

PERIODIC STRUCTURES

FYS3410: PROBLEM SHEET 1

CANDIDATE 33

1. ONE-DIMENSIONAL NaCl CRYSTAL

Figure 1 shows a one-dimensional crystal of sodium chloride. The diatomic array is infinite and periodic. The atoms are equally spaced by a distance a .

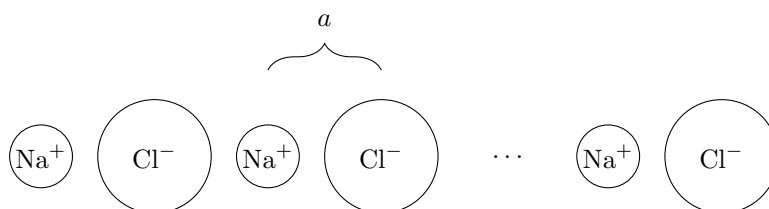
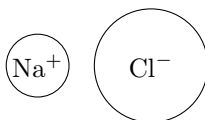


FIGURE 1. Infinite one-dimensional sodium chloride crystal.

1.1. Basis and unit cell. The unit cell is the building block necessary to build the entire crystal. The unit cell one-dimensional crystal in figure 1 is one diatomic set consisting of one sodium ion (Na^+) and one chlorine ion (Cl^-), spaced a apart.



A suitable lattice for this crystal would have lattice points placed $2a$ apart. The lattice vector would point to the right and have length of $2a$. The basis for the crystal is defined by the type, number and arrangement of atoms inside the unit cell. That is, one sodium ion and one chlorine ions placed horizontally in succession, a apart.

1.2. Derivation of Madelung's constant. Madelung's constant is found by first computing the potential energy, or lattice energy of the crystal. This energy is computed from one the viewpoint of an initial ions as a sum of interactions with all other ions in the crystal. For this one-dimensional lattice, the interaction in one of the directions will be

$$(1) \quad U' = \sum_{n=1}^{\infty} -\frac{Qq_n}{r},$$

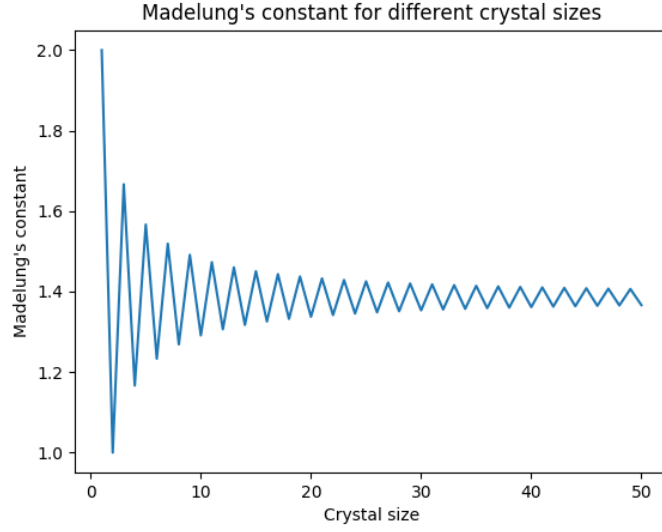


FIGURE 2. Convergence of Madelung's constant

where q is the charge of the starting ion and q_i the charge of some other ion in the lattice. The charges of the ions are the same, but the sign of the product will change. Moreover, the distance to a particular ion is $r = na$. This yields

$$(2) \quad U' = \sum_{n=1}^{\infty} -\frac{q^2(-1)^n}{na} = -\frac{q^2}{a} \sum_{n=1}^{\infty} \frac{(-1)^n}{n}.$$

To include the other direction as well, one needs simply to multiply this by 2

$$(3) \quad U = -\frac{q^2}{a} 2 \sum_{n=1}^{\infty} \frac{(-1)^n}{n}.$$

If

$$(4) \quad U_{\alpha} = -\frac{q^2}{a} \alpha,$$

then Madelung's constant is

$$(5) \quad \alpha = 2 \sum_{n=1}^{\infty} \frac{(-1)^n}{n}.$$

This sum converges towards $2\ln(2) = 1.38629$, which means that the crystal is stable.

1.3. Madelung's constant for a finite crystal. Figure 2 shows a computation of Madelung's constant for different crystal sizes $N \in (1, 50)$. The convergence of the constant is apparent. The script used to generate this plot can be found in appendix A.

1.4. Repulsive and attractive forces. The general condition related to the repulsive and attractive force balance that determines the realisation of a crystal is that the energy should be minimised. The equilibrium lattice constant can be computed numerically. The result of such a simulation is portrayed in figure 3. One can see that as the crystal is increasing in size, it becomes more stable and the

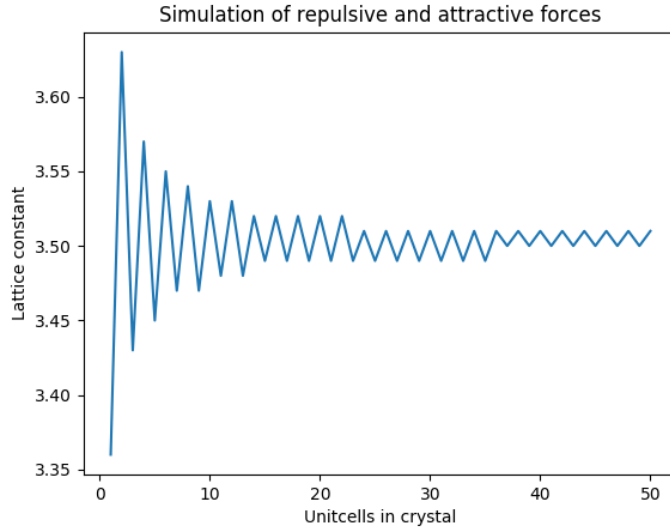


FIGURE 3. Equilibrium of attractive and repulsive forces gives the distance between ions. A larger crystal has a higher lattice constant.

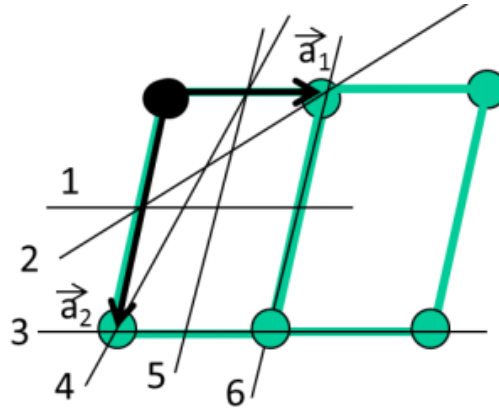


FIGURE 4. Specific planes in a triclinic crystal.

lattice constant decreases. There is a clear convergence in this situation as well. The script that produces this plot can be found in appendix B.

2. RECIPROCAL SPACE IN TRICLINIC CRYSTAL

2.1. Miller indices. Figure 4 shows a triclinic crystal with a set of lattice vectors \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 ¹. The Miller indices for the planes in figure 4 can be found in table 1. The Miller indices are found by the reciprocal intercepts

$$(6) \quad (hkl) = \left(\frac{1}{x_1} \frac{1}{x_2} \frac{1}{x_3} \right).$$

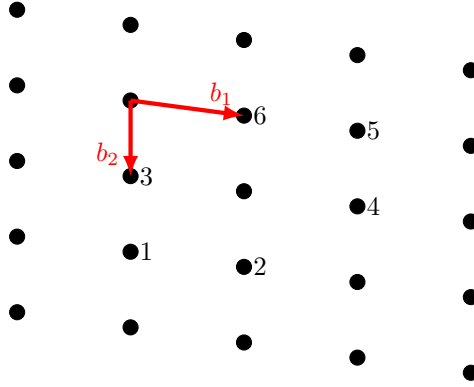
When one are using Miller indices the planes are often referred to as (hkl) planes.

¹ \mathbf{a}_3 is directed toward the reader.

TABLE 1. Miller indices for planes in figure 4

No.	Miller
1	(020)
2	(120)
3	(010)
4	(210)
5	(200)
6	(100)

2.2. Reciprocal lattice points. The (hkl) planes, specified by Miller indices in table 1, can be drawn as points in reciprocal lattice space. Such a space is shown in figure 5, where the numbers of the points correspond to the numbers for the planes in table 1.

FIGURE 5. Reciprocal space with (hkl) planes from table 1 marked as points.

2.3. X-ray diffraction condition. Point 3 in figure 5 corresponds to the plane (010). Imagine a vector to this point from origin, \mathbf{G} . For \mathbf{G} one can check for what vector $\Delta\mathbf{k} = \mathbf{G}$ the Laue condition is satisfied and diffraction happens.

$$\begin{aligned}\Delta\mathbf{k} &= \mathbf{G} \\ \mathbf{k}' - \mathbf{k} &= \mathbf{G} \\ \mathbf{G} + \mathbf{k} &= \mathbf{k}'\end{aligned}$$

For elastic scattering, $k'^2 = k^2$, which gives

$$\begin{aligned}(\mathbf{G} + \mathbf{k})^2 &= k^2 \\ \mathbf{G}^2 + 2\mathbf{k} \cdot \mathbf{G} + k^2 &= k^2 \\ 2\mathbf{k} \cdot \mathbf{G} &= -\mathbf{G}^2 \\ \mathbf{k}_G &= \frac{\mathbf{k} \cdot \mathbf{G}}{\|\mathbf{G}\|} = -\frac{1}{2}\|\mathbf{G}\|.\end{aligned}$$

This means that there will be no diffraction if $k_G < \frac{1}{2}\|\mathbf{G}\|$.

2.4. Brillouin zones. The diffraction condition from the previous section is only valid in one direction. In another direction the vector will have the same projection with the same criteria. By introducing the vector $\mathbf{G}_{(hkl)}$ corresponding to each point in reciprocal space one can determine a zone where the vector has a projection $k_{\mathbf{G}_{(hkl)}} < \frac{1}{2} \|\mathbf{G}_{(hkl)}\|$ for all $\mathbf{G}_{(hkl)}$.

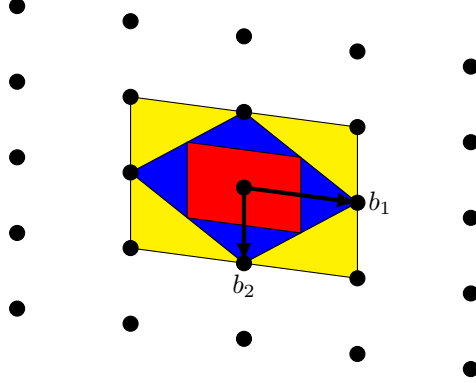


FIGURE 6. Brillouin zones in reciprocal space. Red, blue and yellow are the first second and third Brillouin zone respectively.

3. POINT DEFECTS IN CRYSTALS

3.1. Free energy in a crystal. Vacancies in a crystal lattice can translate into both lower energy and a more preferable system through increased entropy, and higher energy and less preferable system through enthalpy. This result stems from Gibbs free energy

$$(7) \quad G = U + pV - TS = H - TS,$$

where U is internal energy, p is pressure, V is volume, T is temperature, S is entropy and H is enthalpy.

To show that the minimum free energy in a crystal of N sites is reached only when a certain number of vacancies n are available, everything is easier if one simplifies the expression for entropy

$$(8) \quad S = k \ln \left[\frac{N!}{(N-n)!n!} \right],$$

where k is Boltzmann's constant.

First, one must assume that $n \ll N$ and $N \gg 1$, then one can simplify by way of Stirling's approximation

$$\begin{aligned} S &= k(\ln N! - \ln(N-n)! \ln n!) \\ &= k(N \ln N - N - (N-n) \ln(N-n) + (N-n) - n \ln n + n) \\ &= k(N \ln N - (N-n) \ln \left[N \left(1 - \frac{n}{N} \right) \right] - n \ln n) \\ &= k(N \ln N - (N-n) \left[\ln N + \ln \left(1 - \frac{n}{N} \right) \right] - n \ln n) \end{aligned}$$

if $n \ll N$ then $\frac{n}{N}$ is very small and $-\frac{n}{N}$ is a good approximation for $\ln(1 - \frac{n}{N})$. We get

$$\begin{aligned} &\approx k(N \ln N - (N - n) \left(\ln N - \frac{n}{N} \right) - n \ln n) \\ &= k(N \ln N - N \ln N + n \ln N + N \frac{n}{N} - n \frac{n}{N} - n \ln n) \\ &= k(n \ln N - n \ln n + n - \frac{n^2}{N}) \\ &= kn \left(\ln \frac{N}{n} + 1 - \frac{n}{N} \right), \end{aligned}$$

where both 1 and $\frac{n}{N}$ are both negligible compared to $\ln(N/n)$. One is left with

$$(9) \quad S = kn \ln \frac{N}{n}$$

In order to find an optimum for Gibbs free energy one takes the derivative with regards to the number of vacancies

$$\begin{aligned} \frac{\partial G}{\partial n} &= dH - kT \frac{\partial}{\partial n} (n(\ln N - \ln n)) \\ &= dH - kT \left(\ln \frac{N}{n} - 1 \right). \end{aligned}$$

Again one can ignore 1, because it is minuscule compared to the other parts of the equation. The optimum is found in the usual manner

$$\begin{aligned} 0 &= dH - kT \ln \frac{N}{n} \\ \frac{dH}{kT} &= \ln \frac{N}{n} \\ -\frac{dH}{kT} &= \ln \frac{n}{N} \\ n &= Ne^{-dH/kT} > 0. \end{aligned}$$

Thus one can conclude that that the number of vacancies are greater than zero.

3.2. Concentration of vacancies. The change in enthalpy can be written as a function of internal energy, pressure (stress) and volume

$$(10) \quad dH = U + \sigma V.$$

The concentration of vacancies is

$$(11) \quad C_v = \frac{n}{N} = e^{-(U+\sigma V)/kT} = e^{-U/kT} e^{-\sigma V/kT}.$$

One can see that the concentration of vacancies decreases both in volume, internal energy and stress, but increases in temperature.

3.3. Activation energy and activation volume. Activation energy is the energy required to remove an ion from the crystal. Neighboring atoms tend to move into the new vacancy, which creates a tensile stress field. A diffusion creep refers to the deformation of crystalline solids by the diffusion of vacancies through the crystal lattices. Diffusion creep is a mechanism by which the volume of the crystals can increase. The activation volume is the difference in volume between these two states of the crystal; before and after diffusion of vacancies.

Appendices

A. SCRIPT FOR MADELUNG'S CONSTANT

```

import numpy as np
from matplotlib import pyplot as plt

def madelung(N):
    alpha = 0
    for n in range(1, np.int(N)+1):
        alpha += -2.0*(-1)**n/n
    return alpha

crystal_size = np.linspace(1, 50)
madelung_constants = []

for size in crystal_size:
    madelung_constants.append(madelung(size))

plt.plot(crystal_size, madelung_constants)
plt.title("Madelung's constant for different crystal sizes")
plt.xlabel("Crystal size")
plt.ylabel("Madelung's constant")
plt.show()

```

B. SCRIPT FOR SIMULATION OF REPULSIVE AND ATTRACTIVE FORCES

```

import numpy as np
from matplotlib import pyplot as plt

def total_energy(alpha, R, z=2, lambd=1E3, rho=0.32, q=1):
    return z*lambd*np.exp(-R/rho) - alpha*q**2/R

def madelung(N):
    alpha = 0
    for n in range(1, np.int(N)+1):
        alpha += -2.0*(-1)**n/n
    return alpha

crystal_size = np.linspace(1, 50)
d = []

for size in crystal_size:

    alpha = madelung(size)
    r = 0.1

    U_new = total_energy(alpha, r)
    U_old = 100*U_new
    print(U_old, U_new)

```

```

print(U_old-U_new >1E-10)

while (U_old-U_new) > 1E-10:
    r += 0.01
    U_old = U_new
    U_new = total_energy(alpha, r)
    print("r = ", r, " U = ", U_new)

d.append(r)

plt.plot(crystal_size, d)
plt.title("Simulation of repulsive and attractive forces")
plt.xlabel("Unitcells in crystal")
plt.ylabel("Lattice constant")
plt.show()

```