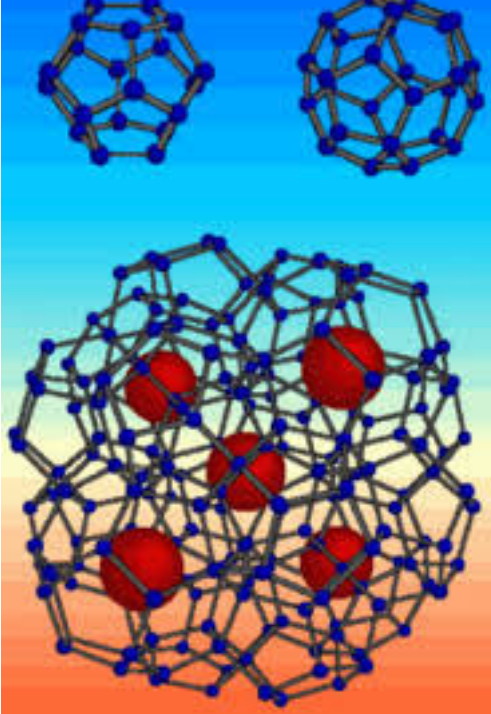




Physics of Condensed Systems

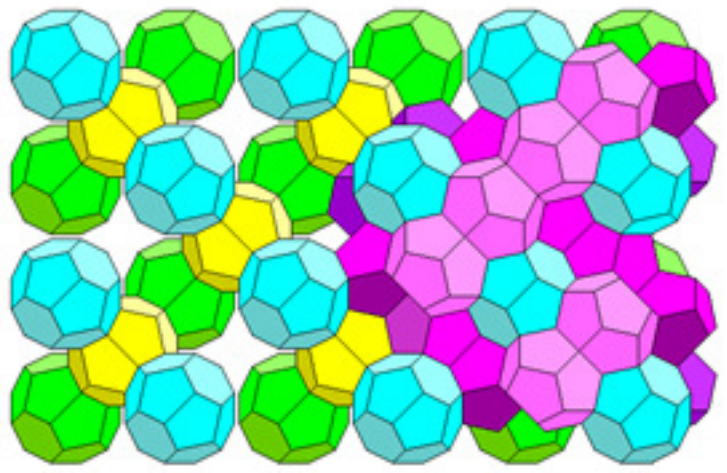
Lecture Notes

Alfonso San Miguel
University Claude Bernard Lyon 1

Copyright © 2016 Alfonso San Miguel

PUBLISHED BY ALFONSO SAN MIGUEL

First printing, July 2016



0. Introduction

What is called "Condensed Matter Physics" is the largest branch of Physics in many aspects. This is mainly due to the variety of concepts which it embraces ranging from superconductivity to phase transitions, from material mechanics to structural macrobiophysics or from quantum condensation to the fundamental effects in electronics, just to cite a few subfields. Many of these subfields are either interdisciplinary or paving the basis of other disciplines. The broad scope of the physics of condensed systems explains that this branch of Physics gathers the largest community of physicist exerting their skills both in industry as well as in academic fundamental or applied research.

A very interesting aspect of Condensed Matter Physics is the depth of many of the concepts that are developed which are common to very different fields. We may cite the famous Higgs boson, which physics basis does not differ from a phenomenon occurring in superconductors; in fact The Higgs mechanism, which gives mass to elementary particles is frequently called the "Anderson-Higgs" mechanism, after the condensed matter physicist Phil Anderson¹ and who described much of the same physics before Peter Higgs². Also, the ideas of the renormalization group (Nobel prize to Kenneth Wilson in 1982) were developed simultaneously in both high-energy and condensed matter physics. Or the ideas of topological quantum field theories, while invented by string theorists as theories of quantum gravity, were discovered in the laboratory by condensed matter physicists!

The nature of researches in physics of condensed systems translates also in applications and we can cite between them the transistor and then all the electronics in today's life, giant-magneto-resistance devices which allowed the fast development of memories, or the development of superconductors used in last generation particle accelerators. In total, either considering their contribution to fundamental or applied physics of condensed systems, the Nobel committee in Sweden has rewarded not less than 50 physicists!

A beautiful aspect of the physics of condensed systems is that it provides answers to many

¹Phil Anderson seems to have been the first physicist to use the term "condensed matter"

²In the standard model, when temperatures are high enough that electroweak symmetry is unbroken, all elementary particles are massless. At a critical temperature, the symmetry is spontaneously broken by condensation, and the W and Z bosons acquire masses.

different day-to-day questions which can appear when observing our closest world: why are metals shiny and why do they feel cold? why is glass transparent? why is water a fluid, and why does fluid feel wet? why is rubber soft and stretchy? In many cases the answers are short and elegant meaning that in fact they include a condensate of brilliant concepts and ideas!

Condensed matter physics plays also a key role in basically any other physics domain as high energy physics, optics, astrophysics, nuclear physics,... . In fact, in addition to the already mentioned convergences between disciplines in the development of theories and models, most of the instrumentation needed in those disciplines is based in condensed matter physics advances (materials, optics, detectors, ...). We may cite as examples the development of lasers and mirrors for the detection of gravitational waves or the development of superconductivity for accelerator physics.

The beauty of the concepts developed in physics of condensed systems - needing the contributions of both quantum physics and statistical physics adds to the magic of the constant interplay between experiments and models, and finally to the interactions between other very complex condensed matter systems: scientist from different domains who cooperate to make science advance!

0.1 Some definitions

Quoting wikipedia, "Condensed matter physics is a branch of physics that deals with the physical properties of condensed phases of matter. Condensed matter physicists seek to understand the behavior of these phases by using physical laws. In particular, they include the laws of quantum mechanics, electromagnetism and statistical mechanics."

The definition of what we understand by *condensed phases of matter* in Condensed Matter Physics (CMP) is not always clear. In general it is admitted that CMP deals with solids, liquids and any other "phases" developed in these systems as superconducting phases, Bose-Einstein condensates, magnetic ordered phases, etc. Gases or individual molecules are in principle excluded from CMP, but molecular solids or liquids make part of CMP. Sometimes plasmas are not considered as CMP systems due to the unbounded nature of positive and negative particles constituting a plasma which then do not correspond with "condensation" concepts. What about fluids beyond the supercritical point? The limits between disciplines are not always evident. For instance, between CMP and molecular physics: which of these disciplines should study large atomic clusters as some nanocrystals? They are in fact systems mid-way between large molecules and solids and both disciplines are interested in them.

0.2 A bit of history

The contribution of ancient Greek philosophers represented an immense turnout in the understanding of our World[J.L.(2015)]. Since that, Condensed Matter Physics (CMP) had to wait essentially the 19th century to make its real start - without, of course, mis-considering the impact of the essential contributions in Physics brought by Copernicus, Kepler, Newton, Galileo, Descartes, Leibniz and many others already from the 17th century.

Many of the basic milestones of physics, as the discovery of the electron or of x-rays, which took place at the edge between the 19th and 20th centuries, were essential for the development of CMP. Nevertheless many important findings and developments were already done during

the 19th century in what we could call the "Macroscopic era of CMP". Some of the important discoveries of that period include the classification of crystal symmetries by Auguste Bravais (published in 1847, few after leaving his professor position at the University of Lyon); the determination of a close relationship between thermal and electrical conductivity in metals (published jointly by G. Wiedemann and R. Franz in 1853) known today as the Wiedemann-Franz law; or the discovery in 1879 of the so-called "classical Hall effect" by Edwin Herbert Hall which can be described as the emergence of a potential difference perpendicularly to the applied magnetic field to a conducting material. The development of statistical physics in the second half of the 19th century with the key contributions of Clausius, Maxwell and Boltzmann followed by the rise of quantum mechanics at the beginning of the 20th century started to pave the way for the development of a mature CMP. In fact those developments set the basis connecting the microscopic and the macroscopic view of condensed systems. Such connection was greatly facilitated by the discovery of x-ray diffraction (Bragg and Laue) which not only allowed to understand Bravais macroscopic views, but also opened the infinitely broad field of crystallography and the relationship between structure at the atomic scale and the physical properties of materials.

The adoption of the concept of CMP had nevertheless to wait the 1940s. Before that time, many different fields as the already mentioned crystallography, but also metallurgy, elasticity, magnetism, electric transport, etc., all of them dealing with diverse aspects of solid matter, were considered as independent and largely autonomous areas of science. In the 1940s these different disciplines consolidated into the newly named discipline of "solid state physics" which, two decades later, was enlarged to include the study of the physical properties of liquids and given the name "condensed matter physics"[Kohn(1999)]

Time	Events/Achievements/People	Nobel Prizes
before 3000 BC 3000-500 BC 500 BC Early Theories ca. 1700 19th century 1851 1853 1879	Stone Age Bronze Age Iron Age Demokritos: Idea that an "atom" exists Aristotle: all metals are a mixture of sulfur and mercury Revival of the idea of an atom by Newton and others Physics is considered to be "solved" by Classical Mechanics, Electromagnetism and Thermodynamics. Metallurgy becomes important and is described by empirical laws. Bravais: Classification of crystal symmetries Wiedemann-Franz law for thermal and electrical conductivity Hall effect	
1897 1900 1905 1907-1913 1911 1912 1913 1920's 1920's 1925-1928 1926-1928 1928-1933 1947	Thompson discovers the electron Drude (and Lorentz): classical electron gas in metals. Fundamentals of Photoemission (Einstein) Specific Heat of solids (Einstein,,Debye,Bor) Onnes (and Holst) discover superconductivity in mercury Max von Laue discovers diffraction of X-rays by crystals W.H.& W.L. Bragg use X-rays to analyze crystals Raman scattering Electron diffraction (Davisson, Thomson) Quantum Mechanics (Schrödinger,Heisenberg,Pauli,Dirac) Sommerfeld,Pauli: the electron gas with Dirac statistics The quantum theory of an electron in a solid: Band structure (Bloch, Peierls, Brillouin, van Vleck) Magnetism(Pauli,Landau,Heisenberg,Bethe) Transistor effect (Shockley,Bardeen,Brattain)	Einstein 1921 Onnes 1913 von Laue 1914 H&L Bragg 1915 Raman 1930 Davisson & Thomson 1937 Anderson, Mott, van Vleck 1977 Anven, Néel 1970 S.,B.,B. 1956
1950's 1950 Late 1950's 1957 1958 1960's 1970's from 1970's 1972 1980 1982 1985 1986 1988 1991 1990's 1995 2003	Development of Quantum Field Theory (Feynman, etc) Ginzburg-Landau: phenomenological theory of superconductors Theory of interacting electrons in solids (Landau,Migdal) Neutron Scattering and Diffraction(Brockhouse,Shull) Bardeen, Cooper, Schrieffer: theory of superconductivity Josephson effect on electron tunneling in superconductors The understanding of the resistance minimum in metals: the Kondo Effect (Kondo, Anderson 1969) Density Functional Theory (Kohn, Pople) Theory of Liquid Crystals The renormalization group Topological phases of matter(Thouless,Haldane,Kosterlitz) Superfluid He ³ (Lee,Osherooff,Richardson) The integer quantum Hall effect The fractional quantum Hall effect(Tsui,Störmer,Laughlin) Fullerenes C ₆₀ (Curl,Kroto,Smalley) Discovery of high temperature superconductivity Giant magnetoresistance Carbon nanotubes (Iijima) Blue emitting diodes (Akasaki, Amano, Nakamura) Experimental Bose-Einstein Condensation(Cornell,Ketterle, Wieman) Single Graphene sheets discovery	Ginzburg,Leggett, Abrikosov,2003 Landau 1962 B. & S. 1994 B.C.S. 1972 Esaki,Giaever, Josephson 1973 1988(Chemistry) de Gennes 1991 Wilson 1982 T.H.K. 2016 L.,O.,R. 1996 von Klitzing 1985 T.S.L. 1998 1996(Chemistry) Müller,Bednorz 1987 Fert,Grunberg 2007 A.A.N. 2014 K.C.W. 2001 Geim,Novoselov 2010

Table 1: Some of the important milestones in the historical development of Condensed Matter Physics. Adapted from [Hoddeson, Baym, and Eckert(1987)]

0.3 Bibliography

There is a huge bibliography on the Physics of Condensed systems. I have used many of the books I discuss below to construct these lecture notes as well as some open resources available in the WWW. I am indebted to all these authors: without their work, which synthesize accomplishments done by generations of physicist over decades, it would have been impossible to write these notes.

In the following I provide a personal list of some of the main books I have consulted and which are available in many libraries.

For the first chapter, devoted to the connexion between statistical physics and CMP I have used mainly two books:

- "Statistical Physics" by F. Mandl.[Mandl(1988)] This is a very easy to read book covering the main aspects needed for an introduction to the subject.
- "Introduction to Modern Statistical Mechanics" by D. Chandler[Chandler(1987)]. More extensive than Mandl, it also covers other aspects as non-equilibrium physics or Montecarlo methods.

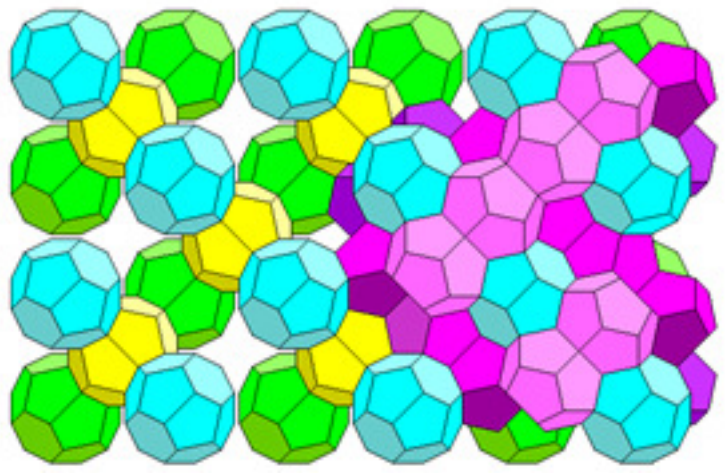
There are of course many other books on Statistical Physics, but these two are particularly synthetic and well written.

The rest of the chapters covered in these lectures find support in one or the other of the books in the following list. As you will see there is a lack of imagination when choosing titles, which makes that most of these books are recalled by their author's names.

- "Solid State Physics" by Ashcroft and Mermin[Ashcroft and Mermin(1976)]. It is one of the classic books on the subject. Very complete and of a very good level. It remains one of the biggest references. It is translated to French.
- "Introduction to Solid State Physics" by Charles Kittel[Kittel(1996)]. This is another "classic". It covers most of the aspects of CMP but in less depth than Ashcroft. Kittel is often considered as more engineering oriented.
- "Solid State Physics" by J.R. Hook and H.E. Hall[Hook and Hall(1991)]. A very good book to get a qualitative introduction on the matter and try to get first the concepts.
- "Physique de la Matière Condensée" by Hung T. Diep [Diep(2003)]. This book covers in a synthetic way all aspects of the course. It allows you also to get an introduction to more advanced subjects including the use of second quantization in condensed matter physics.
- "Solid State Theory" by W.A. Harrison[Harrison(1979)]. As said in the title, this book has a more theoretical approach, but it is a very good introduction book for those thinking about following in the theory field.
- "Solid State Physics" by Giuseppe Grosso and Giuseppe Pastori Parravicini[Grosso and Parravicini(2000)]. This is another advanced book, modern and which has become a classic. A good compromise if you want to extend your knowledge beyond this lectures.
- "Solid State Physics" by David W. Snoke[Snoke(2008)]. A much more modern book than Harrison's for instance. It includes an introduction to group theory and covers many advanced topics using when needed second quantization, Fermi diagrams, etc. Really a more advanced book.
- "States of Matter" by David L. Goodstein[Goodstein(1985)]. This is an interesting book in which condensed matter is brought from the field of thermodynamics. More convenient for an advanced reading or a summer reading after this course !.

Most of the aspects covered in the magnetism chapter can be found in "Magnetism in Condensed Matter" from Stephen Blundell [Blundell(2001)] which is a much more extended book but at a level in good correspondance to the one followed in these lectures. Another interesting book is "Magnétisme" (in French) with various authors and edited by E. du Trémolet de Lacheisserie

[du Trémolet de Lacheisserie (sous la direction de)(2000)].



1. Statistical physics tools

1.1 Introduction

Fortunately, Nature is a many-body system. As a consequence most of the interesting systems drawing the attention of physicist are made of an abominably large number of particles (including physicist themselves!). Such complexity could be somehow discouraging when compared with the already important efforts needed to understand the physics of one atomic nucleus or an isolated atom. Fortunately there are two basic solutions to cope with such defying problem: periodicity (long-range symmetry) and statistics. They are the subject of the first two chapters of this course and will be the basic scaffolding for constructing models of condensed matter systems. Of course, periodicity does not always apply and then statistical physics remains the more general foundations to tackle many-body problems.

It appears then logical to start this course by recalling the main results of statistical physics which will be useful for the study of condensed matter systems. In contrast with the ideal gas, which can be treated classically, condensed matter systems need a quantum treatment. In section 1.2 we will try to understand why it is so. In the following section, 1.3, we will introduce the main statistics (Fermi-Dirac and Bose-Einstein) applying in condensed matter systems. The two next sections will be devoted to one of the very important systems in which these concepts can be applied: free electrons in metals. We will start by the classical Drude model of electron conduction in section 1.4 and then explore the more advanced Sommerfeld model (section 1.5) which really takes advantage of quantum statistics. We will see later in the course how some of the concepts explored here can also be applied in semiconductor materials. A small exploration of Bose-Einstein condensates follows in section 1.6 before turning to the study of the photon gas in section 1.7 which explores the differences with the classical Maxwell-Boltzmann statistics. We will not directly explore in this chapter the applications of the photon gas in condensed matter systems, but we will do it later when studying phonons: the atomic vibrations of solids. To conclude this chapter we will review in the form of appendix (section 1.8) the effect of confinement (particles or quasiparticles are confined to a limited volume) on the determination of the density of states in different systems.

1.2 Quantum versus classic statistics

The first condition needed by a gas of particles to allow for its treatment as a classical gas is that particles do not interact between them. This is what we could call the "idealness" condition for a classical gas. This is a necessary condition for having a classical gas, but it is not sufficient. In fact, the gas should also fulfill what can be called a "classicalness" condition which is basically a condition on the density of particles: if at a given temperature the density of particles is high enough, quantum effects become important. Or in other words, *for a given particle density there is a critical temperature which separates the quantum and the classical behavior of the gas of particles*. The quantum/classical nature of a gas of particles is then not an absolute concept linked to the system itself but depends on its thermodynamic conditions. These ideas are explored in more detail in the following paragraphs.

The classical regime of the perfect gas of particles (described by the Boltzmann-Maxwell statistics which will be recalled later in section 1.7) is characterized by the fact that most of the single-particle states are empty, a very few contain one particle or molecule and it is hardly impossible to find more than one particle/molecule in a single state. Then in classical statistics we are not concerned with the maximum occupation number of single states as basically they are either occupied (by one particle) or unoccupied. Other possibilities can be neglected.

If the considered particles are of quantum nature - if they are sufficiently small - their *de Broglie* associated wavelength can become important (the dual, particle/wave nature of the particle is important). A consequence of this is for instance that the particles can interfere in a diffraction experiment. Today the largest molecules having shown diffraction interference in a two slits experiment are the C_{60} molecules (also called fullerenes). The de Broglie wavelength, λ_{DB} , of a mass quantum particle can be considered as a measure of its spatial extension as a probabilistic object. In quantum mechanics $\lambda_{DB} = h/p$ and represents the minimum size of a wave-packet with momentum p .

In a gas of particles, we can take the average interparticle spacing to be approximately $\ell = (V/N)^{1/3}$ with V the volume of the gas and N the number of particles.

If the average distance between particles, ℓ , is bigger than the *average* de Broglie wavelength of the gas of particles, which is called the "Thermal de Broglie wavelength", λ_{th} , we do not expect quantum interference effects between the particles (seen as waves) which can modify the state occupation statistics. Then if λ_{th} is smaller than ℓ the gas of particles can be treated classically. On the contrary, if λ_{th} is comparable or bigger than ℓ , quantum effects will dominate and the gas will need to be treated either as a Fermi-Dirac gas or a Bose-Einstein gas, depending on the nature of the particles. In the following, we will assimilate the de Broglie wavelength, λ_{DB} , and the thermal de Broglie wavelength, λ_{th} , i.e., $\lambda_{DB} \simeq \lambda_{th}$ and refer to them indifferently.

With this assumption, a gas of particles will need a quantum treatment if:

$$\lambda_{DB}^3 \geq \frac{V}{N} \quad (1.1)$$

The quantum de Broglie wavelength associated to a particle of momentum p and kinetic energy ε is:

$$\lambda_{DB} = \frac{h}{p} = \frac{h}{\sqrt{2m\varepsilon}} = \frac{h}{\sqrt{3mk_B T}} \propto \frac{1}{\sqrt{T}} \quad (1.2)$$

where we have considered $\varepsilon = \frac{3}{2}k_B T$ for structureless particles (equipartition principle for particles having only 3 translation degrees of freedom)

The classical picture of atoms as billiard balls with well-defined trajectories only makes sense then if:

$$\lambda_{DB} \ll \ell = \text{typical spacing between particles} = \left(\frac{V}{N}\right)^{1/3} \quad (1.3)$$

The condition for "classicalness", $\lambda_{th} \propto \frac{1}{\sqrt{T}} \ll (\frac{V}{N})^{1/3}$ is violated either at low T or at high density (at high pressures, for instance).

Remember then that the classical gas picture breaks down if

- "idealness" fails, i.e., if interactions between particles becomes important
- "classicalness" fails, i.e., if the density of particles is high enough so as that quantum effects prevail.

1.3 The Fermi-Dirac and the Bose-Einstein statistics

When a gas of non-interacting particles can not be considered as classical, the Maxwell-Boltzmann statistics is no longer valid. One needs to develop an adapted statistics for such systems and this was one of the important contribution of Fermi, Dirac, Bose and Einstein at the early XXth century. The quantum state of the many particles system is described by the wavefunction $\psi(..., x_a, ..., x_b, ...)$ (we do not worry about how many coordinates we need for each particle : x represents here generalized space coordinates). If the particles are *indistinguishable* then $|\psi(..., x_a, ..., x_b, ...)|^2 = |\psi(..., x_b, ..., x_a, ...)|^2$, i.e, the probability of the state by exchange of two particles is preserved.

In order this to be true, the many-indistinguishable-particles wavefunction can only differ by an overall phase factor upon exchanging the particles,

$$\psi(..., x_a, ..., x_b, ...) = e^{i\phi} \psi(..., x_b, ..., x_a, ...) \quad (1.4)$$

with ϕ a real number between 0 and 2π . It turns out that all fundamental particles correspond to either $\phi = 0$ (or $\phi = 2\pi$), called bosons, or $\phi = \pi$ called fermions. This is a result from relativistic quantum field theory which demonstration is unfortunately not straightforward.

Thus, the wavefunction of a system of fermions is antisymmetric with respect to the exchange of particles:

$$\psi(..., x_a, ..., x_b, ...) = -\psi(..., x_b, ..., x_a, ...) \quad (1.5)$$

and the wavefunction for bosons is symmetric:

$$\psi(..., x_a, ..., x_b, ...) = \psi(..., x_b, ..., x_a, ...) \quad (1.6)$$

The importance of these symmetries are just fantastic: bosons are responsible of superfluidity or superconductivity, i.e., ways to carry flows or currents without dissipation. This is also the case for photons (which are also bosons) which can propagate coherently through the Universe. If our everyday world looks like it is, it is because electrons, which compose all atoms leading to materials are fermions.

Note: *Anyons*, particles whose statistics is neither fermionic nor bosonic, can be found in 2-dimensional systems. In *anyons*, the phase ϕ can take *any* value after permutation of two particles. *Plektons* are the theoretical generalization of the anyons to dimension > 2 and they are subjected to the so-called *braid statistics*. Anyons manifest in the fractional quantum Hall effect which can be described with "quasi-holes" quasiparticles which follow such statistics. It is interesting to note that it is sometimes erroneously proposed that exchanging the particle coordinates two times should be equivalent to no change at all. If we call $\eta = e^{i\phi}$, this would mean $\eta^2 = 1$ leading then to the $\eta = \pm 1$ solutions corresponding to either bosons or fermions. This will imply that anyons should not exist. The error in this argument is that the exchange between particles needs to be done physically through a given path. Then the topology of the considered space and its dimensionality play an important role on the possible statistics. **End of the note**

A major consequence of the antisymmetry of fermions is *Pauli exclusion principle*. This can be illustrated with a two particle example. Here again x_1 and x_2 are generalized position coordinates. The wavefunction of the system of particles $\phi(x_1, x_2)$ must be written as a linear combination of the individual wavefunctions $\phi_1(x)$ and $\phi_2(x)$. An antisymmetric construction of $\phi(x_1, x_2)$ is:

$$\phi(x_1, x_2) = \phi_1(x_1)\phi_2(x_2) - \phi_1(x_2)\phi_2(x_1) \quad (1.7)$$

which in fact verifies antisymmetry :

$$\phi(x_2, x_1) = \phi_1(x_2)\phi_2(x_1) - \phi_1(x_1)\phi_2(x_2) = -\phi(x_1, x_2) \quad (1.8)$$

If we try to locate the two particles in the same position, i.e., $x_1 = x_2$ then $\phi(x_1, x_1) = 0$, canceling the probability that the two particles can be found in the same position. This can be generalized beyond a merely position basis to include also spin. Consequently only one fermion can occupy a state with equal quantum numbers which is the Pauli exclusion principle. On the other side, symmetric wavefunctions, bosons, do not have such limitations in the occupation numbers.

The direct consequence is that the occupation number of a fermionic state can be only 1 or 0 (occupied or empty), whereas in a bosonic state the occupation number can be any integer number (below the total number of particles of the system).

To develop into detail the consequences of the different statistics, we shall introduce the partition function, Z , of a set of N indistinguishable particles. We recall that Z in that case is given by:

$$Z = \frac{1}{N!} Z_1^N \quad \text{with} \quad Z_1 = \sum_n \exp(-\beta E_n) \quad (1.9)$$

here Z_1 is the partition function for one particle. E_n is the energy of the n th state of the particle and $\beta = 1/k_B T$ is the Boltzmann factor. The $1/N!$ prefactor holds to avoid counting equivalent states by exchanging particles. Lets consider more into detail our system.

The state of the quantum system can be specified by the wavefunction $\Phi_v(r_1, r_2, \dots, r_n)$. Φ_v is the v th eigenstate of the Schrödinger's equation for the N -particle system. We are considering non-interacting wavefuctions of individual particles as $\phi_1(r), \phi_2(r), \dots, \phi_j(r), \dots$. In a particular state, say v , $\Phi_v(r_1, r_2, \dots, r_n)$ will be a symmetrized product containing n_1 particles with the single particle wavefunction ϕ_1 , n_2 particles with the single particle wavefunction ϕ_2 , and so on. The numbers $n_1, n_2, \dots, n_j, \dots$ are called the *occupation numbers* of the first, second,..., j th,... single particle states. Our state of independent N particles will be then completely specified by the set of occupation numbers $(n_1, n_2, \dots, n_j, \dots)$:

$$v = \{n_1, n_2, \dots, n_j, \dots\} = v\text{th state.} \quad (1.10)$$

If we consider that the system is grandcanonical (particles can be exchanged with a reservoir)

$$N_v = \sum_j n_j = \text{total number of particles in the } v \text{ state} \quad (1.11)$$

In the canonical ensemble $N = N_v$ for all v . We will follow the canonical ensemble in the following.

The energy of the v th state will be given by

$$E_v = \sum_j \epsilon_j n_j \quad (1.12)$$

where ϵ_j is the energy of the j th single particle state and n_j its corresponding occupation number. For fermions $n_j = 0$ or 1 , and no other possibilities are allowed. The statistics associated to fermions is called the Fermi-Dirac statistics. For bosons the occupation numbers can adopt

any number, only limited by the total number of particles, $n_j = 0, 1, 2, 3, \dots$ and they obey Bose-Einstein statistics.

The development of relativistic quantum mechanics basically spanned from 1920's to 1940's including major contributions from Dirac, Pauli or Majorana. It was in particular demonstrated that bosons need to be integer spin particles whereas fermions are half-integer spin particles. Examples of bosons are photons, gluons, W, Z and Higgs bosons, ^4He atoms or Cooper pairs (pairs of electrons which are responsible of superconductivity). Examples of fermions are electrons (and all leptons), quarks, protons or neutrons, all having $1/2$ spin.

In the following paragraphs we are going to derive the distribution functions of bosons and fermions which allow to determine the mean occupation number at any temperature.

1.3.1 Bose-Einstein distribution function

We will be considering a set of N non-interacting bosons. We are going to consider that particles have a mass and that they can not be neither created or destroyed (this will not be the case for photons or phonons, which will be discussed later).

The total number of particles being fixed, we would be naturally impelled to study the system by considering the canonical partition function, $Z = \sum_n \exp(-\beta E_n)$. In that case we must constrain this sum to those states in which the total number of particles is fixed to N :

$$Z = \sum_{\substack{n_1, n_2, \dots, n_j, \dots \\ \text{such that } \sum_j n_j = N}} \exp \left[-\beta \sum_j n_j \epsilon_j \right] \quad (1.13)$$

The restriction introduced by the summation constraint is a not-easy-to-solve combinatorial problem (the solution is possible, but complicated). For this reason, we will prefer to study the system in the grandcanonical ensemble where such restriction in the sum does not appears. The partition function in the grandcanonical ensemble, Ξ , is:

$$\Xi = \sum_v \exp \left[-\beta (E_v - \mu N_v) \right] = \sum_{n_1, n_2, \dots, n_j, \dots} \exp \left[-\beta \sum_j (\epsilon_j - \mu) n_j \right] \quad (1.14)$$

with v being a state with N_v particles having total energy E_v and μ is the chemical potential (the change in the enthalpy when changing the number of particles of the system and keeping all other variables fixed).

The summation in the exponential can be factorized and we have:

$$\Xi = \prod_j \left\{ \sum_{n_j=0}^{\infty} e^{-\beta(\epsilon_j - \mu)n_j} \right\} = \prod_j \left\{ \frac{1}{1 - e^{\beta(\mu - \epsilon_j)}} \right\} \quad (1.15)$$

Where we have considered that for a geometric series $\sum_{n=0}^{\infty} q^n = 1/(1-q)$. We then have:

$$\ln \Xi = - \sum_j \ln \left[1 - e^{\beta(\mu - \epsilon_j)} \right] \quad (1.16)$$

The average occupation number, $\langle n_j \rangle$, can be then computed from any of the following expressions which are derived in introductive texts to statistical physics:

$$\langle n_j \rangle = \frac{\sum_v n_j e^{-\beta(E_v - \mu N_v)}}{\Xi} = \frac{\partial \Xi}{\partial (-\beta \epsilon_j)} \bigg/ \Xi = \frac{\partial \ln \Xi}{\partial (-\beta \epsilon_j)} \quad (1.17)$$

Replacing the value of $\ln \Xi$ in this last expression and operating we obtain:

$$\langle n_j \rangle = \frac{1}{e^{\beta(\epsilon_j - \mu)} - 1} \quad (1.18)$$

Exercise 1.1 Derive this last expression for $\langle n_j \rangle$ ■

Solution:

$$\langle n_j \rangle = \frac{\partial \ln \Xi}{\partial (-\beta \epsilon_j)} = \frac{\partial}{\partial (-\beta \epsilon_j)} \left[-\sum_{\ell} \ln \left(1 - e^{\beta(\mu - \epsilon_{\ell})} \right) \right] = \quad (1.19)$$

$$= \frac{\partial}{\partial (-\beta \epsilon_j)} \left[-\ln \left(1 - e^{\beta(\mu - \epsilon_j)} \right) \right] = \frac{e^{\beta(\mu - \epsilon_j)}}{1 - e^{\beta(\mu - \epsilon_j)}} \quad (1.20)$$

The average number of particles occupying the j th state is then $\langle n_j \rangle = F(\epsilon_j)$ where $F(\epsilon)$ is the Bose-Einstein distribution function:

$$F(\epsilon)_{\text{B.E.}} = \frac{1}{e^{\beta(\epsilon - \mu)} - 1} \quad (1.21)$$

We note that when $\mu = \epsilon$ the function is singular, i.e., at this energy the mean occupation number diverges and then a macroscopic number of particles pile into the same single particle state. This phenomenon is known by *Bose-Einstein condensation* (BEC) which for instance is a mechanism associated to the superfluidity of He^4 , to the superconducting state observed in many material and which has finally been really observed in ensembles of cold atoms. We will devote a section to this interesting phenomena.

Photons or phonons - this latter will be studied later - are also bosons in the sense that any number of particles can exist in the same single particle state. Photons are mass-less bosons whereas the definition of the mass of a phonon, a collective vibration of atoms, has not real meaning.

1.3.2 Fermi-Dirac distribution function

In the ideal gas of Fermi particles, the Pauli exclusion principle limits the value of the occupation numbers, n_j to only two possibilities $n_j = \{0, 1\}$. Using again the grand canonical ensemble, the partition function writes in an analogous way:

$$\Xi = \sum_{n_1, n_2, \dots, n_j, \dots=0}^1 \exp \left[-\beta \sum_j (\epsilon_j - \mu) n_j \right] \quad (1.22)$$

Again as we have non-interacting particles, the sum in the exponential is factorized and we have:

$$\Xi = \prod_j \left[\sum_{n_j=0}^1 e^{-\beta(\epsilon_j - \mu) n_j} \right] = \prod_j \left[1 + e^{-\beta(\epsilon_j - \mu)} \right] \quad (1.23)$$

and then, this time:

$$\ln \Xi = \sum_j \ln \left[1 + e^{-\beta(\epsilon_j - \mu)} \right] \quad (1.24)$$

we are again interested on the average occupation number:

$$\langle n_j \rangle = \frac{\partial \ln \Xi}{\partial (-\beta \epsilon_j)} = \frac{e^{\beta(\mu - \epsilon_j)}}{1 + e^{\beta(\mu - \epsilon_j)}} = \frac{1}{e^{\beta(\epsilon_j - \mu)} + 1} \quad (1.25)$$

This is the expression of the Fermi-Dirac distribution function:

$$F(\epsilon)_{F.D.} = \frac{1}{e^{\beta(\epsilon - \mu)} + 1} \quad (1.26)$$

We can then summarize the previous and present subsections by:

$$f_{j \text{ F.D.}} \equiv \langle n_j \rangle_{\text{F.D.}} = \frac{1}{e^{\beta(\epsilon_j - \mu)} \pm 1} \quad (1.27)$$

where we have introduced the notation f_i for the distribution function which is frequently used in textbooks. Since the total number of particles, N , is just the sum over all levels of the mean number in each level, we have:

$$N = \sum_i f_i \quad (1.28)$$

valid in both statistics.

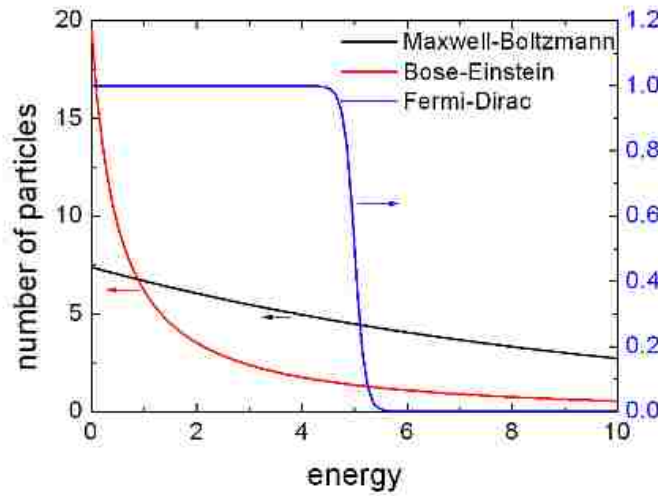


Figure 1.1: Comparison of the Fermi-Dirac and Bose-Einstein distribution functions dependence with energy with the classic Maxwell-Boltzmann distribution function. The arrows indicate which scale needs to be used (rightside or leftside).

In Fig. 1.1 are shown the energy dependency of the two statistics compared with the "classical" Maxwell-Boltzmann statistics distribution function, $f_{M-B} = 1/e^{\beta(\epsilon - \mu)}$.

1.4 The Drude model of metals

1.4.1 introduction

The dynamics of the electrons in a crystal or more generally in a solid is responsible of the electrical conducting properties of most materials (except ion-conduction systems) and also contributes to the thermal conduction of metals. After the discovery of Ohm's law, $R = V/I$,

at the beginning of the XIXth century, we had to wait the discovery of the electron and then the beginning of the XXth century to start to see developing models which could provide an explanation to this empirical law. In fact, in 1900, just 3 years after the discovery of the electron, Drude made the first proposition to explain the resistance of materials to an electric flow. We will confront this approximation which does not take into account the quantum nature of the electron with the semiclassical approach of Sommerfeld which introduces the Fermi-Dirac statistics to account for its quantum nature.

Let's first recall the local Ohm law relating the density of current, $\vec{j}$ and the applied electric field $\vec{E}$:

$$\vec{j} = \bar{\sigma} \vec{E} \quad (1.29)$$

here $\bar{\sigma}$ is the conductivity tensor and $\bar{\rho} \equiv \bar{\sigma}^{-1}$ the resistivity tensor. In the absence of magnetic fields ($\vec{B} = 0$), $\vec{j}$ and $\vec{E}$ are parallel and then $\vec{j} = \sigma \vec{E}$, with σ being then a scalar.

We can put in relation the local and the macroscopic Ohm's law by considering a conducting cylinder like the one represented in figure 1.2

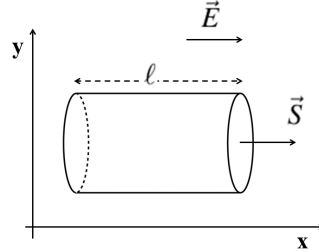


Figure 1.2: A cylinder of cross-section $\vec{S}$ and length ℓ carrying a current.

The intensity, I and the potential difference, V write:

$$I = \vec{j} \cdot \vec{S} = jS \quad V = \vec{E} \cdot \vec{\ell} = E\ell \quad (1.30)$$

and then

$$R = \frac{V}{I} = \frac{E\ell}{\sigma ES} = \frac{\ell}{\sigma S} = \frac{\rho \ell}{S} \quad (1.31)$$

The conductivity of solids is a characteristic of the material and of its thermodynamic conditions. Its value can range from 10^8 to $10^{-18} \Omega^{-1} \text{m}^{-1}$, i.e., more than 25 orders of magnitude between the best conductors and the best insulators!

1.4.2 The Drude classical ideal gas of electrons. Electron mean free path

Drude developed his model assuming that the charge carriers in a solid behave as a classical ideal gas. The first question then to answer is which are the charge carriers in a metal? In many metals the charge carriers are electrons. We will see in the forthcoming chapters that "holes" - the absence of electrons - can also participate to the electrical conduction, i.e., they are also charge carriers in certain metals or semiconductor. In superconductors the charge carriers are Cooper pairs (bound electrons in a certain manner) or the corresponding hole pairs for hole superconductors. Let us concentrate on electron conductors, the only type considered at the time of Drude. As many metals having very different atomic numbers, Z , showed similar conductivity,

it was rapidly understood that not all electrons participate to electrical conduction. It was then assumed that in a metal the electrons of each atoms can be separated between core electrons and valence electrons. Only these last ones participate to the electronic conduction. This is schematized in Figure 1.3.

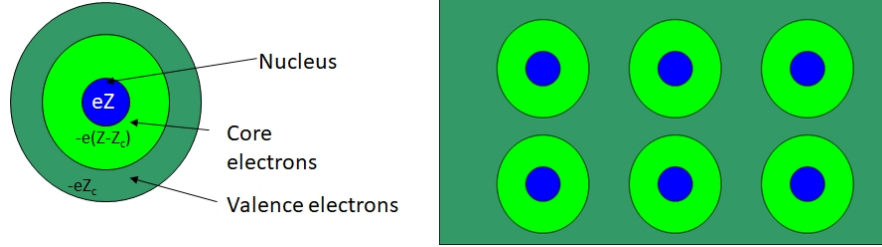


Figure 1.3: (Left) Scheme of an atom in a metal showing the charged particles: Z protons in the nucleus, $Z - Z_c$ core electrons, bound to the atom and not participating to conduction and Z_c (with Z_c usually 1 to 3, depending on the atom), the number of conduction electrons of the atom. (Right) A portion of a metal showing 6 atoms. The valence electrons, are "shared" by all the atoms of the metal (we will talk later about delocalization). For a metal having N atoms, the number of fermions participating to conduction is NZ_c .

The equilibrium speed of the electrons, before applying any external field could be then obtained considering the equipartition theorem ¹:

$$\frac{m_e v_e^2}{2} = \frac{3k_B T}{2} \quad (1.32)$$

At ambient temperature ($T = 300\text{K}$), this leads to $v_e \approx 10^5$ m/s. This is called the thermal velocity. So for Drude, in the absence of external fields, the speed of the electrons was essentially governed by Temperature. Of course, the direction of the speed was stochastic and no net electrical current could appear in the absence of an external field.

When external fields are applied the Lorentz force, $\vec{F} = q\vec{E} + q\vec{v} \wedge \vec{B}$, will lead to the continuous acceleration of the electrons. Drude then introduced the scattering of electrons to be able to limit their acceleration when submitted to an external field. These collisions will be characterized by a mean time between collisions, τ , which will be responsible of a viscous term, a force $\vec{f} = \vec{p}/\tau$, which is opposed to the acceleration of the electrons. Here $\vec{p} = m\vec{v}$ classically. In the quantum approach, $\vec{p}$ is to be identified as the temporal average of the expectation value of the momentum operator, $\hat{p}$, i.e., $\langle \hat{p} \rangle = \langle q | \hat{p} | q \rangle = \hbar q$. The total force on an electron in the presence of an electric, $\vec{E}$ and a magnetic field, $\vec{B}$ will combine the viscous term with the Lorentz force to give:

$$\vec{F} = m_e \frac{d\vec{v}}{dt} = -e(\vec{E} + \vec{v} \wedge \vec{B}) - \frac{\vec{p}}{\tau} \quad (1.33)$$

In stationary conditions $\vec{F} = 0$ and $\vec{v}$ is a constant. If in addition we concentrate only on the effect of an electric field ($\vec{B} = 0$) we have:

$$\vec{p} = m\vec{v} = -e\vec{E}\tau \Rightarrow \vec{v} = -\frac{e\vec{E}\tau}{m} \quad (1.34)$$

This velocity is called the *drift velocity* and strongly differs from the previously calculated, thermal velocity. First of all the drift velocity is directional and not stochastic, meaning that it

¹The equipartition theorem shows that in thermal equilibrium, any degree of freedom (such as a component of the position or velocity of a particle) which appears only quadratically in the energy has an average energy of $1/2 k_B T$

will generate a net electrical current. Secondly, its magnitude is of the order of micrometers per second (as we can calculate once we will evaluate τ) for usual electric fields - i.e., 10-11 orders of magnitude smaller than the thermal velocity - but its directionality makes all the difference. The thermal velocity will be corrected by the Sommerfeld model and become the Fermi velocity. We can now calculate the electrical current, I associated to this steady flow of electrons. Lets consider that the conductor has an electron density n (number of electrons per unit of volume). If we consider a surface $\vec{S}$ perpendicular to the applied field, the number of electrons, dN , going through it in a time dt will be those which have travelled a distance vector $\vec{v}dt$:

$$dN = n\vec{v}dt\vec{S} \Rightarrow I = -e\frac{dN}{dt} = -en\vec{v}\vec{S} \equiv \vec{j}\vec{S} \Rightarrow \vec{j} = -ne\vec{v} \quad (1.35)$$

Combining the results of these two last equations we have:

$$\vec{j} = \frac{ne^2\tau}{m}\vec{E} \quad (1.36)$$

and comparing with the local Ohm's law $\vec{j} = \sigma\vec{E}$ this means that

$$\sigma = \frac{ne^2\tau}{m} \quad (1.37)$$

We can then obtain from experimental values of the conductivity the corresponding time between collisions. For a good metal $\sigma \approx 10^7 \Omega^{-1}m^{-1}$. A typical value of the electron density can be calculated by taking a cell parameter of $a = 1 \text{ \AA}$ and 1 electron per unit cell, which gives $n \approx 10^{29} m^{-3}$. We obtain then:

$$\tau = \frac{m\sigma}{ne^2} \approx \frac{10^{-30}10^7}{10^{-29}10^{-38}} \approx 10^{-14} \text{ s} \quad (1.38)$$

To understand the physical origin of the electron collisions, we have to evaluate the mean free path of the electron, $\bar{\ell}$, which is the mean distance travelled by the electron between two collisions and can be obtained by:

$$\bar{\ell} = \langle \ell \rangle = \sqrt{\langle v^2 \rangle} \tau \quad (1.39)$$

The speed variation due to the application of usual electric fields (drift velocity) is small with respect to the equilibrium thermal speed, so we can consider in first approximation that between two collisions the average velocity is the thermal one.

The Drude model leads then to a mean free path $\bar{\ell} \approx 10^{-9} m = 1 \text{ nm}$. It is then not surprising that Drude considered that the electrons were having collisions with the ions of the crystal which are at distances close to 1 nm.

With our present knowledge, Drude point of view is clearly wrong, as we know now that the periodic potential of the ions or atoms are precisely responsible of the electronic state of the electrons. We will find out and discuss this extensively when developing the electronic band theories in following chapters. The Sommerfeld model of electron conduction which will be discussed next allowed to find the correct origin of electron scattering in metals which limits conductivity to finite values.

1.5 The Sommerfeld model of electron conduction in metals

The Drude Model does not consider the Pauli exclusion principle and then ignores that electrons are fermions. In other words, for Drude, at $T=0 \text{ K}$ all electrons can have zero energy and

consequently all electrons can increase their speed by the application of an electric field or by effect of temperature. This is not compatible with Fermi statistics and consequently some of the predictions of the Drude model failed to reproduce experimental results.

Sommerfeld imagined electrons in metals as a confined gaz of non-interacting fermions submitted to a constant potential, $V(r)$, which we can take arbitrarily as being zero, $V(r) = 0$. In this approximation the electrons of the atoms constituting the metal need to be divided in two types: the electrons in the last electronic shell of the atoms, called the valence electrons and which we consider as free to move and the rest of the electrons which remain trapped in the ions, which are otherwise ignored (core electrons). The effect of the presence of the ions, with their associated potential is not treated in the Sommerfeld model. We will solve this problem when we will include the periodicity of the potential in the forthcoming chapters.

In the Sommerfeld model, the Schrödinger equation for the valence electrons becomes then the free electron equation:

$$-\frac{\hbar^2}{2m}\nabla^2\Psi = \varepsilon\Psi \quad (1.40)$$

with m the mass of the electrons. The solutions are planewaves of the form

$$\Psi(\vec{r}) = \frac{1}{\sqrt{V}}e^{i\vec{k}\vec{r}} \quad (1.41)$$

V being the volume of the solid. The energy eigenvalues are

$$\varepsilon(\mathbf{k}) = \frac{\hbar^2 k^2}{2m} \quad (1.42)$$

We recall here that $\hbar\mathbf{k}$ are the eigenvalues of the momentum operator $\mathbf{p} = \frac{\hbar}{i}\frac{\partial}{\partial\mathbf{r}} = \frac{\hbar}{i}\nabla$ and that $\mathbf{k}$ can be also interpreted as a wave-vector $\mathbf{k} = 2\pi/\lambda$

In doing this we have ignored the electron confinement in the solid which could have been done by introducing a 3-D well potential having an infinite high and solving the Schrödinger equation with such potential. The obtained result in terms of energy quantization is equivalent to the one we are going to get here. Nevertheless, a potential well description will produce wave-function solutions which are stationary-waves instead of propagating plane-waves. Our choice is based in the believe, supporter by experience, that at the usual scales, the positions of the surfaces limiting the solid do not affect the bulk properties of the metal (this is of course not valid in nanoscaled solids as atomic clusters). The physical reason for this lose of spatial coherence is the unavoidable presence of chemical or structural defects in bulk materials. We will then avoid stationary-waves by introducing the periodic Born-von Karman limiting conditions which are presented in the following section. Nevertheless we should here emphasize that the potential well choice for limiting conditions leads to the same results, but with different waves description (this will be shown later in this chapter).

1.5.1 The Born-von Karman periodic conditions

The Born-von Karman boundary conditions (or periodic boundary conditions or sometimes just von Karman periodic conditions) allow to get rid of that problem by introducing a volume of confinement - which will determine the number of quantum states - without introducing surfaces. We recall that the interest in not introducing surfaces is that we avoid the scattering of the electron wavefunctions at that surfaces and hence the formation of stationary waves. This can be easily implemented by considering the electrons confined in a cube of side L . The "trick" is based in

considering that each face of the cube is connected to its opposite in the same direction, so the electrons can never find a boundary. This writes:

$$\Psi(x+L, y, z) = \Psi(x, y+L, z) = \Psi(x, y, z+L) = \Psi(x, y, z) \quad (1.43)$$

which gives by using the plane-wave solution:

$$k_x = \frac{2\pi p}{L}, \quad k_y = \frac{2\pi r}{L}, \quad k_z = \frac{2\pi s}{L} \quad \text{where } p, r, s = 0, \pm 1, \pm 2, \dots \quad (1.44)$$

The k_x, k_y, k_z three dimensional space (known as k -space or even momentum space, as we just need to multiply by the Planck constant to obtain the quantum momentum) is then discretized. For each state we can make correspond a region in k -space of volume $\Delta k = (2\pi/L)^3 = 8\pi^3/V$ which represents the smallest interval of k -volume where a state can hold. If $V \rightarrow \infty$, $\Delta k \rightarrow 0$. A region of k -space of volume Ω will contain then a number of k -states:

$$\frac{\Omega}{(2\pi/L)^3} = \frac{\Omega V}{8\pi^3} \quad (1.45)$$

Or in other words, the number of allowed k -values per unit of volume (of k -space) is:

$$\frac{V}{8\pi^3} \quad (1.46)$$

The Fermi-Dirac statistics tell us that we can place only one electron for each single state level. The one-electrons levels are specified by the wave vectors $\mathbf{k} = (k_x, k_y, k_z)$ and their spin (which can take two values $1/2$ or $-1/2$). Consequently each point of k -space represents 2 electronic levels of different spin with occupations numbers 0 or 1.

We should underline that the introduction of periodic conditions, i.e., introducing the limited volume in which the electrons evolve (even if the Born-von Karman approach partially gets around this) leads to a *discretization of k -states*.

The energy eigenvalues for the electrons in the solid (which we recall are considered as free particles) are

$$\varepsilon = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2}{2m} \left(\frac{2\pi}{L} \right)^2 (p^2 + s^2 + r^2) \quad (1.47)$$

1.5.2 Ground state ($T=0K$). Density of states, Fermi energy

At $T=0$ K the ground state will be constructed by placing two-electrons in the one-electron level $\mathbf{k} = 0$ which has the lowest energy and successively filling the one-electron levels of lowest energy. As energy increases with k^2 , we will progressively fill k -states around the origin in all the 3 directions of k -space. As the number of electrons, N , which we need to place is very large, the occupied region in k -space can be assimilated to a sphere centered in $\mathbf{k} = 0$. The radius of this sphere, corresponding to the highest energy occupied levels, is called k_F (F for Fermi), the Fermi wave vector. The k -space volume of the Fermi sphere is then $4\pi k_F^3/3$.

Then number of allowed states within the sphere is then using 1.46

$$\left(\frac{4\pi k_F^3}{3} \right) \left(\frac{V}{8\pi^3} \right) = \frac{k_F^3}{6\pi^2} V \quad (1.48)$$

Every k -allowed state can hold 2 electrons of different spin. And the total one-electron levels need to accommodate the N electrons of the metal, so:

$$N = 2 \frac{k_F^3}{6\pi^2} V = \frac{k_F^3}{3\pi^2} V \quad (1.49)$$

As the electronic density is $n = N/V$ we have

$$n = \frac{k_F^3}{3\pi^2} \quad (1.50)$$

The sphere of radius k_F is called the *Fermi sphere* and contains the occupied one-electron levels. The surface of the sphere is the *Fermi surface*. The energy of the electrons at the Fermi surface is the *Fermi energy*:

$$\epsilon_F = \frac{\hbar^2 k_F^2}{2m} \quad (1.51)$$

The Fermi energy can then be defined as the maximum energy occupied by an electron at 0K. We can equally define the Fermi momentum $p_F = \hbar k_F$ and the associated Fermi velocity $v_F = p_F/m$. Usual values of the electronic density in metals leads to Fermi energies in the range of 1.5 to 15 electron volts. For instance $\epsilon_F = 7$ eV for copper. One can also define the Fermi temperature, T_F , from $\epsilon_F = k_B T_F$. This leads to values of T_F beyond the melting point of metals. We will further discuss the significance of ϵ_F and T_F .

At $T=0$ K the graphical Fermi-Dirac distribution function is a representation of the occupation statistics of the systems as shown in Figure 1.4

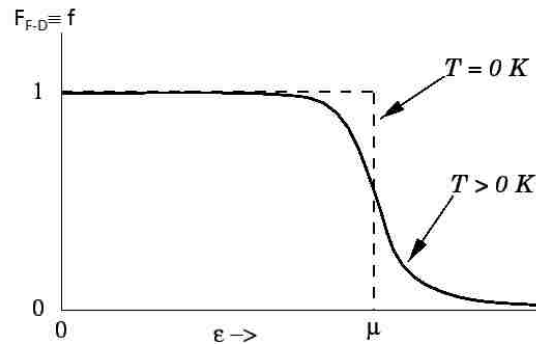


Figure 1.4: The Fermi-Dirac distribution function at $T = 0$ K and at $T > 0$ K.

At $T = 0$ K, the Fermi-Dirac distribution function is a step function. We observe that at $T = 0$ K our definition of Fermi energy corresponds to the chemical potential, $\mu = \epsilon_F$. At $T = 0$ K the occupation number is one below ϵ_F and zero above this value.

For $T > 0$, when electrons will be excited to higher energies, we will verify that the chemical potential remains equal to the Fermi energy to a high degree of precision.

We can now calculate the total energy of this Fermi sea² in the ground state ($T=0$ K):

$$E = 2 \sum_{k < k_F} \frac{\hbar^2}{2m} k^2 \quad (1.52)$$

²In scientific literature we often find this poetic term of "Fermi sea" which somehow makes a parallel between the Fermi surface and the surface of oceans. As it will be discussed, most of the experiments deal with the electrons at the Fermi surface. There was a renown series of conferences entitled "Surfing at the Fermi sea"

In most cases we are dealing with a large number of particles in which case the number of $\mathbf{k}$ states becomes close to a continuum. If we consider then the case of any smooth function $F(\mathbf{k})$ and more concretely the summation over $\mathbf{k}$ -states of that function, it is then possible to adopt an integral form. This is exactly what we want to do with Eq. 1.52 to calculate the energy of the electron Fermi sea. To make the transformation from a discrete sum to an integral, we note that using 1.46 for the $\mathbf{k}$ -space allowed volume for $\mathbf{k}$ value, $\Delta\mathbf{k} = \frac{8\pi^3}{V}$, we can write:

$$\sum_{\mathbf{k}} F(\mathbf{k}) = \frac{V}{8\pi^3} \sum_{\mathbf{k}} F(\mathbf{k}) \Delta\mathbf{k} \quad (1.53)$$

When $\Delta\mathbf{k} \rightarrow 0$ (i.e, $V \rightarrow \infty$) the summation in the right side of the equation will tend to an integral, so:

$$\lim_{V \rightarrow \infty} \frac{1}{V} \sum_{\mathbf{k}} F(\mathbf{k}) = \int \frac{F(\mathbf{k})}{8\pi^3} d\mathbf{k} \quad (1.54)$$

where in addition to evaluation the sum as an integral, we have normalized the obtained value per unit of volum. In that way, we may use this result to evaluate the total energy per unit of volume from 1.52:

$$\frac{E}{V} = \frac{1}{4\pi^3} \int_{\mathbf{k} < k_F} \frac{\hbar^2 k^2}{2m} d\mathbf{k} = \frac{1}{4\pi^3} \frac{\hbar^2}{2m} \int_{\mathbf{k} < k_F} k^2 d\mathbf{k} = \frac{1}{4\pi^3} \frac{\hbar^2}{2m} \int_0^\pi \sin\phi d\phi \int_0^{2\pi} d\theta \int_0^{k_F} k^4 dk = \frac{1}{\pi^2} \frac{\hbar^2 k_F^5}{10m} \quad (1.55)$$

where we have integrated using spherical coordinates. This expression gives us the energy per unit of volume in the system. We can evaluate the energy per electron considering from 1.49 that the number of electrons per unit of volume is $N/V = k_F^3/3\pi^2$, which gives

$$\frac{E}{N} = \frac{3}{10} \frac{\hbar^2 k_F^2}{m} = \frac{3}{5} \varepsilon_F \quad (1.56)$$

which provides an additional significance to ε_F as a measure of the electronic density of energy. Alternatively we can write:

$$\frac{E}{N} = \frac{3}{5} k_B T_F \quad (1.57)$$

A value which we have calculated here at $T = 0$ K and which is always different from zero. This result can be compared with the energy of a particle in a classical gas of non-interacting particles, $\frac{3}{2} k_B T$, which becomes zero when $T = 0$ K. To reach in a classical gas an equivalent value we need to quote the two expressions: $3/5 k_B T_F = 3/2 k_B T$. In other words, we will need then to heat the classical gas to temperatures of $T = \frac{2}{5} T_F \sim 10^4$ K. Such temperatures are well beyond the melting temperature of metals (at ambient or moderate pressures) meaning that electrons in metals are always a statistical quantum system.

1.5.3 The Fermi electron gas at $T > 0$ K

We have seen that in the ground state $\varepsilon_F = \mu$ is in the 1 to 15 eV range. The plot of the Fermi-Dirac distribution in that case, shows that for $T > 0$ K (but T below the metal melting temperature), the distribution function differs from the $T = 0$ K one only in a very small energy domain of the order of $k_B T$ around the position of the Fermi energy. This corresponds to the thermal excitation of those electrons which can have access to available unoccupied states. In

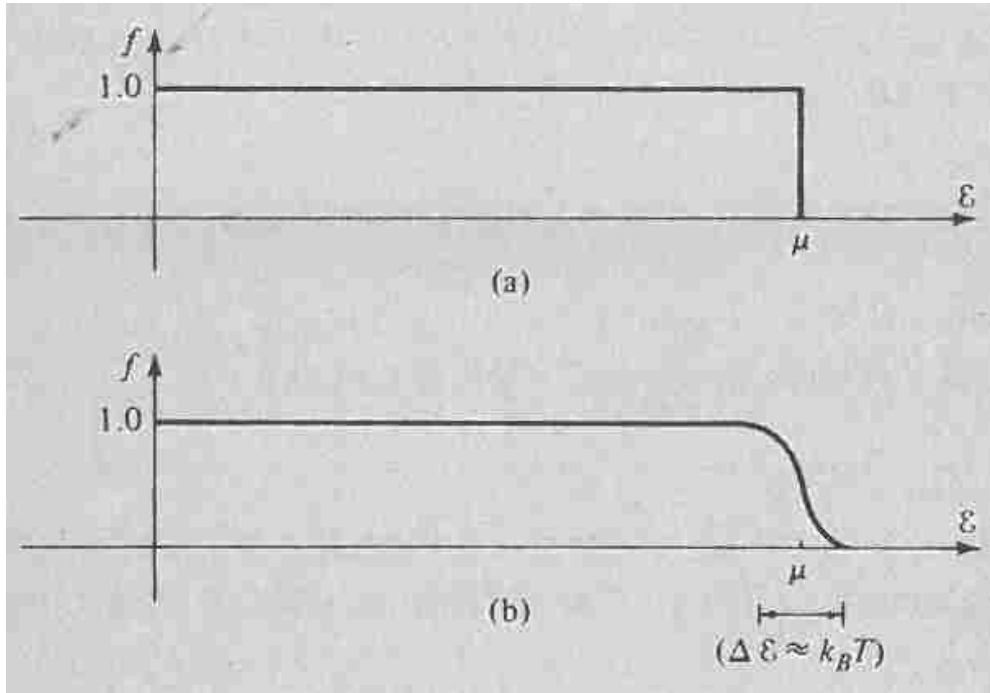


Figure 1.5: Fermi-Dirac function versus ϵ for a given μ at (a) $T = 0$ and (b) $T \approx 0.01\mu$, i.e., of the order room temperature for a typical metallic density. The curves differ only in a region of order $k_B T$ about μ . (From Ashcroft and Mermin)

fact, for instance at $T = 300\text{K}$, the thermal energy $k_B T \sim 25 \text{ meV}$. This is shown in Fig. 1.5 and is frequently referred poetically as the formation of ripples in the Fermi sea.

Under these conditions, it can be shown that μ and ϵ_F differ less than 0.01 %. The difference between the two variables can be evaluated to be (see Subsection 1.8.5 for a demonstration):

$$\mu(T) = \epsilon_F \left[1 - \frac{1}{3} \left(\frac{\pi k_B T}{2\epsilon_F} \right)^2 \right] \quad (1.58)$$

This small correction is sometimes abusively referred as the thermal evolution of the Fermi energy. With the exception of very accurate calculations this thermal correction only becomes important when $\epsilon_F \sim k_B T$, or in other words when $T \sim T_F$. As discussed before, T_F is much higher than metals melting point. Consequently in metallic solids one usually assumes that for the electrons Fermi sea $\epsilon_F = \mu$ at all temperatures.

1.5.4 Temperature effects. The specific heat of the free electron gas (metals)

The specific heat can be obtained from the temperature dependence of the internal energy, U of the electron gas:

$$c_v = \left(\frac{\partial u}{\partial T} \right)_V \quad (1.59)$$

with $u = U/V$ is the energy density. We can evaluate the internal energy as:

$$U = 2 \sum_{\mathbf{k}} \epsilon(\mathbf{k}) f(\epsilon(\mathbf{k})) \quad (1.60)$$

here the sum is done over all the electron state levels (which needs to be multiplied by 2 to account for spin) and each energy level is multiplied by the mean number of electrons in the

level, given by the Fermi-Dirac distribution function, $f \equiv F_{F-D}$. In this expression we have emphasized the dependence of energy with $\mathbf{k}$. Again, we can adopt an integral form for the above expression by dividing by V :

$$u = \frac{2}{V} \sum_{\mathbf{k}} \varepsilon(\mathbf{k}) f(\varepsilon(\mathbf{k})) = \frac{2}{V} \frac{V}{8\pi^3} \sum_{\mathbf{k}} \varepsilon(\mathbf{k}) f(\varepsilon(\mathbf{k})) \Delta\mathbf{k} \xrightarrow{\Delta\mathbf{k} \rightarrow 0} \frac{1}{4\pi^3} \int \varepsilon(\mathbf{k}) f(\varepsilon(\mathbf{k})) d\mathbf{k} \quad (1.61)$$

So the energy density is:

$$u = \int \varepsilon(\mathbf{k}) f(\varepsilon(\mathbf{k})) \frac{d\mathbf{k}}{4\pi^3} \quad (1.62)$$

As we have seen, the total number of particles can be calculated as $N = \sum_{\mathbf{k}} f(\varepsilon(\mathbf{k}))$. Then using the same procedure, the electronic density $n = N/V$ will be:

$$n = \int f(\varepsilon(\mathbf{k})) \frac{d\mathbf{k}}{4\pi^3} \quad (1.63)$$

The expressions of the energy density and of the electronic density only depend on $\mathbf{k}$ through the electronic energy, $\varepsilon = \hbar^2 k^2 / 2m$. We can then evaluate the integrals in spherical coordinates. For instance:

$$n = \int f(\varepsilon(\mathbf{k})) \frac{d\mathbf{k}}{4\pi^3} = \int_0^\infty f(\varepsilon(\mathbf{k})) \frac{k^2 dk}{\pi^2} = \int_0^\infty g(\varepsilon) f(\varepsilon) d\varepsilon \quad (1.64)$$

the last equality (and using $\varepsilon = \hbar^2 k^2 / 2m$ and its derivative) allows to determine $g(\varepsilon)$ which can be written:

$$g(\varepsilon) = \frac{m}{\hbar^2 \pi^2} \sqrt{\frac{2m\varepsilon}{\hbar^2}}, \quad \varepsilon > 0; \quad (1.65)$$

$$= 0, \quad \varepsilon < 0$$

$g(\varepsilon)$ represents the number of one-electron levels in the energy range between ε and $\varepsilon + d\varepsilon$ per unit of volume. In fact, when multiplied by the probability of occupation, $f(\varepsilon)d\varepsilon$ we obtain the corresponding density of occupied levels in the energy interval. $g(\varepsilon)$ is then called the *density of states* or sometimes density of levels per unit volume (or just density of levels). It is somehow equivalent to the degeneracy of the states comprised in the energy range between ε and $\varepsilon + d\varepsilon$ (per unit of volume). Using Equations 1.50 and 1.51 we can also write

$$g(\varepsilon) = \frac{3}{2} \frac{n}{\varepsilon_F} \left(\frac{\varepsilon}{\varepsilon_F} \right)^{1/2}, \quad \varepsilon > 0; \quad (1.66)$$

$$= 0, \quad \varepsilon < 0$$

Of particular importance is to note that in an electron gas in 3-dimensions the density of states increases with energy as $\varepsilon^{1/2}$. We can evaluate the density of states at the Fermi energy which becomes:

$$g(\varepsilon_F) = \frac{3}{2} \frac{n}{\varepsilon_F} \quad (1.67)$$

Then proportional to the electronic density. Combining Eq. 1.67 and Eq. 1.66 one can also write:

$$\varepsilon_F = \frac{\hbar^2}{2m} \left(3\pi^2 n \right)^{2/3} \quad (1.68)$$

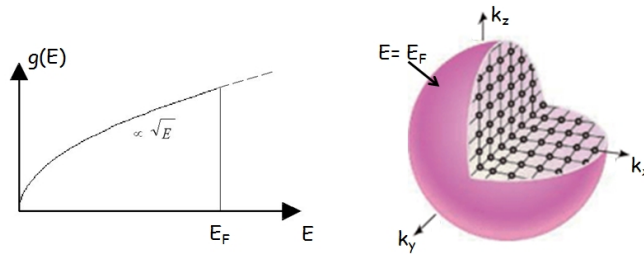


Figure 1.6: Free electron in a 3-dimensional system. Left: density of states. Right: the Fermi Sphere showing the different k -states inside the sphere which are occupied. Each one of the dots contain two states, one for each spin.

We can rewrite the important expression of the electronic density found above and apply the same arguments for the evaluation of the total number of particles in the system and the energy density which gives:

$$n = \int_{-\infty}^{\infty} g(\epsilon) f(\epsilon) d\epsilon \quad (1.69)$$

$$u = \int_{-\infty}^{\infty} \epsilon g(\epsilon) f(\epsilon) d\epsilon \quad (1.70)$$

These integrals (or other similar ones) can be easily evaluated considering the fact that as we have already discussed for almost all temperatures of interest in metals, T is much smaller than the Fermi temperature and then $\mu \approx \epsilon_F$. In such a case:

$$n = \int_0^{\epsilon_F} g(\epsilon) f(\epsilon) d\epsilon \quad (1.71)$$

$$u = \int_0^{\epsilon_F} \epsilon g(\epsilon) f(\epsilon) d\epsilon \quad (1.72)$$

In the following lines, we propose to make an estimative computation of the specific heat of an electron gas in a solid, $c_v = (\partial u / \partial T)_V$. At $T > 0K$ the number of electrons per unit of volume occupying the state ϵ at a temperature T is given by the integral argument of the above integral for the evaluation of the number of occupied states:

$$n(\epsilon, T) = g(\epsilon) f(\epsilon, T) \quad (1.73)$$

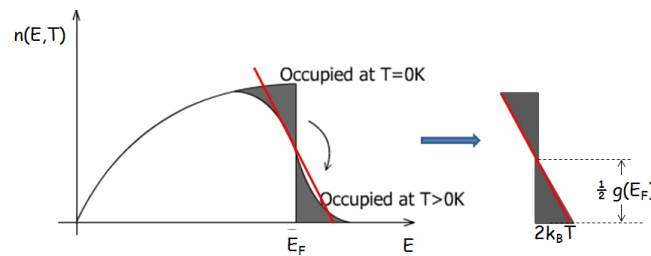


Figure 1.7: Number of electrons as function of energy evolving from $T = 0K$ to $T > 0K$

In Figure 1.7 it is shown the evolution of $n(E, T)$ when $T > 0K$. The $n(E, T)$ evolution just differs from the $n(E, 0)$ from the fact that the electrons from the upper "triangle" have been excited to the lower "triangle" (dark areas of the figure).

We can approach the two gray areas in Fig. 1.7 as 2 triangles which height will be $1/2g(\epsilon_F)$ and base $2k_B T$. In order to see this, it is enough to consider that the curved descending part of $f(\epsilon, T)$ is approximated with a straight line (red line in Fig. 1.7) $f = m\epsilon + a$ with $f = 1/2$ for $\epsilon = \epsilon_F$ and $m = (\partial f / \partial \epsilon)_{\epsilon = \epsilon_F}$.

The number of excited electrons with respect to the $T = 0K$ situation is then given by the area of the lower triangle in the figure, which is $1/2 \times 2k_B T \times 1/2g(\epsilon_F) = 1/2k_B Tg(\epsilon_F)$.

These electrons originate from the upper triangle of the figure and then in average the energy won for each of the electrons is $2k_B T$. The energy won by increasing temperature from $T = 0K$ is then $U = 2k_B T(1/2)k_B Tg(\epsilon_F) = (k_B T)^2 g(\epsilon_F)$.

We can then estimate the electronic contribution to the specific heat:

$$C_v = \frac{\partial U}{\partial T} = 2k_B^2 g(\epsilon_F) T \quad (1.74)$$

as changes in electron states with temperature only take place in this region around ϵ_F (remember the ripples in the Fermi sea).

We have found that $C_v \propto T$ which reproduces well observations at low temperature in metals. In fact, in metals the more complete expression for the specific heat is $C_v = aT^D + bT$. The first contribution is, as we will see later, the phonon contribution to the specific heat which depends on the system dimensionality, D . The second term is the electron contribution to the specific heat. Our above considerations which give this linear dependence on T , where totally independent of dimensionality.

Using the expression of $g(\epsilon_F)$ already calculated (1.67) and replacing it in the expression of C_v we obtain:

$$C_v = 3k_B^2 T \frac{n}{\epsilon_F} = 3nk_B \frac{T}{T_F} \quad (1.75)$$

where the last expression is obtained by using the definition $\epsilon_F = k_B T_F$. The most important result here is that *the contribution of conduction electron to the specific heat of a metal is proportional to the temperature*. It can be easily demonstrated that this result is independent of the dimension of the metallic system. We shall recall here that in a classic gas of monoatomic particles, the specific heat is given by $C_v = 3nk_B$.

If we take in metallic crystals $\epsilon_F \sim 1\text{eV}$, we have $T_F \sim 10^5 K$. Then at ambient temperature $T/T_F \sim 10^{-3}$ and $C_v(\text{electronic}) \sim 10^{-3} 3nk_B$. Again we see that we are far away from the classical conditions and that the systems needs to be treated on quantum grounds.

Conduction electrons are not the only particles contributing to the specific heat of a solid. As we shall see in the following chapters, the atomic vibration of the atoms of the solid, the so called phonons, have a prominent role on heat conduction. In general for a 3D metal we will show that the phonon contribution to the specific heat shows a T^3 dependence. Hence for a 3D metallic solid, $C_v = \gamma T + \beta T^3$. It is practical to plot C_v/T as function of T^2 as we have then $C_v/T = \gamma + \beta T^2$ a linear function on T^2 for which the intercept at the origin is the electron contribution and the slope the phonon one.

1.6 Bose Einstein Condensation

We have already evoked the *Bose-Einstein condensation* (BEC) as a particular configuration of the perfect Bose gaz of particles. The BEC state only concerns non-zero mass particles and not photons. The reason for that is that BEC needs to take place at low temperatures and at low temperatures, if we consider the blackbody radiation, photons disappear in the cavity walls instead of occupying the cavity ground state. This is connected to the fact that the systems of

photons has a vanishing chemical potential at all temperatures, meaning that their number is not conserved when temperature is varied.

So, we consider here bosons of non-zero mass. The Pauli exclusion principle does not apply in this case, and at very low temperature we expect that all particles can drop in the ground state. This phenomenon is known as the Bose-Einstein condensation. First predicted by Einstein in 1925, F. London in 1938 point out that the ^4He superfluid state shows a similar behavior to the BEC.

The Bose-Einstein statistics will then show us how the transition to the BEC state takes place. In some respects the BEC accumulation of particles in a same state can show some analogies to the vapor condensation in the liquid state, and is the reason for its name. Nevertheless, we will see that there are significant differences between BEC and a gaz condensation.

The BE distribution function give us the average occupation number of any state :

$$\langle n_i \rangle = \frac{1}{e^{\beta(\epsilon_i - \mu)} - 1} \quad (1.76)$$

We take the ground state (for $i = 1$) to be zero, i.e., $\epsilon_1 = 0$. Consequently, in order to guarantee that the occupation of this state is a positive number we need to impose that $\mu < 0$. The chemical potential of a BE gaz is then always zero.

We could then evaluate the total number of particles by summing up all contributions:

$$N = \sum_i \frac{1}{e^{\beta(\epsilon_i - \mu)} - 1} \quad (1.77)$$

We may find more interesting to use the density of states to calculate the total number of particles in a BE gaz. This can be done by taking the expression of the density of states which is found in 1.126:

$$f(p)dp = \frac{V4\pi p^2 dp}{h^3} \quad (1.78)$$

which together with $\epsilon = p^2/2m$ gives:

$$f(\epsilon)d\epsilon = f(p)\frac{dp}{d\epsilon}d\epsilon = \frac{V4\pi p^2 dp}{h^3} \frac{dp}{d\epsilon}d\epsilon = \frac{V2\pi(2m)^{3/2}}{h^3} \epsilon^{1/2} d\epsilon \quad (1.79)$$

Now we can evaluate N by integrating the density of states for all possible energies after multiplying it by the occupancy given by the Bose-Einstein distribution and we get

$$\frac{N}{V} = \frac{2\pi(2m)^{3/2}}{h^3} \int_0^\infty \frac{\epsilon^{1/2} d\epsilon}{e^{\beta(\epsilon - \mu)} - 1} \quad (1.80)$$

We are now going to explore the effect of cooling down this boson ensemble while considering that its density (N/V) is kept constant. Consequently, the right side of Eq. 1.80, needs also to remain constant while $\beta = 1/kT$ increases. As in a BE gaz $\mu < 0$, this means that, μ needs to increase while cooling (or $|\mu|$ must decrease). Consequently the integral in Eq. 1.80 defines a temperature $T = T_c$ for which $\mu = 0$ given by :

$$\frac{N}{V} = \frac{2\pi(2m)^{3/2}}{h^3} \int_0^\infty \frac{\epsilon^{1/2} d\epsilon}{e^{(\epsilon/k_B T_c)} - 1} \quad (1.81)$$

This integral can be evaluated by taking as integration variable $z = \varepsilon/k_B T$ and we obtain:

$$\frac{N}{V} = \left(\frac{2\pi m k_B T_c}{h^2} \right)^{3/2} \left[\frac{2}{\sqrt{\pi}} \int_0^\infty \frac{z^{1/2} dz}{e^z - 1} \right] = \left(\frac{2\pi m k_B T_c}{h^2} \right)^{3/2} \times 2.61 \quad (1.82)$$

In the last step, the expression in square brackets, I , has been evaluated knowing that the Riemann function, $\zeta(s)$ and the gamma function, $\Gamma(s)$, verify:

$$\zeta(s)\Gamma(s) = \int_0^\infty \frac{z^{s-1} dz}{e^z - 1} \quad (1.83)$$

and then the expression between brackets can be written $I = 2/\sqrt{\pi} \zeta(3/2) \Gamma(3/2)$, which as $\Gamma(3/2) = \sqrt{\pi}/2$ gives $I = \zeta(3/2) = 2.612\dots$, with all values taken from tabulated resources.

Nevertheless, our derivation done here has a strong weakness which invalidates it. We can see already that its consequences are nonphysical as following it we find that the BE gas cannot be cooled down below T_c . The problem is that writing Eq. 1.80 we have assumed that the discrete sum in Eq. 1.77 could be replaced by an integral form at any temperature. But in a BE gas, when the temperature is sufficiently low, the ground state, with $\varepsilon = 0$ will be dominantly filled, while the integral form of the density of states totally neglects this due to the $\varepsilon^{1/2}$ factor in the integral. To solve this problem, we need explicitly write the contribution of the ground state in its discrete form and add it to Eq. 1.80:

$$N = \frac{1}{e^{-\beta\mu} - 1} + V \frac{2\pi(2m)^{3/2}}{h^3} \int_0^\infty \frac{\varepsilon^{1/2} d\varepsilon}{e^{\beta(\varepsilon-\mu)} - 1} \quad (1.84)$$

which can be written $N = N_1 + N_{\varepsilon>0}$ with the two terms:

$$N_1 = \frac{1}{e^{-\beta\mu} - 1} \quad (1.85)$$

$$N_{\varepsilon>0} = V \frac{2\pi(2m)^{3/2}}{h^3} \int_0^\infty \frac{\varepsilon^{1/2} d\varepsilon}{e^{\beta(\varepsilon-\mu)} - 1} \quad (1.86)$$

as, in fact, for $T > T_c$, the number of particles at the ground state is rather negligible and can be omitted in the evaluation of $N_{\varepsilon>0}$.

We can evaluate $N_{\varepsilon>0}$ by introducing a new integration variable $z = \beta\varepsilon$ and using Eq. 1.82 to get:

$$N_{\varepsilon>0} = N \left(\frac{T}{T_c} \right)^{3/2} \quad (1.87)$$

or

$$N_{\varepsilon>0}/N = \left(\frac{T}{T_c} \right)^{3/2} \quad (1.88)$$

which is the fraction of particles in states with $\varepsilon > 0$. The remaining particles, i.e, the fraction of particles on the ground state is then given by :

$$N_1/N = 1 - \left(\frac{T}{T_c} \right)^{3/2} \quad (1.89)$$

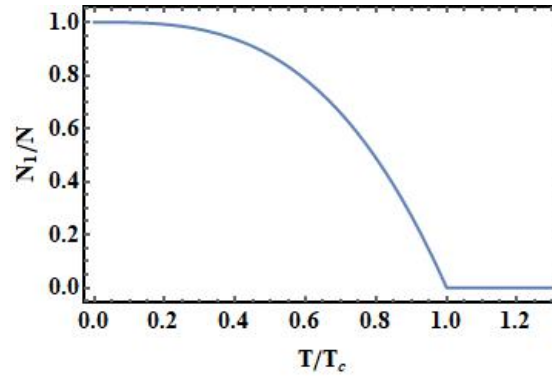


Figure 1.8: Fraction of boson particles crowding into the ground state as function of the normalized temperature T/T_c , with T_c the Bose-Einstein condensation temperature.

expression valid for $T < T_c$. For $T > T_c$ the number of particles in the ground state are negligible and then we can represent the N_1/N evolution with respect to the normalized temperature T/T_c as:

As it can be seen in Fig. 1.8, as T decreases below T_c , the number of particles in the ground state increases considerably and because these particles have zero energy, and hence, zero momentum, they do not contribute to pressure nor do they possess viscosity (viscosity is related to the transport of momentum). This process of accumulation of particles in the zero energy ground state is known as the *Bose-Einstein condensate* (BEC). It is remarkable to note, that whereas in the condensation of a vapor into a liquid, there is a phase separation, in the BEC there is no spatial separation between the two states (condensate and not-condensate). A BE gas at temperatures below T_c is also called degenerated. T_c is known as the *degeneracy temperature* or the *condensation temperature*.

1.6.1 BEC experimental evidence

As it was noted at the beginning of this section, BEC has been found relevant to understand ^4He , which has spin zero and then satisfies BE statistics. ^4He remains liquid at ambient pressure down to absolute zero temperature as, due to its low mass, quantum fluctuations (zero point motion, which derives from the uncertainty principle) overcome the weak van der Waals interaction between molecules in the liquid state. A relatively large pressure of ~ 25 atm is needed to solidify helium close to zero K. The boiling point at ambient pressure of ^4He is 4.2 K, but if we keep cooling liquid ^4He , a sharp transition takes place at 2.17 K. Above this temperature, ^4He behaves as a normal liquid and this phase between 2.17 and 4.2 K is known as Helium-I. Below 2.17 K ^4He flows with no apparent viscosity and is able to flow rapidly through fine capillaries. This new phase is known as Helium-II. Helium-II is described within a two-fluid model mixture of a normal fluid and a superfluid, with no viscous interaction between them. The superfluid has no viscosity and hence no resistance to flow. In the BE gas, for temperatures below T_c we also deal with two kinds of particles which may think that both phenomena are related. There are in fact other similarities, as a similar singular behavior in the specific heat evolution at the transition temperature, known as the *lambda point* which will be described below. Nevertheless, BEC that not allows to correctly predict all the properties of Helium II. This is not surprising as in liquid helium there are interactions between atoms which are not considered in the BEC gas. Helium 3, ^3He , has spin 1/2 and is then a fermion. It exhibits nevertheless a lambda-point transition but a temperature of 2.65 mK, i.e., 3 orders of magnitude lower than for ^4He . Also here a BEC analogy can be found as the superfluid state in ^3He is obtained by the association of pairs of atoms, which are then a boson. Superconductivity has also such analogy as electrons associate in

pairs which are bosons called Cooper pairs, which "condense" in the superconducting state. Nevertheless, none of the above referred cases, ^4He , ^3He or superconductors, correspond to a true BEC, due to the non-negligible interaction between the constituents of the system. The most clear observation of a BEC is due to the use of *cold atoms*, a system which in addition allows to distinguish atoms in the ground state from atoms found in the excited state. The degeneracy temperature is given, using Eq. 1.82 by:

$$T_c = 2.61^{-2/3} \frac{\hbar^2}{2\pi m k_B} \left(\frac{N}{V} \right)^{3/2} = 3.31 \frac{\hbar^2}{m k_B} \left(\frac{N}{V} \right)^{3/2} \quad (1.90)$$

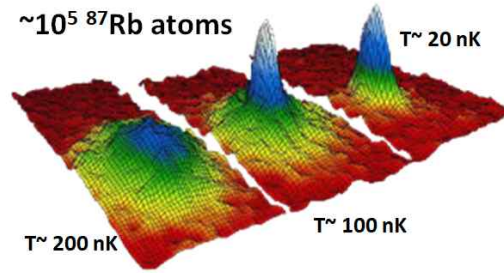


Figure 1.9: Spatial distribution of 10^5 ^{87}Rb atoms with temperature increasing from left to right. These distributions were measured 5 ms after releasing the atom trap. Before opening the trap, the atoms are packed at the center of each image. After opening the trap, the atoms at the ground state, with zero momentum, remain at the center, when the temperature is below T_c (image at the right).

To observe a BEC at the highest temperature we need then light atoms and a high density of atoms. At the same time, we should avoid a too high density, as otherwise, the interatomic distance will introduce interactions between them which will push the system out of the ideal BEC system. Atoms can be cooled down to extremely low temperatures using magneto-optical traps which allow to reach nK temperatures. These methods request to use laser energies which resonate with precise energy transitions of the atoms. This is the reason which makes that the first cold atoms BEC was obtained, not from hydrogen, but from ^{84}Rb atoms. In 1995 Cornell, Weimann and Ketterle cooled 2000 atoms combining magneto-optical traps (MOTs) and evaporative cooling techniques to reach temperatures in the 10^2 nK regime. They managed to detect the BEC formation at $T_c \approx 170$ nK in excellent agreement with Eq. 1.90 when using the atomic density achieved in the experiment of 2.5×10^{12} atoms/cm³.

Fig. 1.9 shows the way the BEC was experimentally detected. These results lead to the 2001 Nobel prize of Physics to Eric Cornell, Wolfgang Ketterle and Carl Wieman. Since then, BEC of many different types of atoms have been produced, including ^4He . We may note that the effect of gravitation limits the lifetime of BECs of cold atoms to fractions of a second (the atoms tend to collide at the bottom of the apparatus). For this reason the same type of experiment has been done in micro-gravity parabolic rocket flights with a record of 6 minutes of experiments in which BECs were kept for ~ 300 ms. A cold atom laboratory has been also installed in the International space station and BEC has been detected for a duration of more than one second. At the time of writing this notes, the coldest temperature reached with cold atoms is of 450 pK. At such temperatures a BEC of ^4He exhibit a de Broglie wavelength of the order of $10 \mu\text{m}$, i.e., the thickness of an hair, offering opportunities for quantum experiments, as entanglement between mass particles, at the macroscopic scale.

1.6.2 BEC specific heat

The evolution with temperature of the specific heat of a system, can constitute a signature of its nature, as for instance the linearity with T at low temperatures in metals. It is then interesting to explore how C_v varies in a BEC. We need for that to consider the energy for a BEC. For $T < T_c$ only particles in the "normal" state will contribute to the energy. Their number is given by $N_{\epsilon>0}$ and the energy of each of the particles is of the order of $k_B T$. Then we can make a fast estimation from Eq. 1.88 that :

$$E \propto N_{\epsilon>0} k_B T = N k_B \frac{T^{5/2}}{T_c^{3/2}} \quad T < T_c \quad (1.91)$$

and then the molar heat capacity is:

$$C_v \propto \frac{5}{2} \left(\frac{T}{T_c} \right)^{3/2} \quad T < T_c \quad (1.92)$$

To obtain a more accurate value, we need to use the Energy expression which can be derived from Eq. 1.86:

$$E = V \frac{2\pi(2m)^{3/2}}{h^3} \int_0^\infty \frac{\epsilon^{3/2} d\epsilon}{e^{\beta(\epsilon-\mu)} - 1} \quad T < T_c \quad (1.93)$$

and changing variables to $z = \beta\epsilon$, we can evaluate the integral and substitute for V from Eq. 1.82 to get (we need this time the values $\zeta(5/2) = 1.3414$ and $\Gamma(5/2) = 3\sqrt{\pi}/4$):

$$E = 0.77 N k_B \frac{T^{5/2}}{T_c^{3/2}} \quad T < T_c \quad (1.94)$$

and finally

$$C_v = 1.926 R \left(\frac{T}{T_c} \right)^{3/2} \quad T < T_c \quad (1.95)$$

We observe that at $T = T_c$, C_v exceeds the classical $3/2R$ value. At high temperature, the classic behavior of course holds. We do not provide here the calculation to show how the heat capacity evolves from high temperatures towards $T = T_c$. Such calculation shows that C_v is continuous at $T = T_c$ but discontinuous in its derivative, showing a characteristic kink as shown in Fig. 1.10.a This evolution shows important similarities with the observed evolution of the heat capacity of ^4He when going through the superfluidity transition as shown in Fig. 1.10.b. This is what lead F. London to suggest this transition in ^4He as a type of BE condensation. This transition shows a characteristic shape which reminds the greek letter lambda, λ . For this reason, the transition between the normal phase of helium (He-I) and its superfluidic phase (He-II) is called the λ -line as shown in Fig. 1.10.c.

The differences between Fig. 1.10.a and Fig. 1.10.b are again the mark of the non negligible interaction between helium atoms in a liquid.

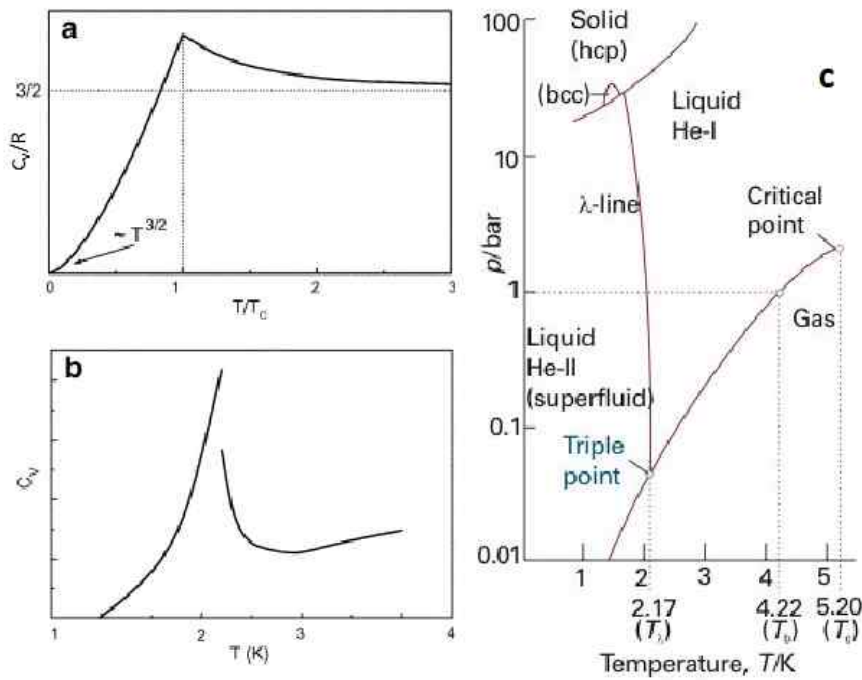


Figure 1.10: (a) Heat capacity dependence with temperature for the ideal BEC close to T_c . (b) The same for ^4He . (c) Low T phase diagram of ^4He . Critical temperature, T_c , boiling temperature, T_b and triple point, T_λ , for the λ -line are shown.

1.7 The photon gas and the Maxwell distribution of photons

1.7.1 The photon gas

A photon gas is an electromagnetic field in thermal equilibrium with its container. It is a result of the quantum theory of the electromagnetic field, that in such a case the Hamiltonian of the systems can be written as a sum of independent terms, each one having the form of a Hamiltonian for a harmonic oscillator of some frequency. We recall that the harmonic oscillator energy can be written as $n\hbar\omega$, with $n = 0, 1, 2, \dots$ (we have omitted the zero point energy). Thus, we can consider our system as made of oscillators having energy $\hbar\omega$ having an occupation number n for each of the oscillators. A state of the free electromagnetic field can then be specified by the number n , the occupation number, for each of the oscillators. This "oscillators" correspond to the concept of photons - single particles of energy $\hbar\omega$ and n can be thought as the number of photons.

The photon gas and the *black body* correspond to the same concept. In fact, a black body is defined as one which absorbs all the radiation incident upon it (a perfect absorber). It also emits the radiation subsequently. If radiation is falling on a black body, its temperature rises until it reaches equilibrium with the radiation. At equilibrium it re-emits as much radiation as it absorbs so there is no net gain in energy and the temperature remains constant. In this case the surface is in equilibrium with the radiation and the temperature of the surface must be the same as the temperature of the radiation. An everyday example of a photon gas is the background radiation in the universe. This photon gas is at a temperature of 2.73 K.

A key feature of the photon gas is that it has a variable particle number and unlike the ideal gas, for which there are three independent variables, N , T , and V , the photon gas has just two independent, controllable variables, T and V . This leads to an essential difference between the photon gas and the ideal gas of molecules: for an ideal gas, an isothermal expansion would

conserve the gas energy, whereas for the photon gas, it is the energy density which is unchanged, the number of photons is not conserved, but proportional to volume in an isothermal change. This is easy to imagine considering an empty piston with zero volume at a given temperature (in contact with a thermal bath). When we increase the volume of the piston quasi statically by pulling, we will generate a photon gas with increasing number of photons which locally will be in equilibrium with the reservoir at temperature T . consequently the photon gas will have a constant energy density dictated by its temperature.

Photons are particle of integer spin (0) and then obey Bose-Einstein statistics. We also note that in the photon gas, photons do not interact between them. This follows from the linearity of Maxwell's equations which allows to superimpose electromagnetic fields (we are nevertheless neglecting an extremely small quantum-mechanical effect which leads to photon-photon scattering). In other word the photon gas is a perfect B-E gas of photons.

The partition function of the photon gas can then be written:

$$Z = Z_{\text{ph}}(T, V) = \sum_{\mathbf{v}} e^{-\beta E_{\mathbf{v}}} = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \dots \exp[-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + \dots)] \quad (1.96)$$

where n_j are the occupation numbers of the photon states of energies $\epsilon_j = \hbar \omega_j$. The independence between photons (then, of the exponential terms) allows us to factorize the exponential into independent portions:

$$Z = \prod_j \left(\sum_{n_j=0}^{\infty} e^{-\beta n_j \epsilon_j} \right) \quad (1.97)$$

with the term in brackets corresponding to a geometrical series, giving:

$$Z = \prod_j \left(\frac{1}{1 - e^{-\beta \epsilon_j}} \right) \quad (1.98)$$

From this expression we can derive many interesting quantities. A particularly interesting one is the average value of the occupation number of the j th state, $\langle n_j \rangle$:

$$\begin{aligned} \langle n_j \rangle &= \frac{\sum_{\mathbf{v}} n_j e^{-\beta E_{\mathbf{v}}}}{\sum_{\mathbf{v}} e^{-\beta E_{\mathbf{v}}}} = \frac{\sum_{n_1, n_2, \dots} n_j e^{-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + \dots + n_j \epsilon_j + \dots)}}{Z} = \\ &= \left[\frac{\partial}{\partial(-\beta \epsilon_j)} \sum_{n_1, n_2, \dots} e^{-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + \dots + n_j \epsilon_j + \dots)} \right] / Z = \\ &= \frac{\partial \ln Z}{\partial(-\beta \epsilon_j)} \end{aligned} \quad (1.99)$$

we now replace the obtained value of Z and we obtain:

$$\begin{aligned} \langle n_j \rangle &= + \frac{\partial}{\partial(-\beta \epsilon_j)} \left[\sum_j -\ln(1 - e^{-\beta \epsilon_j}) \right] = \\ &= e^{-\beta \epsilon_j} / (1 - e^{-\beta \epsilon_j}) \end{aligned} \quad (1.100)$$

which can be written

$$\langle n_j \rangle = \frac{1}{e^{\beta \epsilon_j} - 1} \quad (1.101)$$

which is known as the *Planck distribution function*.

1.7.2 Planck's radiation law

We can now combine this result with the obtained number of photons states in which the photon frequency is in the range ω to $\omega + d\omega$ (see Eq. 1.131 from the complements at the end of this chapter):

$$f(\omega)d\omega = \frac{V\omega^2 d\omega}{\pi^2 c^3} \quad (1.102)$$

Combining this equation with the Planck distribution function and taking into account that for a photon $\varepsilon = \hbar\omega$, we obtain for the number of photons in the frequency range ω to $\omega + d\omega$:

$$dN_\omega = \frac{V}{\pi^2 c^3} \frac{\omega^2 d\omega}{\exp(\beta\hbar\omega) - 1} \quad (1.103)$$

and consequently, for the energy of the radiation in this frequency range:

$$dE_\omega = \hbar\omega dN_\omega = \frac{V\hbar}{\pi^2 c^3} \frac{\omega^3 d\omega}{\exp(\beta\hbar\omega) - 1} \quad (1.104)$$

which allows to obtain the photon energy density in the cavity:

$$u(\omega, T)d\omega = \frac{\hbar\omega^3 d\omega}{\pi^2 c^3 [\exp(\beta\hbar\omega) - 1]} \quad (1.105)$$

This is the Planck's radiation law which, as we have underlined, only depends on the temperature of the cavity and it is independent of its shape and volume. This law gives a description of the black-body radiation in perfect agreement with experiments.

1.7.3 The properties of black-body radiation

In Fig. 1.11 we can see the Planck's radiation law of eq. 1.105 represented at different temperatures (from 3000 to 6000 K). The maximum of the intensity shifts to shorter wavelengths (higher energies) as the black-body temperature increases.

The evolution of $\lambda_{\max}$ or $\nu_{\max}$ can be found by deriving the above expression:

$$\frac{\partial u(\omega, T)}{\partial \omega} = 0 \quad \longrightarrow \quad (3-x)e^x = 3 \quad \text{with} \quad x \equiv \beta\hbar\omega_{\max} = \beta\hbar\nu_{\max} \quad (1.106)$$

This last equation in x is a transcendental equation needing a graphical or numerical solution, which result is:

$$x = \frac{\hbar\omega_{\max}}{k_B T} = \frac{\hbar\nu_{\max}}{k_B T} = 2.822 \quad \implies \quad \lambda_{\max} = \frac{2\pi\hbar}{2.8k_B} \frac{1}{T} = 2.89777 \times 10^6 \text{ nmK/T} \quad (1.107)$$

which is known as Wien's displacement law. This law is extremely well confirmed by experiments and is used as a fast method for calibration of the temperature of hot bodies.

To obtain the total energy density of the black-body radiation at a given temperature, $u(T)$, we need to integrate eq. 1.105 over all frequencies, ω . This gives:

$$u(T) = \int_0^\infty u(\omega, T)d\omega = \alpha T^4 \quad (1.108)$$

with the α value being:

$$\alpha \equiv \frac{\hbar}{\pi^2 c^3} \left(\frac{k_B}{\hbar} \right)^4 \int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\pi^4 k_B^4}{15\hbar^3 c^3} \quad (1.109)$$

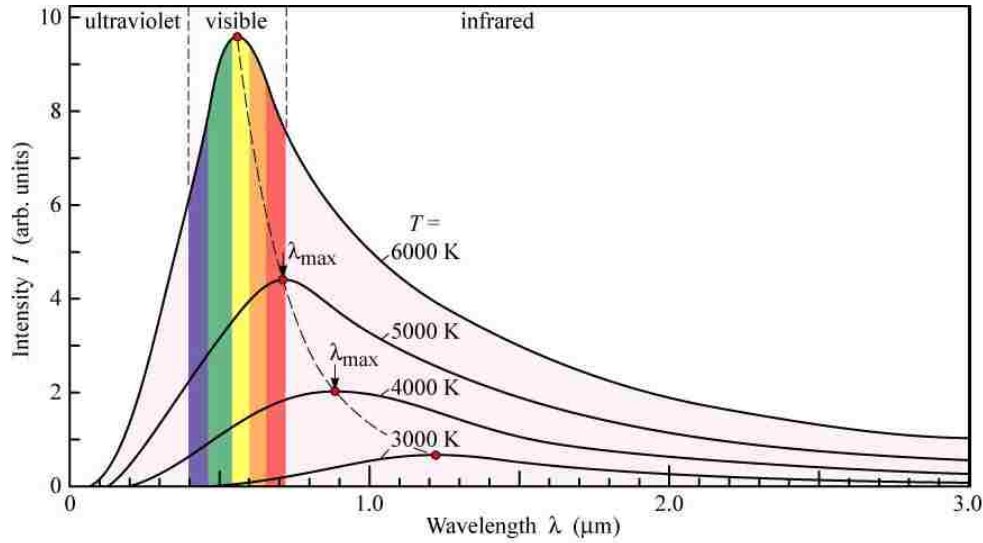


Figure 1.11: Spectral intensity distribution of Planck's black-body radiation as a function of wavelength for different temperatures. The visible region of the spectrum is underlined. Wien displacement law, i.e., the $1/T$ dependence of $\lambda_{\max}$ is also shown (dashed line)

where the value of the integral in the above equation is $I = \pi^4/15$. (see its solution for instance in annex A of Mandle).

Equation 1.108 is the Stefan-Boltzmann law and the constant

$$\sigma \equiv \frac{c}{4} \alpha = \frac{\pi^2 k_B^4}{60 \hbar^3 c^2} = 5.67 \times 10^{-8} \text{ J m}^{-2} \text{ s}^{-1} \text{ K}^{-4} \quad (1.110)$$

is the Stefan-Boltzmann constant. The Stefan-Boltzmann law, $u(T) \propto T^4$, was first obtained experimentally by Joseph Stefan in 1879. Boltzmann, his student, derived theoretically the T^4 dependence using thermodynamic methods. Of course he could not obtain the constant of proportionality which involves Planck's constant.

The reason why σ and not α is called the Stefan-Boltzmann constant is that the total energy radiated per unit of time from a small hole of area A in a black-body is $\sigma T^4 A$. In fact, the kinetic theory of gases can show that $cu(T)/4 = \sigma T^4$ is the energy incident per unit area and time in the walls of the enclosure of the black-body.

1.8 Complements. The density of states

Confinement of particles which can be described with wave equations leads to the discretization of their allowed states. We are going first to quantify such discretization and then determine the associated density of states in the 3D case. We could apply here directly the von Karman periodic conditions previously studied. We will first show that it is also possible to use the quantization in a box as an equivalent approach.

1.8.1 Quantization of the states of waves in a box

For particles in a one-dimensional box of length L , we can take the $V(x) = 0$ inside the box to write the Schrödinger equation as:

$$i\hbar \partial_t \Phi(x, t) = -\frac{\hbar^2}{2m} \partial_x^2 \Phi(x, t) \quad (1.111)$$

Considering stationary waves solutions of the form $\Phi(x, t) = \phi(x)e^{-iEt/\hbar}$ we obtain:

$$\frac{d^2}{dx^2}\phi(x) + k^2\phi(x) = 0 \quad (1.112)$$

where we have taken advantage of the free particle dispersion curve inside the box ($E = \hbar^2 k^2 / 2m$). The 3-D generalization of this expression is:

$$\nabla^2 \phi(\mathbf{r}) + k^2 \phi(\mathbf{r}) = 0 \quad (1.113)$$

the magnitude of the wave vector $\mathbf{k}$, is related to the wavelength, λ by $k = \frac{2\pi}{\lambda}$. We have, the phase velocity v , related to the frequency, ν , by $v = \lambda \nu$. And in terms of circular frequency: $\omega = 2\pi\nu$. Then we have $v = \omega/k$. If we come back to the 1D case, the solutions for the wave equation will be of the type:

$$\phi(x) = A \sin(k_x x) + B \cos(k_x x) \quad (1.114)$$

and imposing that $\phi(x) = 0$ at $x = -a$ and $x = a$ ($L = 2a$) we have a system of 2 equations which can have 2 classes of solutions:

- Either $B = 0$ and $\sin ka = 0$ which means that $ka = n\pi/2$ with $n \in \mathbb{Z}^*$ and n even.
- Either $A = 0$ and $\cos ka = 0$ which means that $ka = n\pi/2$ with $n \in \mathbb{Z}^*$ and n odd.

So we have

- For even solutions $k_n = n\pi/2a$ with $n = 1, 3, 5, \dots$ since $\cos(n\pi a/2a) = \cos(n\pi/2) = 0$
- For odd solutions $k_n = n\pi/2a$ with $n = 2, 4, 6, \dots$ since $\sin(n\pi a/2a) = \cos(n\pi/2) = 0$

The normalizing conditions on the wavefunctions makes that $A = B$.

We then have solutions corresponding to the odd and even values of n :

- $\phi(x) = A \cos(k_n x)$ with $k_n = n\pi/L$ and $n = 1, 3, 5, \dots$
- $\phi(x) = A \sin(k_n x)$ with $k_n = n\pi/L$ and $n = 2, 4, 6, \dots$

where we have replaced $2a = L$. Which are wavefunctions representing stationary states of the particle in the box. The generalization to 3D then leads to a discretization of vector $\mathbf{k}$ states of the form:

$$\mathbf{k} = \left(\frac{\pi}{L} n_1, \frac{\pi}{L} n_2, \frac{\pi}{L} n_3 \right) \quad n_1, n_2, n_3 = 1, 2, \dots \quad (1.115)$$

As already describe, the $\mathbf{k}$ -space is the 3-D space with the components k_x, k_y, k_z as Cartesian axes. Then, for confined waves, not all $\mathbf{k}$ -space values are allowed. In our case, the allowed $\mathbf{k}$ -values form a cubic lattice spaced by π/L and defined only in one octant of the space (n_i values are positive). Then the volume of $\mathbf{k}$ -space associated to an allowed $\mathbf{k}$ -value is $(\pi/L)^3$. In other words, the density of allowed $\mathbf{k}$ -values in $\mathbf{k}$ -space is $(L/\pi)^3$ per unit of volume of $\mathbf{k}$ -space.

1.8.2 Density of states

We are willing to determine the number of waves, $\phi_{n_1, n_2, n_3}(\mathbf{r})$ having wave vectors whose magnitude lies in the interval k and $k + dk$. This number corresponds to the number of $\mathbf{k}$ -points in $\mathbf{k}$ -space lying between two spherical shells or radii k and $k + dk$ in the positive octant (as $k_x > 0, k_y > 0, k_z > 0$, corresponding to $n_i > 0$). This situation is depicted in Fig. 1.12. The volume between the two octants of spheres is $\frac{1}{8}4\pi k^2 dk$, so the number of standing waves having wavevectors between k and $k + dk$ is

$$f(k)dk = \frac{\frac{1}{8}4\pi k^2 dk}{\left(\frac{\pi}{L}\right)^3} = \frac{V k^2 dk}{2\pi^2} \quad (1.116)$$

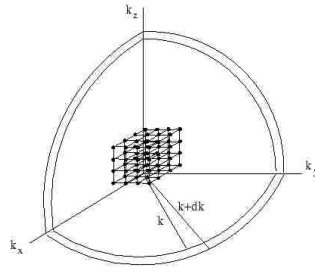


Figure 1.12: $\mathbf{k}$ -space positive octant showing two spherical shells or radii k and $k + dk$.

with $V = L^3$. Alternatively, the number of states with frequencies comprised between ω and $\omega + d\omega$ will take the form:

$$f(\omega)d\omega = \frac{Vk^2}{2\pi^2} \frac{dk}{d\omega} d\omega \quad (1.117)$$

We note that $f(k)$ and $f(\omega)$ represent different functions. The group velocity is defined:

$$v_g = \frac{d\omega}{dk} \quad (1.118)$$

and then using $v = \omega/k$ to replace k :

$$f(\omega)d\omega = \frac{V\omega^2 d\omega}{2\pi^2 v^2 v_g} \quad (1.119)$$

In the case of a non-dispersive medium, i.e., if $v = v_g$:

$$f(\omega)d\omega = \frac{V\omega^2 d\omega}{2\pi^2 v^3} \quad (1.120)$$

We may want to make some comments to our derivation:

- We have made an error by dividing the volume of the spherical shell by that of a cube of side π/L . It is not difficult to show that this error is negligible as soon as $\lambda \ll L$.
- We have derived the above expressions for the case of a cube. The obtained results can be generalized to any arbitrary form, depending finally only on the volume and being independent of the shape of the enclosure.
- It is possible to derive similar results for more general differential equations as for instance $\nabla^2 \phi(\mathbf{r}) + p[k^2 - U(\mathbf{r})]\phi(\mathbf{r}) = 0$ which is the Schrödinger equation for a particle in a potential (and not only for free particles).

We also note that the obtained results are largely independent of the detailed form of the boundary conditions imposed by the surface of the enclosure. We could in particular have adopted the equivalent to the von Karman conditions:

$$\left. \begin{aligned} \phi(0, y, z) &= \phi(L, y, z) \\ \phi(x, 0, z) &= \phi(x, L, z) \\ \phi(x, y, 0) &= \phi(x, y, L) \end{aligned} \right\} \quad (1.121)$$

Which leads to the solution

$$\phi_{n_1, n_2, n_3}(\mathbf{r}) = A \exp(i\mathbf{k}\mathbf{r}) \quad (1.122)$$

with the wavevectors, as we saw, restricted to:

$$\mathbf{k} = \left(\frac{2\pi}{L}n_1, \frac{2\pi}{L}n_2, \frac{2\pi}{L}n_3 \right) \quad n_1, n_2, n_3 = \pm 1, \pm 2, \dots \quad (1.123)$$

The spacing between lattice points is now $2\pi/L$ and the calculation of the density of states is not restricted to one octant as the n_i values can be positive or negative. We then obtain:

$$f(k)dk = \frac{4\pi k^2 dk}{\left(\frac{2\pi}{L}\right)^3} = \frac{Vk^2 dk}{2\pi^2} \quad (1.124)$$

which is exactly the same result as for the precedent case.

1.8.3 Schrödinger free waves in a box

In the case of free particles of mass m , i.e., with zero potential, the Schrödinger equation corresponds to the first case solved in this annex. The energy and momentum of the particle will be then related to the particle by:

$$E = \frac{p^2}{2m}, \quad \mathbf{p} = \hbar \mathbf{k} \quad (1.125)$$

We can then replace

$$f(k)dk = \frac{Vk^2 dk}{2\pi^2} \longrightarrow f(p)dp = \frac{V4\pi p^2 dp}{h^3} \quad (1.126)$$

where $h = 2\pi\hbar$

1.8.4 Electromagnetic waves

The electric field $\mathcal{E}(\mathbf{r}, t)$ of an electromagnetic wave in vacuum travels at the speed of light, c , and verifies the equation

$$\nabla^2 \mathcal{E}(\mathbf{r}, t) - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \mathcal{E}(\mathbf{r}, t) = 0 \quad (1.127)$$

the speed of light is independent of the frequency (there is no dispersion). Considering plane-waves:

$$\mathcal{E}(\mathbf{r}, t) = \mathcal{E}(\mathbf{r})e^{-i\omega t} \quad (1.128)$$

the wave-equation becomes:

$$(\nabla^2 + k^2)\mathcal{E}(\mathbf{r}) = 0 \quad (1.129)$$

with $\omega = kc$ From Eq. 1.129 we may expect to find three independent solutions for a given wave vector $\mathbf{r}$. Nevertheless, Maxwell equations, through the Gauss equation in vacuum, introduces a supplementary constraint:

$$\vec{\nabla} \cdot \mathcal{E}(\mathbf{r}) = 0 \quad (1.130)$$

which reduces the number of solutions to two (and not three), which correspond to the two polarizations of light. Then the number of normal modes of electromagnetic waves in a cavity of volume V is given by:

$$f(\omega)d\omega = \frac{V\omega^2 d\omega}{\pi^2 c^3} \quad (1.131)$$

1.8.5 Sommerfeld Expansion

We are here going to describe an approximation method developed by Arnold Sommerfeld for some characteristic integrals which appear often in statistical physics calculations applied to condensed matter physics. In particular we will apply the method to determine the temperature corrections to the chemical potential with respect to the Fermi energy.

We are often dealing with integral expressions as :

$$E = \int_0^{\infty} \epsilon f_{FD}(\epsilon, T) g(\epsilon) d\epsilon \quad (1.132)$$

or

$$n = \int_0^{\infty} f_{FD}(\epsilon, T) g(\epsilon) d\epsilon \quad (1.133)$$

where E is the internal energy (total energy), n the number of electrons, $f_{FD}(\epsilon, T)$ the Fermi-Dirac distribution function and $g(\epsilon)$ is the density of states. If $g(\epsilon)$ is normalized per unite of volume, so it does the internal energy and the number of particles.

We can write $f_{FD}(\epsilon, T)$:

$$f_{FD}(\epsilon, T) = \frac{1}{\exp(\beta\epsilon - \beta\epsilon_F) + 1} \quad (1.134)$$

the integrals 1.132 and 1.133 are easy to compute if $T=0$, as in that case the Fermi-Dirac distribution function is just a Heaviside function. If $T > 0$, there is no analytical expression for the above mentioned integrals and we need to use an approximative method.

Integrals 1.132 and 1.133 are both of the form:

$$I = \int_0^{\infty} h(x) f_{FD}(x, \mu) dx = \int_0^{\infty} \frac{h(x)}{e^{x-\mu} + 1} dx \quad (1.135)$$

where x replaces $\beta\epsilon$ and μ (here nothing to do with the chemical potential) replaces $\beta\epsilon_F$

As already discussed, in most condensed matter problems, $T_F \gg T$ and for $\epsilon < \epsilon_F$, f_{FD} is equal to 1 except for a small region around ϵ_F (recall figure 1.5.b).

Then the difference

$$\int_0^{\infty} h(\epsilon) f_{FD}(\epsilon, \mu) d\epsilon - \int_0^{\infty} h(\epsilon) d\epsilon = \int_0^{\infty} h(\epsilon) [f_{FD}(\epsilon, \mu) - 1] d\epsilon \quad (1.136)$$

which is zero except for $\epsilon \approx \epsilon_F$. If $h(x)$ is a smooth function of ϵ around ϵ_F , then we may replace its value by its Taylor development around ϵ_F . Equivalently we can take such expansion on $H(x)$, defined as $h(x) = dH(x)/dx$. We have then:

$$H(\epsilon_F) = \sum_{n=0}^{\infty} \frac{d^n}{d\epsilon^n} H(\epsilon) \Big|_{\epsilon=\epsilon_F} \frac{(\epsilon - \epsilon_F)^n}{n!} \quad (1.137)$$

and

$$\int_0^{\infty} \frac{h(x)}{e^{x-\mu} + 1} dx = \int_0^{\infty} \frac{dH(x)}{e^{x-\mu} + 1} = \quad (1.138)$$

which can be solved by integration by parts, $\int u dv = uv - \int v du$:

$$u = \frac{1}{e^{x-\mu} + 1} \rightarrow du = \frac{-e^{x-\mu}}{(e^{x-\mu} + 1)^2} dx ; dv = dH(x) \rightarrow v = H(x) \quad (1.139)$$

$$= \left[\frac{H(x)}{e^{x-\mu} + 1} \right]_0^\infty + \int_0^\infty \frac{e^{x-\mu} H(x)}{(e^{x-\mu} + 1)^2} dx = \quad (1.140)$$

The first term of this expression is obviously zero when $x \rightarrow \infty$. It is also zero at $x = 0$ in the cases we are considering here. In fact $H(x) = dh(x)/dx$ with $h(E)$ being proportional to the density of states. The density of states is proportional to ε^m with $m = -1/2, 0$ and $1/2$ respectively in 1D, 2D and 3D, then leading to $H(0) = 0$. We are then just left with the second term of the last expression

$$\int_{-\infty}^\infty \frac{e^{x-\mu} H(x)}{(e^{x-\mu} + 1)^2} dx \quad (1.141)$$

where we have changed the inferior limit of the integral to $-\infty$ taking into account that the density of states is zero for $\varepsilon < 0$. Making now the change of variable $x' = x - \mu$ we have:

$$\int_{-\infty}^\infty \frac{e^{x'} H(x' + \mu)}{(e^{x'} + 1)^2} dx' \quad (1.142)$$

$$e = -\frac{\Delta\Phi_B}{\Delta t} \quad (1.143)$$

We proceed now with the Taylor development:

$$\begin{aligned} H(x' + \mu) &= H(\mu) + x' H'(\mu) + \frac{x'^2}{2!} H''(\mu) + \dots = H(\mu) + (x' \delta) H(\mu) + \frac{(x' \delta)^2}{2} H(\mu) + \dots = \\ &= \left[1 + x' \delta + \dots + \frac{(x' \delta)^n}{n!} \right] H(\mu) = e^{x' \delta} H(\mu) \end{aligned} \quad (1.144)$$

where we have introduced the differential operator, δ .

We have then:

$$I = \int_{-\infty}^\infty \frac{e^{x'} e^{x' \delta}}{(e^{x'} + 1)^2} H(\mu) dx' = H(\mu) \int_0^\infty \frac{u u^\delta}{(u+1)^2} \frac{du}{u} = H(\mu) \int_0^\infty \frac{u^\delta}{(u+1)^2} du \quad (1.145)$$

where we have made the change of variable $u = e^{x'}$; $du = e^{x'} dx'$; $dx' = du/u$.

Again we integrate by parts the integral:

$$\int_0^\infty \frac{x^\delta}{(1+x)^2} dx = \left[\frac{-x^\delta}{1+x} \right]_0^\infty + \delta \int_0^\infty \frac{x^{\delta+1}}{1+x} = 0 + \frac{\delta \pi}{\sin \delta \pi} \quad (1.146)$$

where we have taken $u = x^\delta$ and $dv = dx/(1+x)^2$ to integrate by parts and we have taken into account that the last integral is a known one ($\int_0^\infty \frac{x^{\delta+1}}{1+x} = \frac{\pi}{\sin \delta \pi}$).

We then have:

$$I = H(\mu) \frac{\pi\delta}{\sin\delta\pi} = H(\mu) \left[1 + \frac{\pi^2\delta^2}{6} + \dots \right] \quad (1.147)$$

where we have used the expansion $1/\sin x = 1/x [1 + x^2/6 + 7x^4/360 + \dots]$.
Our final result is then:

$$I = \int_0^\infty h(x) f_{FD}(x, \mu) dx = H(\mu) \left[1 + \frac{\pi^2\delta^2}{6} + \dots \right] \quad (1.148)$$

with $H(x) = \int h(x) dx$

We consider now the case of a 3-D electron system. In this case the density of states can be written as (see 1.66), $g(\epsilon) = A\epsilon^{1/2}$ and $g'(\epsilon) = 1/2 A\epsilon^{-1/2}$. We take $h(x) = g(\beta\epsilon)$. We have then:

$$\int_0^\infty \frac{h(x)}{e^{x-\mu} + 1} dx = H(\mu) \left[1 + \frac{\pi^2\delta^2}{6} + \dots \right] = H(\mu) + \frac{\pi^2}{6} h'(\mu) \quad (1.149)$$

where as was discussed $x = \beta\epsilon$ and $\mu = \beta\epsilon_F$ and then we have:

$$\begin{aligned} h(\mu) &= g(\beta\epsilon) = A\beta^{1/2} \epsilon^{1/2} \\ H(\mu) &= \int_0^\mu h(x) dx = \int_0^{\epsilon_F} \beta g(\beta\epsilon) d\epsilon \end{aligned} \quad (1.150)$$

we can then write replacing in 1.149

$$\beta^{3/2} \int_0^\infty \frac{g(\epsilon)}{e^{\epsilon-\epsilon_F} + 1} dx = \beta^{3/2} \int_0^{\epsilon_F} g(\epsilon) d\epsilon + \frac{\pi^2}{6} \beta^{-1/2} g'(\epsilon_F) \quad (1.151)$$

which simplifies to

$$\int_0^\infty \frac{g(\epsilon)}{e^{\epsilon-\epsilon_F} + 1} dx = \int_0^{\epsilon_F} g(\epsilon) d\epsilon + \frac{\pi^2}{6\beta^2} g'(\epsilon_F) \quad (1.152)$$

or in its more general form, for any other function $H(E)$

$$\int_0^\infty \frac{H(\epsilon)}{e^{\epsilon-\epsilon_F} + 1} dx \approx \int_0^{\epsilon_F} H(\epsilon) d\epsilon + \frac{\pi^2}{6} k_B T^2 H'(\epsilon_F) \quad (1.153)$$

If we consider free electrons in a solid, we can apply the obtained results to determine the effect of temperature on the Fermi energy.

For this, we apply Eq. 1.153 to the case $H(E) = \rho(E)$. The left side of the equation is then just the number of free electrons in the considered system, n :

$$n = \int_0^\infty \rho(\epsilon) f(\epsilon) d\epsilon \quad (1.154)$$

We consider that this number, n is fixed and then we can calculate it easily at $T = 0$ K:

$$n = \int_0^{\epsilon_F} \rho(\epsilon) d\epsilon \quad (1.155)$$

In fact, replacing $g(\epsilon) = A\epsilon^{1/2}$, we have $n = 2/3 A \epsilon_{F0}^{2/3}$. Here ϵ_{F0} is the Fermi energy at 0 K. Then 1.153 becomes:

$$2/3 A \epsilon_{F0}^{2/3} = 2/3 A \epsilon_F^{2/3} + \frac{\pi^2}{6} k_B T^2 \frac{1}{2} A \epsilon_F^{-1/2} + O(T^4) \quad (1.156)$$

with the final result:

$$\epsilon_F = \epsilon_{F0} \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\epsilon_{F0}} \right)^2 - O(T^4) \right] \quad (1.157)$$

In previous sections, we referred to the Fermi energy at any temperature as the chemical potential, μ , and to the Fermi energy being just defined at zero Kelvin, i.e. $\epsilon_{F0} \equiv \epsilon_F$ so we can also write equivalently:

$$\mu = \epsilon_F \left[1 - \frac{1}{3} \left(\frac{\pi k_B T}{2 \epsilon_F} \right)^2 - O(T^4) \right] \quad (1.158)$$

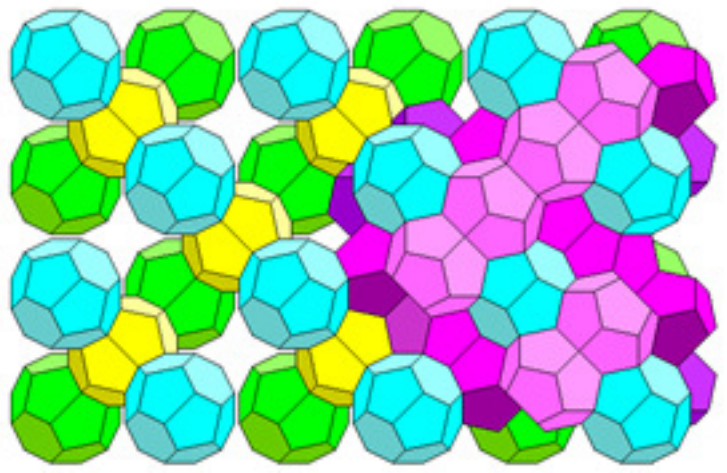
which corresponds to the expression given in 1.58.

In an analogous way, we may determine the temperature correction for the total energy of the 3-dimensional Fermi sea, by taking $h(\epsilon) = \epsilon \rho(\epsilon)$ and obtain:

$$E = E_0 \left[1 + \frac{5\pi^2}{12} \left(\frac{k_B T}{2 \epsilon_F} \right)^2 + O(T^4) \right] \quad (1.159)$$

where E_0 is here the total energy at 0 K.

In both cases, the corrections are important when the Fermi temperature becomes comparable to the considered temperature of the system. As already discussed the Fermi temperature is well above the melting temperature in metals at ambient pressures. Then, except for very fine calculations, the temperature correction may be discarded. White dwarfs are stellar systems in which the electron gas is particularly important as it determines a pressure which conditions its stability. In white dwarfs, $T \sim 25000$ K (for instance for Sirius B), but at the same time the electron density is extremely high leading to Fermi energies close to GeV (from eq. 1.50 one can calculate the Fermi energy from the electron density). Again, here, for white dwarfs, temperature corrections are small. Nevertheless at such high energies the associated Fermi velocity becomes relativistic and needs to be corrected.



2. Crystalline solids

2.1 Introduction

The word "crystal" will have for us a different meaning than from daily life. In solid state physics, a crystal structure is a unique periodic arrangement of atoms or molecules. This periodic arrangement can manifest at the microscopic scale as in the beautiful facets of some natural or artificially grown crystals. Nevertheless such order exists in many materials not exhibiting any apparent sign of it, as in a copper wire.

The physical quantity deciding which crystalline structure will be adopted by a given set of atoms is the cohesive energy. The most stable structure is the one minimizing that quantity. Which crystalline structure depends on the thermodynamic conditions (Pressure, Temperature,...) and consequently structural changes, i.e., phase transitions, can take place when pressure and temperature are varied. The cohesive energy of a crystal is the energy needed to separate the condensed matter system into its constitutive elements, which can be either atoms or molecules. In the case of a molecular crystal (a crystal made of molecules as ice), the usual convention is to consider the molecules as the building blocks of the crystal. By "separation" we mean to put these building blocks far enough one from the other in such a way that all interactions can be neglected.

In this chapter we will discuss first the cohesive energy of crystalline solids in terms of bonding energies. Then we will explore the most important definitions and concepts needed to study crystalline materials.

2.2 The cohesive energy

We will not discuss in this chapter temperature effects which modify the cohesive energy and will need to introduce the Helmholtz energy as well as entropic terms. All calculations in this chapter will be done at $T = 0\text{K}$

The cohesive energy determines the most stable crystalline structure at the given thermodynamic conditions of temperature and pressure. The structure with the lowest (the most negative) cohesive energy is the stable structure in these conditions. For instance at ambient conditions, graphite is the stable structure of carbon. In some cases, it is possible to find in the same thermodynamic conditions other crystalline structures different from the stable one.

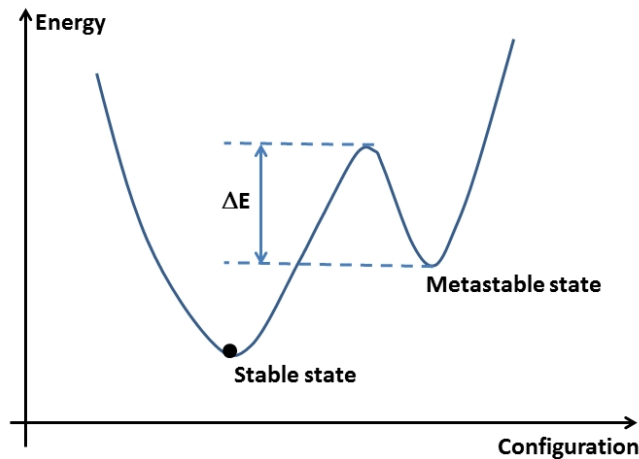


Figure 2.1: Sketch showing the cohesive energy of a system of atoms or molecules as function of the "configuration". By "configuration" we mean a generalized system of coordinates which determines the relative spatial position of the different atoms or molecules.

They are called *metastable* structures, as is the case of diamond or fullerene crystals for the carbon case. The coexistence of these different *polytypes* (structures having the same chemical composition) in the same thermodynamic conditions is explained by the existence of kinetic energy barriers, ΔE which has shown in Fig. 2.1 can be overcome for instance by thermal energy. The cohesive energy is intimately linked to the bond-energy. The bond energy is mainly determined by the predominant interaction type between atoms and molecules. In that respect we can distinguish 5 main types of interactions:

- **Covalent bond** characterized by the spatial localization of the bond electronic density in the bond direction. Covalent crystals are better described within the LCAO model.
- **Metallic bond** The wavefunctions of the conduction electrons are delocalized in the whole crystal and interact with the ions. These crystals can be well described within the quasi-free electron model.
- **Ionic bond** Better described through a coulombian interaction.
- **Hydrogen bond** Interaction between dipoles made of hydrogen and a strong electronegative atom.
- **van der Waals bond** Interaction between static or dynamic dipoles

In the following table are shown some values of the cohesive energy per atom or molecule in some crystals.

As example of metastable structures, with respect to the graphite structure, carbon in its diamond, nanotubes (with diameters larger than 1 nm) or fullerene crystalline arrangements shows a cohesive energy difference of 0.02, 0.05 or 0.37 eV/atom respectively. This is the energy difference between the graphite minimum in Fig. 2.1 (stable state) and the minimum of the alternative structure (metastable state).

2.3 van der Waals interactions

The origin of the van der Waals interaction is the electrostatic dipole-dipole interaction which can have 3 different origins:

1) Orientation effect or Keesom interaction. This is due to the interaction between two permanent

Crystal	Energy (eV/atom)
Covalent	
Si	4.7
C (graphite)	7.4
Metallic	
Hg	0.7
Fe	4.2
W	8.8
Ionic	
NaCl	3.3
MgO	5.2
Hydrogen	
NH ₃	0.36
H ₂ O	0.52
van der Waals	
Ar	0.08
Cl ₂	0.32

Table 2.1: Cohesive energy of some crystals

dipoles, μ_1 and μ_2 separated by a distance R . The associated interaction energy is given by:

$$E_K = -\frac{1}{k_B T} \frac{\mu_1^2 \mu_2^2}{(4\pi\epsilon_0\epsilon)^2} \frac{1}{R^6} \propto \frac{1}{R^6} \quad (2.1)$$

2) Inductive effect or Debye interaction. Due to the interaction of a permanent dipole, μ with the electronic cloud of a non-polar molecule having polarizability α :

$$E_D = -\frac{\mu^2 \alpha}{(4\pi\epsilon_0\epsilon)^2} \frac{1}{R^6} \propto \frac{1}{R^6} \quad (2.2)$$

3) Dispersive effect or London interaction. Due to the fluctuating charges in two non-polar atoms having polarizability α_1 and α_2 :

$$E_L \propto -\alpha_1 \alpha_2 \frac{1}{R^6} \quad (2.3)$$

The three effects can be present simultaneously. The van der Waals energy will be given by:

$$E_{vdW} = E_K + E_D + E_L \propto \frac{1}{R^6} \quad (2.4)$$

The following table gives examples of the importance of the different contributions.

It appears then that the attractive potential energy in the van der Waals interaction decreases rapidly in $1/R^6$. At short distances, the attractive interaction is counterbalanced by a repulsive contribution to the total potential which will be expressed as the sum of both contributions

Crystal	$E_K(\%)$	$E_D(\%)$	$E_L(\%)$	μ (Debye)
Ar	0	0	100	0
HCl	15	5	80	1.03
NH ₃	45	5	50	1.50
H ₂ O	77	4	19	1.83

Table 2.2: The different contributions to the van der Waals energy in 4 crystals. Values are given in percentage of the total van der Waals energy.

(attractive and repulsive). Contributions to the repulsion include the short-distance nuclear-nuclear repulsion and electron-electron repulsions, as well as changes in electronic kinetic energy. The repulsive interaction is often described as being due to the Pauli exchange forces – because of the Pauli Principle, electrons of the same spin and electronic state cannot occupy the same region of space. This reduces electron density between the nuclei, leading to an increase in nuclear-nuclear repulsion. The repulsive component is well modeled by an $1/R^{12}$ potential (positive as it is repulsive). This leads to propose the Lennard-Jones potential as a suitable one to characterize van der Waals interactions by adding the dipole-dipole attractive term to the Pauli repulsive one:

$$V(R) = 4\varepsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right] \quad (2.5)$$

This is a half phenomenological potential, in the sense that, as we will see later, the form of the repulsive term can be determined from experiments, but it is not calculated.

This is a pair potential. In a crystal we will need to consider all pairs of atoms. Due to the very rapid reduction of the interaction potential with distance, the van der Waals potential is then limited just to the first few neighboring atoms interactions.

2.4 Ionic systems

This is usually the main contribution to the cohesive energy in crystals constituted of ions. The van der Waals interaction will contribute too, but it will constitute $\sim 1-2\%$ of the total cohesive energy.

The most important contribution to the cohesive energy, the coulombic part, is called the Madelung energy.

The coulombic potential having a $1/R$ dependence, the ionic interaction has a very long-range nature, involving then a very large number of ions for each ions.

For an ion i , the contribution to the cohesive energy is then:

$$U_i = \sum_{j \neq i} U_{ij} \quad (2.6)$$

with

$$U_{ij} = \lambda \exp\left(\frac{-r_{ij}}{\rho}\right) \pm \frac{1}{4\pi\epsilon_0} \frac{q_i^2}{r_{ij}} \quad (2.7)$$

Here the first term is an alternative semiempirical form of the repulsive potential (Pauli potential) with λ and ρ being parameters. This choice is not important for what follows, as in all cases,

the repulsive part of the potential is only important for first neighbor atoms, as it decreases very rapidly with distance. To make this explicit, we write:

$$U_{ij} = \begin{cases} \lambda e^{-R/\rho} - \frac{1}{4\pi\epsilon_0} \frac{q^2}{R} & \text{for 1st neighbours} \\ \pm \frac{1}{p_{ij}} \frac{1}{4\pi\epsilon_0} \frac{q^2}{R} & \text{for all the others} \end{cases} \quad (2.8)$$

where we have defined $r_{ij} = p_{ij}R$, R being the first neighbors distance.

Then in a system having N positive ions, N negative ions and Z first neighbors atoms we can write:

$$U_{\text{tot}} = NU_i = N \sum_{j \neq i} U_{ij} = N \left(Z\lambda e^{-R/\rho} - \frac{\alpha}{4\pi\epsilon_0} \frac{q^2}{R} \right) \quad (2.9)$$

with

$$\alpha \equiv \sum_{j \neq i} \frac{(\pm)}{p_{ij}} \quad (2.10)$$

α is the *Madelung constant*, which is characteristic of the crystallographic structure as the p_{ij} depend only on the distance relationship between the different shells of ions. A necessary condition for the crystal to be stable is that $\alpha > 0$, otherwise, the crystal will disintegrate due to the Coulombic interaction.

2.4.1 Examples of ionic crystals

Lets consider a simple case, a linear chain of ions made of an alternation of positive and negative ions of the same charge at equal distance, with the first neighbor distance being R . We can then write:

$$\frac{\alpha}{R} = \sum_{j \neq i} \frac{(\pm)}{r_{ij}} = 2 \left[\frac{1}{R} - \frac{1}{2R} + \frac{1}{3R} - \frac{1}{4R} + \dots \right] \quad (2.11)$$

so we have:

$$\alpha = 2 \left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \dots \right] \quad (2.12)$$

Taking profit from the relation:

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \dots \quad (2.13)$$

we have then

$$\alpha = 2 \ln 2 \quad (2.14)$$

In three dimensional crystals, the Madelung constant determination can become more delicate, as depending on how we group the terms in the sum, the series can diverge or we can even find very different results (in mathematics these cases are called conditionally convergent). This reflects the fact that for a given volume the coulombic contribution strongly depends on the surface charge contributions. More elaborated methods (Ewald sums) calculate then the Madelung constant by defining volumes which zero surface charge.

The following table gives the Madelung constant for some important structures:

Structure	Prototype example	Z	α	$(r/R)_{\text{perfect}}$
Zinc Blenda	ZnS	4	1.6381	0.225
Sodium Chloride	NaCl	6	1.7475	0.414
Cesium Chloride	CsCl	8	1.7627	0.73

Table 2.3: Madelung constant, α for some important structures and ionic radius ratio for perfect packing.

We could in principle guess that the more stable structure should then be the one with the higher Madelung constant. The reason that makes that ionic systems also crystallize in the NaCl or ZnS structures is of geometric nature in one side and of electronic one on the other side.

As opposite charges are needed, ionic crystals are composed of two or more ions. The ratio of the ionic ratio between the different species is one of the factors determining the more stable structure. We are going to evaluate this, by considering that the ions can be assimilated to spheres which will need to pack in one or the other structure.

It is interesting in that respect to see that the NaCl and zinc-blend structures can be described as an fcc structure occupied by one of the ions and in which the other ion will either lie in the octahedral interstitial sites (this will give the NaCl structure) or the tetrahedral interstitial sites (giving the ZnS structure). This is shown in Fig. 2.2.

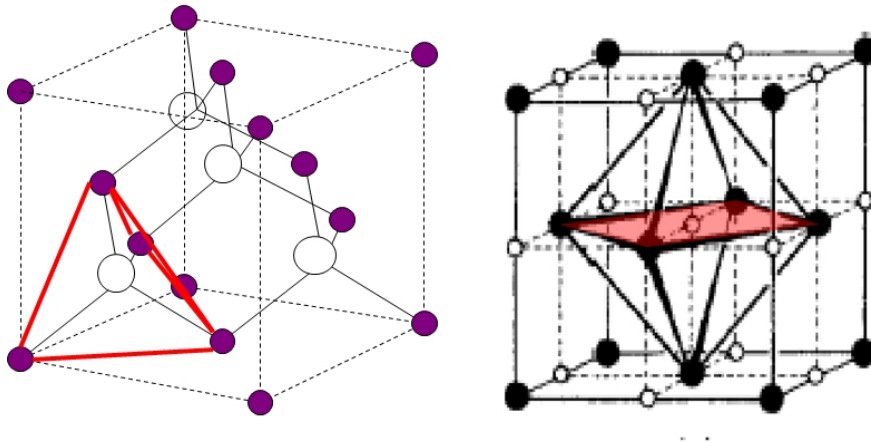


Figure 2.2: ZnS(left) and NaCl(right) structures seen as fcc structures in which the counter-ion has been placed in the interstitial sites of the fcc structure: the tetrahedral one for the ZnS structure and the octahedral one for the NaCl structure

In everyone of the three crystal structures (ZnS, NaCl and CsCl) we can determine the perfect packing condition, i.e. the condition making that the two ions of radius r and R , fill perfectly the space in the structure. Lets consider the case of the NaCl structure. Perfect adjustment will be obtained when the two spheres touch each other in the squared plane depicted at the right of Fig. 2.2.

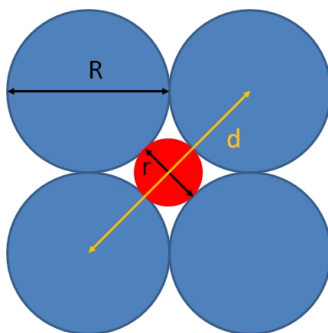


Figure 2.3: Perfect packing in the NaCl structure

This is shown in Fig. 2.3 where we have

$$\begin{cases} d = 2r + 2R \\ d^2 = (2R)^2 + (2R)^2 \end{cases} \quad (2.15)$$

which leads to $r/R = 0.414$. With similar arguments we obtain values of r/R for perfect packing of 0.225 and 0.73 respectively for the ZnS and CsCl structure.

Exercise 2.1 Structure Packing. Calculate the value of r/R for optimum ion packing of the CsCl and ZnS structures).

If we consider the ionic radius in NaCl and CsCl ($r_{\text{Na}^+} = 1.02 \text{ \AA}$, $r_{\text{Cl}^-} = 1.81 \text{ \AA}$, $r_{\text{Cs}^+} = 1.74 \text{ \AA}$) we find $(r/R)_{\text{NaCl}} = 0.563$ and $(r/R)_{\text{CsCl}} = 0.96$ which lie not too far, but higher values than the predicted one. The fact that the calculated r/R in the structure is found bigger than the r/R of the ideal packing in the corresponding structure, means that the packing is favored by larger r which will then reduce the packing by separating the larger ions, until a more favorable packing structure is found. We have then:

$$r/R \quad 0.225 \quad \xrightarrow{Z=4(\text{ZnS})} \quad 0.414 \quad \xrightarrow{Z=6(\text{NaCl})} \quad 0.73 \quad \xrightarrow{Z=8(\text{CsCl})} \quad (2.16)$$

This scheme is of course oversimplified with respect to reality as we are considering anions as perfect spheres. This hypothesis fails when some covalent-type bonding is also participating to the cohesive energy. Important iono-covalent materials crystallize in the ZnS structure, as the III-V (GaAs, GaP) or II-VI semiconductors (ZnS). Some important iono-covalent semiconductors can crystallize in a very similar structure to ZnS having hexagonal symmetry, the würtzite structure as is the case for GaN or CdTe.

2.5 The hydrogen bond

The hydrogen bond is a particular case of polar bond, or dipole-dipole interaction. The reason which makes that it is treated separately from the other van der Waals polar interactions is its strength which is due to the size of the H^+ ion, a proton, which is just 10^{-15} m . This small size, implies that negative ions can found themselves at short equilibrium distance and then in a strong interaction.

Hydrogen bond implies that the proton needs to be found almost "naked" (without electron). In order to do this, the hydrogen atom needs to be bound to a very electronegative atom. It is considered that hydrogen bond is possible when hydrogen is bound either to oxygen(O),

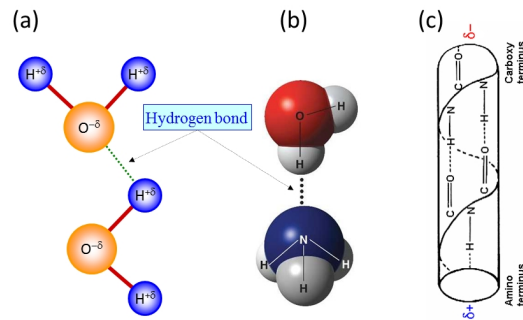


Figure 2.4: Different types of hydrogen bond. (a) homo-molecular in the case of water. (b) Hetero-molecular. (c) Intra-molecular conferring the geometrical stability of the α -helix of a protein.

nitrogen(N) or fluorine(F). This bond is a highly asymmetric covalent bond (iono-covalent) leading to a polar molecule or bond having a high dipole. The hydrogen bond takes place between the H^+ and other polar molecules (case of water) or even inside the molecule (ADN or other biomolecules). In Fig. 2.4 are shown some examples of hydrogen bond. Ionic compounds



Figure 2.5: DFT calculation of the sum of the valence band electron distribution in between two atoms of Germanium (diamond structure), GaAs and ZnSe (zinc blend structure). In germanium the totally symmetric electron charge distribution with a higher concentration in the line relying the two atoms is the sign of the covalent bond. We observe a progressively more ionic character in GaAs (III-V) and ZnSe (II-VI) which translates in the asymmetric electronic distribution.

easily dissolve in solvents like water (H_2O) which are strongly polar due to their hydrogen bonds. The reason is that water molecules strongly interact with the crystal ions to destroy the forces of attraction between the ions. Ionic compounds are insoluble in non-polar solvents like benzene (C_6H_6), carbon tetrachloride (CCl_4), because, being non-polar molecules, their dielectric constants are very low.

2.6 Covalent and metallic systems

We have studied in the previous chapter how the electron wavefunctions can combine either to produce covalent systems (tight binding model) or metallic systems (free electron or quasi-free electron model).

In the case of the covalent bond, the atomic wavefunction of the atoms combine in the LCAO scheme and are then shared between the atoms. This leads to a strong electronic density localization in the direction of the atomic bonds. The calculated electron density for some covalent or iono-covalent systems are shown in Figure 2.5. On the contrary, in metals the electron wavefunctions which participate to the bond are strongly delocalized in the crystal.

The calculation of the cohesion energy for these type of systems can not be done analytically. More advanced numerical methods are then needed. Today, this is done within the framework of the Density Functional Theory (DFT) which is becoming the standard approach to evaluate

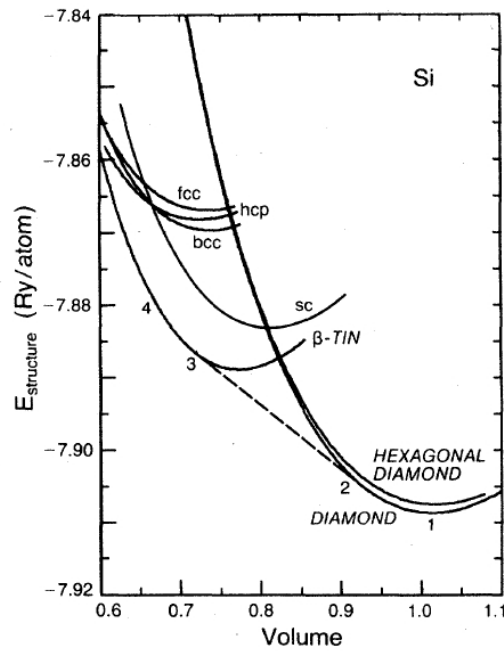


Figure 2.6: DFT calculation of the cohesive energy of silicon in different structures with respect to reduced volume (V/V_0) with V_0 , the volume of the equilibrium structure, diamond, at ambient conditions. The diamond structure of silicon is found to be the lowest energy structure at $V/V_0 = 1$ in good correspondence with observations. When the reduced volume is decreased (which corresponds to an increasing pressure) the β -tin structure (isostructural with white tin, the stable structure of tin between 13 and 162 °C) becomes the stable structure of silicon. This is also in good correspondence with experiments which show the phase transition between the diamond and the β -tin structure of silicon at 11.5 GPa. Other structures are calculated, which are not found to be stable. (from M.T. Yin et M.L. Cohen, Phys Rev B 26 ,5668 (1982))

not only the cohesive energy of solids, but also many of their physical properties including the calculation of the electronic band structure, the phonon dispersion curves, conduction properties, etc.

The DFT theory proposes that the electronic density $n(\vec{r})$ can fully determine the electronic characteristics of the system through functionals, i.e. functions of another function (the $n(\vec{r})$). The basis of the theory were set from 1964 by Hohenberg and Kohn who set the so called Hohenberg–Kohn theorems.

The DFT theory is beyond the scope of this course. We can nevertheless appreciate in Fig 2.6 one result which is the derivation of the cohesive energy of different silicon structures as function of pressure, which allows to predict the sequence of phase transitions.



Figure 2.7: **Video 1.** (scan the QR code with your mobile phone or tablet) This video includes the definition of crystal and lattices and the description of some important crystalline structures

2.7 Crystal structure

A crystal can be described as composed of a lattice and a basis.

Definition 2.7.1 — Lattice. An ensemble of mathematical points all totally equivalent which are defined by translation symmetry through the translation vector :

$$\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3 \quad (2.17)$$

with n_1, n_2 and n_3 integer values and $\vec{a}_i, i = 1, 2, 3$ called the **primitive vectors** or **cell parameters** which lie in different directions and span the lattice.

The space in which the lattice is defined is called **the direct or real space**, as real objects like atoms or molecules lie on it.

Definition 2.7.2 — Basis. Whatever number of atoms or molecules associated to each one of the points of the lattice.

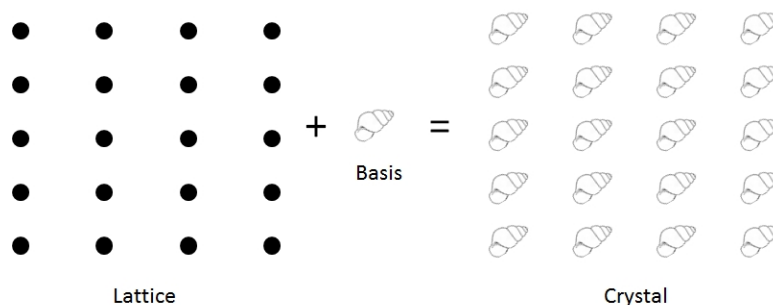


Figure 2.8: A crystal with a non atomic basis.

A basis can contain just one atom which in such a case will usually be defined by coordinates $\vec{r}_1 = (0, 0, 0)$ or can contain thousands of atoms defined by their vector coordinates $\vec{r}_i$. In crystallography lattices are also referred as **Bravais lattices**. Two Bravais lattices are considered as equivalent when the symmetry operations generating the two lattices are the same. Then, there are only 14 possible Bravais lattices in three-dimensional space (see Fig. 2.9).

Definition 2.7.3 — Crystal. A crystal is then defined by a Bravais lattice having associated to each one of its points the same basis:

Crystal = Bravais Lattice + Basis

For a given crystal, the choice of lattice and basis is not unique as illustrated in Figure 2.10. The vectors $\vec{a}_i$, the *cell parameters*, define the cell. If in the crystal only one atom is included in the cell, this is a primitive cell. All unitary cells should have the same surface. A particular and important unitary cell is the Wigner-Seitz cell defined as the locus of points in space that are closer to a lattice point than to any of the other lattice points.

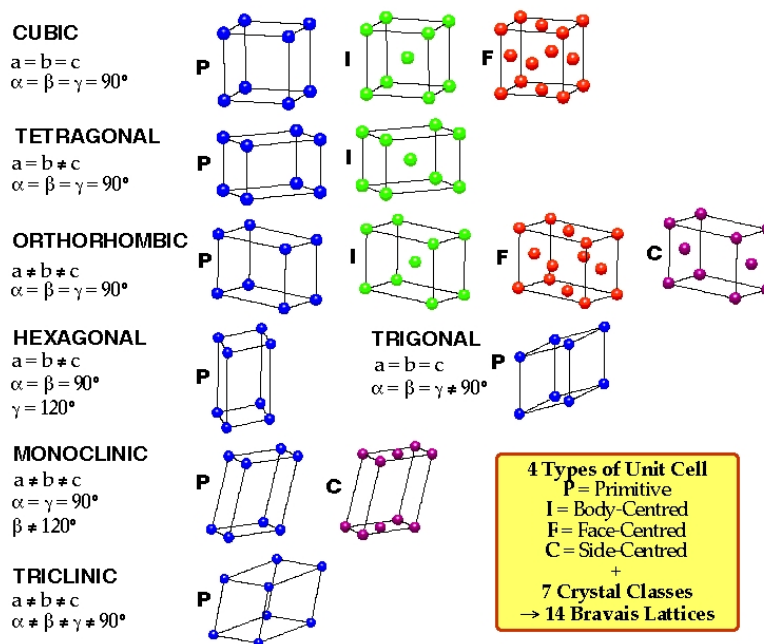


Figure 2.9: The 14 Bravais lattices allowing to describe all 3D crystals. The balls represent not atoms but lattice points. Of course in various particular crystals one atom can be associated to a lattice point.

The lattice points can be grouped in crystallographic planes (or lines in 2-dimensions)

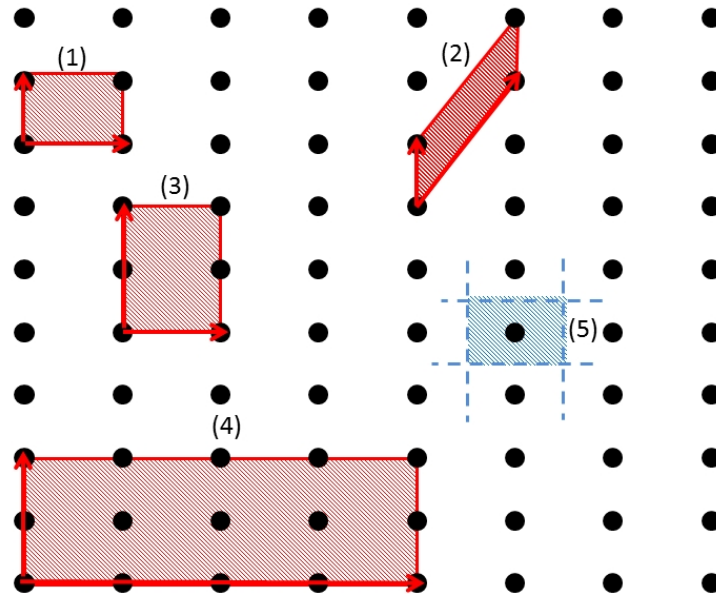


Figure 2.10: Different choices of crystal lattices. Here every dot represents an atom (or a molecule). In (1) and (2) the basis is of only one atom. The associated cells are then unitary cells. In (3) a basis of 2 atoms is needed and in (4) eight atoms are needed to complete the basis. (5) is the Wigner-Seitz cell which is a unitary cell.



Figure 2.11: **Video 2.** (scan the QR code with your mobile phone or tablet) This video includes the following topics :
 - Identification of lattice cells - Other important crystalline structures - Symmetry operations and crystal classification
 - FCC and BCC: primitive and conventional cells

2.8 Diffraction and Reciprocal Space

A number of techniques allow to obtain experimental evidence of the periodicity of atomic structures:

(1) x-ray diffraction (2) neutron diffraction (3) electron diffraction (4) High resolution electron microscopy (5) Atomic force microscopy

(1) and (2) can probe the full crystalline structure, whereas (3), (4) and (5) tend to probe the atoms closer to the surface or even just the surface atoms.

The principle of a diffraction experiment is depicted in Figure 2.12. As it will be later discussed, there are different geometries for such experiments depending on the sample and radiation characteristics.

The two basic and equivalent formulations of the diffraction process are the Bragg law and the Laue law.

In the Bragg point of view, the incoming beam of wavelength λ is scattered elastically by two planes of scatterers (atoms or molecules in general) separated by a distance d , corresponding to a given inter-reticular distance. As shown in Fig. 2.13., the difference of optical path between the beam scattered by the two first planes is $\Delta = XYZ$ (beam 2 lags beam 1 by XYZ). If the beam impinges on the crystal surface with an angle of θ , $\Delta = 2d \sin \theta$. The diffraction condition

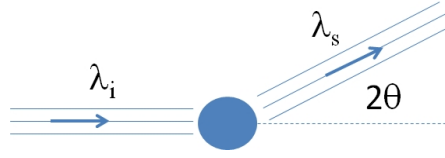


Figure 2.12: Principle of a diffraction experiment. The incoming beam characterized by a wavelength λ_i is scattered by the sample in the direction 2θ with a wavelength λ_s . Diffraction is an elastic process and then $\lambda_i = \lambda_s$. In practice the experiment is designed to determine all the scattering angles needed to obtain the sample structural information.

corresponds to a constructive interference between the 2 beams, i.e., $\Delta = n\lambda$. Then the Bragg condition writes:

$$2d \sin \theta = n\lambda$$

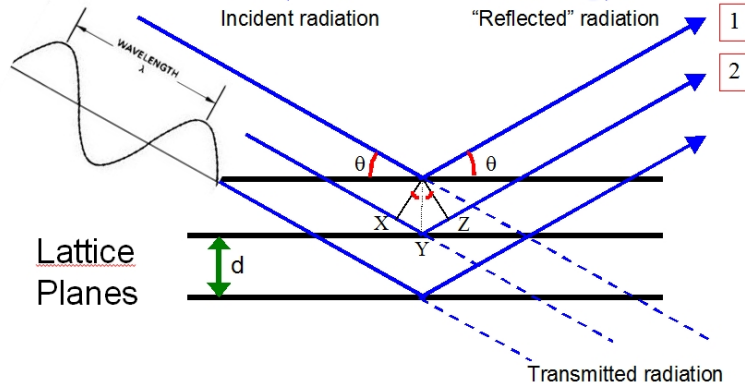


Figure 2.13: Bragg law. Two rays (1 and 2) are diffused elastically by the lattice planes.

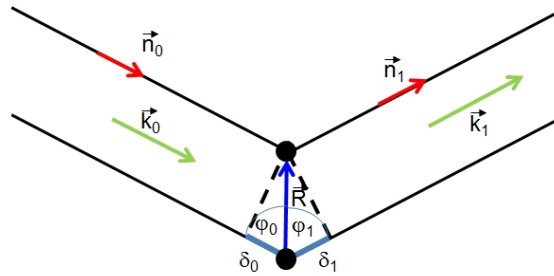


Figure 2.14: Laue law. Two rays are elastically diffused by two lattice points separated by a vector $\vec{R}$.

In the Laue description (Fig. 2.14) we consider a vector $\vec{R}$ connecting 2 lattice points of the periodic lattice. $\vec{R}$ is a lattice vector as it has already been defined. This time we consider the beam of wavenumber $\vec{k}_0 = \frac{2\pi}{\lambda_0} \vec{n}_0$ scattered by the two lattice points in the direction $\vec{k}_1 = \frac{2\pi}{\lambda_1} \vec{n}_1$, where $\vec{n}_0$ and $\vec{n}_1$ are unit vectors. As diffraction is an elastic process $\lambda_0 = \lambda_1 \equiv \lambda$, i.e., the incident and scattered wavenumber moduli are equal, $k_1 = k_0$.

Again we consider the difference of optic paths which is:

$$\delta \equiv \delta_0 + \delta_1 = R \cos \varphi_0 + R \cos \varphi_1 = -\vec{R} \vec{n}_0 + \vec{R} \vec{n}_1 = \vec{R} (\vec{k}_1 - \vec{k}_0) \frac{\lambda}{2\pi} \quad (2.18)$$

The diffraction condition writes this time:

$$\delta = n\lambda \Rightarrow \vec{R} \left(\vec{k}_1 - \vec{k}_0 \right) \frac{\lambda}{2\pi} = n\lambda \Rightarrow \vec{R} \left(\vec{k}_1 - \vec{k}_0 \right) = 2\pi n \quad (2.19)$$

Definition 2.8.1 — The scattering vector. Is the vector difference between the scattered and incident wavevectors:

$$\vec{k} = \vec{k}_1 - \vec{k}_0 \quad (2.20)$$

The Laue condition writes then:

$$\vec{R}\vec{k} = 2\pi n \quad (2.21)$$

or

$$\exp(i\vec{R}\vec{k}) = 1 \quad (2.22)$$

This constitutes, as it will be shown later, an equivalent form of the Bragg diffraction condition. As a consequence, for each $\vec{R}$ value, the Laue condition associates scattering vectors $\vec{k}$ which fulfill the diffraction condition. The Laue condition then makes an association between points (or vectors) between two different spaces.

We will note the $\vec{k}$ vectors verifying the Laue conditions $\vec{G}$ or $\vec{K}$

$$\{\vec{R}\} \leftrightarrow \{\vec{K}\} \quad (2.23)$$

For a given λ this association is unique.

As $\{\vec{R}\}$ constitute the points of a lattice, $\{\vec{K}\}$ are equally points of another lattice.

We call the *direct lattice* or the *Bravais lattice*, the lattice constituted by the $\vec{R}$ vectors:

$$\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3 \quad (2.24)$$

where the $\{\vec{a}_i\}$ are the *real lattice basis*. We call the *reciprocal lattice*, the lattice constituted by the $\vec{K}$ vectors:

$$\vec{K} = h\vec{a}_1^* + k\vec{a}_2^* + \ell\vec{a}_3^* \quad (2.25)$$

with (h, k, ℓ) integers.

and the $\{\vec{a}_i^*\}$ constitute the *reciprocal lattice basis*. The volume defined by the $\{\vec{a}_i^*\}$ is the *reciprocal unit cell*.

The $\{\vec{R}\}$ lattice are points of the so called *real space* $\{\vec{r}\}$ and the $\{\vec{K}\}$ are points of the *reciprocal space* $\{\vec{k}\}$.

For a 1-D crystal with a direct lattice $\vec{R} = n_1 \vec{a}_1 = n_1 a \hat{x}$ with $\hat{x}$ a unitary vector, the Laue condition, $\vec{R}\vec{k} = 2\pi n$, implies:

$$\vec{a}_1^* = \frac{2\pi}{a} \hat{x} \quad \text{and} \quad n_1 h = n \quad (2.26)$$

In a 3-D crystal, $\vec{K}$ should then verify:

$$(n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3) \left(h\vec{a}_1^* + k\vec{a}_2^* + \ell\vec{a}_3^* \right) = 2\pi n \quad (2.27)$$

which needs to be valid for any n_1, n_2 and n_3 integers. This can be verified when:

$$\vec{a}_i \vec{a}_j^* = 2\pi \delta_{ij} \quad (2.28)$$

with δ_{ij} the Kronecker delta function defined as:

$$\delta_{ij} = \begin{cases} 1 & \text{if } i=j \\ 0 & \text{if } i \neq j \end{cases} \quad (2.29)$$

and then the above product becomes:

$$h n_1 + k n_2 + \ell n_3 = n \quad (2.30)$$

which can be verified always if the $\{n_i\}$ and (h, k, ℓ) are integers, which is always the case.

The expression $\vec{a}_i \vec{a}_j^* = 2\pi \delta_{ij}$ can be used to compute efficiently the reciprocal lattice basis vectors.

The integers (h, k, ℓ) have a significance which will be later developed. They are called the *Miller indexes*.

The reciprocal lattice vectors, $\vec{K}$ are also often referred as (hkl) vectors or $\vec{G}_{hkl}$.

It is easily shown that the reciprocal lattice vectors verifying $\vec{a}_i \vec{a}_j^* = 2\pi \delta_{ij}$ can be written as:

$$\vec{a}_1^* = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 (\vec{a}_2 \times \vec{a}_3)} \quad (2.31)$$

$$\vec{a}_2^* = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 (\vec{a}_2 \times \vec{a}_3)} \quad (2.32)$$

$$\vec{a}_3^* = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 (\vec{a}_2 \times \vec{a}_3)} \quad (2.33)$$

where the product $\vec{a}_1 (\vec{a}_2 \times \vec{a}_3)$ represents the volume of the unit cell.

We should note that by symmetry of the expression $\vec{a}_i \vec{a}_j^* = 2\pi \delta_{ij}$, the reciprocal lattice of the reciprocal lattice is the direct lattice. We may also underline that all these considerations are done independently of the crystalline basis. Only the lattice is here considered.

2.9 The significance of Reciprocal Space. Brillouin Zones

To understand the geometrical significance of reciprocal lattice, let's consider a vector $\vec{K}$ of reciprocal lattice. By definition, this vector fulfills the diffraction condition through the Laue expression and is also an scattering vector

$$\vec{K} = \vec{k}_1 - \vec{k}_0 \quad (2.34)$$

with $\vec{k}_0$ and $\vec{k}_1$ the incident and scattered wave-vectors respectively. We can rewrite the preceding expression:

$$\vec{k}_1 - \vec{K} = \vec{k}_0 \quad (2.35)$$

squaring this expression we have:

$$K^2 - 2\vec{K}\vec{k}_1 + k_1^2 = k_0^2 \quad (2.36)$$

As diffraction is an elastic scattering process, $k_0 = k_1$ and then:

$$K^2 = 2\vec{K}\vec{k}_1 \quad (2.37)$$

which can be also written

$$\left(\frac{K}{2}\right)^2 = \frac{\vec{K}}{2} \cdot \vec{k}_1 \quad (2.38)$$

We can derive from this expression has a number of important consequences:

Consequence 1. If we consider as in Fig. 2.15 the vector $\vec{K}$ of the reciprocal lattice and the median plane of this vector, we realize that whatever vector $\vec{k}_1$ having common origin with $\vec{K}$ and its apex on the median plane, fulfills the condition expressed with the above equation.

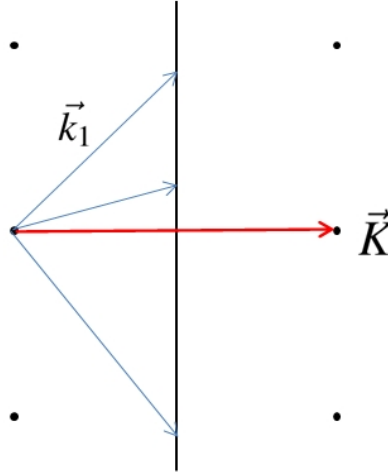


Figure 2.15: Diffraction condition and First Brillouin zone. A median plane for a vector $\vec{K}$ of the reciprocal lattice is shown in black. Three scattered vectors $\vec{k}_1$ are shown.

In other words, for any $\vec{K}$ of the reciprocal lattice, its median plane defines an infinity of scattered vectors, $\vec{k}_1$ which fulfill the diffraction condition.

This allows to define a volume in reciprocal space having as limiting surface precisely the first planes allowing for the diffraction condition. Such a volume is called the *first Brillouin zone* which in fact corresponds to the Wigner-Seitz cell of the reciprocal lattice.

Definition 2.9.1 — First Brillouin Zone. Is the Wigner-Seitz cell in reciprocal space.

Consequence 2. By simple translation of $\vec{k}_1$ and including also $\vec{k}_0$ we can go from Fig. 2.15 to Fig. 2.16

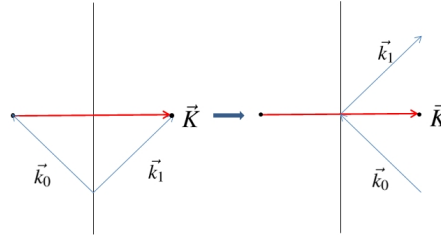


Figure 2.16: A redrawing of the previous Figure by vector translation.

We see in the right sketch of Fig. 2.16 that the median plane defined through the $\vec{K}$ corresponds to the diffracting plane in the Bragg scheme. This demonstrates the equivalence between the Bragg and Laue schemes.

In addition, we conclude that the median planes of each reciprocal lattice vector $\vec{K}$ corresponds to a diffracting plane. This provides a clear geometrical significance to the reciprocal lattice : each vector of the reciprocal lattice is associated to a Bragg plane. Each (h,k,l) correspond to a Bragg plane. Let's demonstrate that in fact, each $\vec{K} = \vec{G}_{hkl}$ represents not a plane, but a family of parallel planes. The Laue condition $\vec{G}\vec{R} = 2\pi n$ means that

$$\vec{G}\vec{R} = 0, \pm 2\pi, \pm 4\pi, \pm 6\pi, \dots \quad (2.39)$$

with $\vec{G}$ being the shortest $\vec{G}$ in the chosen direction. This expression defines a family of parallel planes perpendicular to $\vec{G}$ and having equal distances between them of $d = \frac{2\pi}{|\vec{G}|}$.

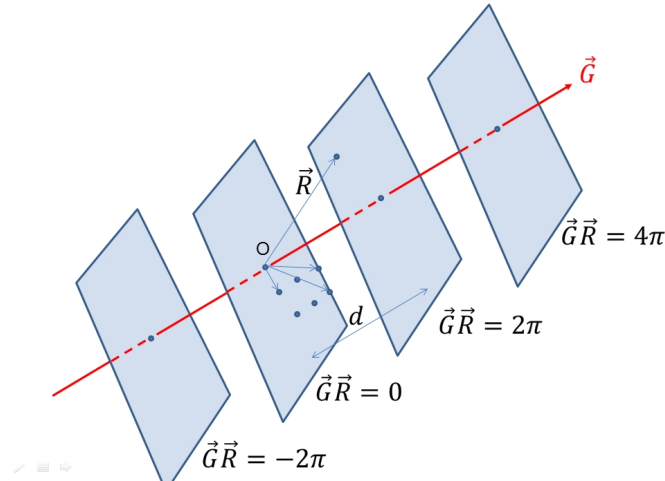


Figure 2.17: A redrawing of the previous Figure by vector translation.

To see this, let us consider Fig. 2.17. In this figure we proceed as follows:

- We plot $\vec{G}$ from a common origin, O, in direct space and reciprocal space.
- The condition $\vec{G}\vec{R} = 0$ defines a plane in direct space cutting O in which all $\vec{R}$, direct lattice vectors, are perpendicular to $\vec{G}$.
- $\vec{G}\vec{R} = \text{constant}$ defines subsequent planes parallel to the preceding one in which all the $\vec{R}$ have the same projection on $\vec{G}$. This projection, d, is the distance between planes :

$$|\vec{R}| \cos \widehat{\vec{G}\vec{R}} = d \quad (2.40)$$

We have then:

$$\vec{G}\vec{R} = 2\pi \implies |\vec{G}|d = 2\pi \implies d = \frac{2\pi}{|\vec{G}|} \quad (2.41)$$

Definition 2.9.2 — $\{h, k, l\}$ family of planes. We note $\{h, k, l\}$ the family of parallel planes associated to a $\vec{G}_{hkl}$ vector of the reciprocal space.

The Miller indexes (hkl) define then a family of parallel planes associated to the reciprocal space vector, $\vec{G}_{hkl}$. The inter-reticular spacing in this family of planes is $d_{hkl} = \frac{2\pi}{|\vec{G}_{hkl}|}$

2.10 Elastic Scattering by Matter

Diffraction is the elastic scattering of radiation by matter. Any radiation can be in principle scattered by matter. Due to practical reasons, X-rays and neutrons are the most extended used radiation for crystalline structure determination. Electrons are also frequently used.

Lets first consider the a Bravais lattice as a density fonction:

$$\rho(\vec{r}) = \sum_i^N \delta(\vec{r} - \vec{R}_i) \quad (2.42)$$

with $\vec{R}$ being all vectors of the direct lattice. In an ideal crystal $N \rightarrow \infty$

Let us compute the Fourier Transform of this lattice:

$$G(\vec{k}) = \int \rho(\vec{r}) e^{i\vec{k}\vec{r}} d\vec{r} = \sum_i^N \int \delta(\vec{r} - \vec{R}_i) e^{i\vec{k}\vec{r}} d\vec{r} = \sum_i^N e^{i\vec{k}\vec{R}_i} = \begin{cases} N(\infty) & \text{if } \vec{k} \in \{\vec{K}\} \\ 0 & \text{otherwise} \end{cases} \quad (2.43)$$

We recall here that normalization factors in the Fourier transform definition can respond to different conventions.

We can then write:

$$G(\vec{k}) = \sum_j \delta(\vec{k} - \vec{K}_j) \quad (2.44)$$

or in other words, the reciprocal lattice is the Fourier transform of the direct lattice.

Diffraction by a Bravais lattice If we consider now the scattered radiation by a solid having scattering centers in each of the direct lattice points, we can consider that for a far observer, each one of the scattering points is emitting a planewave with an amplitude proportional to f_0 , which we define as the diffusion amplitude of a scattering center. The total diffused amplitude reaching a far observer will be:

$$A(\vec{k}) = f_0 \int \rho(\vec{r}) e^{i\vec{k}\vec{r}} d\vec{r} \quad (2.45)$$

Here we have considered the incident amplitude, A_0 normalized to one.

We then find out that the scattering amplitude by a Bravais lattice is proportional to the reciprocal space lattice:

$$A(\vec{k}) = f_0 G(\vec{k}) \quad (2.46)$$

And the detected intensity :

$$I = |A(\vec{k})|^2 = f_0^2 |G(\vec{k})|^2 \quad (2.47)$$

To further progress we need now to include:

- A base of atoms or molecules
- Atoms having finite dimensions (and not only mathematical points)

Diffraction by a crystal.

We apply basically the same formalism with the scattering amplitude written as:

$$A(\vec{k}) = A_0 \int f(\vec{r}) e^{i\vec{k}\vec{r}} d\vec{r} \quad (2.48)$$

where here:

- A_0 is the amplitude of the incident radiation (we choose here not to normalize for more generality).
- $f(\vec{r})$ is the scattering amplitude per unit of sample volume. This magnitude will depend both on the nature of the scatterer (which atom or molecule) and of the radiation (x-ray, neutrons,...).

In a crystal atoms (scatterers) are only found in a finite number of $\vec{r}$ values:

$$\vec{r} = \sum_{n_1=1}^{N_1} \sum_{n_2=1}^{N_2} \sum_{n_3=1}^{N_3} n_j \vec{a}_j + \sum_{i=1}^n \vec{r}_i \quad (2.49)$$

with n_i and n being integers.

Replacing and factorizing, we have:

$$A = A_0 \sum_{n_1=1}^{N_1} \sum_{n_2=1}^{N_2} \sum_{n_3=1}^{N_3} \sum_{i=1}^n f_i e^{i\vec{k}(n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3 + \vec{r}_i)} = A_0 \left[\sum_{n_1, n_2, n_3} e^{i\vec{k}(n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3)} \right] \left[\sum_{i=1}^n f_i e^{i\vec{k}\vec{r}_i} \right] \quad (2.50)$$

where n is the number of atoms in the base. The value of f_i will depend on the radiation and on the nature of the atom sitting in position $\vec{r}_i$.

The first factor is called $L(\vec{k})$ or form factor. The second factor is called $F(\vec{k})$ or structure factor. We have then:

$$A_{\text{diffracted}} = A_0 L(\vec{k}) F(\vec{k}) \quad (2.51)$$

The form factor. To evaluate $L(\vec{k})$ we replace the expression of $\vec{k} = k_x \vec{a}_1^* + k_y \vec{a}_2^* + k_z \vec{a}_3^*$ and $\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$ and using $\vec{a}_i \vec{a}_j^* = 2\pi \delta_{ij}$ we have:

$$L(\vec{k}) = \sum_{n_1=0}^{N_1-1} e^{i2\pi n_1 k_x} \sum_{n_2=0}^{N_2-1} e^{i2\pi n_2 k_y} \sum_{n_3=0}^{N_3-1} e^{i2\pi n_3 k_z} \quad (2.52)$$

in this expression, the n_i are integers, as we are summing over all the lattice points, whereas the k_x , k_y and k_z are real numbers. We are considering here the possibility of having a finite crystal of $N_1 \times N_2 \times N_3$ cells by taking n_i values comprised between 0 and $N_i - 1$ (any translation of this will be equivalent).

Each of the sum terms correspond then to a geometrical series of the form:

$$a_0 + a_0 r + a_0 r^2 + \dots + a_0 r^n = a_0 \frac{1 - r^{n+1}}{1 - r} \quad (2.53)$$

with for instance for the first term of $L(\vec{k})$:

$$a_0 = e^{i2\pi \cdot 0 \cdot k_x} = 1 \quad r = e^{i2\pi k_x} \quad r^{n+1} = e^{iN_1 2\pi k_x} \quad (2.54)$$

We have then:

$$L(\vec{k}) = \left[\frac{1 - e^{iN_1 2\pi k_x}}{1 - e^{i2\pi k_x}} \right] \left[\frac{1 - e^{iN_2 2\pi k_y}}{1 - e^{i2\pi k_y}} \right] \left[\frac{1 - e^{iN_3 2\pi k_z}}{1 - e^{i2\pi k_z}} \right] \quad (2.55)$$

Every one of the numerator or denominator terms in the above equation can be written as:

$$(1 - e^{ix}) = e^{\frac{ix}{2}} (e^{-\frac{ix}{2}} - e^{\frac{ix}{2}}) = -2ie^{\frac{ix}{2}} \sin \frac{x}{2} \quad (2.56)$$

As we are just interested on the modulus of this function and not the phase we have:

$$|L(\vec{k})|^2 = \frac{\sin^2(\pi N_1 k_x)}{\sin^2(\pi k_x)} \frac{\sin^2(\pi N_2 k_y)}{\sin^2(\pi k_y)} \frac{\sin^2(\pi N_3 k_z)}{\sin^2(\pi k_z)} \quad (2.57)$$

If we consider a one-dimensional case to simplify, we have:

$$|L(k_x)|^2 = \frac{\sin^2(\pi N_1 k_x)}{\sin^2(\pi k_x)} \quad (2.58)$$

Figure 2.18, shows the shape of the above function for different values on N_1 .

It is possible to show that:

$$\lim_{N \rightarrow \infty} \frac{\sin^2(\pi N r_1)}{\sin^2(\pi r_1)} \rightarrow \delta_h \quad (2.59)$$

In 3-dimensions this leads to:

$$|L(\vec{k})|^2 \rightarrow \delta_{hkl} \quad (2.60)$$

This results means that for an infinity sized crystal, the diffracted intensity is only different of zero when the diffraction condition is fulfilled. In other words for a crystal of large dimensions :

$$A_{\text{diffracted}} = A_0 L(\vec{k}) F(\vec{k}) = A_0 F(\vec{G}_{hkl}) \quad (2.61)$$

For submicrometric crystals (for grains in fact smaller than about 0.1 to 0.2 μm), it is not possible to consider that the delta function approximation is valid. The diffraction peaks have a

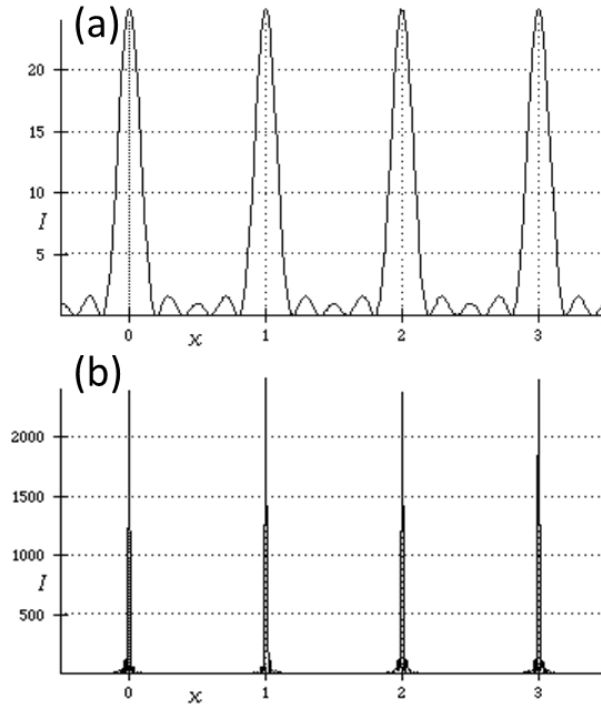


Figure 2.18: The 1-D form factor squared for $N=5$ (a) and $N=50$ (b). The x-axis represents k_x .

fullwidth at half maximum which is inversely proportional to the crystallite domain size. This is the so called *Scherrer effect*.

Structure factor.

For a large enough crystal, the peak intensities will be then evaluated using the structure factor :

$$F(\vec{K}) = \sum_{i=1}^n f_i e^{i\vec{K}\vec{r}_i} \quad (2.62)$$

with $\vec{K}$ the reciprocla lattice vectors, $\vec{K} = h\vec{a}_1^* + k\vec{a}_2^* + l\vec{a}_3^*$ and n the number of atoms in the considered cell (the basis).

If we consider only one atom per unit cell, then:

$$|F(\vec{K})|^2 = f_1^2 \quad (2.63)$$

All family of planes will diffract with an intensity which only is affected by the k -dependence of f_i (see next section).

Let us consider 2 examples:

Example 1. Structure factor of a bcc monoatomic lattice.

We have atoms at positions $\vec{r}_1$ and $\vec{r}_1 + \frac{1}{2}(\vec{a} + \vec{b} + \vec{c})$.

$$F(\vec{K}) = e^{i\vec{K}\vec{r}_1} f_1 \left[1 + e^{i\pi(h+k+l)} \right] \quad (2.64)$$

The term between braces becomes zero when :

$$h + k + l = 2n + 1 \quad (2.65)$$

This is called an *extinction condition* or a *systematic-absence condition*, as all hkl family of planes verifying this condition, will show zero associated diffraction intensity. Extinctions can appear when we have a basis of more than one atom.

Example 2. Structure factor of a bcc diatomic lattice.

We consider here the CsCl salt, which has a bcc structure with the Cs^{+1} ion in one of the basis sites and the Cl^{-1} occupying the other one. Then we have:

$$F(\vec{K}) = f_{\text{Cl}^{-1}} + f_{\text{Cs}^{+1}} e^{i\pi(h+k+l)} \quad (2.66)$$

where we have taken arbitrarily $\vec{r}_1 = (0, 0, 0)$. Then we have:

$$F(\vec{K}) = f_{\text{Cl}^{-1}} + f_{\text{Cs}^{+1}} (-1)^{h+k+l} \neq 0 \quad (2.67)$$

if $f_{\text{Cl}^{-1}} \neq f_{\text{Cs}^{+1}}$

The atomic form factor Also called atomic scattering factor, the term f_i is not in general a constant and depends on the atom considered as scatterer. It also depends on the radiation used in the diffraction experiment (x-rays, neutrons, electrons).

In the case of **x-ray diffraction**, the electromagnetic wave is going to interact with the electrons of the atom, which become the real scatterers. For a given atom with atom number Z the scattered amplitude by the atom will be given by:

$$f_i(\vec{k}) = \sum_{j=1}^Z \int_{\text{atomi}} f_j(\vec{r}_j) e^{i\vec{k}\vec{r}_j} d^3\vec{r}_j \quad (2.68)$$

Where $\vec{r}_j$ is the coordinate position of electron j and $f_j(\vec{r}_j)$ is the diffusion density of that electron. The dominant electron spatial symmetry and the extension of the electronic cloud determines the x-ray atomic form factor which is nothing else than the Fourier transform of the electronic density of the considered atom.

For $k = 0$ the above sum gives $f_i(0) = Z_i$, the number of electrons in the atom.

If we consider as a first approximation that the electronic cloud density can be described by a gaussian profile of full width at half maximum(FWHM) L , the atomic form factor will just be the Fourier transform of that gaussian profile, i.e., another gaussian of FWHM $1/L$. In figure 2.19 the angular dependence of the atomic form factor of different atoms is shown. We can appreciate that $f_i(0) = Z_i$. In figure 2.20 the atomic form factor of different ions having the same number of electrons but different spatial extension is shown. One can then appreciate that the smaller the spatial extension (higher nuclear charge), the wider the atomic forms factor.

The isotropic image of the electronic density is less accurate when d or f orbitals are involved.

Neutron scattering. Not having charge, neutrons interact with the atomic nuclei. The electron spatial extension is several orders of magnitude more important than the nuclei ones and we can assimilate it to a delta fonction:

$$\rho(r) = b\delta(\vec{r}) \quad (2.69)$$

Consequently, we can consider that the neutron form factor will be equivalent to the Fourier transform of a delta function, i.e., a constant independent of k .

$$f(\vec{r}) = b \int \delta(\vec{r}) e^{i\vec{r}\vec{k}} d^3\vec{r} = b \quad (2.70)$$

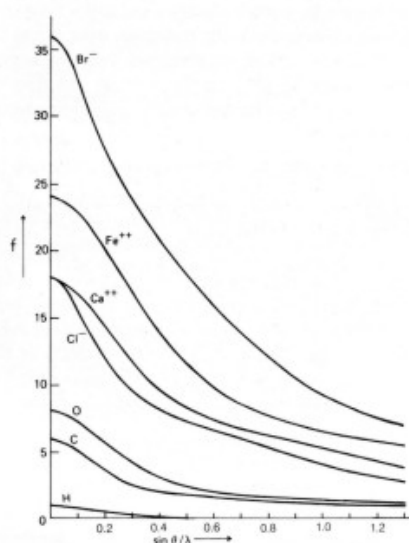


Figure 2.19: Atomic form factor for x-ray scattering for different atoms and ions. Heavy atoms or ions are easy to "see" by x-rays, while light atoms as hydrogen are difficult to detect

Considering adequate prefactors, b can be expressed in units of length and is called the **Fermi length**. Its value changes from one isotope to the another and varies erratically with Z (see Fig. 2.21).

Neutrons having a half integer spin, they can interact with the atom magnetic moment, $\vec{S}_A$. If neutrons are spin polarized, with their spin $\vec{S}_n$ and $\langle \vec{S}_A \vec{S}_n \rangle \neq 0$ then there is also a magnetic component of neutron scattered originated by the magnetic interaction. The magnetic scattering part due to the neutron scattering with the electron spin, will exhibit on its side k -dependence. atomic form factor neutron x-rays

2.11 Diffraction Methods

The application of structure determination are manyfold and include:

- The beginning of material science. As a first step to understand the physico-chemical origin of the properties of a material, we need to determine their structure.
- To study the evolution of systems as a fonction of the thermodynamic conditions of Pressure, Temperature, Magnetic field. This is particularly important in geology, planetology, thermodynamics, physics of materials...
- The application of all this concepts to many domains including history of arts or archeology, material engineering or the one being presently the most developped: structural biology.

We can clasify technics of diffraction depending on the sample type, the source characteristics or the detection methods.

We can distinguish the use of monochromatic sources (λ is fixed) or white sources (also colled polychromatic sources). Then, depending if we study with these sources a single crystal or a polycrystal, we will face different geometries and detection modes.

Let us first consider the diffraction of a single crystal by a monochromatic source. A very useful tool to discuss this diffraction method is the so called **Ewald construction**. Ewald came up with a geometrical construction to help visualise which Bragg planes are in the correct orientation to diffract (Fig. 2.22). We consider the reciprocal space and we plot a sphere having radius $\vec{k}_i = \vec{k}_f$. One needs to fix one point of the sphere surface on one point of the reciprocal lattice that we take as the origin (point O). The sphere needs allways keep this point fixed in reciprocal space and

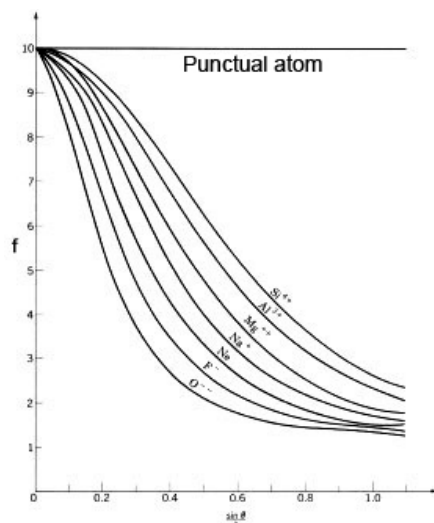


Figure 2.20: Atomic form factor for x-ray scattering for different ions having the same number of electrons as Ne. One can observe that Si^{4+} , having the highest nuclear charge and then the less extended electronic cloud exhibits the largest FWHM. In the case of a punctual atom, the extension of the electronic cloud will be zero and hence the atomic form factor will have an ∞ FWHM

we can make turn it around O (which corresponds to rotate the crystal in a diffraction experiment). When pivoting the sphere around O, the sphere touches another point of the reciprocal lattice, we will find a situation as shown in the figure, in which a vector $\vec{k}_1 - \vec{k}_0 = \delta\vec{k} = \vec{K}$. In fact, any two points of the lattice touching the sphere will be connected by a vector $\vec{K}$ of the reciprocal lattice. The Ewald sphere will then define the diffracting angle 2θ . The Ewald sphere allows then to determine all reciprocal lattice planes attainable for a given λ and provides the diffracting angle for each of them (or equivalently, the crystal orientation needed).

Some consequences are easily derived from the Ewald construction. First of all we note that if $2k_0$ is smaller than the smaller distance between two reciprocal lattice points, no diffraction conditions can be attained. This shows that diffraction needs to be done with small enough wavelengths or in other words with radiation with not too low energies. But what will be the optimum wavelength for a diffraction experiment?

If $2k_0$ is too big with respect to the characteristic distances in reciprocal space, $2\pi/a$, then the number of diffraction peaks will be too important to allow for resolving the different peaks. An optimum is then that $2k_0$ is of the order of a relative small number of times $2\pi/a$. That is $2k_0 \simeq n2\pi/a$ with n of the order of a 3-5 typically. Considering that typical cell parameters range in inorganic crystals in the 3–10 Å range, we end up with a typical optimum value of $\lambda \approx 1$ Å. Of course for large crystal lattices, which can be of hundreds of Å in biomolecular crystals, a larger λ would be more appropriate.

In the case of x-rays, $E_{\text{x-ray}} = hc/\lambda$ which for $\lambda \approx 1$ Å leads to $E_{\text{x-ray}} \approx 10$ keV. This is typically the energy which can be obtained in an x-ray tube or an energy which can be easily extracted in most synchrotron radiation facilities.

In the case of neutrons, as we have a mass particle, $E_n = p^2/2m$ and $p = h/\lambda$. This time considering $\lambda \approx 1$ Å we find $E_n \approx 0.08$ eV. This is much smaller than the energy with which neutrons are expelled from the ^{235}U fission reaction. The energy of neutrons expelled

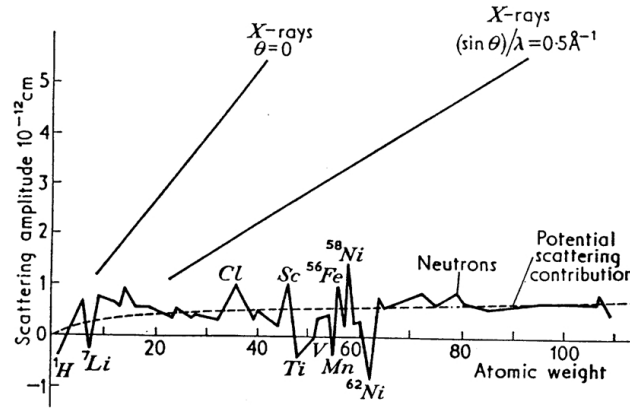


Figure 2.21: Atomic form factor for neutrons and x-rays

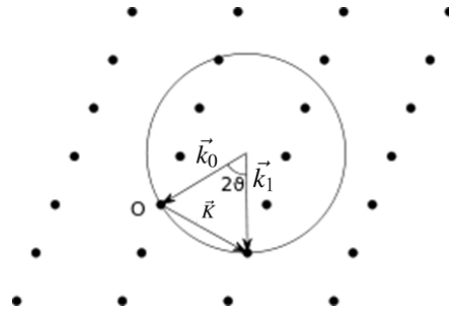
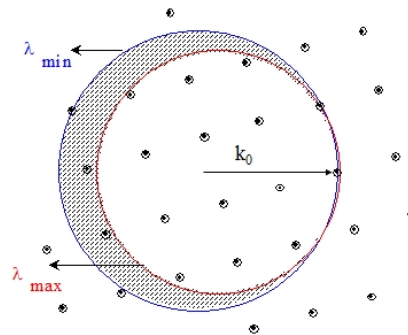


Figure 2.22: The Ewald construction in 2D.

from the reactor core is described by a Maxwell distribution which peaks at about 1 MeV. Neutrons are then cooled down through collisions with molecules in a bath (typically a liquid as water) at ambient temperature ($k_B T_{\text{amb}} \approx 25 \text{ meV}$). Neutrons obtained in such a way, which are typically the ones used in diffraction experiments are called *thermal neutrons*.

The Ewald construction let us also see the expected result when illuminating a single crystal with a polychromatic beam with wavelengths comprised between λ_1 and λ_2 . From Figure 2.23 we can appreciate that without any rotation of the crystal, several reciprocal lattice points will fulfill the diffraction condition and give rise to diffraction at the corresponding diffraction angle provided by the Ewald construction. This is called the Laue method.

Figure 2.23: The Ewald construction for the Laue Method of single crystal diffraction with a white beam having wavelengths comprised between λ_1 and λ_2 .

Powder diffraction

An alternative to the study of single-crystal samples is powder diffraction. Techniques based on powder diffraction use samples made of a very large number of small crystallites having equal probability for any particular crystallite orientation. True randomness may need in some cases to introduce sample rotation orientation.

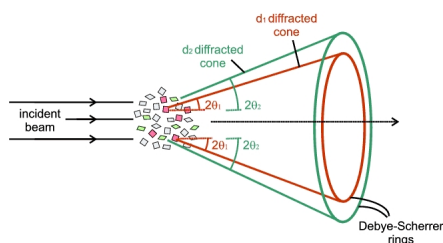


Figure 2.24: Powder diffraction. The figure illustrates the formation of the Debye-Scherrer rings for two different diffraction planes.

As it is shown in Fig. 2.24, the use of a powder sample with a monochromatic beam in angular dispersive mode, leads to the formation of rings on the detector corresponding to each one of the sample diffracting plane. These rings are called the Debye-Scherrer rings. The azimuthal integration of each ring generates a peak at a given angle. The corresponding diffractogram is presented then as shown in Fig. 2.25.

Crystal structure determination from powder diffraction data can be challenging due to the overlap of reflections in a single peak in a powder experiment. The experimental data can be fitted with a model in order to determine the crystalline structure of the studied sample. Rietveld refinement is one of the most used method in powder diffraction. The Rietveld method is a so-called full pattern analysis technique. A crystal structure, together with instrumental and microstructural information, is used to generate a theoretical diffraction pattern that can be compared to the observed data. A least squares procedure is then used to minimize the difference between the calculated pattern and each point of the observed pattern by adjusting model parameters.

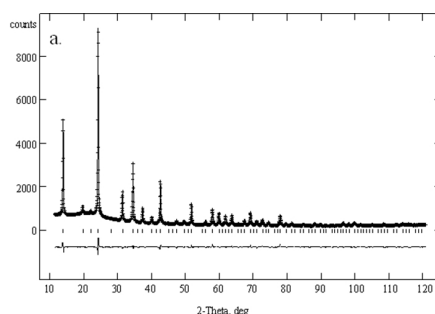
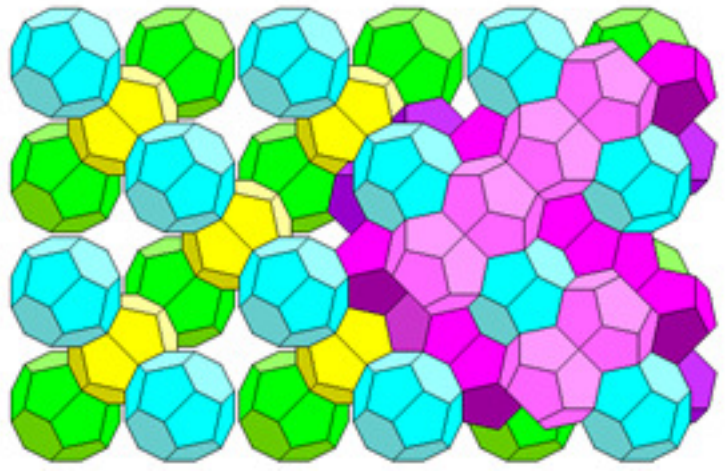


Figure 2.25: X-ray powder diffraction pattern. Crosses are the experimental data. The superimposed line corresponds to the Rietveld refinement of the obtained data. Tick marks are the different diffraction reflexions included in the model and the bottom line is the residual (difference between the model and the data).



Figure 2.26: **Video 3.** (*scan the QR code with your mobile phone or tablet*) This video includes the following topics : - The Ewald sphere and its application to single crystal diffraction - Single crystal diffraction with a white beam - Powder diffraction



3. Dynamics of solids

3.1 Introduction

The heat absorption capability, characterized by the specific heat, C , measures the capacity for acquiring kinetic energy by the particles of the systems. For an ideal mono-atomic gas this is $3/2 k_B T$ for each particle in average which leads to a specific heat at constant volume of $C_V = 3/2 R$. For solids, the empirical law of Dulong and Petit, states that $C_V \approx 3R$, which is in fact verified by the majority of solid metallic chemical elements at room temperature for instance. Nevertheless, this law breaks at low temperatures where a strong dependence with temperature is found both in crystalline metals ($C_V \propto T$) and crystalline electrical insulators ($C_V \propto T^3$). Contrary to the ideal gas, solids present then two different regimes of heat absorption ("low" and "high" temperatures) with a low temperature regime having a different character of the one found in a gas systems. These differences arise from the particularities of the atoms vibrations in a crystal. In the following sections we will study such vibrations from a microscopic point of view and relate them to the macroscopic description of a solid through variables as specific heat or the speed of propagation of sound.

3.2 Dynamics of a mono-atomic 1-D crystal

Let us consider the following 1-D crystal of N identical atoms of mass, m having cell parameter a . The translation vector $t_n = na$ defines for each atom its position at equilibrium. Let us consider that the atoms can be displaced from their equilibrium position by a vector $\vec{u}_n$ which we consider having a modulus always much smaller than a .

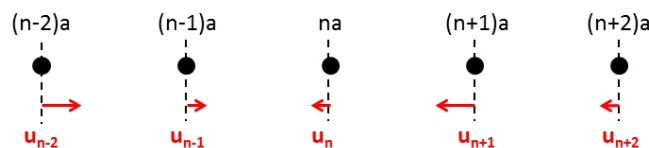


Figure 3.1: A mono-atomic chain of atoms. Atom n can be displaced by $\vec{u}_n$ with respect to its equilibrium position. We consider here only the displacement in the same direction than the axis defining the 1D-chain. The corresponding vibrations are longitudinal vibrations.

We will here consider as shown in the figure *longitudinal* displacements, i.e., vectors $\vec{u}_n$ in the

direction of the chain. The other perpendicular directions are then called *transversal* directions. The system energy can be written as a function of the displacements:

$$E_0(u_1, u_2, \dots, u_N) = E_0(\{u_n\}) \quad (3.1)$$

We can make the Taylor development of this expression around the equilibrium position:

$$E_0(\{u_n\}) = E_0(0) + \frac{1}{2} \sum_{n,n'} \left(\frac{\partial^2 E_0}{\partial u_n \partial u_{n'}} \right)_0 u_n u_{n'} + \frac{1}{6} \sum_{n,n',n''} \left(\frac{\partial^3 E_0}{\partial u_n \partial u_{n'} \partial u_{n''}} \right)_0 u_n u_{n'} u_{n''} + \dots \quad (3.2)$$

In this equation, the subscript 0 denotes that the derivatives are taken around the equilibrium position. We note that the first order derivative terms $(\partial E_0 / \partial u_n)_0 = 0$, as the equilibrium position correspond to a minimum of energy.

The first term, $E_0(0)$ is the energy without any displacement with respect to the equilibrium positions. This term corresponds to the *cohesive energy* of the solid, i.e., the energy needed to break apart the solid in atoms at infinite distance. In our present discussion, this term is not relevant, as we are interested on the effect of atomic displacements.

To further study our system, we adopt the *harmonic approximation* which corresponds to the truncation of the development up to the quadratic term (by extension, the *anharmonic approximation* corresponds to consider higher order terms). In the harmonic approximation we have:

$$E_0^h(\{u_n\}) = E_0(0) + \frac{1}{2} \sum_{n,n'} D_{nn'} u_n u_{n'} \quad (3.3)$$

where we have defined

$$D_{nn'} = \left(\frac{\partial^2 E_0}{\partial u_n \partial u_{n'}} \right)_0 \quad (3.4)$$

The $D_{nn'}$ are called *force constants*. In fact, we see that

$$F_n = -\frac{\partial E_0^h}{\partial u_n} = -\sum_{n'} D_{nn'} u_{n'} \quad n = 1 \dots N \quad (3.5)$$

corresponds to the force on atom n , which is formally identical to the force associated to a spring having spring constant, $k = D_{nn'}$ for which $F = -ku$. Any atom of the crystals behaves as it was linked to all other atoms by springs with force constants, $D_{nn'}^1$.

The $D_{nn'}$ verify a number of symmetries:

¹There is not a 1/2 factor missed in Eq. 3.5 as the two indexes n and n' run over all atoms of the crystal. To see this more clearly, we can imagine the case in which the force constant only applies on first neighbors atoms. In such case $D_{n,n'} \neq 0$ if n and n' differ of an unit. We will have then, if we only explicit terms containing u_n : $E_0^h(\{u_n\}) = E_0(0) + \frac{1}{2} (\dots + D_{n,n+1} u_n u_{n+1} + D_{n,n-1} u_n u_{n-1} + D_{n+1,n} u_{n+1} u_n + D_{n-1,n} u_{n-1} u_n + \dots)$ and taking the derivative $F_n = -\frac{\partial E_0^h}{\partial u_n} = \frac{1}{2} (D_{n,n+1} u_{n+1} + D_{n,n-1} u_{n-1} + D_{n+1,n} u_{n+1} + D_{n-1,n} u_{n-1})$. As $D_{nn'} = D_{mm'}$, $F_n = D_{n,n+1} u_{n+1} + D_{n,n-1} u_{n-1}$, which generalizes to Eq. 3.5 when the restriction of interactions limited to first neighbors is lifted.

- $D_{nn'} = D_{n'n}$ which is a direct consequence of the definition of the force constants as second order derivatives in which the derivation order is not important.
This means that the spring constant between atom n and n' is the same than for atom n' and n which is more than logical!.
- $D_{nn'} = D_{mm'}$ if $t_n - t_{n'} = t_m - t_{m'}$
which states that the spring constant between two atoms of the crystal should be the same than between any two others if they are at the same distance.
- If all the u_n are equal, the situation is equivalent to equilibrium (we are just displacing the crystal as a whole). At equilibrium $F_n = 0 = -u_{n'} \sum_{n'} D_{nn'}$ which implies that $\sum_{n'} D_{nn'} = 0$, expression known as the *sum rule*.

In the harmonic approximation, we can write equation 3.5 as

$$m\ddot{u}_n = - \sum_{n'} D_{nn'} u_{n'} \quad n = 1, 2, \dots, N \quad (3.6)$$

which are the movement equations for the N atoms in the crystal.

The form of eq. 3.6 and the translation symmetry of the $D_{nn'}$ suggest as possible solutions of eq. 3.6 :

$$u_n(t) = A e^{i(qna - \omega t)} \quad n = 1 \dots N \quad (3.7)$$

with $q = 2\pi/\lambda$. We have chosen the symbol q instead of k to underline that the k values can be chosen as belonging to the first Brillouin zone. We will verify this later.

Replacing $u_n(t)$ of eq. 3.7 in eq. 3.6 :

$$-m\omega^2 = - \sum_{n'} D_{nn'} e^{-iq(na - n'a)} \quad (3.8)$$

which can be written:

$$m\omega^2 = D(q) \quad (3.9)$$

with

$$D(q) = \sum_{n'} D_{nn'} e^{-iq(na - n'a)} \quad (3.10)$$

We note that $D(q)$ is the Fourier transform of $D_{nn'}$.

Solving 3.9 allows to determine $\omega(q)$, a fonction on q which is called the *dispersion curve* of the cristal vibrations or the *phonon dispersion curve*.

As $n - n' = n''$ is also an integer we can write:

$$D(q) = \sum_{n'} D_{nn'} e^{-iq(na - n'a)} = \sum_{n''} D_{n''} e^{-iqn''a} \quad (3.11)$$

or as the n'' index is now arbitrary:

$$D(q) = \sum_n D_n e^{-iqna} \quad (3.12)$$

$D(q)$ does not depend on n , which means that it represents an equation of movement for all atoms, which comforts our choice of solution type.

If we shift a given value of q' by a reciprocal lattice vector $n \frac{2\pi}{a}$ and we examine the vibration of atom n which we call u'_n :

$$u'_n(t) = A e^{i((q' + n \frac{2\pi}{a})na - \omega t)} = A e^{i(q'na + n'2\pi - \omega t)} = A e^{in'2\pi} e^{i(q'na - \omega t)} = A e^{i(q'na - \omega t)} = u_n(t) \quad (3.13)$$

we obtain that the amplitude of the vibration is the same that the unshifted q . In other words, we can describe the vibrations in a q domain of extension $2\pi/a$ which if we chose to symmetrize it :

$$-\frac{\pi}{a} \leq q \leq \frac{\pi}{a} \quad (3.14)$$

means that q belongs to the first Brillouin zone.

We have then N solutions of the type $u_n(t)$ which fulfill the dispersion conditions $\omega(q)$. This means that we should have N values of q with their corresponding ω . This discretization of q derives from the crystal periodicity.

In fact, for the N atoms of our chains, this defines its length L as:

$$L = (N-1)a \simeq Na \quad \text{for a large } N \quad (3.15)$$

To be as close as possible to the crystal (∞) paradigm, we apply the *Born von Karman periodic conditions* also known as circular periodic conditions which imposes that the first and the last atom of the chain behave in the same way. If we transpose the idea to an infinite chain of atoms, then any pair of atoms separated by N should behave in the same way:

$$u_n = u_{n+N} \quad (3.16)$$

replacing with our solutions of eq. 3.7 we have then:

$$e^{iqNa} = 1 \Rightarrow qNa = 2\pi n \Rightarrow q = n \frac{2\pi}{L} ; n = 0 \dots N \Rightarrow q = 0, \pm \left(\frac{2\pi}{L}\right), \pm 2 \left(\frac{2\pi}{L}\right), \dots \pm N \left(\frac{2\pi}{L}\right) \quad (3.17)$$

3.3 Monoatomic chain with first neighbours interaction

We consider a mono-atomic chain of atoms as shown in Fig. 3.2. All atoms are at the same distance, a and we consider the interatomic interactions between atoms well represented by a unique spring constant, C . Then the interatomic distance, a is the cell parameter of this 1D crystal. We are first interested in studying the longitudinal vibrations, i.e., the atomic displacements in the direction of the chain, noted u_n . We consider that interactions take place only with the nearest neighbors as represented in the figure.

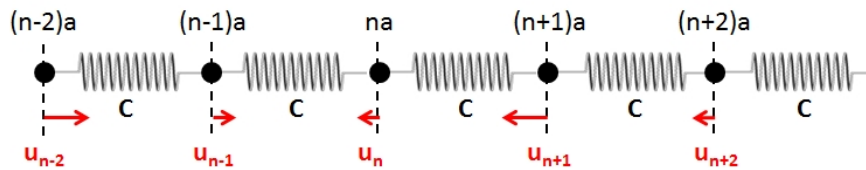


Figure 3.2: A chain of identical atoms of mass m with first neighbours interaction represented by the spring constants C . Again only longitudinal displacements are considered here.

Then, for atom n in the chain, only forces from its closest neighbors need to be considered and the equilibrium equation is written:

$$m\ddot{u}_n = -C(u_n - u_{n-1}) - C(u_n - u_{n+1}) = Cu_{n-1} - 2Cu_n + Cu_{n+1} \quad (3.18)$$

In our previous notation corresponding to the chain energy, we have then the following correspondence:

$$D_{n,n} = D_0 = 2C; \quad D_{n,n-1} = D_{-1} = D_{n,n+1} = D_1 = -C \quad (3.19)$$

With our new notation, the equation of movement simplifies to:

$$m\ddot{u}_n = -C(2u_n - u_{n+1} - u_{n-1}) \quad (3.20)$$

which we can solve considering propagative waves of the form:

$$u_n(t) = Ae^{i(qna - \omega t)} \quad (3.21)$$

Replacing Eq. 3.21 in Eq. 3.20 we have:

$$-m\omega^2 = -C(2 - e^{iqa} - e^{-iqa}) = -2C(1 - \cos(qa)) = -4C \sin^2 \frac{qa}{2} \quad (3.22)$$

where we have used the identities:

$$\cos x = \frac{e^{ix} + e^{-ix}}{2} \quad \text{and} \quad \sin^2 \frac{x}{2} = \frac{1}{2}(1 - \cos x) \quad (3.23)$$

We have then

$$m\omega^2 = 4C \sin^2 \frac{qa}{2} \quad (3.24)$$

with solution:

$$\omega(q) = \sqrt{\frac{4C}{m}} \left| \sin \frac{qa}{2} \right| \quad (3.25)$$

which is the phonon dispersion curve of the monoatomic chain of atoms represented in figure 3.3.

Let's examine the solution in the limit of long wavelengths, $\lambda \gg a$ or $qa \ll 1$, i.e., close to the wavenumber origin. As the sinus function can then be replaced by its argument in the previous equation, we have then:

$$\omega(q) = \sqrt{\frac{4C}{m}} \frac{qa}{2} = \sqrt{\frac{C}{m}} qa \quad (3.26)$$

Here, the group velocity ($d\omega/dq$) and the phase velocity (ω/q) have the same value and are:

$$v_s = \sqrt{\frac{C}{m}} a \quad (3.27)$$

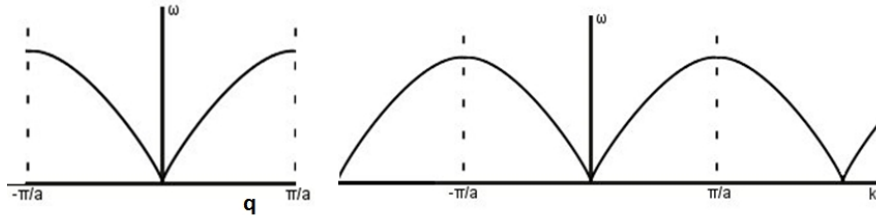


Figure 3.3: Dispersion curve of the monoatomic chain of atoms with first neighbour interaction. In the left side is shown the first Brillouin zone representation. In the right side is shown the extended zone representation, i.e., in all reciprocal space. This last representation let us appreciate that through a translation of a reciprocal lattice $t_n^* = na^* = n2\pi/a$ (with n an integer) it is possible to bring any point of the dispersion curve inside the first Brillouin zone.

In the limit of long-wavelengths this corresponds to the *speed of sound*. We have then found that a macroscopic variable, v_s can be expressed in terms of 3 different microscopic parameters. We also observe that the phonon dispersion curve is bounded by a maximum value

$$\omega_{\max} = \sqrt{\frac{4C}{m}} = \frac{2v_s}{a} \quad (3.28)$$

In order to gain some insight on the orders of magnitude of the involved phonon energies (which we will discuss later correspond to $\hbar\omega$) let's consider that we could apply these 1D results into a bulk crystal like gold. For gold we have $v_s = 2340$ m/s and $a = 0.41$ nm. This leads to $\omega_{\max} \approx 10^{13}$ Hz which situates the energy of the phonon in the infra-red light energy domain. This represents energies on the some meV range or tenths of spectroscopic wavenumbers, $\bar{\nu}$:

$$\bar{\nu} \equiv \frac{1}{\lambda_E} = \frac{E}{hc} \quad (3.29)$$

which for 1 eV represents 8065 cm^{-1} . Phonon modes can attain values up to some thousands it has become a use to call "wavenumbers" also the cm^{-1} units).

We could have made the same calculation for displacements with respect to the equilibrium position in one of the two directions perpendicular to the chain direction. Such displacements probe interatomic interactions in different directions than the longitudinal displacements and then, the corresponding force constants, C_T could be different than C considered before. We will then obtain *a priori* three different phonon dispersion curves: one for each polarization, having the same type of mathematical description. Each phonon dispersion curve will have associated its corresponding speed of sound.

3.4 Diatomic chain with first neighbours interaction

In our second examples two different atomic species will alternate in the chain at equal distances from their neighbours. In that case, the elastic constant, C , will be the same for all first neighbours interactions.

The corresponding movement equation write then:

$$\begin{cases} m_1 \ddot{u}_n = -C(2u_n - v_{n-1} - v_n) \\ m_2 \ddot{v}_n = -C(2v_n - u_n - u_{n+1}) \end{cases} \quad (3.30)$$

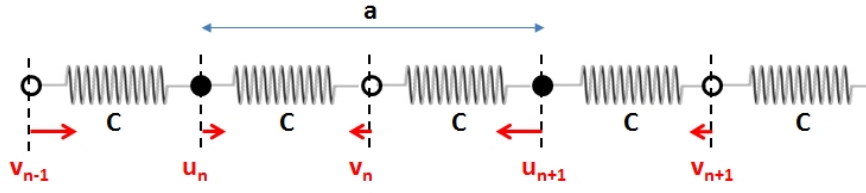


Figure 3.4: *Diatomic chain of atoms at equal distances. The two different atoms, having masses m_1 and m_2 are not equivalent and we should then consider a different amplitude of displacement u and v .*

we remplace in these equations the solutions:

$$\begin{cases} u_n(t) = A_1 e^{i(qna - \omega t)} \\ v_n(t) = A_2 e^{i(q(na + a/2) - \omega t)} \end{cases} \quad (3.31)$$

and we obtain:

$$\begin{cases} -m_1 \omega^2 A_1 = -C \left(2A_1 - A_2 e^{-iqa/2} - A_2 e^{iqa/2} \right) \\ -m_2 \omega^2 A_2 = -C \left(2A_2 - A_1 e^{-iqa/2} - A_1 e^{iqa/2} \right) \end{cases} \quad (3.32)$$

The non-trivial solutions of this system of equations in A_1 and A_2 is obtained by setting the corresponding determinant equal to zero:

$$\begin{vmatrix} 2C - m_1 \omega^2 & -2C \cos qa/2 \\ -2C \cos qa/2 & 2C - m_2 \omega^2 \end{vmatrix} = 0 \quad (3.33)$$

which leads to the solutions:

$$\omega^2 = \frac{C}{m^*} \pm C \left[\left(\frac{1}{m^*} \right)^2 - \frac{4}{m_1 m_2} \sin^2 \frac{qa}{2} \right]^{1/2} \quad (3.34)$$

with m^* being the effective mass of the basis:

$$\frac{1}{m^*} = \frac{1}{m_1} + \frac{1}{m_2} \quad (3.35)$$

The obtained solutions are represented in Fig. 3.5.

We can underline that if we note N the number of crystallographic cells and N_a the total number of atoms of the chain ($N_a = 2N$). We have then N discrete values of q and a total number of states of N_a . Each branch contains then N states or modes.

Let also consider the limiting values of ω at low q . Equation 3.5 can be written then:

$$\omega^2 \approx \frac{C}{m^*} \left[1 \pm \left(1 - \frac{m^{*2}}{m_1 m_2} q^2 a^2 \right)^{1/2} \right] \approx \frac{C}{m^*} \left[1 \pm \left(1 - \frac{m^{*2}}{2m_1 m_2} q^2 a^2 \right) \right] \quad (3.36)$$

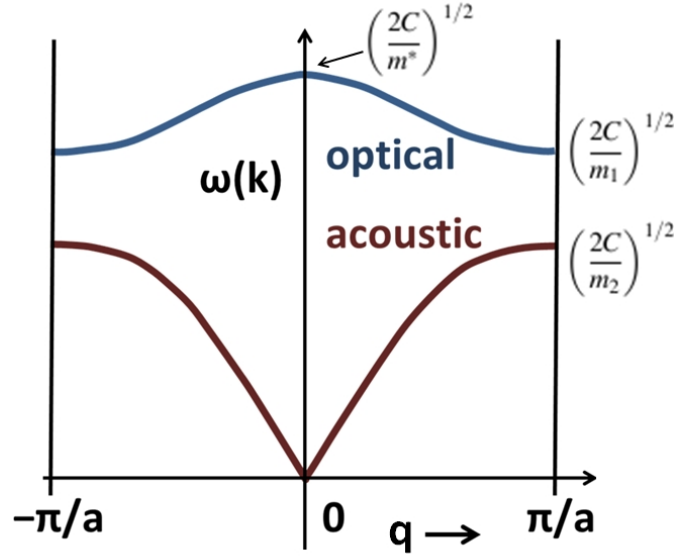


Figure 3.5: Dispersion curve for a diatomic chain of atoms with $m_2 > m_1$. There are two distinct branches called acoustic and optical respectively.

where we have used in the second equality the fact that $\sqrt{1-x} \approx 1-x/2$ for small values of x . We have then two possible solutions:

$$\omega_{\text{optical}}^2 \approx \frac{C}{m^*} \left[2 - \frac{m^{*2}}{2m_1m_2} q^2 a^2 \right] \approx \frac{2C}{m^*} \quad (3.37)$$

$$\omega_{\text{acoustic}}^2 \approx C \frac{m^*}{2m_1m_2} q^2 a^2 = \frac{C}{2(m_1 + m_2)} q^2 a^2 \quad (3.38)$$

Again, the slope of the linear part of $\omega(q)$ for the acoustic branch, corresponds to the speed of sound. To understand the name given to the higher energy branch, let us consider the ratio of the amplitudes A_1 and A_2 as can be derived from Eq. 3.33:

$$\frac{A_1}{A_2} = \frac{2C \cos(qa/2)}{2C - m_1 \omega^2} = \begin{cases} -m_2/m_1 & (\text{optical}) \\ +1 & (\text{acoustic}) \end{cases}$$

In Fig. 3.6 are depicted the corresponding amplitudes in the two cases. For two different bound atoms in a crystal, there will be some asymmetry of charge distribution. Facing an electromagnetic field, such asymmetric distribution will lead to opposite forces, which are able to excite optical type of vibrations, justifying this choice of notation.

Using modern computational techniques, it is possible to determine the phonon dispersion curve of relatively complex structures. This is an important step to verify if the studied structure can exist for instance. In fact, it may happen that the calculations show that for some q values $\omega^2(q) < 0$. This is the signature of a dynamical instability called *Born mechanical instability*. In such case, calculations predict that the structure is dynamically unstable in the studied thermodynamic conditions. This is often the indication that a phase transition towards other more stable structures needs to take place.

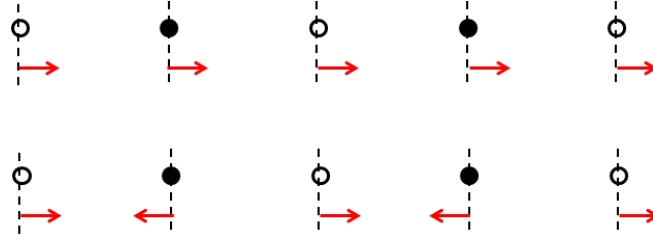


Figure 3.6: Top: representation of an acoustic longitudinal mode in the diatomic chain for long wavelengths. All amplitudes are equal at scales well below λ . The amplitudes will oscillate with time in a given position. Down: representation of an optical longitudinal mode in the same chain of atoms also for long wavelengths.

As with the monoatomic 1D chain, we could now recalculate the phonon dispersion curve for the two transverse vibration directions. In total, we will then obtain 3 acoustic branches (1 longitudinal and 2 transversal) and 3 optical branches (1 longitudinal and 2 transversal). If the corresponding elastic constant are equal then, the corresponding phonon dispersion curves will be equal and we will say that they are degenerated.

3.5 Dynamics of a 3D-crystal

Let us generalize our methodology to 3-dimensional crystals. For this we consider:

- N crystalline cells with positions defined by the translation vector $\vec{t}_n$, $n = 1 \dots N$.
- A base of n_b atoms having positions with respect to their cells $\vec{d}_v = \vec{d}_1, \vec{d}_2, \dots, \vec{d}_{n_b}$.
- Each atom of the crystal is then defined by two indexes n and v and we call the displacement of an atom with respect to its equilibrium position $\vec{u}_{nv}$.

The position of atom (n, v) is then given by $\vec{t}_n + \vec{d}_v + \vec{u}_{nv}$.

Let us consider the Energy of the system in the harmonic approximation:

$$E_0^{\text{har}}(\vec{u}_{n,v}) = E_0(0) + \frac{1}{2} \sum_{\substack{n,v,\alpha \\ n',v',\alpha'}} D_{n,v,\alpha; n',v',\alpha'} u_{n,v,\alpha} u_{n',v',\alpha'} \quad (3.39)$$

with

$$\begin{cases} \alpha, \alpha' = x, y, z \\ v, v' = 1, 2, \dots, n_b \\ n, n' = 1, 2, \dots, N \end{cases} \quad (3.40)$$

α and α' correspond to the polarization directions. In general $\alpha = \alpha'$ corresponding to the longitudinal and transversal directions. Exceptionally, it can be considered that different polarization directions are coupled for instance when considering the normal modes in spiral chains of atoms. In the following, we will consider that $\alpha = \alpha'$ (explicitly or not).

In equation 3.39 we have

$$D_{n,v,\alpha; n',v',\alpha'} = \left(\frac{\partial^2 E_0}{\partial u_{n,v,\alpha} \partial u_{n',v',\alpha'}} \right)_0 \quad (3.41)$$

and first order derivatives are equal to zero as we are considering displacement with respect to the equilibrium position, hence E_0 is at a minimum of energy.

The same type of symmetry relations shown for the linear chain apply here too:

$$D_{n,v} = D_{n',v'} \quad (3.42)$$

$$D_{n,v} = D_{m,v} \quad \text{if} \quad \vec{t}_n - \vec{t}_{n'} = \vec{t}_m - \vec{t}_{m'} \quad (3.43)$$

$$\sum_{n',v'} D_{n,v} = 0 \quad (\text{sum rule}) \quad (3.44)$$

Equations which apply for each polarization direction.

The equations of movement become here for each polarization:

$$m_v \ddot{u}_{n,v} = - \sum_{n',v'} D_{n,v} u_{n',v'} \quad (3.45)$$

with solutions of the form

$$\vec{u}_{n,v} = A_v(\vec{q}, \omega) e^{i(\vec{q}\vec{t}_n - \omega t)} \quad (3.46)$$

Replacing in equation 3.45 we have

$$-m_v \omega^2 A_v = - \sum_{n',v'} D_{n,v} e^{i\vec{q}(\vec{t}_n - \vec{t}_{n'})} A_{v'} \quad (3.47)$$

As for the linear chain, the non-trivial solutions are obtained by considering the resolution of the canonical equation, i.e., by setting the corresponding determinant to zero:

$$\|D_{vv'}(\vec{q}) - m_v \omega^2 \delta_{vv'}\| = 0 \quad (3.48)$$

$$\text{with } D_{vv'}(\vec{q}) \equiv \sum_{n'} D_{n,v} e^{i\vec{q}(\vec{t}_n - \vec{t}_{n'})} \quad (3.49)$$

where the index n becomes dummy, as all cells in the crystals are equivalent. $D_{vv'}$ is called the *crystal dynamical matrix* which has dimension n_b raised to $3n_b$ when considering polarization. This means that the number of phonon branches is $3n_b$ (longitudinal and transversal) and the total number of phonon states is $3Nn_b$.

Correspondingly to the 3 possible sound propagation (1 longitudinal and 2 transverse), there will be for a 3D-crystal always 3 acoustic branches (independently of the value of n_b) and consequently $3n_b - 3$ optical branches.

3.6 Phonons

Up to now, we have been considering the atomic vibrations in a crystal classically. But because we have found that the normal modes of vibration are harmonic and independent one from each other (without interaction), we can adopt an equivalent quantum treatment, considering each vibrational mode characterized by a pulsation ω as a quantum harmonic oscillator having energy:

$$\varepsilon_n = \left(n + \frac{1}{2} \right) \hbar \omega \quad (3.50)$$

The levels are evenly spaced at:

$$\frac{1}{2}\hbar\omega, \frac{3}{2}\hbar\omega, \frac{5}{2}\hbar\omega, \dots \quad (3.51)$$

where $\frac{1}{2}\hbar\omega$ is the zero-point energy of the quantum harmonic oscillator.

An exact amount of energy $\hbar\omega$ must be supplied to the harmonic oscillator lattice to push it to the next energy level. A quantum state of energy ε_n can then be seen as a state of energy $\hbar\omega$ with population n .

In comparison to the photon case when the electromagnetic field is quantized, the quantum of vibrational energy is called a phonon.

Definition 3.6.1 A **phonon** of energy $\hbar\omega$ is the excitation quantum of the vibrational modes of the crystal of frequency ω .

As photons, phonons can be seen as planewaves of infinite extension (ideal crystal) and hence with perfectly characterized momentum $\vec{p} = \hbar\vec{k}$ and energy $\varepsilon = \hbar\omega$. As for photons, phonons will follow Bose-Einstein statistics, and are hence boson quasiparticles.

There are nevertheless a number of differences between phonons and photons which should be underlined:

- Contrarily to photons, phonons are associated to the presence of mass, an organization of masses which constitutes the crystal. *Nevertheless phonons cannot be considered as particles with a mass.* To be more precise, acoustic phonons have an energy which is inversely proportional to their wavelength for long wavelength, as we have in photons ($p = h/\lambda$). Therefore, they are massless, like photons. In the phonon dispersion curve, optical phonons have an energy which goes to a nonzero constant value for long wavelengths. This non-zero constant could then be associated to the mass of the optical phonon with $k = 0$, but for other k -values we do not have a clear method to associate optical phonons with this same mass, due to dispersion. As we will see later, within the Einstein model, which corresponds to an unique oscillator, all phonons are optical ones and with no dispersion. Then we could associate phonons to the mass of that oscillator. Nevertheless the Einstein model is oversimplified and does not reproduce the experimentally measured phonon dispersion curves.
- For phonons $\hbar k$ is not a conventional momentum but we refer to it as crystal momentum, to underline the fact that $\hbar\vec{k}$ and $\hbar(\vec{k} + \vec{\tau}^*)$ are totally equivalent, where $\vec{\tau}^*$ is a vector of the reciprocal lattice.
- Photons have two polarization direction whereas phonons have three (one longitudinal and two transversal).

As phonons are bosons, they can be both created and annihilated, which means that their population, n , can evolve with time.

NOTE. To demonstrate rigorously that the crystal vibrational modes are equivalent to the quantum oscillator, we should demonstrate the equivalence between the corresponding hamiltonians:

$$H = \sum_n \frac{1}{2m} p_n^2 + \frac{1}{2} C \sum_n \left(2u_n^2 - u_n u_{n+1} - u_n u_{n-1} \right) \quad (3.52)$$

for a monoatomic chain of atoms of mass m . And for the harmonic oscillator:

$$H = \sum_q \hbar \omega(q) \left[a_q^\dagger a_q + \frac{1}{2} \right] \quad (3.53)$$

where $a_q^\dagger$ and a_q are respectively the anihilation and creation operators for which:

$$a_q |n\rangle = \sqrt{n} |n-1\rangle \quad (3.54)$$

$$a_q^\dagger |n\rangle = \sqrt{n+1} |n+1\rangle \quad (3.55)$$

3.7 Phonon specific heat. Einstein model

The contribution of phonons to the specific heat of a crystal can be calculated from the temperature dependence of the total phonon energy, E , as:

$$C_v = \frac{dE}{dT} \quad (3.56)$$

Lets consider the contribution to the specific heat of an elemental oscillator, i.e., a phonon of energy $\hbar\omega$ having mean energy $\bar{E}$. If we define as Z the partition function we have:

$$\bar{E} = k_B T^2 \frac{\partial(\ln Z)}{\partial T} \quad (3.57)$$

with k_B the Boltzmann constant.

We then have

$$Z = \sum_{n=0}^{\infty} e^{-\beta E_n} = \sum_{n=0}^{\infty} \exp \left[-\left(n + \frac{1}{2}\right) \frac{\hbar\omega}{k_B T} \right] = e^{-\frac{\beta\hbar\omega}{2}} \left(1 + e^{-\beta\hbar\omega} + e^{-2\beta\hbar\omega} + \dots \right) \quad (3.58)$$

where we have written

$$\beta \equiv \frac{1}{k_B T} \quad (3.59)$$

and considering that the geometrical series writes:

$$1 + x + x^2 + x^3 + \dots = \frac{1}{1-x} \quad (3.60)$$

we obtain

$$Z = e^{-\frac{\beta\hbar\omega}{2}} \left(1 - e^{-\beta\hbar\omega} \right)^{-1} \quad (3.61)$$

We then have:

$$\ln Z = -\frac{\beta \hbar \omega}{2} - \ln(1 - e^{-\beta \hbar \omega}) \quad (3.62)$$

and

$$\frac{\partial(\ln Z)}{\partial T} = \frac{\hbar \omega}{2k_B T^2} + \frac{\frac{\hbar \omega}{k_B T^2} e^{-\frac{\hbar \omega}{k_B T}}}{1 - e^{-\frac{\hbar \omega}{k_B T}}} \quad (3.63)$$

Introducing this result in 3.57

$$\bar{E} = \frac{1}{2} \hbar \omega + \frac{\hbar \omega}{\exp \frac{\hbar \omega}{k_B T} - 1} \quad (3.64)$$

This corresponds to the way Einstein evaluated the specific heat of a crystal and is named the Einstein model. Einstein considered then that all the phonon dispersion curves - not known at that time - could be assimilated to all atoms of the crystal having a unique vibrational mode of frequency, ω_E called the Einstein energy. The total vibrational energy of the system considering that each of the N atoms has 3 vibrational degrees of freedom is:

$$E = 3N\bar{E} = 3N \left(\frac{1}{2} \hbar \omega_E + \frac{\hbar \omega_E}{\exp \frac{\hbar \omega_E}{k_B T} - 1} \right) \quad (3.65)$$

We can calculate for such a solid, the specific heat using Equation 3.56 and if we define $x_E \equiv (\hbar \omega)/(k_B T)$ we get:

$$C_v = 3Nk_B \frac{x^2 e^x}{(e^x - 1)^2} \quad (3.66)$$

Lets consider the behavior at low and high temperature of the specific heat calculated in this model.

At high temperature, $x \rightarrow 0$ and

$$\frac{x^2 e^x}{(e^x - 1)^2} = \frac{x^2(1 + x + \frac{1}{2}x^2 + \dots)}{(x + \frac{1}{2}x^2 + \dots)^2} = \frac{x^2 + \mathcal{O}(x^3)}{x^2 + \mathcal{O}(x^3)} \rightarrow 1 \quad (3.67)$$

where $\mathcal{O}(x^3)$ means "terms of the order of x^3 or bigger.

Consequently we have

$$C_v = 3Nk_B \quad (3.68)$$

which corresponds to the Dulong and Petit law, the observed results for solids at high temperature. In the Einstein model, this expression is valid when $x \rightarrow 0$, which means for temperatures well above the Einstein temperature, T_E , defined as $T_E = \hbar \omega_E / k_B$.

Lets now consider the behavior of the Einstein specific heat at low temperatures, i.e, for $x \gg 1$. We have then

$$C_v = 3Nk_B \frac{x^2 e^x}{e^{2x}} = 3Nk_B x^2 e^{-x} = 3Nk_B \left(\frac{T_E}{T} \right)^2 \exp \left(-\frac{T_E}{T} \right) \quad (3.69)$$

expression valid this time for $T \ll T_E$. This expression shows that C_V tends to zero when the temperature goes to zero, which corresponds also to the observed behavior of solids at low temperatures. Nevertheless, the specific heat in this expression decreases with temperature following an exponential law, which is the dominant term. This does not corresponds exactly to the predictions which show in insulators a T^3 dependence. The Einstein model does not capture the physics of the heat absorption process at low temperature and we need to find another model.

3.8 Phonon specific heat. The Debye model

At low temperature the phonon states which will be first populated are the ones in the acoustic branches. This fact justifies the hypothesis of the Debye model which are:

- There are only acoustic modes
- The acoustic modes follow a linear regime with $\omega = v_s k$
- The number of phonon states is $3N$ for N vibrating atoms. Then there is a maximum frequency of vibration, ω_D , the Debye frequency, given by

$$\int_0^{\omega_D} f(\omega) d\omega = 3N \quad (3.70)$$

where $f(\omega)$ represent the density of states.

To determine the phonon contribution to specific heat through the Debye model, we will evaluate the phonon energy through

$$E = \int_0^{\omega_D} E_n f(\omega) d\omega \quad (3.71)$$

with $E_n = (n + 1/2)\hbar\omega$ the total energy of the phonon state, in which n is the occupancy number given by the Bose statistics:

$$n = \frac{1}{e^{\hbar\omega/k_B T} - 1} \quad (3.72)$$

We need then to calculate $f(\omega)$ which can be determined by the density of states in k -space, $f(k)$, as $f(\omega)d\omega = f(k)dk$. If we consider a solid being a cube of volume $V = L^3$ with L the side of the cube, we have already seen that $\vec{k} = (\frac{2\pi}{L}n_1, \frac{2\pi}{L}n_2, \frac{2\pi}{L}n_3)$ with $n_1, n_2, n_3 = \pm 1, \pm 2, \dots \pm N^{1/3}$. In k -space the different discretized states are separated by $\frac{2\pi}{L}$ in each of the 3-directions of space. We can then associate to each state a volume $\Delta k = \left(\frac{2\pi}{L}\right)^3$.

The volume in k -space between k and $k + dk$ is an spherical shell of volume $4\pi k^2 dk$. Then we can calculate $f(k)$ as

$$f(k)dk = \frac{4\pi k^2 dk}{\left(\frac{2\pi}{L}\right)^3} = V \frac{k^2 dk}{2\pi^2} \quad (3.73)$$

Then

$$f(\omega)d\omega = \frac{V k^2}{2\pi^2} \frac{k}{\omega} d\omega \quad (3.74)$$

and as in the Debye approximation $d\omega/dk = \omega/k = v_s$ we have

$$f(\omega)d\omega = \frac{V \omega^2}{2\pi^2 v_s^3} d\omega \quad (3.75)$$

This is a generic expression for the contribution of a unique phonon branch to the density of states $f(\omega)$. But in a 3-D solid, we need to consider the contributions of two transversal acoustic branches - which we will considerate degenerated - having associated speed of sound v_T and one longitudinal branch with associated speed of sound v_L . Each one of the branches will then contribute to the density of states and we will then have

$$f(\omega)d\omega = \frac{V\omega^2}{2\pi^2 d\omega} \left(\frac{1}{v_L^3} + \frac{2}{v_T^3} \right) \quad (3.76)$$

or defining an average speed of sound as $1/\bar{v}_s^3 = 1/v_L^3 + 2/v_T^3$ we have

$$f(\omega)d\omega = \frac{V\omega^2 d\omega}{2\pi^2 \bar{v}_s^3} \quad (3.77)$$

We can use this result to calculate ω_D :

$$\int_0^{\omega_D} f(\omega)d\omega = 3N \longrightarrow \frac{V}{2\pi^2} \frac{1}{\bar{v}_s^3} \int_0^{\omega_D} \omega^2 d\omega = 3N \quad (3.78)$$

We obtain then

$$\frac{V}{2\pi^2} \frac{1}{\bar{v}_s^3} \omega_D^3 = 3N \longrightarrow \omega_D = (18\pi^2)^{1/3} \frac{\bar{v}_s}{a} \quad (3.79)$$

where we have used $V = Na^3$.

We can then write the density of states as

$$f(\omega)d\omega = \frac{9N}{\omega_D^3} \omega^2 d\omega \quad (3.80)$$

and replace this expression in 3.71 to obtain:

$$E = \frac{9N}{\omega_D^3} \int_0^{\omega_D} \left(\frac{1}{2} \hbar \omega + \frac{\hbar \omega}{e^{\hbar \omega / k_B T} - 1} \right) \omega^2 d\omega = \quad (3.81)$$

$$= \frac{9}{8} N \hbar \omega_D + \frac{9N}{\omega_D^3} \int_0^{\omega_D} \frac{\hbar \omega^3}{e^{\hbar \omega / k_B T} - 1} d\omega \quad (3.82)$$

with the change of variable $x \equiv \hbar \omega / (k_B T)$ and defining the Debye temperature as $T_D = \hbar \omega_D / k_B$ we have

$$C_v = \frac{\partial E}{\partial T} = 9Nk_B \left(\frac{T}{T_D} \right)^3 \int_0^{T_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (3.83)$$

The Debye temperature, as the Einstein temperature, are model-dependent temperatures which values depend on the material under consideration.

We can examine the behavior of the so derived specific heat in the Debye approach in the limits of high and low temperature

At high T , $x \ll 1$ and then the function under the integral above tends just to x^2 and we obtain again the Dulong and Petit limit:

$$C_v = \frac{\partial E}{\partial T} = 9Nk_B \left(\frac{T}{T_D} \right)^3 \int_0^{T_D/T} x^2 dx = 3Nk_B \quad (3.84)$$

At low T , $T_D/T \rightarrow \infty$ and we have then a defined integral which can be demonstrated gives

$$\int_0^\infty \frac{x^4 e^x}{(e^x - 1)^2} dx = \frac{4\pi^4}{15} \quad (3.85)$$

and consequently

$$C_v = \frac{12}{5} Nk_B \pi^4 \left(\frac{T}{T_D} \right)^3 \quad (3.86)$$

The $C_v \propto T^3$ dependence is exactly what is found experimentally. This means that the average integral obtained by integration is $\bar{E} \propto T^4$, which is the analogous result to the Stefan-Boltzmann law of blackbody emission. In both cases, phonons in a crystal and light in a box, we have a confined boson gas, with a linear dispersion curve $p = \hbar\omega/c$ for photons and $\omega = v_s k$ for the Debye phonons.

Both the Einstein model and the Debye model calculate the specific heat of a solid from a simplified version of the phonon dispersion curves. In the case of the Einstein model, the phonon dispersion curves is simplified to $w(k) = w_E$, a constant optical mode without dispersion. In the case of the Debye model, the phonon dispersion curve is simplified to linear acoustic branches. We may then easily understand that at low temperatures, where the thermal energy is only comparable with the acoustic modes, the Einstein model is superior. But the Debye model constitutes a rather good approximation at all temperatures. Why so ? Figure 3.7 provides the explanation : optical modes can be seen as being a prolongation of acoustic ones in an extended zone scheme. This allows the Debye model to approximately reproduce both acoustic and optic modes.

More accurate methods to compute the phonon dispersion curves in crystalline solids require more advanced computation approaches as Density Functional Theory methods.

3.9 Phonon measurements

The most usual methods in the measurement of the phonons of a crystal are based on the inelastic scattering of radiation by the phonons themselves. The used radiation is generally either photons (IR, visible, UV or in the x-ray domain) or neutrons. We can differentiate 4 major methods :

- Brillouin scattering
- Raman scattering
- Inelastic neutron scattering
- Inelastic x-ray scattering

Brillouin and Raman scattering use in general visible photons, but non-visible photons can also be used. In all these inelastic scattering process phonons can be created (Stokes process) or annihilated (anti-Stokes process).

In Figure 3.8 is shown the Stokes and anti-Stokes process of creation and annihilation respectively of a phonon of energy $\hbar\Omega$ and momentum $\hbar\vec{k}$.

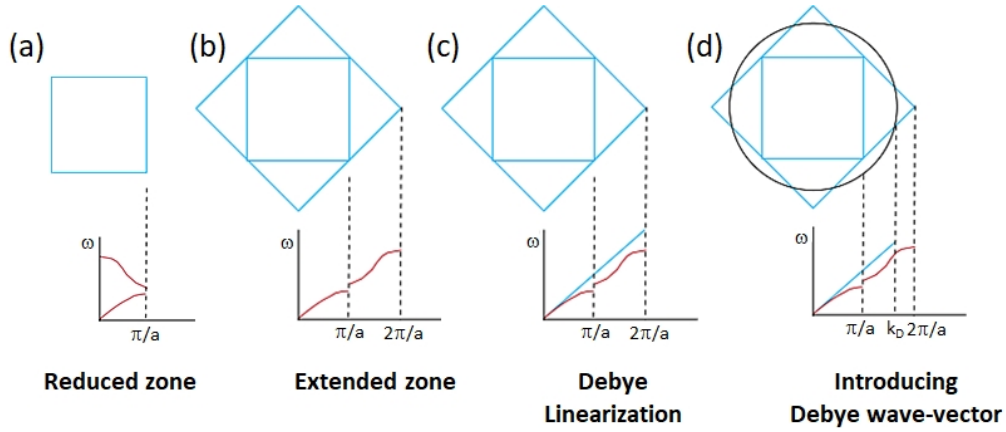


Figure 3.7: Scheme showing why the Debye model produces quite satisfactory results even in the presence of optical modes. (a) Dispersion curves in the reduced zone scheme for transverse modes (for instance) in a 2D diatomic system. On top of it the 1st Brillouin zone (b) Representation in extended zone for the first and second Brillouin zone. (c) Same as (b) but including the linear approximation of the Debye model. (d) Same as (c) introducing the limit the Debye energy and the Debye wave-vector.

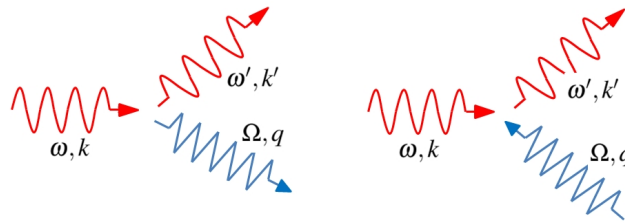


Figure 3.8: Stokes process (left) and anti-Stokes process (right)

Conservation of energy and momentum translates in a crystal in:

$$\begin{cases} \omega = \omega' \pm \Omega \\ \vec{k} = \vec{k}' \pm \vec{q} \pm \vec{G}_{\text{hkl}} \end{cases} \quad (3.87)$$

Here $\vec{G}_{\text{hkl}}$ is any vector of the reciprocal lattice which we can take here as being zero for simplicity (all reciprocal lattice vectors are equivalent). For a photon the dispersion curve is $E = \hbar ck$ where $\hbar c \sim 2 \cdot 10^3 \text{ eV } \text{\AA}$. How large is the momentum, k which can be carried by an optical photon? The photon energy is typically of 1 eV and then $k_{\text{photon}} \sim 1/2 \cdot 10^3 \sim 10^{-3} \text{ \AA}^{-1}$. This value is to be compared with the momentum carried by phonons which extent inside the first Brillouin zone with maximum values $\pi/a \approx 1 \text{ \AA}$. The conclusion is then that the momentum carried by photons is only enough to interact with phonons at the zone center of the Brillouin zone. This is shown in Fig. 3.9 where it is also shown the corresponding values for x-ray photons, which with energies of the order of 10 keV have momentum enough to interact with phonons in all the Brillouin zone.

In the case of neutrons

$$E = \frac{\hbar k^2}{2m} \quad (3.88)$$

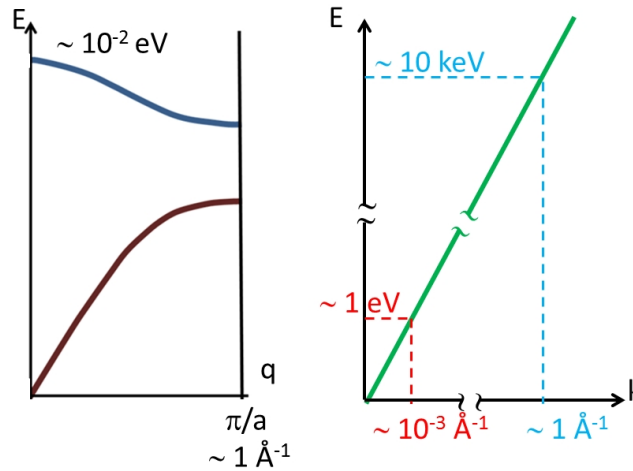


Figure 3.9: Scheme showing the phonon dispersion curve of a diatomic crystal (left) compared with the photon dispersion curve (right). The momentum carried by optical photons only allows interaction with zone center phonons, whereas x-ray photons can interact with all phonons in the first Brillouin zone

Which leads to $E \text{ (meV)} = 2,0716 [k \text{ (\AA}^{-1})]^2$. In research nuclear reactors, neutrons are usually thermalized to energies of the order of 20 meV. Then $k \sim (20/2)^{1/2} \sim 3 \text{ \AA}^{-1}$. Neutrons, as x-rays, have the needed momentum to create or annihilate phonons in all the first Brillouin zone.

It is interesting here to consider the exigences in terms of energy resolution needed in the different studies. In general we should consider that for phonon measurements (~ 10 meV) we need a resolution $\Delta E \sim 10^{-1} \text{ meV}$.

Then for neutrons, we need a resolution $\delta E/E \sim 10^{-1}/20 \sim 10^{-2}$. For optical photons $\delta E/E \sim 10^{-1}/10^3 \sim 10^{-4}$ and for x-rays, being 10^4 times more energetic, we need then $\delta E/E \sim 10^{-8}$. This challenging conditions for x-rays made that the development of inelastic x-ray scattering is more recent than neutron inelastic scattering techniques. Both rely in the 3-axis spectrometer principle (3.10)

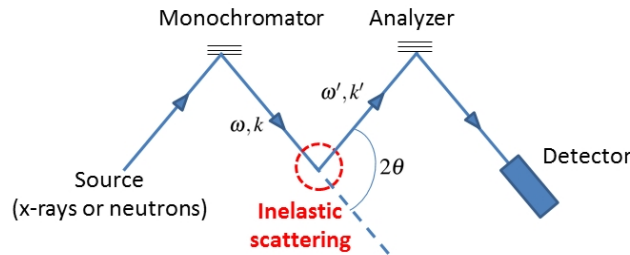


Figure 3.10: Principle of a 3-axis inelastic scattering spectrometer used in neutron and x-ray inelastic scattering techniques. The 3-axis refer to the 3 defined legs after the monochromator. Both monochromator and analyzer use diffraction either to select or to analyze the radiation energy.

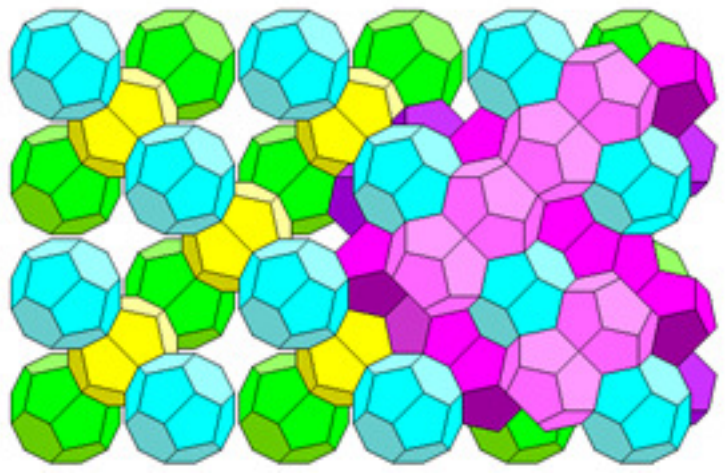
Raman and Brillouin spectroscopy are the names given to the optical photon inelastic scattering techniques used to study optical or acoustic photons respectively. In both cases, as discussed, only zone center phonons will be accessed. Both methods use as exciting radiation a laser

beam. Then as for acoustic phonons, their energy tend to zero as we approach zero momentum transfer, the inelastic scattering process will be done with very low energy exchange. In Brillouin scattering then will be needed to analyze the scattered photons having energies very close to the laser excitation one. In that case, i.e. for Brillouin spectroscopy, Fabry-Perrot interferometers are needed in order to make such energy analysis, whereas in Raman spectroscopy the use of optical gratings, often combined with optical filters allow for an optimal set-up.

Another very frequent method to study phonons is *infra-red absorption spectroscopy*. The Infra-red light energy domain corresponds to the phonon energy domain. This allows for resonant absorption process, i.e. the frequency of the absorbed radiation matches the vibrational frequency. As in Raman spectroscopy only optical zone centre phonons will be probed, as the momentum carried by infra-red (IR) light is again negligible. Nevertheless the phonon measured by IR absorption spectroscopy and Raman spectroscopy are in general different. In fact radiation absorption (IR) and inelastic scattering of radiation (Raman) involve different physical processes. IR absorption is driven by electric dipole moment changes upon a change in the interatomic distance (during the normal vibration) whereas in Raman spectroscopy active vibrations can be detected if the polarizability (field induced dipole moment) is changed during the normal vibration. The application of group theory to the point-group of the crystals leads to further selection rules. These rules determine which optical phonons are detected in IR absorption spectroscopy (they are then called IR-active) and which ones can be detected by Raman spectroscopy (Raman-active). Selection rules allow for some phonon modes to be both Raman- and IR-active.



The magnetic moment of the neutron allows also to use neutron inelastic scattering to measure the dispersion curve of another quasiparticle, *magnons* which are collective excitation of the electron spin structure.)



4. Models of Electrons in Solids

4.1 Introduction

Electrons in solids find some analogies with phonons. In both cases we study waves (normal modes or wavefunctions) in a confined space (the solid) and in the presence of a periodic potential. Spatial confinement will lead to the k-space discretization whereas the periodicity of the potential will make that the electron states would need just to be represented in the first Brillouin zone.

Nevertheless, electrons, particles with half-integer spin, are then fermions while phonons are bosons. They obey to different statistics and this will have important consequences.

The determination of the different electronic states in a crystal is done today with various advanced methods, the ones most widely used being based on the DFT (Density Functional Theory). In this introduction course, we will consider three simpler methods which allow to capture particular aspects of the physics of the systems. In spite of their simplicity, they can in many cases provide an accurate approach to the system description. These models are the free electron model, the tight binding approximation and the nearly-free electron model.

In the free electron model, there is no periodic potential and the electrons are considered as free particles in a box. A variant of this is the empty lattice model which introduces the effect of periodicity but with no interaction potentials. The nearly-free electron model introduces the effect of periodicity in a more realistic way: a non-zero periodic potential is introduced. Finally, in the tight binding model, the dominant effect is the interaction between atoms, even if they will be considered to have a potential not much affected with respect to the free atom.

The different models will be presented almost in this order, with the only modification being that the nearly-free electron model will be the last to be presented in this chapter.

4.2 From the free electron model to the Empty lattice model

4.2.1 Electronic Band Structure

The *empty lattice model* (often incorrectly referred in textbooks as the free electron model) can constitute a first approximation for simple metals. In this approximation we distinguish the electrons in the last electronic shell, the valence electrons which we consider submitted to the periodic potential from the atomic nucleus and the rest of the electrons, $V(r)$ which is considered as constant. We set arbitrarily such constant to zero: $V(r) = 0$. Consequently, the Schrödinger

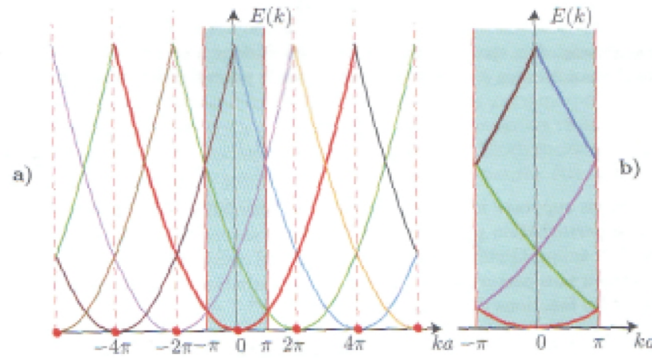


Figure 4.1: Free electron dispersion curve, $E(k)$ of the linear chain crystal. In (a) it is shown the corresponding parabola which can be centered in each one of the reciprocal lattice points (red dots). The shaded central region is the first Brillouin zone. In (b) it is depicted the representation of the band structure in the first Brillouin zone. Each one of the colors correspond to a portion of parabola originated from another reciprocal lattice point. The same result can be obtained by plotting in (a) only the parabola centered at the origin (bold red curve) and by translating through a reciprocal lattice vector inside the first Brillouin zone all regions outside the first Brillouin zone.

equation for the valence electrons becomes the free electron equation:

$$-\frac{\hbar^2}{2m}\nabla^2\Psi = \varepsilon\Psi \quad (4.1)$$

with m the mass of the electrons. The solutions are plane-waves of the form

$$\Psi(\vec{r}) = \frac{1}{\sqrt{V}}e^{i\vec{k}\vec{r}} \quad (4.2)$$

We impose the cyclic limit conditions for a cubic solid of side L and volume $V = L^3$:

$$\Psi(x+L, y, z) = \Psi(x, y+L, z) = \Psi(x, y, z+L) \quad (4.3)$$

which give

$$k_x = \frac{2\pi p}{L} \quad k_y = \frac{2\pi r}{L} \quad k_z = \frac{2\pi s}{L} \quad p, q, r = 0, \pm 1, \pm 2, \dots N^{1/3} \quad (4.4)$$

with N the number of valence electrons in the crystal.

The energy eigenvalues are

$$\varepsilon = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2) \quad (4.5)$$

and the momentum is given by $\vec{p} = \hbar\vec{k}$

Fig. 4.1 shows the energy dispersion parabola of the free electron in 1D (the central parabola in the graph). This unique parabola corresponds to the real free electron model. The empty lattice

model differs from the free electron model by the introduction of periodicity (crystallinity) even if this is done in a virtual way : a periodic potential of zero value. As for any oscillations in a crystal (and the plane-wave wavefunction of the electron is one), any state outside the first Brillouin zone can find its equivalent in the first Brillouin zone by a translation of a reciprocal lattice vector. In Figure 4.1 it is also shown how the 1D free electron dispersion curve is represented in the first Brillouin zone and in the extended scheme. Each one of the curves (with different colors in Figure 4.1) is called an electronic band or just an energy band. For a given k value we have then as many bands as lattice points in the reciprocal lattice, which are infinity for a perfect crystal.

In a three dimensional crystal having an fcc structure, the first Brillouin zone is more complex. To visualize the empty lattice dispersion curve we need to project the dispersion curve in the different high symmetry directions as shown in Fig. 4.2.

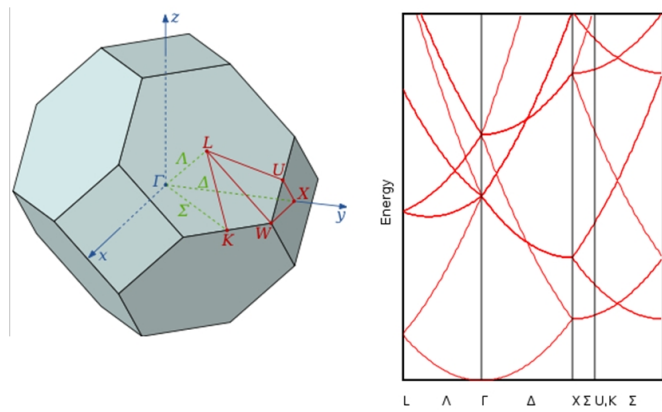


Figure 4.2: Empty lattice dispersion curve, $E(k)$ of the fcc crystal (wright). At the left side is shown the corresponding first Brillouin zone and the high symmetry points. It is observed that in some high symmetry points, several bands converge on a single point, which is then highly degenerated

4.3 The tight binding model

4.3.1 Introduction

The adiabatic approximation let us express the Hamiltonian of a condensed matter system made of atoms of atomic number Z in two different terms which can be treated separately, $H = H_n + H_e$, with

$$H_n = \frac{1}{2M} \sum_{i=1}^{N_n} p_i^2 + \frac{1}{2} Z \sum_{i,j=1; i \neq j}^{N_n} V_c(\vec{R}_i - \vec{R}_j) \quad (4.6)$$

$$H_e = \frac{1}{2m} \sum_{j=1}^{N_e} p_j^2 - \frac{1}{2} Z \sum_i \sum_j V_c(\vec{r}_j - \vec{R}_i) + \frac{1}{2} \sum_{i,j=1; i \neq j}^{N_e} V_c(\vec{r}_i - \vec{r}_j) \quad (4.7)$$

With M and m the mass of the nucleus and of the electron respectively and V_c is the Coulomb potential. Here R_i is the position of the nucleus of atom i and r_j the position of the j electron. The total number of atoms is N_n and the total number of electrons is N_e

Here we consider then only the electronic Hamiltonian, H_e . The electron-electron interaction is the more complex term in this expression. In order to deal with it we will consider that on each electron acts the average interaction from the other electrons. The average distribution of the electrons generate then a potential independent of the position. Within this approximation we will define the atomic potential, V_{at} , as the addition of the last two terms of H_e and then :

$$H_e = \frac{1}{2m} \sum_{j=1}^{N_e} p_j^2 + \sum_i \sum_j^{N_n} V_{at}(\vec{r}_j - \vec{R}_i) = \sum_{j=1}^{N_e} \left[\frac{p_j^2}{2m} + \sum_i^{N_n} V_{at}(\vec{r}_j - \vec{R}_i) \right] = \sum_{j=1}^{N_e} H_j \quad (4.8)$$

H_e is in that way a sum of identical one-electron terms, as each H_j is associated to the impulsion and position of a single electron. V_{at} represents the effect both of the nucleus and of the average distribution of all the electrons. V_{at} decreases rapidly at long distances due to the charge neutrality (screening).

The N_e electron problem has been then simplified to solve a one-electron Schrodinger equation:

$$H_j \Psi_{k_j}(\vec{r}_j) = E_j \Psi_{k_j}(\vec{r}_j) \quad \text{with} \quad H_j = \frac{p_j^2}{2m} + \sum_i^{N_n} V_{at}(\vec{r}_j - \vec{R}_i) \quad (4.9)$$

The complete electron Hamiltonian $H\Psi = E\Psi$ will have then as wavefonctions

$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_{N_e}) = \Psi_{k_1}(\vec{r}_1) \Psi_{k_2}(\vec{r}_2) \dots \Psi_{k_{N_e}}(\vec{r}_{N_e}) \quad (4.10)$$

with $E = \sum_{i=1}^{N_e} E_{k_i}$

As electrons are Fermions, $\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_{N_e})$ needs to be an antisymetric function, so as to follow Pauli exclusion principle. This is easily done by replacing the last expression above of Ψ by the Slater determinant:

$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_{N_e}) = \frac{1}{\sqrt{N_e!}} \begin{vmatrix} \Psi_{k_1}(\vec{r}_1) & \Psi_{k_1}(\vec{r}_2) & \dots & \Psi_{k_1}(\vec{r}_{N_e}) \\ \Psi_{k_2}(\vec{r}_1) & \Psi_{k_2}(\vec{r}_2) & \dots & \Psi_{k_2}(\vec{r}_{N_e}) \\ \dots & \dots & \dots & \dots \\ \Psi_{k_{N_e}}(\vec{r}_1) & \Psi_{k_{N_e}}(\vec{r}_2) & \dots & \Psi_{k_{N_e}}(\vec{r}_{N_e}) \end{vmatrix}$$

We need an additional result to progress in our calculation : the Bloch theorem

4.3.2 The Bloch Theorem

This theorem expresses the consequences of the potential periodicity in a crystal on the solutions of the Schrödinger equation.

Let us consider the 1-dimensional problem with the Schrödinger equation being:

$$-\frac{\hbar^2}{2m} \frac{d^2 \Psi(x)}{dx^2} + V(x) \Psi(x) = E \Psi(x) \quad (4.11)$$

and $V(x)$ a periodic potential verifying:

$$V(x) = V(x + ma) \quad m \in \mathbb{Z} \quad (4.12)$$

The periodicity of $V(x)$ allows us to express it as a linear combination of planewaves of wavenumbers $h_n = n2\pi/a$:

$$V(x) = \sum_{n=-\infty}^{\infty} V_n e^{ih_n x} \quad (4.13)$$

In the particular case in which $V(x) \rightarrow 0$ then

$$\Psi(x) \rightarrow W_k(x) = \frac{1}{\sqrt{L}} e^{ikx} \quad (4.14)$$

a simple plane-wave, where L is the length of the crystal. The eigenvalues are $E(k) = \hbar^2 k^2 / 2m$. We now consider $V(x) \neq 0$ and then apply the Hamiltonian operator $H = p^2 / 2m + V(x) \equiv H_0 + V(x)$ on the wavefunction $W_k(x)$. Using ket notation:

$$H |W_k\rangle = H_0 |W_k\rangle + \sum V_n e^{ih_n x} |W_k\rangle = E(k) |W_k\rangle + \sum V_n |W_{k+h_n}\rangle \quad (4.15)$$

Plane-waves $W_k(x) \propto e^{ikx}$ can be taken as a basis to express $\Psi(x)$. Then, $\Psi(x)$ will be expressed in a closed subspace, $S_k = \{W_k(x), W_{k+h_1}(x), W_{k-h_1}(x), W_{k+h_2}(x), W_{k-h_2}(x), \dots\}$. Consequently the solutions of Eq. 4.11, $\Psi_k(x)$ will be expressed as a linear combination of functions belonging to the subspace, S_k :

$$\Psi_k(x) = \sum_n c_n(k) \frac{1}{\sqrt{L}} e^{i(k+h_n)x} = u_k(x) e^{ikx} \quad (4.16)$$

with

$$u_k(x) = \sum_n c_n(k) \frac{1}{\sqrt{L}} e^{ih_n x} \quad (4.17)$$

Comparing this equation with the expression of $V(x)$ in eq. 4.13, we conclude that $u_n(x)$ has the same periodicity than $V(x)$, i.e., $u_k(x) = u_k(x+a)$.

We can then write Bloch theorem as:

Theorem 4.3.1 The solutions of the Schrödinger equation in a periodic potential are planewaves spatially modulated by a function having the periodicity of that potential.

Figure 4.3 shows a Bloch function in the case of a 1D crystal.

In the case of our 1-D problem we have $\Psi_k(x) = u_k(x) e^{ikx}$ with $u_k(x) = u_k(x+a)$.

If now we consider the value of $\Psi_k(x+t_n)$ with $t_n = na$, we have:

$$\Psi_k(x+na) = e^{ik(x+na)} u_k(x+na) = e^{ik(x+na)} u_k(x) = e^{ikna} e^{ikx} u_k(x) = e^{ikt_n} \Psi_k(x) \quad (4.18)$$

Generalizing to a 3D case, this leads to an equivalent expression of the Bloch theorem:

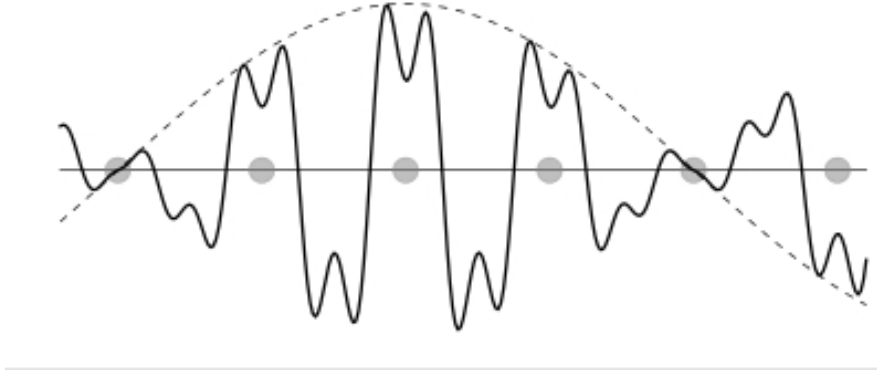


Figure 4.3: A Bloch function in the case of a 1D crystal for a given k value (continuous line). The dashed line is the plane-wave exponential factor and the light circles represent atoms. Credit : Wikipedia

Theorem 4.3.2 $\Psi_{\vec{k}}(\vec{r} + \vec{R}_n) = e^{i\vec{k}\vec{R}_n} \Psi_{\vec{k}}(\vec{r})$ The solutions of the Schrödinger equation in a periodic potential are just modulated by a phase $e^{i\vec{k}\vec{R}_n}$ under a translation by a vector of the lattice, $\vec{R}_n$.

We can note here that two sub-spaces $S_{\vec{k}}$ and $S_{\vec{k}'}$ as defined above are equal if $\vec{k} = \vec{k}' + n2\pi/a$. This allow us to define a k -region $-\pi/a \leq k \leq \pi/a$ from which all other $S_{\vec{k}}$ spaces can be generated. We recognize this as being the first Brillouin zone.

Also here we will introduce the Born-von-Karman periodic conditions to avoid edge effects for a finite size crystal of length $L = Na$:

$$\Psi_{\vec{k}}(x + Na) \equiv \Psi_{\vec{k}}(x) \quad \Rightarrow \quad e^{ikNa} = 1 \quad \Rightarrow \quad k = \frac{2\pi}{Na}n \quad n = 0, \pm 1, \pm 2, \dots \quad (4.19)$$

Again this constitutes a quasicontinuum of states when N is big, which means that all sums over k can be transformed in integrals as was done in Eq. 1.54. We find then N uniformly distributed values of k in the first Brillouin zone.

4.3.3 Crystal momentum

For a free electron, $\Psi_{\vec{k}} = e^{i\vec{k}\vec{r}}$, i.e., a planewave. The application of the momentum operator $\hat{p} = \frac{\hbar}{i} \vec{\nabla}$ gives

$$\hat{p}\Psi_{\vec{k}} = \frac{\hbar}{i} \vec{\nabla} e^{i\vec{k}\vec{r}} = \frac{\hbar}{i} i\vec{k} e^{i\vec{k}\vec{r}} = \hbar\vec{k} \Psi_{\vec{k}} \quad (4.20)$$

so $\hbar\vec{k}$ are eigenvalues of the momentum, $\hat{p}$.

In a crystal we need to consider the application of $\hat{p}$ on Bloch wavefunctions, $\Psi_{\vec{k}} = e^{i\vec{k}\vec{r}} u(\vec{r})$ which gives

$$\hat{p}\Psi_{\vec{k}} = \frac{\hbar}{i} \vec{\nabla} \left(e^{i\vec{k}\vec{r}} u(\vec{r}) \right) = \hbar\vec{k} \Psi_{\vec{k}} + e^{i\vec{k}\vec{r}} \frac{\hbar}{i} \vec{\nabla} u(\vec{r}) \quad (4.21)$$

which is not a constant times $\Psi_{\vec{k}}$, and then $\Psi_{\vec{k}}$ is not a wavefunction of the momentum operator. Consequently *in a crystal it is not correct to assimilate $\hbar\vec{k}$ as corresponding to the crystal momentum*. Nevertheless, it is admitted to refer the momentum axis of the electron dispersion

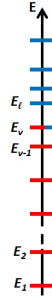


Figure 4.4: Atomic energy levels. Red lines correspond to filled levels and blue to unfilled ones

curves (the band structure) as the momentum axis. It is worth noting that electrons lying in maxima or minima of the band structures can be assimilated to free electrons and then we recover the significance of the momentum.

4.3.4 Energy Bands

We have already seen the energy band structure arising from the free electron model. In the following paragraphs we will see that a band electronic structure is also obtained from the tight binding approach.

We are going to enonciate the main hypothesis of the tight binding model, that is, that the electron wavefunctions in the crystal differ weakly from the atomic wavefunctions, i.e., the electron remain tightly bond to the atoms.

Lets then consider the Schrödinger equation for an isolated atom, which can be written for instance:

$$\left[\frac{\hat{p}^2}{2m} + V_{\text{atomic}}(r) \right] \chi_n(r) = E_n \chi_n(r) \quad (4.22)$$

which gives rises to states of increasing energy $E_1, E_2, \dots, E_{v-1}, E_v, E_e, \dots$ in which the Z electrons of the atoms will lye (see Fig. 4.4). In this notation we call E_v the last occupied energy level (total or partially) and E_e the first totally empty energy level.

We concentrate first on E_v (we will see later why), but what follows will apply to any atomic energy level, occupied or not.

In a crystal the N_n atoms will sit on the lattice positions $\vec{R}_n$. We are then interested on understand how the wavefunctions $\chi_v(\vec{r} - \vec{R}_n)$ centered in each of the $\vec{R}_n$ sites, evolve when we construct the crystal (we could imagine that we make an homotecy of the crystal from infinity distant atoms until the equilibrium position).

The tight binding model makes the hypothesis that the wavefunctions of the N_n atoms in the crystal will have an energy E_k derived from E_v under the following conditions:

- E_k is close to E_v
- E_k is far from E_{v-1} and E_e

In other words, we consider that E_k will remain closer to E_v than to the surrounding atomic energy levels, E_v and E_e :

$$|E_k - E_v| \ll \begin{cases} |E_k - E_{v-1}| \\ |E_k - E_e| \end{cases}$$

Under these conditions it is reasonable (and will be later verified too) to express the wavefunctions

in the crystal, $\Psi_k(\mathbf{r})$ which derive from the $\chi_v(\vec{\mathbf{r}} - \vec{\mathbf{R}}_n)$ as a **L**inear **C**ombination of **A**tomical **O**rbitals (**LCAO** method):

$$\Psi_k(\mathbf{r}) = \frac{1}{\sqrt{N_n}} \sum_{\ell=1}^{N_n} a_{k,\ell} \chi_v(\vec{\mathbf{r}} - \vec{\mathbf{R}}_\ell) \quad (4.23)$$

which can be also written in ket notation as:

$$|\Psi_k\rangle = \frac{1}{\sqrt{N_n}} \sum_{\ell=1}^{N_n} a_{k,\ell} |\vec{\mathbf{R}}_\ell\rangle \quad (4.24)$$

We can then introduce this in the one-electron Schrödinger equation (Eq. 4.9), in which we can consider $j = 1$ as all positions are taken here as being equivalent. Then we have:

$$\sum_{\ell=1}^{N_n} a_{k,\ell} H_1 |\vec{\mathbf{R}}_\ell\rangle = \sum_{\ell=1}^{N_n} a_{k,\ell} E_k |\vec{\mathbf{R}}_\ell\rangle \quad (4.25)$$

$$V_\ell(\mathbf{r}) \equiv \sum_{m=1, m \neq \ell}^{N_n} V_{\text{atomic}}(\vec{\mathbf{r}} - \vec{\mathbf{R}}_m) \quad (4.26)$$

We then separate H_1 in two terms:

$$H_1 = \frac{\hat{\mathbf{p}}^2}{2m} + V_{\text{atomic}}(\vec{\mathbf{r}} - \vec{\mathbf{R}}_\ell) + \sum_{m=1, m \neq \ell}^{N_n} V_{\text{atomic}}(\vec{\mathbf{r}} - \vec{\mathbf{R}}_m) \quad (4.27)$$

The first term represents the Hamiltonian from site ℓ :

$$H_\ell \equiv \frac{\hat{\mathbf{p}}^2}{2m} + V_{\text{atomic}}(\vec{\mathbf{r}} - \vec{\mathbf{R}}_\ell) \quad (4.28)$$

And the second term embraces *all the potentials from all the other sites*, which we call $V_\ell(\mathbf{r})$. Figure 4.5 shows the representation of $V_\ell(\mathbf{r})$ and $V_{\text{atomic}}(\mathbf{r})$ in the case of a linear chain of atoms. We have then :

$$H_1 |\vec{\mathbf{R}}_\ell\rangle = H_\ell |\vec{\mathbf{R}}_\ell\rangle + V_\ell(\vec{\mathbf{r}}) |\vec{\mathbf{R}}_\ell\rangle = E_v |\vec{\mathbf{R}}_\ell\rangle + V_\ell(\vec{\mathbf{r}}) |\vec{\mathbf{R}}_\ell\rangle \quad (4.29)$$

By replacing this in Eq. 4.25 we get:

$$\sum_{\ell=1}^{N_n} a_{k,\ell} \left[E_v |\vec{\mathbf{R}}_\ell\rangle + V_\ell(\vec{\mathbf{r}}) |\vec{\mathbf{R}}_\ell\rangle \right] = \sum_{\ell=1}^{N_n} a_{k,\ell} E_k |\vec{\mathbf{R}}_\ell\rangle \quad (4.30)$$

We now consider that the $|\vec{\mathbf{R}}_\ell\rangle$ constitutes an orthonormed ensemble:

$$\langle \vec{\mathbf{R}}_n | \vec{\mathbf{R}}_\ell \rangle = \delta_{n,\ell} \quad (4.31)$$

This is undoubtedly true when the atoms are far enough. We consider then this property is preserved when the atoms approach to each other to form the crystal.

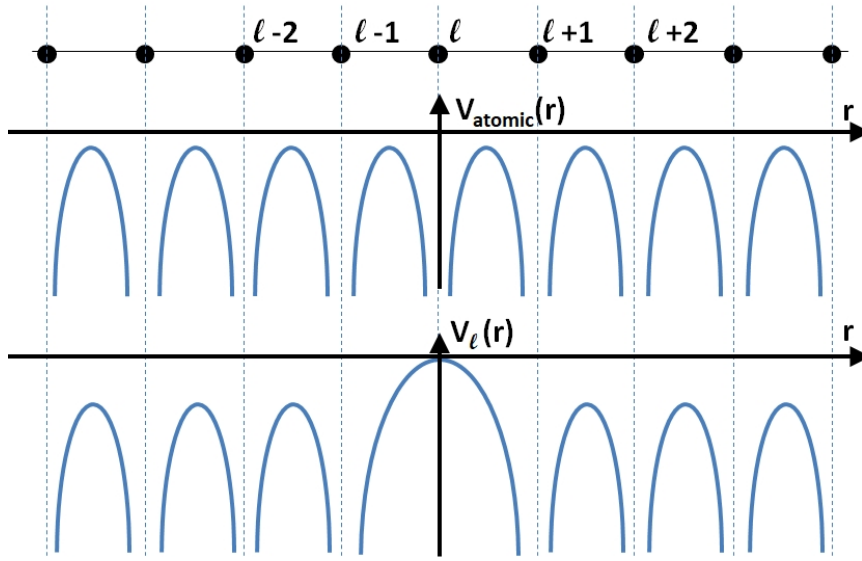


Figure 4.5: Sketch of the $V_{\text{atomic}}(r)$ and $V_{\ell}(r)$ potentials in a linear chain of atoms. In $V_{\ell}(r)$ the contribution of atom ℓ to the chain potential is not considered.

We now apply the bra, $\langle \vec{R}_n |$ in equation 4.30 and if we define the integrals $t_{n,\ell}$, called **overlap integrals** or **transfer integrals**.

$$t_{n,\ell} = -\langle \vec{R}_n | V_{\ell}(r) | \vec{R}_{\ell} \rangle \quad (4.32)$$

(the minus sign is an arbitrary choice which leads more frequently to positive values of the $t_{n,\ell}$ integrals)

we obtain:

$$-\sum_{\ell=1}^{N_n} t_{n,\ell} a_{k,\ell} = (E_k - E_v) a_{k,n} \quad (4.33)$$

This constitutes a system of N_n equations (one for each n value). In that way the equation of Schrödinger is transformed in a matrix eigenvalue problem, with non-trivial solutions obtained by setting its determinant equal to zero.

The $a_{k,n}$ and the $t_{n,\ell}$ values are further constrained.

In fact, if we consider the Born-von Karman limit conditions in 1D crystal of cell parameter a , this translates into $\Psi_k(x + Na) = \Psi_k(x)$, which leads to

$$a_{k,n+N_n} = a_{k,n}. \quad (4.34)$$

On the other side, we have to consider the effect of the translation invariance (two crystal sites should be equivalent), which means that the overlap integrals, $t_{n,\ell}$ will only depend on the distance between the sites n and ℓ and consequently we can express these integrals as a function of a unique index $|n - \ell|$:

$$t_{n,\ell} = t_{|n-\ell|} = t_{\ell} \quad (4.35)$$

where in the last equality we have considered $n = 0$ as all crystal sites are equivalent. Formally, $t_{n,\ell}$ should be forced to be zero for any sites for which $|n-\ell| > N_n$. In practice the overlap integral decreases rapidly with distance and only a few number of terms need to be considered.

In the 1D problem, we can now write Eq. 4.33 singularizing site n and putting together the equidistant terms at the left and the right. We then have:

$$-t_0 a_{k,n} - \sum_{\ell=1}^{N_n/2-1} t_{\ell} (a_{k,n+\ell} + a_{k,n-\ell}) = (E_k - E_v) a_{k,n} \quad (4.36)$$

Grouping terms:

$$- \sum_{\ell=1}^{N_n/2-1} t_{\ell} (a_{k,n+\ell} + a_{k,n-\ell}) = (E_k - E_v + t_0) a_{k,n} \quad (4.37)$$

This is a practical equation to determine E_k which as we will see in the forthcoming examples, leads to a continuum of states, i.e., an energy dispersion curve that we call an energy band.

Now we can use the Bloch theorem to progress in the calculation. In fact, the Hamiltonian H_1 is periodic, so the corresponding eigenfunctions, Ψ_k are Bloch functions and verify (in 1D)

$$\Psi_k(x) = e^{ikx} u_k(x) \quad (4.38)$$

with $u_k(x+a) = u_k(x)$

In our LCAO approximation we have

$$\Psi_k = \frac{1}{\sqrt{N_n}} \sum_{\ell=1}^{N_n} a_{k,\ell} \chi_v(x - R_{\ell}) \quad (4.39)$$

which means then that

$$u_k(x) = \frac{1}{\sqrt{N_n}} \sum_{\ell=1}^{N_n} a_{k,\ell} e^{-ikx} \chi_v(x - R_{\ell}) \quad (4.40)$$

The periodicity of u_k then leads to

$$u_k(x+a) = \frac{1}{\sqrt{N_n}} \sum_{\ell=1}^{N_n} a_{k,\ell} e^{-ika} e^{-ikx} \chi_v(x - R_{\ell-1}) \equiv u_k(x) \quad (4.41)$$

which needs then that

$$a_{k,\ell} e^{-ika} = a_{k,\ell-1} \Rightarrow a_{k,\ell} = a_{k,\ell-1} e^{ika} \quad (4.42)$$

And iterating this, we have

$$a_{k,\ell} = a_{k,0} e^{ik\ell a} \quad (4.43)$$

We can combine this result with Eq. 4.34

$$\left\{ \begin{array}{l} a_{k,n+N_n} = a_{k,n} \\ a_{k,\ell} = a_{k,0} e^{ik\ell a} \end{array} \right\} \Rightarrow e^{ikN_n a} = 1 \Rightarrow k = \frac{2\pi m}{N_n a} \quad m \in \mathbb{Z} \quad (4.44)$$

Now we can include the normalization condition on Ψ_k , $|\Psi_k| = 1 \Rightarrow a_{k,0} = 1$, and then we have

$$a_{k,n} = e^{ikR_n} = e^{ikna} \quad (4.45)$$

All this can be generalized in 3-dimensions, and the wavefunctions of the Schrödinger equation in the LCAO approximation, which verify the Bloch theorem write:

$$\Psi_k(\vec{r}) = \frac{1}{\sqrt{N_n}} \sum_{n=1}^{N_n} e^{ik\vec{R}_n} \chi_v(\vec{r} - \vec{R}_n) \quad (4.46)$$

The wavefunctions $\chi_v(\vec{r} - \vec{R}_n)$ (which we have also written $|\vec{R}_n\rangle$) for which we have admitted that there is no overlap, i.e., $\langle \vec{R}_n | \vec{R}_m \rangle = \delta_{nm}$, are called Wannier functions. The Wannier functions constitute an adequate basis for $\Psi_k(x)$.

4.3.5 Linear chain in first neighbor approximation

Lets consider a linear chain of atoms. As $\chi_v(\vec{r} - \vec{R}_n)$ decreases rapidly as the distance from $\vec{R}_n$ increases, in many cases it is possible to consider that only the t_0 and t_1 integrals differ from zero. We have then:

$$t_n = 0 \quad \text{when} \quad |n| > 1 \quad (4.47)$$

$$t_0 = -\langle R_0 | V_0 | R_0 \rangle = -\langle R_n | V_n | R_n \rangle \quad (4.48)$$

$$t_1 = -\langle R_1 | V_0 | R_0 \rangle = -\langle R_n | V_{n-1} | R_{n-1} \rangle = -\langle R_{n+1} | V_n | R_n \rangle \quad (4.49)$$

We recall that V_0 represents the contribution of all atomic potentials in the crystal except the one at site 0. With these definitions Equation 4.37 then writes:

$$-t_1 (a_{k,n+1} + a_{k,n-1}) = (E_k - E_v + t_0) a_{k,n} \quad (4.50)$$

and using 4.45

$$\left\{ \begin{array}{l} a_{k,n} = e^{ikna} \\ a_{k,n+1} = e^{ik(n+1)a} \\ a_{k,n-1} = e^{ik(n-1)a} \end{array} \right\} \quad (4.51)$$

and then replacing in Eq. 4.50 we get:

$$-t_1 (e^{ika} + e^{-ika}) = (E_k - E_v + t_0) \quad (4.52)$$

which gives

$$E_k = E_v - t_0 - 2t_1 \cos ka \quad (4.53)$$

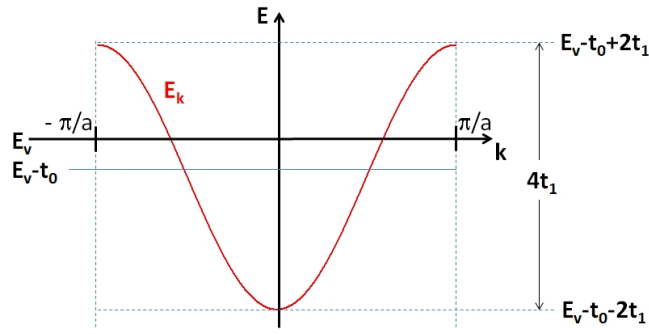


Figure 4.6: Graphic representation of the LCAO 1D band in first neighbors approximation in the first Brillouin zone. **The bandwidth is given by $4t_1$.**

We can then represent $E(k)$ in Fig. 4.6.

We get then a quasi continuum of energy states, i.e. a band of energy. In the k axis we have a total of N_n different values. Each one of these k values can hold 2 different states (spin up and down).

This is the electronic band originated from the electronic state E_v . Obviously, the same can be applied for any of the atomic energy levels (occupied or not) which will produce each of them an energy band. The width of the band is given in each case by the corresponding overlap integral t_1 which mixes through the potential the wavefunction of neighboring atoms. For highly localized states (deep levels in general, or also d or f electronic states), this overlap will be reduced and will lead to narrow bands. In particular, the deepest levels will in principle preserve their atomic character (t_1 negligible).

We can then make a sketch on how the atomic electronic energy levels can evolve in a picture in which the atoms are found initially at infinite distance from each other and in which we progressively reduce the distance r between them. This is shown in Figure 4.7.

The LCAO approximation in the way we are considering it, needs that the maximum of the E_v band does not touch the first excited states from the corresponding band derived from E_c . This means that $E_c - E_v \gg 2t_1$. Such cases need to be treated by considering a linear combination of atomic orbitals from the two energy levels. We speak then of hybridization.

Exercise 4.1 Hybridization. We could find ourselves in the situation in which the electron bands coming from two different levels (for instance s and p carbon levels in a carbon chain) are too close or even overlap at the equilibrium distance formation of the crystal. Without solving the full problem, can you guess how to modify the LCAO model to cope with this difficulty? (do not hesitate to use books or Internet resources to help you). ■

We note also that by replacing k by $k + 2\pi/a$ we do not modify the Bloch LCAO wave function

$$|\Psi_k\rangle = \frac{1}{\sqrt{N_n}} \sum_{\ell=1}^{N_n} e^{ik\ell a} |R_\ell\rangle \quad (4.54)$$

which justifies the representation in the first Brillouin zone.

We see in Eq. 4.54 that:

- For $k = 0$ all $|R_\ell\rangle$ are in phase and we have a minimum of energy.
- For $k = \pm\pi/a$ all consecutive $|R_\ell\rangle$ are in phase opposition and the energy is maximum.

This corresponds respectively to the bonding and antibonding states which are defined in molec-

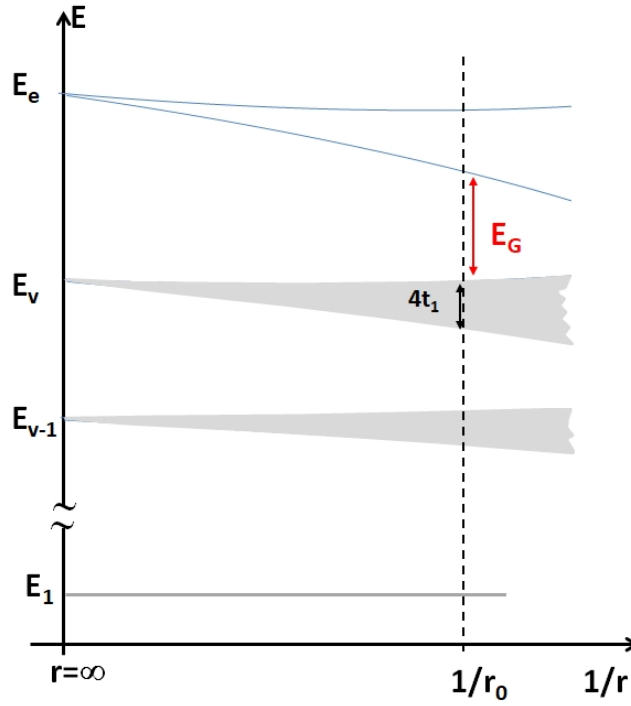


Figure 4.7: Evolution of the atomic energy levels from isolated atoms (left) with decreasing distance, r , until the formation of a crystal at the equilibrium distance r_0 . The deepest atomic energy levels as E_1 are not modified due to the negligible value of their corresponding overlap integrals.

ular systems as shown in Fig. 4.8.

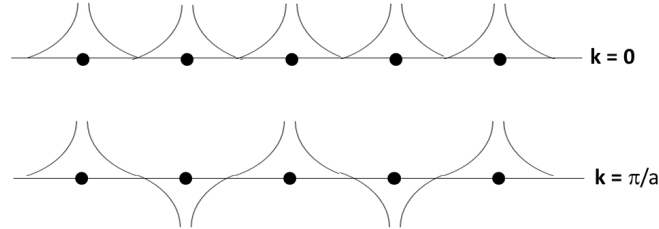


Figure 4.8: Bonding ($k = 0$) and antibonding ($k = \pi/a$ and $k = -\pi/a$) at the center and limits of the first Brillouin zone respectively.

The $|\Psi_k\rangle$ states constitute a complete ensemble, i.e., an orthonormal complete base of the Hilbert space.

To see this, we need to show that $\langle \Psi_{k'} | \Psi_k \rangle = \delta_{k',k}$ with δ to be considered modulo $2\pi/a$ (or any translation in reciprocal space in a general 3D case). In fact,

$$\langle \Psi_{k'} | \Psi_k \rangle = \frac{1}{N_n} \sum_{\ell'} e^{-ik'\ell'a} \langle R_{\ell'} | \sum_{\ell} e^{ik\ell a} | R_{\ell} \rangle = \frac{1}{N_n} \sum_{\ell, \ell'} e^{i(k\ell' - k'\ell)a} \langle R_{\ell'} | R_{\ell} \rangle = \frac{1}{N_n} \sum_{\ell} e^{i(k-k')\ell a} \quad (4.55)$$

where we have taken profit in the last equality of the fact that $\langle R_{\ell'} | R_{\ell} \rangle = \delta_{\ell', \ell}$.

The sum $\langle \Psi_{k'} | \Psi_k \rangle = \frac{1}{N_n} \sum_{\ell} e^{i(k-k')\ell a}$ will be equal to zero for an arbitrary value of $k' - k$ as N_n is a large number.

Only if $k - k' = n2\pi/a$ with $n \in \mathbb{Z}$ we will have $\langle \Psi_{k'} | \Psi_k \rangle = \frac{1}{N_n} N_n = 1$ which is the result that we wanted to demonstrate.

4.3.6 Effective mass

The electron dispersion curve or energy band in the tight binding LCAO approximation can be written in the compact form:

$$E(k) = E'_0 - A \cos ka \quad (4.56)$$

by setting $E'_0 \equiv E_v - t_0$ and $A = 2t_1$. Close to $k = 0$ in the energy minimum, we can approximate

$$\cos ka \sim 1 - \frac{(ka)^2}{2} \Rightarrow E(k) \simeq E''_0 + \frac{Aa^2}{2} k^2 \quad (4.57)$$

with $E''_0 = E'_0 - A$.

We can set arbitrarily our origin of energy to E''_0 . If we now compare the obtained expression with the free electron dispersion curve, it is possible to write:

$$E = \frac{\hbar^2 k^2}{2m^*} \quad (4.58)$$

where we have modified the electron mass by replacing it by an *effective mass* m^* . We can then equate both equations to obtain the value of this effective mass:

$$\frac{Aa^2}{2} k^2 = \frac{\hbar^2 k^2}{2m^*} \Rightarrow m^* = \frac{\hbar^2}{Aa^2} = \frac{\hbar^2}{2t_1 a^2} \quad (4.59)$$

This is graphically shown in Figure 4.9.

Obviously this is applicable to the other maxima and minima of the energy dispersion curve. The obtained results means that when the electrons involved in these maxima or minima can be treated as free electrons by modifying their corresponding electron mass through the effective mass.

The origin of the effective mass, m^* is the interaction of the electron with the periodic potential of the ions and electron-electron (all has been incorporated in the generalized atomic potential). In a more general model the effective mass would include the effect of other interactions as the electron-phonon.

In practice, it is possible to find a value of m^* which allows to treat a particular problem involving electrons (electrical conduction, thermal conduction through electrons, specific heat...). Unfortunately, the values of m^* differ in general depending on the property we want to model, showing the limitations of the model.

We will come later again on the concept of effective mass when we will discuss the electron conduction in Chapter 5.

4.3.7 Electronic density of states

Lets evaluate the electronic density of states for the 1D-chain.

In the first Brillouin ($\Delta k = 2\pi/a$) zone we have N_n possible k -values. In an interval dk the corresponding number of k -values is

$$\frac{N_n a}{2\pi} |dk| = \frac{N_n a}{2\pi} \frac{dE}{|dE/dk|} \quad (4.60)$$

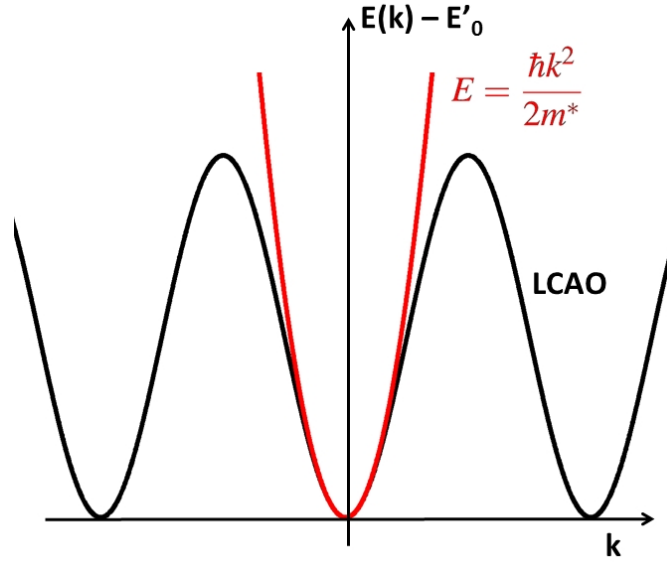


Figure 4.9: Graphic representation of the LCAO 1D band in first neighbors approximation in extended zone. The approximation of the effective mass is shown in red around one minimum of energy

Then the density of states per atom, $D(E)$ is given by

$$D(E) = \frac{a}{\pi} \frac{1}{|dE/dk|} \quad (4.61)$$

in which we have multiplied by 2 to take into account that, due to spin, we have 2 energy states for each k -state.

We take then the dispersion curve for the linear chain $E_k = E_v - t_0 - 2t_1 \cos ka$.

If $|E - (E_v - t_0)| > 2|t_1|$ we are out of the domain of definition of E_k and $D(E) = 0$. Otherwise, we have:

$$|dE/dk| = 2a|t_1 \sin ka| = 2a|t_1| \sqrt{1 - \cos^2 ka} \quad (4.62)$$

And replacing in 4.61 one gets

$$D(E) = \frac{1}{2\pi|t_1|} \frac{1}{\sqrt{1 - (E - E_v + t_0)^2/(4t_1^2)}} \quad \text{if } |E - E_v + t_0| < 2|t_1| \quad (4.63)$$

Figure 4.10 shows the obtained result. We observe that at the energies corresponding to the edges of the bands, the density of states tends to infinity. These are called the *van Hove singularities* and are characteristic of the electronic density of states of 1-dimensional systems. They are of particular importance in systems as the carbon nanotubes, as these singularities constitute an important reservoir of states allowing for resonant phenomena as the photon absorption between two van Hove singularities (the lowest one occupied and the highest energy one empty).

4.3.8 Classification of solids within the TBM

We can evaluate the impact on the electronic transport of the obtained knowledge on the electronic band structure. Let us consider again the 1-D crystal band structure and that the Fermi level

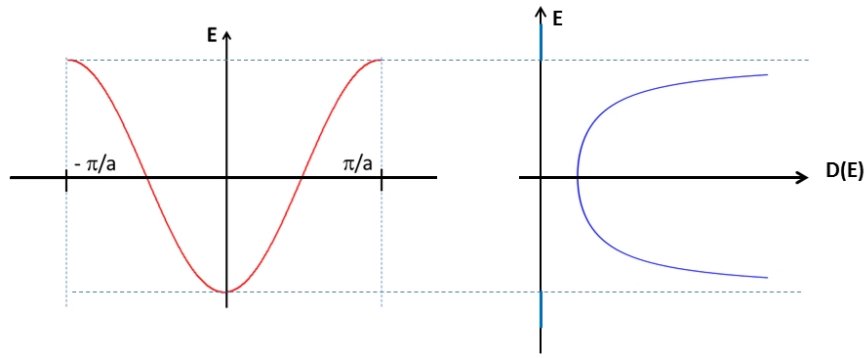


Figure 4.10: Graphic representation of the electronic density of states of a 1-D chain in LCAO in first neighbors approximation (wright). The left panel shows the corresponding electronic band.

lies somewhere close to the maximum of the band as shown in Fig 4.11.a We can now apply an electric field, $\vec{\epsilon}$ as shown in Fig 4.11.b. We have seen that close to the extrema of the band, we can consider that the electrons can be considered as almost free electrons, by introducing an effective mass, and hence also q can still be assimilated to the electron momentum. In that case we can write:

$$\hbar \dot{q} = -e\epsilon \Rightarrow q(t) = q(0) - \frac{e\epsilon t}{\hbar} \quad (4.64)$$

Consequently

- If $q < 0 \Rightarrow |q|$ increases with time
- If $q > 0 \Rightarrow |q|$ decreases with time

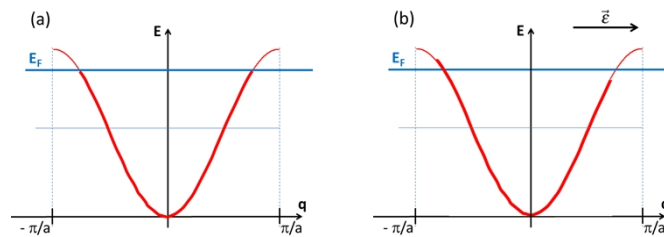


Figure 4.11: Graphic representation of the LCAO 1D band in first neighbors approximation in the first Brillouin zone. (a) The Fermi level has been arbitrarily set close to the maximum of the band. Filled states are represented by a thicker line. (b) Effect of an applied electric field $\vec{\epsilon}$.

The result is shown in Fig 4.11.b. We have then more electrons with negative q value, i.e., a net displacement of the electrons in the negative direction. We have then a current and the material is a conductor. The essential reason for this behavior is the availability of electron empty states just above the Fermi level.

We can now classify crystals in two categories, considering the availability or not of free states above the Fermi level. Figure 4.12 shows the two most important cases. In a metal, the empty states available just above the Fermi level allow for electrical conduction. The incomplete band is called the *conduction band* (CB). In the case of insulators or semiconductors, the Fermi level lies in an energy gap. There is a complete band (the *valence band*, VB) followed by a totally empty band (a conduction band). The application of an electric field will then not allow to change the

energy of the valence band electrons (except for very high electric fields or very small energy gaps).

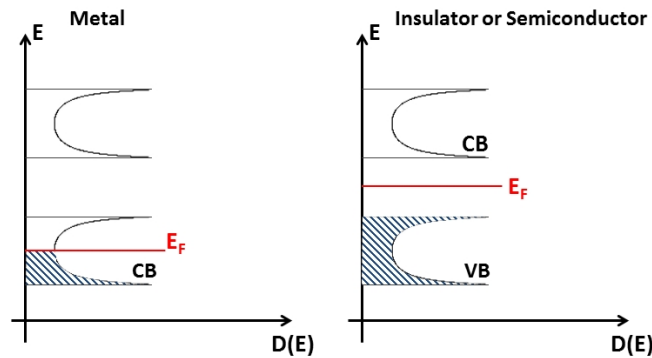


Figure 4.12: Sketch of the band structure of a metal (left) and a semiconductor (right). The conduction band (CB) and valence band (VB) are defined by the position of the Fermi energy, E_F .

In the case of the group I elements, the alkali metals (Li, Na, K, Rb and Cs), each one of the N_n atoms is providing one electron. The valence band can hold $2N_n$ states, so the Fermi level is in the middle of the conduction band. This corresponds to the metal picture in Fig. 4.12 in good agreement with observations (in fact, the alkali metals crystallize in the bcc lattice which has one atom per cell in the primitive cell).

In the group II elements (Be, Mg, Ca, Sr) we have one additional electron per atom. We expect then to totally fill the occupied band, which becomes the valence band. We will be in the situation of an insulator. *This is not what is observed.* The reason is that the band structure needs to be considered in three dimensions and we can have a conduction band lying below the valence band, which will lead to the partial filling of both bands.

We should note that the distinction between a semiconductor and an insulator is only governed by the value of the band-gap energy. It is often assumed that for band-gaps above 3 eV we will consider the system as an insulator. This is somehow arbitrary and depends on the context. We will also read about narrow-gap semiconductors or wide-gap semiconductors.

4.4 Nearly free electron model

In the nearly free electron model we are going to introduce the periodic potential of the ions as a weak perturbation of the free electron model. The quantum perturbation theory can be then used to find out the evolution of the electronic band structure with respect to the free electron model. In this section we will start by rewriting the Schrödinger equation for a periodic potential in momentum space and then to apply this result to the case of a weak potential. This will lead to the same result that the perturbation theory.

4.4.1 The Schrödinger equation for a periodic potential in momentum space

Consider $V(\mathbf{r})$, the periodic potential in a lattice, $V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R})$. We can expand the potential as a linear combination of plane-waves, and due to its periodicity, this restrains the possible wave-vectors in the expansion to vectors of the reciprocal lattice. We have then:

$$V(\mathbf{r}) = \sum_{\mathbf{K}} V_{\mathbf{K}} e^{i\mathbf{K}\mathbf{r}} \quad (4.65)$$

with $\mathbf{K}$ the vectors of the reciprocal lattice. The Fourier coefficients $V_{\mathbf{K}}$ are obtained through inverse Fourier transformation:

$$V_{\mathbf{K}} = \frac{1}{v_c} \int_{\text{cell}} V(\mathbf{r}) e^{i\mathbf{K}\mathbf{r}} d\mathbf{r} \quad (4.66)$$

Where v_c is the volume of the unit cell. We can set the origin of energy freely. A possible choice can be done by setting $V_0 = 0$. In fact, the first Fourier coefficient of the potential expansion represents the average potential energy over the primitive cell. We then fix this value arbitrarily as our energy origin:

$$V_0 = \frac{1}{v_c} \int_{\text{cell}} V(\mathbf{r}) d\mathbf{r} = 0 \quad (4.67)$$

The fact that the potential $V(\mathbf{r})$ is a real number leads to the following symmetry properties on its Fourier components:

$$V_{-\mathbf{K}} = V_{\mathbf{K}}^* \quad (4.68)$$

Most crystals have inversion symmetry, i.e. there is a suitable origin for which $V(\mathbf{r}) = V(-\mathbf{r})$. Then by Eq. 4.66 we have:

$$V_{-\mathbf{K}} = V_{\mathbf{K}} = V_{\mathbf{K}}^* \quad \text{for crystals with inversion symmetry} \quad (4.69)$$

The wavefunction of an electron in a crystal can be expressed in a plane-wave basis:

$$\psi(\mathbf{r}) = \sum_{\mathbf{q}} c_{\mathbf{q}} e^{i\mathbf{q}\mathbf{r}} \quad (4.70)$$

where $\mathbf{q}$ is a vector of the reciprocal space (here not restrained to the first Brillouin zone). We can now replace the above expression of $\psi(\mathbf{r})$ and $V(\mathbf{r})$ in the Schrödinger equation:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}) + V(\mathbf{r}) \psi(\mathbf{r}) = \mathcal{E} \psi(\mathbf{r}) \quad (4.71)$$

The kinetic energy becomes:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}) = \sum_{\mathbf{q}} \frac{\hbar^2}{2m} q^2 c_{\mathbf{q}} e^{i\mathbf{q}\mathbf{r}} \quad (4.72)$$

and the term with the potential energy becomes:

$$U\psi(\mathbf{r}) = \left(\sum_{\mathbf{K}} V_{\mathbf{K}} e^{i\mathbf{K}\mathbf{r}} \right) \left(\sum_{\mathbf{q}} c_{\mathbf{q}} e^{i\mathbf{q}\mathbf{r}} \right) = \sum_{\mathbf{K}, \mathbf{q}} V_{\mathbf{K}} c_{\mathbf{q}} e^{i(\mathbf{K}+\mathbf{q})\mathbf{r}} = \sum_{\mathbf{K}, \mathbf{q}'} V_{\mathbf{K}} c_{\mathbf{q}'-\mathbf{K}} e^{i\mathbf{q}'\mathbf{r}} \quad (4.73)$$

Where we have renamed $\mathbf{K} + \mathbf{q} = \mathbf{q}'$. We now modify in this expression the names of the indices from $\mathbf{K}$ and $\mathbf{q}'$ to $\mathbf{K}'$ and $\mathbf{q}$ in order to write the full Schrödinger equation, which becomes:

$$\sum_{\mathbf{q}} e^{i\mathbf{q}\mathbf{r}} \left[\left(\frac{\hbar^2}{2m} q^2 - \mathcal{E} \right) c_{\mathbf{q}} + \sum_{\mathbf{K}'} V_{\mathbf{K}'} c_{\mathbf{q}-\mathbf{K}'} \right] = 0 \quad (4.74)$$

Since the plane-waves in a crystal are an orthogonal basis, each one of the coefficients between brackets in the above equation needs to cancel:

$$\left(\frac{\hbar^2}{2m} q^2 - \mathcal{E} \right) c_{\mathbf{q}} + \sum_{\mathbf{K}'} V_{\mathbf{K}'} c_{\mathbf{q}-\mathbf{K}'} = 0 \quad (4.75)$$

We can now write this equation for wave-vectors $\mathbf{k}$ lying in the first Brillouin zone. We need then to translate the $\mathbf{q}$ values by the corresponding vector of the reciprocal lattice, $\mathbf{K}$, so as to have $\mathbf{k} = \mathbf{q} + \mathbf{K}$ or $\mathbf{q} = \mathbf{k} - \mathbf{K}$. The previous equation then becomes:

$$\left(\frac{\hbar^2}{2m} (\mathbf{k} - \mathbf{K})^2 - \mathcal{E} \right) c_{\mathbf{k}-\mathbf{K}} + \sum_{\mathbf{K}'} V_{\mathbf{K}'} c_{\mathbf{k}-\mathbf{K}-\mathbf{K}'} = 0 \quad (4.76)$$

and making the change of variables $\mathbf{K}' - \mathbf{K} \rightarrow \mathbf{K}'$ we get:

$$\left(\frac{\hbar^2}{2m} (\mathbf{k} - \mathbf{K})^2 - \mathcal{E} \right) c_{\mathbf{k}-\mathbf{K}} + \sum_{\mathbf{K}'} V_{\mathbf{K}'-\mathbf{K}} c_{\mathbf{k}-\mathbf{K}'} = 0 \quad (4.77)$$

This is nothing else than the Schrödinger equation written in the first Brillouin zone (in momentum space, with $\mathbf{k}$ belonging to the first Brillouin zone) for an electron in a periodic potential. The Schrödinger equation has become an infinite number of equations which for each $\mathbf{k}$ value will produce an infinite number of solutions, one for each vector of the reciprocal lattice, $\mathbf{K}$. In the particular case of the free electron ($V=0$), this corresponds to the different bands originated by the folding of the free energy parabola in the first Brillouin zone.

In other words, this set of infinity equations states that for a given $\mathbf{k}$ we will need to consider only the coefficients $c_{\mathbf{k}}, c_{\mathbf{k}-\mathbf{K}}, c_{\mathbf{k}-\mathbf{K}'}, c_{\mathbf{k}-\mathbf{K}''}, \dots$, in which wave-vectors differ from $\mathbf{k}$ by a reciprocal lattice vector. Then if the wave-vector $\mathbf{q}$ only assumes the values $\mathbf{k}, \mathbf{k}-\mathbf{K}', \mathbf{k}-\mathbf{K}'', \dots$ the wave function adopts the form:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{K}} c_{\mathbf{k}-\mathbf{K}} e^{i(\mathbf{k}-\mathbf{K})\mathbf{r}} \quad (4.78)$$

Result which is obtained by replacing $\mathbf{q}$ by $\mathbf{k}-\mathbf{K}$ in Eq. 4.70. We may note that this writing shows directly that $\psi_{\mathbf{k}}(\mathbf{r})$ are Bloch functions. In fact, we can write this equation as:

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i(\mathbf{k})\mathbf{r}} \left(\sum_{\mathbf{K}} c_{\mathbf{k}-\mathbf{K}} e^{-i\mathbf{K}\mathbf{r}} \right) \quad (4.79)$$

The term between braces is a function, $u(\mathbf{r})$,

$$u(\mathbf{r}) = \sum_{\mathbf{K}} c_{\mathbf{k}-\mathbf{K}} e^{-i\mathbf{K}\mathbf{r}} \quad (4.80)$$

having the periodicity of the lattice, i.e., $u(\mathbf{r}) = u(\mathbf{r} + \mathbf{R})$. Then the form of $\psi_{\mathbf{k}}(\mathbf{r})$ in Eq. 4.81 corresponds to the one of a Bloch function.

4.4.2 Band structure modification

Our starting point are the expression of Bloch functions and of the Schrödinger equations obtained in the previous subsection:

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i(\mathbf{k})\mathbf{r}} \left(\sum_{\mathbf{K}} c_{\mathbf{k}-\mathbf{K}} e^{-i\mathbf{K}\mathbf{r}} \right) \quad (4.81)$$

$$\left(\frac{\hbar^2}{2m} (\mathbf{k}-\mathbf{K})^2 - \mathcal{E} \right) c_{\mathbf{k}-\mathbf{K}} + \sum_{\mathbf{K}'} V_{\mathbf{K}'-\mathbf{K}} c_{\mathbf{k}-\mathbf{K}'} = 0 \quad (4.82)$$

We recall here that $\mathbf{k}$ is only defined in the first Brillouin zone. If we introduce the following notation:

$$\mathcal{E}_q^0 = \frac{\hbar^2}{2m} q^2 \quad (4.83)$$

Then the Schrödinger equation can be written:

$$\left(\mathcal{E} - \mathcal{E}_{\mathbf{k}-\mathbf{K}}^0 \right) c_{\mathbf{k}-\mathbf{K}} = \sum_{\mathbf{K}'} V_{\mathbf{K}'-\mathbf{K}} c_{\mathbf{k}-\mathbf{K}'} \quad (4.84)$$

We consider first the case of the free electron model, i.e., in which the periodic potential is just zero. Then we set in the Schrödinger equation all the Fourier components of the potential equal to zero, $U_{\mathbf{K}} = 0$, and we get:

$$(\mathcal{E}_{\mathbf{k}-\mathbf{K}}^0 - \mathcal{E}) c_{\mathbf{k}-\mathbf{K}} = 0 \quad (4.85)$$

This equation requires that either $c_{\mathbf{k}-\mathbf{K}} = 0$ (the trivial solution without interest) or that $\mathcal{E} = \mathcal{E}_{\mathbf{k}-\mathbf{K}}^0$. For each value of the reciprocal lattice vector, $\mathbf{K}$, we obtain a set of energy values, $\mathcal{E}(\mathbf{k}-\mathbf{K}) = \mathcal{E}_{\mathbf{k}-\mathbf{K}}^0$ which we identify as an energy band.

We can distinguish two cases:

- a) Non degenerate case. For a given value of $\mathcal{E}$ there is only one reciprocal vector verifying $\mathcal{E} = \mathcal{E}_{\mathbf{k}-\mathbf{K}}^0$.
- b) Degenerate case. There is a group of m reciprocal lattice vectors $\mathbf{K}_1, \dots, \mathbf{K}_m$ verifying:

$$\mathcal{E}_{\mathbf{k}-\mathbf{K}_1}^0 = \dots = \mathcal{E}_{\mathbf{k}-\mathbf{K}_m}^0 \quad (4.86)$$

for a given $\mathbf{k}$ value. We should note here that any linear combination of degenerate solutions being also a solution, one has then total freedom in the choice of the coefficients $c_{\mathbf{k}-\mathbf{K}}$ for $\mathbf{K} = \mathbf{K}_1, \dots, \mathbf{K}_m$.

These observations will now become much more substantial when we will allow the periodic potential to have a non zero value. Nevertheless, the distinction between degeneration and non-degeneration will need now to be done not in the basis of exact energy equality, but within differences in energy of the order of V . We consider now on this basis the two different cases (non-degenerate and degenerate).

Case 1. Non-degenerate. We fix a value of $\mathbf{k}$ and consider a particular reciprocal lattice vector $\mathbf{K}_1$ such that $\mathcal{E}_{\mathbf{k}-\mathbf{K}_1}^0$ is far from the values of $\mathcal{E}_{\mathbf{k}-\mathbf{K}}^0$ for $\mathbf{K} \neq \mathbf{K}_1$ compared with V . This corresponds in Fig. 4.13 to the green region inside the first Brillouin zone. We are then considering $\mathbf{k}$ -values for which

$$|\mathcal{E}_{\mathbf{k}-\mathbf{K}_1}^0 - \mathcal{E}_{\mathbf{k}-\mathbf{K}}^0| \gg V \quad \text{for all } \mathbf{K} \neq \mathbf{K}_1 \quad (4.87)$$

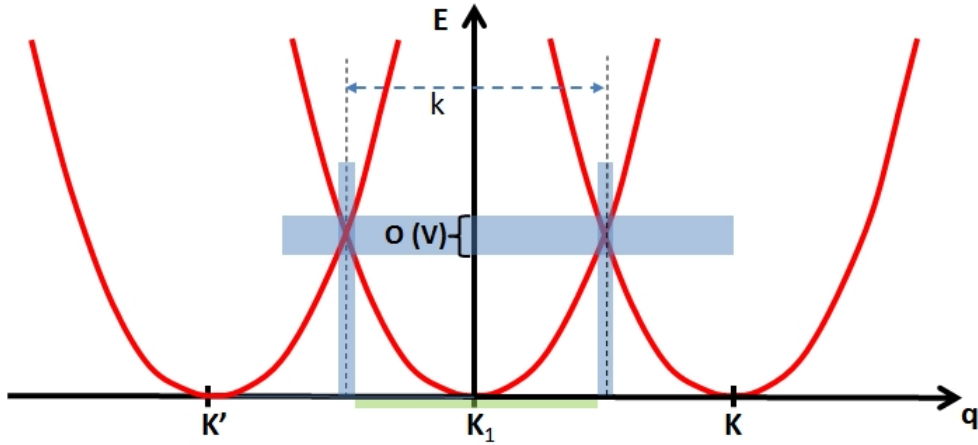


Figure 4.13: The two shaded bands in the k -axis delimit a range of k values for which withing an energy of the order of V , $O(V)$, the free electron bands centered at K_1 and at K or K' , i.e., $\mathcal{E}_{\mathbf{k}-\mathbf{K}_1}^0$ and $\mathcal{E}_{\mathbf{k}-\mathbf{K}}^0$ or $\mathcal{E}_{\mathbf{k}-\mathbf{K}'}^0$, can not be distinguished.

For those k -values, we are willing to evaluate the effect of the perturbation potential on those states corresponding to the free electron levels in the K_1 band, so for

$$\mathcal{E} = \mathcal{E}_{\mathbf{k}-\mathbf{K}_1}^0, \quad c_{\mathbf{k}-\mathbf{K}} = 0 \quad \mathbf{K} \neq \mathbf{K}_1 \quad (4.88)$$

We then consider the Schrödinger equation in its form given by Eq. 4.84 and we just set $\mathbf{K} = \mathbf{K}_1$ and dropping the prime from the dummy summation index:

$$\left(\mathcal{E} - \mathcal{E}_{\mathbf{k}-\mathbf{K}_1}^0 \right) c_{\mathbf{k}-\mathbf{K}_1} = \sum_{\mathbf{K} \neq \mathbf{K}_1} V_{\mathbf{K}-\mathbf{K}_1} c_{\mathbf{k}-\mathbf{K}} \quad (4.89)$$

where the summation excludes the case $\mathbf{K} = \mathbf{K}_1$ because we made the choice of setting our origin of energy for $V_0 = 0$. We are here considering the solution for which $c_{\mathbf{k}-\mathbf{K}}$ vanishes when $\mathbf{K} \neq \mathbf{K}_1$ in the limit of vanishing V . This means that the right side of the equation is the product of two vanishing terms and is then of second order in V . We may explicitly show this by writing Eq. 4.84 in the following way:

$$c_{\mathbf{k}-\mathbf{K}} = \frac{V_{\mathbf{K}_1-\mathbf{K}} c_{\mathbf{k}-\mathbf{K}_1}}{\mathcal{E} - \mathcal{E}_{\mathbf{k}-\mathbf{K}}^0} + \sum_{\mathbf{K}' \neq \mathbf{K}_1} \frac{V_{\mathbf{K}'-\mathbf{K}} c_{\mathbf{k}-\mathbf{K}'}}{\mathcal{E} - \mathcal{E}_{\mathbf{k}-\mathbf{K}}^0} \quad (4.90)$$

where we have separated the term containing $c_{\mathbf{k}-\mathbf{K}_1}$ as it will be an order of magnitude larger than the other terms. We insist that for this being true we need to be in the non-degenerate case, i.e., that all the denominators represent differences in energy large when compared with V . Otherwise, in the degenerate case we will find some $\mathbf{K} \neq \mathbf{K}_1$ for which the denominator will be of the order of V , cancelling the V in the numerator and providing additional terms comparable to the $\mathbf{K} = \mathbf{K}_1$ first term. Therefore, provided that there is no degeneracy we can write:

$$c_{\mathbf{k}-\mathbf{K}} = \frac{V_{\mathbf{K}_1-\mathbf{K}} c_{\mathbf{k}-\mathbf{K}_1}}{\mathcal{E} - \mathcal{E}_{\mathbf{k}-\mathbf{K}}^0} + O(V^2) \quad (4.91)$$

we can then replace this term in Eq. 4.89 to obtain:

$$\left(\mathcal{E} - \mathcal{E}_{\mathbf{k}-\mathbf{K}_1}^0 \right) c_{\mathbf{k}-\mathbf{K}_1} = \sum_{\mathbf{K}} \frac{V_{\mathbf{K}-\mathbf{K}_1} V_{\mathbf{K}_1-\mathbf{K}}}{\mathcal{E} - \mathcal{E}_{\mathbf{k}-\mathbf{K}}^0} c_{\mathbf{k}-\mathbf{K}_1} + O(V^3) \quad (4.92)$$

The terms in the summation are second order in V , so the energy band $\mathcal{E}$ differs from the free electron value $\mathcal{E}_{\mathbf{k}-\mathbf{K}_1}^0$ by terms of the order of V^2 . To solve this equation up to this order, we just need to replace $\mathcal{E}$ in the denominator by $\mathcal{E}_{\mathbf{k}-\mathbf{K}_1}^0$ which gives:

$$\mathcal{E} = \mathcal{E}_{\mathbf{k}-\mathbf{K}_1}^0 + \sum_{\mathbf{K}} \frac{|V_{\mathbf{K}-\mathbf{K}_1}|^2}{\mathcal{E}_{\mathbf{k}-\mathbf{K}_1}^0 - \mathcal{E}_{\mathbf{k}-\mathbf{K}}^0} + O(V^3) \quad (4.93)$$

This shows that the bands in the non-degenerate region (green shaded zone i Fig. 4.13) are modified second order on V which is weak. Every band below $\mathcal{E}_{\mathbf{k}-\mathbf{K}_1}^0$ contributes with a term rising the value of $\mathcal{E}$ and every band above $\mathcal{E}_{\mathbf{k}-\mathbf{K}_1}^0$ contributes with a term lowering the value of $\mathcal{E}$. But again this effect is only second order in V and as we will see in the next section, the weak potential modifies the energy of the degenerate states with a shift which is linear in V , becoming then the most important effect.

Case 2. Degenerate. We will now consider a set of vectors of the reciprocal lattice $\mathbf{K} = \mathbf{K}_1 \dots \mathbf{K}_m$ with associated energy levels $\mathcal{E}_{\mathbf{k}-\mathbf{K}_1}^0, \dots, \mathcal{E}_{\mathbf{k}-\mathbf{K}_m}^0$ equal within order V (this correspond to the blue region in the first Brillouin zone of the figure Fig. 4.13) and far appart from the other $\mathcal{E}_{\mathbf{k}-\mathbf{K}}^0$:

$$|\mathcal{E}_{\mathbf{k}-\mathbf{K}}^0 - \mathcal{E}_{\mathbf{k}-\mathbf{K}_i}^0| \gg V \quad \text{for all } i = 1, \dots, m \quad \mathbf{K} \neq \mathbf{K}_1, \dots, \mathbf{K}_m \quad (4.94)$$

We need then to write eq. 4.89 separating the $i = 1, \dots, m$ contributions:

$$\left(\mathcal{E} - \mathcal{E}_{\mathbf{k}-\mathbf{K}_i}^0 \right) c_{\mathbf{k}-\mathbf{K}_i} = \sum_{j=1}^m V_{\mathbf{K}_j-\mathbf{K}_i} c_{\mathbf{k}-\mathbf{K}_j} + \sum_{\mathbf{K} \neq \mathbf{K}_1, \dots, \mathbf{K}_m} V_{\mathbf{K}-\mathbf{K}_i} c_{\mathbf{k}-\mathbf{K}} \quad i = 1, \dots, m \quad (4.95)$$

We proceed as in the non-degenerate case, writing Eq. 4.84 and separating the energy levels:

$$c_{\mathbf{k}-\mathbf{K}} = \frac{1}{\mathcal{E} - \mathcal{E}_{\mathbf{k}-\mathbf{K}}^0} \left(\sum_{j=1}^m V_{\mathbf{K}_j-\mathbf{K}} c_{\mathbf{k}-\mathbf{K}_j} + \sum_{\mathbf{K}' \neq \mathbf{K}_1, \dots, \mathbf{K}_m} V_{\mathbf{K}'-\mathbf{K}} c_{\mathbf{k}-\mathbf{K}'} \right) \quad \mathbf{K} \neq \mathbf{K}_1, \dots, \mathbf{K}_m \quad (4.96)$$

Since $c_{\mathbf{k}-\mathbf{K}}$ will be at most of order V when $\mathbf{K} \neq \mathbf{K}_1, \dots, \mathbf{K}_m$, we can then rewrite this last equation as:

$$c_{\mathbf{k}-\mathbf{K}} = \frac{1}{\mathcal{E} - \mathcal{E}_{\mathbf{k}-\mathbf{K}}^0} \sum_{j=1}^m V_{\mathbf{K}_j-\mathbf{K}} c_{\mathbf{k}-\mathbf{K}_j} + O(U^2) \quad \mathbf{K} \neq \mathbf{K}_1, \dots, \mathbf{K}_m \quad (4.97)$$

and placing these values in the second summation of eq. 4.95 we obtain:

$$\left(\mathcal{E} - \mathcal{E}_{\mathbf{k}-\mathbf{K}_i}^0 \right) c_{\mathbf{k}-\mathbf{K}_i} = \sum_{j=1}^m V_{\mathbf{K}_j-\mathbf{K}_i} c_{\mathbf{k}-\mathbf{K}_j} + \sum_{j=1}^m \left(\sum_{\mathbf{K} \neq \mathbf{K}_1, \dots, \mathbf{K}_m} \frac{V_{\mathbf{K}-\mathbf{K}_i} V_{\mathbf{K}_j-\mathbf{K}}}{\mathcal{E} - \mathcal{E}_{\mathbf{k}-\mathbf{K}}^0} \right) c_{\mathbf{k}-\mathbf{K}_j} + O(U^3) \quad (4.98)$$

The coefficients in the second term on the right-hand side of these equations are of higher order in V than those in the first term. Then, we can simplify this equation to:

$$\left(\mathcal{E} - \mathcal{E}_{\mathbf{k}-\mathbf{K}_i}^0 \right) c_{\mathbf{k}-\mathbf{K}_i} = \sum_{j=1}^m V_{\mathbf{K}_j-\mathbf{K}_i} c_{\mathbf{k}-\mathbf{K}_j} \quad i = 1, \dots, m \quad (4.99)$$

which constitutes a set of m equations for a system of m quantum levels.

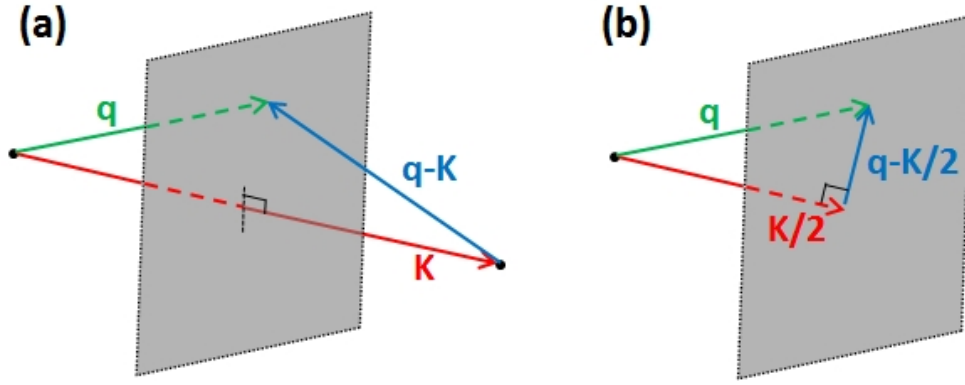


Figure 4.14: (a) The condition $|\mathbf{q}| = |\mathbf{q} - \mathbf{K}|$ imposes that $\mathbf{q}$ lies on the median plane of the $\mathbf{K}$ reciprocal lattice vector, i.e., in the limit of a Brillouin zone. (b) In that case we observe that the vector $\mathbf{q} - 1/2\mathbf{K}$ is parallel to the plane.

4.4.3 Energy levels near a single Bragg plane

We consider as example the one of the Fig. 4.13 when two free electron levels are within order V of each other. Outside of this case, which corresponds to the green shaded $\mathbf{k}$ -values), we have seen that we can consider that the energy levels are not modified up to the order of V . For the near degenerated values, we need to apply Eq. 4.100 which reduces to two equations:

$$\begin{aligned} (\mathcal{E} - \mathcal{E}_{\mathbf{k}-\mathbf{K}_1}^0) c_{\mathbf{k}-\mathbf{K}_1} &= V_{\mathbf{K}_2-\mathbf{K}_1} c_{\mathbf{k}-\mathbf{K}_2} \\ (\mathcal{E} - \mathcal{E}_{\mathbf{k}-\mathbf{K}_2}^0) c_{\mathbf{k}-\mathbf{K}_2} &= V_{\mathbf{K}_1-\mathbf{K}_2} c_{\mathbf{k}-\mathbf{K}_1} \end{aligned} \quad (4.100)$$

By making the following change of variables:

$$\mathbf{q} = \mathbf{k} - \mathbf{K}_1 \quad \text{and} \quad \mathbf{K} = \mathbf{K}_2 - \mathbf{K}_1 \quad (4.101)$$

we get:

$$\begin{aligned} (\mathcal{E} - \mathcal{E}_{\mathbf{q}}^0) c_{\mathbf{q}} &= V_{\mathbf{K}} c_{\mathbf{q}-\mathbf{K}} \\ (\mathcal{E} - \mathcal{E}_{\mathbf{q}-\mathbf{K}}^0) c_{\mathbf{q}-\mathbf{K}} &= V_{-\mathbf{K}} c_{\mathbf{q}} = V_{\mathbf{K}}^* c_{\mathbf{q}} \end{aligned} \quad (4.102)$$

$\mathcal{E}_{\mathbf{q}}^0$ will be equal to $\mathcal{E}_{\mathbf{q}-\mathbf{K}}^0$ for some reciprocal lattice vector only when $|\mathbf{q}| = |\mathbf{q} - \mathbf{K}|$.

This is a reformulation of the Bragg condition as we show it geometrically in Fig. 2.15. In our case this is shown in Fig. 4.14. Then the case of two nearly degenerate levels applies to an electron whose wave vector very nearly satisfies the condition for a single Bragg scattering. Correspondingly, the general case of many nearly degenerate levels applies to the treatment of a free electron level whose wave vector is close to one at which many simultaneous Bragg reflections can occur. Since the nearly degenerate levels (independently of the number of Bragg reflections) are the most strongly affected by a weak periodic potential, we conclude that *a weak periodic potential has its major effects on only those free electron levels whose wave vectors are close to ones at which Bragg reflections can occur.*

To quantitatively determine the effect of the weak potential on the near degenerate levels in our two free electron levels example, we need to solve the system of two equations in Eq. 4.102 which leads by setting the determinant equal to zero:

$$\begin{vmatrix} \mathcal{E} - \mathcal{E}_{\mathbf{q}}^0 & -V_{\mathbf{K}} \\ -V_{\mathbf{K}}^* & \mathcal{E} - \mathcal{E}_{\mathbf{q}-\mathbf{K}}^0 \end{vmatrix} = 0 \quad (4.103)$$

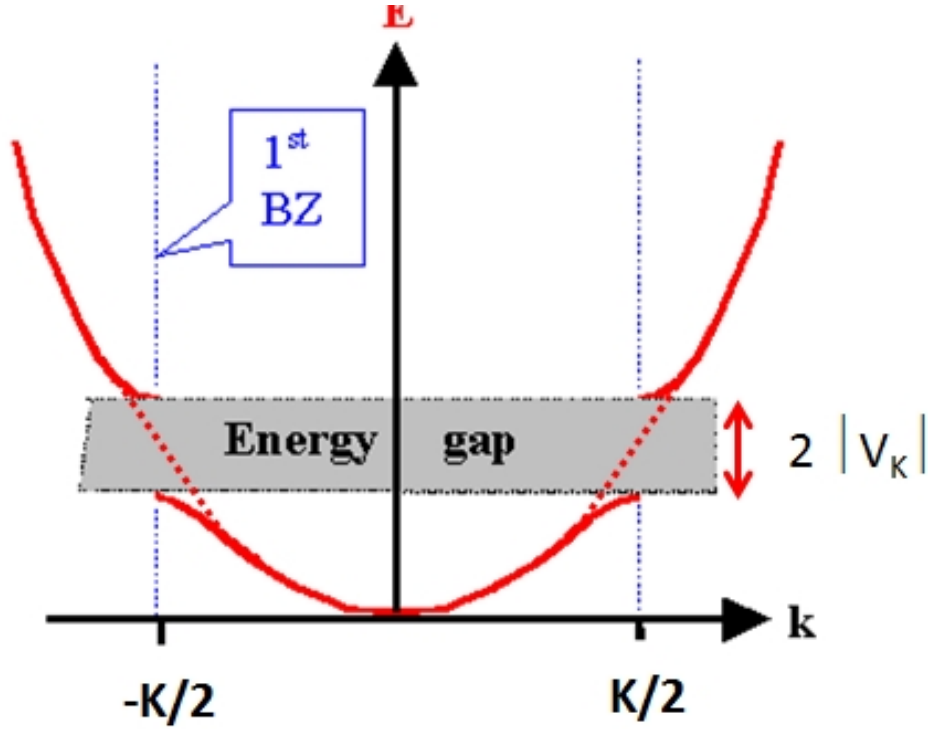


Figure 4.15: Evolution of the energy bands in a projection with $\mathbf{q}$ parallel to $\mathbf{K}$. The lower band corresponds to the minus sign in Eq. 4.105 and the upper band to the plus sign. At the limit of the Brillouin zone, an electronic gap of magnitude $2|V_{\mathbf{K}}|$ opens. When $\mathbf{q}$ is far from the Brillouin zone limit, we fall down in the non-degenerate case and the solution can not be distinguished from the free electron values (the dot lines superimposes to the continuous line)

leading to :

$$(\mathcal{E} - \mathcal{E}_{\mathbf{q}}^0)(\mathcal{E} - \mathcal{E}_{\mathbf{q}-\mathbf{K}}^0) = |V_{\mathbf{K}}|^2 \quad (4.104)$$

having two roots:

$$\mathcal{E} = \frac{1}{2}(\mathcal{E}_{\mathbf{q}}^0 + \mathcal{E}_{\mathbf{q}-\mathbf{K}}^0) \pm \left[\left(\frac{\mathcal{E}_{\mathbf{q}}^0 - \mathcal{E}_{\mathbf{q}-\mathbf{K}}^0}{2} \right)^2 + |V_{\mathbf{K}}|^2 \right]^{1/2} \quad (4.105)$$

The effect of the weak potential on those $\mathbf{q}$ close to the limits of the Brillouin zone (Bragg condition) is shown in Fig. 4.15. When $\mathbf{K}$ is exactly lying in a Bragg plane position, $\mathcal{E}_{\mathbf{q}}^0 = \mathcal{E}_{\mathbf{q}-\mathbf{K}}^0$ and then the two solutions become

$$\mathcal{E} = \mathcal{E}_{\mathbf{q}}^0 \pm |V_{\mathbf{K}}| \quad \text{when } \mathbf{q} \text{ in a single Bragg plane} \quad (4.106)$$

as shown in Fig. 4.15. From Eq. 4.105 we can also see that when $\mathcal{E}_{\mathbf{q}}^0 = \mathcal{E}_{\mathbf{q}-\mathbf{K}}^0$,

$$\frac{\partial \mathcal{E}}{\partial \mathbf{q}} = \frac{\hbar^2}{m} \left(\mathbf{q} - \frac{1}{2} \mathbf{K} \right) \quad (4.107)$$

in other words, when the $\mathbf{q}$ vector lies on the Bragg plane, the gradient of $\mathcal{E}$ is parallel to the plane (see Fig. 4.14.b). Since the gradient is perpendicular to the surfaces on which a function is constant, then the constant-energy surfaces at the Bragg plane are perpendicular to the plane. In Fig 4.16 it is shown how this modifies the Fermi sphere close to the limits of a Brillouin zone.

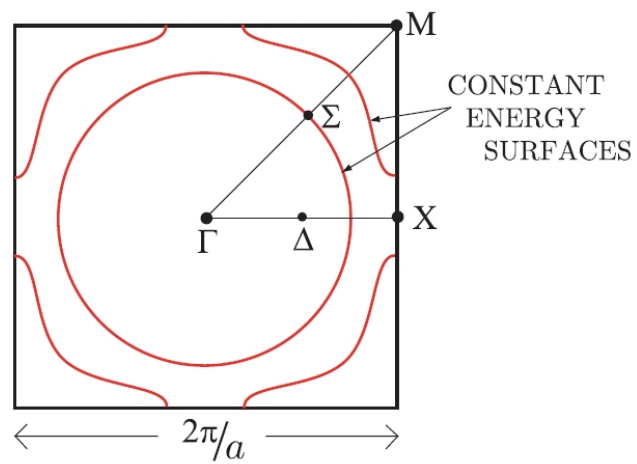
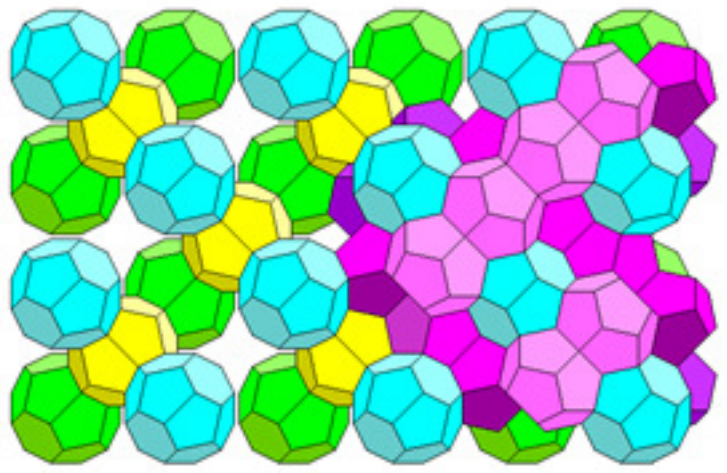


Figure 4.16: Constant energy surfaces in a two-dimensional square lattice in the near free electron model. We see that the Fermi sphere will become modified if lying close to the limits of the Brillouin zone.



5. Electrons in Solids. Physical Properties

5.1 Introduction

The previous chapter has shown the importance of the electronic band structure to describe electrons in a crystalline solid. These electronic bands can be calculated and also measured. Knowledge on the band structure allows to study the response of the electrons in a crystal when submitted to various perturbations as electric or magnetic fields or electromagnetic fields (photons) to cite the more important ones. Engineering the band structure of a system, i.e., modifying at will the important features of the band structure, is today one of the paradigms in condensed matter physics. Playing with dimensionality, topology, scale (nonmetric, mesoscopic), interfaces, defects, are some of the methods used by the condensed matter physicist to tune the electronic structure of a systems. Of course, in the real world we are constrained by the nature of atoms. Nevertheless, atomistic modeling or some designed experiments, for instance using cold atoms, allow recreations with virtual crystal electronic structures which may be inspiring for future developments in the real world.

In this chapter we will first see the consequences of the band structure on the dynamics of the electrons to continue by introducing the central concept of a "hole". Then we will use the acquired knowledge on the electron band structure to explore the classification of semiconductors. We will see the response of crystalline conductor or semiconductor to electric and magnetic fields and explore the Hall effect and the evolution of conductivity with temperature. Finally, we will consider the particular case of metals to study the role played by electrons in their thermal conduction to derive the Wiedemann-Franz law.

5.2 Electron dynamics in band structures

In 1D, close to the minimum of the electronic bands, the parabolic approximation holds and the electron energy in 1D is $\varepsilon = \hbar^2 k^2 / 2m^*$ with m^* being the effective mass. Then the group velocity is given by $v_g = \hbar k / m^* = p / m^*$.

In a semi-classical approach (Sommerfeld), an electron can be considered also as a wave packet defined by the superposition of a number of plane-waves. The electron speed can then be

identified with the group velocity which in 1-Dimension will be:

$$v_g = \frac{\partial \omega(k)}{\partial k} = \frac{1}{\hbar} \frac{\partial \varepsilon(k)}{\partial k} \quad (5.1)$$

or in 3-D:

$$\vec{v}_g = \vec{\nabla}_k \omega(\vec{k}) = \frac{1}{\hbar} \vec{\nabla}_k \varepsilon(\vec{k}) \quad (5.2)$$

where $\varepsilon(\vec{k})$ is to be chosen as the electron energy band in which the conduction electron (or holes) are found.

Let us consider the extrema (maxima or minima) taking place at k_0 for a particular band in a 3D crystal. Then we have for the band under consideration, $\varepsilon_n(\vec{k})$:

$$\nabla_{\vec{k}} \varepsilon_n(\vec{k}) \Big|_{\vec{k}=\vec{k}_0} = 0 \quad (5.3)$$

Making a Taylor development of $\varepsilon(\vec{k})$ around k_0 :

$$\varepsilon_n(\vec{k}) = \varepsilon_n(\vec{k}_0) + \sum_j (\vec{k} - \vec{k}_0)_j \left. \frac{\partial \varepsilon_n}{\partial k_j} \right|_{\vec{k}=\vec{k}_0} + \frac{1}{2} \sum_{i,j} (\vec{k} - \vec{k}_0)_i \left. \frac{\partial^2 \varepsilon_n}{\partial k_i \partial k_j} \right|_{\vec{k}=\vec{k}_0} (\vec{k} - \vec{k}_0)_j + \dots \quad (5.4)$$

with $i, j = x, y, z$. Taking as origin of energy $\varepsilon(k_0)$ and as origin of momentum $\vec{k}_0$ we are then left with:

$$\varepsilon_n(\vec{k}) = \frac{1}{2} \sum_{i,j} (\vec{k})_i \left. \frac{\partial^2 \varepsilon_n}{\partial k_i \partial k_j} \right|_{\vec{k}=0} (\vec{k})_j + \dots \quad (5.5)$$

We have seen that in 3D the speed of electrons in a crystal is described by equations (5.2):

$$a_i = \dot{v}_i = \frac{1}{\hbar} \left[\frac{d}{dt} \left(\vec{\nabla}_k \varepsilon_n(\vec{k}) \right) \right]_i = \frac{1}{\hbar} \sum_j \frac{\partial^2 \varepsilon_n(\vec{k})}{\partial k_i \partial k_j} \dot{k}_j \quad (5.6)$$

where the factor 1/2 has been simplified as we have two equal terms that add for each component of the summation. Here the "dot" over the variables represent the time derivative. We omit from now to explicitly write that the derivatives are taken around the extrema of the band. On the other side we have $\vec{F} = \hbar \dot{\vec{k}}$, so $F_j = \hbar \dot{k}_j$, which replaced in the previous equation gives

$$a_i = \left(\frac{1}{\hbar^2} \frac{\partial^2 \varepsilon_n(\vec{k})}{\partial k_i \partial k_j} \right) F_j \quad (5.7)$$

which defines the inverse of the effective mass tensor (or its inverse here) as :

$$\left[m^{*-1} \right]_{i,j} = \frac{1}{\hbar^2} \frac{\partial^2 \varepsilon_n(\vec{k})}{\partial k_i \partial k_j} \quad (5.8)$$

We can then approximate the band $\varepsilon_n(\vec{k})$ close to its extrema as:

$$\varepsilon_n(\vec{k}) = \varepsilon_n(\vec{k}_0) + \frac{1}{2} m_{i,j}^{*-1} (k_i - k_{0i})(k_j - k_{0j}) + \dots \quad (5.9)$$

As the value of a second derivative does not depend on the differentiation order, quantities $m_{i,j}^{*-1}$ represent a symmetric tensor of the second rank. A symmetric tensor of real numbers, as it is here the case, can be diagonalized, i.e., it is possible to choose a coordinate systems (called a principle coordinate system) in which $m_{i,j}^{*-1} = 0$ for $i \neq j$. Only 3 effective masses are then needed to describe the dynamics of a band: $m_x^* = m_{x,x}^*$, $m_y^* = m_{y,y}^*$ and $m_z^* = m_{z,z}^*$.

For a 1D crystal, the effective mass can then be written $m^* = \hbar^2/(\partial^2 \epsilon_n / \partial k^2)$, i.e., the effective mass is inversely proportional to the curvature of the band around the extrema. For "flat" bands we will have a higher effective mass than for highly curved bands. We will speak in that case of "heavy" or "light" charge carriers respectively.

We should note that if the dispersion relation is not of parabolic type but linear, i.e., with curvature equal to zero, then the effective mass diverges (becomes infinite). This is the case of graphene dispersion curves which is refereed sometimes as a massless dispersion curve, in analogy to the photon dispersion curve, $\epsilon_n = \hbar\omega = \hbar ck$. In fact, the model here presented just does not applies for graphene, as the second order term of the Taylor expansion of ϵ_n does not exists.

5.3 Electrons and holes

If we consider now the sign of the effective mass, $m^* = \hbar^2/(\partial^2 \epsilon / \partial k^2)$, concave bands will have $m^* > 0$ whereas convexe bands would exhibit $m^* < 0$. This corresponds respectively to the conduction and valence band in a semiconductor as shown in the figure, and evidences the fact that the electrons in the valence band will gain velocity in the opposite direction compared to those in the conduction band. We distinguish the type of charge carriers in both bands : conduction in then said to be made by electrons in the conduction band and by *holes* in the valence band.

Let us at this point underline that in practice the effective mass will be considered as positive but applying to these two different types of charge carriers. We will then refer to electron effective mass, m_e^* and holes effective mass, m_h^* .

To better understand the mechanism of hole conduction, let us consider the scheme of Fig. 5.1. The valence band (VB) would be in principle totally filled and then no charge conduction is possible. As all the VB is filled we have the sum over all states of their momentum will give $\sum_{CB} \vec{q} = 0$, as a result of the inversion symmetry of the first Brillouin zone. Lets then consider that we provide enough energy to an electron of momentum $\vec{q}_e$ of the VB so as to transfer it to the conduction band (CB) as shown in Fig. 5.1. We say then that we have created a hole in the VB. Then we will have that if an electron is missing in the valence band, $\sum_{CB} \vec{q} = -\vec{q}_e$. This momentum can be said as being attributed to the hole: $\vec{q}_h = -\vec{q}_e$.

In Fig. 5.1 we have taken as energy origin the top of the VB. The electron which have been extracted had an energy, $-\epsilon_e$, which is negative, i.e., binding. The fact of extracting this energy makes the VB energy increase by a value $\epsilon_h(\vec{k}_h) = -\epsilon_e(\vec{k}_e)$. In other words, we could simulate the hole creation (the absence of an electron in the VB) by associating to it a "hole band" as shown in Fig. 5.2.

The creation of a hole in the VB leads then to the creation of an associated electronic states in the "hole band" symmetric with respect to the origin. The velocity of the hole and the electron are the same as $\nabla \epsilon(\vec{k}_h) = \nabla \epsilon(\vec{k}_e)$.

For an electron in the valence band, the application of an electric field and a magnetic field leads to an equation of movement determined by:

$$\hbar \frac{d\vec{k}_e}{dt} = -e \left(\vec{E} + \vec{v}_e \times \vec{B} \right) \quad (5.10)$$

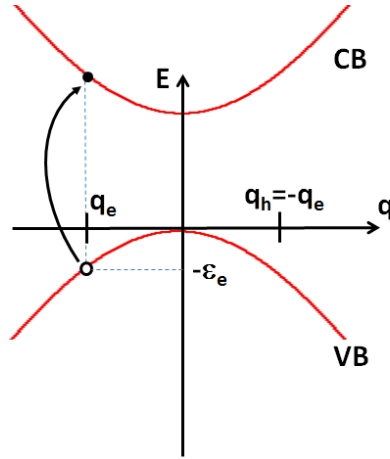


Figure 5.1: Transfer of an electron of momentum k_e between a valence (BV) and a conduction band (CB)

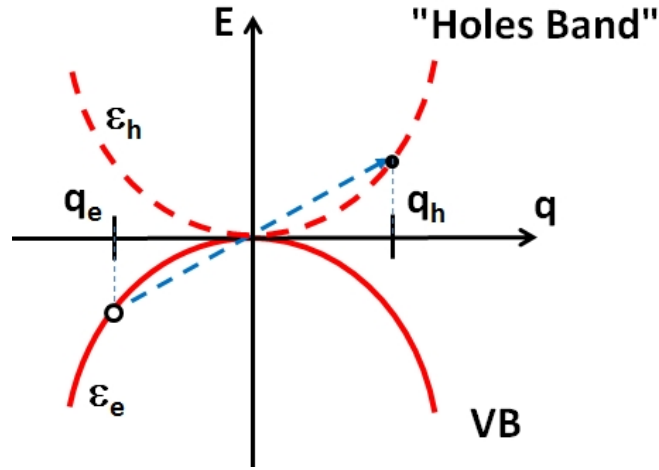


Figure 5.2: Construction of a "hole band" associated to the presence of a hole in the valence band.

To get the equivalent for the hole in the VB we need to replace :

$$\left\{ \begin{array}{l} \vec{k}_e \text{ by } -\vec{k}_h \\ \vec{v}_e \text{ by } \vec{v}_h \end{array} \right\} \quad (5.11)$$

giving

$$\hbar \frac{d\vec{k}_h}{dt} = +e \left(\vec{E} + \vec{v}_h \times \vec{B} \right) \quad (5.12)$$

which is equivalent to the movement of a particle of positive charge.

In Fig.5.3 is sketched what represents from the microscopic point of view hole conduction. The consequence is that hole conduction leads to a contribution to the total current equivalent to the one which will be associated to a free electron. Electron and holes then contribute additively to the conductivity, σ . We can then write:

$$\sigma = ne\mu_e + pe\mu_h \quad \text{with} \quad \mu_e = \frac{e\tau_e}{m_e^*} \quad \text{and} \quad \mu_h = \frac{e\tau_h}{m_h^*} \quad (5.13)$$

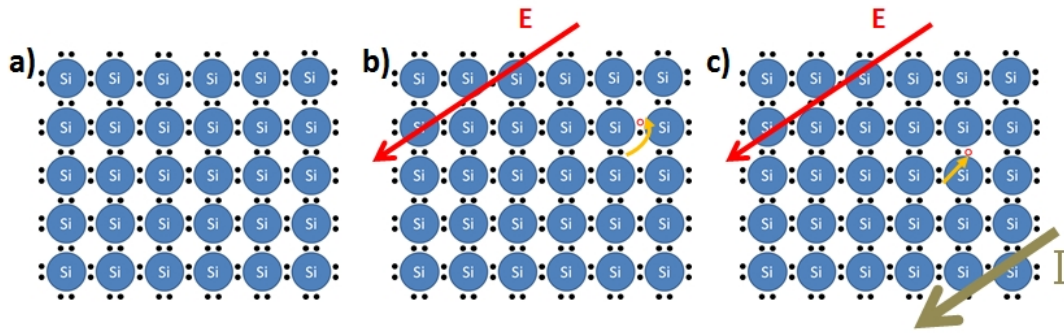


Figure 5.3: Sketch of the microscopic image of hole conduction in a semiconductor. From left to right: (a) an image of a perfect silicon crystal in the Lewis representation. (b) A crystal with a hole (the absence of one of the valence electrons), represented by a red circle. An electrical field, $\vec{E}$ is applied and a neighboring electron, assisted by $\vec{E}$ fills the hole. (c) The same scheme keeps going. The result is a net displacement of electrons in opposite direction to $\vec{E}$, i.e., the production of a current intensity in the same direction than $\vec{E}$

with μ_e and μ_h the electron and hole mobilities respectively.

5.4 Types of semiconductors

We have already made reference to the distinction of semiconductor materials from the value of their gap. In general when the gap is smaller than the silicon one (1.12 eV), one speaks about "narrow gap semiconductors". Examples are : HgTe, InAs or PbSe. Semiconductors are usually referred as being wide-gap when their gaps are larger than 3 eV, but the threshold can be context dependent. Examples are GaN or AlN.

Another important distinction is direct or indirect gap semiconductors. A semiconductor is said to have a direct gap if the maximum of the BV and the minimum of the CB defining the gap do not imply a change in momentum. When a change in momentum is needed, the gap is called indirect.

A semiconductor is said to be extrinsic when the balance of charge carriers is modified by doping. If the concentration of electron carriers is dominant, then the semiconductor is called *n-type* and when hole carriers dominate it is called *p-type*. The corresponding impurities are called *donors* and *acceptors* respectively. For Silicon (column IV in the periodic table), the substitution of Si by column V atoms (P,N), with an excess electrons, is a case of n-doping, and the substitution of column II atoms (B,Ga) leads to p-doping (Fig.5.6)

In physical terms, a donor atom in substitution finds itself in the crystal with an excess electron weakly linked. A small energy is enough to detach the excess electron which will be found as any other electron in the conduction band. The equivalent view in the band structure is to consider that the introduction of donor atoms with a concentration N_D will lead to the introduction of donor level (D.L.) very close to the bottom of the C.B.. At $T=0$ K all the excess electrons are found in that level, but at relatively low temperatures, the donor atoms become ionized, meaning that the electrons of the D.L. are transferred to the C.B. At ambient temperature all the D.L. electrons have been transferred at the C.B. leading to a electron concentration N_D . This is schematized in the left side of Fig. 5.7. For acceptor atoms (right side of 5.7) doping the semiconductor with a concentration N_A , the lacking electron (hole) will easily be replaced by a valence electron of the silicon bonds (V.B). We have then an acceptor level (A.L.) close to the top of the V.B. We can consider either that the A.L. is filled with holes which are easily transferred

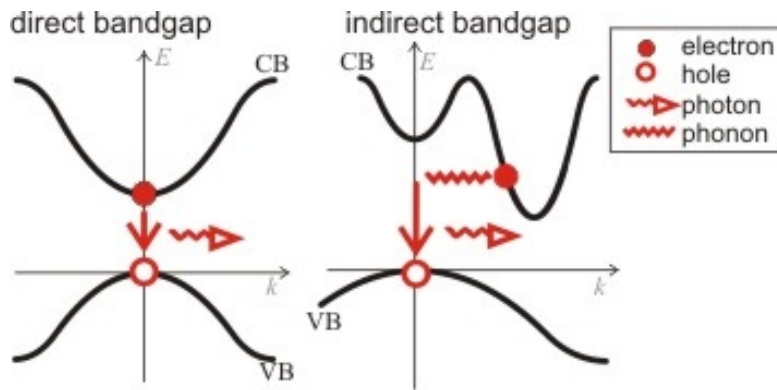


Figure 5.4: In a direct gap semiconductor (left) the recombination between an electron and a hole at the gap leads to the emission of a photon. The reverse process takes also place: a photon of the energy of the gap can be absorbed creating an electron-hole pair. In an indirect gap semiconductor (right) a photon, which has too small momentum, can not be the only particle involved in the recombination (or the creation) of an electron and a hole. A particle with the lacking momentum, usually a phonon, needs to participate in the absorption/emission process.

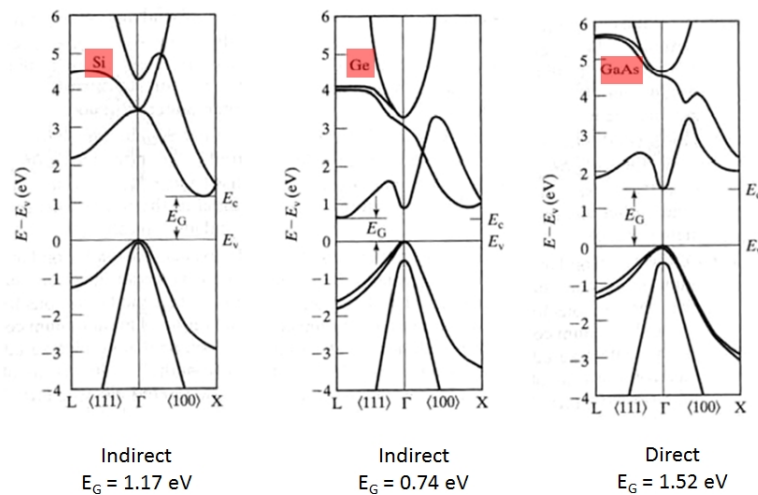


Figure 5.5: Calculated electronic band structure of 3 important semiconductors in two directions of the Brillouin zone. Below each figure is given the experimental value of the gap.

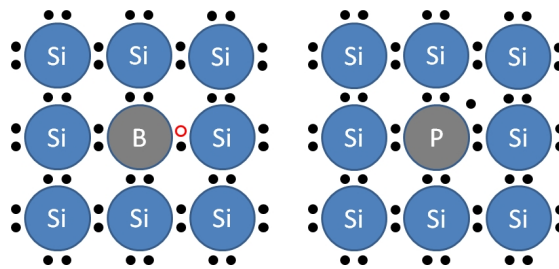


Figure 5.6: Scheme showing p-doping (holes) by group III impurities in silicon (left) and n-doping (electrons) by group V impurities (right).

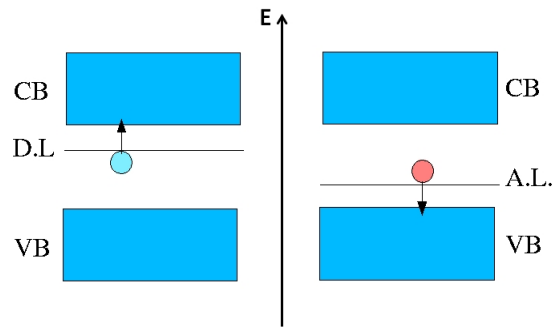


Figure 5.7: Scheme of the band structure of a n-doped semiconductor (left) and of a p-doped semiconductor (right)

to the V.B. or that the A.L. is empty and that it is filled with electrons from the V.B., i.e., creating holes in the V.B.. Again at ambient temperature the concentration of holes in the VB will be N_A if the dopant is provided one hole per impurity.

5.5 Hall effect

This effect is associated to two Nobel prizes. In 1985 Klaus von Klitzing received the Nobel prize for the discovery of the integer quantum Hall effect and in 1998, nationalities, Robert Laughlin, Horst Störmer and Daniel Tsui obtained for their discovery of the fractional quantum Hall effect. These works start all with what is called the "classical" Hall effect due to Edwin Herbert Hall which discovered it in 1879, which is the Hall effect we are going to introduce here.

In short, the Hall effect states that an electrical current submitted to a perpendicular magnetic field generates a tension perpendicular to both. This voltage allows to measure the type of charge carriers of the material and its concentration. In some particular conditions, this tension can increase in steps leading to the integer or fractional Hall effects. It can then be used for metrology purposes.

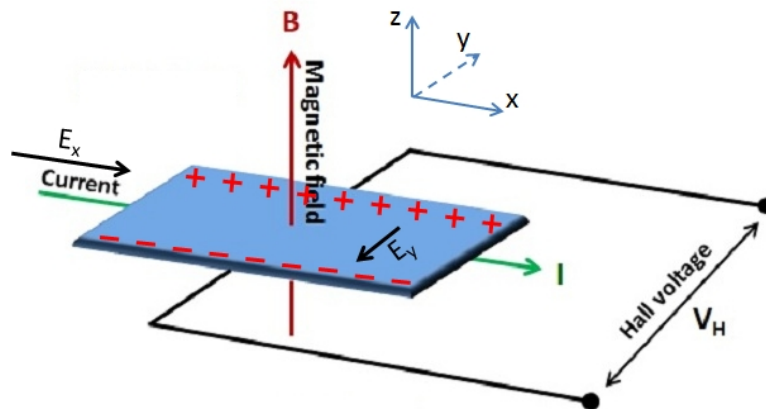


Figure 5.8: Hall effect. A current is applied on a slab of material (in blue) and a magnetic field is applied perpendicularly. A voltage perpendicular to both, the Hall tension V_H is generated.

Let's consider an slab of material as in Fig. 5.8. The current imposed in the x direction is associated to the electric field E_x and if we consider that the charge carriers are electrons, to a movement of electrons from right to left in the x direction. These electrons will be deviated by the

Lorentz force and as shown in the graph they will cumulate in the closest side to us of the slab in the perspective of the figure. The depletion of negative charges generated is represented by the positive charge sign in the other side. These opposite charges generate an electric field in the y direction, E_y . The associate difference of potential, V_H , is the Hall tension.

If the charge carriers would have been positive, for the same current and electric field, they will be travelling from left to right in the x direction. Then the Lorentz force will deviate them also to the slab's closest side to us and consequently E_y will be opposite in sign.

Quantitatively, the Lorentz force responsible of the forces on the charge carriers is $\vec{f} = q(\vec{E} + \vec{v} \wedge \vec{B})$. Let us consider the case of electron charge carriers, i.e., $q = -e$. In stationary conditions we will have:

$$\frac{d\vec{p}}{dt} = -e \left(\vec{E} + \frac{\vec{p}}{m} \wedge \vec{B} \right) - \frac{\vec{p}}{\tau} = 0 \quad (5.14)$$

where $\vec{p}$ represents the momentum operator and τ the time between collisions with defects. We can write the two non-trivial components of the vectorial equation:

$$\begin{aligned} -eE_x - \omega_c \bar{p}_y - \frac{\bar{p}_x}{\tau} &= 0 \\ -eE_y + \omega_c \bar{p}_x - \frac{\bar{p}_y}{\tau} &= 0 \end{aligned} \quad (5.15)$$

with $\omega = \left| \frac{eB}{m} \right|$, which is called the cyclotron frequency.

We have also:

$$j_x = -nev_x = -ne \frac{p_x}{m} \rightarrow p_x = -\frac{m}{ne} j_x \quad \text{and} \quad p_y = -\frac{m}{ne} j_y \quad (5.16)$$

recalling that the conductivity can be written $\sigma_0 = \frac{ne^2\tau}{m}$ we have:

$$\begin{aligned} \sigma_0 E_x &= \omega_c \tau j_y + j_x \\ \sigma_0 E_y &= -\omega_c \tau j_x + j_y \end{aligned} \quad (5.17)$$

The geometry of the experiment in Fig. 5.8 does not allow for a current flow in the y direction and then $j_y = 0$. We are then left with:

$$\begin{aligned} j_x &= \sigma_0 E_x \\ E_y &= -\left(\frac{\omega_c \tau}{\sigma_0} \right) j_x = -\frac{B}{ne} j_x \end{aligned} \quad (5.18)$$

The second equation allows to determine the Hall tension. We can first define the Hall coefficient, R_H

$$R_H = -\frac{1}{ne} \quad (5.19)$$

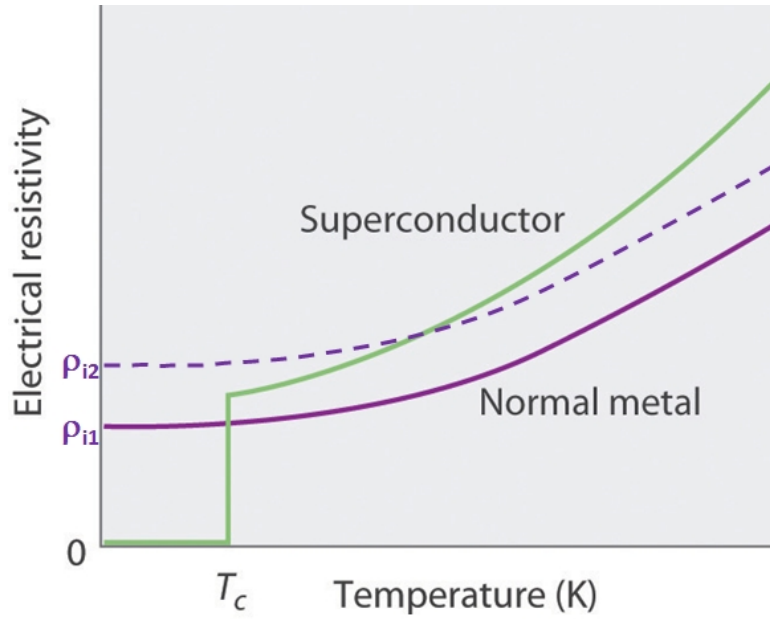


Figure 5.9: Temperature evolution of the resistivity of metals. The two violet curves show the evolution for a same metal having two different concentrations of impurities. The green curve illustrates the behavior of a superconducting metal, characterized by zero resistivity conduction below the superconducting critical temperature, T_c .

R_H is independent of τ . If we call W the width of the slab in the y direction we have $E_y = R_H B j_x$, the Hall field and $V_H = E_y W$, the Hall tension.

For the alkali metals one finds $R_H(\text{calculated})/R_H(\text{experiments}) \approx 1$. Another success of the free electron model !.

On the other side, for the alkaline earth metals $R_H(\text{calculated})/R_H(\text{experiments}) < 0$, which means that the charge carriers are positive, i.e., holes. That is also the result for p-doped semiconductors.

We need then to consider that the Hall constant can be positive or negative depending on the type of charge carriers. For electrons $R_H = -\frac{1}{n_e e}$ and for holes $R_H = \frac{1}{n_h e}$.

The measure of V_H allows then to determine the sign and value of R_H , i.e., the type of charge carriers and their density.

5.6 Electrical conductivity as a function of temperature

In metals the number (or the density of charge carriers) does not evolve with temperature. The conductivity is ruled by the scattering of charge carriers either with impurities (with characteristic time τ_i) or with lattice phonons (τ_L). We can see charge transport associated to each one of the scattering processes as circuits associated in series which will lead to a total resistivity $\rho = \rho_L + \rho_i$ or in terms of time between collisions $\frac{1}{\tau} = \frac{1}{\tau_L} + \frac{1}{\tau_i}$. The two terms are independent one from the other as long as the concentration impurities is not too high to start to disturb the lattice. ρ_i will depend on the concentration of impurities and then be temperature independent. On the other side ρ_L will increase with temperature as does the phonon concentration.

We have then $\rho(T) = \rho_L(T) + \rho_i$ with $\rho(0) = 0$. In Fig. 5.9 is shown this evolution for two samples of the same metal having two different concentrations of impurities and consequently two different values of ρ_i (violet curves).

It is also depicted in Fig. 5.9 the case of a superconductor (green curve). In an important

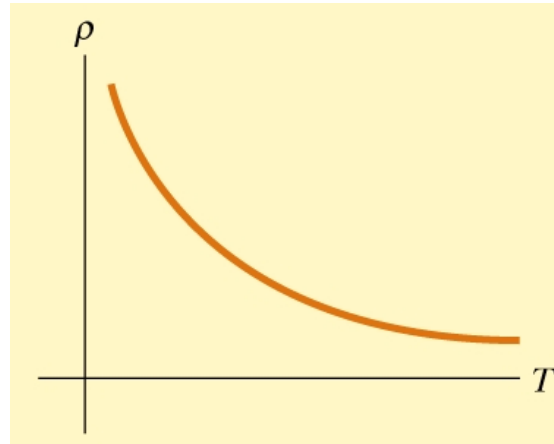


Figure 5.10: Temperature evolution of the resistivity of an intrinsic semiconductor..

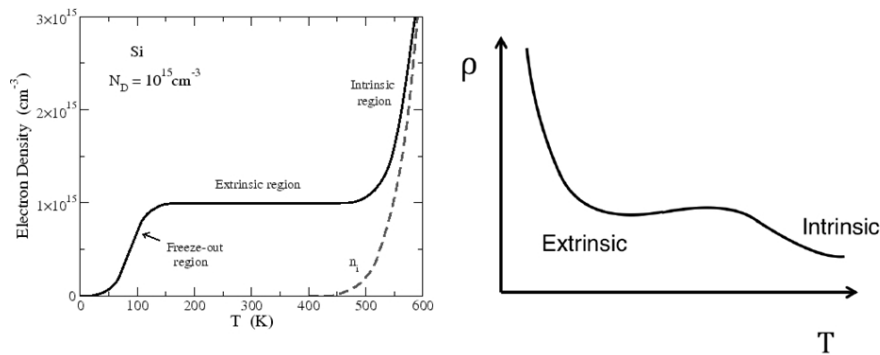


Figure 5.11: Evolution with temperature of the concentration of charge carriers (left) and of resistivity (right) for an extrinsic semiconductor. The example of n-doped silicon is given. The discontinuous line shows the evolution of the electron density in the case of intrinsic silicon.

number of metals, at low enough temperatures, the electrical resistivity drops to zero for a critical temperature, T_c . The regime for $T < T_c$ is called the superconductor state and is characterized by the coupling of electron in pairs called Cooper pairs. In what is called *BCS superconductivity*, the electrons are coupled between them through their interaction with phonons, called the electron-phonon coupling.

In normal metals, the ratio between the resistivity at 293 K and at liquid He temperature (4.2 K), $\rho(293)/\rho(4.2)$ is frequently used as an indicator of purity. This ratio can vary from 10^6 for specimens having exceptionally high purities to ~ 1 for highly impure metals.

The case of semiconductors is totally different. Let us consider intrinsic semiconductors. At $T = 0K$ there are no charge carrier available and the resistivity is infinite. When temperature is increased, electrons from the VB can be excited into the CB and pairs of electron-hole carriers will be created leading to a progressive reduction of the resistivity. As shown in Fig.5.10, the resistivity evolution with temperature is totally different from the one of a metal. The $\rho(T)$ dependence is commonly used to distinguish the metallic from the semiconducting character of a material.

In the case of an extrinsic semiconductor, the behaviour is similar to the intrinsic one, except that there is a much stronger reduction of resistivity at very low temperatures due to the ionization of the dopants. Once all dopants have been ionized, the resistivity does not evolve significantly until the intrinsic regime is reached again. Fig. 5.11 shows how this evolution translates both in terms of charge carriers and of resistivity evolution.

5.7 Thermal conductivity of metals and the Wiedemann-Franz law

In metals heat can be carried both by electrons or by phonons. In metals, the first one is dominant and we will concentrate on it. Fourier's law of thermal conduction, states that the heat flow $\vec{J}_Q$ is proportional to the temperature gradient:

$$\vec{J}_Q = -k_T \vec{\nabla} T \quad (5.20)$$

the proportionality constant, k_T is the *thermal conductivity*. If we consider electrons in a metal as a gaz of particles, we can use the kinetic theory of gas results which states that for a property, P its flux J_P is related to its gradient ∇P by :

$$J_P = -\frac{1}{3} \ell \bar{v} \nabla P \quad (5.21)$$

where ℓ is the mean free path of the gaz particles (here the electrons) and $\bar{v}$ their average velocity. If this result is applied to the heat flow we have :

$$J_Q = -\frac{1}{3} \ell \bar{v} \nabla Q = -\frac{1}{3} \ell \bar{v} \frac{dQ}{dT} \nabla T = -\frac{1}{3} \ell \bar{v} c_v \nabla T \quad (5.22)$$

whith c_v in our case the electron specific heat. We can then write, considering that $\ell = \bar{v} \tau$:

$$k_T = \frac{1}{3} \ell \bar{v} c_v = \frac{1}{3} \bar{v}^2 \tau c_v \quad (5.23)$$

We go now out from this totally classical description by considering the Fermi statistics, which imposes that the only electrons which can be excited are those at the Fermi level, having $\bar{v} = v_F$. Then $k_T = \frac{1}{3} v_F^2 \tau c_v$. We can relate v_F to the Fermi temperature using $k_B T_F = 1/2 m v_F^2$, which gives $v_F^2 = (2k_B T_F)/m$. Consideting that in the high temperature limit we found that the electron specific heat could be written as $c_v \approx 3nk(T/T_F)$ we are left with :

$$k_T \approx \frac{2nk_B^2 T \tau}{m} \quad (5.24)$$

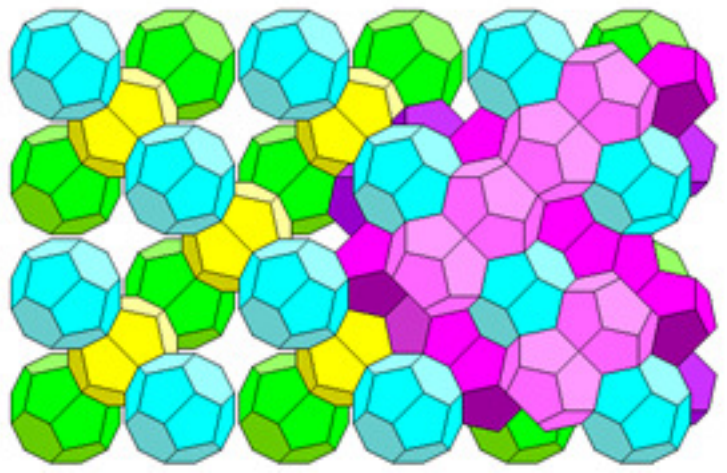
A more precise calculation gives a slightly different expression

$$k_T = \frac{\pi^2 nk_B^2 T \tau}{3m} \quad (5.25)$$

Compared with the electrical conductivity, $\sigma = \frac{ne^2 \tau}{m}$ by defining L as:

$$L \equiv \frac{k_T}{\sigma T} = \frac{\pi^2}{3} \left(\frac{k_B}{3} \right)^2 = 2.45 \cdot 10^{-8} \text{ W}\Omega\text{K}^{-2} \quad (5.26)$$

This is the Wiedemann-Franz law, which states that the Lorenz number, L , is a constant independently of the nature of the metal. An important assumption in its derivation is that the scattering process of electrons for heat flow or charge flow is equivalent, i.e., we have assumed that τ was the same both in the expressions of the thermal and of the electrical conductivity. In fact, many simple metals verify the Wiedemann-Franz law in a large domain of temperature, but other do not. In principle, any physical phenomena which can move electrons apart from the ideal gas description, i.e., inelastic collisions for instance, would contribute to the Wiedemann-Franz law failure. This can be electron-phonon interactions, electron-electron, electron-magnon or any inelastic interaction in general.



6. Magnetic properties

6.1 Introduction

Magnetism is a property observed in materials already by the ancient Greeks and exploited since more than one thousand years by Chinese (Fig. 6.1). Magnetic materials are present in all houses, cars, industrial installations, hospitals, etc., but the understanding of magnetism in materials has no more of 100 years, which is not really surprising when we consider that the origin of magnetism in materials is a quantum-relativistic phenomena !

The magnetic moment of a free atom can be due to:

- The electron spin
- The orbital magnetic moment of the electrons
- Induced electronic orbital magnetic moments by the application of a magnetic field
- Nuclear magnetic moment, which in general is of the order of 1000 times smaller than the electronic magnetic moments.

Nuclear magnetism is important nevertheless in some cases as the distinction between ortho and para hydrogen (H_2) or in nuclear magnetic resonance (NMR) techniques.

In condensed phases, the intensity of magnetic effects is measured through the non dimensional quantity, χ , the magnetic susceptibility, which we can define in different ways depending the type of materials:

a) LHI (Lineal homogeneous and isotropic) materials. in which the magnetization $\mathbf{M}$ is proportional to the applied field $\vec{H}$:

$$\mathbf{M} = \chi \mathbf{H} \quad (6.1)$$

If χ is positive the material is paramagnetic If χ is negative the material is diamagnetic We will discuss these two cases in detail in the following subsections.

b) Anisotropic materials. The magnetic response will depend of the direction of the applied magnetic field. The magnetization does not need in that case to be collinear with the field, which means that the susceptibility can be represented by a tensor, $\vec{\chi}$. This is the case of single crystals.

$$\vec{M} = \vec{\chi} \vec{H} \quad (6.2)$$

c) Non Linear magnetic material Those non-linear effects appear as a consequence of a non-homogenous local magnetization (domains) and lead to history-dependent magnetism and the

presence of hysteresis cycles as shown in Fig. 6.1 We may want to define a differential magnetic susceptibility

$$\chi = \left(\frac{dM}{dH} \right) \quad (6.3)$$

which should integrate also the history of the material. Ferromagnetic materials can be considered as the most important part of this type of systems. As shown in Fig. 6.1 in ferromagnets, the presence of hysteresis loops which dependence on the maximum applied fields (and also on the magnetic history of the material) makes difficult the definition of a magnetic susceptibility. Non linear effects can be also observed in linear or anisotropic materials at high magnetic fields.

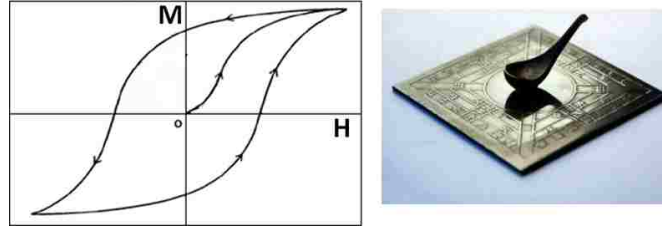


Figure 6.1: Left: A typical magnetization curve of a ferromagnet: a non linear magnetic material. Right: An ancient Chinese magnetic compass

The magnetic susceptibility can vary from -10^{-5} for the weakest diamagnets to 10^6 for the best ferromagnets.

6.1.1 From macro to microscopic magnetism

The applied magnetic field, $\mathbf{H}$ (units A/m in SI), will be affected inside a condensed system by the charges and currents present in the material and we will need to consider the magnetic field $\mathbf{B}$ (units of Tesla in SI). In most literature both $\mathbf{B}$ and $\mathbf{H}$ are referred as "magnetic fields" and are related by:

$$\mathbf{H} = (1/\mu_0)\mathbf{B} - \mathbf{M} \quad \text{or} \quad \mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M}) \quad (6.4)$$

where $\mathbf{M}$ is the macroscopic magnetization.

At $T = 0$ the magnetization $\mathbf{M}$ of a quantum mechanical system of volume V in an uniform magnetic field $\mathbf{H}$ is defined to be:

$$M(H) = -\frac{1}{\mu_0 V} \frac{\partial E_0(H)}{\partial H} \quad (6.5)$$

where we have dropped the vectorial character assuming for simplicity that $\mathbf{M}$ and $\mathbf{H}$ are parallel (otherwise the susceptibility which we are going to define macroscopically below will be a tensor). In this expression $E_0(H)$ is the ground-state energy in the presence of the field H . If the system is in thermal equilibrium at temperature T , we will need to consider the magnetization associated to each state $E_n(H)$ and then:

$$M(H, T) = \frac{\sum_n M_n(H) e^{-E_n/k_B T}}{\sum_n e^{-E_n/k_B T}} \quad (6.6)$$

where

$$M_n(H) = -\frac{1}{\mu_0 V} \frac{\partial E_n(H)}{\partial H} \quad (6.7)$$

Which can be written in the thermodynamic form:

$$M = -\frac{1}{\mu_0 V} \frac{\partial F}{\partial H} \quad (6.8)$$

with F the magnetic Helmholtz free energy, defined by the fundamental statistical mechanical rule:

$$e^{-F/k_B T} = \sum_n e^{-E_n(H)/k_B T} \quad (6.9)$$

The dimensionless magnetic susceptibility is defined as:

$$\chi = \frac{\partial M}{\partial H} = -\frac{1}{\mu_0 V} \frac{\partial^2 F}{\partial H^2} \quad (6.10)$$

We will find this expression as very interesting to compute the magnetic susceptibility or the magnetization from the energy of the system. This expression also allows to see that we can measure the magnetization by recording the force exerted on the sample by an inhomogeneous magnetic field that varies slowly over the sample. In fact, in that case, the change in free energy when moving the sample from x to $x + dx$ is:

$$dF = F(H(x + dx)) - F(H(x)) = \frac{\partial F}{\partial H} \frac{\partial H}{\partial x} dx = -\mu_0 V M \frac{\partial H}{\partial x} dx \quad (6.11)$$

and therefore the force per unit volume f exerted on the sample by the magnetic field is:

$$f = -\frac{1}{V} \frac{dF}{dx} = \mu_0 M \frac{\partial H}{\partial x} \quad (6.12)$$

as $\frac{\partial H}{\partial x}$ is given by the experimental conditions, the measured force on the specimen allows to measure the magnetization.

We will not discuss in this course the origin of the magnetism in the different atoms or ions which is typically studied in quantum physics courses and which allows to explain the variability of the atomic or ionic magnetic moments. We will concentrate in this lectures in the coupling between magnetic momentum and the relation with the macroscopic magnetic properties of solids. We just recall here briefly the main results on the magnetism of atoms and ions.

The magnetic moment of an atom or an ion is a vectorial quantity, μ which can be written as:

$$\mu = -\mu_B (\mathbf{L} + 2\mathbf{S}) \quad (6.13)$$

where $\mu_B = e\hbar/(2m_e) = 9.274 \cdot 10^{-24} \text{ J T}^{-1}$ is the Bohr magneton and $\hbar\mathbf{L} = \hbar \sum \ell$ and $\hbar\mathbf{S} = \hbar \sum \mathbf{s}$ are the sums over the electrons of the atoms of the vectorial operators of angular magnetic moment (ℓ) and spin ($\mathbf{s}$) respectively. The contributions of a closed shell of electrons to $\mathbf{L}$ or $\mathbf{S}$ is zero, so that permanent dipole moments only occur in atoms or ions with incomplete shells. In condensed matter systems, the most external incomplete shells are frequently completed either through electron exchange (case of ionic interactions) or through electron sharing (case of covalent interactions). For this reason atoms or ions in condensed systems exhibiting a permanent magnetic moment are those having *deep incomplete shells* (not involved in bonding) as transition metals (Fe, Co, Ni, Mn,...) or rare earths (Lanthanides as Gd, Er,...) ions, which have incomplete 3d and 4f shells receptively.

In weak magnetic fields the angular momenta $\hbar\mathbf{L}$, $\hbar\mathbf{S}$ and $\hbar\mathbf{J}$ ($= \hbar\mathbf{L} + \hbar\mathbf{S}$) associated with the incomplete shells in *isolated* atoms or ions of these elements are determined by the Russell-Saunders coupling scheme (called also the L-S coupling; the j-j coupling is only important for the very heavy atoms). According to the L-S coupling scheme the stationary states of the shell are eigenstates of $\mathbf{L}^2$, $\mathbf{S}^2$ and $\mathbf{J}^2$ with eigenvalues $L(L+1)$, $S(S+1)$ and $J(J+1)$ respectively. The values of L , S and J for the state of lowest energy are given by Hund's rules.

6.1.2 Atomic susceptibilities

We consider a system of non-interacting atoms. Each atom is treated in a central field approximation in which the atomic hamiltonian of electrons in the Z electron atom can be reduced to Z one-electron hamiltonians:

$$\hat{H}_0 = \sum_{i=1}^Z \left[-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{r_i} + U_{\text{eff}}(r_i) \right] \quad (6.14)$$

with m and e the mass and charge of the electron respectively and U_{eff} being an effective potential including the effect of all other electrons. The effect of the application of a magnetic field on electron i can be introduced by considering its associated potential vector, $\mathbf{A}_i$ which leads to the modification of the momentum of the electron i : $\mathbf{p}_i \rightarrow \mathbf{p}_i + e\mathbf{A}_i$ with $\mathbf{A}_i = -(\mathbf{r}_i \times \mathbf{B})/2$ (we take the Coulomb gauge: $\mathbf{B} = \nabla \times \mathbf{A}$ and $\nabla \cdot \mathbf{A} = 0$).

The term of kinetic energy of the Hamiltonian is then modified becoming:

$$\frac{1}{2m} (\hat{\mathbf{p}}_i - e\mathbf{A}_i)^2 \quad (6.15)$$

lets evaluate the term between brackets:

$$(\hat{\mathbf{p}}_i - e\mathbf{A}_i)^2 = \left(\hat{\mathbf{p}}_i + \frac{e}{2} \mathbf{r}_i \times \mathbf{B} \right)^2 = \hat{\mathbf{p}}_i^2 + \frac{e}{2} (\hat{\mathbf{p}}_i \cdot (\mathbf{r}_i \times \mathbf{B}) + (\mathbf{r}_i \times \mathbf{B}) \cdot \hat{\mathbf{p}}_i) + \frac{e^2}{4} (\mathbf{r}_i \times \mathbf{B})^2 \quad (6.16)$$

Here $\mathbf{B}$ is not an operator but a vectorial constant. Then all observable operators commute with $\mathbf{B}$ and we can write, using the rules of vector calculus:

$$(\hat{\mathbf{p}}_i - e\mathbf{A}_i)^2 = \hat{\mathbf{p}}_i^2 + \frac{e}{2} (\mathbf{B} \cdot (\hat{\mathbf{p}}_i \times \mathbf{r}_i) - (\mathbf{r}_i \times \hat{\mathbf{p}}_i) \cdot \mathbf{B}) + e^2 \left(\frac{1}{2} \mathbf{r}_i \times \mathbf{B} \right)^2 \quad (6.17)$$

where the angular momentum of atom i appears as

$$\hbar \mathbf{L}_i = \mathbf{r}_i \times \hat{\mathbf{p}}_i = -\hat{\mathbf{p}}_i \times \mathbf{r}_i \quad (6.18)$$

and the Hamiltonian in the presence of a magnetic field can then be written:

$$\hat{H} = \hat{H}_0 + \sum_{i=1}^Z \left[\mu_B \mathbf{B} \cdot \mathbf{L}_i + \frac{e^2}{2m} \left(\frac{1}{2} \mathbf{B} \times \mathbf{r}_i \right)^2 \right] \quad (6.19)$$

We need also to consider the spin contribution, which will include an additional energy term $-\mu_s \cdot \mathbf{B}$ with

$$\mu_s = -\frac{e}{m} \hat{\mathbf{S}} \quad (6.20)$$

where the electron spin operator, $\hat{\mathbf{S}}$ has eigenstates $\pm 1/2\hbar$ (to be compared with the equivalent expression of the electronic spin magnetic moment $\mu_s = -2\mu_B \hat{\mathbf{S}}$ in which the eigenvalues of $\hat{\mathbf{S}}$ are $\pm 1/2$). Our Hamiltonian becomes:

$$\hat{H} = \hat{H}_0 + \sum_{i=1}^Z \left[\mu_B \mathbf{B} \cdot (\hat{\mathbf{L}}_i + 2\hat{\mathbf{S}}_i) + \frac{e^2}{2m} \left(\frac{1}{2} \mathbf{B} \times \mathbf{r}_i \right)^2 \right] \quad (6.21)$$

If we now consider $\mathbf{B} = (0, 0, B)$:

$$\mathbf{B} \times \mathbf{r}_i = B(x_i \mathbf{e}_y - y_i \mathbf{e}_x) \rightarrow \left(\frac{1}{2} \mathbf{B} \times \mathbf{r}_i \right)^2 = \frac{B^2}{4} (x_i^2 + y_i^2) \quad (6.22)$$

and then:

$$\hat{H} = \hat{H}_0 + \mu_B B \sum_{i=1}^Z (\hat{L}_{z_i} + 2\hat{S}_{z_i}) + \frac{e^2 B^2}{8m} \sum_{i=1}^Z (x_i^2 + y_i^2) \quad (6.23)$$

Where in general the last term is a sum on the squared electronic average orbital radius perpendicular to the applied field, $r_{\perp}^2$. We call ϵ_n , the eigenvalue of $\hat{H}_0$. If we consider the effect of the applied magnetic field, the energy shifts produced are ~ 0.1 meV and are very small as compared to atomic energy scales (eV). This justifies the use perturbation theory which gives the perturbed eigenvalue up to second order in H:

$$\Delta\hat{H} = \mu_B B \sum_{i=1}^Z (\hat{L}_{z_i} + 2\hat{S}_{z_i}) + \frac{e^2 B^2}{8m} \sum_{i=1}^Z (x_i^2 + y_i^2) \quad (6.24)$$

and

$$\epsilon_n \rightarrow \epsilon_n + \Delta\epsilon \quad (6.25)$$

where the energy change $\Delta\epsilon$ due to the magnetic field is for a given energy level $\langle n |$ up to second order in $\hat{H}$:

$$\Delta\epsilon_n = \langle n | \Delta\hat{H} | n \rangle + \sum_{n' \neq n} \frac{|\langle n | \Delta\hat{H} | n' \rangle|^2}{\epsilon_n - \epsilon_{n'}} \quad (6.26)$$

And hence in our Z electron system we have:

$$\Delta\epsilon_n = \underbrace{\frac{e^2 B^2}{8m} \sum_{i=1}^Z \langle \psi_i | x_i^2 + y_i^2 | \psi_i \rangle}_{(1) \text{ diamagnetic term}} + \underbrace{\mu_B B \sum_{i=1}^Z \langle \psi_i | \hat{L}_{z_i} + 2\hat{S}_{z_i} | \psi_i \rangle}_{(2) \text{ paramagnetic term}} + \underbrace{B \sum_{i=1}^Z \sum_{n' \neq n} \frac{|\langle \psi_i | \mu_B (\hat{L}_{z_i} + 2\hat{S}_{z_i}) | \psi'_i \rangle|^2}{\epsilon_{n_i} - \epsilon_{n'_i}}}_{(3) \text{ van Vleck paramagnetic term}} \quad (6.27)$$

The term (1) contains the expected value of the electron precession around the z axis due to the presence of the magnetic field. Is the diamagnetic term which we will discuss here. The term (2) (and (3)) contain the total magnetic moment of the atom and is different of zero if we have incomplete electronic shells (see annex). Term (2) is the one that will contribute to the usual paramagnetism of the material and term (3) is a more "exotic" form of diamagnetism related to field induced electronic transitions. In general the separation between the different electronic states is large and then the van Vleck term is in general small. This term will be no further discussed in this course and we will concentrate on the two first terms in the following sections.

6.1.3 Diamagnetism

We discuss here term (1) in Eq. 6.27.

In diamagnetic materials the application of an applied magnetic field, creates an induced magnetic field in the material having a direction opposite to the applied magnetic field. Consequently the material is repelled by the applied magnetic field. This behavior is opposite to the one exhibited by paramagnetic materials.

Diamagnetism is present in all materials, but in general it is only relevant when other magnetic effects (paramagnetism, ferromagnetism, etc) are absent. In that case the material is called a *diamagnet* and corresponds to what ordinarily is referred as a non-magnetic material. Diamagnetism is a weak property and its effects are not observable in everyday life.

We will discuss here the diamagnetism found in materials containing atoms with closed shells (dielectrics or insulators). This is referred as Langevin diamagnetism as Langevin developed a classical model for this case. We will here make a quantum description (often referred as Larmor diamagnetism). Both approaches lead to the same value of the magnetic susceptibility.

If the electron wave-function has spherical symmetry ($x_i^2 \equiv y_i^2 \equiv z_i^2$ and $x_i^2 + y_i^2 + z_i^2 = r_i^2$) then $3x_i^2 = r_i^2$ and $x_i^2 + y_i^2 = 2x_i^2$ giving:

$$\langle \psi_i | x_i^2 + y_i^2 | \psi_i \rangle = \frac{2}{3} \langle \psi_i | r_i^2 | \psi_i \rangle \quad (6.28)$$

The diamagnetic energy of one ion can then be computed as:

$$\epsilon_d = \frac{e^2 B^2}{8m} \sum_{i=1}^Z \langle \psi_i | r_i^2 | \psi_i \rangle \approx \frac{Ze^2 \mu_0^2 H^2}{12m} \langle r^2 \rangle \quad (6.29)$$

with $\langle r^2 \rangle$ being the mean square distance of the electrons of the ion to the atomic nucleus. We just need to multiply by the number of ions N in a system of volume V to obtain the total energy $E_d = N\epsilon_d$. The dimensionless diamagnetic susceptibility can then be calculated as:

$$\chi = -\frac{N}{\mu_0 V} \frac{\partial^2 \epsilon_d}{\partial H^2} = -\frac{nZ\mu_0 e^2}{6m} \langle r^2 \rangle \quad (6.30)$$

with $n = N/V$ being the ion density. This results describes the magnetic response of solid noble gases or simple ionic crystals as alkali halides, as in these crystals the ions are only slightly distorted by their crystalline environments (the atomic picture holds). In the diamagnetic response, the susceptibility is negative and rather small (10^{-5}). The magnetization is opposite to the external field – it opposes the external field like in Lenz's law.

The Larmor theory (or the Langevin theory) does not apply to metals because they have non-localized electrons. The theory for the diamagnetism of a free electron gas is called Landau diamagnetism, and instead considers the weak counter-acting field that forms when the electron trajectories are curved due to the Lorentz force.

When a material contains ions with partially filled electronic shells its magnetic behavior is going to be dominated by term 2 in equation 6.27 which is now different of zero. Before we can apply this we could consider the atomic magnetic moment in the next section. As both paramagnetic as well as diamagnetic effects are rather small, the magnetization modifications of the external magnetic field can be neglected and the external magnetic field can be identified with the internal one. We recall that for the moment we are considering that the interaction between the magnetic moments associated to the ions can be neglected.

6.1.4 Interaction of a permanent moment with an applied magnetic field

We consider a magnetic field $\mathbf{B}$ taken to be along the z -axis acting on an atom of magnetic moment μ . The corresponding hamiltonian is:

$$H_m = -\mu \mathbf{B} = -\mu_z B \quad (6.31)$$

The effect of the magnetic field is to break the degeneracy of the ground state (provided by Hund rules (see annex) and determining the values of L, S and J) leading to $2J+1$ levels having energy

$$E_m = g_J \mu_B m_J B \equiv -\mu_{m_J} B \quad (6.32)$$

with $\mu_{m_J} = g_J \mu_B m_J$ and $m_J = -J, \dots, -1, 0, 1, \dots, J$ (m_J is also frequently noted J_z) and g_J the Landé g -factor being in most cases:

$$g_J = \frac{3}{2} - \frac{L(L+1) - S(S+1)}{2J(J+1)} \quad (6.33)$$

We have then $2J+1$ equally spaced energy levels, with a separation $g_J\mu_B B$ and a corresponding effective magnetic moment (by comparison with eq. 6.31):

$$\mu_{\text{eff}} = -g_J\mu_B m_J \mathbf{J} = -\mu_{m_J} \mathbf{B} \quad (6.34)$$

The Landé g-factor gives the number of Bohr magnetons associated with the effective moment, and in a simple geometrical model it arises because μ ($\propto (\mathbf{L} + 2\mathbf{S})$) is not parallel to μ_{eff} ($\propto (\mathbf{L} + \mathbf{S})$).

6.1.5 Paramagnetism of ions. Curie paramagnetism

We consider here a number of magnetic ions in a condensed systems without interaction between them and we want to determine the evolution of the magnetic moment of the system when applying a magnetic field as function of temperature. Such paramagnetic behavior will be observed for substances having magnetic ions at distances far enough to avoid magnetic interactions between such ions. This will be the case in a gas of atoms or magnetic molecules, in diluted salts of rare earths or transition metals or even in some oxides of rare earths.

If the permanent magnetic moments behave then independently one from the other, then at a temperature T , the relative occupation of the magnetic energy levels will be given by the Boltzmann factor (we have independent ion/atom magnetic moments behaving classically in terms of statistics but with a quantized magnetic energy):

$$\exp(-E_{m_J}/k_B T) = \exp(g_J\mu_B B m_J/k_B T) = \exp(\beta \mu_{m_J} B) \quad (6.35)$$

with $\beta = 1/k_B T$. The net magnetization, M for a system of N magnetic moments per unit of volume is therefore given by:

$$M = N \langle \mu \rangle = N \sum_{m_J=-J}^{m_J=J} -\mu_{m_J} \exp(\beta \mu_{m_J} B) / \sum_{m_J=-J}^{m_J=J} \exp(\beta \mu_{m_J} B) \quad (6.36)$$

Or alternatively we can use the partition function:

$$Z = \sum_{m_J=-J}^{m_J=J} \exp(\beta \mu_{m_J} B) \quad (6.37)$$

and write:

$$M = -\frac{Nk_B T^2}{B} \left(\frac{\partial \ln Z}{\partial T} \right)_B = -\frac{Nk_B T^2}{B} \frac{1}{Z} \left(\frac{\partial Z}{\partial T} \right)_B \quad (6.38)$$

We can set $x \equiv g_J\mu_B B\beta J$, which is essentially a dimensionless measure of the magnetic field. Then the partition function is a geometric series of $2J+1$ terms with first term being $\exp(x)$ and ratio $\exp(-x/J)$, which gives as result¹:

$$Z = \frac{e^x(1 - e^{-(2J+1)x/J})}{1 - e^{-x/J}} = \sinh \left[\left(\frac{2J+1}{2J} \right) x \right] / \sinh \left(\frac{x}{2J} \right) \quad (6.39)$$

Introducing this expression of the partition function in ref.[?] we obtain:

$$M = Ng_J\mu_B JB_J(x) \quad (6.40)$$

¹The sum of a geometric series of n terms, with a_1 being the first term and r the common ratio is : $S_n = a_1(1 - r^n)/(1 - r)$. We recall also that $\sinh x = (e^x - e^{-x})/2$ and $\cosh x = (e^x + e^{-x})/2$

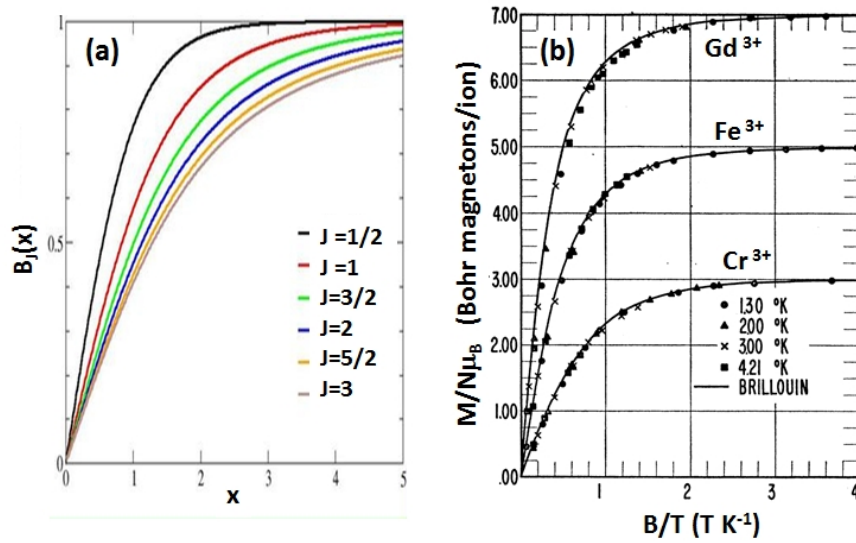


Figure 6.2: (a) The Brillouin function for different values of J . (b) Magnetization curves for different ions (Gd^{3+} , Fe^{3+} and Cr^{3+}) in a non magnetic matrix. The different symbols correspond to measurements done at different temperatures (from 1.3 to 4.21 K) varying the applied magnetic field. As shown the magnetization is a function of B/T . The curves are obtained from equation 6.40 setting $g_J = 2$ and values for J of $3/2$, $5/2$ and $7/2$ for Cr^{3+} , Fe^{3+} and Gd^{3+} respectively. The J values for Gd^{3+} and Fe^{3+} correspond in fact to the predictions of Hund's law whereas for Cr^{3+} agreement is only obtained when setting $L \approx 0$ and consequently $J \approx S$. This is an effect of a non-central crystal field (the effect of the other atoms around the ion) which lead to the so-called "quench of the orbital moment". (data from W.E. Henry, Phys. Rev. **88**, 559 (1952)).

where $B_J(x)$ is the so-called Brillouin function defined by:

$$B_J(x) = \frac{2J+1}{2J} \coth \left[\left(\frac{2J+1}{2J} \right) x \right] - \frac{1}{2J} \coth \left(\frac{x}{2J} \right) \quad (6.41)$$

As can be seen in Fig. 6.2.a, the behavior of the Brillouin function is qualitatively similar for all values of J : it increases linearly with x and saturates to 1 for large x values. The magnetization evolves then in the same way with increasingly large magnetic fields, approaching the saturation magnetization $Ng_J\mu_B J$ at large fields. The saturation magnetization corresponds to the maximum alignment of the magnetic moments with the applied field. The changeover in behavior from linear to saturation occurs when $x \approx J$, that is when $g_J\mu_B B/k_B T \approx 1$. For $g_J = 1$ this corresponds to a field of the order of 450 T at $T = 300$ K and hence to a field of order 1.5 T at $T = 1$ K. Static fields beyond 10 T need large instrument facilities with present limiting magnetic fields of about 100 T. Consequently, paramagnetic saturation can only be attained at low temperatures. Fig. 6.2.b shows three examples of magnetization measurements showing an excellent agreement with the calculated values using the Brillouin function.

For small x , $B_J(x) \approx (J+1)x/3J$, so that in weak fields²:

$$M = \frac{Ng_J^2\mu_B^2 J(J+1)B}{3k_B T} \quad (6.42)$$

Before using this results to deduce the susceptibility χ we must recall that the magnetic field, B that we are considering is the one "felt" by the ions, i.e., the local field inside the material, and

²we need for this to consider that for $x \ll 1$, $\coth x \approx 1/x + x/3$

in principle it will differ from the applied magnetic field, H , due to the magnetization screening. Nevertheless, for small values of χ we have that $\mu_0 M \ll B$, then $H \approx B/\mu_0$, i.e., the difference between the local and applied fields are negligible. We then obtain:

$$\chi = \frac{M}{H} = \mu_0 \frac{M}{B} = \frac{Np^2 \mu_B^2 \mu_0}{3K_B T} \quad (6.43)$$

where we have set $p \equiv g_J[J(J+1)]^{1/2}$. This notation is used because the expression in Eq. 6.43 correspond to the classical calculation made by Langevin for ions of magnetic momentum $p\mu_B$. Our calculation relates the value of p to the properties of the ion. Equation 6.43 explains the **Curie law** of a paramagnet, i.e., $\chi = C/T$ with $C = Np^2 \mu_B^2 \mu_0 / 3K_B$, known as the **Curie constant**. Pierre Curie discovered experimentally this law during his PhD thesis entitled "Propriétés magnétiques des corps à diverses températures" (1895) and Paul Langevin explained it with the tools of statistical physics publishing his conclusions in 1905.

Using Eq. 6.43 it is possible to deduce values for p^2 from measured values of the magnetization dependence with T . The agreement is remarkable for most rare-earth ions (4f electrons) but for most transition metals it is obtained a much better agreement when replacing J by S , which means that $L = 0$. It is then said that the orbital angular momentum is **quenched**. At the origin of orbital angular momentum quenching we find the electric field produced by neighboring ions, which is called the **crystal field**. In simple terms, due to this environmental electric field the electrons responsible of magnetism cannot occupy with the same probability the different 3d(or 4f) orbitals as for the case of the free ion (we recall that these orbitals have different spatial distributions provided by the modulus of the corresponding spherical harmonics $Y_\ell^{m_\ell}$). This results in an anisotropy of the spin-orbit coupling and then in a disruption of the third Hund rule. When the crystal field (non radial) is dominant (case of transition metals), the symmetry of the environment is such that the eigenstates determined by the crystal field have $\langle L_x \rangle = \langle L_y \rangle = \langle L_z \rangle = 0$ and the contribution of the orbital momentum vanishes. See for instance chapter 7 of reference [du Trémolet de Lacheisserie (sous la direction de)(2000)] for a more detailed description.

The crystal field is better screened by the outermost electron shell in the case of the 4f electrons (at least 8 electrons, $5s^2 5p^6$, in the external shells) than in the case of the 3d electrons (the outermost level contains at most two electrons, $4s^2$). Also the 4f electrons are spatially more localized than the 3d ones and the electric field gradient, which is at the end responsible of the effect, is less important in 4f electrons. These are the reasons which make that usually there is no quench of orbital momentum in rare-earth systems.

6.1.6 Paramagnetism of conduction electrons. Pauli Paramagnetism

The model developed in the previous section cannot be applied when the permanent magnetic moment is not carried by atoms but by conduction electrons. The reason is that the behavior of these last ones is dominated by the Pauli exclusion principle, hence by Fermi statistics. The component of the spin magnetic moment can take values $\pm \mu_B$ parallel to the applied field. The energies of the electrons with their magnetic moment parallel to the field B (labeled $\uparrow$) are lowered by $\mu_B B$ and the energies of electrons with moments anti-parallel to the field (labeled $\downarrow$) are raised by $\mu_B B$. We can write:

$$\begin{aligned} E_\downarrow &= E - \mu_B B \\ E_\uparrow &= E + \mu_B B \end{aligned} \quad (6.44)$$

We are going to consider here two different, but equivalent, evaluations of the associated magnetic susceptibility. The first method is graphical and the second one is analytical.

a) Graphical Evaluation

This leads to an evolution of the electron density of states as shown in Figure 6.3. From Figure

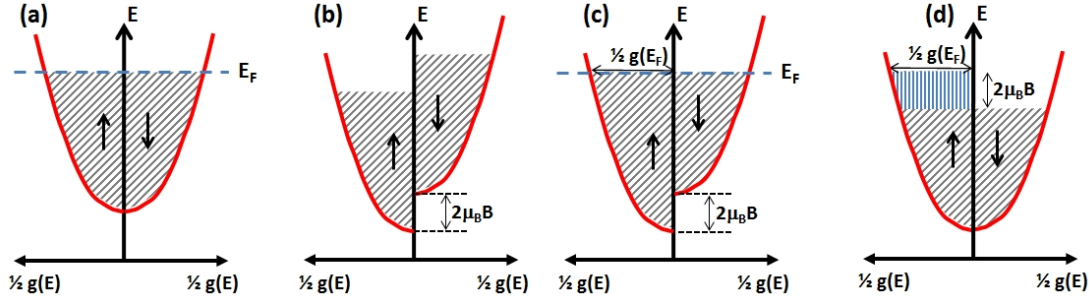


Figure 6.3: Pauli paramagnetism. (a) Occupied states for conduction electrons in a free-electron model at $T=0$ in the absence of magnetic field. The density of states has been shared between electrons with up and down spin. (b) Energy splitting of the two sub-bands due to the application of a magnetic field. (c) Relaxed electronic structure in which the Fermi energy is recovered. (d) The spin down sub-band is artificially down-shifted to show that the difference between the number of electrons per unit of volume up and down corresponds to the area vertically dashed.

6.3.d we can compute the excess of spin up electrons as the vertically dashed area:

$$N_{\uparrow} - N_{\downarrow} = g(E_F) \mu_B B \quad (6.45)$$

and the magnetization will be:

$$M = \mu_B (N_{\uparrow} - N_{\downarrow}) = \mu_B^2 g(E_F) B \quad (6.46)$$

For free electrons we have using eq. 1.66:

$$g(E_F) = \frac{3}{2} \frac{N}{E_F} \quad (6.47)$$

And neglecting the material magnetization (valid for weak magnetic fields), we have $B \approx \mu_0 H$ and then the associated magnetic susceptibility becomes:

$$\chi_P = \frac{M}{H} = \mu_0 \mu_B^2 g(E_F) = \frac{3}{2} \frac{N \mu_0 \mu_B^2}{E_F} \quad (6.48)$$

where the "P" index holds for **Pauli spin paramagnetism**, which is the name given to this effect. If we would have not considered the Fermi statistics (or the exclusion principle), we could have used the classical (Maxwellian) Curie law prediction of eq. 6.43 by putting $J = S = 1/2$, $g = 2$, which gives $p^2 = 3$ and then

$$\chi_{\text{clas}} = \frac{N \mu_B^2 \mu_0}{K_B T} \quad (6.49)$$

and recalling that $E_F = k_B T_F$ we can write:

$$\chi_P = \frac{2}{3} \frac{T_F}{T} \chi_{\text{clas}} \quad (6.50)$$

The classical result will be only achieved for temperatures of the order of T_F which as we have seen are in general well above the melting temperatures of metals.

The Pauli paramagnetism obtained from this free electron picture is not exact as it does not integrate the real band structure of metals. Nevertheless within a factor of ~ 2 it predicts rather well the experimental values of simple metals as the alkali metals.

b) Analytical Evaluation

We consider the density of states of each electron spin population $g(E \uparrow)$ and $g(E \downarrow)$ to evaluate the magnetization:

$$M = \mu_B \int_0^\infty [g(E \uparrow)f(E \uparrow) - g(E \downarrow)f(E \downarrow)] dE \quad (6.51)$$

With $f(E)$ being the Fermi-Dirac distribution function. If the applied magnetic field is weak, we can consider that $g(E \uparrow) = g(E \downarrow) = g(E)$ (see Fig. 6.3), as $\rho(E)$ changes slowly. We can also replace $f(E \uparrow)$ and $f(E \downarrow)$ by a first order development around E :

$$\begin{aligned} f(E \uparrow) &\approx f(E) - \frac{\partial f}{\partial E}(E \uparrow - E) \\ f(E \downarrow) &\approx f(E) - \frac{\partial f}{\partial E}(E \downarrow - E) \end{aligned} \quad (6.52)$$

Replacing, we obtain:

$$M \approx \mu_B^2 B \int_0^\infty g(E) \left(-\frac{\partial f}{\partial E} \right) dE \quad (6.53)$$

At low or moderate temperatures $\frac{\partial f}{\partial E}$ is only important close to E_F and then:

$$M \approx \mu_B^2 B g(E_F) \int_0^\infty \left(-\frac{\partial f}{\partial E} \right) dE = \mu_B^2 B g(E_F) (f(0) - f(\infty)) = \mu_B^2 B \rho(E_F) \quad (6.54)$$

Again as the magnetic field is assumed to be weak, we can neglect the material magnetization and then $B \approx \mu_0 H$ giving:

$$\chi_P = \frac{M}{H} = \mu_0 \mu_B^2 g(E_F) \quad (6.55)$$

which is the same result than with the graphical method. The Pauli paramagnetic susceptibility is then independent of temperature. We could compute the value of M at a higher order in T . For this we should take equation 6.53, make its integration by parts and then apply the Sommerfeld development method discussed at the end of the chapter devoted to Statistical Physics. We find then that χ_P is a constant plus a T^2 term of the form :

$$\chi_P = \mu_0 \mu_B^2 g(E_F) \left[1 + \frac{\pi^2}{12} \left(\frac{k_B T}{E_F} \right)^2 \right] \quad (6.56)$$

6.2 Interacting magnetic moments

In the case of ferromagnets, antiferromagnets, ferrimagnets and other magnetic materials as spin glasses, helical magnets, frustrated magnets... the interaction between the magnetic ions of the

materials becomes important and needs to be considered. We will consider here the *Heisenberg hamiltonian* to describe this interaction :

$$H = -\frac{1}{2} \sum_i \sum_{j \neq i} J_{ij} \vec{S}_i \cdot \vec{S}_j \quad (6.57)$$

where $\vec{S}_i$ represents the magnetic moment of the atom or ion i and is often just called the localized spin or just the spin of the atom. The value J_{ij} is called the *exchange integral* and carries the physics of the interaction between magnetic moments. We will not derive here the exchange integral, but its origin combines the repulsive coulombic interaction between the electrons of the two atoms and the Pauli exclusion principle. This integral depends then on the distance between the considered ions or atoms. The factor $1/2$ avoids counting twice every pair of interacting atoms. The exchange integral decreases very rapidly when the distance increases and in the following we will only consider that it is different of zero for first neighbors. In that case we will write the Heisenberg hamiltonian as:

$$H = -J \sum_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j \quad (6.58)$$

where we have introduced the notation $\langle i,j \rangle$ which runs over all $i-j$ first neighbors and allowing then to omit the $1/2$ term. If J is positive, the ferromagnetic interaction (parallel spins) and if J is negative, we favor the antiferromagnetic interaction (anti-parallel spins).

In the presence of a magnetic field, $\vec{B}$ the Heisenberg Hamiltonian needs to include the interaction of the spin with the applied field, which adds an additional term:

$$H = -J \sum_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j - g_J \mu_B \sum_{i=1}^N \vec{S}_i \cdot \vec{B} \quad (6.59)$$

where g_J is the Landé factor or gyromagnetic factor.

The exchange energy between neighboring magnetic atoms is of the order of 10 to 10^3 meV/atom. This is a relatively large energy which makes that in general the angle between spin is very close to zero ($J > 0$) or π ($J < 0$). If we consider that only these two extreme situations (parallel or antiparallel spins) are allowed, the corresponding description of magnetism is the *Ising model*.

6.2.1 Magnetic anisotropy and magnetic domains

Crystalline structure leads to non-isotropic magnetic properties, i.e., an applied magnetic field will align easier the magnetic moments in certain directions with respect to others. This is known as *magnetic anisotropy*. To account for the differences in magnetic energy in different crystalline directions, we introduce H_A , the anisotropy contribution to the hamiltonian:

$$H_A = K_x \sum_i (S_i^x)^2 + K_y \sum_i (S_i^y)^2 + K_z \sum_i (S_i^z)^2 \quad (6.60)$$

with K_x , K_y and K_z the constants of anisotropy or magnetocrystalline constants, which depend on the crystalline structure.

In a cubic material, $K_{x,y,z} = K$ and H_A becomes a constant of value $KS(S+1)$ independent of the orientation of the spin of the atoms with respect to the crystalline structure. Nevertheless,

magnetic anisotropy is also present in cubic crystals. In that case, an anisotropy hamiltonian including terms up to 4 order in power of S_i^x , S_i^y and S_i^z is needed.

An interesting case is uniaxial anisotropy, i.e., when there exists an easy magnetization direction, called the easy magnetization axis or just easy axis. In general the easy axis correspond with one of the crystallographic axis. In that particular case, the anisotropy hamiltonian can be written:

$$H_A = K_x S^2 \sin^2 \theta \quad (6.61)$$

with θ being the angle between the easy axis and the system magnetization vector (M).

In other terms, the easy axis is the direction inside a crystal, along which small applied magnetic field is sufficient to reach the saturation magnetization. Hard axis is the direction inside a crystal, along which large applied magnetic field is needed to reach the saturation magnetization. For instance for fcc Ni the $\langle 111 \rangle$ is lowest packed direction and it is the easy axis. $\langle 100 \rangle$ is the hard axis.

Magnetic order appears when the magnetic energy is more important than the thermal energy. There exists then a temperature beyond which magnetic order does not persist and that the spins are randomly oriented. The material is then paramagnetic beyond this temperature and has zero magnetization (macroscopic). This critical temperature is the Curie temperature, T_C , in the case of ferromagnets and the Néel temperature, T_N , in the case of antiferromagnets.

In general the anisotropy constants, K_i are much less important than the exchange integral, J . Consequently, anisotropy does not play a significant effect in the paramagnetic phase, but it may be important in the magnetic ordered phase. In fact, in ferromagnets, antiferromagnets or ferrimagnets, spins can be locally organized in magnetic domains also called Weiss domains. The transient region between domain, usually about 100 nm thick is the domain wall or Bloch wall. The reason leading to domain formation is the combined effect of exchange energy and magnetocrystalline energy. The domain evolution under a magnetic field leads to the hysteresis cycle in the magnetization curve.

6.2.2 Mean Field Approximation

The Heisenberg quantum hamiltonian makes that the magnetic hamilton equation only soluble exactly in some cases (Ising model in 1D for instance). The mean field approximation, is an approach allowing to characterize a number of magnetic properties without having to solve the quantum Heisenberg Hamilton equation.

The meanfield approach consist oin neglecting spin fluctuations given by $\Delta \vec{S}_i = \vec{S}_i - \langle \vec{S}_i \rangle$. Here $\langle \vec{S}_i \rangle$ is the average spin on site i . We may then write:

$$\vec{S}_i = \langle \vec{S}_i \rangle + (\vec{S}_i - \langle \vec{S}_i \rangle) = \langle \vec{S}_i \rangle + \Delta \vec{S}_i \quad (6.62)$$

We now compute the product $\vec{S}_i \vec{S}_j$ and we neglect quadratic terms $\Delta \vec{S}_i \Delta \vec{S}_j$ and we have:

$$\vec{S}_i \vec{S}_j = \vec{S}_i \langle \vec{S}_j \rangle + \langle \vec{S}_i \rangle \vec{S}_j - \langle \vec{S}_i \rangle \langle \vec{S}_j \rangle \quad (6.63)$$

In a ferromagnetic material, the average value is independent of position, i.e., $\langle \vec{S}_i \rangle = \langle \vec{S} \rangle$ and then

$$\vec{S}_i \vec{S}_j = \vec{S}_i \langle \vec{S} \rangle + \langle \vec{S} \rangle \vec{S}_j - \langle \vec{S} \rangle \langle \vec{S} \rangle \quad (6.64)$$

In the case of an antiferromagnetic material or in a ferrimagnetic material, one will need to make the distinction between the average spin of the two sublattices (spin up and spin down sublattices). We consider here the case of a ferromagnet which leads then replacing in the Heisenberg hamiltonian to:

$$H = -J \sum_{\langle i,j \rangle} \left(\vec{S}_i \cdot \vec{S}_j + \langle \vec{S}_i \cdot \vec{S}_j \rangle - \langle \vec{S}_i \cdot \vec{S}_j \rangle \right) - g_J \mu_B \sum_i \vec{S}_i \cdot \vec{B} =$$

$$JNz \langle \vec{S} \rangle^2 - g_J \mu_B \sum_i \vec{S}_i \cdot \left(\frac{Jz}{g_J \mu_B} \langle \vec{S} \rangle + \vec{B} \right) \quad (6.65)$$

where z is the number of first neighbors. In that way we may write the hamiltonian as:

$$H = JNz \langle \vec{S} \rangle^2 - g_J \mu_B \sum_i \vec{S}_i \cdot \vec{B}_{\text{eff}} \quad (6.66)$$

where we have introduced an *effective magnetic field* given by:

$$\vec{B}_{\text{eff}} = \vec{B} + \frac{Jz \langle \vec{S} \rangle}{g_J \mu_B} \quad (6.67)$$

We can define the system magnetization as

$$\vec{M} = \sum_{i=1}^N \langle \vec{S}_i \rangle \quad (6.68)$$

where the average spin on site i will correspond to its thermal expectation value which can be calculated from the partition function

$$Z = \sum_{\text{conf}} e^{-\beta H_i} = \sum_{\text{conf}} e^{\beta g_J \mu_B \vec{S}_i \cdot \vec{B}_{\text{eff}}} \quad (6.69)$$

where we have taken $H_i = -g_J \mu_B \vec{S}_i \cdot \vec{B}_{\text{eff}}$ omitting the term independent of $\vec{B}_{\text{eff}}$, as in what follows we will need to derive with respect to $\vec{B}_{\text{eff}}$. The sum runs over all possible spin configurations on site i and $\beta = 1/(k_B T)$

Then we have:

$$\langle \vec{S}_i \rangle = \frac{\text{Tr}(\vec{S}_i e^{-\beta H_i})}{Z} \quad (6.70)$$

and we can compute the magnetization as:

$$\vec{M} = \sum_{i=1}^N \frac{\text{Tr}(\vec{S}_i e^{-\beta H_i})}{Z} = \frac{1}{Z} \sum_{i=1}^N \vec{S}_i e^{-\beta H_i} = \frac{1}{\beta Z} \frac{\partial Z}{\partial \vec{B}_{\text{eff}}} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial \vec{B}_{\text{eff}}} \quad (6.71)$$

6.3 Annex.Magnetism of one and many electrons. Hund's Rules

We introduce a semi-classical formulation of the orbital magnetic moment, μ_o of an electron. The electrical current of a circulating electron in an atomic orbit of radius r would be $i = -e/\tau$ with $\tau = 2\pi r v$ we have $i = -e/(2\pi r v)$. The orbital magnetic moment associated to a single whorl is $\mu_o = i \mathbf{a}$ where $\mathbf{a}$ is the vector area of the whorl: $|\mathbf{a}| = \pi r^2$ and then $\mathbf{a} = \pi r^2 \mathbf{u}$, with $\mathbf{u}$ a unitary vector perpendicular to the area (following right hand rule of current circulation). We have then:

$$\mu_o = \frac{-ev}{2\pi r} \mathbf{a} = -\frac{ev}{2} r \mathbf{u} \quad (6.72)$$

The orbital angular momentum is quantized giving $mvr = |\hbar \ell|$ which let us write:

$$\mu_o = -\frac{e\hbar}{2m} \ell = -\mu_B \ell \quad (6.73)$$

with μ_B the Bohr magneton. We recall here that the above equality becomes a relation between operators and not between vectors. On its side the spin magnetic moment is :

$$\mu_s = -g_0 \mu_B \mathbf{s} \approx -1 \mu_B \mathbf{s} \quad (6.74)$$

where g_0 is the gyromagnetic ratio for the self-spinning electron, which is twice bigger than the value for an orbiting electron. In the framework of relativistic quantum mechanics its value is :

$$g_0 = 2 \left(1 + \frac{\alpha}{2\pi} + O(\alpha^2) \right) \approx 2 \quad (6.75)$$

The total spin of an electron is then given by:

$$\mu = -\mu_B \ell - 2\mu_B \mathbf{s} = -\mu_B (\ell + 2\mathbf{s}) \quad (6.76)$$

For a system of electrons in an atom or an ion we will have a total angular and spin momentum given by $\mathbf{L} = \sum \ell$ and $\mathbf{S} = \sum \mathbf{s}$ with

$$\mu = -\mu_B (\mathbf{L} + 2\mathbf{S}) \quad (6.77)$$

It can also be shown that $\mu = -g_J \mu_B \mathbf{J}$ with $\mathbf{J} = \mathbf{L} + \mathbf{S}$ and g_J the Landé factor being :

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} = \frac{3}{2} + \frac{1}{2} \frac{S(S+1) + L(L+1)}{J(J+1)} \quad (6.78)$$

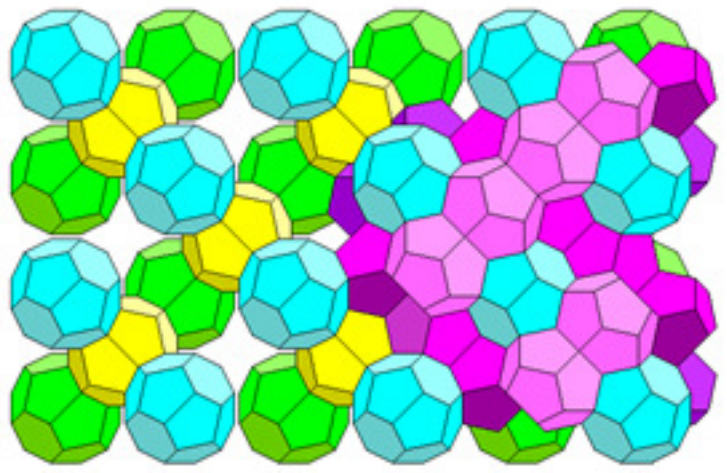
The Hund rules as applied to atoms and ions affirm that electrons will occupy orbitals in such a way that the ground state is characterized by the following:

- 1. $|\mathbf{S}|$ is maximum respecting Pauli's exclusion principle;
- 2. $|\mathbf{L}|$ is maximum (once rule 1 has been respected)
- 3. $|\mathbf{J}| = |\mathbf{L} - \mathbf{S}|$ if the level is less than half filled. $|\mathbf{J}| = |\mathbf{L} + \mathbf{S}|$ if the level is more than half filled. (if the energy level is half-filled, then $L = 0$ and we do not need rule 3 and $\mathbf{J} = \mathbf{S}$).

The application of Hund's rules to atoms or ions having one or more d-shell or f-shell electrons is shown in Fig. 6.4 including the spectroscopic notation of the level occupation: $2S+1 L_J$ with the following notation for the L values: S,P,D,F,G,H,I for $L=0,1,2,3,4,5$ and 6 respectively.

<i>d</i> -shell ($l = 2$)									
n	$l_z = 2,$	$1,$	$0,$	$-1,$	-2	S	$L = \Sigma l_z $	J	SYMBOL
1	↓					1/2	2	3/2	$\left. \begin{array}{l} {}^2D_{3/2} \\ {}^3F_2 \\ {}^4F_{3/2} \\ {}^5D_0 \\ {}^6S_{5/2} \end{array} \right\} J = L - S $
2	↓	↓				1	3	2	
3	↓	↓	↓			3/2	3	3/2	
4	↓	↓	↓	↓		2	2	0	
5	↓	↓	↓	↓	↓	5/2	0	5/2	
6	↑↑	↑	↑	↑	↑	2	2	4	$\left. \begin{array}{l} {}^5D_4 \\ {}^4F_{9/2} \\ {}^3F_4 \\ {}^2D_{5/2} \\ {}^1S_0 \end{array} \right\} J = L + S$
7	↑↑	↑↑	↑	↑	↑	3/2	3	9/2	
8	↑↑	↑↑	↑↑	↑	↑	1	3	4	
9	↑↑	↑↑	↑↑	↑↑	↑	1/2	2	5/2	
10	↑↑	↑↑	↑↑	↑↑	↑↑	0	0	0	
<i>f</i> -shell ($l = 3$)									
n	$l_z = 3,$	$2,$	$1,$	$0,-1,-2,-3$		S	$L = \Sigma l_z $	J	
1	↓					1/2	3	5/2	$\left. \begin{array}{l} {}^2F_{5/2} \\ {}^3H_4 \\ {}^4I_{9/2} \\ {}^5I_4 \\ {}^6H_{5/2} \\ {}^7F_0 \\ {}^8S_{7/2} \end{array} \right\} J = L - S $
2	↓	↓				1	5	4	
3	↓	↓	↓			3/2	6	9/2	
4	↓	↓	↓	↓		2	6	4	
5	↓	↓	↓	↓	↓	5/2	5	5/2	
6	↓	↓	↓	↓	↓	3	3	0	
7	↓	↓	↓	↓	↓	7/2	0	7/2	
8	↑↑	↑	↑	↑	↑	3	3	6	$\left. \begin{array}{l} {}^7F_6 \\ {}^6H_{15/2} \\ {}^5I_8 \\ {}^4I_{15/2} \\ {}^3H_6 \\ {}^2F_{7/2} \\ {}^1S_0 \end{array} \right\} J = L + S$
9	↑↑	↑↑	↑	↑	↑	5/2	5	15/2	
10	↑↑	↑↑	↑↑	↑	↑	2	6	8	
11	↑↑	↑↑	↑↑	↑↑	↑	3/2	6	15/2	
12	↑↑	↑↑	↑↑	↑↑	↑	1	5	6	
13	↑↑	↑↑	↑↑	↑↑	↑↑	1/2	3	7/2	
14	↑↑	↑↑	↑↑	↑↑	↑↑	0	0	0	

Figure 6.4: Ground states of ions with partially filled *d*- or *f*-shells, as constructed from Hund's rules.



7. Dynamics of phonons: anharmonicity

7.1 Introduction

In Fig. 7.1 is depicted in red the harmonic potential and its quantized vibrational states. The difference of distance dependence between the attractive and repulsive part of the potential that composes the interatomic potentials, leads to its asymmetry as depicted by the blue curve in Fig. 7.1. At low temperature, when only the firsts vibrational states are concerned, there is not much difference between the harmonic and the real interatomic potential, but that can be very different at high temperature.

The harmonic assumption - quadratic description of the potential - which we used when describing phonons, allowed us to apply the adiabatic approximation, i.e., to separate the lattice vibrations in *independent* vibrational modes.

The inclusion of anharmonic terms (beyond second order) in the Taylor expansion of the potential, leads then to the loss of independence between phonons, they become coupled or they can be represented as suffering collisions.

Phonon collisions will limit the phonon thermal conductivity which otherwise would have no limits for a perfect and infinite crystal (to avoid interaction of phonons with boundaries).

The anharmonic term is also responsible of the thermal expansion of solids. in fact, as shown in

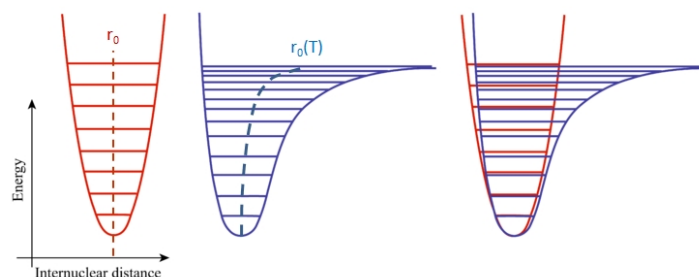


Figure 7.1: Harmonic interatomic potential (red) and the corresponding quantized vibrational states and anharmonic potential (blue). The average equilibrium position, r_0 does not change with temperature in the harmonic case meaning that there is no thermal expansion, contrarily to the anharmonic case.

Fig. 7.1, in the harmonic potential, the equilibrium position will be not affected with temperature, as the oscillation of the interatomic distance around the equilibrium position is symmetric at all temperatures. In the anharmonic potential, at high temperatures, the average interatomic distance increases with temperature and thermal expansion takes place.

7.2 Thermal expansion

The volumetric thermal expansion is thermodynamically given by

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \left(\frac{\partial p}{\partial T} \right)_V = \frac{1}{B} \left(\frac{\partial p}{\partial T} \right)_V \quad (7.1)$$

where we have used the definition of the bulk modulus (inverse of the isothermal compressibility, κ_T):

$$B \equiv \frac{1}{\kappa_T} \equiv -V \left(\frac{\partial P}{\partial V} \right)_T \quad (7.2)$$

And the following relation:

$$\underbrace{\left(\frac{\partial V}{\partial T} \right)_p = - \left(\frac{\partial S}{\partial p} \right)_T}_{\text{Maxwell relation}} = - \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial p} \right)_T = - \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial p} \right)_T \quad (7.3)$$

where we have used for the last equality the Maxwell relation:

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V \quad (7.4)$$

The expression of the thermal expansion can be expressed in terms of the Helmholtz free Energy, $F = E - TS$, by recalling that

$$p = - \left(\frac{\partial F}{\partial V} \right)_T \quad (7.5)$$

We have then

$$\beta = -\frac{1}{B} \left(\frac{\partial^2 F}{\partial V \partial T} \right) \quad (7.6)$$

We can recognize two different contributions : $F = E_{\text{coh}} + E_{\text{ph}}$, where E_{coh} is the cohesive energy due to the interatomic interactions and E_{ph} is the contribution of phonons to the total energy. $E_{\text{ph}} = \sum f_i$ where f_i is the contribution of one phonon mode and $3N$ the number of phonons in a system having N atoms.

$$f_i = \frac{\hbar \omega}{2} + \frac{\hbar \omega}{e^{\hbar \omega_i / k_B T} - 1} \quad (7.7)$$

If we consider the harmonic approximation, ω is independent of the volume (see our calculation in 1D: $\omega(k)$ was independent of the cell parameter, a), and then E_{ph} will not contribute to β . On the other side, E_{coh} is dependent on the volume but - apart from entropic effects, only important in few rare cases - in general independent on T . Then E_{coh} does not contribute neither to β and in the harmonic approximation $\beta = 0$, in correspondence with our above qualitative description.

Let us now turn to the anharmonic case. We shall see that the dependence of ω with V is the dominant contribution to β . Let's start by computing the pressure :

$$p = - \left(\frac{\partial E_{\text{coh}}}{\partial V} \right) - \sum_i \frac{\partial f_i}{\partial V} = - \left(\frac{\partial E_{\text{coh}}}{\partial V} \right) - \sum_i \hbar \frac{\partial \omega_i}{\partial V} \left[1/2 + \frac{1}{e^{\hbar \omega_i / k_B T} - 1} \right] \quad (7.8)$$

the population of the phonon state ω_i is $n_i = \frac{1}{e^{\hbar \omega_i / k_B T} - 1}$, so we have neglected the volume variation of the population of phonon states with respect to temperature variation which will be considered later. This is a reasonable hypothesis for liquid and solids which are much less compressible than a gas. We can then write:

$$p = - \left(\frac{\partial E_{\text{coh}}}{\partial V} \right) - \sum_i (n_i + 1/2) \frac{\partial \hbar \omega_i}{\partial V} \quad (7.9)$$

Then when computing β we have:

$$\beta = \frac{1}{B} \left(\frac{\partial p}{\partial T} \right)_V = - \frac{1}{B} \sum_i \frac{\partial n_i}{\partial T} \frac{\partial \hbar \omega_i}{\partial V} \quad (7.10)$$

Let us define, what is called the total *Grüneisen parameter*, γ_T as:

$$\gamma_T \equiv \frac{\sum_i \frac{\partial n_i}{\partial T} \left(-V \frac{\partial \hbar \omega_i}{\partial V} \right)}{\sum_i \hbar \omega_i \frac{\partial n_i}{\partial T}} \quad (7.11)$$

To understand the physical significance of the Grüneisen parameter, we recall that:

$$E_{\text{ph}} = \sum_i \hbar \omega_i \left(n_i + \frac{1}{2} \right) \rightarrow c_v = \frac{\partial E_{\text{ph}}}{\partial T} = \sum_i \hbar \omega_i \frac{\partial n_i}{\partial T} = \sum_i c_v(\omega_i, T) \quad (7.12)$$

The Grüneisen parameter is an average value of the variation of the phonon frequency with volume, weighted by their contribution to the specific heat, $c_v(\omega_i, T_i)$.

We have then the relation:

$$\beta = \frac{\gamma_T c_v}{B V} \quad (7.13)$$

The Grüneisen parameter depends weakly on temperature and is a characteristic constant of a material having values comprised in general between 1 and 3. As the bulk modulus B of solids depends also weakly on temperature, this expression shows that the dependence on T of the thermal expansion coefficient is essentially the same as the one of c_v which we have already studied.

If we consider a solid with only one phonon mode (Einstein model), the Grüneisen parameter becomes:

$$\gamma = \frac{-V \frac{\partial \omega}{\partial V}}{\omega} = - \frac{d(\ln \omega)}{d(\ln V)} \quad (7.14)$$

It is frequent to define in an analogous way the Grüneisen parameter for the different phonon modes of a crystal, which is sometimes referred as the microscopic Grüneisen parameter :

$$\gamma_i = - \frac{d(\ln \omega_i)}{d(\ln V)} = - \frac{V}{\hbar \omega_i} \frac{\partial \hbar \omega_i}{\partial V} \quad (7.15)$$

That allows us to write:

$$\gamma_T = \frac{\sum_i \gamma_i c_v(\omega_i, T)}{\sum_i c_v(\omega_i, T)} \quad (7.16)$$

7.3 Grüneisen parameter and anharmonic potential

Let us consider the expansion of the interatomic potential, $V(r)$ up to 3rd order, around the equilibrium position $r = a$:

$$V(r) = V(a) + \frac{(r-a)^2}{2} \left(\frac{\partial^2 V}{\partial r^2} \right)_{r=a} + \frac{(r-a)^3}{6} \left(\frac{\partial^3 V}{\partial r^3} \right)_{r=a} \quad (7.17)$$

In the harmonic approximation the interatomic spring constant is given by $K = \left(\frac{\partial^2 V}{\partial r^2} \right)_{r=a}$. Let us consider the spring constant when the distance between atoms is displaced to a position a' :

$$K = \left(\frac{\partial^2 V}{\partial r^2} \right)_{r=a'} = \left(\frac{\partial^2 V}{\partial r^2} \right)_{r=a} + (a' - a) \left(\frac{\partial^3 V}{\partial r^3} \right)_{r=a} = V'' + V'''_x \quad (7.18)$$

Where we have made a 1st order development around $r = a$. Let us consider a cubic crystal ($V = a^3$) and a single phonon so as to write:

$$\gamma = -\frac{V}{\omega} \frac{\delta \omega}{\delta V} = -\frac{a}{3\omega} \frac{\delta \omega}{\delta a} = -\frac{a}{6K} \frac{\delta K}{\delta a} \quad (7.19)$$

where in the last equality we have considered that $\omega \propto K^{1/2}$ and hence $\omega \propto 1/2 K^{-1/2} \delta K$. We identify then

$$V''' = \frac{\partial K}{\partial x} = \frac{\delta K}{\delta a} \quad (7.20)$$

Replacing in the expression of γ we have:

$$\gamma = \frac{a}{6} \frac{\left(\frac{\partial^3 V}{\partial r^3} \right)_{r=a}}{\left(\frac{\partial^2 V}{\partial r^2} \right)_{r=a'}} \quad (7.21)$$

which shows that the Grüneisen parameter constitutes a measure of the relative importance of the anharmonic terms with respect to the harmonic ones.

The curvature of the interatomic potentials determine also the elastic constants of a material (Young modulus, shear modulus,...). The anharmonicity then translates also into a dependence of the elastic moduli with V and hence with pressure.

Certain materials can exhibit negative values of the thermal expansion coefficient. They are called NTE (for negative thermal expansion) materials. Others like invar (a Fe-Ni alloy), have values of β close to zero. Invar is used in applications where the dimensional stability is required as in precision instruments. In invar, a magneto-volumetric effect compensates the anharmonic term in a large temperature domain.

7.4 Thermal conductivity

We have already discussed that the introduction of anharmonic terms implies the breakout of the phonon independent approximation characteristic of the harmonic approach. In other words, in the anharmonic approximation, phonons can interact and their interaction, which can be viewed as collisions, will have an important impact on the phonon driven thermal conductivity. Phonon thermal conduction is the dominant thermal conduction process in insulators.

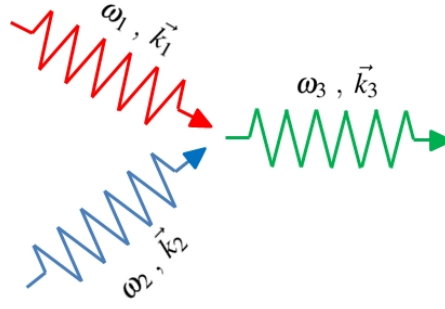


Figure 7.2: Diagram of a 2-phonon collision leading to their annihilation and the creation of a 3rd one : $1 + 2 \rightarrow 3$.

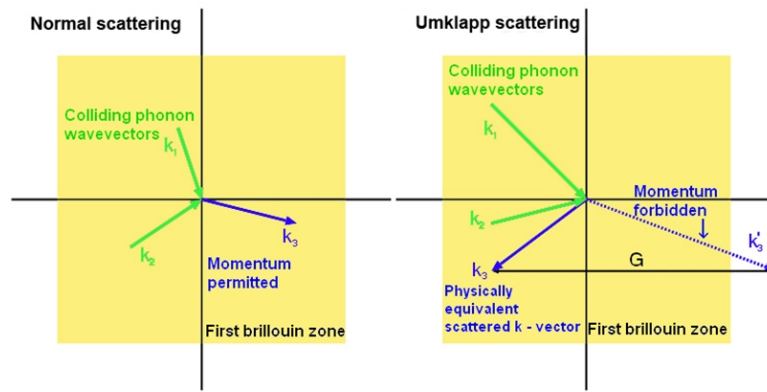


Figure 7.3: $1 + 2 \rightarrow 3$ Normal (left) and Umklapp (right) phonon collisions.

In a phonon collision the energy and momentum conservation hold. If we consider the collision of two phonons leading to their annihilation and the creation of a third one as depicted in Fig. 7.2 we should have $\hbar\omega_1 + \hbar\omega_2 = \hbar\omega_3$ and $\vec{k}_1 + \vec{k}_2 = \vec{k}_3 + \vec{G}_{hkl}$. The last expression, which takes into account that we need to consider the lattice momentum conservation, implies that two possible collisions are possible which are also called N-process (N for Normal) and U-process (U for Umklapp, from German) shown in Fig. 7.3 in a 2D-case. In the normal process, the sum $\vec{k}_1 + \vec{k}_2$ remains in the first Brillouin zone and we do not need to add a reciprocal lattice vector to have all the physics description in the first Brillouin zone. In the Umklapp scattering, the sum $\vec{k}_1 + \vec{k}_2$ goes out of the first Brillouin zone and we need to bring it back by adding a $\vec{G}_{hkl}$. The result is that the resulting phonon travels backwards, i.e., a U-process reduces the phonon thermal conductivity.

As for photons, the corpuscular nature of phonons can be obtained by considering wave-packets resulting by the superposition of plane-waves. This allows for having different phonon populations in regions of the solid having different temperatures.

In the harmonic case and in a perfect solid, there is nothing to perturbate the phonon flux due to a temperature gradient and the thermal conductivity will be infinite.

In a real crystal 3 factors will modify this: a) crystal imperfections; b) the finite size of the crystal and c) anharmonicity (phonon collisions).

We can consider phonons as a gas of particles and apply here again the kinetic theory of a gas to evaluate the phonon thermal conductivity, K_{ph} which will write:

$$K_{ph} = \frac{1}{3} \bar{v} \ell c_v^{ph} \quad (7.22)$$

With $\bar{v}$ the phonon mean velocity, ℓ the phonon mean free path (resulting from collisions) and c_v^{ph} the phonon specific heat.

Lets try to evaluate the evolution of K_{ph} with temperature, by inspecting the T dependence of the 3 terms in this expression.

If we consider for simplicity a crystal having a unitary cell, there will be only acoustic branches, from which we can find $\bar{v} = v_{\text{sound}} = \text{constant}$. This will be valid for low k, but at higher momentum $d\omega/dk \rightarrow 0$, so we can consider $\bar{v} \approx v_{\text{sound}}$ a good approximation.

We have already studied $c_v^{\text{ph}}(T)$ which is constant at high temperatures (beyond Debye temperature) and follows a T^3 dependence at low T.

Concerning ℓ , the phonon mean free path, we can consider that it will be inversely proportional to the phonon population. We can then consider 3 different regimes:

A) High Temperature. $C_v = \text{constant}$ and $\bar{v} = \text{constant}$.

The phonon population at high T:

$$n(k) = \frac{1}{e^{\hbar\omega/k_B T} - 1} \approx \frac{k_B T}{\hbar\omega_k} \propto T \rightarrow \ell \propto \frac{1}{T} \quad (7.23)$$

Consequently we could expect that the phonon thermal temperature follow the same dependence as ℓ . Experiments show that $K_{\text{ph}} \propto 1/T^x$ with $1 < x < 2$. This difference comes from the fact that the theory is more complex as it needs to include phonon collision processes which can involve a larger number of phonons.

B) Low Temperature. $C_v \propto T^3$ and $\bar{v} = \text{constant}$.

The phonon population goes this time:

$$n(k) = \frac{1}{e^{\hbar\omega/k_B T} - 1} \approx e^{-\hbar\omega/k_B T} \quad (7.24)$$

and hence, the phonon mean free path increases exponentially and ℓ becomes comparable with the size of the crystal.

Then we find $K_{\text{ph}} \propto T^3$ with a value which will increase proportionally to the size of the crystal (low T size effect).

C) Which will be the behavior at intermediate temperatures, i.e., when $T \rightarrow \theta_{\text{Debye}}$. This is the domain in which the U-process will start to become important and then lead to an inflexion of the K_{th} evolution. The U-process is favored by those phonons having energies close to $k_B \theta_{\text{Debye}}$. The energy of those phonons is not precisely determined by their population will vary approximately as $n_U \propto e^{-\theta_{\text{Debye}}/T}$ (Boltzmann term) and consequently $\ell \propto e^{\theta_{\text{Debye}}/T}$. This exponential dependence will dominate the T^n dependence of c_v , and consequently $K_{\text{ph}} \propto e^{\theta_D/T}$. Experimentally it is found $K_{\text{ph}} \propto e^{\theta_D/bT}$ with $2 \lesssim b \lesssim 3$.

Figure 7.4 synthesizes the above discussion

In Fig. 7.5 illustrates this for the case of silicon. We note that the K_{min} is the value which would correspond to the ℓ value reduced to the interatomic distances. In general we can consider that ℓ will result from the superposition of its limitation from the different effects: size effects, pressence of defects, phonons (U-process). We can then write:

$$\frac{1}{\ell} = \frac{1}{\ell_{\text{size}}} + \frac{1}{\ell_{\text{defects}}} + \frac{1}{\ell_U} \quad (7.25)$$

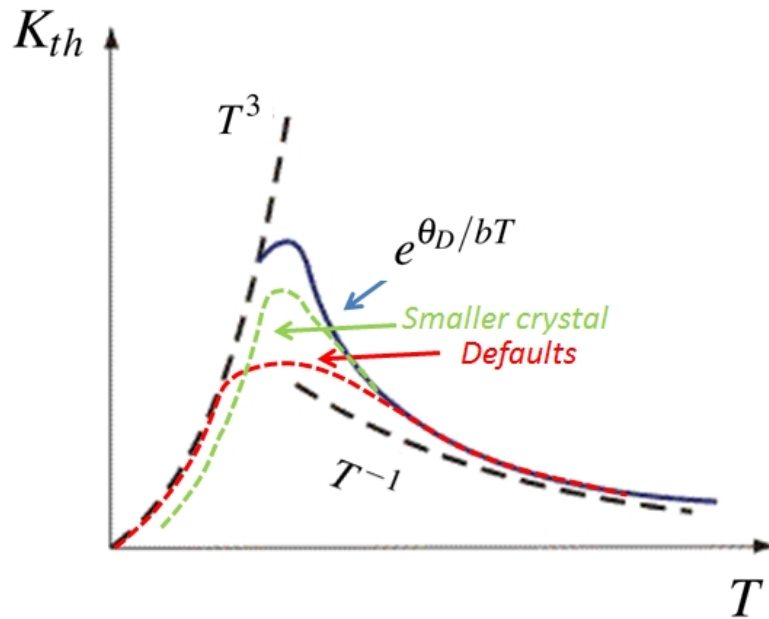


Figure 7.4: Thermal conductivity of a non-metal as function of temperature showing the 3 temperature regimes discussed in the text. The effect of defects and crystal size are also depicted

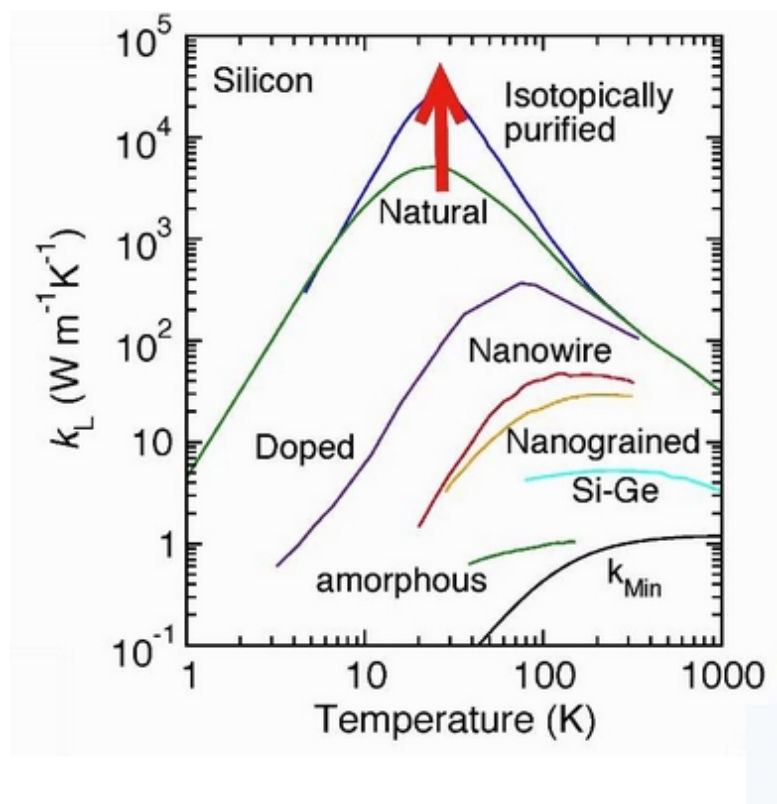
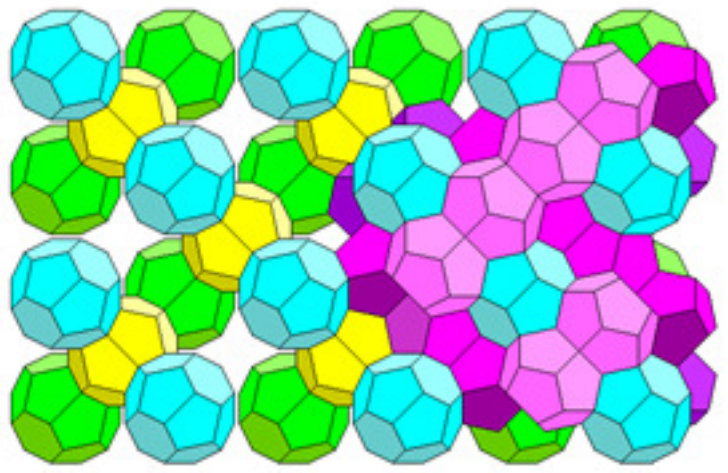
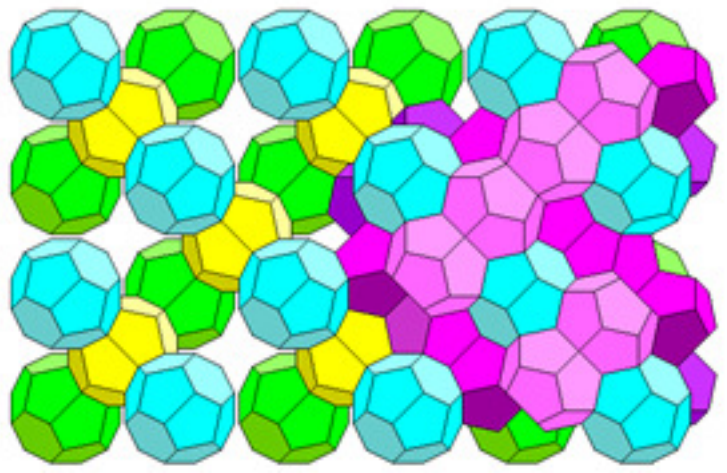


Figure 7.5: Thermal conductivity of silicon in different forms.



Bibliography



Bibliography

- [J.L.(2015)] H. J.L., *Physics - A short history* (Oxford University Press, Oxford, 2015).
- [Kohn(1999)] W. Kohn, *Rev. Mod. Phys.* **71**, S59 (1999).
- [Hoddeson, Baym, and Eckert(1987)] L. Hoddeson, G. Baym, and M. Eckert, *Rev. Mod. Phys.* **59**, 287 (1987).
- [Mandl(1988)] F. Mandl, *Statistical Physics*, 2nd ed. (John Wiley & Sons, Inc., New York, 1988).
- [Chandler(1987)] D. Chandler, *Introduction to Modern Statistical Mecahnics* (Oxford University Press, New York, 1987).
- [Ashcroft and Mermin(1976)] N. Ashcroft and N. Mermin, *Solid State Physics* (Saunders College, Philadelphia, 1976).
- [Kittel(1996)] C. Kittel, *Introduction to Solid State Physics*, 7th ed. (John Wiley & Sons, Inc., New York, 1996).
- [Hook and Hall(1991)] J. Hook and H. Hall, *Solid State Physics*, 2nd ed. (John Wiley & Sons, 1991).
- [Diep(2003)] H. T. Diep, *Physique de la Matière Condensée* (Dunod, Paris, 2003).
- [Harrison(1979)] W. A. Harrison, *Solid State Theory* (Dovers Publications, New York, 1979).
- [Grosso and Parravicini(2000)] G. Grosso and G. P. Parravicini, *Solid State Physics* (Elsevier Academic Press, London, 2000).
- [Snoke(2008)] D. W. Snoke, *Solid State Physics. Essential Concepts* (Addison-Wesley, 2008).
- [Goodstein(1985)] D. L. Goodstein, *States of Matter* (Dovers Publications, Toronto, 1985).
- [Blundell(2001)] S. Blundell, *Magnetism in Condensed Matter* (Oxford University Press, New York, 2001).
- [du Trémolet de Lacheisserie (sous la direction de)(2000)] E. du Trémolet de Lacheisserie (sous la direction de), *Magnétisme* (EDP Sciences, Grenoble, 2000).