Phys. 12c 2015, Lecture Notes (Week 6)

Statistical Mechanics of Fermions and Bosons

(First Look...)

Consider "Perfect" gas $\equiv$ no interactions

Last time we found Grand Partition Function for single state E_i:

$$\mathcal{Z}_{FD}(E_i) = \sum_{N_S=0}^{1} \exp[(\mu N_S - N_S E_i)/\tau];\ \text{fermions}$$

$$\mathcal{Z}_{BE}(E_i) = \sum_{N_S=0}^{\infty} \exp[(\mu N_S - N_S E_i/\tau]; \text{bosons}$$

FD $\equiv$ Fermi-Dirac and BE $\equiv$ Bose-Einstein

Upper limit for BE is actually N (= # of particles in system), but for N large we take the upper limit to ∞.

Much of the physics from average occupation number of state E_i:

$$f(E_i) = \langle N_i \rangle$$

Fermi-Dirac Occupation:

Average occupation number

$$f_{FD}(E_i) \equiv \langle N_i \rangle = \frac{\sum_{N_S=0}^{1} N_S \exp[(N_S\mu - N_S E_i)/\tau]}{\mathcal{Z}_{\mathcal{FD}}}$$

or

$$f_{FD}(E_i) = \frac{e^{(\mu - E_i)/\tau}}{1 + e^{(\mu - E_i)/\tau}}$$

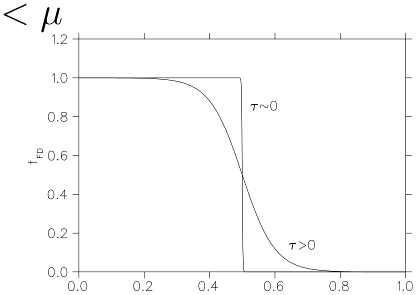
or

$$f_{FD}(E_i) = \frac{1}{e^{(E_i - \mu)/\tau} + 1}$$

Consider behavior of f_{FD}: let $x = E_i - \mu$

Look first at low temperature:

$$\lim_{\tau \to 0} \left(\frac{1}{e^{x/\tau} + 1} \right) = \begin{matrix} 0 \text{ if } x > 0,\ \text{or } E_i > \mu \\ 1 \text{ if } x < 0,\ \text{or } E_i < \mu \end{matrix}$$



Thus all states filled with 1 particle up to $E_{max} = \mu(\tau = 0) \equiv E_F$ Fermi Energy

What is μ for $\tau > 0$?

Require $\sum_i^\infty \langle N_i \rangle = N =$ total number of particles.

Then we can solve for μ via:

$$\sum_{states} f(E_i) = \sum_{states} \frac{1}{e^{(E_i-\mu)/\tau}+1} = N \text{ to find } \mu(\tau).$$

Bose-Einstein Occupation:

$$f_{BE}(E_i) \equiv \langle N_i \rangle = \frac{\sum_{N_S=0}^{\infty} N_S \exp[(\mu N_S - N_S E_i)/\tau]}{\mathcal{Z_{BE}}}$$

Let $x = e^{(\mu - E_i)/\tau}$; then only $x < 1$ leads to physically convergent results:

$$\begin{aligned} f_{BE}(E_i) &= \frac{\sum_{N_S=0}^{\infty} N_S x^{N_S}}{\sum_{N_S=0}^{\infty} x^{N_S}} = \frac{x \frac{d}{dx}\left(\frac{1}{1-x}\right)}{\frac{1}{1-x}} \\ &= \frac{x}{1-x} = \frac{1}{\frac{1}{x}-1} \\ \text{and } f_{BE}(E_i) &= \frac{1}{e^{(E_i-\mu)/\tau}-1} \end{aligned}$$

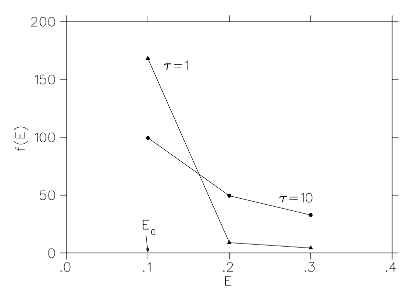
Note similiarity of f_{BE} and photon occupation:$\langle N_{photon} \rangle = \frac{1}{e^{\hbar\omega_i/\tau}-1}$ for $\mu_{photon} = 0$
Behavior of f_{BE}: let $y = E_i - \mu$

$$\lim_{\tau \to 0} \left(\frac{1}{e^{y/\tau}-1} \right) = 0 \;\Rightarrow \text{for } y > 0 \text{ or } E_i > \mu \;\; \text{(empty states)}$$

if $f_{BE} = \langle N_i \rangle = 0$ at $\tau = 0$ where are all the particles?
$\hookrightarrow$ All must be in the ground state E_0
with $\mu \leq E_0$ for $\tau \gtrsim 0$ such that

$$f_{BE}(E_0) = \frac{1}{e^{(E_0-\mu)/\tau}-1} \approx \frac{1}{(1+\frac{E_0-\mu}{\tau}+\cdots)-1} \approx N$$

$$\mu \simeq E_0 - \frac{\tau}{N}$$



Again, for any τ can find $\mu(\tau)$ via

$$\sum_i \langle N_i \rangle = \sum_i \frac{1}{e^{(E_i-\mu)/\tau}-1} = N$$

Quantum approach to classical gas:

For classical limit need small occupation numbers, ie. need

$$f_{FD}(E) << 1 \text{ for all } E$$

and

$$f_{BE}(E) << 1 \text{ for all } E$$

Therefore, need $\frac{E_i-\mu}{\tau} >> 1$ or $\tau << E_i - \mu$ for all E_i *(see later)*
(seems to imply low τ? *NO!*)
Then $f_{class}(E_i) = f_{FD}^{\tau<<E-\mu}(E_i) = f_{BE}^{\tau<<E-\mu}(E_i) = e^{-(E_i-\mu)/\tau} \Rightarrow$ classical distribution function. Solving for μ:

$$\begin{aligned} \textstyle\sum_i f_{class}(E_i) = N \ &= \textstyle\sum_i e^{\mu/\tau} e^{-E_i/\tau} \\ &= e^{\mu/\tau}(Z_1) \end{aligned}$$

Z_1 is the single particle partition function. $Z_1 = n_Q V$ with $n_Q = (\frac{m\tau}{2\pi\hbar^2})^{3/2}$.
Thus $N = e^{\mu/\tau}(n_Q V)$ or $\mu_{class} = \tau \ln\left(\frac{n}{n_Q}\right)$ (where $n = \frac{N}{V}$) as before.
And classical limit requires

$$\tau << E_i - \mu_{class}$$

for all E_i (even gnd. state $E_0 \simeq 0$)
Thus need

$$\tau << -\mu_{class}$$

$$\tau << -\tau \ln\left(\frac{n}{n_Q}\right)$$

$$n << n_Q$$

$$n << \left(\frac{m\tau}{2\pi\hbar^2}\right)^{3/2}$$

$$\tau >> \frac{2\pi\hbar^2 n^{2/3}}{m} \text{ classical limit}$$

Let $\tau_Q \equiv \dfrac{2\pi\hbar^2 n^{2/3}}{m} \Rightarrow$Quantum temp.
How cold is τ_Q?
For N_2 at atmospheric number density $n \simeq 2.5 \cdot 10^{19}/cc$,
$\tau_Q = \dfrac{2\pi(197MeV - fm)^2 n^{2/3}}{mc^2} \approx 0.01^\circ K$

Concluding Topics for Ideal Classical Gas:

1. 1. **Classical gas with internal degrees of freedom:**

   In canonical ensemble recall (classically)

$$Z_N = \frac{(Z_1^{class})^N}{N!}$$

$$Z_1^{class} = \sum_{states} e^{-E_i/\tau}$$

   Previously we derived $Z_1^{class} = V n_Q$ with $E_i = \frac{P_i^2}{2m}$.

For more complicated system (eg. molecule)

$$\text{Hamiltonian} = E = E_T + E_E + E_R + E_V$$

E_T=translational K.E.

E_E=electronic states

E_R=rotational states

E_V=vibration states

with $E_i = E_T + E_E + E_R + E_V$

E_T given by $\frac{P^2}{2m}$

E_E are electronic energy levels ($\Delta E_E \sim$ few eV $\Rightarrow$ can ignore at room temperature

since $\tau_{room} << \Delta E_E$, but not in stars)

E_R given by $\frac{\hbar^2 J(J+1)}{2I}$, where I is the moment of inertia

($\Delta E_R \sim 10^{-3} - 10^{-4}$ eV. Therefore important at room temperature).

E_V given by $\hbar\omega(n+\frac{1}{2})$. ($\Delta E_V \sim$0.1 eV, few levels may be important at τ_{room}.)

Then $Z_1^{class} = \sum_{T,E,R,V} e^{-[E_T+E_E+E_R+E_V]/\tau}$

Generally different energies are independent (e.g. independent quantum numbers)

Thus

$$\begin{aligned} Z_1^{class} &= (\textstyle\sum_T e^{-E_T/\tau})(\sum_E e^{-E_E/\tau})\cdots \\ &= Z_1^T Z_1^E Z_1^R Z_1^V \\ &= \underbrace{(Z_1^T)}_{n_Q V \text{as before}} \times \underbrace{(Z_{int})}_{\text{internal degrees of freedom}} \end{aligned}$$

Thus standard thermo parameters receive additional contributions: eg.

$$\begin{aligned} \Rightarrow F &= -\tau \ln Z_N = -\tau[N \ln Z_1^T + \underbrace{N \ln Z_{int}}_{F_{int}=-\tau N \ln Z_{int}} - \ln N!] \\ &= F_T + F_{int} \\ \Rightarrow \sigma &= -\left(\frac{\partial F}{\partial \tau}\right)_V = \sigma_T + \sigma_{int} \\ \Rightarrow \mu &= \left(\frac{\partial F}{\partial N}\right)_V = \tau \ln\left(\frac{n}{n_Q}\right) - \tau \ln Z_{int} \end{aligned}$$

2. 2. **Heat Capacity**

Recall

$$C_V = \tau \left(\frac{\partial \sigma}{\partial \tau}\right)_V$$

$$\sigma_{ideal} = N\left[\ln\left(\frac{n_Q}{n}\right) + \frac{5}{2}\right]; \quad n_Q = \left(\frac{m\tau}{2\pi\hbar^2}\right)^{\frac{3}{2}}$$

Then

$$C_V = \tau\left[N\left(\frac{3}{2}\right)\frac{1}{\tau}\right] = \frac{3}{2}N$$

Also useful to define another heat capacity

$$C_P \equiv \tau\left(\frac{\partial\sigma}{\partial\tau}\right)_P$$

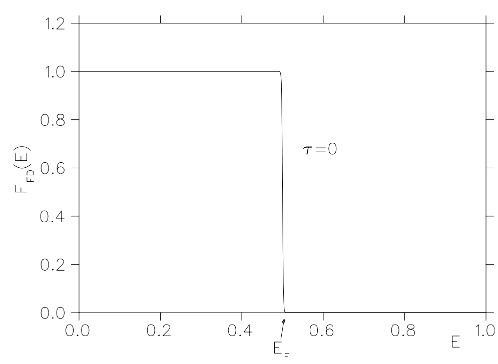
For constant pressure use equation of state $PV = N\tau$ or $V = \frac{N\tau}{P}$
then $\sigma = N\left[\ln(\frac{\tau n_Q}{P}) + \frac{5}{2}\right]$ and $C_P = \tau[N(\frac{5}{2})\frac{1}{\tau}] = \frac{5}{2}N$
Can define:

$$\gamma \equiv \text{ratio of } \underbrace{\text{specific heats}}_{\text{heat capacity per gram}} = \frac{C_P}{C_V}\ \left(= \frac{5}{3} \text{ for ideal gas}\right).$$

Fermi Gas:

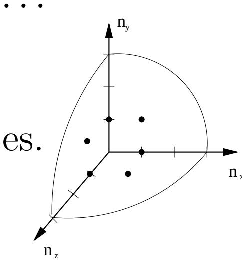
Fermi Energy

Fermi Energy defined at $\tau = 0$ where all energy levels filled , up to E_F.
How big is E_F?



Fill 3-d box ($L \times L \times L$) with N Fermions.
Energy levels are:

$$E_{n_T} = \frac{\hbar^2\pi^2 n_T^2}{2mL^2}; \ n_T^2 = n_x^2 + n_y^2 + n_z^2, \quad n_x, n_y, n_z = 1, 2, 3, \cdots$$



Each unit cube has 1 state.
Therefore the number of states = Volume = number of unit cubes.
All states filled up to surface of sphere (Fermi surface).

Therefore, the number of filled states $= N = (\frac{4}{3}\pi n_{max}^3)(\frac{1}{8})(2)$ where
$(\frac{1}{8})$ results since n_x, n_y, n_z are positive and only one octant of sphere is allowed, and factor of (2) is for the 2 spin states (at least) per particle.
Generally there is a factor of $2s + 1$ where s is the spin
(spin $\frac{1}{2}$ has 2, spin $\frac{3}{2}$ has 4,$\cdots$).

Solving for n_{max} gives $n_{max} = (3N/\pi)^{\frac{1}{3}}$ and for E_F we have:

$$\begin{aligned} E_F &= \frac{\hbar^2\pi^2 n_{max}^2}{2mL^2} \\ &= \frac{\hbar^2\pi^2}{2mL^2}\left[\frac{3N}{\pi}\right]^{\frac{2}{3}} = \frac{\hbar^2}{2m}\left(\frac{\pi^3 3N}{L^3\pi}\right)^{\frac{2}{3}} \end{aligned}$$

and

$$E_F = \frac{\hbar^2}{2m}(3\pi^2 n)^{\frac{2}{3}} \quad \text{for a spin } \frac{1}{2} \text{ Fermi gas}$$

For the case of arbitrary half-integer spin, $n_{max} = \left(\frac{6N}{(2s+1)\pi}\right)^{\frac{1}{3}}$ and

$$E_F = \frac{\hbar^2}{2m}\left(\frac{6\pi^2 n}{2s+1}\right)^{\frac{2}{3}} \quad \text{for a spin } s \text{ Fermi gas}$$

Total Energy for Spin $\frac{1}{2}$ Fermi Gas at τ=0

$$U(\tau = 0) = 2\sum_{n_T}^{n_{max}} E_{n_T} = 2\sum_{n_x}\sum_{n_y}\sum_{n_z} E_{n_T} \Rightarrow 2\int_0^{n_{max}} E_{n_T}\frac{4\pi n_T^2 dn_T}{8}$$

2 spin states $\nearrow$

$$U(\tau = 0) = \frac{\hbar^2\pi^3}{2mL^2}\int_0^{n_{max}} n_T^4 dn_T = \frac{\hbar^2\pi^3 n_{max}^5}{10mL^2} = \underbrace{\left(\frac{\hbar^2\pi^2 n_{max}^2}{2mL^2}\right)}_{E_F}\frac{\pi n_{max}^3}{5}$$

and with $n_{max}^3 = \frac{3N}{\pi}$ we get

$$U(\tau = 0) = \frac{3}{5}NE_F$$

Thus there's lots of energy in a Fermi Gas at τ=0.

Fermi Gas at $\tau > 0$

For $\tau > 0$ we have e.g. $U = \langle E\rangle = 2\sum_{n_x}\sum_{n_y}\sum_{n_z} E_{n_T}[f_{FD}(E_{n_T})]$

[*2 for spin $\frac{1}{2}$ and $f_{FD}(E_{n_T})$ is the occupation probability of state E_{n_T}.*]

For N large convert sum into integral; and since $f_{FD}(E)$ need integral over dE. Thus

$$\begin{aligned} \langle A(E)\rangle = \sum\sum\sum A(E) f_{FD}(E) &\Rightarrow \tfrac{2}{8}\int_0^\infty 4\pi n_T^2 dn_T A(E) f_{FD}(E) \\ &\Rightarrow \int_0^\infty A(E) f_{FD}(E)\rho(E) dE \end{aligned}$$

$\hookrightarrow \rho(E)$ - called density of states - from change of variables $n_T \Rightarrow E$.
Note: K^2 uses $\mathcal{D}(E) = \rho(E)$)

To find $\rho(E)$, note:

$$\text{for } E_{n_T} = \frac{\pi^2\hbar^2}{2mL^2} n_T^2; \;\; n_T^2 = n_x^2 + n_y^2 + n_z^2$$

then

$$\begin{aligned} \left(\frac{2}{8}\right)(4\pi n_T^2) dn_T &= \rho(E)dE \\ \pi \left(\frac{2mL^2}{\pi^2\hbar^2}\right) E dn_T &= \rho(E)dE \end{aligned}$$

and since

$$dE = \left(\frac{\pi^2\hbar^2}{2mL^2}\right)(2n_T dn_T)$$

we have

$$dn_T = \left(\frac{2mL^2}{\pi^2\hbar^2}\right)^{\frac{1}{2}} \left(\frac{1}{2}\right) \frac{1}{E^{\frac{1}{2}}} dE$$

leading to

$$\rho(E)dE = \frac{\pi}{2}\left(\frac{2mL^2}{\pi^2\hbar^2}\right)^{\frac{3}{2}} E^{\frac{1}{2}} dE$$

$$\Rightarrow \rho(E) = \frac{V}{2\pi^2\hbar^3}(2m)^{\frac{3}{2}} E^{\frac{1}{2}} \Rightarrow \text{Density of states in 3D for spin } \frac{1}{2}$$

or in general

$$\Rightarrow \rho(E) = \left(\frac{2s+1}{2}\right)\frac{V}{2\pi^2\hbar^3}(2m)^{\frac{3}{2}} E^{\frac{1}{2}} \Rightarrow \text{Density of states for arbitrary spin } s$$

Thus for general Fermi Gas problem use:

$$\begin{aligned} N &= \int_0^\infty \rho(E) f_{FD}(E) dE \;\; \text{to solve } \mu(\tau) \\ \text{and } U &= \int_0^\infty E\rho(E) f_{FD}(E) dE \end{aligned}$$

[Note: all τ dependence in $f_{FD}(E)$]

Applications of Fermi Gas:

1. **Heat Capacity from Conduction electrons in metals**

   Recall: from elastic oscillations of solid (phonons) at low temperature:

   $$C_V^{phonons} = \left(\frac{2V\pi^2}{5\hbar^3 v^3}\right)\tau^3 = \frac{12\pi^2 N}{5}\left(\frac{\tau}{\hbar\omega_D}\right)^3$$

(Debye theory) (this fails at low temperature for metals).

In metals, typically 1 "free" e^-/atom, therefore

consider contribution to C_V from free e^-.

If e^- are classical gas then $C_V^{e^-} = \frac{3}{2}N_{e^-}$ (much too big)

Check e^- density compared to n_Q: for Cu ($\rho = 9g/cm^3$)

$$\begin{aligned} n_{free\ e^-} &\simeq n_{atoms} = \frac{(9g/cm^3)6 \cdot 10^{23} atm/mole}{64g/mole} \\ &\simeq 10^{23}/cm^3. \end{aligned}$$

Then at $\tau = \tau_{room} = \frac{1}{40}\text{eV},\ n_Q = (\frac{m_e\tau}{2\pi^2\hbar^2})^{\frac{3}{2}} \simeq 2 \cdot 10^{18}/cm^3.$

Thus $n_{free\ e^-} >> n_Q \Rightarrow$ Quantum Gas

and Fermi Energy for free electrons is

$$\begin{aligned} E_F &= \frac{\hbar^2}{2m_e}(3\pi^2 n_{free\ e^-})^{\frac{2}{3}} \\ &\simeq 8eV \gg \tau_{room} \end{aligned}$$

If $\tau \ll E_F$ system called degenerate Fermi gas.

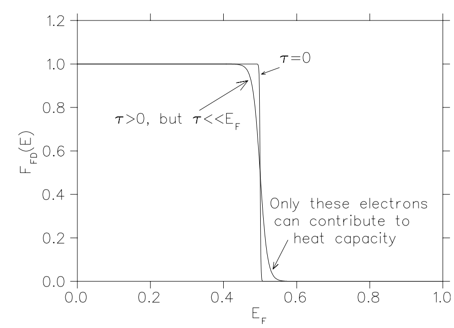
Now include contribution of e^- (as degenerate Fermi Gas) to heat capacity of metals

$\hookrightarrow$ (Triumph of Quantum Statistical Mechanics)

Assuming e^- are almost a degenerate Fermi Gas.

Then

$$U = \frac{(2m)^{\frac{3}{2}}V}{2\pi^2\hbar^3}\int_0^\infty \frac{(E)E^{\frac{1}{2}}dE}{e^{(E-\mu)/\tau}+1}$$



use Brute force

Although $\mu = \mu(\tau)$ let's assume $\mu \simeq E_F$

(since $\tau << E_F$) and let $x = \frac{E}{\tau}$ then

$$U = \frac{(2m)^{\frac{3}{2}}V}{2\pi^2\hbar^3}(\tau)^{\frac{5}{2}} \underbrace{\int_0^\infty \frac{x^{\frac{3}{2}}dx}{e^{-\alpha}e^x+1}}; \quad \alpha \equiv \frac{E_F}{\tau}$$

Note: if $\alpha \gg 1$, $\displaystyle\int_0^\infty \frac{\phi(x)dx}{e^{x-\alpha}+1} \simeq \int_0^\alpha \phi(x)dx + \frac{\pi^2}{6}\left(\frac{d\phi}{dx}\right)_{x=\alpha} + \frac{7\pi^4}{360}\left(\frac{d^3\phi}{dx^3}\right)_{x=\alpha} + \cdots$

see $*$.

Thus:

$$U \simeq \frac{(2m)^{\frac{3}{2}}V}{5\pi^2\hbar^3}E_F^{\frac{5}{2}}\left[1+\frac{5\pi^2}{8}\left(\frac{\tau}{E_F}\right)^2-\frac{7\pi^4}{384}\left(\frac{\tau}{E_F}\right)^4+\cdots\right]$$

Noting that $3\pi^2\left(\frac{N}{V}\right)=\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}E_F^{\frac{3}{2}} \Rightarrow \frac{(2m)^{\frac{3}{2}}V}{\pi^2\hbar^3}=\frac{3N}{E_F^{\frac{3}{2}}}$

we get:

$$U \simeq \underbrace{\frac{3}{5}NE_F}_{\tau=0 \text{ limit}}\left[1+\frac{5\pi^2}{8}\left(\frac{\tau}{E_F}\right)^2\right] \quad \text{ignoring higher order terms}$$

then

$$C_V=\left(\frac{\partial U}{\partial \tau}\right)=\left(\frac{3\pi^2N}{4}\right)\left(\frac{\tau}{E_F}\right)$$

$$\hookrightarrow \text{and for } \tau \ll E_F,\ C_V \ll \tfrac{3}{2}N$$

giving

$$C_V^{Total}=\underbrace{a\tau^3}_{phonons}+\underbrace{b\tau}_{electrons} \quad \Leftarrow \text{good agreement with experiment for metals}$$

$*$ From Sommerfeld's Lemma, A. Sommerfeld Z. Physik **47**, 1 (1928).