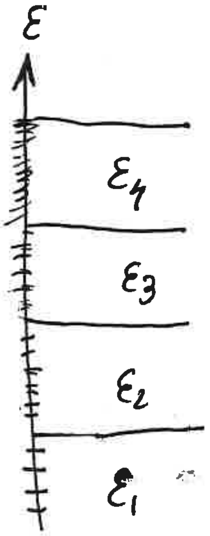
# Chapter 6

## THEORY OF SIMPLE GASES

We will discuss some of the basic properties of simple gases that follow Quantum Statistics

## (6.1) An Ideal Gas in Q.M. microcanonical Ens-

* Gas of $N$ particles indistinguishable non-interacting
  $(E, V, N)$ – specify micocanonical ensemble.
  As usual, we need to calculate $\Omega(E, V, N)$.
* TD limit : Large $V \rightarrow$ dense energy levels.
  - We can coarse grain to energy cells $\varepsilon_i$.
  - Then, each $\varepsilon_i$ has $g_i \gg 1$ energy levels.
  - Particles are distributed among the levels:
    $n_1$ in $\varepsilon_1$, $n_2$ in $\varepsilon_2$ etc..




As usual, there are two constraints:

$$\sum_i n_i = N$$

$$\sum_i n_i \varepsilon_i = E$$

And we can write the number of states:

$$\Omega(N, V, E) = \sum_{\{n_i\}}{}' W\{n_i\}$$

where $W\{n_i\}$ = number of distinct states $\{n_i\}$

$\sum'$ = sum over all $\{n_i\}$ that obey constraints.

- We can write $W\{n_i\}$ as a product

$$W\{n_i\} = \prod_i \omega(i) \quad \text{with } \omega(i) = \left\{\begin{matrix}\#\text{ distinct } \mu\text{-states}\\ \text{of the } i\text{-th cell}\end{matrix}\right\}$$

- This number $\omega(i)$ is the number of distinct ways to divide $n_i$ indistinguishable particles among the $g_i$ energy levels.

* For Bose-Einstein statistics :

Any number of particles can be at a certain energy level and therefore

$$\omega_{BE}(i) = \frac{(n_i + g_i - 1)!}{n_i!\,(g_i - 1)!} \qquad \left[\begin{matrix}\text{setting } g_i - 1 \text{ walls}\\ \text{between } n_i \text{ particles}\end{matrix}\right]$$

and

$$W_{BE}\{n_i\} = \prod_i \frac{(n_i + g_i - 1)!}{n_i!\,(g_i - 1)!}$$

* For Fermi-Dirac Statistics :

Not more than one particle can be at a certain energy level and therefore

$$\omega_{FD}(i) = \frac{g_i!}{n_i!\,(g_i - n_i)!} \qquad (\text{note that } n_i \le g_i)$$

So that

$$W_{FD}\{n_i\} = \prod_i \frac{g_i!}{n_i!\,(g_i - n_i)!}$$

* The classical limit is Boltzmann-Maxwell statistics

We can calculate it in two ways :

(i) As the classical distribution of distinguishable particles. In this case there are $(g_i)^{n_i}$ such partitions. But there are

$\frac{N!}{n_1!\, n_2! \cdots}$ partititions with the distribution $\{n_i\}$.

Dividing by the Gibbs factor we get the weight $\frac{1}{n_1!\, n_2! \dots} = \prod_i \frac{1}{n_i!}$

And the number of such distributions is

$$W_{MB}\{n_i\} = \prod_i \frac{(g_i)^{n_i}}{n_i!}$$

(ii) We can get this result by taking the limit $g_i \gg n_i$ of either $W_{FD}\{n_i\}$ or $W_{BE}\{n_i\}$.

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Now we can calculate the entropy of the system

$$S(N,V,E) = \ln \Omega(N,V,E) = \ln \left[ \sum_{\{n_i\}}' W\{n_i\} \right]$$

As usual there is a dominant maximal value of $W\{n_i\}$, so we can approximate

$$S(N,V,E) = \ln \Omega(N,V,E) \simeq \ln W\{n_i^*\}.$$

- To find this maximal value, we use the method of Lagrange multipliers.

We will minimize the function:

$$\mathcal{L} = \ln W\{n_i^*\} - \alpha \sum_i n_i - \beta \sum n_i \varepsilon_i$$

$$N = \sum_i n_i \qquad E = \sum_i n_i \varepsilon_i$$

Let's calculate first the factor $\ln W\{n\}$

$$\ln W\{n_i\} = \sum_i \ln \omega(i) \quad \text{with}$$

$$\omega(i) = \begin{cases} \dfrac{(g_i+n_i-1)!}{(g_i-1)!\, n_i!} & \text{for B.E.} \\[2ex] \dfrac{g_i!}{n_i!\,(n_i-g_i)!} = \dbinom{g_i}{n_i} & \text{for F.D.} \end{cases}$$

Using Stirling's approximation $\ln x! \simeq x \ln x - x$ we find:

(i) BE:

$$\ln \omega(i) = (g_i+n_i-1)\ln(g_i+n_i-1) - \cancel{(g_i+n_i-1)} - \left[(g_i-1)\ln(g_i-1) - \cancel{(g_i-1)}\right] - \left[n_i \ln n_i - \cancel{n_i}\right]$$

Assume $g_i, n_i \gg 1$

$$= (g_i+n_i)\ln(g_i+n_i) - g_i \ln g_i - n_i \ln n_i$$

$$= g_i \ln(g_i+n_i) - g_i \ln g_i + n_i \ln(g_i+n_i) - n_i \ln n_i$$

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

(ii) FD:

$$\ln \omega(i) = g_i \ln g_i - n_i \ln n_i - (g_i-n_i)\ln(g_i-n_i)$$

$$= -g_i \ln(g_i-n_i) + g_i \ln g_i + n_i \ln(g_i-n_i) - n_i \ln n_i$$

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

- We can write these two expressions together as

$$\boxed{\ln \omega(i) = n_i \ln\left(\frac{g_i}{n_i}-a\right) - \frac{g_i}{a}\ln\left(-a\frac{n_i}{g_i}+1\right)}$$

with $a=+1$ for F.D and $a=-1$ for B.E.

- The derivative with respect to $n_i$ is

$$\frac{\partial \ln \omega(i)}{\partial n_i} = \ln\left(\frac{g_i}{n_i}-a\right) + n_i\left(\frac{1}{\frac{g_i}{n_i}-a}\right)\left(-\frac{g_i}{n_i^2}\right) - \frac{g_i}{a}\,\frac{\frac{a}{g_i}}{a\frac{n_i}{g_i}-1}$$

The last two terms cancel and

$$\frac{\partial \ln w(i)}{\partial n_i} = \ln\left(\frac{g_i}{n_i} - a\right)$$

And the derivative of the Lagrangian is:

$$\frac{\partial \mathcal{L}}{\partial n_i} = \ln\left(\frac{g_i}{n_i} - a\right) - \alpha - \beta \varepsilon_i = 0$$

$$\frac{g_i}{n_i^*} - a = e^{\alpha + \beta \varepsilon_i}$$

$$\Rightarrow \quad n_i^* = \frac{g_i}{a + e^{\alpha + \beta \varepsilon_i}}$$

This implies that the most probable occupancy of each of the energy levels in the cell $\{\varepsilon_i, g_i\}$ is

$$\boxed{\frac{n_i^*}{g} = \frac{1}{e^{\alpha + \beta \varepsilon_i} + a}}$$

- From this we can derive TD. In the microcanonical ensemble we start by calculating $S$, the entropy.

$$S = \ln W\{n_i^*\} = \sum_i \ln w(i) = \sum_i \left[n_i^* \ln\left(\frac{g_i}{n_i^*} - a\right) - \frac{g_i}{a} \ln\left(1 - a\frac{n_i^*}{g_i}\right)\right]$$

$$= \sum_i \left\{n_i^* (\alpha + \beta \varepsilon_i) + \frac{g_i}{a} \ln\left[1 + a e^{-\alpha - \beta \varepsilon_i}\right]\right\}$$

$$\sum n_i^* \alpha = \alpha N \; ; \; \sum_i n_i^* \beta \varepsilon_i = \beta E$$

$$S = \alpha N + \beta E + \frac{1}{a} \sum_i g_i \ln\left(1 + a e^{-\alpha - \beta \varepsilon_i}\right)$$

The lagrange multipliers are $\beta = \left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T}$; $\alpha = \left(\frac{\partial S}{\partial N}\right)_{V,E} = -\frac{\mu}{T}$

We see that

$$S - \alpha N - \beta E = \frac{TS + \mu N - E}{T} = \frac{G - (E - TS)}{T} = \frac{PV}{T}$$

Such that the pressure - temperature - volume relation

$$\boxed{\frac{PV}{T} = \frac{1}{a}\sum_i \left\{g_i \ln\left[1 + a e^{-\alpha-\beta E_i}\right]\right\}}$$

- In the classical limit $\quad w(i) = \dfrac{g_i^{\,n_i}}{n_i!}$

  $\ln w(i) = n_i \ln g_i - n_i \ln n_i + n_i = n_i\left(\ln \dfrac{g_i}{n_i} + 1\right)$

  which is the $a \to 0$ limit

  $\left(\text{or} \qquad \dfrac{n_i^*}{g_i} = \dfrac{1}{e^{\alpha+\beta\varepsilon_i} + a} \longrightarrow e^{-\alpha-\beta\varepsilon_i}\right)$

  This yields the ideal gas law

$$\frac{PV}{T} \simeq \sum_i g_i \frac{1}{\cancel{a}} \cancel{a} e^{-\alpha-\beta E_i} = \sum_i n_i^* = N$$

## 6.2 An ideal gas in the other ensembles

- The canonical ensemble is derived from the partition function:

$$Q_N(T, V) = \sum_E e^{-\beta E}$$

  The total energy is $\quad E = \sum_\varepsilon n_\varepsilon \varepsilon$

  with the numbers $\{n_i\}$ obeying $\quad N = \sum_\varepsilon n_\varepsilon$

- Then, we can write

$$Q_N(V, T) = \sum_{\{n_\varepsilon\}}{}' g\{n_\varepsilon\} e^{-\beta \sum_\varepsilon n_\varepsilon \varepsilon}$$

  sum over all distributions $\{n_\varepsilon\}$ that obey $\sum_\varepsilon n_\varepsilon = N$

- In this case we do not need to group the energy levels to cells, so in each level $\underline{g_i = 1}$.

Then

$$\begin{cases} g_{BE}\{n_\varepsilon\} = \prod\limits_{\varepsilon} \dfrac{(g+n_\varepsilon-1)!}{(g-1)!\; n_\varepsilon!} = \prod\limits_{\varepsilon} \dfrac{n_\varepsilon!}{n_\varepsilon!} = 1 \\[2ex] g_{FD}\{n_\varepsilon\} = \prod\limits_{\varepsilon} \dbinom{1}{n_\varepsilon} = \begin{cases} 1 & \text{if } n_\varepsilon = 0,1 \\ 0 & \text{otherwise} \end{cases} \\[2ex] g_{MB}\{n_\varepsilon\} = \prod\limits_{\varepsilon} \dfrac{1}{n_\varepsilon!} \end{cases}$$

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In the FD case, we get

$$Q_N(V,T) = \sum_{\{n_\varepsilon\}}{}' e^{-\beta \sum_\varepsilon n_\varepsilon \varepsilon}$$

where the sum is over all states with $n_\varepsilon = 0,1$ with $\sum_\varepsilon n_\varepsilon = N$

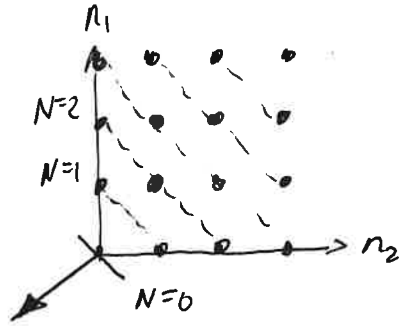
In the BE we get a similar sum, but without the limitation $n_\varepsilon = 0,1$, but $n_\varepsilon = 0,1,2\ldots\infty$

It turns out that these sums are cumbersome to calculate, and instead we can calculate the <u>grand-canonical</u> partition function

$$\mathcal{Q}(z,V,T) = \sum_{N=0}^{\infty} z^N \sum_{\{n_\varepsilon\}}{}' e^{-\beta \sum_\varepsilon n_\varepsilon}$$

$$= \sum_{N=0}^{\infty} \sum_{\{n_\varepsilon\}}{}' \prod_\varepsilon \left(z e^{-\beta}\right)^{n_\varepsilon}$$

The summation can be replaced by an unconstrained summation




$$= \sum_{n_0 n_1 \ldots} \left(z e^{-\beta\varepsilon_0}\right)^{n_0} \left(z e^{-\beta\varepsilon_1}\right)^{n_1} \cdots$$

$$= \left[\sum_{n_0} \left(z e^{-\beta\varepsilon_0}\right)^{n_0}\right] \left[\sum_{n_1} \left(z e^{-\beta\varepsilon_1}\right)^{n_1}\right] \cdots$$

The summation, of course, is different for BE / FD.

For BE $n_\varepsilon = 0, 1, 2 \dots \infty$ (any non-negative integer)

For FD $n_\varepsilon = 0, 1$

Therefore,

$$\mathcal{Q}(z, V, T) = \begin{cases} \prod_\varepsilon (1 - z e^{-\beta\varepsilon})^{-1} & : BE \\ \prod_\varepsilon (1 + z e^{-\beta\varepsilon}) & : FD \end{cases}$$

Such that

(where $-$ for BE, $+$ for FD)

$$\boxed{\frac{PV}{T} = \ln \mathcal{Q} = \mp \sum_\varepsilon \ln(1 \mp z e^{-\beta\varepsilon})}$$

For the M.B. case we can assume $z e^{-\beta\varepsilon} \ll 1$

and

$$\frac{PV}{T} \simeq \mp \mp z \sum_\varepsilon e^{-\beta\varepsilon} = z \sum_\varepsilon e^{-\beta\varepsilon} = z Q_1$$

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With $a = -1$ for BE ; $a = 1$ for FD ; $a = 0$ for MB

$$\boxed{\frac{PV}{T} = \ln \mathcal{Q} = \frac{1}{a} \sum_\varepsilon \ln(1 + a z e^{-\beta\varepsilon})}$$

The number is calculated from

$$\bar{N} = z \left(\frac{\partial \ln \mathcal{Q}}{\partial z}\right)_{V,T} = \frac{1}{a} \sum_\varepsilon \frac{z a e^{-\beta\varepsilon}}{1 + a z e^{-\beta\varepsilon}}$$

$$= \sum_\varepsilon \frac{1}{e^{\beta\varepsilon}/z + a}$$

Similary

$$\bar{E} = -\left(\frac{\partial \ln \mathcal{Q}}{\partial \beta}\right)_{z,V} = -\frac{1}{a} \sum_\varepsilon \frac{-\varepsilon z a e^{-\beta\varepsilon}}{1 + a z e^{-\beta\varepsilon}} =$$

$$= \sum_\varepsilon \frac{\varepsilon}{e^{\beta\varepsilon}/z + a}$$

$$\bar{E} = -\left(\frac{\partial \ln \mathcal{Q}}{\partial \beta}\right)_{z,V} = \sum_{\varepsilon} \frac{\varepsilon}{z^{-1} e^{\beta\varepsilon} + a}$$

The occupancy of a certain energy level, say $\varepsilon_0$, can be calculated from the definition of the grand-potential

$$\mathcal{Q}(z,V,T) = \left[\sum_{n_0} (z e^{-\beta\varepsilon_0})^{n_0}\right]\left[\sum_{n_1} (z e^{-\beta\varepsilon_1})^{n_1}\right] \cdots\cdots$$

$$-\frac{1}{\beta}\frac{1}{\mathcal{Q}}\left(\frac{\partial \mathcal{Q}}{\partial \varepsilon_0}\right) = -\frac{1}{\beta \mathcal{Q}}\left[\sum_{n_0} z^{n_0} (-\beta n_0) e^{-\beta \varepsilon_0 n_0}\right] \cdots$$

$$= \frac{1}{\mathcal{Q}}\left[\sum_{n_0} (z e^{-\beta\varepsilon_0})^{n_0} n_0\right]\left[\cdots\cdots\right] = \langle n_0 \rangle$$

Therefore -

$$\langle n_0 \rangle = -\frac{1}{\beta}\frac{\partial \ln \mathcal{Q}}{\partial \varepsilon_0} = + \frac{1}{\cancel{\beta}}\,\frac{1}{\cancel{a}}\,\frac{\cancel{(-\beta)}\,\cancel{a} z e^{-\beta\varepsilon_0}}{1 + a z e^{-\beta\varepsilon_0}}$$

$$\boxed{\langle n_0 \rangle = \frac{1}{z^{-1} e^{\beta\varepsilon_0} + a}}$$

We already saw this result in the $\mu$-canonical ens.

$$\frac{n_i^*}{g_i} = \frac{1}{e^{\beta\varepsilon}/z + a} ;$$

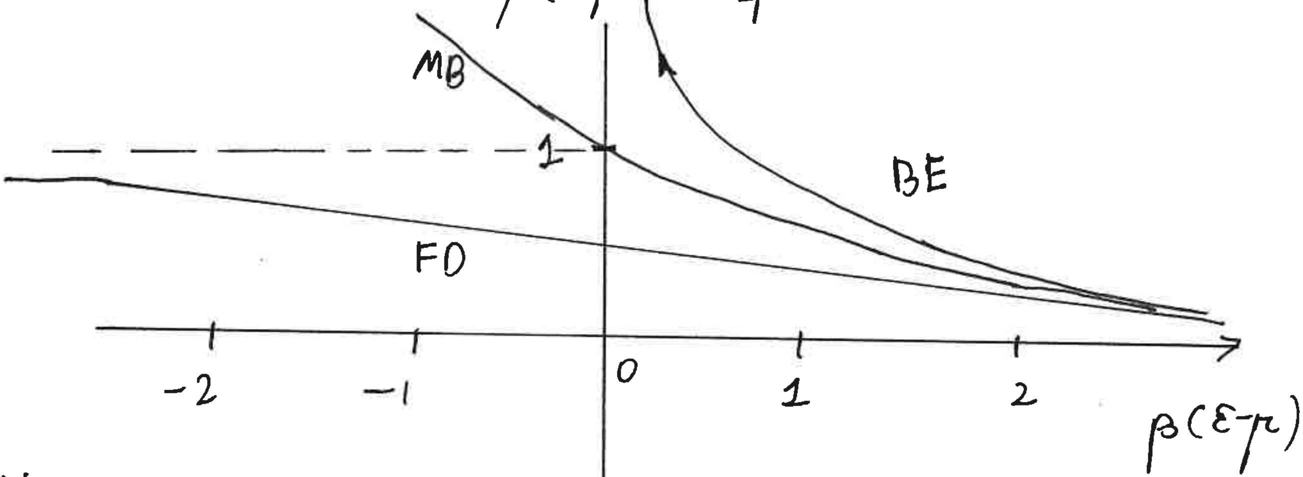
$\Rightarrow$ we see that the average = most probable.

## 6.3 Statistics of occupation numbers

The mean occupation number in a single-particle state with energy $\varepsilon$ is:

$$\boxed{\langle n_\varepsilon \rangle = \frac{1}{e^{\beta(\varepsilon-\mu)} + a}} \qquad z = e^{\beta\mu}$$

Let's see how it changes with temperature, as a function of $\beta(\varepsilon-\mu) = \frac{\varepsilon-\mu}{T}$




We see:

(i) Bose-Einstein condensation $\quad \langle n_\varepsilon \rangle \longrightarrow \infty$ when $\varepsilon \to \mu$

(ii) Classical limit

$$e^{(\varepsilon-\mu)/T} \gg 1 \longrightarrow \langle n_\varepsilon \rangle_{FD} \simeq \langle n_\varepsilon \rangle_{BE} \simeq \langle n_\varepsilon \rangle_{MB}$$

(iii) Pauli's exclusion

At low $T$ $\quad \langle n_\varepsilon \rangle_{FD} \to 1$ its upper limit

* The intuition for the classical limit:

At this limit $\langle n_\varepsilon \rangle \ll 1$ so the only probable values are $n_\varepsilon = 0, 1$ and therefore

$$g_{MB} = \prod_i \frac{1}{n_i!} = 1 = g_{FD} = g_{BE}$$

* In the classical limit we know that
$\mu \ll 0$ such that $z \ll 1$ $(z = e^{\mu/T})$
We already calculated and showed that the equivalent condition is

$$\frac{\mu}{T} = \ln\left(\frac{N \lambda^3}{V}\right) \rightarrow z = \frac{N\lambda^3}{V} \ll 1$$

$$\Rightarrow \frac{N}{V} \ll \frac{1}{\lambda^3} \qquad \lambda = \frac{h}{\sqrt{2\pi m T}} \ll \left(\frac{V}{N}\right)^{1/3}$$

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Next, we discuss statistical fluctuations $\quad \langle n_\varepsilon \rangle = \dfrac{1}{e^{\beta\varepsilon}/z + a}$

We saw $\quad \langle n_\varepsilon \rangle = -\dfrac{1}{\beta}\dfrac{\partial \ln Q}{\partial \varepsilon_0} = -\dfrac{1}{\beta}\dfrac{1}{Q}\dfrac{\partial Q}{\partial \varepsilon}$

Similarly $\quad \langle n_\varepsilon^2 \rangle = \left[\dfrac{1}{Q}\left(-\dfrac{1}{\beta}\dfrac{\partial}{\partial \varepsilon}\right)^2 Q\right]$

Hence,
$$\langle n_\varepsilon^2 \rangle - \langle n_\varepsilon \rangle^2 = \frac{1}{\beta^2}\frac{1}{Q}\frac{\partial^2 Q}{\partial \varepsilon^2} - \frac{1}{\beta^2}\left(\frac{1}{Q}\frac{\partial Q}{\partial \varepsilon}\right)^2$$
$$= \frac{1}{\beta^2}\frac{\partial^2 \ln Q}{\partial \varepsilon^2} = -\frac{1}{\beta}\frac{\partial \langle n_\varepsilon \rangle}{\partial \varepsilon}$$

$$\langle \Delta n_\varepsilon^2 \rangle = \langle n_\varepsilon^2 \rangle - \langle n_\varepsilon \rangle^2 = -\frac{1}{\beta}\frac{\beta z^{-1} e^{\beta\varepsilon}}{(z^{-1}e^{\beta\varepsilon}+a)^2} = \frac{z^{-1}e^{\beta\varepsilon}}{(z^{-1}e^{\beta\varepsilon}+a)^2}$$

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As for the relative fluctuations

$$\frac{\langle \Delta n_\varepsilon^2 \rangle}{\langle n_\varepsilon \rangle^2} = -\frac{1}{\beta}\frac{1}{\langle n_\varepsilon \rangle^2}\frac{\partial \langle n_\varepsilon \rangle}{\partial \varepsilon} = \frac{1}{\beta}\frac{\partial}{\partial \varepsilon}\left[\frac{1}{\langle n_\varepsilon \rangle}\right]$$

$$= \frac{1}{\beta}\frac{\partial}{\partial \varepsilon}\left[z^{-1}e^{\beta\varepsilon} + a\right] = z^{-1}e^{\beta\varepsilon} = e^{\beta(\varepsilon-\mu)}$$

We can rewrite it as

$$\boxed{\frac{\langle \Delta n_\varepsilon^2 \rangle}{\langle n_\varepsilon \rangle^2} = \frac{1}{\langle n_\varepsilon \rangle} - a}$$

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It is instructive to discuss the three cases:

(i) Classical M.B. $(a=0)$ $\quad \dfrac{\langle \Delta n_\varepsilon^2 \rangle}{\langle n_\varepsilon \rangle^2} = \dfrac{1}{\langle n_\varepsilon \rangle}$

because the distribution is normal.

(ii) F.D. $(a=1)$ is below normal and the variance vanishes when $\langle n_\varepsilon \rangle = 1$, since the energy level is full

(iii) B.E. is above normal $\quad \dfrac{\langle \Delta n_\varepsilon^2 \rangle}{\langle n_\varepsilon \rangle^2} = \dfrac{1}{\langle n_\varepsilon \rangle} + 1$

If $\langle n_\varepsilon \rangle$ is large $\quad \dfrac{\langle \Delta n_\varepsilon^2 \rangle}{\langle n_\varepsilon \rangle^2} = 1 \rightarrow$ strong fluctuations

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There are averages and variances, but let's look at the distribution itself.

We know that $\quad p(n_\varepsilon) = \dfrac{(ze^{-\beta\varepsilon})^n}{\sum_n (ze^{-\beta\varepsilon})^n}$

- For BE this is $\quad p(n_\varepsilon) = (ze^{-\beta\varepsilon})^n (1 - ze^{-\beta\varepsilon})$

$$p(n) = \left(\frac{\langle n_\varepsilon \rangle}{\langle n_\varepsilon \rangle + 1}\right)^n \frac{1}{\langle n_\varepsilon \rangle + 1} \quad \Leftarrow \quad \langle n_\varepsilon \rangle = \frac{ze^{-\beta\varepsilon}}{1 - ze^{-\beta\varepsilon}}$$

$$\boxed{p(n) = \frac{\langle n_\varepsilon \rangle^n}{(\langle n_\varepsilon \rangle + 1)^{n+1}}}$$

- For FD we get $\quad p(n) = \dfrac{(ze^{-\beta\varepsilon})^n}{1 + ze^{-\beta\varepsilon}} \quad \begin{cases} p(0) = 1 - \langle n_\varepsilon \rangle \\ p(1) = \langle n_\varepsilon \rangle \end{cases}$

- In Maxwell-Boltzmann (MB)

$$p(n) = \frac{(ze^{-\beta})^n / n!}{\exp(ze^{-\beta})} = \frac{\langle n_\varepsilon \rangle^n}{n!} e^{-\langle n_\varepsilon \rangle}$$

- This is a Poisson distribution of uncorrelated particles.

In contrast the BE distribution decays only geometrically... (shows correlation

## 6.4 Kinetic Considerations

We have seen

$$\frac{PV}{T} = \ln \mathcal{Q} = \frac{1}{a} \sum_{\varepsilon} \ln(1 + a z e^{-\beta \varepsilon})$$

* For large volumes we can replace by integration

$\sum_{\varepsilon} \to \sum_{p}$ . Remember that $\sum_{k} \to \frac{V}{(2\pi)^3} \int d^3k$

$$\to \frac{V}{(2\pi\hbar)^3} \int d^3p$$

$$\frac{P\cancel{V}}{T} = \frac{1}{a} \frac{\cancel{V}}{h^3} \int_0^\infty 4\pi p^2 dp \ln\left[1 + a z e^{-\beta \varepsilon(p)}\right]$$

$$P = \frac{T}{a h^3} \int 4\pi p^2 dp \ln\left[1 + a z e^{-\beta \varepsilon(p)}\right] =$$

Integration by parts

$$= \frac{4\pi T}{\cancel{a} h^3} \left[ \cancel{\frac{p^3}{3} \ln[\;] \Big|_0^\infty} - \int_0^\infty \frac{p^3}{3} \cdot \frac{\cancel{a} z e^{-\beta \varepsilon(p)}}{1 + a z e^{-\beta \varepsilon(p)}} \cdot \left(-\beta \frac{d\varepsilon}{dp}\right) \right]$$

integrand vanishes at $p = 0, \infty$

$$\to \boxed{P = \frac{4\pi}{3h^3} \int_0^\infty \frac{1}{z^{-1} e^{\beta \varepsilon(p)} + a} \left(p \frac{d\varepsilon}{dp}\right) p^2 dp}$$

* As for the total number of particles

$$\boxed{N = \frac{V}{h^3} \int \langle n_p \rangle d^3p = \frac{4\pi V}{h^3} \int_0^\infty \underbrace{\frac{1}{z^{-1} e^{\beta \varepsilon(p)} + a}}_{\langle n_p \rangle} p^2 dp}$$

By comparing we find

$$\dot{q} = \frac{\partial \mathcal{H}}{\partial p}$$

$$P = \frac{1}{3} \frac{N}{V} \left\langle p \frac{d\varepsilon}{dp} \right\rangle = \frac{1}{3} n \langle p u \rangle$$

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If the energy-momentum relation is $\varepsilon \sim p^s$ then

$$P = \frac{1}{3} n \left\langle p \frac{d\varepsilon}{dp} \right\rangle = \frac{1}{3} n s \langle \varepsilon \rangle$$

$$\varepsilon = \alpha p^s$$

$$p \frac{d\varepsilon}{dp} = s \alpha p^s = s\varepsilon$$

$$\boxed{P = \frac{s}{3} \frac{N}{V} \frac{E}{N} = \frac{s}{3} \frac{E}{V}}$$

- Note that this holds for all statistics ($a=1$ F.D; $a=-1$ B.E; $a=0$ M.B)
- $s=2$ is non-relativistic; $s=1$ is relativistic.

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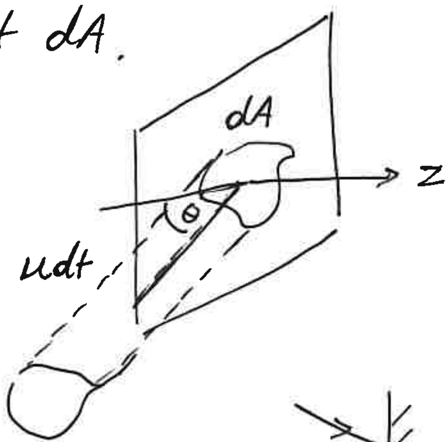
The last formula suggests that the pressure is a matter of kinetic considerations $P = \frac{n}{3} \langle p u \rangle$.

To see this consider an area element $dA$.

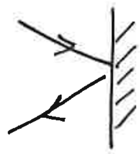
The velocity distribution is $f(\bar{u})$

$$\int_{\bar{u}} f(\bar{u})\, d^3u = 1$$




The number of particles in the range $[u, u+du]$ that hits $dA$ is

$$dN(\bar{u}) = \underbrace{(d\bar{A} \cdot \bar{u})\, dt}_{\text{volume of cylinder}} \times \underbrace{n f(\bar{u})\, d\bar{u}}_{\text{density of particles in } [\bar{u}, \bar{u}+d\bar{u}]}$$



Each collision reverses the z-momentum $p_z \to -p_z$, such that the momentum transferred to the wall is $2p_z$.

Thus, the momentum transfer per unit time per unit area is:

$$2p_z \frac{dN(\bar{u})}{dA \cdot dt} = 2p_z \left[ u_z n f(\bar{u})\, d\bar{u} \right]$$

$$P = \frac{\Delta \text{ momentum}}{dA \cdot dt} = 2n \int_{u_x=-\infty}^{\infty} \int_{u_y=-\infty}^{\infty} \int_{u_z=0}^{\infty} (p_z u_z)\, f(\bar{u})\, du_x\, du_y\, du_z$$

Since $f(\bar{u})$ and $(p_z u_z)$ are even functions

$$P = n \int_{\bar{u}} (p_z u_z) f(\bar{u})\, d\bar{u} = n \langle p u \cos^2\theta \rangle$$

pu is symmetric

$$= n \langle pu \rangle \langle \cos^2\theta \rangle$$

$$\langle \cos^2\theta \rangle = \frac{2\pi \int \cos^2\theta \, d(\cos\theta)}{4\pi} = \frac{1}{2} \left. \frac{\cos^3\theta}{3} \right|_{-1}^{+1} = \frac{1}{3}$$

$$\boxed{P = \frac{1}{3} n \langle pu \rangle}$$

## Effusion

The escape of particles from a unit area is

$$R = n \int_{u_x=-\infty}^{+\infty} \int_{u_y=-\infty}^{+\infty} \int_{u_z=0}^{+\infty} u_z f(u)\, du_x\, du_y\, du_z$$

$$= n \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi/2} \int_{u=0}^{\infty} [u\cos\theta\, f(u)][u^2\, d(\cos\theta)\, du\, d\phi\, d\theta]$$

$$= (2\pi)\left(\frac{1}{2}\right) n \int du\, u^3 f(u) = n\pi \int_0^\infty f(u)\, u^3\, du$$

Taking into account $\int \underbrace{[4\pi f(u)]}_{\rho(u)} u^2 du = 1$

We find that

$$\boxed{R = \frac{1}{4} n \langle u \rangle}$$

* Note that the effusing particles have non-zero momentum and therefore the vessel recoils.
* The particles are faster than average, since faster particles leave in larger numbers.

Hence, the vessel cools down.