Level 2 Foundations of Physics 2B/3C Phys2591/3671
CMP – 14 Lectures by Prof. Peter D Hatton,
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Lecture 1 – 19th November 2020

Recommended Text: is "The Oxford Solid State Basics" by Steven H. Simon, published by OUP ISBN: 9780199680771 (Library: 530.41 SIM)
– see lecture 1 handout and information on duo for more details of alternative and additional texts.

This course provides an introduction to "Condensed Matter Physics".
In simple terms Condensed Matter Physics is about the Physical properties of solids. In practice it goes much further than that. We know that: solids are composed of atoms, atoms composed of protons, neutrons and electrons, and that protons and neutrons are composed of sub-atomic particles (quarks); electrons are thought to be fundamental point-like particles (or waves).

Condensed Matter Physics is concerned with the study of matter where the atoms are very close together or in very close proximity, and importantly arranged in a well-defined periodic arrangement. The interaction between adjacent atoms (generally as a result of the interaction between electrons) gives rise to a huge variety of physical phenomena. In this course we will develop models to:
- describe the structure of matter
- explain observed physical properties of matter
- compare these theories with experimental data.

In reality Condensed Matter Physics is concerned with three broad classes of materials: crystalline solids, amorphous solids and liquids. We will explore these later in the course.

The most immediately obvious examples of condensed matter are solids and liquids. However today we know about much more exotic phases which are considered part of condensed matter physics. Examples of these are:
- Ferromagnetic and anti-ferromagnetic phases (interaction of spins)
- Superconductivity (resulting from quantum interaction of electrons at very low temperatures)
- Bose-Einstein condensates resulting from interactions of neighbouring atoms at ultra-low temperatures. You will know from statistical physics that bosons can occupy the same quantum state, whereas fermions do not. At ultralow temperatures where ensembles of atoms all occupy the lowest quantum state then quantum effects can manifest themselves on a macroscopic scale.
- Ferrofluids – a liquid strongly magnetised in the presence of a magnetic field
- Ferroelectrics – systems which have a spontaneous electric field which can be modified or reversed by an external electric field.

Condensed Matter Physics describes matter in its various forms by using some key fundamental physical laws:
- Quantum mechanics (theory of small particles)
- Statistical physics (how to count small particles)
- Thermodynamics (how to work out the energy of a system of particles)

- Electromagnetism (theory of interaction between charged particles)

Overall aim of the course:

In any solid (or condensed matter system) we have in excess of 10^{23} atoms (this is Avogadro's number). Any problem involving such a system will involve what we call a many-body problem. This has no exact solution – so instead we will aim to develop a range of approximations to describe the properties of these systems based are based on straightforward physical principles. That is the overall aim of this course.

Richard Feynman the well-known Physicist won the Nobel Prize in 1965 for Quantum Electrodynamics (describes how light and matter interact bringing together quantum mechanics and special relativity). He is also credited with creating the field of nanotechnology in 1959 giving a lecture called "*There's plenty of room at the bottom*" where he discussed the possibility of manipulating individual atoms as an alternative to synthetic chemistry. Feynman was also an outstanding communicator of science.

> "*Upto now we have been content to dig in the ground to find minerals, ... ultimately in the great future we can arrange the atoms the way we want.*"
>
> - Richard P. Feynman, 1959
> The man who dared to think small

Feynman quotation from the text book "Six easy pieces"

> "If, in some cataclysm, all of scientific knowledge were to be destroyed, and only one sentence passed on to the next generations of creatures, what statement would contain the most information in the fewest words? I believe it is the *atomic hypothesis* (or the atomic *fact*, or whatever you wish to call it) *that all things are made of atoms – little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling on being squeezed into one another*. In that one sentence, you will see, there is an *enormous* amount of information about the world, if just a little imagination and thinking are applied."

Prerequisites

I will assume that you are familiar with chapters in the recommended Level 1 text "University Physics" by Young and Freedman which provide relevant background material (13th edition)

- Chapter 18 – Thermal properties of matter
  - Equations of state
  - Molecular properties of matter
  - Kinetic-molecular mode of an ideal gas
  - Heat capacities
  - Molecular speeds

- o Phases of matter

- Chapter 27 – Magnetic field and magnetic forces
  - o Motion of charged particles

- Chapter 42 – Molecules and condensed matter
  - o Types of bond
  - o Molecules and molecular spectra
  - o Solids and their structure
  - o Energy bands
  - o Free electron model of metals
  - o Semiconductor crystals and devices
  - o Superconductivity (not covered in this module)

See also the introductory summary PowerPoint on duo (Background material) which briefly reviews these pre-requisites.

Introduction

We begin with a question – What is Matter?
Matter is the substance of which the physical universe is composed.

Matter can be characterised by a range of physical properties – mass, density, strength, electrical conductivity, thermal conductivity, interaction with electromagnetic fields, optical properties …

Where does matter come from?
Matter comes from processes occurring in the centre of stars. Clouds of hydrogen coalesce to form more dense regions eventually leading to the formation of a star. Nuclear fusion leads to the formation of heavier elements going through the periodic table to iron (atomic mass 56). Supernovae explosions form heavier elements which are ejected into space to begin the process all over again.

All matter is described in a systematic manner by the periodic table of the elements. This is based on the number of protons in the nucleus of an atom.
Matter can exist in different *forms* or *phases*. For example water H_2O can exist as a solid, liquid or gas. These different *phases* have different physical properties although the chemical composition is unchanged.
The environment in which matter exists is also important and has an effect on its physical characteristics. For example heating ice produces water and then produces steam. However other parameters also affect the physical state of the system – e.g. pressure.
The *phase diagram* illustrates how this can occur:
Young and Freedman Chapter 18, Figure 18.24
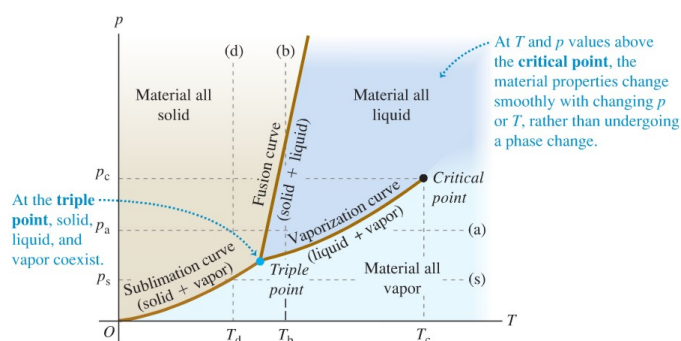
This introduces some new important physical parameter for matter:

Critical Point – above this there is no distinction between a gas and a liquid.
Triple Point – a place where each phase co-exists in equilibrium.

For water the triple point is T = 0.01 ^{O}C and P = 4.58 mm Hg (0.0006 Atmospheres).

At a constant pressure a substance can change from solid - liquid - vapour as the temperature is increased.
At a constant temperature a substance can go from vapour - liquid - solid as the pressure is increased.
Each phase is separated by a well-defined phase boundary e.g. solid/liquid or liquid/vapour.

During this lecture course we will be looking at simple physical models to explain properties of matter.
For example:
The parameters which determine the phase of a substance are:
1. the forces between atoms
   and
2. temperature (which is equivalent to the kinetic energy of the atoms [Thermodynamics])

We can postulate a simple physical model to explain the behaviour of different phases of water in one of four possible phases.

Simple Phases: Gases - dominated by temperature
- ignore interatomic binding forces (atoms are free to move throughout the gas)
- use models to derive thermal properties

Solids - Interatomic binding dominates (atoms are fixed relative to each other)
- derive mechanical and thermal properties

Complex Phases   Liquids   - temperature and interatomic binding forces are comparable
- It is like a gas or a solid?
- derive thermal and mechanical properties

Plasmas   - a phase which exists a very high temperatures
- completely dominated by temperature where thermal energy has ionised the gas into positive and negative charges (e.g. the sun)

Increasing	*Solid* binding energy >> kinetic energy of atoms
Kinetic	*Liquid* binding energy ~ kinetic energy of atoms
Energy	*Gas* binding energy << kinetic energy of atoms
↓	*Plasma* Ionization energy << kinetic energy of atoms

Before developing theories of the properties of matter further we must introduce the notation used to describe matter (atoms and molecules).

Review of Previous Material

(How we quantify matter)

The Periodic Table

Use the standard notation for the periodic table:

$$_{Z}^{A}R$$

R is the name of the element (determined from the Z or proton number)
Z is the atomic number
A is the total number of protons and neutrons and gives the mass of the nucleus.
Some examples:

$$_{2}^{4}He \qquad\qquad _{6}^{12}C \qquad\qquad _{6}^{14}C$$

Atoms with the same Z but different A are called isotopes.

Mass

Many elements have a range of naturally occurring isotopes e.g. Cl has two common isotopes:

$_{17}^{35}Cl$ 75%	$_{17}^{37}Cl$ 25%
5.807×10^{-26} kg	6.138×10^{-26} kg

Masses can be measured by a mass spectrometer (see Young and Freedman Ch. 27.5 p 897 13th edition).

An "average" atom of chlorine has a mass of:

$$\left(5.807\times10^{-26}\times0.75\right)+\left(6.138\times10^{-26}\times0.25\right)=5.890\times10^{-26} \text{ kg}$$

Atomic masses are expressed in terms of the unified mass unit (symbol u). Young and Freedman p597 (section 18.2)

This is *defined* as 1/12 × mass of a neutral $_{6}^{12}C$ atom. Thus, the mass of one $_{6}^{12}C$ atom is 12 u.

$$1u = 1.6606 \times 10^{-27} \text{ kg}$$

The *relative atomic mass* is also used to describe the mass of atoms. We define this as:

Relative atomic mass (M_A) = Mass of average atom / Unified mass unit

e.g. for chlorine:

$$M_A = \frac{5.890\times10^{-26}}{1.6606\times10^{-27}} = 35.4$$

To obtain the mass of a particular atom multiply M_A by the unified mass unit.
In many cases groups of atoms form the basis of matter rather than individual atoms.
These groups of atoms are referred to as molecules.

e.g. H_2 N_2 H_2O H_2SO_4 etc...

We can also define a relative molecular mass:

M_R = *Mass of molecule / unified mass unit*

e.g. for HCl:
$$M_R = (1u + 35.4u) / 1 u = 36.4$$
The mass of atoms and molecules occurs in the range of $10^{-25} - 10^{-27}$ kg. In 1 kg of material there are ~ $10^{25} - 10^{27}$ atoms/molecules.

The number of atoms/molecules (or amount) of a substance is expressed in moles. A *mole* is defined as an amount of material which has the same number of $^{12}_{6}C$

atoms as in 12 g of $^{12}_{6}C$ (i.e. 0.012 kg)

A mole of a substance contains:
$$\frac{12 \times 10^{-3}}{1.993 \times 10^{-26}} = 6.022 \times 10^{23} \text{ atoms or molecules.}$$
(Young and Freedman p618)

This number is called Avogadro's number symbol N_A.

To obtain the number of moles of a substance n = Mass of substance / relative mass
e.g. 1 kg of HCl contains:
$$\frac{1}{36.4 \times 1.66 \times 10^{-27} \times 6.022 \times 10^{23}} = 27.5 \text{ moles}$$

Size
How big are atoms and molecules?

We can estimate the atomic size from the density of the substance assuming the atoms are packed in three dimensions. Although atoms are approximately spherical, we assume each occupies a cube of volume d^3.

The density of a substance in given by:
$$\rho = \frac{M_{atom}}{V_{atom}} \approx \frac{M_{av}}{d^3}$$
where M_{av} is obtained from the periodic table.

e.g. copper has a density of ρ = 8930 kg m^{-3}, M_{av} = 63.55 u so d^3=1.181×10^{-29} and d = 2.28×10^{-10} m = 0.23 nm.

Generally, we find that the diameters of atoms and molecules are in the range 0.15 - 0.5 nm

[Note the size of the nucleus is ~10^{-15} m and is given approximately by radius R ~ $R_0 M_A^{1/3}$ where R$_0$ = 1.2×10^{-15} m = 1.2 fm e.g. gold Au R ~ 7 fm]

Equipartition Theorem
This states that:
When a substance is in equilibrium there is an average energy of ½k_BT per molecule or ½RT per mole associated with <u>each degree of freedom</u>.

A degree of freedom is a motion of translation, rotation, vibration and potential energy of vibration.

Heat Capacity of Solids

The heat capacity of a solid is determined by the equipartition theorem. In a crystalline solid the atoms vibrate about their mean position so there will be a potential and kinetic energy associated with the vibration in 3 dimensions. The total energy per atom is obtained from the three translational and three vibrational degrees of freedom:

$$\frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 + \frac{1}{2}\alpha x^2 + \frac{1}{2}\alpha y^2 + \frac{1}{2}\alpha z^2$$

There are 6 degrees of freedom which give a total internal energy *per mole* of $U_{Mole} = 3\,R\,T$, and a molar heat capacity of

$$C_{Vm} = \frac{dU_m}{dT} = 3R$$

This is known as the *Dulong and Petit Law*.

Compressing Solids

The behaviour of a solid under compression is described by a parameter called the **Isothermal Bulk Modulus:**

$$B = \frac{\Delta P}{\Delta V / V}$$

the ratio of the change in pressure to the fractional decrease in volume. This is usually written as:

$$-V\frac{dP}{dV}$$

In compressing a solid the work done is $-PdV$. From the first law of thermodynamics we get $dU = -PdV + dQ$ where dU is the change in internal energy. In an isothermal process there is no change in thermal energy so finally:

$$B = -V\frac{dP}{dV} = V\frac{d^2U}{dV^2}$$

The bulk modulus verifies the microscopic properties of the solid. The internal energy is:

$$U = \frac{1}{2}Nn_nV(r)$$

where N is the number of atoms and n_n the number of nearest neighbours.

Stretching Solids

The behaviour of a solid which is stretched is described by **Young's Modulus**.

$$Y = \frac{F/A}{\Delta L/L} = \frac{F/A}{\left(\dfrac{F}{A}\right)r_0\left(\dfrac{-dr}{dF(r)}\right)\bigg|_{r=r_0}} = \frac{-1}{r_0}\left(\frac{dF(r)}{dr}\right)$$

The atomic force *F(r)* is given by

$$F(r) = \frac{-dU(r)}{dr}$$

so

$$Y = \frac{1}{r_0}\left(\frac{d^2V}{dr^2}\right)_{r=r_0}$$

This relates the macroscopic Young's Modulus to the microscopic interatomic potential $U(r)$. This interatomic potential function arises from the behaviour of the electrons in the bonds.

Key Concepts – for group discussion in lecture

1. What is the single most expensive endeavour ever undertaken by humankind?
2. Johannes Kepler famously said "*ubi materia, ibi geometria*"
   a. What does this mean? What are the implications for describing condensed matter?
3. Crystals can be modelled as classical or quantum systems when considering atoms and their interactions.
   a. What are the implications of using each of these approaches to describe crystals?
   b. What are the differences in approaches when describing the phase diagram of water?
4. Electrons can be described using a classical or quantum description.
   a. What is the difference between a classical and a quantum description of electrons?
   b. What are the implications of these different approaches when thinking about the interaction between electrons and crystals?

Summary of key points made:

1. Geometry enable periodic functions to be used to describe the properties of matter.
2. Physical properties of matter result from the periodic arrangement of atoms in a solid, which will have certain symmetries.
3. Modelling crystals as classical system does not limit or restrict the motion. The classical equipartition theorem is used to model the distribution of energy within a crystal assigning equal energy to each mode. This can work well at high temperature.
4. Modelling crystals as quantum systems imposes restrictions on the motion of the atoms, motion is quantised. The quantisation becomes more significant at lower energies (lower temperatures).
5. Water has an unusual phase diagram where the slope of the solid liquid boundary is opposite to other materials. This means water can be denser in liquid form than solid and is a consequence of the crystal structure of ice.
6. Modelling an electron as a classical particle moving in a solid places little restriction on the motion of the electron, the electron energy is determined by the equipartition theorem.
7. Modelling the electron as a quantum particle restricts the energy to quantised states. Considering the electron as a wave means that certain waves will fit easily into a crystal whereas other waves will not. This occurs when the electron wavelength is related to the periodicity of the atoms in the crystal. (We will revisit this again at the end of the course when thinking about energy band gaps).

Course Overview

1. Review of Level 1 CMP course introduction, key concepts
2. Describing crystals: lattices, Miller indices
3. Reciprocal lattice and wave diffraction
4. X-rays and the structure factor
5. Bonding: Van der Waals, Leonard-Jones potential, ionic bonding, hydrogen bonding, metallic bonding
6. Static lattice failure, vibrating atoms, waves and phonon dispersion
7. Phonons with two atom basis, thermal properties of crystals
8. Electrons, classical Drude Model, Wiedemann-Franz law
9. Quantum Sommerfield model of electrons, density of states, periodic boundary conditions
10. Fermi Dirac statistics, electron occupation
11. Magnetic properties of free electron model
12. The crystal lattice and the nearly free electron model, Bloch states
13. Energy Bands: metals, insulators
14. Course Review and summary

Models covered in lecture course

Structural	**Lecture**
1. Structure of crystals – description	**[2]**
2. Probing structure – x-ray waves (structure, amplitude) (Reciprocal lattice coordinate describing crystals as periodic)	**[3-4]**
Mechanical and thermal	
3. Bonding	**[5]**
4. Vibrating atoms – phonons a "quantum" model	**[6-7]**
Electrical	
Classical Electron	
5. Electrons classical particles	**[8]**
Quantum Free Electron	
6. Electron quantum particles	**[9-10]**
7. Magnetic properties	**[11]**
Quantum Nearly Free Electron	
8. Nearly free electron energy bands, Bloch states	**[12**]
9. Metals, insulators, semiconductors	**[13]**
10. Review of course	**[14]**