1. **Quantum solid.** In a quantum solid the dominant repulsive energy is the zero-point energy of the atoms. Consider a crude of one-dimensional model of crystalline He\textsuperscript{4} with each He atom confined to a line segment of length \(L\). In the ground state the wave function within each segment is taken as a half wavelength of a free particle. Find the zero point kinetic energy per particle.

Solution:

\[
\varepsilon = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 (2\pi)^2}{2m\lambda^2} = \frac{\hbar^2}{2m\lambda^2}.
\]

With the assumption, \(L = \frac{\lambda}{2}\). Then \(\varepsilon = \frac{\hbar^2}{2m(2L)^2} = \frac{\hbar^2}{8mL^2}\).

2. **Cohesive energy of bcc and fcc neon.** Using the Lennard-Jones potential, calculate the ratio of the cohesive energies of neon in the bcc and fcc structures (Answer: 0.956). The lattice sums for the bcc structures are:

\[
\sum_j p^{-12}_j = 9.11418; \quad \sum_j p^{-6}_j = 12.2533.
\]

Solution:

\[
U_{\text{tot}} = 2N \varepsilon \left[ \sum_j \frac{1}{p^{12}_j} \left( \frac{\sigma}{R} \right)^{12} - \sum_j \frac{1}{p^6_j} \left( \frac{\sigma}{R} \right)^6 \right] = 2N \varepsilon \left[ \alpha \left( \frac{\sigma}{R} \right)^{12} - \beta \left( \frac{\sigma}{R} \right)^6 \right].
\]

Here \(\alpha \equiv \sum_j \frac{1}{p^{12}_j}\) and \(\beta \equiv \sum_j \frac{1}{p^6_j}\).

Let \(\frac{dU_{\text{tot}}}{dR} = 0\). \(-12\alpha \frac{\sigma^{12}}{R^{13}} + 6\beta \frac{\sigma^6}{R^7} = 0\) This gives the equilibrium position \(R_0\).

\[
\frac{\sigma}{R_0^6} = \frac{\beta}{2\alpha}
\]

Substitute this into \(U_{\text{tot}}\), we have

\[
U_{\text{tot}} = 2N \varepsilon \left[ \alpha \left( \frac{\sigma}{R} \right)^{12} - \beta \left( \frac{\sigma}{R} \right)^6 \right] = 2N \varepsilon \left[ \alpha \left( \frac{\beta}{2\alpha} \right)^{12} - \beta \frac{\beta}{2\alpha} \right] = -\frac{N\varepsilon \beta^2}{2\alpha}.
\]

The cohesive energy is \(-U_{\text{tot}} = \frac{N\varepsilon \beta^2}{2\alpha}\).

\[
\frac{-U_{\text{tot}}(\text{bcc})}{-U_{\text{tot}}(\text{fcc})} = \frac{12.2533^2 / 9.11418}{14.45392^2 / 12.13188} = \frac{16.474}{17.220} = 0.957.
\]
3. **Solid molecular hydrogen.** For H\(_2\) one finds from measurements on the gas that the Lennard-Jones parameters are \(\varepsilon = 50 \times 10^{-16}\) erg and \(\sigma = 2.96\) Å. Find the cohesive energy in kJ per mole of H\(_2\); do the calculation for an fcc structure. Treat each H\(_2\) molecule as a sphere. The observed value of the cohesive energy is 0.751 kJ/mol., much less than we calculated, so that quantum corrections must be very important.

**Solution:**
\[
U_{tot}(R_0) = -\frac{N\varepsilon\beta^2}{2\alpha} = -N\varepsilon \frac{14.45392^2}{2 \times 12.13188} = -8.61N\varepsilon .
\]

For 1 mol, \(N = 6.022 \times 10^{23}\),
\[
U_{tot}(R_0) = -8.61 \times 6.022 \times 10^{23} \times 50 \times 10^{-16} = -2.59 \times 10^{10} \text{erg/mol} = -2.59 \text{kJ/mol} .
\]

4. **Linear ionic crystal.** Consider a line of 2N ions of alternating charge ±q with a repulsive potential energy \(A/R^n\) between nearest neighbors. (a) Show that at the equilibrium separation

(CGS)
\[
U(R_0) = -\frac{2Nq^2 \ln 2}{R_0} \left(1 - \frac{1}{n}\right) .
\]

(b) Let the crystal be compressed so that \(R_0 \rightarrow R_0(1 - \delta)\). Show that the work done in a compressing a unit length of the crystal has the leading term \(C\delta^2/2\), where

(CGS)
\[
C = \frac{(n-1)q^2 \ln 2}{R_0} .
\]

To obtain the results in SI, replace \(q^2\) by \(q^2/4\pi\varepsilon_0\). Note: We should not expect to obtain this result from the expression for \(U(R_0)\), but we must use the complete expression for \(U(R)\).

**Solution:**

(a)

\[\begin{array}{cccccc}
-q & +q & -q & +q & -q & +q \\
\end{array}\]

\(R\)

\[
u(R) = \begin{cases} 
\frac{A}{r^n} - \frac{q^2}{r} & r/R = \text{odd} \\
\frac{A}{r^n} + \frac{q^2}{r} & r/R = \text{even}
\end{cases}
\]

\[
U_{tot}(R) = \frac{1}{2} (2N) \left[ \sum_j \frac{A}{p_j^n R^n} + \sum_j (-1)^{p_j} q^2 \right] .
\]
\[
\frac{dU_{\text{tot}}(R)}{dR} = -N \left[ \sum_j \frac{n A}{p_j^n R_0^{n+1}} + \sum_j \frac{(-1)^{p_j} q^2}{p_j R^2} \right]
\]

\[
\frac{d^2 U_{\text{tot}}(R)}{dR^2} = N \left[ \sum_j \frac{n(n+1)A}{p_j^n R_0^{n+2}} + \sum_j \frac{2(-1)^{p_j} q^2}{p_j R^3} \right].
\]

At equilibrium, \(\frac{dU_{\text{tot}}(R_0)}{dR} = 0\).

\[
\sum_j \frac{n A}{p_j^n R_0^{n+1}} + \sum_j \frac{(-1)^{p_j} q^2}{p_j R_0^2} = 0, \quad A = \frac{1}{R_0^n} \sum_j \frac{(-1)^{p_j}}{p_j} \cdot nR_0.
\]

Then

\[
U_{\text{tot}}(R_0) = N \left[ -\sum_j \frac{1}{p_j^n} \sum_j \frac{(-1)^{p_j}}{p_j} \cdot \frac{q^2}{nR_0} + \sum_j \frac{(-1)^{p_j}}{p_j} \cdot \frac{q^2}{R_0} \right]
\]

\[
= \frac{Nq^2}{R_0} \left( 1 - \frac{1}{n} \right) \sum_j \frac{(-1)^{p_j}}{p_j} = \frac{2Nq^2}{R_0} \left( 1 - \frac{1}{n} \right) \left( -\frac{1}{1} + \frac{1}{2} - \frac{1}{3} + \frac{1}{4} - \ldots \right)
\]

The factor 2 comes from negative \(j\) summation.

Note \(\ln(1 + x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \ldots\).

Let \(x=1\), \(\ln 2 = 1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \ldots\).

Therefore, \(U_{\text{tot}}(R_0) = -\frac{2Nq^2}{R_0} \ln 2 \left( 1 - \frac{1}{n} \right)\).

(b)

\[
U_{\text{tot}}(R) = U_{\text{tot}}(R_0) + \frac{dU_{\text{tot}}(R_0)}{dR}(R-R_0) + \frac{1}{2} \frac{d^2 U_{\text{tot}}(R_0)}{dR^2}(R-R_0)^2 + \ldots
\]

\[
\approx U_{\text{tot}}(R_0) + \frac{1}{2} \frac{d^2 U_{\text{tot}}(R_0)}{dR^2}(R-R_0)^2
\]

Thus the work done by compress \(R_0 \to R_0(1-\delta)\) equals the energy increase.
\[ W = U_{\text{tot}} (R(1 - \delta)) - U_{\text{tot}} (R_o) \approx \frac{1}{2} \frac{d^2 U_{\text{tot}} (R_o)}{dR^2} R_o^2 \delta^2. \]

From (a),

\[
\frac{d^2 U_{\text{tot}} (R_o)}{dR^2} = N \left[ \sum_j \frac{n(n+1)A}{p_{ij}^n R_0^{n+2}} + \sum_j \frac{2(-1)^{p_j} q^2}{p_j R_0^3} \right]
\]

\[
= N \left[ -\sum_j \frac{1}{p_{ij}^n} \sum_j (-1)^{p_j} \frac{(n+1)q^2}{nR_0^3} + \sum_j \frac{2(-1)^{p_j} q^2}{p_j R_0^3} \right]
\]

\[
= \frac{Nq^2}{nR_0^3} [2 - (n+1)] \sum_j (-1)^{p_j} = \frac{2Nq^2}{nR_0^3} (n-1) \ln 2
\]

Then \[ W = \frac{1}{2} \frac{d^2 U_{\text{tot}} (R_o)}{dR^2} R_o^2 \delta^2 = \frac{Nq^2}{nR_0^3} (n-1) \ln 2 \cdot \delta^2. \] There are 2N atoms. The work done to each atom is

\[
w = \frac{W}{2N} = \frac{q^2}{2nR_0} (n-1) \ln 2 \cdot \delta^2 = \frac{1}{2} C \delta^2 \text{ with } C = \frac{q^2}{nR_0} (n-1) \ln 2.\]