Physics 489 S 04 Lecture 2
Quantum Theory of Metals (Ashcroft and Mermin chapter 2)
Equilibrium Properties

1. Overview
   In metals electrons are not "attached" to nuclei but are free to move
   Quantum Mechanics explains the two key points:
   - Electrons are able to move even at T=0, *unlike any classical picture*
   - Yet the contribution to specific heat is much less than expected classically

2. Experimental specific heat of solids
   Classical theory: $C_V = \frac{3}{2}k_B$ x total number of degrees of freedom: nuclei and electrons
   But classical value of $3k_B$ *per nucleus* found only at High T.
   Contribution of electrons much less than classical value.
   (Also $C_V \propto T^3$ at low T from nuclear contribution. More on this later.)

3. Quantum Mechanics and exclusion principle explain shell structure of atoms
   Pauli, Dirac and Fermi (1926-7) applied exclusion principle to free electrons
   Sommerfeld (1928) showed linear T-dependence from electrons, seen at low T.
   Predicted first - found experimentally later!

4. Homogeneous electron gas. Free, independent electrons.
   (Here we consider 3-dimensions; 2 dimensions given in homework.)
   Schrödinger equation with periodic boundary conditions inside cube of volume $V = L^3$
   Eigenstates labeled by $\mathbf{k} = \frac{2\pi}{L}(n_x, n_y, n_z)$ with $\psi_{\mathbf{k}} = e^{i\mathbf{k}\cdot\mathbf{r}}$; $E_{\mathbf{k}} = \frac{\hbar^2}{2m}k^2$
   Consider $\mathbf{k}$ as a vector: $\mathbf{p} = \hbar\mathbf{k}$; $\mathbf{v} = \frac{\hbar}{m}\mathbf{k}$
   Sums over eigenstates per unit volume always have the form $\frac{1}{V}\sum_{\mathbf{k}} f(\mathbf{k})$
   Volume of k-space occupied by each state $= (\frac{2\pi}{L})^3 = \frac{(2\pi)^3}{V}$
   In continuum limit we replace $\frac{1}{V}\sum_{\mathbf{k}} \rightarrow (\frac{1}{2\pi})^3 \int d^3\mathbf{k}$
   We will use this in crystals also!

5. Ground state
   As in atoms, fill states from the lowest energy levels, obeying exclusion principle.
   Highest occupied levels have Fermi wavevector k_F and Fermi energy $E_F = \frac{\hbar^2}{2m}k_F^2$
   Fermi surface in $\mathbf{k}$-space separates filled from empty states.
   Counting electrons leads to
   - $n = \frac{N}{V} = 2(\frac{1}{2\pi})^3 \int_{k<k_F} d^3\mathbf{k}$
   - or $n = \frac{2}{(2\pi)^3}\frac{4\pi}{3}k_F^3 = \frac{1}{3\pi^2}k_F^3$

   Volume inclosed by Fermi surface $V_{FS} = \frac{4\pi}{3}k_F^3 = 3\pi^2 n$

6. Useful units for numerical estimates.
   n =3D density of free (valence) electrons in a metal.
   n is represented by radius of electron r_s, $n = \frac{1}{\frac{4\pi}{3}r_s^3}$ usually expressed in units of Bohr radius, $a_0 = \frac{\hbar^2}{2me^2} = 0.529A$
   Then $k_F = \frac{1.92}{r_s}$ and $E_F = \frac{1}{2}\frac{e^2}{a_0}(k_F a_)^2 = \frac{50.1eV}{(r_s/a_0)^2}$

7. Derived thermodynamic quantities (3D).
   Average energy per electron, $u/n = (3/5)E_F$
   Bulk modulus (electronic contribution), $B = (2/3)nE_F$
   Surprisingly good agreement with actual values of B.

8. Density of states per unit energy energy. (Assume spin 1/2)
   In continuum limit $2\frac{1}{V}\sum_{\mathbf{k}}$ is replaced by $\int dEg(E)$, where $g(E)$ = number of states per unit volume per unit energy.
   In 3D, $g(E) = \frac{2}{3}\frac{n}{E_F}(\frac{E}{E_F})^{1/2}$
   Result for free electron case, concept is general - applies to all quantum problems.
   In 1D, $g(E) \propto E^{-1/2}$; in 2-D $g(E) \propto E^0$, i.e. $g(E)$ is independent of E.

9. Use Fermi-Dirac distribution at finite temperature.
   Since the number of particles is conserved, the chemical potential μ must in general change as a function of T
   Sommerfeld expansion (see also problem) show the magnitude of the shift
   In 3-D μ shifts to lower energy as T increases(Figure given in Kittel)
   For $T >> E_F$, $\mu < 0$ and the distribution approaches the Maxwell distribution

10. Linear electronic specific heat. (Ashcroft and Mermin p 46-7; Kittel gives simpler derivation)
    $C_V = g(E_F)k_B^2 T$; $g(E_F) = \frac{2}{3}\frac{n}{E_F} \propto m$
    In ordinary materials dominates measured C_V at very low T.
    Note that for a given density, $C_V \propto mass$
    "Heavy fermion" materials have anomalously large C_V with mass of order 1000 m_e.

11. Atomic units: $\hbar = m_e = e = 4\pi\epsilon_0 = 1$
    Leads to the fundamental units (see notes by E. Koch for derivation):

a_0	$= 4\pi\epsilon_0\hbar^2 / m_e e^2$	$\approx 5.2918 \cdot 10^{-11}$m	Bohr radius
m_e	$=$	$\approx 9.1095 \cdot 10^{-31}$kg	electron mass
t_0	$= (4\pi\epsilon_0)^2\hbar^3 / m_e e^4$	$\approx 2.4189 \cdot 10^{-17}$s	elementary unit of time
e	$=$	$\approx 1.6022 \cdot 10^{-19}$C	elementary charge