18. Electrons

May 29, 2018

Fermi energy

In solid state physics books,

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

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

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

In one dimension,

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

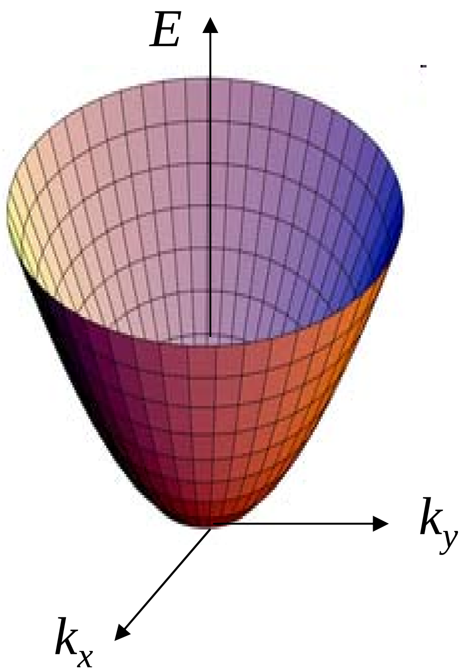
$$E_F = \frac{\pi^2\hbar^2 n^2}{8m}$$

Free particles in 2-d

Density of states

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

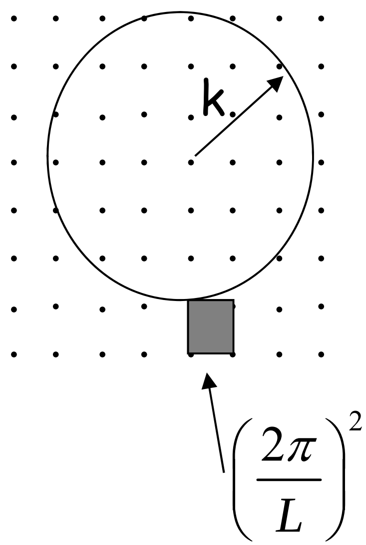
$$k = \frac{\sqrt{2mE}}{\hbar}$$



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

Free particles in 2-d

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



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

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

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

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

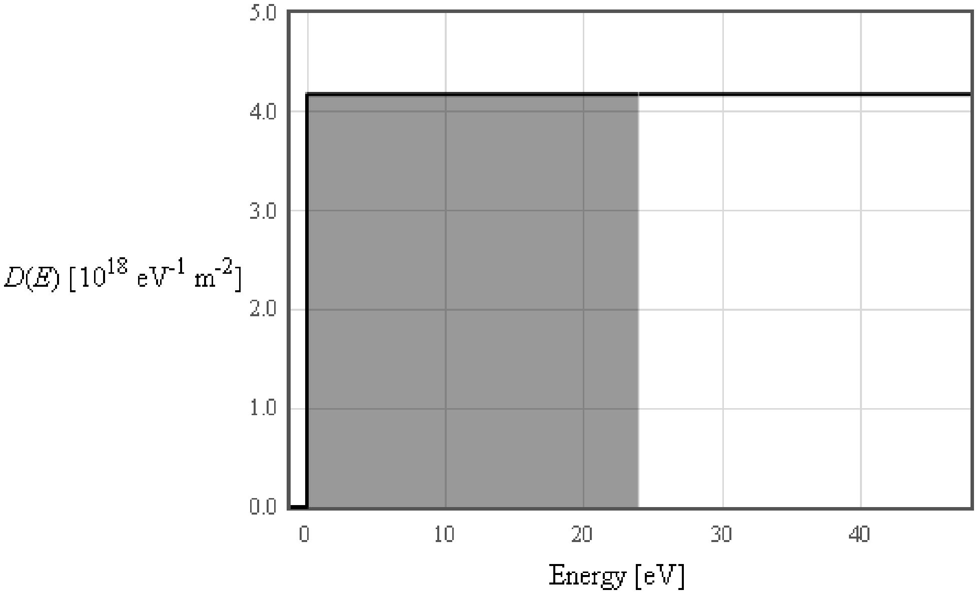
$$D(E) = D(k)\frac{dk}{dE}$$

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

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

Free particles in 2-d

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



At $T = 0$:

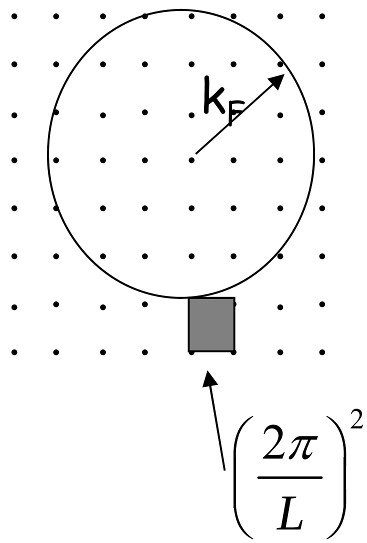
$$n = \int_0^{E_F} D(E)dE$$

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

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

Fermi circle

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



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

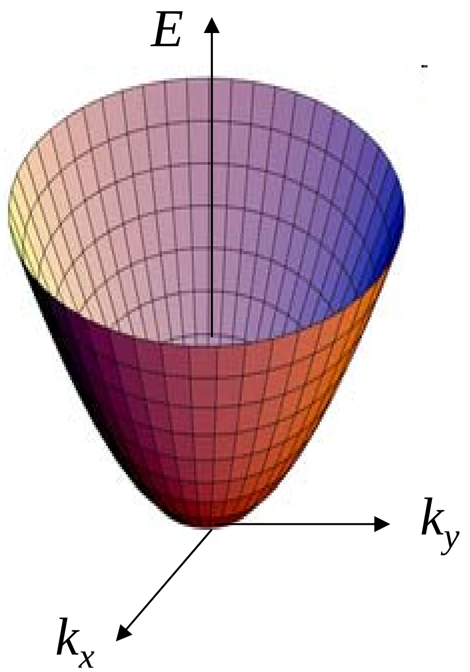
$$k_F = \sqrt{2\pi n}$$

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

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

Free particles in 3-d

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



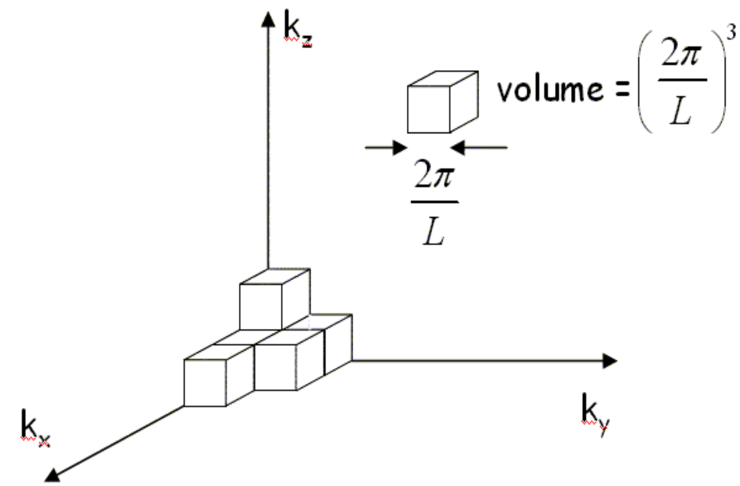
Density of states

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

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

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

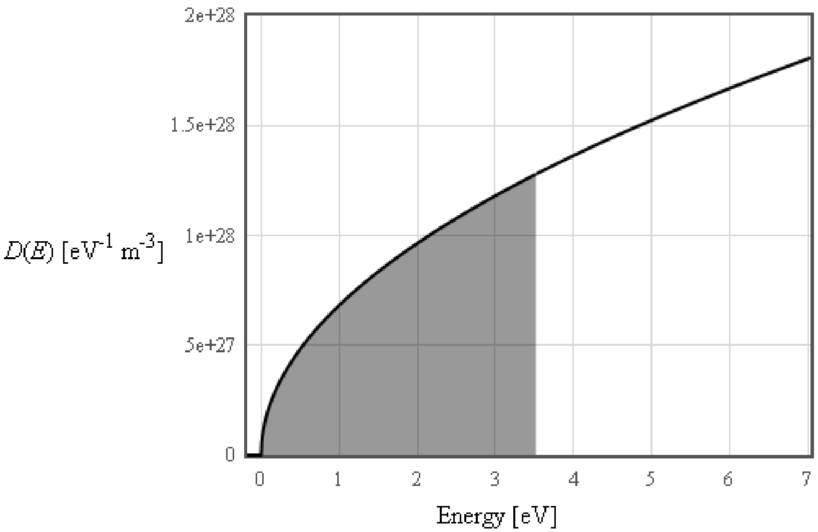
$$D(E) = D(k)\frac{dk}{dE}$$



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

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

Free particles in 3-d



At $T = 0$:

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

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

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

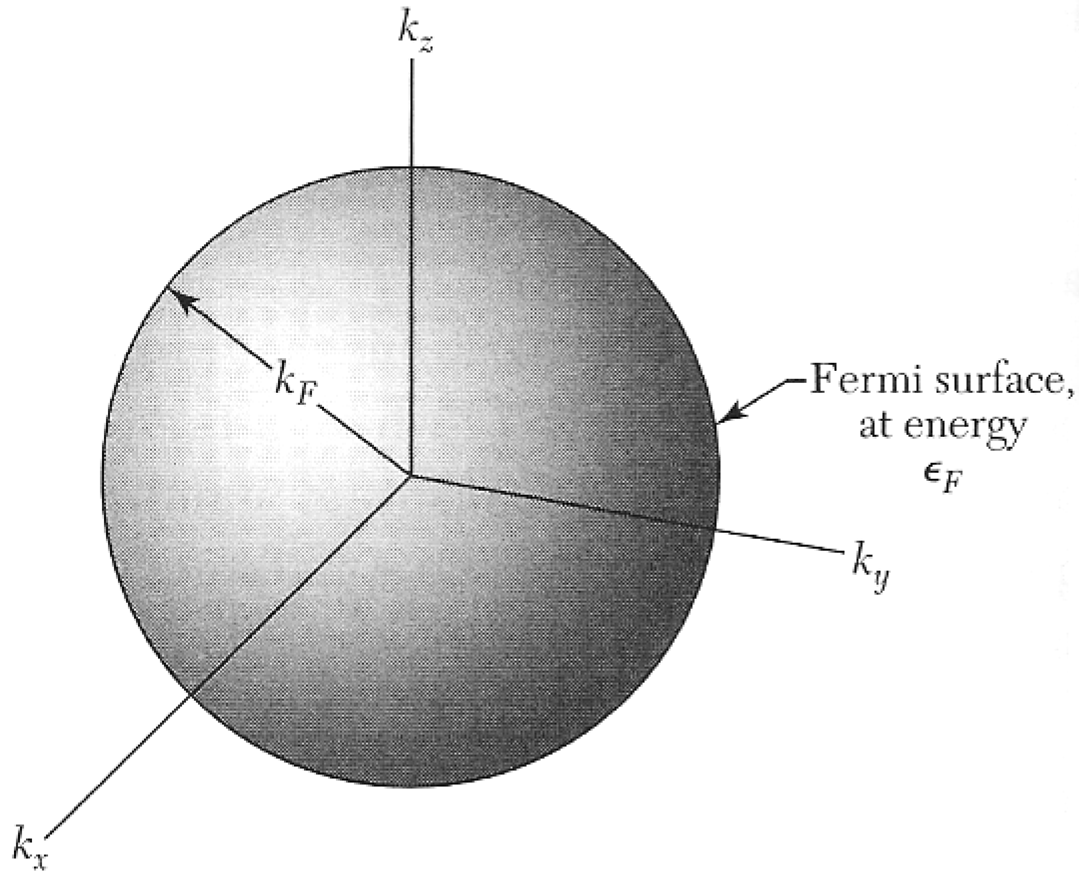
Fermi sphere

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

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.

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

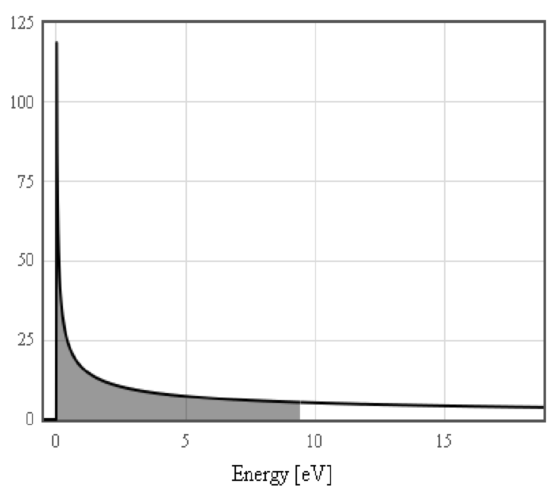
$$E_F >> k_B T$$

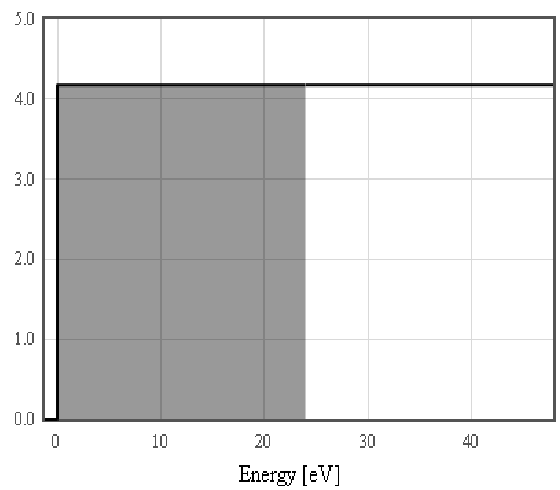
Free electron Fermi gas

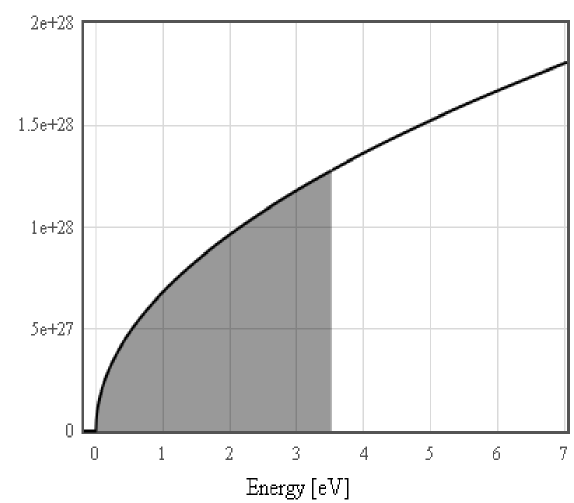
1 - d
$$D(E)=\sqrt{\frac{2m}{\hbar^2\pi^2E}}=\frac{n}{2\sqrt{E_FE}}\qquad \mathrm{J^{-1}m^{-1}}$$

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

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







Average electron energy

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

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

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

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

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

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

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

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

$$B = -V\frac{\partial P}{\partial V}$$

$$P = -\left(\frac{\partial U}{\partial V}\right)_N = \frac{\hbar^2\left(9\pi^4 N^5/V^5\right)^{\frac{1}{3}}}{5m}$$

$$P \propto V^{-5/3}$$

$$B = \frac{5}{3}P = \frac{10}{9}\frac{U}{V} = \frac{2}{3}nE_F = \frac{\hbar^2\left(3\pi^4 n^5\right)^{\frac{1}{3}}}{m} \qquad \text{N/m}^2$$

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 $D(E)=D(k)\frac{dk}{dE}$	$D\left(E\right)=\frac{1}{\pi\hbar}\sqrt{\frac{2m}{E}}=\frac{n}{2\sqrt{E_FE}}$ J^{-1}m^{-1}	$D\left(E\right)=\frac{m}{\pi\hbar^2}=\frac{n}{E_F}$ J^{-1}m^{-2}	$D\left(E\right)=\frac{(2m)^{\frac{3}{2}}}{2\pi^2\hbar^3}\sqrt{E}=\frac{3n}{2E_F^{3/2}}\sqrt{E}$ 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
$D(E_F)$	$D\left(E_F\right)=\frac{4m}{\pi^2\hbar^2n}$ J^{-1}m^{-1}	$D\left(E_F\right)=\frac{m}{\pi\hbar^2}$ J^{-1}m^{-2}	$D\left(E_F\right)=\frac{m\left(3n\right)^{\frac{1}{3}}}{\pi^{\frac{4}{3}}\hbar^2}$ J^{-1}m^{-3}
$D'(E_F)=\left.\frac{dD}{dE}\right\|_{E=E_F}$	$D'(E_F)=\frac{-16m^2}{\pi^4\hbar^4n^3}$ J^{-2}m^{-1}	$D'(E_F)=0$ J^{-2}m^{-2}	$D'(E_F)=\frac{m^2}{\hbar^4\sqrt[3]{3\pi^8n}}$ 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 $\approx\frac{\hbar^2}{2m}\left(3\pi^2n\right)^{\frac{2}{3}}-\frac{\pi^{\frac{2}{3}}m}{[illegible]}\left(k_BT\right)^2$ J

Arnold Sommerfeld

Sommerfeld Expansion

We would like to perform integrals of the form

$$\int_{-\infty}^{\infty} H(E) f(E) dE$$

Examples:

$$n = \int_{-\infty}^{\infty} D(E) f(E) dE \qquad u = \int_{-\infty}^{\infty} E D(E) f(E) dE$$

Integrate by parts (Partielle Integration)

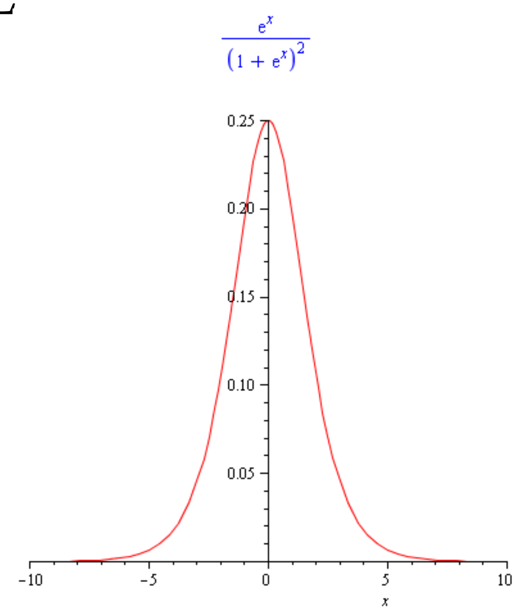
$$\int_{-\infty}^{\infty} \frac{dK(E)}{dE} f(E) dE = K(\infty) f(\infty) - K(-\infty) f(-\infty) - \int_{-\infty}^{\infty} K(E) \frac{df(E)}{dE} dE$$

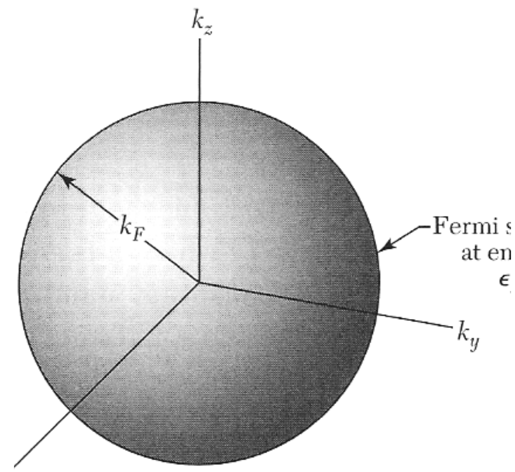
$$K(E) = \int_{-\infty}^{E} H(E') dE' \qquad H(E) = \frac{dK(E)}{dE}$$

Sommerfeld Expansion

$$\int_{-\infty}^{\infty} H(E)\,f(E)\,dE = -\int_{-\infty}^{\infty} K(E)\frac{df(E)}{dE}\,dE$$

$$\frac{-df(E)}{dE} = \frac{\dfrac{1}{k_BT}\exp\left(\dfrac{E-\mu}{k_BT}\right)}{\left(1+\exp\left(\dfrac{E-\mu}{k_BT}\right)\right)^2}$$





Expand $K(E)$ around $E = \mu$

$$K(E) \approx K(\mu) + \left.\frac{dK}{dE}\right|_{E=\mu}(E-\mu) + \frac{1}{2}\left.\frac{d^2K}{dE^2}\right|_{E=\mu}(E-\mu)^2 + \cdots$$

Sommerfeld Expansion

$$x = \frac{E-\mu}{k_B T}$$

$$\int_{-\infty}^{\infty} \frac{e^x}{\left(1+e^x\right)^2} dx = 1$$

$$\int_{-\infty}^{\infty} \frac{xe^x}{\left(1+e^x\right)^2} dx = 0$$

$$\int_{-\infty}^{\infty} \frac{x^2 e^x}{\left(1+e^x\right)^2} dx = \frac{\pi^2}{3}$$

$$\int_{-\infty}^{\infty} \frac{x^3 e^x}{\left(1+e^x\right)^2} dx = 0$$

$$\int_{-\infty}^{\infty} \frac{x^4 e^x}{\left(1+e^x\right)^2} dx = \frac{7\pi^4}{15}$$

Sommerfeld Expansion

$$\int_{-\infty}^{\infty} H(E) f(E) dE \approx K(\mu) + \frac{\pi^2}{6}\left(k_B T\right)^2 \left.\frac{dH(E)}{dE}\right|_{E=\mu} + \frac{7\pi^4}{360}\left(k_B T\right)^4 \left.\frac{d^3 H(E)}{dE^3}\right|_{E=\mu} + \cdots$$

$$K(\mu) = \int_{-\infty}^{\mu} H(E) dE \qquad H(E) = \frac{dK(E)}{dE}$$

Sommerfeld Expansion: chemical potential

$$\int_{-\infty}^{\infty} H(E)f(E)dE = K(\mu) + \frac{\pi^2}{6}\left(k_B T\right)^2 \left.\frac{dH(E)}{dE}\right|_{E=\mu} + \frac{7\pi^4}{360}\left(k_B T\right)^4 \left.\frac{d^3H(E)}{dE^3}\right|_{E=\mu} + \cdots$$

For μ in 3-d:

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

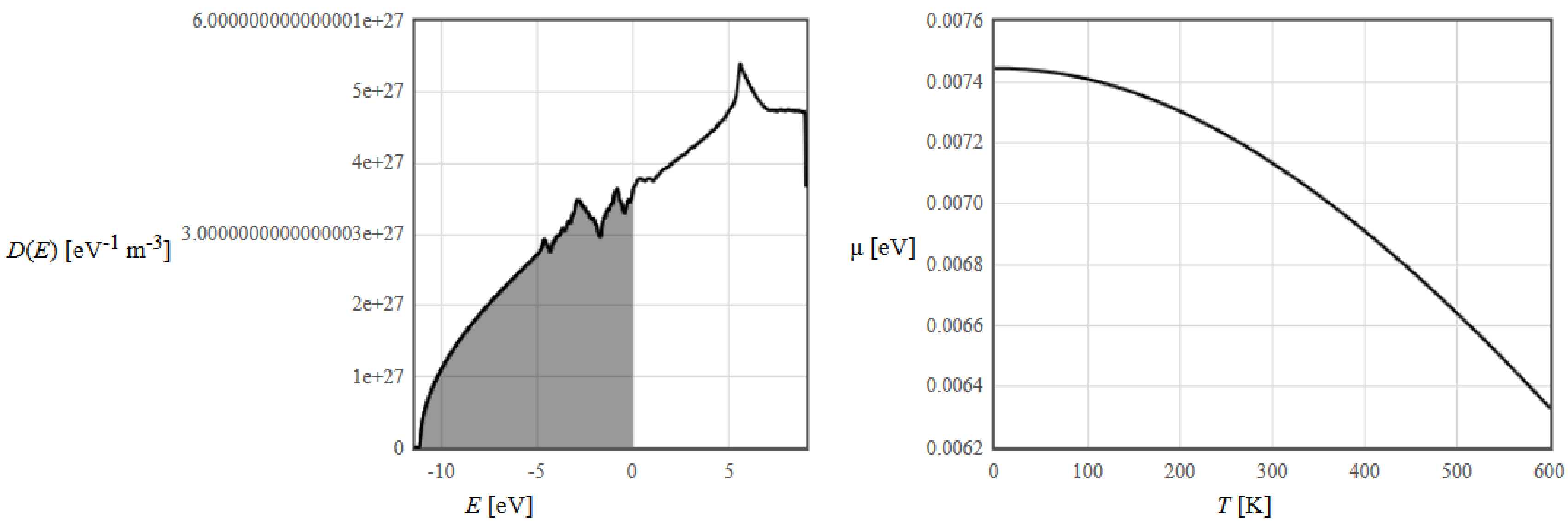
$$n = \int_{-\infty}^{\mu} D(E)dE + \frac{\pi^2}{6}\left(k_B T\right)^2 D'(E_F) + \cdots$$

$$K(\mu) = \int_{-\infty}^{\mu} D(E)dE = \int_{-\infty}^{E_F} D(E)dE + \int_{E_F}^{\mu} D(E)dE \approx n + \left(\mu - E_F\right)D(E_F)$$

Sommerfeld Expansion: chemical potential

$$n = n + (\mu - E_F) D(E_F) + \frac{\pi^2}{6}(k_B T)^2 D'(E_F)$$

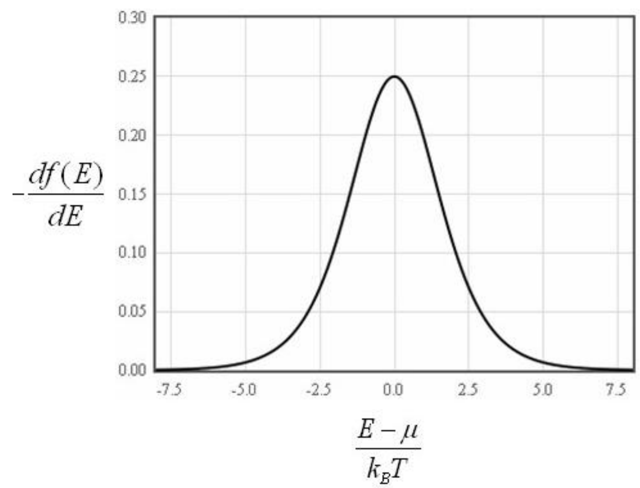
$$\boxed{\mu \approx E_F - \frac{\pi^2}{6}(k_B T)^2 \frac{D'(E_F)}{D(E_F)}}$$

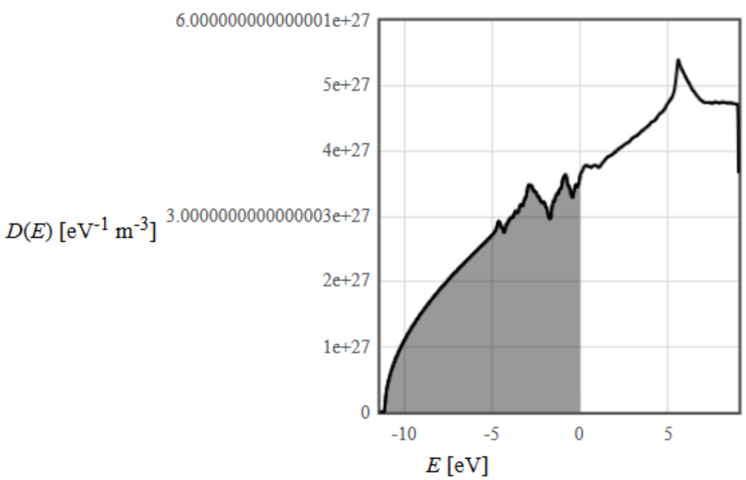


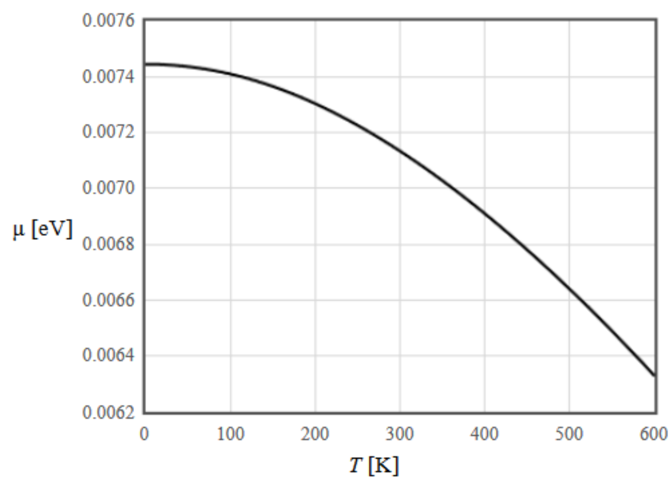
Aluminum

Sommerfeld Expansion: chemical potential

$$n = -\int_{-\infty}^{\infty} K(E)\frac{df(E)}{dE}dE = \int_{-\infty}^{\infty} \frac{K(E)\exp\left(\frac{E-\mu}{k_BT}\right)dE}{k_BT\left(\exp\left(\frac{E-\mu}{k_BT}\right)+1\right)^2}.$$







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