

PH-207 Condensed Matter I

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Contents

Lectures

Lecture 1.1

Course is about... (Introduction)

Books

Outline

Entropy decreases implies heat flows out; energy comes from bonding

Example of order: spherical close packing; demonstrate that this is FCC.

Derive FCC packing fraction: 4 spheres; Pythagoras to relate a and r .

HCP as an aside. Focusing on cubic lattices. There are 14 Bravais lattice, 3 of which are cubic.

Show the cubic lattices. Count sphere in each. Suggest packing fraction as exercise for students.

Lecture 1.2

Recap

lattice: collection of points with some properties

cubic family: SC, BCC, FCC

Today

mathematics of the lattice

lattice vectors

- Illustrate some valid lattice vectors on simple square.

Integer summation; can be used to define lattice.

Conventional vs primitive

- centered square lattice
- show that $a\hat{x}$ and $a\hat{y}$ are not sufficient
- show valid primitive lattice vectors
- show that conventional is simpler, but need to also record where points are; avoid double counting

Describing BCC, FCC using conventional + extra points

- **convolve** basis with lattice (means "copy" basis to every point)

Lattice, Basis, Convolution

- maths of this
- only doing convolution with point-like objects
- $FT[a \otimes b] = FT[a] \times FT[b]$

Graphene as 2D example

- sketch 2D hexagonal lattice
- ask whether vector joining nn points along x-axis is LV
- demonstrate that it is not because LV must join LP and only LP
- show valid LV for 2D hexagonal lattice and identify 2 point basis

Lecture 1.3

Last week, met lattices:

- collection of points with *translational symmetry*
- all points which we can reach with *integer sums of lattice vectors*.

Describe crystals by copying something to every lattice point.

e.g. NaCl is FCC with two atoms associated with every point

Can also describe a collection of points which does not *strictly* fulfil the lattice requirement

- e.g. graphene; illustrate that has to be 2-point basis

Similarly, Diamond lattice

- consider (without rotation!) the situation of (1) atom at cube vertex cf (2) atom 1/4 along body diagonal
- (1) has neighbour immediately 1/4 along body diagonal; (2) has no such neighbour.
- i.e. lattice does **not** look identical from each atom; therefore each atom is **not** a lattice point

Today, related idea of **Unit cell**

- region of space which we copy to every point
- tiles space without gaps or overlap
- illustrations: Simple Square; Centred Square

Some types of unit cell

- **Conventional** which is a cube
- **Primitive** which always contains exactly one lattice point

Together with the constraint that these tile space without gaps or overlap, for a given lattice, any primitive unit cell has the same volume (and a conventional unit cell containing n lattice points has n times the volume of the primitive unit cell).

- Primitive unit cell:
 - Parallelepiped ($\mathbf{r} = \sum_i x_i \mathbf{a}_i$ for $0 \leq x_i < 1$)
 - Wigner–Seitz (region of space nearest a given lattice point)

Some great visualisations at Physics in a Nutshell page on BCC.

Diffraction

1D – require integer number of 2π phase diff to get constructive interference

2D – don't labour geometry of 2D because generalising to 3D now

3D – diagram showing two LPs connected by \mathbf{d} .

- Input \mathbf{k} . Explain e^{ikx} generalised to vectors.
- Outgoing \mathbf{k}' . Projection of k and k' along d .
- Argue for $\mathbf{k} \cdot \mathbf{d} = \mathbf{k}' \cdot \mathbf{d}$
- Note that \mathbf{d} is a LV i.e. \mathbf{R}_n
- Find $\mathbf{G} = \Delta \mathbf{k}$ such that $\mathbf{G} \cdot \mathbf{R}_n = 2\pi p$.

Lecture 1.4

Diffraction

- Recap vector diagram
- result was $\Delta \mathbf{k} \cdot \mathbf{R}_n = 2\pi \times p$ where p is an integer
- Find set of vectors $\mathbf{G} = \Delta \mathbf{k}$ that fulfil this condition

Show solution and demonstrate that it works

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}; \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}; \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

Show that $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij}$ (Kronecker delta)

And hence that $\mathbf{G}_m = \sum_i m_i \mathbf{b}_i$ satisfies $\mathbf{G}_m \cdot \mathbf{R}_n = 2\pi \times p$.

Reciprocal lattice

For any real-space lattice, there is an associated *reciprocal* lattice.

Exists in *momentum space*, just like $\hbar k$ is a momentum and $k = 2\pi/\lambda$ has units of inverse metres.

$\hbar \mathbf{G}_m$ is the set of discrete momentum kicks that a lattice can impart to a wave through diffraction.

Real experiments are more messy; here, we're assuming crystal is infinite, which makes this result exact.

*RLV: SC example:

Powder x-ray camera

See how we can use this in an experiment.

Ideally, monocrystalline sample, and record full diffracted pattern for all incident angles.

However, takes a long time, and often difficult to obtain large monocrystalline sample.

Instead, **powdered sample** i.e. lots of small crystals; incident plane waves; record angle of diffracted light.

Consider **elastic scattering** $|k| = |k'|$.

Diagram; derive $\sin(\theta/2) = \dots$

Can use for all cubic family crystals (SC, BCC, FCC, and derived e.g. diamond or NaCl) but must account for the extra points inside the conventional unit cell.

Structure factor

Write down integral for diffraction. Split into lattice bit and unit cell bit.

Lecture 1.5

Last time, did 3D scattering. Now generalise to not just two points, but a continuum of points: an integral
Wrote this integral down last time, but was a bit rushed.

Will find "lattice" bit and "unit cell" bit.

Integral -> Structure factor

(Make sure to subst in $\Delta k = G_m$.)

This is a messy integral in general, but when treating **cubic** crystal (FCC, BCC etc) with **conventional** vectors, then we have several **points** in the **conventional** unit cell; then we can make progress.

Geometric structure factor

Unit cell contains several Dirac delta functions.

Convolution with Dirac delta just picks out value of function at that point.

Integral goes to a sum over phase at each point. (Just as in 3D scattering which we wrote down originally.)

GSF must be non-zero; there are **selection rules** which (h, k, l) must follow.

Derive BCC's GSF. State SC, BCC, FCC rules. Remind that can work this out; perhaps helpful to recall, but most important is to understand the procedure.

e.g. A crystal is illuminated with x-rays of wavelength $\lambda = 1\text{\AA}$. The first few observed diffraction orders are at $\sin(\theta/2) = (0.289, 0.333, 0.471)$. Find the crystal structure and the lattice constant.

Lecture 1.6

Show diffraction orders: mag (hkl) GSF

- some magnitudes not possible
- some magnitudes possible with several (hkl) values
- use this to solve the past paper question (values given in notes)

Lattice planes

- Diffraction can be considered as coming from parallel planes
- Label these planes with Miller indices (hkl) (all integers)
- Plane is orthogonal to vector \mathbf{G}_{hkl}
- In general, a plane is defined by three points
- Plane (hkl) intersects at \mathbf{a}_1/h , \mathbf{a}_2/k , \mathbf{a}_3/l
- Example of (100) and (111); show pictures

Miller indices

- (hkl): planes
- [hkl]: direction

von Laue

- vector mathematical way to describe diffraction
- derive $2\mathbf{k} \cdot \mathbf{G} = G^2$
- justifying $\Delta\mathbf{k} = \mathbf{G}$
- quasi-crystals (reference WS1 & crystallographic restriction theorem)

Lecture 2.1

So far, we have considered **static** properties of lattice.

Now, we look at **dynamic** properties, including **wave propagation**

- Wave prop
 - notation
- Phonons
 - properties

Lecture 2.2

Have moved on to Lattice II and **dynamic** properties of the lattice, inc **wave propagation**
Going to use **heat capacity** as a window into the microscopic

Heat capacity

- start with classical theory: equipartition
- $(1/2)k_B T$ per quadratic DoF
- Treat atoms as harmonic oscillators, with equilibrium position and spring constant
- (this comes from the bonding, of course, but not relevant just now)
- Can vibrate in x,y,z
- Energy of HO: $(1/2)mv^2 + (1/2)kx^2$
 - two DoF; $(1/2)kT$ / DoF * 2 DoF/HO * 3 HO/atom * N atoms
 - Internal energy $U = 3Nk_B T$
 - Heat capacity $(\partial U/\partial T) = 3Nk_B$
 - Compare with typical plot.

try to explain this result

1D **monatomic** lattice

Next time

1D **diatomic** lattice

Perhaps show some key ideas/pictures

Look ahead. . .

- Phonons are *quantized*
- They obey quantum statistics: Bosons or Fermions
- Phonons can be excited by *heat*
- Therefore, phonons contribute to **specific heat capacity**
- We can build simple models and see whether they agree with experiment
 - Equipartition
 - * Fully classical
 - * Doesn't work at low temperature
 - Einstein model
 - * Bose statistics
 - * Considers only single phonon energy
 - * Sort of works. . .
 - Debye model
 - * Bose statistics still
 - * Considers range of phonon energies
 - * Works really well!
 - * (As simple as possible, and no simpler)

Lecture 2.3

Sketch diatomic lattice. Careful of a and indexing

- a spans both M and m
- small atoms *even* indices; big atoms *odd* indices

Step through derivation; get to quadratic in ω^2 i.e. quartic equation

Show dispersion curve. Two distinct branches.

Animations

- low k of acoustic branch
- BZ edge of acoustic branch
- low k of optical branch: still a high frequency, cf. acoustic branch
- BZ edge of optical branch

Zone boundary modes

- acoustic/optical have same k but different frequencies
- acoustic: small atoms stationary; optical: big atoms stationary (must be because heavy things move slower for same spring constant)

Optical branch

- charge separation
- high frequency for low k vector
- possible to couple to, and match energy and momentum with, a **photon**

Measure by spectroscopy: optical frequency dependent absorption by a thin sample of the crystal

Show NaCl dispersion

- crystal directions
- overlapping lines because different modes
- general idea captured despite simplicity of our model

Lecture 3.1

Heat capacity because heat is made of phonons

- microscopic theory makes testable predictions

Recall definition

Recall Equipartition: $3HO/\text{atom} * 2DoF/HO * (1/2)kBT/DoF = 3kBT/\text{atom}$

Consider phonons of a single frequency: Einstein model

High T limit

Low T limit

Plot full curve and Low T curve

Show that it doesn't fit experiment at low T

Motivate Debye model

Lecture 3.2

Debye model

Rather than a single frequency ω_E , vibrational energy spread over range of frequencies up to some maximum ω_D .

$$3n = \int_0^{\omega_D} g(\omega) d\omega$$

$$u_{\text{Lat}}^{\text{Deb}} = \int_0^{\omega_D} \hbar\omega \dots$$

Recover Einstein by setting $g(\omega) = 3n\delta(\omega - \omega_E)$.

$g(\omega)$ is a **density of states**. $g(\omega)\delta\omega$ is number of states in frequency interval $\omega, \omega + \delta\omega$.

Attack this by considering allowed frequencies in crystal by imposing boundary conditions.

Lecture 3.3

Remind of Debye model

Debye model: next steps

Debye model: finding the heat capacity

Show full expression

- careful guide through limiting cases

Compare with experiment

- zoom in on low temperature

works well because

- largest contribution to heat capacity from low energy phonons
- low energy phonons very well described by no dispersion approximation
- high T: classical limit, which is independent of phonons etc

Not full story for metals because **electrons**

Lecture 4.1 Drude

Electrons

- Drude
- Sommerfeld

Drude

- intro
- DC conductivity
- cf expt
- AC conductivity
- Optical properties and cf experiment

Lecture 4.2 finish Drude; start Sommerfeld

Lecture 4.3 Sommerfeld

Recap ingredients to model

Recap thermal occupation

Recap effect of external electric field

Need also **density of states**

- density per unit energy or per unit k state. (Density per unit volume is assumed.)
- affects ability of electrons to change state; i.e. more able if there are denser packed states
- simple equation in Sommerfeld model; lattice causes interesting deviations from this

Notation: $g_e(k)$ vs $g_e(E)$ or simply $g(E)$, implying density per unit k -state or per unit energy, respectively

Draw Fermi sphere and show counting states in a shell; maths shortcut is to use derivative.

Calculate density of states. Emphasise $g_k(k)dk = g_E(E)dE$. Substitute in E . Calculate at Fermi energy.

Density of **occupied** states is product $g(E)f(E)$.

Lecture 4.4 Bloch, binding, reduced zone

Talked about allowed k-states, occupation.

Three topics today

- Bloch waves
- Tight binding
- Kronig–Penney

Bloch waves Talk about wavefunction for electrons in the lattice.

An electron travelling through a crystal is subject to a periodic potential.

Result

- wavefunctions are $\psi = e^{ik \cdot r} u(r)$ where $u(r + R_n) = u(r)$.
- illustrate

Tight binding

Talk about **how** having atoms arranged in crystals means that some electrons are free to roam the lattice

- free atom potential and energy levels
- sketch many atoms side-by-side
- show that lower states are unaffected
- show that higher states must affect each other, by Fermi exclusion
- now look at periodic potential

Kronig–Penney

Simplest model of periodic potential

1D arrangement of finite potential wells

Can solve exactly. We won't do this here.

Show dispersion curve atop free electron curve.

Explain gaps – same k but can be either localised at regions of high potential, or at regions of low potential; hence different energies for same k.

Reduced zone

k conserved up to a change in reciprocal lattice vector. In 1D, any change of $2\pi/a$ leaves wave unchanged. (See directly from Bloch wave result.)

Reduced zone scheme redraws dispersion curve inside first Brillouin zone.

Point out similarity with diatomic 1D phonon dispersion curve. In this system, there's a ladder of increasingly high energy wavefunctions.

Filled bands

If number of electrons in material such that band is half filled, then this is a metal. e free to move when E field applied.

If band is exactly filled, then electrons cannot move. Shift by π/a and redraw.

Now, **if** electrons are excited across the band (somehow) they can move. Also, the **empty** site allows other electrons in the lower band to move.

Effective mass