

Heat Capacity of the Quantum Free Electron Gas

Actual electron population distribution (density),

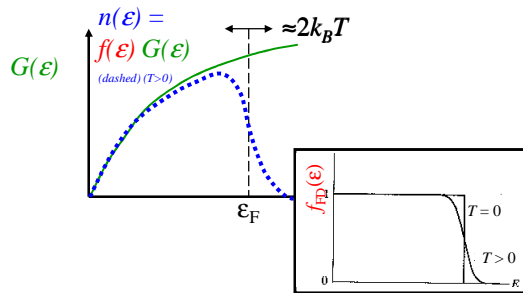
$n(\epsilon) = \text{probability distribution function} \times \text{density of states function}$

So at temperature T the total energy of electrons is: $\epsilon_{el} = \int_0^\infty \epsilon f(\epsilon) G(\epsilon) d\epsilon = \int_0^\infty \frac{\epsilon G(\epsilon)}{e^{(\epsilon - \epsilon_F)/kT} + 1} d\epsilon$, and $C_{el} = \frac{d\epsilon_{el}}{dT}$

The exact answer to this complicated integral is derived in more advanced texts:

$$C_{el} = \frac{\pi^2}{3} k_B^2 G(\epsilon_F) T \quad \boxed{C_{el} \propto T!}$$

- So why does this “quantum” derivation give a different answer to that derived using a classical description?
- Because we should only consider electrons that can actually be excited, and not count those that can't. *i.e.*, only those within $k_B T$ of ϵ_F



A Rough and Ready Estimate of C_{el}

We can estimate C_{el} in just a few lines in order to confirm the linear dependence on temperature:

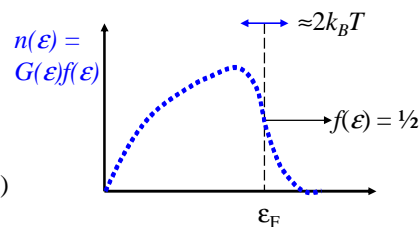
$$\begin{aligned} \# \text{ electrons that can absorb thermal energy} &\cong (2k_B T) G(\epsilon_F) \overbrace{f(\epsilon_F)}^{1/2} \\ &\cong k_B T G(\epsilon_F) \end{aligned}$$

$$\begin{aligned} \text{total thermal energy of electrons at } T &\epsilon(T) \cong \epsilon_0 + \left(\frac{3}{2} k_B T\right) k_B T G(\epsilon_F) \\ &\epsilon(T) \cong \epsilon_0 + \frac{3}{2} k_B^2 T^2 G(\epsilon_F) \end{aligned}$$

$$\text{FEG heat capacity at } T \quad C_{el} = \frac{d\epsilon_{el}}{dT} \cong 3k_B^2 G(\epsilon_F) T$$

The above approximation is remarkably close to the exact result!

$$\boxed{C_{el} = \frac{\pi^2}{3} k_B^2 G(\epsilon_F) T = \gamma T}$$



Heat Capacity of Metals: Theory vs. Expt. at low T

But this linear dependence is impossible to measure directly, since the heat capacity of a **REAL** metal has two contributions:

$$C(T) = C_{el} + C_{lattice} = \gamma T + \alpha T^3$$

dominant term for **VERY** low temperatures

Very low temperature measurements reveal γ (Sommerfeld parameter) by plotting C/T vs $T^2 \rightarrow$

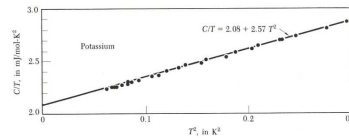


Figure 9 Experimental heat capacity values for potassium, plotted as C/T versus T^2 . (After W. H. Linden and N. E. Phillips.)

Results for simple metals (in units mJ/mol K) show that the FEG values are in reasonable agreement with experiment, but are always too high:

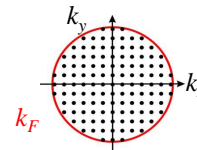
Metal	γ_{expt}	γ_{FEG}	$\gamma_{\text{expt}}/\gamma_{\text{FEG}} = m^*/m$
Li	1.63	0.749	2.18
Na	1.38	1.094	1.26
K	2.08	1.668	1.25
Cu	0.695	0.505	1.38
Ag	0.646	0.645	1.00
Au	0.729	0.642	1.14
Al	1.35	0.912	1.48

The discrepancy is accounted for by defining an **effective electron mass m^*** (later) that is due to the neglected electron-ion and electron-electron interactions



Electrical conductivity in reciprocal space (the “quantum picture”)

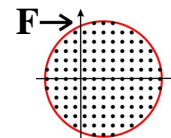
- In the absence of an electric field ($\mathbf{F} = 0$), there are the same number of electrons moving in the $\pm x$, $\pm y$, and $\pm z$ directions, so the net current is zero (symmetry)



- But when a field E is applied along the x -direction, $F = -eE = dp/dt = \hbar \delta k / \delta t = \hbar \Delta k / \tau$ the Fermi sphere is shifted by an amount related to the net change in momentum of the FEG:

- Every orbital has its k -vector changed by $\Delta k = -eE\tau/\hbar$ *i.e* whole Fermi sphere is displaced.
- This creates a net current flow since more electrons move in the $+x$ direction than the $-x$ direction. So the incremental velocity is $v = \hbar \Delta k / m = -eE\tau / m$
- And, in a constant electric field E : (Ohm’s Law)

τ is collision time (collisions maintain steady state)



$$J = N_e q v = N_e q (\hbar \Delta k / m) = N_e e^2 \tau E / m = \sigma E$$

$$\sigma = \left(\frac{N_e e^2 \tau}{m} \right)$$



Quantum version of the Wiedemann–Franz Law and Lorenz Number

Our quantum description gives the correct L ...

Use the simple form of the DoS (quantum) in the box on slide 2-5 together with the equation for C_{el} (3-1) to get the heat capacity of the quantum FEG per unit volume:

$$C'_{el} = \frac{\pi^2}{2} k_B^2 N_{el} \frac{T}{\mathcal{E}_F}$$

The thermal conductivity per unit volume is , $K' = \frac{\pi^2 k_B^2 N_{el} \tau T}{3m}$

$$L_{QFEG} = \frac{K}{\sigma T} = \frac{\pi^2 k_B^2}{3e^2} = 2.45 \times 10^{-8} \left(\frac{J}{CK} \right)^2$$

Note: This is independent of N_{el} , m , and even τ !!

The agreement with experiment (right) is quite good, although the value of L is about a factor of 10 less at temperatures near 10K... more at end of course.

	L = $\kappa/\sigma T$ 10^{-8} (J/CK) ²	
Metal	0 °C	100 °C
Cu	2.23	2.33
Ag	2.31	2.37
Au	2.35	2.40
Zn	2.31	2.33
Cd	2.42	2.43
Mo	2.61	2.79
Pb	2.47	2.56



Limitations of the Quantum FEG Model—and Beyond

As we've seen, the FEG model of Drude plus QM can predict many of the basic properties of metals (*e.g.* heat capacity, electrical and thermal conductivity, WF-law). However, strict quantitative agreement with experiment is not achieved.

Importantly, it does not explain why some materials are metals, some insulators and some are semiconductors

That leads to the question: How do the electrons respond to an applied field?

Electrons in the crystal are arranged in bands separated by gaps in which there are no allowed electron states.

These energy/band gaps result from the interaction of the electron wavefunction with the periodic potential of the ion cores.

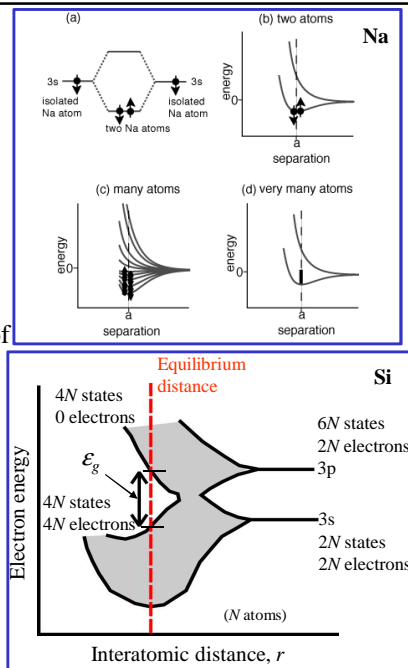
Therefore we must take into account the periodic lattice, which leads to the concept of effective mass (later)

We continue to ignore interactions between electrons (we use the single electron Schrodinger equation). Why is this valid?



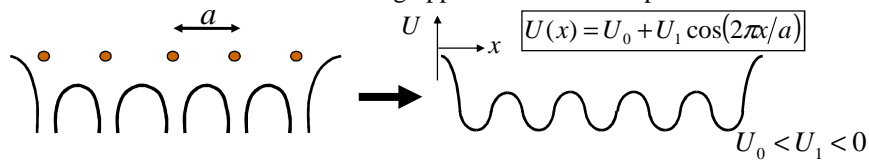
The Idea of Energy Bands and Gaps!

- Consider Na, valency 1 (3s)
- (a,b) Bonding and antibonding energy levels and their occupation for a molecule of two Na atoms. The interaction yields two levels that are delocalised over entire structure.
- (c) For N atoms, the N energy levels will split into N non-degenerate molecular levels/ Half of these will be occupied by 2 electrons each.
- (d) There is a quasi-continuum (i.e. band) of states between the lowest and highest filled states. The Fermi level lies so that the band is half filled: metal (WHY?)
- In Si, we see quite a different behaviour... Silicon is a non-metal, with a band gap (e_g)



Nearly free electron gas model

- The lattice periodicity has the effect that the electron wavefunctions are no longer sinusoidal traveling waves of constant amplitude, instead exhibiting the lattice periodicity in their amplitudes
- The electrons may be scattered by the lattice. When the de-Broglie wavelength of the electron corresponds to a periodicity in the spacing of the ions the electron interacts particularly strongly with the lattice **Bragg Scattering**
- Bragg reflection of electron waves is the cause of energy gaps, which in turn dictate the conductivity of the material
- The model we use makes the following approximation of the potential:



Nearly free electron gas model: Electron Wavefunctions in a Periodic Potential

Now consider the following cases (solutions to 1D time-independent SE, [slide 2-5](#)) :

$U_1 = 0$ Wavefunctions are plane waves and energy bands are parabolic: $\psi = Ae^{i(kx-\alpha t)}$ $\epsilon = \frac{\hbar^2 k^2}{2m}$ **i.e., Free Electron Gas ($m_e = m_0$, later!)**

$U_1 \neq 0$
 $k \ll \frac{\pi}{a}$ Electrons wavelengths much larger than a , so wave functions and energy bands are nearly the same as above

$U_1 \neq 0$
 $k \leq \frac{\pi}{a}$ Electrons wavelengths approach a , so waves begin to be strongly back-scattered :

$$\psi_{\pm} = Ae^{i(kx-\alpha t)} \pm Be^{-i(kx-\alpha t)} \quad B < A$$

$U_1 \neq 0$
 $k = \frac{\pi}{a}$ Electron waves are strongly back-scattered (Bragg scattering) so standing waves are formed:

$$\psi_{\pm} = C(e^{i(kx-\alpha t)} \pm e^{-i(kx-\alpha t)}) = \frac{1}{\sqrt{2}} A(e^{ikx} \pm e^{-ikx})e^{-i\alpha t}$$