Electrons

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:

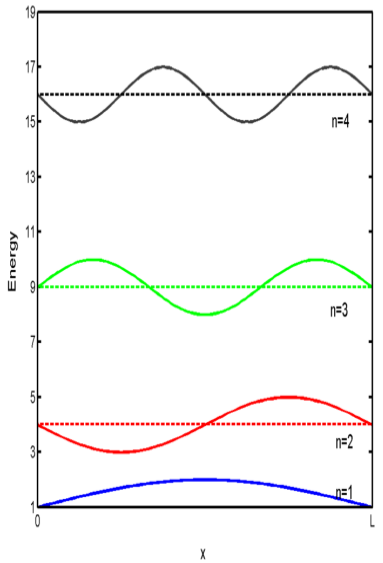
Solve the Schrödinger equation instead of the wave equation.

Electrons are fermions not bosons.

Free particles in 1-d

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

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

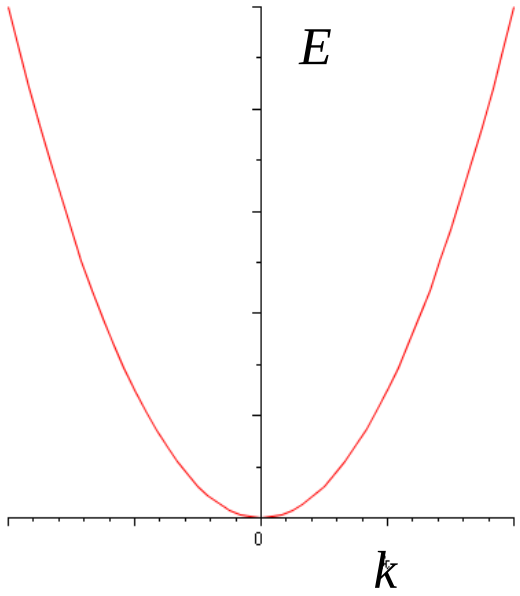


$$\lambda = \frac{2L}{n}$$

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



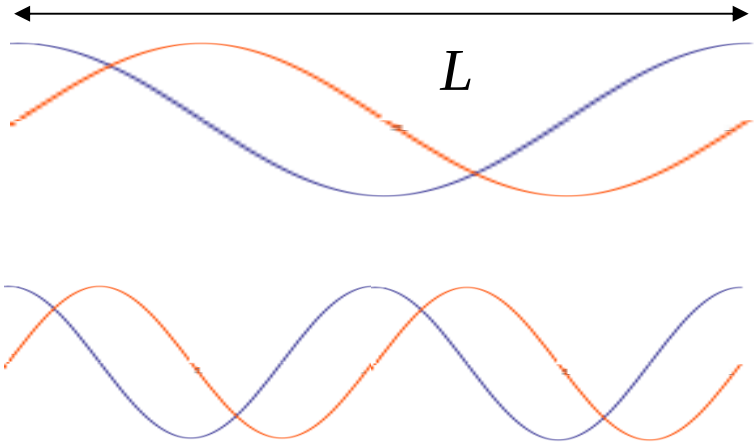
Eigenvalues of T:

$$T\psi_k = A_k e^{i(k(x+a)-\omega t)} = A_k e^{ika} e^{i(kx-\omega t)} = e^{ika}\psi_k$$

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

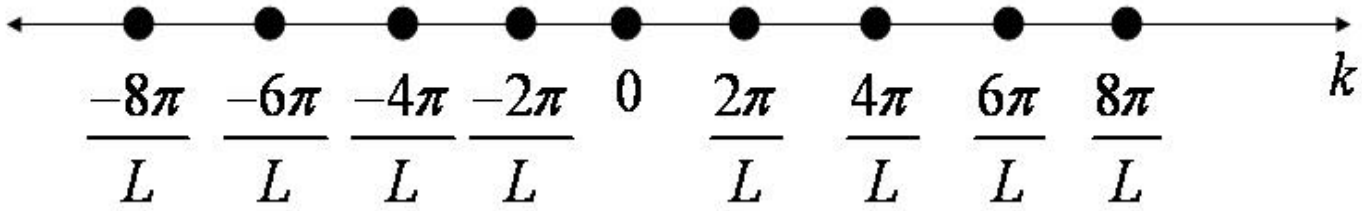
Periodic boundary conditions

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



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

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



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

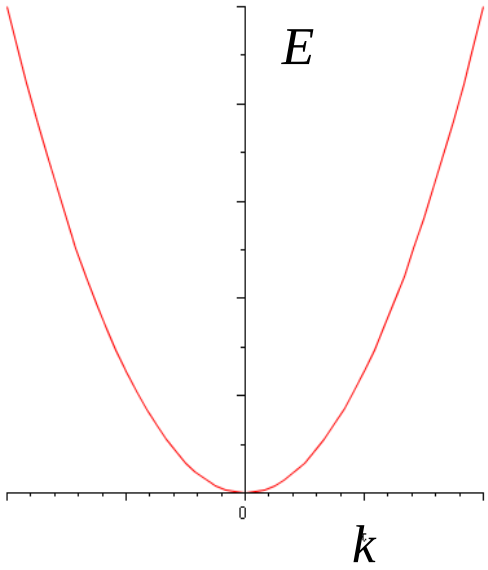
Density of states:

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

← Spin

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

Free particles in 1-d



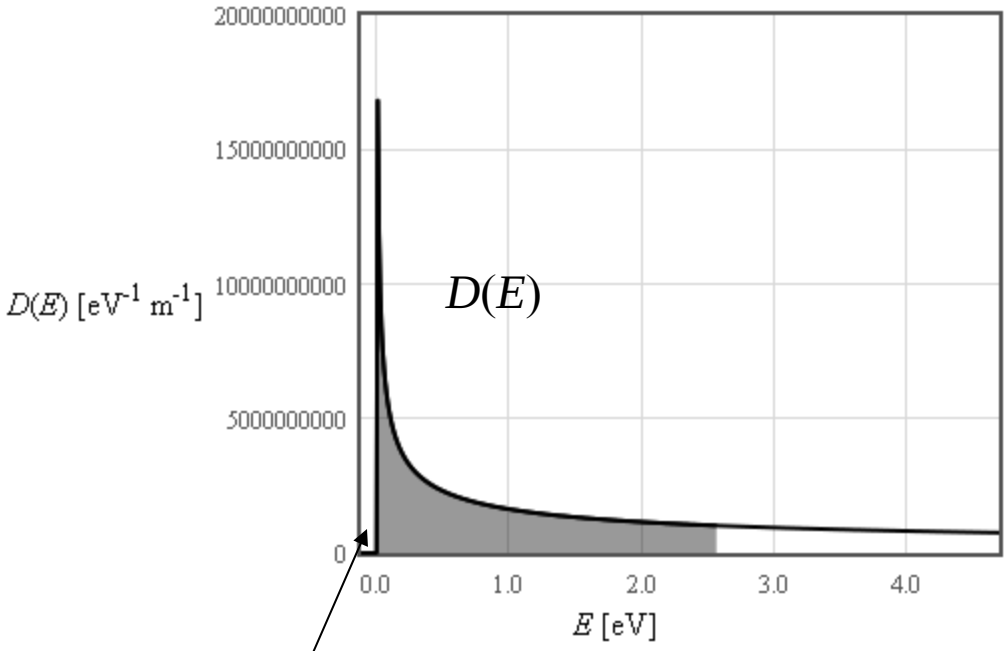
$$D(k) = \frac{2}{\pi} \longleftarrow \text{Spin}$$

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

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

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

Density of states



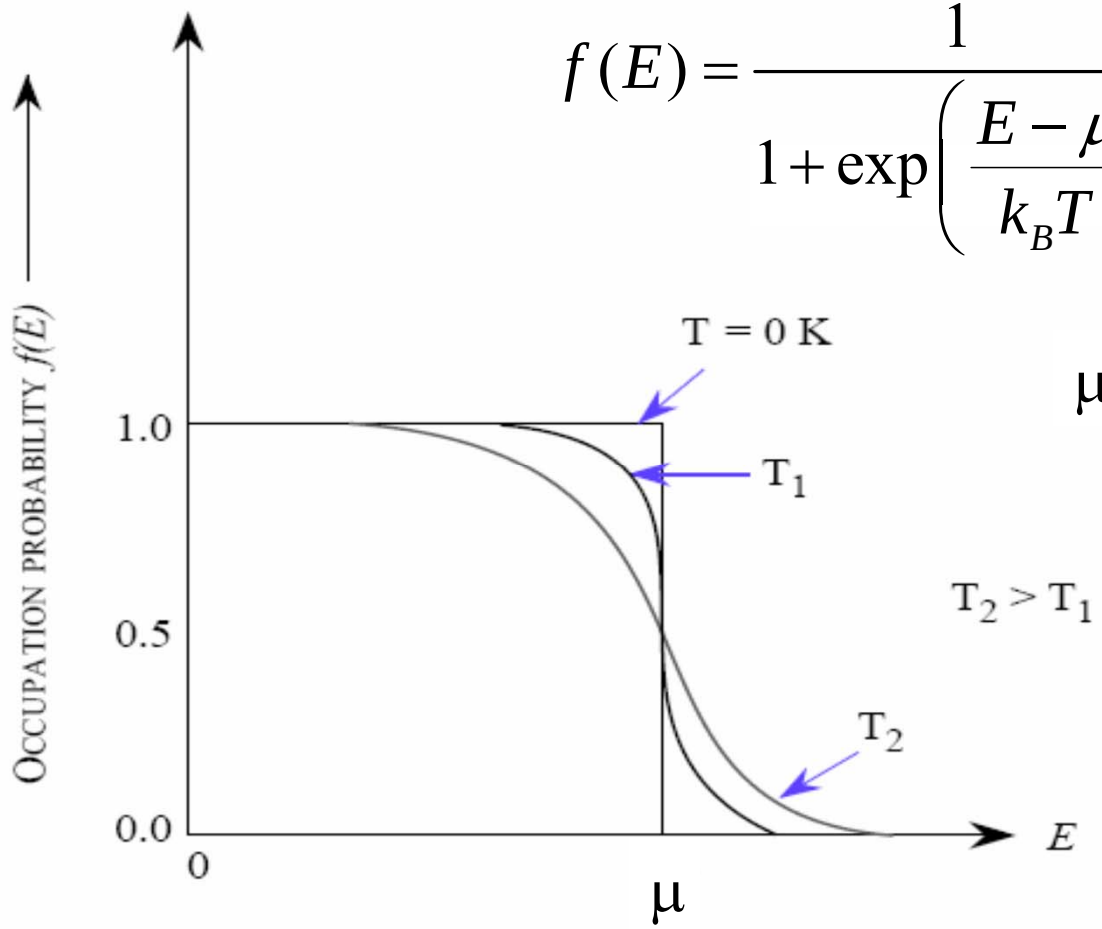
Van Hove singularity

E

Fermi function

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

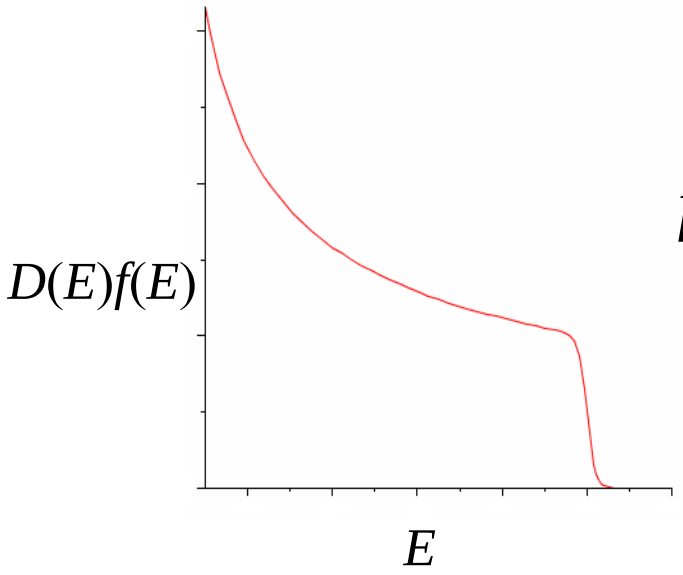
$$f(E) = \frac{1}{1 + \exp\left(\frac{E - \mu}{k_B T}\right)}$$



μ = chemical potential

Chemical potential

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



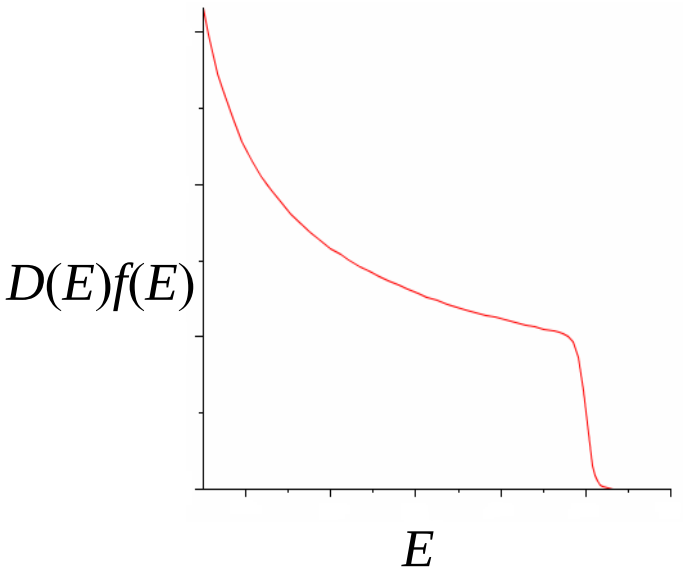
$$f(E) = \frac{1}{1+\exp\left(\dfrac{E-\mu}{k_B T}\right)}$$

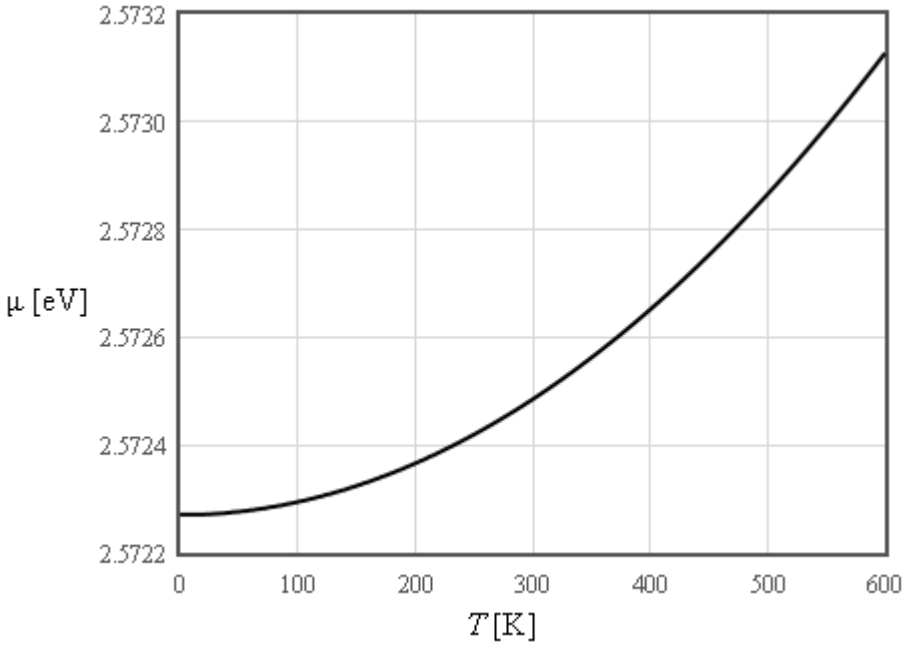
The chemical potential is implicitly defined as the energy that solves the following equation.

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

Here N is the total number of electrons.

Chemical potential





μ is temperature dependent

Fermi energy

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

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

At $T = 0$ $$n = \int_{-\infty}^{E_F} D(E)dE$$

In one dimension,

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

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

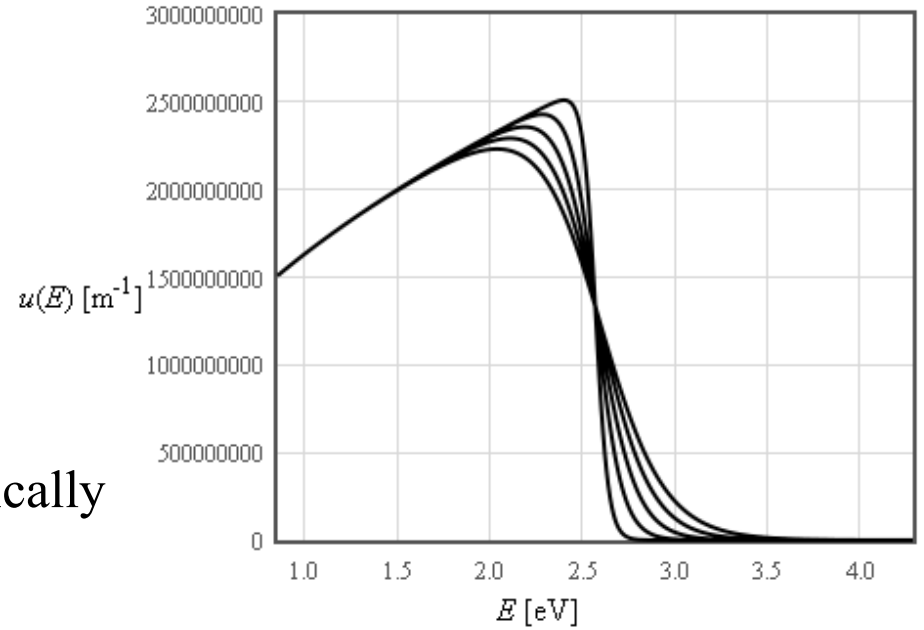
Free particles in 1-d

internal energy spectral density

$$u(E) = ED(E)f(E) = \frac{\sqrt{2mE}}{\pi\hbar}\frac{1}{\exp\left(\frac{E-\mu}{k_B T}\right)+1}$$

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

$$c_v = \frac{du}{dT}$$



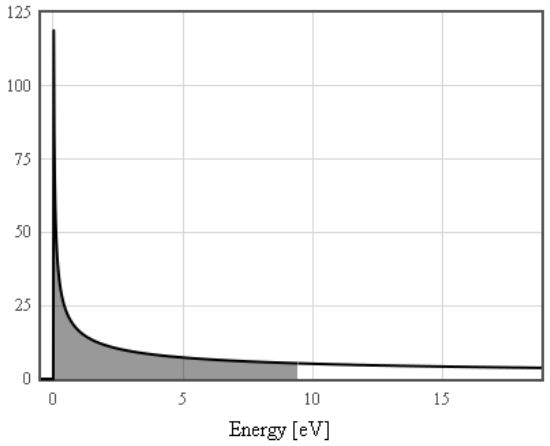
Not possible to do this integral analytically

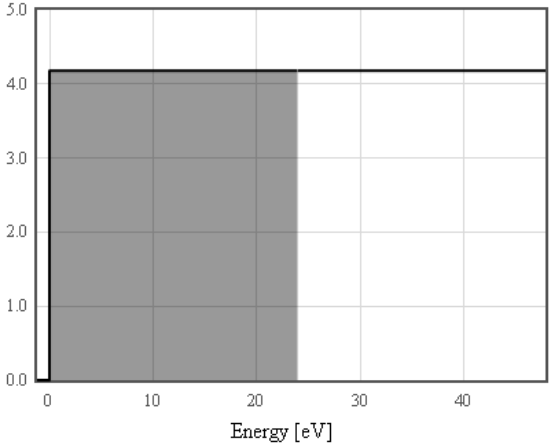
analog to the Planck curve for electrons in 1-d

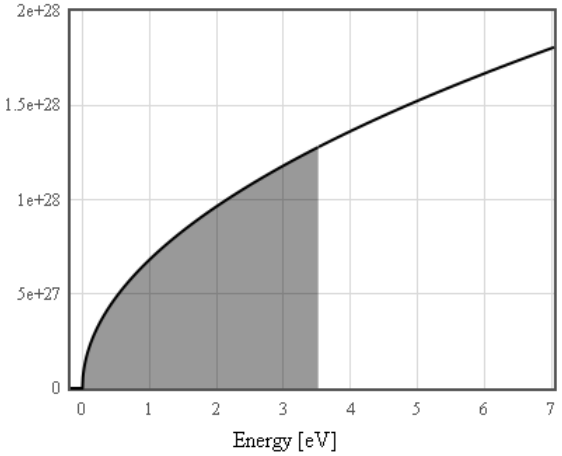
Free electron Fermi gas

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

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







The free electron model is a one parameter model

	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	$D(k)=\frac{2}{\pi}$	$D(k)=\frac{k}{\pi}$ m^{-1}	$D(k)=\frac{k^2}{\pi^2}$ m^{-2}
Density of states $D(E)=D(k)\frac{dk}{dE}$	$D(E)=\frac{1}{\pi\hbar}\sqrt{\frac{2m}{E}}=\frac{n}{2\sqrt{E_F E}}$ $\mathrm{J}^{-1}\mathrm{m}^{-1}$	$D(E)=\frac{m}{\pi\hbar^2}=\frac{n}{E_F}$ $\mathrm{J}^{-1}\mathrm{m}^{-2}$	$D(E)=\frac{(2m)^{\frac{3}{2}}}{2\pi^2\hbar^3}\sqrt{E}=\frac{3n}{2E_F^{3/2}}\sqrt{E}$ $\mathrm{J}^{-1}\mathrm{m}^{-3}$
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 $\approx\frac{\hbar^2}{2m}\left(3\pi^2n\right)^{\frac{2}{3}}-\frac{\pi^{\frac{2}{3}}m}{2\hbar^2 3^{\frac{10}{3}}n^{\frac{2}{3}}}\left(k_BT\right)^2$ J
Internal energy distribution $u(E)=E\frac{D(E)}{\exp\left(\frac{E-\mu}{k_BT}\right)+1}$	$u(E)=\frac{n}{2}\sqrt{\frac{E}{E_F}}\frac{1}{\exp\left(\frac{E-\mu}{k_BT}\right)+1}$ m^{-1} $=\frac{1}{\pi\hbar}\sqrt{2mE}\frac{1}{\left(E-\mu\right.}$ m^{-1}	$u(E)=\frac{n}{E_F}\frac{E}{\exp\left(\frac{E-\mu}{k_BT}\right)+1}$ m^{-2} $=\frac{m}{\pi\hbar^2}\frac{E}{\left(E-\mu\right.}$ m^{-2}	$u(E)=\frac{3n}{2}\left(\frac{E}{E_F}\right)^{3/2}\frac{1}{\exp\left(\frac{E-\mu}{k_BT}\right)+1}$ m^{-3} $=\frac{1}{2\pi^2\hbar^3}\left(2mE\right)^{3/2}$ m^{-3}

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:

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

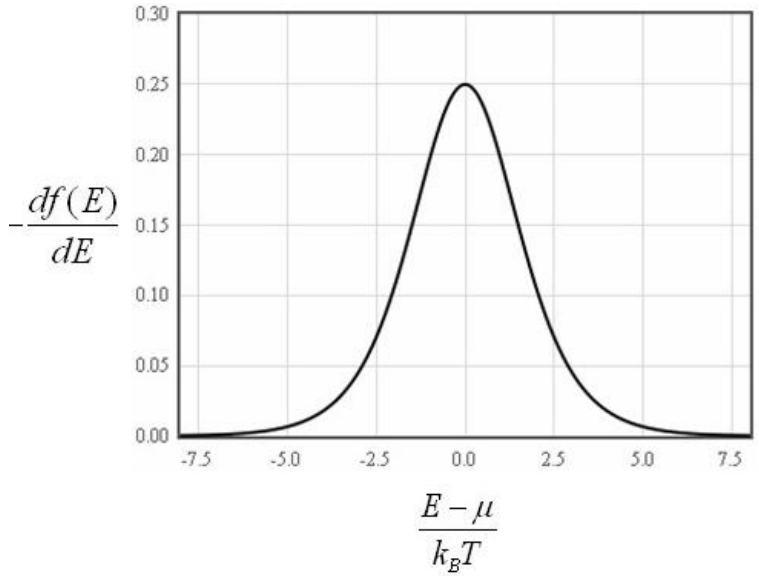
DoS → cv(T)

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

Properties of metals depend mostly on the electron states at the Fermi surface

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

$$n = \int_{-\infty}^{\infty} D(E) f(E) dE = K(\infty) f(\infty) - K(-\infty) f(-\infty) - \int_{-\infty}^{\infty} K(E) \frac{f(E)}{dE} dE.$$



http://lampx.tugraz.at/~hadley/ss1/materials/thermo/dos2mu.html