So far: Canonical ensemble.

Now: Grand canonical ensemble

$$\mathcal{Q}(z, V, T) = Tr\left(e^{-\beta(\hat{\mathcal{H}} - \mu\hat{N})}\right)$$

$$= \sum_N Tr\left(e^{-\beta(\hat{\mathcal{H}} - \mu N)}\right)$$

$z = e^{\mu\beta} \rightarrow$ $$= \sum_N z^N \, Tr\left(e^{-\beta\hat{\mathcal{H}}}\right)$$

$$= \sum_N z^N \, Q(N, V, T)$$

density matrix $$\hat{\rho}_G = \frac{e^{-\beta(\hat{\mathcal{H}} - \mu\hat{N})}}{Tr\left(e^{-\beta(\hat{\mathcal{H}} - \mu\hat{N})}\right)}$$

average $$\langle \hat{A} \rangle = Tr\left(\hat{\rho}_G \hat{A}\right)$$

$$= \frac{Tr\left(e^{-\beta(\hat{\mathcal{H}} - \mu\hat{N})}\hat{A}\right)}{Tr\left(e^{-\beta(\hat{\mathcal{H}} - \mu\hat{N})}\right)}$$

$$= \frac{\sum_N z^N \, Tr\left(\hat{\rho}_{can}\hat{A}\right)}{\sum_N z^N \, Tr\left(\hat{\rho}_{can}\right)}$$

Last: Microcanonical ensemble

We had defined:

$$\Gamma(E) = \frac{1}{N!\,h^{3N}} \int_{E < \mathcal{H}(\vec{p},\vec{q}) < E+\Delta E} d^{3N}p \, d^{3N}q$$

classical statistical mechanics

note: the units of $\delta(E-\mathcal{H})$ are energy^{-1}: $\delta(E-\mathcal{H})\Delta E$ is dimensionless

$\Gamma(E)$ counts the number of states

Rewrite: ($\Delta E \to 0$ limit)

$$\Gamma(E) = \frac{\Delta E}{N!\,h^{3N}} \int \delta(E - \mathcal{H}(\vec{p},\vec{q}))\, d^{3N}p \, d^{3N}q$$

We had defined: $S(N,E,V) = k \log(\Gamma(E))$

density matrix:

(normalization factor $1/\Gamma(E)$ is included)

$$\rho_{MC} = \begin{cases} \frac{1}{\Gamma(E)} & \text{for } E < \mathcal{H} < E+\Delta E \\ 0 & \text{otherwise} \end{cases}$$

In $\Delta E \to 0$ limit: $\rho_{MC} = \frac{\Delta E}{\Gamma(E)} \delta(E - \mathcal{H}(\vec{p},\vec{q}))$

$$\langle A \rangle = \frac{1}{N!\,h^{3N}} \iint \rho_{MC}\, A \; d^{3N}p \, d^{3N}q$$

Just as a reminder: $\Gamma(E)$ is volume of energy shell in classical statistical mechanics

Now, we "translate" this into quantum statistical mechanics.

$\Gamma(E)$ is equal to the number of states (i.e., energy eigenstates) in the interval $[E, E+\Delta E]$

→ all states contribute with equal weight

$$\rightarrow \hat{\rho}_{MC} = \sum_n \frac{1}{\Gamma(E)} |\psi_n\rangle\langle\psi_n|$$

n in energy shell

Note: $Tr(\hat{\rho}_{MC}) = 1$

$$= \sum_n p(E_n) |\psi_n\rangle\langle\psi_n|$$

$$\text{where } p(E_n) = \begin{cases} \frac{1}{\Gamma(E)} & \text{for } E < E_n < E+\Delta E \\ 0 & \text{otherwise} \end{cases}$$

Letting $\Delta E \to 0$:

$$\hat{\rho}_{MC} = \frac{\Delta E}{\Gamma(E)}\,\delta(\hat{\mathcal{H}} - E) = \frac{1}{\omega(E)}\,\delta(\hat{\mathcal{H}} - E)$$

$\omega(E)\,\hat{\rho}_{MC} = \delta(\hat{\mathcal{H}} - E)$

$\Rightarrow$ taking Tr on both sides and using $\mathrm{Tr}(\hat{\rho}_{MC}) = 1$

$\leadsto \omega(E) = \mathrm{Tr}(\delta(\hat{\mathcal{H}} - E))$

and $\frac{1}{\Delta E}\Gamma(E) = \mathrm{Tr}\,\delta(\hat{\mathcal{H}} - E) = \omega(E)$ ← density of states

$$\langle \hat{A} \rangle = \mathrm{Tr}(\hat{\rho}_{MC}\,\hat{A})$$

recall: $\omega(E) \mathrel{\hat{=}}$ density of states

As in classical statistical mechanics, we have

$$S(N, E, V) = k \log \Gamma(E)$$

in quantum statistical mechanics.

Sec. 8.4: Let's think about entropy at zero temperature.

$\Gamma(E)$: number of states in energy interval

$$\Rightarrow k \log(\Gamma(E)) = k \log 1 = 0$$

provided we have no degeneracies!

But: $k \log \Gamma(E) \neq 0$ if the ground state is degenerate

⇝ recall: we have encountered degenerate gr. states in homework assignment

let degeneracy be G.

$\Rightarrow \quad S = k \log G$

entropy per atom/molecule : $\frac{S}{N} = k \frac{\log G}{N}$

So: no degeneracy → 3rd law of thermodynamics holds "strictly"

$S \to 0$ as $T \to 0$

degeneracy → $\frac{S}{N}$ some constant finite value that is (typically) $\leq k \frac{\log N}{N}$

8.5 The ideal gases: Microcanonical ensemble

Ideal gas → no interactions

$$\hat{\mathcal{H}} = \sum_{i=1}^{N} \frac{\hat{\vec{p}}_i^{\,2}}{2m}$$

assume non-relativistic

Particles are either bosons or fermions

we are talking about elementary particles

the N-particle eigenstates are symmetric under the exchange of any pair of coordinates ($\vec{r}_i$, spin, isospin) – we're really exchanging the particles:

$$\psi(\vec{q}_1, \vec{q}_2, \dots, \vec{q}_N) = + \psi(\vec{q}_2, \vec{q}_1, \dots, \vec{q}_N)$$

the N-particle states are anti-symmetric under the exchange of any pair of coordinates:

$$\psi(\vec{q}_1, \vec{q}_2, \dots, \vec{q}_N) = - \psi(\vec{q}_2, \vec{q}_1, \dots, \vec{q}_N)$$

$\vec{q}_i$: all "labels" of i^{th} particles

What is the likelihood to find two identical fermions at the same location, or better, in exactly the same "state"?

Zero!

"Fermions are anti-social" / avoid each other

Examples: will be done on page 180...

Bosons: photon, Higgs boson, W boson, ...

Fermions: electron, muon, quark, ...

What about atoms or molecules?

$\hookrightarrow$ it depends...

let's assume that the temperature is sufficiently low so that we do not see the "internal" structure of the atom e.g.: H-atom

↳ proton + electron
(spin-$\frac{1}{2}$) (spin-$\frac{1}{2}$)

two spin-$\frac{1}{2}$ particles couple to spin zero or spin one
→ integer spin

⇒ H-atom can be considered a composite boson at low temperature

D-atom

↳ proton + neutron + electron
(spin-$\frac{1}{2}$) (spin-$\frac{1}{2}$) (spin-$\frac{1}{2}$)

three spin-$\frac{1}{2}$ particles couple to half-integer spin

⇒ D-atom can be considered a composite fermion at low T

T-atom

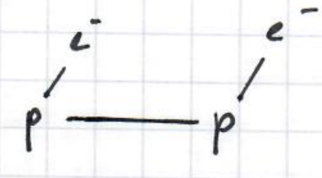
↳ proton + neutron + neutron + electron

⇒ T-atom can be considered a composite boson at low T

What about molecules?

Look at H_2 (molecular hydrogen) as an example.

treat H_2 as basic unit



need to think about
- nuclear
- electronic
- vibrational
- rotational

degrees of freedom

relevant for exchange of nuclei

symmetric nuclear fct. × odd rotational wave fct. ($l = 1, 3, 5, \ldots$)

or

anti-symmetric nuclear fct. × even rotational wave fct. ($l = 0, 2, 4, \ldots$)

$\Rightarrow$ total wave fct. (excluding electr. degrees) is anti-symmetric
(must be the case since nuclei are fermions)

Recall: $$Y_{lm}(\hat{r}) = (-1)^l \, Y_{lm}(-\hat{r})$$

nuclear wave fct.: singlet (1×)
triplet (3×)

singlet: $\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)$

triplet: $\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right)$

$|\uparrow\uparrow\rangle$

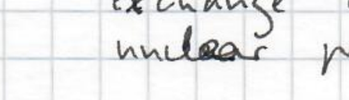
$|\downarrow\downarrow\rangle$

spin of protons (formal treatment equivalent to electron spin)

Note: We also have electronic spin

$\rightsquigarrow$ In the lowest electronic state, the electrons form a spin singlet (anti-symmetric electronic wave fct.)

Why are we looking at nuclear × rotational wave fct. part?



internuclear distance:

exchange of protons involves nuclear part, rotational part, vibrational part

symmetric (dependent on r)

even l

At low T: para-hydrogen (or molecular para-hydrogen)

and ortho-hydrogen (or molecular ortho-hydrogen)

odd l

We can calculate rotational partition fct.:

$$Q_{rot,para} = \sum_{l=0,2,\ldots} (2l+1)\, e^{-\beta l(l+1)\frac{\hbar^2}{2J}}$$

$$Q_{rot,ortho} = \sum_{l=1,3,\ldots} (2l+1)\, e^{-\beta l(l+1)\frac{\hbar^2}{2J}}$$

no conversion from ortho- to para-hydrogen.

Now: When l even $\rightsquigarrow$ nuclear spin degeneracy = 1.

When l odd $\rightsquigarrow$ " " " = 3.

Equilibrium ratio of ortho- and para-molecular hydrogen at $T \sim 300K$?

$$\frac{N_{ortho}}{N_{para}} = \frac{3\sum_{l\,odd} (2l+1)\, e^{-\beta l(l+1)\hbar^2/2J}}{\sum_{l\,even} (2l+1)\, e^{-\beta l(l+1)\hbar^2/2J}}$$

Note: At 300 K, we should be ok with Boltzmann factors $\rightsquigarrow$ do not need to consider fully symmetrized partition function
or anti-symmetrized

What is the value of $\frac{\hbar^2}{2J}$ for H_2?

$\frac{\hbar^2}{2J} = k\ 85\,K$

At room temperature, vibrational and electronic degrees are frozen (to a good approximation).

Back to ideal gas in microcanonical ensemble:

main topic of Sec. 8.5

- ideal Bose gas
- ideal Fermi gas
- ideal Boltzmann gas

How many states $\Gamma(E)$ do we have between E and $E + \Delta E$?

Or: how do we count for ideal Bose gas, ideal Fermi gas, ideal Boltzmann gas?

$\boxed{\text{For now: no spin!}}$ need to include spin later eigenenergies of $\underbrace{\text{single particle}}_{\substack{\text{3D box with} \\ \text{volume } V \\ (V = L^3)}}$: $\varepsilon_{\vec{k}} = \frac{\hbar^2 k^2}{2m}$

$$\vec{k} = \frac{2\pi}{L} \vec{n}$$

$n_x = 0, \pm 1, \pm 2, \ldots$
$n_y = \ldots$
$n_z = \ldots$

as $V \to \infty$, the energy levels get closer and closer.

$$\Rightarrow \sum_{\vec{k}} \ldots \longrightarrow \frac{V}{(2\pi)^3} \int \ldots \, d^3k$$

$$dk_x = \frac{2\pi}{L} \Delta n$$

$$\Rightarrow dk_x dk_y dk_z = \left(\frac{2\pi}{L}\right)^3$$

sum $\longrightarrow$ integration

Up to now, single-particle picture.

Now: State of ideal system can be described by specifying a set of occupation numbers $\{n_{\vec{k}}\}$:

$n_{\vec{k}}$ particles have momentum $\hbar\vec{k}$ in the state under consideration.

this assumes no interactions $\longrightarrow$ $E = \sum_{\vec{k}} \varepsilon_{\vec{k}}\, n_{\vec{k}}$ (total energy)

$N = \sum_{\vec{k}} n_{\vec{k}}$ (total number of particles)

For spinless bosons and fermions, $\{n_{\vec{k}}\}$ uniquely defines a state of the system

$n_{\vec{k}} = 0, 1, 2, \ldots$	for bosons
$n_{\vec{k}} = 0, 1$	for fermions

Boltzmann gas: $n_{\vec{k}} = 0, 1, 2, \ldots$ but now there exist $\dfrac{N!}{\prod_{\vec{k}} (n_{\vec{k}}!)}$ states for the N-particle system

For example:

Let $n_{000} = 1$ and $n_{100} = 1$

We have two plane wave single-particle states:

$\frac{1}{\sqrt{V}}$ and $\frac{1}{\sqrt{V}} e^{ik_x x}$ $\rightsquigarrow$ call them $\varphi_1(\vec{r})$ and $\varphi_2(\vec{r}_2)$.

* Wave function for two identical bosons with position vectors $\vec{r}_1$ and $\vec{r}_2$:

$$\frac{1}{\sqrt{2}}\left(\varphi_1(\vec{r}_1)\,\varphi_2(\vec{r}_2) + \varphi_2(\vec{r}_1)\,\varphi_1(\vec{r}_2)\right)$$

one wave fct.

* Wave function for two identical fermions with position vectors $\vec{r}_1$ and $\vec{r}_2$:

$$\frac{1}{\sqrt{2}}\left(\varphi_1(\vec{r}_1)\,\varphi_2(\vec{r}_2) - \varphi_2(\vec{r}_1)\,\varphi_1(\vec{r}_2)\right)$$

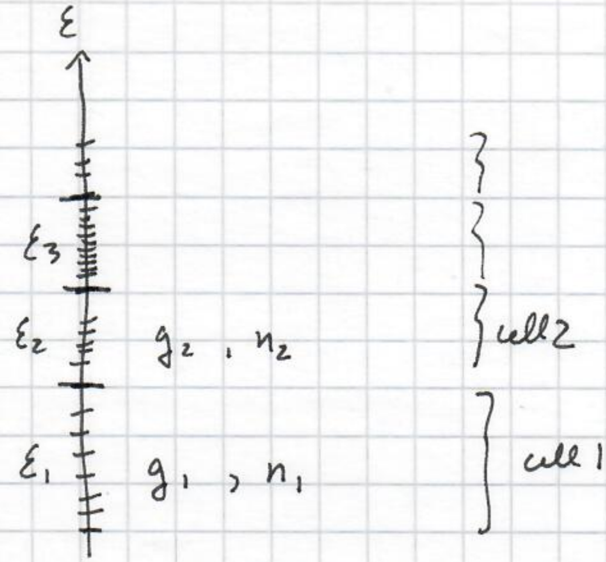
one wave fct.

* Wave functions for two Boltzmann particles:

$$\left.\begin{array}{l} \varphi_1(\vec{r}_1)\,\varphi_2(\vec{r}_2) \\ \& \ \varphi_2(\vec{r}_1)\,\varphi_1(\vec{r}_2) \end{array}\right\} \text{two wave fcts.}$$

How do we obtain $\Gamma(E)$?

Divide single-particle energy levels into cells.
The i^{th} cell contains n_i particles with average single-particle energy ε_i.
Let g_i be number of levels in i^{th} cell.



$g_i \gg 1$

We demand: $\sum_i n_i = N$ (*)

$$\sum_i n_i \varepsilon_i = E \quad (**)$$

$$\Rightarrow \Gamma(E) = \sum_{\{n_i\}} \underbrace{W\{n_i\}}$$

no of states of the system associated with the set $\{n_i\}$

↓

the sum extends over all sets of integers $\{n_i\}$ that satisfy conditions (*) and (**)

Let's work this out for

- identical bosons
- identical fermions
- distinguishable particles

Identical bosons: Each level can be occupied by any number of particles

i^{th} cell: g_i energy levels (or g_i subcells with $g_i - 1$ partitions

$$0 \,|\, 0 \,|\, 0 \,|\, 0 \;\ldots\; | \, 0$$

sub-cell 1, sub-cell 2

partition 1

partition $g_i - 1$

Write $W\{n_i\} = \prod_i w_i$

number of distinct microstates associated with the i^{th} cell (cell has n_i particles to distribute among g_i levels)

E.g.: $n_i = 6$, $g_i = 2$

$\Rightarrow w_i = \frac{7!}{6!1!} = 7$

allowed occupations:
60, 51, 42, 33, 24, 15, 06
(7 possibilities)

$$\Rightarrow \quad w_i = \frac{(n_i + g_i - 1)!}{n_i!\,(g_i - 1)!}$$

and $$W\{n_i\} = \prod_i w_i = \prod_i \frac{(n_i + g_i - 1)!}{n_i!\,(g_i - 1)!}$$

Identical fermions: The number of particles in each of the g_i subcells of the i^{th} cell is either zero or one.

$\Rightarrow$ w_i is equal to the number of ways in which n_i things can be chosen from g_i things:

$$w_i = \binom{g_i}{n_i} = \frac{g_i!}{n_i!\,(g_i - n_i)!}$$

$$\Rightarrow W\{n_i\} = \prod_i w_i = \prod_i \frac{g_i!}{n_i!\,(g_i - n_i)!}$$

Distinguishable particles: $$W\{n_i\} = \prod_i \frac{g_i^{\,n_i}}{n_i!}$$

The three different "rules" for counting states give rise to the terminology

- Bose statistics
- Fermi statistics
- Boltzmann statistics

Can we make this more concrete with an example?

Say, we have three cells with average energy $\underbrace{\varepsilon}_{\varepsilon_1}$, $\underbrace{2\varepsilon}_{\varepsilon_2}$ and $\underbrace{3\varepsilon}_{\varepsilon_3}$.

Say, we have a system with energy $E = 2000\,\varepsilon$ and $N = 1000$ particles.

$\Rightarrow \quad (n_1, n_2, n_3) = (0, 1000, 0)$ one set of occupation numbers

$(500, 0, 500)$ another set of occupation numbers

$\vdots$

all fulfill the condition that $N = \sum_i n_i$

$E = \sum_i n_i \varepsilon_i$

For concreteness, let us say that each cell contains 1000 energy levels, i.e.,

$$g_1 = 1000$$
$$g_2 = 1000$$
$$g_3 = 1000$$

Consider the set $(n_1, n_2, n_3) = (0, 1000, 0)$

For identical fermions: $w_1 = \dfrac{(1000)!}{0!\,(1000-0)!} = 1$

$$w_2 = \frac{(1000)!}{(1000)!\ 0!} = 1$$

$$w_3 = 1$$

$$\Rightarrow W = 1 \cdot 1 \cdot 1 = 1$$

for $n_1, n_2, n_3 = 0, 1000, 0$

there exists exactly one way to arrange the 1000 fermions

For identical bosons: $w_1 = \dfrac{(999)!}{0!\,(999)!} = 1$

$$w_2 = \frac{(1999)!}{(1000)!\ (999)!}$$

$$W_3 = 1$$

$$\Rightarrow W = \frac{(1999)!}{(1000)!\,(999)!}$$

for $n_1, n_2, n_3 = 0, 1000, 0$

For distinguishable particles: $W = \frac{(1000)^0}{0!} \cdot \frac{1000^{1000}}{(1000)!} \cdot 1$

$$= \frac{1000^{1000}}{(1000)!}$$

So $W_{dist.} > W_{boson} > W_{fermion}$

Note: we have many possible sets (n_1, n_2, n_3)

Recall:

$$\Gamma(E) = \sum_{\{n_i\}} W\{n_i\}$$

sum over all sets that give the "correct" energy and number of particles !

$$\Rightarrow S = k \log \underbrace{\Gamma(E)}$$

we know now how to calculate this...
... in principle ...

Counting all $W\{n_i\}$ is hard to impossible...

$\rightsquigarrow$ Replace sum over $\{n_i\}$ by most probable value (i.e., the set of $n_1, n_2, \ldots$ that maximizes W)

this is justified assuming the fluctuations are small

$$S = k \log \sum_{\{n_i\}} W\{n_i\} \Longrightarrow \boxed{S = k \log W\{\bar{n}_i\}}$$

This leaves the task of finding the set $\{\bar{n}_i\}$.

$$\Rightarrow \quad \delta \log W\{n_i\} - \Big[\alpha \underbrace{\sum_i \delta n_i}_{\text{particle number constraint}} + \beta \underbrace{\sum_i \varepsilon_i \delta n_i}_{\text{energy constraint}}\Big] = 0$$

undetermined Lagrange multipliers (at the moment: unknown). Will turn out to be $\beta = (kT)^{-1}$ and $\alpha = -\beta\mu$.

use $\log W\{n_i\} = \sum_i \log w_i$

$$\approx \sum_i \left[n_i \log\left(\frac{g_i}{n_i} - a\right) - \frac{g_i}{a} \log\left(1 - a\frac{n_i}{g_i}\right)\right]$$

Stirling appr.

$$a = \begin{cases} -1 & \text{bosons} \\ +1 & \text{fermions} \end{cases}$$

(see pages 190a and 190b for the derivation)

Identical bosons: $w_i = \dfrac{(n_i+g_i-1)!}{n_i!\,(g_i-1)!}$

$$\Rightarrow \log w_i = \log\left(\frac{(n_i+g_i-1)!}{n_i!\,(g_i-1)!}\right)$$

$$= \log\left((n_i+g_i-1)!\right) - \log(n_i!) - \log\left((g_i-1)!\right)$$

assuming $g_i \gg 1$ and $n_i \gg 1$ ⟶ Stirling appr. ⟶

$$\approx (n_i+g_i-1)\log(n_i+g_i-1)$$
$$- n_i \log n_i$$
$$- (g_i-1)\log(g_i-1)$$
$$- (n_i+g_i-1) + n_i + (g_i-1)$$

$$= n_i\left[\log(n_i+g_i-1) - \log n_i\right]$$
$$+ (g_i-1)\left[\log(n_i+g_i-1) - \log(g_i-1)\right]$$

$$= n_i \log\left(\frac{n_i+g_i-1}{n_i}\right)$$
$$+ (g_i-1)\log\left(\frac{n_i+g_i-1}{g_i-1}\right)$$

$$= n_i \log\left(\frac{g_i-1}{n_i} - (-1)\right)$$
$$- (-g_i)\log\left(1-(-1)\frac{n_i}{g_i-1}\right)$$
$$- \log\left(1-(-1)\frac{n_i}{g_i-1}\right)$$

$g_i \gg 1 \Rightarrow$ second line can be dropped compared to first

$$\approx n_i \log\left(\frac{g_i}{n_i} - a\right) - \frac{g_i}{a}\log\left(1 - a\frac{n_i}{g_i}\right)$$

$g_i \gg 1$

$\Rightarrow g_i - 1 \approx g_i$

where $a = -1$

Identical fermions: $W_i = \dfrac{g_i!}{n_i!\,(g_i - n_i)!}$

$$\Rightarrow \log W_i \approx g_i \log g_i - n_i \log n_i - (g_i - n_i)\log(g_i - n_i)$$

Stirling

$$= g_i\left[\log g_i - \log(g_i - n_i)\right]$$

$$+ n_i\left[\log(g_i - n_i) - \log n_i\right]$$

$$= n_i \log\left(\frac{g_i - n_i}{n_i}\right) - g_i \log\left(\frac{g_i - n_i}{g_i}\right)$$

$$= n_i \log\left(\frac{g_i}{n_i} - 1\right) - g_i \log\left(1 - \frac{n_i}{g_i}\right)$$

$$= n_i \log\left(\frac{g_i}{n_i} - a\right) - \frac{g_i}{a}\log\left(1 - a\frac{n_i}{g_i}\right)$$

where $a = 1$

$$\Rightarrow \sum_i \left[\log\left(\frac{g_i}{n_i} - a\right) - \alpha - \beta\, \varepsilon_i\right]_{n_i = \bar{n}_i} \delta n_i = 0$$

(see p. 191 b for details)

but δn_i is arbitrary

$$\Rightarrow \log\left(\frac{g_i}{\bar{n}_i} - a\right) - \alpha - \beta\varepsilon_i = 0$$

$$\Downarrow$$

$$\bar{n}_i = \frac{g_i}{e^{\alpha + \beta\varepsilon_i} + a}$$

$$\text{or} \quad \frac{\bar{n}_i}{g_i} = \frac{1}{e^{\alpha+\beta\varepsilon_i} + a}$$

most probable number of particles per energy level in the i^{th} cell

Explicitly:

$$\bar{n}_i = g_i \frac{1}{z^{-1} e^{\beta\varepsilon_i} - 1} \qquad \text{bosons}$$

$$\bar{n}_i = g_i \frac{1}{z^{-1} e^{\beta\varepsilon_i} + 1} \qquad \text{fermions}$$

$$\bar{n}_i = g_i \frac{1}{z^{-1} e^{\beta\varepsilon_i}} \qquad \text{Boltzmann}$$

Variation with respect to n_i : (Details for calc. on page 191)

look at $n_i \log\left(\frac{g_i}{n_i} - a\right) - \frac{g_i}{a}\log\left(1 - a\frac{n_i}{g_i}\right)$

$$= n_i \log(g_i - n_i a) - n_i \log(n_i)$$

$$- \frac{g_i}{a}\log(g_i - a n_i) + \frac{g_i}{a}\log(g_i)$$

Vary n_i : $\delta n_i \log(g_i - n_i a) + n_i \frac{a}{g_i - n_i a}(-\delta n_i)$

(need to vary n_i outside of log and inside of log!!!)

$$- \delta n_i \log n_i - n_i \frac{1}{n_i}\delta n_i$$

$$- \frac{g_i}{a}\left(\frac{1}{g_i - a n_i}\right)(-a\,\delta n_i)$$

$$= \delta n_i \left[\log\left(\frac{g_i - n_i a}{n_i}\right)\right]$$

$$+ \delta n_i \left[\frac{n_i a}{n_i a - g_i} - 1 + \frac{g_i}{g_i - a n_i}\right] = \log\left(\frac{g_i}{n_i} - a\right)\delta n_i$$

$$\frac{-n_i a + g_i - (g_i - a n_i)}{g_i - a n_i}$$

$$= 0$$

We identified $e^{\alpha} = z^{-1}$ or $z = e^{-\alpha}$

fugacity

$$\beta = \frac{1}{kT}$$

This can be seen by writing the energy $\rightarrow \beta$ and number constraint equations $\rightarrow \alpha$

Reinterpret:
($i \rightarrow \vec{k}$ and no g_i factors)

$$\bar{n}_{\vec{k}} = \frac{1}{z^{-1} e^{\beta \varepsilon_{\vec{k}}} - 1} \qquad \text{bosons}$$

$$\bar{n}_{\vec{k}} = \frac{1}{z^{-1} e^{\beta \varepsilon_{\vec{k}}} + 1} \qquad \text{fermions}$$

$$\bar{n}_{\vec{k}} = z\, e^{-\beta \varepsilon_{\vec{k}}} \qquad \text{Boltzmann}$$

Using $g_i \gg 1$, we obtain

$$\frac{S}{k} = \log W\{\bar{n}_i\} = \begin{cases} \sum_i \left[\bar{n}_i \log\left(1+\frac{g_i}{\bar{n}_i}\right) + g_i \log\left(1+\frac{\bar{n}_i}{g_i}\right)\right] & \text{Bosons} \\ \sum_i \left[\bar{n}_i \log\left(\frac{g_i}{\bar{n}_i}-1\right) - g_i \log\left(1-\frac{\bar{n}_i}{g_i}\right)\right] & \text{Fermions} \\ \sum_i \bar{n}_i \log\left(\frac{g_i}{\bar{n}_i}\right) & \text{Boltzmann} \end{cases}$$

Look at Boltzmann gas:

$$N = \sum_i n_i = z \sum_i g_i e^{-\beta\varepsilon_i} = z \sum_{\vec{k}} e^{-\beta\varepsilon_{\vec{k}}}$$

$$= z \frac{V}{(2\pi)^3} 4\pi \int_0^\infty e^{-\beta\hbar^2 k^2/(2m)} k^2\, dk = \frac{zV}{\lambda^3}$$

replacing the sum over $\vec{k}$ by an integral (see p. 181) and converting to spherical coordinates, with the 4π coming from the integration over the angles

$$\lambda = \sqrt{\frac{2\pi\hbar^2}{mkT}}$$

de Broglie wave length (or thermal wave length)

$$\Rightarrow z = \lambda^3 \frac{1}{\frac{V}{N}} = \frac{\lambda^3}{v} \qquad \text{So: } \boxed{z = \frac{\lambda^3}{v}}$$

$$E = \sum_i n_i \varepsilon_i = z \sum_i g_i \varepsilon_i e^{-\beta\varepsilon_i} = z \sum_{\vec{k}} \varepsilon_{\vec{k}} e^{-\beta\varepsilon_{\vec{k}}}$$

$$= z \frac{V}{(2\pi)^3} 4\pi \int_0^\infty \frac{\hbar^2 k^2}{2m} e^{-\beta \hbar^2 k^2/(2m)} k^2 \, dk$$

$$\boxed{E = \frac{3}{2} N k T}$$

from previous page: $\frac{S}{k} = \sum_i \bar{n}_i \log\left(\frac{g_i}{\bar{n}_i}\right)$

Last:

$$= \sum_i \left(\bar{n}_i \log g_i - \bar{n}_i \log \bar{n}_i\right) = \sum_i \left[\bar{n}_i \log g_i - \bar{n}_i \underbrace{\log\left(z g_i e^{-\beta\varepsilon_i}\right)}_{\log g_i + \log z - \beta\varepsilon_i}\right]$$

$$\frac{S}{k} = z \sum_{\vec{k}} e^{-\beta\varepsilon_{\vec{k}}} \left(\beta\varepsilon_{\vec{k}} - \log z\right) = \beta E - N \log z$$

$$\boxed{\frac{S}{k} = \frac{3}{2} N - N \log\left(\frac{N}{V}\left(\frac{2\pi\hbar^2}{mkT}\right)^{3/2}\right)}$$

plugging in for E and z

The Bose and Fermi gas converge toward the Boltzmann gas at high T. At low T, the Boltzmann gas does not provide a description of a physical system.