Mandatory assignment FYS3400

Candidate number: 110

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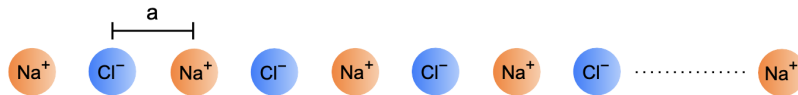
Exercise 1 module assignment I

Figure 1: Infinite 1D NaCl lattice with nearest neighbor separation a

1. Choose the basis and the unit cell for this lattice:

   The basis are the 2 atoms of Sodium and Chloride. We can attach each base to a lattice point to form the crystal. The unit cell corresponds to a segment $2a$ long centered in each lattice point. Note that the chose is arbitrary. In addition, this crystal is an Ionic crystal.

2. Derive an analytical expression for the Madelung constant:

   We can calculate the Madelung constant by looking at the potential $(U_i = \sum_j U_{ij})$, which is felt by an atom (i). This potential has 2 components: The repulsive interaction and electrostatic interaction. The former $(U_{ij}^{rep} = \lambda e^{-\frac{r_{ij}}{\rho}})$ acts only in the short-range between the ion cores, the latter $(U_{ij}^{el} = \frac{1}{4\pi\epsilon_0}\frac{q_i q_j}{r_{ij}})$ outweigh the repulsive component in longer distances. The main contribution to the binding energy of the crystal is electrostatic. So the total potential felt by an atom is:

$$U_i = \sum_j U_{ij}^{rep} + U_{ij}^{el}$$

$$= (z\lambda e^{-\frac{a}{\rho}} - \alpha\frac{1}{4\pi\epsilon_0}\frac{q^2}{a})$$

   Where n indicate the number of neighbours and α is the Madelung constant. So calculate the Madelung constant we can set up the origin in an arbitrary atom i. Let's choose a positive atom as reference atom:

$$U_i^{el} = 2(\frac{1}{4\pi\epsilon_0}\frac{q(-q)}{a} + \frac{1}{4\pi\epsilon}\frac{q(q)}{2a} + \frac{1}{4\pi\epsilon_0}\frac{q(-q)}{3a}\cdots$$

$$= 2(\frac{q^2}{4\pi\epsilon_0 a}(-1 + \frac{1}{2} - \frac{1}{3}\cdots$$

$$= -2\frac{q^2}{4\pi\epsilon_0 a}\sum_{n=1}^{\infty}\frac{(-1)^{n-1}}{n}$$

$$= -\frac{q^2}{4\pi\epsilon_0 a}(2ln(2))$$

   The sum is the Taylor expansion of $ln(1 + x)$. The factor 2 is needed because there are 2 ions at equal distance: one on the right and one on the left. Note that this assumption provides a better estimation of the Madelung constant when the lattice size increases. In conclusion, the Madelung constant α for a 1D chain is equal to: $2ln(2)$

3. Assume this crystal a finite size crystal varying from 1 to 50 unit cells and plot the Madelung constant as a function of the crystal size; plot the corresponding interaction energy evolution.

The way of thinking to find the Madelung constant for a finite chain of atoms is quite the same as shown in the previous point, although this time we have to make some consideration to the sum. In fact in this case if we take a central atom as reference where start calculate the sum, the Madelung constant becomes:

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

However, we can complicate the problem choosing an atom at the beginning of the chain or at the end. In the latter case we cannot put the 2 factor, and we have to calculate 2 sums one that takes into account how many atoms there are on the left of the atom taken as reference and the other sum has to take into account the number of atoms on the left. In the following plots N indicates the number of atoms in the chain.
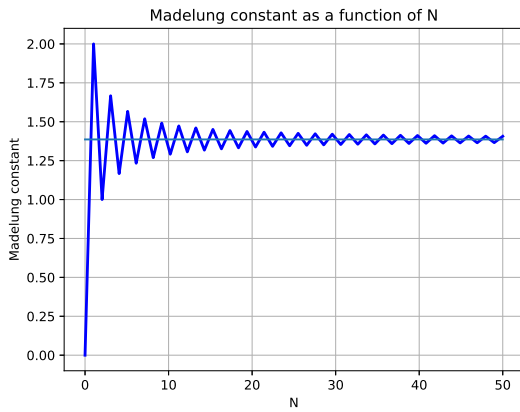

Figure 2: Madelung constant value as a function of number of atoms. We can clearly see that the value of the Madelung constant converges sharply to the theoretical value $\alpha = 2ln(2)$ with increasing the chain size.
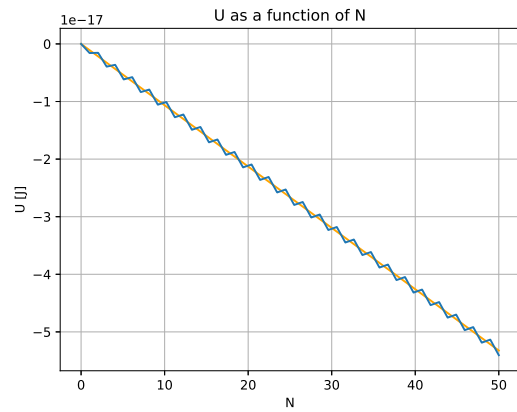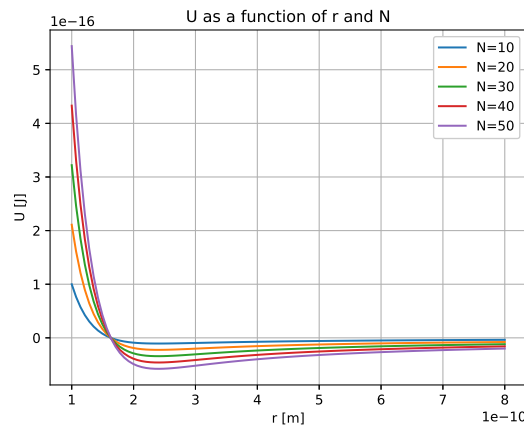
Figure 3: Interaction energy evolution. The energy U_{tot} is calculated at $r = a$ for different sizes of the crystal. The aim of this chart is to show that the energy decreases and fluctuates around the theoretical value with $\alpha = 2ln(2)$.

4. Is there a condition related to the repulsive/attractive force balance determining the potential realization of such crystals? Assume that the Pauli repulsion is similar to that for three-dimensional $NaCl$, $\lambda = 1keV$ and $\rho = 0.32$Å, and plot the equilibrium separation a_0 between Na^+ and Cl^- ion as a function of the crystal size.

We can find the minimum differentiating $U_{tot}(r) = NU_i(r)$ with respect to r and find where $U'_{tot}(r) = 0$. The value of r that minimize the function U_{tot} has to satisfy the following condi-

tion:

$$r_{min}^2 e^{-\frac{r_{min}}{\rho}} = \frac{\rho \alpha q^2}{z \lambda} \tag{1}$$

By looking at this equation we see that $r^2 e^{-\frac{r_{min}}{\rho}}$ is upper limited for $r \geq 0$. So the equation(1) has a solution only when the maximum is greater than $\frac{\rho \alpha q^2}{z \lambda}$. The maximum value of $r^2 e^{-\frac{r}{\rho}}$ is given for $r = 2\rho$; and by substituting this value in the equation(1) we get:

$$4\rho e^{-2} = \frac{\alpha q^2}{z \lambda}$$

Hence, in light of the above the condition on the parameters for the realisation of the crystal is:

$$\rho < \frac{e^2 \alpha q^2}{4z \lambda}$$

As $U_{tot}(r)$ has a minimum, and the position r that gives the minimum value of the function doesn't depend on the crystal size. I estimated numerically the equilibrium separation through the Newton method. The simulation that I implemented converges at $r_0 = 2.4 \text{Å}$.

Exercise 7 module assignment I

Text

Consider a crystal having N sites and a certain number of vacancies (n).

(a) Derive an expression for the equilibrium concentration of vacancies $c_v = n/N$ as a function of temperature T and applied stress σ. Show that the minimum free energy is reached only for a certain concentration of vacancies.

(b) Explain the roles of the formation energy and the activation volume.

Solution:

According to thermodynamics the change in the free energy of a chemical reaction in a close system is:

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

which ΔH is the enthalpy variation and ΔS the entropy variation. From a thermodynamic point of view, a solid containing vacancies constitutes a solid solution where the vacancies are dissolved in. In analogy with equilibrium problems with liquid solvent and solution, we can treat the solid like a solvent and the vacancies as a solute, and the problem may be treated in terms of the thermodynamics of chemical reactions and solutions.

I approached the problem as a reaction that starts from a perfect crystal with N sites and 0 vacancies (G_0), and ends up in a crystal with N sites and n vacancies (G_n).

Hence: $\Delta G = G_n - G_0$.

First of all, to evaluate the free energy we need to know the terms that compose it: $\Delta H = H_n - H_0$ and $\Delta S = S_n - S_0$. Let's start with entropy, that in thermodynamics is defined:

$$S = k_b ln(\Omega) \tag{2}$$

Where Ω represents all the possible microstates of the system, which describe all of the possible ways that a system could be found.

$$\Omega = \frac{N!}{(N - n)!(n!)} \tag{3}$$

If $n = 0$ we obtain $\Omega = 1$ and S_0 is null. The enthalpy is defined as follow:

$$H = U + \sigma V$$

where the stress σ is a generalisation of the pressure p. In our case, the H_0 is a constant independent on the number of vacancies, nonetheless, H_n has a linear dependence on the number of vacancies n. This is because the enthalpy shows how much energy and work are required to create a vacancy. If we assume that the enthalpy required to create a vacancy is $H_{vac} = U_{vac} + \sigma V_{vac}$, hence the H_n term is proportional to n: $H_n = n(U_{vac} + \sigma V_{vac})$.

Our aim is to find the minimun of the free energy, to do that we impose the derivative of ΔG equal to 0:

$$0 = \frac{d}{dn}\Delta G = \frac{d}{dn}\Delta H - T\frac{d}{dn}\Delta S$$

$$0 = \frac{d}{dn}nH_{vac} - Tk_B\frac{d}{dn}ln(\Omega)$$

$$0 = H_{vac} - Tk_B ln(\frac{N - n}{n})$$

$$\frac{n}{N - n} = e^{-\frac{H_{vac}}{k_B T}}$$

By considering the limit where the number of vacancies is much smaller than the number of possible sites ($n \ll N$), the equation becomes:

$$c_{n_{Vac}} = \frac{n}{N} = e^{-\frac{U_{vac} + \sigma V_{vac}}{k_B T}}$$

Here we have found that only for a certain density of vacancies the minimum is reached.

(b) The formation energy illustrates the energy that requires to create a vacancy, in other words, the energy that necessitates removing an atom from a lattice site. The activation volume is the difference between the volume of the state after a vacancy is removed and the volume before vacancy is removed.

Exercise 2 module assignment II

Text

Derivation of the phonon density of states (DOS) in a 1D lattice containing containing N atoms

1. Introduce periodic boundary conditions, derive DOS in the k-space, and plot $DOS(k)$

2. Use the 1D dispersion equation as obtained by solving Problem 1, i.e., $\omega = \omega_0|sin(ka/2)|$, to find DOS as a function of ω and plot $DOS(\omega)$.

3. Pay attention to the relative "simplicity" of $DOS(k)$ and significantly bigger "complexity" of $DOS(\omega)$, providing an argument for calculating DOS in k-space.

Solution

(a) The periodic boundary conditions are: $u_s = u_{s+N}$, where u is the displacement of a single particle in lattice space. Is known, that the displacement for a single particle in the lattice can be written as follow: $u_s = u(0)e^{iska}e^{-i\omega t}$.

Assuming that the lattice vibrates at the same frequency, the boundary conditions are:

$$u(0)e^{iska}e^{-i\omega t} = u(0)e^{i(s+N)ka}e^{-i\omega t}$$

$$e^{iska} = e^{iska}e^{iNka}$$

$$1 = e^{iNka}$$

The last equations is satisfied only if kL (where $L = Na$) is an integer multiple of 2π, that introduces a discretization on k vector, so only specific k vector are allowed:

$$k = n\frac{2\pi}{L}$$

In this case, n determines which normal modes are allowed in the crystal. Since the wave vector is bounded in the first Brillouin zone ($-\frac{\pi}{a} \leq k \leq \frac{\pi}{a}$) the n integer factor spaces from $-\frac{N}{2}$ to $\frac{N}{2}$. The DOS in the k-space is defined as follows: "number of normal modes per unit range of k". In fact, there is one normal mode for each unit range of K ($\Delta k = \frac{2\pi}{L}$).

Hence, we obtain that the $DOS(k) = \frac{dN}{dk} = \frac{1}{\Delta(k)} = \frac{L}{2\pi}$. This is correct because, the total number of normal modes allowed are N:

$$\# \text{ Normal modes} = \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} DOS(k)dk$$

$$= \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} \frac{L}{2\pi}dk$$

$$= \frac{L}{2\pi}(\frac{2\pi}{a})$$

$$= \frac{L}{a} \quad \text{L=Na}$$

$$= N$$

(b) The $DOS(\omega)$ is defined as $\frac{dN}{d\omega}$. In other words, $DOS(\omega)$ is the number of modes per unit range in ω space.

$$\frac{dN}{d\omega} = \frac{dN}{dk}\frac{dk}{d\omega} = \frac{dN}{dk}\frac{1}{\frac{d\omega}{dk}} = \frac{dN}{dk}\frac{1}{v_g}$$

From the previous point, we've already found the number of modes per unit range in k ($\frac{dN}{dk} = \frac{L}{2\pi}$). Now

the only thing left is to calculate the group velocity using the dispersion relation $\omega(k)$.

$$
\begin{aligned}
v_g = \frac{d\omega}{dk} &= \frac{d}{dk}\omega_0(sin(\frac{ka}{2})) \\
&= \frac{a\omega_0}{2}cos(\frac{ka}{2}) \\
&= \frac{a\omega_0}{2}\sqrt{1 - sin^2(\frac{ka}{2})} \\
&= \frac{a}{2}\sqrt{\omega_0^2 - \omega_0^2 sin^2(\frac{ka}{2})} \\
&= \frac{a}{2}\sqrt{\omega_0^2 - \omega^2}
\end{aligned}
$$

In conclusion, the density of states in the ω space is:

$$
DOS(\omega) = \frac{L}{2\pi}\frac{1}{v_g} = \frac{L}{\pi a}\frac{1}{\sqrt{\omega_0^2 - \omega^2}}
$$

There is a singularity in $DOS(\omega)$ every time $\omega = \omega_0$, or whenever the group velocity is 0.
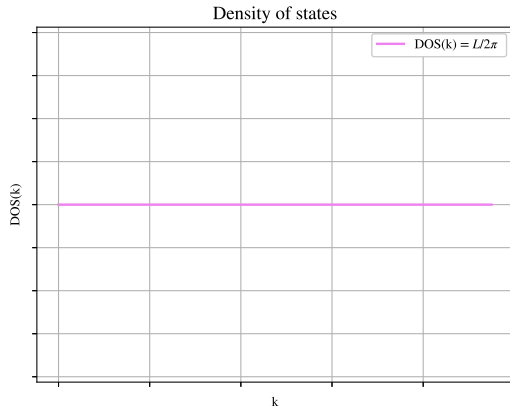

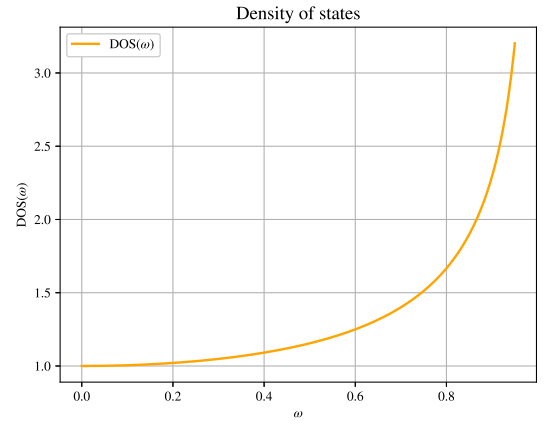Figure 4: The dimensional units have been scaled in order to illustrate the function's shape better

Figure 5: The dimensional units have been scaled in order to illustrate the function's shape better

Exercise 4 module assignment II

Text

A two-dimensional (2D) finite hexagonal lattice has a spacing of $a = 3\text{Å}$. Assuming the sound velocity in this material to be $c = 10^3 m/s$, what is the Debye frequency ω_D?

Solution

In a solid, the total number of normal modes allowed in a solid is a finite number, this corresponds to impose a constrain to the frequency allowed, otherwise the crystal will break. There is a limit to the highest phonon frequency that is allowed in the crystal. Let this highest cutoff frequency be ω_D or Debye frequency. Therefore, to this frequency corresponds a cutoff wavevector $|k_D|$ linked by the following dispersion relation ($|k|c = \omega$) to frequency. On Debye model wavevectors larger in module than k_D are not allowed. In other words, there is is an upper limit on normal mode frequency, that they cannot overstep the highest frequency ω_D:

$$\#\text{Normal modes} = \int_0^{\omega_D} DOS(\omega)d\omega = \int_0^{k_D} DOS(k)dk$$

Let's start considering a finite 2D hexagonal lattice with N atoms as shown in *figure 6*. First of all,
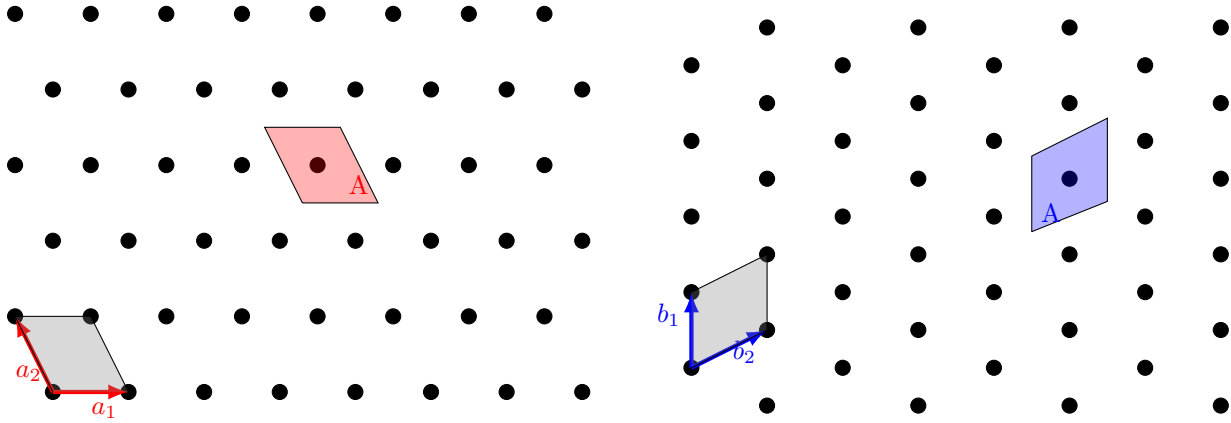

Figure 6: hexagonal lattice

Figure 7: Reciprocal lattice

we need to calculate the boundary conditions; to do this we have to impose that at the border the total displacement of a particle is equal to 0. We assumed a finite lattice formed by N atoms spacing of $a = 3\text{Å}$, so we're going to consider a lattice of length $L_{a_1} = N_{a_1}a$ along a_1 axes and a length $L_{a_2} = N_{a_2}a$ along the a_2 axes. The displacement of a particle in 2 dimension can be written:

$$u_{s_i} = u_s(0)e^{-i\omega t}sin(sk_i a) \quad \text{where } i = a_1, a_2$$

in the light of the above we impose $u_0 = 0 = u_{N_{a_1}+1}$ and $u_0 = 0 = u_{N_{a_2}+1}$. As a result, the wavevector k can assume only precise values by the boundary conditions:

$$k_i = n_i\frac{\pi}{L_i} \quad \text{with } i = a_1, a_2 \text{ and } n_i = 1, 2, 3 \dots N_i - 1$$

Now we are in the reciprocal lattice, we clearly see from *figure 7* that there is 1 mode for each primitive cell. The area of this primitive cell is equal to $A = \frac{\sqrt{3}}{2}\frac{\pi^2}{L^2}$ (for the sake of explanation, we assumed $L_{a_1} = L_{a_2}$, this does not change the physics of the problem).

In view that there is a limit on the module of the k vector all the possible normal mode are enclosed in the positive (no negative k) quarter of a circle with radius k_D. In addition, each normal vibrational mode of polarisation p (in this case 1 along every base component) has the form of a standing wave. Hence, we have to take into account that in 2 dimension we have 2 possible polarisation. So the number of modes allowed in this quarter of circle is per definition:

$$n(k) = 2\frac{(\frac{\pi k^2}{4})}{A}$$
$$= 2\frac{(\frac{\pi k^2}{4})}{\frac{\sqrt{3}}{2}\frac{\pi^2}{L^2}} = \frac{L^2 k^2}{\pi\sqrt{3}}$$

If $\frac{1}{k} \ll L$, follow $DOS(k) = \frac{dn(k)}{dk} = \frac{2L^2 k}{\pi \sqrt{3}}$.

From the previous exercise, we know that $DOS(\omega) = DOS(k)\frac{1}{c} = \frac{2L^2 k}{c\pi\sqrt{3}} = \frac{2L^2 \omega}{c^2 \pi \sqrt{3}}$, since ω is related to k. As long as it is defined

$$\int_0^{\omega_D} DOS(\omega) d\omega = \# \text{ Normal modes}$$

the total number of allowed normal modes are the number of atoms multiplied by the degree of freedom minus the number of constrain, this statement can simply translate in a mathematical expression: $\#$ Normal modes$= (2N - N_{a_1} - N_{a_2})$. Is reasonable to assume that $N \gg N_{a_1}$ and $N \gg N_{a_2}$, hence the total number of modes in the system are approximately $2N$. Moreover, if we look back at *figure 6* we can clearly see that the whole surface of the 2D solid is entirely covered by N unit cells with area A, the result of this is that the total surface of the solids is $= \frac{\sqrt{3}}{2} L^2 = N \frac{\sqrt{3}}{2} a^2$.

Now we have all the tools to calculate the Debye frequency:

$$\int_0^{\omega_D} \frac{2L^2 \omega}{c^2 \pi \sqrt{3}} d\omega = 2N$$

$$\frac{L^2 \omega_D^2}{c^2 \pi \sqrt{3}} = 2N$$

$$\omega_D^2 = \frac{2N\pi\sqrt{3}c^2}{L^2}$$

$$\omega_D = \sqrt{\frac{2\pi\sqrt{3}c^2}{a^2}}$$

In conclusion, evaluating the last equation, using all the parameters of the problem, we get:

$$\omega_D \approx 1.1 \times 10^{13} s^{-1}$$