Electrons

Free particles in 1-d

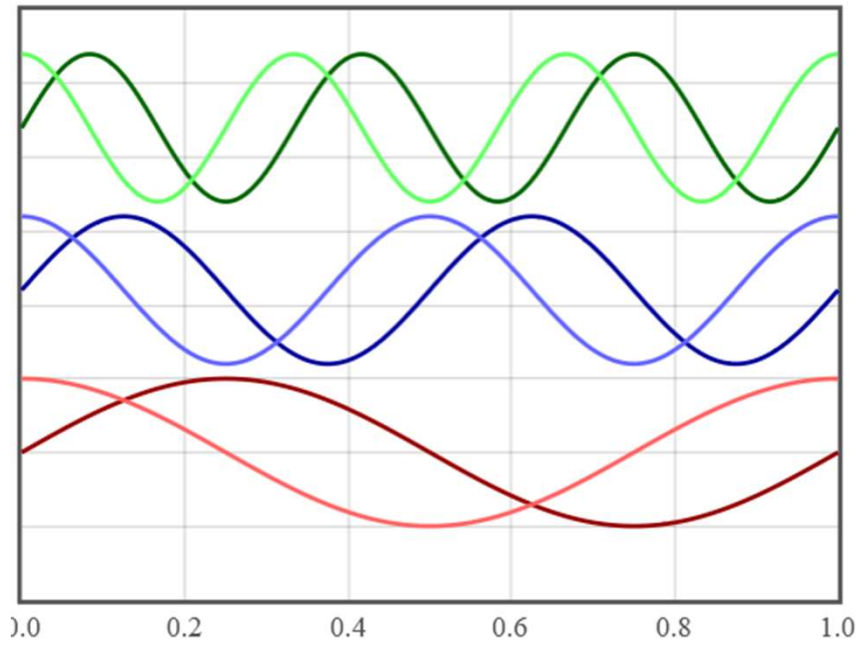
Fill the electrons states like in an atom.

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

$$V(x) = 0$$

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

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

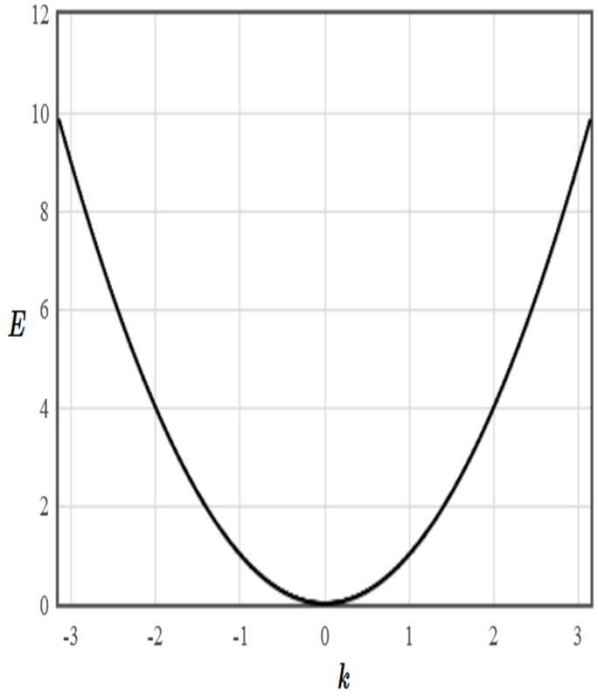


Free particles in 1-d

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

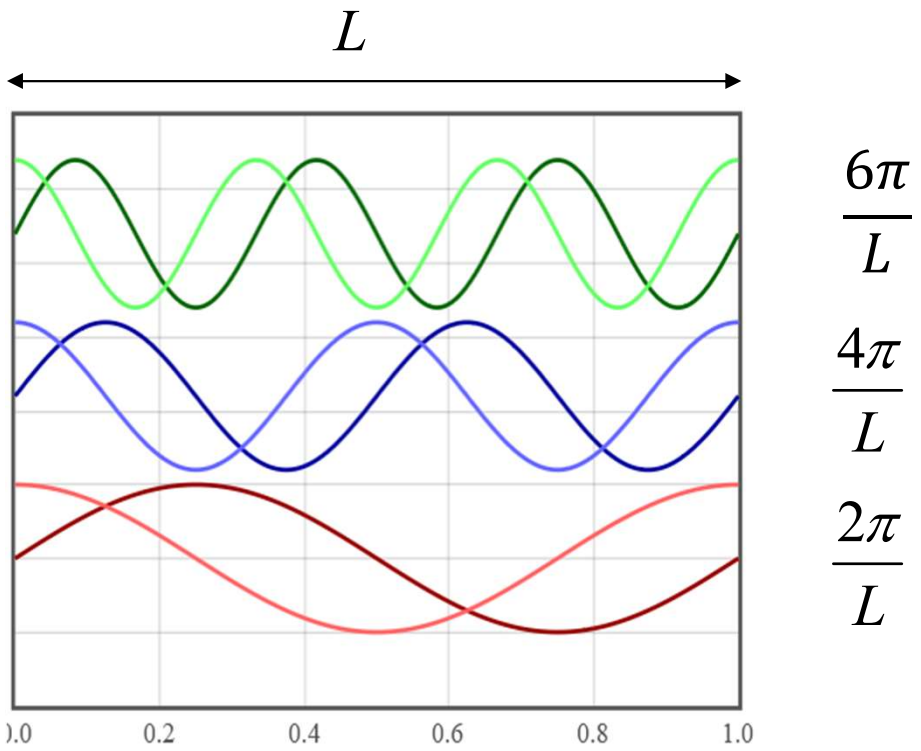
Eigen function solutions: $\psi_k = \dfrac{e^{i(kx-\omega t)}}{\sqrt{L}}$

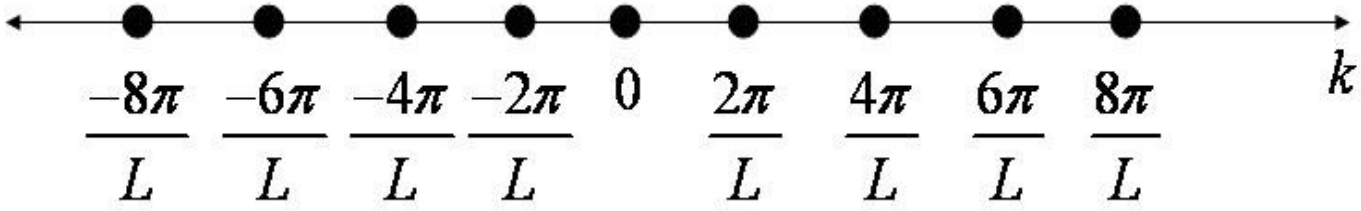
Dispersion relation: $E = \hbar\omega = \dfrac{\hbar^2 k^2}{2m} = \dfrac{1}{2}mv^2$



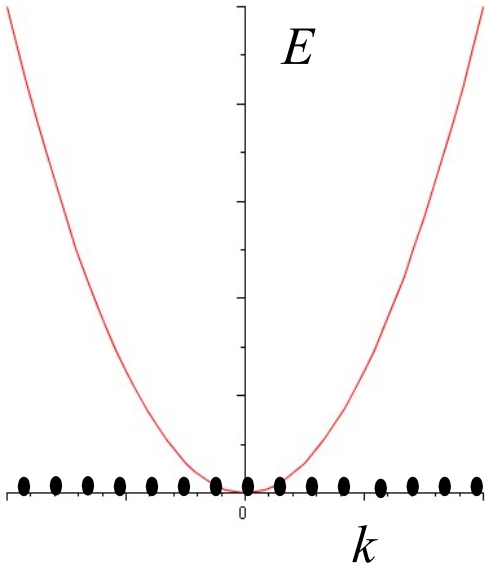
Periodic boundary conditions

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

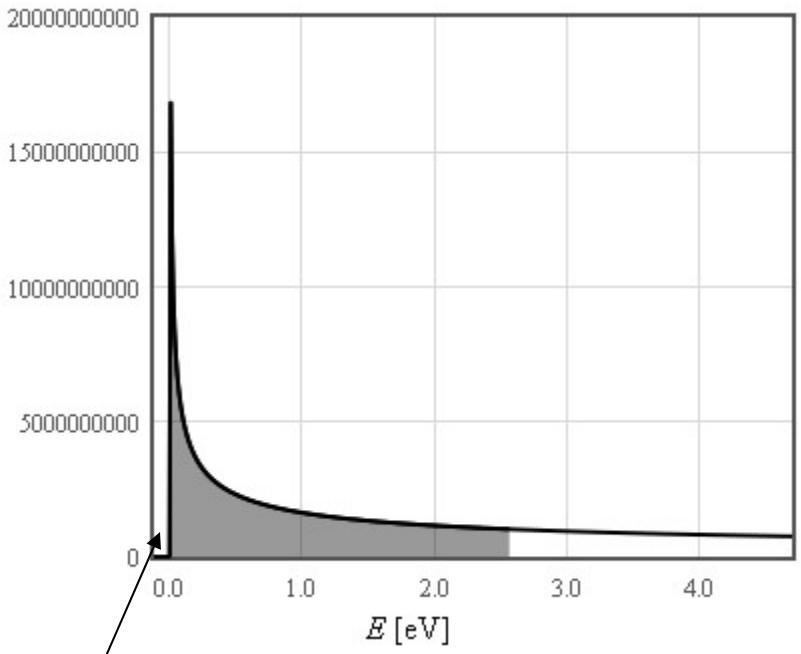




Free particles in 1-d



Density of states



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

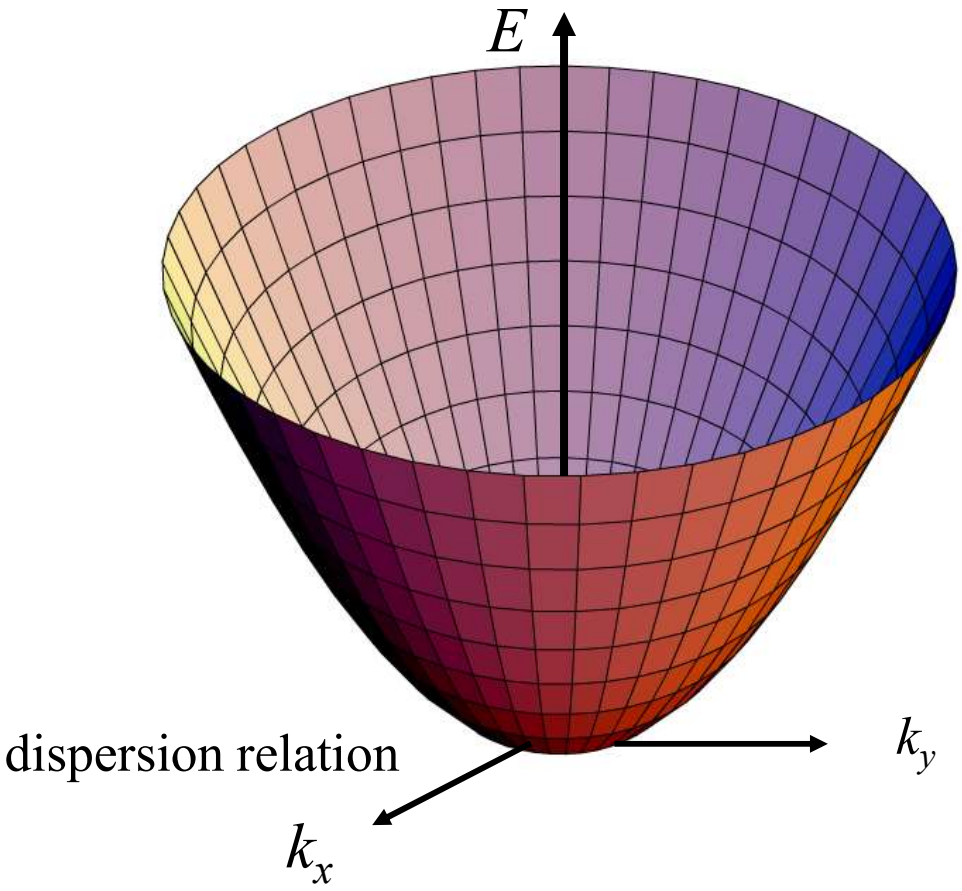
Van Hove singularity

E

free electrons (simple model for a metal)

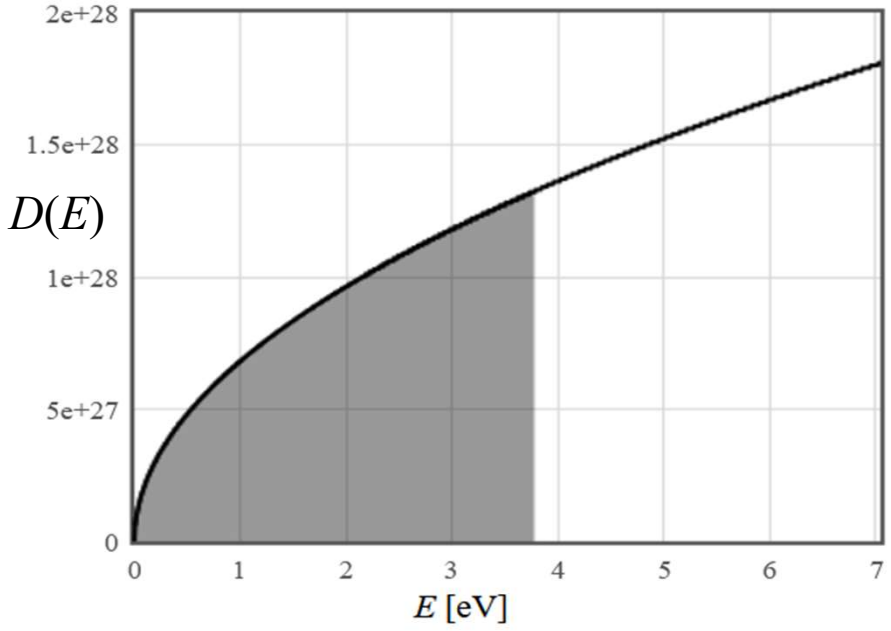
$$\vec{p} = \hbar\vec{k}$$

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



dispersion relation

3-d density of states

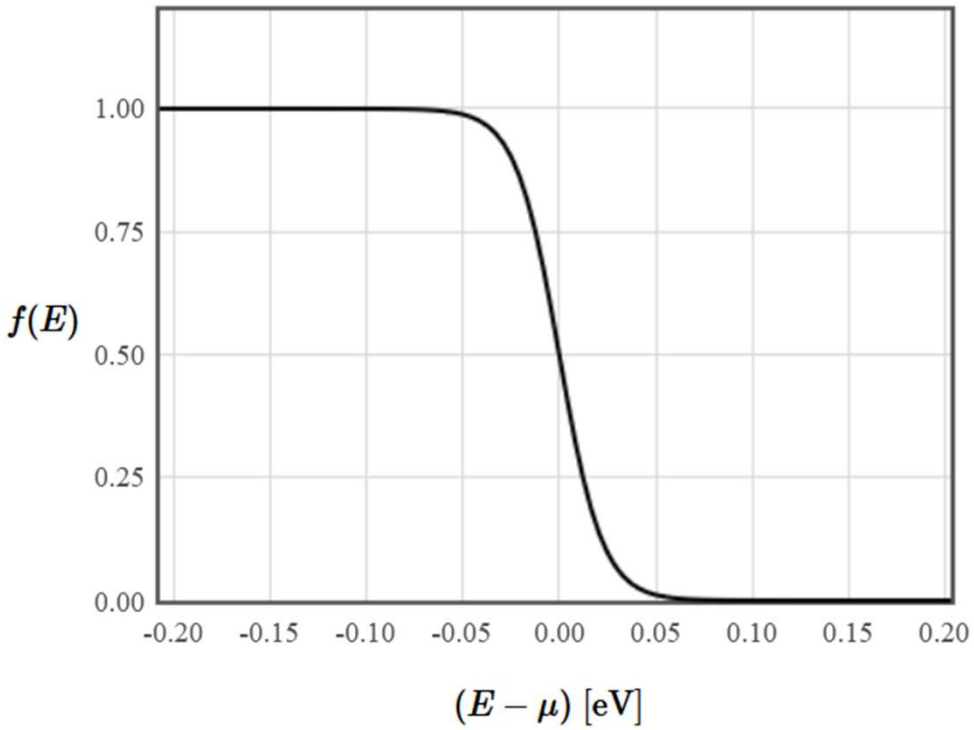


$$D(E) = \begin{cases} 0 & \text{for} \quad E < 0 \\ \dfrac{(2m)^{3/2}}{2\pi^2\hbar^3}\sqrt{E} & \text{for} \quad E > 0 \end{cases}$$

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

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

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,

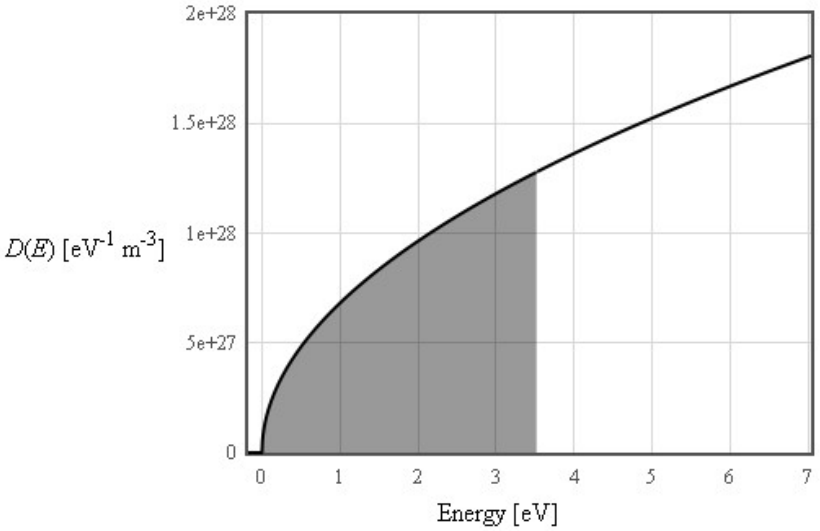
$$E_F = \mu(T=0).$$

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 $T = 0$:

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

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

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

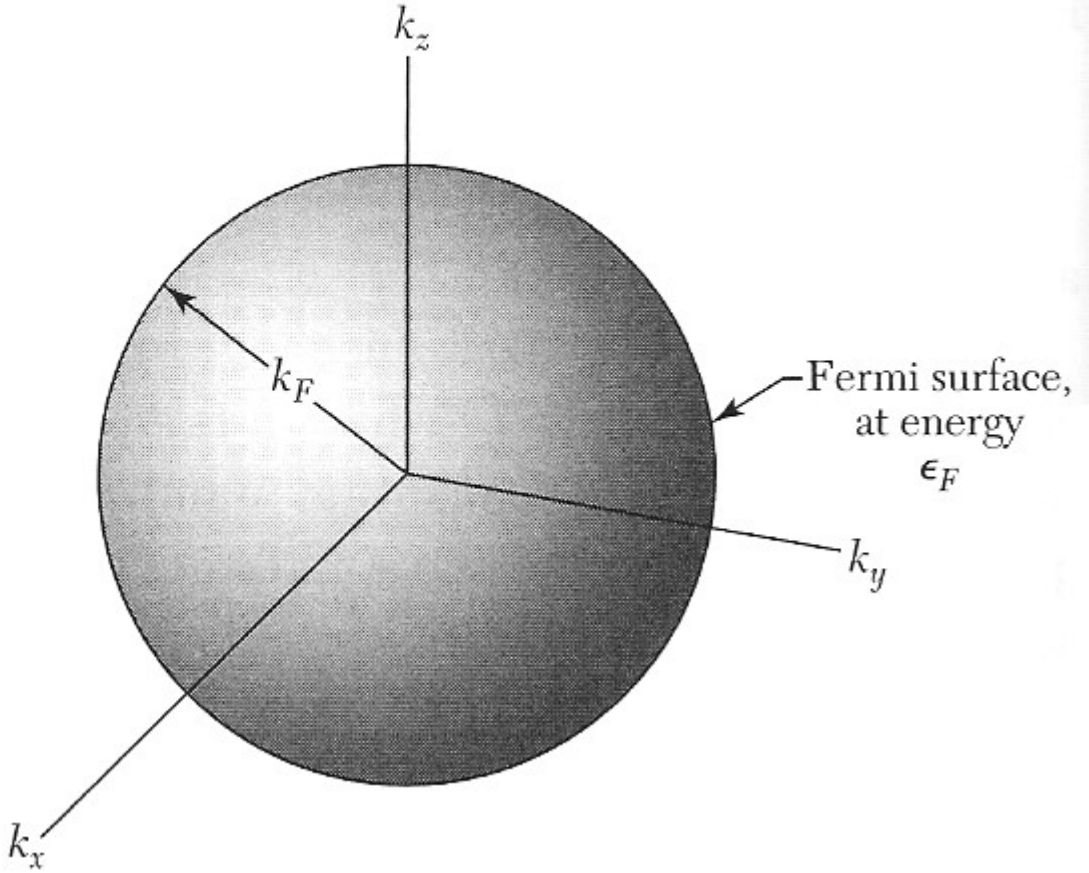
Fermi sphere

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

spin

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

n = electron density



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

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

Internal energy density at $T = 0$

$$u = \int_{-\infty}^{\infty} ED(E)dE = \int_{0}^{E_f} ED(E)dE$$

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

$$u = \int_{0}^{E_f} \frac{(2m)^{\frac{3}{2}}}{2\pi^2\hbar^3}E^{3/2}dE = \frac{(2m)^{\frac{3}{2}}}{5\pi^2\hbar^3}E_f^{\frac{5}{2}}$$

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

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

Pressure 3-D

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

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

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

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

Bulk modulus

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

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

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

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

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/CM^2 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).

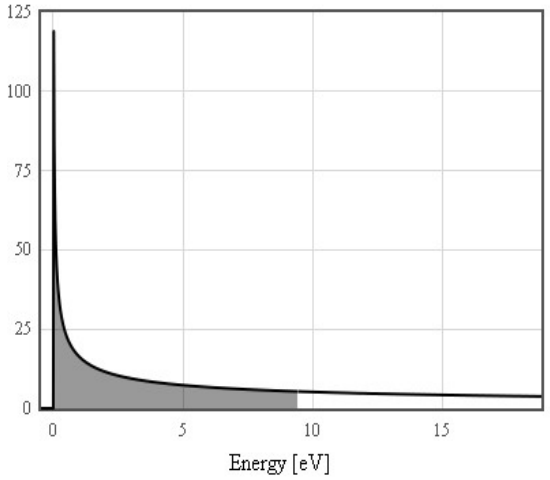
Ashcroft and Mermin

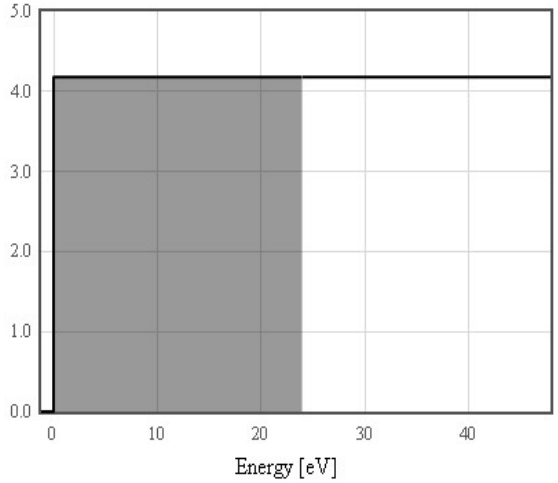
Free electron Fermi gas

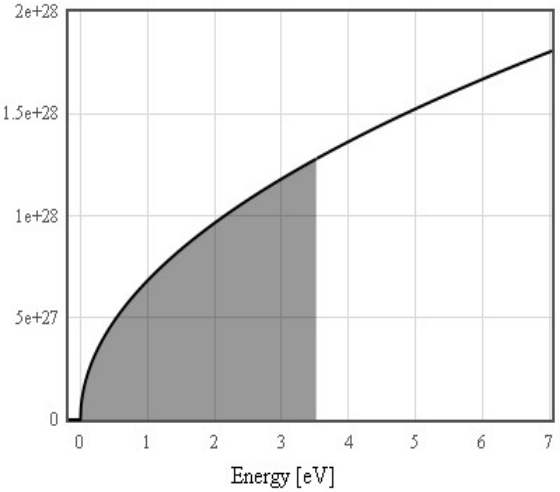
1 - d $$D(E) = \sqrt{\frac{2m}{\hbar^2 \pi^2 E}} = \frac{n}{2\sqrt{E_F E}} \quad \mathrm{J^{-1}m^{-1}}$$

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

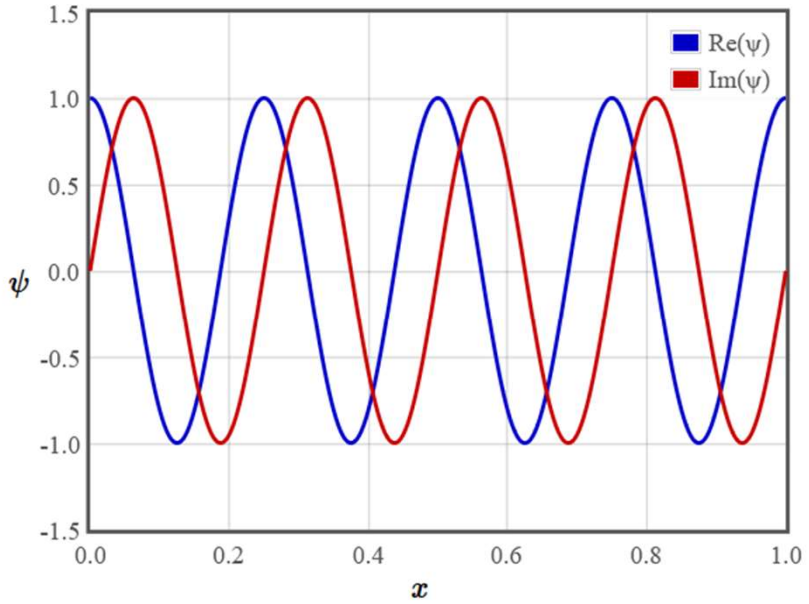
3 - d $$D(E) = \frac{\pi}{2}\left(\frac{2m}{\hbar^2 \pi^2}\right)^{3/2} \sqrt{E} = \frac{3n}{2E_F^{3/2}} \sqrt{E} \quad \mathrm{J^{-1}m^{-3}}$$







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	$D(k) = \frac{2}{}$	$D(k) = \frac{k}{} \quad \mathrm{m}^{-1}$	$D(k) = \frac{k^2}{} \quad \mathrm{m}^{-2}$

Electronic specific heat

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

$$c_{v,total} = \gamma T + AT^3$$

electrons phonons

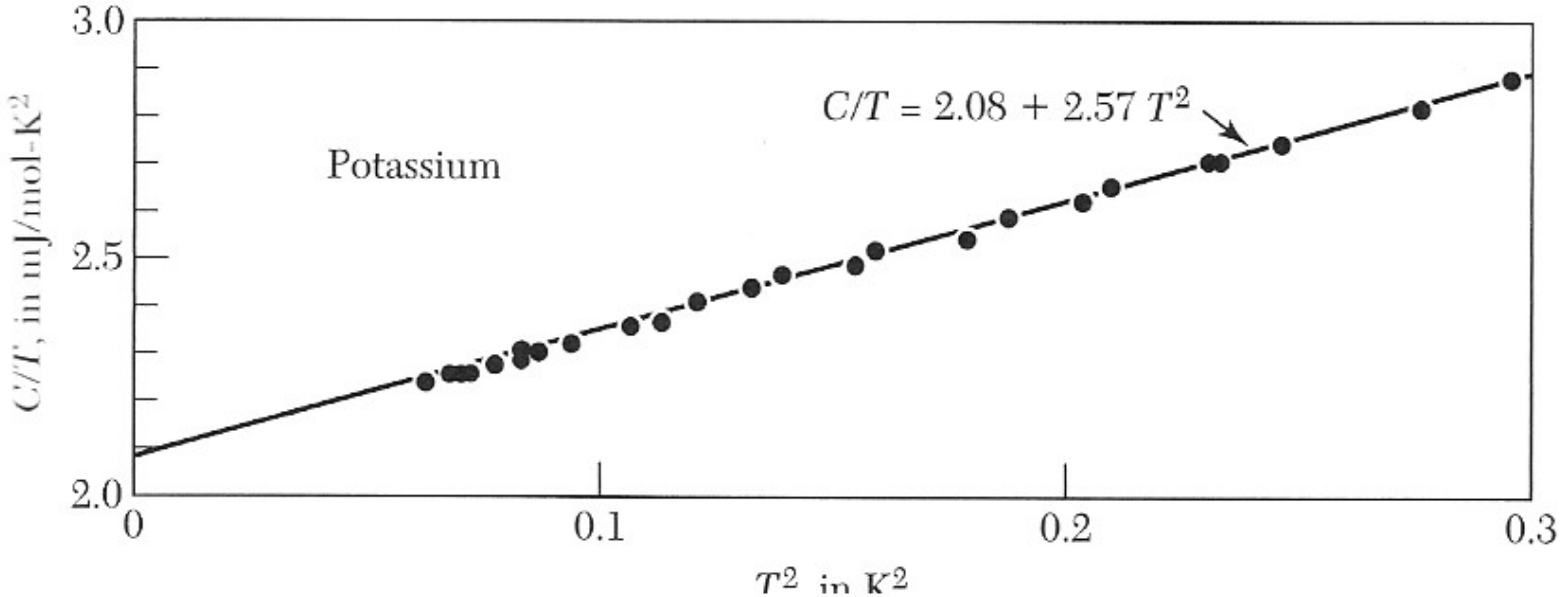


Table 2 Experimental and free electron values of electronic heat capacity constant γ of metals

(From compilations kindly furnished by N. Phillips and N. Pearlman. The thermal effective mass is defined by Eq. (38).)

Observed γ in mJ mol^{-1} K^{-2}.
Calculated free electron γ in mJ mol^{-1} K^{-2}
m_{th}/m = (observed γ)/(free electron γ).

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

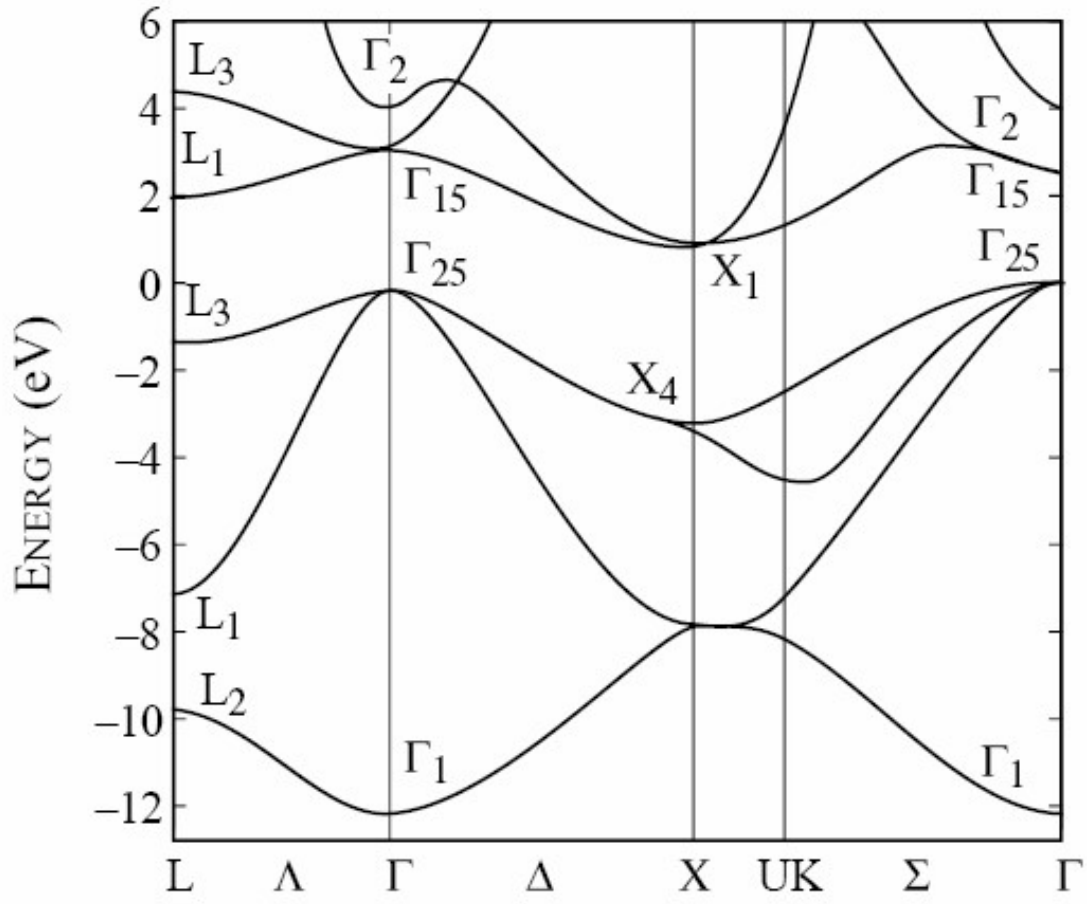
$u \approx \frac{3}{5} n E_F + \frac{\pi^2}{4} \frac{n}{E_F} (k_B T)^2 \quad \mathrm{J\,m^{-3}}$
$c_v \approx \frac{\pi^2}{2} \frac{n}{E_F} k_B^2 T \quad \mathrm{J\,K^{-1}\,m^{-3}}$
$s \approx \frac{\pi^2}{2} \frac{n}{E_F} k_B^2 T \quad \mathrm{J\,K^{-1}\,m^{-3}}$
$f \approx \frac{3}{5} n E_F - \frac{\pi^2}{4} \frac{n}{E_F} (k_B T)^2 \quad \mathrm{J\,m^{-3}}$
$P \approx \frac{2}{5} n E_F + \frac{\pi^2}{6} \frac{n}{E_F} (k_B T)^2 \quad \mathrm{N\,m^{-2}}$
$B \approx \frac{2}{3} n E_F + \frac{\pi^2}{18} \frac{n}{E_F} (k_B T)^2 \quad \mathrm{N\,m^{-2}}$
$h \approx n E_F + \frac{5\pi^2}{12} \frac{n}{E_F} (k_B T)^2 \quad \mathrm{J\,m^{-3}}$
$g \approx n E_F - \frac{\pi^2}{12} \frac{n}{E_F} (k_B T)^2 \quad \mathrm{J\,m^{-3}}$

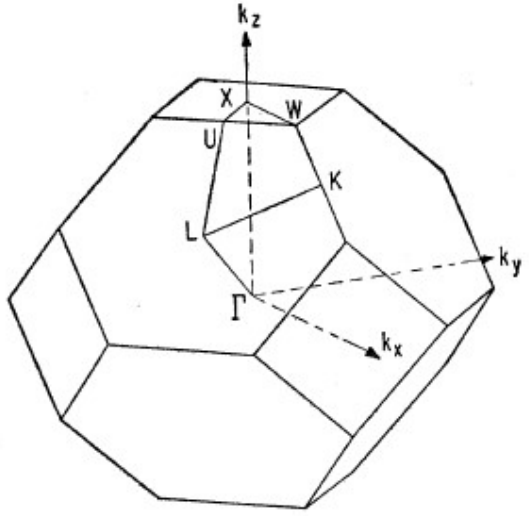
All properties depend on n and m

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

Electron Band Theory

Calculate the dispersion relation for electrons in a crystal

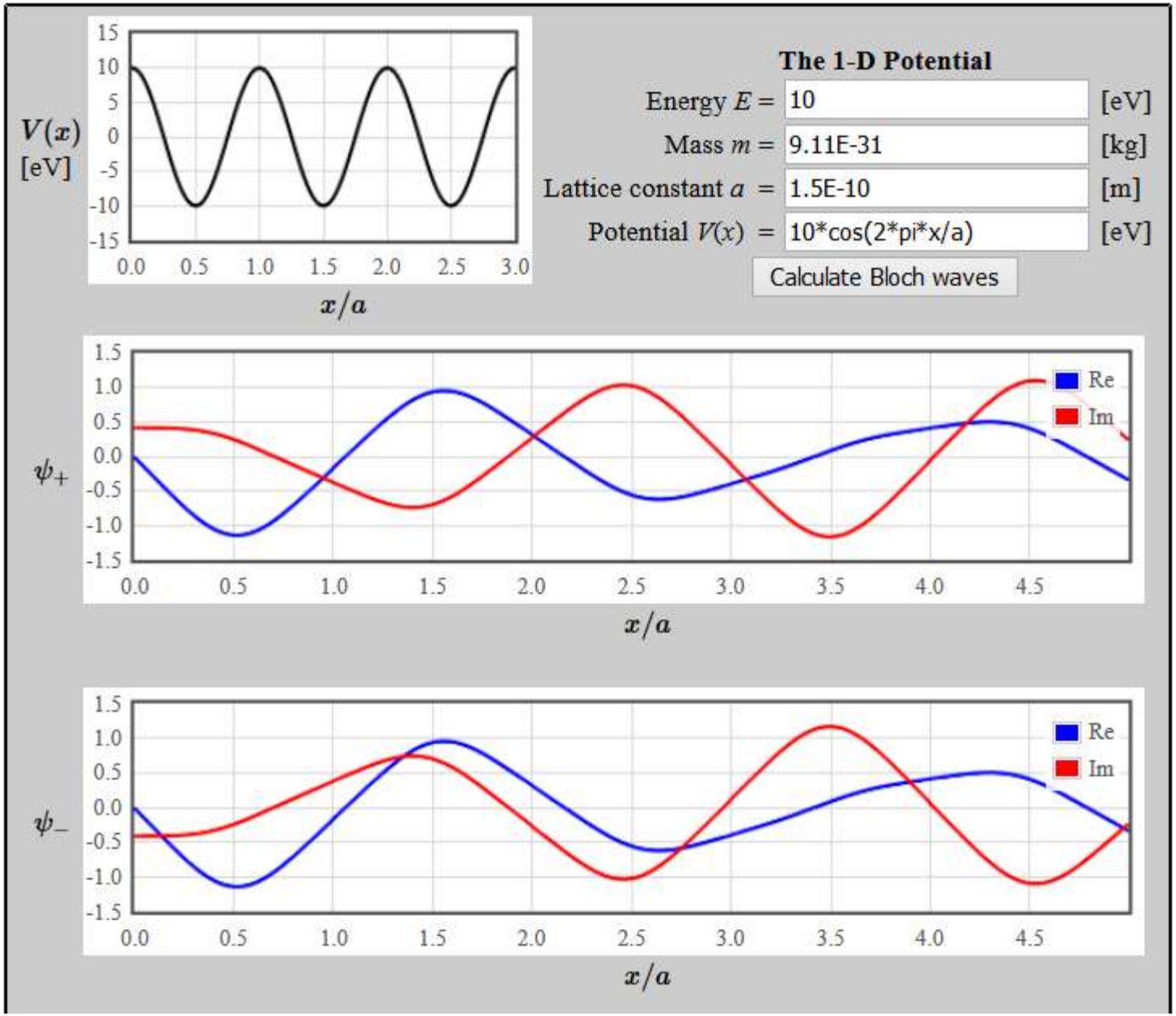




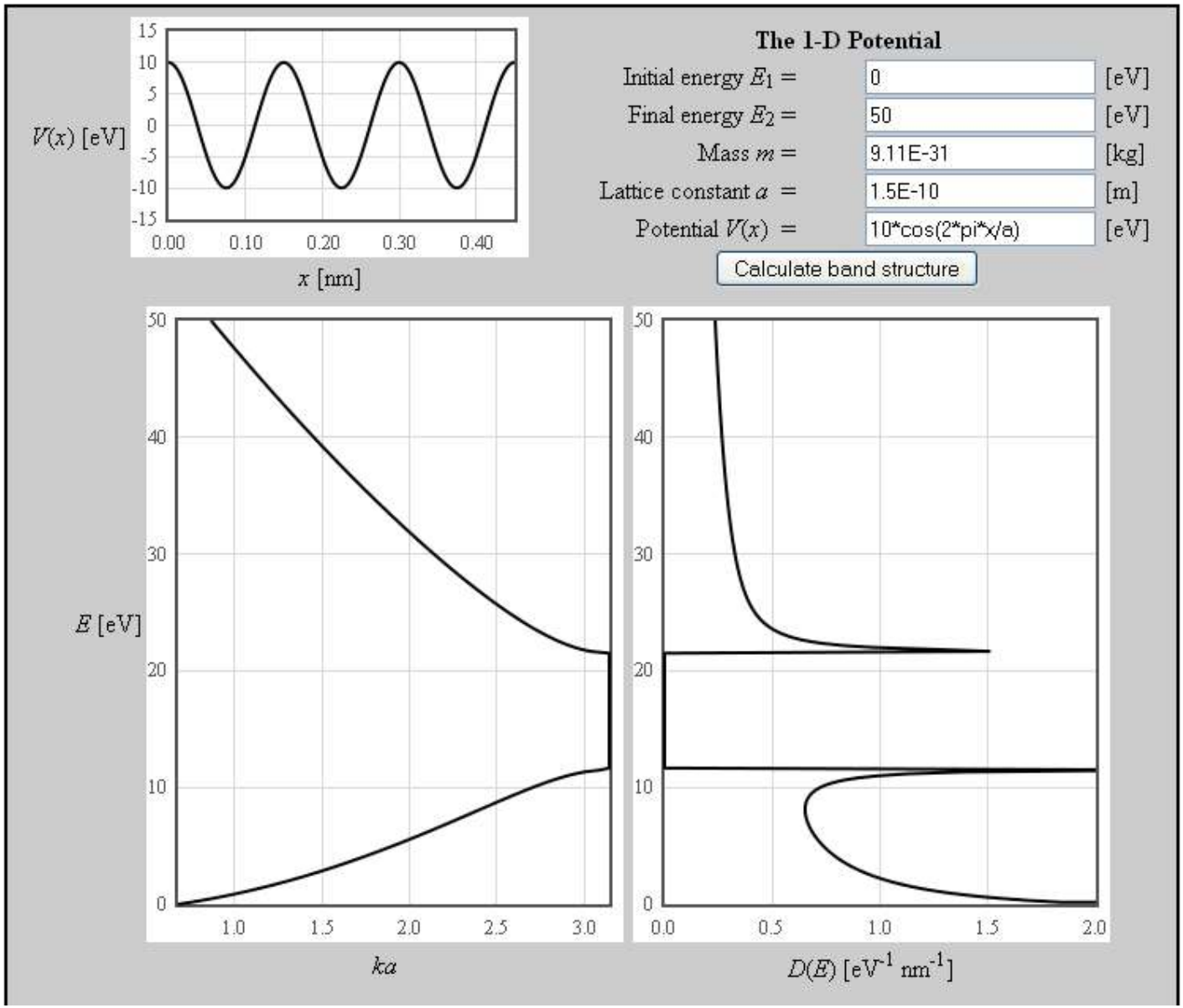
silicon

Bloch waves in 1-D

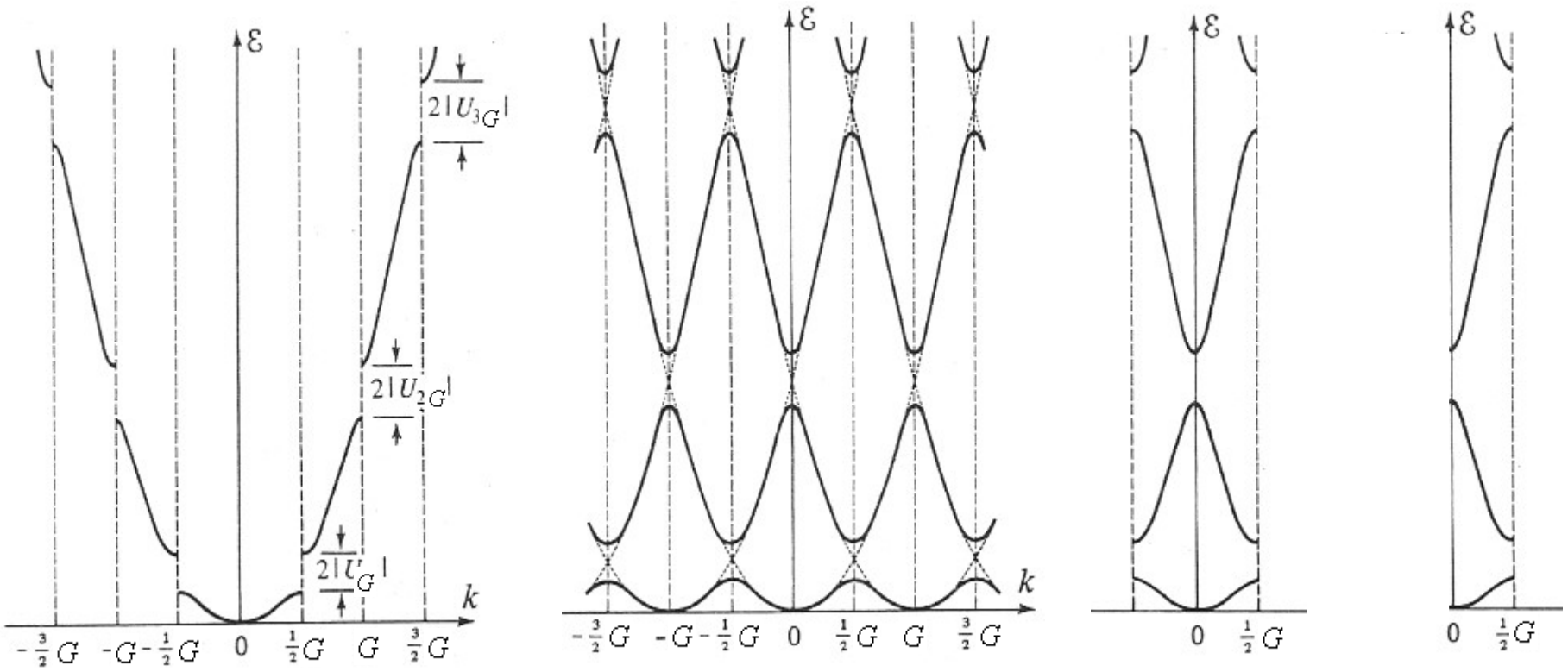
$$\psi = e^{ikx} u_k(x)$$



Band structure in 1-D



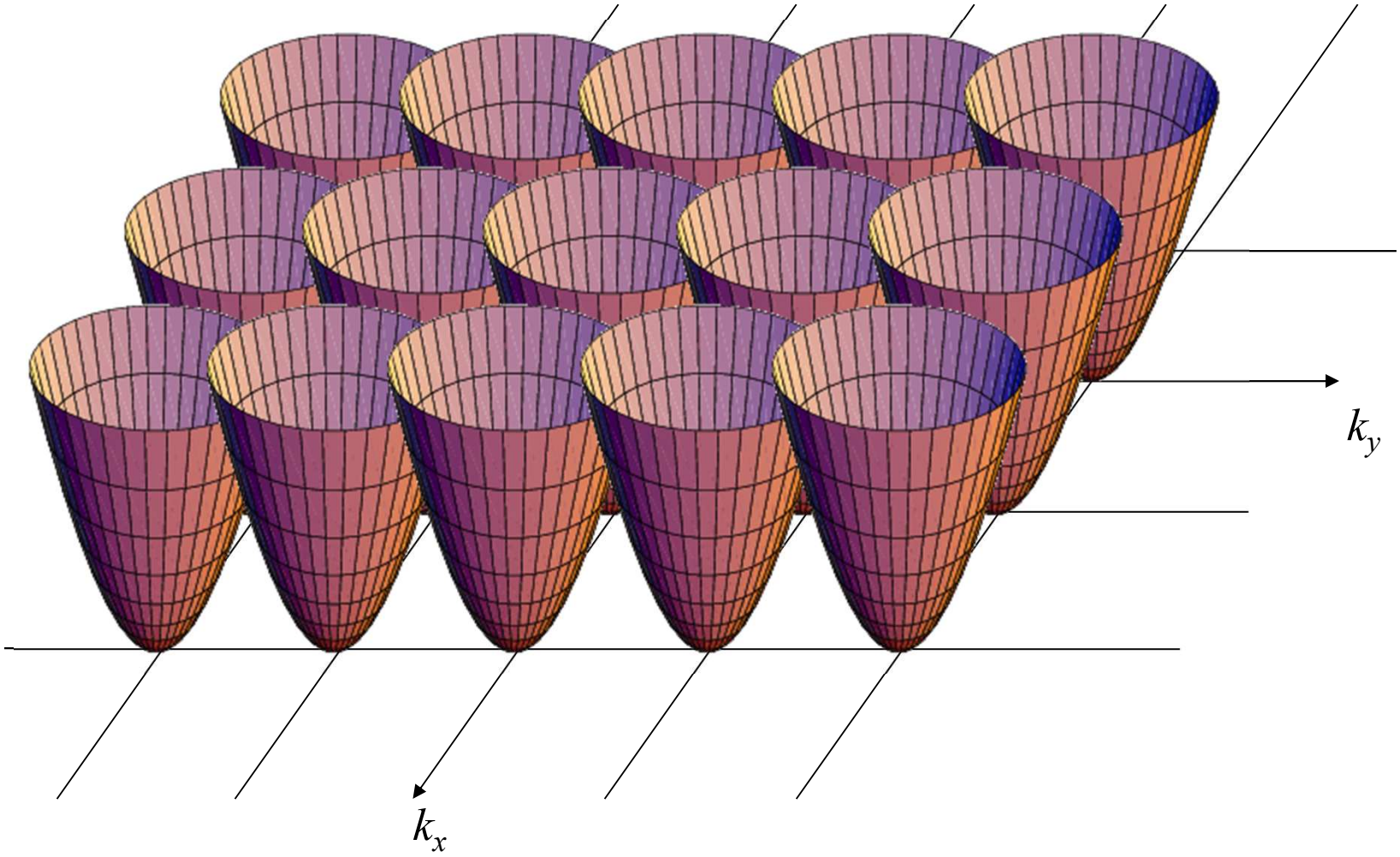
Empty lattice approximation



Extended Repeated Reduced

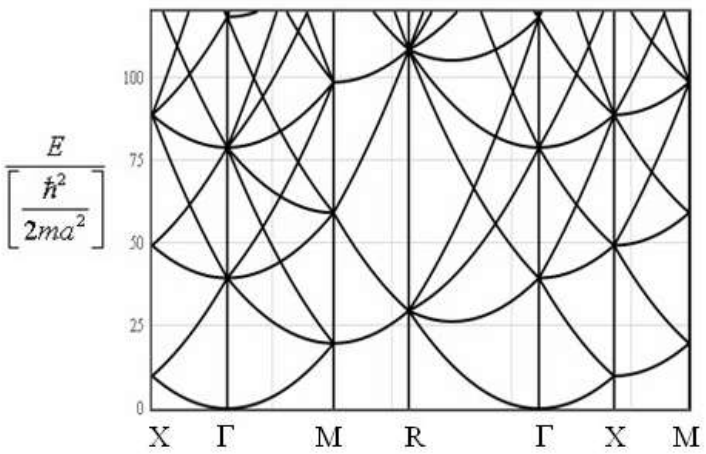
$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \sum_{\vec{G}} C_{\vec{G}} e^{i\vec{G}\cdot\vec{r}} = e^{i\vec{k}\cdot\vec{r}} \underbrace{e^{i\vec{G}_0\cdot\vec{r}} e^{-i\vec{G}_0\cdot\vec{r}}}_{1} \sum_{\vec{G}} C_{\vec{G}} e^{i\vec{G}\cdot\vec{r}} = e^{i\left(\vec{k}+\vec{G}_0\right)\cdot\vec{r}} \sum_{\vec{G}} C_{\vec{G}} e^{i\left(\vec{G}-\vec{G}_0\right)\cdot\vec{r}}$$

Empty lattice approximation



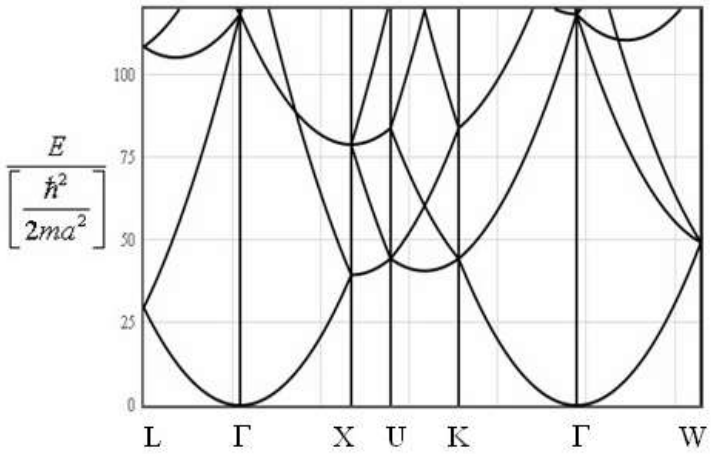
Empty lattice approximation

Simple cubic



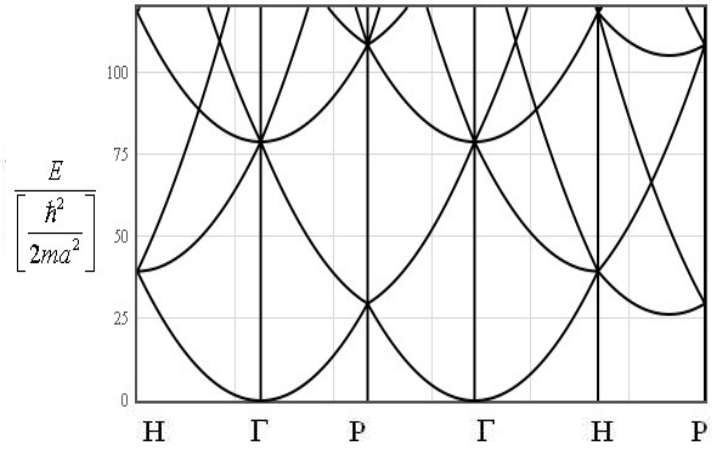
Choose a different order for the symmetry points

Face centered cubic

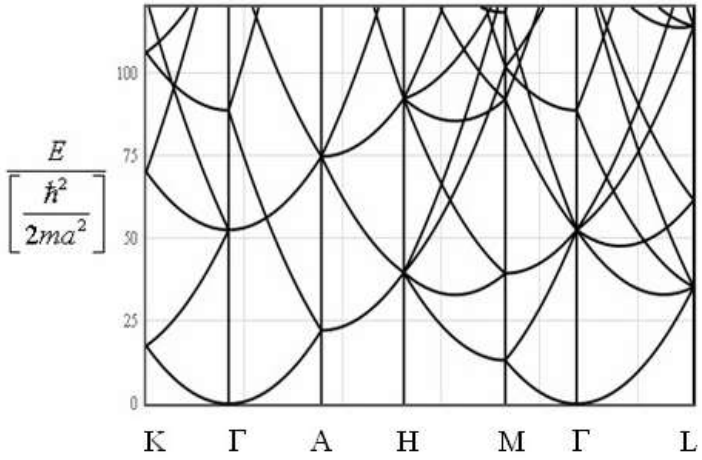


Choose a different order for the symmetry points

Body centered cubic



Hexagonal



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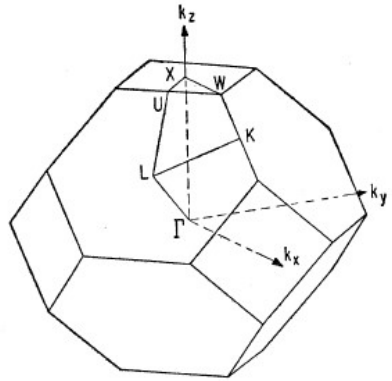
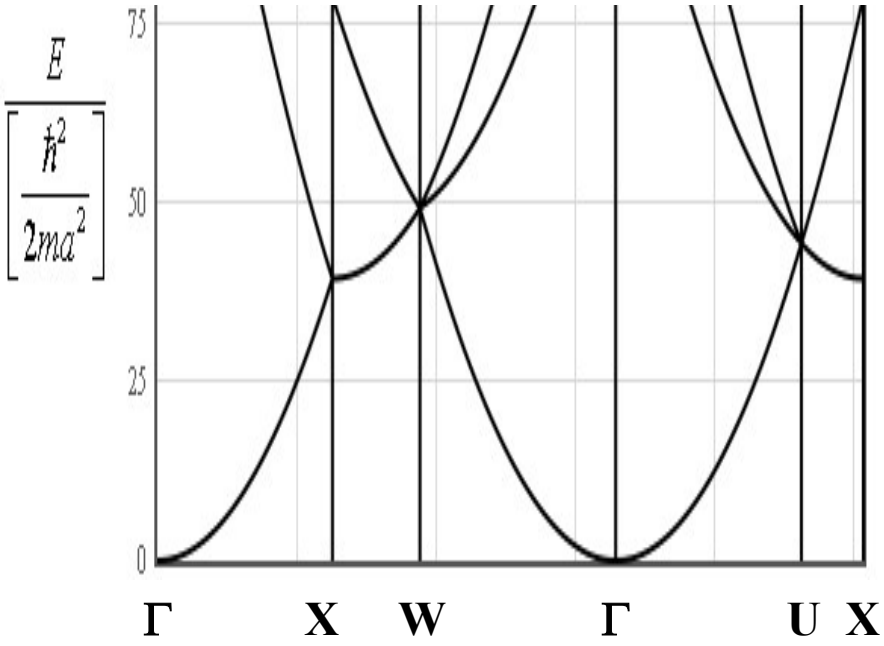
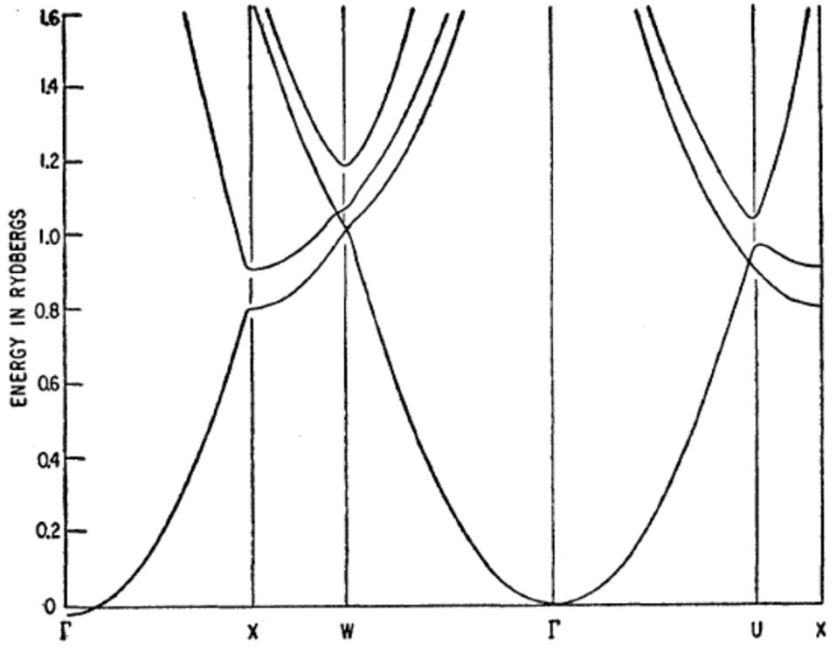
Band Structure of Aluminum

WALTER A. HARRISON
General Electric Research Laboratory, Schenectady, New York

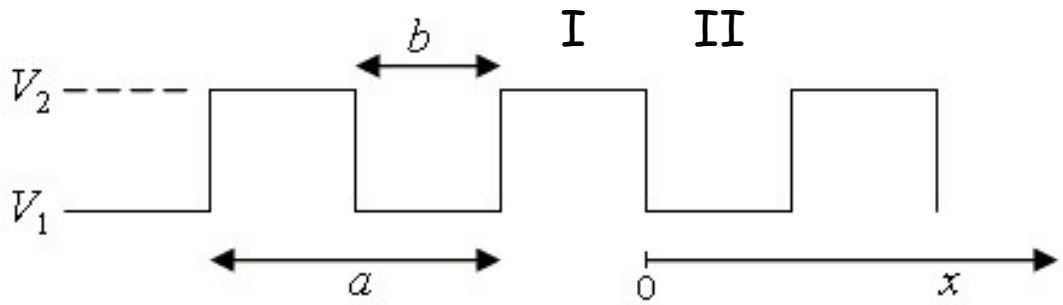


empty lattice approximation





A separable potential

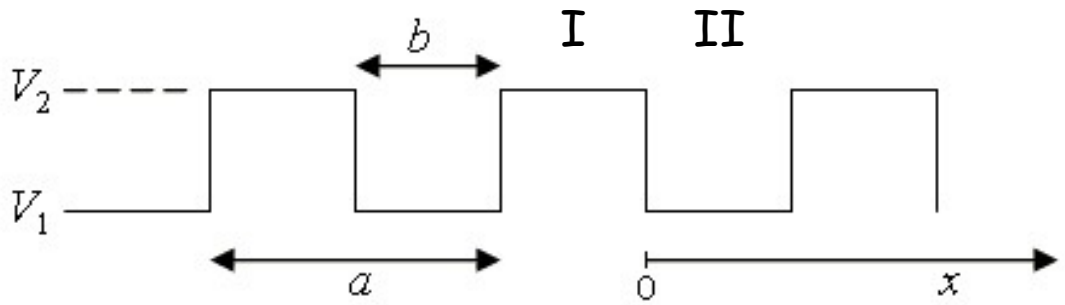


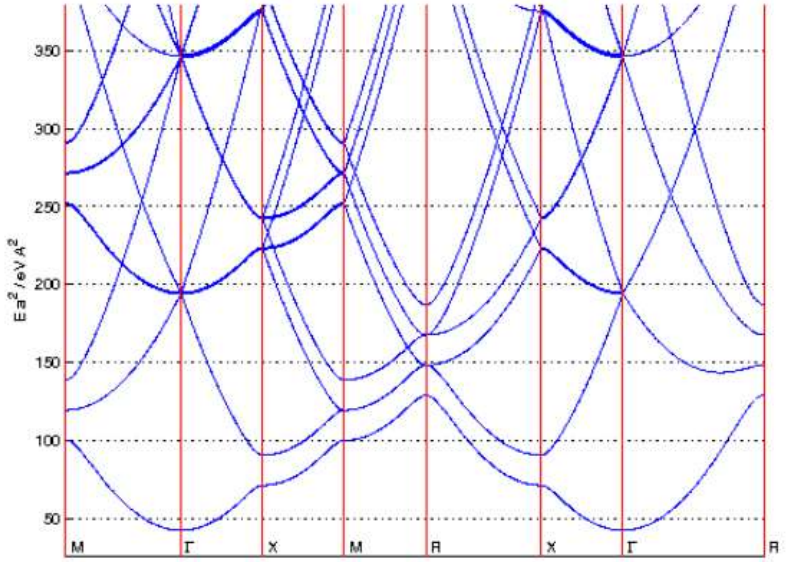
$$-\frac{\hbar^2}{2m}\nabla^2\Psi+(V(x)+V(y)+V(z))\Psi=E\Psi$$

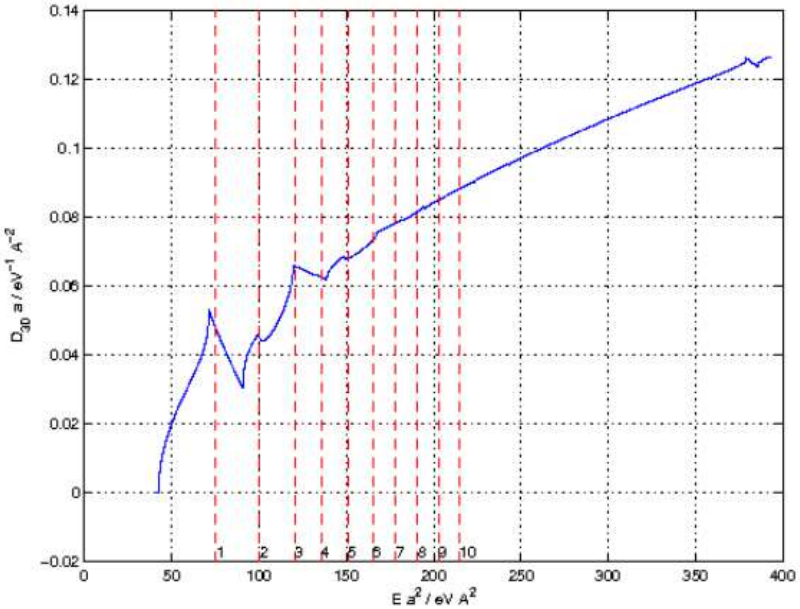
Ψ is the product of the solutions to the Kronig-Penney model.

$$\Psi(x,y,z)=\psi_{KP}(x)\psi_{KP}(y)\psi_{KP}(z)$$

A separable potential







http://lampx.tugraz.at/~hadley/ss1/separablecrystals/thermo.html