E. Dilute Gas[+]

- Non-interacting gas $\Rightarrow$ can talk about single-particle states

- We have seen that:

$$W_{FD}(\{n_i\}) = \prod_i \frac{g_i!}{n_i!\,(g_i-n_i)!} \quad \text{gives Fermi-Dirac distribution}$$

$$W_{BE}(\{n_i\}) = \prod_i \frac{(n_i+g_i)!}{n_i!\,g_i!} \quad \text{gives Bose-Einstein distribution}$$

- We now show that:

$$W(\{n_i\}) = \prod_i \frac{g_i^{n_i}}{n_i!} \quad \text{gives Maxwell-Boltzmann distribution}$$

AND for $\underbrace{\frac{n_i}{g_i}}_{}\ll 1$, the result is valid

requires low density and high temperature
i.e., [$\lambda_{thermal} \ll$ particle separation]
and thus can be used in classical stat. mech. problems.

[+] A gas of "classical particles". But what are "classical particles"?

- Look at $W_{FD}(\{n_i\})$ in the limit $n_i \ll g_i$ for all cells i.

For each cell,

$$\frac{g_i!}{n_i!\,(g_i-n_i)!} = \frac{\overbrace{g_i(g_i-1)(g_i-2)\cdots(g_i-n_i+1)}^{\text{there are } n_i \text{ factors}}}{n_i!}$$

since $g_i \gg n_i$, each term in numerator $\approx g_i$

$$\therefore \frac{g_i!}{n_i!\,(g_i-n_i)!} \approx \frac{g_i^{n_i}}{n_i!}$$

OR

$$\boxed{W_{FD}(\{n_i\}) \approx \prod_i \frac{g_i^{n_i}}{n_i!} \quad \text{for } \frac{n_i}{g_i} \ll 1 \text{ for all } i}$$

- Look at $W_{BE}(\{n_i\})$ in the limit $n_i \ll g_i$ for all cells i.

For each cell,

$$\frac{(g_i+n_i)!}{g_i!\,n_i!} = \frac{\overbrace{(g_i+1)(g_i+2)\cdots(g_i+n_i)}^{n_i \text{ factors}}}{n_i!} \approx \frac{g_i^{n_i}}{n_i!}$$

$$\therefore \boxed{W_{BE}(\{n_i\}) \approx \prod_i \frac{g_i^{n_i}}{n_i!} \quad \text{for } \frac{n_i}{g_i} \ll 1 \text{ for all } i}$$

$\therefore$ When $n_i \ll g_i$,

$$W_{FD}(\{n_i\}) = W_{BE}(\{n_i\}) \cong \prod_i \frac{g_i^{n_i}}{n_i!}$$

and the most probable distribution becomes the Maxwell-Boltzmann distribution, as we now show.

Consider

$$W(\{n_r\}) = \prod_i \frac{g_i^{n_i}}{n_i!}$$

Interpretation:

- Inside each cell i, there are many possible arrangements
  - There are g_i states in cell i
  - Let's say each particle in cell i can be placed in any of the g_i states and there is no restriction on the occupancy of each state.
  - For n_i particles in cell i, there are $\approx \frac{g_i^{n_i}}{n_i!}$ possible arrangements^{+} inside cell i.
  - Number of microstates corresponding to a distribution $\{n_1, n_2, \ldots\}$ is

$$W(\{n_r\}) = \prod_i \frac{g_i^{n_i}}{n_i!}$$

$^{+}$ The number $\frac{g_i^{n_i}}{n_i!}$ works increasing well when $n_i \ll g_i$.

- To get the most probable distribution, we want to maximize $\ln W$ subjected to the constraints

$$\sum_{\text{cells } i} n_i = N = \text{constant}$$

$$\sum_{\text{cells } i} n_i \varepsilon_i = E = \text{constant}$$

$$\ln W = \sum_r (n_r \ln g_r - \ln n_r!)$$

$$= \sum_r (n_r \ln g_r - n_r \ln n_r + n_r)$$

Note: We used Stirling's formula for $\ln n_r!$

Since we grouped single-particle states into cells, we can choose $g_r \gg 1$ so that it is possible that $n_r \gg 1$ even if $\frac{n_r}{g_r}$ (# particle per state) is small ($\ll 1$).

$$\delta \ln W = \sum_r \delta n_r (\ln g_r - \ln n_r) = 0$$

Constraints: $\sum_r n_r = N \Rightarrow \sum_r \delta n_r = 0$ (Lagrange multiplier α)

$\sum_r \varepsilon_r n_r = E \Rightarrow \sum_r \delta n_r \varepsilon_r = 0$ (Lagrange multipler β)

- Using the method of Lagrange multiplers:

$$\sum_r (\ln g_r - \ln n_r - \alpha - \beta\varepsilon_r)\,\delta n_r = 0$$

$$\therefore \ln g_r - \ln n_r - \alpha - \beta \varepsilon_r = 0$$

$$\Rightarrow \ln\left(\frac{n_r}{g_r}\right) = -\alpha - \beta\varepsilon_r$$

Maxwell-Boltzmann distribution

$$\Rightarrow \boxed{\frac{n_r}{g_r} = e^{-\alpha}\, \underbrace{e^{-\beta\varepsilon_r}}}$$ (Key result)

≈ "probability" that a single-particle state of energy ε_r is occupied [# particles per available state]

[this is just the Boltzmann distribution, but now applied to a single particle!]

OR $\boxed{n_r = g_r\, \underline{e^{-\alpha}} e^{-\beta\varepsilon_r}}$

particles in cell r

states of energy ε_r [depends on confining potential]

particles per state of energy ε_r [does not depend on g_r]

As $\sum_r n_r = N \Rightarrow e^{-\alpha} \sum_r g_r e^{-\beta\varepsilon_r} = N$

$$\Rightarrow e^{-\alpha} = \frac{N}{\sum_r g_r e^{-\beta\varepsilon_r}}$$ (fixed α by a constraint)

$$\therefore n_r = N \frac{g_r e^{-\beta\varepsilon_r}}{z}, \quad z = \sum_r g_r e^{-\beta\varepsilon_r}$$

= single-particle partition function

$$\Rightarrow \boxed{\frac{n_r}{N} = \frac{g_r e^{-\beta\varepsilon_r}}{z}}$$

Prob. of finding a particle in a cell r (energy level ε_r)

[Again, this is just a special case of our general result in Ch. V. But now, we need the particles to be non-interacting.]

Remark: Formally, β comes in as a Lagrange multipler. To establish its physical meaning of $\frac{1}{kT}$, we need to apply the result to a problem of known results (e.g. ideal gas) and then identify $\beta = \frac{1}{kT}$. Since we already discussed the more general canonical ensemble approach, we will not do this here.

Summary / Validity (Dilute gas regime)

- Starting with (considering single-particle states)

$$W(\{n_r\}) \propto \prod_r \left(\frac{g_r^{n_r}}{n_r!} \right)$$

(not been careful about the quantum nature of particles)

Maximize $\ln W$ with the constraints:

$$\sum_r n_r = N \quad ; \quad \sum_r \varepsilon_r n_r = E$$

(this is based on what we know about isolated systems),

we get

$$\frac{n_r}{g_r} = N \frac{e^{-\beta \varepsilon_r}}{\sum_r g_r e^{-\beta \varepsilon_r}}$$

OR

$$\frac{n_r}{N} = \frac{g_r e^{-\beta \varepsilon_r}}{\sum_r g_r e^{-\beta \varepsilon_r}} = \frac{g_r e^{-\beta \varepsilon_r}}{Z}$$

Z ← single-particle partition function

- Can be regarded as applying our canonical ensemble result to a system of a single-particle. In doing so, implicitly, we require the single particle can only be weakly interacting with the other particles. Also, particles seldom go into the same state ($n_r \ll g_r$) and thus no need to worry about fermionic/bosonic effect.

Q: When is $W(\{n_r\}) \propto \prod_r \left(\frac{g_r^{n_r}}{n_r!} \right)$ good?

- Each of the n_r particles can be in any one of the g_r states

  - Will NOT cause problem if

    $$\frac{n_r}{g_r} \ll 1 \quad \text{(OK)} \quad \text{[classical statistics]}$$

    - since the chance of placing two or more particles in the same state is tiny if $n_r \ll g_r$

    AND

    if identical particles do NOT occupy the same state, why do we need to care about they are fermions or bosons?

    (i.e., quantum nature of particles is not important if $n_r \ll g_r$)

    [indistinguishability still needs to be considered]

  - Will cause problem if

    $$n_r \approx g_r \quad \text{(not OK)} \quad \text{[quantum statistics]}$$

    - then we need to consider the restriction on occupying single-particle states

    → [Fermi-Dirac or Bose-Einstein statistics]

Claiming a result:

"Classical ideal gas"

$$z = \frac{1}{h^3}\int dx\int dy\int dz\int dp_x\int dp_y\int dp_z\; e^{-\beta\frac{p_x^2+p_y^2+p_z^2}{2m}}$$

$$= \frac{V}{h^3}\left(\int dp\; e^{-\frac{\beta p^2}{2m}}\right)^3$$

$$= \frac{V}{h^3}\left(\frac{2m\pi}{\beta}\right)^{3/2} = V\cdot\left(\frac{2\pi mkT}{h^2}\right)^{3/2}$$

$\therefore$ In a classical gas, $\frac{n_r}{N} = \frac{g_r e^{-\beta\varepsilon_r}}{z}$

$$\frac{n_r}{g_r} = \frac{N e^{-\beta\varepsilon_r}}{V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}} = \frac{e^{-\beta\varepsilon_r}\left(\frac{h^2}{2\pi mkT}\right)^{3/2}}{\left(\frac{V}{N}\right)} \propto \frac{\lambda_{th}^3}{\left(\frac{V}{N}\right)}$$

$$\boxed{\begin{array}{l}\text{Define:}\\ \lambda_{thermal} \equiv \text{thermal de Broglie wavelength}\\ = \sqrt{\frac{h^2}{2\pi mkT}} = \sqrt{\frac{2\pi\hbar^2}{mkT}} \qquad \text{quantum aspect}\end{array}}$$

$n_r \ll g_r$ if

$\lambda_{th} \ll \left(\frac{V}{N}\right)^{1/3}$ = average separation between particles in the gas

$\Rightarrow$ high temp. and/or dilute

[then we don't need to consider quantum feature seriously]

A by-product...

On p. VII-(21), α is fixed by the constraint $\sum_r n_r = N$ to be

$$e^{-\alpha} = \frac{N}{\sum_r g_r e^{-\beta\varepsilon_r}} = \frac{N}{z}$$

We just found that for classical ideal gas

$$z = V\cdot\left(\frac{2\pi mkT}{h^2}\right)^{3/2} = \frac{V}{\lambda_{th}^3}$$

$$\therefore\; e^{-\alpha} = \frac{N}{z} = \frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2} = \frac{N}{V}\lambda_{th}^3$$

$$\Rightarrow \alpha = -\ln\left[\frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2}\right]$$

$$= \ln\underbrace{\left[\frac{V}{N}\frac{1}{\lambda_{th}^3}\right]}_{\gg 1 \text{ for classical ideal gas}}$$

Previously, we have

$\mu = -kT\ln\left[\frac{V}{N}\frac{1}{\lambda_{th}^3}\right]$ for classical ideal gas

chemical potential

Comparing: $\underbrace{\alpha = -\frac{\mu}{kT} = -\beta\mu}$

we used this relationship in rewriting $f_{FD}(\varepsilon)$ and $f_{BE}(\varepsilon)$. Here is an illustration that it is indeed the case for classical gas.

Remark

- The Maxwell-Boltzmann (classical) statistics also works for N distinguishable particles.

  # ways for N particles to realize a division into $\{n_1, n_2, \dots\}$ for the cells $= \dfrac{N!}{n_1!\, n_2! \cdots}$

  Inside a cell (g_i states), each particle (out of n_i) can take on any state

  $\Rightarrow$ # ways of arranging n_i particles among g_i states $= g_i^{n_i}$

$$W(\{n_r\}) = \frac{N!}{n_1!\, n_2! \cdots}\, g_1^{n_1} \cdot g_2^{n_2} \cdots$$

$$= N! \prod_i \frac{g_i^{n_i}}{n_i!} \propto \prod_i \frac{g_i^{n_i}}{n_i!}$$

Maximizing this W with the constraints gives the Maxwell-Boltzmann result.