

The free electron gas

The free electron gas is a model for electrons in metals. It assumes the electrons do not interact and that the only effect of the ions is to keep the electrons from leaving the material. The model is solved quantum mechanically for 1 electron and then the N -electron configuration is constructed by hand, respecting the Pauli principle.

The contents of these notes are likely not new to you. But it is nevertheless essential since it introduces some key terminology, like Fermi sphere and density of states. If you have never seen this before, please study these notes in detail. If you have seen this before, I suggest you just read it quickly for review.

Additional reading

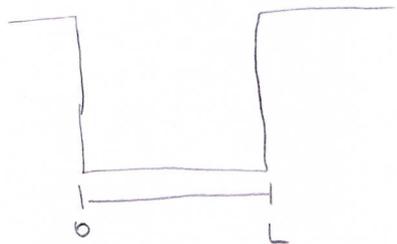
- Ashcroft and Mermin, chapter 2
- the Oxford Solid State Basics, Simon, chapter 4.

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A particle in a box

We begin by revisiting the first model you ever saw in quantum mechanics: a particle in an infinite well.



But we do so with a small twist: we use periodic boundary conditions. This allows us to maintain translation invariance, even though the box is finite.

The Hamiltonian of the system is

$$H = \frac{\hat{p}^2}{2m} \quad (1)$$

We don't need to diagonalize H . We can simply diagonalize \hat{p} . Its eigenvalue equation is written as

$$\hat{p} |k\rangle = \hbar k |k\rangle \quad (2)$$

I set $\hbar=1$. If you don't do that, then you may write $\hbar k$ instead. To figure out the allowed values of k , we go to the coordinate representation, where $\hat{p} = -i \partial_x$. Then, if we define

$$\phi_k(x) = \langle x | k \rangle \quad (3)$$

we get

$$-i \partial_x \phi_k = k \phi_k \quad (4)$$

The solution of this equation is

$$\phi_u(x) = \frac{e^{ikx}}{\sqrt{L}} \quad (5)$$

where the factor of $1/\sqrt{L}$ was included so that

$$\int_0^L dx |\phi_u(x)|^2 = 1 \quad (6)$$

Next we impose the PBC:

$$\phi_u(x+L) = \phi_u(x) \quad (7)$$

This implies that

$$e^{ikL} = 1 \quad \Rightarrow \quad k = \frac{2\pi l}{L}, \quad l = 0, \pm 1, \pm 2, \dots \quad (8)$$

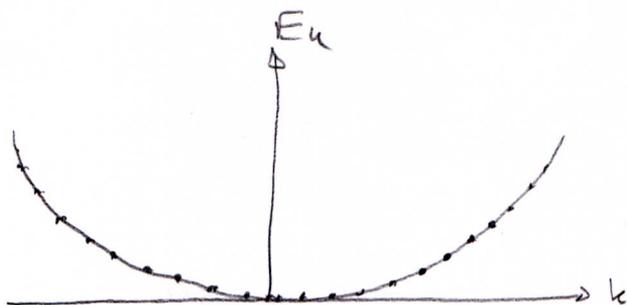
This is exactly the type of quantization we found in the notes on Fourier analysis. Momentum is always quantized like this.

Now, back to H . Since $H \propto \hat{p}^2$, the eigenvectors of H will be the same as those of \hat{p} . Moreover, the energies will be

$$E_k = \frac{k^2}{2m} \quad (9)$$

[If $A|\psi\rangle = \lambda|\psi\rangle$ then $(\alpha A^2)|\psi\rangle = \alpha\lambda^2|\psi\rangle$].

Eq (9) is the dispersion relation for a particle in a box. It looks like this:



The plot is actually discrete, since k is discrete. However, the spacing is

$$\Delta k = \frac{2\pi}{L} \quad (10)$$

which becomes tiny when L is large.

— " —

It is straightforward to extend everything to 3D. Now

$$H = \frac{\hat{P}^2}{2m} \quad (11)$$

The eigenvectors of \hat{P}_x , \hat{P}_y and \hat{P}_z (which commute and may thus be simultaneously diagonalized) are

$$|k\rangle = |k_x, k_y, k_z\rangle \quad (12)$$

And they satisfy

$$\hat{P}_i |k\rangle = k_i |k\rangle \quad (13)$$

the eigenfunctions are

$$\phi_{\mathbf{k}}(\mathbf{r}) = \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}} \quad (14)$$

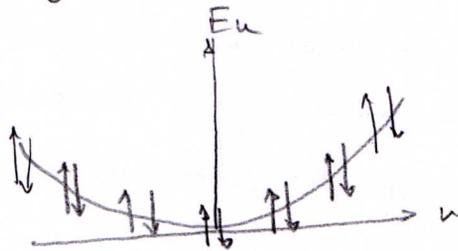
where V is the volume of the box. Finally, the dispersion relation reads

$$E_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m}, \quad k = |\mathbf{k}| \quad (15)$$

Fermi stuff

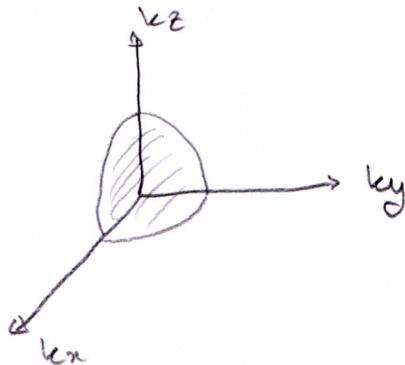
We have thus far considered a single electron in a box. Now I want to consider N of them and ask, what is the ground state of the system. We assume they do not interact, but they must satisfy the Pauli exclusion principle.

This means that in the ground state the electrons will populate the different k states in order of increasing energy. Something like this



Each k state can take 2 particles, one with spin up and the other with spin down.

The energy depends only on $|k|$. Thus, in 3D the electrons will actually fill out a sphere in k -space.



This sphere is called the Fermi sphere and everything associated with it is called the "Fermi something".

The most important names are

$$k_F = \text{Fermi momentum} \quad (16)$$

= Radius of the sphere

$$E_F = \text{Fermi energy} = \frac{k_F^2}{2m} \quad (17)$$

= Fermi level

The Fermi momentum is therefore the momentum of the highest filled state. And E_F is the corresponding energy.

An important question is how k_F is related to the number of electrons in the system N . The easiest way to answer this question is by means of the formula

$$N = 2 \sum_{\mathbf{k}} \Theta(k_F - k) \quad (18)$$

where the factor of 2 is to account for spin and where $\Theta(x)$ is the Heaviside function,

$$\Theta(x) = \begin{cases} 1 & x > 0 \\ 0 & x < 0 \end{cases} \quad (19)$$

Eq (18) therefore says that N is a sum over all \mathbf{k} states with weight 1 if $k < k_F$ and 0 otherwise. Makes sense!

To our time we convert the sum to an integral using the recipe

$$\sum_{\mathbf{k}} \rightarrow \frac{V}{(2\pi)^3} \int d^3k \quad (20)$$

we then get

$$N = 2 \frac{V}{(2\pi)^3} \int d^3k \Theta(k_F - k)$$

We now move to spherical coordinates and integrate over the solid angle, which gives a factor of 4π . We then get

$$\begin{aligned} N &= 2 \frac{V}{(2\pi)^3} 4\pi \int_0^{\infty} dk k^2 \Theta(k_F - k) \\ &= \frac{V}{\pi^2} \int_0^{k_F} dk k^2 \\ &= \frac{V}{\pi^2} \frac{k_F^3}{3} \end{aligned}$$

thus, k_F is related to the density N/V according to

$$k_F = (3\pi^2 N/V)^{1/3} \quad (21)$$

The Fermi energy is then simply

$$E_F = \frac{(3\pi^2 N/V)^{2/3}}{2m} \quad (22)$$

Another thing we can do is compute the total energy of the system. It is defined as

$$U = 2 \sum_{\mathbf{k}} \frac{\hbar^2 \mathbf{k}^2}{2m} \Theta(k_F - k)$$

Following the same procedure we get

$$\begin{aligned} U &= 2 \frac{V}{(2\pi)^3} 4\pi \int_0^{k_F} dk \frac{\hbar^2 k^4}{2m} \\ &= \frac{V}{\pi^2} \frac{k_F^5}{5} \frac{1}{2m} \end{aligned}$$

we may write this as

$$U = \underbrace{\frac{V k_F^3}{3\pi^2}}_N \frac{3}{5} \underbrace{\frac{\hbar^2 k_F^2}{2m}}_{E_F}$$

Thus

$$U = \frac{3}{5} N E_F$$

(23)

The average energy per electron is therefore $\frac{3}{5} E_F$, which is a little bit above $\frac{1}{2} E_F$.

The density of states (DOS)

Sometimes it is easier to think in terms of energy. But this can be tricky because the states are labelled by l, m and many l, m values have the same $E_{l, m}$ (all l, m values in the same shell l, m). To account for this we define the density of states, such that

$$D(\epsilon)d\epsilon = \text{number of states with energy between } \epsilon \text{ and } \epsilon + d\epsilon \quad (24)$$

The actual formula for $D(\epsilon)$ is

$$D(\epsilon) = (2S+1) \sum_{l, m} \delta(\epsilon - E_{l, m}) \quad (25)$$

* More about this in the end of the next page

Here $S=1/2$ is the spin of the electron. I just leave it there so you know which part of $D(\epsilon)$ comes from spin.

The DOS appears most often when you have a sum over l, m of some function $f(E_{l, m})$ that depends only on $E_{l, m}$. We may then write

$$(2S+1) \sum_{l, m} f(E_{l, m}) = \int d\epsilon D(\epsilon) f(\epsilon) \quad (26)$$

To see that (25) and (26) are equivalent, we write

$$\begin{aligned}\int dE D(E) f(E) &= \int dE \left[(2S+1) \sum_{\mu} \delta(E - E_{\mu}) \right] f(E) \\ &= (2S+1) \sum_{\mu} \int dE \delta(E - E_{\mu}) f(E) \\ &= (2S+1) \sum_{\mu} f(E_{\mu})\end{aligned}$$

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Let me try to clarify (25): convert the sum to an integral in order to get

$$D(E) = (2S+1) \frac{V}{(2\pi)^3} \int d^3k \delta\left(E - \frac{\hbar^2 k^2}{2m}\right)$$

You are integrating over all momentum space, but the δ chops off only that part for which $\frac{\hbar^2 k^2}{2m} = E$. That is how you define the density of states.

Example: particle in a box in 3D

Let us find $D(E)$ for $E_n = \hbar^2 k^2 / 2m$. We have

$$\begin{aligned}\sum_{\mathbf{k}} f(E_{\mathbf{k}}) &= \frac{V}{(2\pi)^3} \int d^3 k f(E_{\mathbf{k}}) \\ &= \frac{V}{(2\pi)^3} 4\pi \int dk k^2 f(E_{\mathbf{k}})\end{aligned}$$

Now we change variables to $E = \hbar^2 k^2 / 2m$. We get

$$k = \sqrt{2mE}$$

$$dk = \frac{\sqrt{2m}}{2\sqrt{E}}$$

$$k^2 dk = (2m)^{3/2} \frac{\sqrt{E}}{2} dE$$

this then gives

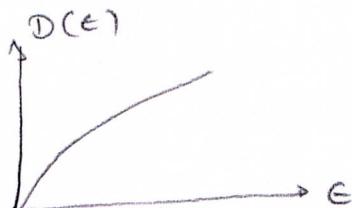
$$\sum_{\mathbf{k}} f(E_{\mathbf{k}}) = \frac{V}{2\pi^2} (2m)^{3/2} \int dE \frac{\sqrt{E}}{2}$$

Thus we recognize the DOS as

$$D(E) = (2S+1) \frac{V}{4\pi^2} (2m)^{3/2} \sqrt{E} \quad (27)$$

[If I substitute $S=1/2$, the 2 will mix with all the other two's].

From (27) we see that the DOS increases with E



The Fermi energy is now defined from the relation

$$N = \int_0^{E_F} D(E) dE \quad (28)$$

Let's check:

$$\begin{aligned} N &= \frac{(2S+1)}{4\pi^2} V (2m)^{3/2} \int_0^{E_F} \sqrt{E} dE \\ &= \frac{2}{4\pi^2} V (2m)^{3/2} E_F^{3/2} \frac{2}{3} \end{aligned}$$

so

$$(2m E_F)^{3/2} = 3\pi^2 N/V$$

or

$$E_F = \frac{(3\pi^2 N/V)^{2/3}}{2m}$$

which is exactly (22).

We can also compute the total energy as

$$U = \int_0^{E_F} dE E D(E) \quad (29)$$

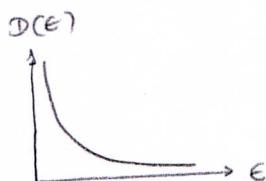
I will leave for you to check that this is indeed (23)

Table of some useful densities of states

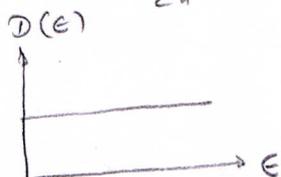
For the non-relativistic dispersions $E_{\mathbf{k}} = |\mathbf{k}|^2 / 2m$, in 1D, 2D and 3D, we have

$$E_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m}$$

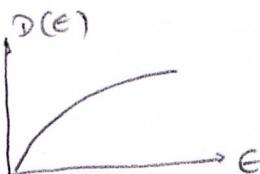
$$1D: \quad \mathcal{D}(E) = (2S+1) \frac{L}{4\pi} \sqrt{2m} \frac{1}{\sqrt{E}} \quad (30a)$$



$$2D: \quad \mathcal{D}(E) = (2S+1) A \frac{(2m)}{2\pi} \quad (30b)$$



$$3D: \quad \mathcal{D}(E) = (2S+1) \frac{V}{4\pi^2} (2m)^{3/2} \sqrt{E} \quad (30c)$$



In 1D the DOS diverges at $E=0$. This is called a van Hove singularity.

I will also write down the result for the relativistic dispersion

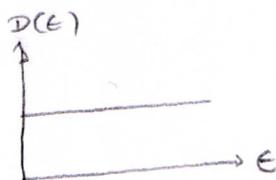
$$E_{ik} = c|k| \quad (31)$$

This will appear often in condensed matter. It is also the dispersion for photons. Since we are using $\hbar=1$, $E_{ik} = \omega_{ik}$, so you can also write down the dispersion for ω .

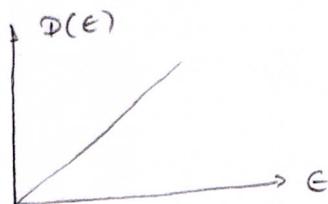
The results are

$$E_{ik} = c|k|$$

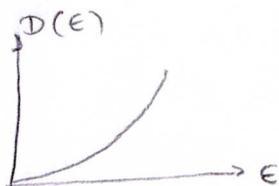
$$1D: \quad D(E) = \text{const} \times \frac{1}{2\pi c} \quad (32a)$$



$$2D: \quad D(E) = \text{const} \times \frac{E}{2\pi c^2} \quad (32b)$$



$$3D: \quad D(E) = \text{const} \times \frac{E^2}{2\pi^2 c^3} \quad (32c)$$



I wrote "const" instead of $(2S+1)$ because massless particles are delicate. Think about "const" as the number of polarizations. For photons $\text{const} = 2$. Even though the photon has spin 1, the fact that it is massless prohibits the occupation of the $S_z = 0$ state. Thus, it is left with only two spin polarizations.

The DOS and Green's functions (optional)

Consider a system with Hamiltonian H and eigenstuff equation

$$H |k\rangle = E_k |k\rangle \quad (33)$$

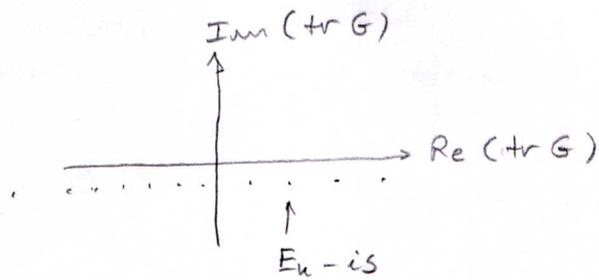
I wrote the quantum number as k for obvious reasons, but it could be a vector like \mathbf{k} . We define the retarded Green's function of H as

$$G(E) = \lim_{\delta \rightarrow 0} \frac{1}{E + i\delta - H} \quad (34)$$

Explanation: (i) δ is a tiny number to ensure G doesn't blow up, we set it to zero in the end. (ii) G is an operator because H is an operator. (iii) $\frac{1}{A}$ is just a nice way of writing A^{-1} , the matrix inverse of the operator A . If I forget to write $\lim_{\delta \rightarrow 0}$, then it should be implicit. The Green's function contains the DOS inside it. To see that, take its trace using $|k\rangle$ as basis

$$\begin{aligned} \text{tr } G(E) &= \sum_k \langle k | \frac{1}{E + i\delta - H} | k \rangle \\ &= \sum_k \frac{1}{E + i\delta - E_k} \\ &= \sum_k \frac{(E - E_k) - i\delta}{(E - E_k)^2 + \delta^2} \end{aligned} \quad (35)$$

We see that $\text{tr } G(E)$ shows poles at $E = E_n - i\epsilon$.



The pole structure of $\text{tr } G$ therefore reveals the eigenvalues of H . Now let us look at the imaginary part and consider the identity

$$\lim_{\epsilon \rightarrow 0} \frac{\epsilon}{(\epsilon - E_n)^2 + \epsilon^2} = \pi \delta(\epsilon - E_n) \quad (36)$$

We then get

$$\text{Im}[\text{tr}(G)] = -\pi \sum_n \delta(\epsilon - E_n) \quad (37)$$

via (25)! Thus we conclude that

$$D(\epsilon) = -\frac{1}{\pi} \text{Im}[\text{tr}(G)] \quad (38)$$

Or, if you want to write it explicitly,

$$D(\epsilon) = -\frac{1}{\pi} \text{Im} \sum_n \frac{1}{\epsilon + i\epsilon - E_n} \quad (39)$$

with the limit $\epsilon \rightarrow 0$ being left implicit, this Eq. can be useful in evaluating $D(\epsilon)$ numerically.

The trace in Eq (17) can be taken with respect to any basis. Let $|f_m\rangle$ be some other basis (maybe a localized orbital). Then we may write

$$D(\epsilon) = -\frac{1}{\pi} \text{Im} \sum_m \langle f_m | G | f_m \rangle \quad (40)$$

This introduces us to the idea of decomposing the DOS into its projections in a given basis. We define

$$D(\epsilon, f_m) = -\frac{1}{\pi} \text{Im} \langle f_m | G | f_m \rangle \quad (41)$$

$$\Rightarrow D(\epsilon) = \sum_m D(\epsilon, f_m) \quad (42)$$

Thus, $D(\epsilon, f_m)$ describes the part of the DOS corresponding to the state $|f_m\rangle$. For instance, we could have a tight-binding model with two orbitals. Then we can examine the individual DOS of each orbital. Or we could have a magnetic system and then analyze the spin up and spin down DOSs.