Electronic structure of Solids I

université de BORDEAUX

Free electron gas model (Fermi gas)

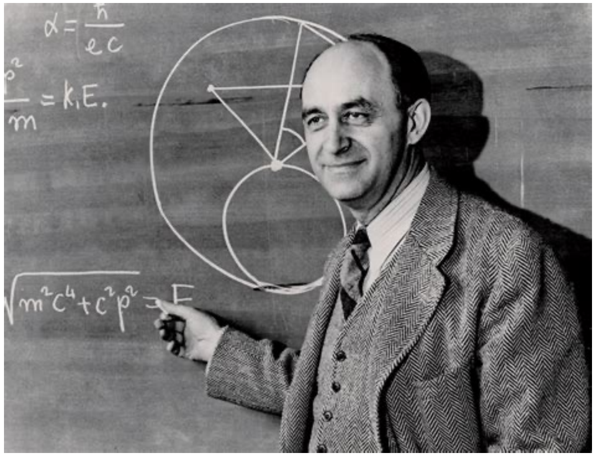
A free electron model is the simplest way to represent the electronic structure of solids such as metals.

Although the free electron model is a great oversimplification of the reality, is able to describe many important properties of conductors.

Fermi Gas :

- Valence electrons are considered to travel freely throughout the crystal, neglecting the interaction of electrons with ions of the lattice and the interaction between electrons

- Pauli principle is taken into account.



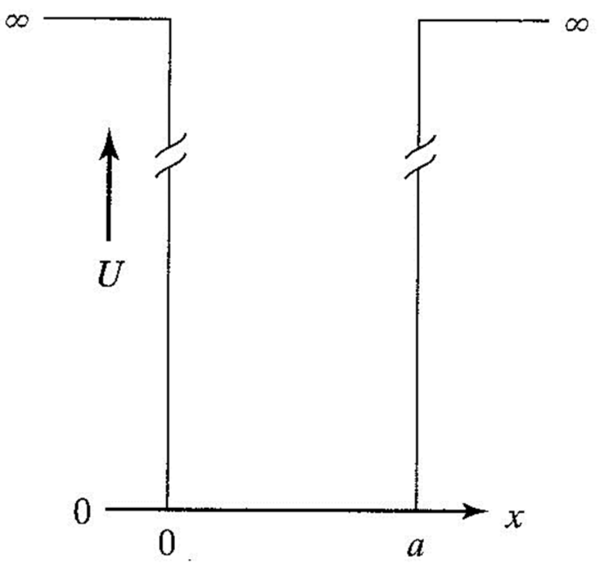
Enrico Fermi (1901 – 1954)

Free electron gas model

1D-conductor = "particle in a 1D-box"

We assume that an electron of mass m is confined to a length L by infinite potential barriers.

$$H\psi_n(x) = \frac{p^2}{2m}\psi_n(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_n(x) = E_n\psi_n(x)\,.$$



Free electron gas model

1D-conductor = "particle in a 1D-box"

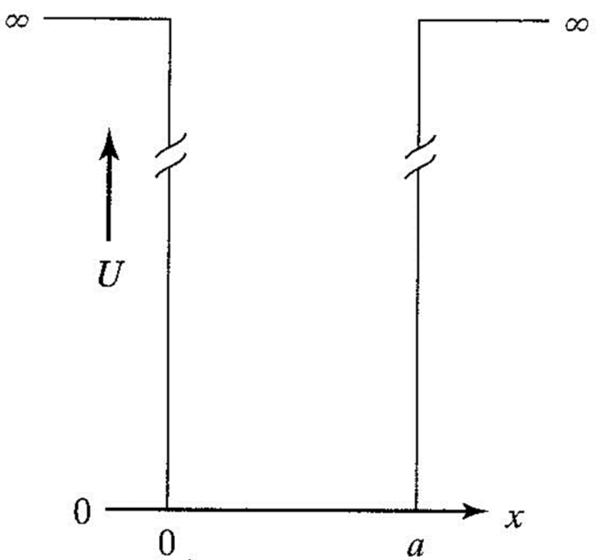
We assume that an electron of mass m is confined to a length L by infinite potential barriers.

$$H\psi_n(x) = \frac{p^2}{2m}\psi_n(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_n(x) = E_n\psi_n(x) \,.$$

SOLUTIONS :

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

$$E_n = \frac{\hbar^2}{2m}\left(\frac{\pi n}{L}\right)^2$$

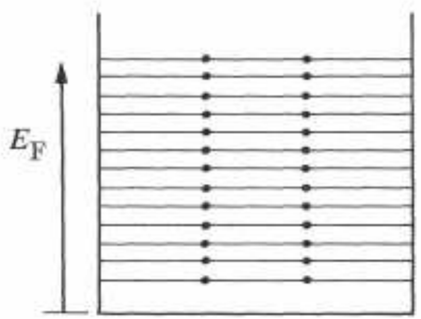


Free electron gas model

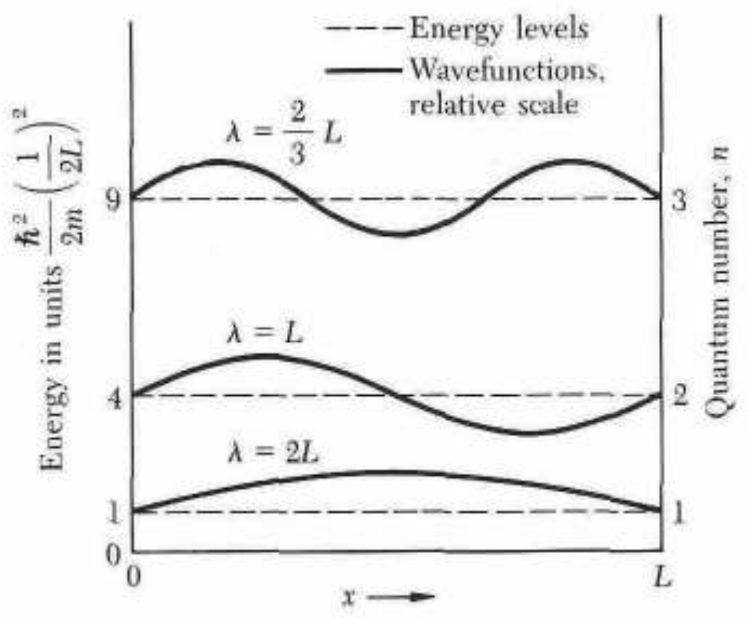
<u>Fermi energy</u> <u>(for a system of N electrons)</u>

One need to accomodate N electrons in the various quantum states of the particle in a box.

The highest occupied state = Fermi level



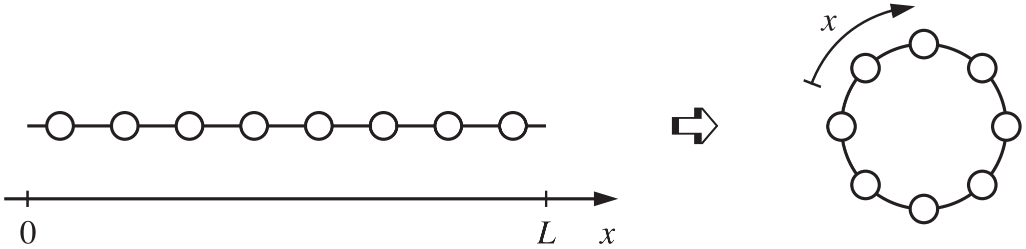
$$E_F = \frac{\hbar^2}{2m}\left(\frac{\pi N}{2L}\right)^2$$



Free electron gas model

3D-conductor = particle in periodic box

Periodic boundary conditions = we assume that the crystal is infinite in x, y and z



The solution of the Schrödinger equation which satisfies these boundary conditions, called Born - von Karman periodic conditions, has the form of a traveling plane wave:

$$\psi_{\mathbf{k}}(\mathbf{r}) = A\exp(i\mathbf{k}\cdot\mathbf{r})$$

With a quantized wave vector **k**:

$$k_x = \frac{2\pi n_x}{L}; \quad k_y = \frac{2\pi n_y}{L}; \quad k_z = \frac{2\pi n_z}{L}$$

$$E_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right)$$

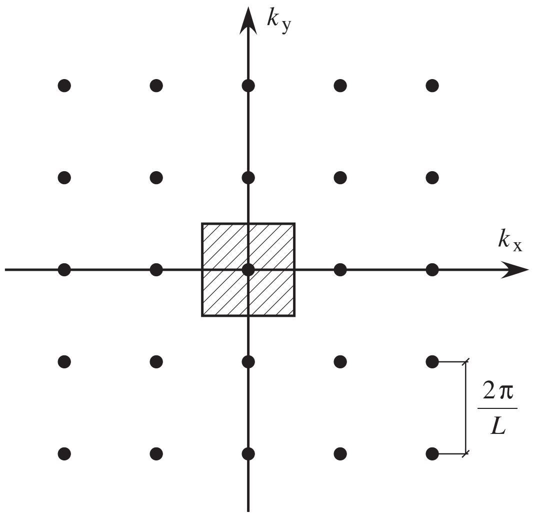
Quantization of electronic energy

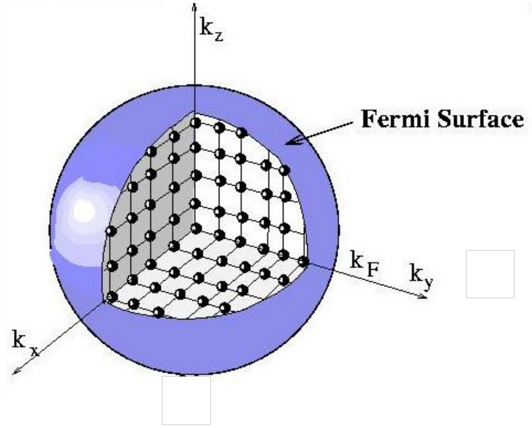
Free electron gas model

3D-conductor = particle in periodic box

Fermi wave-vector

In the ground state, a system of N electrons occupies states with lowest possible energies.





Therefore all the occupied states lies inside the sphere of radius k_F (Fermi sphere)

$$E_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right)$$

Free electron gas model

3D-conductor = particle in periodic box

Fermi energy

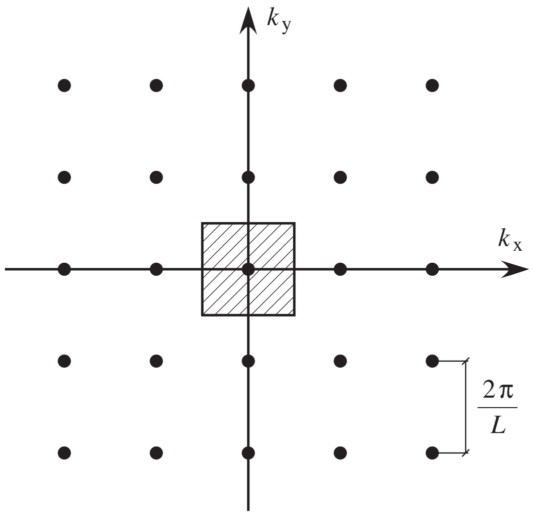
$$E_F = \frac{\hbar^2 k_F^2}{2m}$$

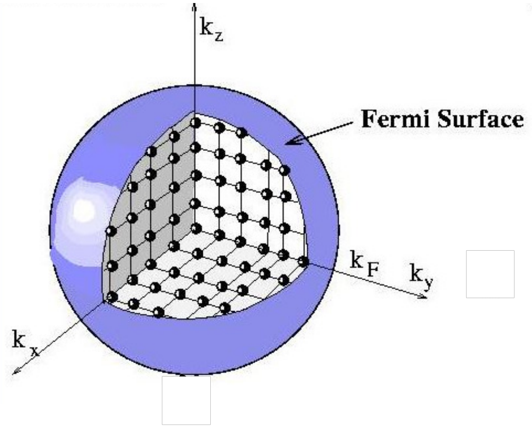
$$E_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

Fermi temperature

$$T_F = E_F / k_B$$

Fermi wave-vector





Free electron gas model

3D-conductor = particle in periodic box

Fermi energy

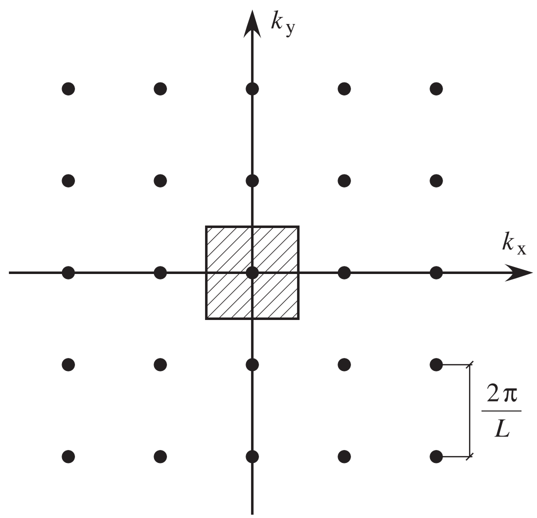
$$E_F = \frac{\hbar^2 k_F^2}{2m}$$

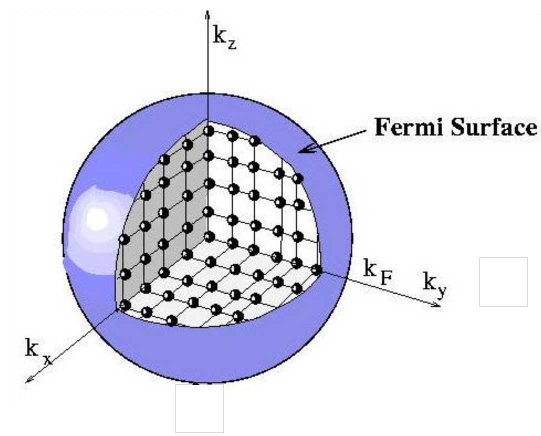
$$E_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

Fermi temperature

$$T_F = E_F / k_B$$

Fermi wave-vector





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

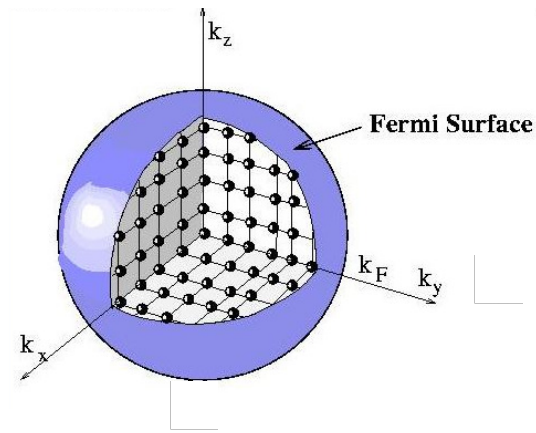
N is the total number of valence electrons in the crystal

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

Free electron gas model

Fermi temperature

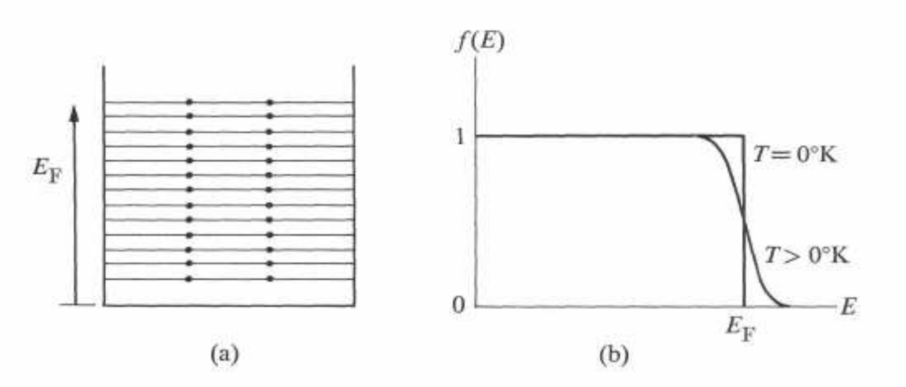
Element	r_s/a_0	E_F	T_F	k_F	v_f
Li	3.25	4.74eV	5.51×10^4K	1.12×10^8cm^{-1}	1.29×10^8cm/sec
Na	3.93	3.24	3.77	0.92	1.07
K	4.86	2.12	2.46	0.75	0.86
Rb	5.20	1.85	2.15	0.70	0.81
Cs	5.62	1.59	1.84	0.65	0.75
Cu	2.67	7.00	8.16	1.36	1.57
Ag	3.02	5.49	6.36	1.20	1.39
Au	3.01	5.53	6.42	1.21	1.40
Be	1.87	14.3	16.6	1.94	2.25
Mg	2.66	7.08	8.23	1.36	1.58
Ca	3.27	4.69	5.44	1.11	1.28
Sr	3.57	3.93	4.57	1.02	1.18
Ba	3.71	3.64	4.23	0.98	1.13
Nb	3.07	5.32	6.18	1.18	1.37
Fe	2.12	11.1	13.0	1.71	1.98
Mn	2.14	10.9	12.7	1.70	1.96
Zn	2.30	9.47	11.0	1.58	1.83
Cd	2.59	7.47	8.68	1.40	1.62
Hg	2.65	7.13	8.29	1.37	1.58
Al	2.07	11.7	13.6	1.75	2.03



Application: Na (bcc) with a = 0.42 nm and one valence electron per atom - det. k_F, E_F, T_F, v_F ?

Free electron gas model

Fermi-Dirac distribution : how to fill the quantum states with electrons ?



$$f(E) = \begin{cases} 1, & E < E_F \\ 0, & E > E_F \end{cases}$$ T = 0 K

$$f(E) = \frac{1}{e^{(E-\mu)/k_B T} + 1}$$ T ≠ 0 K

f(E) = probability that the level E is occupied by electrons

f(E) = 1 -> level completely filled (2 electrons)
f(E) = 0 -> level empty

Free electron gas model

Density of states (DOS)

An important quantity which characterizes electronic properties of a solid is the density of states (DOS), which is the number of electronic states per unit energy range.

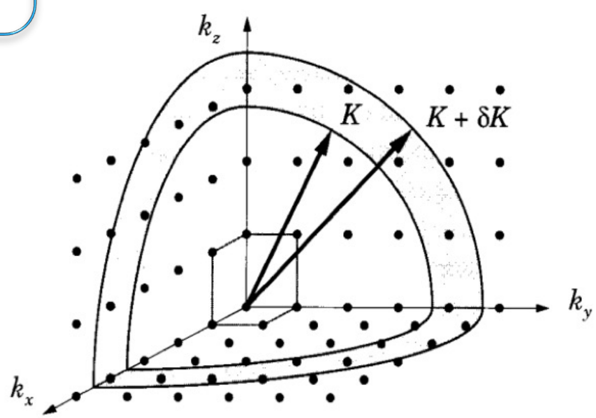
Let $\phi(E)$ be the total number of electronic states of energy < E within a 3D-conductor:

$$\phi(E) = \frac{V}{3\pi^2}\left(\frac{2mE}{\hbar^2}\right)^{3/2}$$

Then density of states $g(E)$ is defined as:

$$g(E) = \frac{d\phi}{dE}$$

$$g(E) = \frac{d\phi}{dE} = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$$

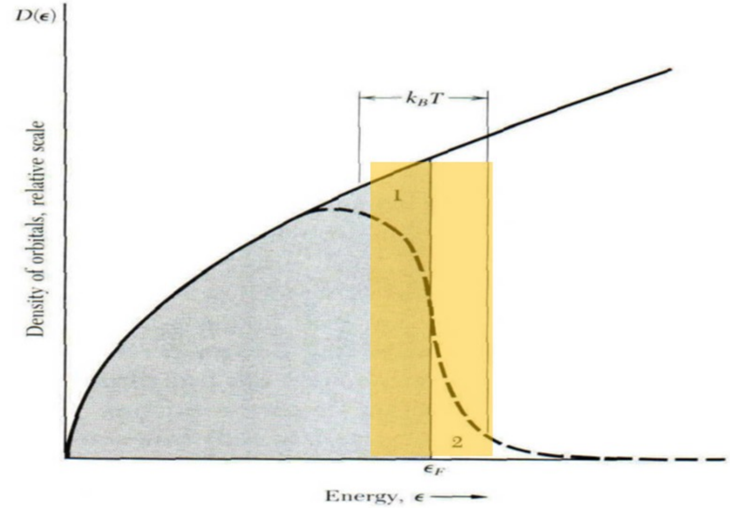


Free electron gas model

Density of states (DOS)

Density of states in a 3D-conductor:

$$g(E) = \frac{d\phi}{dE} = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$$



Normalization:

$$N = \int_0^{E_F} g(E)dE \qquad T = 0\ K$$

$$N = \int_0^{+\infty} g(E)f(E,T)dE \qquad T \neq 0\ K$$

Where *f(E, T)* is the Fermi distribution function.

Heat capacity of solids – electronic contribution

At low temperature $k_B T << E_F$

$$U = \int_0^{+\infty} E g(E) f(E,T) dE$$

Since only the distribution function depends on Temperature:

$$C_{el} = \frac{dU}{dT} = \int_0^{+\infty} E g(E) \frac{df(E,T)}{dT} dE$$

Using: $$0 = E_F \frac{dN}{dT} = E_F \int_0^{+\infty} g(E) \frac{df(E,T)}{dT} dE$$

we obtain:

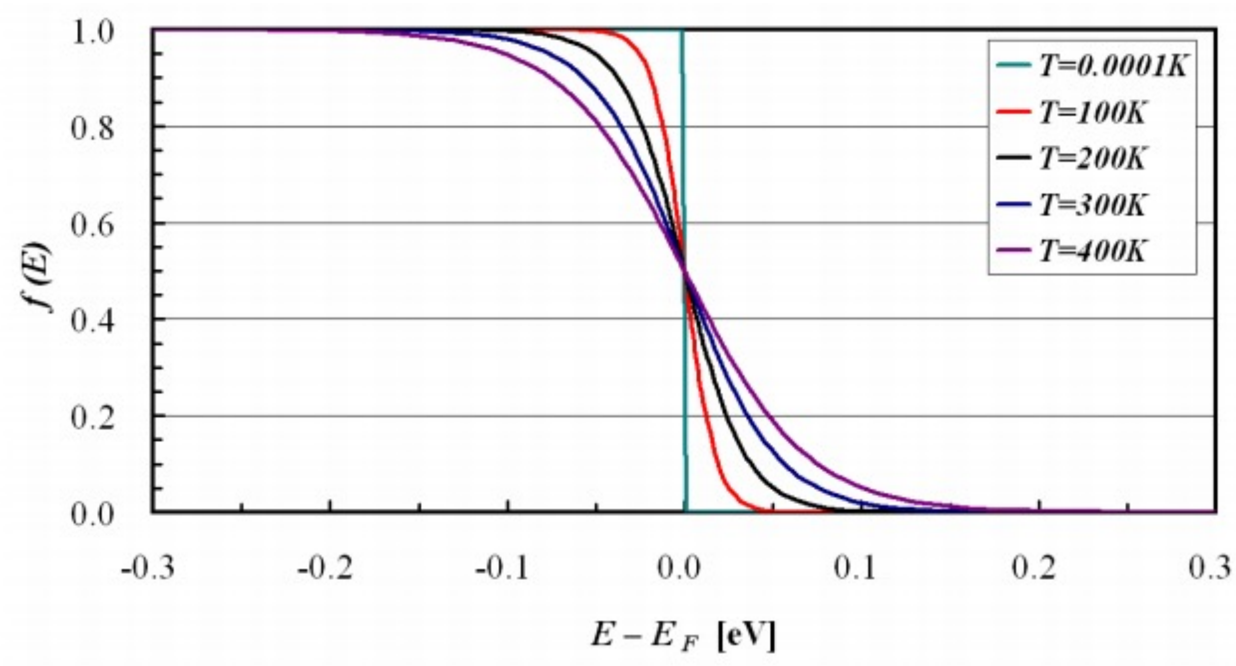
$$C_{el} = \int_0^{+\infty} (E - E_F) g(E) \frac{df(E,T)}{dT} dE$$

Free electron gas model

Heat capacity of solids – electronic contribution

At low temperature $k_B T << E_F$

df/dT is large only at energies which lie close to the Fermi energy:

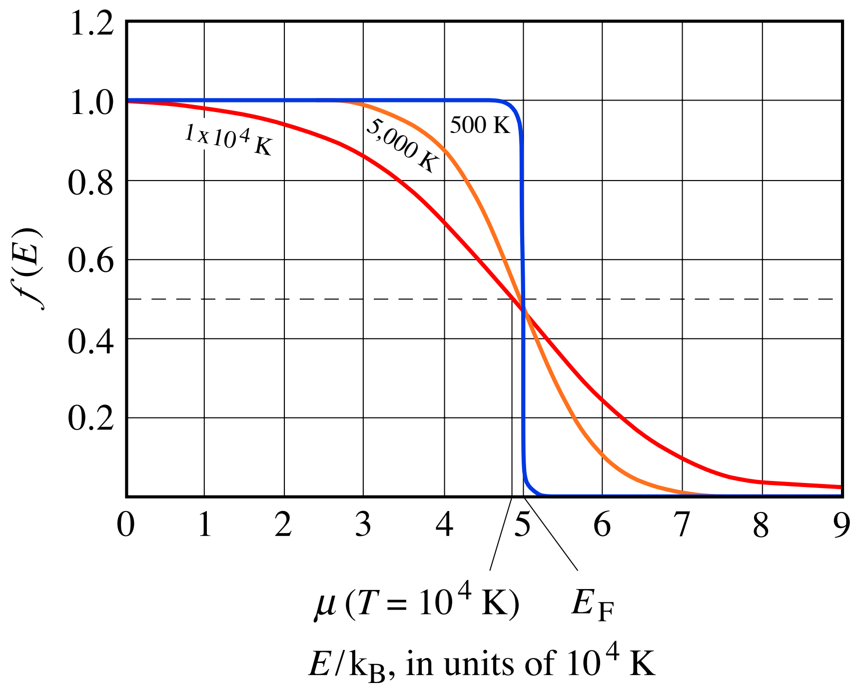


So that: $$C_{el} = g(E_F)\int_0^{+\infty}(E - E_F)\,\frac{df(E,T)}{dT}dE$$

Free electron gas model

Heat capacity of solids – electronic contribution

We also ignore the variation of the chemical potential with temperature and assume that $\mu = E_F$ which is a good approximation at room temperature and below.



$$f(E) = \frac{1}{e^{(E-\mu)/k_BT} + 1}$$

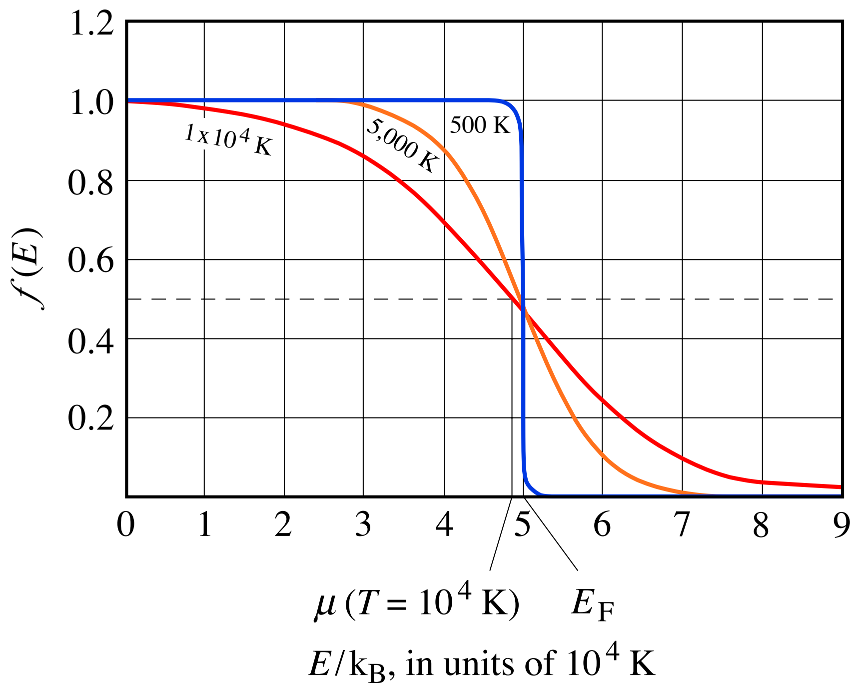
Important to note that $f(E) = 1/2$ when $E = \mu$

Additionally, it can be shown that: $\mu = E_F \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{E_F} \right)^2 \right]$

Free electron gas model

Heat capacity of solids – electronic contribution

We also ignore the variation of the chemical potential with temperature and assume that $\mu = E_F$ which is a good approximation at room temperature and below.



$$f(E) = \frac{1}{e^{(E-\mu)/k_B T} + 1}$$

Important to note that $f(E) = 1/2$ when $E = \mu$

And at room temperature μ deviates from E_F by less than 0.01 %

Free electron gas model

Heat capacity of solids – electronic contribution

Then:

$$C_{el} = g(E_F)\int_0^{+\infty} \frac{(E-E_F)^2}{k_B T^2} \frac{e^{(E-E_F)/k_BT}}{\left[e^{(E-E_F)/k_BT}+1\right]^2} dE = g(E_F)\int_{-E_F/k_BT}^{+\infty} \frac{x^2 (k_BT)^3}{k_BT^2} \frac{e^x}{[e^x+1]^2} dx$$

Using: $E_F >> k_BT$

we obtain: $$C_{el} = g(E_F)\, k_B^2 T \underbrace{\int_{-\infty}^{+\infty} \frac{x^2 e^x}{[e^x+1]^2} dx}_{\pi^2/3} = \frac{\pi^2}{3} g(E_F) k_B^2 T$$

Finally: $$C_{el} = \frac{\pi^2}{2} N k_B \frac{T}{T_F}$$

Fermi temperature: $T_F = E_F / k_B$

Experimentally the heat capacity at low temperatures below can be represented as a sum of electronic and phononic contributions:

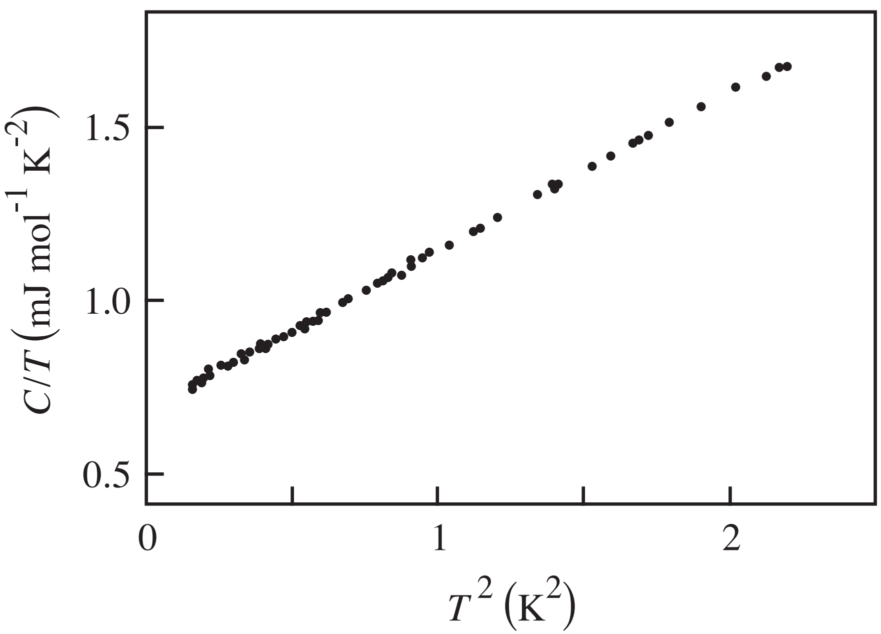
$$C = C_{el} + C_{ph} = \alpha T + \beta T^3$$

Free electron gas model

Heat capacity of solids – electronic contribution

Experimentally the heat capacity at low temperatures below can be represented as a sum of electronic and phononic contributions:

$$C = C_{el} + C_{ph} = \alpha T + \beta T^3$$



Heat capacity of Gold (Au)