

Solution to Exercise 2.1-1 Free Electron Gas with Constant Boundary Conditions

Illustration

Consider the free electron gas model but let the boundary conditions be: $\psi(\mathbf{0}) = \psi(L) = \mathbf{0}$, i.e. we have fixed boundary conditions.

Derive the solution to the Schrödinger equation and the density of states for this case.

Show that the number of states is the same as for the periodic boundary conditions as given in the backbone.

For the basic solution and the dispersion relation (energy vs. momentum / wave vector), due to the boundary conditions we now obtain

$$\psi(x, y, z) = A_{\mathbf{k}} \cdot \sin(k_x \cdot x) \cdot \sin(k_y \cdot y) \cdot \sin(k_z \cdot z)$$

$$E = \frac{\hbar^2 \cdot k^2}{2m}$$

Obviously, the boundary conditions $\psi(x=0) = \psi(x=L) = \mathbf{0}$ (and analogously so for y and z) are satisfied by

$$k_x = \frac{n_x \cdot \pi}{L}$$

$$n_x = 1, 2, 3, \dots$$

and analogously so for the y and z direction. The amplitude factor $A_{\mathbf{k}}$ follows from the condition that the probability to have the electron in the "box" equals 1:

$$1 = |A_{\mathbf{k}}|^2 \int_0^L \sin^2(k_x \cdot x) dx \int_0^L \sin^2(k_y \cdot y) dy \int_0^L \sin^2(k_z \cdot z) dz$$

Hence, here we have $|A_{\mathbf{k}}|^2 = (2/L)^3$, independent of \mathbf{k} .

The number of states $Z(\mathbf{k})$ up to a wave vector \mathbf{k} is generally given by

$$Z(\mathbf{k}) = \frac{\text{Volume of sphere with radius } E(\mathbf{k})}{\text{Volume of state}}$$

For fixed boundary conditions we have

$$Z(\mathbf{k}) = \frac{1}{8} \cdot \frac{4/3 (\pi \cdot k)^3}{(\pi/L)^3} = \frac{(k \cdot L)^3}{6\pi^2}$$

This is exactly what we would get for the periodic boundary conditions – thanks to the factor $1/8$.

Where does this factor come from? Easy – since the quantum numbers \mathbf{n} are restricted to positive integers in this case, we can not count states in 7 of the 8 octants of the complete sphere and must divide the volume of the complete sphere by 8.

This becomes clear if we look at a drawing of the possible states in phase space:

