STEFANO
CURTAROLO

QM THEORY OF SOLIDS

- INTRODUCTION
- BORN-VON KARMAN
- FERMI ENERGY, MOM, TEMP
- FERMI-DIRAC STATISTICS
- DENSITY OF STATES
- ENERGIES
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QM1 - QM5
FD1 - FD7
SPIN 1 - SPIN 6

SOMMERFELD THEORY ELECTRON GAS
CHAP 2 AM.

Free electrons in a box

STATIONARY SCHRÖDINGER EQUATION (TIME INVARIAT (stationary)

$i\hbar\frac{\partial}{\partial t}\psi \Rightarrow$ general

→ $\hat{H}\psi = E\psi \Rightarrow$ defines ψ

└ stationary

$\left[i\hbar\frac{\partial}{\partial t}\right]\psi$

~~ħω~~=

$e^{i\omega t} \Rightarrow \frac{\partial}{\partial t} = i\omega$

$i\hbar\omega i = -\hbar\omega =$

$e^{i(\bar{k}\cdot\bar{r}-\omega t)}$

→ real solutions are eigen-vectors / functions $[\psi(x)]_n$ of Hamiltonian operator (Energy) with Energy(n)

n can be discrete or continuum

→ ψ is wave function

$$\int\psi^*\psi\,dx = 1$$

$$|\psi(\bar{x})|^2 d^3\bar{x} = \psi^*\psi\,d^3x$$ = prob to have electron in $[x_0]$ volume d^3x

→ Other properties are operators

$$O = \langle\hat{O}\rangle \equiv \int\psi^*(x)\,\hat{O}\,\psi(x)\,dx = \sum(\psi^T)(\hat{O})(\psi)$$

↑ properties   ↑ average of an operator over the density

↳ but this is Real $\Rightarrow O^* = O \Rightarrow \hat{O} = \hat{O}^\dagger$

self adjoint

adjoint for matrix would be
- complex conjugate
- transport

$\hat{H}$ = Energy operator $\Rightarrow -\frac{\hbar^2}{2m}\left(\frac{\partial}{\partial x}\right)^2 + V(x) = \hat{H}(x)$

Hamiltonian $\hat{T} + \hat{V}$

$\frac{\hat{p}^2}{2m} + V$

$e^{i(\bar{k}\bar{x}-\omega t)}$

$\hat{p} = \hbar k$

$\hat{p} = -i\hbar\frac{\partial}{\partial x} \Leftarrow -\hbar i\left(\frac{\partial}{\partial x} = +ik\right) = \hbar k$

DE BROGLIE says
POSTULATE

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

$p = \frac{h}{\lambda} = \frac{hk}{2\pi} \Rightarrow \underline{p = \hbar k}$

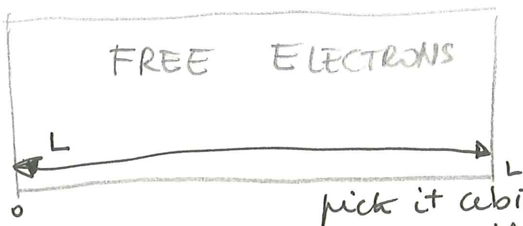
QM 1

How to go to macroscopic
what happens
at the border?

$$\psi(0) = \psi(L) \overset{\uparrow}{=} 0 \;?$$

NO!!
too restrictive.

METAL
= HUGE BOX
$\Rightarrow \infty$



pick it cubic
$V = L^3$

we can state BORN-VON KARMAN
$\psi(0) = \psi(L) \Rightarrow$ & $L \to \infty$
$\psi(x,y,z) = \psi(x+L,y,z)$
$= \psi(x,y+L,z) \equiv \psi(x,y,z+L)$

$\psi \simeq \psi_0 e^{ik_x}$

$\Rightarrow$ S. eq in $\hat{H}\psi = E\psi$

$$\frac{\hat{p}^2}{2m}\psi = E\psi \Rightarrow \quad -\frac{\hbar^2}{2m}\nabla^2\psi = E\psi$$

free wave

$$1 = \int_V \psi^*\psi\, d^3x \Rightarrow \int_V \psi_0^2 e^{-i\bar{k}\cdot\bar{r}} e^{i\bar{k}\cdot\bar{r}}\, dV = 1$$

$$\Rightarrow \psi_0 = \frac{1}{\sqrt{V}}$$

$$\psi = \frac{e^{i\bar{k}\cdot\bar{r}}}{\sqrt{V}}$$

but which $\bar{k}$

and energy $\displaystyle\int \psi^*\hat{H}\psi\, dx = E \Rightarrow E = -\frac{\hbar^2}{2m}(ik)^2 = \frac{\hbar^2k^2}{2m}$ $(p^2 ??)$

$$\mathcal{E}(k) = \frac{\hbar^2k^2}{2m}$$

energy of 1 electron with wave vector k (or momentum)

~~$\psi(x+L$~~ $\psi(x+L) = \psi(x) \Rightarrow \quad \psi \sim \underbrace{e^{ik_xx}}_{=1} \quad k_x = \frac{2\pi n_x}{L} \to e^{ik_xL} = 1$

$\Rightarrow$ BORN - VON KARMAN

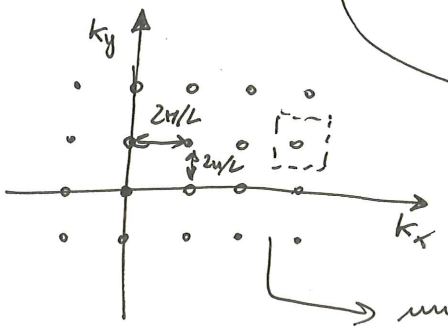
$$\Rightarrow 1 = e^{ik_xL} = e^{ik_yL} = e^{ik_zL} = 1 \Rightarrow$$

$$k = (k_x, k_y, k_z) = \left(\frac{2\pi n_x}{L}, \frac{2\pi n_y}{L}, \frac{2\pi n_z}{L}\right)$$

n_x, n_y, n_z integer

$\to$ QUANTIZATION OF SOLUTIONS!!

in 2D



$\to$ unit volume in $\bar{k}$ space

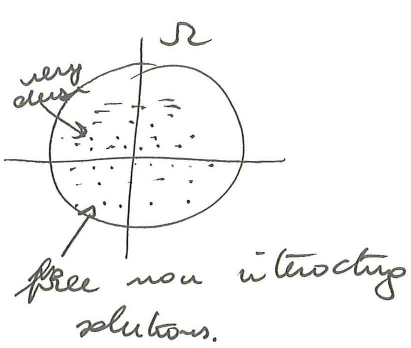
$$(\delta k)^3 = \left(\frac{2\pi}{L}\right)^3 = \frac{8\pi^3}{V} \;!!$$

very small

QM2.

⇒ a volume Ω in $\bar{k}$ space,

contains $\frac{\Omega}{(\delta k)^3} = \frac{\Omega V}{(8\pi^3)}$ points



⇒ SPIN $\pm\frac{1}{2}$ of electrons ⇒ 2 electrons per state $\bar{k}$ solution

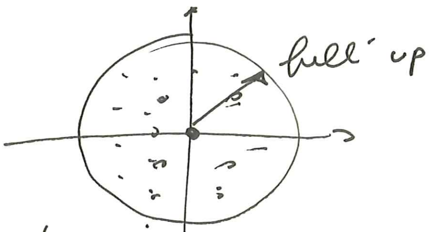
Now let's count them.

— take metal, volume V

— extract all free electrons $N = nV$ $\left(n = \frac{N}{V}\right)$ density

— put 1 → $\varepsilon = 0$, 2 $\varepsilon = 0$

— then put ~~it~~ other 2 in it to fill $\varepsilon(n_x = 1, n_y = 0, n_z = 0)$ and again



then fill up sphere with radius $\bar{k}_F$ (Fermi MOMENTUM)

⇒ all states with $|k| < k_F$ are occupied (2 e per point)!,

Volume $\Omega = \frac{4}{3}\pi k_F^3$ ⇒

$$\#\text{kpoints} = \frac{\Omega}{(\delta k)^3} = \cdot\frac{4}{3}\frac{\pi k_F^3 V}{8\pi^3}$$

$$N = 2 * \#\text{kpoints}$$

$$\Rightarrow N = \cancel{2}\cdot\frac{\cancel{4}}{3}\frac{\cancel{\pi} k_F^3}{\cancel{8}\pi^{\cancel{3}\,2}} V \qquad \boxed{k_F = \sqrt[3]{3\pi^2 n}}$$

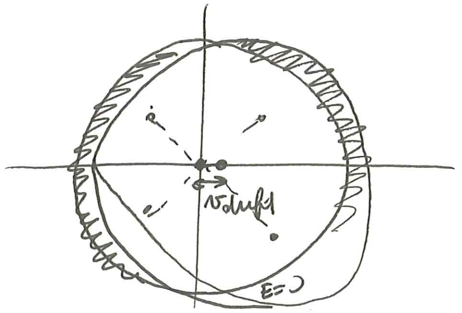
∀e with $\bar{k}$
there is an e with $-\bar{k}$
⇒ tot current = 0

$$n = \frac{N}{V} = \frac{1}{3}\frac{k_F^3}{\pi^2} \Rightarrow$$

ΦH3

~~Ø~~ $v_k = \frac{\hbar k_F}{m_e}$ $\Rightarrow$ if apply Force (E field) $\Rightarrow v_{\text{drift}}$

k shifts



$\forall$ e ~~w~~ with k, there is e with $-k$ only if far from surface $\Rightarrow$ ONLY electrons with $|k| \sim k_F$ are important in conduction

$$v_F \sim 10^6 \frac{m}{s} \sim \frac{1}{100} c \;!!$$

$$\overset{!}{=} \left(\frac{\hbar k_F}{m} \right)$$

fast

surprising results

at $T=0$ all e should have $v_{TH} = 0$

$\llcorner$ but for QM there are $v \approx c/100$ in all direction (conservation of mass)

$$\boxed{\mathcal{E}_F = \frac{\hbar^2 k_F^2}{2m} = \underbrace{\frac{1}{2} m v_F^2}_{= k_B T_F} =} \sim \overset{\cancel{1.8}}{1.0} \text{ and } 15 \text{ eV}$$

Fermi energi $\llcorner \approx 10-100$ k HOT!!!

Total energy $\Rightarrow$ all k with $|k| \leq k_F$ are occupied

~~ener~~

every state has energy $\mathcal{E}(k) = \frac{\hbar^2 k^2}{m}$

2e per state

$\cancel{E = \int_{|k| \leq k_F}}$

$$E = 2 \sum_{|k| \leq k_F} \frac{\hbar^2}{2m} k^2$$

so many and $(\delta k)^3$ is small

$$\Rightarrow \sum_{|k| \leq k_F} \longrightarrow \int_{|k| \leq k_F} \frac{d^3k}{(\delta k)^3} = \frac{1}{(2\pi)^3/V} \int d^3k$$

$$\boxed{\sum_{|k| \leq k_F} \Longleftrightarrow \frac{V}{(2\pi)^3} \int d^3k} \; \llcorner =$$

QM 4

$$E = \frac{2V}{(2\pi)^3}\int_{|k|\le k_F} \frac{\hbar^2}{2m} k^2\, d^3k = \frac{V\hbar^2}{8\pi^3 m}\int_{|k|\le k_F} k^2\, d^3k \; \cancel{= \frac{V\hbar^2}{8\pi^3}\,\frac{1}{3}}$$

$$d^3k = 4\pi k^2 dk$$

spherical symmetry

$$= \frac{V\hbar^2 \cancel{4\pi}}{\cancel{8}_{2}\pi^3 m}\int_0^{k_F} k^4\, dk = \frac{V\hbar^2}{2\pi^2 m}\,\frac{k_F^5}{5}$$

$$\underbrace{\frac{k^5}{5}\Big|_0^{k_F} = k_F^5/5}$$

$$E = \frac{V\hbar^2 k_F^5}{10\pi^2 m} \Rightarrow k_F = \sqrt[3]{3\pi^2 n} \Rightarrow k_F^3 = 3\pi^2\frac{N}{V}$$

$$= \frac{\cancel{V}\hbar^2 k_F^2}{10\cancel{\pi^2} m}\, 3\cancel{\pi^2}\frac{N}{\cancel{V}} \Rightarrow \frac{E}{N} = \frac{3}{10}\frac{\hbar^2 k_F^2}{m} = \frac{3}{5}\varepsilon_F$$

$$\Rightarrow \boxed{\langle E\rangle \text{ per electron} = \frac{3}{5}\varepsilon_F}$$

ε_F TABLES ~ 2~3 eV

T_F TABLES ~50 000 ~100000 K!!

1eV ⇒ 11604 K!

$$k_B T_F = \varepsilon_F$$

BULK COMPRESSIBILITY

$$dE = -p\,dV + T\,dS + \mu\, dN$$

pressure of gas. $P = -\frac{\partial E}{\partial V}\Big|_{S,N} =$

$$E = \frac{3}{5}N\varepsilon_F \quad \varepsilon_F \propto k_F^2 \propto (n^{1/3})^2$$

$$\Rightarrow E \propto \left(\frac{1}{V}\right)^{2/3} = V^{-\frac{2}{3}}$$

$$\Rightarrow \frac{\partial E}{\partial V} = -\frac{2}{3}\frac{E}{V}$$

$$\Rightarrow \boxed{P = \frac{2}{3}\frac{E}{V} \;!!}$$

compressibility at const T

$$B = \frac{1}{\kappa} = -V\frac{\partial P}{\partial V}\Big|_T$$

$$E \sim V^{-2/3} \quad P \sim V^{-5/3} \Rightarrow \frac{\partial P}{\partial V} = -\frac{5}{3}\frac{P}{V} \Rightarrow$$

$$B = \frac{5}{3}P = \frac{10}{9}\frac{E}{V}$$

$$\boxed{B = \frac{10}{9}\frac{E}{V}}$$

QMs

FERMI-DIRAC STATISTICS

$T>0$ N electrons. Thermal equilibrium

particle with energy E, probability of

occupancy states with Energy E $P_N(E) \propto e^{-\beta E}$ $\beta = \frac{1}{k_B T}$

$\Rightarrow$ sum $\forall E$ possible energy

Prob state with Energy E is occupied

$$P_N(E) = \frac{e^{-\beta E}}{\sum_{\text{states}} e^{-\beta E}}$$

$$\sum_{\text{states}} \Leftrightarrow \sum_{\text{energy}} \underbrace{\#\text{states with energy}}_{\Omega(E)}$$

But $S = k \log \Omega(E)$

$$\Omega(E) = e^{\beta(TS)}$$

$$\sum_{\text{energy}} e^{-\beta \underbrace{(E-TS)}_{F}} = e^{-\beta F}$$

F → Helmoltz Free energy

$dE = -pdV + TdS + \mu dN$

$dF = -pdV - SdT + \mu dN$

$$= \frac{e^{-\beta E_\alpha}}{\sum_{\text{states}} e^{-\beta E_\alpha} = e^{-\beta F}}$$

$$\Rightarrow P_N(E_\alpha) = e^{-\beta(E_\alpha^N - F_N)}$$

probability of a macroscopic states with N electrons in Thermal equilibrium & total energy $= E$

Now pick 1 electron in level i $\left(\varepsilon_i = \frac{\hbar^2 k_i^2}{2m}\right.$ for JELLO$\left.\right)$

prob that there is an electron in level i $\ni$ in a system of N electrons in T. eq is

$$f^N(i) = \sum_{\text{all states}} P_N(E_\alpha^N)$$

density of prob for <u>1</u> electron

FD 1

$$+ \quad f^N(i) = 1 - \sum_{\eta \in \left\{\begin{array}{l}\text{all states}\\ \underline{\text{without}} \text{ electron}\\ \text{in state } i\end{array}\right\}} P_N(E_\eta^N)$$

+ pick $N+1$ system = energy E^{N+1}

with 1 electron in level i with energy $\varepsilon_i \Rightarrow E_\gamma^{N+1}$ ↳ states with 1 electron in i

⇒ the N system has energy without electron in i has energy

$$\underset{\substack{\downarrow\\ 0 \text{ electrons in } i}}{E_\eta^N} = \underset{\substack{\uparrow\\ 1 \text{ electrons in } \underline{i}}}{E_\gamma^{N+1}} - \varepsilon_i$$

$$\Rightarrow f^N(i) = 1 - \sum_{\gamma \in \left\{\begin{array}{l}\text{states of } N+1 \text{ system}\\ \text{with 1 electron}\\ \text{in state } i\end{array}\right\}} P_N(E_\gamma^{N+1} - \varepsilon_i)$$

but

$$P_N(E_\eta) = e^{-\beta(E_\eta^N - F_N)}$$

$$P_N(E_\gamma^{N+1} - \varepsilon_i) = e^{\beta\varepsilon_i} \underset{\substack{\uparrow\\ N \text{ particles}}}{P_N}(E_\gamma^{N+1} \overset{\text{energy}}{)} =$$

$$= e^{+\beta\varepsilon_i} e^{-\beta(E_\gamma^{N+1} - F_N)}$$

$$-F_N \to -F_{N+1} + \underbrace{(F_{N+1} - F_N)}_{\Delta F = F_{N+1} - F_N \text{ for 1 particle}}$$

$$e^{-\beta(E_\gamma^{N+1} - F_{N+1})} = P_{N+1}(E_\gamma^{N+1})$$

$\lim\limits_{T \to 0} \mu = \varepsilon_F$

$$P_{N+1}(E_\gamma^{N+1}) \underbrace{e^{\beta(\varepsilon_i - \Delta F)}}_{e^{\beta(\varepsilon_i - \mu)}}$$

$$dF = -pdV - SdT + \mu dN$$

$$\mu = \partial F) \Rightarrow \Delta F \equiv \mu$$

FD 2.

$$\Rightarrow \quad f^N(i) = 1 - \sum_{\gamma\ i\,\text{occupied}} e^{\beta(\varepsilon_i - \mu)} \underbrace{P_{N+1}(E_\gamma^{N+1})}_{i\ \text{occupied}}$$

$$\cancel{\Rightarrow} \; 1 - e^{\beta(\varepsilon_i - \mu)} f^{N+1}(i)$$

$$\Rightarrow \quad f^N(i) = 1 - e^{\beta(\varepsilon_i - \mu)} f^{N+1}(i)$$

* $N \sim N_a = 10^{23}$ 1 extra electron does not change probability $\Rightarrow$ $f^N = f^{N+1}$

$$\Rightarrow \quad f^N(i)\left(1 + e^{\beta(\varepsilon_i - \mu)}\right) = 1$$

$$\boxed{f^N(i) = \frac{1}{e^{\beta(\varepsilon_i - \mu)} + 1}}$$

prob of state

Fermi-Dirac Distribution for 1 electron in state $\underline{i}$ with energy ε_i, in a system with a lot of electrons in thermal equilibrium

$$\boxed{{}^{*}N = \sum_{i\ \text{states}} f(i)}$$

number of electrons = sum in all states

$T \to 0$

we filled up all states at $\varepsilon \le \varepsilon_F$

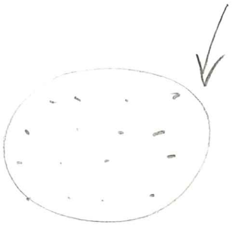
$$\Rightarrow \quad T=0 \quad f(i) < \begin{matrix} 1 & \varepsilon_i \le \varepsilon_F \\ 0 & \varepsilon_i > \varepsilon_F \end{matrix}$$

$$\lim_{T\to 0} f(i) < \begin{matrix} 1 & \varepsilon_i \le \mu \\ 0 & \varepsilon_i > \mu \end{matrix} \qquad \varepsilon_F = \lim_{T\to 0} \mu$$

$T > 0$

TOTAL for N electrons internal energy $U(T)$ = sum of all electronic energy

T



$$U(T) = \sum_k 2\,\varepsilon(k)\, \underbrace{f(\varepsilon(k))}$$

2 electrons per state

at $T=0$ was 1 for $|k| \le k_F$

$$\sum_k \Leftrightarrow \int \frac{d^3k}{\frac{(2\pi)^3}{V}} \qquad \Rightarrow \quad u = \frac{U}{V}$$

$$U = \frac{V\,2}{(2\pi)^3}\int d^3k\ \varepsilon(k)\, f(\varepsilon(k)) \quad \Rightarrow \quad u = \frac{2}{(2\pi)^3}\int \varepsilon(k)\, f(\varepsilon(k))\, d^3k$$

spoa

$$\int \frac{2}{(2\pi)^3}\, d^3k \Leftrightarrow \int d\varepsilon\, g(\varepsilon) \qquad \varepsilon = \frac{\hbar^2 k^2}{2m}$$

$$f(\varepsilon) \Rightarrow \qquad d^3k \Rightarrow 4\pi k^2\, dk$$

density of states ⇒ # electronic states between ε and $\varepsilon + d\varepsilon$

FD 4

$$\varepsilon = \frac{\hbar^2}{2m} k^2 \Rightarrow \text{spherical symmetry}$$

$$d^3k = 4\pi k^2 dk$$

$$\int \frac{\cancel{2}}{(\cancel{2}\pi)^3} \cancel{4\pi}\, k^2 dk = \frac{1}{\pi^2}\int k^2 dk -$$

$$k = \sqrt{\frac{2m\varepsilon}{\hbar^2}}$$

$$\varepsilon = \frac{\hbar^2}{2m} k^2 \qquad d\varepsilon = \frac{\hbar^2 \cancel{2}}{\cancel{2}m} k\, dk$$

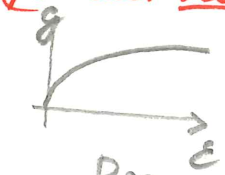
$$\Rightarrow k^2 dk = \frac{m}{\hbar^2} k\, d\varepsilon = \frac{m}{\hbar^2}\sqrt{\frac{2m}{\hbar^2}}\, \varepsilon^{1/2} d\varepsilon$$

$$\frac{1}{\pi}$$

$$\Rightarrow \int_{k^3} \frac{2}{(2\pi)^3} d^3k\, (\varepsilon) \quad \int_0^\infty g(\varepsilon)\, d\varepsilon$$

one-electron density of states in $\varepsilon, \varepsilon + d\varepsilon$ (per unit volume)

$$g(\varepsilon) = \begin{cases} \dfrac{m}{\hbar^2\pi^2}\sqrt{\dfrac{2m\varepsilon}{\hbar^2}} & \varepsilon > 0 \\ = 0 & \varepsilon < 0 \end{cases}$$



Parabola = free electrons

$$k_F = \sqrt[3]{3\pi^2 n} \Rightarrow$$

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

$$g(\varepsilon) = \frac{m\, k_F}{\hbar^2\pi^2}\sqrt{\frac{\varepsilon}{\varepsilon_F}}$$

$$n = \frac{k_F^3}{3\pi^2} = k_F \cdot \frac{k_F^2}{3\pi^2} = \frac{k_F}{3\pi^2}\,\varepsilon_F\frac{2m}{\hbar^2} \Rightarrow k_F = \frac{3\pi^2\hbar^2 n}{2m\varepsilon_F}$$

$$g(\varepsilon) = \frac{\cancel{m}}{\cancel{\hbar^2\pi^2}}\,\frac{3\cancel{\pi^2}\cancel{\hbar^2} n}{2\cancel{m}\varepsilon_F}\,(\;) \Rightarrow g$$

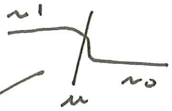
$$\boxed{g(\varepsilon) = \frac{3}{2}\frac{n}{\varepsilon_F}\left(\frac{\varepsilon}{\varepsilon_F}\right)^{1/2} \quad \varepsilon > 0}$$

FD 45

$$U = \int \varepsilon(k)\, f(\varepsilon(k)) \underbrace{\frac{2}{(2\pi)^3} d^3k}_{g(\varepsilon)\,d\varepsilon}$$

$$U = \int_0^\infty \cancel{\varepsilon(k)}\ \varepsilon\, g(\varepsilon)\, f(\varepsilon)\, d\varepsilon = \int_0^\infty \varepsilon f(\varepsilon) g(\varepsilon) d\varepsilon$$

energy, # of states, FD distrib (occupancy of 1 state)



$$n = \int f(\varepsilon(k)) \frac{2}{(2\pi)^3} d^3k \Rightarrow n = \int_0^\infty f(\varepsilon) g(\varepsilon) d\varepsilon$$

$g(\varepsilon)$ → because geometry

$f(\varepsilon)$ → because T

⇒ everything important happens ~ ~~Effn~~ μ
around μ

⇒ smooth function $H(\varepsilon)$ (no singularities around $\varepsilon \sim \mu$) → Taylor around μ

$$\Rightarrow \int_0^\infty H(\varepsilon) f(\varepsilon) d\varepsilon = \int_0^\mu H(\varepsilon) d\varepsilon + \sum_{n=1}^\infty (kT)^{2n} a_n \frac{d^{2n-1}}{d\varepsilon^{2n-1}} H(\varepsilon)\Big|_{\varepsilon=\mu}$$

SOMMERFELD EXPANSION

$$H(\varepsilon) < \begin{matrix} \varepsilon g(\varepsilon) \sim \varepsilon^{3/2} & \text{for } u \\ g(\varepsilon) \sim \varepsilon^{1/2} & \text{for } n \end{matrix}$$ good

get n, but $\frac{\partial n}{\partial T} = 0$ ⇒ $\boxed{\mu = \varepsilon_F \left[1 - \frac{1}{3}\left(\frac{\pi k_B T}{2\varepsilon_F}\right)^2\right]}$

$$\mu = \varepsilon_F - \frac{\pi^2}{6}(kT)^2 \frac{g'(\varepsilon_F)}{g(\varepsilon_F)}$$ general

for free electrons

get U ⇒ ~~U = U_0 T→0 lost~~

$$\boxed{U = U_0 + \frac{\pi^2}{6}(kT)^2 g(\varepsilon_F)}$$ energy.

FD 6

$$dE = -p\,dV + \underbrace{T\,dS}_{\delta Q} + \mu\,dN$$

$$C = \frac{\delta Q}{\delta T} \Rightarrow C_V = \left.\frac{\partial E}{\partial T}\right|_{\underbrace{V,N}_{n \text{ constant}}}$$

$$\Rightarrow C_V = \left.\frac{\partial U}{\partial T}\right|_{n} = \frac{\pi^2}{3} k_B^2\, g(\varepsilon_F)\, T$$

↳ ε_F constant

↳ generic $g(\varepsilon)$ ⇒

free electrons

$$C_V = \frac{\pi^2}{2}\left(\frac{k_B T}{\varepsilon_F}\right) \underset{\uparrow}{n} k_B \sim \frac{T \cdot n}{\varepsilon_F} \quad \text{LINEAR}$$

density of free electrons

Real one is $C_V = \underbrace{\gamma T}_{\text{electrons}} + \underbrace{A T^3}_{\text{phonon degrees of freedom but quantum}}$

$$U = \frac{3}{2}(kT) \quad \text{electrons}$$

$$\Rightarrow \boxed{C_V = \frac{3}{2} k n} \quad \text{CLASSIC} = [illegible]$$

per 1 electron

FD 7

2 SPIN SYSTEMS: SINGLET + TRIPLET

— PAULI PRINCIPLE

total wavefunction of fermion ([illegible]) must be antysimetric an exchange of fermionic index

$$\psi^{TOT}(\text{space}, \text{spin}) = \psi^{SP}(\text{space})\,\eta(\text{SPIN})$$

for

$$\psi^{TOT}(1,2) = \psi^{SP}(r_1, r_2)\,\eta(s_1, s_2)$$

$$\text{if } 1 \to 2 \Rightarrow \psi(2,1) = -\psi(1,2)$$

CHOICHES

$$a)\ \underbrace{\psi^{\text{space}}(1,2) = -\psi^{\text{SPACE}}(2,1)}_{\text{antisimetric}} \Rightarrow \underbrace{\eta(1,2) = \eta(2,1)}_{\text{simetric}}$$

TRIPLET
(3 solutions)

$$b)\ \underbrace{\psi^{\text{space}}(1,2) = \psi^{\text{space}}(2,1)}_{\text{symetric}} \Rightarrow \underbrace{\eta(2,1) = -\eta(1,2)}_{\text{antisimetric}}$$

SINGLET
(only 1 solution)

WHAT DO WE KNOW

$[\hat{H}, \hat{L}^2] = 0 \qquad [\hat{H}, \hat{L}_z] = 0$ eigenfunction of H $\psi_{n,m\ell}$

$\hat{L}_z \psi_{\cancel{m\ell m}\,n\ell m} = m\hbar\, \psi_{n\ell m}$

$[\hat{L}_i, \hat{L}_j] = i\hbar \varepsilon_{ijk} \hat{L}_k \qquad \hat{L}^2 \psi_{n\ell m} = \ell(\ell+1)\hbar^2 \psi_{n\ell m}$

Same for S!

For a state of 1 spin ↑+ or ↓− $\quad \eta(\varepsilon) \quad \varepsilon = \pm 1$

$$S_z\, \eta(\varepsilon) = \varepsilon \frac{\hbar}{2} \eta(\varepsilon)$$

(bring $\frac{\hbar}{2}$ outside so $\varepsilon = \pm 1$)

$$S^2 \eta(\varepsilon) = \frac{3}{4}\hbar^2 \eta(\varepsilon)$$

$m_z = \frac{1}{2}\varepsilon$

m_z in $-\ell_z, -\ell_z+1, \dots, \ell_z$

for 1 state $\ell_z = \frac{1}{2}$

$m_z = -\frac{1}{2}, \frac{1}{2} \quad (\varepsilon = \pm 1)$

$\ell_z(\ell_z+1) = \frac{1}{2}\left(\frac{1}{2}+1\right) = \frac{3}{4}$

2 particles

$$\Rightarrow \quad \Psi(r_1, r_2, \varepsilon_1, \varepsilon_2) = \psi(r_1, r_2)\, \eta(\varepsilon_1, \varepsilon_2)$$

basis of $\eta(\varepsilon_1, \varepsilon_2)$ = all possible configurations!

$$\eta(+,+),\ \eta(+,-),\ \eta(-,+),\ \eta(-,-)$$

how are they?

SPIN 2

How single spin operator acts?

$S_1^2 \eta(\varepsilon_1, \varepsilon_2) = \frac{3}{4}\hbar^2 \eta(\varepsilon_1, \varepsilon_2)$ $\quad$ $S_{1z}\eta(\varepsilon_1 \varepsilon_2) = \varepsilon_1 \frac{\hbar}{2} \eta(\varepsilon_1 \varepsilon_2)$

$S_2^2 \eta(\varepsilon_1, \varepsilon_2) = \frac{3}{4}\hbar^2 \eta(\varepsilon_1, \varepsilon_2)$ $\quad$ $S_{2z}\eta(\varepsilon_1 \varepsilon_2) = \varepsilon_2 \frac{\hbar}{2} \eta(\varepsilon_1 \varepsilon_2)$

TOTAL SPIN

$S = S_1 + S_2$, how it commutes? $\quad [S_1, S_2] = 0$

S_1 & S_2 doesn't speak $[S_{1i}, S_{2j}] = 0$

$$[S_x, S_y] = [S_{1x} + S_{1y}, S_{2x} + S_{2y}]$$

$$= [S_{1x}, S_{1y}] + [S_{2x}, S_{2y}]$$

$$= i\hbar S_{1z} + i\hbar S_{2z} = i\hbar(S_{1z} + S_{2z}) = \underline{\underline{i\hbar S_z}}$$

$$S^2 = (S_1 + S_2)^2 = S_1^2 + S_2^2 + 2 S_1 \cdot S_2$$

$$\overset{!}{=} S_1^2 + S_2^2 + 2(S_{1x}S_{2x} + S_{1y}S_{2y} + S_{1z}S_{2z})$$

$$\overset{!}{=} S_1^2 + S_2^2 + 2\left[S_{1z}S_{2z} + \frac{1}{2}(S_{1+}S_{2-} + S_{1-}S_{2+})\right]$$

S_+ brings spin up if down, otherwise $= 0$ $\quad S_\pm = S_x \pm i S_y$

$S_+ \eta(+) = 0 \quad S_+ \eta(-) = \hbar \eta(+)$

$S_- \eta(+) = \hbar \eta(-) \quad S_- \eta(-) = 0$

SPIN 3

calculation of S_z and S^2 on total spin

$$S_z\,\eta(\varepsilon_1\,\varepsilon_2) = (S_{1z}+S_{2z})\,\eta(\varepsilon_1,\varepsilon_2) = \frac{\hbar}{2}(\varepsilon_1+\varepsilon_2)\,\eta(\varepsilon_1\,\varepsilon_2)$$

$\Rightarrow$ $\eta(\varepsilon_1,\varepsilon_2)$ eigenstate with eigenvalue

$$\underbrace{M_z = \frac{1}{2}(\varepsilon_1+\varepsilon_2)}\qquad (*\hbar)$$

$$\varepsilon_1,\,\varepsilon_2 = \pm 1 \quad\Rightarrow\quad M_z = \underset{(--)}{-1},\ \underset{\substack{(+-)\\(-+)}}{0},\ \underset{(++)}{1}$$

$\uparrow$ degenerate $\Rightarrow$ get eigenvectors

linear combination

$$\begin{pmatrix}1\\0\\0\\0\end{pmatrix}=(++)\quad \begin{pmatrix}0\\1\\0\\0\end{pmatrix}=(+-)\quad \begin{pmatrix}0\\0\\1\\0\end{pmatrix}=(-+)\quad \begin{pmatrix}0\\0\\0\\1\end{pmatrix}=(--)$$

in this representation

$$\Rightarrow\ \bar{S_z} = \hbar\begin{pmatrix}1&0&0&0\\0&0&0&0\\0&0&0&0\\0&0&0&-1\end{pmatrix}$$

$$S^2\,\eta(\varepsilon_1\,\varepsilon_2) \Rightarrow \qquad S^2 = S_1^2 + S_2^2 + 2S_{1z}S_{2z} + S_{1+}S_{2-} + S_{1-}S_{2+}$$

$$S^2\eta(++) = \left(\frac{3}{4}\hbar^2 + \frac{3}{4}\hbar^2\right)\eta(++) + \frac{1}{2}\hbar^2\eta(++) = 2\hbar^2\eta(+,+)$$

$$S^2\eta(+-) = (\qquad)\,\eta(+-) - \frac{1}{2}\hbar^2\eta(+-) + \hbar^2\eta(-,+) \ \ldots = \hbar^2\big(\eta(+-)+\eta(-+)\big)$$

$$S^2\eta(-+) = \hbar^2\big(\eta(-+) + \eta(+,-)\big)$$

$$S^2\eta(--) = 2\hbar^2\eta(--)$$

eig $(++)$ $S^2 = 2\hbar^2$

$$\Rightarrow\ S^2 = \hbar^2\begin{pmatrix}2&0&0&0\\0&1&1&0\\0&1&1&0\\0&0&0&2\end{pmatrix}$$

$\rightarrow$ eig?

eig $(--)$ $\longrightarrow$ $S^2 = 2\hbar^2$

SPIN 4

$\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \Rightarrow$ eigenvalue problem

$\det\begin{pmatrix} 1-\lambda & 1 \\ 1 & 1-\lambda \end{pmatrix} = 0 \qquad (1-\lambda)^2 - 1 = 0 \qquad \lambda = 0, 2$

$\lambda = 0 \qquad \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}\begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = 0 \qquad x_1 + x_2 = 0$

$x_1 = -x_2$

$\Rightarrow$ norm $\Rightarrow \left(0, \frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}}, 0\right)$

$\Rightarrow$

$\frac{1}{\sqrt{2}}\begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} - \frac{1}{\sqrt{2}}\begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix} = \frac{1}{\sqrt{2}}\left(\eta(+,-) - \eta(-,+)\right) \Longrightarrow \lambda = 0$

$\lambda = 2 \qquad \begin{pmatrix} 1-2 & 1 \\ 1 & 1-2 \end{pmatrix}\begin{pmatrix} x_1 \\ x_2 \end{pmatrix} \Rightarrow x_1 - x_2 = 0 \qquad x_1 = +x_2$

norm $\left(0, \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0\right)$

wave $\Rightarrow \frac{1}{\sqrt{2}}\begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} + \frac{1}{\sqrt{2}}\begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix} = \frac{1}{\sqrt{2}}\left(\eta(+,-) + \eta(-,+)\right)$

$\Rightarrow$

SPIN S

SUMMARIZE

if sum 2 spin $\Rightarrow$ STATES

$$\frac{1}{\sqrt{2}}\left[\eta(+,-)-\eta(-,+)\right] = \text{singlet} \qquad S_z = 0 \quad M = 0 \qquad S^2 = 0$$

ANTY~~I~~SIMMMETRIC $\varepsilon_1 \Leftrightarrow \varepsilon_2$

TRIPLET

$\eta(+,+)$ $\qquad M = 1 \quad S_z = \hbar$

$\eta(--)$ $\qquad$ triplet $\qquad M = -1 \quad S_z = -\hbar \qquad S^2 = 2\hbar^2$

$\frac{1}{\sqrt{2}}\left[\eta(+,-)+\eta(+,-)\right]$ $\qquad M = 0 \quad S_z = 0$

$0 \quad + \quad 0$

SIMMETRIC

$\varepsilon_1 \Leftrightarrow \varepsilon_2$

$l_s(l_s+1)$

$1\ (1+1) = 2$

$\Rightarrow$

$M = -1, 0, 1$ $\quad$ Ok

$(2\,l_s + 1)$ values

$$\psi^{tot} = \psi(\quad)\,\eta(\quad) = \text{ANTY} \quad \varepsilon_1 \Leftrightarrow \varepsilon_2$$

SIMM $\quad$ ANTI

ANTI $\quad$ SIMM

SPIN 6

Table 2.1

FERMI ENERGIES, FERMI TEMPERATURES, FERMI WAVE VECTORS, AND FERMI VELOCITIES FOR REPRESENTATIVE METALS[a]

ELEMENT	r_s/a_0	$\mathcal{E}_F$	T_F	k_F	v_F
Li	3.25	4.74 eV	5.51×10^4 K	$1.12 \times 10^8\ \mathrm{cm}^{-1}$	1.29×10^8 cm/sec
Na	3.93	3.24	3.77	0.92	1.07
K	4.86	2.12	2.46	0.75	0.86
Rb	5.20	1.85	2.15	0.70	0.81
Cs	5.62	1.59	1.84	0.65	0.75
Cu	2.67	7.00	8.16	1.36	1.57
Ag	3.02	5.49	6.38	1.20	1.39
Au	3.01	5.53	6.42	1.21	1.40
Be	1.87	14.3	16.6	1.94	2.25
Mg	2.66	7.08	8.23	1.36	1.58
Ca	3.27	4.69	5.44	1.11	1.28
Sr	3.57	3.93	4.57	1.02	1.18
Ba	3.71	3.64	4.23	0.98	1.13
Nb	3.07	5.32	6.18	1.18	1.37
Fe	2.12	11.1	13.0	1.71	1.98
Mn	2.14	10.9	12.7	1.70	1.96
Zn	2.30	9.47	11.0	1.58	1.83
Cd	2.59	7.47	8.68	1.40	1.62
Hg	2.65	7.13	8.29	1.37	1.58
Al	2.07	11.7	13.6	1.75	2.03
Ga	2.19	10.4	12.1	1.66	1.92
In	2.41	8.63	10.0	1.51	1.74
Tl	2.48	8.15	9.46	1.46	1.69
Sn	2.22	10.2	11.8	1.64	1.90
Pb	2.30	9.47	11.0	1.58	1.83
Bi	2.25	9.90	11.5	1.61	1.87
Sb	2.14	10.9	12.7	1.70	1.96

[a] The table entries are calculated from the values of r_s/a_0 given in Table 1.1 using $m = 9.11 \times 10^{-28}$ grams.

assumes that the electronic energy per unit volume in a 1-cm cube of copper is the same as in a 2-cm cube).

Using (2.29) to evaluate (2.27), we find that the energy density of the electron gas is:

$$\frac{E}{V} = \frac{1}{4\pi^3}\int_{k<k_F} d\mathbf{k}\,\frac{\hbar^2k^2}{2m} = \frac{1}{\pi^2}\frac{\hbar^2k_F^{\,5}}{10m}. \tag{2.30}$$

To find the energy per electron, E/N, in the ground state, we must divide this by $N/V = k_F^{\,3}/3\pi^2$, which gives

$$\frac{E}{N} = \frac{3}{10}\frac{\hbar^2k_F^{\,2}}{m} = \frac{3}{5}\mathcal{E}_F. \tag{2.31}$$

We can also write this result as

$$\frac{E}{N} = \frac{3}{5}k_BT_F \tag{2.32}$$

where T_F, the *Fermi temperature*, is

$$\boxed{T_F = \frac{\mathcal{E}_F}{k_B} = \frac{58.2}{(r_s/a_0)^2} \times 10^4\ \text{K}.} \tag{2.33}$$

Note, in contrast to this, that the energy per electron in a classical ideal gas, $\frac{3}{2}k_BT$, vanishes at $T = 0$ and achieves a value as large as (2.32) only at $T = \frac{2}{5}T_F \approx 10^4$ K.

Given the ground-state energy E, one can calculate the pressure exerted by the electron gas from the relation $P = -(\partial E/\partial V)_N$. Since $E = \frac{3}{5}N\mathcal{E}_F$ and $\mathcal{E}_F$ is proportional to $k_F{}^2$, which depends on V only through a factor $n^{2/3} = (N/V)^{2/3}$, it follows that[16]

$$P = \frac{2}{3}\frac{E}{V}. \tag{2.34}$$

One can also calculate the compressibility, K, or bulk modulus, $B = 1/K$, defined by:

$$B = \frac{1}{K} = \left(-V\frac{\partial P}{\partial V}\right)_T \tag{2.35}$$

Since E is proportional to $V^{-2/3}$, Eq. (2.34) shows that P varies as $V^{-5/3}$, and therefore

$$B = \frac{5}{3}P = \frac{10}{9}\frac{E}{V} = \frac{2}{3}n\mathcal{E}_F \tag{2.36}$$

or

$$B = \left(\frac{6.13}{r_s/a_0}\right)^5 \times 10^{10}\ \text{dynes/cm}^2. \tag{2.37}$$

In Table 2.2 we compare the free electron bulk moduli (2.37) calculated from r_s/a_0, with the measured bulk moduli, for several metals. The agreement for the heavier alkali metals is fortuitously good, but even when (2.37) is substantially off, as it is in

Table 2.2
BULK MODULI IN 10^{10} DYNES/CM^2 FOR SOME TYPICAL METALS[a]

METAL	FREE ELECTRON B	MEASURED B
Li	23.9	11.5
Na	9.23	6.42
K	3.19	2.81
Rb	2.28	1.92
Cs	1.54	1.43
Cu	63.8	134.3
Ag	34.5	99.9
Al	228	76.0

[a] The free electron value is that for a free electron gas at the observed density of the metal, as calculated from Eq. (2.37).

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[16] At nonzero temperatures the pressure and energy density continue to obey this relation. See (2.101).

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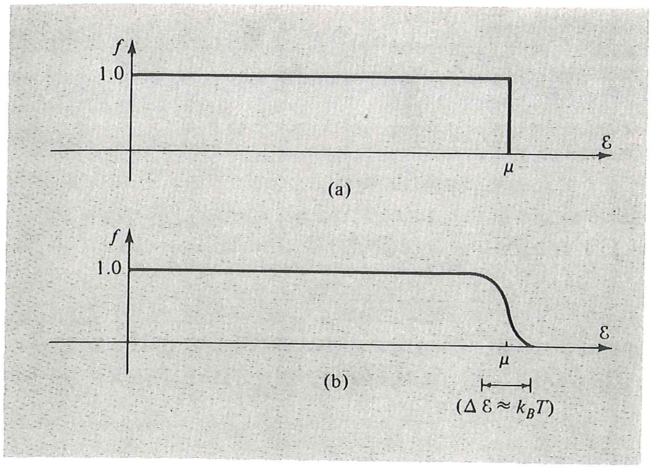

Figure 2.3
The Fermi function, $f(\mathcal{E}) = 1/[e^{\beta(\mathcal{E}-\mu)}+1]$ versus $\mathcal{E}$ for given μ, at (a) $T = 0$ and (b) $T \approx 0.01\mu$ (of order room temperature, at typical metallic densities). The two curves differ only in a region of order k_BT about μ.

and (2.67) remain valid for any set of noninteracting (that is, independent) electrons.[23] Thus we shall later be able to apply results deduced from (2.66) and (2.67) to considerably more sophisticated models of independent electrons in metals.

In general, the integrals (2.66) and (2.67) have a rather complex structure. There is, however, a simple systematic expansion that exploits the fact that at almost all temperatures of interest in metals, T is very much smaller than the Fermi temperature (2.33). In Figure 2.3 the Fermi function $f(\mathcal{E})$ is plotted at $T = 0$ and at room temperature for typical metallic densities ($k_BT/\mu \approx 0.01$). Evidently f differs from its zero temperature form only in a small region about μ of width a few k_BT. Thus the way in which integrals of the form $\int_{-\infty}^{\infty} H(\mathcal{E})f(\mathcal{E})\,d\mathcal{E}$ differ from their zero temperature values, $\int_{-\infty}^{\mathcal{E}_F} H(\mathcal{E})\,d\mathcal{E}$, will be entirely determined by the form of $H(\mathcal{E})$ near $\mathcal{E} = \mu$. If $H(\mathcal{E})$ does not vary rapidly in the energy range of the order of k_BT about μ, the temperature dependence of the integral should be given quite accurately by replacing $H(\mathcal{E})$ by the first few terms in its Taylor expansion about $\mathcal{E} = \mu$:

$$H(\mathcal{E}) = \sum_{n=0}^{\infty} \frac{d^n}{d\mathcal{E}^n} H(\mathcal{E})\bigg|_{\mathcal{E}=\mu} \frac{(\mathcal{E}-\mu)^n}{n!}. \tag{2.68}$$

Sommerfelt expansion

This procedure is carried out in Appendix C. The result is a series of the form:

$$\int_{-\infty}^{\infty} H(\mathcal{E})f(\mathcal{E})\,d\mathcal{E} = \int_{-\infty}^{\mu} H(\mathcal{E})\,d\mathcal{E} + \sum_{n=1}^{\infty} (k_BT)^{2n} a_n \frac{d^{2n-1}}{d\mathcal{E}^{2n-1}} H(\mathcal{E})\bigg|_{\mathcal{E}=\mu} \tag{2.69}$$

which is known as the Sommerfeld expansion.[24] The a_n are dimensionless constants of the order of unity. The functions H one typically encounters have major variations on an energy scale of the order of μ, and generally $(d/d\mathcal{E})^n H(\mathcal{E})|_{\mathcal{E}=\mu}$ is of the order of $H(\mu)/\mu^n$. When this is the case, successive terms in the Sommerfeld expansion are

---

[23] See Chapter 8.

[24] The expansion is not always exact, but is highly reliable unless $H(\mathcal{E})$ has a singularity very close to $\mathcal{E} = \mu$. If, for example, H is singular at $\mathcal{E} = 0$ (as is the free electron density of levels (2.63)) then the expansion will neglect terms of the order of $\exp(-\mu/k_BT)$, which are typically of order $e^{-100} \sim 10^{-43}$. See also Problem 1.

The prediction of a linear specific heat is one of the most important consequences of Fermi-Dirac statistics, and provides a further simple test of the electron gas theory of a metal, provided one can be sure that degrees of freedom other than the electronic ones do not make comparable or even bigger contributions. As it happens, the ionic degrees of freedom completely dominate the specific heat at high temperatures. However, well below room temperature their contribution falls off as the cube of the

Table 2.3

SOME ROUGH EXPERIMENTAL VALUES FOR THE COEFFICIENT OF THE LINEAR TERM IN T OF THE MOLAR SPECIFIC HEATS OF METALS, AND THE VALUES GIVEN BY SIMPLE FREE ELECTRON THEORY

$r_s = \left(\frac{\gamma}{0{,}169 z} \right)^{1/2}$

	ELEMENT	r_s	FREE ELECTRON γ (in 10^{-4} cal-mole^{-1}-K^{-2})	MEASURED γ (in 10^{-4} cal-mole^{-1}-K^{-2})	RATIO[a] (m^*/m)
	Li	3,26	1.8	4.2	2.3
	Na	3,92	2.6	3.5	1.3
	K	4,87	4.0	4.7	1.2
	Rb	5,2	4.6	5.8	1.3
	Cs	5,6	5.3	7.7	1.5
	Cu		1.2	1.6	1.3
	Ag		1.5	1.6	1.1
	Au		1.5	1.6	1.1
	Be		1.2	0.5	0.42
z=2	Mg	2,66	2.4	3.2	1.3
	Ca		3.6	6.5	1.8
	Sr		4.3	8.7	2.0
	Ba		4.7	6.5	1.4
	Nb		1.6	20	12
	Fe		1.5	12	8.0
	Mn		1.5	40	27
	Zn		1.8	1.4	0.78
	Cd		2.3	1.7	0.74
	Hg		2.4	5.0	2.1
(z=3)	Al	2,08	2.2	3.0	1.4
	Ga		2.4	1.5	0.62
	In		2.9	4.3	1.5
	Tl		3.1	3.5	1.1
	Sn		3.3	4.4	1.3
	Pb		3.6	7.0	1.9
	Bi		4.3	0.2	0.047
	Sb		3.9	1.5	0.38

[a] Since the theoretical value of γ is proportional to the density of levels at the Fermi level, which in turn is proportional to the electronic mass m, one sometimes defines a specific heat effective mass m^* so that m^*/m is the ratio of the measured γ to the free electron γ. Beware of identifying this specific heat effective mass with any of the many other effective masses used in solid-state theory. (See, for example, the index entries under "effective mass.")

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metal, H. A. Lorentz showed, using the classical Maxwell-Boltzmann velocity distribution, that an energy-dependent relaxation time would lead to temperature dependence in the DC and AC conductivities, as well as to a nonvanishing magnetoresistance and a field- and temperature-dependent Hall coefficient. As one might now expect from the inappropriateness of the classical velocity distribution, none of these corrections were in any way able to bring the discrepancies of the Drude model into better alignment with the observed facts about metals.[31] Furthermore, we shall see (Chapter 13) that when the correct Fermi-Dirac velocity distribution is used, adding an energy dependence to the relaxation time has little significant effect on most of the quantities of interest in a metal.[32] If one calculates the DC or AC conductivities, the magnetoresistance, or the Hall coefficient assuming an energy-dependent $\tau(\mathcal{E})$, the results one finds are the same as those one would have calculated assuming an energy-independent τ, equal to $\tau(\mathcal{E}_F)$. In metals these quantities are determined almost entirely by the way in which electrons near the Fermi level are scattered.[33] This is another very important consequence of the Pauli exclusion principle, the justification of which will be given in Chapter 13.

PROBLEMS

1. *The Free and Independent Electron Gas in Two Dimensions*

(a) What is the relation between n and k_F in two dimensions?

(b) What is the relation between k_F and r_s in two dimensions?

(c) Prove that in two dimensions the free electron density of levels $g(\mathcal{E})$ is a constant independent of $\mathcal{E}$ for $\mathcal{E} > 0$, and 0 for $\mathcal{E} < 0$. What is the constant?

(d) Show that because $g(\mathcal{E})$ is constant, every term in the Sommerfeld expansion for n vanishes except the $T = 0$ term. Deduce that $\mu = \mathcal{E}_F$ at any temperature.

(e) Deduce from (2.67) that when $g(\mathcal{E})$ is as in (c), then

⇒ 1ST ORDER ↑

$\mu = \mathcal{E}_K + kT\log(1-e^{-\beta\mathcal{E}_F})$

$$\mu + k_BT\ln(1 + e^{-\mu/k_BT}) = \mathcal{E}_F. \qquad (2.95)$$

EXACT

$\Rightarrow \mu = \mathcal{E}_F + \frac{\ln(1-e}{\beta}$

(f) Estimate from (2.95) the amount by which μ differs from $\mathcal{E}_F$. Comment on the numerical significance of this "failure" of the Sommerfeld expansion, and on the mathematical reason for the "failure." See stat. mech. notes, [illegible] 8.3

1st order $\mu = \mathcal{E}_F -$

2. *Thermodynamics of the Free and Independent Electron Gas*

(a) Deduce from the thermodynamic identities

$$c_v = \left(\frac{\partial u}{\partial T}\right)_n = T\left(\frac{\partial s}{\partial T}\right)_n, \qquad (2.96)$$

---

[31] The Lorentz model is, however, of considerable importance in the description of semiconductors (Chapter 29).

[32] The thermopower is a notable exception.

[33] These assertions are correct to leading order in $k_BT/\mathcal{E}_F$, but in metals this is always a good expansion parameter.

from Eqs. (2.56) and (2.57), and from the third law of thermodynamics ($s \to 0$ as $T \to 0$) that the entropy density, $s = S/V$ is given by:

$$s = -k_B \int \frac{d\mathbf{k}}{4\pi^3} [f \ln f + (1 - f) \ln (1 - f)], \tag{2.97}$$

where $f(\mathcal{E}(\mathbf{k}))$ is the Fermi function (Eq. (2.56)).

(b) Since the pressure P satisfies Eq. (B.5) in Appendix B, $P = -(u - Ts - \mu n)$, deduce from (2.97) that

$$P = k_B T \int \frac{d\mathbf{k}}{4\pi^3} \ln \left(1 + \exp\left[-\frac{(\hbar^2 k^2/2m) - \mu}{k_B T}\right]\right). \tag{2.98}$$

Show that (2.98) implies that P is a homogeneous function of μ and T of degree 5/2; that is,

$$P(\lambda\mu, \lambda T) = \lambda^{5/2} P(\mu, T) \tag{2.99}$$

for any constant λ.

(c) Deduce from the thermodynamic relations in Appendix B that

$$\left(\frac{\partial P}{\partial \mu}\right)_T = n, \qquad \left(\frac{\partial P}{\partial T}\right)_\mu = s. \tag{2.100}$$

(d) By differentiating (2.99) with respect to λ show that the ground-state relation (2.34) holds at any temperature, in the form

$$P = \tfrac{2}{3} u. \tag{2.101}$$

(e) Show that when $k_B T \ll \mathcal{E}_F$, the ratio of the constant-pressure to constant-volume specific heats satisfies

$$\left(\frac{c_p}{c_v}\right) - 1 = \frac{\pi^2}{3}\left(\frac{k_B T}{\mathcal{E}_F}\right)^2 + O\left(\frac{k_B T}{\mathcal{E}_F}\right)^4.$$

(f) Show, by retaining further terms in the Sommerfeld expansions of u and n, that correct to order T^3 the electronic heat capacity is given by

$$\begin{aligned} c_v &= \frac{\pi^2}{3} k_B{}^2 T g(\mathcal{E}_F) \\ &\quad - \frac{\pi^4}{90} k_B{}^4 T^3 g(\mathcal{E}_F) \left[15\left(\frac{g'(\mathcal{E}_F)}{g(\mathcal{E}_F)}\right)^2 - 21 \frac{g''(\mathcal{E}_F)}{g(\mathcal{E}_F)}\right]. \end{aligned} \tag{2.102}$$

3. *The Classical Limit of Fermi-Dirac Statistics*

The Fermi-Dirac distribution reduces to the Maxwell-Boltzmann distribution, provided that the Fermi function (2.56) is much less than unity for every positive $\mathcal{E}$, for in that case we must have

$$f(\mathcal{E}) \approx e^{-(\mathcal{E}-\mu)/k_B T}. \tag{2.103}$$

The necessary and sufficient condition for (2.103) to hold for all positive $\mathcal{E}$ is

$$e^{-\mu/k_B T} \gg 1. \tag{2.104}$$

(a) Assuming that (2.104) holds, show that

$$r_s = e^{-\mu/3k_B T}\, 3^{1/3} \pi^{1/6} \hbar (2mk_B T)^{-1/2}. \tag{2.105}$$

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In conjunction with (2.104) this requires that

$$r_s \gg \left(\frac{\hbar^2}{2mk_BT}\right)^{1/2}, \tag{2.106}$$

which can also be taken as the condition for the validity of classical statistics.

(b) What is the significance of the length r_s must exceed?

(c) Show that (2.106) leads to the numerical condition

$$\frac{r_s}{a_0} \gg \left(\frac{10^5\ \text{K}}{T}\right)^{1/2}. \tag{2.107}$$

(d) Show that the normalization constant $m^3/4\pi^3\hbar^3$ appearing in the Fermi-Dirac velocity distribution (2.2) can also be written as $(3\sqrt{\pi}/4)n(m/2\pi k_BT_F)^{3/2}$ so that $f_B(0)/f(0) = (4/3\sqrt{\pi})(T_F/T)^{3/2}$.

4. *Insensitivity of the Distribution Function to Small Changes in the Total Number of Electrons*

In deriving the Fermi distribution (page 41) we argued that the probability of a given level being occupied should not change appreciably when the total number of electrons is changed by one. Verify that the Fermi function (2.56) is compatible with this assumption as follows:

(a) Show, when $k_BT \ll \mathcal{E}_F$, that when the number of electrons changes by one at fixed temperature, the chemical potential changes by

$$\Delta\mu = \frac{1}{Vg(\mathcal{E}_F)}, \tag{2.108}$$

where $g(\mathcal{E})$ is the density of levels.

(b) Show, as a consequence of this, that the most the probability of any level being occupied can change by is

$$\Delta f = \frac{1}{6}\frac{\mathcal{E}_F}{k_BT}\frac{1}{N}. \tag{2.109}$$

[Use the free electron evaluation (2.65) of $g(\mathcal{E}_F)$.] Although temperatures of millidegrees Kelvin can be reached, at which $\mathcal{E}_F/k_BT \approx 10^8$, when N is of order 10^{22} then Δf is still negligibly small.