LECTURE #17

AT FINITE TEMPERATURES, WE MUST CONSIDER THE THERMAL DISTRIBUTIONS THAT WE DERIVED USING QUANTUM STATISTICAL MECHANICS.

RECALL: $$N = \sum_{n=1}^{\infty} N_n$$

$$U = E_{TOTAL} = \sum_{n=1}^{\infty} N_n E_n$$

ASSUMING THAT dE BETWEEN STATES IS SMALL AND MORE THAN ONE STATE IS OCCUPIED, THESE SUMS CAN BE REPLACED BY INTEGRALS:

$$n = \frac{N}{V} = \int_0^{\infty} g(E) f(E)\, dE \quad \leftarrow \text{PARTICLE DENSITY}$$

$$u = \frac{U}{V} = \int_0^{\infty} E g(E) f(E)\, dE \quad \leftarrow \text{ENERGY DENSITY}$$

DO THESE INTEGRALS YIELD RESULTS THAT ARE CONSISTENT WITH OUR PREVIOUS RESULTS FOR e^- AT $T = 0K$?

AT $T = 0K$, THE FERMI-DIRAC DISTRIBUTION IS:

$$f(E) = \left\{ \begin{array}{ll} 1, & E < \mu(0) \\ 0, & E > \mu(0) \end{array} \right\} \Rightarrow \mu(0) = E_F$$

$$\therefore\ n = \int_0^{E_F} \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}\, dE = \frac{1}{3\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} E_F^{3/2}$$

$$\Rightarrow\ E_F = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3} = \frac{\hbar^2 k_F^2}{2m} \quad \text{(AS EXPECTED)}$$

$$E_{TOTAL} = \int_0^{E_F} \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{3/2}\, dE$$

$$= \frac{V}{5\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E_F^{5/2} = \frac{V}{5\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left(\frac{\hbar^2 K_F^2}{2m}\right)^{5/2}$$

$$= \frac{\hbar^2 K_F^5 V}{10\pi^2 m} \quad \text{(AS EXPECTED)}$$

NOTE: THE AVERAGE ENERGY PER ELECTRON IS:

$$\langle E \rangle = \frac{E_{TOTAL}}{N} = \frac{\hbar^2 K_F^5}{10\pi^2 m}\frac{V}{N} = \frac{\hbar^2}{10\pi^2 m}(3\pi^2 n)^{5/3}\frac{1}{n}$$

$$= \frac{3}{5}\left(\frac{\hbar^2}{2m}\right)(3\pi^2 n)^{2/3} = \frac{3}{5}E_F$$

$$\therefore \langle E \rangle = \frac{3}{5}E_F \quad \text{AT } T = 0K$$

NOTE: THIS IS MARKEDLY DIFFERENT THAN CLASSICAL FREE PARTICLES THAT POSSESS $\langle E \rangle = 0$ AT $T = 0K$.

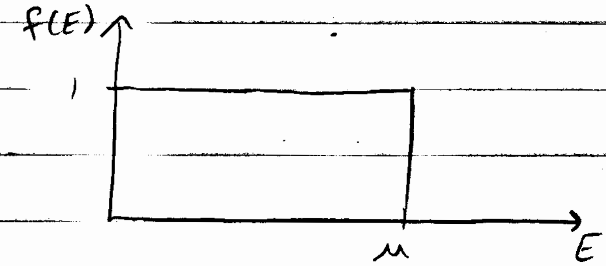
WHAT IS THE CONSTANT VOLUME SPECIFIC HEAT CAPACITY OF THE FREE ELECTRON GAS?

$$C_V = \left(\frac{\partial u}{\partial T}\right)_V, \quad u = \frac{U}{V} = \frac{E_{TOTAL}}{V}$$

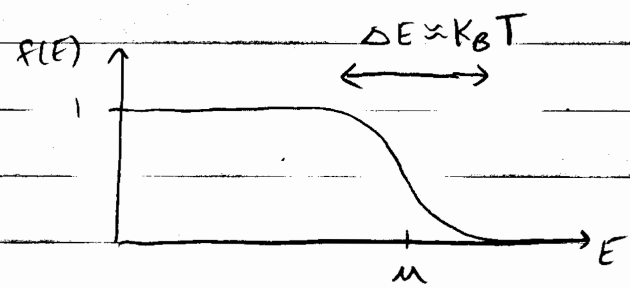
WHERE $u = \int_0^\infty E g(E) f(E)\, dE$

IN GENERAL, INTEGRALS CONTAINING THE FERMI-DIRAC DISTRIBUTION ARE DIFFICULT (IF NOT POSSIBLE) TO EVALUATE ANALYTICALLY

AT $T = 0K$,



AT $T > 0K$,



$\therefore$ $f(E)$ ONLY DIFFERS FROM ITS ZERO TEMPERATURE VALUES IN A SMALL REGION ABOUT μ OF WIDTH $\sim K_B T$.

NOTE: IN TYPICAL METALS, $\frac{K_B T}{\mu} \approx 0.01$ AT ROOM TEMPERATURE.

$\therefore$ FOR AN ARBITRARY FUNCTION $H(E)$, INTEGRALS OF THE FORM $\int_{-\infty}^{\infty} H(E) f(E)\, dE$ DIFFER FROM THEIR ZERO TEMPERATURE VALUES, $\int_{-\infty}^{E_F} H(E)\, dE$, BASED ON THE FORM OF $H(E)$ NEAR $E = \mu$.

ASSUMING THAT $H(E)$ DOES NOT VARY RAPIDLY NEAR μ, THE TEMPERATURE DEPENDENCE OF THE INTEGRAL CAN BE APPROXIMATED BY TAYLOR SERIES EXPANDING $H(E)$ ABOUT $E = \mu$:

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

"THE SOMMERFELD EXPANSION"

ASSUME $H(E) \to 0$ AS $E \to -\infty$ AND DIVERGES AS SOME POWER OF E AS $E \to \infty$.

FURTHER DEFINE $K(E) = \int_{-\infty}^{E} H(E')\,dE'$

$$\Rightarrow \quad H(E) = \frac{dK(E)}{dE}$$

WE WANT TO EVALUATE $\int_{-\infty}^{\infty} H(E) f(E)\,dE$

INTEGRATE BY PARTS: $u = f(E)$ $\quad dv = H(E)\,dE$

$du = \frac{\partial f}{\partial E}$ $\quad v = K(E)$

$$\therefore \int_{-\infty}^{\infty} H(E) f(E)\,dE = f(E) K(E)\Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} K(E) \frac{\partial f}{\partial E}\,dE$$

SINCE $f(E) \to 0$ AS $E \to \infty$ AND $K(E) \to 0$ AS $E \to -\infty$,

$$\int_{-\infty}^{\infty} H(E) f(E)\,dE = \int_{-\infty}^{\infty} K(E)\left(-\frac{\partial f}{\partial E}\right)dE$$

TAYLOR SERIES EXPAND $K(E)$ ABOUT $E = \mu$:

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

SINCE $\int_{-\infty}^{\infty} K(\mu)\left(-\frac{\partial f}{\partial E}\right)dE = K(\mu) f(E)\Big|_{\infty}^{-\infty} = K(\mu) = \int_{-\infty}^{\mu} H(E)\,dE$

AND $-\frac{\partial f}{\partial E}$ IS AN EVEN FUNCTION OF $(E-\mu)$

(THUS ONLY EVEN VALUES OF n CONTRIBUTE TO THE INTEGRAL $\int_{-\infty}^{\infty} K(E)\left(-\frac{\partial f}{\partial E}\right)dE$),

$$\int_{-\infty}^{\infty} H(E) f(E)\, dE = \int_{-\infty}^{\mu} H(E)\, dE + \sum_{n=1}^{\infty} \int_{-\infty}^{\infty} \frac{(E-\mu)^{2n}}{(2n)!}\left(-\frac{\partial f}{\partial E}\right) dE \; \frac{d^{2n-1}}{dE^{2n-1}} H(E)\Big|_{E=\mu}$$

LET $\frac{E-\mu}{K_B T} = x$,

$$\therefore \int_{-\infty}^{\infty} H(E) f(E)\, dE = \int_{-\infty}^{\mu} H(E)\, dE + \sum_{n=1}^{\infty} a_n (K_B T)^{2n} \frac{d^{2n-1}}{dE^{2n-1}} H(E)\Big|_{E=\mu}$$

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

NOTE: $a_1 = \frac{\pi^2}{6}$, $a_2 = \frac{7\pi^4}{360}$, ...

$$\therefore \boxed{\begin{array}{l} \int_{-\infty}^{\infty} H(E) f(E)\, dE = \int_{-\infty}^{\mu} H(E)\, dE + \frac{\pi^2}{6}(K_B T)^2 H'(\mu) \\ \qquad + \frac{7\pi^4}{360}(K_B T)^4 H'''(\mu) + \ldots \end{array}}$$

RETURN TO THE PROBLEM OF C_V FOR THE FREE e^- GAS.

$u = \int_0^{\infty} E g(E) f(E)\, dE$ LET $H(E) = \begin{cases} E g(E), & E > 0 \\ 0, & E < 0 \end{cases}$

$$\therefore u \approx \int_0^{\mu} E g(E)\, dE + \frac{\pi^2}{6}(K_B T)^2 \left[\mu g'(\mu) + g(\mu)\right]$$

$n = \int_0^{\infty} g(E) f(E)\, dE$ LET $H(E) = \begin{cases} g(E), & E > 0 \\ 0, & E < 0 \end{cases}$

$$\therefore n \approx \int_0^{\mu} g(E)\, dE + \frac{\pi^2}{6}(K_B T)^2 g'(\mu)$$

ASSUME THAT μ DIFFERS FROM E_F BY TERMS OF ORDER T^2.

$\therefore$ TO ORDER T^2, $\int_0^{\mu} H(E)\,dE = \int_0^{E_F} H(E)\,dE + (\mu - E_F) H(E_F)$

APPLYING THIS EXPANSION AND REPLACING μ BY E_F IN THOSE TERMS ALREADY OF ORDER T^2,

$$u = \int_0^{E_F} E g(E)\,dE + E_F\left[(\mu - E_F) g(E_F) + \frac{\pi^2}{6}(k_B T)^2 g'(E_F)\right] + \frac{\pi^2}{6}(k_B T)^2 g(E_F)$$

$$n = \underbrace{\int_0^{E_F} g(E)\,dE}_{n \text{ AT } T = 0K} + \left[(\mu - E_F) g(E_F) + \frac{\pi^2}{6}(k_B T)^2 g'(E_F)\right]$$

SINCE WE ARE CALCULATING C_V AT CONSTANT VOLUME,

$n = \frac{N}{V}$ IS INDEPENDENT OF TEMPERATURE

$$\therefore \quad (\mu - E_F) g(E_F) + \frac{\pi^2}{6}(k_B T)^2 g'(E_F) = 0$$

$$\therefore \quad \mu = E_F - \frac{\pi^2}{6}(k_B T)^2 \frac{g'(E_F)}{g(E_F)}$$

RECALL: $g(E_F) = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E_F^{1/2}$

$$\left.\frac{dg}{dE}\right|_{E_F} = g'(E_F) = \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E_F^{-1/2}$$

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

NOTE: THE SHIFT OF μ FROM E_F IS OF THE ORDER OF T^2 (AS WE ASSUMED)

NOTE: AT ROOM TEMPERATURE $\frac{k_B T}{E_F} \simeq 0.01$ IN MOST METALS $\Rightarrow$ μ DIFFERS FROM E_F BY $\sim 0.01\%$.

$\therefore$ WE WILL OFTEN USE μ AND E_F INTERCHANGEABLY IN MATERIALS SCIENCE.

SINCE $(\mu - E_F) g(E_F) + \frac{\pi^2}{6}(k_B T)^2 g'(E_F) = 0$,

$$u = \int_0^{E_F} E g(E)\, dE + \frac{\pi^2}{6}(k_B T)^2 g(E_F)$$

$$\therefore c_V = \left(\frac{\partial u}{\partial T}\right)_V = \frac{\pi^2}{3} k_B^2 T g(E_F)$$

SINCE $g(E_F) = \frac{3}{2}\frac{n}{E_F}$, $\boxed{c_V = \frac{\pi^2}{2}\left(\frac{k_B T}{E_F}\right) n k_B}$

HOWEVER, IN A METAL, AT HIGH TEMPERATURES, $c_V \to 3 n k_B$, WHICH IS APPROXIMATELY A FACTOR OF 100 GREATER THAN THE FREE e^- RESULT.

FURTHERMORE, AT INTERMEDIATE TEMPERATURES,

$$c_V = \underbrace{\gamma T}_{\text{FREE } e^- \text{ RESULT}} + \underbrace{A T^3}_{\text{ADDITIONAL TERM THAT SUGGESTS THAT FREE } e^- \text{ THEORY IS INCOMPLETE}}$$