Solids

Talk about behavior of electrons in many-atom systems.
No few approximation schemes, but we'll learn a theorem.

A solid is a crystal of nuclei & electrons around them.
Crystal can vibrate, such normal modes are called
PHONONS (analogous to photons).

But we concatenate on electrons, with nuclei as fixed
background.

Is each electron bound to one atom? Or are they
shared around? Depends on substance.

For many metals, useful to treat electrons as free to
move.

Free Electron Gas

Zeroth order approx: only effect of nuclei is to
confine electrons to solid. Otherwise treat them as free.

So, e⁻ move in 3D square well, sides length \(a, b, c\).

\[
\psi_{n_x, n_y, n_z}(x, y, z) = \sqrt{\frac{8}{l_x l_y l_z}} \sin\left(\frac{n_x \pi x}{l_x}\right) \sin\left(\frac{n_y \pi y}{l_y}\right) \sin\left(\frac{n_z \pi z}{l_z}\right)
\]

\[
E_{n_x, n_y, n_z} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2}\right) = \frac{\hbar^2 k^2}{2m}
\]

\(n_x, n_y, n_z\) nonnegative integers.

\[
k^2 = \pi^2 \left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2}\right)
\]

Fill out grid in \(k\)-space, spacings \(\frac{\pi}{l_i}\).

Each block has \(k\)-volume \(\frac{l_x l_y l_z \pi^3}{2}\).

Note \(k\)-vol \(\sim\) \(\frac{1}{V}\).
(Consider N electrons. (Generally valence electrons of atoms.)

Pauli exclusion says lowest energy state has only 2 electrons (both spins) per grid point (x,y,z), filling up lowest first.

For many electrons, ignore discreteness of grid, just say there are 2 e⁻ per k-volume \( \frac{\pi^3}{V} \).

k-volume filled: \( \frac{N}{2} \frac{\pi^3}{V} = \frac{N \pi^3}{2} \)

\( n = \text{density of electrons vol.} \)

Fill positive octant of sphere up to \( k = k_F \) "Fermi momentum"

\[ \frac{N \pi^3}{2} = \frac{8}{3} \pi^3 k_F^3 \implies k_F = \left( \frac{3\pi^2 n}{8} \right)^{1/3} \]

This sphere called "Fermi surface."

Energy of the electron at Fermi surface is

\[ E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m} \left( \frac{3\pi^2 n}{8} \right)^{2/3} \]

This is not total energy.

\[ E_{tot} = \int_{0}^{E_F} dE \text{ integrate up all single-particle states} \]

\[ dE = \frac{\hbar^2 k^2}{2m} \frac{dN}{dE} \text{ for each particle} \]

\[ dN = \binom{\text{# electrons}}{\text{k-vol.}} (\text{k-vol at } k) \]

\[ = \frac{2}{\pi^2} \frac{1}{2} \int_{0}^{k_F} d^3k \]

\[ = \frac{1}{\pi^2} k_F^3 \text{ possible octant shell in } k\text{-space} \]
\[ E_{\text{tot}} = S_0 \cdot \frac{\hbar^2}{10\pi^3 m} k_F^4 \frac{dE}{dk} = \frac{\hbar^2}{10\pi^3 m} k_F^5 \cdot \frac{1}{(3\pi^2 N)^{5/3}} \]

\[ E_{\text{tot}} = \frac{\hbar^2}{10\pi^3 m} (3\pi^2 N)^{5/3} V^{-2/3} \]

For fixed particle number \( N \), smaller volume \( \rightarrow \) bigger energy.

\[ dE = \frac{\hbar^2}{3 \pi^2 m} V^{-5/3} = \frac{2}{3} \frac{E}{V} dV \]

since \( dE = -P dV \), \( P = \frac{2}{3} \frac{E}{V} \) "degeneracy pressure."

\[ P = \frac{\hbar^2}{15\pi^2 m} (3\pi^2 N)^{5/3} \cdot n^{5/3} \]

High pressure \( @ \) high density.

White dwarf star can be treated as giant free electron gas; pressure of degeneracy resists gravity.

- At zero temperature, Fermi surface filled.
- For metal at higher temperature, some electrons excited out of Fermi surface.
- Still a good picture for temperature much smaller than Fermi temperature, which goes like density.

\[ E_F \approx kT_F : \quad kT \ll kT_F \Rightarrow \frac{\hbar^2}{2m} \left( \frac{2\pi^2 n}{\hbar^2} \right)^{2/3} \ll \frac{2\pi^2 n}{\hbar^2} \]

Typical metal: \( E_F \approx 0.1 \, eV \approx 10^8 \, K \) \( \left( \frac{1}{4\pi^2 n} \frac{k}{eV} \right) \)

Metals are "cold" electron gases.

White dwarf: \( E_F \approx 10^5 \, eV \approx 10^8 \, K \).