1 Module 1

Exercise 1

(a)

The basis vector is a vector that starts from an atom and goes to the closer atom of the same type. For example we can choose the leftmost Na^+ as the origin and we draw a vector until the second Na^+. The base unit cell is made of a couple $Na^+ + Cl^-$

(b)

Let us take a Na^+ atom at position x and suppose that the chain is infinitely long both at the left and at the right. Each Cl^- atom exerts an attractive force (negative potential) on the Na^+ atom and each other Na^+ exerts a repulsive one (positive potential). Hence, in atomic units

$$V(x) = 2 \cdot \left[\frac{1}{a} - \frac{1}{2a} + \frac{1}{3a} - \dots\right] = \frac{2}{a}\sum_{n=1}^{+\infty}\frac{(-1)^{n+1}}{n} = \frac{2\ln 2}{a}$$

Then the Madelung constant is $M = 2\ln 2$

(c)

A consequence of the presence of only a finite number of atoms is that symmetry is broken: each atom has now a different number of atoms on its right and left (except for the central one) and this effect becomes smaller as the number of atoms increases (more atoms can be approximated as "centrals"). Remember that the Madelung constant is a geometrical factor related to the energy per molecule in the crystal. One can now proceed in two different ways which will be equivalent in the limit of large N as shown in figure 1.

1. Neglect border effects and consider each atom as "central". This can be reasonable since the Coulomb potential decreases rapidly with the atom index. In this case the total energy of the lattice is approximately $U = NU_i$ where

$$U_i = 2\sum_{n=1}^{N/2}\frac{(-1)^n}{na} = \frac{\alpha}{a}$$

   and α is the Madelung constant.

2. Consider the border effects and the fact that not all atoms have the same energy. In this case the value of the Madelung constant would depend on the chosen atom, so we calculate an "average" Madelung constant by calculating the average energy of each molecule in the crystal as $V_{tot}/N_{molecules} = V_{tot}/(N/2)$ and use that expression to evaluate the Madelung constant.
   The total energy of the system can be computed as a sum over all the particles' interactions. If we begin the chain with a Na^+ atom, the charge of the $n-th$ atom in the chain is in atomic units $(-1)^n$, hence

$$U = \frac{1}{2}\sum_{i\neq j}\frac{(-1)^i(-1)^j}{r_{ij}} = \frac{1}{2}\sum_{i\neq j}\frac{(-1)^{i+j}}{|i-j|\,a} = \frac{N\alpha}{2a}$$

   and this provides an estimation for the Madelung constant. The factor 2 in the last expression has been added to consider the fact that the madelung constant is related to the energy of a molecule and not an atom.

The Madelung constant for both models as a function of the number of atoms is plotted in figure 1.

(d)

To simply the calculation we here neglect border effects and calculate the energy of the crystal as the sum of the electrostatic energy and the Pauli repulsion energy (nearest neighbour only). Let us denote with a the interatomic distance of the lattice. Each atom in the center of the crystal has energy equal to

$$U_i(a) = 2\sum_{i\neq j}U_{ij}(a) = 2\left(\lambda e^{-a/\rho} - \sum_{i\neq j}\frac{1}{r_{ij}}\right) = 2\left(\lambda e^{-a/\rho} - \sum_{n=1}^{N/2}\frac{(-1)^n}{n}\right)$$

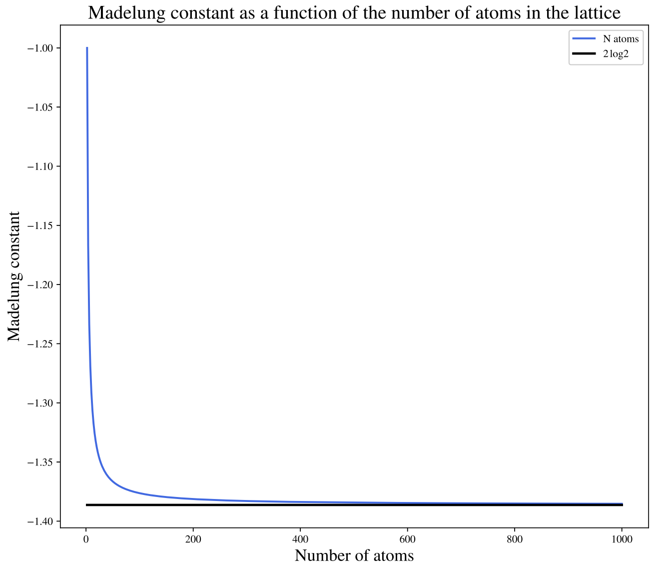

Figure 1: Madelung constant as a function of the number of atoms

The equilibrium distance can be obtained by searching the minimum of the energy per atom

$$\frac{\partial U_i}{\partial a} = 0$$

The equation can be solved numerically and the the result is reported in figure **??**

Exercise 2

(a)

$$N = 12 \cdot \frac{1}{6} + 2 \cdot \frac{1}{2} + 3 \cdot 1 = 6$$

(b)

Let us consider the tetrahedon composed by two adiacent atoms in the lowest layes, the central atom in the lowest layer and the closest atom in the middle layer. Since the tetrahedon is regular, all the sides are of the same length. The distance x of the projection of the middle layer point to the lowest layer from a vertex of the triangle is

$$x = \frac{a}{2} \frac{1}{\cos \frac{\theta}{2}} = \frac{a}{\sqrt{3}}$$

Hence the height of the middle point is

$$h = \sqrt{a^2 - \frac{a^2}{3}} = \sqrt{\frac{2}{3}} a$$

hence the height of the base cell is $c = 2h = \sqrt{8/3}a$ and the c/a ratio is $\sqrt{8/3}$.

(c)

Exercise 3

Let us choose a set of parallel planes. From this set we choose the plane closer to the origin. The idea is to calculate the distance between planes as the distance from the origin to this plane. Let us suppose that the plane intersects the x, y, z axes of a cube respectively in positions x_1, x_2, x_3: the crystal requires that

$$x_1 = n_1 a$$
$$x_2 = n_2 a$$
$$x_3 = n_3 a$$

where a is the lattice constant.
The Miller indices of the plane are defined as

$$(hkl) \equiv (h, k, l) \equiv C\left(\frac{1}{n_1 a}, \frac{1}{n_2 a}, \frac{1}{n_3 a}\right)$$

where N is a constant that guarantees that (hkl) is a set of integer numbers (the minimum integers that keeps the reciprocal proportionality). Without loss of generalisation we can assume N to be equal to 1; in fact, otherwise, N would be a common multiple of n_1, n_2, n_3 and we can return to the case above defining $n'_k = n_k/N \quad \forall k$.
If one takes the general equation of a plane

$$ax + by + cz + d = 0$$

it is possible to define the distance of the plane π to a point P via the formula

$$d(P, \pi) = \frac{|ax_p + by_p + cz_p + d|}{\sqrt{a^2 + b^2 + c^2}} \tag{1}$$

Equation 1 can be rewritten as

$$\frac{x}{c_1} + \frac{y}{c_2} + \frac{y}{c_3} = 1 \tag{2}$$

and in this form the parameters c_1, c_2, c_3 assume the geometrical significance of intercepts of the axes (just check by setting x, y, z equal to 0 in couples). This particularly useful in our case, since we can write the equation of our plane as

$$\frac{x}{n_1 a} + \frac{y}{n_2 b} + \frac{y}{c_3} = 1$$

and using 1 for the origin

$$d(O, \pi) = \frac{1}{\sqrt{(\frac{1}{n_1 a})^2 + (\frac{1}{n_2 a})^2 + (\frac{1}{n_3 a})^2}}$$

or

$$d(O, \pi) = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Exercise 4

(a)

1. (010)
2. (210)
3. (010)
4. (120)
5. (010)
6. (100)

(c) and (d)

Diffraction occurs if the von Laue condition is satisfied, that its

$$2\mathbf{k} \cdot \mathbf{G} + G^2 = 0$$

1. if $\mathbf{k} \cdot \mathbf{G} > 0$ the above expression is always positive, hence the result is trivial
2. if $\mathbf{k} \cdot \mathbf{G} < 0$ then

   $$\mathbf{k} \cdot \; veG = -k_g G > -\frac{G^2}{2}$$

   hence

   $$2\mathbf{k} \cdot \mathbf{G} + G^2 > -2\frac{G^2}{2} + G^2 = 0$$

Exercise 7

(a)

Suppose that we have N sites, and n of them are vacancies. Let us calculate the entropy of the system as

$$S = k_B \ln \omega$$

If we imagine the sites as a 1D sequence we can calculate the number of possible ways to combine n objects of type A with $N-n$ objects of type B. In this case

$$\omega(N,n) = \frac{N!}{n!(N-n)!}$$

Let us take the logarithm of this expression and use the Stirling's approximation

$$\ln \omega = \ln(N!) - \ln(n!) - \ln((N-n)!) \approx N \ln N - n \ln n - (N-n)\ln(N-n)$$

If temperature and pressure are constant, then the equilibrium state of the system is the one that minimizes the free energy

$$G = H - TS = U + pV - TS$$

If we assume $G = 0$ at $T = 0$ we can then search for the minimum of

$$\Delta G = \Delta U + \Delta(PV) - \Delta(TS)$$

and ΔU is energy variation due to the formation of vacancies, hence we can write it as $\Delta U = nE_f$ where E_f is the energy required to remove a vacancy. But if we assume pressure, volume and temperature constant

$$\Delta G = \Delta U - T\Delta S$$

we can search for the minimum in this way

$$0 = \frac{d\Delta G}{dn} = \frac{\partial \Delta U}{\partial n} - k_B T \frac{\partial \Delta S}{\partial n} = E_f - T\left[-\ln n - 1 + \ln(N-n) + 1\right]$$

$$\frac{E_f}{T} = \ln\left(\frac{N-n}{n}\right)$$

or

$$\frac{n}{N-n} = \exp\left(-\frac{E_f}{k_B T}\right)$$

and if $n << N$

$$c_v = \frac{n}{N} = \exp\left(-\frac{E_f}{k_B T}\right)$$

This is the concentrarion of vacancies as a function of the temperature at constant pressure, temperature and volume.

(b)

In this context the formation energy is the energy required to form a vacancy, that is the energy to bring an atom from the crystal to the surface.
The activation volume is

2 Module 2

I start with a brief review of useful concepts to go trough Kittel's book

General information about waves

Let us consider the wave equation

$$\frac{\partial^2 u(x,t)}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 u(x,t)}{\partial t^2}$$

One solution is the function

$$u(x,t) = Ae^{i(kx-\omega t)}$$

where k and ω are two numbers such that $v^2 = \omega^2/k^2$ and the minus sign at the exponent is purely conventional.
One first important consideration is that

$$u(x-vt,0) = Ae^{i(kx-kvt)} = Ae^{i(kx-\omega t)} = u(x,t)$$

this means that the value of the function u at position x at time t is equal to the value of the function t seconds before, in a position traslated from x to the same distance that a particle with velocity v would cover in the time t. In other words, these types of solutions are rigid waves that traslates in time and space without deforming with velocity v. If at time t the point of a wave is at position x_1 where do we find it at time $t_2 = t + t_0$? From what just said the same point will be at position $x(t_2) = x(t) + vt_0$. In general a wave point motion equation is $x(t) = x(0) + vt = x(0) + \frac{\omega}{k}t)$ so it moves with a velocity v (called *phase velocity*).
Since the wave equation is a linear equation (derivatives do not "mix"), a linear combination of functions of the previous form is still a solution. Hence, chosen $k_1, \ldots, k_N$ and $\omega_1, \ldots, \omega_n$ such that $\omega_i/k_i = v$, the function

$$u(x,t) = \sum_{n=1}^{N} A(k_n)e^{i(k_n x - \omega(k_n)t)}$$

is still a solution of the equation (can be verified by direct subsitution and imposing polynomials identity).
In particular we can take a "continous" linear combination such that

$$u(x,t) = \int_{-\infty}^{+\infty} A(k)e^{i(kx-\omega(k)t)}\, dk \tag{3}$$

This function can be viewed as the Fouries transform of a function $u(k,t) = A(k)e^{ikx}$. Every function (wave) $A(k)$ sufficiently regular can be written in terms of a linear combination of sines and cosines (indeformable waves).
Now suppose that $A(k)$ is peaked around a value k_0 so that we can expand $\omega(k)$ at first order

$$\omega(k) \simeq \omega(k_0) + \frac{d\omega(k)}{dk}(k-k_0)$$

Equaton 3 can be rewritten as

$$u(x,y) \simeq A(k_0)e^{i(k_0 x - w(k_0)t)} \int_{-\infty}^{+\infty} e^{i(\omega'(k)(k-k_0))t}\, dk \equiv f(x,t)\cdot g(t)$$

The first factor $f(x,t) = A(k_0)e^{i(k_0 x - w(k_0)t)}$ is a plane wave with phase velocity $\omega_0 \equiv \omega(k_0)$, while the second factor $g(t) = \int_{-\infty}^{+\infty} e^{i(\omega'(k)(k-k_0))t}\, dk$ modulates the wave in time as an envelope that moves with velocity $\omega'(k)$, called the *group velocity*.