Chapter 4 : Ideal (non-interacting) systems

Simplified evaluation of partition functions and all thermodynamic properties.

N-particle system

micro state defined by an N-particle state ⇒ Decomposed into N one-particle states → focus in this chapter

Such factorization is accurate when the particles are non-interacting, i.e., particles are independent of each other. They do not influence each other's trajectories. No inter-particle potentials.

$\therefore H = H_1 + H_2 + H_3 + \ldots\ldots$

Hamiltonian of N-particle system = Sum of Hamiltonians for each particle

(No cross-terms arising from interaction between particles).

$$H\psi = (H_1 + H_2 + H_3 + \ldots)(\psi_1 \psi_2 \psi_3 \ldots)$$

$$\because \psi = \psi_1 \psi_2 \psi_3 \ldots\ldots$$

Total wavefunction → Product of one-particle wavefunctions (for non-interacting particles)

$$\therefore H\psi = \psi_2 \psi_3 \ldots H_1 \psi_1 + \psi_1 \psi_3 \ldots H_2 \psi_2 + \psi_1 \psi_2 \ldots H_3 \psi_3 + \ldots$$

$$H\psi = \psi_2 \psi_3 \ldots \varepsilon_1 \psi_1 + \psi_1 \psi_3 \ldots \varepsilon_2 \psi_2 + \psi_1 \psi_2 \ldots \varepsilon_3 \psi_3 + \ldots$$

$$E\psi = \psi_1 \psi_2 \psi_3 \ldots (\varepsilon_1 + \varepsilon_2 + \varepsilon_3 + \ldots)$$

$$\therefore \quad E\psi = (\varepsilon_1+\varepsilon_2+\varepsilon_3+\dots)\,\psi$$

$$\therefore \quad E = \varepsilon_1+\varepsilon_2+\varepsilon_3+\dots$$

Energy of N-particle eigenstate

sum of energies of N one-particle eigenstates

(Only for non-interacting particles)

Approximate for weakly interacting particles ⇒ can exchange energy via direct collisions or collisions with walls, but no inter-molecular forces, ⇒ e.g. ideal gas (density low enough such that negligible inter-molecular interaction but equilibrium maintained by collisions)

Partition function ⇒

$$Q = \sum_j e^{-\beta E_j} \qquad j \text{ N-particle states}$$

$$Q = \sum_j e^{-\beta(\varepsilon_1^j+\varepsilon_2^j+\varepsilon_3^j+\dots)}$$

energy of each one of a No of one-particle states for the j^{th} N-particle state.

Subscript can label a given particle

i.e we assume particles are distinguishable

$$Q = \sum_j \left(e^{-\beta\varepsilon_1^j}\, e^{-\beta\varepsilon_2^j}\dots\right)$$

$$= \left(\sum_j e^{-\beta\varepsilon_1^j}\right)\left(\sum_j e^{-\beta\varepsilon_2^j}\right)\dots$$

$$Q = q_1 q_2 \dots$$

partition function for each particle

This factorization can be over

a) different degrees of freedom of a molecule (translation, vib, rotation).

phonons ← b) independent vibrational modes of a monoatomic crystal

c) molecules adsorbed on independent sites on a solid surface

so not just restricted to particles. Over any set of uncorrelated collective variables. or uncorrelated quasi-particles

finding groupings that are uncorrelated. Correlations within a group.

variable that depends upon the co-ordinates or states of a large collection of particles.

In above case, if factorization over quasi-particles that are identical then: $q_1 = q_2 = q_3 \dots = q$

$$Q = q^N$$

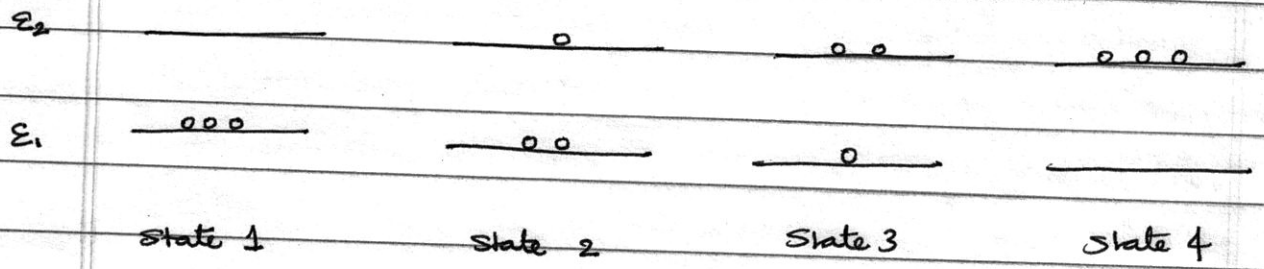
q is Boltzmann sum over states for single particle

Now all we have to do is evaluate the one-particle partition function and raise it to N^{th} power.

Thus reduction of N-body problem ⇒ one-body problem.

Let's consider N-particle system where $N = 1000$ and 5 possible one-particle microstates. Total number of states/terms $= 5^{1000}$ to be sampled when evaluating Q.

However, by factorization over independent identical quasi-particles we explicitly enumerate only 5 states



Four states of a 3-particle system with two single-particle states

A state ν can be characterized by n_1 particles in 1^{st} single-particle state, n_2 in 2^{nd}, ... and so on.

These numbers $(n_1, n_2, \ldots n_N)$ are called occupation numbers.

A set of these numbers specifies the state ν completely. For indistinguishable particles (~~even the order is not important~~.

Any more information is tantamount to distinguishing particles.

In above case

State 1: $n_1 = 3$ $n_2 = 0$
State 2: $n_1 = 2$ $n_2 = 1$
State 3: $n_1 = 1$ $n_2 = 2$
State 4: $n_1 = 0$ $n_2 = 3$

Note ⇒ an occupation number is a collective variable

$$\sum_i n_i = N, \text{ total \# of particles}$$

i ⇒ sum over all 1-particle states

$$\sum_i \varepsilon_i n_i = E_\nu \text{ energy in } \nu^{th} \text{ state.}$$

$n_i = 0$ or 1 for some class of particles, known as fermions

$n_i = 0, 1, 2, 3, \ldots$ for another class, known as bosons.

Note partition function for single particles can be further factorized into partition functions for every degree of freedom, provided these are uncorrelated. For molecules,

$$\therefore q = q_{trans}\, q_{rot}\, q_{vib}\, q_{elec} \dots$$

$$\therefore \varepsilon = \varepsilon^{i}_{trans} + \varepsilon^{j}_{rot} + \varepsilon^{k}_{vib} + \varepsilon^{l}_{elec} + \dots$$

$$\therefore Q = \left(q_{trans}\, q_{rot}\, q_{vib}\, q_{elec}\right)^{N}$$

Problem of indistinguishability

If two particles are indistinguishable then $\varepsilon_1^{j}+\varepsilon_2^{k}$ is equivalent to $\varepsilon_1^{k}+\varepsilon_2^{j}$. These two arrangements cannot be distinguished from one another.

Therefore, in the Boltzmann sums these should be counted only once i.e. nature considers them as one and the same arrangement.

∴ A term in Q of form

$$e^{-\beta(\varepsilon_1^{j}+\varepsilon_2^{k}+\varepsilon_3^{l}+\dots)}$$

where each particle (1, 2, 3, ...) is ~~a~~ in a diffrent one-particle quantum state (j, k, l, ...). where $j \neq k \neq l \neq \dots$ then this term occurs N! times. Because N particles can be permuted over their N occupied states N! ways.

∴ Dividing q^N by N! can get rid of this over-counting.

But situation is more complicated due to terms where particles are in same 1-particle state because 1) this may not even be allowed → Fermi-Dirac statistics 2) if this is allowed (Bose-Einstein statistics) then N! is not proper correction factor

→ terms like $e^{-\beta(\varepsilon_1^{j}+\varepsilon_2^{j}+\varepsilon_3^{j}+\dots)}$ not allowed to appear.

At high temperature, number of single particle states available is very large compared to the number of particles. Particles rarely in same state. For particles that are not distinguishable, each N-particle state occurs N! times, corresponding to the number of ways of assigning N distinct one-particle states to the N indistinguishable particles. Hence correct partition function is

$$\frac{1}{N!}\, q^N$$

Without 1/N! we would be over-counting distinguishable states.

—x—

Energies of these quasi-particles uncorrelated. Consider a two-particle system

$$\text{then} \quad E = E^{(1)} + E^{(2)}$$

$$Q = \sum_{n,m} \exp^{-\beta(E^{(1)} + E^{(2)})}$$

$$\text{so} \quad \langle E^{(1)} E^{(2)} \rangle = \frac{1}{Q} \sum_{n,m} E_n^{(1)} E_m^{(2)} \exp^{-\beta(E_n^{(1)} + E_m^{(2)})}$$

correlation between these two energy values

$$= \frac{1}{Q} \left(\sum_n E_n^{(1)} \exp^{-\beta E_n^{(1)}} \right) \cdot \left(\sum_m E_m^{(2)} \exp^{-\beta E_n^{(2)}} \right)$$

$$= \frac{1}{Q} \left(\partial q_1 / \partial(-\beta) \right) \left(\partial q_2 / \partial(-\beta) \right)$$

$$= \left(\frac{\partial \ln q_1}{\partial(-\beta)} \right) \left(\frac{\partial \ln q_2}{\partial(-\beta)} \right)$$

$$= \langle E^{(1)} \rangle \langle E^{(2)} \rangle$$

Correlations $\langle E^{(1)} E^{(2)} \rangle - \langle E^{(1)} \rangle \langle E^{(2)} \rangle = 0$

No correlation between energy of one particle w.r.t another.

∴ Quantum statistics →	Classical statistics
Particles occupy discrete well separated quantum states	At high temperature a continuum of states.
Low temperature high density	OR At low densities of particles

Quantum statistics

So at low temperatures & high density, discrete states dominant and there's likelihood of two particles occupying the same state and hence special considerations are required.

Two types of particles in nature

"Force carrying" particles	Particles constituting matter.
⇒ Integer spin	⇒ Spin a multiple of ½
⇒ Spin is an additional dimension.	⇒ Spin is an additional dimension.
$s=1$, spinning by 360° once exposes the same face to a static observer.	$s=\frac{1}{2}$, Here spinning twice exposes the same face to a static observer.
⇒ Two-particle wave-function symmetric under particle exchange. $\psi_a^{(1)}\psi_b^{(2)} = +\psi_a^{(2)}\psi_b^{(1)}$	⇒ Two-particle wave-function anti-symmetric under particle exchange. $\psi_a^{(1)}\psi_b^{(2)} = -\psi_a^{(2)}\psi_b^{(1)}$
$\psi = \frac{1}{\sqrt{2}}(\psi_a\psi_b + \psi_b\psi_a)$	$\psi = \frac{1}{\sqrt{2}}(\psi_a\psi_b - \psi_b\psi_a)$.
$\therefore \psi_a^{(1)}\psi_a^{(2)} = +\psi_a^{(2)}\psi_a^{(1)}$ ~~i.e ψ_a can be any wave-function can hold two particles.~~	$\psi_a^{(1)}\psi_a^{(2)} = -\psi_a^{(2)}\psi_a^{(1)}$ $\therefore \psi_a^{(1)}\cdot\psi_a^{(2)} = 0$

Two particles can be in the same state	Two particles cannot be in the same state. (Pauli exclusion)
"gregarious" ~~particles~~ waves can overlap completely any number of them can occupy the same quantum state. ⇒ they prefer to crowd into same quantum state In special cases, bosons can condense to give superfluids (no viscosity) and superconductors	"anti-social" particles. wavefunctions cannot overlap. That's what gives matter it's rigidity and strength Matter occupies volume due to this and cannot be squeezed too closely ⇒ stability of matter results from this.

Bosons

Consider an ideal gas of bosons. Say N of them.
Thermodynamic properties can be described by canonical partition function:

$$Q = \sum_{\nu} \exp^{-\beta E_\nu}$$

In terms of occupation numbers $\{n_1, n_2, n_3, \ldots\}$

$$Q = \sum_{\substack{n_1, n_2, \ldots \\ = 0,1,2,\ldots}} \exp^{-\beta \sum_i n_i \varepsilon_i}$$

This sum is non-trivial to calculate ∵ there is a constraint on the set of occupation numbers i.e $\sum_i n_i = N$
You can't consider all possible sets of occupation numbers.

Switching to a grand canonical ensemble simplifies this problem. Instead of constraining system to have N particles

You can immerse the system in a bath of such bosons so that N can fluctuate. No constraint on N or on the set of occupation numbers. You can now sum over all possible sets.

$$\Xi = \sum_{\nu} e^{-\beta E_\nu + \beta\mu N}$$

$$= \sum_{\substack{n_1,n_2,n_3\ldots \\ =0,1,2,\ldots}} e^{-\beta\left(\sum_i \varepsilon_i n_i \overset{-}{\cancel{+}} \sum_i \mu n_i\right)}$$

$$= \sum_{\substack{n_1,n_2,n_3\ldots \\ =0,1,2,\ldots}} \prod_i e^{-\beta(\varepsilon_i-\mu)n_i}$$

$$= \prod_i \sum_{n=0,1,2,\ldots} e^{-\beta(\varepsilon_i-\mu)n}$$

$$= \prod_i \sum_n \left(e^{-\beta(\varepsilon_i-\mu)}\right)^n$$

For $\varepsilon > \mu$ this term is < 1

$$\Xi \approx \prod_i \frac{1}{\left(1-e^{-\beta(\varepsilon_i-\mu)}\right)}$$

$$\ln \Xi = -\sum_i \ln\left(1-e^{\beta(\mu-\varepsilon_i)}\right)$$

What is the average population i.e. occupation number of i^{th} quantum state.

$$\bar{n}_i = \frac{\sum_\nu n_i e^{-\beta E_\nu + \beta\mu N}}{\Xi} = \frac{1}{\Xi}\left(\frac{\partial \Xi}{\partial(-\beta\varepsilon_i)}\right) = \frac{\partial \ln\Xi}{\partial(-\beta\varepsilon_i)}$$

$$\overline{n_i} = \frac{e^{\beta(\mu-\varepsilon_i)}}{1-e^{\beta(\mu-\varepsilon_i)}}$$

$$\overline{n_i} = \frac{1}{e^{\beta(\varepsilon_i-\mu)}-1}$$

For $\bar{n}_i$ to be positive (it's an occupation number!), $\varepsilon_i - \mu > 0$ or μ has to be smaller than ε_i, i.e. the smallest ε_i. If ground state energy $= 0$, μ has to be negative.

$\therefore$ $\mu = \left(\frac{\partial E}{\partial N}\right)_{\beta,V}$ this implies that adding particles to a boson gas decreases it's total energy. This has interesting implications. As more and more particles are added we will see from the form of $\bar{n}_i(\varepsilon_i-\mu)$, particles tend to pile together in the ground state. Higher the particle density greater the likelihood to pile-up in the ground state thus reducing the total energy as particles are added.

This implies an "attraction" between particles. Even though there are no inter-particle forces between particles, particles are correlated due to wave function symmetry requirements. The symmetric nature of the two-particle wave-function leads to an "attraction" - (a quantum correlation) between particles.

Ideal gas of fermions

$$\Xi = \sum_{\substack{n_1, n_2, \dots \\ = 0 \text{ or } 1}} e^{-\beta E_\nu + \beta \mu N}$$

$$= \sum_{\substack{n_1, n_2, \dots \\ = 0 \text{ or } 1}} e^{-\beta\left(\sum_i \varepsilon_i n_i \overset{-}{\cancel{+}} \sum_i \mu n_i\right)}$$

$$= \sum_{\substack{n_1, n_2, \dots \\ = 0 \text{ or } 1}} \prod_i e^{-\beta(\varepsilon_i - \mu) n_i}$$

$$= \prod_i \sum_{n = 0 \text{ or } 1} e^{-\beta(\varepsilon_i - \mu) n}$$

$$\Xi = \prod_i \left(1 + e^{-\beta(\varepsilon_i - \mu)}\right)$$

$$\ln \Xi = \sum_i \ln\left(1 + e^{-\beta(\varepsilon_i - \mu)}\right)$$

$$\bar{n}_i = \frac{\partial \ln \Xi}{\partial(-\beta \varepsilon_i)} = \frac{1}{1 + e^{-\beta(\varepsilon_i - \mu)}} \, e^{-\beta(\varepsilon_i - \mu)}$$

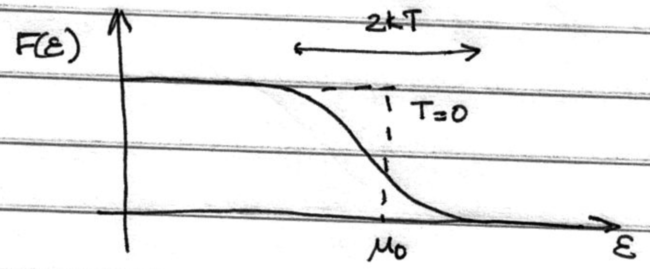
$$\bar{n}_i = \frac{1}{e^{\beta(\varepsilon_i - \mu)} + 1}$$

Thus for quantum gases $\bar{n}_i = \dfrac{1}{e^{\beta(\varepsilon_i - \mu)} \pm 1}$

(FERMI-DIRAC STATISTICS) fermion ← +   − → boson. (BOSE-EISTEIN STATISTICS)

Just one change in sign has dramatic implications in the statistics of particles and resulting properties

Above function expressed as a continuous function of ε is known as the Fermi function $F(\varepsilon)$. ie $\langle n_j \rangle$ or $\overline{n_j} = F(\varepsilon_j)$



Note $\overline{n_i}$ can only be between 0 and 1 as seen from the function

Note there is no restriction on μ for fermions

At $T=0$ or $\beta=\infty$ → or very low relative to μ_0

$\varepsilon<\mu_0$, $F = \dfrac{1}{e^{-\infty}+1} = 1$

$\varepsilon>\mu_0$, $F = \dfrac{1}{e^{\infty}+1} = 0$

A step function

States of energy below μ_0 filled with one particle each.

States above μ_0 empty.

Even at zero temperature, particles occupy most possible states.

At non-zero T, (Note μ is somewhat diff from μ_0 due to chemical potential's temp dependence)

F is <1 right below $\varepsilon=\mu$, states becomes slightly depopulated

F is >1 right above $\varepsilon=\mu$, states become slightly populated

& $F = 1/2$ at $\varepsilon=\mu$.

The transition from $F=1$ to $F=0$ broadens as T ↑. Breadth is given by $2kT$.

μ in this case is the chemical potential of the fermions in the bath. Thus the levels in the system/gas are populated upto an energy given by this chemical potential.

Note $\mu = \left(\dfrac{\partial E}{\partial N}\right)_\beta$, thus addition of one particle to system "fermionic" repulsion.

increases system energy by μ. i.e. energy state filled is close in energy to μ. Note μ in general is a function of temperature It's value at T=0 is denoted by μ_0.

Now in a bath, μ_0 is determined by the bath. The total N occupying the energy levels can fluctuate. But for a large system it takes an average value which ~~is given by~~ does not fluctuate significantly.

$$\bar{N} = \sum_i \bar{n}_i = \sum_i \frac{1}{e^{\beta(\varepsilon_i-\mu)}+1}$$

electrons/ particles from bath fill system energy levels until $\varepsilon = \mu_{bath}$ reached.

Now due to equivalence of ensembles of large systems we know that a fixed number N of fermions would distribute themselves also as per above equation and N would then determine μ, the chemical potential of the N-fermion system. of course μ would also depend on β

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

We can look at a specific example of how this works.
Above Fermi-Dirac distribution encodes quantum mechanical correlations. Even though particles do not interact via any interparticle forces, they are correlated due to symmetry requirements of their mutual wavefunctions.
These quantum correlations are important at low temperature and/or high densities.
↳ high enough such that wavefunctions overlap.

So this model is useful for describing high particle density electrons

systems such as electrons in a metal or white dwarf stars and "nuclear" gases.

Conduction
<u>Electrons in a metal</u> ⇒ Conduction Electrons form a sea.

also conduction electrons in a semiconductor (from doping)

Typical densities $10^{22}/cm^3$ or $10/nm^3$. Thus several electrons are within one De-Broglie wavelength of each other. Thus, the electrons can interfere quantum mechanically.
(i.e. Wavefunctions overlap).

$\rightarrow \frac{h}{\boxed{mv}} = \lambda$

electron mass is small. So DeBroglie wavelength is longer.

Let's see how energy levels are packed. (Density of energy states)

Consider N particles in a volume V in the shape of a cube of edge L.
$V = L^3$. Possible energy states are

$$\varepsilon(l_x, l_y, l_z) = \frac{h^2(l_x^2 + l_y^2 + l_z^2)}{8mL^2} \longrightarrow$$

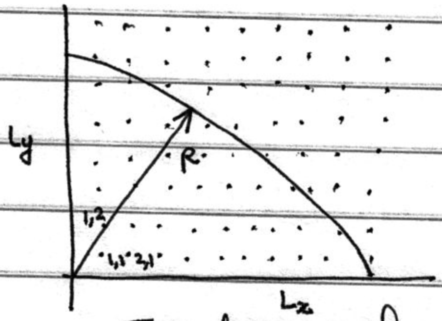
discrete, well separated for small m, small L

$l_x, l_y, l_z = 1, 2, 3, \ldots$ quantum numbers in 3-dimensions

each set specifies a different wave-function.

In a 3D space of these quantum numbers $l_x l_y l_z$ there is one-to-one correspondence between a point in this space and a possible molecular quantum state

in positive quadrant only ∵ $l_x, l_y, l_z \geq 0$.



Two dimensional projection of this space

Therefore there is one quantum state per unit volume $1 \times 1 \times 1$ of this space.

A sphere of radius R in this space where

$$R^2 = L_x^2 + L_y^2 + L_z^2$$

contains within it all states of energy less than or equal to ε where

$$\varepsilon = \frac{h^2 R^2}{8mL^2}$$

$$\therefore R^2 = \frac{8mV^{2/3}}{h^2}\varepsilon.$$

Thus the number of allowed quantum states with energy ε or less is given by the number of states within the positive quadrant of this sphere, the volume of which is $\frac{\pi R^3}{6}$

$\because$ there is 1 quantum state per unit volume.

$$\therefore \text{No of states with energy} \leq \varepsilon = \frac{\pi R^3}{6} = \frac{\pi}{6}\left(\frac{8m\varepsilon}{h^2}\right)^{3/2} \cdot V$$

$\downarrow$

call this $\phi(\varepsilon)$.

We argued that classical mechanics applies when $\phi(\varepsilon) \gg N$

$\because$ number of available states is much greater than the number of particles. Particles rarely try to occupy same state.

So the symmetry imposed quantum corrections are not important.

$$\text{Now} \quad \phi(\varepsilon) = \frac{\pi}{6}\left(\sqrt{\frac{8m\varepsilon}{h^2}}\right)^3 \cdot V$$

$$= \frac{4\pi}{3}\left(\frac{\sqrt{2m\varepsilon}}{h}\right)^3 \cdot V$$

$$\text{Now} \quad \lambda = \frac{h}{mv} \qquad \text{where} \qquad v = 2\sqrt{\frac{\varepsilon}{2m}}$$

de-Broglie wavelength

higher the λ greater the wave nature

$$\therefore \quad \phi(\varepsilon) = \frac{4\pi}{3}\left(\frac{1}{\lambda}\right)^3 \cdot V.$$

$$\phi(\varepsilon) >> N$$

$$\text{implies} \qquad \frac{V}{\lambda^3} >> N$$

$$\therefore \quad \lambda^3 << \frac{V}{N}$$

volume occupied by one particle

de-Broglie wavelength cubed.

volume occupied by the delocalized wave of the quantum particle. in a given state

∴ If the above inequality is valid the wave functions of two particles do not overlap at all and classical counting (statistics is valid. (i.e wavelength λ << interparticle distance $\left(\frac{V}{N}\right)^{1/3}$

When λ ~ interparticle distance, gas exhibits quantum nature

If above inequality does not hold then Fermi - Dirac Statistics needs to be ~~accounted for~~ used to describe the populating of available states. Since particles cannot occupy the same state successive particles take up higher and higher energy ~~energy~~ configurations (more nodes in the wave).

isolated from any of its surroundings (i.e. canonical ensemble)

In the fermionic system constituted by N electrons. we know at T=0K, electrons are filled, until electrons exhausted. This determines ~~upto an energy~~ μ_0.
There are two flavors of electrons spin $=+1/2$ or spin $=-1/2$ so each state can accomodate two electrons

distinguishable via spin.

$$\therefore \quad 2\times\frac{\pi}{6}\left(\frac{8m\mu_0}{h^2}\right)^{3/2}\cdot V = N$$

$$\therefore \quad \frac{N}{V} = \frac{\pi}{3}\left(\frac{8m\mu_0}{h^2}\right)^{3/2}$$

$$\therefore \quad \mu_0 = \left(\frac{3N}{\pi V}\right)^{2/3}\cdot\frac{h^2}{8m}$$

1/molar volume

$$\mu_0 = \left(\frac{N}{V}\right)^{2/3}\left(\frac{3}{8\pi}\right)^{2/3}\frac{h^2}{2m}$$

μ_0 for a Fermionic system is +ve and depends on the particle density

For sodium, molar volume 23.7 cm³/mole, each atom contributes one electron to the electron sea. As a result we find $\mu_0 = 3.1$ eV. Thus conduction electrons in sodium occupy energy levels up to 3.1 eV (due to Pauli exclusion principle ⇒ only two electrons can occupy each state).

μ_0 is known as the Fermi-energy of the metal and is typically 1-5 eV. (A metal is typically a source/sink of electrons with this energy. In a chemical bath, μ is determined by the bath and so the metal can gain electrons if $\mu_{bath} > \mu_0$ or lose electrons if $\mu_{bath} < \mu_0$ until the Fermi level of metal equilibriates with the chemical potential of bath ⇒ described by grand canonical ensemble, i.e. μ_{bath} determines $\bar{N}$ of metal)

Now $\beta = 1/kT$, $kT \approx 0.025\,\text{eV}$ at room temperature

$\therefore$ $\beta\mu_0$ at room temperature $\approx O(100)$

$\therefore$ Compared to a characteristic temperature μ_0/k known as a Fermi temperature T_F, room temperature is two orders magnitude smaller and can be considered almost zero and the Fermi-distribution still looks like a step function. Only very close to μ_0 in energy is there deviation from the step function.

Fermi temperatures are typically thousands of degrees Kelvin. Most of the electrons never have a chance to be excited to energies above μ until this temperature is reached.

Energy of N-fermion gas

at 0K

$$\searrow E_0 = 2\int_0^{\infty} \omega(\varepsilon)\cdot\varepsilon\,\overline{n_i}\,d\varepsilon$$

factor of 2 for spin +1/2 and -1/2

Note for continuous energies

$$\sum_i \overline{n_i}\,\varepsilon_i = \int_{\phi} \overline{n_i}\,\varepsilon\,d\phi = \int_{\varepsilon} \overline{n_i}\,\varepsilon\,\omega(\varepsilon)\,d\varepsilon$$

where $\omega(\varepsilon) = \dfrac{d\phi}{d\varepsilon}$ = density of states

where $\omega(\varepsilon)$ = density of states $= \dfrac{d\phi(\varepsilon)}{d\varepsilon} = \dfrac{\pi}{6}\left(\dfrac{8m}{h^2}\right)^{3/2}\cdot V\,\dfrac{3}{2}\,\varepsilon^{1/2}$

$$\omega(\varepsilon) = \frac{4\pi}{2}\left(\frac{2m}{h^2}\right)^{3/2} V\varepsilon^{1/2} = 2\pi\left(\frac{2m}{h^2}\right)^{3/2} V\varepsilon^{1/2}$$

$$\therefore E_0 = 2\int_0^{\mu_0} \omega(\varepsilon)\cdot\varepsilon\,d\varepsilon + 2\int_{\mu_0}^{\infty} \omega(\varepsilon)\cdot\varepsilon\cdot 0\cdot d\varepsilon$$

$$E_0 = 4\pi\left(\frac{2m}{h^2}\right)^{3/2} V \int_0^{\mu_0} \varepsilon^{1/2}\cdot\varepsilon\,d\varepsilon = 4\pi\left(\frac{2m}{h^2}\right)^{3/2} V\cdot \left.\frac{\varepsilon^{5/2}}{5/2}\right|_0^{\mu_0}$$

$$E_0 = \frac{8\pi}{5}\left(\frac{2m}{h^2}\right)^{3/2} V\cdot \mu_0^{5/2}$$

$$\mu_0^{3/2} = \frac{N}{V} \cdot \frac{3}{8\pi} \cdot \left(\frac{h^2}{2m}\right)^{3/2}$$

$$\therefore \left(\frac{2m}{h^2}\right)^{3/2} \cdot 8\pi \cdot V = \frac{3N}{\mu_0^{3/2}}$$

$$E_0 = \frac{3}{5}\frac{N}{\mu_0^{3/2}} \cdot \mu_0^{5/2} = \frac{3}{5}N\mu_0$$

$\therefore$ E_0 is zero-point energy of a Fermi-Dirac gas.

$\because$ $\frac{\partial E_0}{\partial T} = 0$ $\Rightarrow$ contribution of conduction electrons to the heat capacity is zero.

In order to contribute to heat capacity, electrons must be able to be excited to higher quantum states by absorbing thermal energy $\because$ $\mu_0 >> kT$ (@ room temperature), only small number of particles are within kT from the top of the distribution (near μ_0) where there are vacant states lying above. Thus a very small fraction of electrons can contribute to the heat capacity, and so experimental heat capacity (due to conduction electrons) is almost zero.

How about the pressure of the N-fermion system $\Rightarrow$

We know in the grand canonical ensemble

PV is natural function

i.e. $pV = kT \ln \Xi$

$$\therefore p = \frac{kT}{V} \sum_i \ln(1 + e^{\beta(\mu_0 - \varepsilon_i)})$$

$$= \frac{kT}{V} \int_0^{\mu_0} \ln(1 + e^{\beta(\mu_0 - \varepsilon_i)}) \, \mathbf{2} \cdot a(\varepsilon) \, d\varepsilon$$

factor of 2 to account for spin 1/2 and spin -1/2 particles

$$P_0 = \frac{kT}{V} \cdot 4\pi \left(\frac{2m}{h^2}\right)^{3/2} V \int_0^{\mu_0} \ln\left(1 + e^{\beta(\mu_0 - \varepsilon)}\right) \cdot \varepsilon^{1/2} d\varepsilon.$$

We can assume $e^{\beta(\mu_0-\varepsilon)} >> 1$ ∵ for most of the integration except for states very close to μ_0. The higher β (lower the temperature) the more this assumption is valid for most states.

$$\therefore \quad P_0 = \frac{kT}{V} \cdot 4\pi \left(\frac{2m}{h^2}\right)^{3/2} \cdot V \int_0^{\mu_0} \beta(\mu_0 - \varepsilon)\varepsilon^{1/2} d\varepsilon$$

$$P_0 = 4\pi \left(\frac{2m}{h^2}\right)^{3/2} \cdot \left(\frac{\mu_0 \varepsilon^{3/2}}{3/2} - \frac{\varepsilon^{5/2}}{5/2}\right)\Bigg|_0^{\mu_0}$$

$$P_0 = 4\pi \left(\frac{2m}{h^2}\right)^{3/2} \cdot \left(\frac{2\mu_0^{5/2}}{3} - \frac{2\mu_0^{5/2}}{5}\right)$$

$$P_0 = 4\pi \left(\frac{2m}{h^2}\right)^{3/2} \cdot \frac{4}{15} \mu_0^{5/2}.$$

→ zero-point pressure is a quantum effect ⇒ indicated by appearance of h.

$$\text{Note } \mu_0^{3/2} = \frac{N}{V} \cdot \left(\frac{3}{8\pi}\right)\left(\frac{h^2}{2m}\right)^{3/2}$$

$$\therefore \quad 4\pi \left(\frac{2m}{h^2}\right)^{3/2} = 1/\left(\frac{2V}{3N} \cdot \mu_0^{3/2}\right)$$

$$\therefore \quad P_0 = \frac{3N}{2V} \frac{4}{15} \frac{\mu_0^{5/2}}{\mu_0^{3/2}}$$

$$P_0 = \frac{2}{5} \frac{N}{V} \cdot \mu_0$$

zero-point pressure → O(10^5) atm

↓

quantum effect

We know for the grand canonical ensemble.

$$G = N\mu_0 = E_0 - TS_0 + p_0V$$

$$S_0 = \frac{E_0 + p_0V - N\mu_0}{T}$$

$$S_0 = \frac{\frac{3}{5}N\mu_0 + \frac{2}{5}N\mu_0 - N\mu_0}{T} \qquad \text{at } 0K$$

$$S_0 = 0 \qquad \text{at } 0K$$

Only one way to put N indistinguishable particles into the lowest $\overset{\text{in energy}}{}$ possible N-particle quantum state.

What temperature/density does classical statistics apply?

$$\phi(\varepsilon) = \frac{\pi}{6}\left(\frac{8m\varepsilon}{h^2}\right)^{3/2}\cdot V$$

$$\phi(\varepsilon) = \frac{4\pi}{3}\left(\frac{\sqrt{2m\varepsilon}}{h}\right)^{3}\cdot V$$

Now $\varepsilon \approx kT$, equipartition theorem

↳ average energy of a state accessible at temperature T.

$$\therefore \phi(\varepsilon) = \frac{4\pi}{3}\left(\frac{\sqrt{2mkT}}{h}\right)^{3}\cdot V$$

higher the thermal energy smaller is the spread of a matter wave.

classical statistics applies when

$$\phi(\varepsilon) >> N$$

$$\therefore \frac{4\pi}{3}\left(\frac{\sqrt{2mkT}}{h}\right)^{3} >> \frac{N}{V}$$

$$\therefore \underbrace{\left(\frac{\sqrt{2mkT}}{h}\right)}_{\frac{1}{\text{thermal wavelength}}}^{3} >> \frac{3}{4\pi}\,\frac{N}{V}$$

$$\therefore \frac{2mkT}{h^2} >> \left(\frac{3}{4\pi}\right)^{2/3}\left(\frac{N}{V}\right)^{2/3}$$

$$\therefore \overbrace{kT}^{\text{thermal energy}} >> \left(\frac{3}{4\pi}\right)^{2/3}\underbrace{\left(\frac{N}{V}\right)^{2/3}}_{\text{particle density}}\cdot\frac{h^2}{2m}$$

For example of fermions $\therefore kT >> \mu_0$

Thus we explicitly show that the temperature has to be high relative to the particle density (encoded in μ_0 for fermions) for classical statistics to apply.

Now let's evaluate partition function Q for Boltzmann statistics
Due to the Legendre transform relationship

$$\ln Q(\bar{N},V,T) = \ln \Xi(\mu,V,T) - \beta\mu\bar{N}$$

$$\ln Q = -\beta\mu\bar{N} \pm \sum_i \ln\left(1 \pm e^{\beta(\mu-\varepsilon_i)}\right)$$

upper (lower) sgin for fermions (bosons)

We know $e^{\beta(\varepsilon_i-\mu)}$ is a large number so $e^{\beta(\mu-\varepsilon_i)}$ is a very small number

From $\ln(1 \pm x) \approx \pm x$ for $x \approx 0$

$$\therefore \quad \ln Q = -\beta\mu\bar{N} + \sum_i e^{\beta(\mu-\varepsilon_i)}$$

$$\ln Q = -\beta\mu\bar{N} + \bar{N}$$

$$Q = e^{\bar{N}(1-\beta\mu)}$$

$$\therefore Q = \left(e^{(1-\beta\mu)}\right)^{\bar{N}}$$

$$Q = e^{\bar{N}} \cdot \left(e^{-\beta\mu}\right)^{\bar{N}}$$

$$Q = e^{\bar{N}} \cdot \left[\frac{\left(\sum_i e^{-\beta\varepsilon_i}\right)}{\bar{N}}\right]^{\bar{N}} \qquad \because \quad \bar{N} = e^{\beta\mu}\sum_i e^{-\beta\varepsilon_i}$$

$$Q = \frac{\left(\sum_i e^{-\beta\varepsilon_i}\right)^N}{(N/e)^N}$$

from Stirling's approximation

$$Q = \frac{\left(\sum_i e^{-\beta\varepsilon_i}\right)^N}{N!}$$

$q \Rightarrow$ single partificle partition function

$$Q = \frac{q^N}{\boxed{N!}} \Rightarrow \text{similar to what we argued before}$$

indistinguishability
no other quantum effects

Boltzmann or classical statistics

At high temp or low density $(kT >> \mu)$

$$\overline{n_i} = \frac{1}{e^{\beta(\varepsilon_i-\mu)} \pm 1}$$

but we have $\overline{n_i} << 1$ ∵ many more states than particles. No where close to 1 particle in each state.

$$\therefore e^{\beta(\varepsilon_i-\mu)} \pm 1 \Rightarrow \text{is a large number}$$

$$\therefore e^{\beta(\varepsilon_i-\mu)} >> 1$$

$$\therefore \overline{n_i} \simeq \frac{1}{e^{\beta(\varepsilon_i-\mu)}}$$

$$\therefore \overline{n_i} = e^{-\beta(\varepsilon_i-\mu)}$$

Now $\overline{N} = \sum \overline{n_i} = \sum e^{-\beta(\varepsilon_i-\mu)}$

Probability of particle in i^{th} state

$$P_i = \frac{\overline{n_i}}{\overline{N}} = \frac{e^{-\beta(\varepsilon_i-\mu)}}{\sum e^{-\beta(\varepsilon_i-\mu)}} = \frac{e^{-\beta\varepsilon_i}}{\sum e^{-\beta\varepsilon_i}} \cdot \frac{e^{+\beta\mu}}{e^{\beta\mu}}$$

$$\therefore P_i = \frac{e^{-\beta\varepsilon_i}}{\sum e^{-\beta\varepsilon_i}}$$ .... familiar Boltzmann statistics

Both Fermi-Dirac & Bose-Einstein statistics converge to Boltzmann statistics. No more quantum correlations included.

Note ⇒ quantum correlations are included via μ. For FD statistics μ is a large +ve energy. B.E statistics are represented by negative value of μ.