-R|\equiv r'}{=} \sum_{i=1}^{N} \int d^3r' \; e^{-iq(r'+R)} \rho_a(r')$$

positions of atom in the xtal

$$= \underbrace{\left(\sum_{i=1}^{N} e^{-iqR_i}\right)}_{W(\bar{q})} \underbrace{\left(\int d^3r' \; e^{-iqr'} \rho_a(r')\right)}_{f(\bar{q})}$$

$W(\bar{q}) = \sum_{i=1}^{N} e^{-iqR_i}$ = $\boxed{\text{xtal form factor}}$

$f(\bar{q})$ [atomic form factor]

Let's now assume that we know $f(q)$:
e.g. from the NIST web site,

then the elastic scattering

$$\frac{d\sigma}{d\Omega} \sim |F(q)|^2 \text{ and}$$

is essentially defined by

$$\boxed{\text{STATIC STRUCTURE FACTOR} \quad S(q) \equiv \frac{1}{N} \langle\langle |W(q)|^2 \rangle\rangle}$$

$\langle\langle \;\rangle\rangle$ is called thermal average

$S(q)$ is very different for different R_i positions as the phases e^{-iqR_i} are very different.

Optional; but extremely useful for experimentalists.

Relation between $S(q)$ & correlations

In condensed system atomic positions are determined by the probability distribution function (p.d.f.)

Q: Can we use X-rays to measure $S(\bar{q})$ and from it deduce the p.d.f.?

A: Yes.

Recall, the scattering amplitude $F(q)$ is the sum but we measure $|F(q)|^2$ $\xrightarrow{\text{many}}$ pairwise interference terms which depends on the positions and and relative orientations of the pairs of atoms.

Define a two-point distribution function

$$n^{(2)}(r, r') \equiv \left\langle\left\langle \sum_{i \neq j} \delta(r - r_i') \cdot \delta(r' - r_j) \right\rangle\right\rangle$$

from $S(q) = \frac{1}{N} \langle\langle |W(q)|^2 \rangle\rangle$

Prove this

we find $\boxed{S(q) = 1 + n \int d^3r \, e^{iqr} g(\bar{r})}$

where

$$g(r) = n^{(2)}(r,0)/n^2.$$

$g(r)$ is called the pair distribution function (pdf)

e.g. if particles are random
$g(r) = 1$

in liquid $g(r) \equiv g(|\vec{r}|)$
and $g(r) \to 1$ at large r

if we define, then for liquid $h(r) \underset{r\to\infty}{=} 0$

$$h(r) \equiv g(r) - 1$$

i.e. $h(r) \neq 0$ if particles correlate or positions not random.

we get

$$\boxed{\begin{aligned} S(q) &= N\delta_{q,0} + 1 + \tilde{h}(q) \\ \text{where} \quad \tilde{h}(q) &\equiv n\int d^3r\, e^{iqr} h(r) \end{aligned}}$$

What is the difference between liquid and Solid State?

Pair correlation function is found in the expression for x-rays b/c

X-ray scatt. amplitude ~ F.T. of atomic density:

$$F(q) = f(q)\,W(q) =$$

$$= \left(\sum_{i}^{N} e^{-iqR_i}\right)\left(\int d^3r'\, e^{-iqr'} \rho_a(r')\right)$$

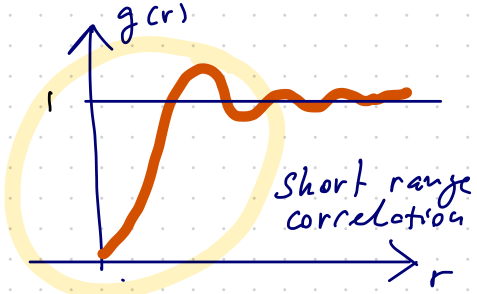
$I \sim |F(q)|^2 \Rightarrow$ it contains interference terms

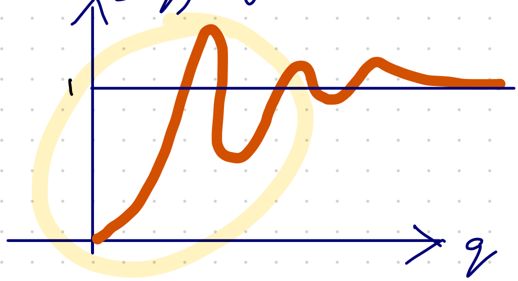
$\Downarrow$

2-body pair correlation function enters into the formula $h^{(2)}$

Let's try to understand $h^{(2)}$ for various states of matter.

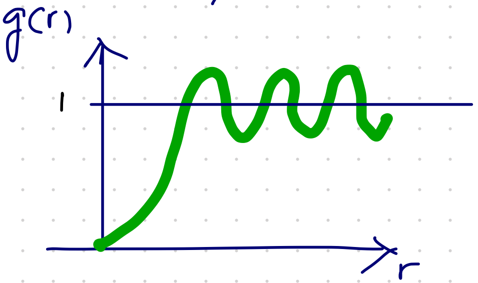
- at high T all phases are liquids or gases.

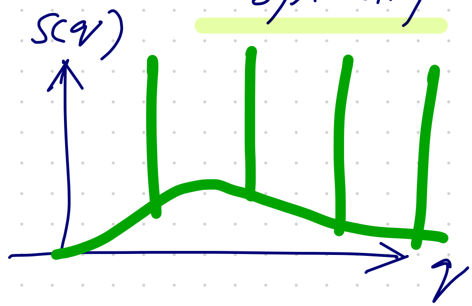




- At low T most materials order

Long-range order with spontaneously-broken symmetry





Fun fact:

And the revolution happened in 1984!

new class of alloys called quasicrystals is discovered!

X-ray show long-range order with FIVE-FOLD ROTATIONAL SYMMETRY!!! ← imposible??!! in Solids?

in the next lecture we will learn about Lattices & symmetry

<read Ch 3 of the main text>.

THE END.