Electrons

Thermodynamic properties

Free electrons

Fermi surfaces

Band structure calculations

- Empty lattice approximation
- Plane wave method
- Tight binding

Thermodynamic properties of non-interacting fermions

The grand canonical partition function is

$$Z_{gr} = \sum_q \exp\left(\frac{\mu}{k_B T}\right)^{N_q} \exp\left(-\frac{E_q}{k_B T}\right) = \sum_q \exp\left(-\frac{E_q - \mu N_q}{k_B T}\right)$$

Here q sums over the macro states. Only one fermion is allowed per microscopic quantum state.

$$N_q = \sum_i n_{qi} \qquad E_q = \sum_i n_{qi}\varepsilon_i \qquad n_{qi} \in 0,1$$

n_{qi} are occupation numbers that specify if microstate i is occupied in macrostate q

http://lamp.tu-graz.ac.at/~hadley/ss2/fermigas/thermo/thermo.php

Thermodynamic properties of non-interacting fermions

$$Z_{gr} = \sum_q \exp\left(-\frac{E_q - \mu N_q}{k_B T}\right) = \sum_q \exp\left(-\frac{\sum_i n_{qi}\left(\varepsilon_i - \mu\right)}{k_B T}\right) = \sum_q \prod_i \exp\left(-\frac{n_{qi}\left(\varepsilon_i - \mu\right)}{k_B T}\right)$$

The sum over all possible macrostates can also be written as the sum over all possible microstates.

$$Z_{gr} = \sum_{n_{0i}=0}^{1} \sum_{n_{1i}=0}^{1} \cdots \sum_{n_{q\max i}=0}^{1} \prod_i \exp\left(-\frac{n_{qi}\left(\varepsilon_i - \mu\right)}{k_B T}\right) = \prod_i \left(\exp\left(-\frac{\left(\varepsilon_i - \mu\right)}{k_B T}\right) + 1\right)$$

Pull the $n_{0\mathrm{i}}$ factors through the other sums then write out the sum over 0 and 1.

Thermodynamic properties of non-interacting fermions

Grand potential: $\Phi = U - TS - \mu N = -k_B T \ln(Z_{gr})$

$$\Phi = -k_B T \sum_i \ln\left(\exp\left(-\frac{(\varepsilon_i - \mu)}{k_B T}\right) + 1\right)$$

Approximate the sum by an integral over the density of states.

$$\phi = \frac{\Phi}{V} = -k_B T \int_{-\infty}^{\infty} D(E) \ln\left(\exp\left(-\frac{(E - \mu)}{k_B T}\right) + 1\right) dE$$

Differentiate to find the number density.

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

Fermi function

Thermodynamic properties

Grand potential density:

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

Helmholz free energy density:

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

Entropy density:

$$s = -\frac{\partial \phi}{\partial T} = \frac{1}{T}\int_{-\infty}^{\infty} D(E)\left(\frac{(E-\mu)}{1+\exp\left(\frac{(E-\mu)}{k_B T}\right)} - k_B T \ln\left(\exp\left(-\frac{(E-\mu)}{k_B T}\right)+1\right)\right) dE$$

http://lamp.tu-graz.ac.at/~hadley/ss2/fermigas/thermo/thermo.php

Thermodynamic properties

Chemical potential (implicitly defined by):

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

DoS → mu

Internal energy density:

$$u = \phi + Ts + \mu n = \int_{-\infty}^{\infty} \frac{ED(E)}{1+\exp\left(\frac{E-\mu}{k_B T}\right)} dE$$

DoS → u(T)

Energy spectral density:

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

DoS → u(E)

Specific heat:

$$c_v = \frac{\partial u}{\partial T} = \int_{-\infty}^{\infty} \frac{ED(E)(E-\mu)\exp\left(\frac{E-\mu}{k_B T}\right)}{k_B T^2 \left(1+\exp\left(\frac{E-\mu}{k_B T}\right)\right)^2} dE$$

DoS → cv(T)

http://lamp.tu-graz.ac.at/~hadley/ss2/fermigas/thermo/thermo.php

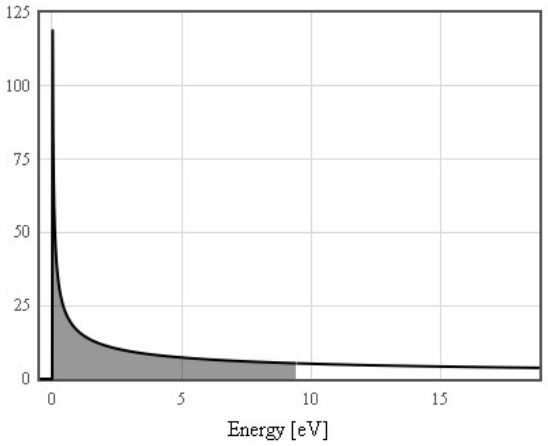
	1-D Schrödinger equation for a free particle $i\hbar\frac{d\psi}{dt}=-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}$	2-D Schrödinger equation for a free particle $i\hbar\frac{d\psi}{dt}=-\frac{\hbar^2}{2m}\left(\frac{d^2\psi}{dx^2}+\frac{d^2\psi}{dy^2}\right)$	3-D Schrödinger equation for a free particle $i\hbar\frac{d\psi}{dt}=-\frac{\hbar^2}{2m}\left(\frac{d^2\psi}{dx^2}+\frac{d^2\psi}{dy^2}+\frac{d^2\psi}{dz^2}\right)$
Eigenfunction solutions	$\psi_k = A_k \exp\left(i\left(kx-\omega t\right)\right)$	$\psi_k = A_{\vec{k}} \exp\left(i\left(\vec{k}\cdot\vec{r}-\omega t\right)\right)$	$\psi_k = A_{\vec{k}} \exp\left(i\left(\vec{k}\cdot\vec{r}-\omega t\right)\right)$
Eigenvalues of the translation operator $T\psi_k(\vec{r})=\psi_k(\vec{r}+\vec{R})=\lambda_k\psi_k(\vec{r})$	$\lambda_k = \exp\left(ikR\right)$	$\lambda_{\vec{k}} = \exp\left(i\vec{k}\cdot\vec{R}\right)$	$\lambda_{\vec{k}} = \exp\left(i\vec{k}\cdot\vec{R}\right)$
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	$D(k)=\frac{2}{\pi}$	$D(k)=\frac{k}{\pi}$ $\mathrm{m^{-1}}$	$D(k)=\frac{k^2}{\pi^2}$ $\mathrm{m^{-2}}$
Density of states $D(E)=D(k)\frac{dk}{dE}$	$D(E)=\frac{1}{\pi\hbar}\sqrt{\frac{2m}{E}}=\frac{n}{2\sqrt{E_F E}}$ $\mathrm{J^{-1}m^{-1}}$	$D(E)=\frac{m}{\pi\hbar^2}=\frac{n}{E_F}$ $\mathrm{J^{-1}m^{-2}}$	$D(E)=\frac{(2m)^{\frac{3}{2}}}{2\pi^2\hbar^3}\sqrt{E}=\frac{3n}{2E_F^{3/2}}\sqrt{E}$ $\mathrm{J^{-1}m^{-3}}$
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
$D(E_F)$	$D(E_F)=\frac{4m}{\pi^2\hbar^2n}$ $\mathrm{J^{-1}m^{-1}}$	$D(E_F)=\frac{m}{\pi\hbar^2}$ $\mathrm{J^{-1}m^{-2}}$	$D(E_F)=\frac{m(3n)^{\frac{1}{3}}}{\pi^{\frac{4}{3}}\hbar^2}$ $\mathrm{J^{-1}m^{-3}}$
$D'(E_F)=\left.\frac{dD}{dE}\right\|_{E=E_F}$	$D'(E_F)=\frac{-16m^2}{\pi^4\hbar^4n^3}$ $\mathrm{J^{-2}m^{-1}}$	$D'(E_F)=0$ $\mathrm{J^{-2}m^{-2}}$	$D'(E_F)=\frac{m^2}{\hbar^4\sqrt[3]{3\pi^8n}}$ $\mathrm{J^{-2}m^{-3}}$
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 $\approx\frac{\hbar^2}{2m}\left(3\pi^2n\right)^{\frac{2}{3}}-\frac{\pi^{\frac{2}{3}}m}{2\hbar^2 3^{\frac{10}{3}}n^{\frac{2}{3}}}\left(k_BT\right)^2$ J
Internal energy distribution $u(E)=E\frac{D(E)}{\exp\left(\frac{E-\mu}{k_BT}\right)+1}$	$u(E)=\frac{n}{2}\sqrt{\frac{E}{E_F}}\frac{1}{\exp\left(\frac{E-\mu}{k_BT}\right)+1}$ $\mathrm{m^{-1}}$ $=\frac{1}{\pi\hbar}\sqrt{2mE}\frac{1}{\exp\left(\frac{E-\mu}{k_BT}\right)+1}$ $\mathrm{m^{-1}}$	$u(E)=\frac{n}{E_F}\frac{E}{\exp\left(\frac{E-\mu}{k_BT}\right)+1}$ $\mathrm{m^{-2}}$ $=\frac{m}{\pi\hbar^2}\frac{E}{\exp\left(\frac{E-\mu}{k_BT}\right)+1}$ $\mathrm{m^{-2}}$	$u(E)=\frac{3n}{2}\left(\frac{E}{E_F}\right)^{3/2}\frac{1}{\exp\left(\frac{E-\mu}{k_BT}\right)+1}$ $\mathrm{m^{-3}}$ $=\frac{1}{2\pi^2\hbar^3}\left(2mE\right)^{3/2}\frac{1}{\exp\left(\frac{E-\mu}{k_BT}\right)+1}$ $\mathrm{m^{-3}}$

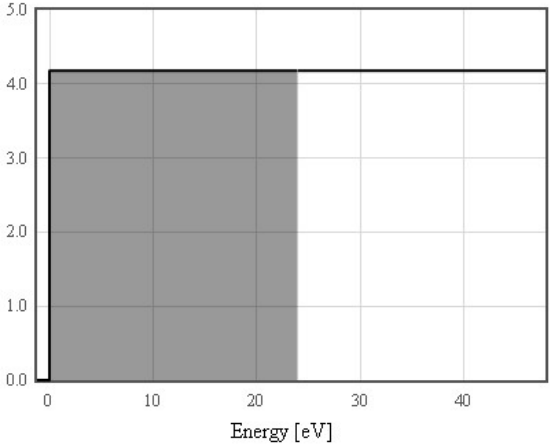
Free electron Fermi gas

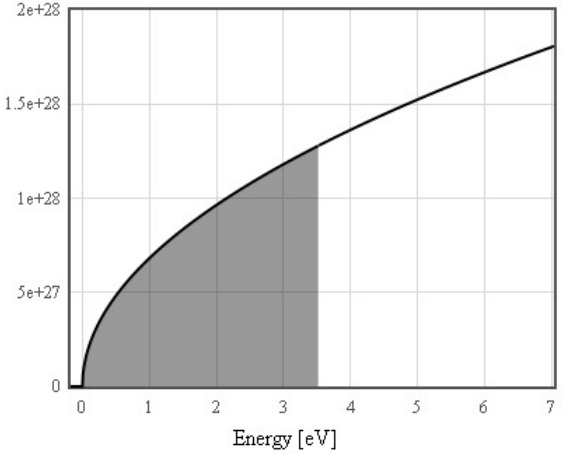
1 - d $$D(E) = \sqrt{\frac{2m}{\hbar^2 \pi^2 E}} = \frac{n}{2\sqrt{E_F E}} \qquad \mathrm{J^{-1}m^{-1}}$$

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

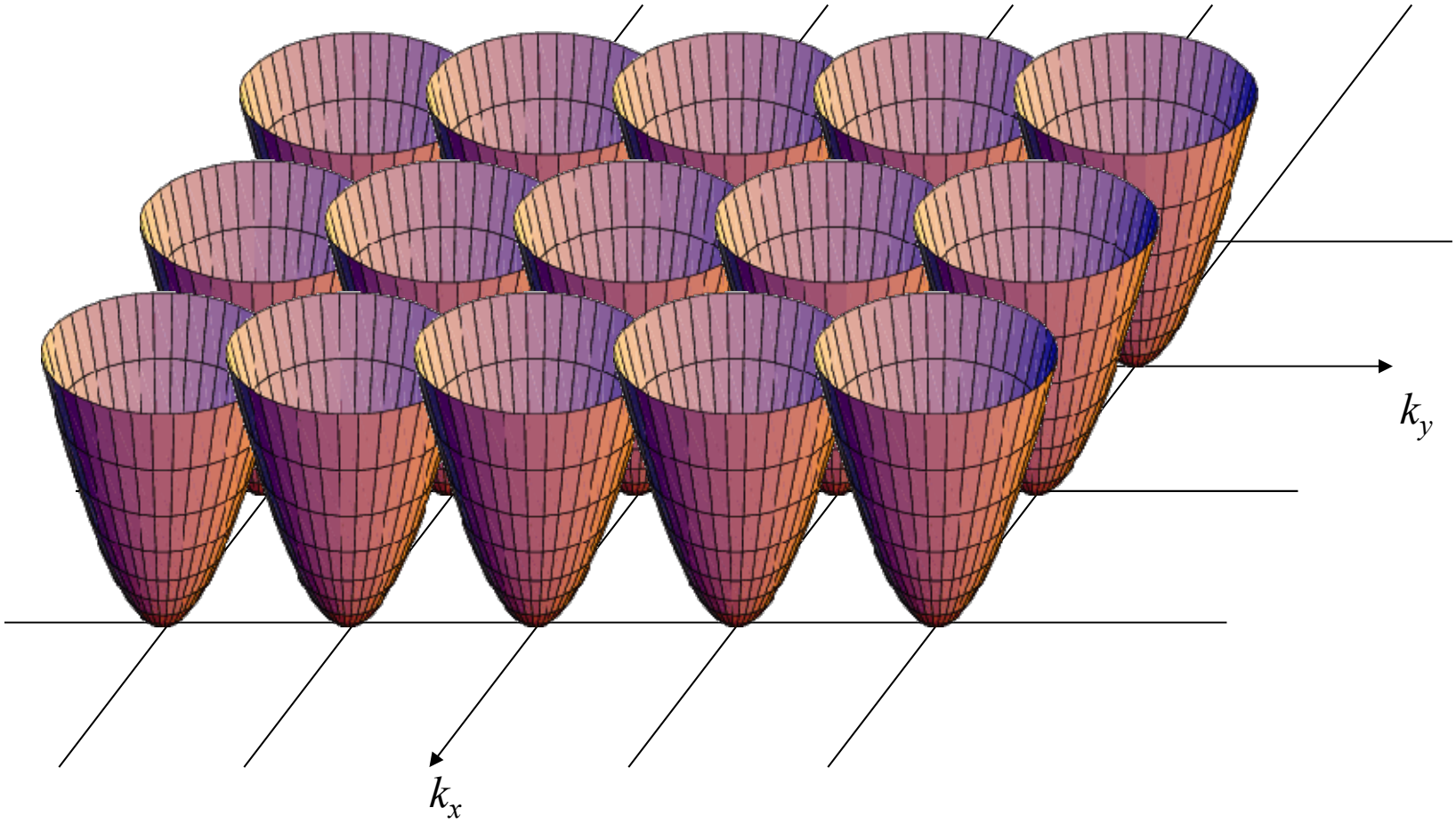
3 - d $$D(E) = \frac{\pi}{2}\left(\frac{2m}{\hbar^2 \pi^2}\right)^{3/2} \sqrt{E} = \frac{3n}{2E_F^{3/2}} \sqrt{E} \qquad \mathrm{J^{-1}m^{-3}}$$





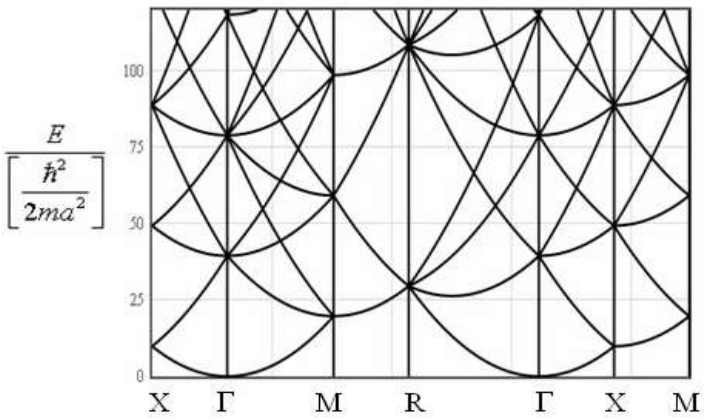


Empty lattice approximation



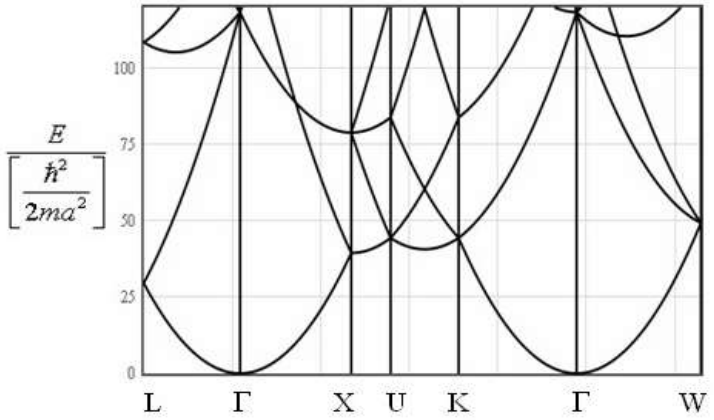
Empty lattice approximation

Simple cubic



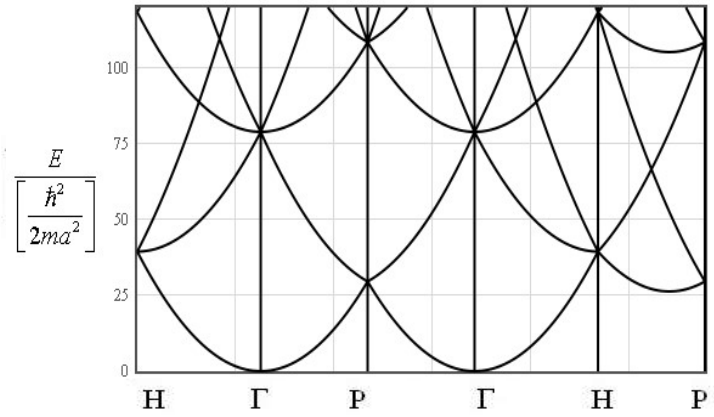
Choose a different order for the symmetry points

Face centered cubic

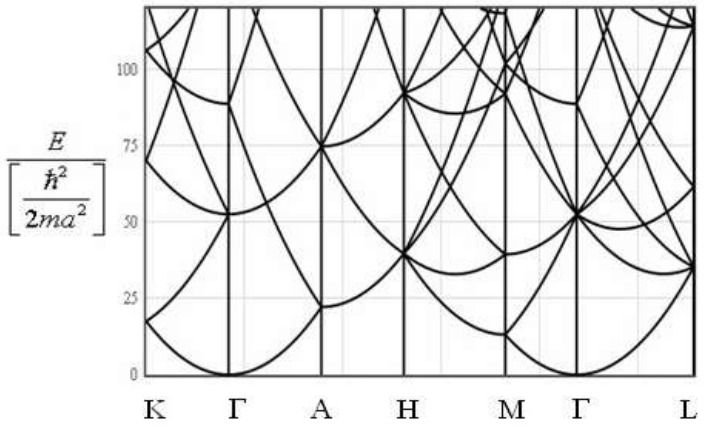


Choose a different order for the symmetry points

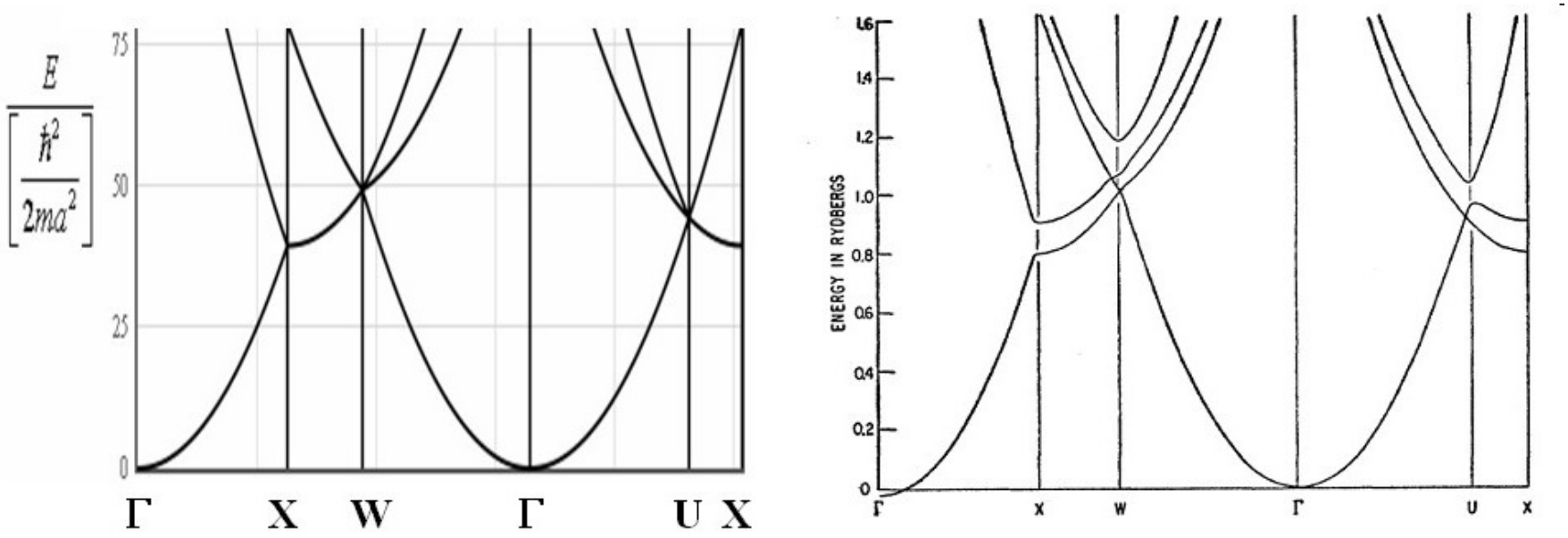
Body centered cubic



Hexagonal

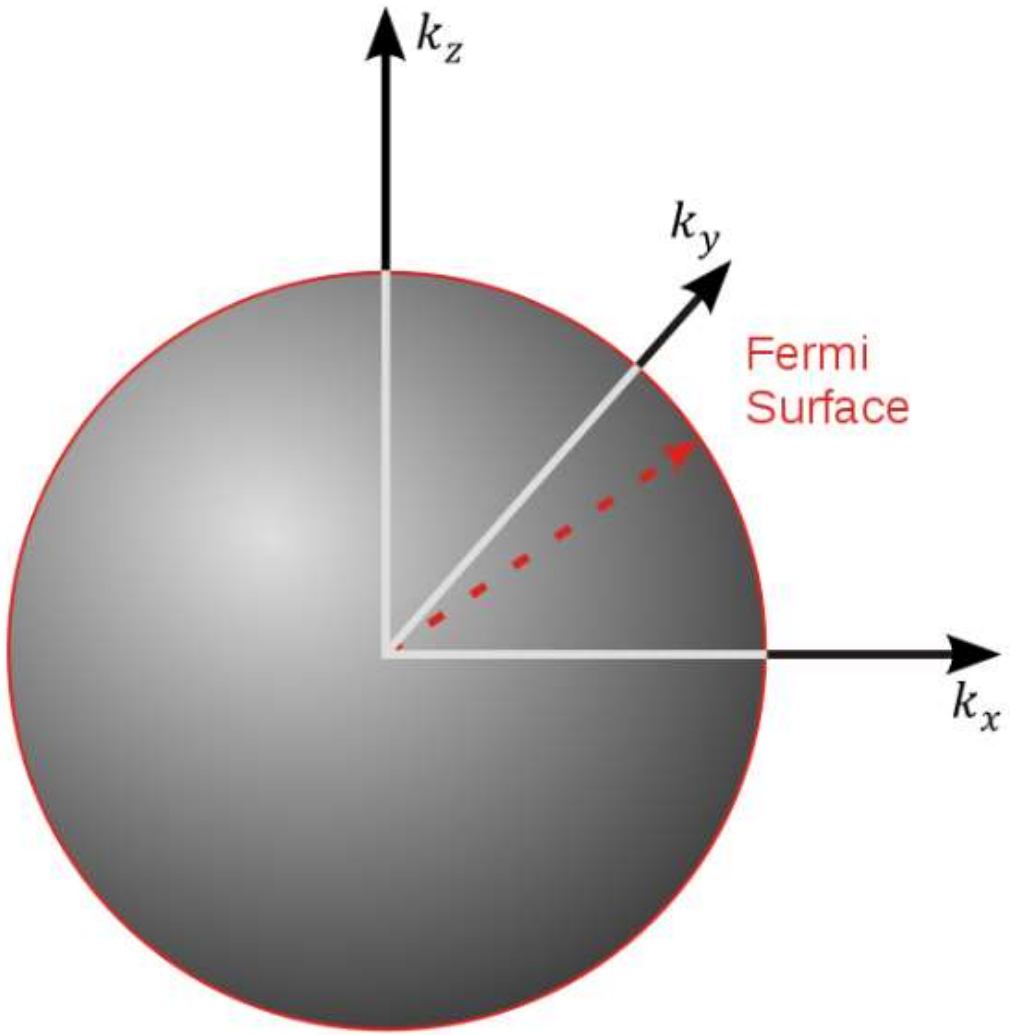


Empty lattice approximation



aluminum

Fermi surface for free electrons



2N states per Brillouin zone

A crystal $L \times L \times L$ has $N = \frac{L^3}{a^3}$ unit cells.

The first Brillouin zone contains $N = \frac{\left(\frac{2\pi}{a}\right)^3}{\left(\frac{2\pi}{L}\right)^3} = \frac{L^3}{a^3}$ k points.

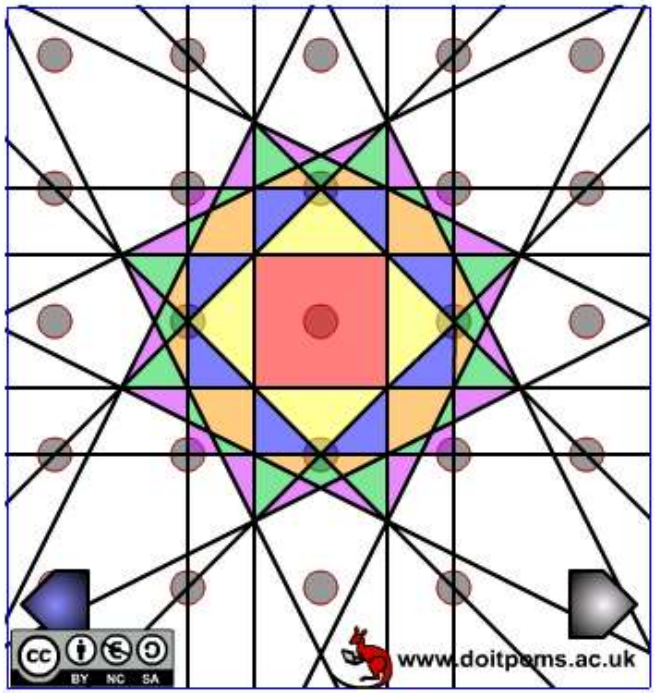
There are N translational symmetries.

Each k state can hold 2 electrons (spin).

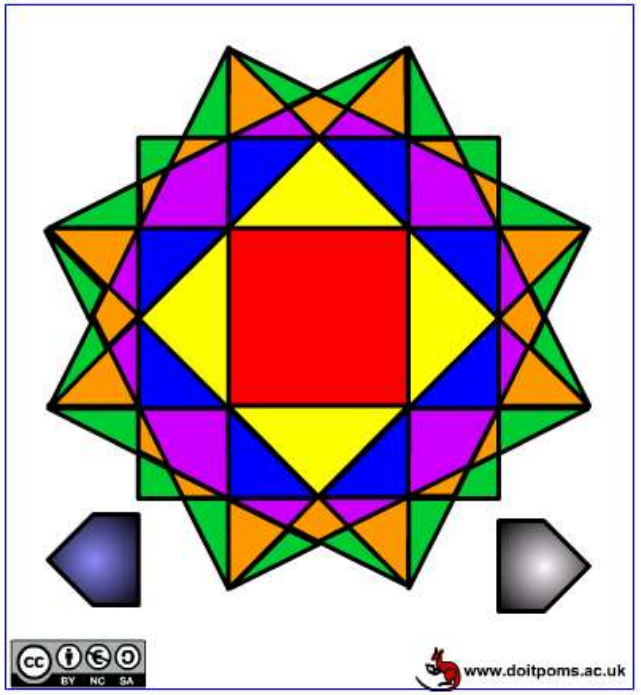
There are $2N$ per Brillouin zone.

Constructing Brillouin zones

2-D square lattice



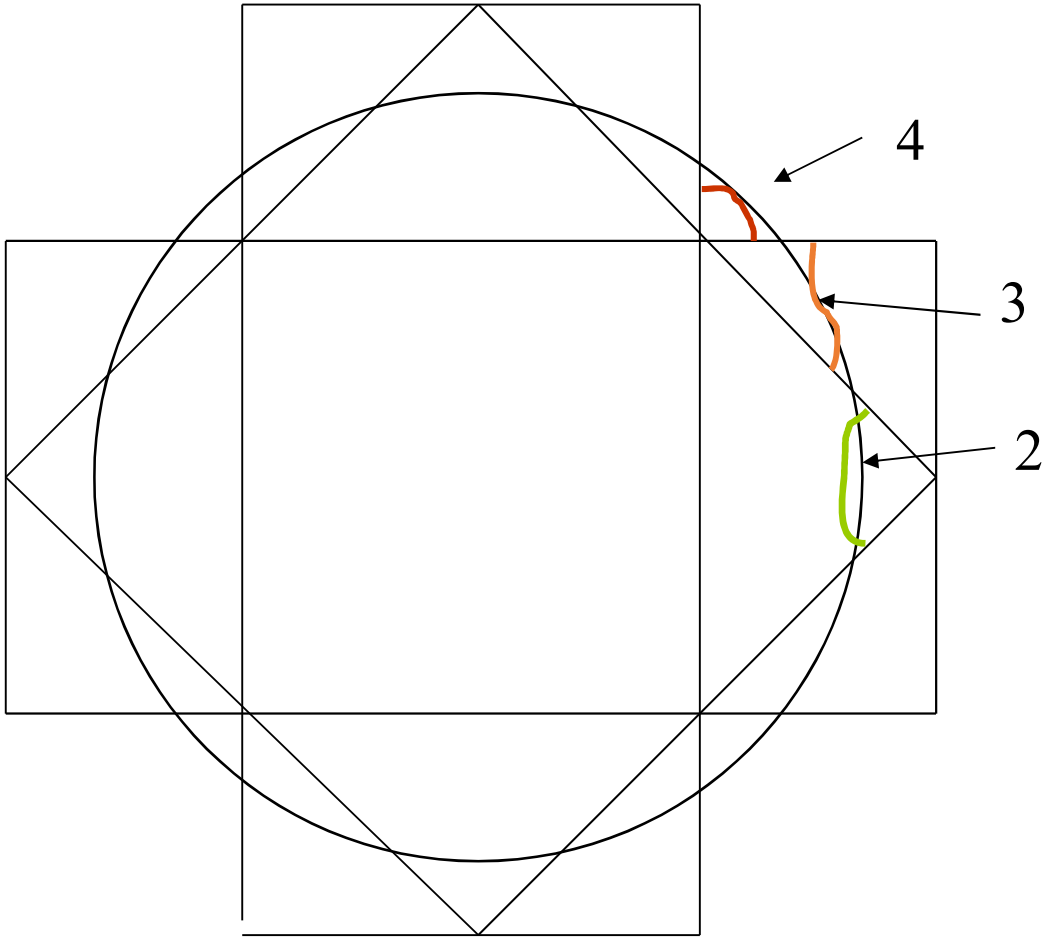
2-D square Zone folding



http://lamp.tu-graz.ac.at/~hadley/ss1/crystaldiffraction/construct.php

http://lamp.tu-graz.ac.at/~hadley/ss1/crystaldiffraction/folding.php

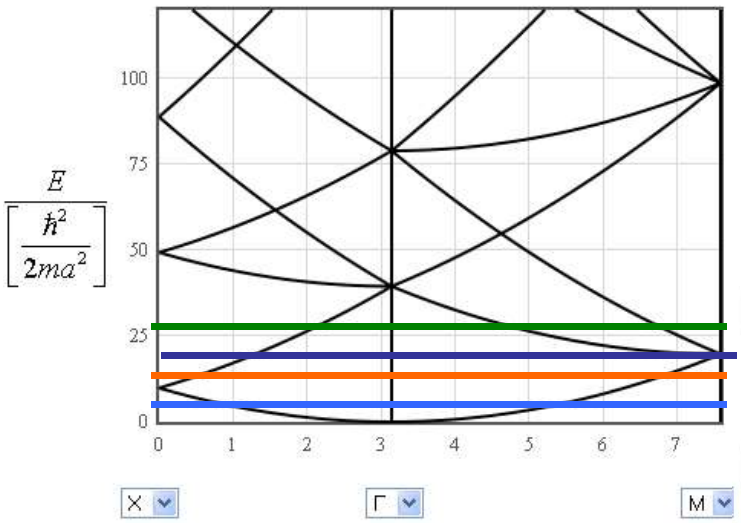
Constructing Fermi surface



No Fermi surface in the 1st Brillouin zone

2d square

$2N$ electron states in a Brillouin zone



The Fermi surface strikes the Brillouin zone boundary at 90°.