PHYSICS 315

Physics of materials

Summary of lectures by

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Course web site: http://www.physics.ubc.ca/~birger/n315.toc/index.html

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Chapter 1

Course organization

The preparation and use of *materials* play important roles in all civilizations. In recognition of this fact we label early cultures by the material which dominated technology at the time (stone, bronze and iron age). Today thousands of new materials continue to revolutionize our everyday existence. In the early part of this century the availability of inexpensive steel made it possible to mass produce automobiles. During the last 50 years improvements in semiconductor technology led to the computer revolution. More recently, improved understanding of "soft matter", liquid crystals, polymers and biological materials is likely to bring profound changes in medicine and other aspects of our lives.

In this course we study the physical properties of materials that have more structure than simple liquids and gases. We start by considering crystalline solids, first from the point of view of structure and then from the point of view of the cohesive energy. Next, we study the elastic properties and move on to defects and their effect on the strength of materials. This is followed by a discussion of thermal and transport properties due to electrons and phonons. Next there is some discussion on dielectric response and screening. After a short discussion of the Hall effect I use the positve sign of the Hall coefficient in metals such as Aluminum to motive the need for a discussion of electronic band structure. Finally, since it often is said that we now live in the "silicon age" I conclude with a section on intrinsic and doped semiconductors.

I will assume that the students in this course will have taken the usual complement of second year mathematics courses (MATH 200, 215 and 221). A first course in thermodynamics such as PHYS 213, or the corresponding courses in chemistry or earth sciences will be assumed. Some knowledge of modern physics (e.g. PHYS 200), and mechanics (e.g. PHYS 216) will be helpful, but is not required.

There is no assigned text, but these notes will cover most of the course. In previous years the course included a section on "soft matter". This material is not included in these notes. References to appropriate sources are given as we move along.

I have "borrowed" freely from old exams prepared by my colleagues David Balzarini , Meyer Bloom , Roland Cobb , Dan Murray and Murray Neuman when selecting problems and examples.

The course description in the UBC Calendar is

315 (3) *Physics of Materials*-Crystal structure, elasticity and phonons, elementary electronic transport, defects, alloys, liquid crystals and polymers. Prerequisite: PHYS 203 or 213 or CHEM 201 or 205. Corequisite MATH 215.[3-0-0].

Chapter 2

Solid structure

The materials with the highest degree of order are the crystalline solids. Most solids exhibit such order at least to some degree. This chapter is concerned with the geometrical arrangement of atoms in a crystal. In particular we will discuss classification of crystals and how their crystalline properties are measured. We will also briefly mention amorphous or glassy materials towards the end of the chapter. For further reading on the material in this chapter I recommend the books by Ashcroft and Mermin [2], Christman [5], Kittel [6] and Omar [8].

2.1 Bravais lattices and lattices with a basis

The most characteristic feature of a *crystalline solid* is its *periodic structure*. A crystal can be thought to be made up of a space filling arrangement of basic building blocks called *unit cells* such that the local arrangement of the atoms in any cell is reproduced exactly in all the other cells. We define a lattice vector $\mathbf{R}$ as a vector which extends from a position in one cell to an equivalent position in another cell. A translation by a lattice vector leaves the local environment unchanged, and we say that a crystal exhibits translational symmetry, when the reference is shifted by a lattice vector.

The concept of a perfect crystal is an idealization which cannot be completely realized for several reasons

- The periodicity of a crystal will always be interrupted by its surface.
- In practice it is not possible to grow crystals without imperfections.
- At any non-zero temperature the atoms will vibrate about their equilibrium positions and this will destroy the translational symmetry.

As we shall see later, lattice imperfections are responsible for many of the physical properties of a solid, such as its strength, toughness, electronic properties and some of its optical properties. However, before we can talk about the defects we must define the ideal which they disturb.

Crystallography is concerned with the geometrical properties of a crystal. A fundamental concept is that of a *Bravais lattice.* Such a lattice is a set of points

$$\mathbf{R} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c} \tag{2.1}$$

where n_1, n_2, n_3 are integers (negative, positive or zero). All the sites of a Bravais lattice are equivalent and the local environment is identical at each lattice point. The three vectors **a**, **b**, **c** are called *primitive lattice vectors.* The primitive lattice vectors must be non co-planar, but they need not be orthogonal to each other. We define α to be the angle between **b** and **c**, β the angle between **c** and **a**, γ the angle between **a** and **b** (see figure 2.1.a). The three primitive lattice vectors span a volume (figure 2.1.b) whose magnitude is

$$v_c = |\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})| \tag{2.2}$$

We refer to this volume as a *primitive unit cell.* If a crystal structure is a Bravais lattice with one atom at each lattice point, each primitive unit cell will have a volume $v_c = V/N$ where V is the volume and N is the number of atoms of the crystal. Sometimes it convenient to work with a unit cell which is larger than the primitive unit cell. To qualify as a unit cell it must still be possible to use it as building block in a repeated pattern that fills the lattice. There are generally many possible ways of choosing the primitive unit cell for a given crystal structure, but the volume of the primitive unit cell will always be the same, and the volume of a non-primitive unit cell is always an integer multiple of the volume of the primitive unit cell

2.1.1 Common crystal structures

We now apply the definitions which we have just made to the most common crystal structures.

Simple cubic lattice

The primitive unit cell is (as the name indicates) a cube. We take the side of the unit cube to be a and choose the edges to be parallel to the three axes of a Cartesian coordinate system as shown in figure (2.2-a)

$$\mathbf{a} = a\hat{\mathbf{x}},\ \mathbf{b} = a\hat{\mathbf{y}},\ \mathbf{c} = a\hat{\mathbf{z}}$$

The volume of the primitive unit cell is a^3.

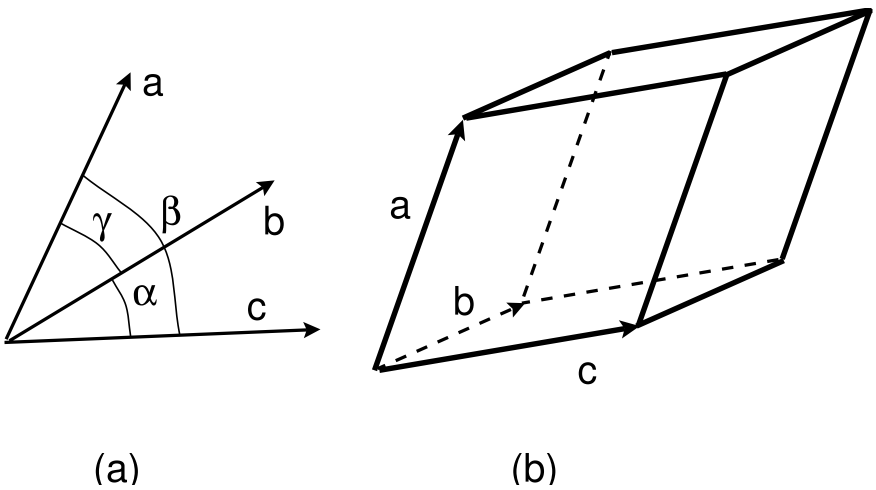

Figure 2.1: (a) Primitive lattice vectors. (b) Primitive unit cell

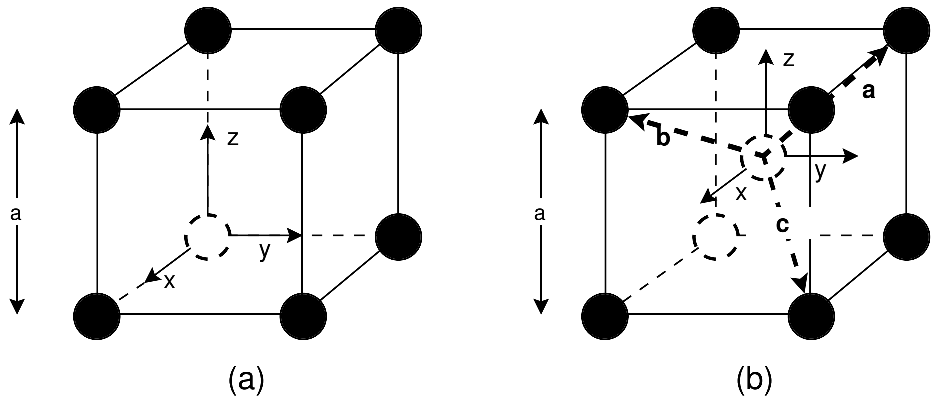

Figure 2.2: (a) Simple cubic lattice. (b) Body centered cubic lattice

Body centered cubic lattice (bcc)

In the bcc structure identical atoms are located at the corners and at the center of a cube. The unit cube is not a primitive unit cell - it is, however, a unit cell. We can construct the primitive cell from the three lattice vectors **a**, **b** and **c** of figure 2.2-b.

$$\mathbf{a} = \frac{a}{2}(-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}); \quad \mathbf{b} = \frac{a}{2}(\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}}); \quad \mathbf{c} = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}}) \tag{2.3}$$

The volume of the primitive cell is from (2.2) $\frac{1}{2}a^3$. This result could be expected from the following argument: assume that there are atoms at all the points of the bcc lattice. Each atom in the center of a unit cube belongs to that unit exclusively, while each of the eight corner atoms are shared by seven other cubes. The number of atoms per unit cube is thus 8/8 + 1 = 2. Since the volume of the unit cube is a^3, the volume of the primitive unit cell must be $v_c = a^3/2$.

Face centered cubic lattice (fcc)

The fcc lattice is another common Bravais lattice see figure (2.3). A possible choice of primitive lattice vectors is

$$\mathbf{a} = \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}}); \quad \mathbf{b} = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{z}}); \quad \mathbf{c} = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}}) \tag{2.4}$$

The volume of the primitive unit cell is

$$\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c}) = \frac{a^3}{4}$$

This result can also be found by noting that each of the six face centers of the unit cube is shared by one other cube, while each corner is shared by seven other corners. Thus, there are 6/2 + 8/8 = 4 atoms per unit cube. The volume of the primitive unit cell must thus be $a^3/4$.

Triangular lattice

So far we assumed a three-dimensional Bravais lattice. It is easy to generalize to the case of two dimensions. In this case the Bravais lattice is made up of the integer set $\{n_1, n_2\}$ of points

$$\mathbf{R} = n_1\mathbf{a} + n_2\mathbf{b}$$

where **a** and **b** are primitive lattice vectors. The *area* of the primitive unit cell is

$$A_c = |\mathbf{a} \times \mathbf{b}|$$

The lattice is shown in figure 2.4(a). We choose the primitive lattice vectors to be

$$\mathbf{a} = a\hat{\mathbf{x}}; \quad \mathbf{b} = \frac{a}{2}\hat{\mathbf{x}} + a\frac{\sqrt{3}}{2}\hat{\mathbf{y}}$$

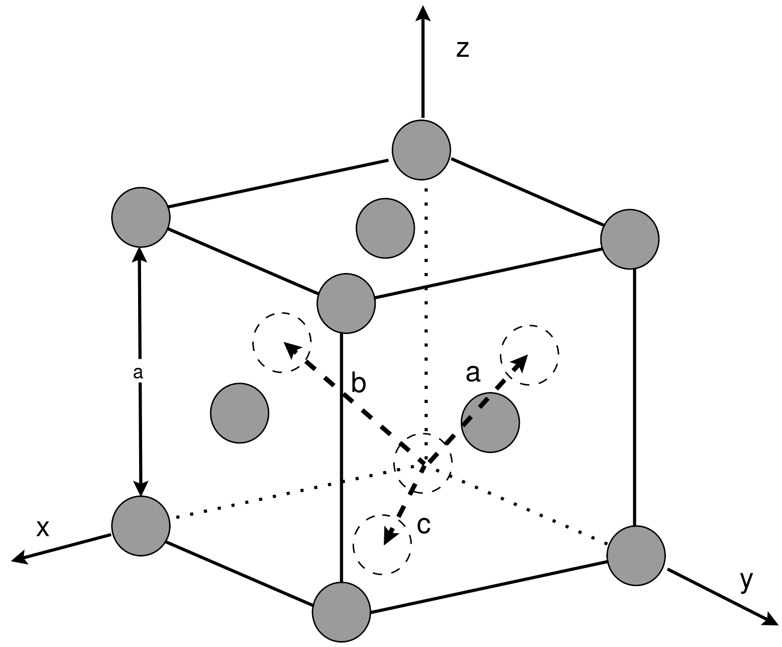

Figure 2.3: Face centered cubic lattice

giving $A_c = a^2\sqrt{3}\ /2$ for the area of the unit cell.

Not all crystalline lattices are Bravais lattices. If we remove 1/3 of the lattice sites of the triangular lattice we get the *honey-comb lattice* of figure 2.4(b) We notice from figure 2.4(b) that the honey-comb lattice is made up of two distinct types of sites which we have respectively labeled (i) and (ii) (or by filled and empty circles). The situation is unlike a Bravais lattice, where all sites are equivalent. However, if we consider the sites of type (i) separately, we note they form a triangular lattice which is rotated by 30^o with respect to the original triangular lattice. The primitive lattice vectors of this triangular lattice can be taken to be

$$\mathbf{a} = a(\frac{3}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}}{2}\hat{\mathbf{y}});\ \ \mathbf{b} = a\sqrt{3}\mathbf{y}$$

A translation by the vector $\mathbf{d}= a\hat{\mathbf{x}}$ takes one from a site of type (i) to a site of type(ii). We call the vector $\mathbf{d}$ a *basis vector*. The honey-comb lattice is an example of a *lattice with a basis*: all the lattice sites are *either* on a Bravais lattice site

$$\mathbf{R} = n_1\mathbf{a} + n_2\mathbf{b}$$

or on a Bravais lattice site displaced by a basis vector

$$\mathbf{R} = n_1\mathbf{a} + n_2\mathbf{b} + \mathbf{d}$$

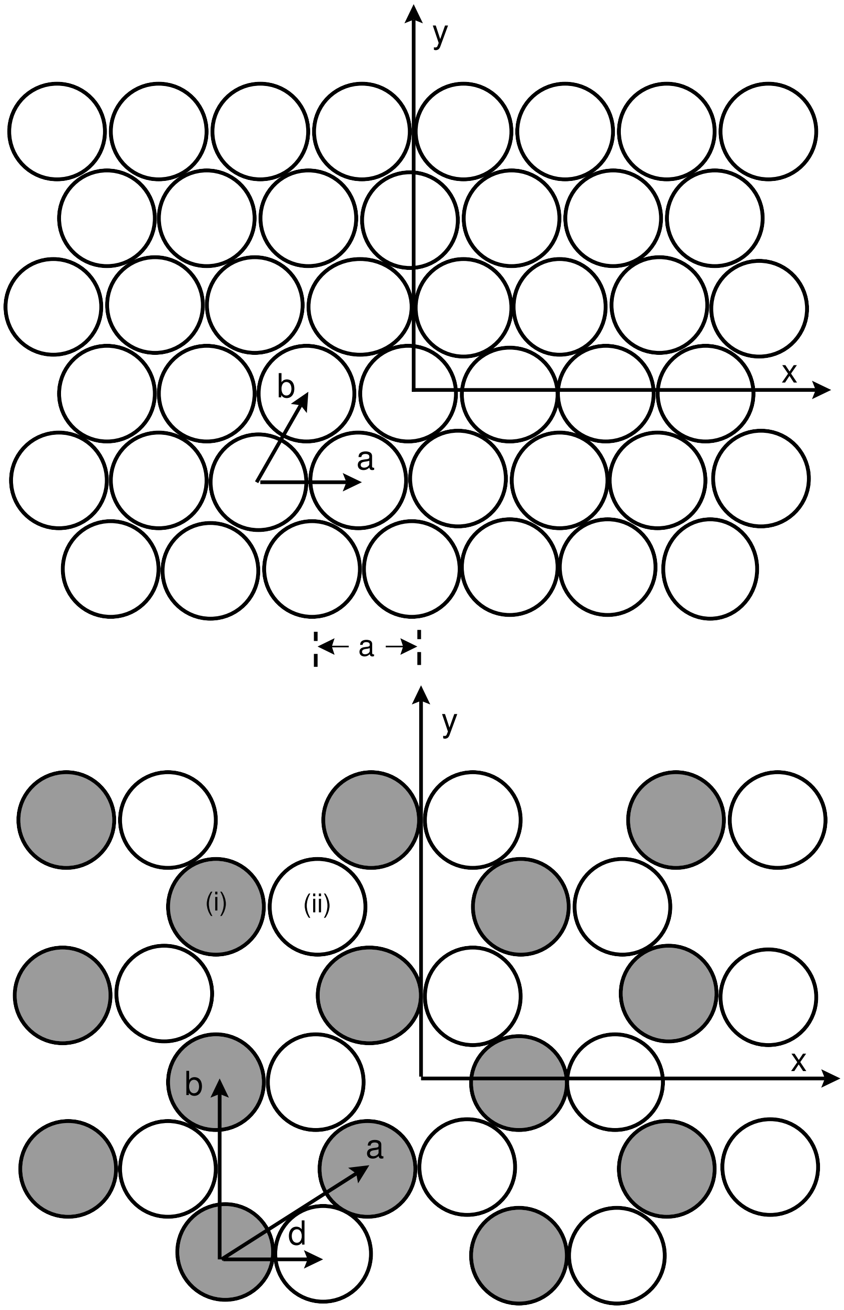

Figure 2.4: (a) Triangular lattice. (b) Honey-comb lattice

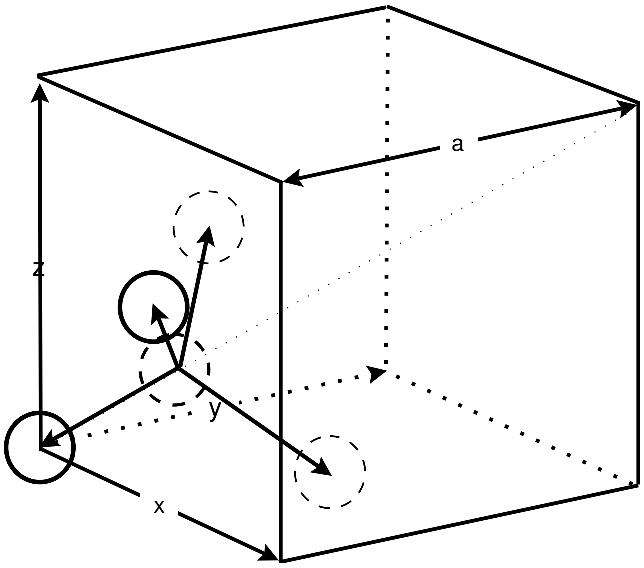

Figure 2.5: Tetrahedral bond in diamond lattice

The concept of a lattice with a basis can be generalized in a straight forward manner to three dimensions and the case where there are more than two non equivalent sites in the primitive unit cell. A lattice with a n-point basis $d_1 \cdots d_n$ has its lattice points at one of the n types of sites

$$\mathbf{R} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c} + \mathbf{d}_i, \quad i = 1, 2...n$$

Diamond structure

The lattice points of the diamond structure are localized either on a fcc lattice or on a fcc lattice point displaced by a basis vector

$$\mathbf{d} = \frac{a}{4}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$$

A characteristic feature of the diamond structure is the tetrahedral bond (figure 2.5). The orientation of the four tetrahedral directions are different for the fcc lattice points and on the points displaced by the basis vector. The two types of sites are therefore not equivalent and the diamond lattice is not a Bravais lattice.

In a number of compounds the two distinct sites of the diamond lattice are occupied by atoms of different species. The structure is then called the *zinc blende (ZnS) structure* . A number of semiconductors such as GaAs and InSb crystallize in this structure, while the elemental semiconductors silicon and germanium crystallize in the diamond structure.

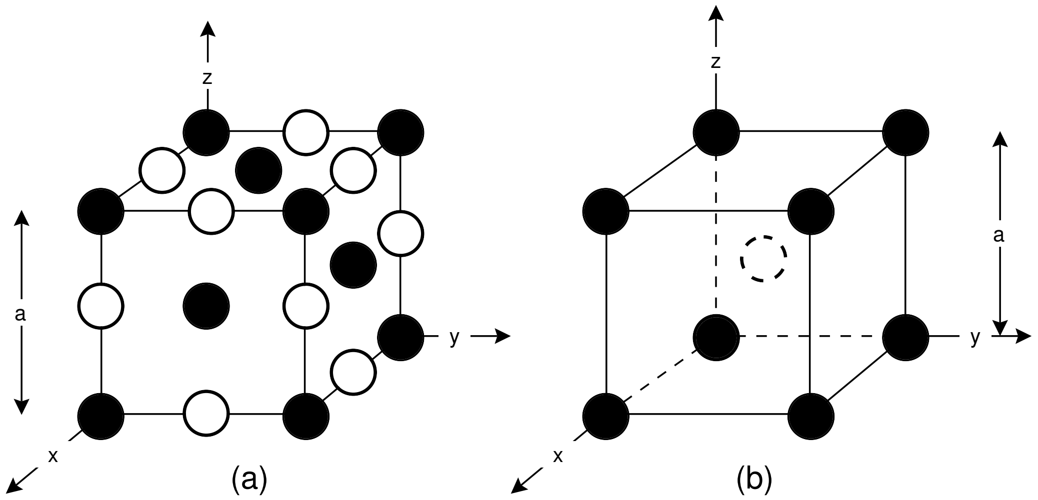

Figure 2.6: (a)NaCl lattice. (b) CsCl structure

Compound structures

All compounds (materials made up of more than one element) will necessarily crystallize in a lattice with basis. An important crystal structure for compounds is the *sodium chloride (NaCl) structure*(figure 2.6(a)) which is fcc with the basis $\mathbf{d} = \frac{a}{2}\hat{\mathbf{x}}$.

A third fairly common compound structure is that of *cesium chloride* in figure 2.6(b) . This structure is simple cubic with a basis vector $\mathbf{d} = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$. It differs from the bcc lattice only in that the body center and corner sites are occupied by atoms of different species in the CsCl structure.

2.1.2 Packing fraction and coordination number

There are a number of factors that dictate which crystal structure will be realized for a given compound. As we indicated earlier, the tetrahedral covalent bond favors the diamond (or zinc blende) structure. In the case where the forces that hold the crystal together are not directional, as in the case of the covalent bond, packing considerations are often important. A convenient measure of the packing efficiency of a given structure is the *packing fraction* f . We draw a sphere of radius r around each atom (or ion). We first assume that we are dealing with a substance in which the atoms are all of the same kind and which crystallizes in a Bravais lattice. We choose the radius r so that the atoms touch, but do not penetrate each other. The packing fraction is then defined as

$$f = \frac{4\pi r^3}{3v_c}$$

where $v_c is$ the volume of the primitive unit cell.

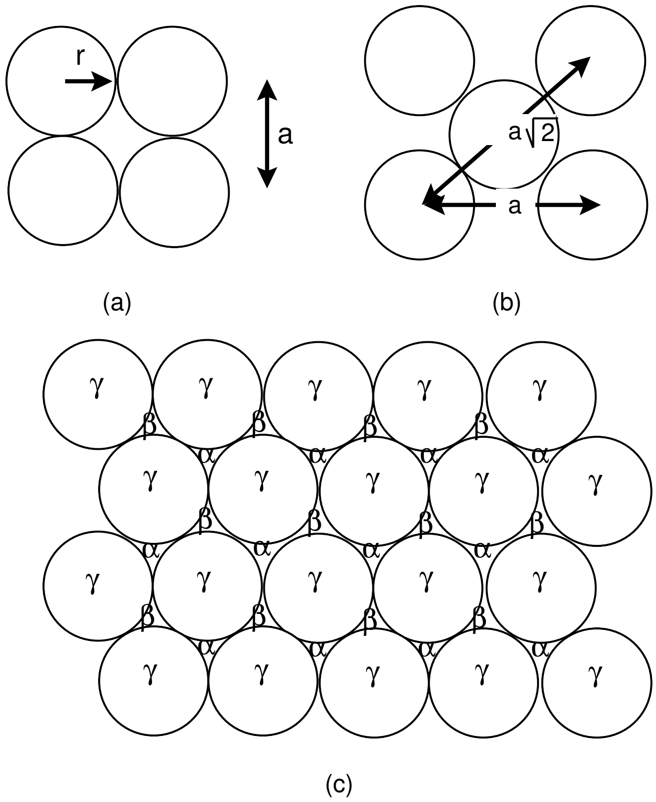

Figure 2.7: Packing fraction of (a) the simple cubic lattice. (b) The fcc lattice. (c) Close packing of spheres.

Another important characteristic of a crystal structure is the *coordination number* . For a Bravais lattice the coordination number is the number of *nearest neighbors*, or number of atoms that touch each other. Generally, a high coordination number and a high packing fraction go together. In the case of a compound the coordination number may be different for the different constituents.

Simple cubic lattice

From figure 2.7(a) we see that r= $\frac{a}{2}$. The volume of the unit cell is a^3. The packing fraction is thus

$$f_{sc} = \frac{4\pi}{3 \times 8} = \frac{\pi}{6} = 0.5236$$

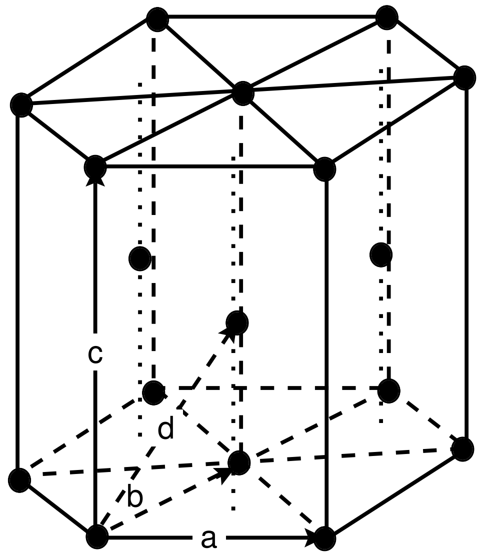

Figure 2.8: The hexagonal closed packed lattice.

Fcc lattice

Figure 2.7(b) shows the packing arrangement on one of the cube faces. We see from the figure that 4r= $a\sqrt{2}$. Since there are four spheres per unit cube the packing fraction is

$$f_{fcc} = \frac{4 \times 4\pi}{3}\left(\frac{\sqrt{2}}{4}\right)^3 = \frac{\pi\sqrt{2}}{6} = 0.7405$$

The coordination number of the fcc lattice is 12.

Hexagonal closed packed lattice

The most efficient packing of spheres in a single two-dimensional layer is the triangular lattice (figure 2.7(c)), with coordination number 6. We can construct a closed packed three dimensional lattice by adding successive triangular layers on top of the original layer. The best way to do this is to put the next layer either above the sites marked α or the sites marked β in figure 2.7(c). The reader may convince her or himself that if the stacking sequence of successive layers is $\cdots\gamma\alpha\beta\gamma\alpha\beta\gamma\alpha\beta\cdots$ we recover the fcc lattice. Another possible sequence which gives the same packing fraction is $\cdots\gamma\alpha\gamma\alpha\gamma\alpha\cdots$ The resulting crystal structure (figure 2.8) is called hexagonal closed packed (hcp). This lattice structure is *not* a Bravais lattice since the local environment of the atoms in γ and α layers are different. The set of $\gamma - points$ in the hcp structure does form a Bravais lattice, the *hexagonal lattice.* The primitive lattice vectors of this lattice can be chosen as

$$\mathbf{a} = a\hat{\mathbf{x}}; \;\; \mathbf{b} = a(\frac{1}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}}{2}\hat{\mathbf{y}}); \mathbf{c} = c\hat{\mathbf{z}}$$

The hcp lattice is then hexagonal with basis

$$\mathbf{d} = \frac{1}{2}\mathbf{c} + \frac{1}{3}(\mathbf{a}+\mathbf{b}) = a(\frac{1}{2}\hat{\mathbf{x}} + \frac{1}{2\sqrt{3}}\hat{\mathbf{y}}) + \frac{1}{2}c\hat{\mathbf{z}}$$

The coordination number of the hcp is 12, just as for the fcc lattice.

The concept of packing fraction can be extended to compounds. Consider an ideal crystal A^+B^- in which the A^+ and B^- separately form a Bravais lattice with volume v_c of the primitive unit cell. We associate an ionic radius r_+ and r_- to each species. Assuming that the closest approach of two positive, to negative and ions of opposite kind are $2r_+, 2r_-$ and $(r_+ + r_-)$, respectively, we define the packing fraction as

$$f = \frac{4\pi}{3v_c}({r_+}^3 + {r_-}^3)$$

2.1.3 The 14 Bravais lattices

There are 14 possible Bravais lattice for a three dimensional crystal (see figure 2.9). With the angles α, β and γ defined as in (figure 2.1) these lattices are tabulated in 2.1. The reader may well wonder why are there just 14 three dimensional Bravais lattices. Why e.g. do we not include a base centered cubic lattice? We do not consider this lattice to be a distinct lattice since it is a special case of the simple tetragonal lattice, as is the base centered tetragonal lattice. We refer the interested reader to [2] for a more detailed discussion of the classification of the lattices.

The structure and cell dimensions of some elements and compounds are listed in table 5.1 below.

A standard notation has evolved to describe crystallographic directions and distances. We write for a general lattice vector

$$\mathbf{R} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c} = [n_1 n_2 n_3]$$

(note the square bracket and the absence of commas). If some of the numbers are negative, it is conventional to put the minus sign above the number rather than in front, e.g.

$$\mathbf{R} = \mathbf{a} - \mathbf{b} + \mathbf{c} = [1\bar{1}1]$$

Often several crystallographic directions are equivalent e.g. the [100] and [010] directions in a cubic crystal. We indicate collectively all directions which are equivalent to $[n_1 n_2 n_3]$ as $\langle n_1 n_2 n_3 \rangle$ (angular brackets).

In the case of the cubic crystals it is conventional to let the indices n_1, n_2, n_3 refer to the sides of the unit cube rather than the primitive lattice vectors. For example, the three lattice vectors (2.3) of the bcc lattice are written as

$$\left[\frac{\bar{1}}{2}\frac{1}{2}\frac{1}{2}\right];\quad \left[\frac{1}{2}\frac{\bar{1}}{2}\frac{1}{2}\right];\quad \left[\frac{1}{2}\frac{1}{2}\frac{\bar{1}}{2}\right]$$

Table 2.1: 3-D Bravais lattices.

Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^o$
Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90^o$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^o, \gamma = 120^o$
Simple monoclinic Body centered monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90^o \neq \gamma$
Simple orthorombic Base centered orthorombic Body centered orthorombic Face centered orthorombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^o$
Simple tetragonal Body centered tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^o$
Simple cubic Body centered cubic Face centered cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^o$

2.1.4 Polycrystalline and noncrystalline solids

It is rare to find a large *single crystal* in which the periodic arrangement extends throughout the solid. When such crystals are cut one may see flat faces or *facets* such as in gemstones. The facet planes will normally correspond to high symmetry directions of the structure which are the ones for which the normals to the planes correspond to low index directions such as the $\langle 100 \rangle$, $\langle 110 \rangle\rangle$ or $\langle 111 \rangle$ direction. A single crystal will be *anisotropic*, i.e. mechanical, optical and transport properties will be different in different directions depending on the orientation of the crystalline axes. Single crystals are difficult to grow, the process must be done very slowly and under carefully controlled circumstances.

Most solids are polycrystalline, i.e. contain many small crystallites separated by grain boundaries. Polycrystalline materials will be *isotropic* (the same in all directions) on length scales which are large compared to the size of the individual grains.

Some solids lack any regular arrangement of the constituent atoms or ions on length scales more than a few lattice spacings. When this happens the solid is said to be amorphous or glassy. Generally, in order to obtain an amorphous solid from a melt, the cooling has to be rapid. In the

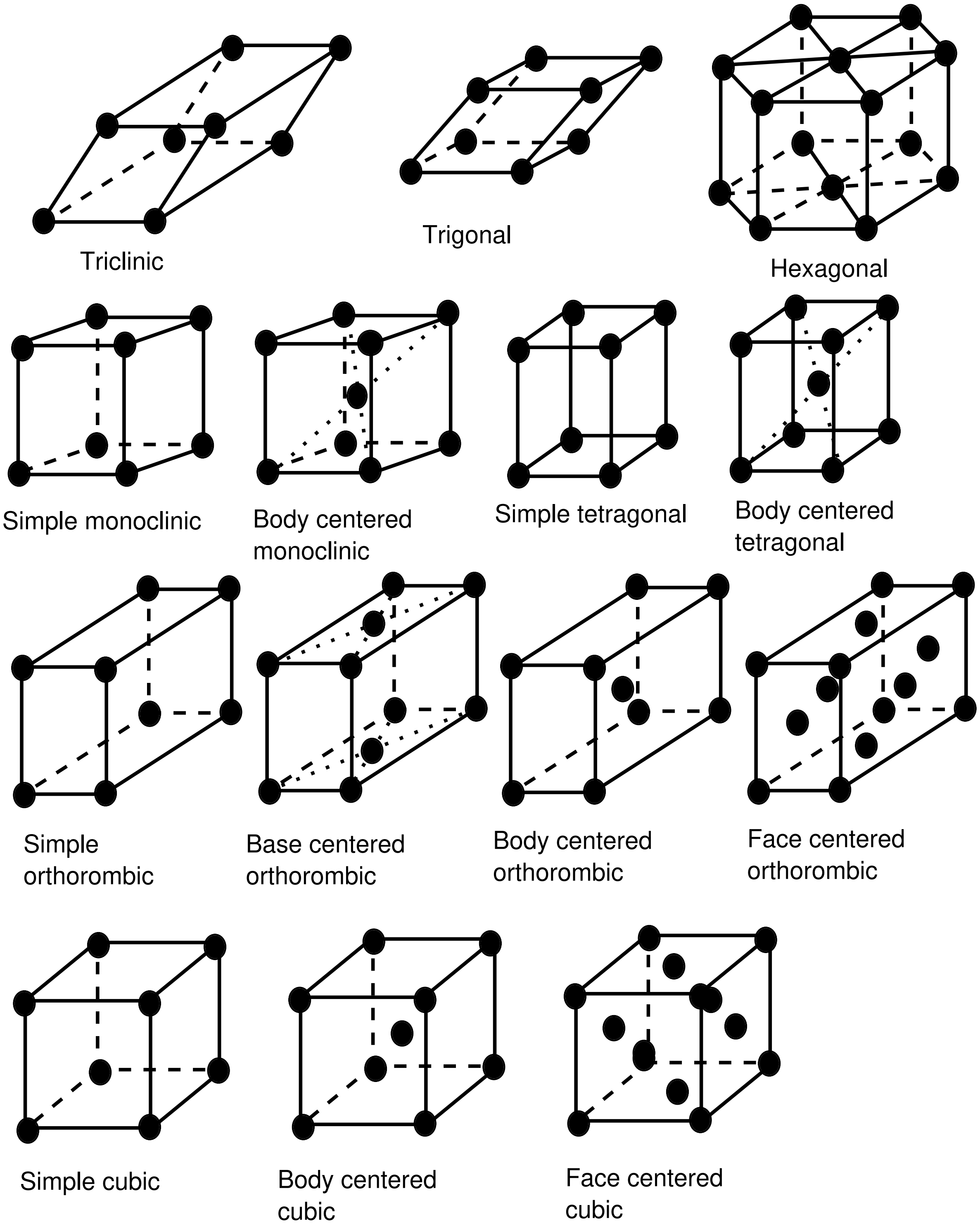

Figure 2.9: The 14 Bravais lattices.

case of metals or other materials with a simple crystal structure the cooling has to be extremely rapid. Such a rapid *quenching* can typically only be achieved for thin strips and films. Certain materials, which crystallize into very complicated structures, order only with difficulty and are easy to produce in a glassy form. The freezing transition between a liquid and a crystalline solid is a sharp *phase transition*. In the case of a liquid and a glass the transition is gradual and the distinction is not that sharp. Typically, one defines the transition from a liquid to a glass to take place when the *viscosity* (resistance to flow) exceeds a certain value. Of particular importance are the silicate glasses used to make window glass and bottles. Solids made up of organic polymers can be polycrystalline or amorphous.

2.1.5 Problems

Problem 2.1-1:

Compute the packing fraction f for the bcc lattice

Problem 2.1-2:

(a) Show that the packing fraction f for the diamond lattice is $\pi\sqrt{3}/16$.

(b) What is the packing fraction and coordination number of the honeycomb lattice?

Problem 2.1-3:

Consider the hexagonal closed packed lattice:

(a) Show that $c = a\sqrt{8/3} = 1.633a$. Frequently a crystal structure is called hcp even if c is not exactly equal to the ideal value.

(b) Show that the packing fraction for the ideal hcp lattice is $\pi\sqrt{2}/6 = 0.7405$.

Problem 2.1-4:

The ionic compound A^+B^- crystallizes in the NaCl structure (see figure 2.6). Plot the packing fraction as a function of the ratio $\xi = r_+/r_-$. Assume that $\xi < 1$.

Problem 2.1-5:

Repeat the calculation of problem 2.1-4 for the CsCl structure.

Problem 2.1-6:

Use the information in table 5.1 to calculate the densities (in kgm^{-3}) of the following solids: **(a)** Aluminum, **(b)** Iron, **(c)** Silicon and **(d)** Zinc. Atomic weights of some common elements are listed in table 5.2.

Problem 2.1-7:

SrTiO_3 crystallizes in the *perovskite* structure. The strontium atoms are at the corners of cubes with side a, the titanium atoms are at the body centers, while the oxygen atoms occupy the cube faces.

(a). What is the Bravais lattice type?

(b). Verify that the primitive unit cell contains one Sr, one Ti and three O atoms.

(c). Write down a set of primitive lattice vectors and basis vectors for the perovskite structure.

Problem 2.1-8:

The primitive lattice vectors of a certain bravais lattice can be written

$$\mathbf{R} = \frac{1}{2}(n_1 + 2n_2)a\hat{\mathbf{x}} + \frac{1}{2}n_1 b\hat{\mathbf{y}} + n_3 c\hat{\mathbf{z}}$$

What is the lattice type?

Problem 2.1-9:

In each of the following cases indicate whether the structure is a Bravais lattice. If it is, give three primitive lattice vectors, if it is not describe it as a Bravais lattice with as small as possible basis. In all cases the length of the side of the unit cube is a.

(a) Base centered cubic (simple cubic with additional points in the centers of the horizontal faces of the cubic cell).

(b) Side centered cubic (simple cubic with additional points in the centers of the vertical faces of the cubic cell).

(c) Edge centered cubic (simple cubic with additional points at the midpoints of the lines joining nearest neighbors).

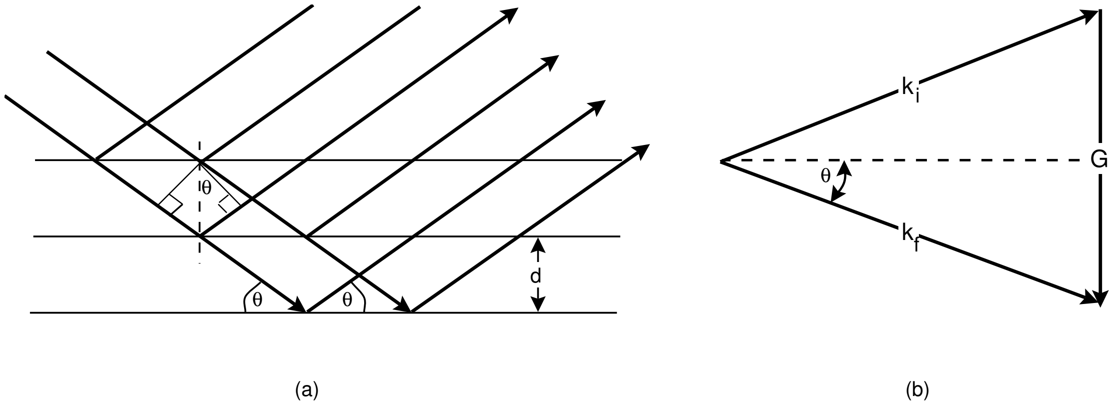

Figure 2.10: (a) Bragg's law.(b) Elastic scattering.

2.2 Structure determination

2.2.1 Reciprocal lattice

The elementary theory of crystal structure determination by *diffraction* is based on *Bragg's law* (figure 2.10) We imagine a crystal as made up of *lattice planes.* An incoming plane wave is reflected by these planes . We assume that the angle of incidence is the same as the angle of reflection (specular reflection). We also assume that the wavelength of the reflected light is the same as the wavelength of the reflected light (elastic scattering). If the wavelength of the incoming wave is λ, the angle of incidence is θ, and the perpendicular distance between the planes is d, we have constructive interference between waves reflected from a family of parallel planes if

$$2d \sin\theta = n\lambda \tag{2.5}$$

where n is an integer. Consider a Bravais lattice. We define a lattice plane as any plane which contains at least three points that do not lie on the same line (non co-linear points). A *family of planes* is a set of lattice planes which together include *all* points of the Bravais lattice. The equation for a plane is in vector notation

$$\mathbf{R} \cdot \hat{\mathbf{n}} = c$$

where $\mathbf{R}$ is a vector to a point in the plane, $\hat{\mathbf{n}}$ is a unit vector normal to the plane and c is the perpendicular distance from the origin to the plane. Let us now return to the Bragg condition (2.5) and let $\mathbf{k}_i$ be the wave vector of the incident beam, $\mathbf{k}_f$ the wave vector of the elastically scattered beam and

$$\mathbf{G} = \mathbf{k}_f - \mathbf{k}_i$$

the *scattering vector.* We have

$$\lambda = \frac{2\pi}{k}$$

and find that with θ the angle of incidence

$$G = 2k \sin\theta$$

and (2.5) becomes

$$\mathbf{R} \cdot \mathbf{G} = 2\pi n \tag{2.6}$$

As n runs through the set of integers equation (2.6) defines a family of planes. The vector $\mathbf{G}$ is called a *reciprocal lattice vector.* Let $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$ be a set of primitive lattice vectors of a Bravais lattice, we can construct a set of *primitive reciprocal lattice vectors* from

$$\begin{array}{lll} \mathbf{A}\cdot\mathbf{a} = 2\pi; & \mathbf{A}\cdot\mathbf{b} = 0; & \mathbf{A}\cdot\mathbf{c} = 0 \\ \mathbf{B}\cdot\mathbf{a} = 0; & \mathbf{B}\cdot\mathbf{b} = 2\pi; & \mathbf{B}\cdot\mathbf{c} = 0 \\ \mathbf{C}\cdot\mathbf{a} = 0; & \mathbf{C}\cdot\mathbf{b} = 0; & \mathbf{C}\cdot\mathbf{c} = 2\pi \end{array} \tag{2.7}$$

with the solution

$$\mathbf{A} = \frac{2\pi\mathbf{b}\times\mathbf{c}}{\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c})}; \;\; \mathbf{B} = \frac{2\pi\mathbf{c}\times\mathbf{a}}{\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c})}; \;\; \mathbf{C} = \frac{2\pi\mathbf{a}\times\mathbf{b}}{\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c})}; \tag{2.8}$$

We can now construct a Bravais lattice of reciprocal lattice vectors

$$\mathbf{G} = h\mathbf{A} + k\mathbf{B} + l\mathbf{C} \tag{2.9}$$

where h, k, l are integers. If $\mathbf{R}$ is a general vector (2.1) of the *direct lattice* we see that (2.7) gives

$$\mathbf{G}\cdot\mathbf{R} = 2\pi(n_1 h + n_2 k + n_3 l) = 2\pi n$$

Suppose $\mathbf{K}$ is the *shortest* reciprocal lattice vector in a given direction, then $\mathbf{K}\cdot\mathbf{R} = 2\pi n$ defines a family of planes, and the coefficients $h, k.l$ of this family are called *Miller indices.* The distance between the planes is $2\pi/K$ and it is customary to use the Miller indices to specify a reciprocal lattice vector as

$$\mathbf{G} = (hkl)$$

It can be seen from (2.8) that the volume of the reciprocal primitive unit cell is

$$V_c = |\mathbf{A}\cdot(\mathbf{B}\times\mathbf{C})| = \frac{(2\pi)^3}{|\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c})|} = \frac{(2\pi)^3}{v_c} \tag{2.10}$$

In the case of cubic crystals it is customary to let the Miller indices refer to unit cube *not* the primitive unit cell. Figure (2.11) show some crystallographic planes and their Miller indices for a cubic crystal. In a cubic crystal the (100),$(0\bar{1}0)$and (001) planes are equivalent. It is conventional to refer collectively to {hkl} as the (hkl) family of planes as well as all the symmetry related ones.

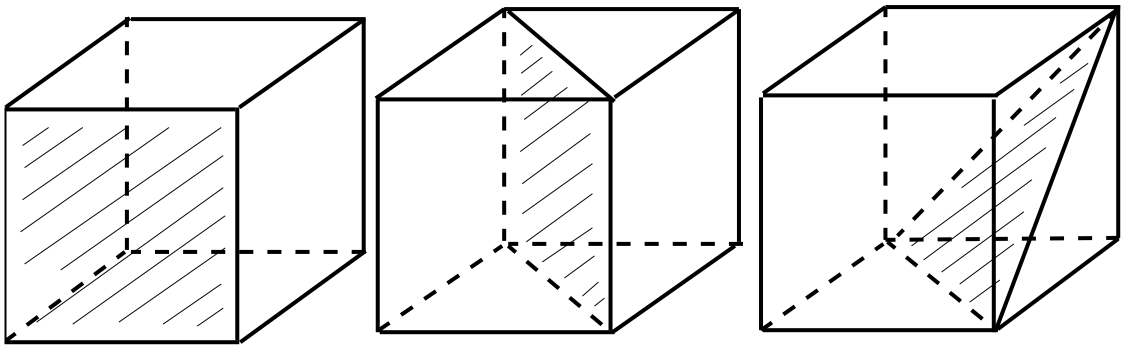

Figure 2.11: Some crystallographic planes of a cubic crystal.

2.2.2 Reciprocal lattice of a fcc lattice

Applying (2.8) to (2.4) we find

$$\mathbf{A} = \frac{2\pi}{a}(-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}); \;\; \mathbf{B} = \frac{2\pi}{a}(\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}}); \;\; \mathbf{C} = \frac{2\pi}{a}(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}}) \tag{2.11}$$

and we see from (2.4) that the reciprocal of the fcc is a body centered cubic lattice with side of unit cube $\frac{4\pi}{a}$, if a is the side of the unit cube of the original fcc lattice. Similarly, the reciprocal to the bcc lattice is fcc.

2.2.3 Ewald construction

We can illustrate some of the more common experimental methods of determining crystal structures by a simple geometric construction called the Ewald construction (figure 2.12) We choose one of the reciprocal lattice points in figure 2.12 as the origin. We assume that there is an incoming beam for which the magnitude and direction of the wave-vector $\mathbf{k}_i$ is held fixed. If the beam undergoes *elastic scattering* the magnitude of the scattered wave vector $\mathbf{k}_f$ must be the same as the magnitude of the incoming wave vector. The possible wave vectors of the diffracted beam must therefore lie on the surface of a sphere which is called the *Ewald sphere*. This surface of this sphere will in most cases only contain one reciprocal lattice vector - the one at the base of $\mathbf{k}_i$. Whenever another reciprocal lattice vector touches the sphere the condition for Bragg reflection is satisfied. There are two main methods to obtain *x-ray diffraction* from a single crystal. In the *Laue method* one uses a beam which contains a continuous spectrum of wave vectors $k_{min} < k_i < k_{max}$ but the orientation of the crystal studied and the direction of the beam is held fixed. From figure 2.13 we see that the reciprocal lattice points in the crescent shaped volume between the two spheres will cause scattering and can be picked up on a film surrounding the crystal under study or by a detector. The Laue

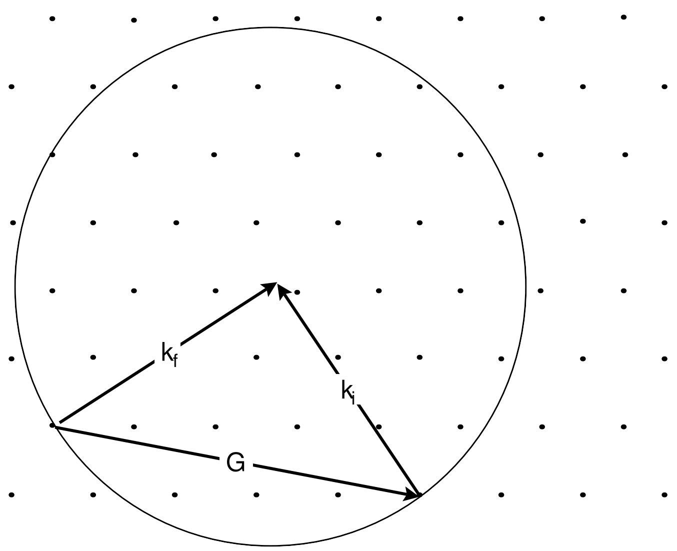

Figure 2.12: Ewald construction.

method is frequently used to orient a single crystal with respect to a fixed axis in an experimental set up. Another important method, *the rotating crystal method*, uses a monochromatic beam. The arrangement has the crystal mounted on a spindle located at the axis of a cylinder (see figure 2.14), with an opening for the incoming beam and an x-ray film mounted on the inner surface. For some orientations the Ewald condition will be satisfied and the diffracted beam will produce a black spot on the film.

Diffraction from a powder sample works in a similar fashion as the rotating crystal method. The randomly oriented crystallites in the powder diffracts like a single grain which has been rotated very many different ways.

X-rays are not the only available probes for diffraction experiments. Electron and neutron beams are commonly used. The wavelength of a particle beam is given by the de Broglie relation $\lambda = h/p$, where h is Planck's constant and p the momentum. For diffraction to be a useful tool in structure analysis, the wavelength should be of the same order of magnitude as typical lattice spacings i.e. ∼Å. Using the formula for the energy $E = p^2/2m$, where m is the mass of a particle, one can show that the wavelength of a neutron in Å can be written

$$\lambda = \frac{0.28}{\sqrt{E}}$$

if the energy E is given in electron volts (eV). For the wavelength to be 1 Å the energy would have to be 0.08 eV. Since the thermal energy $k_B T$ at room temperature is 0.025 eV, the neutrons used in diffraction experiments are referred to as *thermal neutrons*.

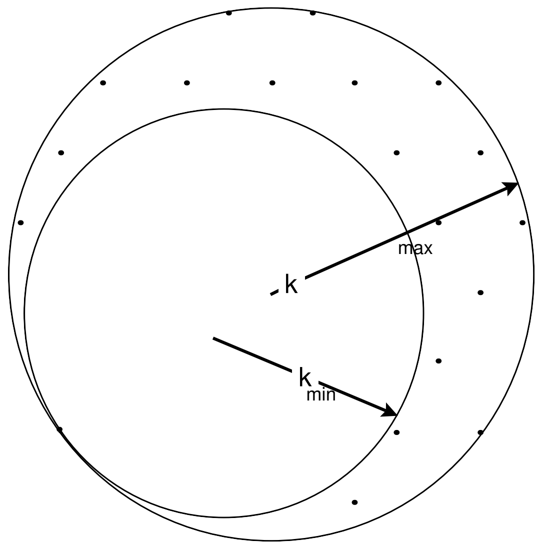

Figure 2.13: Ewald construction for the Laue method.

In the case of electrons the wavelength in Å can be written

$$\lambda = \frac{12.25}{\sqrt{E}}$$

where again the energy is given in eV. At energies where λ is of the order a few Ångström the penetration depth of electrons is typically only a few lattice spacings. Low energy electron diffraction (LEED) is for this reason mostly used for studies of the surface properties of materials.

2.2.4 The Wigner-Seitz cell and the Brillouin zone

It is often practical to divide a crystal into unit cells in a different way than what we did in figure 2.1. Consider the cell defined by the following construction (for the two dimensional version of this see figure 2.15). First draw lattice vectors connecting a lattice point at the origin with neighboring lattice points. Then draw planes bisecting these vectors. The smallest volume which is enclosed by such planes and includes the point at the origin is a *Wigner Seitz cell.* This cell is frequently used as a primitive unit cell. In this way the crystal is divided into volumes which have the property that all points inside each cell are closer to the lattice point at its origin than to any other lattice point.

The Wigner Seitz construction can also be carried out for the *reciprocal lattice*. The resulting unit cell is then called a *Brillouin zone* The Wigner Seitz cell can be generalized to non crystalline structures. For a disordered set of points the resulting cell will be bounded by planes forming the

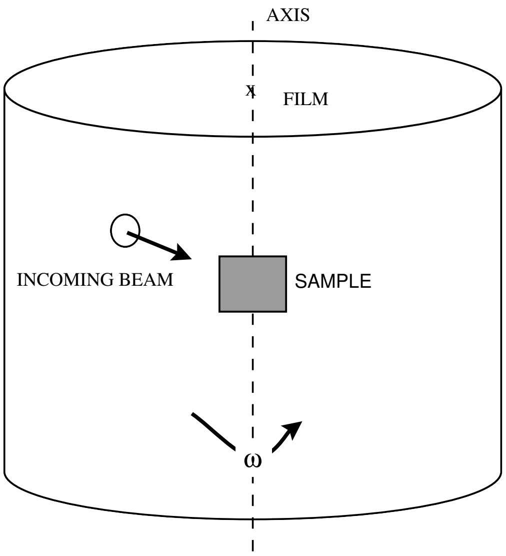

Figure 2.14: Rotating crystal method.

Voronoy polyhedra. The shape of each Voronoy polyhedron will generally depend on which point it surrounds. The plane normals connecting the neighboring points form a network which is referred to as the *Delaunay tessellation.* The Delaunay tessellation has many uses outside solid state physics. For example, in geography one is often required to produce topographical maps where contours correspond to point of equal altitude, mean rainfall, temperature, atmospheric pressure etc. These maps must be generated from a grid of observation stations. The Delaunay tessellation of this grid forms a useful basis for computer generated interpolation schemes.

2.2.5 Problems

Problem 2.2-1:

An x-ray source emits an x-ray line of wavelength $\lambda = 1.54$ Å. The lattice constant and crystal structures of iron and aluminum are found in table 5.1.

(a) Find the Bragg angle(s) for reflections from the (111) plane of Al.

(b) Find the Bragg angle(s) for reflections from the (110) planes of Fe

Problem 2.2-2:

The construction (2.9) of the reciprocal lattice assumes that the direct vectors **a, b, c** of (2.8) are *primitive* lattice vectors. If instead of using the primitive vectors one uses the lattice vectors of the unit cube of e.g. the fcc or bcc lattices, what happens is that (2.9) predicts some reciprocal

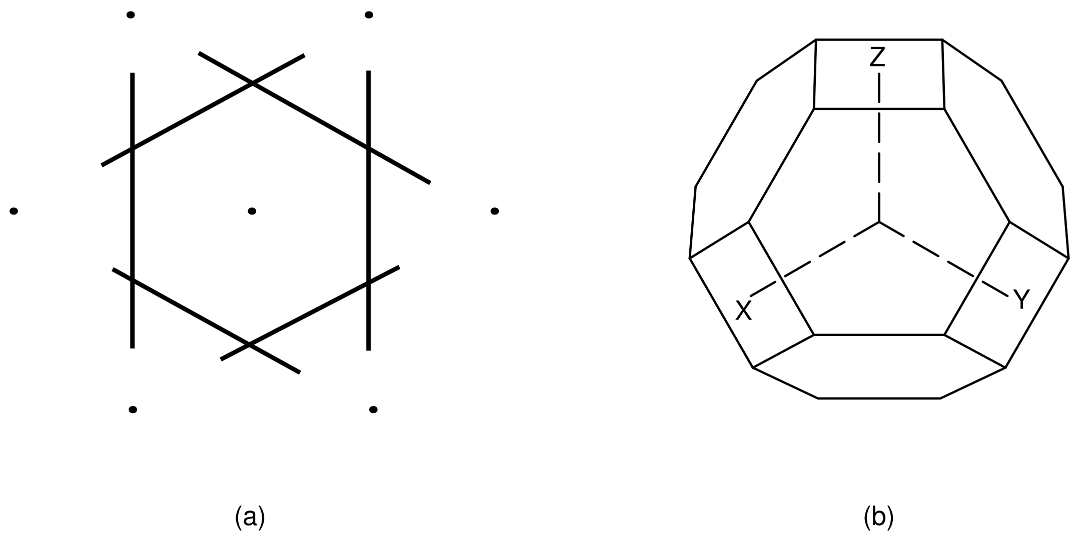

Figure 2.15: Wigner Seitz cell , (a) for the triangular lattice, (b) for the bcc lattice. In the latter case the square faces are perpendicular to the [100] , [010] and [001] directions, while the hexagonal faces are perpendicular to the [111] and symmetry equivalent directions.

lattice points that should not be there. Consider a simple cubic (sc) lattice for which the side of the primitive unit cube is a. Construct the reciprocal lattice of this structure.

(a) Which of the reciprocal lattice vectors of the sc lattice are missing in the reciprocal lattice constructed from the fcc lattice with the same unit cube side a.

(b) Which of the reciprocal lattice vectors of the sc lattice are missing in the reciprocal lattice constructed from the bcc lattice with a unit cube of side a.

Problem 2.2-3:

It is observed that crystals generally cleave most easily along the crystal planes which are furthest apart. Clearly, these are also the planes which have the highest density of atoms per unit area. From (2.6) we see that the perpendicular distance between nearby lattice planes is $2\pi/G$ where $\mathbf{G}$ is the shortest reciprocal reciprocal lattice vector in the direction normal to the planes. The shortest reciprocal lattice vectors for the fcc lattice are normal to the (111) planes, while the (110) planes are normal to the shortest reciprocal lattice vectors for the bcc lattice. Assume that the side of the unit cube is a.

(a) What is the density of atoms (number per unit area) on a (111) plane of a fcc lattice?

(b) What is the density of atoms on a (110) plane of a bcc lattice?

Problem 2.2-4:

The primitive lattice vectors of a 2-dimensional triangular lattice are

$$\mathbf{a} = a\hat{\mathbf{x}}; \;\; \mathbf{b} = \frac{a}{2}\hat{\mathbf{x}} + \frac{a\sqrt{3}}{2}\hat{\mathbf{y}}$$

where a is the nearest neighbor distance.

(a) Find the reciprocal lattice

(b) Draw the Wigner Seitz cell and locate the coordinates of its corners.

(c) Draw the Brillouin zone and locate the coordinates of its corners.

Problem 2.2-5:

Find the coordinates of the corners of the Wigner Seitz cell for the bcc lattice (figure 2.15 (b)).

Problem 2.2-6:

An X-ray reflection from a certain crystal occurs at an angle of incidence of 45° when the crystal is maintained at $0°C$. When it is heated to $150°C$ the angle changes by 6.4 minutes of arc. What is the linear thermal expansion coefficient of the material?

Chapter 3

Static properties

3.1 Atomic structure

Depending on the type of material, we will consider matter as made up of either *atoms*, *molecules*, or *ions*. An tom is made up of a nucleus surrounded by electrons. The nucleus is in turn made up of protons and neutrons. The mass of an electron is $m_e = 0.109 \times 10^{-31} kg$, many times smaller than the mass of a proton, $m_p = 1.6726 \times 10^{-27} kg$, or neutrons $m_n = 1.6749 \times 10^{-27} kg$. The mass of an atom thus rests almost exclusively in the nucleus and is often given in terms of the atomic mass unit or a.m.u. ($1 a.m.u. = 1.6605 \times 10^{-27} kg$). A chemical element is specified by the number of protons in the nucleus. Atoms which differ only in the number of neutrons in their nuclei are called *isotopes*. Different isotopes of the same element have except for the mass difference essentially identical properties.

Molecules are tightly bound groups of atoms, covalently bonded by the sharing of electrons. Ions are atoms that have a net electric charge because they have either given up one or more electrons or accepted extra electrons.

The electrons in an atom are characterized by 4 quantum numbers. Electrons with *principal quantum number* $n = 1, 2, 3, 4...$ are referred to as $K, L, M, N..$ electrons, respectively. The electrons with the lowest principal quantum are closest to the nucleus and most tightly bound. We refer to these as *core electrons*. The electrons with the highest values of n are the *valence electrons* and they are less tightly bound to the nuclei than the core electrons. The chemical properties of a material depend almost exclusively on how the valence electrons are distributed among the atoms, molecules and ions. Energies associated with chemical change are typically of the order *electron-volts* per atom, which makes this a convenient unit of energy ($1eV = 1.6022 \times 10^{-19} J$

The second quantum number l specifies the *orbital angular momentum* of an electron. The possible values of l are $0, 1, \ldots n-1$. According to quantum mechanics the angular momentum is $\sqrt{l(l+1)}\hbar$, where $\hbar$ is Planck's constant h divided by 2π. Electrons with $l = 0, 1, 2, 3..$ are referred to as $s, p, d, f..$ electrons respectively. The number of electrons in the different n, l states specifies the *electronic configuration*, e.g. the ground state of the element argon with chemical symbol Ar is $1s^2 2s^2 2p^6 3s^2 3p^6$ indicates that there are 2 electrons in the $K-$shell with $n = 1$, these are both s-electrons, i.e. have $l = 0$. There are 8 electrons in the L shell 2 of then $s-$electrons and 6 $p-$electrons with $l = 1$. There are also 2 $s-$electrons and 6 $p-$electrons in the $M-$shell.

The third quantum number m is associated with the component of the orbital angular momentum along a suitably chosen axis. This quantum number can take on any of the $2l+1$ values $m = -l, -l+1, \ldots l-1, l$. In an isolated atom electrons with different m quantum number have the same energy. The energy levels will be split, however, in a magnetic field and may also be split inside a crystal where different orientations need not be equivalent.

Finally, electrons carry an intrinsic angular momentum, called *spin*. The component of the spin may take on one of two different values $\sigma = \pm\frac{1}{2}\hbar$ with respect to any axis. Electrons satisfy the *Pauli exclusion principle*, only one electron may occupy a given quantum state. The main importance of the spin degree of freedom for us will come when we need to count states - the effect is to double the number of available states.

3.2 Lattice sums, binding energy and bulk modulus

What holds the crystal together? In all materials the forces are of electrostatic origin, but the detailed mechanism varies widely. On the basis of the dominant mechanism for bonding we classify crystals as either

- molecular
- ionic
- covalent
- metallic
- hydrogen bonded

We will discuss these types of bonding in turn – unfortunately it is only in the two first cases that we are able to go beyond very qualitative arguments.

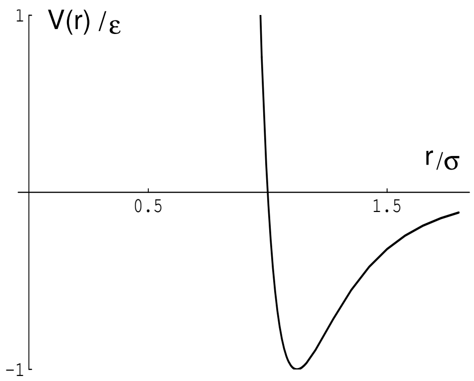

Figure 3.1: Lennard-Jones potential.

3.2.1 Molecular crystals

The constituents of a molecular crystal are atoms and molecules with an inert electronic configuration. This configuration remains intact when the material is cooled down from the gas phase through the liquid state into a crystal. To a reasonable approximation, the interaction between the atoms or molecules can be described by a *pair potential* $v(\mathbf{r}_i - \mathbf{r}_j)$. The simplest cases are the crystals formed from the inert gases neon (Ne), argon (Ar), krypton (Kr) and xenon (Xe). In this case the atoms have spherical symmetry and the potential is *central* $v = v(|\mathbf{r}_i - \mathbf{r}_j|)$ This potential can be thought of as made up of two parts. At short range when the atomic cores overlap there is a *strong repulsion*, whose origin lies in the *Pauli exclusion principle.* Since two electrons cannot occupy the same state, the core states will have to be strongly distorted when two atoms get too close together, and there is a large energy cost associated with such distortions. At larger distances there is no significant overlap between the electron states of neighboring atoms. The dominant force is then due to the *van der Waals attraction.* The corresponding potential falls off as the sixth power of the distance– and since force is minus the gradient of the potential, the corresponding force will be $\sim 1/R^7$. This r dependence can be understood from the following argument:

If an atom is exposed to an electric field $\mathcal{E}$ the force on the negatively charged electrons and the positively charged nucleus will be in opposite directions. This will induce a *dipole moment*

$$\mathbf{p_j} = \alpha\vec{\mathcal{E}} \tag{3.1}$$

where α is the *polarizability.* If the electric field is absent the average dipole moment will be zero, but there will still be a fluctuating dipole moment due to quantum effects (zero point motion). The electric field due to a dipole falls off as the inverse third power of the distance, and it will induce a dipole moment in neighboring atoms which is proportional to the field according to (3.1). The

Table 3.1: Lennard-Jones parameters for the inert gases

Element	σ [Å]	ϵ [eV]
Ne	2.74	0.0031
Ar	3.40	0.0104
Kr	3.65	0.0140
Xe	3.98	0.0200

interaction energy will then be of the form

$$\langle -\mathbf{p}_j \cdot \vec{\mathcal{E}_i} \rangle = \alpha < \mathcal{E}_i^2 >$$

where $\mathbf{p}_j$ is the induced dipole moment on atom j due to the fluctuating field $\vec{\mathcal{E}_i}$ from atom i. The angular brackets $\langle\rangle$ indicate *average value.* The average value of the fluctuating electric field is $\langle\mathcal{E}\rangle = 0$, while the mean square value will be non-zero. Since the fluctuating field falls off as the inverse third power of the distance, the mean square field will be proportional to the inverse sixth power of the distance to the fluctuating atom. The van der Waals interaction energy is thus $\sim 1/r^6$.

An approximate way of combining the repulsive and attractive interactions between the atoms in a molecular crystal is the *Lennard-Jones potential*

$$v(r) = \frac{A}{r^{12}} - \frac{B}{r^6} = 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6] \tag{3.2}$$

where A and B are constants which depend on which atom or molecule is involved. It is conventional to parameterize the potential in terms of an energy parameter ϵ and length parameter σ, in terms of which A= $4\epsilon\sigma^{12}$, B= $4\epsilon\sigma^6$. We plot the Lennard -Jones potential in figure 3.1.

The potential changes sign at $r = \sigma$. By differentiating (3.2) we find that the potential has minimum at $r = 2^{1/6}\sigma$. The value of the potential at the minimum is $-\epsilon$. In the case of the inert gases one can estimate the potential parameters using data obtained from measurements of corrections to the ideal gas law in the gas phase (virial coefficients). Some typical values are listed in table 3.1.

If we assume that all the atoms are at their equilibrium positions in the perfect lattice, we can estimate the *cohesive energy* U of the crystal as

$$U = \frac{N}{2}\sum_{\mathbf{R}} v(R) \tag{3.3}$$

where the sum in (3.3) is over the lattice. Substituting (3.2) we find

$$U = 2N\epsilon \sum_{\mathbf{R}} \left(\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6} \right) = 2N\epsilon \left(\left(\frac{\sigma}{r_{nn}}\right)^{12} \sum_{\mathbf{R}} \left(\frac{r_{nn}}{R}\right)^{12} - \left(\frac{\sigma}{r_{nn}}\right)^{6} \sum_{\mathbf{R}} \left(\frac{r_{nn}}{R}\right)^{6} \right) \tag{3.4}$$

where r_{nn} is the nearest neighbor distance. We define the geometrical constants

$$A_n = \sum_{\mathbf{R}} \left(\frac{r_{nn}}{R}\right)^{n} \tag{3.5}$$

The constants A_n can easily be evaluated numerically for different lattice types. The inert gases crystallize in the fcc structure at low temperatures. For the fcc lattice one finds $A_6 = 14.44862$, $A_{12} = 12.13188$ Using (3.5) in (3.4) we find for the cohesive energy

$$U = 2N\epsilon \left\{ A_{12} \left(\frac{\sigma}{r_{nn}}\right)^{12} - A_6 \left(\frac{\sigma}{r_{nn}}\right)^{6} \right\} \tag{3.6}$$

if we differentiate (3.6) with respect to r_{nn} we find that the cohesive energy has a minimum for

$$r_{nn} = \left(\frac{2A_{12}}{A_6}\right)^{1/6} \sigma = 1.09\sigma \tag{3.7}$$

for the fcc lattice. At this equilibrium separation we find $U = -8.6N\epsilon$ for the cohesive energy. Another quantity which can easily be evaluated in this model is the bulk modulus

$$B = -V\frac{\partial P}{\partial V} \tag{3.8}$$

where V is the volume per particle and P is the pressure which at low temperatures reduces to

$$P = -\frac{\partial U}{\partial V}$$

It is convenient to introduce $u = U/N$ and $v_c = V/N$. We find

$$B = v_c \frac{\partial^2 u}{\partial {v_c}^2} \tag{3.9}$$

For the fcc lattice with a the side of the unit cube we have $v_c = a^3/4$, $r_{nn} = a/\sqrt{2}$, hence $v_c = r_{nn}^3/\sqrt{2}$ and

$$\frac{\partial}{\partial v_c} = \frac{\sqrt{2}}{3{r_{nn}}^2}\frac{\partial}{\partial r}$$

we find after some algebra

$$B = \frac{4\epsilon (A_6)^{\frac{5}{2}}}{\sigma^3 (A_{12})^{\frac{3}{2}}} \tag{3.10}$$

In table 3.2 we compare the predictions of our simple theory with experiment

Table 3.2: Some properties of inert gas crystals

Element	r_{nn}[Å] theory	r_{nn}[Å] exper.	u[eV] theory	u[eV] exper.	B[10^9 Pa] theory	B[10^9 Pa] exper.
Ne	2.99	3.13	-0.027	-0.02	1.81	1.1
Ar	3.71	3.75	-0.089	-0.08	3.18	2.7
Kr	3.98	3.99	-0.120	-0.11	3.46	3.5
Xe	4.34	4.33	-0.172	-0.17	3.81	3.6

We see that the agreement for r_{nn} is quite good, the cohesive energy agrees well only for the heavier elements and the discrepancy is somewhat larger for the bulk modulus. The systematic dependence of the error on atomic mass suggest that the discrepancies have something to do with the quantum zero point motion which decreases with mass. One whole, table 3.2 indicates that the rare gas solids are well understood, at least qualitatively. There is one somewhat embarrassing fact. The rare gas atoms crystallize in the fcc rather than in the hcp lattice. The latter has $A_{12} = 12.13229$ and $A_6 = 14.45489$. If one calculates the cohesive energy for the hcp lattice one finds $u = -8.61106N\epsilon$ which is slightly lower than the value $u = -8.61077N\epsilon$ one finds by substituting (3.7) into (3.6). Since the difference is so minute, other factors such as the zero-point energy and three-body corrections to the potential come into play.

3.2.2 Ionic crystals

As we shall see, the ionic crystals are another group of solids for which it is possible to construct a simple theory of the cohesive energy that agrees reasonably well with experiment. To be specific we consider a structure such as $CsCl$ or $NaCl$, and assume that there are two singly charged ions per primitive unit cell. There are N primitive unit cells in the crystal so that there are altogether $2N$ ions. The largest contribution to the cohesive energy will come from the Coulomb interaction

$$\frac{e_1 e_2}{4\pi\epsilon_0}\frac{1}{r} \tag{3.11}$$

between two ions of charge e_1 and e_2 separated by a distance r.

Proceeding as in (3.4) we find for the Coulomb energy of the crystal

$$U_{coul} = -\frac{Ne^2}{4\pi\epsilon_0 d}\left(1 + \sum_{\mathbf{R}\neq 0}\left\{\frac{d}{|\mathbf{R}+\mathbf{d}|} - \frac{d}{R}\right\}\right) \tag{3.12}$$

Table 3.3: Madelung constant for some crystal structures

Structure	α
NaCl	1.7476
CsCl	1.7627
ZnS	1.6381

The sum over $\mathbf{R}$ is over the Bravais lattice. The term inside the ()

$$\alpha = 1 + \sum_{\mathbf{R}\neq 0} \left\{ \frac{d}{|\mathbf{R}+\mathbf{d}|} - \frac{d}{R} \right\} \tag{3.13}$$

is called the *Madelung constant.* It is a purely geometric factor which depends only on the crystal structure and not on the lattice constant. When evaluating (3.13) we run up against the problem that the series is *not convergent,* and depending on the order in which the terms are summed one can add up the series to different results. To see this let us attempt to evaluate the sum by splitting it up into two contributions

$$\sum_{\mathbf{R}\neq 0} \left\{ \frac{d}{|\mathbf{R}+\mathbf{d}|} - \frac{d}{R} \right\} = \sum_{\mathbf{R}\neq 0, R>R_0} \left\{ \frac{d}{|\mathbf{R}+\mathbf{d}|} - \frac{d}{R} \right\} + \sum_{R>R_0} \left\{ \frac{d}{|\mathbf{R}+\mathbf{d}|} - \frac{d}{R} \right\}$$

$$\approx \sum_{\mathbf{R}\neq 0, R<R_0} \left\{ \frac{d}{|\mathbf{R}+\mathbf{d}|} - \frac{d}{R} \right\} - \frac{Nd}{V} \int_{R>R_0} R^2\, dR \int_0^{2\pi} d\phi \int_{-\theta}^{\theta} d\theta \frac{|\mathbf{R}+\mathbf{d}| - R}{|\mathbf{R}+\mathbf{d}|R}$$

For fixed angles ϕ and θ the integrand will approach a value which is approximately independent of R for large R. The value of the integral will thus depend on the *shape* of the crystal volume V. The physical origin of this problem is that the long range of the Coulomb interaction small surface charges can cause a significant change in the electrostatic potential, which in turn can effect the sum in (3.13). At equilibrium the net charge and dipole moment of the crystal will be zero. The series will be summed correctly if the terms are summed up in blocks that have no net charge, dipole moment nor quadrupole moment. The sum over blocks will then be convergent, and the value of this sum is the correct Madelung constant . The value of α for some crystal structures is given in table 3.1

In addition to the Coulomb interaction we need to consider the core-core repulsion in estimating the lattice constant, bulk modulus and cohesive energy. One way to proceed is to write the cohesive energy on the form

$$U = U_{coul} + U_{core} = -\frac{N\alpha e^2}{4\pi\epsilon_o r_{nn}} - \frac{NC}{(r_{nn})^m} \tag{3.14}$$

where C is a constant. In the case of molecular crystals we chose $m = 12$ for convenience. Since there is no free parameter associated with the Coulomb term we can now afford to use m as an adjustable parameter. If we e.g. use experimental data to fit C and m to the observed nearest neighbor distance r_{nn} and bulk modulus B (3.9) one can test the theory by comparing theoretical values of the cohesive energy with experimental data. In the case of simple ionic crystals with the NaCl structure, the theoretical and experimental values for the cohesive energy differ by at most a few percent and it would appear that he simple theory we have outlined is qualitatively correct. The form (3.14) for the core- core interaction is somewhat arbitrary. Another common two parameter form for U_{core} is

$$U_{core} = A \exp(-r_{nn}/\lambda)$$

with A and λ adjustable parameters. These parameters can be fitted in a similar spirit to what we used for C and m of (3.14).

3.2.3 Other common forms of bonding

The *covalent crystal* can be thought of as giant molecules and the cohesive energy comes about largely from the chemical energy of contributing bonds. This type of bond comes about by the sharing of electrons between adjacent atoms, and it is quantum mechanical in origin. Reasonable semi-quantitative results for the binding energy can be obtained using chemical rules of thumb, the subject is beyond the scope of this course.

Similarly, there is no simple theory for cohesion in *metals* . The valence (or conduction) electrons occupy delocalized orbits percolating through the crystal and can be thought of as constituting an electron fluid which is confined within the crystal by the requirement of charge neutrality. There are important contributions to the energy from the attractive interaction between electrons and the positive ions and the repulsive electron-electron interaction. The Pauli exclusion principle raises the energy by forcing the electrons to occupy electron states with a nonzero kinetic energy. Quantum mechanical considerations play a dominant role and the electrons participate in a complicated quantum dance in which they avoid each other and take advantage of the attraction to the ions. This energy contribution is called the *exchange and correlation energy* .

The *hydrogen bond* index Hydrogen bond is even more subtle, but is responsible for the complicated structure of a number of important materials such as ice and many organic materials e.g. the spatial configuration of proteins owes much to the hydrogen bond.

3.2.4 Problems

Problem 3.2-1

Derive (3.10) from (3.7) and (3.9) and use the data in table (5.1) to verify the numbers in the 6'th column of table (3.2).

Problem 3.2-2

The lattice parameters of KCl are given in table 5.1

(a) Calculate the Coulomb energy between a K^+ and a Cl^- ion at the nearest neighbor distance in units of eV.

(b) Assume that the parameters σ and ϵ of the van der Waals attraction between the ions (the term proportional to $1/r^6$ in the Lennard -Jones potential) are the same as for Ar (table 3.1). Calculate the van der Waals energy between a K^+ and a Cl^- ion at the nearest neighbor distance of KCl. Compare with the result found under (a).

Problem 3.2-3

The cohesive energy of an ionic crystal can be approximated as

$$U = N\left\{-\frac{\alpha e^2}{4\pi\epsilon_o r} + \frac{C}{r^m}\right\}$$

where N is the number of unit cells, each assumed to contain one positive and one negative charge $\pm e$. In the formula α is the Madelung constant (see table 3.3), r is the nearest neighbor distance, and C and m are adjustable parameters. The cohesive energy of $NaCl$ has be measured to be $U/N = -1.27 \times 10^{-18} J$, (For details of the NaCl structure see table 5.1 and figure 2.6).

(a). Use the above data to determine the constants C and m.

(b). Show that the bulk modulus can be determined from

$$B = -V\frac{\partial P}{\partial V} = V\frac{\partial^2 U}{\partial V^2} = \frac{(m-1)}{18}\frac{\alpha e^2}{4\pi\epsilon_o r^4}$$

where V is the volume of a crystal containing N unit cells.

(c). Calculate the bulk modulus of NaCl.

3.3 Stress and strain

In this section we will consider solids which differs from perfect crystals in that the atoms are displaced from their equilibrium positions by a small amount[1]. We consider the stresses and strains associated with static external forces, and postpone to section 4.1 a discussion of elastic waves. One purpose in discussing the theory of elasticity is to lay the foundation for understanding the strength of materials.

Consider a solid which is deformed by external forces. The position of a given atom in the crystal will only differ from that of a perfect crystal by a small amount if the forces causing the deformation are weak. We write

$$\mathbf{r} = \mathbf{R} + \mathbf{u}$$

Here $\mathbf{r}$ is the actual position of an atom which was at $\mathbf{R}$ before the crystal was deformed. The vector $\mathbf{u}(\mathbf{R})$ represents the *displacement* of an atom which used to be at $\mathbf{R}$. If the displacement vector $\mathbf{u}$ is constant the only thing which has happened is that the crystal has moved a distance $\mathbf{u}$, and there is no elastic energy associated with this. In elastic theory one is interested in how the displacements *change* in space. We define the deformation tensor (or matrix)

$$\begin{bmatrix} \epsilon_{xx} & \epsilon_{xy} & \epsilon_{xz} \\ \epsilon_{yx} & \epsilon_{yy} & \epsilon_{yz} \\ \epsilon_{zx} & \epsilon_{zy} & \epsilon_{zz} \end{bmatrix} = \begin{bmatrix} \frac{\partial u_x}{\partial x} & \frac{\partial u_y}{\partial x} & \frac{\partial u_z}{\partial x} \\ \frac{\partial u_x}{\partial y} & \frac{\partial u_y}{\partial y} & \frac{\partial u_z}{\partial y} \\ \frac{\partial u_x}{\partial z} & \frac{\partial u_y}{\partial z} & \frac{\partial u_z}{\partial z} \end{bmatrix} \tag{3.15}$$

Equation (3.15) can be written more compactly as

$$\epsilon_{\alpha\beta} = \frac{\partial u_\beta}{\partial x_\alpha} \tag{3.16}$$

where $x_\alpha = x, y$ or z and $u_\beta = u_x, u_y$ or u_z. Let $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, $\hat{\mathbf{z}}$ be unit vectors in three Cartesian directions inside a solid. After the deformation the new axes are given by the vectors $\mathbf{x}'$, $\mathbf{y}'$ and $\mathbf{z}'$ (figure 3.2(a)). The three new axes need no longer be perpendicular to each other, but we do require the deformation to be small. After the deformation we have for the new x-axis

$$\mathbf{x}' = (1 + \frac{\partial u_x}{\partial x})\hat{\mathbf{x}} + \frac{\partial u_y}{\partial x}\hat{\mathbf{y}} + \frac{\partial u_z}{\partial x}\hat{\mathbf{z}}$$

and in general

$$\begin{bmatrix} \mathbf{x}' \\ \mathbf{y}' \\ \mathbf{z}' \end{bmatrix} = \begin{bmatrix} 1+\epsilon_{xx} & \epsilon_{xy} & \epsilon_{xz} \\ \epsilon_{yx} & 1+\epsilon_{yy} & \epsilon_{yz} \\ \epsilon_{zx} & \epsilon_{zy} & 1+\epsilon_{zz} \end{bmatrix} \begin{bmatrix} \hat{\mathbf{x}} \\ \hat{\mathbf{y}} \\ \hat{\mathbf{z}} \end{bmatrix} \tag{3.17}$$

It is conventional to define the *strain tensor* $e_{\alpha\beta}$ in terms of the symmetric part of the deformation

[1]An elementary, but more detailed discussion than is presented here can be found in Barber and Loudon [3]. For a more advanced treatment of elasticity theory see Landau and Lifschitz [7].

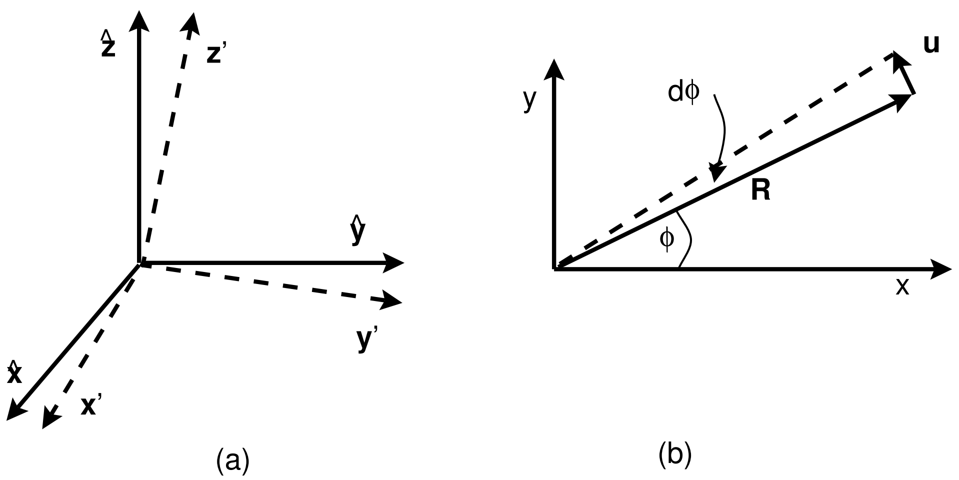

Figure 3.2: (a) Distortion of a Cartesian coordinate system. (b) Rotation about the z-axis

tensor

$$\begin{bmatrix} e_{xx} & e_{xy} & e_{xz} \\ e_{yx} & e_{yy} & e_{yz} \\ e_{zx} & e_{zy} & e_{zz} \end{bmatrix} = \begin{bmatrix} \epsilon_{xx} & \epsilon_{xy}+\epsilon_{yx} & \epsilon_{xz}+\epsilon_{zx} \\ \epsilon_{xy}+\epsilon_{yx} & \epsilon_{yy} & \epsilon_{yz}+\epsilon_{zy} \\ \epsilon_{xz}+\epsilon_{zx} & \epsilon_{yz}+\epsilon_{zy} & \epsilon_{zz} \end{bmatrix} \tag{3.18}$$

The reason for this is that the anti-symmetric part of the deformation tensor is associated with a *rotation* of the whole crystal and just as in the case of uniform translation there is no elastic energy associated with a pure rotation. To see why, consider as an example a rotation of a vector $\mathbf{R}$ in the $x-y$ plane by a small angle $d\phi$ as shown in figure 3.2(b). Before the rotation the polar coordinates of the vector were r,ϕ.

$$\mathbf{R} = \mathbf{x} + \mathbf{y} = r\cos\phi\hat{\mathbf{x}} + r\sin\phi\hat{\mathbf{y}}$$

$$\mathbf{u} = d\mathbf{R} = -r\sin\phi d\phi\hat{\mathbf{x}} + r\cos\phi d\phi\hat{\mathbf{y}} = -yd\phi\hat{\mathbf{x}} + xd\phi\hat{\mathbf{y}}$$

The associated deformation matrix is

$$\begin{bmatrix} \epsilon_{xx} & \epsilon_{xy} & \epsilon_{xz} \\ \epsilon_{yx} & \epsilon_{yy} & \epsilon_{yz} \\ \epsilon_{zx} & \epsilon_{zy} & \epsilon_{zz} \end{bmatrix} = \begin{bmatrix} 0 & d\phi & 0 \\ -d\phi & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

We see that the small rotation is associated with a deformation tensor whose only nonzero components are $\epsilon_{yx} = -d\phi$, $\epsilon_{xy} = d\phi$. The result of the small rotation is thus an anti-symmetric deformation tensor.

The notation in (3.18) is the one commonly used. It is somewhat awkward in that it might

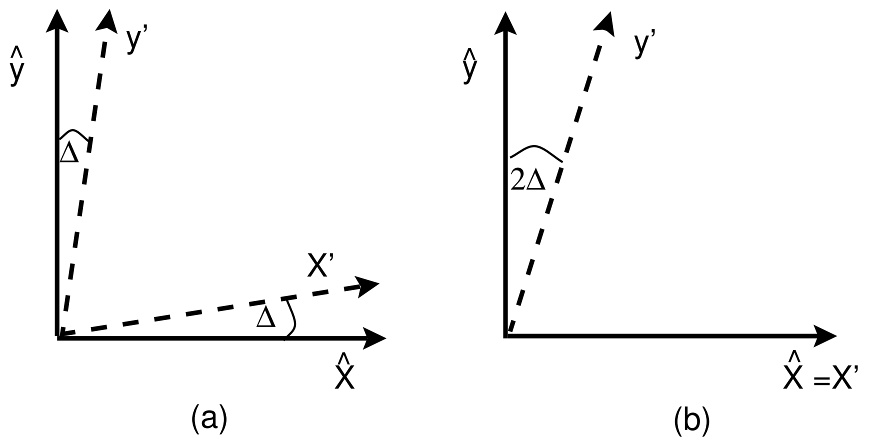

Figure 3.3: Two distortions with the same shear strain.

have been more logical to define the strain tensor as

$$\eta_{\alpha\beta} = \frac{1}{2}\left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha}\right)$$

as is done in [7].

Consider next the *shear* deformation of figure 3.3 in which the x- and y-axes are deformed in the opposite directions by a rotation by a small angle Δ. Using $\sin\Delta \simeq \Delta$, $\cos\Delta \simeq 1$ we have

$$\mathbf{x}' = \cos\Delta\ \hat{\mathbf{x}} + \sin\Delta\ \hat{\mathbf{y}} \simeq\ \hat{\mathbf{x}} + \Delta\ \hat{\mathbf{y}}$$

$$\mathbf{y}' = \cos\Delta\hat{\mathbf{y}} + \sin\Delta\hat{\mathbf{x}} \simeq \hat{\mathbf{y}} + \Delta\hat{\mathbf{x}}$$

We find $\epsilon_{xy} = \epsilon_{yx} = \Delta$, $e_{xy} = e_{yx} = 2\Delta$, i.e. the deformation is symmetric.

If instead the deformation had been on the form depicted in figure 3.3(b), in which the x-axis is held fixed but the y-axis is rotated clockwise by 2Δ we find

$$\mathbf{x}' = \hat{\mathbf{x}}$$

$$\mathbf{y}' = \cos(2\Delta)\hat{\mathbf{y}} + \sin(2\Delta)\hat{\mathbf{x}} \simeq \hat{\mathbf{y}} + 2\Delta\hat{\mathbf{x}}$$

We now have $\epsilon_{xy} = 0$, $\epsilon_{yx} = 2\Delta$, but the strain tensor is unchanged $e_{xy} = e_{yx} = 2\Delta$. The two configurations have the same strain, since, for small deformations, they only differ by a rotation by the angle Δ.

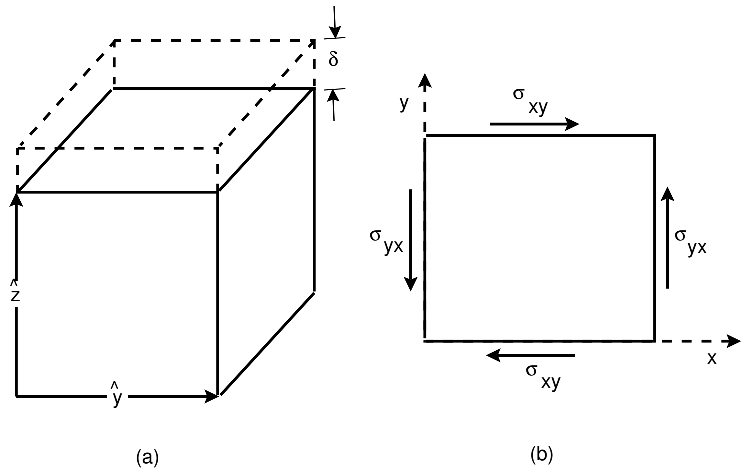

Figure 3.4: (a) Dilation strain $e_{zz} = \delta$. (b) For equilibrium the shear stress $\sigma_{xy} = \sigma_{yx}$

Figure 3.4(a) depicts a situation in which there is a change of volume as a consequence of the stretching of a crystal in the z-direction. Suppose a volume V is deformed into a volume V'. We define the *dilation* as

$$\delta = \frac{V' - V}{V} \tag{3.19}$$

The volume of the parallelepiped formed by three vectors **a**, **b** and **c** can be written (see figure 2.1(b))

$$\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c}) = \begin{vmatrix} a_x & a_y & a_z \\ b_x & b_y & b_z \\ c_x & c_y & c_z \end{vmatrix}$$

and we find

$$V' = 1 + \delta = \begin{vmatrix} 1 + \epsilon_{xx} & \epsilon_{xy} & \epsilon_{xz} \\ \epsilon_{yx} & 1 + \epsilon_{yy} & \epsilon_{yz} \\ \epsilon_{zx} & \epsilon_{zy} & 1 + \epsilon_{zz} \end{vmatrix}$$

or

$$\delta \simeq \epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz} + terms\ of\ order\ \epsilon^2$$

Only the diagonal components of the strain tensor gives rise to a volume change for small distortions. A positive volume change is a dilation while a negative change is a compression.

Since the strain tensor is symmetric only six of its nine component are independent and it is

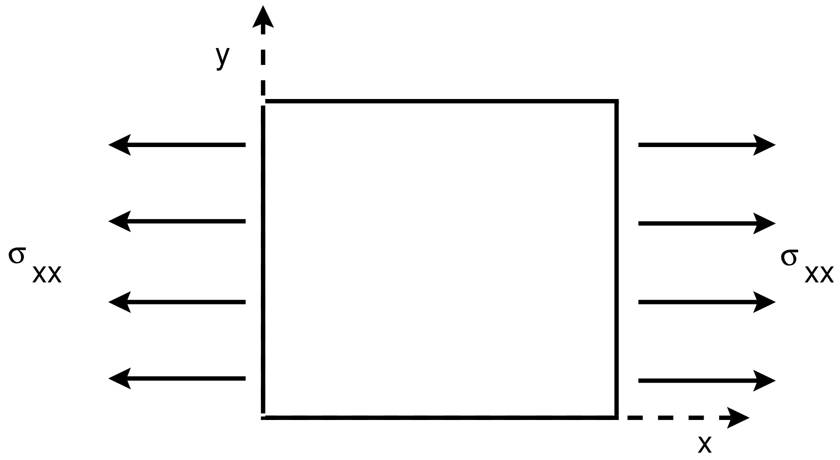

Figure 3.5: Tensile stress

conventional to number the components:

$$
\begin{aligned}
e_1 &= e_{xx} &&= \epsilon_{xx} \\
e_2 &= e_{yy} &&= \epsilon_{yy} \\
e_3 &= e_{zz} &&= \epsilon_{zz} \\
e_4 &= e_{yz} &&= \epsilon_{yz} + \epsilon_{zy} \\
e_5 &= e_{xz} &&= \epsilon_{xz} + \epsilon_{zx} \\
e_6 &= e_{xy} &&= \epsilon_{xy} + \epsilon_{xy}
\end{aligned}
\tag{3.20}
$$

In general one needs to apply a force in order to produce strain. Force per unit area is called *stress*. We let $\sigma_{\alpha\beta}$ represent the force in the α direction acting on a surface whose normal is in the β direction. If the force is parallel to the surface (perpendicular to the normal) we have *shear* stress (figure 3.4(b)), while if the force is parallel to the normal (perpendicular to the surface) we are dealing with *tension* or *compression*, (figure 3.5). The diagonal components of the stress tensor represents tensile forces when positive, compaction forces when negative.

For a material in equilibrium the forces acting on a volume element must be balanced and there can be no net torques. In the case of shear stresses this will give rise to a *double couple* situation as depicted in figure 3.4(b). The consequence is that for equilibrated stresses the stress tensor will be symmetric, i.e. $\sigma_{\alpha\beta} = \sigma_{\beta\alpha}$. Of the 9 components of the strain tensor only 6 are thus distinct. In analogy with (4-8) we write for these components

$$\begin{aligned}
\sigma_1 &= \sigma_{xx} \\
\sigma_2 &= \sigma_{yy} \\
\sigma_3 &= \sigma_{zz} \\
\sigma_4 &= \sigma_{yz} &= \sigma_{zy} \\
\sigma_5 &= \sigma_{xz} &= \sigma_{zx} \\
\sigma_6 &= \sigma_{xy} &= \sigma_{yx}
\end{aligned} \tag{3.21}$$

In the theory of elasticity one assumes that stresses and strains are proportional to each other according to *Hooke's law.* Complications arise from the fact that a given component of stress may affect more than one strain component and vice versa. For example, if a beam is elongated due to tensile stress the cross sectional area will also change. The most general form of Hooke's law is

$$\sigma_i = \sum_{j=1}^{6} C_{ij} e_j \tag{3.22}$$

The coefficients C_{ij} are called *elastic constants* .

3.3.1 Elastic constants for a cubic crystal

There are 36 possible elastic constants, but they will not be independent because of symmetry requirements. The number of independent elastic constants will depend on the crystal structure and we refer to [7] for details on this point. We will here limit our attention to crystals of cubic symmetry and argue that there are then 3 independent elastic constants.

To be specific the [100],[010] and [001] directions are equivalent in a cubic crystal. We must thus have $C_{11} = C_{22} = C_{33}$, $C_{12} = C_{21} = C_{13} = C_{31} = C_{23} = C_{32}$ and $C_{44} = C_{55} = C_{66}$. All the other off-diagonal elastic constants will be zero. To see that $C_{36} = 0$, assume that a crystal is strained so that $e_6 = e_{xy} \neq 0$. A nonzero C_{36} would mean that there is a resulting tensile stress in the z-direction. If we relabel the axes so that $\hat{\mathbf{x}} \to \hat{\mathbf{y}}$, $\hat{\mathbf{y}} \to -\hat{\mathbf{x}}$ we see that in the new coordinate system the e_4 strain will change sign (figure 3.6). If $C_{36} \neq 0$, the σ_{zz} stress would also change sign, say, from tension to compression. However, this is clearly impossible since the crystal hasn't changed. Similar arguments can be used to show that the remaining off-diagonal elastic constants are zero. To summarize: for a cubic crystal Hooke's law takes the form

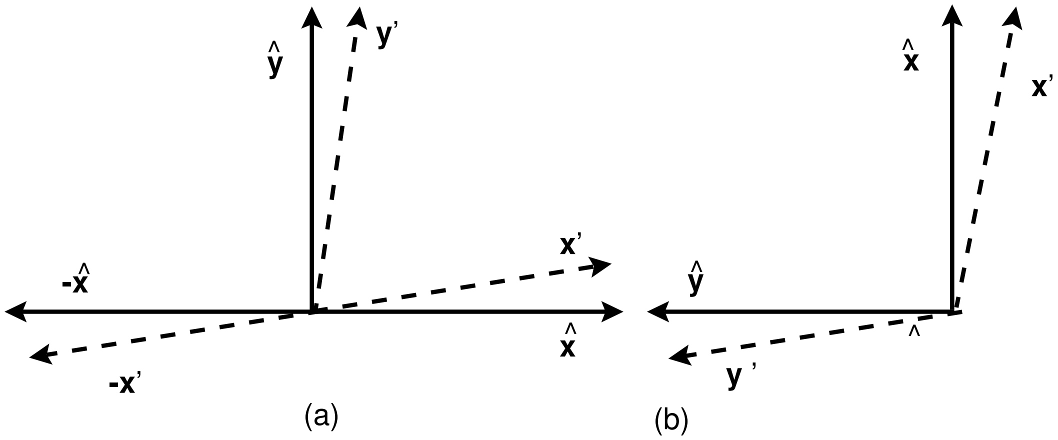

Figure 3.6: Relabeling the axes

$$\begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{bmatrix} \begin{bmatrix} e_1 \\ e_2 \\ e_3 \\ e_4 \\ e_5 \\ e_6 \end{bmatrix} \tag{3.23}$$

Cubic crystal under uniaxial compression strain

As an example consider a crystal with cubic symmetry which is put in a vise so that there is a uniform compression in the $[1\bar{1}0]$ direction (figure 3.7). The dilation of the crystal is from the figure given by -δ. Let us find the components of the strain and stress tensor. We find $\epsilon_{xx} = \epsilon_{yy} = -\frac{\delta}{2}$, $\epsilon_{xy} = \epsilon_{yx} = \frac{\delta}{2}$, so that the strain tensor becomes

$$\mathbf{e} = \begin{bmatrix} -\frac{\delta}{2} & \delta & 0 \\ \delta & -\frac{\delta}{2} & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

giving $e_1 = -\frac{\delta}{2}$, $e_2 = -\frac{\delta}{2}$, $e_3 = 0$, $e_4 = 0$, $e_5 = 0$, $e_6 = \delta$. Substitution into (3.23) gives

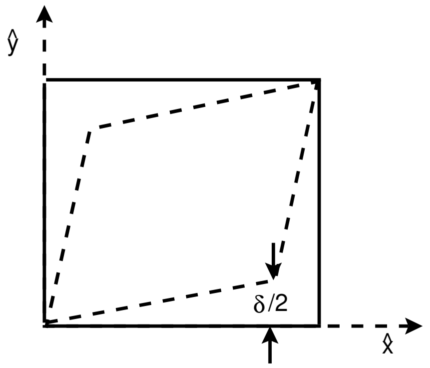

Figure 3.7: Compression perpendicular to the $(1\bar{1}0)$ plane

$$\begin{aligned}
\sigma_1 &= \sigma_{xx} &&= -\tfrac{\delta}{2}(C_{11} + C_{12}) \\
\sigma_2 &= \sigma_{yy} &&= -\tfrac{\delta}{2}(C_{12} + C_{11}) \\
\sigma_3 &= \sigma_{zz} &&= -\delta C_{12} \\
\sigma_4 &= \sigma_{yz} &&= 0 \\
\sigma_5 &= \sigma_{xz} &&= 0 \\
\sigma_6 &= \sigma_{xy} &&= \delta C_{44}
\end{aligned} \tag{3.24}$$

Note that while there is no strain component in the z-direction there will be a compressional stress.

3.3.2 Elastic constants of an isotropic material

If we have the stress components in one coordinate system we can find the stresses acting on any lattice plane by the rules of vector addition, taking into account the fact that *stress is force per unit area* . E.g. when the Cartesian components of the stress is given by (3.24), the stress normal to the $(1\bar{1}0)$ plane is,

$$\sigma_n = \frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}(\sigma_{xx} - \sigma_{xy} + \sigma_{yy} - \sigma_{yx}) = -\frac{\delta}{2}(C_{11} + C_{12} + 2C_{44}) \tag{3.25}$$

where the first factor of $\frac{1}{\sqrt{2}}$ comes from taking the *component* of a force in the $x-$direction (or $y-$direction). The second factor comes that the $(1\bar{1}0)$ plane of a unit cube has *area* $\sqrt{2}$. There will be no shear stress on this plane in our example.

Consider next a pure compression δ in the [100] direction, $e_1 = -\delta$, $e_2 = e_3 = e_4 = e_5 = e_6 = 0$. We find for a cubic material

$$\sigma_1 = -\delta C_{11},\ \sigma_2 = -\delta C_{12},\ \sigma_3 = -\delta C_{12},\ \sigma_4 = \sigma_5 = \sigma_6 = 0. \tag{3.26}$$

A polycrystalline or amorphous material will be *isotropic.* For an isotropic system we must require that if the dilation is the same, the normal stress is the same, irrespectively of the plane chosen for the application of the strain. By comparing (3.25) with (3.26) we then find for an isotropic system

$$C_{11} = C_{12} + 2C_{44} \tag{3.27}$$

It is conventional to describe an isotropic system in terms of the the two *Lamé constants*

$$\lambda = C_{12}, \ \mu = C_{44} \tag{3.28}$$

From (3.27) an isotropic system must have $C_{11} = \lambda + 2\mu$. We conclude that Hooke's law for an isotropic system takes the form

$$\begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix} = \begin{bmatrix} \lambda + 2\mu & \lambda & \lambda & 0 & 0 & 0 \\ \lambda & \lambda + 2\mu & \lambda & 0 & 0 & 0 \\ \lambda & \lambda & \lambda + 2\mu & 0 & 0 & 0 \\ 0 & 0 & 0 & \mu & 0 & 0 \\ 0 & 0 & 0 & 0 & \mu & 0 \\ 0 & 0 & 0 & 0 & 0 & \mu \end{bmatrix} \begin{bmatrix} e_1 \\ e_2 \\ e_3 \\ e_4 \\ e_5 \\ e_6 \end{bmatrix} \tag{3.29}$$

Uniaxial stress of an isotropic solid.

An isotropic solid is subject to uniaxial tension T in the $x-$ direction. We wish to find the strain components.

If $\sigma_1 = T$, $\sigma_2 = \sigma_3 = \sigma_4 = \sigma_5 = \sigma_6 = 0$ we find the following equations for the strains

$$\begin{aligned} T &= (\lambda + 2\mu)e_1 + \lambda e_2 + \lambda e_3 \\ 0 &= \lambda e_1 + (\lambda + 2\mu)e_2 + \lambda e_3 \\ 0 &= \lambda e_1 + \lambda e_2 + (\lambda + 2\mu)e_3 \end{aligned} \tag{3.30}$$

in addition to $e_4 = e_5 = e_6 = 0$. The solution to (3.30) is

$$\begin{aligned} e_1 &= \frac{T(\lambda + \mu)}{\mu(3\lambda + 2\mu)} \\ e_2 = e_3 &= \frac{-T\lambda}{2\mu(3\lambda + 2\mu)} \end{aligned} \tag{3.31}$$

The *Poisson ratio* of an isotropic material is defined as

$$-\frac{e_2}{e_1} = \frac{\lambda}{2(\lambda + \mu)} \tag{3.32}$$

The *Young's modulus* is defined as the ratio of an *uniaxial stress* T and the tensile strain component along T. If the stress is acting in the $x-$direction we have $Y = T/e_1$. We find that

$$Y = \frac{\mu(3\lambda + 2\mu)}{\lambda + \mu} \tag{3.33}$$

for an isotropic material.

3.3.3 Problems

Example problem:

Find the Young's modulus of a cubic crystal with elastic constants C_{11}, C_{12} and C_{44}

(a) if uniaxial tension is applied in the [100] direction?

(b) if uniaxial tension is applied in the [110] direction?

(c) if uniaxial tension is applied in the [111] direction?

Check that your formulas reduce to (3.33) if the elastic constants satisfy (3.27)(3.28).

Solution

(a)

We have

$$T = C_{11}e_1 + C_{12}e_2 + C_{12}e_3$$

$$0 = C_{12}e_1 + C_{11}e_2 + C_{12}e_3$$

$$0 = C_{12}e_1 + C_{12}e_2 + C_{11}e_3$$

$$0 = C_{44}e_4 = C_{44}e_5 = C_{44}e_6$$

giving for Young's modulus

$$Y = \frac{T}{e_1} = \frac{C_{11}^2 + C_{11}C_{12} - 2C_{12}^2}{C_{12} + C_{11}}$$

(b)

We have

$$\frac{T}{2} = C_{11}e_1 + C_{12}e_2 + C_{12}e_3$$

$$\frac{T}{2} = C_{12}e_1 + C_{11}e_2 + C_{12}e_3$$

$$0 = C_{12}e_1 + C_{12}e_2 + C_{11}e_3$$

$$0 = C_{44}e_4 = C_{44}e_5$$

$$\frac{T}{2} = C_{44}e_6$$

To see this note that the net force on a (110) surface of a unit cube is $T\sqrt{2} = stress \times area$. This force is distributed equally on the (100) and(010) surfaces, i.e. the net force on the (100) surface is $F = T/\sqrt{2}$ with components σ_1 and σ_6 equal $F/\sqrt{2} = T/2$. The solutions to the coupled equations are

$$e_1 = e_2 = \frac{TC_{11}}{2(C_{11}^2 + C_{12}C_{11} - 2C_{12}^2)}$$

$$e_6 = \frac{T}{2C_{44}}$$

Let us imagine that the origin of the unit cube is held fixed. The $x-$component of the distortion at [110] is

$$\epsilon_{xx} + \epsilon_{xy} = e_1 + \frac{1}{2}e_6$$

similarly, the $y-$component is

$$\epsilon_{yy} + \epsilon_{yx} = e_2 + \frac{1}{2}e_6 = e_1 + \frac{1}{2}e_6$$

The distortion $(e_1+\frac{1}{2}e_6)\sqrt{2}$ is in the [110] direction and the strain in this direction is $(distortion/distance) = e_1 + \frac{1}{2}e_6$. The Young's modulus (stress/strain) is thus

$$Y = \frac{1}{\frac{C_{11}}{2(C_{11}^2+C_{12}C_{11}-2C_{12}^2)} + \frac{1}{4C_{44}}}$$

which simplifies to

$$Y = \frac{4C_{44}(C_{11}^2 + C_{12}C_{11} - 2C_{12}^2)}{2C_{11}C_{44} + C_{11}^2 + C_{12}C11 - 2C_{12}^2}$$

(c)

If the uniaxial stress in the [111] direction is T, the force on a (111) surface is $T\sqrt{3}$. On the unit cube this force is distributed equally on (100),(010) and (001) surfaces of unit area. The net force on any one of these surfaces is thus $T\sqrt{3}/3 = T/\sqrt{3}$. This force has three equal components $T/3$ in the x, y and z directions. We thus have

$$\frac{T}{3} = C_{11}e_1 + C_{12}e_2 + C_{12}e_3$$

$$\frac{T}{3} = C_{12}e_1 + C_{11}e_2 + C_{12}e_3$$

$$\frac{T}{3} = C_{12}e_1 + C_{12}e_2 + C_{11}e_3$$

$$\frac{T}{3} = C_{44}e_4 = C_{44}e_5 = C_{44}e_6$$

The solution is

$$e_1 = e_2 = e_3 = \frac{T}{3(C_{11} + 2C_{12})}$$

$$e_4 = e_5 = e_6 = \frac{T}{3C_{44}}$$

Again let the origin be held fixed. The $x-$component of the distortion at the diagonally opposite [111] corner is

$$\epsilon_{xx} + \epsilon_{xy} + \epsilon xz = e_1 + \frac{1}{2}(e_5 + e_6) = e_1 + e_4$$

Similarly the $y-$ and $z-$components of the distortion will be

$$\epsilon_{yx} + \epsilon_{yy} + \epsilon_{yz} = e_1 + e_4$$

$$\epsilon_{zx} + \epsilon_{zy} + \epsilon_{zz} = e_1 + e_4$$

The net distortion will be $\sqrt{3} \times$ *distortion component* in either direction. The net strain will be the *net distortion*$/\sqrt{3}$ i.e. $e_1 + e_4$. We find

$$Y = \frac{1}{\frac{1}{3C_{11}+2C_{12}} + \frac{1}{3C_{44}}}$$

which simplifies to

$$Y = \frac{3C_{44}(C_{11} + 2C_{12})}{C_{44} + C_{11} + 2C_{12}}$$

Example problem

A polycrystalline material has Young's modulus $Y = 2.5 \times 10^{10}\ N\ m^{-2}$ and Poisson ratio 0.46.

(a) What are the elastic constants λ and μ?

(b) What is the bulk modulus?

(c) A person weighing $75kg$ stands on a $1cm^3$ sample shaped like a cube, what is the change in volume? what is the change in height?

(d) A sample of the material is dumped into the ocean and lands at the depth of $1000m$. What is the fractional change in volume?

Solution

(a)

$$0.46 = \frac{\lambda}{2(\lambda + \mu)}$$

$$Y = \frac{\mu(3\lambda + 2\mu)}{\lambda + \mu} = 2.5 \times 10^{10} Nm^{-2}$$

giving

$$\mu = 0.856 \times 10^{10} Nm^{-2};\ \lambda = 9.846 \times 10^{10} Nm^{-2}$$

(b)

$$B = \lambda + \frac{2}{3}\mu = 10.4 \times 10^{10} Nm^{-2}$$

(c)

$$\Delta h = 0.01 \times \frac{75 \times 9.8}{10^{-4} Y} = 3 \mu m$$

(d) At $1000m$ depth the pressure is approximately 100 $atm = 10^7 Nm^{-2}$. The fractional volume change is then $\delta = -\frac{P}{B} = 10^{-4}$.

Problem 3.3-1:

An isotropic material with elastic constants λ and μ is put under uniform hydrostatic pressure ($\sigma_1 = \sigma_2 = \sigma_3 = -P$, $\sigma_4 = \sigma_5 = \sigma_6 = 0$). Show that the bulk modulus is

$$B = -V \frac{\partial P}{\partial V} = \lambda + \frac{2}{3} \mu \tag{3.34}$$

Problem 3.3-2:

A cubic crystal with elastic constants C_{11}, C_{12} and C_{44} is put under uniform hydrostatic pressure ($\sigma_1 = \sigma_2 = \sigma_3 = -P$, $\sigma_4 = \sigma_5 = \sigma_6 = 0$). Assume that the stresses act normal to the (100), (010) and (001) planes. Find the bulk modulus.

3.4 Defects

So far, we have been concerned with perfect crystals in which the unit cell is repeated without error in all directions throughout space. Any real crystal will contain imperfections. Many bulk properties, such as the elastic behavior, discussed in the previous section, and the thermal properties to be discussed later are relatively insensitive to a small amount of imperfections. Other properties, such as the strength of materials, and electric conduction, are strongly affected by defects.

3.4.1 Point defects

Figure 3.8 illustrates four different types of point defects. *Vacancies* are simply missing atoms or ions. If the removed atom or ion is allowed to migrate to the surface we have a *Schottky defect.* On the other hand, if the missing atom is stuck in an *interstitial* position we have a *Frenkel* defect. Another common form of defect, is an *impurity.* A *substitutional* impurity simply consists of a foreign atom replacing a host atom on one of the lattice sites. This is the common form of impurity if the guest and host atoms are of comparable size. If the impurity atom is much smaller than the host it can sometimes find room in the empty space between the atoms, we then say that the impurity is interstitial. The point defects of figure 3.8 are always present in small amounts in a

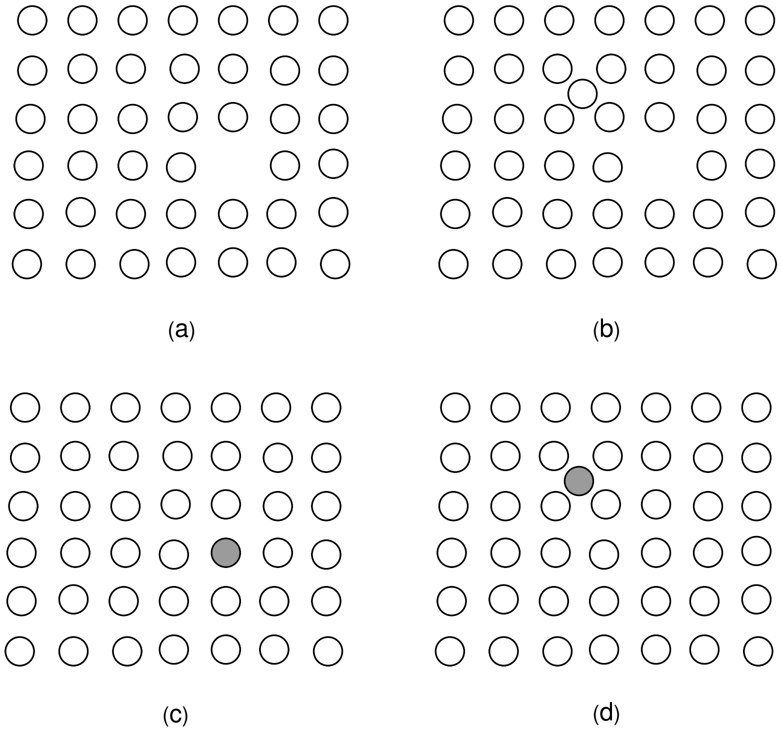

Figure 3.8: Point defects: (a) Schottky defect, (b) Frenkel defect, (c) Substitutional impurity, (d) Interstitial impurity

crystal at equilibrium. We will here concentrate on vacancies. Let E_v be the *vacancy formation energy*, which for a Schottky defect is the energy of removing an atom or ion and placing it on the surface of a crystal. The equilibrium concentration n_V of Schottky vacancies will then be approximately given by a *Boltzmann factor*

$$n_V = \frac{N_V}{N} = e^{-\beta E_V}$$

where N_V is the number of vacancies, N the total number of sites in the crystal and $\beta = \frac{1}{k_B T}$. Typical vacancy formation energies for metals and ionic crystals are in the range 0.5-1.5 eV. At room temperatures and below the equilibrium vacancy concentration will be very low (at room temperature $\beta \simeq 40$ eV^{-1} and $e^{-40} \simeq 4. \times 10^{-18}$). At elevated temperatures the vacancy concentration will be much higher, e.g. at $1000K$ the Boltzmann factor is $\simeq 10^{-5}$.

In an *ionic crystal* the positive ion is often smaller than the negative counter ion. The vacancy formation energy for the positive ion may then be significantly smaller than the corresponding energy for the negative ion. If this leads to a charge imbalance a huge negative electrostatic potential will develop in the interior of the crystal and prevent the escape of any more positive ions. We can thus write

$$E_+ = \epsilon_+ + e\phi; \quad E_- = \epsilon_- - e\phi$$

where E_+ (E_-) is the true vacancy formation energy of a positive (negative) ion and ϵ_+, and ϵ_- are the corresponding quantities at constant electrostatic potential, e is the ion net charge and ϕ is the electrostatic potential difference between surface and bulk. This potential will be established by a layer of surface dipoles called the *Debye layer* and as a consequence we have for the positive (negative) ion vacancy concentration n_+ (n_-)

$$n_+ \simeq n_- = e^{-\frac{\beta}{2}(\epsilon_+ + \epsilon_-)} \tag{3.35}$$

$$n_+ n_- = e^{-\beta(\epsilon_+ + \epsilon_-)} \tag{3.36}$$

Equation (3.37) is a special case of the *law of mass action* . One way of introducing a larger equilibrium vacancy concentration is by *doping*. Consider e.g. a K^+Cl^- crystal that contains a concentration n_{Ca} of calcium impurities. The calcium ions are divalent and as a consequence we must replace (3.35) by

$$n_+ - n_- = n_{Ca} \tag{3.37}$$

while (3.36) remains valid. If n_{Ca} is much larger than the equilibrium vacancy concentration in the absence of doping (3.36) and (3.37) will give $n_+ \simeq n_{Ca}$. One consequence of this is that although a calcium ion is heavier than a potassium ion the density of a crystal will be reduced by doping.

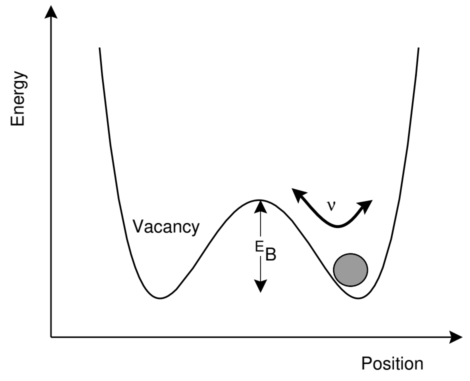

Figure 3.9: Potential energy barrier for atom next to vacancy

In practice, a crystal at room temperature and lower will often have a vacancy concentration which is much higher than predicted by equilibrium theory. To understand how this comes about we must consider vacancy *diffusion.* A vacancy will move to a neighbor site in a crystal if an atom from that site jumps into the empty site. In order to do so it will, however, have to overcome an energy barrier E_B figure (3.9). We write for the *jump rate* p (probability per unit time that a neighbor will jump into the empty site)

$$p = \nu e^{-\beta E_B} \tag{3.38}$$

Here ν is the *attempt frequency*, the rate at which the atom or ion attempts to overcome the barrier. This rate is of the order of a typical lattice vibration frequency (see section 4.1). The Boltzmann factor exp(-βE_B) represent the probability that an attempt to jump over the barrier will be successful. We let $n(x)$ be the number of vacancies per unit volume, and assume that the concentration depends on a coordinate x in a direction normal to a family of lattice planes. The concentration of vacancies per unit area in these planes will be a $n(x)$ where a is the spacing between planes. The *particle current density*, i.e the number of vacancies per unit area moving in the positive x direction minus the number moving in the negative x-direction will then be

$$j = -a^2 \frac{dn}{dx} \nu e^{-\beta E_B} \tag{3.39}$$

Conventionally one writes

$$j = -D \frac{dn}{dx} \tag{3.40}$$

where D is the *diffusion constant.* We thus have

$$D = \nu a^2 e^{-\beta E_B} \tag{3.41}$$

A typical value for the factor νa^2 for a metal or ionic crystal is $10^{-6} m^2/s$. The energy barrier E_B will normally be a few tenths of an electron volt. At room temperature the Boltzmann factor $\exp(-\beta E_B)$ may then be of the order 10^{-16}, yielding a diffusion constant of the order $10^{-22}\ m^2/s$. You will have learned in other courses that the typical time t it takes to travel a distance x will be

$$x \simeq \sqrt{Dt}$$

If x is $1mm = 10^{-3}m$, we find $t \simeq 10^{16}s$, which is a significant fraction of the age of the universe. On the other hand if we increase the temperature from room temperature to $1000K$ the diffusion time will be reduced to times of the order days. Typically a crystal will be grown from a melt of the order $1000K$, at these temperatures the vacancy concentration will be quite high. The extent to which the vacancy concentration will have time to reach its equilibrium value, as a crystal is cooled down, will then depend critically on the cooling rate.

3.4.2 Dislocations

The type of defect that influences the mechanical properties of a material the most is dislocations. Imagine that we remove a half-plane of atoms in a family of lattice planes as shown in figure 3.10. The edge of this half-plane is perpendicular to the plane of the figure. The associated *line defect* is called an *edge dislocation* . In the immediate neighborhood of the edge there is considerable distortion of the crystal, while further away the crystal appears almost regular. The presence of the dislocation will still be felt far away. To see this, imagine the following "walk" on a lattice plane perpendicular to the edge: go 8 lattice spacings W, then 8 lattice spacings S, then 8 spacings E and finally 8 spacings N. If this walk takes place in an undistorted part of the crystal it would take us back to the starting point, but if we go *around* an edge dislocation we would be one lattice spacing short. The vector $\mathbf{b}$ by which the walk is short of returning is called *Burger's vector* .

A *screw dislocation* can be obtained by making a cut along a half-plane and shifting the parts on either side by one lattice spacing (figure 3.11). After this distortion the lattice planes perpendicular to the edge of the cut forms a helicoidal surface (somewhat analogous to the parking floors in a parkade). Both in the case of edge and of screw dislocations, we refer to the region near the edge of the cut, where the crystal is most distorted, as the *core*. If we make the same walk as we did before, around the edge, we would be short one lattice spacing parallel to the edge of the cut. *The Burger's vector of a screw dislocation is parallel to the dislocation core for a screw dislocation, and perpendicular to it for an edge dislocation.* In both cases the associated strain away from the axis will be approximately 1 lattice spacing divided by the distance to the axis, i.e the strain field will be inversely proportional to the distance to the dislocation core. Since the strain falls off so slowly with distance the energy associated with dislocations will be large compared to vacancies. Thermal

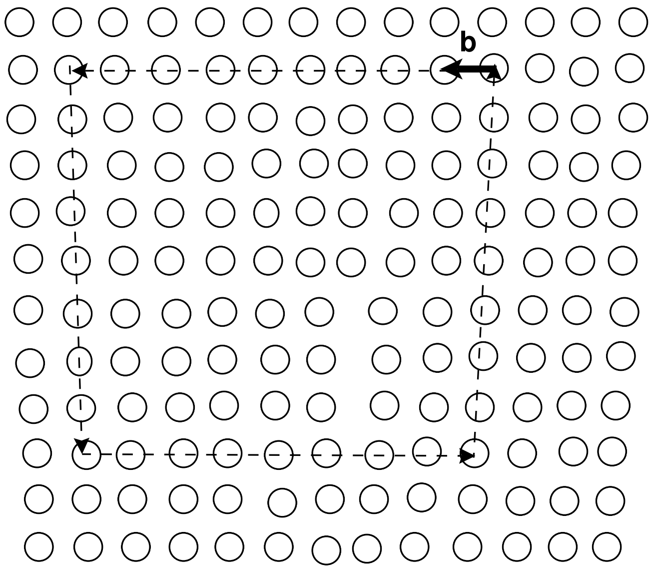

Figure 3.10: Edge dislocation

energies are therefore too small to create dislocations. Once formed they can migrate, but not be got rid of, without a major rearrangement of the atoms in the crystal. The pattern of dislocations depends on the history of the crystal. It is almost impossible to grow a dislocation free crystal, and further dislocations are formed in a crystal subject to bending and other forms of severe stain.

3.4.3 Problems

Example Problem

A Na^+Cl^- crystal contains small amount of the radioactive isotope Na^{22}. The sodium ions in Na^+Cl^- occupy a fcc lattice. Assume that the Na^{22} ions can jump to one of the 12 nearest neighbor positive ion site, only if it contains a vacancy, otherwise it is stuck. Assume that the effective value for νa^2 in the formula (3.40) for the diffusion constant is $10^{-6}m^2/s \times$ the positive ion vacancy concentration. Also assume that the jump activation energy E_B is $0.5eV$. Estimate the diffusion constant for Na^{22} at 600K if

(a). The vacancy concentration is $e^{-\beta\epsilon}$ with $\epsilon = 1eV$.

(b). The crystal contains 1% Ca^{++}.

(c). How long would it typically take for a Na^{22} ion to diffuse $1mm$ in the two cases.

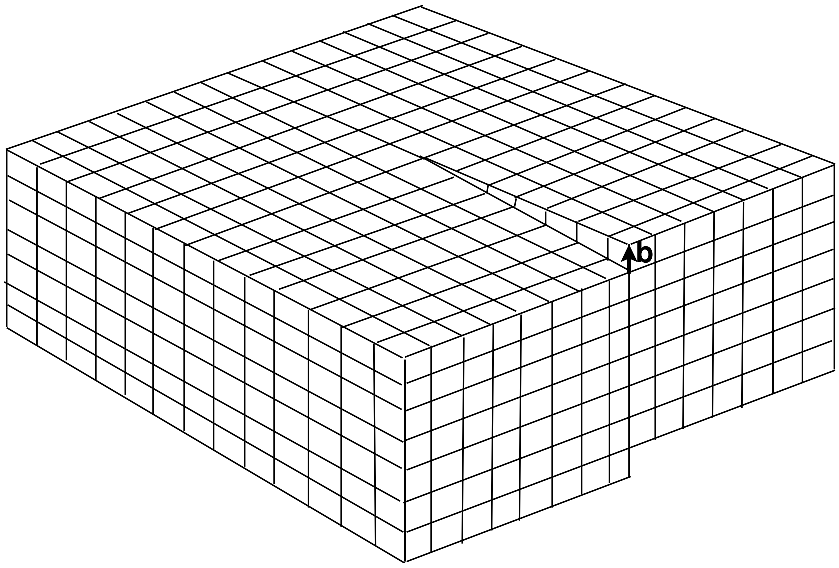

Figure 3.11: Screw dislocation.

Solution

Writing n for the vacancy concentration we find for the diffusion constant

$$D = \nu a^2 n e^{-\beta E_B}$$

We have $k_B = 0.86205 \times 10^{-4} eV\ K^{-1}$
(a) We have

$$D = 10^{-6} \exp\left(-\frac{1+0.5}{600 \times 0.86205 \times 10^{-4}}\right) = 2.5 \times 10^{-19} m^2 s^{-1}$$

(There is some room for interpretation of the effective jump rate prefactor νa^2: is it per neighbor, or per jump "in the right direction"? Since equation (3.41) was derived for one-dimensional diffusion and is applied to the three dimensional case. The difference is qualitatively insignificant considering the large exponents in the Boltzmann factors and the uncertainty in the activation energies)
(b). With $1\% Ca^{++}$.

$$D = 10^{-6} \exp\left(-\frac{0.5}{600 \times 0.86205 \times 10^{-4}}\right) = 6.3 \times 10^{-13} m^2 s^{-1}$$

(c). If x is the distance the time will typically be

$$t \approx \frac{x^2}{D} = \begin{cases} 4 \times 10^{12} s & \approx 10^5 years \quad \textit{in case } \mathbf{a} \\ 1.6 \times 10^6 s & \approx 18 days \quad \textit{in case } \mathbf{b} \end{cases}$$

Problem 3.4-1:

Consider a crystal which contains two edge dislocations with cores parallel to the z-axis. One cut-out half-plane extends from the origin in the positive x-direction. The second dislocation core intersects the $x-y$ plane at $L(-\hat{x}+\hat{y})$, where the distance L corresponds to many lattice spacings. Find the Burger's vector for a counter clockwise (seen from the positive z-axis) path around (i) the first dislocation, (ii) the second dislocation, (iii) both dislocations if the second half-plane that has been cut out extends

(a). in the negative x-direction

(b). in the positive y-direction.

3.5 Strength of materials

If a material is put under sufficient stress it will undergo permanent damage and the material will not return to its original shape if the stress is removed. The theoretical *shear strength* of a perfect crystal can be estimated by the following simple argument. Consider two nearby lattice planes in a sheared crystal as seen in cross-section in figure 3.12. We assume that in the undistorted crystal the lattice planes are directly above each other, and let x be the shear displacement of an atom in one lattice plane relative to the next plane a distance d below. The lattice spacing in the x-direction is a. The strain is $e_{xy} = e_6 = x/d$. For small displacements the shear stress will be

$$\sigma_{xy} = Ge_{xy} = \frac{Gx}{d} \tag{3.42}$$

where in our case the shear modulus is $G = C_{66}$. If we increase the strain, the shear stress cannot continue to increase linearly with the strain without limit. When the relative slip between the two planes reaches a full lattice spacing we recover the periodic crystal and the stress is zero. The stress will also be zero, corresponding to unstable equilibrium, when the successive planes are slipped by one half lattice spacing as shown in figure (3.12). We conclude that the stress must be a *periodic* function of the strain with period a. The simplest way to model this is to assume a sinusoidal variation of the stress with the strain. We require that we recover (3.42) for small strains and obtain

$$\sigma_{xy} \approx \frac{Ga}{2\pi d}\sin(\frac{2\pi x}{a}) \tag{3.43}$$

Equation (3.43) predicts that there is a *maximum shear stress* σ_c beyond which the crystal will yield. In our simple model this stress is given by

$$\sigma_c = \frac{Ga}{2\pi d} \tag{3.44}$$

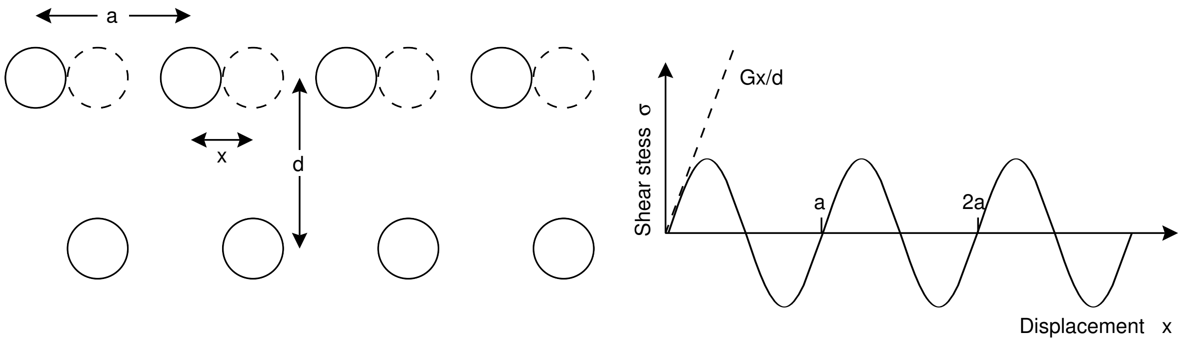

Figure 3.12: The shear stress is a periodic function of the strain.

Table 3.4: Yield stress and shear modulus for aluminum

Material	$G\ Nm^{-2}$	$\sigma_c\ Nm^{-2}$	G/σ_c
Single crystal Al	$2.8{\times}10^{10}$	$4.0{\times}10^{5}$	60 000
Pure polycrystalline Al	2.5×10^{10}	2.6×10^{7}	900
Commercial drawn Al wire	2.5×10^{10}	3.8×10^{7}	250
Duralumin	2.5×10^{10}	3.6×10^{8}	70

Since a and d will be about the same size, (3.44) predicts that the shear modulus should at most be one order of magnitude larger the the yield stress. This prediction is very far from the truth. In table 3.4 we list some typical values of G and σ_c for aluminum samples of varying quality. Similar values would obtain for other materials. We note that not only is the disagreement between theory and experiment quite bad. More embarrassing, considering that the theory was developed for a perfect crystal, is the fact that the disagreement gets worse the better the quality of the crystal. It is now generally accepted that shear slip is mediated by *dislocations*. Consider the edge dislocation of figure 3.10. If the edge is slipped, one lattice spacing at the time, to the right, this is equivalent to a shear deformation of the top part of the crystal, relative to the bottom part by one lattice spacing. Since it is only the edge which is moving, and not the whole lattice plane, the required stress is much less than it would be in a perfect crystal without dislocations.

An analogous situation occurs if one tries to pull a heavy carpet across the floor in an empty room. Brute force pulling requires more strength than most of us possess. A much easier method is to produce a wrinkle at one end of the carpet and push the wrinkle across. We can now understand why σ_c increases in a crystal with an increasing number of imperfections. Dislocations can not easily cross grain boundaries of a polycrystalline material. The strain produced by drawing an aluminum wire will produce a tangle of dislocations that pin other dislocations. The process of increasing the strength of a material through dislocation producing deformations is called *work hardening*. The impurities of an alloy such as duralumin also act as pinning centers. Returning to our carpet analogy, the wrinkle method of pulling a carpet does not work too well if the room is full of furniture.

A *ductile* material can be subjected to *plastic deformation*, if the strain exceeds an elastic limit. Figure 3.13 describes the outcome of a typical tensile test of a ductile material. In the test a cylindrical sample is subject to uniaxial tension σ, and the strain component $\epsilon = e_{11}$ is measured. We start with an unstressed sample (a). When the stress is increased to (b) the behavior is elastic, the stress is proportional to the strain as predicted by Hooke's law, and the sample will return to its original shape if the stress is released. The point (b) is called the *yield point*. Beyond this point the relationship between stress and strain is nonlinear. If the stress is released at (c) the sample will not return to its original shape but there will be a *plastic deformation*. We now must distinguish between two ways of registering the stress. The *true stress* is defined as

$$\sigma_t = \frac{tensile\ force}{actual\ area}$$

and the *engineering stress* is given by

$$\sigma_e = \frac{tensile\ force}{original\ area}$$

The dashed line in figure 3.13 represents the true stress, while the full line corresponds to the engineering stress. The marked difference between the two curves arises because the reduction in cross sectional area tends not to be uniform, but concentrated in a "neck". If the stress is reapplied at (d) the new yield point (e) will typically be somewhat higher than the old one, due to work hardening. Finally there is a maximum stress which the sample can endure before it breaks.

Some materials are *brittle* and break suddenly rather than undergo plastic deformation. Important examples are glass and rocks. In brittle materials small voids called *cracks* develop when a sample is stressed. In order to explain the importance of cracks we need to comment on how nonuniform stress is distributed. Consider a medium which is subject to a spatially varying stress consisting possibly both of a shear component and tensile stress. The requirement that forces and torques are balanced, leads to a symmetric stress tensor which satisfies the partial differential equation

$$\sum_{j=x,y,z} \frac{\partial \sigma_{ij}}{\partial r_j} = 0 \tag{3.45}$$

where $i = x, y$ or z. One can solve (3.45) for a spherical cavity. The boundary condition is uniaxial tensile stress σ_∞ far away, and zero normal component of the stress on the cavity surface. At the top

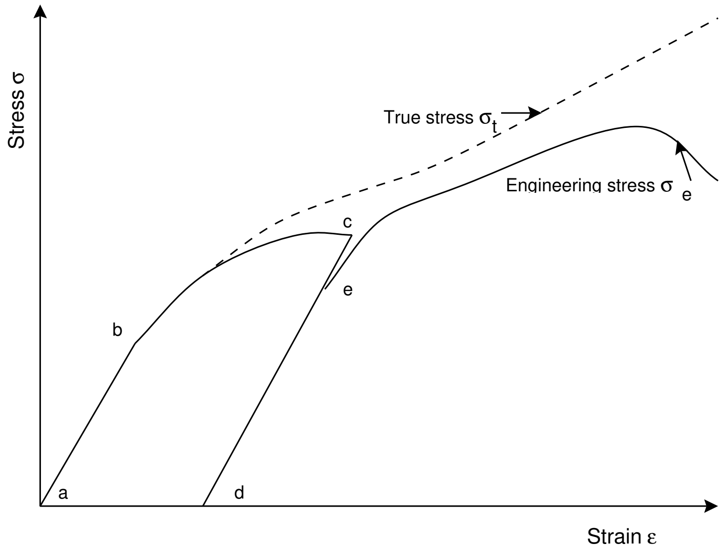

Figure 3.13: Stress vs. strain for a ductile material.

and bottom there will be a compressive stress equal to σ_∞. At the equator the stress is tensile and enhanced to $3\sigma_\infty$. If the void is an oblate ellipsoid of revolution with the tensile stress σ_∞ applied parallel to the minor axis b, the stress enhancement at the equator is even more pronounced and given by

$$\sigma_{eq} = \sigma_\infty(1 + \frac{2c}{b})$$

where c is the major axis.

In the case of a long thin crack the stress enhancement can thus be enormous and we see that once a crack opens up, the stress enhancement at the tip makes it tend to grow, drastically weakening the strength of a sample. As shown in figure (3.14) there are three main crack propagation modes. We note that the deformation associated with a mode II crack is the same as for an edge dislocation, while a mode III crack is analogous to a screw dislocation. A complication is that the material near the tip of a crack may be subject to chemical corrosion. As anyone who has had to cut a glass pane to fit a frame would know, it is easier to crack glass when it is wet. Corrosion processes can be very slow and this can give rise to the phenomenon of *static fatigue*. A window pane subject to a steady stress may suddenly, for no apparent reason, decide to shatter. Similarly a ductile material may become brittle if the dislocation density gets to high due to excessive work hardening. This phenomenon is called *dynamic fatigue*. . For further reading on strength of materials see the book by Callister [1]. For a discussion of ductile materials see also the article by Sprackling [10], a readable discussion of the properties of brittle materials can be found in Scholz [9].

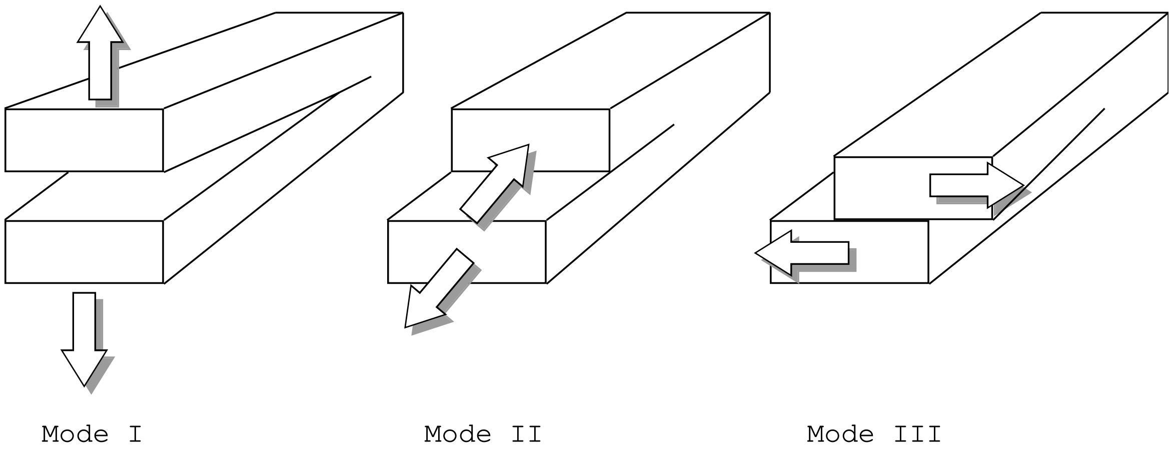

Figure 3.14: The three crack propagation modes.

We conclude this section by defining a few more different properties associated with the strength of materials:

- **Hardness** is a measure of the resistance of a material to plastic deformations such as dents and scratches. A somewhat arbitrary but often used index of hardness is the Mohs scale. This scale is based on the idea that a harder material can scratch a softer material. The hardest known material is diamond which is given an index of 10 on the Mohs scale. Next are corundum and sapphire with 9, topaz with 8, quartz 7, orthoclase (a feldspar mineral) 6, apatite (calcium fluorophoshate) 5, fluorite 4, calcite 3, gypsum 2 and talc 1. There are a number of more quantitative hardness measures such as the Brinell hardness number. In a Brinell test a spherical indenter of tungsten carbide or hardened steel with a diameter of typically $1cm$ is applied for a specified length of time and with a specified force. The diameter of the indentation is then measured and converted to a hardness number using a chart. The Rockwell hardness test is a similar method.

- **Resilience** is the ability of a material to return to its original shape after being bent, compressed or stretched. The resilience modulus U_r is the energy per unit volume which is stored and can be retrieved before the yield point (point b in figure 3.13). This energy is given by

$$U_r = \int_0^{\epsilon_y} \sigma d\epsilon = \frac{1}{2}\sigma_y d\epsilon_y$$

  where σ and ϵ are engineering stress and strain. A related property which is more difficult to quantify is **Toughness**. It is defined as the ability to absorb energy up to fracture or other failure.

3.5.1 Problems

Problem 3.5-1: Weibull statistics

There are a number of situations, e.g. in problems involving *fracture* or *failure* where what matters is not the *average* property of the system, but rather the behavior of the *weakest link*. An empirical approach to such problems was taken by the Swedish engineer Waloddi Weibull.

Consider a fiber of length n in some unit. Assume a segment i of unit length has a yield threshold stress σ_i which may depend on microscopic flaws and will vary from segment to segment. We assume the probability that a segment breaks with a stress σ is given by

$$P(\sigma) = 1 - e^{-\phi(\sigma)}$$

The probability that the link will *not* break is then $e^{-\phi(\sigma)}$, where $\phi(\sigma)$ is some monotonically increasing function of σ. If any one of the links fails the whole chain fails. Therefore, the probability that the fiber survives is $e^{-n\phi(\sigma)}$ and the probability that it will break under stress σ is

$$P_{chain} = 1 - e^{-n\phi(\sigma)} \tag{3.46}$$

Weibull suggested the form

$$\phi(\sigma) = a(\sigma - \sigma_0)^{\rho}; \quad for\ \sigma > \sigma_0 \tag{3.47}$$

where σ_0 is some minimum failure stress (which may be zero). The exponent ρ must be expected to be a property of the fiber material (Weibull found $\rho \approx 3$ for steel, and $\rho \approx 1.46$ for cotton.). The proportionality constant a in (3.47) will from (3.46) not be a material property, but will also depend on the unit of length chosen and σ_0 will depend on the manufacturing process.

(a). If length is measured in feet rather than meters, and stresses in *lb per square inches* rather than Nm^{-2} by what factor will the constant a change for steel? for cotton?

(b). A $10m$ long fishing line will withstand a certain force 99 times out of a hundred. What is the probability that a $100m$ long fishing line of the same material can support the same force?

(c). Plot the probability that *(i)* a steel and *(ii)* a cotton fibber will support the stress σ in units where $a = \sigma_0 = 1$. The length of the fiber is 1 in these units.

Chapter 4

Electrons and phonons

We will in this chapter treat the properties of solids related to the *motion* of the atoms or ions and of the electrons. The vibrations of atoms and ions in the lattice will be discussed mainly for their importance in understanding the *thermal properties* of solids. In the case of the electrons we will also be concerned with the electric and optical conductivity.

4.1 Lattice vibrations

In our discussion of the structure of solids we have assumed that the atoms (or ions) sit still at their equilibrium positions. We now wish to turn to lattice vibrations. Our formal development will be based on classical mechanics and the basic assumption of a harmonic lattice. At low temperatures the theory must be modified to take into accounts quantum mechanical effects and we introduce the concept of phonons. We then show that most thermal properties of solids can be explained by an idealized model due to Debye. Two important effects which cannot be explained in the harmonic approximation are thermal expansion and the lattice contribution to thermal conduction. We come back to these effects towards the end of this section.

4.1.1 The harmonic approximation

In order to establish a manageable formalism we will make two important simplifying assumptions which allow us to picture the vibrating lattice as a system of masses and springs. Firstly, since the electrons in a solid are very light compared with the atoms, the electrons will respond very fast to a disturbance of the ion positions. It is thus natural to make the approximation that the electrons will adjust instantaneously to the ion position when the ions move. This implies that the potential energy of the ions can be expressed as a function of the ion coordinates alone.

Let $\mathbf{R}_i$ be the equilibrium position of the i'th ion, $\mathbf{u}_i$ the displacement of this ion from the rest position. The actual position of the ion is then

$$\mathbf{r}_i = \mathbf{R}_i + \mathbf{u}_i$$

We write $u_{i\alpha}$ ($\alpha = x, y, z$) for the components of the displacement. The components of the force on the i'th ion is

$$f_{i\alpha} = -\frac{\partial V(\mathbf{r}_1, \mathbf{r}_2, ..\mathbf{r}_i, ..\mathbf{r}_N)}{\partial r_{i\alpha}}$$

or in the more compact vector notation

$$\mathbf{f}_i = -\frac{\partial V}{\partial \mathbf{r}_i} \tag{4.1}$$

For small amplitude vibrations we can make a Taylor series expansion of the potential energy function

$$V(\mathbf{r}_1, \mathbf{r}_2, ..\mathbf{r}_N) = V(\mathbf{R}_1, \mathbf{R}_2, ..\mathbf{R}_N) + \sum_{i\alpha} u_{i\alpha} \left. \frac{\partial V(\mathbf{r}_1, \mathbf{r}_2, ..\mathbf{r}_N)}{\partial r_{i\alpha}} \right|_{r_{i\alpha}=R_{i\alpha}\ for\ all\ i} +$$

$$+\frac{1}{2} \sum_{ij\alpha\beta} u_{i\alpha} u_{j\beta} \left. \frac{\partial^2 V(\mathbf{r}_1, \mathbf{r}_2, ..\mathbf{r}_N)}{\partial r_{i\alpha} \partial r_{j\beta}} \right|_{r_{i\alpha}=R_{i\alpha}\ for\ all\ i} + \cdots \tag{4.2}$$

When all the ions are at their equilibrium positions, the net force (4.1) on them is zero. The second term on the right hand side of (4.2) must therefore vanish. The second assumption necessary to establish the *harmonic approximation* consists of stopping at the last term on the right hand side of (4.2). This allows us to think of the lattice can be thought of as made up a set of masses connected by springs. Each spring is represented by a spring constant

$$\Phi_{ij\alpha\beta} = \left. \frac{\partial^2 V(\mathbf{r}_1, \mathbf{r}_2, \cdots \mathbf{r}_N)}{\partial r_{i\alpha} \partial r_{j\beta}} \right|_{r_{i\alpha}=R_{i\alpha}} \quad \text{for all } i \tag{4.3}$$

The equation of motion for the α'component of the displacement of the i'th atom is then according to Newton's second law.

$$m\ddot{u}_{i\alpha} = f_{i\alpha} = -\sum_{j\beta} \Phi_{ij\alpha\beta} u_{j\beta} \tag{4.4}$$

Because the motion is three dimensional, the notation is a bit cumbersome, and it is instructive to consider some simple special cases before we return to the general case (4.4).

4.1.2 Harmonic chain

Consider a long chain consisting of N masses m connected by springs with spring constant K (figure 4.1). Let a be the equilibrium spacing between the masses, so that $x = na$ is the equilibrium position of the n'th mass. The actual position of the n'th mass is

$$r_n = na + u(n)$$

and the potential energy of the spring connecting the n'th and the $(n+1)$'st mass is $\frac{K}{2}[u(n+1) - u(n)]^2$. We assume *periodic boundary conditions,* i.e. we let the N'th mass be connected with the first mass. Formally, we do this by requiring that $u(N+1) = u(1)$ and in general

$$u(N+n) = u(n) \tag{4.5}$$

The force on the n'th mass is $K[u(n+1) + u(n-1) - 2u(n)]$ and Newton's second law gives rise to a coupled set of differential equations

$$m\ddot{u}(n) = K[u(n+1) + u(n-1) - 2u(n)] \tag{4.6}$$

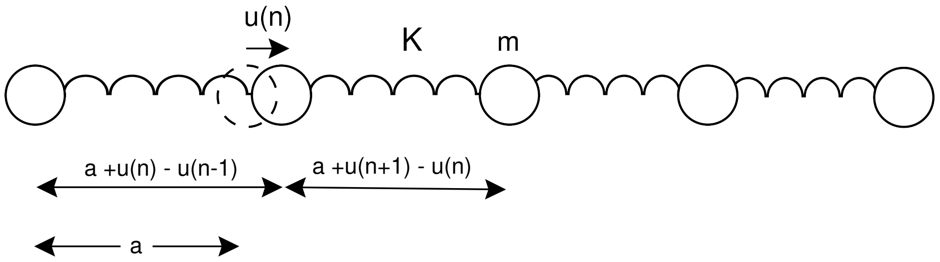

Figure 4.1: The harmonic chain

We can find solutions to (4.6) on the form

$$u(n) = Ae^{i(nka-\omega t)} \tag{4.7}$$

where k is the wave vector . Substitution of (4.7) into (4.6) yields

$$-m\omega^2 Ae^{i(nka-\omega t)} = AK\left\{e^{i[(n+1)ka-\omega t]} + e^{i[(n-1)ka-\omega t]} - 2e^{i[nka-\omega t]}\right\}$$

or

$$\omega^2 = \frac{2K}{m}[1-\cos(ka)]$$

We use the trigonometric identity

$$2\sin^2(\frac{ka}{2}) = [1-\cos(ka)] \tag{4.8}$$

By convention the frequency ω is positive and we find

$$\omega = 2\sqrt{\frac{K}{m}}\left|\sin\frac{ka}{2}\right| \tag{4.9}$$

The periodic boundary condition (4.5) determines which values of k are allowed. Substitution of (4.7) into (4.5) gives

$$e^{ikNa} = 1$$

or $k = \frac{2\pi l}{Na}$ with l an *integer.* From (4.7) we see that $l' = l + N$ and l give rise to identical solutions, and we can without loss of generality restrict l to the values

$$l = -\frac{N}{2}, \frac{N}{2} - 1, \cdots 1, 2, ..\frac{N}{2} - 1 \tag{4.10}$$

From (4.10) we note that there are N distinct values of l. This result is compatible with the fact that the system has N degrees of freedom. The restriction on the wave vector is

$$-\frac{\pi}{a} \leq k < \frac{\pi}{a} \tag{4.11}$$

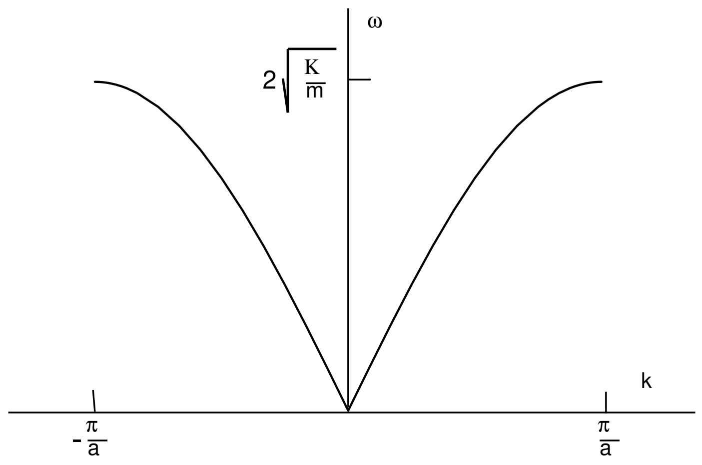

Figure 4.2: The harmonic chain

We note that $G = \frac{2\pi}{a}$ is a *reciprocal lattice vector* of the one dimensional lattice consisting to the chain atoms being located in their equilibrium positions. The restriction (4.11) is then equivalent to saying that k is *within the Brillouin zone.* The relationship (4.9) between frequency and wave vector is plotted in figure (4.2) The physical displacement is, of course, real. Since the differential equation (4.6) is linear and real, both the real and imaginary part of a complex solution are also solutions. With these considerations the general solution to (4.6) is then with A, B, C_l and S_l arbitrary constants of integration

$$u(n) = \sum_{l=-\frac{N}{2},l\neq 0}^{\frac{N}{2}-1} \left[C_l \cos(\frac{2\pi l n}{N} - \omega_l t) + S_l \sin(\frac{2\pi l n}{N} - \omega_l t) \right] + A + Vt \tag{4.12}$$

The case $l = 0$ in (4.12 requires special attention. If $l = 0$ the wave vector $k = 0$. This means that all displacements u are the same. The differential equation (4.6) now becomes

$$m\ddot{u}(n) = 0$$

with solution $u = A + Vt$ where A and V are constants. Usually the situation where the chain moves uniformly (as a whole) is not of much interest in lattice vibrational problems, but it is important when considering the *recoil* in the decay of a radioactive nucleus in the lattice (as in the Mössbauer effect), or in particle detectors analyzing or particles from cosmic rays or high energy accelerators.

It is instructive to solve the harmonic chain problem with various boundary conditions. First, consider the situation where we "pluck" the chain by displacing the atom at the origin by a fixed amount δ.

The initial conditions are then

$$u(0,t=0)=\delta;\ \ u(n,t=0)=0\ \ for\ \ n\neq 0 \tag{4.13}$$

$$\dot{u}(n,t=0)=0\ for\ all\ n \tag{4.14}$$

It is convenient to use the complex form for the normal mode expansion

$$u(n)=\sum_{l=-N/2,l\neq 0}^{N/2-1} A_l e^{i(2\pi nl/N-\omega t)}+A+Vt$$

giving

$$u(n,t=0)=\sum_{l=-N/2,l\neq 0}^{N/2-1} A_l e^{i(2\pi nl/N)}+A \tag{4.15}$$

$$0=\dot{u}(n,t=0)=\sum_{l=-N/2,l\neq 0}^{N/2-1} -i\omega A_l e^{i(2\pi nl/N)}+V \tag{4.16}$$

The fundamental formula for inverting discrete Fourier series is

$$\sum_{n=0}^{N-1} e^{2\pi i(l-l')n/N}=\begin{cases}\frac{1-e^{2\pi i(l-l')}}{1-e^{2\pi i(l-l')/N}}=0; & for\ \ l\neq l'\\ N; & for\ \ l=l'\end{cases} \tag{4.17}$$

Equating (4.13) and (4.15) and multiplying by $e^{i\pi l'n/N}$ and summing over n gives

$$A=A_l=\frac{\delta}{N}$$

i.e. all modes are excited with equal amplitude. The actual motion is the real part of the solution giving

$$u(n)=\frac{\delta}{N}\left(\sum_{l=-N/2,l\neq 0}^{N/2-1}\cos(2\pi nl/N-\omega t)+1\right) \tag{4.18}$$

Next consider the case where the atom at the origin is given a "kick" so that it has velocity v (in units of lattice spacings per unit time) starting at the origin with all the other atoms at rest. The initial condition is now

$$\dot{u}(0,t=0)=v;\ \ u(n,t=0)=0\ \ forn\neq 0 \tag{4.19}$$

$$u(n,t=0)=0\ for\ all\ n \tag{4.20}$$

We find equating (4.16) and (4.19) using the Fourier transform formula (4.17)

$$V=\frac{v}{N}$$

and

$$A_l = \frac{iv}{\omega N}$$

The actual motion of the masses is obtained by taking the real part or

$$u(n) = \frac{v}{N}\left(-\sum_{l=-N/2,l\neq 0}^{N/2-1} \frac{1}{\omega}\sin(2\pi nl/N - \omega t) + t\right) \tag{4.21}$$

Returning to the general case: we refer to the individual terms in the [ ] of 4.12 as *normal modes* and to (4.11) as a normal mode expansion.

From (4.9) we note that there is a maximum frequency

$$\omega_{max} = 2\sqrt{\frac{K}{m}}$$

If an atom is subject to a periodic force with frequency $\omega < \omega_{max}$ this will set up traveling waves with wave vectors satisfying (4.9). The *phase velocity* of this wave is

$$v_p = \frac{\omega}{k} = \frac{2}{k}\sqrt{\frac{K}{m}}\left|\sin(\frac{ka}{2})\right|$$

while the group velocity is

$$v_g = \frac{\partial\omega}{\partial k} = a\sqrt{\frac{K}{m}}\cos(ka)$$

Note that the group velocity $\to 0$ as $\omega \to \omega_{max}$. A local disturbance with frequency $> \omega_{max}$ cannot propagate through the lattice, but stays trapped. In the long wave length limit $k \to 0,\ \lambda = 2\pi/k \to \infty$ the phase and group velocities approach a common limit

$$s = a\sqrt{\frac{K}{m}}$$

We refer to long wave length lattice vibrations as *sound waves* with s the speed of sound.

4.1.3 Diatomic chain

We next consider a slightly more complicated case in which there are two atoms per unit cell with mass m and M, respectively. The equilibrium size of the unit cell is a and nearest neighbors are connected by springs with spring constant K (see figure 4.3). The equations of motion for the two masses are

$$m\ddot{u}_1 = K[u_2(n) + u_2(n-1) - 2u_1(n)]$$

$$M\ddot{u}_2 = K[u_1(n+1) + u_1(n) - 2u_2(n)] \tag{4.22}$$

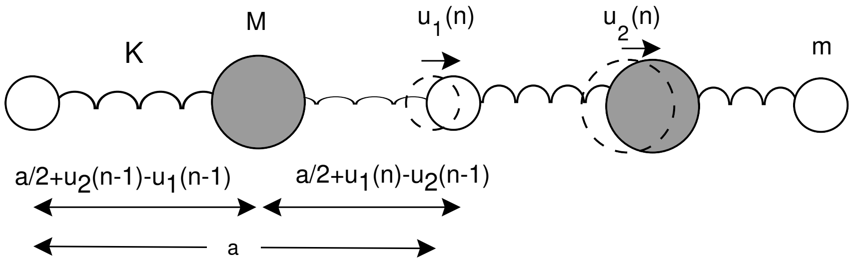

Figure 4.3: The diatomic harmonic chain

The amplitude of vibration for the two masses will now be different and we look for solutions of (4.22) on the form

$$u_1 = \epsilon_1 e^{i(kna-\omega t)}$$
$$u_2 = \epsilon_2 e^{i(kna-\omega t)} \tag{4.23}$$

Substitution of (4.23) into (4.22) gives

$$(m\omega^2 - 2K)\epsilon_1 + K(1+e^{-ika})\epsilon_2 = 0$$
$$K(1+e^{ika})\epsilon_1 + (M\omega^2 - 2K)\epsilon_2 = 0 \tag{4.24}$$

For (4.24) to have a solution we must have

$$\begin{vmatrix} m\omega^2 - 2K & K(1+e^{-ika}) \\ K(1+e^{ika}) & M\omega^2 - 2K \end{vmatrix} = mM\omega^4 - 2K(m+M)\omega^2 + 2K^2[1-\cos(ka)] = 0$$

Using (4.8) we find the solutions

$$\omega^2 = \frac{K}{\mu}(1 \pm \sqrt{1 - \frac{4Mm}{(M+m)^2}\sin^2(\frac{ka}{2})})$$

where $\mu = \frac{mM}{m+M}$ is the reduced mass. The allowed values of the wave vector k are the same as for the case of the monatomic chain (4.10),(4.11). For each allowed wave vector there are now two frequencies.

The top branch of figure 4.4 is called *optical* and the bottom branch *acoustic*. The highest allowed frequency $\omega_{max} = \sqrt{\frac{2K}{\mu}}$ occurs for k= 0. At the zone boundary k= $\frac{\pi}{a}$ the frequencies are given by

$$\omega^2 = \frac{K}{\mu}(1 \pm |\frac{M-m}{M+m}|)$$

and the two roots are $\omega = \sqrt{\frac{2K}{M}}$ and $\omega = \sqrt{\frac{2K}{m}}$. Suppose $M > m$. We see that there is an intermediate band of frequencies

$$\sqrt{\frac{2K}{M}} < \omega < \sqrt{\frac{2K}{m}}$$

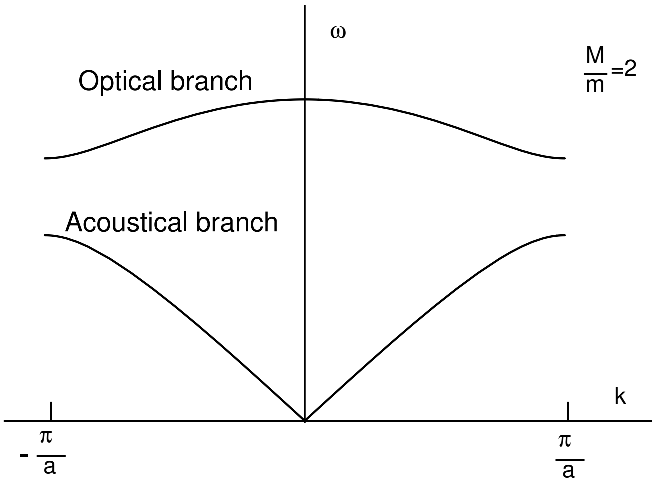

Figure 4.4: The frequency vs. wave-vector for the diatomic chain.

for which no lattice wave can propagate. Finally let us consider the acoustical branch near $k = 0$. We find

$$\omega \simeq k\sqrt{\frac{Ka^2}{2(M+m)}}$$

and the sound velocity is given by

$$s = \sqrt{\frac{Ka^2}{2(M+m)}}$$

Once the frequencies are found one can find the ratio ϵ_1/ϵ_2 and thus get a qualitative idea of the nature of the vibrations. Simple calculations show that for the acoustic branch near $k = 0$ $\epsilon_1 \simeq \epsilon_2$ i.e. the light and heavy atom vibrate together. As one moves up the acoustic branch the amplitude ϵ_1 of the lighter atom is reduced and at the Brillouin zone boundary only the heavier atom moves. Along the optical branch near $k = \frac{\pi}{a}$ only the lighter atom moves while near $k = 0$ neighboring atoms move in opposite directions in such a way that the center of mass is stationary.

4.1.4 Lattice vibrations in three dimensions

We now return to the general problem (4.3) (4.4). If the crystal potential is known, e.g. if the atoms interact pairwise via a Lennard–Jones potential (3.2) , the force constants (4.3) can be computed by straightforward if tedious algebra. Suppose we are dealing with a crystal in which the equilibrium positions of the atoms form a Bravais lattice. In analogy with (4.7) we assume a solution to (4.4) on the form

$$\mathbf{u}_j = \vec{\epsilon} e^{i(\mathbf{k}\cdot\mathbf{R_i}-\omega\mathbf{t})} \tag{4.25}$$

From the translational symmetry of the crystal it is clear that the force constant (4.3) is a function of the distance $\mathbf{s} = \mathbf{R_j} - \mathbf{R_i}$.

$$\Phi_{ij\alpha\beta} = \Phi_{\alpha\beta}(\mathbf{s})$$

Substitution of (4.25) into (4.4) gives

$$-m\omega^2 \epsilon_\alpha = -\sum_{\mathbf{s},\beta} \Phi_{\alpha\beta}(\mathbf{s}) e^{i\mathbf{k}\cdot\mathbf{s}} \epsilon_\beta$$

The Fourier transform of the force constant matrix Φ is the *dynamical matrix*

$$D_{\alpha\beta}(\mathbf{k}) = \sum_{\mathbf{s}} \mathbf{\Phi}_{\alpha\beta}(\mathbf{s}) \mathbf{e}^{\mathbf{ik}\cdot\mathbf{s}}$$

The determination of the normal mode frequencies involves solving the determinantal equation

$$\begin{vmatrix} D_{xx}(\mathbf{k}) - m\omega^2 & D_{xy}(\mathbf{k}) & D_{xz}(\mathbf{k}) \\ D_{yx}(\mathbf{k}) & D_{yy}(\mathbf{k}) - m\omega^2 & D_{yz}(\mathbf{k}) \\ D_{zx}(\mathbf{k}) & D_{zy}(\mathbf{k}) & D_{zz}(\mathbf{k}) - m\omega^2 \end{vmatrix} = 0 \tag{4.26}$$

The dynamical matrix will be *real* since if $\mathbf{s}$ is a Bravais lattice vector so is $-\mathbf{s}$. From (4.3) we see that the dynamical matrix will be *symmetric.* It is a theorem of linear algebra that a real symmetric matrix has positive eigenvalues and that the eigenvectors $\vec{\epsilon}$ will be orthogonal to each other. The cubic equation which results when one multiplies out the determinant in (4.26) will thus have three positive roots for ω^2. If we take the square root of ω^2 we thus get real frequencies. One can show that for small values of $\mathbf{k}$ one of the eigenvectors $\vec{\epsilon}$ will be parallel to $\mathbf{k}$, i.e. the vibrations will be *longitudinal.* The two other modes will have $\vec{\epsilon}$ perpendicular to $\mathbf{k}$ and the vibrations will be *transverse.* In the general case the amplitude vector will not be exactly parallel or perpendicular to $\mathbf{k}$, but the three vectors $\vec{\epsilon}$ corresponding to a given $\mathbf{k}$ will be orthogonal to each other.

The restrictions on the allowed values of $\mathbf{k}$ are analogous to what we had in the case of the linear chain. It is clear from (4.25) that adding a reciprocal lattice vector to $\mathbf{k}$ will not lead to any change in the displacement vector $\mathbf{u}$. We thus restrict $\mathbf{k}$ to the *Brillouin zone* . The allowed values of $\mathbf{k}$ inside the Brillouin zone depends on the boundary conditions. Suppose a crystal is made up of L unit cells in the directions of each of the three primitive lattice vectors $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$, and we apply periodic boundary conditions . A little reflection should convince the reader that the allowed $\mathbf{k}$-values can be written

$$\mathbf{k} = \frac{n_1}{L}\mathbf{A} + \frac{n_2}{L}\mathbf{B} + \frac{n_3}{L}\mathbf{C} \tag{4.27}$$

where n_1, n_2 and n_3 are integers and $\mathbf{A}$, $\mathbf{B}$ and $\mathbf{C}$ are the reciprocal lattice vectors. Just as we found in connection with our discussion of (4.10) the total number of allowed $\mathbf{k}$-vectors inside the

Brillouin zone will be $L \times L \times L = N$, where N is the total number of unit cells. There will thus be $3N$ normal modes, which is expected from the fact that each atom can vibrate in three different directions.

If we are dealing with a lattice which is not a Bravais lattice, but a Bravais lattice with a basis, the situation becomes more complex and we will skip the details. In analogy with what we did for the diatomic chain we will have an expression on the form (4.25) for each atom in the basis. For a lattice with a p-point basis the diagonalization of the resulting dynamical matrix will give rise to a $3p \times 3p$ determinant which must be put equal to zero. In analogy with what we found for the diatomic chain 3 of the normal modes will be acoustic (i.e. the frequency approaches zero in the long wave length limit) and the remainder optical (with a non-zero frequency in the long wavelength limit).

4.1.5 Density of states

In what follows we will need to calculate thermal averages which involves summing over contributions from all the individual modes. For this purpose we need to find a way to convert sums over allowed $\mathbf{k}$-values into a volume integral over d^3k. The volume of the primitive unit cell of the reciprocal lattice is from (2.10)

$$|\mathbf{A} \cdot (\mathbf{B} \times \mathbf{C})| = \frac{(2\pi)^3}{v_c} \tag{4.28}$$

where v_c is the volume of the primitive unit cell of the direct lattice. We have for the total volume

$$V = L^3 v_c$$

Consider the modes for which the integers n_1, n_2 and n_3 in (7-22) are between

n_1 and $n_1 + dn_1$

n_2 and $n_2 + dn_2$

n_3 and $n_3 + dn_3$

The total number of such modes is

$$dn_1 dn_2 dn_3 = d^3n$$

From (4.27) and (4.28) we see that these modes occupy a 'volume' in k-space

$$d^3k = \frac{(2\pi)^3}{V} d^3n$$

If the volume V is macroscopically large the k-values for successive normal modes are very close together and we can replace a sum of allowed k-states by an integral according to

$$\sum_{\mathbf{k}} = \frac{V}{(2\pi)^3} \int d^3k \tag{4.29}$$

Equation (4.29) will prove quite useful later on.

4.1.6 Phonons

We treat the normal modes of the lattice as a set of independent harmonic oscillators. According to quantum mechanics the energies of the individual oscillators are *quantized* with energy levels

$$E_n = (n + \frac{1}{2})\hbar\omega \tag{4.30}$$

where n can take on integer values 0,1,2... , $\hbar$ is Planck's constant divided by 2π and ω is the normal mode frequency. The energy of the lowest state, the ground state energy, is $\frac{1}{2}\hbar\omega$ and an excitation with energy $\hbar\omega$ above the ground state energy is called a *phonon*. The probability $p(n)$ that an oscillator will be in the n'th state will be proportional to the Boltzmann factor

$$e^{-\beta E_n} = e^{-\beta(n+\frac{1}{2})\hbar\omega}$$

where $\beta = \frac{1}{k_BT}$. The probabilities have to add up to 1 so that

$$p(n) = \frac{1}{Z}e^{-\beta(n+\frac{1}{2})\hbar\omega}$$

where

$$Z = \sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2})\hbar\omega} = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}$$

The average energy stored in each mode is then

$$< E >= \sum_{n=0}^{\infty} E_n p(n) = \frac{1}{Z}\sum_{n=0}^{\infty}(n+\frac{1}{2})\hbar\omega e^{-\beta(n+\frac{1}{2})\hbar\omega} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}$$

Straightforward algebra gives

$$< E >= \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}$$

Each mode will contribute a term

$$\frac{\partial < E >}{\partial T} = \frac{\partial < E >}{\partial \beta}\frac{\partial \beta}{\partial T} = \frac{1}{k_BT^2}\frac{(\hbar\omega)^2 e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}$$

to the specific heat. At high temperatures $\beta \to 0$, and

$$e^{\beta\hbar\omega} \to 1 + \beta\hbar\omega = 1 + \frac{\hbar\omega}{k_BT}$$

and the contribution to the specific from each mode approaches k_B. If the crystal has N atoms there are 3N normal modes. We thus find that the heat capacity in the high temperature limit will be close to 3Nk_B. This result is known as the *law of Dulong and Petit.*

In general, the lattice heat capacity will be the sum of the contributions from the individual modes. We find

$$C_V = \frac{1}{k_B T^2} \sum_{k,\alpha} \frac{[\hbar\omega(\mathbf{k},\alpha)]^2 e^{\beta\hbar\omega(\mathbf{k},\alpha)}}{(e^{\beta\hbar\omega(\mathbf{k},\alpha)}-1)^2} = \frac{V}{(2\pi)^3}\frac{1}{k_B T^2}\sum_\alpha \int_{BZ} d^3k \frac{[\hbar\omega(\mathbf{k},\alpha)]^2 e^{\beta\hbar\omega(\mathbf{k},\alpha)}}{(\exp[\beta\hbar\omega(\mathbf{k},\alpha)]-1)^2} \tag{4.31}$$

Here, $\omega(\mathbf{k},\alpha)$ is the frequency of one of the three modes with wave vector $\mathbf{k}$. The integral in (4.31) is over the Brillouin zone.

4.1.7 Debye model

We next describe a simplified model which allows us to evaluate (4.31), to a good approximation. In the *Debye model* one makes the following assumptions:

(1). The frequency of a normal mode with wave vector $\mathbf{k}$ is approximated as

$$\omega(\mathbf{k},\alpha) = sk \tag{4.32}$$

where s is an average sound velocity.

(2). The Brillouin zone is approximated by a sphere. The radius q_D of the sphere is given by the requirement that the number of allowed wave vectors inside the sphere should be equal to the number of atoms N

$$\frac{4\pi}{3}{q_D}^3\frac{V}{(2\pi)^3} = N$$

or

$$q_D = (6\pi^2\frac{N}{V})^{1/3} \tag{4.33}$$

The maximum phonon frequency in the Debye model is called the *Debye frequency*

$$\omega_D = sq_D \tag{4.34}$$

We also define the *Debye temperature* as

$$\theta_D = \frac{\hbar\omega_D}{k_B} \tag{4.35}$$

We substitute (4.32) into (4.31)

$$C_V = \frac{3V}{(2\pi)^3}\frac{4\pi}{k_B T^2}\int_0^{q_D} k^2 dk \frac{\hbar^2 s^2 k^2 e^{\beta\hbar sk}}{(e^{\beta\hbar sk}-1)^2}$$

Table 4.1: Debye temperatures of some elements and compounds

Element	$\theta_D[K]$	Compound	$\theta_D[K]$
Li	335	$NaCl$	280
Na	156	KCl	230
K	91	CaF_2	470
Cu	343	LiF	680
Ag	226	Quartz	255
Au	162		
Al	428		
Ge	378		
Si	647		
Diamond	1860		

(The factor of 3 comes from the sum over α.). We introduce the dimension less variable $x = \beta\hbar sk$ and find

$$C_V = \frac{3V}{2\pi^2}\frac{{k_B}^2T^3}{\hbar^3 s^3}\int_0^{\beta\hbar s q_D}\frac{x^4e^x dx}{(e^x-1)^2}$$

which simplifies, using (4.33) (4.34) and (4.35), to

$$C_V = 9Nk_B(\frac{T}{\theta_D})^3\int_0^{\theta_D/T}\frac{x^4e^x dx}{(e^x-1)^2} \tag{4.36}$$

Equation (4.36) can be evaluated analytically in some limits. At low temperatures $\theta_D/T \to \infty$. The integral in (4.36) can the be evaluated analytically to

$$\int_0^\infty \frac{x^4e^x dx}{(e^x-1)^2} = \frac{4\pi^4}{15}$$

and we get

$$\lim_{T\to 0} C_V = \frac{12\pi^4}{5}Nk_B\left(\frac{T}{\theta_D}\right)^3 \tag{4.37}$$

i. e. the low temperature specific heat will be proportional to T^3. For high temperatures we note that for small values of x the integrand in (4.36) is $\simeq x^2$. The integral is then $\simeq \frac{1}{3}(\theta_D/T)^3$ and we recover the Dulong and Petit heat capacity. Finally, we not that if we plot the specific heat per mol vs. the temperature in units of the Debye temperature, (4.36) predicts a universal curve (see figure

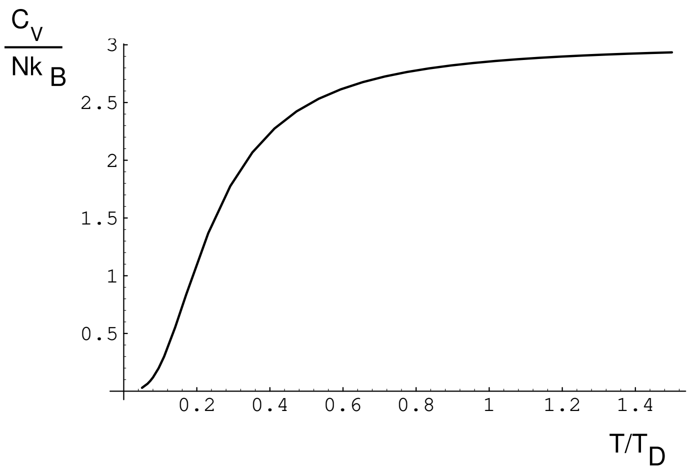

Figure 4.5: Heat capacity in the Debye model.

4.5). This prediction is remarkably accurate. To get the good agreement the Debye temperature should be considered as a fitting parameter, i.e. the value of θ_D was chosen which gave the best overall fit. Some fitted Debye temperatures are tabulated below.

4.1.8 Problems

Example

Consider a linear chain of atoms. Each atom interacts with its nearest neighbor on either side via a Lennard-Jones potential (3.2). Assume parameter values appropriate to krypton (tables 3.1and 5.2).

(a). Find the equilibrium spacing between the atoms.

(b). Find the sound velocity.

(c). What is the maximum frequency?

Solution

Each atom interacts with its nearest neighbor on either side via a Lennard-Jones potential with $\sigma = 3.65\text{Å}$, $\epsilon = 0.014eV$. The interatomic potential is

$$v(r) = 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6}]$$

(a). The equilibrium spacing can be obtained from

$$\frac{\partial v}{\partial r} = 0 = -\frac{4\epsilon}{r}[12(\frac{\sigma}{r})^{12} - 6(\frac{\sigma}{r})^{6}]$$

with solution

$$r = a = 2^{1/6}\sigma = 4.0970 \times 10^{-10} m$$

(b). The mass of a Krypton atom is $m = 83.80 \times 1.66042 \times 10^{-27} = 1.39 \times 10^{-25} kg$ The force constant of the chain is

$$K = \left(\frac{\partial^2 v}{\partial r^2}\right)_{r=a} = \frac{4\epsilon}{r^2}[12 \times 13(\frac{\sigma}{r})^{12} - 6 \times 7(\frac{\sigma}{r})^6] = 0.92 N m^{-1}$$

The sound velocity is then

$$s = a\sqrt{\frac{K}{m}} = 1070 m s^{-1}$$

(c). The maximum frequency is

$$\omega_{max} = 2\sqrt{\frac{K}{m}} = 5.2 \times 10^{12} rad\ s^{-1}$$

Problem 4.1-1:

The harmonic chain model can be solved also when the interaction between the masses extends beyond the nearest neighbors. Consider the case when the n'th mass is connected to masses $n+1$ and $n-1$ with the spring constant K_1 and to masses $n+2$ and $n-2$ with the spring constant K_2. The equation of motion for the $n'th$ mass is now

$$m\ddot{u} = K_1(u_{n+1} + u_{n-1} - 2u_n) + K_2(u_{n+2} + u_{n-2} - 2u_n) \tag{4.38}$$

Assume periodic boundary conditions and solutions of the form

$$u_n = Ae^{i(kan - \omega t)} \tag{4.39}$$

where a is equilibrium lattice spacing.
(a) Find a formula for ω as a function of k.
(b) Plot $\omega\sqrt{m/K_1}$ vs. ka for the special case $K_1 = K_2$.

Problem 4.1-2:

Plot the state of a monatomic chain of 100 atoms with periodic boundary conditions that has been "kicked" or "plucked" by evaluating (4.18) and (4.21) for a sequence of times. Give a physical interpretation of the evolving pattern, by making use of the fact that the sound velocity increases with increasing wavelength.

4.2 Sommerfeld model for electrons

In order to find the electronic states in a crystal one must solve the Schrödinger equation for the electrons in the presence of a potential with the periodicity of the lattice. The resulting *electronic band structure calculation* represents a problem which is beyond this course. Instead we will address an idealized problem in which the electrons experience a constant potential. This is the so called *Sommerfeld model*, and it turns out to be sufficient to explain a number of qualitative properties of metals.

4.2.1 Electron gas

The volume of the box is $V = L^3$. First consider the simplest case of periodic boundary conditions. The wave function of the particle satisfies

$$\psi(x=0) = \psi(x=L).$$

The quantum eigenstates of the system are then given by

$$\psi(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot r} = \frac{1}{\sqrt{V}} \exp(i[k_x x + k_y y + k_z z])$$

where

$$k_x = \frac{2\pi n_x}{L}, k_y = \frac{2\pi n_y}{L}, k_z = \frac{2\pi n_z}{L}$$

and n_x, n_y, n_z can take on the values $0, \pm1, \pm2...$ i.e. are integers. The x-component of the momentum is $p_x = \hbar k_x = hn_x/L$ and we have similar expressions for the other components. Consider now a volume in phase space $W = L^3 \Delta p_x \Delta p_y \Delta p_z$ where the components are in the intervals

$$\begin{aligned} p_1 &< p_x < p_1 + \Delta p_x \\ p_2 &< p_x < p_2 + \Delta p_y \\ p_3 &< p_z < p_3 + \Delta p_z \end{aligned} \tag{4.40}$$

We find that the number of states in W is given by

$$N_W = \frac{L^3 \Delta p_x \Delta p_y \Delta p_z}{h^3} = \frac{W}{h^3} \tag{4.41}$$

The counting rule (4.41) must be applied with some discretion. Suppose we change the boundary conditions and consider a box with hard walls. The boundary condition is $\psi = 0$ at surface. The eigenstates are now

$$\psi = \sqrt{\frac{8}{\pi}} \sin(k_x x) \sin(k_y y) sin(k_z z)$$

with

$$k_x = \frac{\pi n_x}{L},\ k_y = \frac{\pi n_y}{L},\ k_z = \frac{\pi n_z}{L} \tag{4.42}$$

Note the absence of the factor of 2 in (4.42). The number of states in the interval (4.40) is then

$$\frac{2^3 \Delta p_x \Delta p_y \Delta p_z L^3}{h^3} = \frac{8W}{h^3}$$

The reason for this apparent paradox is that the 'standing wave' states associated with the hard wall boundary condition must be considered to be mixtures of states propagating back and forth. The states k_x and -k_x are not distinct. So while

$$\frac{\#\ of\ states}{Volume\ of\ phase\ space} = 8\ times\ larger$$

only 1/8 th of the momentum states are distinct.

4.2.2 Free electron gas at zero temperature

At zero temperature the system will be in its lowest energy state, the *ground state*. Electrons are *Fermions* and the Pauli exclusion principle for Fermions states that no two particles can occupy the same state. The single particle states can be characterized by a wave vector $\mathbf{k}$ and spin σ. The number of allowed k-values inside a "volume" d^3k in k-space is from (4.41), noting the relation $p = \hbar k$ between momentum and wave-vector

$$\frac{Vd^3k}{(2\pi)^3}$$

When summing over allowed k-states we can replace a sum by an integral in the large V, or continuum limit

$$\sum_{\mathbf{k}} \to \frac{V}{(2\pi)^3} \int d^3k \tag{4.43}$$

We will neglect the interaction between the electrons. The energy of a state with wave vector k is $E_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m}$, i.e. it increases monotonically with increasing k. The lowest energy state then has all momentum states occupied up to a maximum wave vector k_F, the *Fermi wave vector* . The number of states with wave vector less than k_F is then (including a factor 2 for spin)

$$N = V\frac{2 \times 4\pi {k_F}^3}{3(2\pi)^3} = \frac{V{k_F}^3}{3\pi^2}$$

We refer to the k-space volume with $k < k_F$ as the *Fermi sphere* and its surface as the *Fermi surface* . The momentum of a particle with wave vector k_F is called the *Fermi momentum* $p_F = \hbar k_F$. The energy of a particle with wave vector k_F is the *Fermi energy*

$$\epsilon_F = \frac{{p_F}^2}{2m} \tag{4.44}$$

The free electron gas is often used as a starting point to describe the electronic properties of metals. Let us make some order of magnitude estimates from this application.

Length: The *Wigner-Seitz radius* r_s is defined as the ratio

$$\frac{radius\ of sphere\ containing\ one\ electron}{Bohr\ radius}$$

so that

$$\frac{V}{N} = \frac{4\pi {a_0}^3 {r_s}^3}{3}$$

Here $a_0 = 0.529 \times 10^{-10} m$ is the Bohr radius. If Z is the valence of a metal then the number of conduction electrons is $N = ZN_{atoms}$. From tables of the density, atomic weight and Avogadro's number one can then work out the value of r_s. For the metallic elements one typically has $2 < r_s < 6$. Aluminum is a high density metal with $r_s = 2.07$, cesium is a low density metal with $r_s = 5.62$.

Wave vectors: We have

$$\frac{{k_F}^3}{3\pi^2} = \frac{N}{V} = \frac{3}{4\pi {a_0}^3 {r_s}^3} \tag{4.45}$$

giving

$$a_0 k_F = \left(\frac{9\pi}{4}\right)^{1/3} \frac{1}{r_s} = \frac{1.92}{r_s} \tag{4.46}$$

The Fermi wave vector k_F is of the order of the inverse Bohr radius.

Velocity: The *Fermi velocity* is given by

$$v_F = \frac{\hbar k_F}{m} = \frac{4.2}{r_s} \times 10^6 ms^{-1}$$

This velocity is of the order 1% of the velocity of light, or 1000 times a typical sound velocity. We conclude that electrons in metals are supersonic, but non-relativistic.

Energy: It is instructive to compare the Fermi energy with the Rydberg, the ground state energy of the hydrogen atom. We have

$$1Ry = \frac{e^2}{4\pi\epsilon_0 2a_0} = 13.6eV$$

From (4.46)

$$\epsilon_F = \frac{\hbar^2 {k_F}^2}{2m} = \frac{\hbar^2}{2m{a_0}^2} \left(\frac{9\pi}{4}\right)^{2/3} \frac{1}{{r_s}^2} \tag{4.47}$$

Substituting numbers gives

$$\epsilon_F = \frac{50.1eV}{{r_s}^2}$$

For aluminum, $\epsilon_F = 11.7eV$, for cesium $\epsilon_F = 1.59eV$. The model which we have described above is commonly called the Sommerfeld model. We have neglected the electron-electron interaction. Real electrons are charged particles. The energy associated with the Coulomb repulsion between two electrons a distance r apart is

$$\frac{e^2}{4\pi\epsilon_0 r}$$

A typical nearest neighbor distance between electrons is $\sim a_0 r_s$ and we see that the Coulomb energy and the kinetic energy is comparable. Nevertheless, the Sommerfeld model explains many of the qualitative properties of the physics of metals. Since the kinetic energy is $\sim 1/{r_s}^2$ and the model will work best when r_s is small- and for many purposes aluminum is the most free electron like metal.

Temperature: Thermal energies available to electrons are of the order $k_B T$. It is instructive to compare this quantity to the Fermi energy. For this purpose one can define the Fermi temperature as

$$T_F = \epsilon_F / k_B$$

The Fermi temperature is $13.6 \times 10^4 K$ for Al and 1.84×10^4 for cesium. These are high temperatures compared to room temperature.

4.2.3 Low temperature electronic specific heat

At nonzero temperatures not all the electrons will occupy states inside the Fermi sphere. Some electrons will be excited from states inside the Fermi sphere to an electronic state outside the sphere leaving a *hole* behind, see figure 4.7(b). Let $f(\epsilon)$ be the probability that a state is occupied and $1 - f(\epsilon)$ the probability that it is not. We also introduce the chemical potential μ. If $\epsilon < \mu$ the normal state of the affairs is that the state is occupied, while for $\epsilon > \mu$ it is normally empty. We require that the ratio satisfies

$$\frac{f(\epsilon)}{1 - f(\epsilon)} = e^{-\beta(\epsilon - \mu)} \tag{4.48}$$

i.e. the ratio is given by a Boltzmann factor. From (4.48) the probability that a state with energy ϵ is occupied is given by the *Fermi-Dirac* distribution (figure 4.6)

$$f(\epsilon) = \frac{1}{e^{\beta(\epsilon - \mu)} + 1} \tag{4.49}$$

The mean number of particles is then given by

$$\langle N \rangle = 2\frac{V}{(2\pi)^3} \int d^3k f(\epsilon_k) \tag{4.50}$$

The condition (4.50) determines the chemical potential μ. For $T = 0$ we have $\mu = \epsilon_F$, while for $T \neq 0$ μ will be a slowly varying function of T. When discussing thermodynamic properties of the Fermi gas it is convenient to change the integration variable from wave vector to energy. We have

$$\epsilon = \frac{\hbar^2 k^2}{2m}, d^3k = 4\pi k^2 dk, \quad d\epsilon = \frac{\hbar^2 k}{m} dk$$

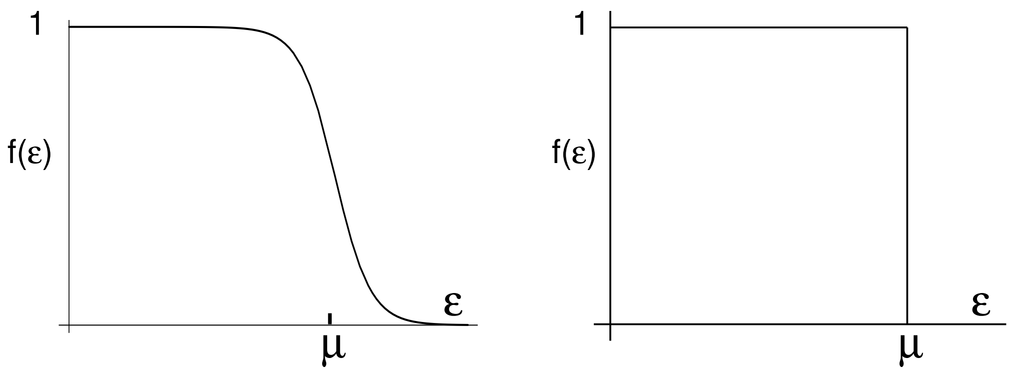

Figure 4.6: (a) The Fermi-Dirac distribution at non-zero temperature. (b) Fermi-Dirac distribution at $T = 0$

$$\langle N \rangle = \int_{-\infty}^{\infty} d\epsilon\, \mathcal{D}(\epsilon) f(\epsilon)$$

where the *density of states* is given by (see figure 4.7)

$$\mathcal{D}(\epsilon) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\epsilon}$$

The density of states is a convenient quantity when taking thermal averages. The internal energy of the ideal Fermi gas is e.g.

$$U = \int_{-\infty}^{\infty} \mathcal{D}(\epsilon) \epsilon f(\epsilon) d\epsilon \tag{4.51}$$

Let us use this result to find a formula for the specific heat

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{VN}$$

The only quantity in (4.51) which depends on temperature is $f(\epsilon)$. The trouble is that the other independent variable is μ not N. When differentiating f with respect to T we must therefore consider μ to be an implicit function of T, N, V. We can obtain the leading term in a low temperature expansion for the specific heat by noting that for $T = 0, \mu = e_F$. The temperature dependence of U at constant N comes about because of *thermal excitations* in which particles are excited into previously unoccupied states outside the Fermi surface leaving *holes* behind (figure 4.7 (b)).

We use ϵ_F as our *reference energy*: Then $\epsilon - \epsilon_F =$ is the excitation energy of a particle outside Fermi surface. Similarly the excitation energy of a hole, i.e. a particle missing from a single particle state of energy ϵ is $\epsilon_F - \epsilon$. The change in internal energy due to thermal excitations is then

$$\Delta U = \int_{\epsilon_F}^{\infty} d\epsilon (\epsilon - \epsilon_F) f(\epsilon) \mathcal{D}(\epsilon) + \int_{-\infty}^{\epsilon_F} d\epsilon (\epsilon_F - \epsilon)(1 - f(\epsilon)) \mathcal{D}(\epsilon)$$

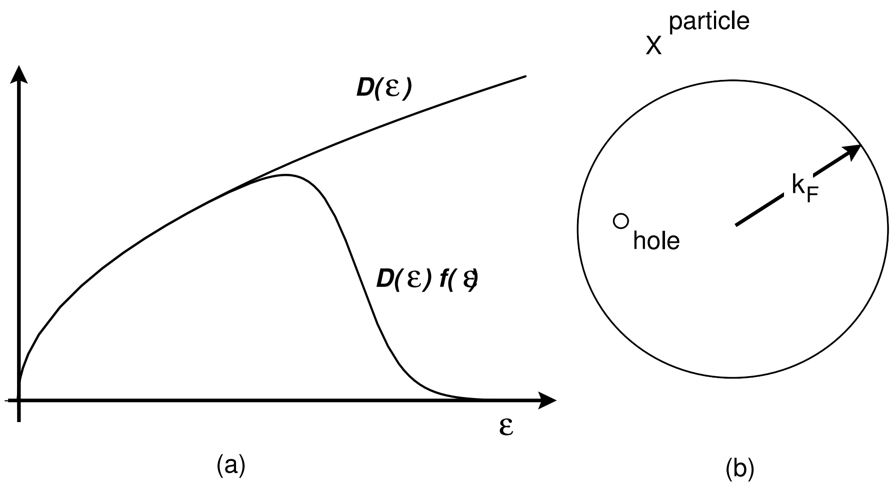

Figure 4.7: (a)Density of states of free electrons. (b) Particles and holes.

We differentiate inside the integrand to get

$$C_V = \int_{-\infty}^{\infty} d\epsilon(\epsilon - \epsilon_F)\frac{\partial f}{\partial T}\mathcal{D}(\epsilon) \tag{4.52}$$

We now approximate $\mu \simeq \epsilon_F$ and neglect the temperature dependence of μ

$$\frac{\partial f}{\partial T} = \frac{\epsilon - \epsilon_F}{k_B T^2}\frac{e^{\beta(\epsilon-\epsilon_F)}}{(e^{\beta(\epsilon-\epsilon_F)}+1)^2}$$

Because of the factor $\partial f/\partial T$ the integrand in (4.52) will be sharply peaked near $\epsilon = \epsilon_F$. If we assume that near $\epsilon = \epsilon_F, \mathcal{D}(\epsilon) \simeq \mathcal{D}(\epsilon_F)$ and put $x = \beta(\epsilon - \epsilon_F)$ we get

$$C_V \simeq {k_B}^2 T\mathcal{D}(\epsilon_F)\int_{-\infty}^{\infty} dx \frac{x^2 e^x}{(e^x+1)^2} \tag{4.53}$$

The integral in (4.53) can be evaluated to yield $\frac{\pi^2}{3}$ and we get the formula for the electronic specific heat

$$C_V = \frac{T\pi^2 {k_B}^2}{3}\mathcal{D}(\epsilon_F) \tag{4.54}$$

Note that we have not made use of the formula $\epsilon = \frac{\hbar^2 k^2}{2m}$ for the electron energy. In a metal electrons occupy *energy bands* where $\epsilon_{\mathbf{k}}$ may be a complicated function of $\mathbf{k}$. Equation (4.54) still remains valid in this situation.

If we substitute the free electron value for the energy we get

$$C_V = \frac{\pi^2 N k_B}{2}\frac{T}{T_F} \tag{4.55}$$

An important aspect of (4.54) and (4.55) is the linear temperature dependence. It can be shown that for low temperatures the contribution to the specific heat from lattice vibrations will be proportional to T^3. Therefore, the specific heat of metals at low temperatures (T$\leq 10K$) will be dominated by the electronic contribution. This contribution is still small. The factor T/T_F in (4.55) indicates that only a small fraction of the conduction electrons will be thermally excited even at room temperature. At ordinary temperatures the lattice specific heat dominates.

4.2.4 Problems

Problem 4.2-1:

In sodium metal each ions contributes one conduction electron. Using the data in table 5.1 calculate for sodium

(a). The Fermi energy
(b). The Fermi velocity
(c). The Fermi temperature.

Problem 4.2-2:

^3He atoms can be considered as Fermi particles. At low temperatures ^3He forms a liquid with a volume of $4.62 \times 10^{-29} m^3$ per helium atom. The mass of a ^3He atom is $5 \times 10^{-27} kg$. Estimate the Fermi temperature of ^3He.

Problem 4.2-3:

Show that the kinetic energy of a three dimensional gas of N free electrons is $\frac{3}{5} N \epsilon_F$.

Problem 4.2-4:

Estimate the electronic and lattice specific heats for Al at temperatures $1K,\ 10K,\ 100K$ in units of $J\ mol^{-1} K^{-1}$. Use the Sommerfeld model for the electrons and the Debye model for the phonons. Aluminum is trivalent.

4.3 Drude model

In this section we will discuss *transport properties* associated with the conduction electrons, mainly the conductivity of a metal subject to a DC electric field or an alternating electromagnetic field. The latter extension of the theory will also will allow us to discuss the optical properties of a metal.

We will employ a simple classical model, the Drude model. For simplicity we will assume that the metal is isotropic and neglect all band structure effects. Our discussion will of necessity be rather brief and we refer the reader to Ashcroft and Mermin [2], Callaway [4], Wooten [12] and Ziman [11] for a more extensive discussion.

Let us first consider the *DC conductivity* of a metal containing n conduction electrons per unit volume. Each electron will have a velocity $\mathbf{v}$ which will be some fraction of the Fermi velocity, but in the absence of an electric field the electrons are equally likely to move in any direction, so the average velocity $\langle \mathbf{v} \rangle = 0$. However , if we apply an electric field $\vec{\mathcal{E}}$ the electrons will be accelerated in the field, and there will be an average nonzero *drift velocity* $\mathbf{v}_{drift}$. We let the charge of the electrons be $e = -|e|$ and the mass be m_e. From time to time the electrons will undergo collisions with impurities and phonons and we assume that after each collision the electron will be equally likely to travel in any direction, so that immediately after each collision the average velocity is zero. Let $\mathbf{v}(\mathbf{0})$ be the velocity immediately after a collision. Some time t after that collision, but before the next collision the electron velocity will be

$$\mathbf{v}(t) = \mathbf{v}(0) + \frac{e\vec{\mathcal{E}}t}{m_e} \tag{4.56}$$

The average time between collisions, τ, is commonly called the *relaxation time.* We see from (4.56) that the drift velocity in our simple model will be

$$\mathbf{v}_{drift} = \langle \mathbf{v}(\tau) \rangle = \frac{e\vec{\mathcal{E}}\tau}{m_e} \tag{4.57}$$

The electric current density (current per unit area) is then

$$\mathbf{j} = ne\mathbf{v}_{drift} = \frac{ne^2\tau}{m_e}\vec{\mathcal{E}} \tag{4.58}$$

According to Ohm's law the electric field needed to produce a given current is given by

$$\vec{\mathcal{E}} = \rho \mathbf{j}$$

where ρ is the *resistivity.* Conversely we put

$$\mathbf{j} = \sigma_0 \vec{\mathcal{E}}$$

with σ_0 the *DC conductivity.* We thus find in the Drude model

$$\sigma_0 = \frac{ne^2\tau}{m_e} \tag{4.59}$$

It is instructive to construct a differential equation for the average velocity $\langle \mathbf{v}(t) \rangle$. If the average time between collisions is τ, the probability of a collision taking place in the time interval dt will be dt/τ. The mean speed will then increase by

$$d\langle \mathbf{v}(t) \rangle = \frac{e\vec{\mathcal{E}}dt}{m_e} \tag{4.60}$$

with probability $(1 - dt/\tau)$ or drop to zero with probability dt/τ. Neglecting terms of order dt^2 we find

$$\frac{d\langle \mathbf{v}(t) \rangle}{dt} = \frac{e\vec{\mathcal{E}}}{m_e} - \frac{\langle \mathbf{v}(t) \rangle}{\tau}$$

In the steady state $\langle \mathbf{v}(t) \rangle \rightarrow \mathbf{v}_{drift}$ and

$$\mathbf{v}_{drift} = \frac{e\vec{\mathcal{E}}\tau}{m_e}$$

and we get the same result as before.

We can also consider the response to a AC electric field

$$\vec{\mathcal{E}} = Re[\vec{\mathcal{E}}(\omega)e^{-i\omega t}]$$

Assuming a steady state response

$$\langle \mathbf{v}(t) \rangle = \mathbf{v}(\omega)e^{-i\omega t} \tag{4.61}$$

we find

$$-i\omega \mathbf{v}(\omega) = \frac{e\vec{\mathcal{E}}(\omega)}{m_e} - \frac{\mathbf{v}(\omega)}{\tau}$$

Putting $\mathbf{j}(t) = Re[\mathbf{j}(\omega)e^{-i\omega t}]$ we write

$$\mathbf{j}(\omega) = \sigma(\omega)\vec{\mathcal{E}}(\omega)$$

and we find after some algebra

$$\sigma(\omega) = \frac{\sigma_0}{1 - i\omega\tau} \tag{4.62}$$

We see that (4.62) exhibits two distinct régimes: a low frequency régime where $\omega\tau << 1$ in which the current is approximately in phase with the field, and a high frequency régime $\omega\tau >> 1$ in which the current will be approximately 90^o out of phase .

Another way of looking at the system is in terms of a complex dielectric constant.

$$\epsilon(\omega) = \epsilon_r(\omega)\epsilon_0$$

where ϵ_r is the relative dielectric constant and ϵ_0 is the permittivity of vacuum. We have

$$\vec{\mathcal{D}} = \epsilon_0\vec{\mathcal{E}} + \vec{\mathcal{P}}$$

where $\vec{\mathcal{D}}$ is the *electric displacement* and $\vec{\mathcal{P}}$ the *electric polarization* per unit volume, $\vec{\mathcal{P}} = ne\mathbf{u}$ and $\mathbf{u}$ is the displacement of an electron, caused by the applied field

$$\frac{d\mathbf{u}}{dt} = \mathbf{v}$$

In analogy with (4.61) we put $\mathbf{u} = \mathbf{u}(\omega)e^{-i\omega t}$ and find $-i\omega\mathbf{u}(\omega) = \mathbf{v}(\omega)$ and after a little algebra we find

$$\epsilon_r = 1 + \frac{i\sigma(\omega)}{\epsilon_0\omega} \tag{4.63}$$

We define the *Plasma frequency* as

$$\Omega_{pl} = \sqrt{\frac{ne^2}{\epsilon_0 m}} \tag{4.64}$$

The formula (4.63) for the relative dielectric constant can be rewritten as

$$\epsilon_r = 1 - \frac{\Omega_{pl}}{\epsilon_0\omega(\omega + i/\tau)} \tag{4.65}$$

You will learn from other courses that an electromagnetic wave with frequency ω propagates in a medium with dielectric constant ϵ_r with wave vector $\mathbf{q} = \mathbf{q}_0\sqrt{\epsilon_r}$ where $q_0 = \omega/c$ is the wave vector in vacuum. If the dielectric constant is complex the wave will be damped and it is customary to write

$$\sqrt{\epsilon_r} = n + ik$$

where n and k are *optical constants*. The normal incidence reflectivity from vacuum can be shown to be given in terms of the optical constants as

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \tag{4.66}$$

In figure 4.8 we plot the optical constants and the reflectivity in the Drude model. For frequencies which are small compared to the plasma frequency the imaginary part of the index of refraction will be large and electromagnetic waves can only penetrate a short distance in a metal (skin effect). The intensity of the wave will decay according to

$$I \propto \mathcal{E}^2 \propto \exp\left(-\frac{2\omega k}{c}z\right)$$

where z is the penetration depth.

For frequencies higher than the plasma frequencies k will typically be very small and the metal will be transparent to electromagnetic radiation. Similarly, the reflectivity of a metal will be high for frequencies below the plasma frequency, and low for higher frequencies.

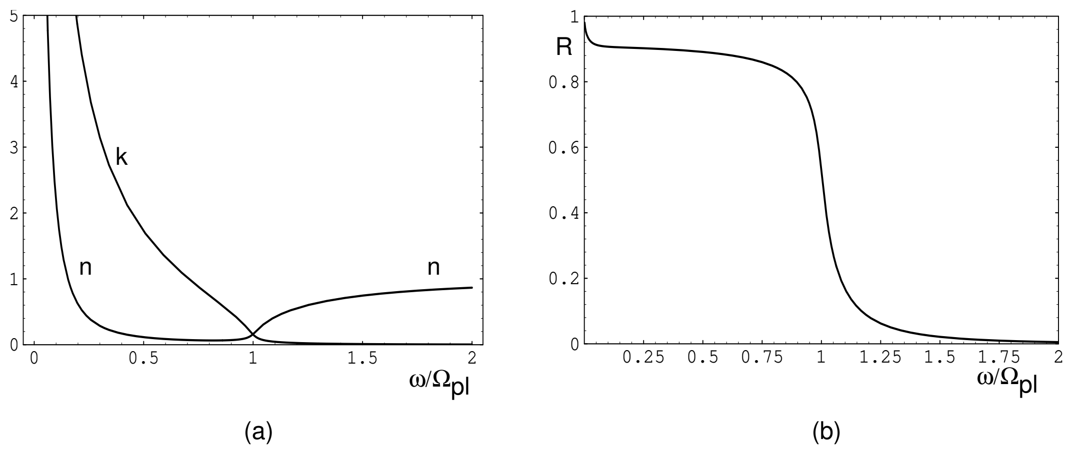

Figure 4.8: (a) Optical constants n and k and (b) normal incidence reflectivity in the Drude model. Frequencies are shown in units of the plasma frequency Ω_{pl} and the curves are drawn for the case $\Omega_{pl}\tau = 20$

4.4 Problems

Problem 4.3-1

(a). The relaxation time τ for an aluminum sample is $0.8 \times 10^{-14}s$. Calculate the DC resistivity.
(b). Calculate the plasma frequency for Aluminum (note that Al is trivalent, values of required physical constants can be found near the end of Part I of the lecture notes).
(c). To what electromagnetic wavelength in vacuum will the plasma frequency correspond in Aluminum.

Problem 4.3-2

Consider a metal for which $\omega_{pl}\tau >> 1$. The dielectric constant for frequencies larger than the plasma frequencies will then be approximately real, but less than one. The *phase velocity* for electromagnetic waves is ω/q, with the wave vector $q = 2\pi/\lambda$. The phase velocity for $\omega > \Omega_{pl}$ will then be faster than the speed of light. This will not violate special relativity since signals propagate with the *group velocity* given by $v_{group} = d\omega/dq$.

(a). Show that the group velocity of light is less that the speed of light for $\omega > \Omega_{pl}$ in the Drude model.

(b). One consequence of the fact that for $\omega > \Omega_{pl}$ the index of refraction $n < 1$ in the Drude model is that there will be *total reflection* of X-rays impinging with an angle of incidence larger than a critical angle given by $\sin(\theta_c) = n$. Calculate the critical angle of incidence for light with frequency $2\Omega_{pl}$.

Problem 4.3-3

Calculate the penetration depth at which the intensity of an electromagnetic wave in Aluminum relaxation time $\tau = 0.8 \times 10^{-14} s$ will be reduced by a factor of 2 at the frequency of

(a). $\omega = 2\pi 10^7 Hz$.

(b).$\omega = 2\pi 10^{14} Hz$.

Chapter 5

Review

5.1 Midterm review problems

Problem 5.1-1:

(a). Which crystal planes of the copper metal structure have the highest density of atoms?

(b). What is the density of atoms per cm^2 in these planes?

(c). Find the Bragg angle(s) for reflection of x-rays of wave-length 1.50 Å against these planes?

(d). Calculate the density of copper in g/cm^3 from the data in 5.1. The atomic weight of Copper is $63.54g/mol$

Problem 5.1-2:

(a). Describe the diamond lattice. Is it a Bravais lattice? If not, describe it as a Bravais lattice with the smallest possible number of basis vectors.

(b). Find the angle between any two of the lines (bonds) joining a site of the diamond lattice to its four nearest neighbors.

Problem 5.1-3:

The primitive lattice vectors of a lattice are

$$\mathbf{a} = \frac{a}{2}(-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}); \quad \mathbf{b} = \frac{a}{2}(\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}}); \quad \mathbf{c} = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}})$$

where $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, $\hat{\mathbf{z}}$ are three unit vectors along Cartesian axes.

(a). What is the Bravais lattice?

(b). Find three primitive reciprocal lattice vectors.

(c). Which lattice plane has the highest density of atoms? Calculate the density of atoms per unit area for this plane.

Problem 5.1-4:

(a). Which of the following crystal structures are Bravais lattices: the hexagonal closed packed, the body centered cubic, the face centered cubic, the diamond structure?

(b). Find a set of primitive reciprocal lattice vectors for the structures listed above.

Problem 5.1-5:

Zinc crystallizes in the hexagonal closed packed structure, with a c/a ratio slightly different from the ideal value $\sqrt{8/3}$). The atomic weight of Zn is 65.37. Calculate the mass density of Zn.

Problem 5.1-6:

(a). Explain the effect of dislocations on the mechanical strength of materials.

(b). Discuss the strengths of very well prepared crystals, perfect crystals, and relatively poorly prepared crystals. Which are strongest or weakest and why?

(c) In an ionic crystal such as NaCl the vacancy formation energy will be different for positive and negative ion vacancies. Nevertheless, if the crystal is pure the concentration of positively and negatively charged vacancies will be roughly the same. Describe the mechanism through which this comes about.

(d) Define Burger's vector.

5.2 Old Midterms

Midterm examination February 1992

"Closed book exam"

1:

Silicon crystallizes in the diamond structure (fcc with a basis vector $\frac{1}{4}[111])and$a= 5.43 Å the side of the unit cube. The atomic number of Si is 28.09.

(a). Calculate the density of Si in kg/m^3.

(b). What type of structure is the reciprocal lattice of Si?

(c). Write down a set of primitive reciprocal lattice vectors for Si.

2:

The element Xe crystallizes in the fcc structure at low temperatures. Assume an interatomic Lennard-Jones potential with $\sigma = 3.98$ Å and $\epsilon = 0.020eV$. Calculate the nearest neighbor distance in Å of Xe and the cohesive energy in $eV/atom$ at low temperatures.

3:

Describe briefly the *Ewald construction* and its use in the rotating crystal method of crystal structure determination.

Some formulas:

Avogadro's number is 6.022×10^{23}, an atomic mass unit is $1.67 \times 10^{-27} kg$. 1Å$= 10^{-10}m$. The Lennard Jones potential is

$$v(r) = 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6]$$

$$A_n = \sum_{\mathbf{R}} (\frac{r_{nn}}{R})^n$$

$A_6 = 14.45$, $A_{12} = 12.13$ for the fcc lattice.

Midterm examination February 1993

Allowed aids: 2 page handwritten “Cheat sheet”, calculator. Answer all questions.

1:

A certain lattice has a primitive unit cell with the dimensions $a = 3$Å, b= 4Å, c= 5Å, $\alpha = \beta = 90°$, $\gamma = 60°$.

(a). Write down a set of primitive lattice vectors **a, b** and **c** on Cartesian form.

(b). Construct a set of primitive reciprocal lattice vectors.

2:

Iron is a body centered cubic metal. The edge of the unit cube is $a = 2.87$Å.

(a). Which lattice planes of the iron structure have the highest density of atoms?

(b). What is the density of $atoms/m^2$ in these planes? (1 Å$= 10^{-10}m$).

(c). Find the Bragg angle(s) for reflection against these planes if x-rays of wavelength 1.54 Å are employed. (The formula for Bragg scattering is $2d \sin\theta = n\lambda$).

3:

(a). Sketch the Wigner Seitz cell of the triangular lattice.

(b). Define edge and screw dislocations.

(c). What is the difference between the bulk modulus B and Young's modulus Y? Which one will be largest of the two? (Describe the difference in words, no formulas are required).

Midterm examination February 1994

Allowed aid: Calculator, 2 page "cheat sheet"
Answer all 3 questions.

1:

In each of the following cases indicate if the structure is a Bravais lattice. If it is, give three primitive lattice vectors, if it is not describe it as a Bravais lattice with as small as possible basis. In all cases the side of the unit cube is a.

(a). Base centered cubic (simple cubic with additional points in the centers of the horizontal faces of the cubic cell).

(b). Side centered cubic (simple cubic with additional points in the centers of the vertical faces of the cubic cell).

(c). Edge centered cubic (simple cubic with additional points at the midpoints of the lines joining nearest neighbors).

2:

(a). Write down a set of Bravais primitive lattice vectors **a, b** and **c** and basis vector **d** for the hexagonal close packed lattice.

(b). Show that the ideal c/a ratio is $\sqrt{8/3}$.

(c). Zinc has atomic weight 65.37 and crystallizes in a hexagonal closed packed structure with $a = b = 2.66$Å, $c = 4.95$Å, i.e. the c/a ratio is slightly different from the ideal. Calculate the mass density of Zinc in g/cm^3.

3:

An isotropic elastic material is shaped like a cube. The faces of the cube are subject to a uniform pressure P, and no other stresses.

(a). Express the components of the strain in terms of P and the Lamé coefficients λ and μ defined by $C_{11} = \lambda + 2\mu$, $C_12 = \lambda$, $C_{44} = \mu$.

(b). Find the dilation (fractional volume change).

(c). Define the Young's modulus and the bulk modulus. Why are they different?

Values of physical constants

Atomic mass unit $amu = 1.66042 \times 10^{-27}$ kg

Avogadro's number $N_A = 6.0225 \times 10^{23} mol^{-1}$

Midterm examination February 1995

Allowed aid: Calculator, 2 page "cheat sheet"

Answer all 3 questions.

1: Zinc crystallizes in the hexagonal closed packed structure, with $a = 2.66$ Å, $c = 4.95$ Å (The c/a ratio is slightly different from the ideal value $\sqrt{8/3}$). The atomic weight of Zn is 65.37, $1 a.m.u. = 1.6604 \times 10^{-27} kg$.

(a). Calculate the mass density of Zn.

(b). Write down a set of reciprocal lattice vectors.

(c). Calculate the distance between the (011) planes.

2: The element Kr crystallizes in the fcc structure at low temperatures. Assume an interatomic Lennard-Jones potential

$$v(r) = 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6]$$

We have $A_6 = 14.45$, $A_{12} = 12.13$ for the fcc lattice with

$$A_n = \sum_{\mathbf{R}} (\frac{r_{nn}}{R})^n$$

The nearest neighbor distance is $r_{nn} = 3.99$ Å for Kr and the cohesive energy is -0.120 $eV/atom$ at low temperatures.

(a). Derive formulas which express the cohesive energy and the nearest neighbor distance in terms of σ and ϵ.

(b). Calculate the Lennard-Jones parameters σ and ϵ.

3: An isotropic elastic material is subject to a uniform tension T in the $z-$direction and no other stresses.

(a). Express the components of the strain in terms of T and the Lamé coefficients λ and μ defined by $C_{11} = \lambda + 2\mu$, $C_{12} = \lambda$, $C_{44} = \mu$.

(b). Find the dilation (fractional volume change).

Solution to 1995 midterm

1:

(a):

The volume per unit cell is

$$v_c = ca^2 \frac{\sqrt{3}}{2}$$

Since there are two Zinc atoms per primitive unit cell the mass density is

$$\rho = \frac{2m_{Zn}}{v_c} = \frac{4 \times 65.37 \times 1.6604 \times 10^{-27}}{\sqrt{3}4.95 \times 2.66^2 \times 10^{-30}} = 7156 kg\ m^{-3}$$

(b):

If we choose the direct lattice vectors to be

$$\mathbf{a} = a\hat{\mathbf{x}};\ \mathbf{b} = a(\frac{\hat{\mathbf{x}}}{2} + \frac{\sqrt{3}\hat{\mathbf{y}}}{2});\ \mathbf{c} = c\hat{\mathbf{z}}$$

we find the following set of primitive reciprocal lattice vectors

$$\mathbf{A} = \frac{2\pi \mathbf{b} \times \mathbf{c}}{v_c} = \frac{2\pi}{a}(\hat{\mathbf{x}} - \frac{\hat{\mathbf{y}}}{\sqrt{3}});\ \mathbf{B} = \frac{2\pi \mathbf{c} \times \mathbf{a}}{v_c} = \frac{4\pi \hat{\mathbf{y}}}{a\sqrt{3}};\ \mathbf{C} = \frac{2\pi \mathbf{a} \times \mathbf{b}}{v_c} = \frac{2\pi}{c}$$

(c):

The distance between the (011) planes is

$$d = \frac{2\pi}{|\mathbf{B} + \mathbf{C}|} = \frac{a}{\sqrt{\frac{4}{3} + \frac{a^2}{c^2}}} = 2.09 \mathring{A}$$

2:

(a):

The internal energy per particle is

$$\frac{U}{N} = 2\epsilon \left\{ A_{12} \left(\frac{\sigma}{r_{nn}} \right)^{12} - A_6 \left(\frac{\sigma}{r_{nn}} \right)^6 \right\}$$

has a minimum when

$$\frac{\partial U}{N \partial r_{nn}} = 0 = -\frac{12}{r_{nn}} A_{12} \left(\frac{\sigma}{r_{nn}} \right)^{12} + \frac{6}{r_{nn}} A_6 \left(\frac{\sigma}{r_{nn}} \right)^6$$

giving

$$\left(\frac{\sigma}{r_{nn}}\right)^6 = \frac{A_6}{2A_{12}}$$

or

$$r_{nn} = \left(\frac{2A_{12}}{A_6}\right)^{1/6}\sigma$$

If we substitute this result into the expression for the internal energy we find

$$\frac{U}{N} = \frac{\epsilon}{2}\frac{A_6^2}{A_{12}}$$

(b):

We have

$$\sigma = r_{nn}\left(\frac{A_6}{2A_{12}}\right)^{1/6} = 3.66\mathring{A}$$

and

$$\epsilon = \frac{2UA_{12}}{A_6^2} = 0.0139eV$$

3:

(a):

We have

$$\begin{bmatrix} 0 \\ 0 \\ T \\ 0 \\ 0 \\ 0 \end{bmatrix} = \begin{bmatrix} \lambda+2\mu & \lambda & \lambda & 0 & 0 & 0 \\ \lambda & \lambda+2\mu & \lambda & 0 & 0 & 0 \\ \lambda & \lambda & \lambda+2\mu & 0 & 0 & 0 \\ 0 & 0 & 0 & \mu & 0 & 0 \\ 0 & 0 & 0 & 0 & \mu & 0 \\ 0 & 0 & 0 & 0 & 0 & \mu \end{bmatrix} \begin{bmatrix} e_1 \\ e_2 \\ e_3 \\ e_4 \\ e_5 \\ e_6 \end{bmatrix}$$

We find $e_4 = e_5 = e_6 = 0$. This gives

$$\begin{aligned} 0 &= (\lambda+2\mu)e_1 + \lambda e_2 + \lambda e_3 \\ 0 &= \lambda e_1 + (\lambda+2\mu)e_2 + \lambda e_3 \\ T &= \lambda e_1 + \lambda e_2 + (\lambda+2\mu)e_3 \end{aligned}$$

The solution is

$$e_3 = \frac{T(\lambda+\mu)}{\mu(3\lambda+2\mu)}$$

$$e_1 = e_2 = \frac{-T\lambda}{2\mu(3\lambda+2\mu)}$$

(b):

The dilation is given by

$$\delta = e_1 + e_2 + e_3 = \frac{T}{2\mu+3\lambda}$$

Midterm exam February 1996

Allowed aids: Calculator, 2 page "cheat sheet".

Answer all questions

1: The CsCl structure is simple cubic with a basis vector $\mathbf{d} = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$. It is a common lattice structure for ionic materials and differs from the *bcc* lattice only in that the body center and corner sites are occupied by atoms of different species.

(a) If the two types of ions in the CsCl are of the same size what is the packing fraction f?

(b) What is the packing fraction if the radius of one type of ions is twice that of the other type?

2: Iron is a *bcc* metal with $a = 2.87$ Å.

(a) Find a set of primitive reciprocal lattice vectors for iron.

(b) Find the scattering angles (angles between incident and scattered wave vectors) for x-rays of wave vector$\lambda = 1.54$ Å impinging upon a powder sample of iron. (Bragg's law of scattering is $2d \sin\theta = n\lambda$, where θ is the angle of incidence and d is the distance between lattice planes).

3: In an isotropic material it is conventional to describe the elastic constants in terms of the Lamé constants $\lambda = C_{12}$ and $\mu = C_{44}$. The elastic constant C_{11} is then given by $\lambda + 2\mu$. In a certain material $\lambda = 1. \times 10^{10}$ Nm^{-2}, $\mu = 0.5 \times 10^{10}$ Nm^{-2}. A wire made of this material of cross section 1 mm^2 is pulled (subject to uniaxial tension) so that its length increases by 1%.

(a) What is the force required to pull the wire?

(b) What is the change in the cross sectional area of the wire?

5.3 Old finals

April 1993 Final

Time 3 hours. Allowed aids: One double sided 'cheat sheet', calculator. Answer 5 out of the 7 questions. All questions have equal value. If you answer more than 5 questions you will be given credit for the 5 best answers.

1:

An A^+ B^- ionic solid crystallizes in the $NaCl$ structure (i.e. the lattice is fcc with a basis vector $\mathbf{d} = \frac{a}{2}\hat{\mathbf{x}}$, where a is the side of the unit cube).

(a). Assuming that the positive and negative ions have equal size what is the packing fraction of the material?

(b). If the positive ion has a radius which is $\frac{1}{2}$ that of the negative ion what would the packing fraction be?

2:

(a). What is the Ewald construction?

(b). Describe the Laue method of X-ray diffraction.

(c). Describe the rotating crystal method of crystal structure determination.

3:

An isotropic elastic material is shaped like a cube. The faces which are parallel to the $x - z$ and $y - z$ planes are subject to a uniform pressure P, while the faces parallel to the $x - y$ plane are not subject to any external force. The elastic constants of the material are $C_{11} = \lambda + 2\mu$, $C_{12} = \lambda$ and $C_{44} = \mu$.

(a). Find the components of the strain.

(b). What are the stresses acting on a (110) surface?

4:

Aluminum is face centered cubic with the side of the unit cube $a = 4.05 \times 10^{-10}$ m. The Debye temperature is $428K$.

(a). Find the Debye wave vector q_D.

(b). What is the sound velocity?

5:

Beryllium has the h.c.p. structure with lattice constants $a = 2.27 \times 10^{-10} m$, $c = 3.59 \times 10^{-10} m$. Each ion contributes 2 conduction electrons. Assuming Beryllium to be a free electron metal

(a). Calculate the Fermi energy of Beryllium.

(b). Calculate the Fermi velocity.

6:

(a). What is chirality?

(b). Describe the features of chiral nematic liquid crystals which makes them useful as thermometer materials.

7:

(a). Describe the micellar and lamellar phases of soaps.

(b). Describe how a polymer dispersed liquid crystal display works.

April 1994 final

Time 2 1/2 hours. Allowed aids: One double sided hand written 'cheat sheet', calculator. Answer 4 out of the 5 questions. All questions have equal value. If you answer more than 4 questions you will be given credit for the 4 best answers.

1:

Given the table of physical properties of sodium and the values of the physical constants listed at the end of the paper find

a: the nearest neighbor distance of two sodium ions.

b: a set of primitive reciprocal lattice vectors.

c: the scattering angles (angle between incident and scattered wave vector) ϕ for x-rays of wavelength $\lambda = 1.54$ Åimpinging upon a powder sample of sodium. (Bragg's law of scattering is $2d \sin\theta = n\lambda$, where θ is the angle of incidence, and d is the distance between planes.)

2:

Assume that the conductivity σ of sodium is given by $\sigma = ne^2\tau/m$, where n is the number of valence electrons per unit volume, e the electron charge, and m the electron mass. Use the table of physical properties of sodium and the values of the physical constants listed at the end of the paper to find

a: the relaxation time τ

b: the electron drift velocity if a current of $10^5 Amp\, m^{-2}$ passes through a sodium sample.

c: Assume that the sodium specific heat is given by the Dulong-Petit value $C_V = 3Nk_B$. How fast will the temperature rise if a current of $10^5 Amp\, m^{-2}$ passes through a sodium sample and no heat is transported away?

3:

Use the table of physical properties of sodium and the values of the physical constants listed at the end of the paper to estimate

a: the sound velocity

b: the Fermi velocity

c: the Fermi energy of sodium in electron volts.

4:

a: What is a plastic deformation?

b: Why is the maximum shear stress σ_c of a material usually much less than the theoretical value predicted for a perfect crystal?

c: Define Burger's vector and draw pictures showing the Burger's vector for an edge and a screw dislocation.

5:

a: What is the micellar phase of a soap solution?

b: What is a chiral nematic liquid crystal?

c: Why are chiral nematics useful as thermometer materials?

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Some properties of Sodium Metal

Valence	+1	Structure	body centered cubic	Debye temperature	156 K
Density	0.97 g cm^{-3}	Conductivity	$0.21\times10^{6}\ \Omega^{-1}cm^{-1}$	Weight of 1 mol	22.99 g

April 1995 final

Time 2 1/2 Hours. Allowed aids: One double sided hand written 'cheat sheet', calculator. Answer 4 of the 5 questions. If you answer all the questions you will be given credit for the 4 best answers. All questions have equal value. You will find values of some physical constants on the last page.

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1:

Potassium is a bcc metal with one valence electron per potassium ion. The side of the unit cube is $a = 5.23$ Å. The Debye temperature is $91K$ and the atomic weight of potassium is $39.10gmol^{-1}$. What is

a: The plasma frequency Ω_{pl}?

b: The velocity of sound?

c: The heat capacity at room temperature of $1kg$ of potassium (in JK^{-1})?

d: The Fermi energy (in electron volts)?

————————————

2:

Consider a linear chain of N atoms. Each atom interacts with its nearest neighbor on either side with a potential

$$V(x) = V_0 + \frac{K}{2}(x-a)^2$$

where x is the distance between two nearest neighbor atoms and V_0, K and a are constants.

a: Find the velocity of sound.

b: Find the phase and group velocity of a lattice wave with wave vector $k = \frac{\pi}{4a}$.

c: Sketch the displacements u along the chain for the lattice wave in **(b)** at an instant in time when the amplitude of an atom at the origin is at its maximum value.

————————————

3:

In a good conductor the relaxation time τ will be sufficiently long that $\omega\tau >> 1$, when the frequency ω is larger than the plasma frequency Ω_{pl}. The relative dielectric function ϵ_r can then be taken as real, as can the index of refraction $n = \sqrt{\epsilon_r}$. An electromagnetic wave propagates in such a metal with wave vector $\mathbf{q} = n\mathbf{q}_0$, where $q_0 = \omega/c$ and c is the velocity of light in vacuum. Consider a metal for which

$$\epsilon_r = 1 - \frac{\Omega_{pl}^2}{\omega^2}$$

a: Find the phase velocity $v_p = \omega/q$ for the wave when $\omega > \Omega_{pl}$.

b: Find the group velocity $v_g = d\omega/dq$ for the wave when $\omega > \Omega_{pl}$.

c: Show that $v_g v_p = c^2$.

d: Give a numerical answer to **(a)** and **(b)** when $\omega = 2\Omega_{pl}$.

4:

a: What type of crystal exhibits optical phonons?

b: Outline the main features of the Debye model of lattice vibrations.

c: Show that in the Debye model a solid will satisfy the Dulong-Petit law for the heat capacity for temperatures much higher than the Debye temperature.

5:

a: Describe the principles behind the twist nematic liquid crystal cell in a liquid crystal display.

b: What is chirality? Give an example of an object which is chiral and one which is not.

c: What is a chiral nematic?

Solution to April 95 final

1:

a:

The plasma frequency is given by

$$\Omega_{pl} = \sqrt{\frac{ne^2}{\epsilon_0 m_e}}$$

The electron density n is, since potassium has valence one,

$$n = \frac{1}{v_c} = \frac{2}{a^3}$$

Putting the terms together we find

$$\underline{\Omega_{pl} = 6.67 \times 10^{15} rads^{-1}}$$

b:

The sound velocity is given by

$$s = \frac{\theta_D k_B}{\hbar q_D}$$

we have

$$q_D = (6\pi^2 n)^{1/3} = 9.39 \times 10^9 m^{-1}$$

and find

$$\underline{s = 1270 ms^{-1}}$$

c:

The heat capacity of a sample of mass M is

$$C_V = \frac{3N_A k_B M}{m_w}$$

where m_w is the molecular weight. We find

$$\underline{C_V = 638 J\ kg^{-1}\ K^{-1}}$$

d: The Fermi energy is

$$\epsilon_F = \frac{\hbar^2 k_F^2}{2m_e}$$

we have

$$k_F = (6\pi^2 n)^{1/3} = 7.45 \times 10^9 m$$

Substituting numbers using $1eV = 1.602 \times 10^{-19}\ J$ we find

$$\epsilon_F = 2.11 eV$$

2:

a:

The equation of motion for the displacement u_n of the n'th atom on the chain is

$$m\ddot{u} = K(u_{n+1} + u_{n-1} - 2u_n)$$

The normal mode solutions can be written with l an integer

$$u_n = A_n e^{i(2\pi l n - \omega t)}$$

where with $k = \frac{2\pi l n}{a}$

$$\omega^2 = \frac{4K}{m}\sin^2(\pi l n) = \frac{4K}{m}\sin^2\frac{ka}{2}$$

for small k:

$$\omega \approx \sqrt{\frac{K}{m}}ka$$

giving for the sound velocity

$$s = \sqrt{\frac{K}{m}}a$$

b:

The phase velocity is in general

$$v_{ph} = \frac{\omega}{k} = \frac{2a}{k}\sqrt{\frac{K}{m}}\sin\frac{ka}{2}$$

for $k = \frac{\pi}{4a}$ we find

$$v_{ph} = \frac{8a}{\pi}\sqrt{\frac{K}{m}}\sin(\frac{\pi}{8}) = .97a\sqrt{\frac{2K}{m}}$$

The group velocity is in general

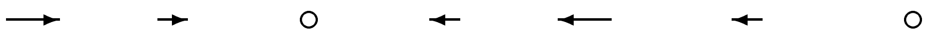
$$v_g = \frac{\partial\omega}{\partial k} = a\sqrt{\frac{4K}{m}}\cos\frac{ka}{2}$$

or for $k = \frac{\pi}{4a}$ we find

$$v_g = a\sqrt{\frac{K}{m}}\cos\frac{\pi}{8}$$

c:

We plot the displacements along the chain when $k = \frac{\pi}{4a}$ below



3:

We have for the wave vector

$$q = \frac{\omega}{c}\sqrt{1 - \frac{\Omega_{pl}^2}{\omega^2}}$$

Solving for ω gives

$$\omega = \sqrt{c^2q^2 + \Omega_{pl}^2}$$

a:

The phase velocity is

$$v_p = c\sqrt{1 + \frac{\Omega_{pl}^2}{c^2 q^2}}$$

b:

The group velocity is

$$v_g = \frac{c^2 q}{\sqrt{c^2 q^2 + \Omega_{pl}^2}} = \frac{c}{\sqrt{1 + \frac{\Omega_{pl}^2}{c^2 q^2}}}$$

c:

The way the formulas are written it is obvious that $v_g v_p = c^2$.

d:

When $\omega = 2\Omega_{pl}$, we have $c^2 q^2 = 3\Omega_{pl}^2$. The phase velocity is then $2c/\sqrt{3} = 3.46 \times 10^8 ms^{-1}$, while the group velocity is $c\sqrt{3}/2 = 2.60 \times 10^8 ms^{-1}$.

4:

a:

Optical phonons are found in crystals which exhibit lattices with a basis, i.e. in which there are more than one molecule or atom per primitive unit cell.

b:

The key features of the Debye models are

- The frequency of a normal mode with wave vector $k < q_D$ is given as $\omega = sk$ in terms of an average sound velocity s.
- The Brillouin zone is approximated by a sphere with radius $q_D = (\frac{6\pi^2 N}{V})^{3/2}$. This value of q_D assures that the number of allowed wave vectors is equal to the total number of atoms.
- The normal modes are quantized and the mean energy in each mode is

$$\langle E \rangle = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\beta\hbar\omega - 1}}$$

c:

In the limit that the temperature becomes large compared to the maximum frequency ω_D the average energy in each mode is

$$\langle E \rangle = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\beta\hbar\omega - 1}} \approx \frac{1}{\beta} = k_B T$$

The heat capacity in each mode is then just k_B and the total heat capacity becomes

$$C_V = 3Nk_B$$

which is the Dulong-Petit law.

Question **5** contains essay type questions and we refer to course handouts for details.

April 1996 final

Time $2\frac{1}{2}$ Hours. Allowed aids: One double sided hand written 'cheat sheet', calculator. Answer 4 of the 5 questions. If you answer all the questions you will be given credit for the 4 best answers. All questions have equal value. You will find values of some physical constants on the last page.

1:

(a) Describe the main types of point defects in crystals.

(b) Consider an ionic crystal of the type A^+B^-. Assume that the energy associated with moving a positive or negative ion from the bulk of the crystal to its surface is respectively ϵ_+ and ϵ_-. Derive formulas for the equilibrium vacancy concentration (% vacant sites) of positive and negative ions for *(i)*pure crystals and where c % of the positive ions have been replaced by divalent C^{++} ions.

(c) Often the actual concentrations of vacancies in a crystal is much larger than the equilibrium concentration. Discuss how this can happen.

(d) Discuss why a small amount of edge dislocations reduces the shear strength of a crystal, while adding more dislocations and/or impurities can increase the strength of a crystal.

2:

Consider a chain of atoms, all of mass m. The equilibrium distance between nearest neighbor atoms are alternatively a_1 and a_2 so that the length of the unit cell is

$$a = a_1 + a_2$$

and there are two atoms per unit cell. The spring constant of the bond of length a_1 is K_1, while the spring constant of the bond of length a_2 is K_2.

(a) Write down the equations of motion for the displacements u_1 and u_2 for the two atoms in a unit cell.

(b) Find solutions to the equation of motion on the form

$$u_1 = e_1 e^{i(kna-\omega t)}$$

$$u_2 = e_2 e^{i(kna-\omega t)}$$

and find an equation for the frequency ω as a function of the wave-vector k.

(c) Consider the special case $k = \pi/a$ and find the possible values of the frequency ω.

(d) Describe the vibrational modes when $k = \pi/a$.

3:

(a) Outline the main features of Debye model of lattice vibrations.

(b) Gold is face centered cubic with the side of unit cube $4.08 \times 10^{-10}m$. The atomic weight of gold is 197 $a.m.u.$ and the Debye temperature is $\theta_D = 162K$. Find the Debye wave-vector q_D.

(c) Estimate the sound velocity in gold.

(d) What is the room temperature heat capacity of a $1kg$ gold bar?

4:

(a). Outline the main features of the Sommerfeld (free electron) model of the conduction electrons in a metal.

(b). Present an argument why the electronic specific heat of a metal C_V is proportional to the temperature T and inversely proportional to the Fermi temperature T_F.

(c). K (potassium) is a monovalent, body centered cubic metal with $a = 5.23 \times 10^{-10}m$. Find the Fermi wave vector k_F.

(d). Find the plasma frequency Ω_{pl}.

5:

(a) Show that the kinetic energy of N free electrons at temperature $T = 0$ is $\frac{3}{5}N\epsilon_F$ where ϵ_F is the Fermi energy.

(b) The relaxation time τ for an aluminum sample is $0.8 \times 10^{-14}s$. Calculate the DC conductivity of Al. (Aluminum is face centered cubic with $a = 4.05 \times 10^{-10}m$, and trivalent).

(c) Calculate the real and imaginary part of the relative dielectric constant of Aluminum at the frequency $\omega = 2\pi \times 10^{14} rad\ s^{-1}$.

Table 5.1: Crystal structure of some common substances. Unless specified the temperature is $300K$

Substance	Structure	a,Å	cÅ	Substance	Structure	a,Å	cÅ
Ag	fcc	4.09		Ge	diamond	5.66	
Al	fcc	4.05		InSb	ZnS	6.46	
AgBr	NaCl	5.77		K	bcc	5.23	
Ar[at 4K]	fcc	5.31		KCl	NaCl	6.29	
Au	fcc	4.08		Kr[at 4K]	fcc	5.64	
Be	hcp	2.27	3.59	Na	bcc	4.23	
C(diamond)	diamond	3.57		NaCl	NaCl	5.63	
CdS	ZnS	5.82		Ne[at 4K]	fcc	4.46	
Co	hcp	2.51	4.07	Pb	fcc	4.95	
Cr	bcc	2.88		Si	diamond	5.43	
CsCl	CsCl	4.11		Xe[at 4K]	fcc	6.13	
Cu	fcc	3.61		Zn	hcp	2.66	4.95
CuCl	ZnS	5.41		ZnS	ZnS	5.41	
Fe	bcc	2.87					

5.4 Values of physical constants

1 Å$=10^{-10}m = 10nm$

Atomic mass unit $amu = 1.66042 \times 10^{-27}$ kg

Avogadro's number $N_A = 6.0225 \times 10^{23} mol^{-1}$

Bohr radius $a_0 = 0.52918$ Å

Boltzmann constant $k_B = 1.381 \times 10^{-23} J/K$

Electron charge $e = -1.602 \times 10^{-19} C$

Electron mass $m_e = 9.109 \times 10^{-31} kg$

Permittivity of vacuum $\epsilon_0 = 8.8542 \times 10^{-12} F/m$

Planck's constant $\hbar = 1.054 \times 10^{-34} kg\ m^2/s$

Speed of light $c = 2.998 \times 10^8 ms^{-1}$

Table 5.2: Atomic weights of selected elements

Element name	Symbol	Atomic weight
Aluminum	Al	26.982
Argon	Ar	39.948
Copper	Cu	63.55
Iron	Fe	55.847
Krypton	Kr	83.80
Silicon	Si	28.086
Zinc	Zn	65.38

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