Problem 2.58

In a monovalent metal, one electron per atom is free to roam throughout the object. What holds such a material together—why doesn't it simply fall apart into a pile of individual atoms? Evidently the energy of the composite structure must be *less* than the energy of the isolated atoms. This problem offers a crude but illuminating explanation for the cohesiveness of metals.

(a) Estimate the energy of N isolated atoms, by treating each one as an electron in the ground state of an infinite square well of width a (Figure 2.23(a)).

(b) When these atoms come together to form a metal, we get N electrons in a much larger infinite square well of width Na (Figure 2.23(b)). Because of the Pauli exclusion principle (which we will discuss in Chapter 5) there can only be one electron (two, if you include spin, but let's ignore that) in each allowed state. What is the lowest energy for this system (Figure 2.23(b))?

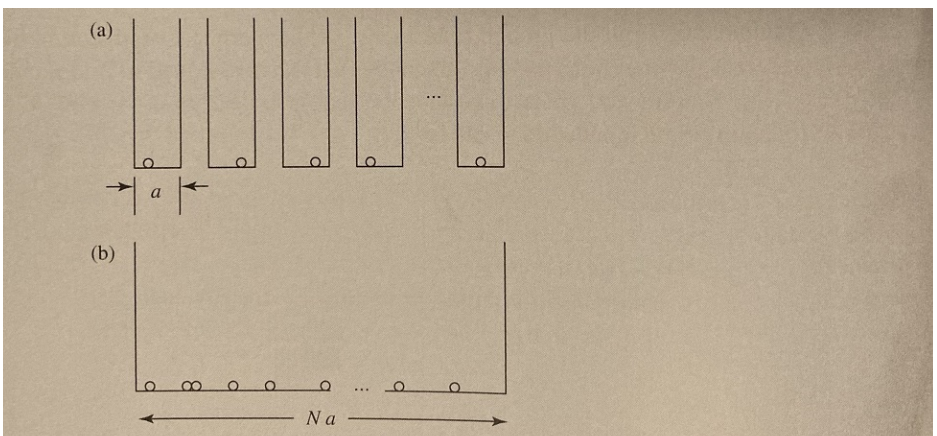

Figure 2.23: (a) N electrons in individual wells of width a. (b) N electrons in a single well of width Na.

(c) The difference of these two energies is the **cohesive energy** of the metal—the energy it would take to tear it apart into isolated atoms. Find the cohesive energy per atom, in the limit of large N.

(d) A typical atomic separation in a metal is a few Ångström (say, $a \approx 4$ Å). What is the numerical value of the cohesive energy per atom, in this model? (Measured values are in the range of 2–4 eV.)

Solution

Part (a)

The energy of an electron in the ground state is

$$E_1 = \frac{\pi^2\hbar^2}{2m_e a^2},$$

so if there are N isolated wells, the total energy is

$$NE_1 = \frac{N\pi^2\hbar^2}{2m_e a^2}.$$

Part (b)

The lowest energy occurs when the N electrons occupy the bottom N states of the infinite square well.

$$\begin{aligned}
E &= \frac{1^2\pi^2\hbar^2}{2m_e(Na)^2} + \frac{2^2\pi^2\hbar^2}{2m_e(Na)^2} + \cdots + \frac{(N-1)^2\pi^2\hbar^2}{2m_e(Na)^2} + \frac{N^2\pi^2\hbar^2}{2m_e(Na)^2} \\
&= \sum_{n=1}^{N} \frac{n^2\pi^2\hbar^2}{2m_e(Na)^2} \\
&= \frac{\pi^2\hbar^2}{2m_eN^2a^2}\sum_{n=1}^{N} n^2 \\
&= \frac{\pi^2\hbar^2}{2m_eN^2a^2} \cdot \frac{N(N+1)(2N+1)}{6} \\
&= \frac{\pi^2\hbar^2}{2m_ea^2} \cdot \frac{(N+1)(2N+1)}{6N}
\end{aligned}$$

Part (c)

The cohesive energy is the difference in energies when the atoms are together versus when they're apart.

$$\begin{aligned}
\text{CE} &= NE_1 - E \\
&= \frac{N\pi^2\hbar^2}{2m_ea^2} - \frac{\pi^2\hbar^2}{2m_ea^2} \cdot \frac{(N+1)(2N+1)}{6N} \\
&= \frac{\pi^2\hbar^2}{2m_ea^2}\left[N - \frac{(N+1)(2N+1)}{6N}\right] \\
&= \frac{\pi^2\hbar^2}{2m_ea^2}\left[\frac{6N^2 - 2N^2 - N - 2N - 1}{6N}\right] \\
&= \frac{\pi^2\hbar^2}{2m_ea^2}\left[\frac{4N^2 - 3N - 1}{6N}\right]
\end{aligned}$$

Since there are N atoms, the cohesive energy per atom is

$$\frac{\text{CE}}{N} = \frac{\pi^2\hbar^2}{2m_ea^2}\left[\frac{4N^2 - 3N - 1}{6N^2}\right].$$

Take the limit as $N \to \infty$.

$$\lim_{N\to\infty} \frac{\text{CE}}{N} = \lim_{N\to\infty} \frac{\pi^2\hbar^2}{2m_ea^2}\left[\frac{4N^2 - 3N - 1}{6N^2}\right] = \frac{\pi^2\hbar^2}{2m_ea^2}\left(\frac{4}{6}\right) = \frac{\pi^2\hbar^2}{3m_ea^2}$$

Part (d)

$$\begin{aligned}\hbar &\approx 1.05 \times 10^{-34} \text{ J} \cdot \text{s} \\ m_e &\approx 9.11 \times 10^{-31} \text{ kg} \\ a &\approx 4 \text{ Å} = 4 \times 10^{-10} \text{ m} \\ \pi &\approx 3.14\end{aligned}$$

Plug these numbers into the formula for the cohesive energy per atom in the limit of large N.

$$\lim_{N\to\infty} \frac{\text{CE}}{N} = \frac{\pi^2\hbar^2}{3m_e a^2} \approx 2.49 \times 10^{-19} \cancel{\text{J}} \times \frac{1 \text{ eV}}{1.6 \times 10^{-19} \cancel{\text{J}}} \approx 1.56 \text{ eV}$$

Using 2.5 Å $< a <$ 3.5 Å instead results in the 2–4 eV range.