

Free electron model

Lecture 2

see, for instance, Kittel Chapter 6

Recap

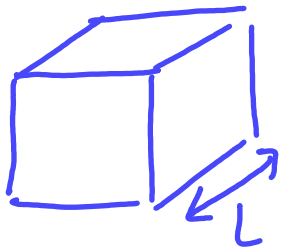
Free electron model in 3D

"simplest way to represent the electronic structure of a metal"

* the valence e^- of the atoms become conduction e^-
i.e. a monovalent crystal with N atoms, there will be N conduction e^-

* Assumptions of the model : no interactions between e^- and the nuclei and other e^-

Solid seen as $1e^-$ trapped in an ∞ -well potential
(energy \rightarrow Kinetic - analogy Kinetic theory of gases)



$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}) = E \psi(\vec{r})$$

Periodic boundary conditions $\psi(x+L, y, z) = \psi(x, y, z)$

$\Rightarrow \psi(\vec{r}) = A \exp(i\vec{K} \cdot \vec{r})$
travelling plane wave

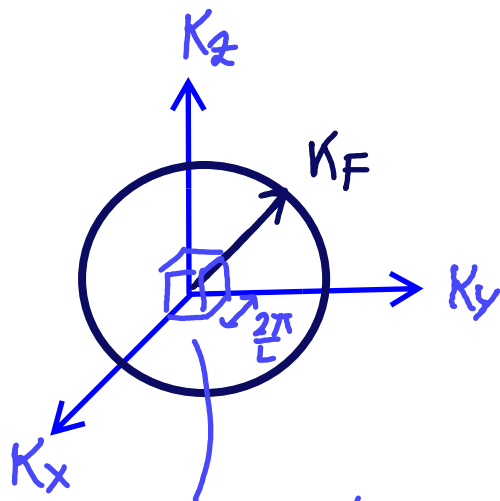
wavevector
 $K_i = \frac{2\pi}{L} n_i$
quantum numbers
posit./neg integers

$E_K = \frac{\hbar^2 K^2}{2m} = \frac{\hbar^2}{2m} (K_x^2 + K_y^2 + K_z^2)$
Dispersion relation for e^-

Recap

the N electrons are accommodated in the lowest possible states following Pauli exclusion principle.

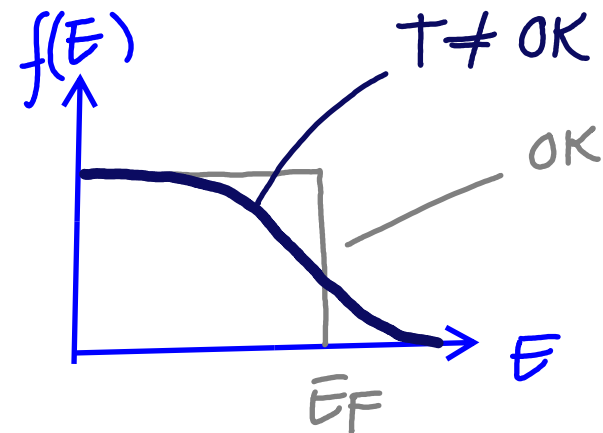
⇒ thus, all occupied states (orbitals) are inside a sphere of radius k_F in k -space.



each state occupies $(\frac{2\pi}{L})^3$ in k -space.

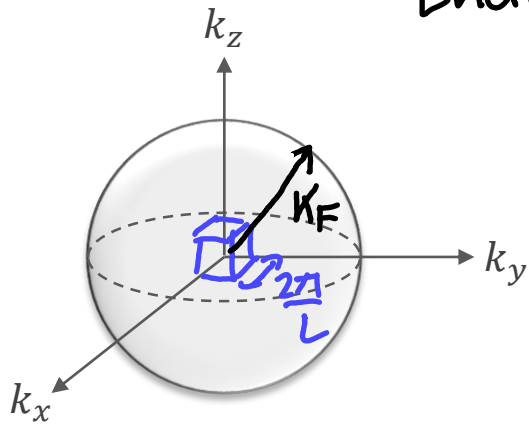
Fermi level: highest occupied state
Fermi energy: energy of the highest occupied state

Remember: Fermi-Dirac distribution function



Fermi energy

Energy at the Fermi surface : $E_F = \frac{\hbar^2 K_F^2}{2m}$



* Total number of states : $N = 2 \frac{4/3 \pi K_F^3}{(2\pi/L)^3} = \frac{V}{3\pi^2} K_F^3$

Annotations:
 - 2 possible spin states (pointing to the factor 2)
 - Volume of sphere of radius K_F (pointing to $4/3 \pi K_F^3$)
 - Volume of 1 K -state in K space (pointing to $(2\pi/L)^3$)

* Wavevector at Fermi surface $K_F = \left(3\pi^2 \frac{N}{V}\right)^{1/3} = \left(3\pi^2 n\right)^{1/3}$

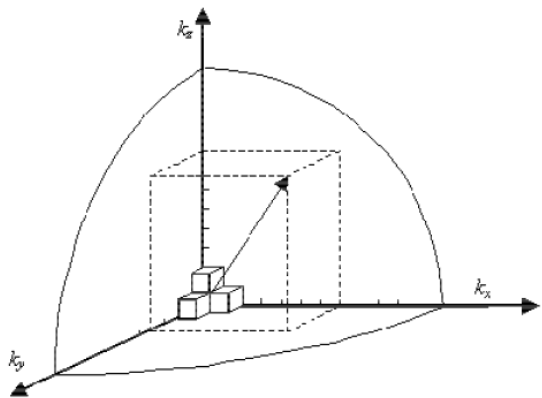
Annotation:
 - $n = \frac{N}{V} =$ electron density (pointing to N/V)

* Fermi energy $= \frac{\hbar^2 K_F^2}{2m} = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}$

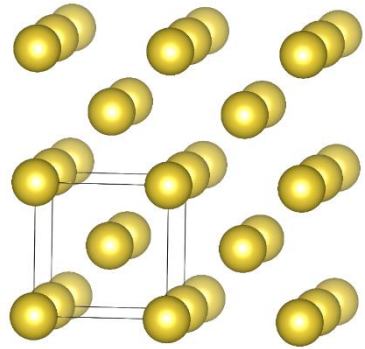
* Fermi velocity $v = \frac{\hbar K_F}{m} = \frac{\hbar^2}{m} (3\pi^2 n)^{1/3}$

* Fermi Temperature $T_F = \frac{E_F}{K_B}$

all them depend on electron concentration!



A few estimates for Na



$a = 4.2 \text{ \AA}$

- BCC structure with lattice parameter $a = 4.2 \text{ \AA}$
- 1 valence e^- per atom

→ since there are atoms per unit cell:

$$e^- \text{ concentration} = \frac{N}{V} = \frac{1}{(4.2)^3} \approx 3 \cdot 10^{22} \text{ cm}^{-3}$$

$$\text{Fermi wavevector } k_F = (3\pi^2 n)^{1/3} \sim 10^8 \cdot \text{m}^{-1} \sim 1 \text{ \AA}^{-1}$$

$$\text{Fermi energies } E_F = \frac{\hbar^2 k_F^2}{2m} \sim 3.3 \text{ eV}$$

$$\text{Fermi Temperature } T_F \sim 40000 \text{ K}$$

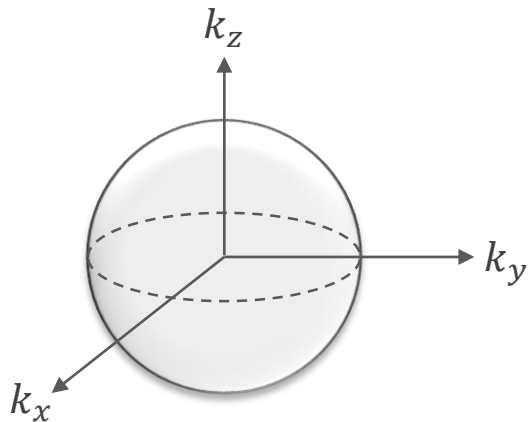
$$\text{Fermi velocity } v_F = 10^8 \frac{\text{cm}}{\text{s}}$$

Berechnete Parameter der Fermiflächen für freie Elektronen in Metallen bei Zimmertemperatur
(Nur für Na, K, Rb, Cs bei 5 K und für Li bei 78 K)

Wertigkeit	Metall	Elektronen- konzentration in cm^{-3}	Radius- parameter ^a r_s	Fermi- Wellenvektor in cm^{-1}	Fermi- geschwindigkeit in cm s^{-1}	Fermi- energie in eV	Fermitemperatur $T_F = \varepsilon_F/k_B$ in K
1	Li	$4,70 \times 10^{22}$	3,25	$1,11 \times 10^8$	$1,29 \times 10^8$	4,72	$5,48 \times 10^4$
	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
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
	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(ω)	14,48	2,23	1,62	1,88	10,03	11,64

^a Der dimensionslose Radiusparameter ist definiert als $r_s = r_0/a_H$; dabei ist a_H der erste Bohrsche Radius und r_0 der Radius einer Kugel, die ein Elektron enthält.

Density of states = number of states per unit energy range

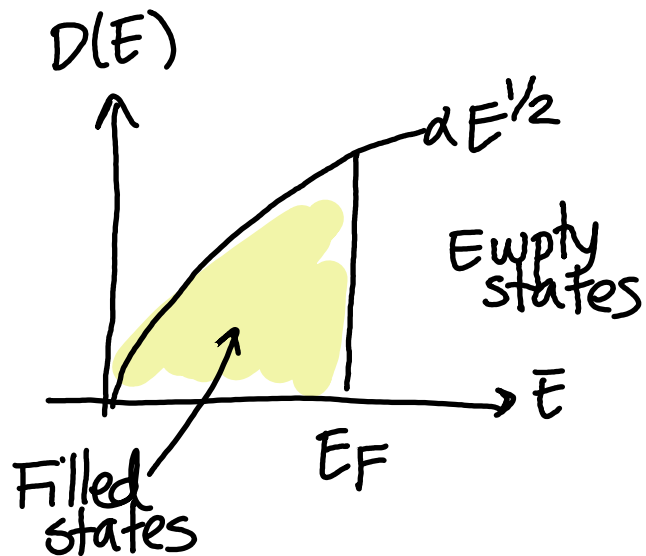


$$N(E) = \frac{V}{3\pi^2} K^3 = \frac{V}{3\pi^2} \left(\frac{2mE}{\hbar^2} \right)^{3/2}$$

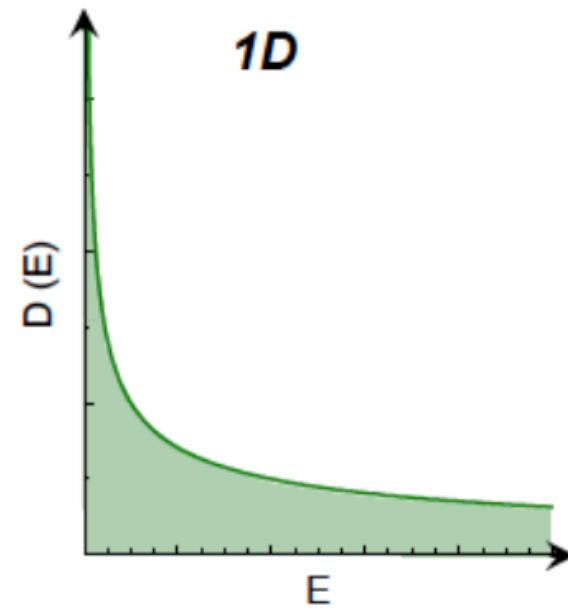
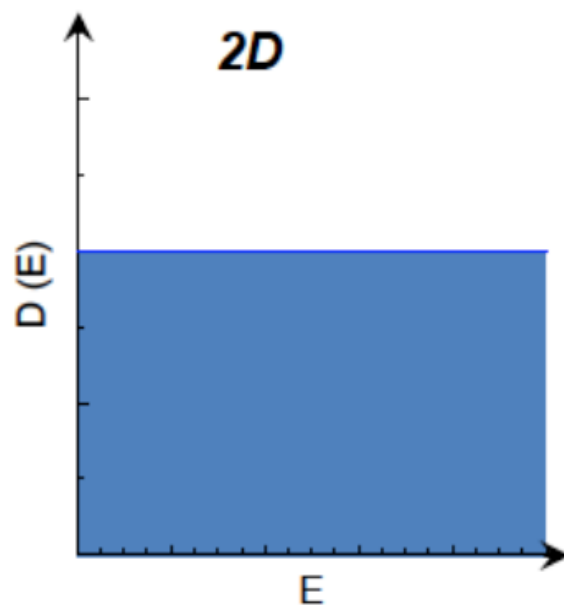
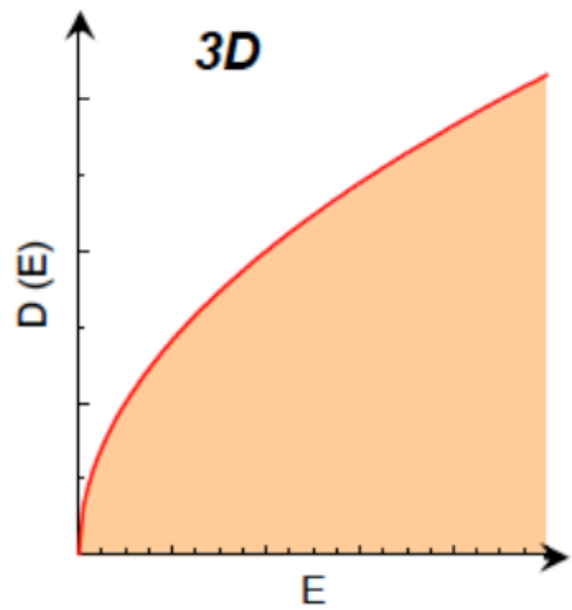
\uparrow
 $E = \frac{\hbar^2 K^2}{2m}$

Density of states: $D(E) = \frac{dN}{dE} = \frac{V}{3\pi^2} \frac{3}{2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{1/2}$

$$\Rightarrow D(E) = \frac{3}{2} \frac{N}{E}$$



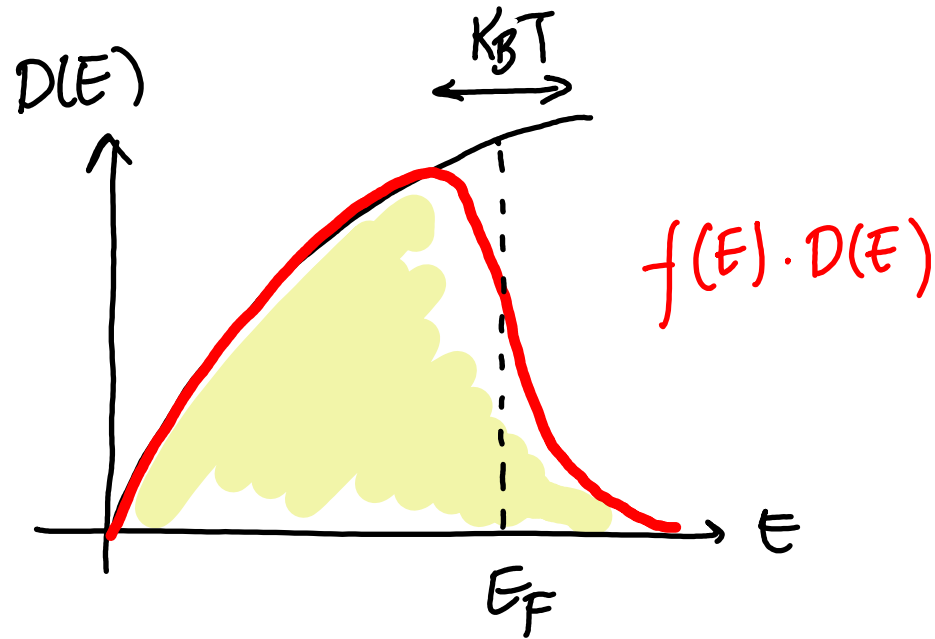
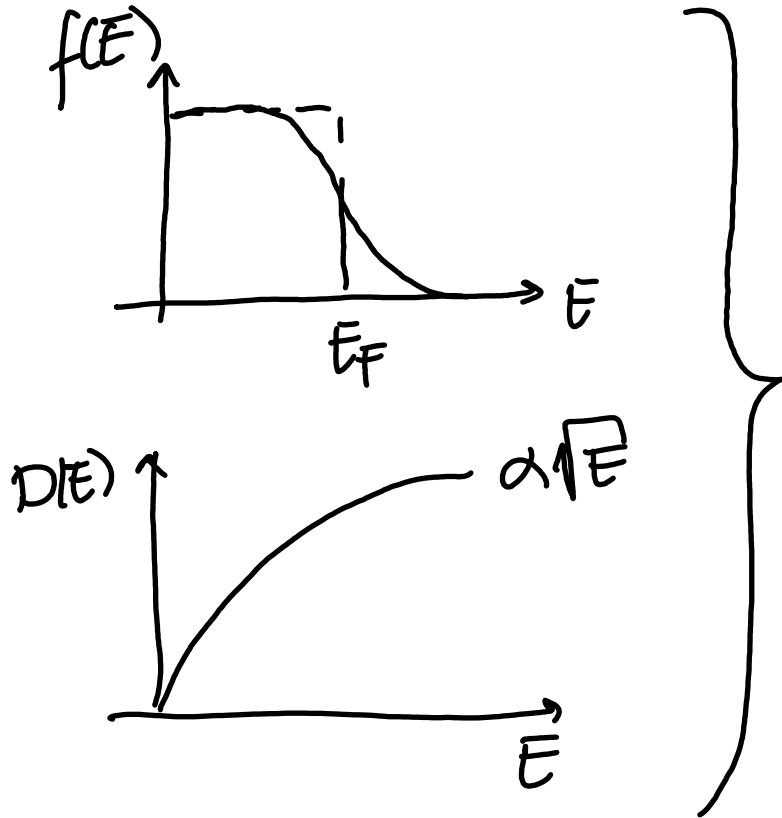
OK



Zustandsdichte für ein 1D-, 2D- und 3D-Elektronengas.

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

$T > 0K$ We should consider Fermi distribution: $N = \int_0^{\infty} D(E) \cdot f(E) \cdot dE$



Typical values for free electrons

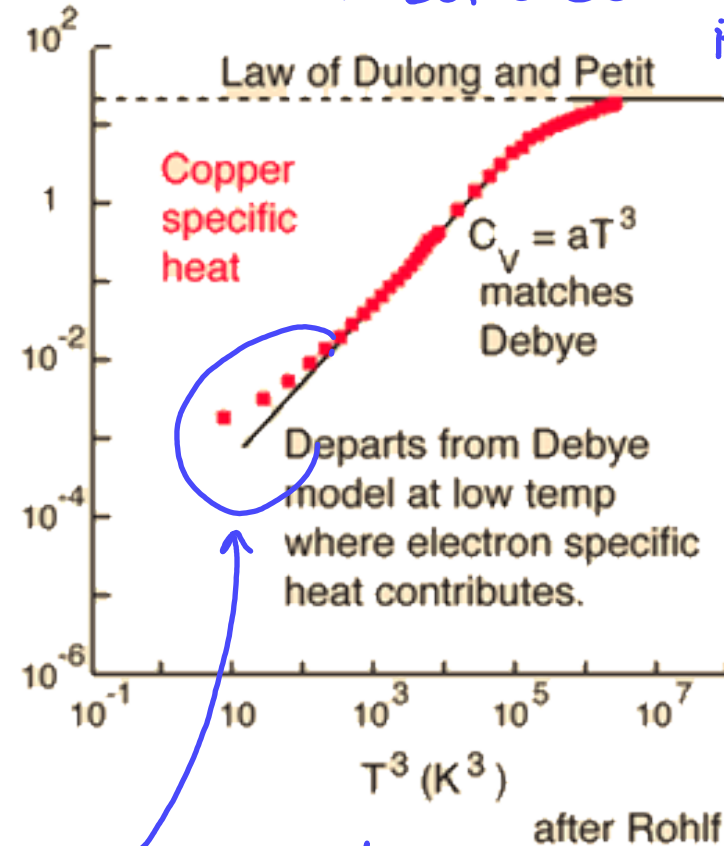
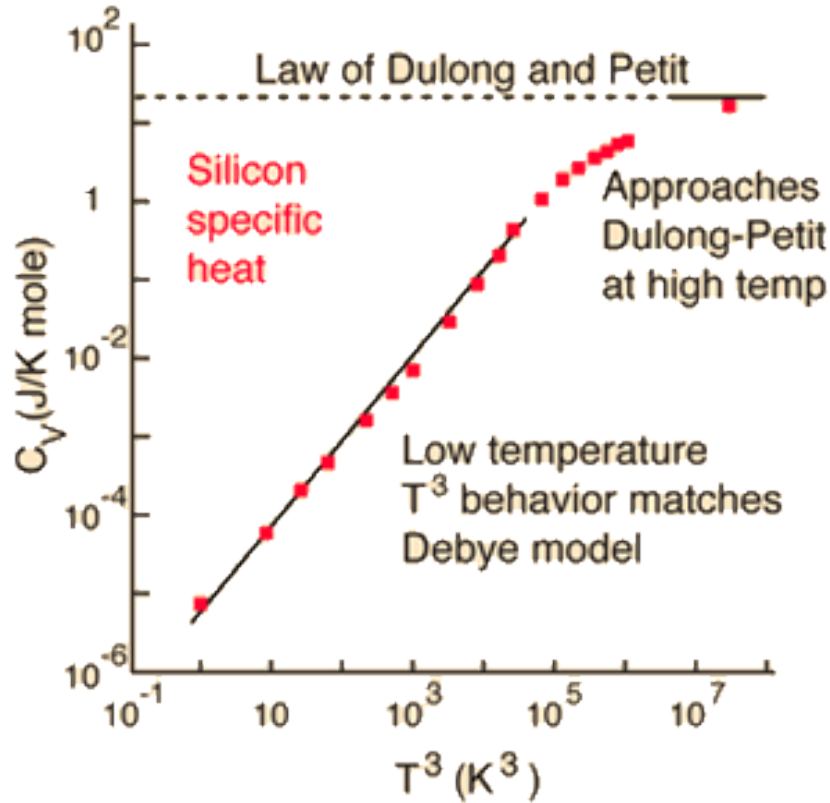
Metal	Valence	Fermi energy E_F	Fermi Temperature $T_F = E_F/k_B$
Li	1	4.72 eV	5.5×10^4 K
Na	1	3.23 eV	3.75×10^4 K
Al	3	11.63 eV	13.5×10^4 K

For typical metals, the Fermi energy temperature is much greater than ordinary temperatures
Transition from $f(E)=1$ to $f(E)=0$ is rather sharp at room temperature

Heat capacity of metals

Puzzle in C-metals: from classical statistics, one expects that electronic contribution to heat capacity $\sim \frac{3}{2} N K_B$ (if N atoms each giving $1 e^-$)

→ but observed value at low T is typically 0.01 smaller

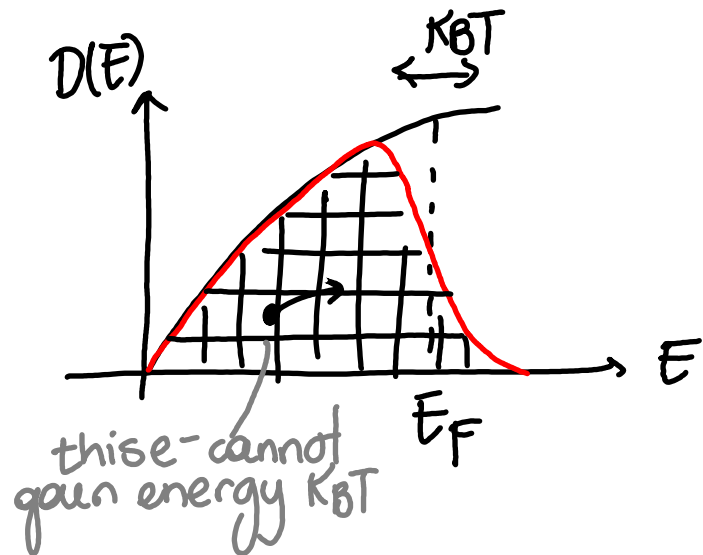


↓
Resolved when Pauli exclusion principle and Fermi distribution function were discovered

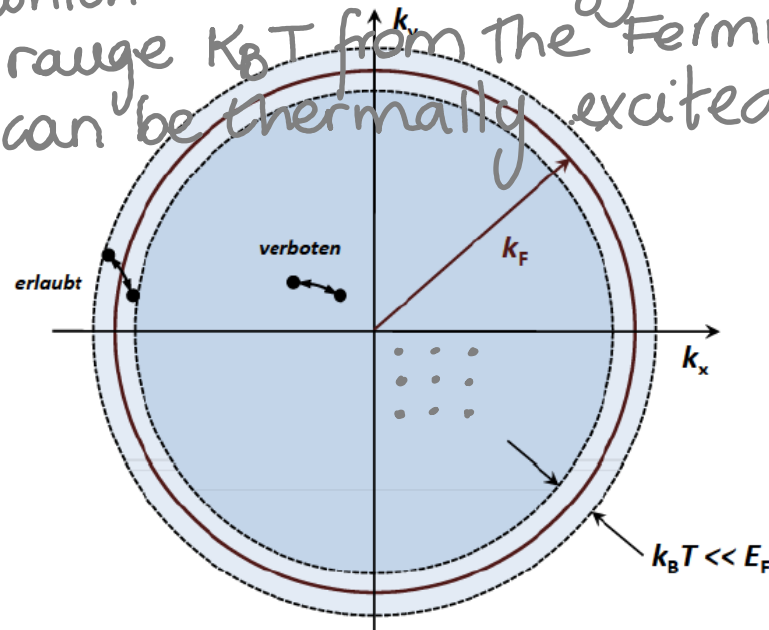
→ see

at low T it deviates from phonons results $C_{ph} \propto T^3$ instead, in metals $C \propto T$ at low T

Heat capacity of electrons



Not every electron gains an energy $\sim K_B T$ as expected classically but only those which have the energy within a range $K_B T$ from the Fermi level can be thermally excited.



N : total number of electrons

only fraction $\frac{K_B T}{E_F}$ of e^- can be excited at T

$$\Rightarrow U = N \left(\frac{K_B T}{E_F} \right) \underbrace{K_B T}_{\text{energy } e^-}$$

$$\Rightarrow C_{el} = \left[\frac{dU}{dT} \right] \sim N K_B \left(\frac{K_B T}{E_F} \right) \rightarrow \boxed{C_{el} \propto T} \text{ in agreement with experiment}$$

at RT, C_{el} is smaller than classical value $\sim K_B T$ by a factor of 0.01 (in agreement with experiment)

Only electron states near E_F participate in excitation processes

Heat capacity of electrons

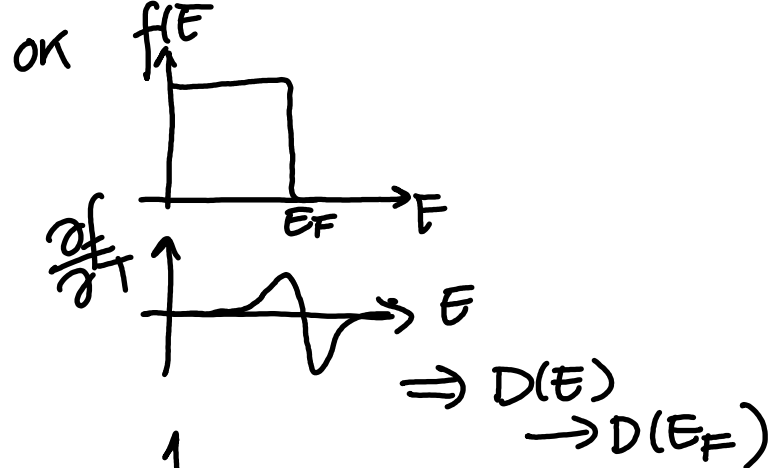
Total Energy for a system of $N e^-$

$$U(T) = \int_0^{\infty} \underbrace{D(E)}_{\text{Density of states}} \cdot E \cdot \underbrace{f(E,T)}_{\text{Fermi Dirac Distribution function}} dE$$

Density of states

Fermi Dirac Distribution function

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



$$\text{Heat Capacity } C = \frac{dU}{dT} = \int_0^{\infty} E D(E) \frac{df(E,T)}{dT} dE = \int_0^{\infty} (E - E_F) D(E) \frac{df(E,T)}{dT} dE$$

Remember $N = \int_0^{\infty} D(E) \cdot f(E) \cdot dE \Rightarrow 0 = E_F \frac{dN}{dT} = E_F \int_0^{\infty} D(E) \cdot \frac{df}{dT} dE$

Considering $k_B T \ll E_F$: $D(E) \rightarrow D(E_F)$ and assuming $\mu = E_F$:

$$\boxed{C_{el} = D(E_F) k_B^2 T \int_{-\infty}^0 \frac{x^2 (k_B T)^3}{k_B T^2} \frac{e^x}{(e^x + 1)^2} dx = \frac{\pi^2}{3} D(E_F) k_B^2 T = \frac{\pi^2}{2} N k_B \frac{T}{T_F}} \quad C_{el} = \gamma T$$

with $x \equiv \frac{E - E_F}{k_B T}$

$D(E) = \frac{N}{E_F}$
 $E_F = k_B T_F$

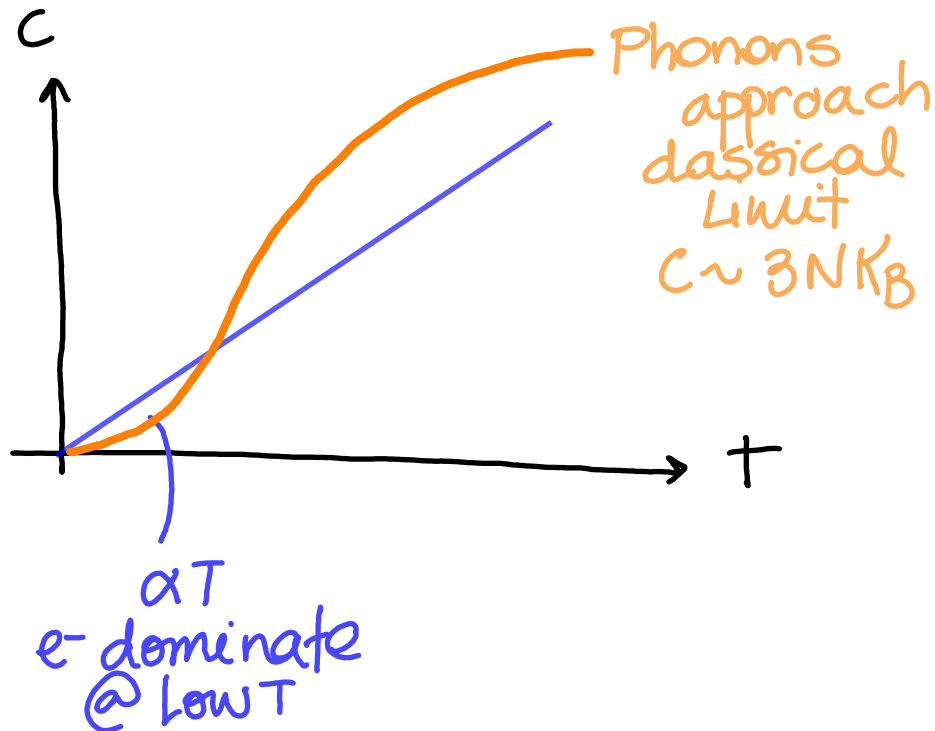
Heat capacity of metals

$$C = C_{el} + C_{ph} = \gamma T + AT^3$$

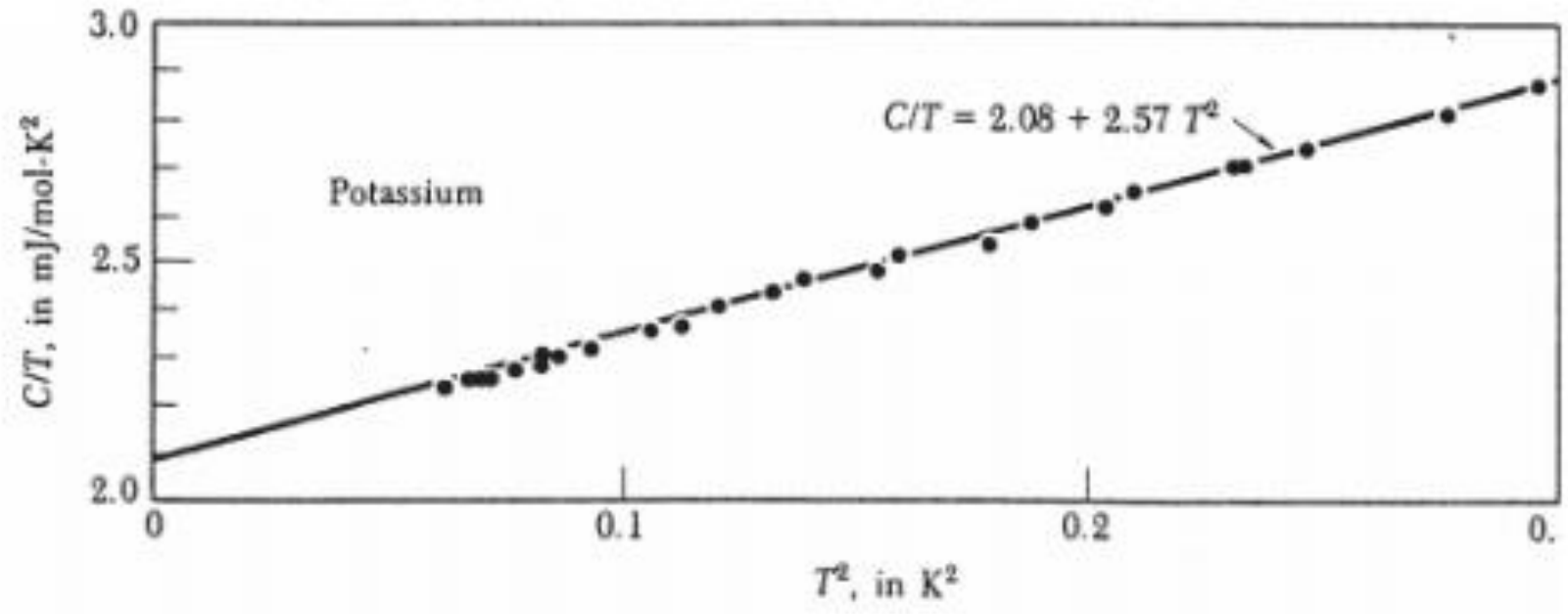
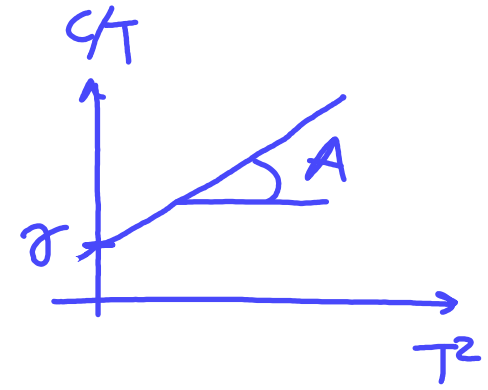
Electronic term
dominates at
Low Temp.

Constants γ and A can be obtained from experimental fitting.

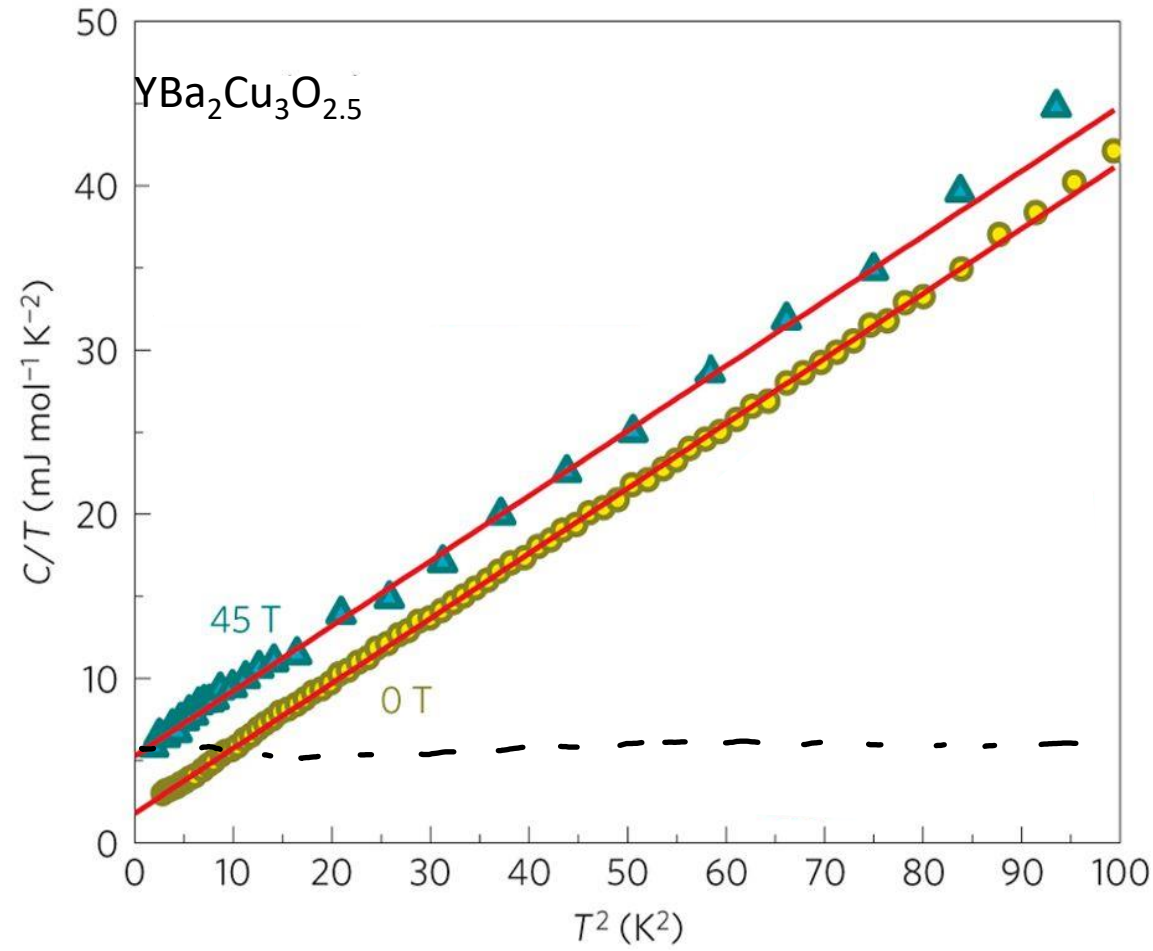
Note that from γ one can calculate $D(E_F)$ for metals



$$C = \gamma T + AT^3 \rightarrow \text{often convenient to plot: } \frac{C}{T} = \gamma + AT^2$$



Experimental heat capacitance



$$\gamma(\text{observed}) = \frac{5 \text{ mJ}}{\text{mol K}^2}$$

S. Riggs *et al.*, *Nature Physics* 7, 332 (2011)

Low temperature heat capacity coefficient for some metals

in units of 10^{-4} J/(mol-K)

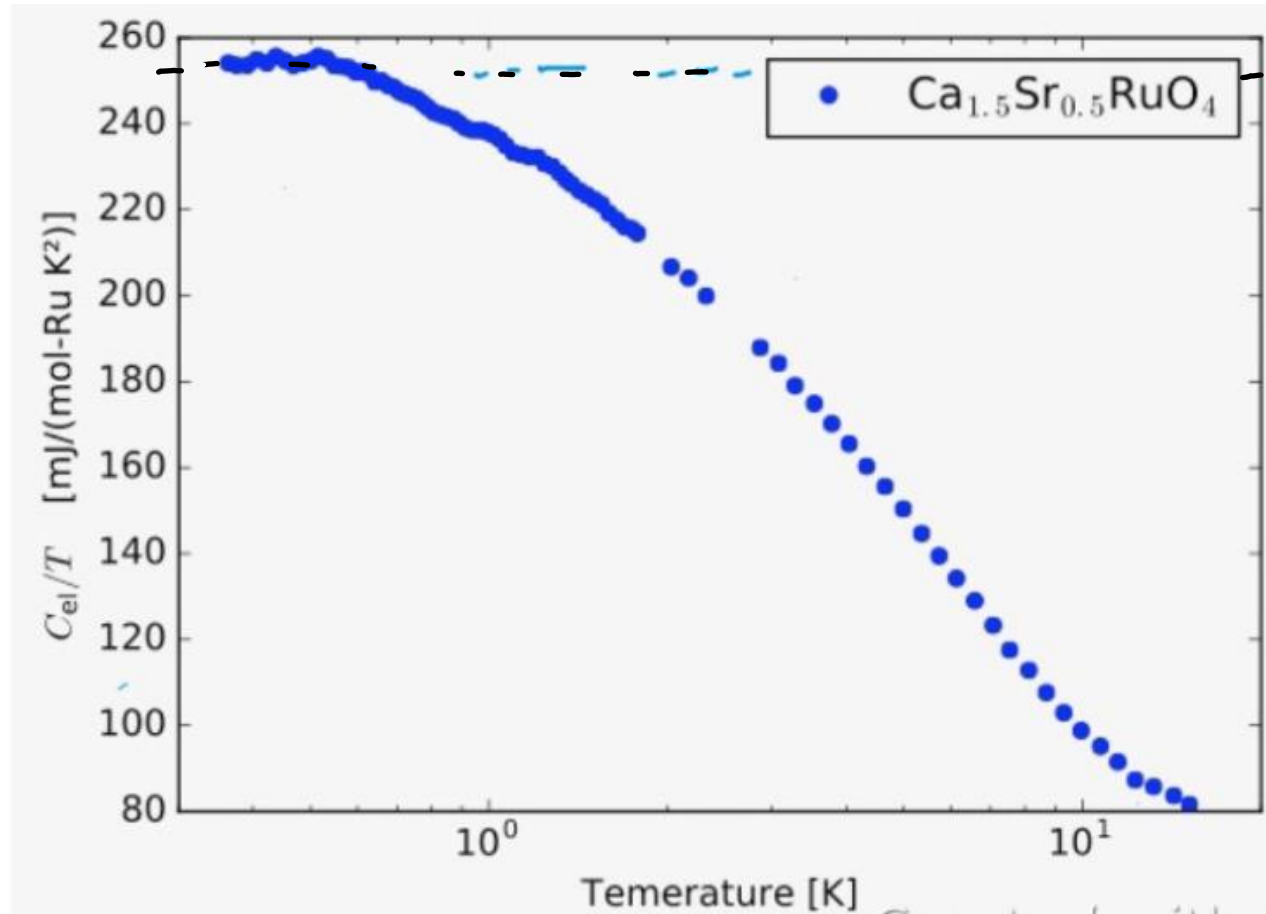
Material	γ_{exp}	γ_{th}
Li	18	7.4
Na	15	11
K	20	17
Cu	7	5.0
Ag	7	6.4
Be	2	2.5
Bi	1	5.0
Mn	170	5.2

thermal effective mass

$$\frac{m_{th}}{m} = \frac{\gamma(\text{observed})}{\gamma(\text{free } e^- \text{ calculation})}$$

(because interaction of conduction e^- with phonons, with other e^- , ... has not been considered)

Heavy fermions



huge

— $\gamma(\text{observed})$
 $= 250 \frac{\text{mJ}}{\text{mol K}^2} !!$

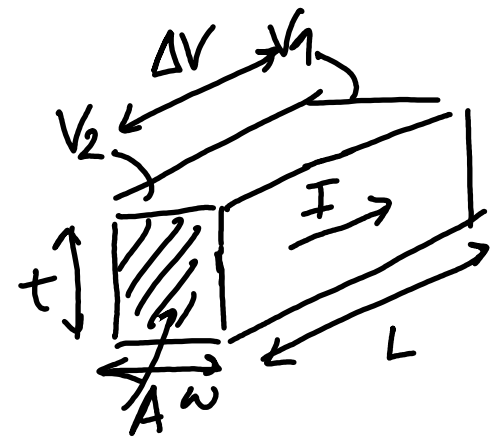
Electronic transport - Drude model

4 major assumptions

- Electrons are treated as classical particles within free electron model approximation.
- Electrons move freely only between collisions with scattering centers.
- An electron experience a collision with a probability $1/\tau$.
 τ =relaxation time (collision time), i.e. average time between two consecutive scattering events
- Electrons achieve thermal equilibrium with their surroundings only through collisions.

Drude model for electrical conductivity

Ohm's Law $V = IR$
 $\underbrace{\hspace{1.5cm}}$ Resistance (depends on dimensions)



Current density: $\boxed{\vec{j} = \sigma \vec{E}}$ $\sigma = \text{conductivity}$

$$\left. \begin{array}{l} j = \frac{I}{A} \\ v = E \cdot L \end{array} \right\} \frac{I}{A} = \sigma \frac{V}{L} \Rightarrow R = \frac{L}{\sigma A} = \rho \frac{L}{A} = \rho \frac{L}{wt}$$

resistivity $\rho = \frac{1}{\sigma} = \frac{A}{L} R$

property of the material
 it does not depend on dimensions

$$[\rho]: \Omega \cdot m$$

$$[\sigma]: S/m$$

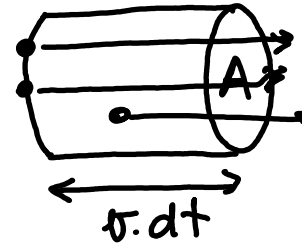
" ∇ in microscopic quantities"

n : e⁻ per unit volume

v : velocity of e⁻ \Rightarrow current density will be $\parallel v$

$n(v \cdot dt)A$: number of e⁻ that will cross area $A \perp$ to the flow

$-e$: charge of e⁻



Current density: $\left[\vec{j} = -ne\vec{v} \right]$
(charge crossing A in time dt)
average electronic velocity or drift velocity

$$* E = 0 \Rightarrow \langle v \rangle = 0 \Rightarrow j = 0$$

* $E \neq 0 \Rightarrow$ drift velocity will opposite to the field

@ $t_0 = 0, \vec{v}_0$

@ time t since the last collision, $\vec{v}_0 + \left(\frac{-eE t}{m} \right)$

since direction
is assumed randomly.
after collision: \vec{v}_0 contribution
to average electronic
velocity $\rightarrow 0$

\Rightarrow Drift velocity: $\boxed{\vec{v} = - \frac{eE\tau}{m}}$

\Rightarrow Current density: $\boxed{\vec{j} = -ne\vec{v} = - \frac{ne^2\tau}{m} \vec{E}}$

conductivity $\boxed{\sigma = \frac{ne^2\tau}{m}}$

• relaxation time values can be determined
from electrical conductivity measurements

metals: typically $\rho_{RT} \sim 1-10 \mu\Omega \text{ cm} \Rightarrow \tau \sim 10^{-14} \text{ s}$