

To get the quantum heat capacity ~~accurately~~ accurately, must evaluate integrals like

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$$u = \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) \varepsilon f(\varepsilon)$$

and
$$n = \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) f(\varepsilon)$$

general form is

$$I = \int d\varepsilon H(\varepsilon) f(\varepsilon)$$

at $T = 0$

$$I_0 = \int_{-\infty}^{\varepsilon_F} d\varepsilon H(\varepsilon)$$

at $T \neq 0$, I differs from I_0 by

the variation of $H(\varepsilon)$ near $\varepsilon = \mu$

Therefore, we need a Taylor expansion of $H(\varepsilon)$ about $\varepsilon = \mu$

$$\Rightarrow H(\varepsilon) = \sum_{n=0}^{\infty} \frac{d^n}{d\varepsilon^n} H(\varepsilon) \Big|_{\varepsilon=\mu} \frac{(\varepsilon-\mu)^n}{n!}$$

This is actually done in Appendix C by defining another function

$$K(\epsilon) = \int_{-\infty}^{\epsilon} H(\epsilon') d\epsilon'$$

$$H(\epsilon) = \frac{dK(\epsilon)}{d\epsilon}$$

which allows an integration by parts, resulting in:

$$\int_{-\infty}^{\infty} H(\epsilon) f(\epsilon) d\epsilon = \int_{-\infty}^{\infty} K(\epsilon) \left(-\frac{\partial f}{\partial \epsilon} \right) d\epsilon$$

Then,

$$K(\epsilon) = K(\mu) + \sum_{n=1}^{\infty} \left[\frac{(\epsilon - \mu)^n}{n!} \right] \left[\frac{d^n K(\epsilon)}{d\epsilon^n} \right]_{\epsilon = \mu}$$

Substituting gets the desired result, namely

$$\int_{-\infty}^{\infty} H(\epsilon) f(\epsilon) d\epsilon = \int_{-\infty}^{\mu} H(\epsilon) d\epsilon + \sum_{n=1}^{\infty} a_n (k_B T)^{2n} \left. \frac{d^{2n-1}}{d\epsilon^{2n-1}} H(\epsilon) \right|_{\epsilon = \mu}$$

Sommerfeld
Expansion

where

$$a_n = \int_{-\infty}^{\infty} \frac{x^{2n}}{(2n)!} \left(-\frac{d}{dx} \frac{1}{e^x + 1} \right) dx$$

and

$$x = \frac{\epsilon - \mu}{k_B T}$$

Note: $\int_{-\infty}^{\infty} \left(-\frac{\partial f}{\partial \epsilon} \right) d\epsilon = 1$

integral of delta function

The a_n are coefficients which can be calculated mathematically (see Appendix C)

The Sommerfeld expansion can be ^(written down) evaluated to get the first and most important terms:

$$\Rightarrow \int_{-\infty}^{\infty} H(\epsilon) f(\epsilon) d\epsilon = \int_{-\infty}^{\mu} H(\epsilon) d\epsilon + \frac{\pi^2}{6} (k_B T)^2 H'(\mu) + \frac{7\pi^4}{360} (k_B T)^4 H'''(\mu) + O\left(\frac{k_B T}{\mu}\right)^6$$

For u , $H(\epsilon) = \epsilon g(\epsilon)$

n , $H(\epsilon) = g(\epsilon)$

$$\Rightarrow u = \int_0^{\mu} \epsilon g(\epsilon) d\epsilon + \frac{\pi^2}{6} (k_B T)^2 [\mu g'(\mu) + g(\mu)] + O(T^4)$$

$$n = \int_0^{\mu} g(\epsilon) d\epsilon + \frac{\pi^2}{6} (k_B T)^2 g'(\mu) + O(T^4)$$

expand $\int_0^{\mu} H(\epsilon) d\epsilon$ about ϵ_F

$$\rightarrow \int_0^{\epsilon_F} H(\epsilon) d\epsilon + (\mu - \epsilon_F) H(\epsilon_F)$$

Finally, one can get:

$$u = \int_0^{\epsilon_F} \epsilon g(\epsilon) d\epsilon + \epsilon_F \left\{ (\mu - \epsilon_F) g(\epsilon_F) + \frac{\pi^2}{6} (k_B T)^2 g'(\epsilon_F) \right\} + \frac{\pi^2}{6} (k_B T)^2 g(\epsilon_F) + O(T^4) \quad (45)$$

$$n = \int_0^{\epsilon_F} g(\epsilon) d\epsilon + \left\{ (\mu - \epsilon_F) g(\epsilon_F) + \frac{\pi^2}{6} (k_B T)^2 g'(\epsilon_F) \right\}$$

In the ground state,

$$\mu = \epsilon_F \quad \text{and} \quad T = 0$$

\Rightarrow first term in each expression is the ground state value

$$\int_0^{\epsilon_F} \epsilon g(\epsilon) d\epsilon \quad \& \quad \int_0^{\epsilon_F} g(\epsilon) d\epsilon$$

\otimes for $C_V \Rightarrow$ constant volume \Rightarrow constant density

$$\Rightarrow n \neq f(T)$$

$$\Rightarrow \left\{ (\mu - \epsilon_F) g(\epsilon_F) + \frac{\pi^2}{6} (k_B T)^2 g'(\epsilon_F) \right\} = 0$$

This determines $\mu(T)$

$$\Rightarrow \mu = \epsilon_F - \frac{\pi^2}{6} (k_B T)^2 \frac{g'(\epsilon_F)}{g(\epsilon_F)}$$

For free electrons, $g(\epsilon) \propto \epsilon^{1/2}$

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

Thermal energy density thus simplified to:

$$u = u_0 + \frac{\pi^2}{6} (h_B T)^2 g(\epsilon_F)$$

$$u_0 = \int_0^{\epsilon_F} \epsilon g(\epsilon) d\epsilon$$

$$\Rightarrow C_v = \left(\frac{\partial u}{\partial T} \right)_n = \frac{\pi^2}{3} k_B^2 T g(\epsilon_F)$$

more general expression

for free electrons,

$$g(\epsilon_F) = \frac{3}{2} \frac{n}{\epsilon_F}$$

$$\Rightarrow C_v = \frac{\pi^2}{2} \left(\frac{k_B T}{\epsilon_F} \right) n k_B$$

for free electrons

compared to classical expression

$$C_v^{\text{class}} = \frac{3}{2} n k_B$$

$\Rightarrow C_v$ is smaller than C_v^{class} by about ~~about~~
a factor of 10^{-2}

$$\text{i.e. } C_v \sim 10^{-2} C_v^{\text{class}}$$

Sommerfeld theory: velocity distribution

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of 1-electron levels (including both spin \uparrow and spin \downarrow)
in volume element $d\vec{h}$ about \vec{h} in h -space is:

$$\frac{V}{4\pi^3} d\vec{h}$$

occupancy probability is

$$f(\epsilon(\vec{h}))$$

of electrons in $d\vec{h}$ is

$$\frac{V}{4\pi^3} f(\epsilon(\vec{h})) d\vec{h}$$

$$\vec{v} = \frac{\hbar \vec{h}}{m}$$

\Rightarrow how many electrons in volume $d\vec{v}$ about \vec{v} ?

$$dv_x = \frac{\hbar}{m} dh_x$$

$$dv_y = \frac{\hbar}{m} dh_y$$

$$dv_z = \frac{\hbar}{m} dh_z$$

$$\Rightarrow d\vec{v} = \left(\frac{\hbar}{m}\right)^3 d\vec{h}$$

⇒ number of electrons in volume V within $d\vec{v}$ about \vec{v} is:

$$dN = \frac{V}{(4\pi)^3} f(\mathcal{E}) \left(\frac{m}{\hbar}\right)^3 d\vec{v}$$

⇒ number of electrons/unit volume within $d\vec{v}$ about \vec{v} is:

$$dn = \frac{(m/\hbar)^3}{(4\pi)^3} f(\mathcal{E}) d\vec{v}$$

$$dn = f(\vec{v}) d\vec{v}$$

$$\Rightarrow f(\vec{v}) = \frac{(m/\hbar)^3}{(4\pi)^3} \frac{1}{e^{(\frac{1}{2}mv^2 - \mu)/k_B T} + 1}$$

Fermi-Dirac velocity distribution

Question becomes for what situations will the classical theory, using F-D velocity-distribution, be valid? (49)

for electron with momentum $\hbar k_F = p$

Δp must be small with respect to p

we have $\Delta x \Delta p \sim \hbar$

$$\Rightarrow \Delta x \sim \frac{\hbar}{\Delta p}$$

which should be much larger than $\frac{\hbar}{p}$ for good classical description

$$\Rightarrow \frac{\hbar}{\Delta p} \gg \frac{\hbar}{p} = \frac{1}{k_F}$$

$$\Rightarrow \Delta x \gg \frac{1}{k_F}$$

but $\frac{1}{k_F} \sim r_s \Rightarrow \underbrace{\Delta x \gg r_s}_{\text{condition for good classical description}}$

\Rightarrow classical description not good if

$$\Delta x \sim r_s$$

~~⊗~~ Read also text of A+M: p. 51

Useful Consequences of Fermi-Dirac statistics for properties of metals.

1. mean free path

$$l = v_F \tau$$

\Rightarrow l 's of $\sim 10^2 \text{ \AA}$ at room temp.

2. thermal conductivity, Lorenz number

$$K = \frac{1}{3} v^2 \tau C_v$$

$C_v \sim 10^2$ smaller than C_v^{class}

$v^2 \sim 10^2$ larger

$$\frac{K}{\sigma T} = 2.44 \times 10^{-8} \text{ watt-ohm/K}^2$$

3. Thermopower

~~$$Q = -\frac{C_v}{3ne}$$~~

$$Q = -\frac{\frac{\pi^2}{2} \left(\frac{k_B T}{E_F} \right) n k_B}{3ne}$$

which is smaller by $\frac{k_B T}{E_F}$ ~~is~~,

\Rightarrow good agreement with measurements.