Thermal conductivity

$$\vec{j}_U = \bar{E}\vec{j}$$

Average particle energy

$$u = \bar{E}n$$

internal energy density

$$\vec{j}_U = -\bar{E}D\nabla n = -D\nabla u$$

$$\vec{j}_U = -D\frac{du}{dT}\nabla T = -Dc_v\nabla T$$

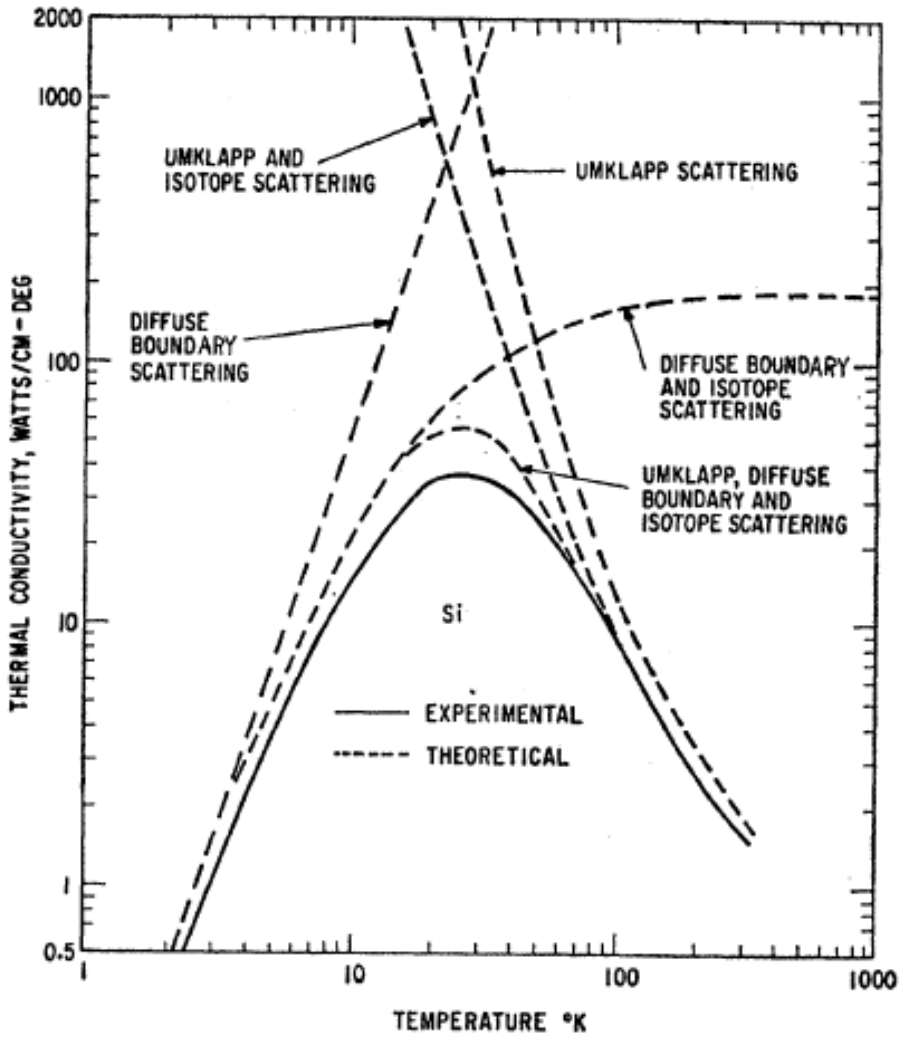
$$\vec{j}_U = -K\nabla T$$

Thermal conductivity

$$K = Dc_v$$

$$K \to 0 \quad \text{as} \quad T \to 0$$

Thermal conductivity $\vec{j}_U = -K\nabla T$



Imperfections in the crystal or grain boundaries decrease the mean free path and the thermal conductivity.

At high temperatures, the mean free path is limited by Umklapp processes. At low temperatures the Umklapp processes freeze out and the mean free path is limited by imperfections.

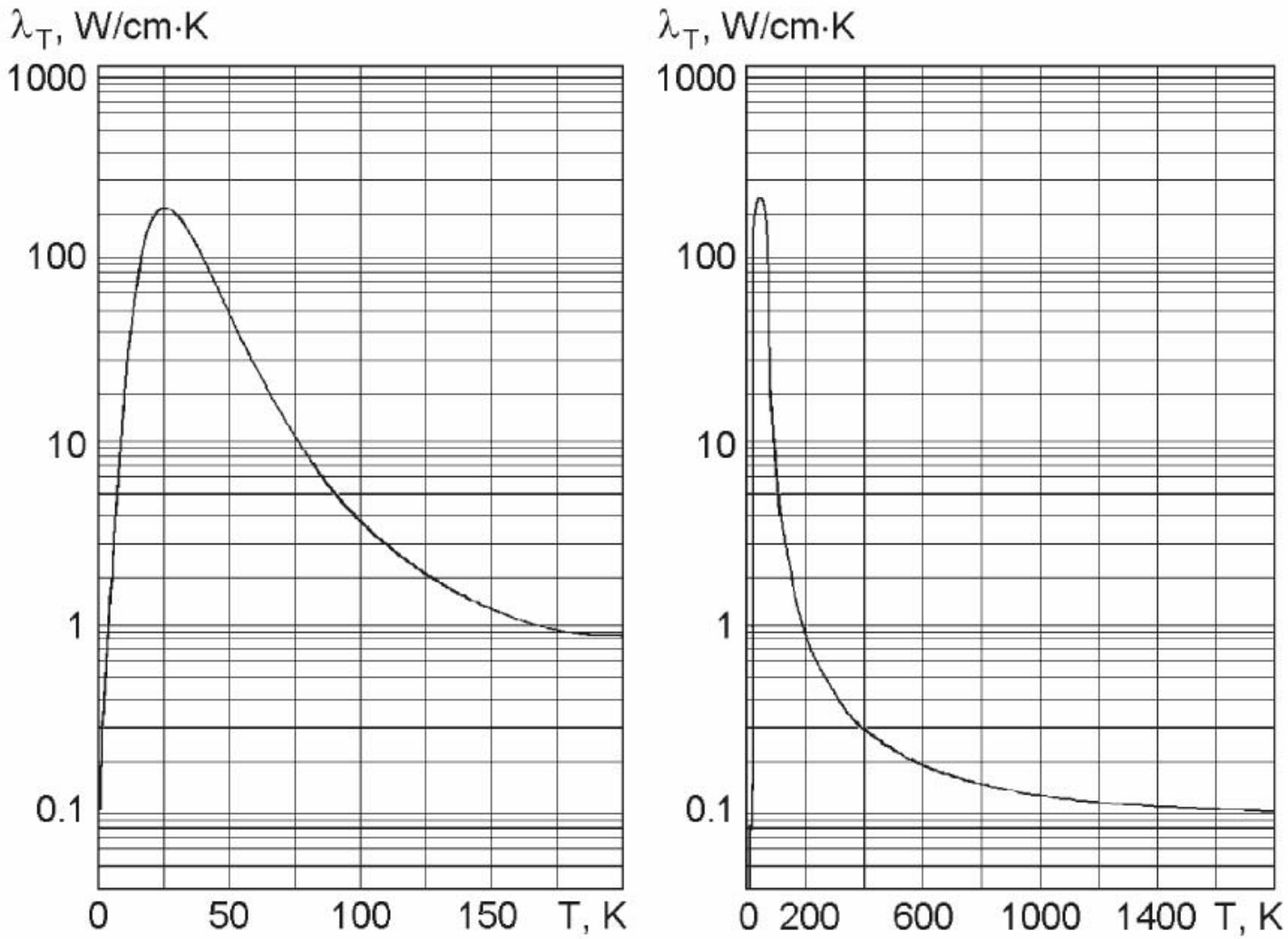
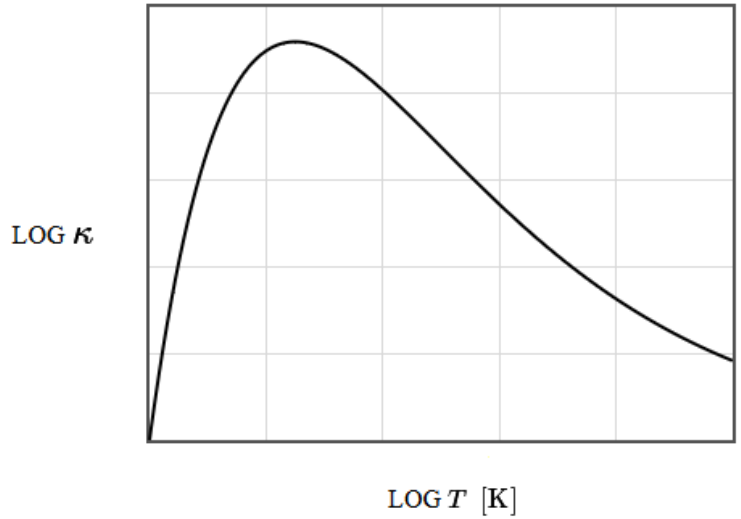


Fig. 2.69 Temperature dependence of the thermal conductivity coefficient for sapphire: (**a**) low temperatures; (**b**) high temperatures

Thermal conductivity

$$\vec{j}_U = -K\nabla T$$

Material	Thermal conductivity W/(m·K)
Glass	1.1
Concrete, stone	1.7
Ice	2
Sandstone	2.4
Sapphire	35
Stainless steel	12.11 ~ 45.0
Lead	35.3
Aluminum	237
Aluminum alloys	120—180
Gold	318
Copper	401
Silver	429
Diamond	900 - 2320
Graphene	(4840±440) - (5300±480)



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:

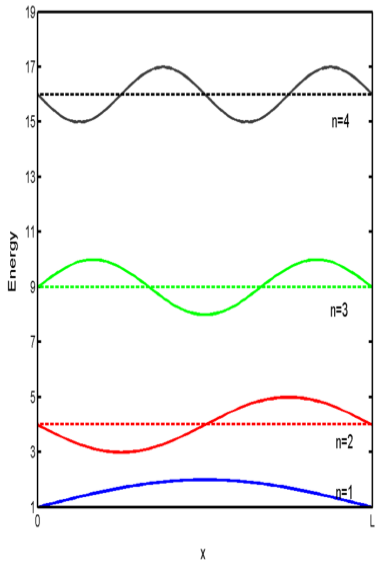
Solve the Schrödinger equation instead of the wave equation.

Electrons are fermions not bosons.

Free particles in 1-d

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

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

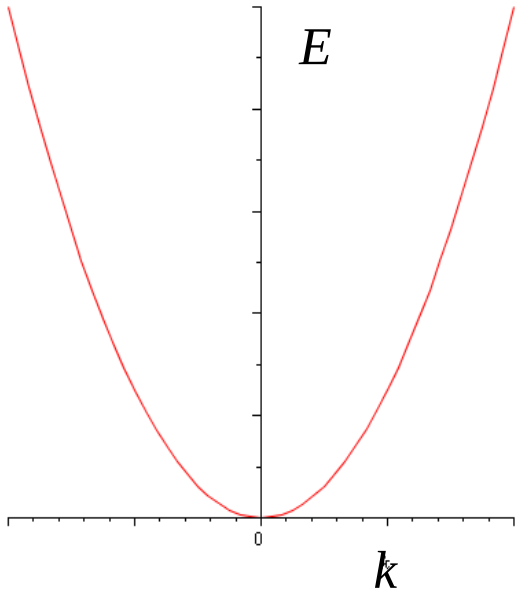


$$\lambda = \frac{2L}{n}$$

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



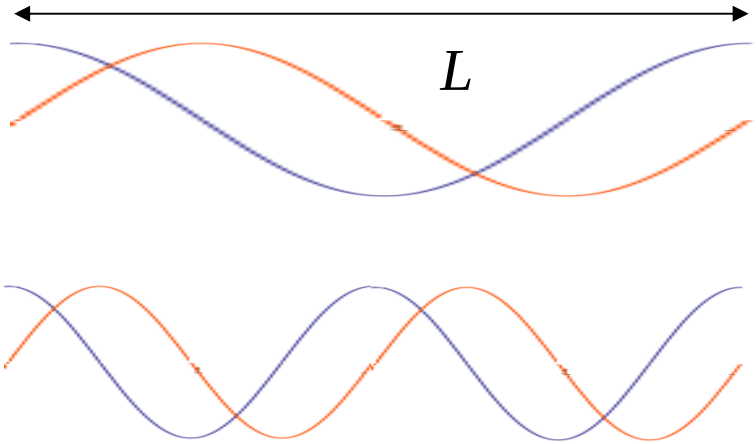
Eigenvalues of T:

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

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

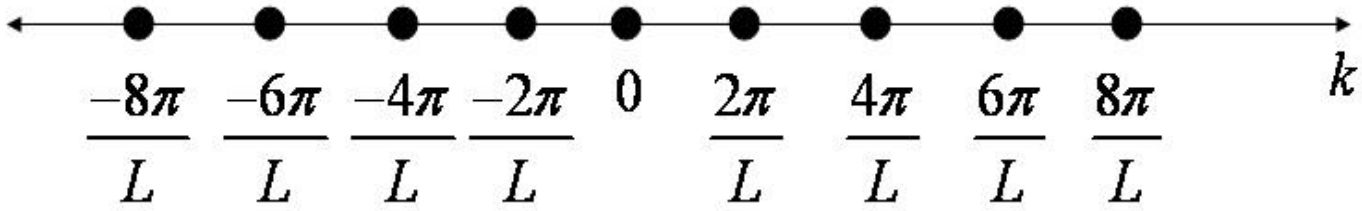
Periodic boundary conditions

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



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

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



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

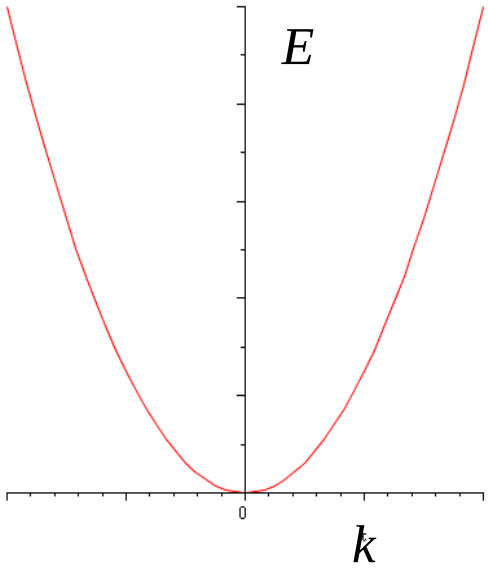
Density of states:

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

← Spin

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

Free particles in 1-d



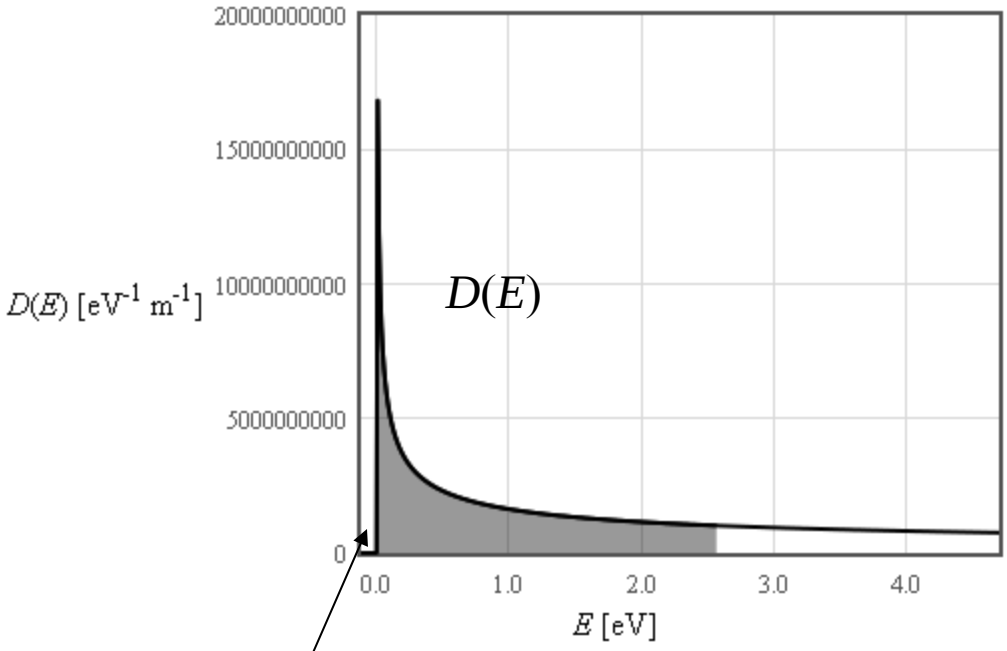
$$D(k) = \frac{2}{\pi} \longleftarrow \text{Spin}$$

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

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

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

Density of states



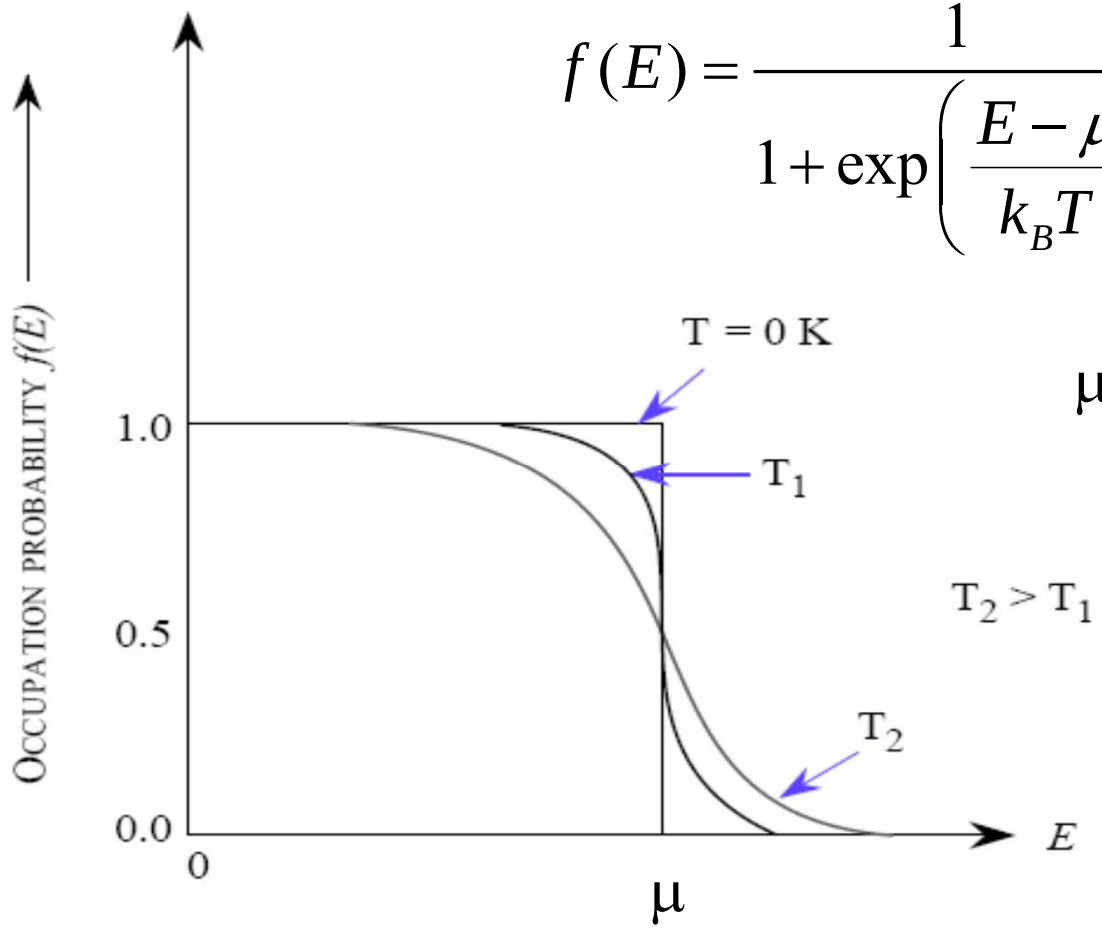
Van Hove singularity

E

Fermi function

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

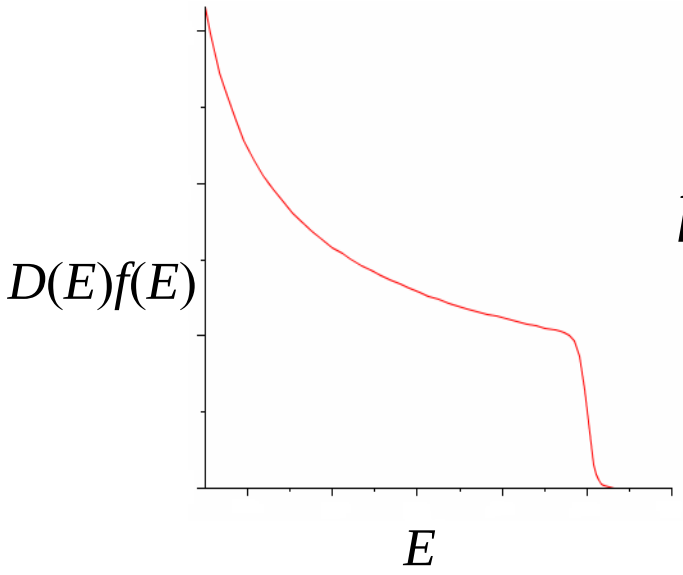
$$f(E) = \frac{1}{1 + \exp\left(\frac{E - \mu}{k_B T}\right)}$$



μ = chemical potential

Chemical potential

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



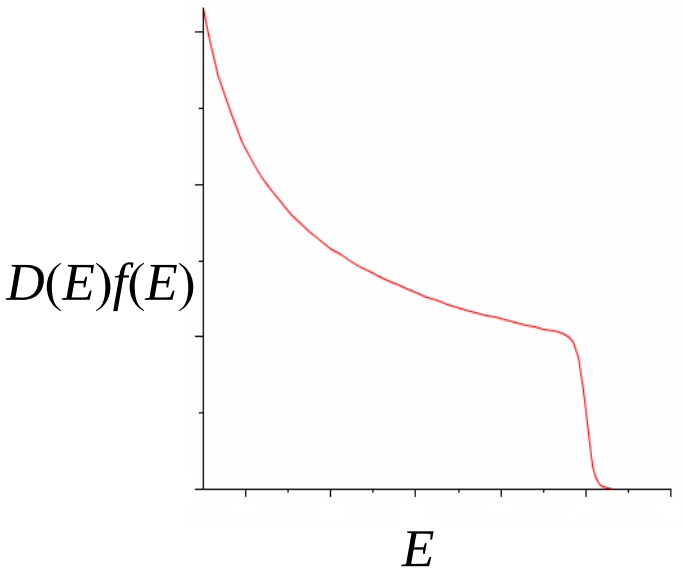
$$f(E) = \frac{1}{1+\exp\left(\dfrac{E-\mu}{k_B T}\right)}$$

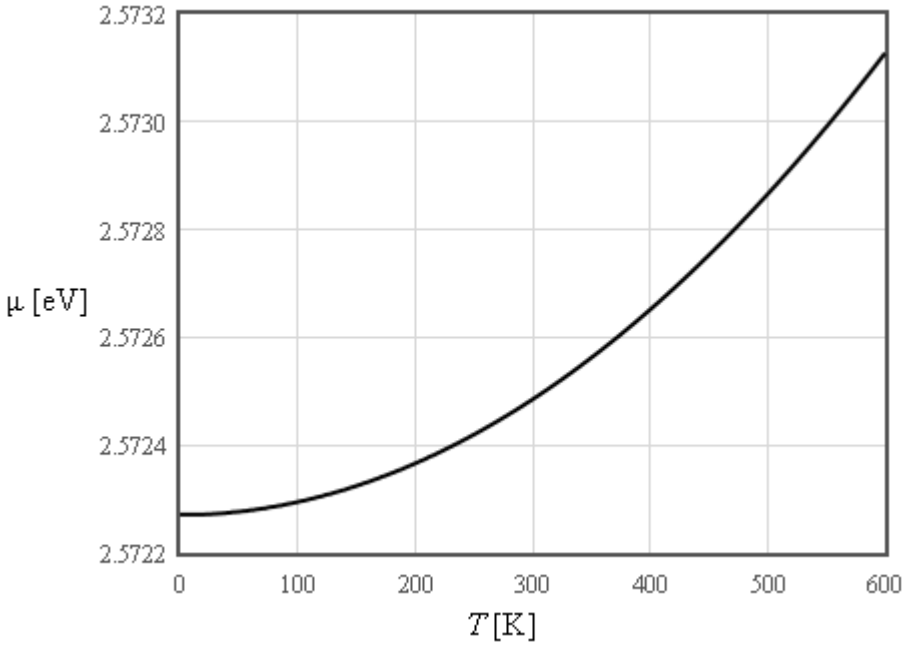
The chemical potential is implicitly defined as the energy that solves the following equation.

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

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,

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

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

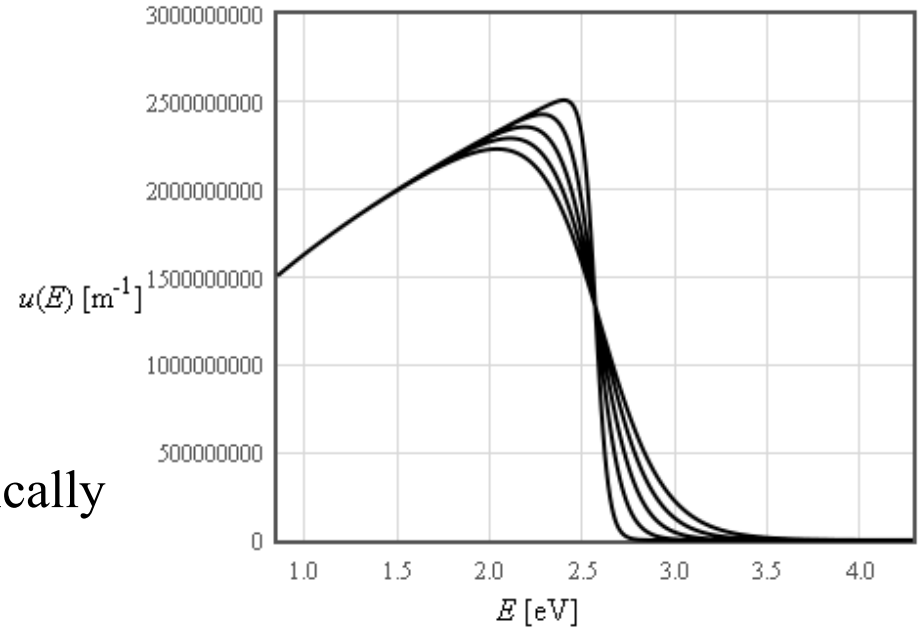
Free particles in 1-d

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

Thermodynamic properties

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

From the density of states, the thermodynamic properties can be calculated.

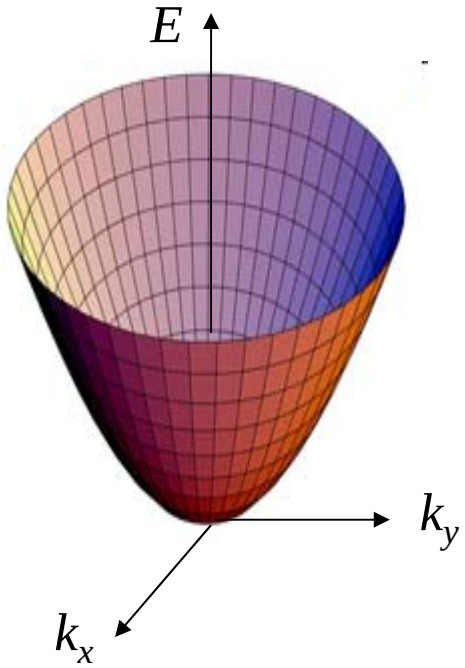
Internal energy $u = \int_{-\infty}^{\infty} ED(E)f(E)dE$	$u \approx \frac{1}{3}nE_F + \frac{\pi^2 D(E_F)}{6}(k_B T)^2$ J m^{-1} $\approx \frac{\pi^2\hbar^2 n^3}{24m} + \frac{2m}{3\hbar^2 n}(k_B T)^2$ J m^{-1}
Specific heat $c_v = \left(\frac{\partial u}{\partial T}\right)_{V=const}$	$c_v \approx \frac{\pi^2 D(E_F)}{3}k_B^2 T$ J K^{-1}m^{-1} $\approx \frac{4m}{3\hbar^2 n}k_B^2 T$ J K^{-1}m^{-1}
Entropy $s = \int \frac{c_v}{T}dT$	$s \approx \frac{\pi^2 D(E_F)}{3}k_B^2 T$ J K^{-1}m^{-1} $\approx \frac{4m}{3\hbar^2 n}k_B^2 T$ J K^{-1}m^{-1}
Helmholtz free energy $f = u - Ts$	$f \approx \frac{1}{3}nE_F - \frac{\pi^2 D(E_F)}{6}(k_B T)^2$ J m^{-1} $\approx \frac{\pi^2\hbar^2 n^3}{24m} - \frac{2m}{3\hbar^2 n}(k_B T)^2$ J m^{-1}
Pressure $P = -\left.\frac{\partial F}{\partial V}\right\|_{N,T}$	$P \approx \frac{2}{3}nE_F + \frac{\pi^2 D(E_F)}{3}(k_B T)^2$ N $P \approx \frac{\pi^2\hbar^2 n^3}{12m} + \frac{4m}{3\hbar^2 n}(k_B T)^2$ N
Bulk modulus $B = -V\frac{\partial P}{\partial V}$	$B \approx 2nE_F - \frac{\pi^2 D(E_F)}{3}(k_B T)^2$ N $B \approx \frac{\pi^2\hbar^2 n^3}{4m} - \frac{4m}{3\hbar^2 n}(k_B T)^2$ N

Free particles in 2-d

Density of states

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

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



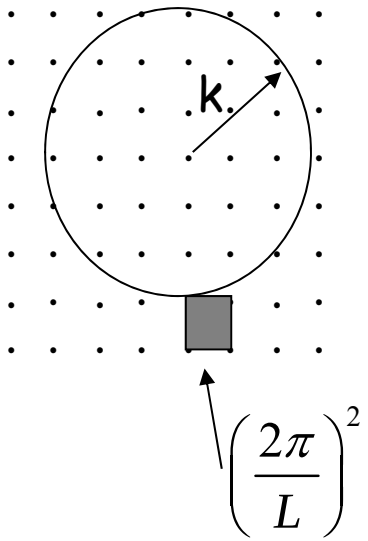
$$\frac{dk}{dE} = \frac{1}{2\hbar}\sqrt{\frac{2m}{E}}$$

Free particles in 2-d

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

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

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



$$L^2 D(k)dk = \frac{2 \cdot 2\pi k dk}{\left(\frac{2\pi}{L}\right)^2}$$

$$D(k) = \frac{k}{\pi} \qquad \mathrm{m}^{-1}$$

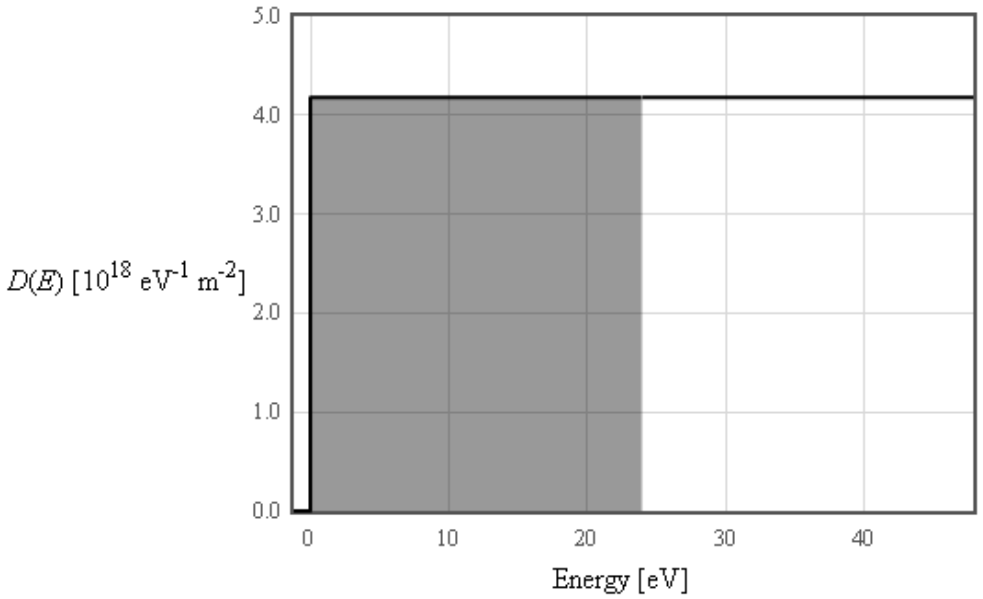
$$D(E) = D(k)\frac{dk}{dE}$$

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

$$\boxed{D(E) = \frac{m}{\pi\hbar^2}}$$

Free particles in 2-d

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



At $T = 0$:

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

$$n = \frac{N}{L^2} = \frac{m}{\pi\hbar^2}\int_0^{E_F} dE = \frac{m}{\pi\hbar^2}E_F$$

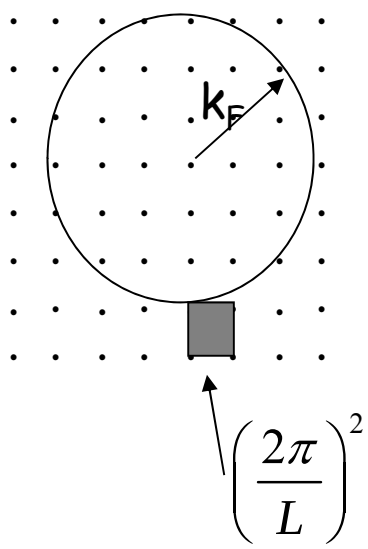
$$E_F = \frac{\pi\hbar^2 n}{m}$$

Fermi circle

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

$$k_F = \sqrt{2\pi n}$$

$n = N/L^2$ = electron density

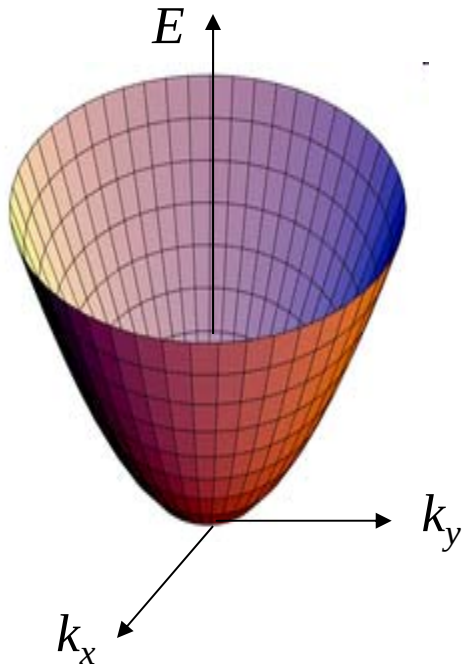


$$E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\pi \hbar^2 n}{m}$$

At $T = 0$, all states inside the Fermi circle are occupied and those outside are empty.

Free particles in 3-d

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



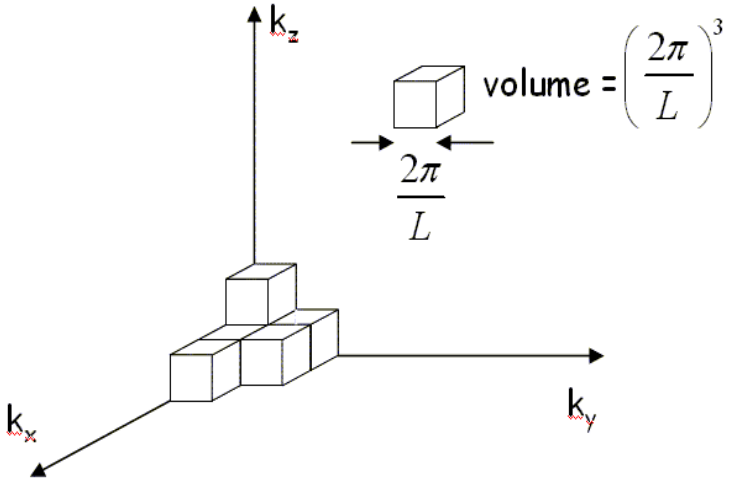
Density of states

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

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

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

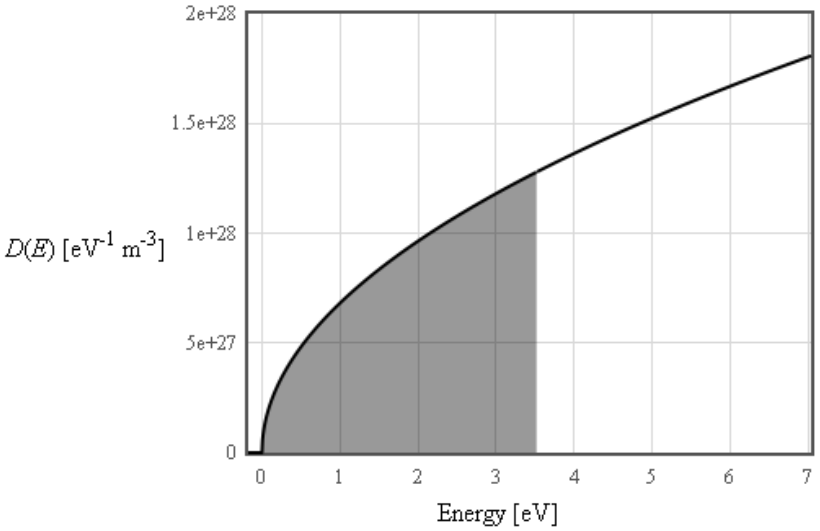
$$D(E) = D(k)\frac{dk}{dE}$$



$$k_x, k_y, k_z = \ldots, \frac{-4\pi}{L}, \frac{-2\pi}{L}, 0, \frac{2\pi}{L}, \frac{4\pi}{L}, \ldots$$

$$D(E) = \frac{(2m)^{\frac{3}{2}}}{2\pi^2\hbar^3}\sqrt{E}$$

Free particles in 3-d



At $T = 0$:

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

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

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

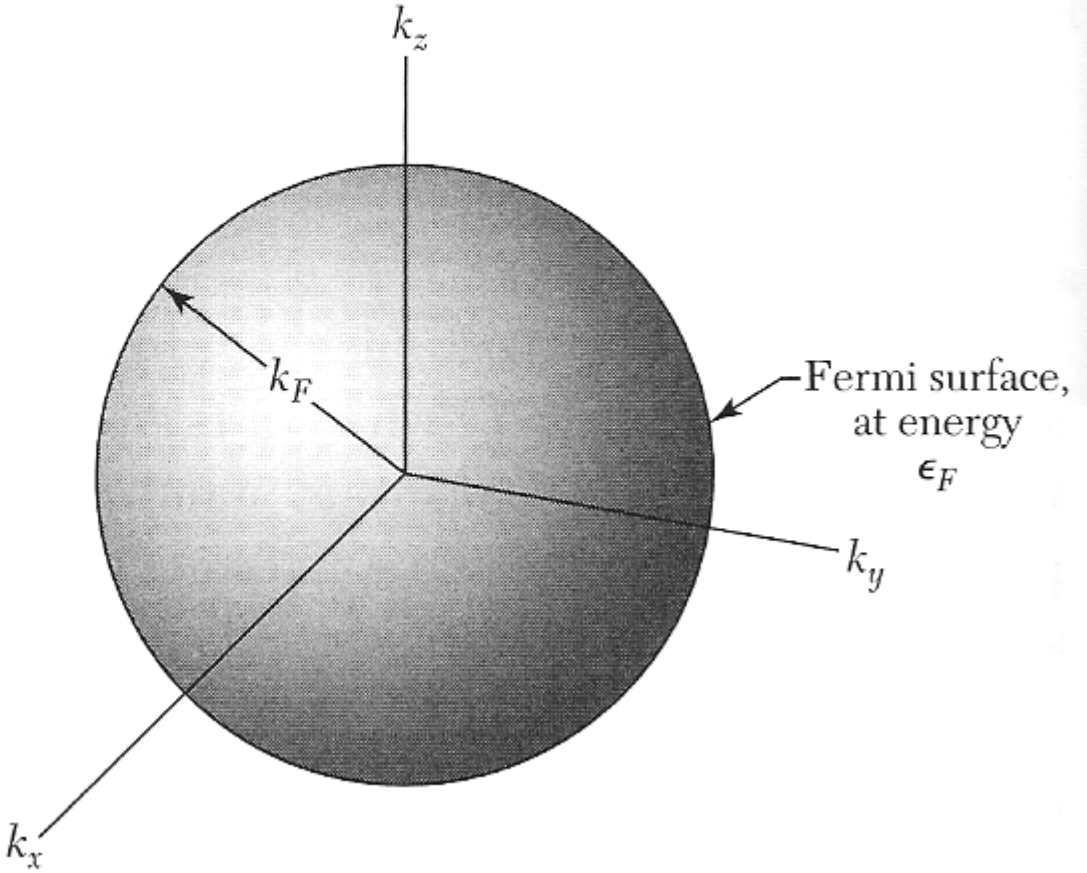
Fermi sphere

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

spin

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

n = electron density



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

$$v_F = \frac{\hbar k_F}{m}$$

$$T_F = \frac{E_F}{k_B}$$

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

Table 1 Calculated free electron Fermi surface parameters for metals at room temperature

(Except for Na, K, Rb, Cs at 5 K and Li at 78 K)

Valency	Metal	Electron concentration, in cm^{-3}	Radius[a] parameter r_n	Fermi wavevector, in cm^{-1}	Fermi velocity, in cm s^{-1}	Fermi energy, in eV	Fermi temperature $T_F \equiv \epsilon_F/k_B$, in deg K
1	Li	4.70×10^{22}	3.25	1.11×10^{8}	1.29×10^{8}	4.72	5.48×10^{4}
	Na	2.65	3.93	0.92	1.07	3.23	3.75
	K	1.40	4.86	0.75	0.86	2.12	2.46
	Rb	1.15	5.20	0.70	0.81	1.85	2.15
	Cs	0.91	5.63	0.64	0.75	1.58	1.83
	Cu	8.45	2.67	1.36	1.57	7.00	8.12
	Ag	5.85	3.02	1.20	1.39	5.48	6.36
	Au	5.90	3.01	1.20	1.39	5.51	6.39
2	Be	24.2	1.88	1.93	2.23	14.14	16.41
	Mg	8.60	2.65	1.37	1.58	7.13	8.27
	Ca	4.60	3.27	1.11	1.28	4.68	5.43
	Sr	3.56	3.56	1.02	1.18	3.95	4.58
	Ba	3.20	3.69	0.98	1.13	3.65	4.24
	Zn	13.10	2.31	1.57	1.82	9.39	10.90
	Cd	9.28	2.59	1.40	1.62	7.46	8.66
3	Al	18.06	2.07	1.75	2.02	11.63	13.49
	Ga	15.30	2.19	1.65	1.91	10.35	12.01
	In	11.49	2.41	1.50	1.74	8.60	9.98
4	Pb	13.20	2.30	1.57	1.82	9.37	10.87
	Sn(w)	14.48	2.23	1.62	1.88	10.03	11.64

[a]The dimensionless radius parameter is defined as $r_n = r_0/a_H$, where a_H is the first Bohr radius and r_0 is the radius of a sphere that contains one electron.

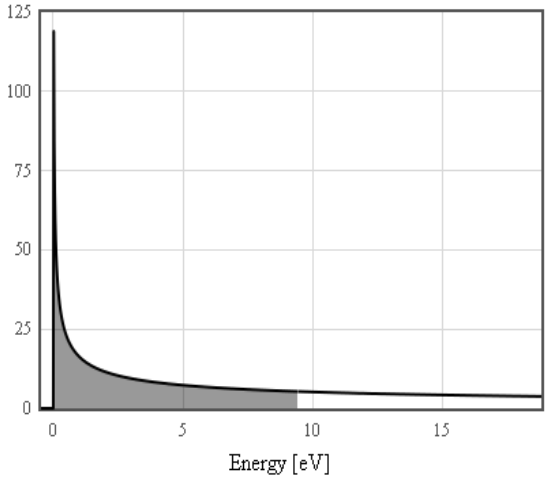
$$k_F = \left(3\pi^2 n\right)^{1/3} \qquad E_F >> k_B T$$

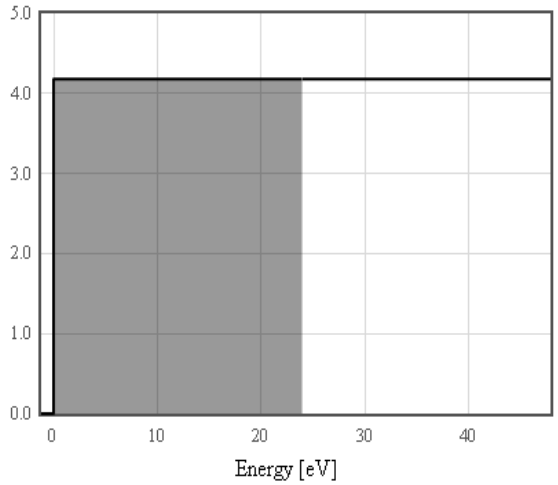
Free electron Fermi gas

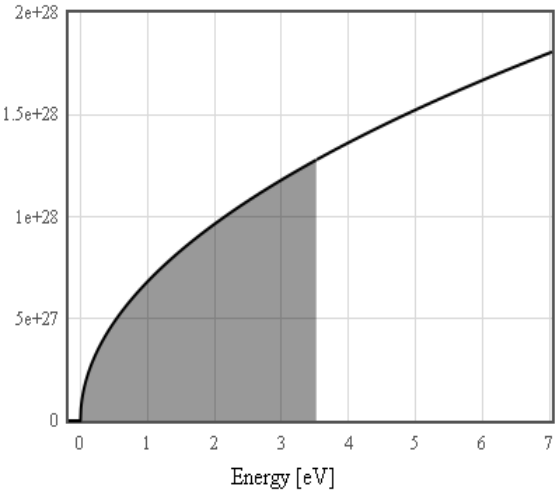
1 - d $$D(E) = \sqrt{\frac{2m}{\hbar^2 \pi^2 E}} = \frac{n}{2\sqrt{E_F E}} \quad \mathrm{J^{-1}m^{-1}}$$

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

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







Average electron energy

$$n\langle E\rangle = \int_0^{E_F} ED(E)dE$$

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

$$n\langle E\rangle = \int_0^{E_F} \frac{3n}{2E_F^{3/2}} E^{\frac{3}{2}} dE = \frac{3}{5}nE_F$$

$$\boxed{\langle E\rangle = \frac{3}{5}E_F}$$

$$u(T=0) = \frac{3}{5}nE_F$$

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

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

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