[1] One dimensional ionic crystal

We consider a straight chain of $2N \gg 1$ ions with alternating electric charges regularly spaced with an interatomic distance $r$. Because of the electrostatic potential, each ion interact with all the others. Additionally, there is a repulsive interaction between nearest neighbors only with a potential energy of the form $a/r^n$.

\[ \cdots - \quad + \quad - \quad + \quad \cdots \quad - \quad + \quad \cdots \]

FIG. 1: One dimensional ionic crystal

(a) Express the total cohesion energy $E$ of the crystal (Note: Using the Taylor development of $\ln(1 + x)$ around $x = 0$, you can verify that $\sum_{k=1}^{\infty} (-1)^{k-1} \frac{1}{k} = \ln(2)$).

The interaction potential energy between ions $i$ & $j$ is

\[ U_{ij} = \frac{a}{r^2} \left( \delta_{i,j+1} + \delta_{i,j-1} \right) + (-1)^{i-j} \frac{q^2}{4\pi \varepsilon_0 |i-j| r} \]

So, the total interaction energy is:

\[ E = \frac{1}{2} \sum_{i \neq j} U_{ij} = \frac{1}{2} \sum_{i \neq j} \frac{a}{r^2} \left( \delta_{i,j+1} + \delta_{i,j-1} \right) + \frac{1}{2} \sum_{i \neq j} (-1)^{i-j} \frac{q^2}{4\pi \varepsilon_0 |i-j| r} \]

\[ E = \frac{2Na}{r^n} + \frac{1}{2} \sum_{k=1}^{2N} \sum_{k+i \neq k+0} (-1)^{k-1} \frac{q^2}{4\pi \varepsilon_0 |k| r} \quad \text{with the range of summation over } k \text{ depending on } i. \]

With $N \gg 1$, most atoms are far enough from the ends of the chain for the series in $k$ to have already "converged" be for the ends of the chain to be reached so the summation in $k$ can be considered to run from $-\infty$ to $+\infty$.

\[ E = \frac{2Na}{r^n} + \frac{1}{2} \sum_{k=1}^{\infty} \sum_{k+i \neq k+0} (-1)^{k-1} \frac{q^2}{4\pi \varepsilon_0 |k| r} = \frac{2Na}{r^n} + \frac{2Nq^2}{4\pi \varepsilon_0 r} \left( \sum_{k=1}^{\infty} \frac{(-1)^{k-1}}{k} \right) \]

With a Taylor development

\[ \ln (1 + x) = \frac{x}{1} - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \cdots = -\sum_{k=1}^{\infty} \frac{(-1)^{k-1} x^k}{k} \]

& for $x = 1 \quad \ln (2) = -\sum_{k=1}^{\infty} (-1)^{k-1} \frac{1}{k}$,

So

\[ E = 2N \left[ \frac{a}{r^n} - \frac{q^2}{4\pi \varepsilon_0 r} \ln (2) \right] \]

Note: Taylor development of $f(a)$ around $a_0$:

\[ f(a) = f(a_0) + (a-a_0) \frac{df}{da} \bigg|_{a=a_0} + \frac{(a-a_0)^2}{2} \frac{d^2f}{da^2} \bigg|_{a=a_0} + \cdots \]

\[ = \sum_{n=0}^{\infty} \frac{(a-a_0)^n}{n!} \frac{d^n f}{da^n} \bigg|_{a=a_0} \]
(b) Express the equilibrium interatomic distance \( r_0 \).

Equilibrium is characterized by:

\[
\frac{\partial E}{\partial r} \bigg|_{r = r_0} = 0 = 2N \left[-\frac{\mathbf{a}}{r_0^{n+1}} + \frac{\frac{9}{2} \mathbf{b} \mathbf{a}^2}{4\pi \varepsilon_0 r_0^2}\right]
\]

So

\[
r_0 = \frac{4\pi \varepsilon_0 \mathbf{a}}{\frac{9}{2} \mathbf{b} \mathbf{a}^2}
\]

(c) Compute the work \( W(\eta) \) required to stretch the string by a factor \( 1 + \eta \) with \( \eta \ll 1 \), starting from equilibrium. Expressing the work as \( W = \frac{N \eta^2}{4\pi \varepsilon_0 \mathbf{a}^2} f(n) \eta^2 \) and specify \( f(n) \).

The change in energy during the transformation is the work done on the system:

\[
W = E((1 + \eta) r_0) - E(r_0) = E(r_0) + \eta r_0 \frac{\partial E}{\partial r} \bigg|_{r_0} + \frac{\eta^2 r_0^2}{2} \frac{\partial^2 E}{\partial r^2} \bigg|_{r_0} + \cdots - E(r_0) = \frac{\eta r_0}{2} \frac{\partial^2 E}{\partial r^2} \bigg|_{r_0}
\]

Earlier we found:

\[
\frac{\partial E}{\partial r} = 2N \left[-\frac{\mathbf{a}}{r^{n+1}} + \frac{\frac{9}{2} \mathbf{b} \mathbf{a}^2}{4\pi \varepsilon_0 r^2}\right]
\]

So

\[
\frac{\partial^2 E}{\partial r^2} = 2N \left[\frac{\eta(n+1) \mathbf{a}}{r^{n+2}} - \frac{\frac{9}{2} \mathbf{b} \mathbf{a}^2}{4\pi \varepsilon_0 r^3}\right]
\]

and \( W = \frac{\eta r_0}{2} \frac{\partial^2 E}{\partial r^2} \bigg|_{r_0} = \frac{\eta r_0}{2} \frac{\partial^2 E}{\partial r^2} \bigg|_{r_0} = \frac{\eta r_0}{2} \frac{\partial^2 E}{\partial r^2} \bigg|_{r_0}
\]

and we know that \( \frac{\frac{9}{2} \mathbf{b} \mathbf{a}^2}{4\pi \varepsilon_0 r_0^2} = \frac{\mathbf{a}}{r_0^3} \) so

\[
W = \frac{N \eta^2 \mathbf{a}^2}{4\pi \varepsilon_0 r_0^2} f(n) \eta^2 \text{ with } f(n) = \mathbf{a} \mathbf{b} (n - 1)
\]
We now consider a three dimensional crystal with \( N \) atoms at sites \( R_{n_x,n_y,n_z} = r(n_x\hat{x} + n_y\hat{y} + n_z\hat{z}) \) where \( r \) is the interatomic distance used as a scale factor for the crystal. Each atom interacts only with its nearest neighbor through a Morse potential \( U(r) = U_0 \left( e^{-2a(r-d)} - 2e^{-a(r-d)} \right) \) with \( U_0, a \) and \( d \) parameters which are established experimentally.

**FIG. 2: Cubic crystal**

(a) Assuming the kinetic energy is zero, express the energy of the crystal \( E(r) \)

\[
E = \frac{3}{2} N U(r)
\]

(b) Express the equilibrium interatomic distance \( r_e \).

At equilibrium \( \frac{\partial E}{\partial r} \bigg|_{r_e} = 0 \) so

\[
3N U_0 \left( -2a e^{-2a(r_e-d)} + 2a e^{-a(r_e-d)} \right)
\]

so \( r_e = d \)

(c) Express the equilibrium bulk modulus \( B \)

By definition \( B = -\nabla \frac{\partial P}{\partial V} \) and at constant temperature \( P = -\frac{\partial E}{\partial V} \)

The volume of the crystal is \( V = N r^3 \) so \( dV = 3N r^2 \, dr \)

So \( P = -\frac{\partial (3N U(r))}{3N r^2 \, \partial r} = -\frac{U_0}{r^2} \left( -2a e^{-2a(r-d)} + 2a e^{-a(r-d)} \right) \)

\[
B = -2a U_0 \frac{N r_e^3}{3N r^2} \frac{\partial}{\partial r} \left[ \frac{1}{r^2} \left( -2a e^{-2a(r-d)} + 2a e^{-a(r-d)} \right) \right]_{r=r_e}
\]

\[
B = -\frac{2}{3} a U_0 r_e \left[ -\frac{2}{r_e^3} \left( e^{-2a(r_e-d)} - e^{a(r_e-d)} \right) + \frac{1}{r_e^2} \left( -2a e^{-2a(r_e-d)} + a e^{-a(r_e-d)} \right) \right]
\]

so \( B = \frac{2a U_0}{3 r_e} \)
[3] Relation between elastic constants. The bulk modulus is defined as \( B = -\frac{V \frac{dP}{dV}}{V} \) where \( V \) is the volume and \( P \) is the pressure. The Young modulus is defined as \( Y = \frac{E}{\epsilon} \) where \( \tau \) is the stress, a tensile or compressive force per unit area, and \( \epsilon \) is the resulting strain. The Poisson ratio \( \nu \) is defined as \( \epsilon_y = -\nu \epsilon_x \) where \( \epsilon_x \) is the stress along direction \( x \) and \( \epsilon_y \) is the relative change in dimension in any direction \( y \) perpendicular to \( x \). Finally, the modulus of rigidity is defined as \( G = \frac{\sigma}{\alpha} \) where \( \sigma \) is a shear stress and \( \alpha \) is the resulting shear angle.

In the following two questions you are going to establish relations between \( B, Y, \eta \) and \( G \). For this, you may consider a cube of side \( l \) made of an isotropic solid material.

(a) Establish the relation \( Y = 3B(1-2\nu) \) (Hint: Write in terms of the pressure the strain along one direction resulting from the compressive stress and the Poisson ratio. Then express the relative change in volume. Finally, use your results in the bulk modulus definition.).

The strain along one direction results from the compressive effect of the pressure \( \Delta P \) is reduced (its absolute value) by the effect of Poisson ratio: \( \epsilon_x = -\frac{P}{Y} + \nu \frac{P}{Y} + \nu \frac{P}{Y} = -\frac{P(1-2\nu)}{Y} \). 

To leading order, the relative change in volume resulting from the establishment of pressure \( P \) is \( \frac{\delta V}{V} = \epsilon_x + \epsilon_y + \epsilon_z = 3\epsilon_x = -\frac{3P(1-2\nu)}{Y} \). 

The definition of the bulk modulus gives \( B = -\frac{V \frac{dP}{dV}}{V} = \frac{Y}{3(1-2\nu)} \) and indeed \( Y = 3B(1-2\nu) \).

(b) Establish the relation \( Y = 2G(1+\nu) \) (Hint: Express the relative increase in length of a diagonal of the side of the cube. Then identify this change to that resulting from the combined effect of an equivalent compressive and tensile stress along the two diagonals of the same side of the cube.).

First, let's write the relative change in length of the diagonal of the side of the cube

\[ \delta = \frac{OA'}{OA} = \frac{\sqrt{a^2 + (a + \alpha)^2} - \sqrt{2}a}{\sqrt{2}a} \]

Considering \( \alpha \ll a \),

\[ \epsilon = \frac{\sqrt{2a^2 + 2a\alpha} - \sqrt{2}a}{\sqrt{2}a} = 1 + \frac{1}{2} \frac{\alpha}{a} - 1 \]

\[ \epsilon = \frac{\alpha}{2} = \frac{\sigma}{2G} \] with \( \sigma \sqrt{2}a \) the shear stress responsible for the shear angle \( \alpha \).
In order to make the connection with the Young modulus, we can consider the same deformation resulting from compressive & tensile stress $\tau$ acting along the diagonals. With $\tau$ & $\sigma$ being forces per unit area, we have $\tau = \sigma$ as the cross section perpendicular to the diagonals is $\sqrt{2} a^2$.

In this picture, the relative change in length of the diagonal results from the Young modulus & the Poisson ratio combined:

$$\varepsilon = \frac{\tau}{Y} + \nu \frac{\tau}{Y} = \frac{1 + \nu}{Y} \tau$$

Comparing this to our earlier expression:

$$\varepsilon = \frac{\sigma}{2G} = \frac{\tau}{2G} = \frac{1 + \nu}{Y} \tau$$

we indeed obtain

$$Y = 2G(1 + \nu)$$