4. ***Free electron gas*** (a) Show that the kinetic energy of a free electron gas at absolute zero is $E = \frac{3}{5} N E_F$ where E_F is the Fermi energy. (b) Derive expressions for the pressure $P = -\frac{\partial E}{\partial V}$ and the bulk modulus $B = -V(\frac{\partial p}{\partial V})$. (c) Estimate the contribution of the conduction electrons to B for potassium and compare your answer to the experimentally measured bulk modulus 0.37×10^{10} $\mathrm{Nm^{-2}}$. Potassium has a bcc structure of lattice parameter $5.225\,\mathring{A}$.

(a) Volume per state $= \underbrace{\frac{1}{2}}_{\text{spin}} \cdot \frac{(2\pi)^3}{V} \Rightarrow$ States per unit volume in k-space $= \frac{V}{4\pi^3}$

$\therefore$ States within the shell k and k + dk $= \frac{V}{4\pi^3} \cdot 4\pi k^2 dk = \frac{Vk^2 dk}{\pi^2}$

$\Rightarrow$ Energy of the free electron gas $= E = \int_0^{k_F} \frac{Vk^2 dk}{\pi^2} \cdot \frac{\hbar^2 k^2}{2m} = \frac{V\hbar^2 k_F{}^5}{10m\pi^2}$ ---(1)

To find a relationship between k_F and N:

$$\int_0^{k_F} \frac{Vk^2 dk}{\pi^2} = N \Rightarrow \frac{Vk_F{}^3}{3\pi^2} = N \quad \text{---(2)}$$

We also have $\frac{\hbar^2 k_F{}^2}{2m} = E_F$ ---(3)

$(2)\times(3) \Rightarrow \frac{V\hbar^2 k_F{}^5}{6m\pi^2} = NE_F \Rightarrow \frac{3}{5}\times\frac{V\hbar^2 k_F{}^5}{6m\pi^2} = \frac{V\hbar^2 k_F{}^5}{10m\pi^2} = \frac{3}{5}NE_F$

Compare this result with (1), $\therefore\ \underline{\underline{E = \frac{3}{5}NE_F}}$

(b) $E = \frac{3}{5}NE_F$, note that N is a constant.

$$\therefore\ p = -\frac{\partial E}{\partial V} = -\frac{3}{5}N\frac{\partial E_F}{\partial V}$$

$$(2) \Rightarrow \frac{Vk_F{}^3}{3\pi^2} = N \Rightarrow k_F{}^3 = \frac{3\pi^2 N}{V}$$

$$\Rightarrow E_F = \frac{\hbar^2 k_F{}^2}{2m} = \frac{\hbar^2}{2m}\left(3\pi^2 N\right)^{2/3} V^{-2/3} \quad \text{---(4)}$$

$$\therefore\ p = -\frac{3}{5}N\frac{\partial E_F}{\partial V} = -\left(\frac{3}{5}N\right)\frac{\hbar^2}{2m}\left(3\pi^2 N\right)^{2/3}\left(-\frac{2}{3}V^{-5/3}\right)$$

$$= \frac{2}{5}\frac{N}{V}\frac{\hbar^2}{2m}\left(3\pi^2 N\right)^{2/3} V^{-2/3}$$

$$= \underline{\underline{\frac{2}{5}\frac{NE_F}{V}}} \quad \text{(from (4))}$$

$$B = -V\frac{\partial p}{\partial V}$$

From before, $p = \frac{2}{5}N\frac{\hbar^2}{2m}\left(3\pi^2 N\right)^{2/3}V^{-5/3}$

$$\therefore\; B = -V\frac{\partial p}{\partial V} = -VN\frac{\partial}{\partial V}\left[\frac{2}{5}\frac{\hbar^2}{2m}\left(3\pi^2 N\right)^{2/3}V^{-5/3}\right]$$

$$= -VN\frac{2}{5}\frac{\hbar^2}{2m}\left(3\pi^2 N\right)^{2/3}\left(-\frac{5}{3}\right)\left(V^{-8/3}\right)$$

$$= \frac{2}{3}N\frac{\hbar^2}{2m}\left(3\pi^2 N\right)^{2/3}V^{-5/3}$$

$$= \frac{2}{3}\frac{N}{V}\frac{\hbar^2}{2m}\left(3\pi^2 N\right)^{2/3}V^{-2/3}$$

$$= \underline{\underline{\frac{2}{3}\frac{NE_F}{V}}}$$

(c) (4) $\Rightarrow E_F = \frac{\hbar^2}{2m}\left(3\pi^2 N\right)^{2/3}V^{-2/3} = \frac{\hbar^2}{2m}\left(3\pi^2 n\right)^{2/3}$ ---(4)

$n = N/V$

For bcc with lattice parameter $= 5.225\times 10^{-10}$ m (valence = 1)

$$n = \frac{2}{\left(5.225\times 10^{-10}\right)^3} = 1.402\times 10^{28}\ \text{m}^{-3}$$

$$E_F = \frac{\left(1.055\times 10^{-34}\right)^2}{2\times 9.11\times 10^{-31}}\times\left(3\times\pi^2\times 1.402\times 10^{28}\right)^{2/3} = 3.4\times 10^{-19}\,\text{J}$$

$$\therefore\; B = \frac{2}{3}\frac{NE_F}{V} = \frac{2}{3}nE_F = \frac{2}{3}\times 1.402\times 10^{28}\times 3.4\times 10^{-19} = 0.32\times 10^{10}\ \text{Nm}^{-2}$$

$\therefore$ Compare to the real (measured) value of 0.37×10^{10} Nm^{-2}, kinetic energy of the free electrons is a major component to the bulk modulus of potassium.