Electrons

Free electron Fermi gas

A simple model for a metal is electrons confined to box with periodic boundary conditions.

Like the problem of photons in a box except:

- Solve the Schrödinger equation instead of the wave equation.
- Electrons are fermions not bosons.

Free electrons

$$\left(-\sum_i^N \frac{\hbar^2}{2m}\nabla_i^2\right)\Psi(\vec{r}_1,\vec{r}_2,\cdots,\vec{r}_N) = E\Psi(\vec{r}_1,\vec{r}_2,\cdots,\vec{r}_N)$$

No potential, no *e*-*e* interactions, periodic boundary conditions.
This separates into "molecular orbital' Hamiltonians

$$-\frac{\hbar^2}{2m}\nabla_i^2\psi_i(\vec{r}_i) = E_i\psi_i(\vec{r}_i)$$

$$\Psi(\vec{r}_1,\vec{r}_2,\cdots,\vec{r}_N) = \mathcal{A}\left(\psi_1(\vec{r}_1)\uparrow\psi_1(\vec{r}_1)\downarrow\psi_2(\vec{r}_2)\uparrow\psi_2(\vec{r}_2)\downarrow\cdots\right),$$

$$E = E_1\uparrow + E_1\downarrow + E_2\uparrow + E_2\downarrow + \cdots.$$

Free particles in 1-d

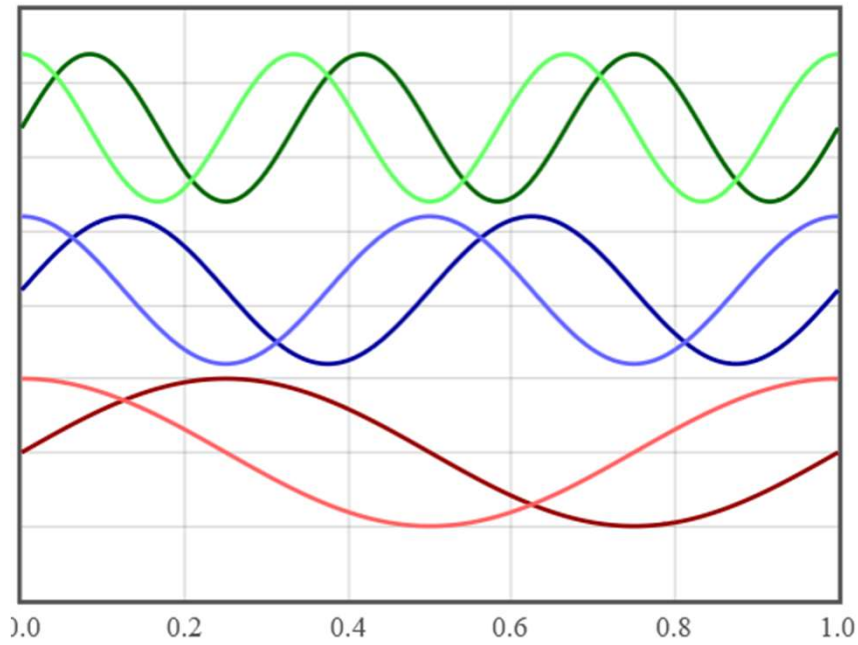
Fill the electrons states like in an atom.

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$$

$$V(x) = 0$$

$$\psi_k = \frac{e^{i(kx-\omega t)}}{\sqrt{L}}$$

$$\psi_k^{\,*}\,\psi_k = \frac{1}{L}$$



Non interacting fermions

$$\psi = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}}$$

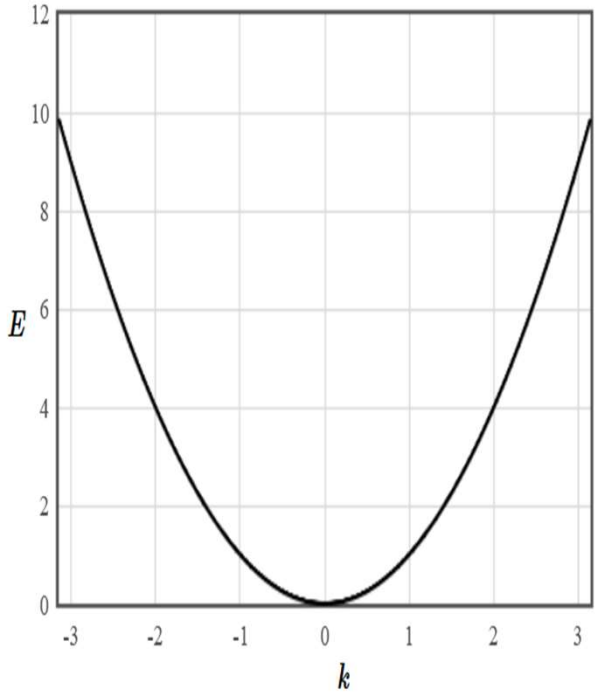
$$\psi^* \psi = \frac{1}{V}$$

Free particles in 1-d

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} \qquad V = 0$$

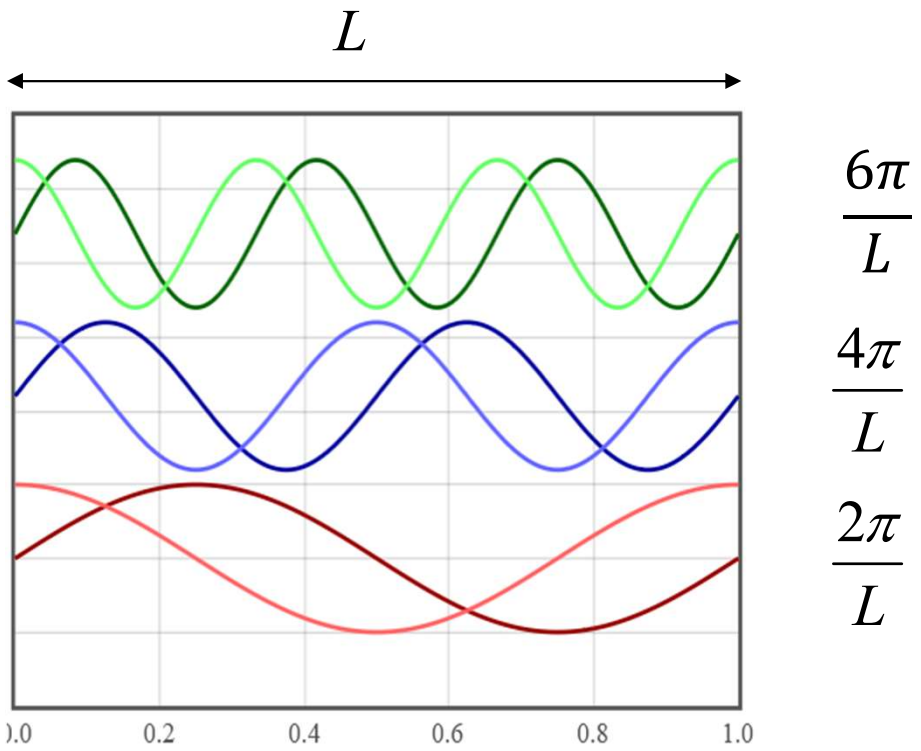
Eigen function solutions: $\psi_k = \dfrac{e^{i(kx-\omega t)}}{\sqrt{L}}$

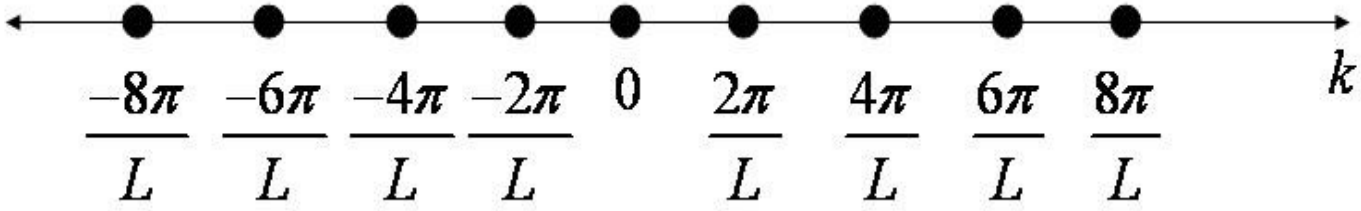
Dispersion relation: $E = \hbar\omega = \dfrac{\hbar^2 k^2}{2m} = \dfrac{1}{2}mv^2$



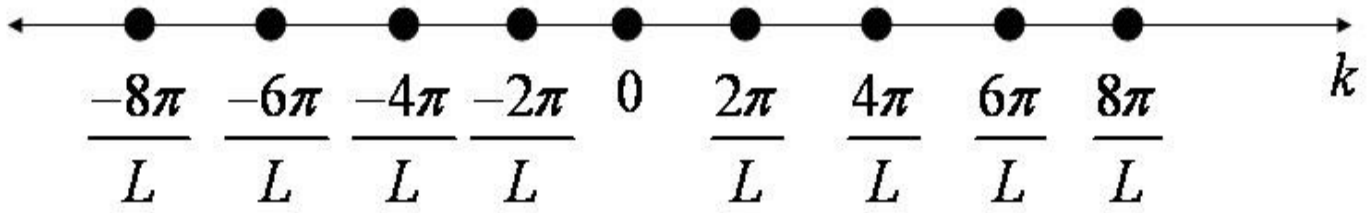
Periodic boundary conditions

$$\psi_k = \frac{e^{i(kx-\omega t)}}{\sqrt{L}}$$





Periodic boundary conditions



Left and right

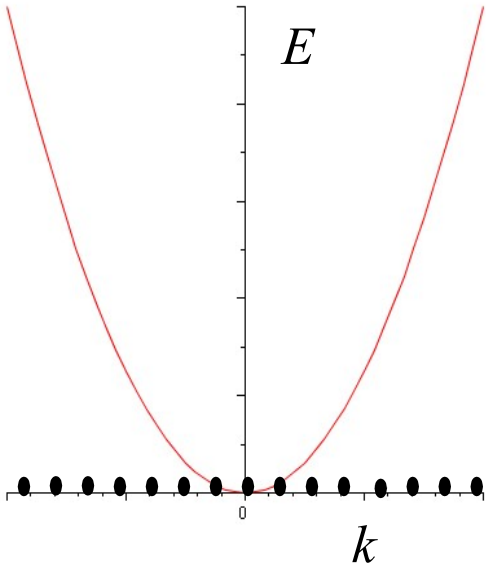
Spin

$$LD(|k|)dk = \frac{2 \cdot 2dk}{\frac{2\pi}{L}}$$

Density of states in k: $D(|k|) = \frac{2}{\pi}$

Number of states between $|k|$ and $|k|+dk$ is $LD(|k|)dk$

Free particles in 1-d

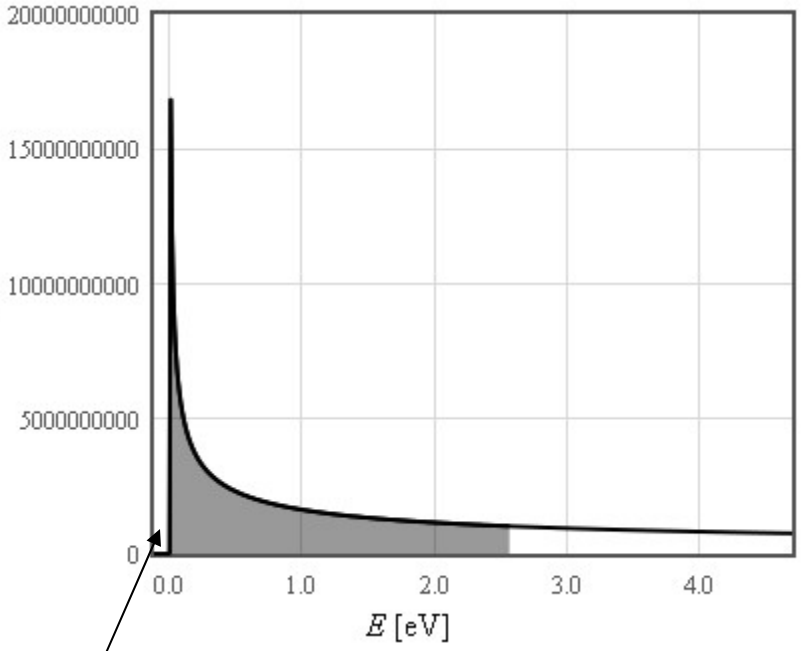


$$D(k) = \frac{2}{\pi} \longleftarrow \text{Spin}$$

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

$$\frac{dk}{dE} = \frac{1}{2\hbar}\sqrt{\frac{2m}{E}}$$

Density of states



$$D(E) = \frac{1}{\pi\hbar}\sqrt{\frac{2m}{E}}$$

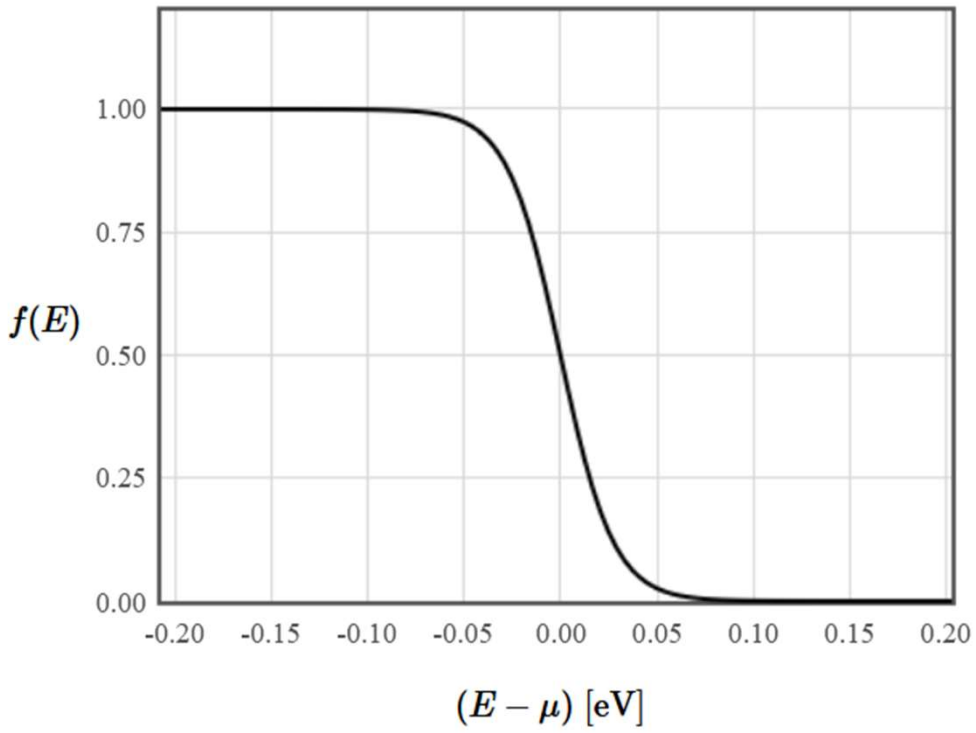
Van Hove singularity

E

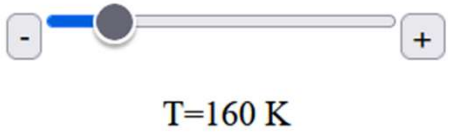
Fermi function

$f(E)$ is the probability that a state at energy E is occupied.

$$f(E) = \frac{1}{1 + \exp\left(\frac{E - \mu}{k_B T}\right)}$$



μ = chemical potential

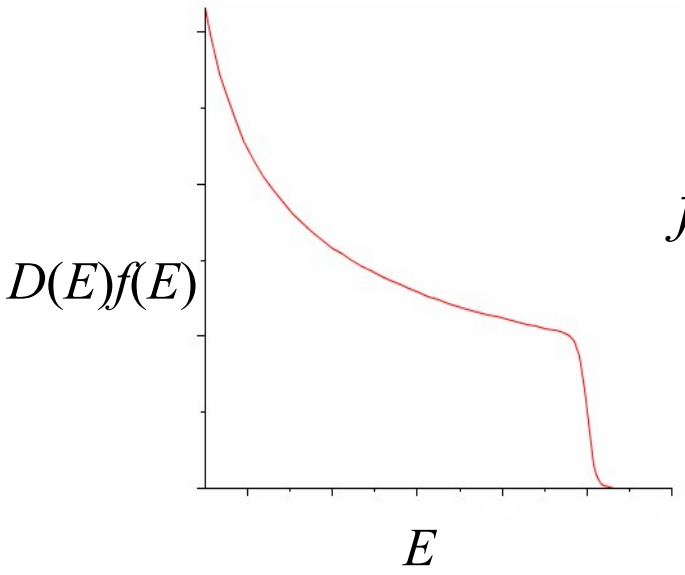


T=160 K

http://lampz.tugraz.at/~hadley/ss1/materials/thermo/gp/gp/Fermi-function.html

Chemical potential

$$D(E) = \frac{1}{\pi\hbar}\sqrt{\frac{2m}{E}}$$



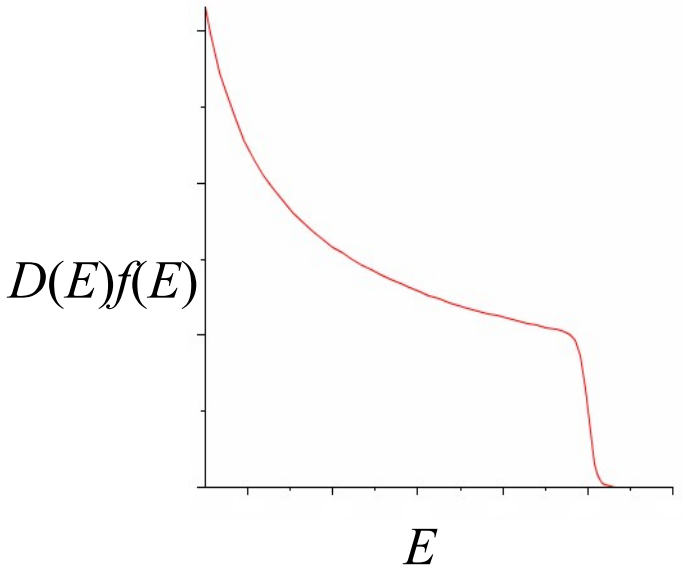
$$f(E) = \frac{1}{1+\exp\left(\dfrac{E-\mu}{k_B T}\right)}$$

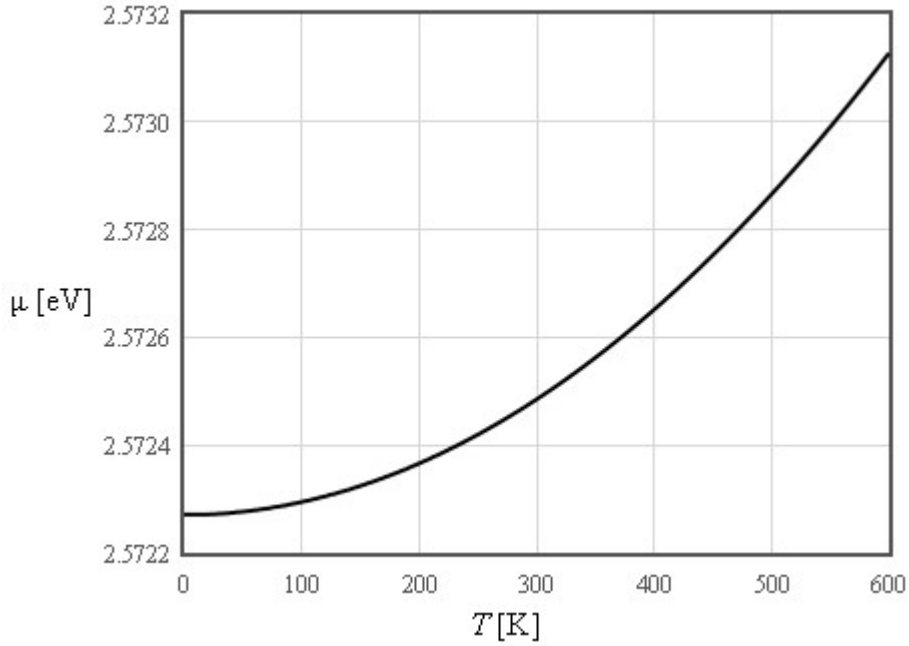
The chemical potential is implicitly defined as the energy that solves the following equation.

$$n = \frac{N}{L} = \int_{-\infty}^{\infty} D(E) f(E) dE = \int_{-\infty}^{\infty} \frac{D(E)dE}{1+\exp\left(\dfrac{E-\mu}{k_B T}\right)}$$

Here N is the total number of electrons.

Chemical potential





μ is temperature dependent

Fermi energy

In solid state physics books,

$$E_F = \mu(T=0).$$

In semiconductor books, $E_F(T) = \mu(T)$.

At $T = 0$ $$n = \int_{-\infty}^{E_F} D(E)dE$$

In one dimension,

$$n = \int_0^{E_F} \frac{1}{\pi\hbar}\sqrt{\frac{2m}{E}}dE = \frac{2}{\pi\hbar}\sqrt{2mE_F}$$

$$E_F = \frac{\pi^2\hbar^2 n^2}{8m}$$

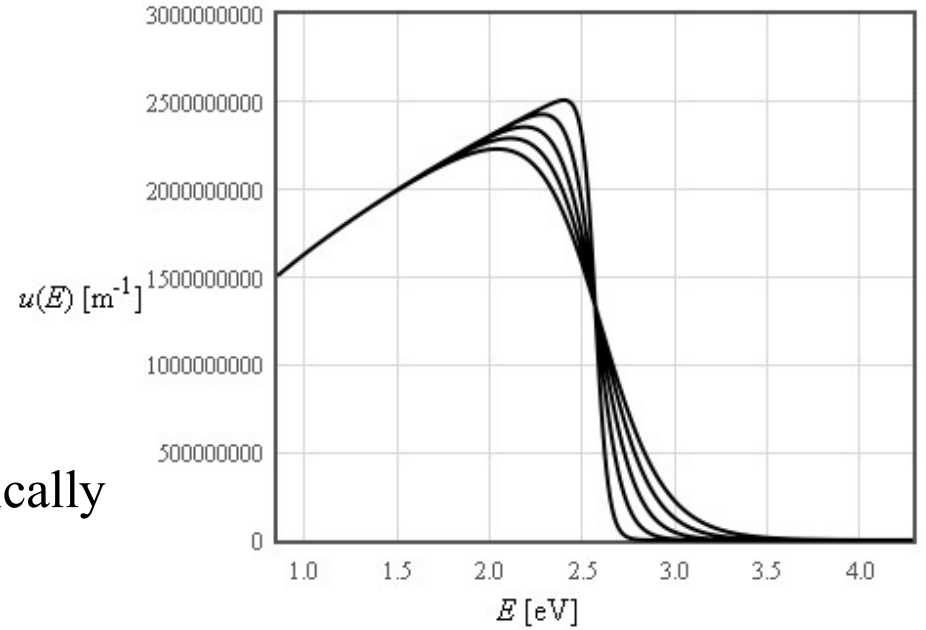
Free particles in 1-d

internal energy spectral density

$$u(E) = ED(E)f(E) = \frac{\sqrt{2mE}}{\pi\hbar}\frac{1}{\exp\left(\frac{E-\mu}{k_B T}\right)+1}$$

$$u = \int_{-\infty}^{\infty} u(E)dE$$

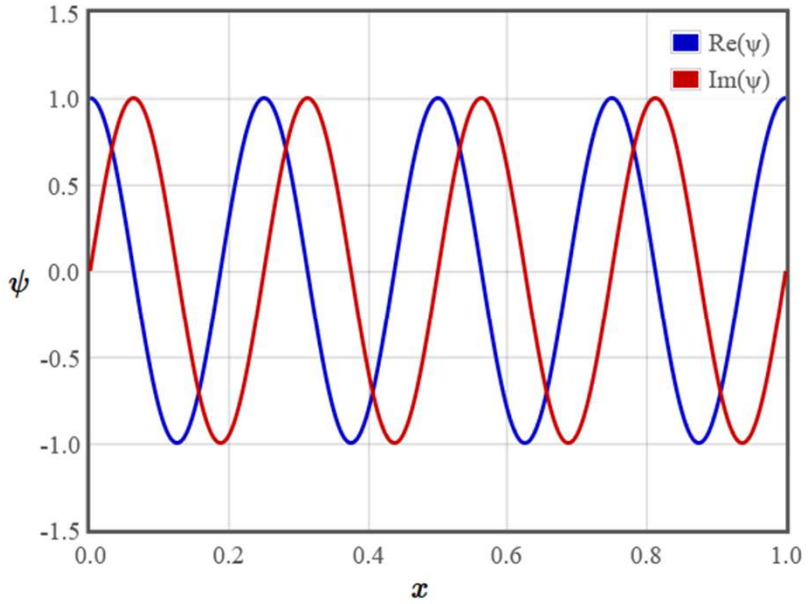
$$c_v = \frac{du}{dT}$$



Not possible to do this integral analytically

analog to the Planck curve for electrons in 1-d

Free-electron model



$n_x = 4$ [+] [-]

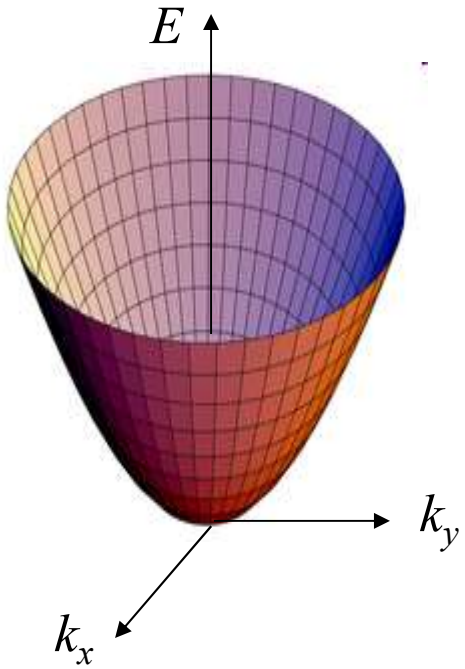
Single particle solutions to Schrödinger equation	$\psi(\vec{r}) = \frac{1}{\sqrt{L}} e^{ikx} \quad \frac{1}{\sqrt{\mathrm{m}}}$	$\psi(\vec{r}) = \frac{1}{\sqrt{L^2}} e^{i\vec{k}\cdot\vec{r}} \quad \frac{1}{\mathrm{m}}$	$\psi(\vec{r}) = \frac{1}{\sqrt{L^3}} e^{i\vec{k}\cdot\vec{r}} \quad \frac{1}{\mathrm{m}^{3/2}}$
Allowed k values	$k_x = \frac{2\pi n_x}{L} \quad \frac{1}{\mathrm{m}}$ $n_x = \cdots -2, -1, 0, 1, 2, \cdots$	$\vec{k} = \left[\frac{2\pi n_x}{L}, \frac{2\pi n_y}{L}\right] \quad \frac{1}{\mathrm{m}}$ $n_x, n_y = \cdots -2, -1, 0, 1, 2, \cdots$	$\vec{k} = \left[\frac{2\pi n_x}{L}, \frac{2\pi n_y}{L}, \frac{2\pi n_z}{L}\right] \quad \frac{1}{\mathrm{m}}$ $n_x, n_y, n_z = \cdots -2, -1, 0, 1, 2, \cdots$
Density of electron states in reciprocal space	$D(\vec{k}) = \frac{2}{2\pi}$	$D(\vec{k}) = \frac{2}{(2\pi)^2}$	$D(\vec{k}) = \frac{2}{(2\pi)^3}$
Density of electron states in reciprocal space	$D(k) = \frac{2}{}$	$D(k) = \frac{k}{} \quad \mathrm{m}^{-1}$	$D(k) = \frac{k^2}{} \quad \mathrm{m}^{-2}$

Free particles in 2-d

Density of states

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

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



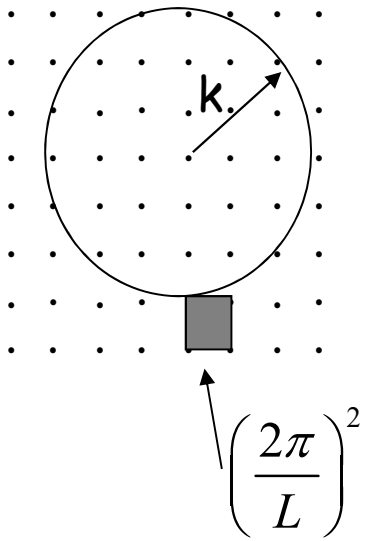
$$\frac{dk}{dE} = \frac{1}{2\hbar}\sqrt{\frac{2m}{E}}$$

Free particles in 2-d

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

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

$$\frac{dk}{dE} = \frac{1}{2\hbar}\sqrt{\frac{2m}{E}}$$



$$L^2 D(|k|)dk = \frac{2 \cdot 2\pi k dk}{\left(\frac{2\pi}{L}\right)^2}$$

$$D(|k|) = \frac{k}{\pi} \quad \mathrm{m}^{-1}$$

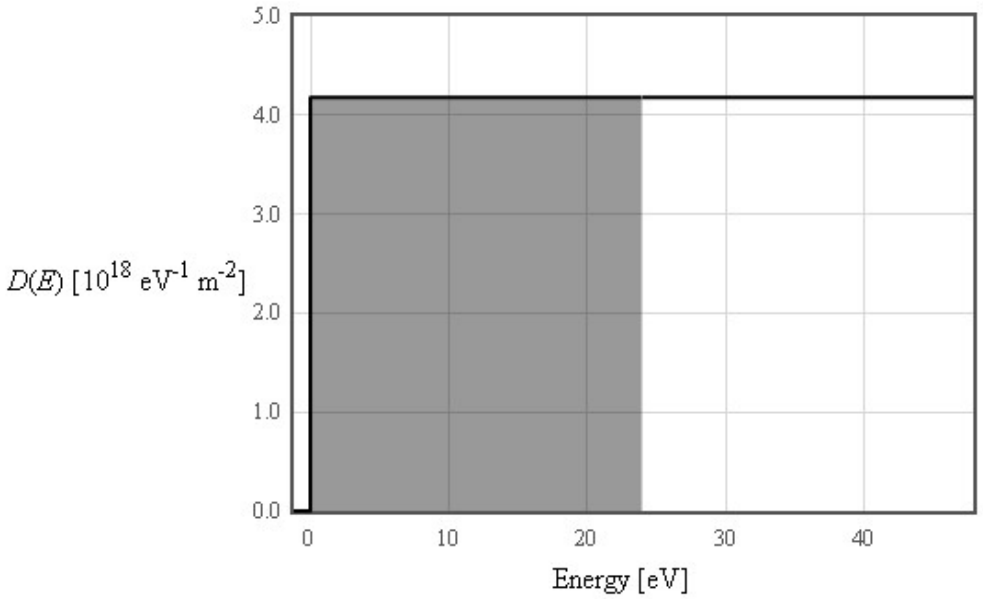
$$D(E) = D(|k|)\frac{dk}{dE}$$

$$D(E) = \frac{k}{\pi}\frac{dk}{dE} = \frac{\sqrt{2mE}}{\hbar\pi}\frac{1}{2\hbar}\sqrt{\frac{2m}{E}}$$

$$\boxed{D(E) = \frac{m}{\pi\hbar^2}}$$

Free particles in 2-d

$$D(E) = \frac{m}{\pi\hbar^2}$$



At $T = 0$:

$$n = \int_0^{E_F} D(E)dE$$

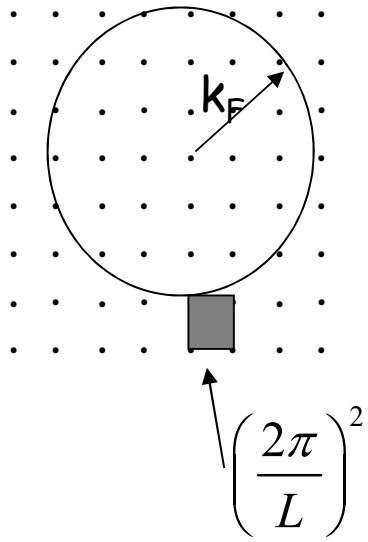
$$n = \frac{N}{L^2} = \frac{m}{\pi\hbar^2}\int_0^{E_F} dE = \frac{m}{\pi\hbar^2}E_F$$

$$E_F = \frac{\pi\hbar^2 n}{m}$$

Fermi circle

spin

$$N = \frac{2\pi k_F^2}{\left(\frac{2\pi}{L}\right)^2}$$



$n = N/L^2$ = electron density

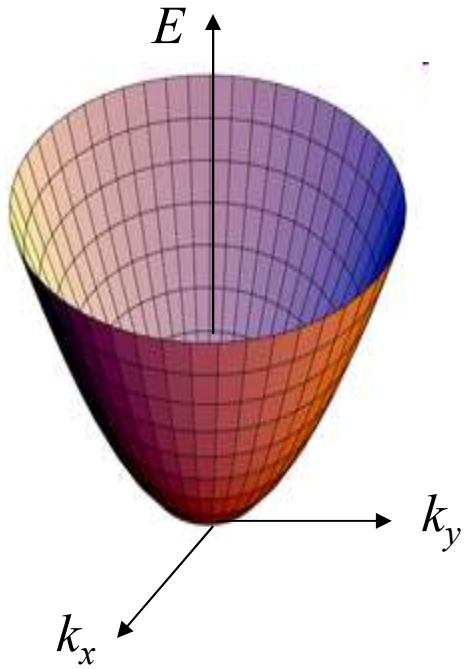
$$k_F = \sqrt{2\pi n}$$

$$E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\pi \hbar^2 n}{m}$$

At $T = 0$, all states inside the Fermi circle are occupied and those outside are empty.

Free particles in 3-d

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



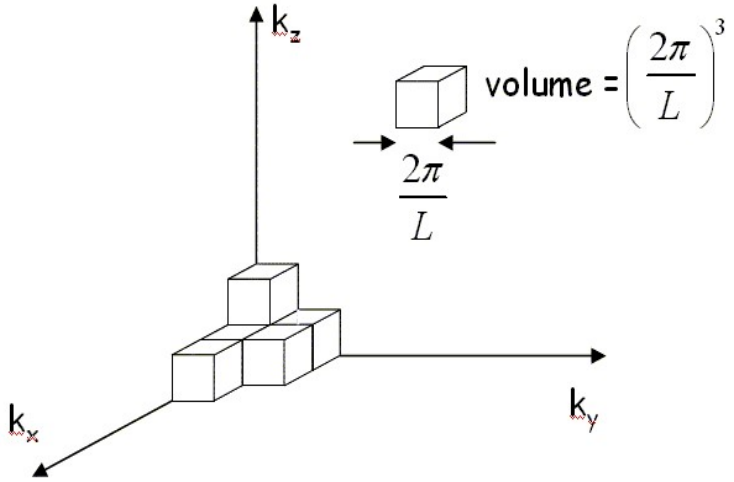
Density of states

$$D(|k|) = \frac{k^2}{\pi^2}$$

$$\frac{dk}{dE} = \frac{1}{2\hbar}\sqrt{\frac{2m}{E}}$$

$$k^2 = \frac{2mE}{\hbar^2}$$

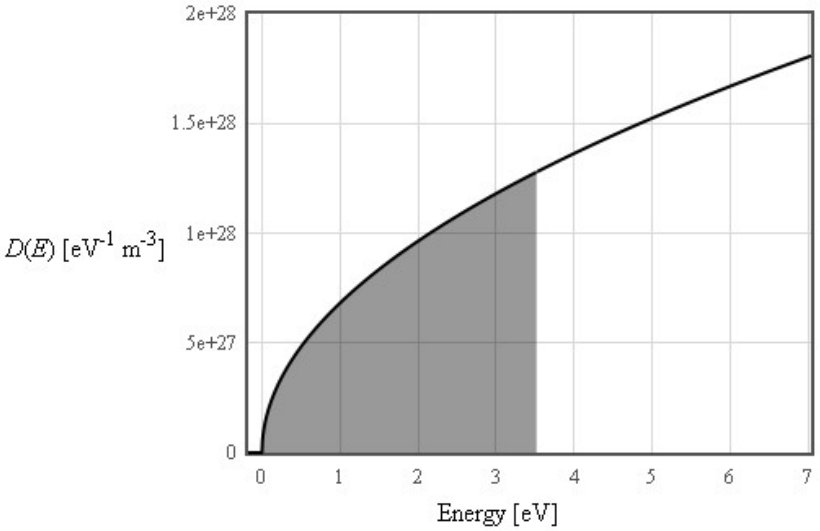
$$D(E) = D(|k|)\frac{dk}{dE}$$



$$k_x, k_y, k_z = \ldots, \frac{-4\pi}{L}, \frac{-2\pi}{L}, 0, \frac{2\pi}{L}, \frac{4\pi}{L}, \ldots$$

$$\boxed{D(E) = \frac{(2m)^{\frac{3}{2}}}{2\pi^2\hbar^3}\sqrt{E}}$$

Free particles in 3-d



At $T = 0$:

$$n = \int_0^{E_F} D(E)dE$$

$$n = \frac{N}{L^3} = \frac{\sqrt{2}m^{3/2}}{\pi^2\hbar^3}\int_0^{E_F}\sqrt{E}dE = \frac{(2m)^{3/2}}{3\pi^2\hbar^3}E_F^{3/2}$$

$$E_F = \frac{\hbar^2}{2m}\left(3\pi^2 n\right)^{2/3}$$

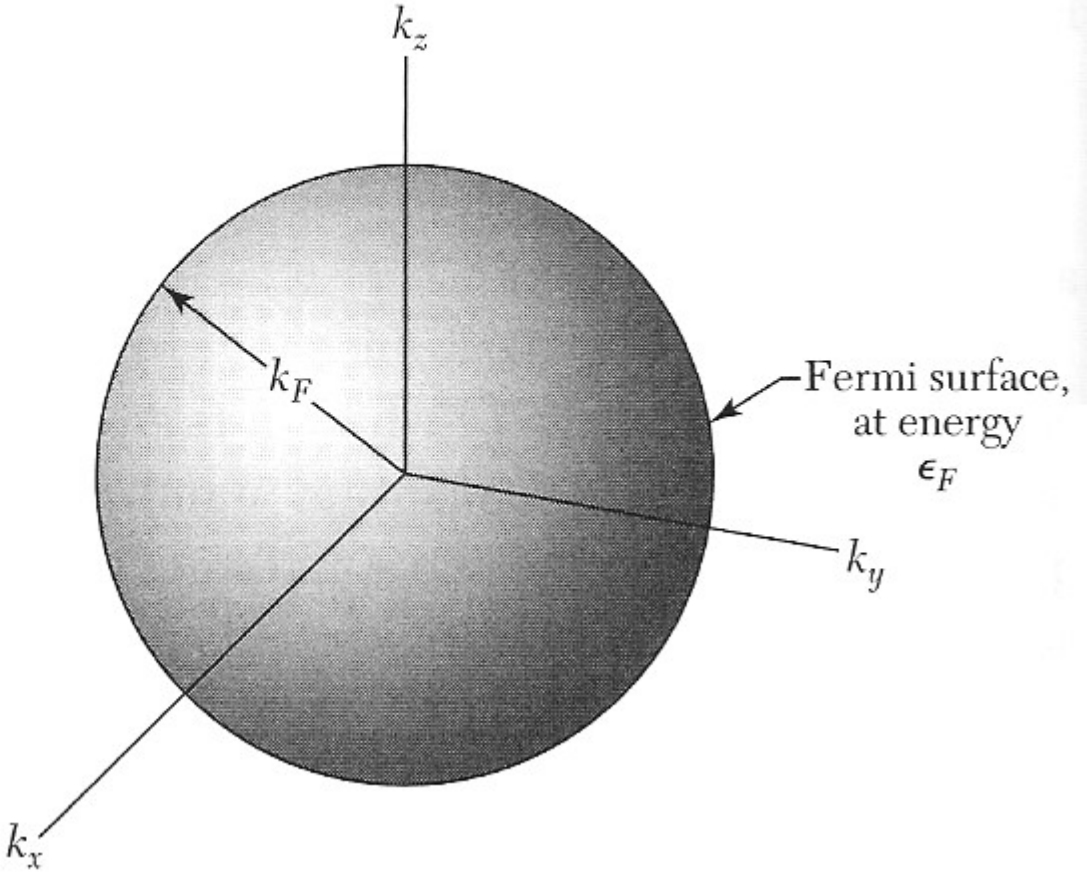
Fermi sphere

$$N = 2\frac{4\pi k_F^3}{3\left(\frac{2\pi}{L}\right)^3}$$

spin

$$k_F = \left(3\pi^2 n\right)^{1/3}$$

n = electron density



$$E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2\left(3\pi^2 n\right)^{2/3}}{2m}$$

$$v_F = \frac{\hbar k_F}{m}$$

$$T_F = \frac{E_F}{k_B}$$

The thermal and electronic properties depend on the states at the Fermi surface.

Table 1 Calculated free electron Fermi surface parameters for metals at room temperature

(Except for Na, K, Rb, Cs at 5 K and Li at 78 K)

Valency	Metal	Electron concentration, in cm^{-3}	Radius[a] parameter r_n	Fermi wavevector, in cm^{-1}	Fermi velocity, in cm s^{-1}	Fermi energy, in eV	Fermi temperature $T_F \equiv \epsilon_F/k_B$, in deg K
1	Li	4.70×10^{22}	3.25	1.11×10^{8}	1.29×10^{8}	4.72	5.48×10^{4}
	Na	2.65	3.93	0.92	1.07	3.23	3.75
	K	1.40	4.86	0.75	0.86	2.12	2.46
	Rb	1.15	5.20	0.70	0.81	1.85	2.15
	Cs	0.91	5.63	0.64	0.75	1.58	1.83
	Cu	8.45	2.67	1.36	1.57	7.00	8.12
	Ag	5.85	3.02	1.20	1.39	5.48	6.36
	Au	5.90	3.01	1.20	1.39	5.51	6.39
2	Be	24.2	1.88	1.93	2.23	14.14	16.41
	Mg	8.60	2.65	1.37	1.58	7.13	8.27
	Ca	4.60	3.27	1.11	1.28	4.68	5.43
	Sr	3.56	3.56	1.02	1.18	3.95	4.58
	Ba	3.20	3.69	0.98	1.13	3.65	4.24
	Zn	13.10	2.31	1.57	1.82	9.39	10.90
	Cd	9.28	2.59	1.40	1.62	7.46	8.66
3	Al	18.06	2.07	1.75	2.02	11.63	13.49
	Ga	15.30	2.19	1.65	1.91	10.35	12.01
	In	11.49	2.41	1.50	1.74	8.60	9.98
4	Pb	13.20	2.30	1.57	1.82	9.37	10.87
	Sn(w)	14.48	2.23	1.62	1.88	10.03	11.64

[a]The dimensionless radius parameter is defined as $r_n = r_0/a_H$, where a_H is the first Bohr radius and r_0 is the radius of a sphere that contains one electron.

$$k_F = \left(3\pi^2 n\right)^{1/3} \qquad E_F >> k_B T$$

Free electron Fermi gas

1 - d $$D(E) = \sqrt{\frac{2m}{\hbar^2 \pi^2 E}} = \frac{n}{2\sqrt{E_F E}} \quad \mathrm{J^{-1}m^{-1}}$$

2 - d $$D(E) = \frac{m}{\hbar^2 \pi} = \frac{n}{E_F} \quad \mathrm{J^{-1}m^{-2}}$$

3 - d $$D(E) = \frac{\pi}{2}\left(\frac{2m}{\hbar^2 \pi^2}\right)^{3/2} \sqrt{E} = \frac{3n}{2E_F^{3/2}} \sqrt{E} \quad \mathrm{J^{-1}m^{-3}}$$