Thermal conductivity, Free Electrons

Thermal conductivity

$$\vec{j}_U = \bar{E}\vec{j}$$

Average particle energy

$$u = \bar{E}n$$

internal energy density

$$\vec{j}_U = -\bar{E}D\nabla n = -D\nabla u$$

$$\vec{j}_U = -D\frac{du}{dT}\nabla T = -Dc_v\nabla T$$

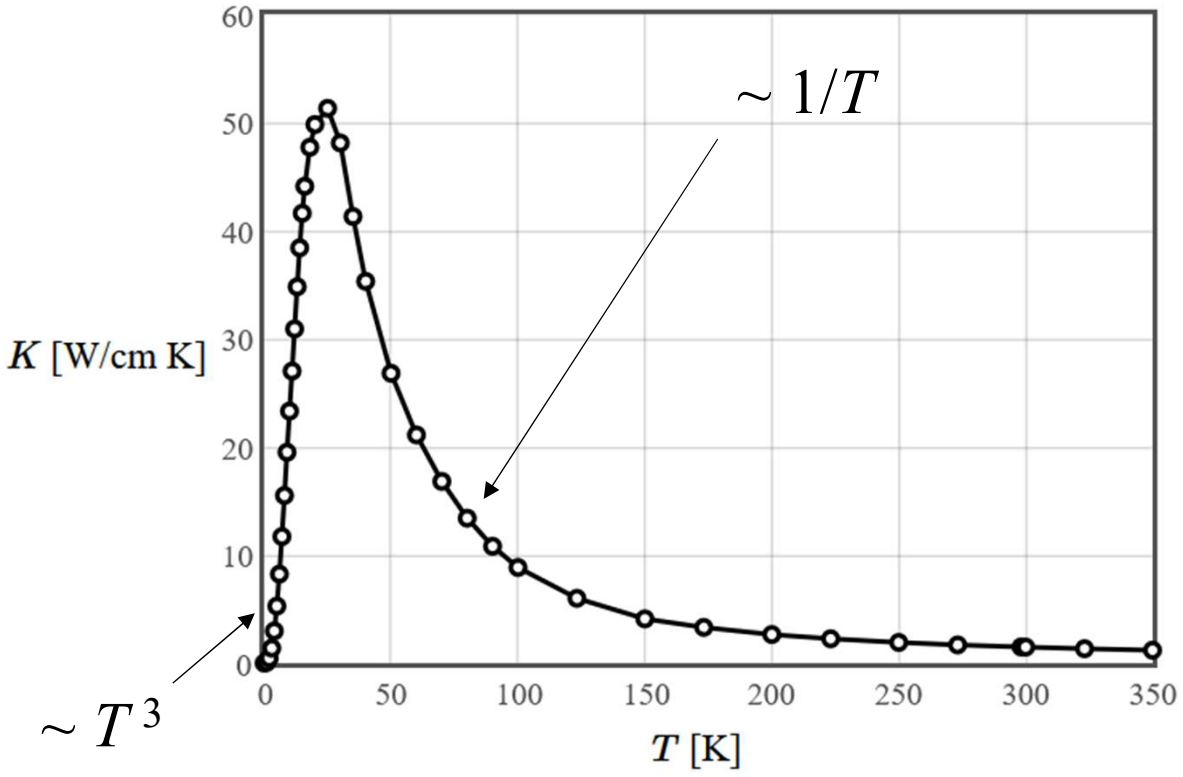
$$\vec{j}_U = -K\nabla T$$

Thermal conductivity

$$K = Dc_v$$

$$K \to 0 \quad \text{as} \quad T \to 0$$

Thermal conductivity $\vec{j}_U = -K\nabla T$

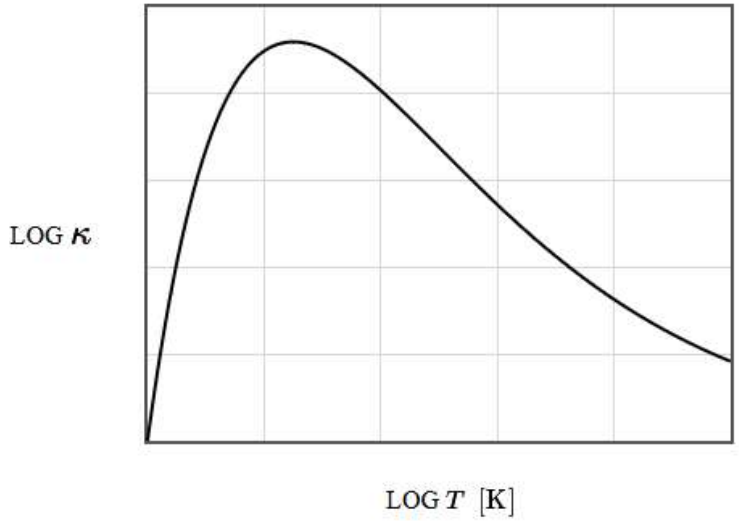


The thermal conductivity of silicon.[1]

Thermal conductivity

$$\vec{j}_U = -K\nabla T$$

Material	**Thermal conductivity W/(m·K)**
Glass	1.1
Concrete, stone	1.7
Ice	2
Sandstone	2.4
Sapphire	35
Stainless steel	12.11 ~ 45.0
Lead	35.3
Aluminum	237
Aluminum alloys	120—180
Gold	318
Copper	401
Silver	429
Diamond	900 - 2320
Graphene	(4840±440) - (5300±480)



Phonon student projects

Calculate a dispersion relation for some other Bravais lattice.

Finish the Javascript calculation of the phonon density of states for fcc.

Calculate one column of the phonon table: hcp, NaCl, CsCl, ZnS, diamond, ...

Calculate the temperatures at which ZnO goes through phase transitions.

Free electron Fermi gas

Kittel, chapter 6

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

Like the problem of photons in a box except:

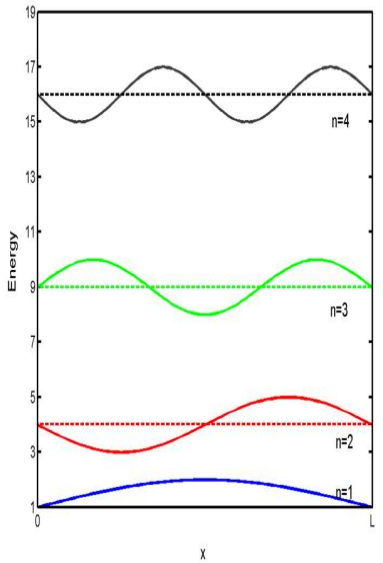
Solve the Schrödinger equation instead of the wave equation.

Electrons are fermions not bosons.

Free particles in 1-d

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

$$E = \frac{n^2h^2}{8mL^2} = \frac{h^2}{2m\lambda^2} = \frac{p^2}{2m} = \frac{\hbar^2k^2}{2m} = \frac{mv^2}{2}$$



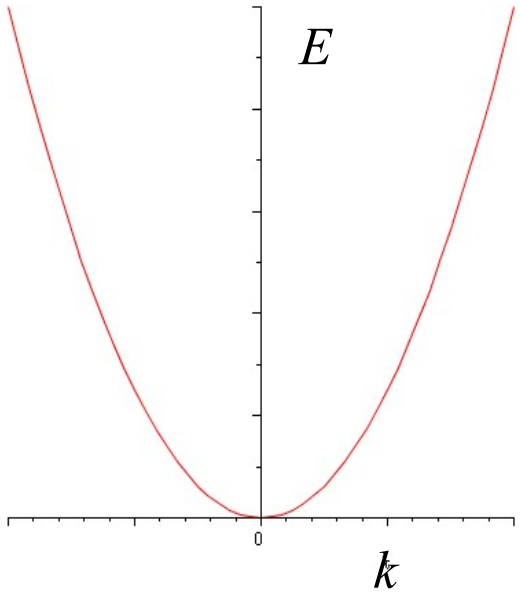
$$\lambda = \frac{2L}{n}$$

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: $\psi_k = A_k e^{i(kx-\omega t)}$

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



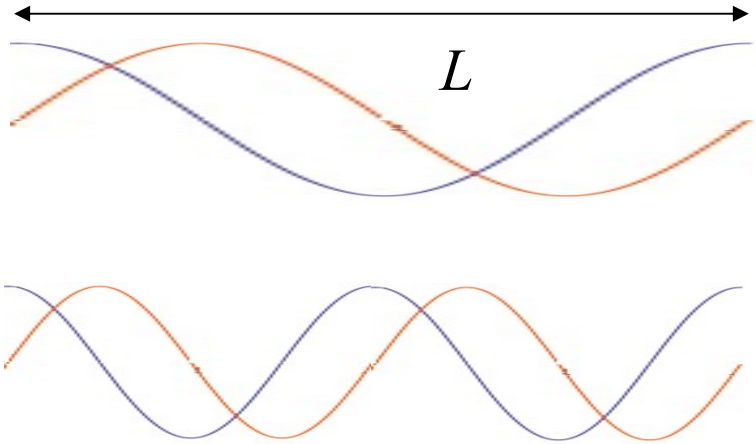
Non interacting fermions

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

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

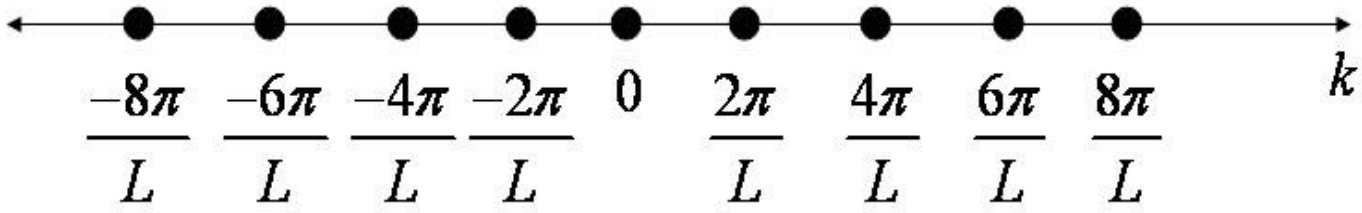
Periodic boundary conditions

$$\psi = A_k e^{i(kx-\omega t)}$$



$$\frac{2\pi}{L}$$

$$\frac{4\pi}{L}$$



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

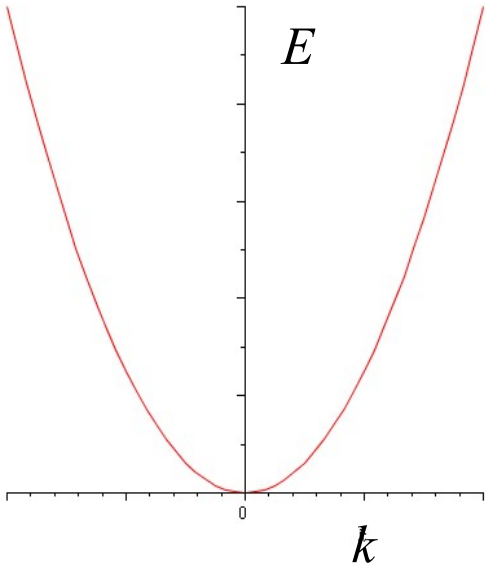
Density of states:

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

← Spin

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

Free particles in 1-d



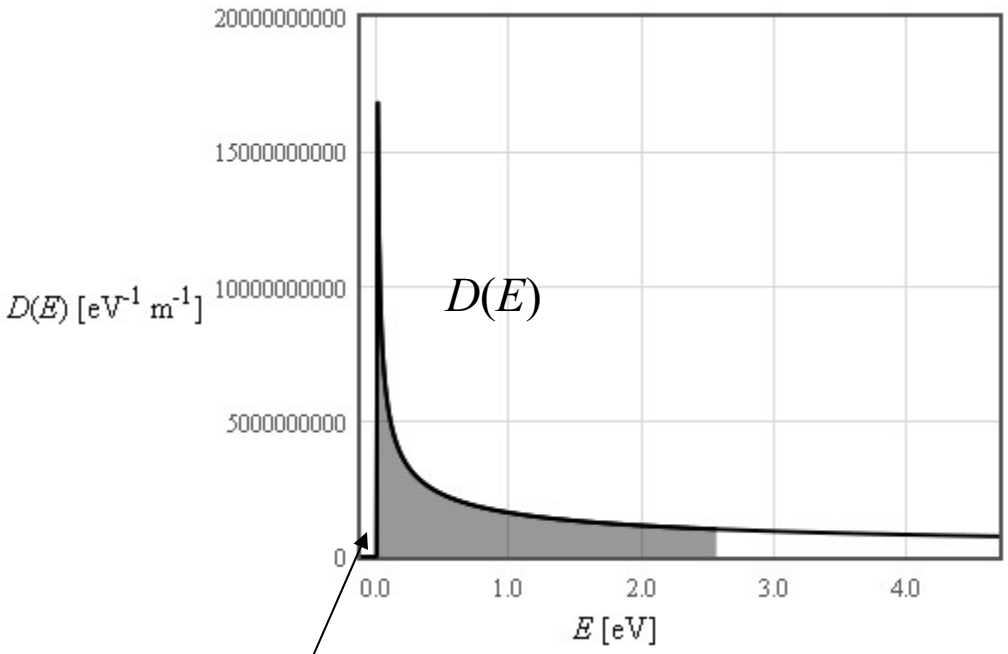
$$D(k) = \frac{2}{\pi} \longleftarrow \text{Spin}$$

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

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

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

Density of states



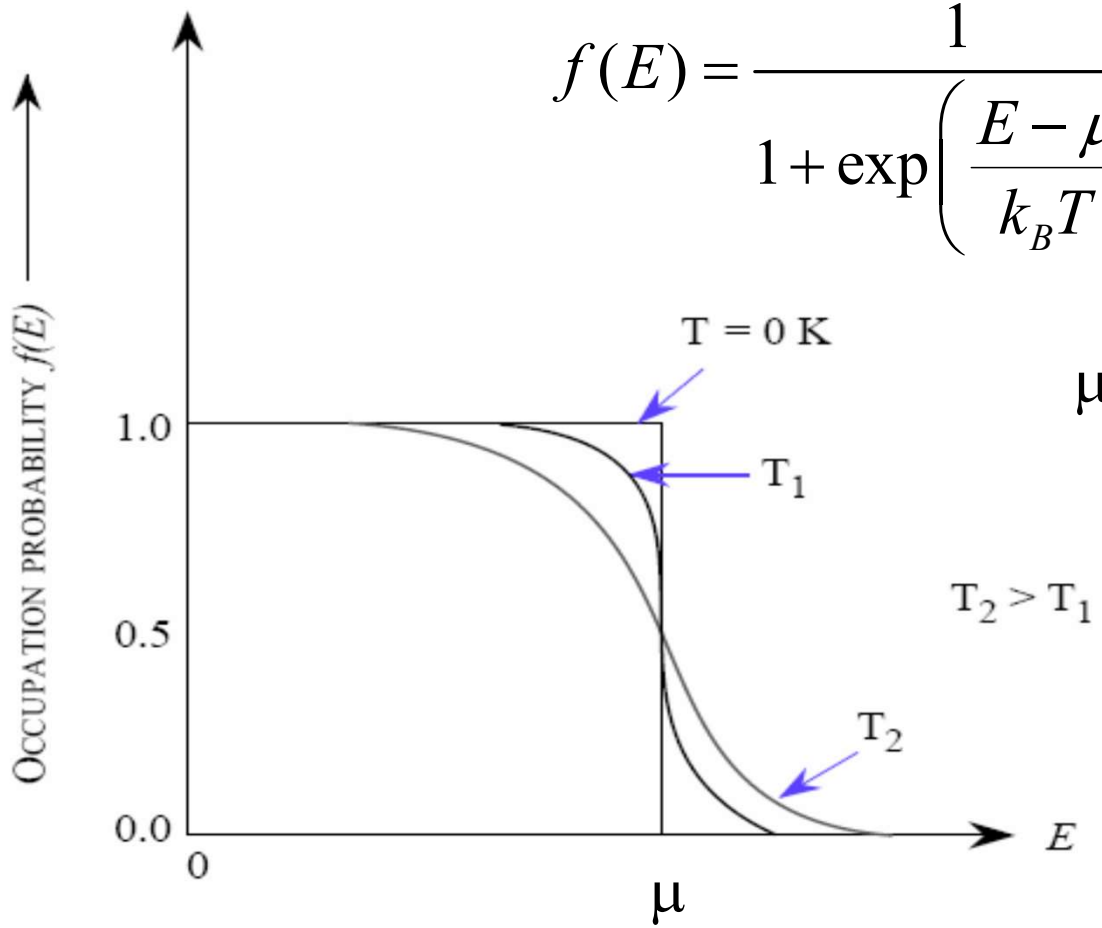
Van Hove singularity

E

Fermi function

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

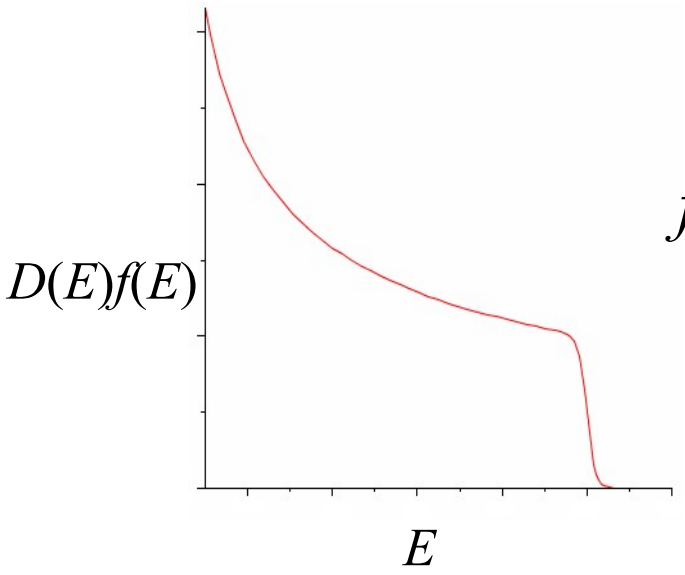
$$f(E) = \frac{1}{1 + \exp\left(\frac{E - \mu}{k_B T}\right)}$$



μ = chemical potential

Chemical potential

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



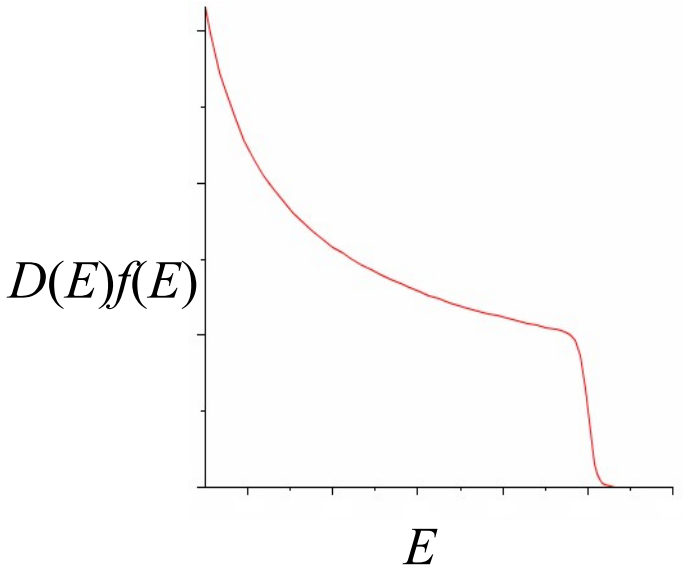
$$f(E) = \frac{1}{1+\exp\left(\dfrac{E-\mu}{k_B T}\right)}$$

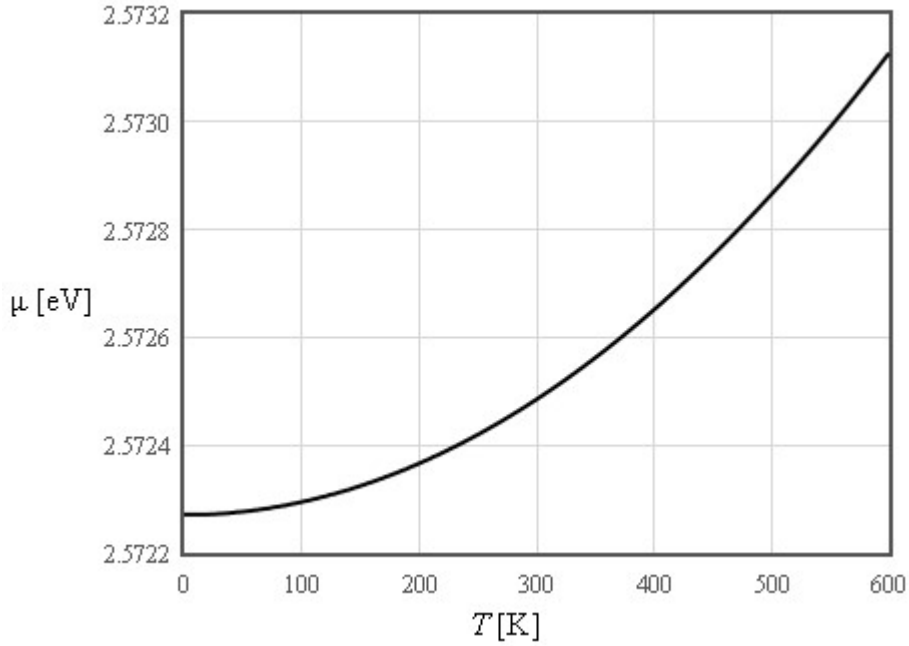
The chemical potential is implicitly defined as the energy that solves the following equation.

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

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,

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

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

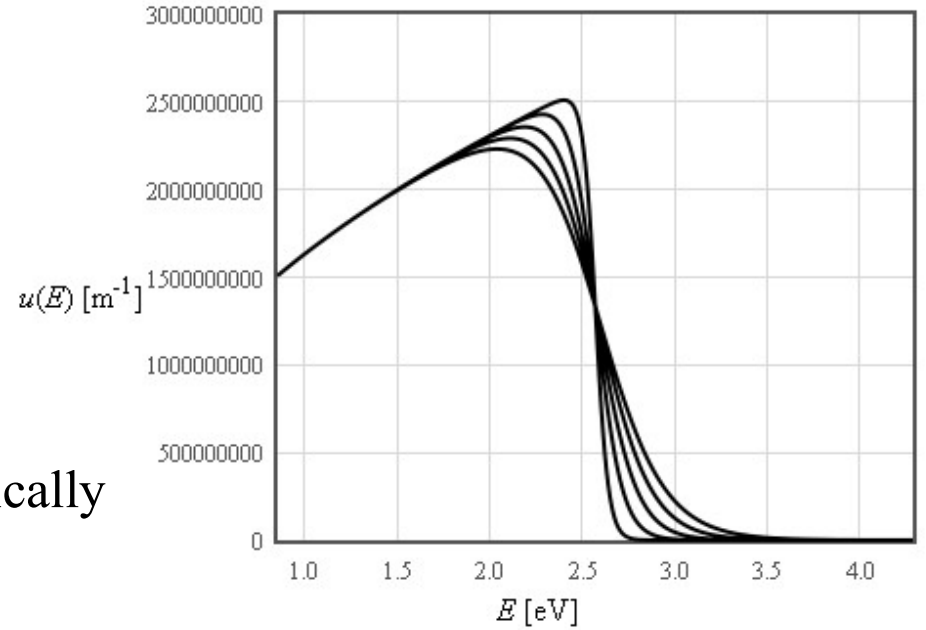
Free particles in 1-d

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

Thermodynamic properties

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

From the density of states, the thermodynamic properties can be calculated.

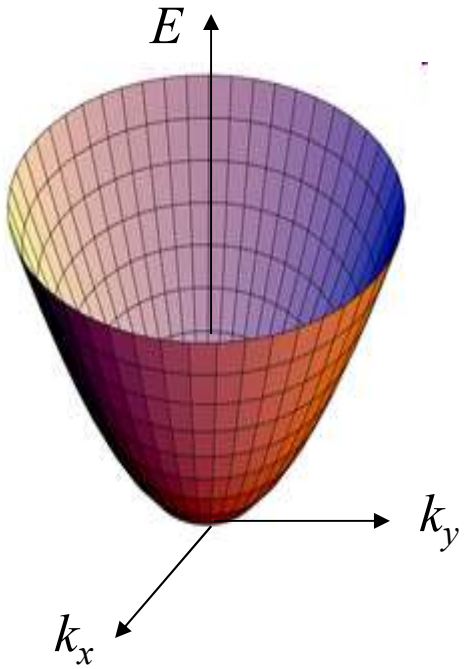
Internal energy $u = \int_{-\infty}^{\infty} ED(E)f(E)dE$	$u \approx \frac{1}{3}nE_F + \frac{\pi^2 D(E_F)}{6}(k_B T)^2$ J m^{-1} $\approx \frac{\pi^2\hbar^2 n^3}{24m} + \frac{2m}{3\hbar^2 n}(k_B T)^2$ J m^{-1}
Specific heat $c_v = \left(\frac{\partial u}{\partial T}\right)_{V=const}$	$c_v \approx \frac{\pi^2 D(E_F)}{3}k_B^2 T$ J K^{-1}m^{-1} $\approx \frac{4m}{3\hbar^2 n}k_B^2 T$ J K^{-1}m^{-1}
Entropy $s = \int \frac{c_v}{T}dT$	$s \approx \frac{\pi^2 D(E_F)}{3}k_B^2 T$ J K^{-1}m^{-1} $\approx \frac{4m}{3\hbar^2 n}k_B^2 T$ J K^{-1}m^{-1}
Helmholtz free energy $f = u - Ts$	$f \approx \frac{1}{3}nE_F - \frac{\pi^2 D(E_F)}{6}(k_B T)^2$ J m^{-1} $\approx \frac{\pi^2\hbar^2 n^3}{24m} - \frac{2m}{3\hbar^2 n}(k_B T)^2$ J m^{-1}
Pressure $P = -\left.\frac{\partial F}{\partial V}\right\|_{N,T}$	$P \approx \frac{2}{3}nE_F + \frac{\pi^2 D(E_F)}{3}(k_B T)^2$ N $P \approx \frac{\pi^2\hbar^2 n^3}{12m} + \frac{4m}{3\hbar^2 n}(k_B T)^2$ N
Bulk modulus $B = -V\frac{\partial P}{\partial V}$	$B \approx 2nE_F - \frac{\pi^2 D(E_F)}{3}(k_B T)^2$ N $B \approx \frac{\pi^2\hbar^2 n^3}{4m} - \frac{4m}{3\hbar^2 n}(k_B T)^2$ N

Free particles in 2-d

Density of states

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

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



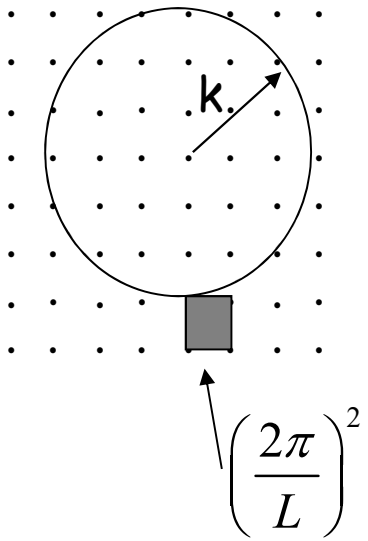
$$\frac{dk}{dE} = \frac{1}{2\hbar}\sqrt{\frac{2m}{E}}$$

Free particles in 2-d

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

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

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



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

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

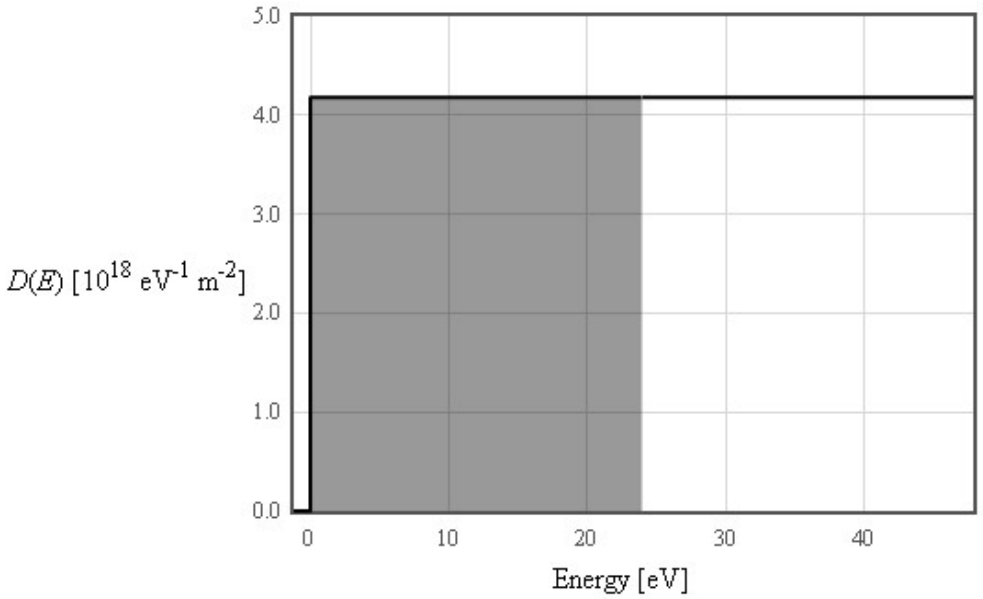
$$D(E) = D(k)\frac{dk}{dE}$$

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

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

Free particles in 2-d

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



At $T = 0$:

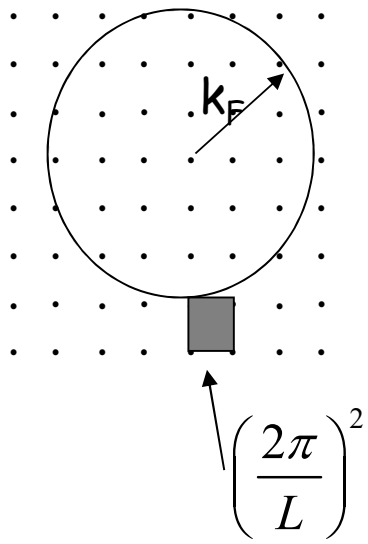
$$n = \int_0^{E_F} D(E)dE$$

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

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

Fermi circle

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



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

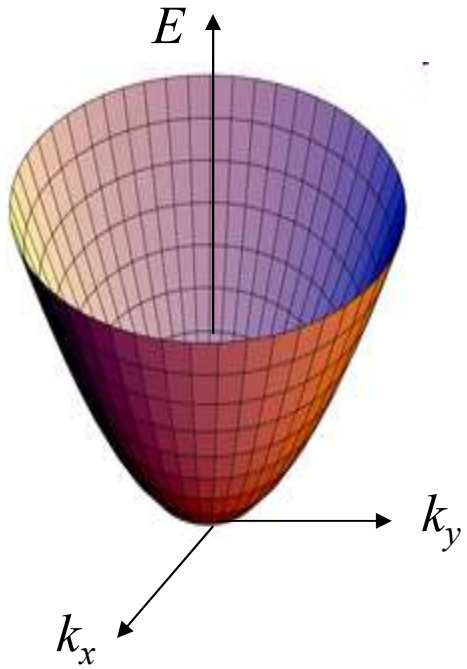
$$k_F = \sqrt{2\pi n}$$

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

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

Free particles in 3-d

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



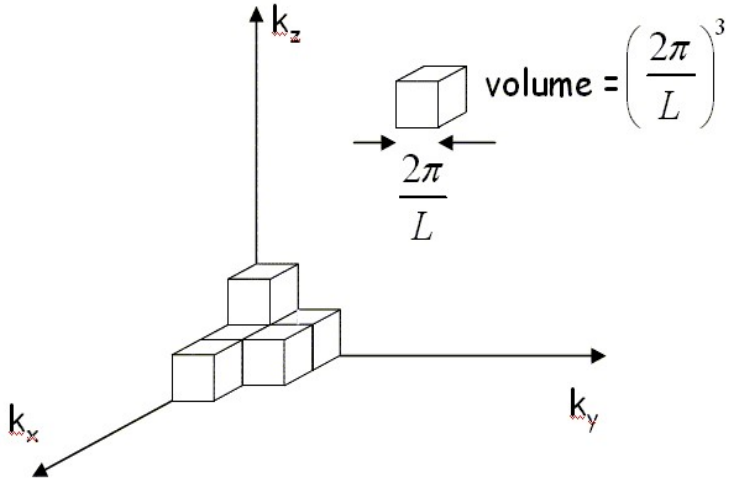
Density of states

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

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

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

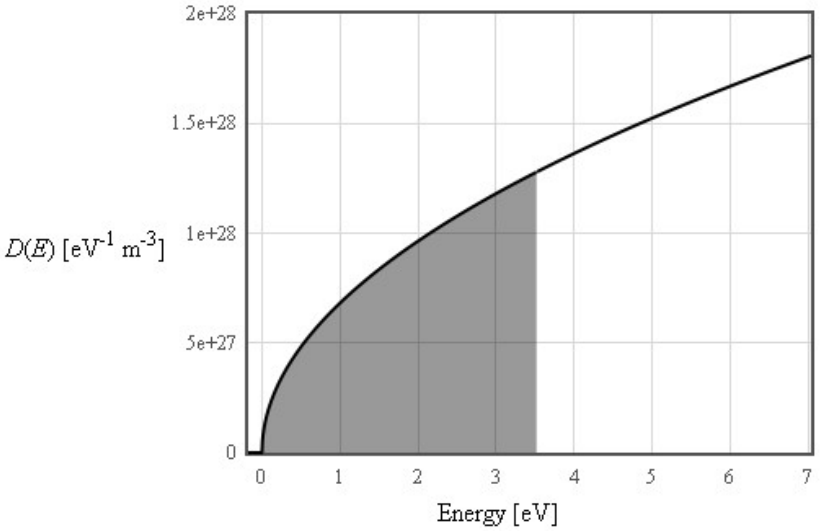
$$D(E) = D(k)\frac{dk}{dE}$$



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

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

Free particles in 3-d



At $T = 0$:

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

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

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

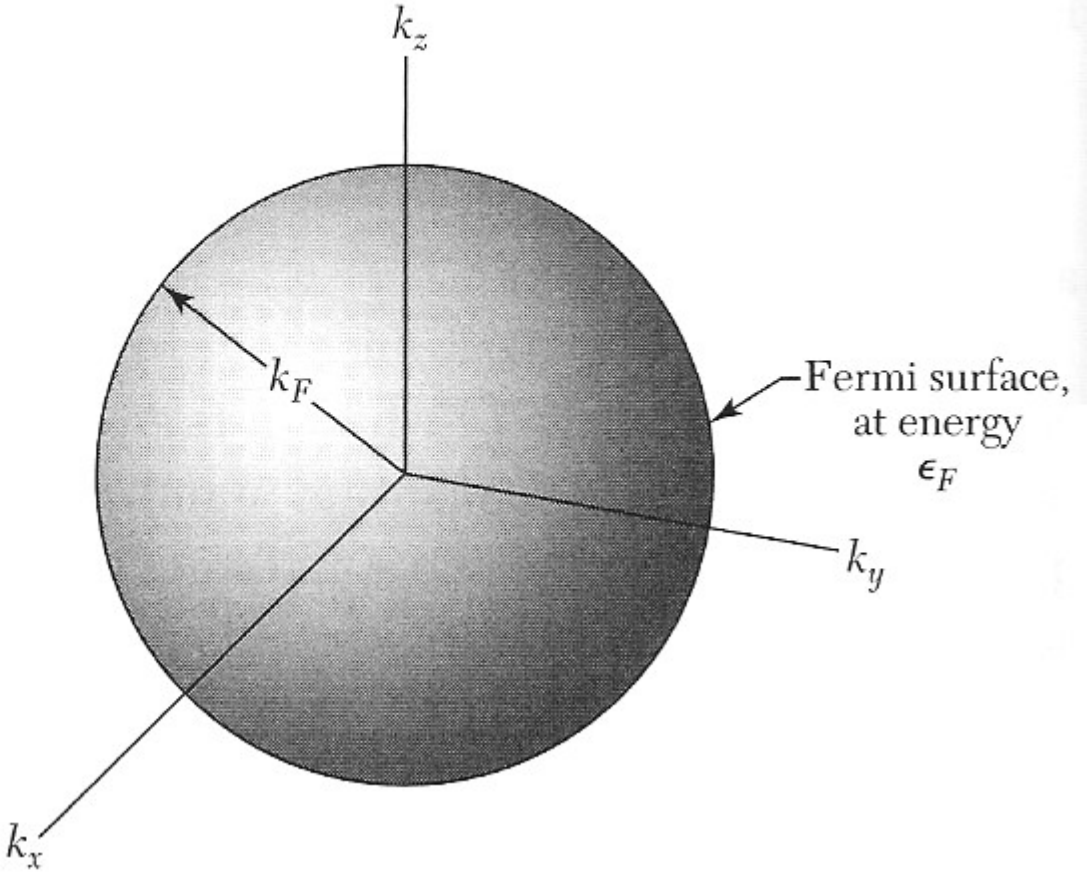
Fermi sphere

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

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.

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