Condensed Matter Physics I – FK7060, Jan. 18, 2018.

Lecture 2 – Sommerfeld theory of metals

Reading

Ashcroft & Mermin, Ch. 2, pp. 30 – 53. Ch. 3, pp. 58 – 62 (for overview).

Content

- Fermi-Dirac distribution
- Free electrons, boundary conditions
- Density of levels
- Fermi energy, chemical potential
- Electron specific heat
- Mean free path
- Thermal conductivity & thermopower
- Unexplained questions

Central concepts

- **Fermi-Dirac distrubution**

  The Pauli exclusion principle strongly modifies classical (Maxwell-Boltzmann) expressions for electronic specific heat and electron velocities. Sommerfeld theory ≈ Drude + Fermi-Dirac distribution.

$$f_{MB} = Ae^{-\varepsilon/k_BT}$$
$$f_{FD} = \frac{1}{e^{(\varepsilon-\mu)/k_BT}+1}$$

- **Free electrons, boundary conditions**

  Schrödinger equation

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r})$$

  Free electrons: no potential U. Plane-wave solution

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}}e^{i\mathbf{k}\cdot\mathbf{r}}$$

$$\varepsilon(\mathbf{k}) = \frac{\hbar^2k^2}{2m}$$

  Applying momentum operator $\hat{\mathbf{p}} = -i\hbar\nabla$ gives eigenvalue $\mathbf{p} = m\mathbf{v} = \hbar\mathbf{k}$.

  The vector $\mathbf{k}$ can be interpreted as a wave vector with de Broglie wavelength

$$\lambda = \frac{2\pi}{k}$$

  Applying periodic boundary conditions $\psi(x+L) = \psi(x)$ etc., $L = V^{1/3}$ gives allowed wave vector components

$$k_x = \frac{2\pi n_x}{L}, \quad k_y = \frac{2\pi n_y}{L}, \quad k_z = \frac{2\pi n_z}{L}, \quad n_x, n_y, n_z \text{ integers}$$

- **Density of levels**

  Volume of **k**-space per level: $(2\pi/L)^3$. Number of levels per volume in **k**-space: $V/8\pi^3$. Each **k**-state can also take spin up or down.

- **Fermi energy, chemical potential**

  Since energy increases with k, there is a *Fermi sphere* of radius k_F, defined to contain all N states at $T = 0$.

$$N = 2\left(\frac{4\pi k_F^3}{3}\right)\left(\frac{V}{8\pi^3}\right)$$

  which gives ($n = N/V = N_{\text{ions}}Z/V$ for valence Z)

$$k_F = (3\pi^2 n)^{1/3}$$

  corresponding to a Fermi energy

$$\varepsilon_F = \frac{\hbar^2 (3\pi^2 n)^{2/3}}{2m}$$

  Definition of Fermi temperature

$$\varepsilon_F = k_B T_F$$

  Average energy per electron in ground state

$$\langle\varepsilon\rangle = \frac{3}{5}\varepsilon_F$$

  Compare $\varepsilon_F \simeq 2 - 10$ eV in metals with thermal energy $k_B T \simeq 25$ meV at room temperature.

  Equation for chemical potential μ (arbitrary temperature)

$$N = \sum_i \frac{1}{e^{(\varepsilon_i - \mu)/k_B T} + 1} = \sum_i f_{FD,i} = \int_{\varepsilon=0}^{\infty} f_{FD}(\varepsilon) D(\varepsilon) d\varepsilon$$

  Density of states (2.61)

$$D(\varepsilon) d\varepsilon = 2\frac{V}{8\pi^3} 4\pi k^2 dk$$

$$D(\varepsilon) = \frac{V}{2\pi^2} \frac{(2m)^{3/2}}{\hbar^3} \sqrt{\varepsilon}$$

$$g(\varepsilon) = \frac{D(\varepsilon)}{V} = \frac{3}{2}\frac{n}{\varepsilon_F}\left(\frac{\varepsilon}{\varepsilon_F}\right)^{1/2}$$

  Difference between Fermi energy ε_F and chemical potential μ (2.78)

$$\mu = \varepsilon_F\left[1 - \frac{1}{3}\left(\frac{\pi k_B T}{2\varepsilon_F}\right)^2\right]$$

- **Electron specific heat**

  Internal energy U

$$U = \int_0^{\infty} \varepsilon D(\varepsilon) f(\varepsilon) d\varepsilon = U_0 + \frac{\pi^2}{6}(k_B T)^2 D(\varepsilon_F)$$

  Specific heat (2.80)

$$c_{v,\text{el}} = \frac{\partial u}{\partial T} = \frac{\pi^2}{3} g(\varepsilon_F) k_B^2 T = \frac{\pi^2}{2} n k_B \left(\frac{k_B T}{\varepsilon_F}\right) = \gamma T$$

  Strong experimental deviations from this number are observed for, for instance, Nb, Fe, Mn, Bi, and Sb (Table 2.3).

- **Mean free path - revisited**

  Typical electron velocity is v_F so that

$$l = v_F \tau$$

- **Thermal conductivity & thermopower - revisited**

  Using $\varepsilon_F = m v_F^2/2$, the thermal conductivity becomes

$$\kappa = \frac{c_v v_F^2 \tau}{3} = \frac{2 c_v \varepsilon_F \tau}{3m} = \frac{\pi^2}{3} \frac{n\tau}{m} k_B^2 T$$

  giving a Lorenz number

$$L = \frac{\kappa}{\sigma T} = \frac{\pi^2}{3} \frac{k_B^2}{e^2}$$

  Thermopower (2.94)

$$Q = -\frac{1}{3} \frac{c_v}{ne} = -\frac{\pi^2}{6} \frac{k_B}{e} \left(\frac{k_B T}{\varepsilon_F} \right) = -1.42 \left(\frac{k_B T}{\varepsilon_F} \right) \times 10^{-4} \quad \text{V/K}$$

Unexplained questions (Ch. 3)

- **Transport experiments**

  - Hall coefficient sign

  - Magnetoresistance field dependence

  - Colors of Cu, Au

- **Thermodynamic experiments**

  - Size of linear term specific heat for metals such as Fe, Mn

  - Cubic term specific heat

- **Fundamental observations**

  - Why are some elements nonmetals? What determines the number of conduction electrons?