Chap 6 The free Fermi gas and single electron model

(Sommerfeld, 1927)

1926:
Schrodinger eq.,
FD statistics

- Fermi energy
- density of states
- specific heat

Note: Free electron model is most accurate for alkali metals.

It gives good result on electron specific heat, electric and thermal conductivities… etc.

Dept of Phys

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Electronic degrees of freedom

Free electron

Chap 6

$$\mathcal{H} = -\sum_{j}^{N_e} \frac{\hbar^2}{2m} \nabla_j^2$$

Electron in lattice

Chap 7, 8

$$-\sum_{j}^{N_e}\sum_{\alpha}^{N_i} \frac{Z_\alpha e^2}{|\vec{r}_j - \vec{R}_\alpha|}$$

Chap 10

Realistic calculations

Electron-electron interaction

Chap 9

$$+\sum_{j\ll k}^{N_e} \frac{e^2}{|\vec{r}_j - \vec{r}_k|}$$

Ionic degrees of freedom

Phonon

Chap 13

$$\mathcal{H} = -\sum_{\alpha}^{N_i} \frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2 + \sum_{\alpha\ll\beta}^{N_j} \frac{Z_\alpha Z_\beta e^2}{|\vec{R}_\alpha - \vec{R}_\beta|}$$

Electrons interact with EM fields, impurities, phonons … etc (next semester)

Free electron model

$$\left(-\frac{\hbar^2}{2m}\nabla^2+0\right)\psi(\vec{r})=\varepsilon\psi(\vec{r})$$

separable, assume

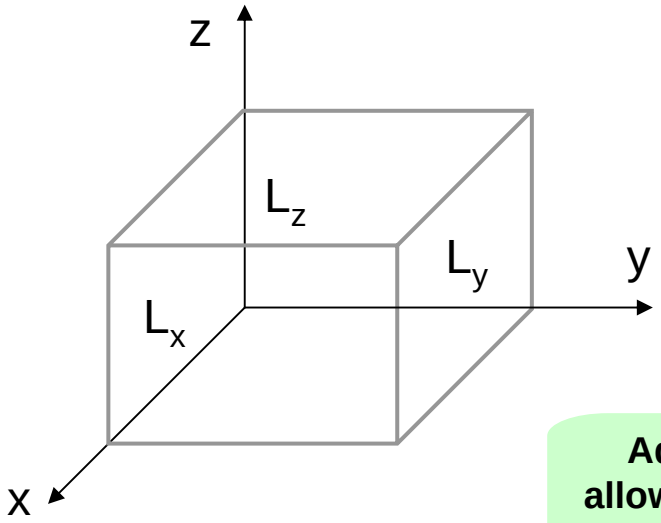
$$\psi(\vec{r})=\phi_x(x)\phi_y(y)\phi_z(z)$$

then

$$\begin{cases}\dfrac{d^2}{dx^2}\phi_x(x)+k_x^2\phi_x(x)=0,\\ \dfrac{d^2}{dy^2}\phi_y(y)+k_y^2\phi_y(y)=0,\\ \dfrac{d^2}{dz^2}\phi_z(z)+k_z^2\phi_z(z)=0,\end{cases}$$

$$k_x^2+k_y^2+k_z^2=\frac{2m\varepsilon}{\hbar^2}$$

$$\Rightarrow\quad \phi(\vec{r})=\frac{1}{\sqrt{V}}e^{i\vec{k}\cdot\vec{r}}$$



Advantage: allows travelling waves

Periodic Boundary Condition (PBC):

$$\phi_x(L_x)=\phi_x(0);\ \phi_y(L_y)=\phi_y(0);\ \phi_z(L_z)=\phi_z(0)$$

$$\Rightarrow\quad k_x=\frac{2\pi}{L_x}n_x,\quad n_x\in Z$$

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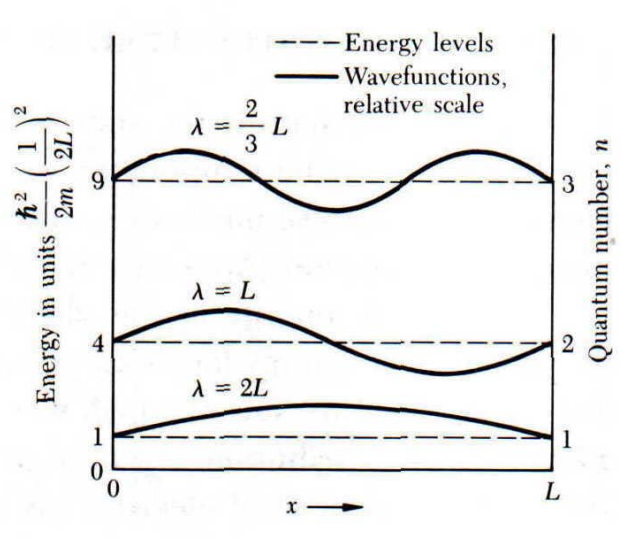
Box BC vs Periodic BC

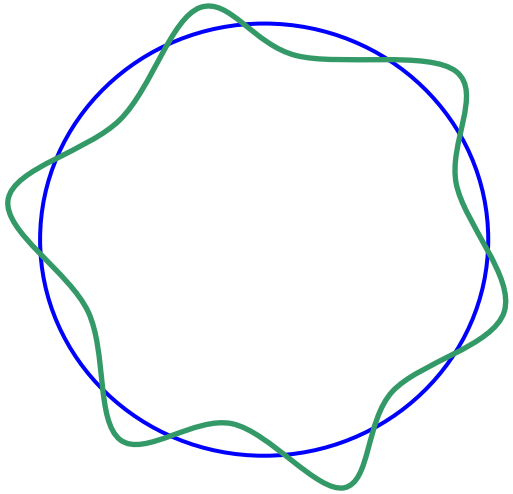
Plane wave solution $\psi(x) = Ae^{ikx} + Be^{-ikx}, \quad \varepsilon(k) = \hbar^2 k^2 / 2m$

- "Box" BC

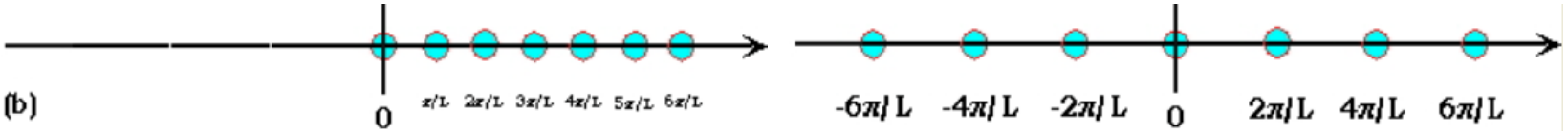


k = π /L, 2 π /L, 3 π /L…

- Periodic BC

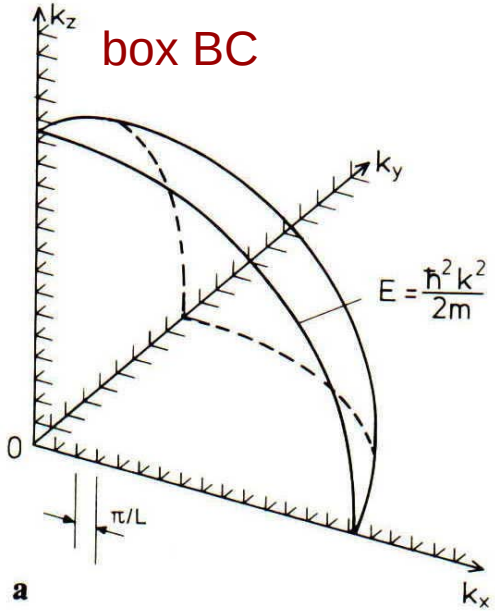


k = ±2 π /L, ±4 π /L, ±6 π /L…

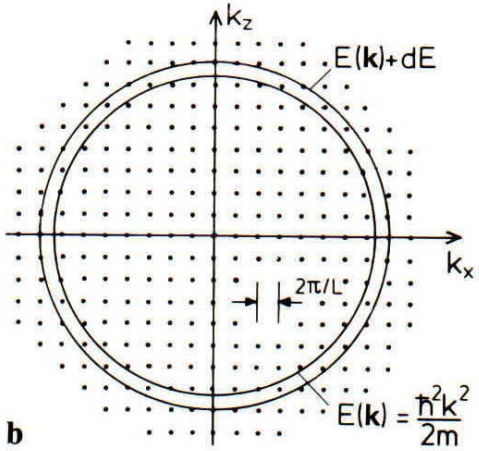


Box BC vs Periodic BC

box BC



periodic BC



• Each point allows 2 electrons (due to spin). After filling in N electrons, the occupied points form a Fermi sphere. Its radius is called the Fermi wave vector, and the energy of the outermost electron is called the Fermi energy.

• Different BCs give the same Fermi wave vector and the same energy

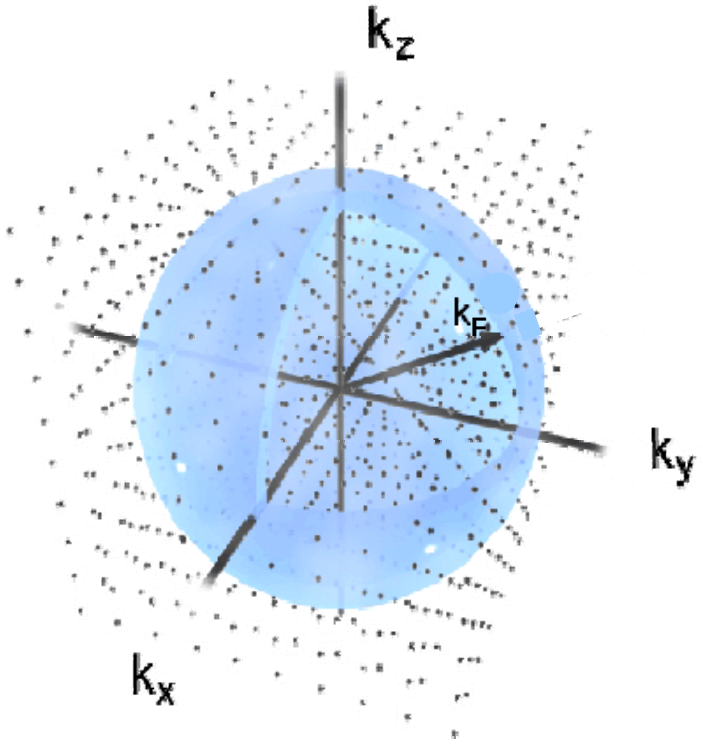
box BC $N = 2\frac{1}{8}\frac{(4\pi/3)k_F^3}{(\pi/L)^3}$ periodic BC $N = 2\frac{(4\pi/3)k_F^3}{(2\pi/L)^3}$

Connection between electron density and Fermi energy

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

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

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



For K, the electron density N/V=1.4×10^{28} m^{-3}, therefore

$$\varepsilon_F = 3.40\times10^{-19}\,J = 2.12eV \qquad k_F = 0.746\ A^{-1}$$

- ε_F is roughly the order of the atomic energy levels
- k_F is of the order of a^{-1}.

Fermi temperature and Fermi velocity

$$\varepsilon_F = k_B T_F = \frac{m}{2} v_F^2$$

- The Fermi temperature is of the order of 10^4 K

ELEMENT	r_s/a_0	ε_F	T_F	k_F	v_F
Li	3.25	4.74 eV	5.51×10^4 K	1.12×10^8 cm^{-1}	1.29×10^8 cm/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	6.38	1.20	1.39
Au	3.01	5.53	6.42	1.21	1.40

important

- Some useful formulas:

T=0

$$N = \sum_{\text{filled } \alpha} 1 \qquad \alpha = (\vec{k}, s)$$

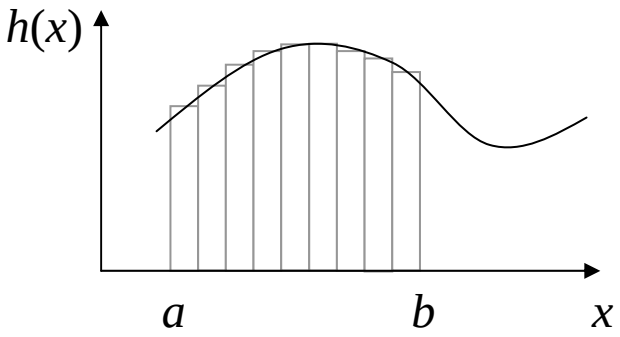
$$E = \sum_{\text{filled } \alpha} \varepsilon_\alpha$$

T≠0

$$N = \sum_{\text{filled } \alpha} f_\alpha \qquad \text{where } f(\varepsilon_\alpha) = \frac{1}{e^{(\varepsilon_\alpha - \mu)/kT} + 1}$$

$$E = \sum_{\text{filled } \alpha} \varepsilon_\alpha f_\alpha$$

- Connection between summation and integral



$$\int_a^b dx h(x) = \lim_{\Delta x \to 0} \sum_i \Delta x \cdot h(x_i), \text{ or}$$

$$\sum_i h(x_i) \cong \int_a^b \frac{dx}{\Delta x} h(x).$$

Similarly in 2D and 3D, e.g.,

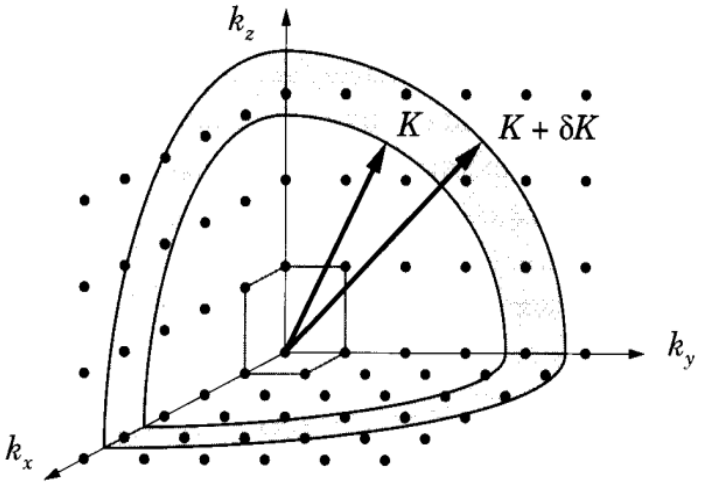
$$\sum_{\vec{k}} f(E_{\vec{k}}) \cong \int \frac{d^3k}{\Delta^3 k} f(E_{\vec{k}})$$

important

- Density of states $D(\varepsilon)$ (DOS, 態密度)

$D(\varepsilon)d\varepsilon$ is the number of states within the energy surfaces of ε and $\varepsilon + d\varepsilon$

$$D(\varepsilon)d\varepsilon = \frac{\int_{shell} d^3k}{\Delta^3 k}, \quad \Delta^3 k = \left(\frac{2\pi}{L}\right)^3$$



- Once we know the DOS, we can reduce the 3-dim ***k***-integral to a 1-dim ε -integral.

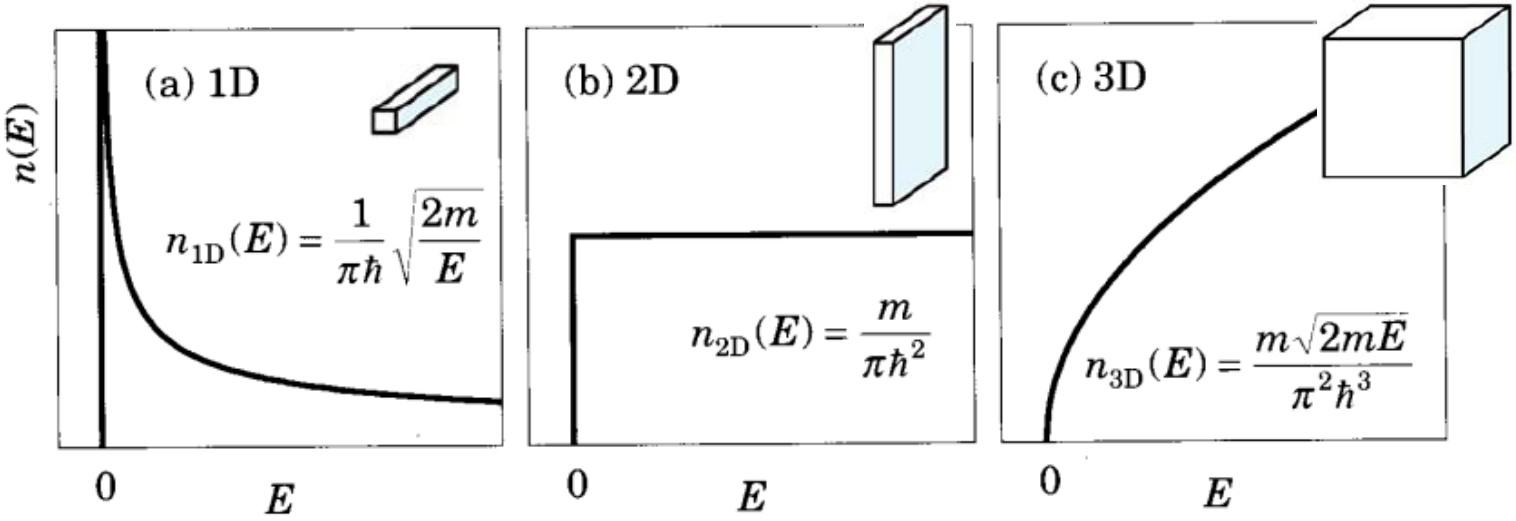
$$\int \frac{d^3k}{\Delta^3 k} h(\varepsilon_{\vec{k}}) = \int d\varepsilon D(\varepsilon) h(\varepsilon)$$

- For a 3D Fermi sphere,

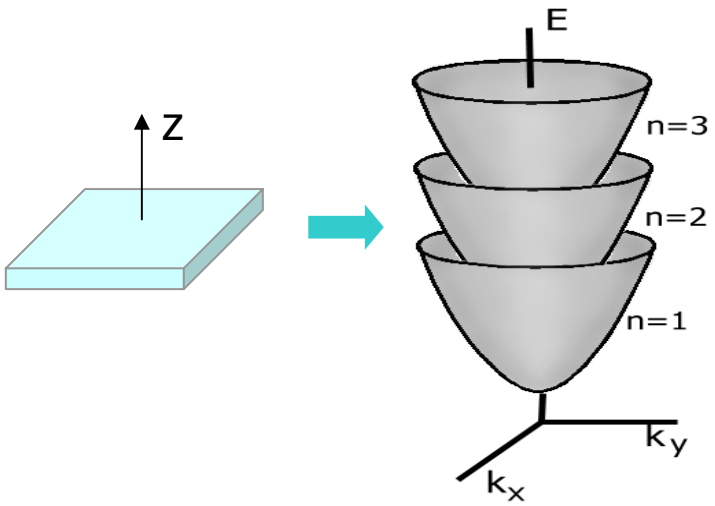
$$D(\varepsilon)d\varepsilon = 2\int_{shell} \frac{d^3\vec{k}}{(2\pi/L)^3} \qquad \varepsilon(\vec{k}) = \frac{\hbar^2 k^2}{2m}$$

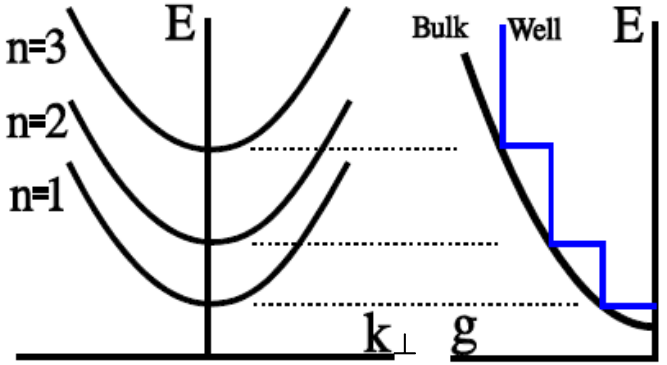
$$= 2\frac{4\pi k^2 dk}{(2\pi/L)^3} \qquad \Rightarrow D(\varepsilon) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{\varepsilon}$$

• Free electron DOS (per volume) in 1D, 2D, and 3D



• Multiple bound states in 2D





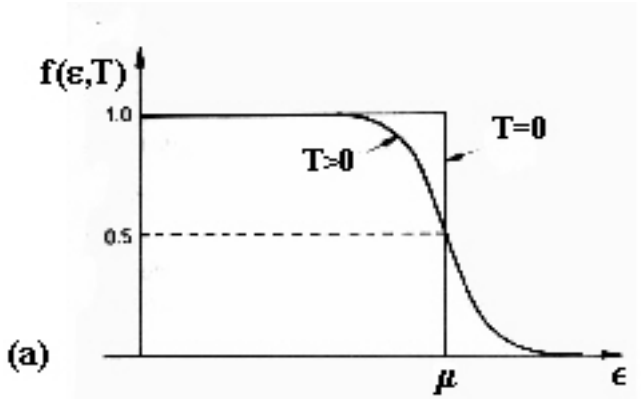
- Thermal distribution of electrons

Recall $2\sum_{\vec{k}} f(\varepsilon_{\vec{k}}) \rightarrow 2\int \frac{d^3\vec{k}}{\Delta^3\vec{k}} f(\varepsilon_{\vec{k}}) = \int d\varepsilon D(\varepsilon) f(\varepsilon)$

where $f(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/kT}+1}, \qquad f(\mu) = 1/2$

$\mu(T=0K) = \varepsilon_F$

$\mu(T>0K) \neq \varepsilon_F$



- Combine DOS *D(ε)* and thermal dist *f(ε ,T)*

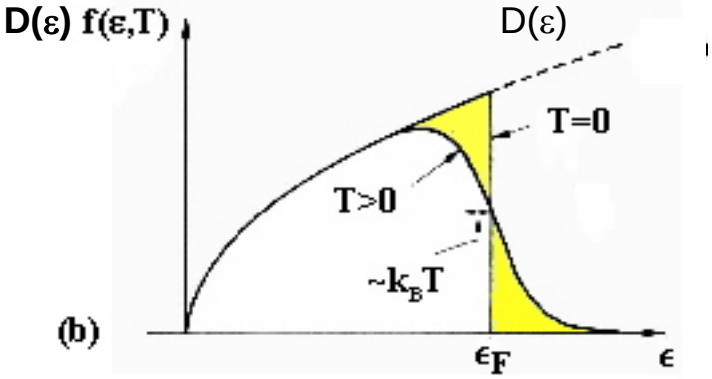
Hotel rooms

$N = 2\sum_{\vec{k}} f_k \rightarrow \int d\varepsilon D(\varepsilon) f(\varepsilon,T)$

tourists

$E(T) = 2\sum_{\vec{k}} f_k \varepsilon_k \rightarrow \int d\varepsilon D(\varepsilon) f(\varepsilon,T)\varepsilon$

money



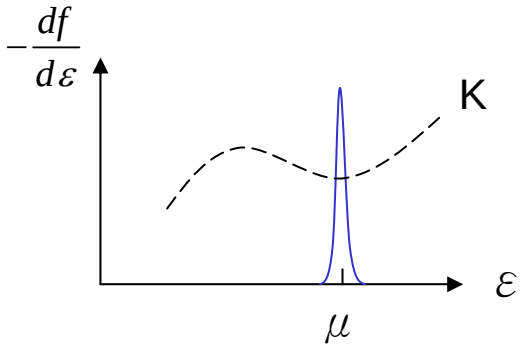
Sommerfeld expansion

Integral of the form (*h* is arbitrary)

$$\int_0^\infty d\varepsilon\, h(\varepsilon) f(\varepsilon), \qquad h(\varepsilon) \equiv \frac{dK}{d\varepsilon}$$

$$= \cancel{Kf}\Big|_0^\infty - \int_0^\infty d\varepsilon\, K \frac{df}{d\varepsilon}$$

sharp around μ



If K is smooth near ε_F, then expand K around μ (not ε_F):

$$K(\varepsilon) = K(\mu) + \left.\frac{dK}{d\varepsilon}\right|_\mu (\varepsilon - \mu) + \frac{1}{2!}\left.\frac{d^2K}{d\varepsilon^2}\right|_\mu (\varepsilon - \mu)^2 + \ldots$$

$$\Rightarrow \int_0^\infty d\varepsilon\, h(\varepsilon) f(\varepsilon) = \int_0^\mu d\varepsilon\, h(\varepsilon) + \frac{\pi^2}{6}(k_B T)^2 \frac{dh}{d\mu} + \ldots$$

unknown

$$\int_0^\infty d\varepsilon \left(-\frac{df}{d\varepsilon}\right) = 1$$

$$\int_0^\infty d\varepsilon (\varepsilon - \mu)\left(-\frac{df}{d\varepsilon}\right) = 0$$

$$\int_0^\infty d\varepsilon (\varepsilon - \mu)^2 \left(-\frac{df}{d\varepsilon}\right) = \frac{\pi^2}{3}(k_B T)^2$$

Chemical potential at finite temperature (n=N/V, g=D/V)

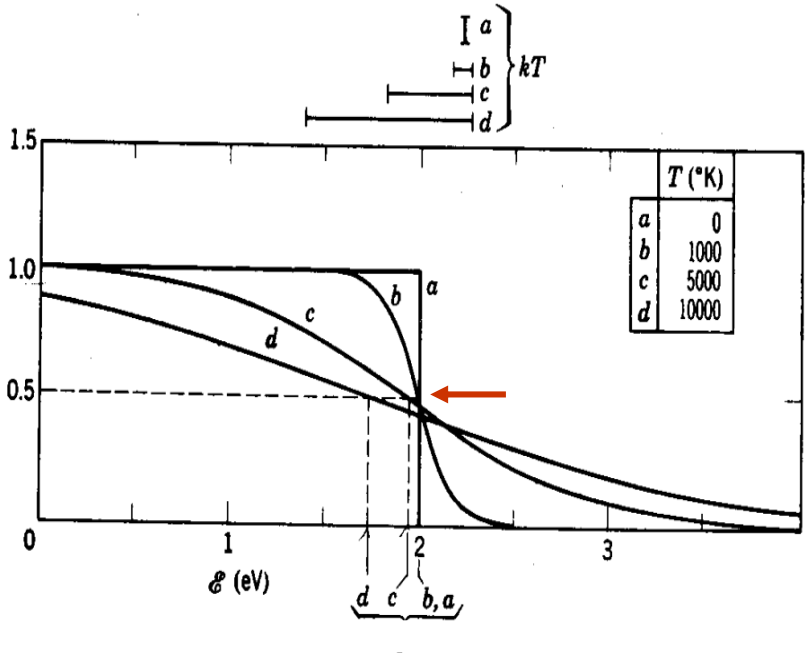
$$n = \int_{-\infty}^{\infty} g(\varepsilon) f(\varepsilon) d\varepsilon = \int_{-\infty}^{\mu} g(\varepsilon) d\varepsilon + \frac{\pi^2}{6} (k_B T)^2 g(\mu)' + O\left(\frac{k_B T}{\mu}\right)^4$$

$$\simeq \int_{0}^{\varepsilon_F} g(\varepsilon) d\varepsilon + \underbrace{\int_{\varepsilon_F}^{\mu} g(\varepsilon) d\varepsilon}_{\approx(\mu-\varepsilon_F) g(\varepsilon_F)} + \frac{\pi^2}{6} (k_B T)^2 g(\varepsilon_F)'$$

$$\rightarrow (\mu - \varepsilon_F) g(\varepsilon_F) + \frac{\pi^2}{6} (k_B T)^2 g(\varepsilon_F)' =$$

$$\mu = \varepsilon_F - \frac{\pi^2}{6} (k_B T)^2 \frac{g(\varepsilon_F)'}{g(\varepsilon_F)}$$

$$= \varepsilon_F \left(1 - \frac{1}{3}\left(\frac{\pi k_B T}{2\varepsilon_F}\right)^2\right)$$



Electronic specific heat (u=U/V)

$$u = \int_0^{\mu} d\varepsilon\, \varepsilon g(\varepsilon) + \frac{\pi^2}{6}(k_B T)^2 \frac{d(\varepsilon g)}{d\mu} +$$

$$\int_0^{\mu} d\varepsilon\, \varepsilon g \simeq \int_0^{\varepsilon_F} d\varepsilon\, \varepsilon g(\varepsilon) + \underbrace{(\mu - \varepsilon_F)\varepsilon_F g}_{-\varepsilon_F \frac{\pi^2}{6}(k_B T)^2}$$

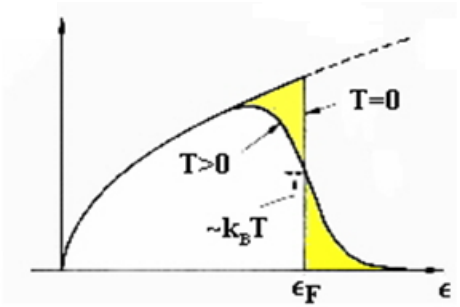
$$\Rightarrow u = u_0 + \frac{\pi^2}{6}(k_B T)^2 g(\varepsilon_F) + \ldots$$

$$c_v = \left(\frac{\partial u}{\partial T}\right)_V = \frac{\pi^2}{3}(k_B)^2 T g(\varepsilon_F) = \frac{\pi^2}{2}\left(\frac{k_B T}{\varepsilon_F}\right) n k_B$$

$$\propto \quad T$$

Heuristic argument

D(ε)f(ε)



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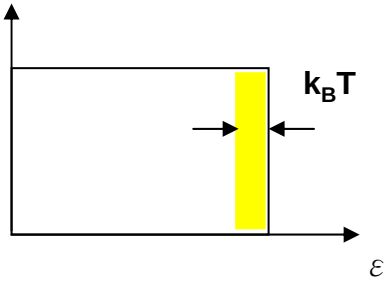
D(ε)f(ε)



- Electrons near the Fermi surface are excited by thermal energy *kT*. Their number is of the order of $N' = N_A\ (kT/\ \varepsilon_F)$

- The energy absorbed by the electrons is

$$U(T)\text{-}U(0) \approx N_A\,(kT)^2/\ \varepsilon_F$$

- specific heat $C_e \approx dU/dT$

$$= 2R\ kT/\ \varepsilon_F = 2R\ T/T_F$$

a factor of T/T_F smaller than classical result

$$\gamma = \frac{C_e}{T}$$

Table 2 Experimental and free electron values of electronic heat capacity constant γ of metals

(From compilations kindly furnished by N. Phillips and N. Pearlman. The thermal effective mass is defined by Eq. (38).

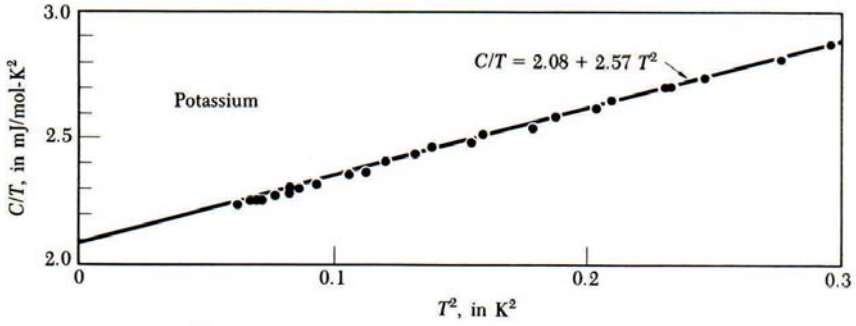
Observed γ in mJ mol^{-1} K^{-2}.
Calculated free electron γ in mJ mol^{-1} K^{-2}
m_{th}/m = (observed γ)/(free electron γ).

Li	Be											B	C	N
1.63	0.17													
0.749	0.500													
2.18	0.34													
Na	Mg											Al	Si	P
1.38	1.3											1.35		
1.094	0.992											0.912		
1.26	1.3											1.48		
K	Ca	Sc	Ti	V	Cr	Mn(γ)	Fe	Co	Ni	Cu	Zn	Ga	Ge	As
2.08	2.9	10.7	3.35	9.26	1.40	9.20	4.98	4.73	7.02	0.695	0.64	0.596		0.19
1.668	1.511									0.505	0.753	1.025		
1.25	1.9									1.38	0.85	0.58		
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn (w)	Sb
2.41	3.6	10.2	2.80	7.79	2.0	—	3.3	4.9	9.42	0.646	0.688	1.69	1.78	0.11
1.911	1.790									0.645	0.948	1.233	1.410	
1.26	2.0									1.00	0.73	1.37	1.26	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg(α)	Tl	Pb	Bi
3.20	2.7	10.	2.16	5.9	1.3	2.3	2.4	3.1	6.8	0.729	1.79	1.47	2.98	0.008
2.238	1.937									0.642	0.952	1.29	1.509	
1.43	1.4									1.14	1.88	1.14	1.97	

- In general $C_V = C_e + C_p$

$$= \gamma T + AT^3$$

C_e is important only at very low T



... Sommerfeld does not seem to have asked why the ions did not influence the electrons between collisions, or why the effects arising from motion of the ions could be neglected. As Bethe recalls, "he didn't even care terribly much why the electrons were free, which I thought was a very important thing to know."[89] Neglect of the ions also disturbed other physicists, including Heisenberg and Frenkel;[90] Schottky wrote to Sommerfeld that "to assume a field free condition inside a metal appears to me to be too specialized for the problem."[91] Sommerfeld was aware of these problems, but, as Peierls reflected recently, he was optimistic that in one way or another they would be resolved.[92]

L. Hoddeson et al, Out of the crystal maze, p.104