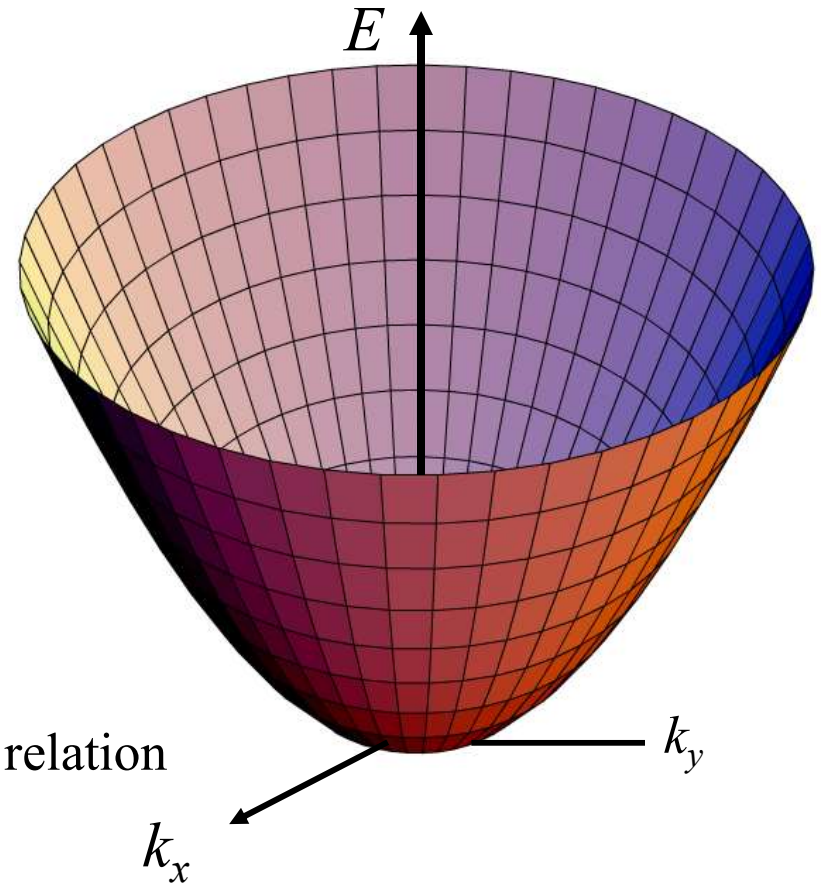
Electrons

free electrons (simple model for a metal)

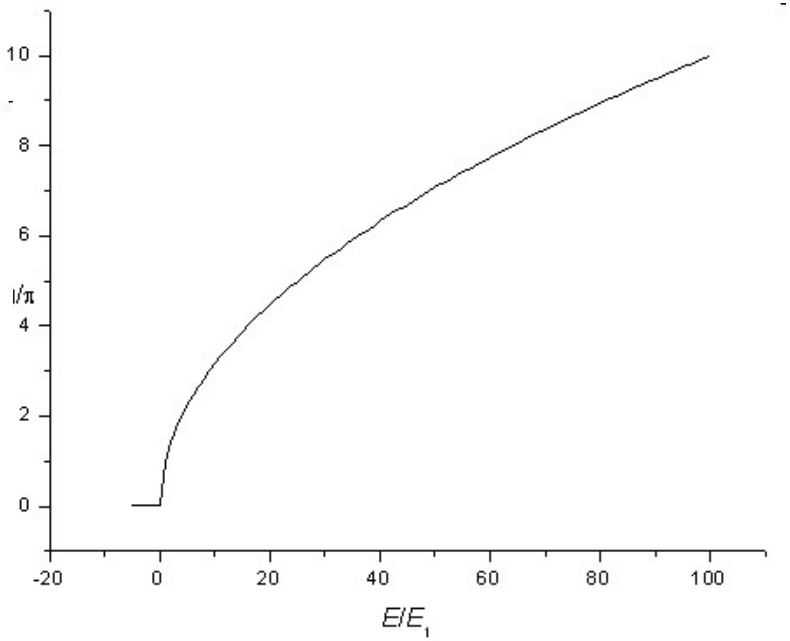
$$p = \hbar k$$

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



dispersion relation

3-d density of states

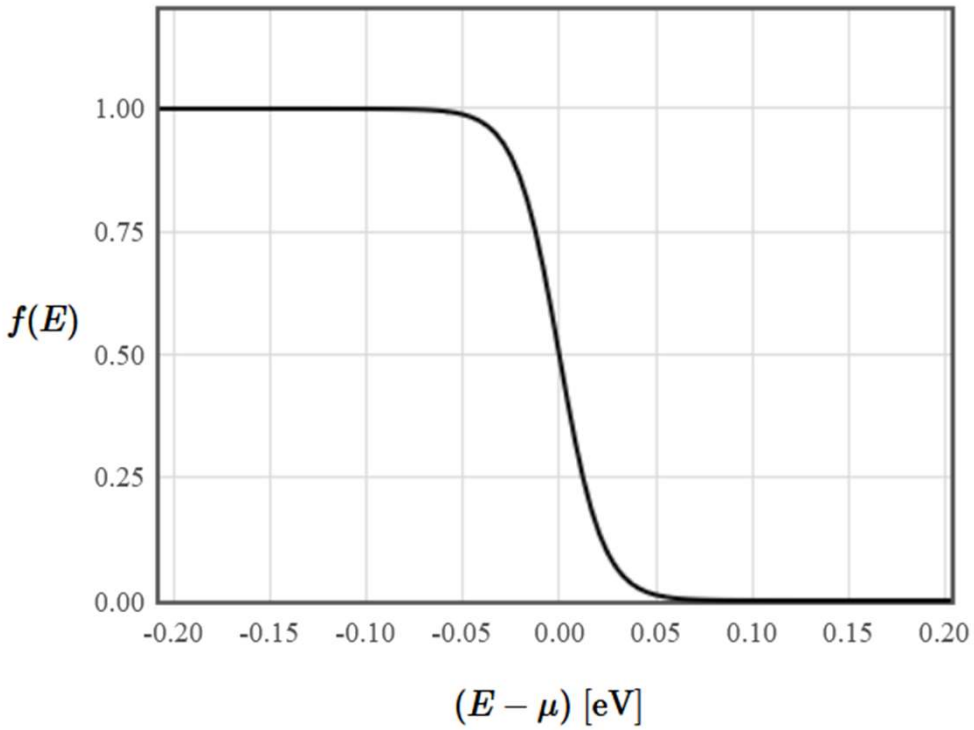


$$D(E) = \begin{cases} 0 & \text{for} \quad E < 0 \\ \dfrac{(2m)^{3/2}}{2\pi^2\hbar^3}\sqrt{E} & \text{for} \quad E > 0 \end{cases}$$

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,

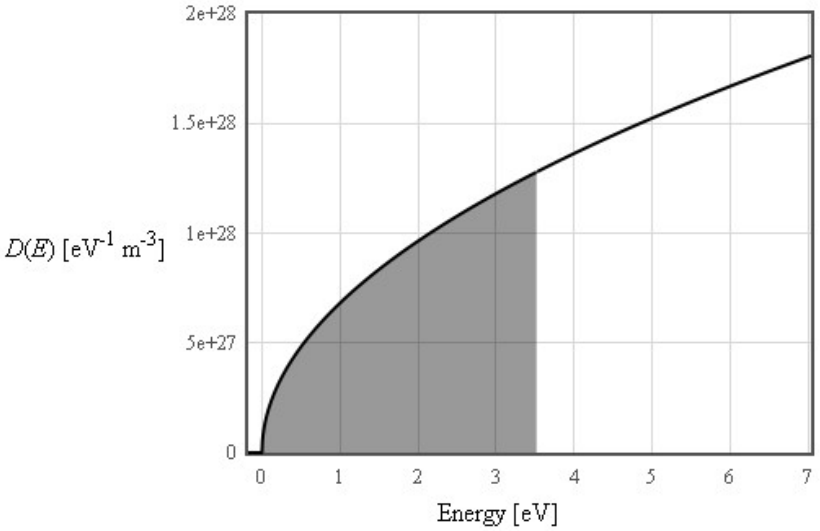
$$E_F = \mu(T=0).$$

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 $T = 0$:

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

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

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

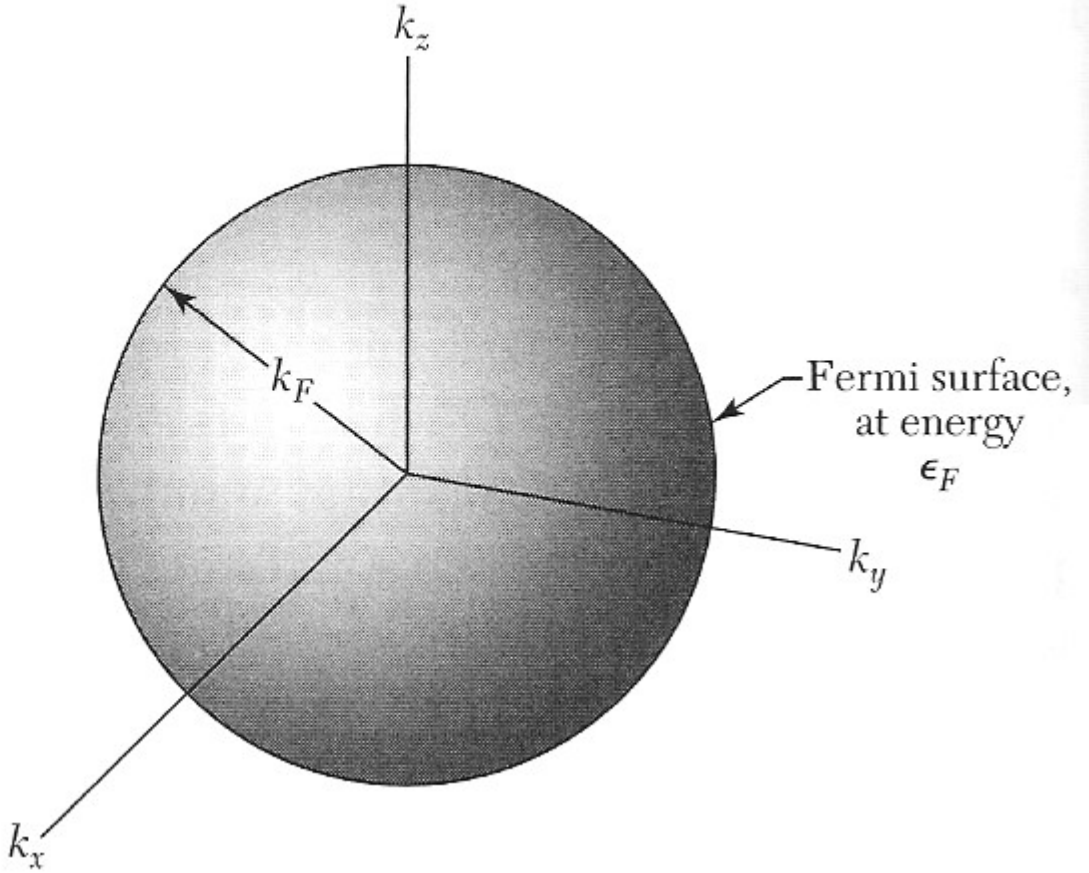
Fermi sphere

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

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

Results of the quantization of the Schrödinger equation for free fermions in 1, 2, and 3 dimensions.

A simple model for metals is the free electron model where the potential energy of the electrons is zero and the electron-electron interactions are ignored. This is equivalent to any system of noninteracting fermions with zero potential energy. In this model the thermodynamic properties only depend on one parameter, the particle density n. In the table below, n denotes the number of particles per meter in one-dimension, the number of particle per square meter in two-dimensions, and the number of particles per cubic mter in three dimensions.

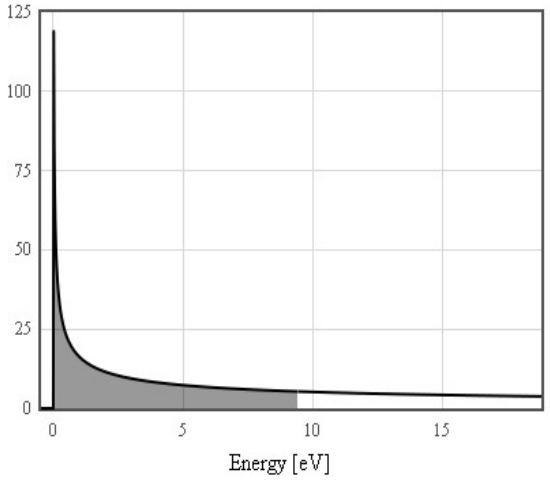
	1-D Schrödinger equation for a free particle $i\hbar\frac{d\psi}{dx}=-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}$	**2-D Schrödinger equation for a free particle** $i\hbar\frac{d\psi}{dx}=-\frac{\hbar^2}{2m}\left(\frac{d^2\psi}{dx^2}+\frac{d^2\psi}{dy^2}\right)$	**3-D Schrödinger equation for a free particle** $i\hbar\frac{d\psi}{dx}=-\frac{\hbar^2}{2m}\left(\frac{d^2\psi}{dx^2}+\frac{d^2\psi}{dy^2}+\frac{d^2\psi}{dz^2}\right)$
Eigenfunction solutions	$A_k\exp\left(i\left(kx-\omega t\right)\right)$	$A_{\vec{k}}\exp\left(i\left(\vec{k}\cdot\vec{r}-\omega t\right)\right)$	$A_{\vec{k}}\exp\left(i\left(\vec{k}\cdot\vec{r}-\omega t\right)\right)$
Dispersion relation	$E=\hbar\omega=\frac{\hbar^2k^2}{2m}$ J	$E=\hbar\omega=\frac{\hbar^2k^2}{2m}$ J	$E=\hbar\omega=\frac{\hbar^2k^2}{2m}$ J
Density of states	$D(k)=\frac{2}{\pi}$	$D(k)=\frac{k}{\pi}$ m^{-1}	$D(k)=\frac{k^2}{\pi^2}$ m^{-2}
Density of states $D(E)=D(k)\frac{dk}{dE}$	$D(E)=\frac{1}{\pi\hbar}\sqrt{\frac{2m}{E}}=\frac{n}{2\sqrt{E_FE}}$ $\mathrm{J}^{-1}\mathrm{m}^{-1}$	$D(E)=\frac{m}{\pi\hbar^2}=\frac{n}{E_F}$ $\mathrm{J}^{-1}\mathrm{m}^{-2}$	$D(E)=\frac{(2m)^{\frac{3}{2}}}{2\pi^2\hbar^3}\sqrt{E}=\frac{3n}{2E_F^{3/2}}\sqrt{E}$ $\mathrm{J}^{-1}\mathrm{m}^{-3}$
Fermi energy E_F $n=\int_{-\infty}^{E_F}D(E)dE$	$E_F=\frac{\pi^2\hbar^2n^2}{8m}$ J	$E_F=\frac{\pi\hbar^2n}{m}$ J	$E_F=\frac{\hbar^2}{2m}\left(3\pi^2n\right)^{\frac{2}{3}}$ J
$D(E_F)$	$D(E_F)=\frac{4m}{\pi^2\hbar^2n}$ $\mathrm{J}^{-1}\mathrm{m}^{-1}$	$D(E_F)=\frac{m}{\pi\hbar^2}$ $\mathrm{J}^{-1}\mathrm{m}^{-2}$	$D(E_F)=\frac{m(3n)^{\frac{1}{3}}}{\pi^{\frac{4}{3}}\hbar^2}$ $\mathrm{J}^{-1}\mathrm{m}^{-3}$
$D'(E_F)=\left.\frac{dD}{dE}\right\|_{E=E_F}$	$D'(E_F)=\frac{-16m^2}{\pi^4\hbar^4n^3}$ $\mathrm{J}^{-2}\mathrm{m}^{-1}$	$D'(E_F)=0$ $\mathrm{J}^{-2}\mathrm{m}^{-2}$	$D'(E_F)=\frac{m^2}{\hbar^4\sqrt[3]{3\pi^8n}}$ $\mathrm{J}^{-2}\mathrm{m}^{-3}$
Chemical potential μ $n=\int_{-\infty}^{\infty}D(E)f(E)dE$	$\mu\approx E_F-\frac{\pi^2}{6}\left(k_BT\right)^2\frac{D'(E_F)}{D(E_F)}$ J $\approx\frac{\pi^2\hbar^2n^2}{8m}+\frac{2m}{3\hbar^2n^2}\left(k_BT\right)^2$ J	$\mu=k_BT\ln\left(\exp\left(\frac{E_F}{k_BT}\right)-1\right)$ J $=k_BT\ln\left(\exp\left(\frac{\pi\hbar^2n}{mk_BT}\right)-1\right)$ J	$\mu\approx E_F-\frac{\pi^2}{6}\left(k_BT\right)^2\frac{D'(E_F)}{D(E_F)}$ J $\approx\frac{\hbar^2}{2m}\left(3\pi^2n\right)^{\frac{2}{3}}-\frac{\pi^{\frac{2}{3}}m}{2\hbar^2\sqrt[3]{3}^{\frac{10}{3}}}\left(k_BT\right)^2$ J

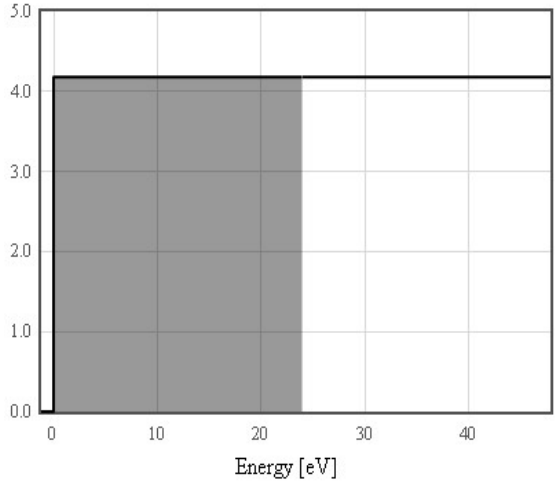
Free electron Fermi gas

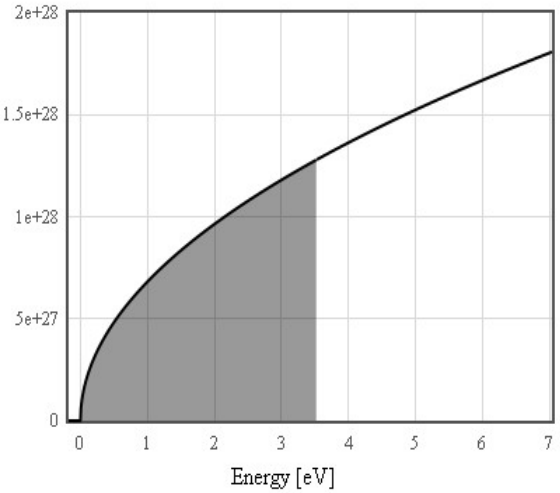
1 - d $$D(E) = \sqrt{\frac{2m}{\hbar^2 \pi^2 E}} = \frac{n}{2\sqrt{E_F E}} \quad \mathrm{J^{-1}m^{-1}}$$

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

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





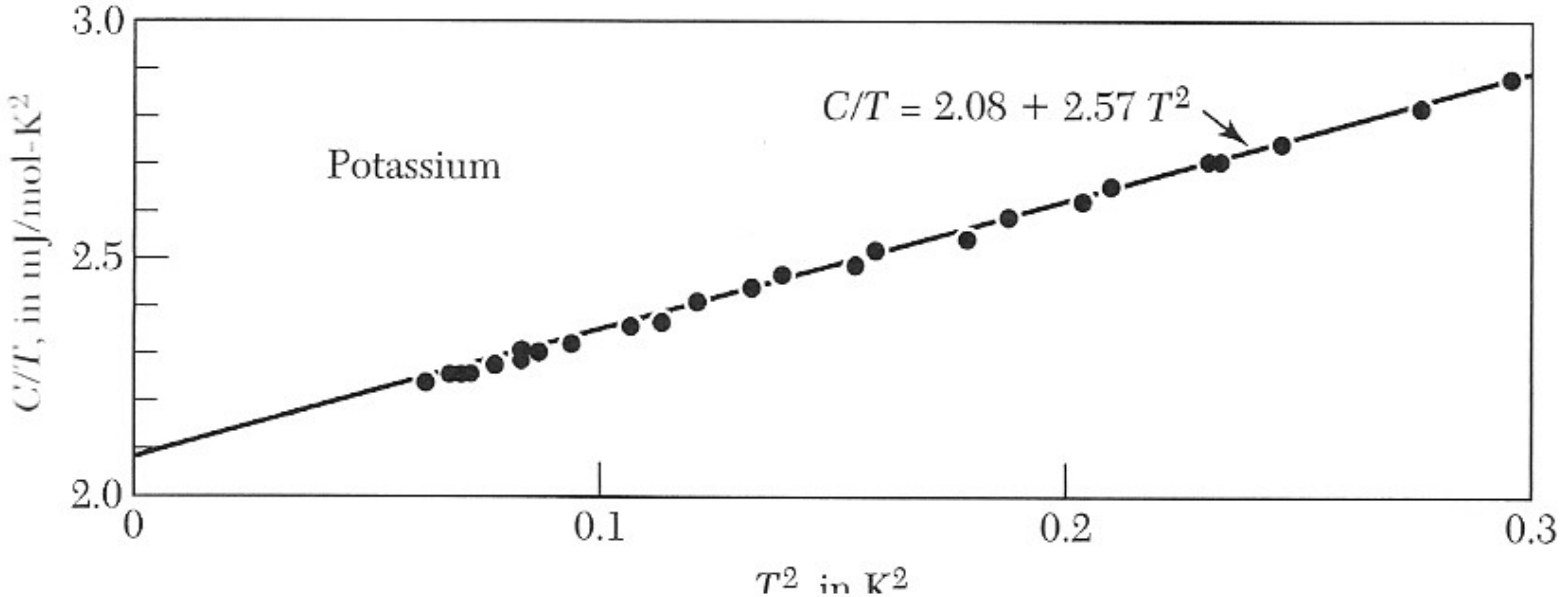


Electronic specific heat

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

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

electrons phonons



Effective mass

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

$$C_v = \gamma T + AT^3$$

$$\frac{m^*}{m} = \frac{\gamma_{observed}}{\gamma} = \frac{D(E_F)_{observed}}{D(E_F)_{free\ electron}}$$

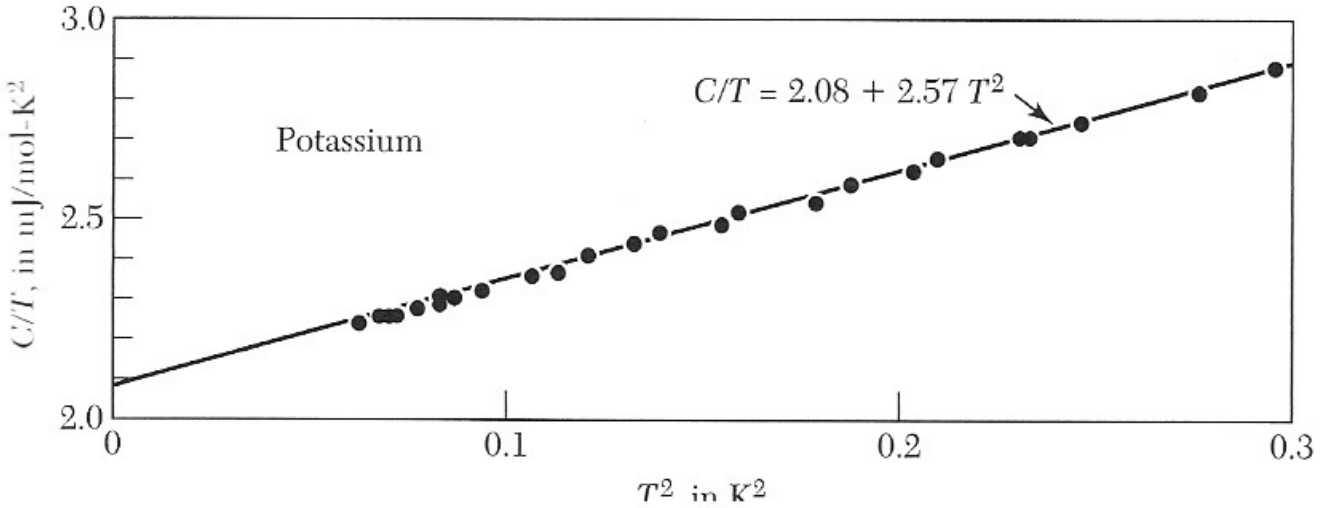


Table 2 Experimental and free electron values of electronic heat capacity constant γ of metals

(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

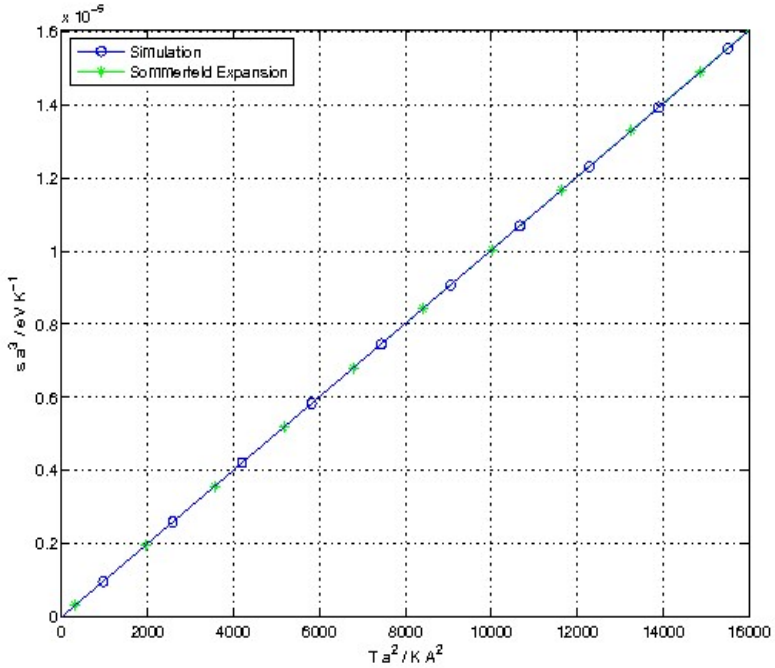
Entropy

$$c_v = \frac{du}{dT} \approx \frac{\pi^2 D(E_F)}{3} k_B^2 T \quad \text{J K}^{-1}\text{m}^{-3}$$

$$\frac{c_v}{T} = \frac{\partial s}{\partial T}\bigg|_{N,V} \approx \frac{\pi^2 D(E_F)}{3} k_B^2 \quad \text{J K}^{-1}\text{m}^{-3}$$

free electrons: $s \approx \left(\frac{\pi}{3}\right)^{\frac{2}{3}} \frac{m n^{\frac{1}{3}}}{\hbar^2} k_B^2 T \quad \text{J K}^{-1}\text{m}^{-3}$

Entropy density



Helmholtz free energy

$$s \approx \frac{\pi^2 D(E_F)}{3} k_B^2 \mathrm{T} \quad \mathrm{J\,K^{-1}m^{-3}}$$

free electrons: $$\approx \left(\frac{\pi}{3}\right)^{\frac{2}{3}} \frac{m n^{\frac{1}{3}}}{\hbar^2} k_B^2 T \quad \mathrm{J\,K^{-1}m^{-3}}$$

Helmholtz free energy density

$$f = u - Ts \approx \int_{-\infty}^{E_F} E D(E) dE - \frac{\pi^2 D(E_F)}{6} \left(k_B T\right)^2 \quad \mathrm{J\,m^{-3}}$$

free electrons: $$f \approx \frac{\hbar^2}{10m} \left(\pi^4 3^5 n^5\right)^{\frac{1}{3}} - \frac{m\left(3\pi^2 n\right)^{\frac{1}{3}}}{6\hbar^2} \left(k_B T\right)^2 \quad \mathrm{J\,m^{-3}}$$

Results of the quantization of the Schrödinger equation for free fermions in 1, 2, and 3 dimensions.

A simple model for metals is the free electron model where the potential energy of the electrons is zero and the electron-electron interactions are ignored. This is equivalent to any system of noninteracting fermions with zero potential energy. In this model the thermodynamic properties only depend on one parameter, the particle density n. In the table below, n denotes the number of particles per meter in one-dimension, the number of particle per square meter in two-dimensions, and the number of particles per cubic mter in three dimensions.

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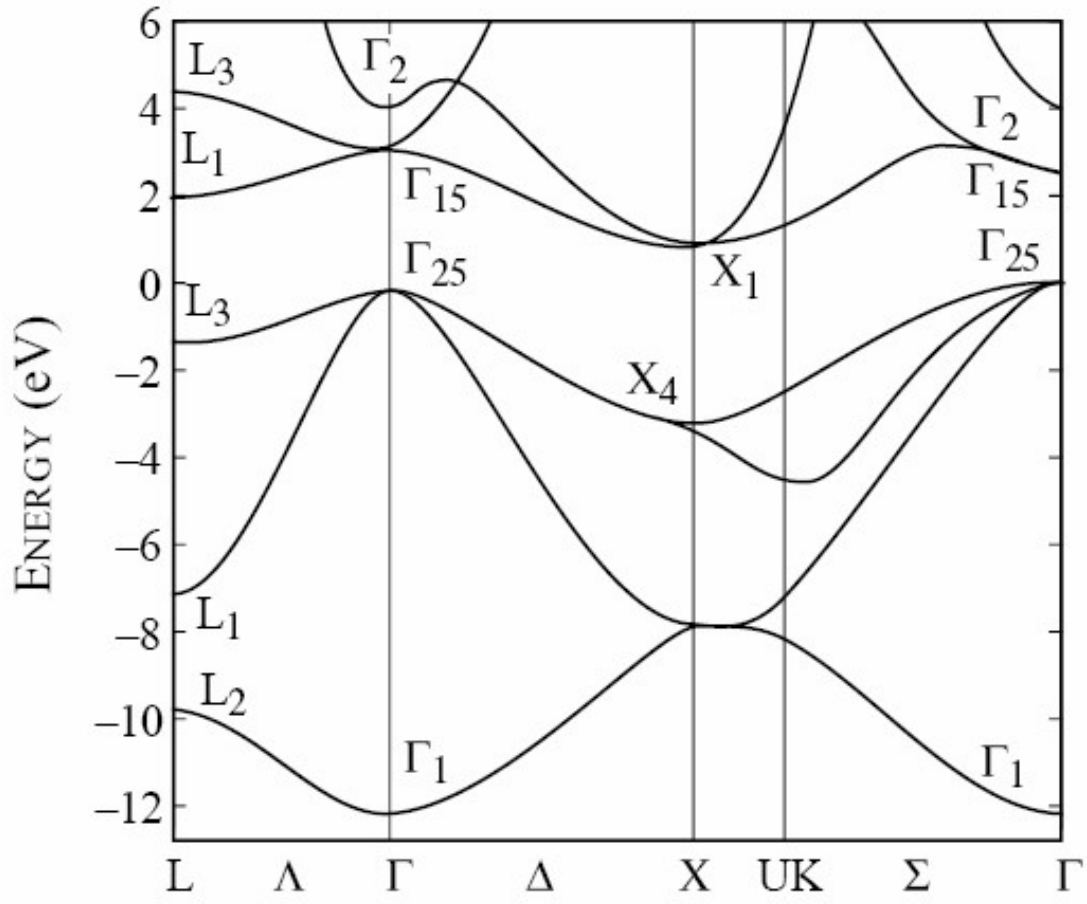
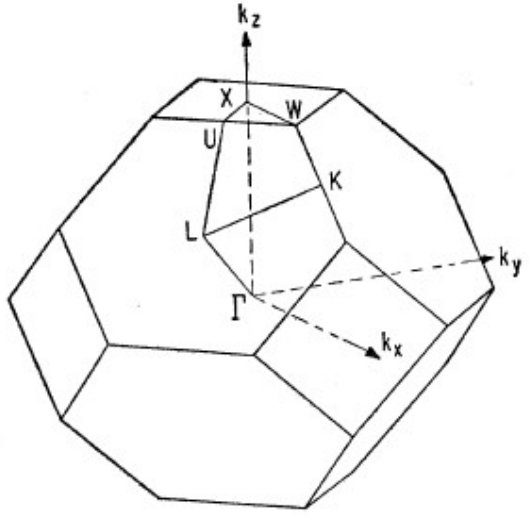
Eigenfunction solutions	$A_k\exp\left(i\left(kx-\omega t\right)\right)$	$A_{\vec{k}}\exp\left(i\left(\vec{k}\cdot\vec{r}-\omega t\right)\right)$	$A_{\vec{k}}\exp\left(i\left(\vec{k}\cdot\vec{r}-\omega t\right)\right)$
Dispersion relation	$E=\hbar\omega=\frac{\hbar^2k^2}{2m}$ J	$E=\hbar\omega=\frac{\hbar^2k^2}{2m}$ J	$E=\hbar\omega=\frac{\hbar^2k^2}{2m}$ J
Density of states	$D(k)=\frac{2}{\pi}$	$D(k)=\frac{k}{\pi}$ m^{-1}	$D(k)=\frac{k^2}{\pi^2}$ m^{-2}
Density of states $D(E)=D(k)\frac{dk}{dE}$	$D(E)=\frac{1}{\pi\hbar}\sqrt{\frac{2m}{E}}=\frac{n}{2\sqrt{E_FE}}$ $\mathrm{J}^{-1}\mathrm{m}^{-1}$	$D(E)=\frac{m}{\pi\hbar^2}=\frac{n}{E_F}$ $\mathrm{J}^{-1}\mathrm{m}^{-2}$	$D(E)=\frac{(2m)^{\frac{3}{2}}}{2\pi^2\hbar^3}\sqrt{E}=\frac{3n}{2E_F^{3/2}}\sqrt{E}$ $\mathrm{J}^{-1}\mathrm{m}^{-3}$
Fermi energy E_F $n=\int_{-\infty}^{E_F}D(E)dE$	$E_F=\frac{\pi^2\hbar^2n^2}{8m}$ J	$E_F=\frac{\pi\hbar^2n}{m}$ J	$E_F=\frac{\hbar^2}{2m}\left(3\pi^2n\right)^{\frac{2}{3}}$ J
$D(E_F)$	$D(E_F)=\frac{4m}{\pi^2\hbar^2n}$ $\mathrm{J}^{-1}\mathrm{m}^{-1}$	$D(E_F)=\frac{m}{\pi\hbar^2}$ $\mathrm{J}^{-1}\mathrm{m}^{-2}$	$D(E_F)=\frac{m(3n)^{\frac{1}{3}}}{\pi^{\frac{4}{3}}\hbar^2}$ $\mathrm{J}^{-1}\mathrm{m}^{-3}$
$D'(E_F)=\left.\frac{dD}{dE}\right\|_{E=E_F}$	$D'(E_F)=\frac{-16m^2}{\pi^4\hbar^4n^3}$ $\mathrm{J}^{-2}\mathrm{m}^{-1}$	$D'(E_F)=0$ $\mathrm{J}^{-2}\mathrm{m}^{-2}$	$D'(E_F)=\frac{m^2}{\hbar^4\sqrt[3]{3\pi^8n}}$ $\mathrm{J}^{-2}\mathrm{m}^{-3}$
Chemical potential μ $n=\int_{-\infty}^{\infty}D(E)f(E)dE$	$\mu\approx E_F-\frac{\pi^2}{6}\left(k_BT\right)^2\frac{D'(E_F)}{D(E_F)}$ J $\approx\frac{\pi^2\hbar^2n^2}{8m}+\frac{2m}{3\hbar^2n^2}\left(k_BT\right)^2$ J	$\mu=k_BT\ln\left(\exp\left(\frac{E_F}{k_BT}\right)-1\right)$ J $=k_BT\ln\left(\exp\left(\frac{\pi\hbar^2n}{mk_BT}\right)-1\right)$ J	$\mu\approx E_F-\frac{\pi^2}{6}\left(k_BT\right)^2\frac{D'(E_F)}{D(E_F)}$ J $\approx\frac{\hbar^2}{2m}\left(3\pi^2n\right)^{\frac{2}{3}}-\frac{\pi^{\frac{2}{3}}m}{2\hbar^2\sqrt[3]{3}^{\frac{10}{3}}}\left(k_BT\right)^2$ J

Electron Band Theory

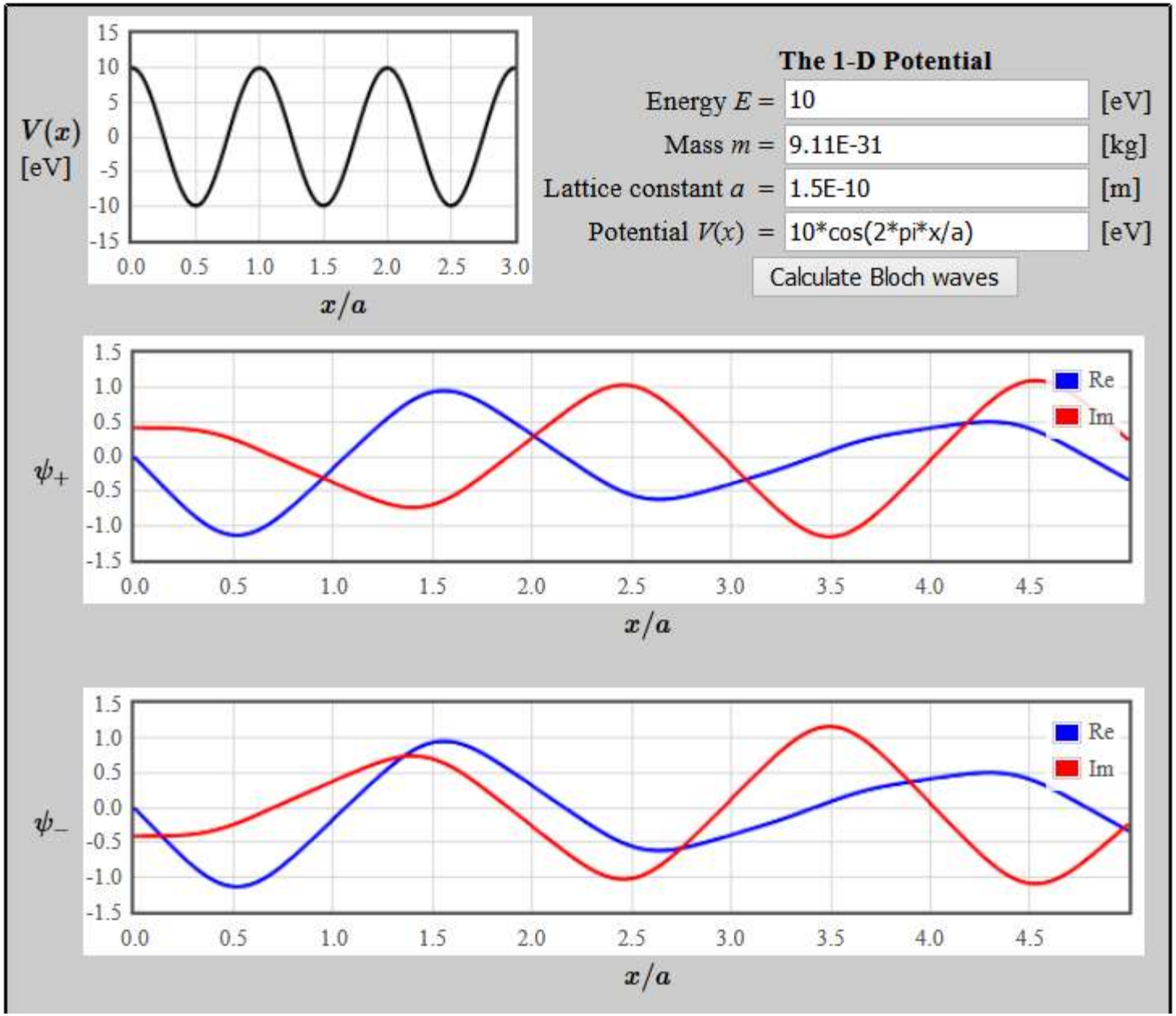
Calculate the dispersion relation for electrons in a crystal



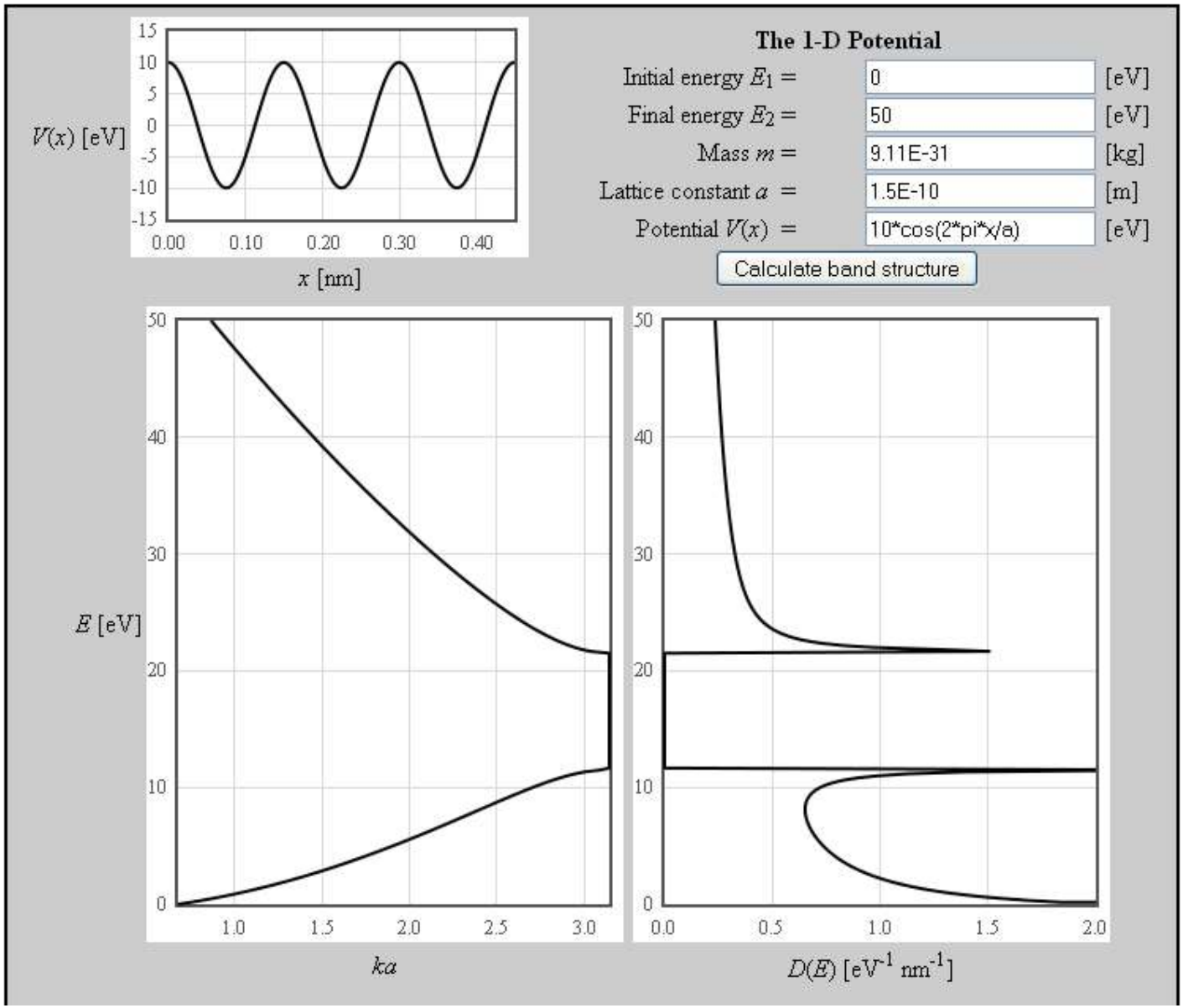


silicon

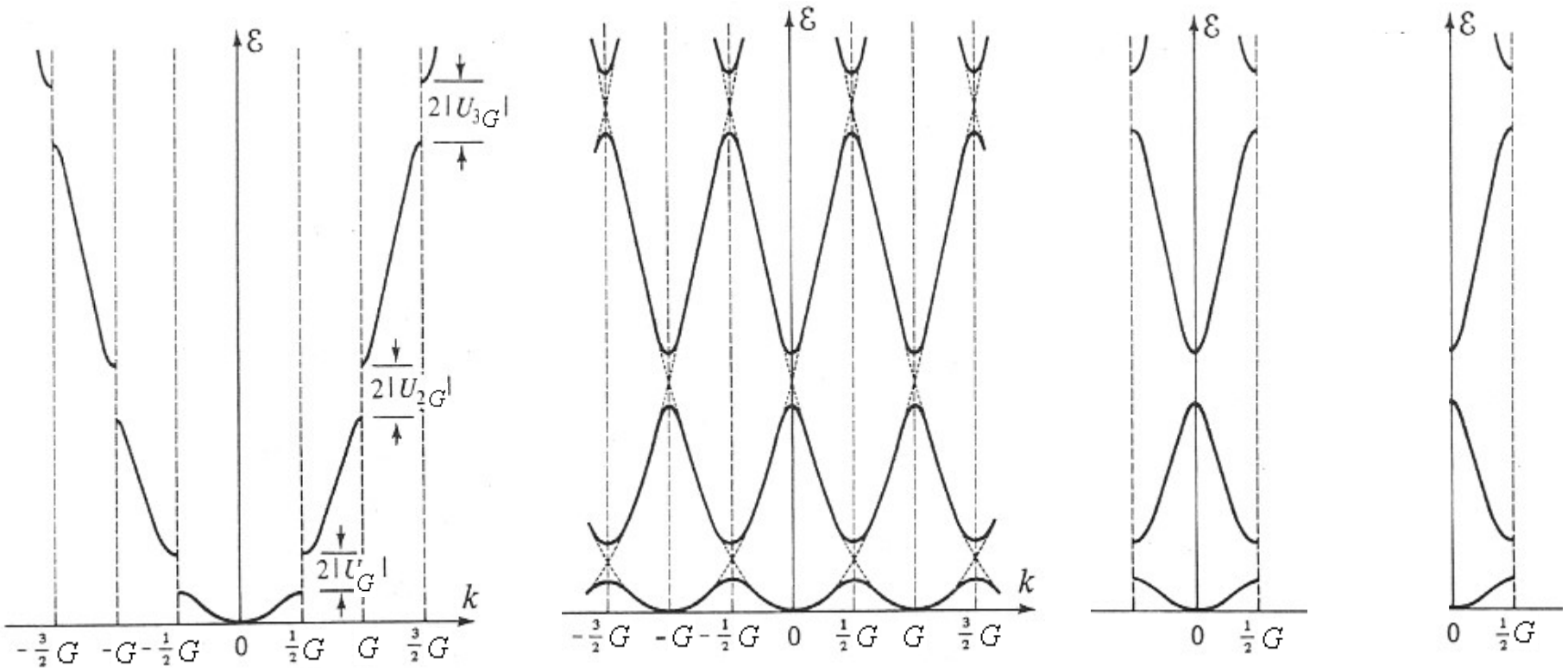
Bloch waves in 1-D



Band structure in 1-D



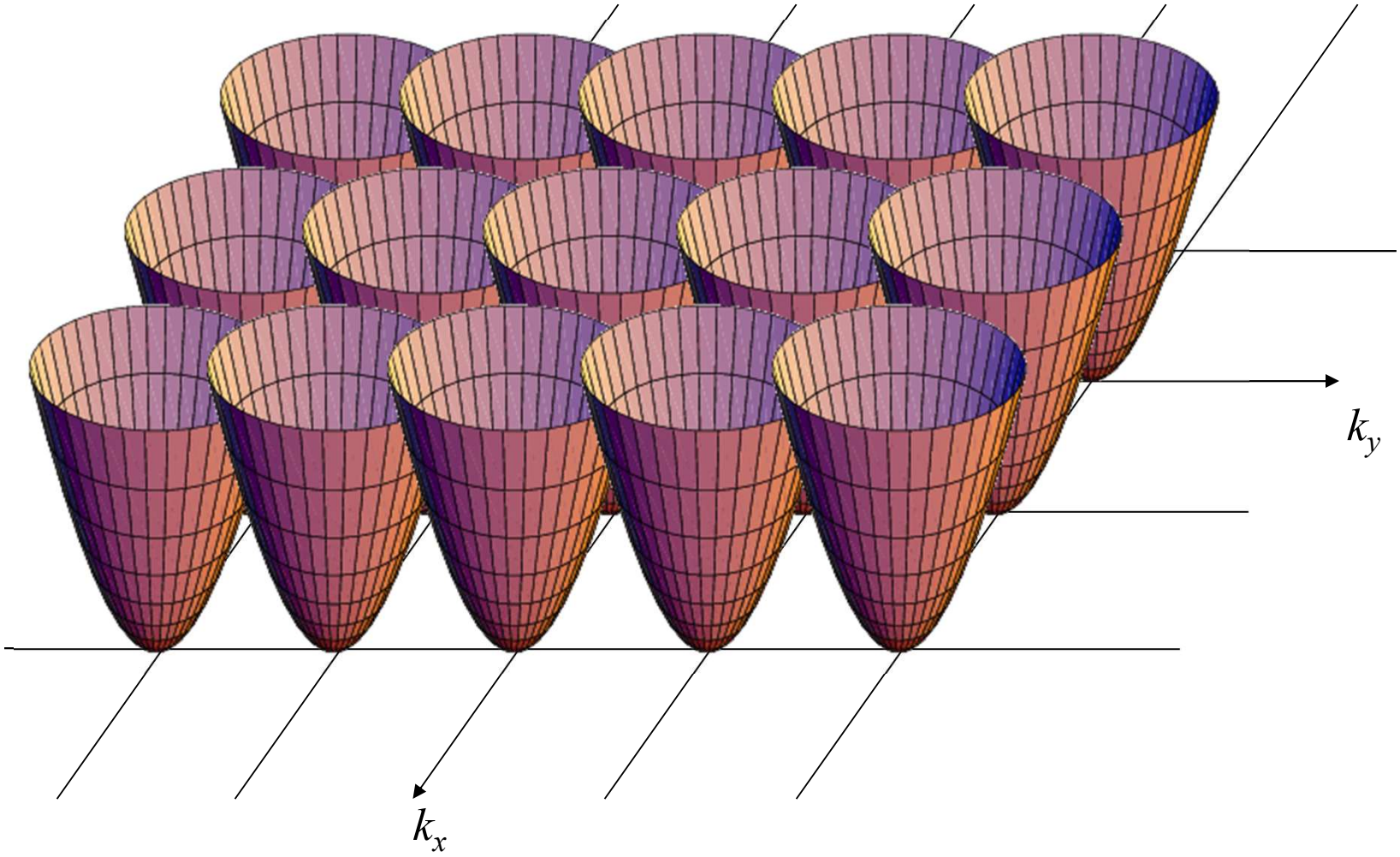
Empty lattice approximation



Extended Repeated Reduced

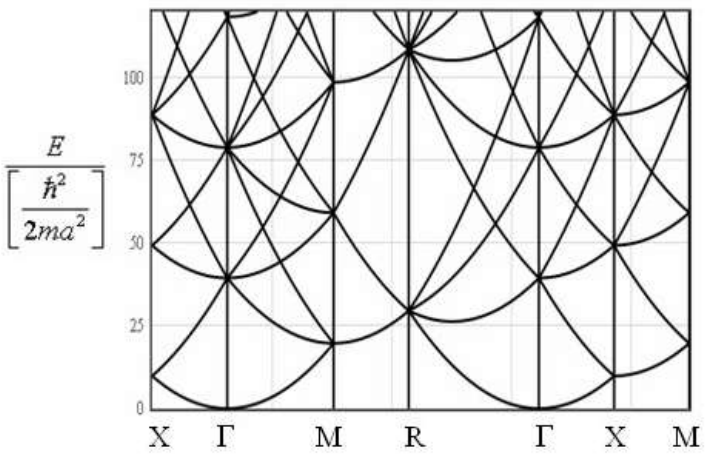
$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \sum_{\vec{G}} C_{\vec{G}} e^{i\vec{G}\cdot\vec{r}} = e^{i\vec{k}\cdot\vec{r}} \underbrace{e^{i\vec{G}_0\cdot\vec{r}} e^{-i\vec{G}_0\cdot\vec{r}}}_{1} \sum_{\vec{G}} C_{\vec{G}} e^{i\vec{G}\cdot\vec{r}} = e^{i\left(\vec{k}+\vec{G}_0\right)\cdot\vec{r}}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

Empty lattice approximation



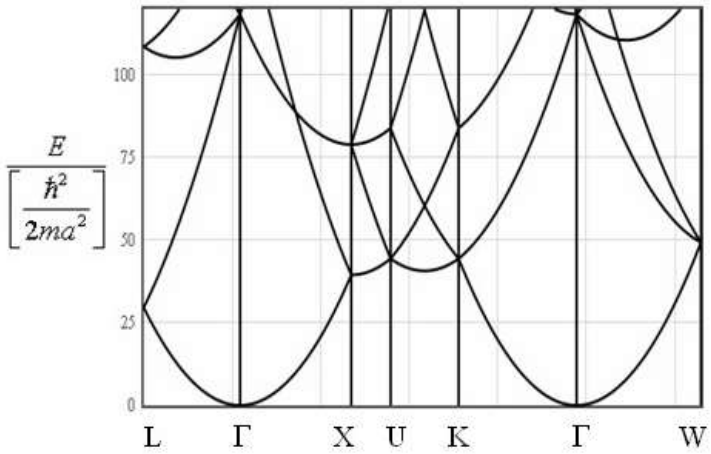
Empty lattice approximation

Simple cubic



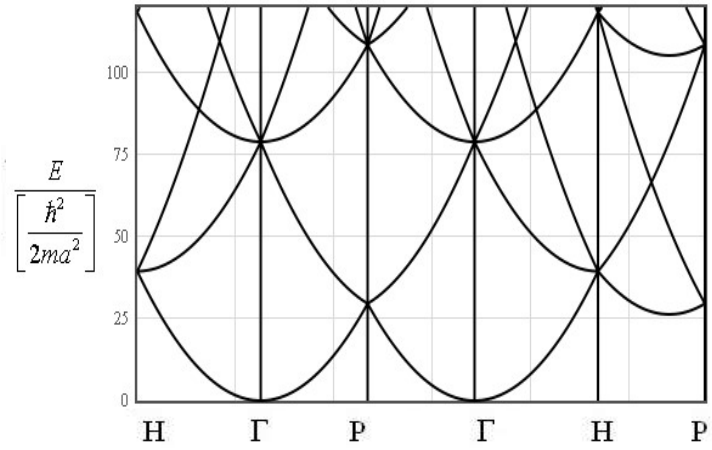
Choose a different order for the symmetry points

Face centered cubic

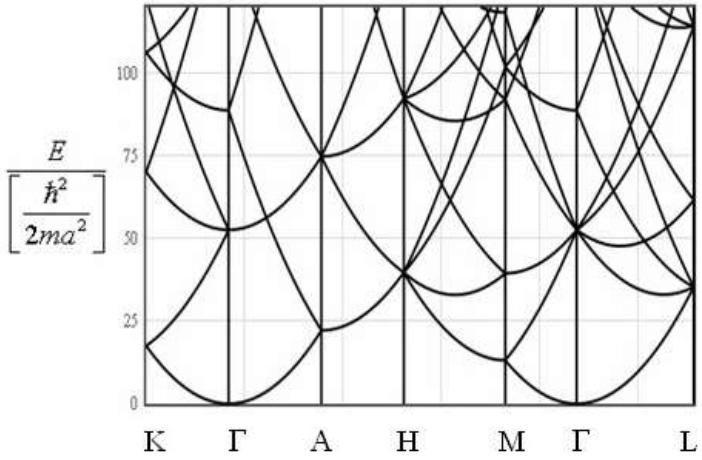


Choose a different order for the symmetry points

Body centered cubic



Hexagonal



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Band Structure of Aluminum

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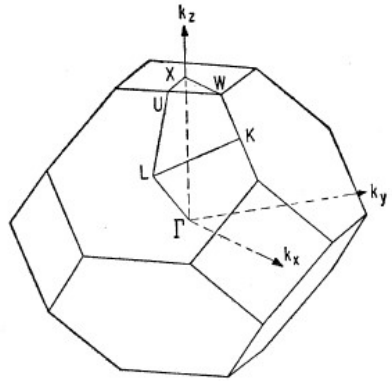
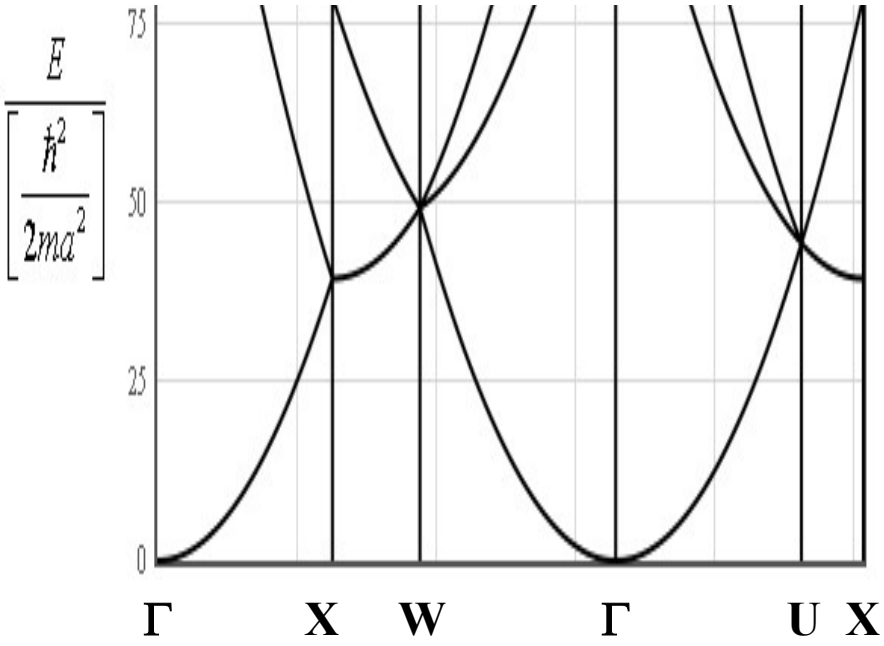
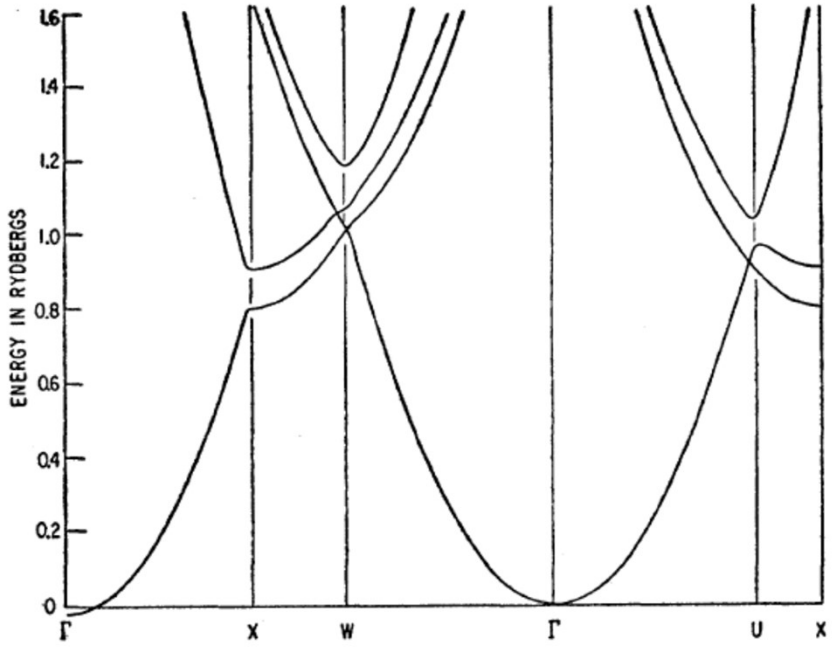
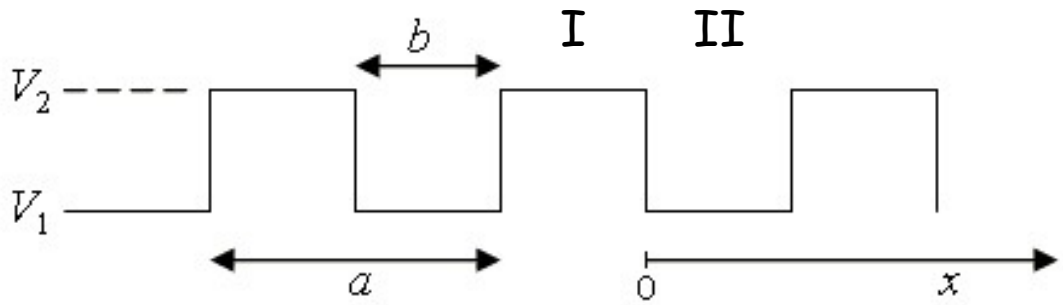


empty lattice approximation





A separable potential

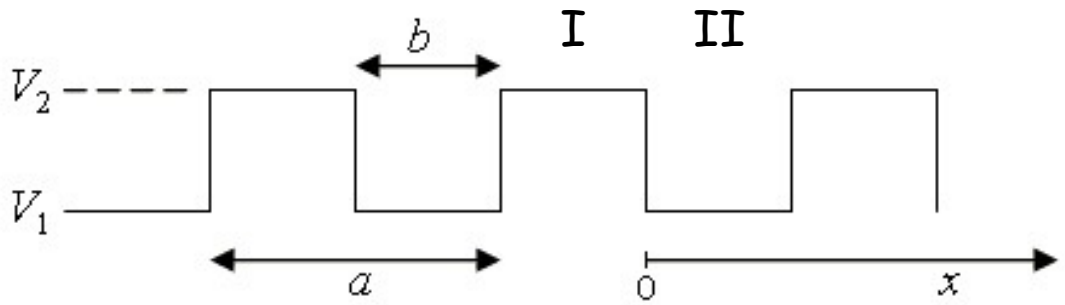


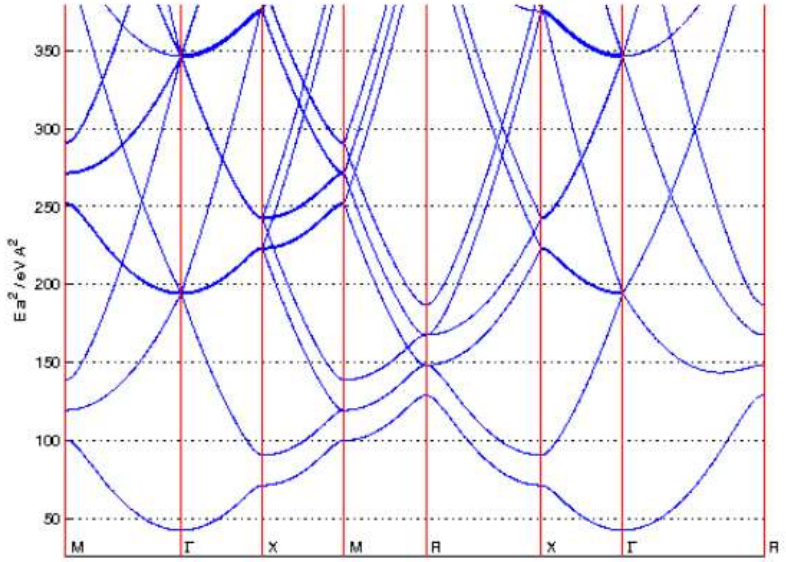
$$-\frac{\hbar^2}{2m}\nabla^2\Psi+(V(x)+V(y)+V(z))\Psi=E\Psi$$

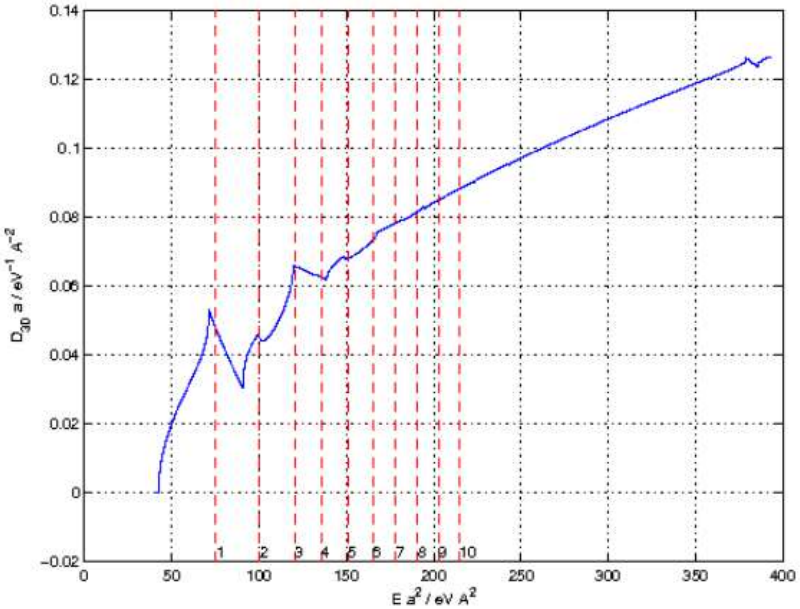
Ψ is the product of the solutions to the Kronig-Penney model.

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

A separable potential







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