Solid State Theory

0. Introduction + Motivation

What is condensed matter physics?

Quoting Wikipedia:

Condensed matter physics is the field of physics that deals with the macroscopic and microscopic properties of matter. In particular, it is concerned with the "condensed" phases of matter that appear whenever the number of constituents in a system are extremely large and the interactions between the constituents are strong. The most familiar examples of condensed phases are solids and liquids, which arise from electromagnetic forces between atoms.

The use of the term "condensed matter", being more general than just the study of solids, was coined and promoted by Nobel laureate Phil Anderson.

Condensed matter physics is by far the largest single subfield of physics. The annual meeting of condensed matter physicists by the American Physical Society is attended by some 10,000 people each year! The DPG spring meeting of condensed matter physicists draws some 5,000 people.

Why do we study condensed matter physics?

- It describes the world around us.
  Why are metals shiny and why do they feel cold?
  Why is glass transparent?
  Why is water a fluid, and why does it feel wet?

- It is useful.
  New materials change the world, e.g. semiconductor technology.

- It is exceptionally broad.

  Topics included in this field range from the very practical to the absurdly abstract, from down-to-earth engineering to mathematical topics that border on string theory.

- It is deep.

  The questions that arise in condensed matter physics are as deep as those you might find anywhere. In fact, many of the ideas that are now used in other fields of physics can trace their origins to condensed matter physics.
  - Anderson-Higgs mechanism, which explains how elementary particles acquire their mass
  - ideas of the renormalization group developed simultaneously in both high-energy and cond-mat physics
  - topological quantum field theories, invented by string theorists, materialize in cond-mat experiments

- Reductionism does not always work.

  Subsequent questions of "What is it made of?" not always provide ultimate insight.

  water → molecules → atoms → electrons + protons → quarks → ... ?

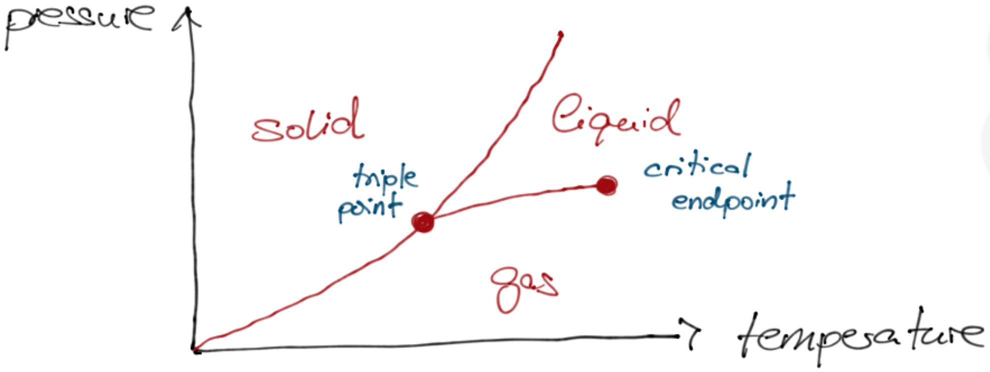
  <u>But:</u> Putting many electrons together, new particles may <u>emerge</u> that carry only <u>1/3</u> of the charge of an electron (fractional quantum Hall effect)

- It is a laboratory.

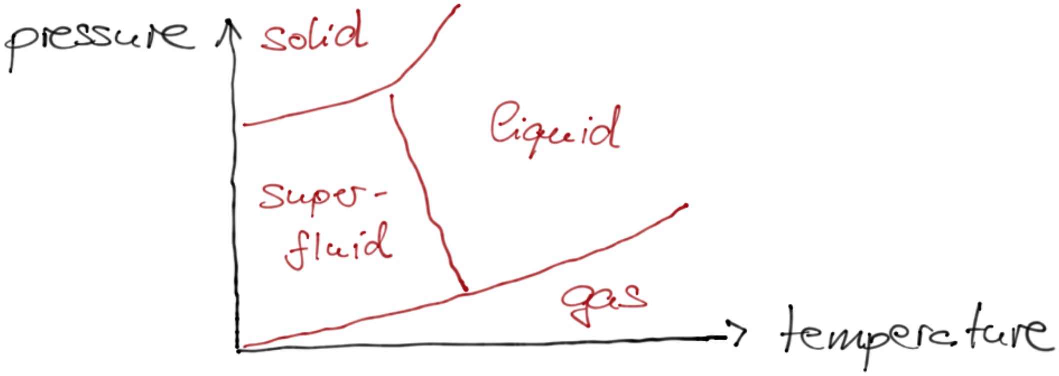
  Condensed matter physics is perhaps the best laboratory we have for studying quantum physics and statistical physics.

1. Solids

Fundamental states of matter: solid, liquid, gas

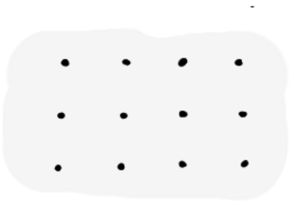


At sufficiently small temperatures matter almost always assumes a solid state.
Exception: Helium (He) → superfluid state (Nobel prize 1996)



1.1 Crystaline solids

Most solids are crystals characterized by a periodic arrangement of their constituents.



In contrast to amorphous solids like glasses.

Solid crystals break translation and rotation invariance of space.
Consequences: → solid state is separated from the liquid and gas state by a symmetry-breaking phase transition, i.e. a liquid or gas cannot be continuously transformed into a solid.

→ The solid exhibits a structural rigidity.
This structural rigidity allows for long-distance transmission of forces, i.e. dissipationless momentum and angular momentum flows.
(similar to a superconductor that allows for dissipationless charge flow.)

→ A solid crystal exhibits low-energy excitations (Goldstone modes) that are the acoustic phonons.
Phonon velocities are determined by the elastic moduli like bulk and shear modulus that quantify the rigidity of the crystal.

→ When a liquid freezes and solidifies it usually does not lead to a macroscopic solid composed of a single crystal. It often consists of a large number of smaller crystals (so-called domains), which have broken the symmetries in different fashions.
Such a material is a polycristal.

1.2 Crystal structures

(crash course, for more details consult exp. lecture + books)

The geometrical properties of a periodic structure are characterized by the Bravais lattice.

A (three-dimensional) Bravais lattice consists of all points with position vectors $\vec{R}$ of the form

$$\boxed{\vec{R}_n = n_1 \cdot \vec{a}_1 + n_2 \cdot \vec{a}_2 + n_3 \cdot \vec{a}_3}$$

with $n_i \in \mathbb{Z}$. The primitive vectors $\vec{a}_i$ are linearly independent.

Note: choice of primitive vectors is not unique.

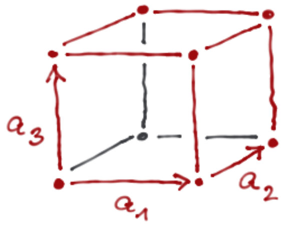
Theorem (Auguste Bravais 1848):

There exist only 14 such Bravais lattices in three spatial dimensions.

Examples

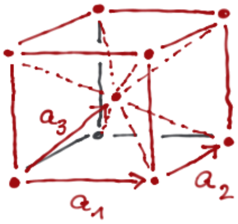
- simple cubic lattice (sc)

$$\vec{a}_1 \perp \vec{a}_2 \perp \vec{a}_3 \quad \text{with} \quad |\vec{a}_1| = |\vec{a}_2| = |\vec{a}_3|$$



- body-centered cubic lattice (bcc)

$$\vec{a}_1 = a\hat{x} \qquad \vec{a}_2 = a\hat{y} \qquad \vec{a}_3 = \frac{a}{2}(\hat{x}+\hat{y}+\hat{z})$$

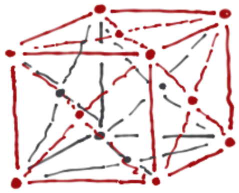


(sc plus an additional point at the center of each cube.)

- face-centered cubic lattice (fcc)

$$\vec{a}_1 = \frac{a}{2}(\hat{y}+\hat{z}) \qquad \vec{a}_2 = \frac{a}{2}(\hat{z}+\hat{x})$$

$$\vec{a}_3 = \frac{a}{2}(\hat{x}+\hat{y})$$



(sc plus an additional point at the center of each square face.)

Coordination number z

Number of nearest neighbors of each lattice point.

(Nearest neighbors = points in a Bravais lattice closest to a given point.)

	fcc	bcc	sc	diamond*	hyperhoneycomb*
z	12	8	6	4	3

* not Bravais lattices

The fcc and bcc Bravais lattices are very important as an enormous variety of solids crystallize in these forms with an atom or ion at each lattice site (→ sphere packing realizations). Usually, the fcc lattice is prefered at low temperatures due to its larger coordination number z. In contrast, the sc, diamond or hyperhoneycomb lattices are very rarely realized.

Unit cell

The unit cell is a volume of space that, when translated through a subset of the vectors of the Bravais lattice, just fills all of space w/o overlapping itself or leaving voids (→ tilings).

Primitive unit cell (PUC)

A unit cell containing exactly a single lattice point.

Note: There is no unique way of choosing a primitive unit cell for a given Bravais lattice. However, its volume is fixed by the density of points in the Bravais lattice

$$V_{PUC} = \frac{1}{n}$$

One possible choice is

$$PUC = \left\{ x_1\vec{a}_1 + x_2\vec{a}_2 + x_3\vec{a}_3 \;\middle|\; 0 \le x_i < 1, \quad i = 1,2,3 \right\}.$$

For a given PUC an arbitrary vector $\vec{R}$ is uniquely defined as

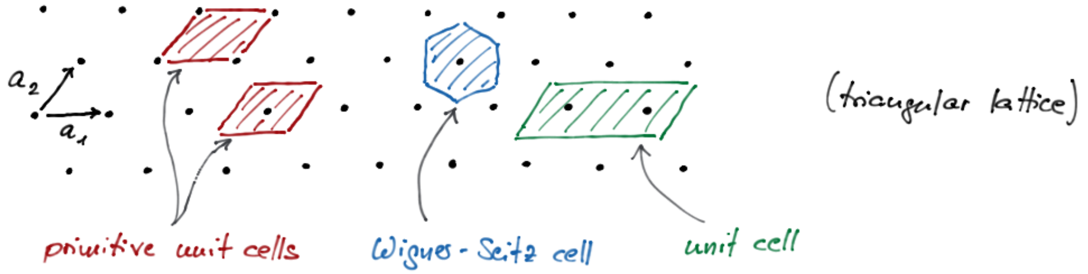
$$\vec{R} = \vec{R}_n + \vec{x} \qquad \text{with } \vec{x} \in PUC \quad \text{and } \vec{R}_n = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$$

Wigner-Seitz primitive cell

A primitive unit cell around a lattice point containing the region of space that is closer to the point than to any other lattice point.

The Wigner-Seitz cell possesses the full symmetry of the Bravais lattice.

Examples for a two-dimensional Bravais lattice:



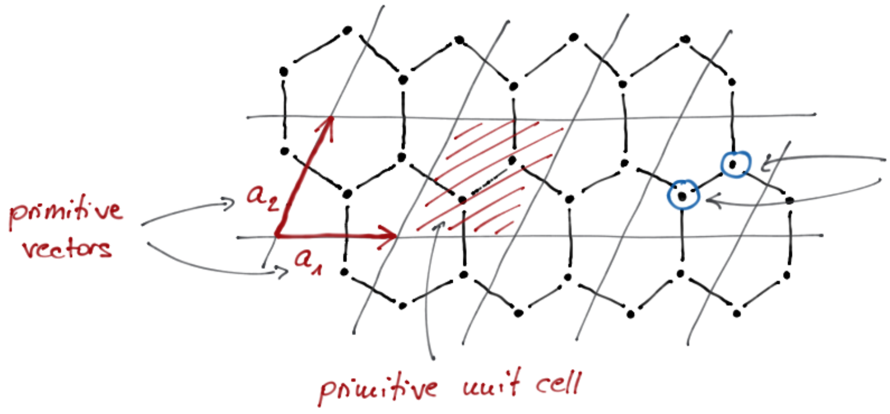
Crystal structure

The crystal structure consists of identical copies of the same physical unit, called the basis, located at all the points of a Bravais lattice.
In particular, the basis specifies the position of atoms within a unit cell.

Examples

- monatomic Bravais lattice
  A crystal structure with a basis consisting of a single atom or ion positioned for example at the points of the Bravais lattice
  Examples: fcc crystal structure of Al, Cr, Au, Pb, Ni, Cu, Ag, …
  bcc crystal structure of Li, Na, K, Fe, Mo, Cs, …

- two-dimensional honeycomb lattice (realized e.g. in graphene)



basis contains two points at $\{\frac{1}{3}(\vec a_1 + \vec a_2), \frac{2}{3}(\vec a_1 + \vec a_2)\}$

→ honeycomb lattice itself is not a Bravais lattice

- diamond lattice
  fcc lattice with two point basis $\{\vec 0, \frac{a}{4}(\hat x + \hat y + \hat z)\}$

- hexagonal close-pack structure
  Simple hexagonal Bravais lattice ≙ stacked two-dimensional triangular lattices
  primitive vectors $\vec a_1 = a\hat x$, $\vec a_2 = \frac{a}{2}\hat x + \frac{\sqrt{3}a}{2}\hat y$, $\vec a_3 = c\hat z$
  with two-point basis $\{\vec 0, \frac{1}{3}\vec a_1 + \frac{1}{3}\vec a_2 + \frac{1}{2}\vec a_3\}$

This structure of close-packed spheres is of similar importance as the monatomic bcc and fcc lattices.

- structures necessarily described by a basis because there are two/multiple types of ions/atoms present:
  - sodium chloride ($NaCl$)
    fcc lattice, basis: Na at $\vec{0}$ and Cl at $\frac{a}{2}(\hat{x}+\hat{y}+\hat{z})$
  - cesium chloride ($CsCl$)
    bcc lattice, basis: Cs at $\vec{0}$ and Cl at $\frac{a}{2}(\hat{x}+\hat{y}+\hat{z})$
- zincblende structure (sphalerite, zinc sulfide ZnS)
  diamond lattice structure, but the two positions specified by the basis are occupied by different ions/atoms

Classification of crystal structures

(subject of crystallography, here only very superficial)

Crystal structures are classified according to their symmetries.

Point group

The point group is composed of all symmetry operations that leave a particular ion/atom of the crystal fixed like reflections, inversion, rotations, combined rotation-reflection, rotation-inversion.

There are in total 32 crystallographic point groups.

Symmetries of the point group are important to determine e.g. the number of independent components of tensor quantities that characterize properties of the crystal/solid such as the conductivity σ_{ij}, polarizability α_{ij}, susceptibility χ_{ij} or piezoelectric tensor d_{ijk}.

Space group

The space group is composed of the symmetry operations of the point group and in addition

- translations via Bravais lattice vectors
- combined translation-rotation (screw-axis) and translation-reflection (glide planes) symmetry operations

and combinations thereof.

There are in total $\underline{\underline{230}}$ space groups.

1.3 Reciprocal lattice

Consider a function, e.g. a potential, with the periodicity of a Bravais lattice

$$V(\vec{r}+\vec{R}_n) = V(\vec{r}) \qquad \text{with } \vec{R}_n = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$$

Fourier transform: $V(\vec{r}) = \sum_m V_{\vec{G}_m} \, e^{i\vec{G}_m\cdot\vec{r}}$

where the momenta $\vec{G}_m$ have the property $\boxed{e^{i\vec{G}_m\cdot\vec{R}_n} = 1}$

or alternatively $\vec{G}_m\cdot\vec{R}_n = 2\pi N$ with $N\in\mathbb{Z}$.

The momenta are then given by

$$\boxed{\begin{array}{ll} \vec{G}_m = m_1\vec{b}_1 + m_2\vec{b}_2 + m_3\vec{b}_3 & m_i\in\mathbb{Z}, \ i=1,2,3 \\ \text{with} \quad \vec{a}_i\cdot\vec{b}_j = 2\pi\,\delta_{ij} & \end{array}}$$

Explicitly:

$$\vec{b}_1 = 2\pi\,\frac{\vec{a}_2\times\vec{a}_3}{\vec{a}_1(\vec{a}_2\times\vec{a}_3)}$$

← volume of the primitive unit cell $V_{PUC} = \vec{a}_1(\vec{a}_2\times\vec{a}_3)$

$$\vec{b}_2 = 2\pi\,\frac{\vec{a}_3\times\vec{a}_1}{\vec{a}_1(\vec{a}_2\times\vec{a}_3)}$$

$$\vec{b}_3 = 2\pi\,\frac{\vec{a}_1\times\vec{a}_2}{\vec{a}_1(\vec{a}_2\times\vec{a}_3)}$$

The vectors $\vec{b}_i$ are the primitive vectors of the <u>reciprocal lattice</u>.
It is a Bravais lattice in Fourier space.

Examples

Bravais lattice	sc	fcc	bcc	simple hexagonal
reciprocal lattice	sc	bcc	fcc	simple hexagonal

First Brillouin zone

Wigner-Seitz primitive cell of the reciprocal lattice.

Arbitrary vector in momentum space: $\vec{k} = \vec{G}_n + \vec{p}$ with $\vec{p} \in 1.\ BZ$

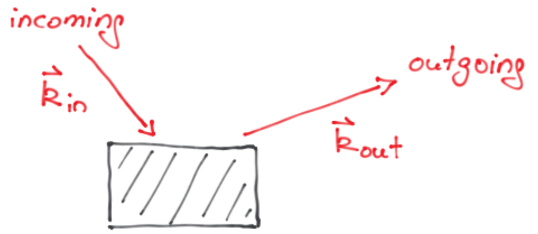
volume: $V_{1BZ} = \vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3) = \dfrac{(2\pi)^3}{V_{PUC}}$

Conventions / Notations

- directions in the Bravais lattice:
  $[n_1\ n_2\ n_3] \hat{=}$ direction specified by the vector $n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$
- planes in the Bravais lattice: Miller indices
  $(m_1\ m_2\ m_3)$ plane that is normal to the vector $m_1\vec{b}_1 + m_2\vec{b}_2 + m_3\vec{b}_3$

1.4 Scattering from a crystal

Consider a typical setup for a scattering experiment



Typical interatomic distances in a solid: $a \sim 1\,\text{Å} = 10^{-10}\,m$

Typical energies needed for scattering: $\hbar\omega = \dfrac{hc}{\lambda} \sim \dfrac{hc}{1\,\text{Å}} \approx 12\ \text{keV}$

→ x-ray energies

Consider matrix element of the scattering potential $V(\vec r)$

$$\langle \vec k_{out} | V(\vec r) | \vec k_{in} \rangle = \frac{1}{vol.} \int d^3\vec r \; e^{-i\vec k_{out}\cdot\vec r} \, V(\vec r) \, e^{i\vec k_{in}\cdot\vec r}$$

$$= \frac{1}{vol.} \int d^3\vec r \sum_{\vec G_m} V_{\vec G_m} \, e^{i(\vec k_{in} + \vec G_m - \vec k_{out})\cdot\vec r}$$

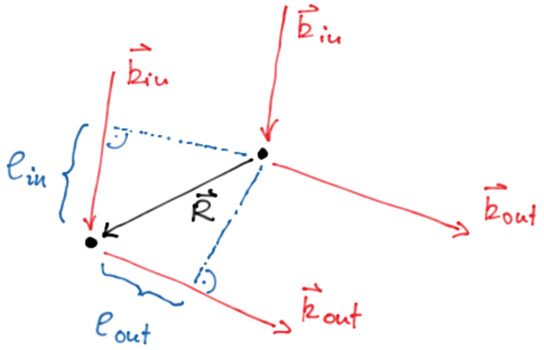
$$= \sum_{\vec G_m} V_{\vec G_m} \cdot \delta_{\vec k_{in} + \vec G_m, \, \vec k_{out}}$$

So, we obtain the selection rule: $\boxed{\vec k_{out} = \vec k_{in} + \vec G_m}$

with a reciprocal lattice vector $\vec G_m$.

Geometric interpretation:

Consider two ions/atoms in the crystal separated by a Bravais lattice vector $\vec R_n$ that both scatter an incoming wave



von-Laue condition for constructive interference:

The two scattering events interfere constructively if the path difference is an integer multiple of the wavelength λ

$$\vec\ell_{in} + \vec\ell_{out} = \lambda \cdot N \qquad \text{with } N \in \mathbb{Z}$$

with $\vec\ell_{in} = \vec R \cdot \hat k_{in}$ and $\vec\ell_{out} = -\vec R \cdot \hat k_{out}$

and assuming elastic scattering, i.e. $\vec k_{in} = \frac{2\pi}{\lambda} \hat k_{in}$, $\vec k_{out} = \frac{2\pi}{\lambda} \hat k_{out}$

$$\Rightarrow \vec R \cdot (\vec k_{in} - \vec k_{out}) = 2\pi N \qquad \text{with } N \in \mathbb{Z}$$

$\Rightarrow$ $\vec k_{in} - \vec k_{out}$ is a reciprocal lattice vector.

Scattering experiments allow for example to

- determine the Bravais lattice of a solid (Debye-Scherrer method)
- orient the crystal (Laue method)
- obtain information about the basis of a crystal via the geometrical structure factor and the atomic form factor.