

# Electronic Properties of Metals

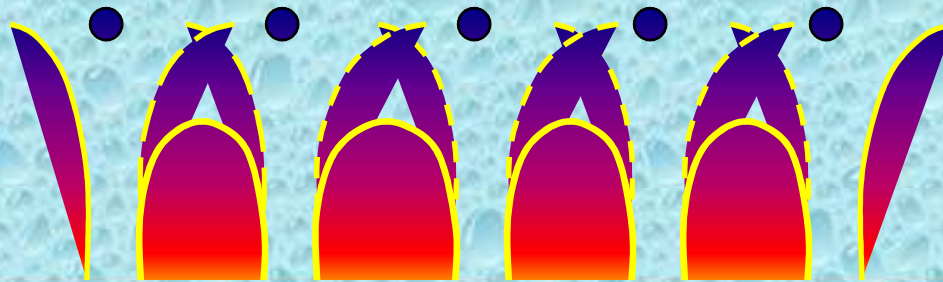
- A. The Free Electron Gas (FEG) Model
- B. Properties of the FEG: Fermi Energy  $E_F$  and Density of States  $N(E)$
- C. Heat Capacity of the FEG



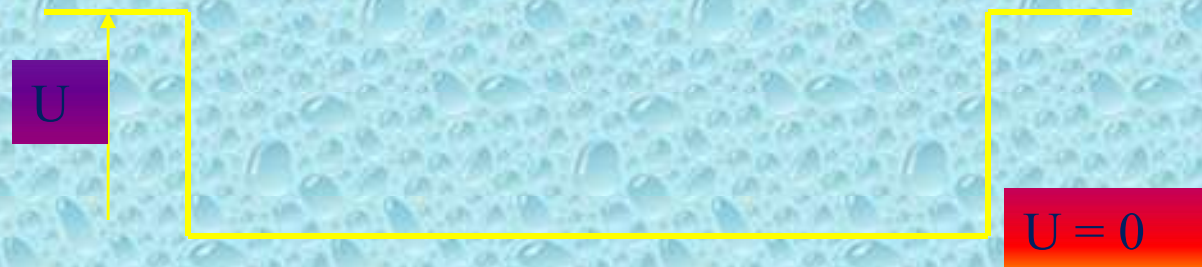
Having studied the structural arrangements of atoms in solids, and the thermal and vibrational properties of the lattice, we now consider the electronic properties of solids in terms of a very simple model.

## A. The Free Electron Gas Model

Plot  $U(x)$  for a 1-D crystal lattice:



Simple and crude finite-square-well model:



Can we justify this model? How can one replace the entire lattice by a constant (zero) potential?



## E. Heat Capacity of the FEG

19<sup>th</sup> century puzzle: each monatomic gas molecule in sample at temperature  $T$  has energy  $\frac{3}{2}kT$ , so if the  $N$  free electrons in a metal make up a classical “gas” they should behave similarly.

$$E_{el} = N\left(\frac{3}{2}kT\right)$$

or expressed per mole:

$$\frac{E_{el}}{n} = \frac{3}{2} \frac{N}{n} kT = \frac{3}{2} N_A kT = \frac{3}{2} RT$$

So the electronic contribution to the molar heat capacity would be expected to be

$$C_{el} = \frac{d}{dT} \left( \frac{E_{el}}{n} \right) = \frac{3}{2} R$$

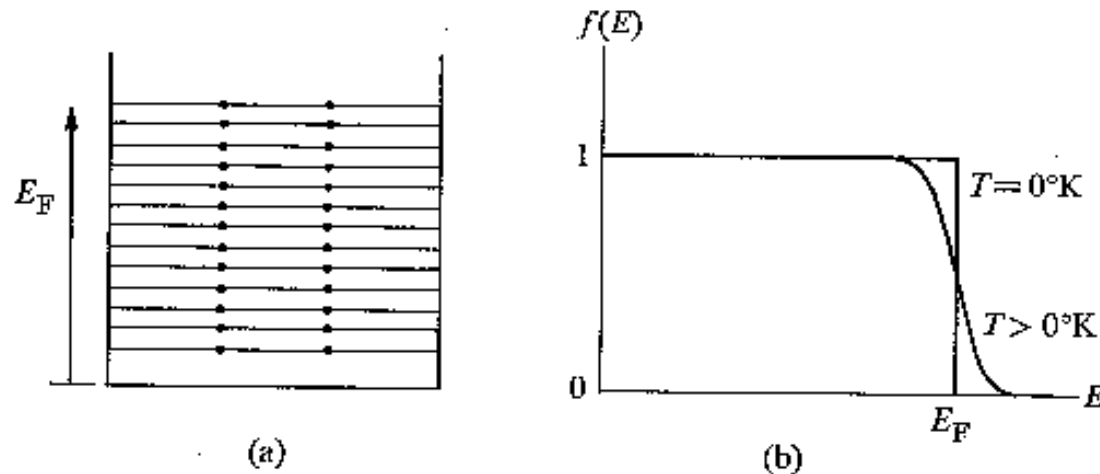
This is half of the  $3R$  we found for the lattice heat capacity at high  $T$ . But experiments show that the total  $C$  for metals is only slightly higher than for insulators—which conflicts with the classical theory!

# Heat Capacity of the Quantum-Mechanical FEG

Quantum mechanics showed that the occupation of electron states is governed by the Pauli exclusion principle, and that the probability of occupation of a state with energy  $E$  at temperature  $T$  is:

$$f(E) = \frac{1}{e^{(E-\mu)/kT} + 1}$$

where  $\mu =$  chemical potential  $\approx E_F$  for  $kT \ll E_F$



**Fig. 4.6** (a) Occupation of energy levels according to the Pauli exclusion principle. (b) The distribution function  $f(E)$  versus  $E$ , at  $T = 0^\circ\text{K}$  and  $T > 0^\circ\text{K}$ .



# Heat Capacity of the Quantum-Mechanical FEG

So at temperature  $T$   
the total energy is:

$$E_{el} = \int_0^{\infty} E f(E) N(E) dE = \int_0^{\infty} \frac{EN(E)}{e^{(E-E_F)/kT} + 1} dE$$

And the electronic  
heat capacity is:

$$C_{el} = \frac{dE_{el}}{dT} = \frac{1}{kT^2} \int_0^{\infty} \frac{EN(E)(E - E_F)e^{(E-E_F)/kT}}{(e^{(E-E_F)/kT} + 1)^2} dE$$

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

$$C_{el} = \frac{\pi^2}{3} k^2 N(E_F) T$$

$$C_{el} \propto T!$$

## A Rough and Ready Estimate

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

# electrons that  
can absorb  
thermal energy

$$\begin{aligned} &\cong (2kT) N(E_F) f(E_F) \\ &\cong kT N(E_F) \end{aligned}$$

total thermal energy  
of electrons at T

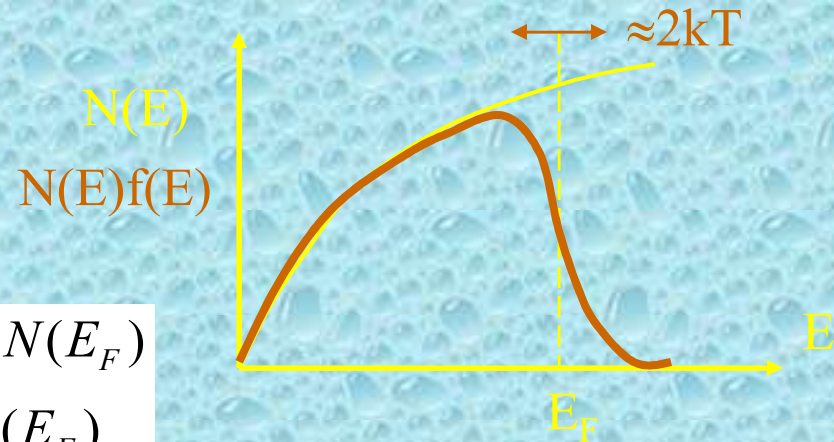
$$\begin{aligned} E(T) &\cong E_0 + \left(\frac{3}{2} kT\right) kT N(E_F) \\ E(T) &\cong E_0 + \frac{3}{2} k^2 T^2 N(E_F) \end{aligned}$$

FEG heat  
capacity at T

$$C_{el} = \frac{dE_{el}}{dT} \cong 3k^2 N(E_F) T$$

Remarkably close  
to the exact result!

$$C_{el} = \frac{\pi^2}{3} k^2 N(E_F) T = \gamma T$$



But this linear dependence is impossible to measure directly, since the heat capacity of a metal has two contributions. Now for a metal at low temperatures we can write the total heat capacity:

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

Assuming we can measure  $C(T)$  for a metal, how can we test this relationship?



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

Very low temperature measurements reveal:

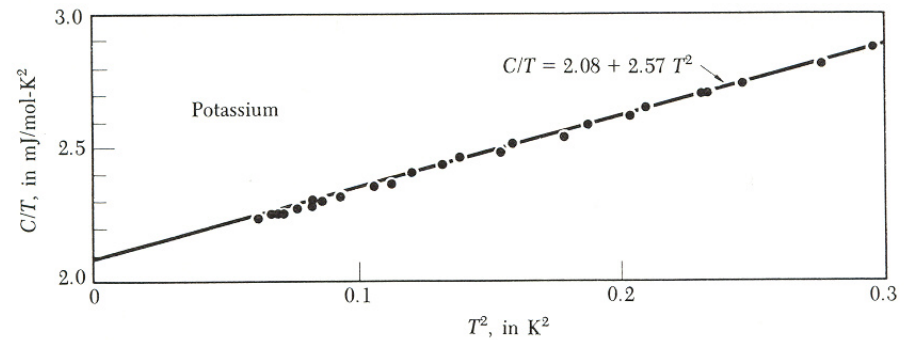


Figure 9 Experimental heat capacity values for potassium, plotted as  $C/T$  versus  $T^2$ . (After W. H. Lien and N. E. Phillips.)

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	$\gamma_{\text{expt}}$	$\gamma_{\text{FEG}}$	$\gamma_{\text{expt}}/\gamma_{\text{FEG}} = m^*/m$
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  $m^*$  that is due to the neglected electron-ion interactions