

Electrons

Electrons

Electrons move like waves but exchange energy and momentum like particles.

$$E = \hbar\omega \quad \vec{p} = \hbar\vec{k}$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(x)\psi = i\hbar\frac{\partial\psi}{\partial t}$$

Probability of finding an electron

$$\int_{-\infty}^{\infty} \psi^* \psi dx$$

Infinite square well

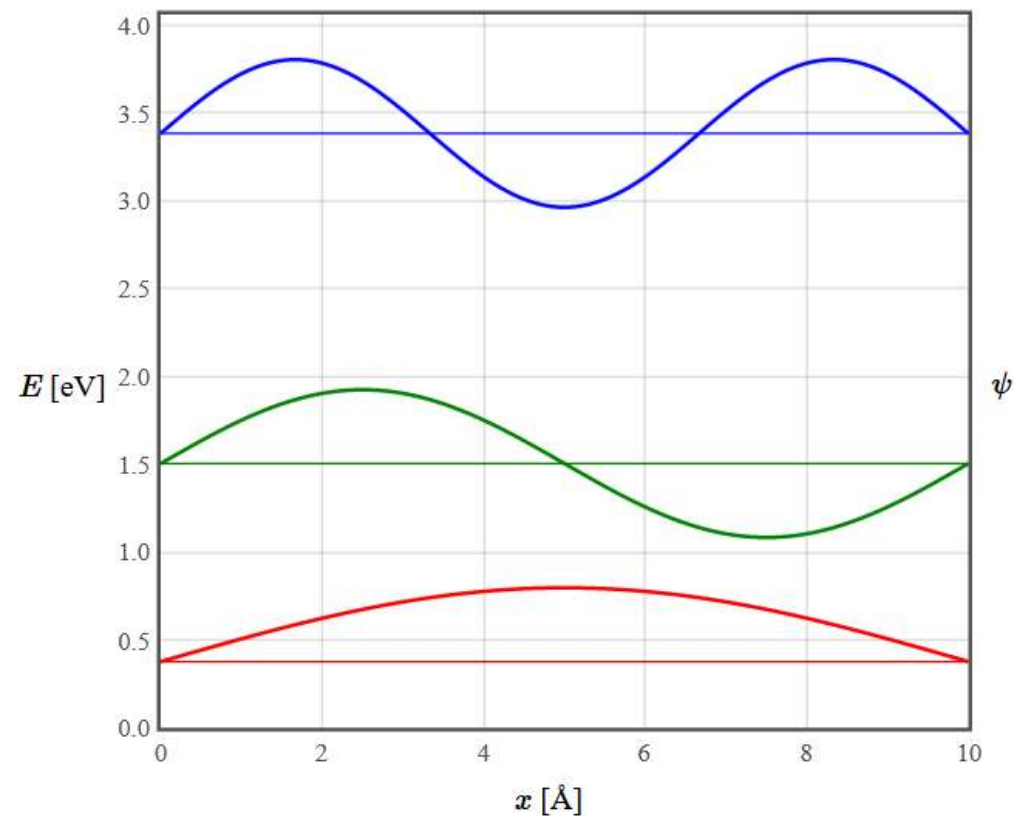
Fill the electrons states like in an atom.

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

$$V(x) = \begin{cases} 0 & 0 < x < L \\ \infty & \text{otherwise} \end{cases}$$

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

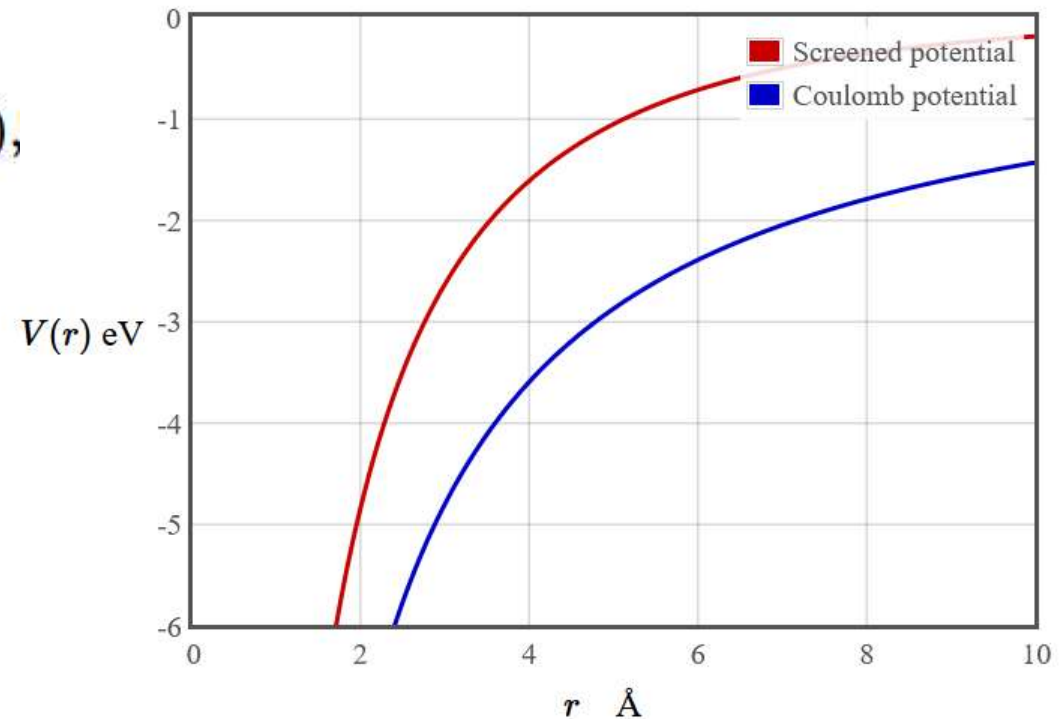
$$E_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2$$



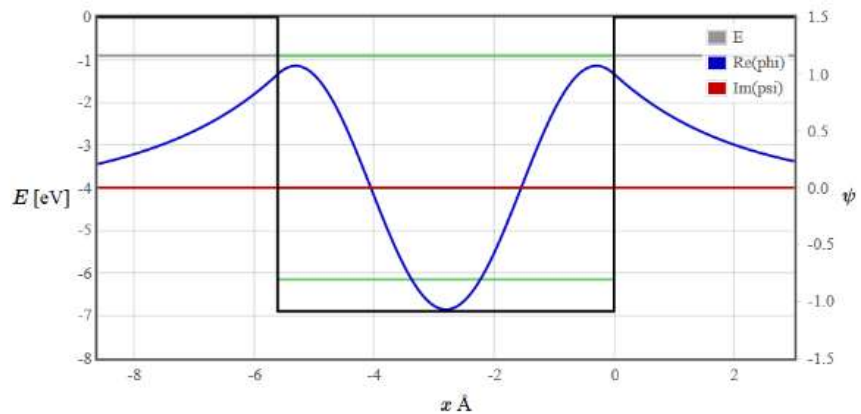
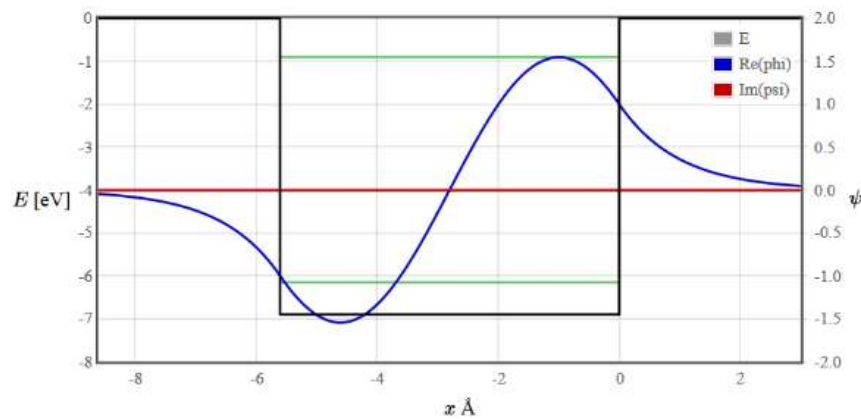
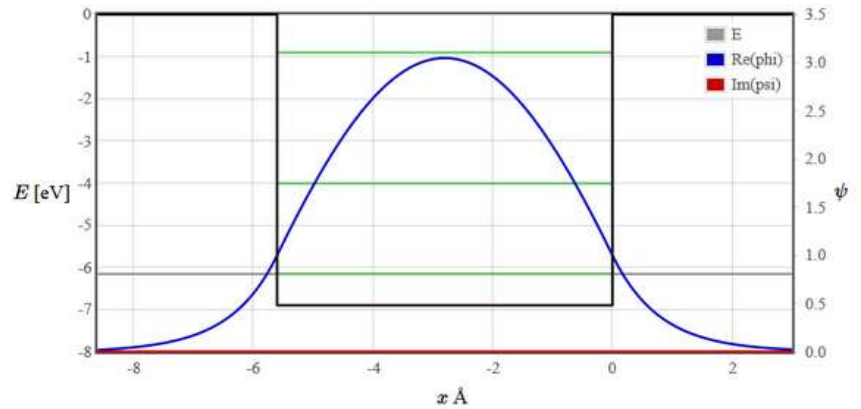
Screened potential

Fill the electrons states like in an atom.

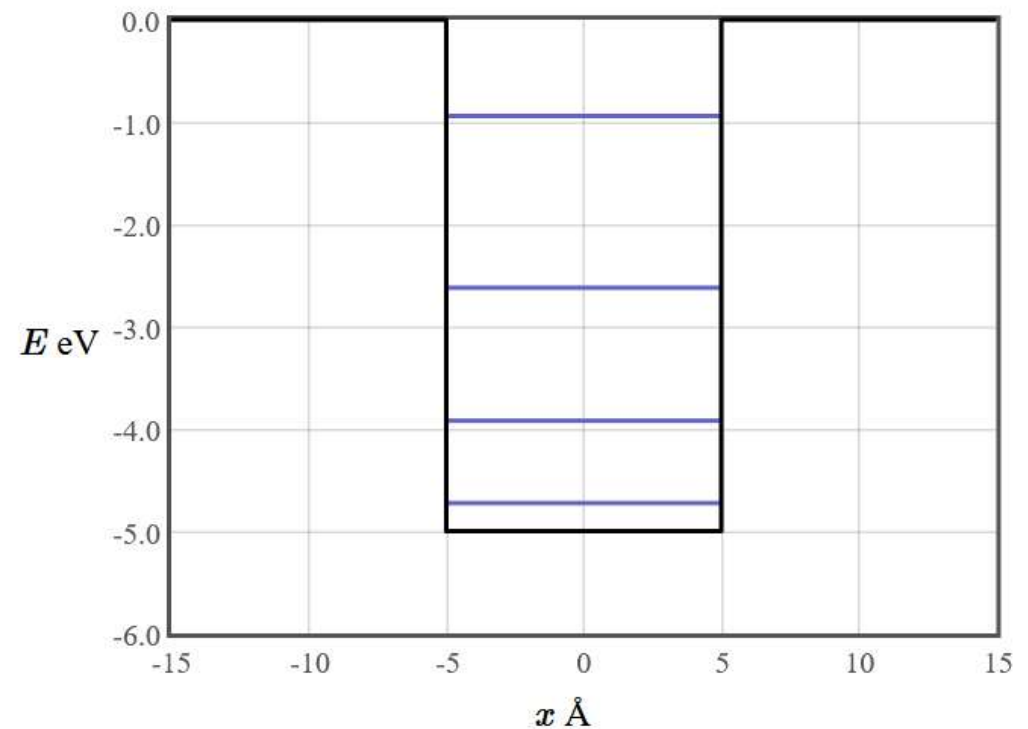
$$V = \frac{e}{4\pi\epsilon_0|\vec{r} - \vec{r}'|} \exp(-k_s|\vec{r} - \vec{r}'|),$$



The valence electrons become unbound



Finite square well potential



Free particles in 1-d

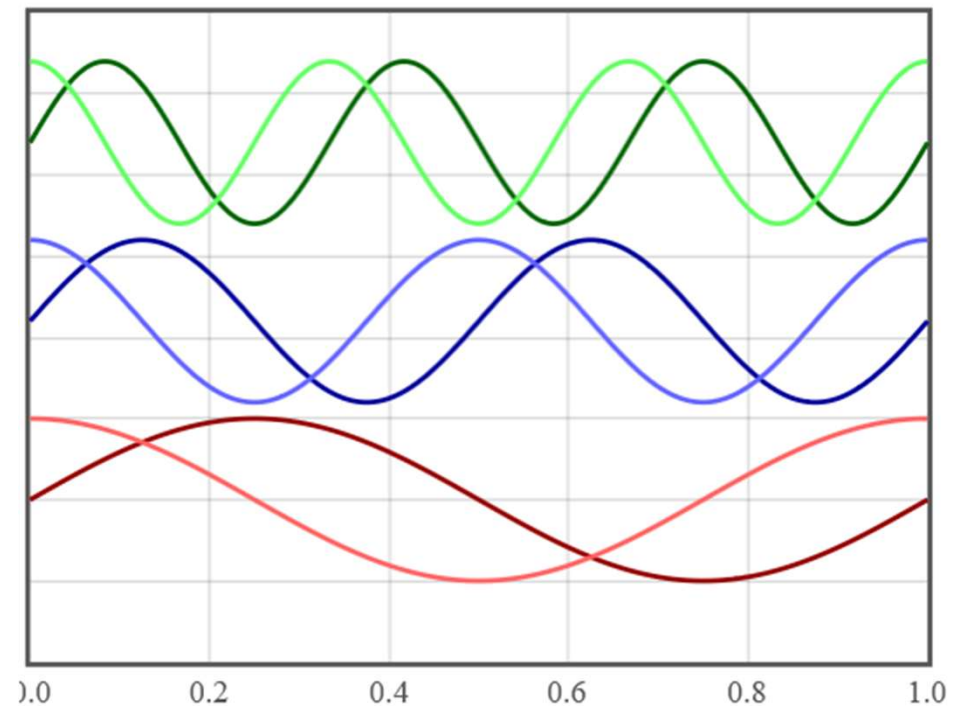
Periodic boundary conditions

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(x)\psi = i\hbar\frac{\partial\psi}{\partial t}$$

$$V(x) = 0$$

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

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

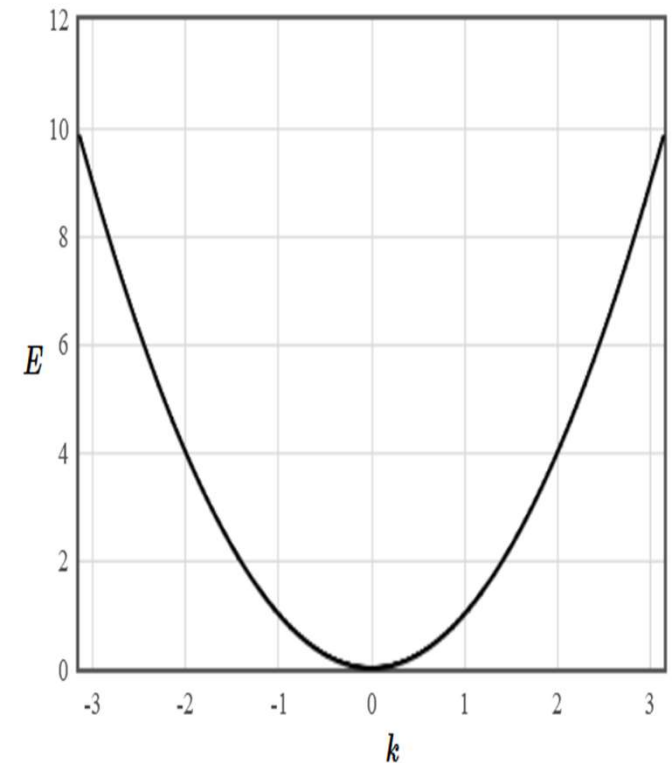


Free particles in 1-d

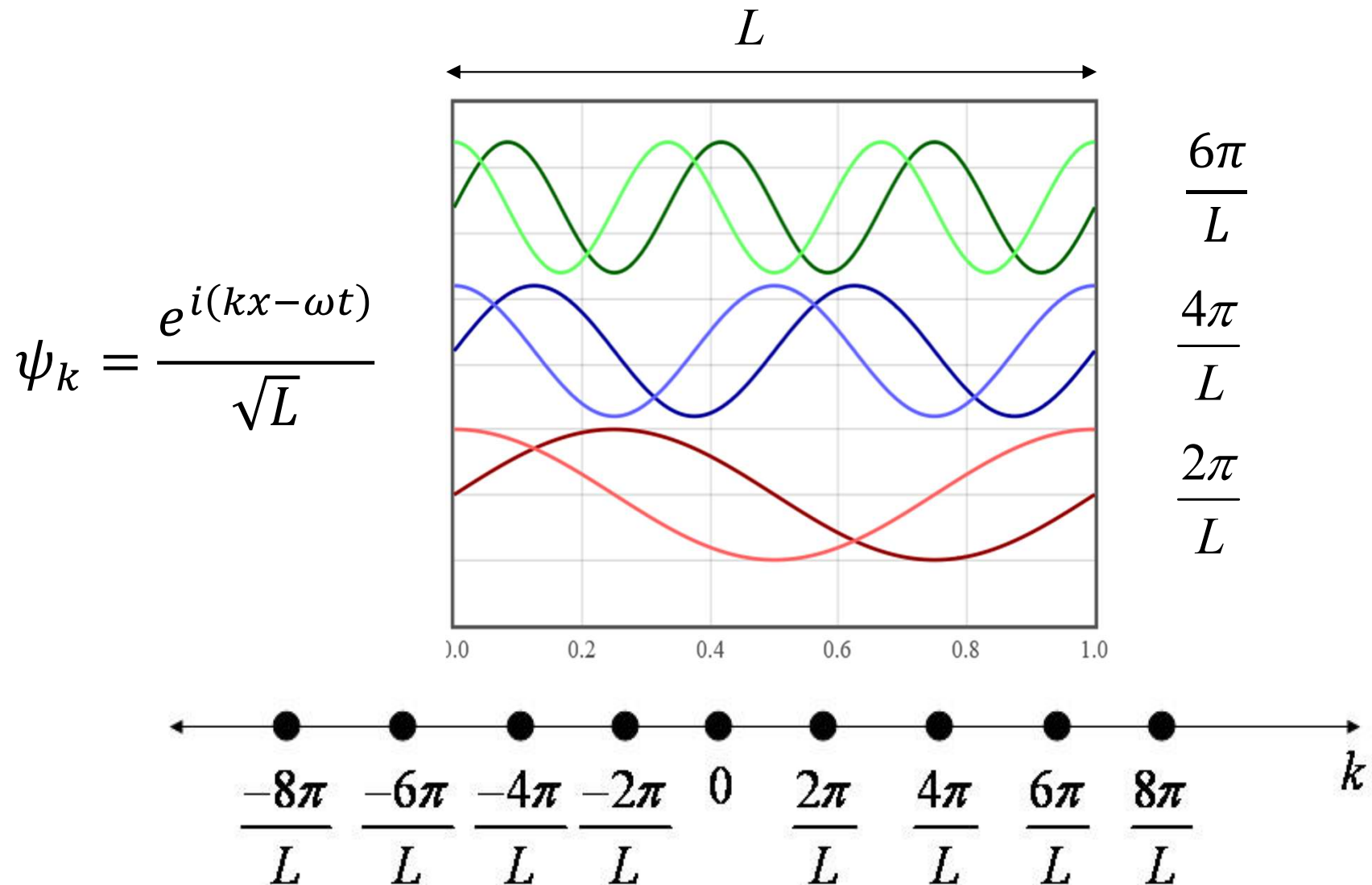
$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} \quad V = 0$$

Eigen function solutions: $\psi_k = \frac{e^{i(kx - \quad)}}{\sqrt{L}}$

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

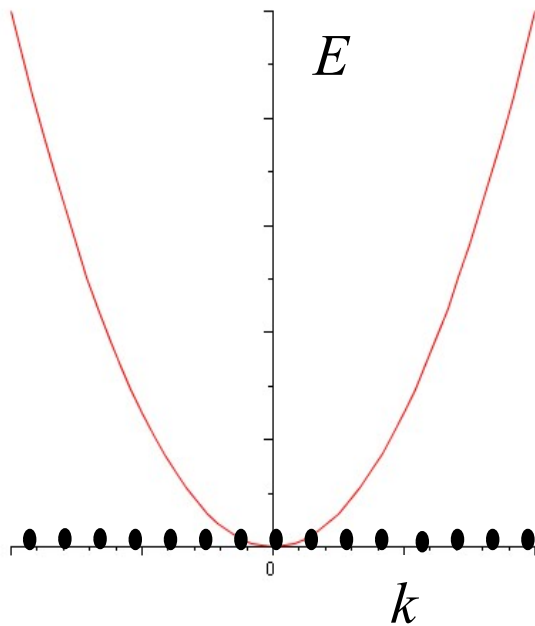


Periodic boundary conditions

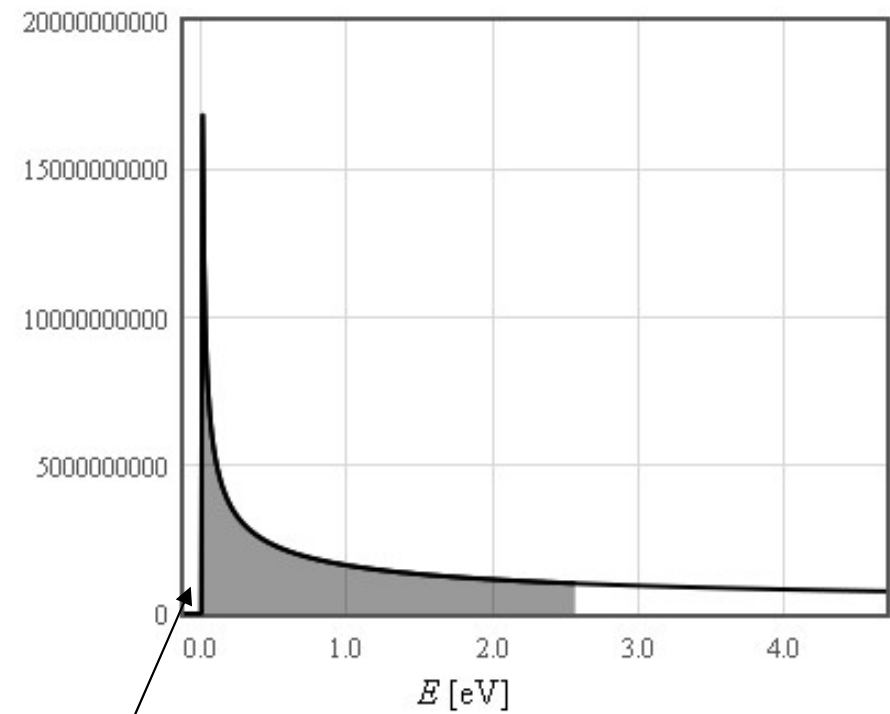


Free particles in 1-d

Density of states



$D(E)$



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

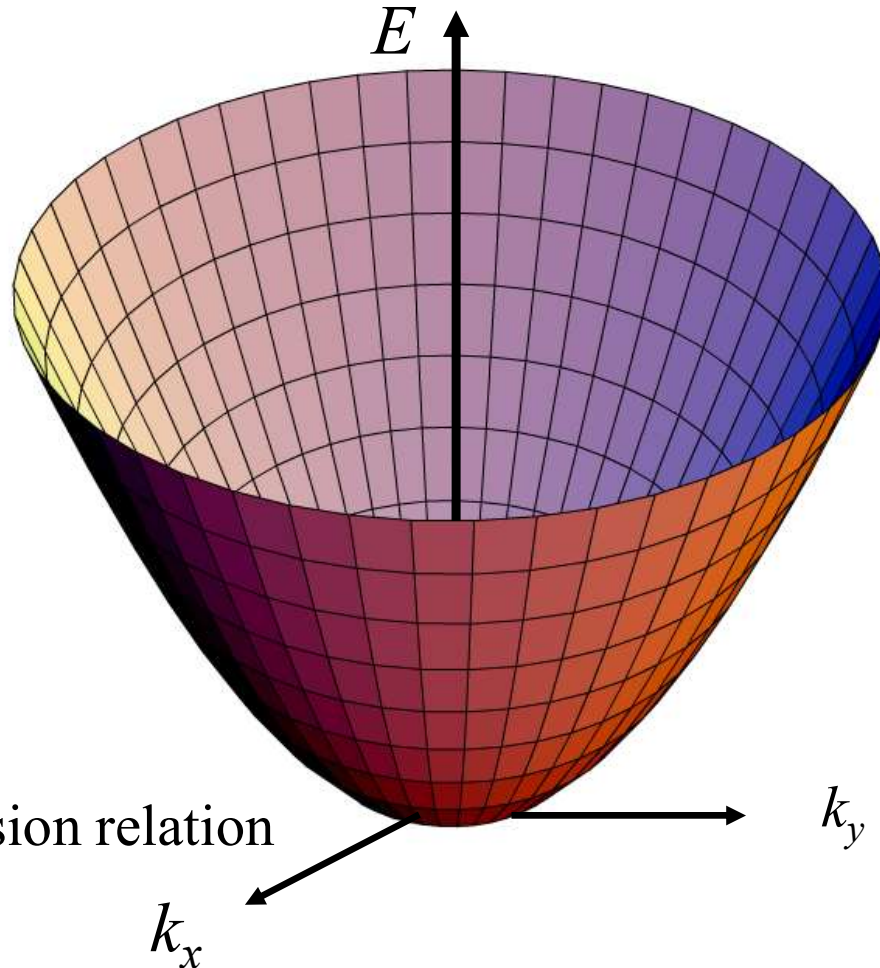
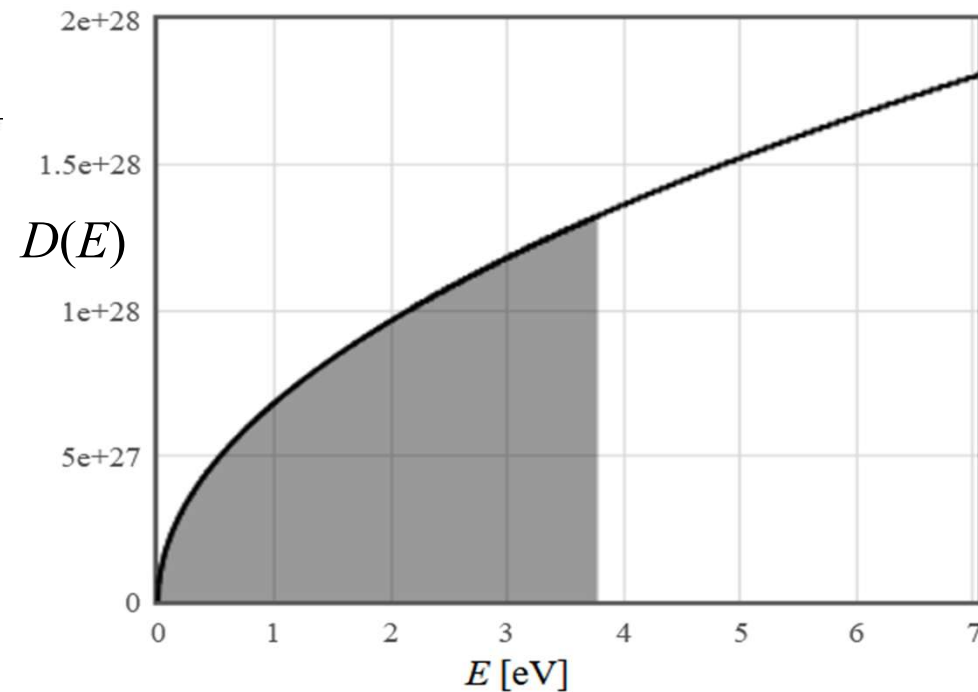
Van Hove singularity E

free electrons (simple model for a metal)

$$\vec{p} = \hbar \vec{k}$$

$$E(\vec{k}) = \frac{1}{2}mv^2 = \frac{p^2}{2m} = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2)$$

3-d density of states



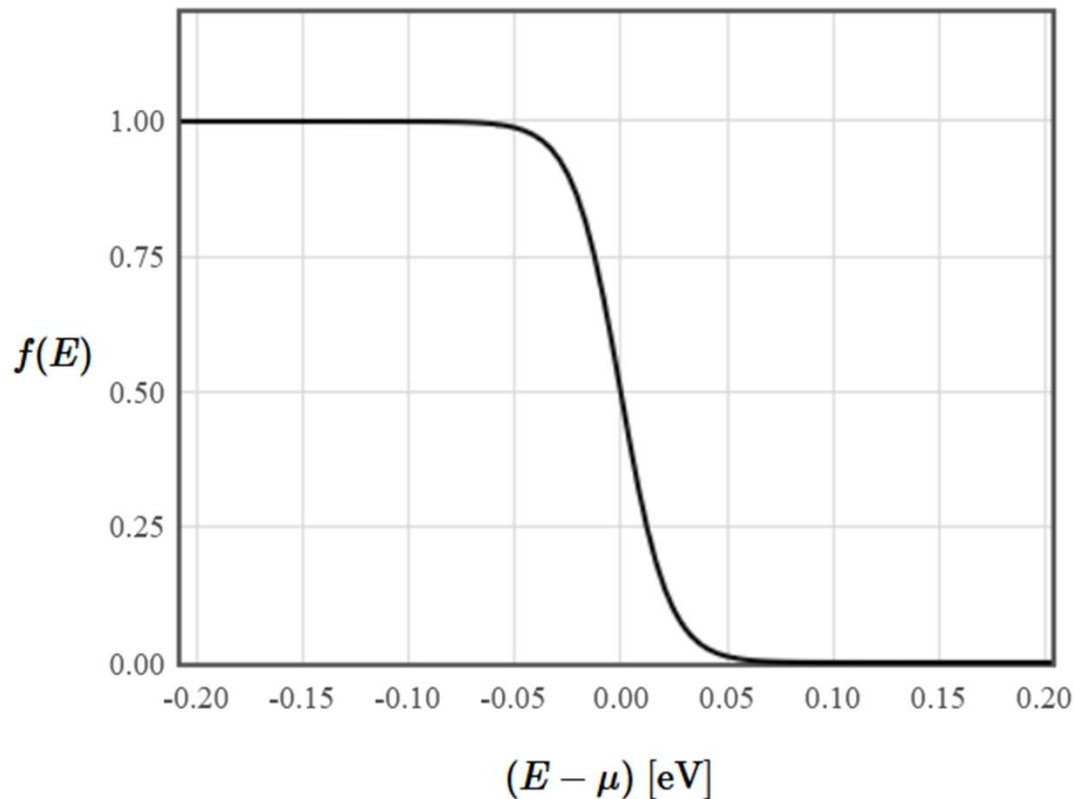
$$0 \quad \text{for } E < 0$$

$$D(E) = \frac{(2m)^{3/2}}{2\pi^2 \hbar^3} \sqrt{E} \quad \text{for } E > 0$$

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

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

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

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

Here n is the electron density.

Fermi energy

In solid state physics books,

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

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

At $T = 0$

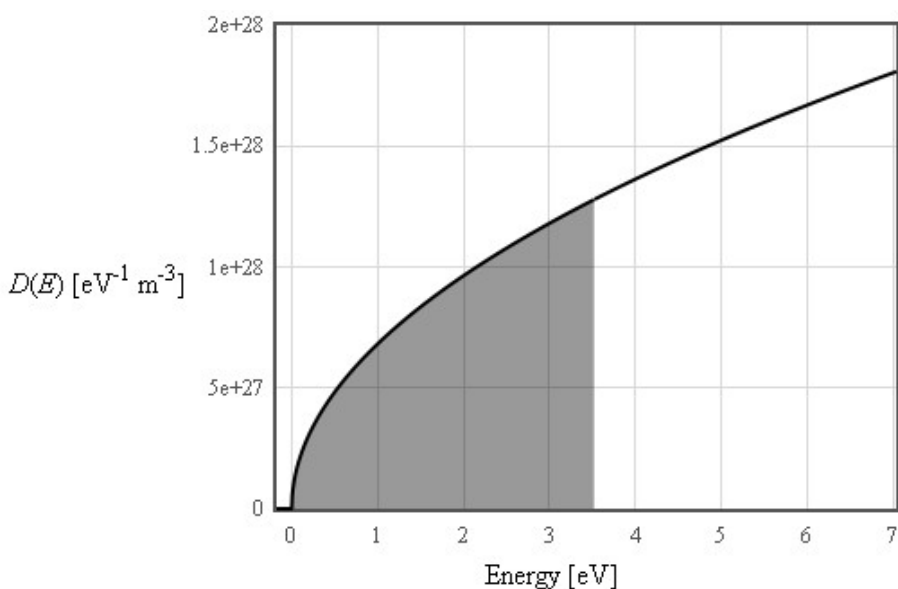
$$n = \int_{-\infty}^{E_F} D(E) dE$$

Free particles in 3-d

At $T = 0$:

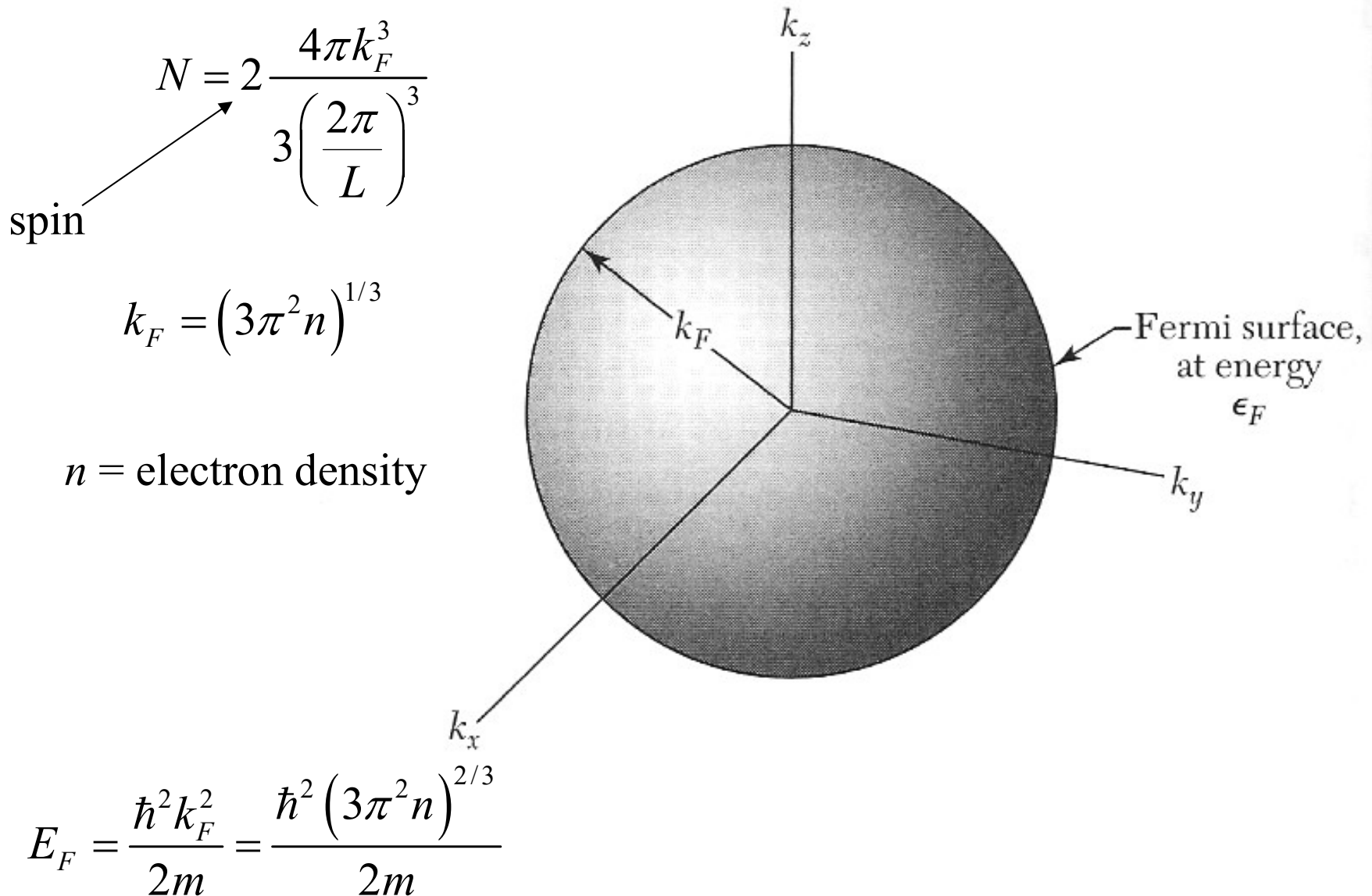
$$n = \int_0^{E_F} D(E) dE$$

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



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

Fermi sphere



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

Internal energy density at $T = 0$

$$u = \int_{-\infty}^{\infty} ED(E)dE = \int_0^{E_f} ED(E)dE$$

$$D(E) = \frac{(2m)^{\frac{3}{2}}}{2\pi^2\hbar^3} \sqrt{E} \quad \text{J}^{-1} \text{m}^{-3}$$

$$u = \int_0^{E_f} \frac{(2m)^{\frac{3}{2}}}{2\pi^2\hbar^3} E^{3/2} dE = \frac{(2m)^{\frac{3}{2}}}{5\pi^2\hbar^3} E_f^{\frac{5}{2}}$$

$$E_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3} \quad u(T=0) = \frac{3}{5} n E_F$$

$$u(T=0) = \frac{\pi^{\frac{4}{3}} \hbar^2}{10m} (3n)^{\frac{5}{3}} = \frac{\pi^{\frac{4}{3}} \hbar^2}{10m} \left(\frac{3N}{V} \right)^{\frac{5}{3}}$$

Pressure 3-D

$$P = - \left(\frac{\partial U}{\partial V} \right)_N$$

$$u(T = 0) = \frac{\pi^{\frac{4}{3}} \hbar^2}{10m} (3n)^{\frac{5}{3}} = \frac{\pi^{\frac{4}{3}} \hbar^2}{10m} \left(\frac{3N}{V} \right)^{\frac{5}{3}}$$

$$U = V u \propto V^{-2/3}$$

$$P = - \left(\frac{\partial U}{\partial V} \right)_N = \frac{2}{3} \frac{U}{V} = \frac{2}{5} n E_F = \frac{\hbar^2 (9\pi^4 n^5)^{\frac{1}{3}}}{5m}$$

Bulk modulus

$$B = -V \frac{\partial P}{\partial V}$$

$$P = -\left(\frac{\partial U}{\partial V}\right)_N = \frac{\hbar^2 \left(9\pi^4 N^5 / V^5\right)^{\frac{1}{3}}}{5m}$$

$$P \propto V^{-5/3}$$

$$B = \frac{5}{3} P = \frac{10}{9} \frac{U}{V} = \frac{2}{3} n E_F = \frac{\hbar^2 \left(3\pi^4 n^5\right)^{\frac{1}{3}}}{m} \quad \text{N/m}^2$$

See: Landau and Lifshitz, Statistical Physics 1
or Ashcroft and Mermin, Solid State Physics

Bulk modulus

Table 2.2

BULK MODULI IN 10^{10} DYNES/CM² FOR SOME TYPICAL METALS^a

METAL	FREE ELECTRON B	MEASURED B
Li	23.9	11.5
Na	9.23	6.42
K	3.19	2.81
Rb	2.28	1.92
Cs	1.54	1.43
Cu	63.8	134.3
Ag	34.5	99.9
Al	228	76.0

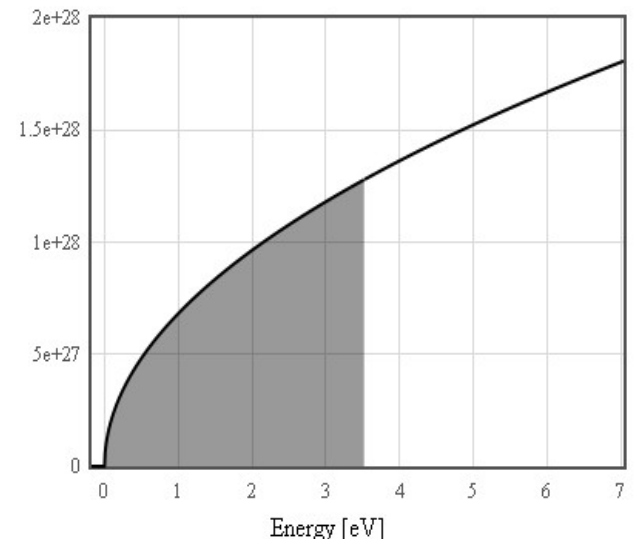
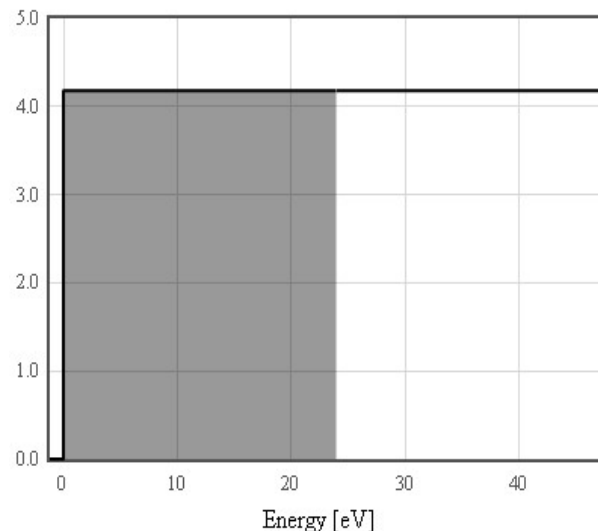
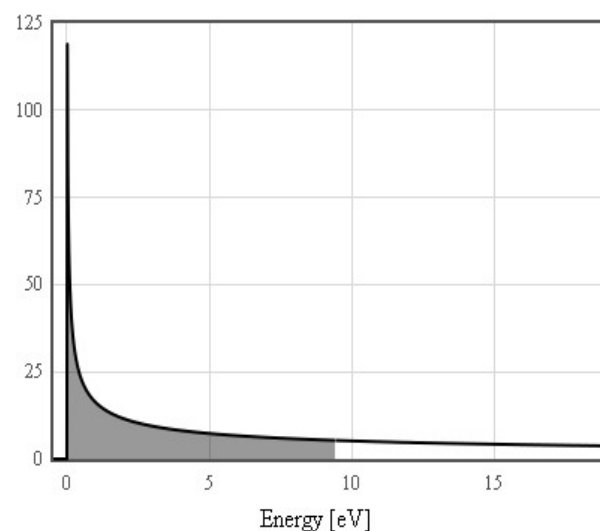
^a The free electron value is that for a free electron gas at the observed density of the metal, as calculated from Eq. (2.37).

Free electron Fermi gas

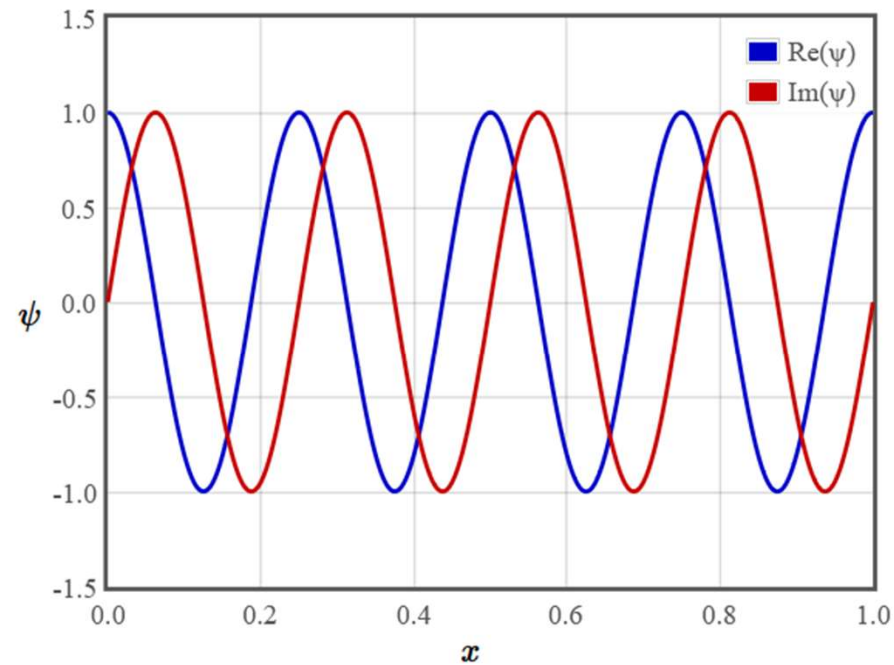
1 - d
$$D(E) = \sqrt{\frac{2m}{\hbar^2 \pi^2 E}} = \frac{n}{2\sqrt{E_F E}} \quad \text{J}^{-1} \text{m}^{-1}$$

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

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



Free-electron model



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

Sommerfeld expansion

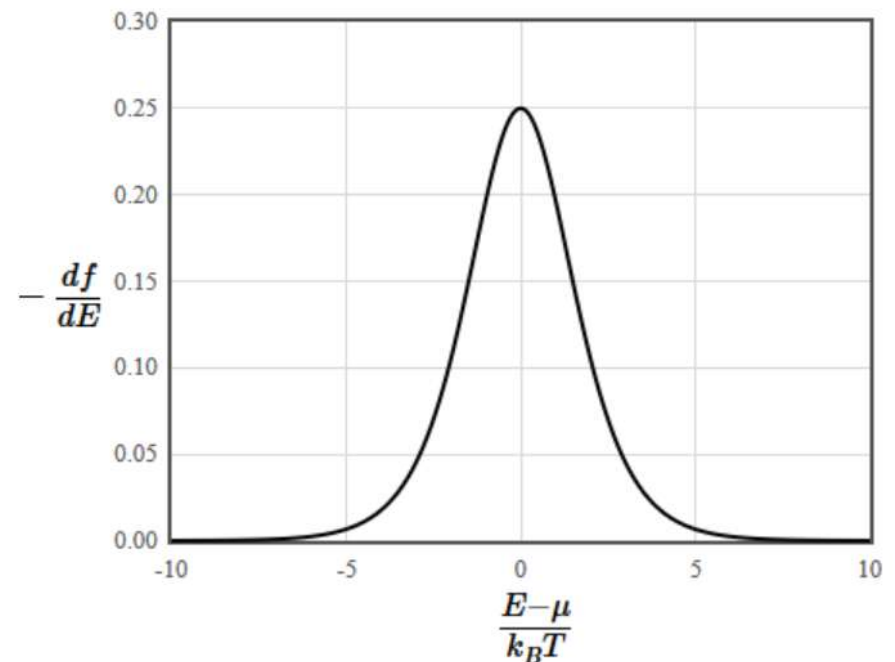
$$\int_{-\infty}^{\infty} H(E) f(E) dE,$$

$$\int_{-\infty}^{\infty} H(E) f(E) dE = K(\infty)f(\infty) - K(-\infty)f(-\infty) - \int_{-\infty}^{\infty} K(E) \frac{df}{dE} dE,$$

$$K(E) = \int_{-\infty}^E H(E') dE'$$

$$\int_{-\infty}^{\infty} H(E) f(E) dE = - \int_{-\infty}^{\infty} K(E) \frac{df}{dE} dE,$$

$$-\frac{df(E)}{dE} = \frac{\exp\left(\frac{E-\mu}{k_B T}\right)}{k_B T \left(\exp\left(\frac{E-\mu}{k_B T}\right) + 1\right)^2}$$



Electronic specific heat

$$c_{v,electrons} = \frac{du}{dT} \approx \left(\frac{\pi}{3}\right)^{\frac{2}{3}} \frac{mn^{\frac{1}{3}}}{\hbar^2} k_B^2 T \quad \text{J K}^{-1} \text{m}^{-3}$$

$$c_{v,total} = \underset{\substack{\uparrow \\ \text{electrons}}}{\gamma T} + \underset{\substack{\uparrow \\ \text{phonons}}}{AT^3}$$

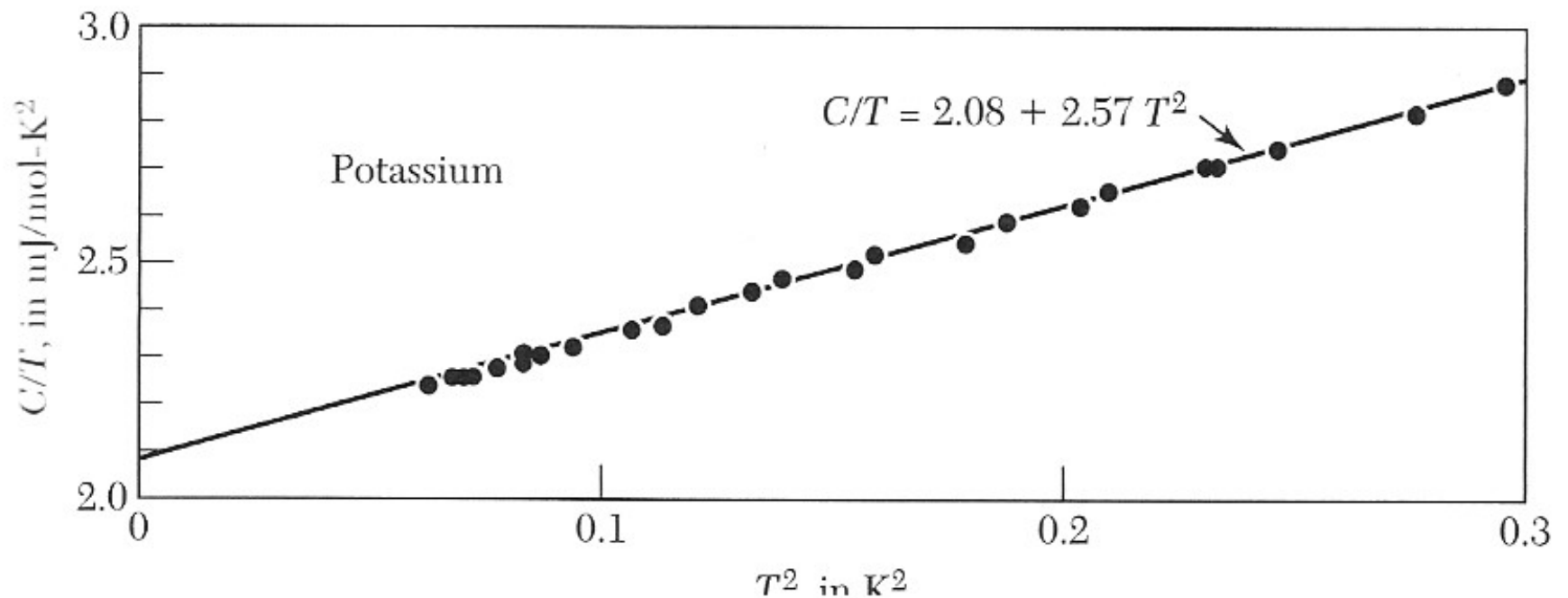


Table 2 Experimental and free electron values of electronic heat capacity constant γ of metals														
(From compilations kindly furnished by N. Phillips and N. Pearlman. The thermal effective mass is defined by Eq. (38).)														
Observed γ in $\text{mJ mol}^{-1} \text{K}^{-2}$.														
Calculated free electron γ in $\text{mJ mol}^{-1} \text{K}^{-2}$														
$m_{\text{th}}/m = (\text{observed } \gamma)/(\text{free electron } \gamma)$.														
Li	Be											B	C	N
1.63	0.17													
0.749	0.500													
2.18	0.34													
Na	Mg											Al	Si	P
1.38	1.3											1.35		
1.094	0.992											0.912		
1.26	1.3											1.48		
K	Ca	Sc	Ti	V	Cr	Mn(γ)	Fe	Co	Ni	Cu	Zn	Ga	Ge	As
2.08	2.9	10.7	3.35	9.26	1.40	9.20	4.98	4.73	7.02	0.695	0.64	0.596		0.19
1.668	1.511									0.505	0.753	1.025		
1.25	1.9									1.38	0.85	0.58		
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn (w)	Sb
2.41	3.6	10.2	2.80	7.79	2.0	—	3.3	4.9	9.42	0.646	0.688	1.69	1.78	0.11
1.911	1.790									0.645	0.948	1.233	1.410	
1.26	2.0									1.00	0.73	1.37	1.26	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg(α)	Tl	Pb	Bi
3.20	2.7	10.	2.16	5.9	1.3	2.3	2.4	3.1	6.8	0.729	1.79	1.47	2.98	0.008
2.238	1.937									0.642	0.952	1.29	1.509	
1.43	1.4									1.14	1.88	1.14	1.97	

from Kittel