



Metals – A First Glimpse



The Metallic Question

- Why do metals have “high” bulk modulus?
- Main new ideas
 - Three Dimensional Problems in QM
 - 3D Particle in a Box
 - Degeneracy and Density of States
 - Fermi Energy
- How many electrons are there per unit volume in a metal?



Higher Dimensions

- Essentially no difference!
- State is described by $\Psi(\mathbf{r}, t)$
- Position operator R , $\langle R \rangle = \int \Psi^*(\mathbf{r}, t) \mathbf{r} \Psi(\mathbf{r}, t) d\mathbf{r}$
- Momentum operator $P = -i\hbar \nabla$
- Commutation relation $[R_i, P_j] = i\hbar \delta_{ij}!$
- Schrödinger equation $i\hbar \frac{\partial \Psi}{\partial t} = H\Psi$
- Our first example will be a metal



Particle in a 3D box - Simplest Model of a Metal

- Particles confined to $0 \leq x_1 \leq L, 0 \leq x_2 \leq L, 0 \leq x_3 \leq L$
- $\psi(x_1, x_2, x_3)$ vanishes on the faces of the box
- Energy eigenstates satisfy
$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial x_3^2} \right) \psi = E\psi$$
- Energy levels are given by

$$E_{n_1, n_2, n_3} = \frac{\hbar^2 \pi^2}{2mL^2} (n_1^2 + n_2^2 + n_3^2)$$

- Eigenstate ($V = L^3$) $\psi_{n_1, n_2, n_3}(x_1, x_2, x_3) = \sqrt{\frac{8}{V}} \sin\left(\frac{n_1 \pi x_1}{L}\right) \sin\left(\frac{n_2 \pi x_2}{L}\right) \sin\left(\frac{n_3 \pi x_3}{L}\right)$



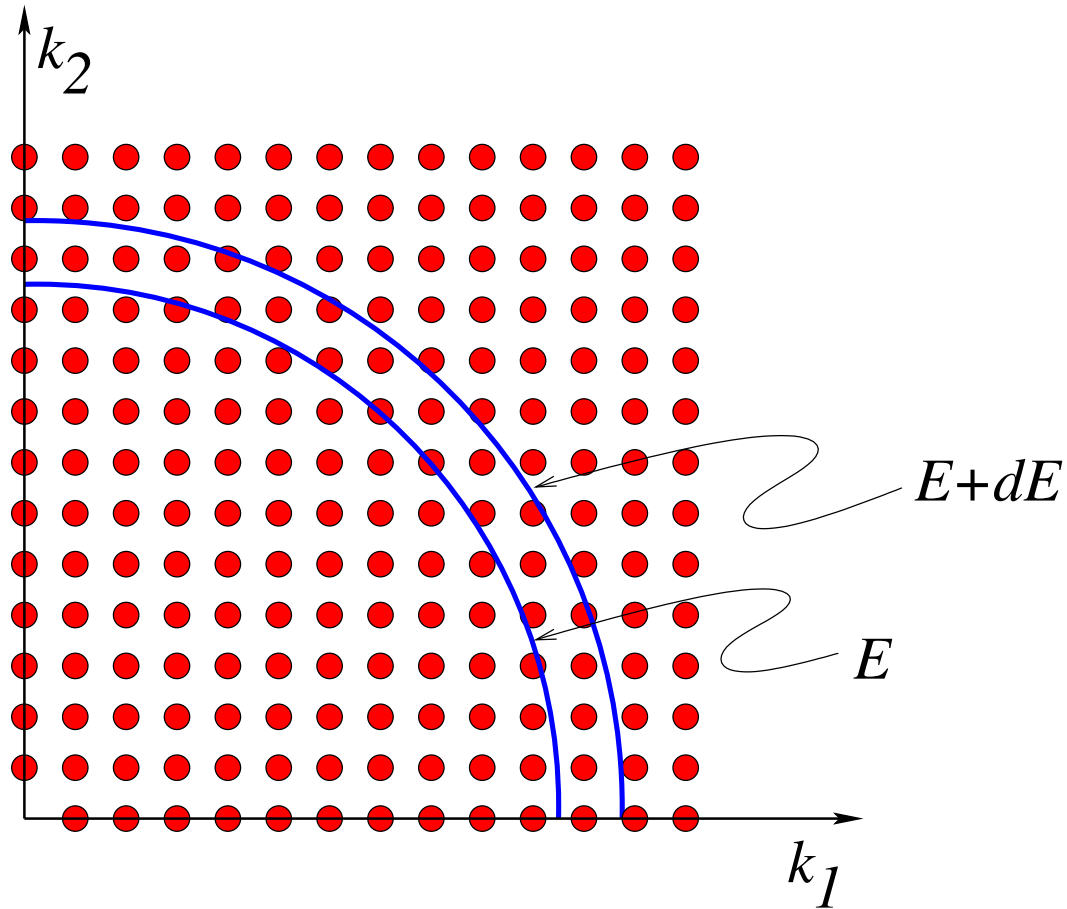
Particle in a 3D Box

- What is the ground state (lowest energy state)?
- Corresponds to $n_1 = 1, n_2 = 0, n_3 = 0$
- Hey, also $n_1 = 0, n_2 = 1, n_3 = 0$ and $n_1 = 0, n_2 = 0, n_3 = 1$
- There are three different (in fact, orthogonal) wavefunctions which have the ground state energy!
- The ground state is termed “degenerate”, in this case, three fold degenerate
- If we call $k_1 = \frac{n_1\pi}{L}$, etc.,

$$E_{k_1, k_2, k_3} = \frac{\hbar^2}{2m} (k_1^2 + k_2^2 + k_3^2)$$

Particle in a 3D Box

- The states can be depicted in k -space





How do we use this to study metals?

- Take number density of electrons to be ρ
- Have to accommodate $N = \rho V$ electrons
- Each energy state (k_1, k_2, k_3) can accommodate only two electrons (of different spin...Pauli's principle)!
- Question: What will be the highest occupied energy level?
- Best studied using the concept of density of states (which will appear in all of solid state physics)!
- Density of states: $g(E)$ defined as number of states between E and $E + dE$
- What is the density of states for free electrons?



The Fermi Energy

- As we add more electrons, the set of occupied states starts to look like a sphere in k -space
- The radius of the k -space sphere when all electrons have been accommodated is k_F
- Number of states per unit volume of k -space $= \left(\frac{2V}{\pi^3}\right)$ (the factor 2 accounts for spin)
- The total number of states in the sphere of $k_F = \left(\frac{2V}{\pi^3}\right) \cdot \frac{4\pi k_F^3}{24}$ must be N
- The radius of the “Fermi sphere” $k_F = (3\pi^2\rho)^{1/3}$
- The “Fermi energy” $E_F = \frac{\hbar^2}{2m}(3\pi^2\rho)^{2/3}$



Another way to The Fermi Energy

- Call $k^2 = k_1^2 + k_2^2 + k_3^2$, then $E_{k_1, k_2, k_3} = \frac{\hbar^2}{2m} k^2$
- The total number of states in a sphere of radius $k = \left(\frac{2V}{\pi^3}\right) \frac{4\pi k^3}{24} = \frac{V}{3\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} E^{3/2}$
- This implies density of states $g(E) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$
- Clearly, $\int_0^{E_F} g(E) dE = N$, implies $E_F = \frac{\hbar^2}{2m} (3\pi^2 \rho)^{2/3}$, in agreement with previous result



Fermi Energies in Metals

FERMI ENERGIES, FERMI TEMPERATURES, FERMI WAVE VECTORS, AND FERMI VELOCITIES FOR REPRESENTATIVE METALS^a

ELEMENT	r_s/a_0	ε_F	T_F	k_F	v_F
Li	3.25	4.74 eV	5.51×10^4 K	$1.12 \times 10^8 \text{ cm}^{-1}$	$1.29 \times 10^8 \text{ cm/sec}$
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
Be	1.87	14.3	16.6	1.94	2.25
Mg	2.66	7.08	8.23	1.36	1.58
Ca	3.27	4.69	5.44	1.11	1.28
Sr	3.57	3.93	4.57	1.02	1.18
Ba	3.71	3.64	4.23	0.98	1.13
Nb	3.07	5.32	6.18	1.18	1.37
Fe	2.12	11.1	13.0	1.71	1.98
Mn	2.14	10.9	12.7	1.70	1.96
Zn	2.30	9.47	11.0	1.58	1.83
Cd	2.59	7.47	8.68	1.40	1.62
Hg	2.65	7.13	8.29	1.37	1.58
Al	2.07	11.7	13.6	1.75	2.03
Ga	2.19	10.4	12.1	1.66	1.92
In	2.41	8.63	10.0	1.51	1.74
Tl	2.48	8.15	9.46	1.46	1.69
Sn	2.22	10.2	11.8	1.64	1.90
Pb	2.30	9.47	11.0	1.58	1.83
Bi	2.25	9.90	11.5	1.61	1.87
Sb	2.14	10.9	12.7	1.70	1.96

^a The table entries are calculated from the values of r_s/a_0 given in Table 1.1 using $m = 0.11 \times 10^{-28}$ grams

Ashcroft and Mermin



Total Energy

- Total energy U in the metal (at zero T)

$$U = \int_0^{E_F} E g(E) dE = \frac{3}{5} N E_F = \frac{3}{5} N \frac{\hbar^2}{2m} \left(3\pi^2 \frac{N}{V} \right)^{2/3}$$

goes as $V^{-\frac{2}{3}}$

- Pressure $P = -\frac{\partial U}{\partial V} = \frac{3}{5} U V$ varies as $V^{-\frac{5}{3}}$
- Bulk modulus $B = -V \frac{\partial P}{\partial V} = \frac{5}{3} P!$
- Compare with real data



Fermi Energies in Metals

BULK MODULI IN 10^{10} DYNES/CM² FOR SOME TYPICAL METALS^a

METAL	FREE ELECTRON B	MEASURED
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

Ashcroft and Mermin



Summary

- Took first steps outside 1D
- ...with great reward!
- A simple, yet powerful, model for metals
- Fermi energies are very large energies compared to usual thermal energies