

3-D FREE ELECTRONS AND THE PAULI EXCLUSION PRINCIPLE

(The Free Electron Fermi Gas)

1. One electron in 3-D

The **3-D Schrodinger's Equation** is:

$$(-\hbar^2/2m) \nabla^2 \psi(x,y,z,t) + PE(x,y,z) \psi(x,y,z,t) = i\hbar \partial \psi(x,y,z,t) / \partial t$$

where $\nabla^2(f) = \partial^2(f)/\partial x^2 + \partial^2(f)/\partial y^2 + \partial^2(f)/\partial z^2$ (in rectangular coordinates).

The method of solution is again to set $PE(x,y,z) = 0$ for free electrons and then to try separation of variables: let

$$\psi(x,y,z,t) = S(x,y,z) T(t) .$$

After dividing both sides of the Schrodinger Equation by ψ we again get two equations:

$$(-\hbar^2/2m) [\nabla^2 S(x,y,z)] / S(x,y,z) = E = i\hbar [\partial T(t) / \partial t] / T(t) .$$

The $T(t)$ equation is identical to the 1-D case and so has the same solution as before:

$$T(t) = B e^{-i\omega t} , \quad \text{where } \omega = E/\hbar .$$

The $S(x,y,z)$ equation can also be solved via separation of variables.

We try: $S(x,y,z) = X(x) Y(y) Z(z)$ to get:

$$(-\hbar^2/2m) [Y(y) Z(z) \partial^2 X(x) / \partial x^2 + X(x) Z(z) \partial^2 Y(y) / \partial y^2 + X(x) Y(y) \partial^2 Z(z) / \partial z^2] / S(x,y,z) = E$$

and now dividing through by $S(x,y,z) = X(x) Y(y) Z(z)$, we get:

$$(-\hbar^2/2m) [\{\partial^2 X(x) / \partial x^2\} / X(x) + \{\partial^2 Y(y) / \partial y^2\} / Y(y) + \{\partial^2 Z(z) / \partial z^2\} / Z(z)] = E .$$

We can see that the three terms each have only one variable (and hence the partial derivatives can be replaced with total derivatives), so each of these terms is a constant as far as the other terms go. If we let

$$\mathbf{k}^2 = 2mE/\hbar^2$$

as we did for the 1-D case, then we can identify each of the constants as

$$k_x^2 + k_y^2 + k_z^2 = k^2 , \quad \text{where}$$

$$d^2 X(x) / dx^2 = -k_x^2 X(x), \quad d^2 Y(y) / dy^2 = -k_y^2 Y(y), \quad d^2 Z(z) / dz^2 = -k_z^2 Z(z) .$$

Each of these equations is identical to the 1-D case which gave us $X(x) = A \sin(kx + \theta)$ and after applying the **boundary conditions**, $k = n\pi/L$; therefore we have:

$$\mathbf{k}_x = n_x \pi / L_x , \quad \mathbf{k}_y = n_y \pi / L_y , \quad \text{and} \quad \mathbf{k}_z = n_z \pi / L_z .$$

Now from $k^2 = 2mE/\hbar^2 = k_x^2 + k_y^2 + k_z^2$, and using the above we get:

$$\mathbf{E} = \hbar^2 (n_x^2 / L_x^2 + n_y^2 / L_y^2 + n_z^2 / L_z^2) \pi^2 / 2m .$$

Note the existence of **three quantum numbers: n_x , n_y , and n_z** . The **fourth quantum number** is that of **spin** ($n_{\text{spin}} = \pm 1/2$) and does not come out of the Schrodinger Equation - we must put it into the theory. It does come

out automatically from the relativistic Schrodinger's equations (the Dirac Equation), but that is beyond the level of this course.

Also recall from the 1-D case that $p = \hbar k$. In the 3-D case we have

$$\mathbf{p}_x = \hbar \mathbf{k}_x, \quad \mathbf{p}_y = \hbar \mathbf{k}_y, \quad \mathbf{p}_z = \hbar \mathbf{k}_z; \quad \text{and} \quad \mathbf{p} = \hbar \mathbf{k} = m\mathbf{v} \quad (\text{momentum}).$$

2. Many electrons and the Pauli Exclusion Principle

Since electrons obey the Pauli Exclusion Principle, no two electrons in the same area of space (the "free" electrons in the same solid in this case) can have the same set of quantum numbers. Hence when we consider many "free" electrons in a solid, we must consider their energy (and momentum) in light of the Pauli Exclusion Principle. [Note: the other bound electrons of the atoms are not free to roam in the whole space and so have their individual quantum numbers within each atom. It is only the free valence electrons that we are talking about here that are able to roam the whole space of the solid. These free (valence) electrons are thus like electrons bound to the whole solid rather than to an individual atom, and we can think of these free electrons as being in an "atom" of the whole solid – and they do have four quantum numbers similar to the electrons bound to their atom, but in this case the quantum numbers are the n_x , n_y , n_z , and spin.]

3. Filling up energy levels at T=0 K

At absolute zero all the electrons will be in the lowest possible state - which does not mean that all electrons will have the quantum numbers $n_x=1$, $n_y=1$, and $n_z=1$ due to the Pauli Exclusion Principle. **The highest level filled at T = 0K is called the Fermi Energy, ϵ_F , and the k value of this level is called the Fermi wavevector, k_F .**

To find the Fermi Energy and the Fermi wavevector, we need to know how many "free" electrons are in the solid as well as how big the solid is. This suggests that the density of electrons will be important.

For any reasonable size solid, the number of electrons will be huge! [$N_a = 6 \times 10^{23}$ /mole] Thus as we did before we will replace the summation based on the integers, n_i , with an integral over dk_i (where the i refers to x , y , and z). To accomplish this we then need to know the density of states. From the boundary conditions, we obtained (see above) that:

$$k_x = n_x \pi / L_x, \quad ,$$

where we applied the standing wave boundary condition which gave us only positive k values. If we apply the **periodic boundary condition**, this gives us only half the values of k but allows both positive and negative values:

$$\mathbf{k}_x = n_x 2\pi / L_x .$$

To get a density of states, we simply look for $D(k) = \Delta n / \Delta k$ and $D(\epsilon) = \Delta n / \Delta \epsilon$ so that

$$N = 2 \iiint D(k_x) D(k_y) D(k_z) dk_x dk_y dk_z = \int D(\epsilon) d\epsilon ,$$

where the 2 in front of the integral is from the fact that there are two spin states for each k state. From the equation $k_x = 2n_x \pi / L_x$ we can get $n_x = (L_x / 2\pi) k_x$ and so

$$D(k_x) \equiv dn_x / dk_x = (L_x / 2\pi) .$$

We further use the conversion from rectangular to spherical form:

$$dk_x dk_y dk_z = (dk) (k d\theta_k) (k \sin[\theta_k] d\phi_k) = 4\pi k^2 dk$$

where the last step assumes spherical symmetry ($\int_0^{2\pi} d\phi = 2\pi$, $\int_0^\pi \sin\theta d\theta = 2$).

Therefore we can write the expression for N to be:

$$N = 2 (L_x / 2\pi) (L_y / 2\pi) (L_z / 2\pi) \int_0^{k_F} 4\pi k^2 dk = 2 (V / 8\pi^3) (4\pi k_F^3 / 3),$$

or solving for k_F , the **Fermi wavevector**, we get: $k_F^3 = (N/V) (24\pi^3 / 8\pi)$, or $\mathbf{k}_F = [3\pi^2 N/V]^{1/3}$.

To get the **Fermi energy**, we simply recall that $\epsilon = \hbar^2 k^2 / 2m$ to get:

$$\epsilon_F = \hbar^2 k_F^2 / 2m = (\hbar^2 / 2m) (3\pi^2 N/V)^{2/3} .$$

To get the **Fermi velocity**, v_F , (that is the velocity of the electron that is in the highest filled state at $T=0$), we recall that $\hbar k = p = mv$:

$$v_F = \hbar k_F / m_e .$$

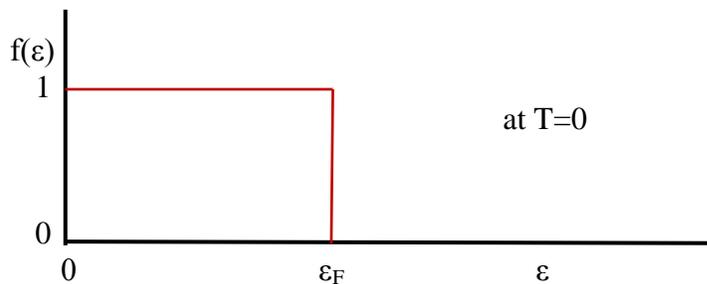
Finally we can define a **Fermi Temperature**: $k_B T_F \equiv \epsilon_F$.

You are to use the above relations in [homework problem 21](#).

4. The Fermi-Dirac distribution: A Replacement for the Planck distribution

For **photons** and **phonons** we had the **Planck distribution** that gave us the average number of photons or phonons created at any temperature. For electrons, we do not "create" electrons. Instead the electrons "fill" different energy states. We **need a distribution function that will give us the probability of an electron filling any particular state**.

This distribution function at $T=0K$ should look like the following:



This function should be equal to 1 for $\epsilon < \epsilon_F$, that is the fraction of states filled [or the probability of the state being filled] is 1 for all energies less than the Fermi energy, and the function should be equal to 0 for all energies greater than the Fermi energy. Recall that this is only for $T=0K$.

At higher temperatures, the function should begin to decrease from 1 for energies less than the Fermi energy and increase from zero for energies greater than the Fermi energy - since with a little energy some of the electrons near the Fermi energy will be able to gain a little energy and move up to a higher energy state.

We will NOT derive this function here (we do it in PHYS 447), only state it and then show that it does indeed have the above properties:

$$f_{\text{Fermi-Dirac}}(\epsilon) = 1 / [e^{(\epsilon-\mu)/kT} + 1] , \quad (\text{Fermi-Dirac distribution})$$

where μ is called the **chemical potential**. At $T=0K$, $\mu = \epsilon_F$. First note how this distribution function differs from the Planck distribution:

$$\langle n \rangle = 1 / [e^{\epsilon/kT} - 1] \quad (\text{Planck distribution}) .$$

There are two main differences: the existence of μ and the change of sign of the 1 in the denominator from - 1 in the Planck to + 1 in the Fermi-Dirac. See the excel spreadsheet on [Distributions](#).

Let's first consider the sign change. With a minus sign in the denominator of the Planck distribution, the denominator can become less than 1, which means that the function can be greater than 1. This is fine for photons and phonons that do NOT obey the Pauli Exclusion Principle. With a plus sign in the denominator of the Fermi-Dirac distribution, the denominator can never be less than 1, and hence the function can never be greater than 1. This is required by the Pauli Exclusion Principle.

Next let's consider the chemical potential, μ . At $T=0K$, if ϵ is less than μ , then the exponential has a negative infinity in the exponent, which makes the exponential function zero, which makes the value of the distribution function equal to 1. If ϵ is greater than μ , then the exponential has a positive infinity in the exponent, so the exponential is infinite, and the distribution function is 0. This is what is required in filling up the energy levels at $T=0K$!

Finally, note that at any temperature, **when $\epsilon=\mu$** , the exponent is zero so the exponential function is 1 and **the distribution function is equal to $1/2$** . **Only at $T=0K$ does $\mu=\epsilon_F$** . **At higher temperatures, μ increases, that is, $\mu=\mu(T)$; the Fermi energy, ϵ_F , does not change since it is simply the highest level filled at $T=0K$.**

5. The Chemical Potential, $\mu(T)$

To solve for $\mu(T)$, we can employ our summation (integration) of states to find N . We must include the fraction of states occupied to do this:

$$N = \int_0^{\infty} f_{FD}(\epsilon, T) D(\epsilon) d\epsilon .$$

To do this, we need to figure out the density of states based on energy rather than wavevector as we have done before. Recall that

$$\begin{aligned} dN &= 2(L/2\pi)^3 4\pi k^2 dk = (V/\pi^2) k^2 dk, & \text{and} \\ \epsilon &= \hbar^2 k^2 / 2m \quad \text{so} \quad d\epsilon = (2\hbar^2 k / 2m) dk \quad \text{where } k = (2m\epsilon/\hbar^2)^{1/2}. \end{aligned}$$

Therefore: $k^2 = (2m/\hbar^2)\epsilon$ and $dk = (2m/\hbar^2)^{1/2} (1/2\epsilon^{-1/2}) d\epsilon$, and so

$$dN = (V/\pi^2) (2m/\hbar^2)^{3/2} 1/2 \epsilon^{1/2} d\epsilon = D(\epsilon) d\epsilon .$$

Thus in 3-D we have:

$$N = \int_0^{\infty} [1 / \{e^{(\epsilon-\mu)/kT} + 1\}] (V/\pi^2) (2m/\hbar^2)^{3/2} 1/2 \epsilon^{1/2} d\epsilon ,$$

which is the **relation to get $\mu(T)$** (since ϵ is integrated out and all the other parameters do not depend on T). This is not a nice integral to do. However, in 2-D the integral is much nicer.

Homework problem 22 requires you to set the 2-D problem up and then solve for $\mu(T)$.

Hint: Find a new dN for the 2-D case that will give you a new $D(\epsilon)$ to use in equation: $N = \int_0^{\infty} f_{FD}(\epsilon, T) D(\epsilon) d\epsilon$.

For *homework problem 23* you are required to find the kinetic energy of the electrons in the solid at $T=0$. Since the electrons are not all in the lowest state, there will be some kinetic energy even at $T=0K$. To do this, consider how to find the average energy:

$$\langle \epsilon \rangle = \int \epsilon f(\epsilon, T) D(\epsilon) d\epsilon / \int f(\epsilon, T) D(\epsilon) d\epsilon .$$

Also, the total energy is just the number of electrons, N , times the average energy per electron: $U_{T=0} = N \langle \epsilon \rangle$. Finally, recall that at $T=0K$, $f(\epsilon, 0) = 1$ for $0 < \epsilon < \epsilon_F$ and $f(\epsilon, 0) = 0$ for $\epsilon > \epsilon_F$.

You should be able to do *Homework problem 24* now.