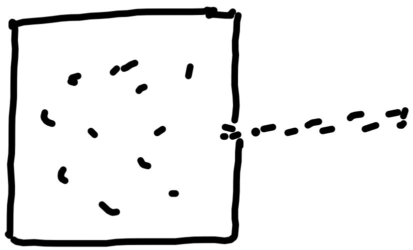
10/6

Effusion: occurs when molecules can escape through a hole in the wall of the container with diameter $D \ll \lambda$



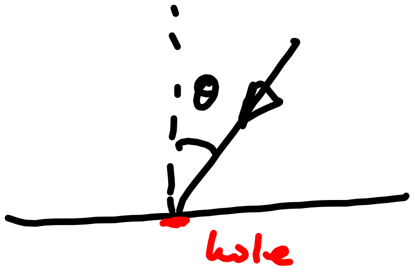
λ: medium free path (no collisions between the molecules when they go through the hole.

- If the hole is very large there is hydrodynamic flow instead of effusion. (non equilibrium process).

Last time we found that

$$\phi(\bar{v}) = f(\bar{v})\, v \cos\theta$$

# of molecules per unit time and unit area that hit a wall and have speed between v and $v + dv$ and direction θ – $\theta + d\theta$.

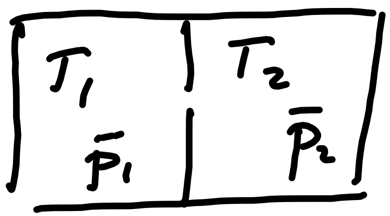


The number of particles that will get through the hole is

$$A\,\phi(\bar{v})\, d^3v \propto A\, f(v)\, v \underbrace{\cos\theta}_{\sim 1}\, v^2\, dv\, d\Omega \propto e^{-\frac{mv^2}{2kT}}\, v^3\, dv\, d\Omega$$

only particles with $\bar{v} \perp$ wall go through.

Then we see that the distribution of velocities has an extra factor v compared with the distribution of velocities inside the container.



- If the hole were large equilibrium is reached when T and p become the same for both gases.

- If the hole is $d \ll \lambda$ then equilibrium occurs when $n_1 \bar{v}_1 = n_2 \bar{v}_2$ (1)

Same flow in both directions.

We know that $\bar{p}_i = n_i kT$ eq. of state for ideal gas.

$$n_i = \frac{\bar{p}_i}{kT_i}$$

and $\bar{v}_i \propto \sqrt{\frac{kT_i}{m_i}}$

$$n_i \bar{v}_i \propto \frac{\bar{p}_i}{kT_i}\sqrt{\frac{kT_i}{m_i}} \propto \frac{\bar{p}_i}{\sqrt{T_i m_i}}$$

$$\frac{\bar{p}_1}{\sqrt{T_1 m_1}} = \frac{\bar{p}_2}{\sqrt{T_2 m_2}}$$

You also can use $e^{-\frac{m v^2}{2kT}} v^3 \, dv \, dz$ to evaluate $\langle v \rangle$, $\langle v^2 \rangle$ and $\tilde{v}$ for the particles that go out. You can see that $\langle v \rangle$, etc. will be higher for the effused particles than for the particles in the container.

Quantum Statistics of Ideal Gases (Ch. 9.)

In quantum mechanics particles of the same kind are indistinguishable.

Consider a gas : (weak interactions)

N identical particles.

V volume of container

Q_i all the coordinates of particle i.

s_i : quantum state of particle i.

Single particle approach is valid.

The gas is described by

$\{s_1, s_2, \ldots, s_N\}$ quantum state.

$\Psi_{\{s_1, s_2, \ldots, s_N\}}(Q_1, Q_2, \ldots, Q_N)$: wave function of the gas.

a) classical case. (~ high T limit of quantum)

- Distinguishable particles. (unphysical and leads to problems with S (entropy) and Gibbs' paradox. → Maxwell-Boltzmann statistics.

No symmetry requirements.

b) Particles with integer spin (bosons):

ψ has to be symmetric under the exchange of two particle.

$$\psi(Q_1 \ldots Q_i \ldots Q_j \ldots Q_N) = \psi(Q_1 \ldots Q_j \ldots Q_i \ldots Q_N)$$

→ Bose-Einstein's statistics,

c) Particles with half-integer spin (fermions):

ψ has to be antisymmetric under exchange of two particles.

$$\psi(Q_1 \dots Q_i \dots Q_j \dots Q_N) = -\psi(Q_1 \dots Q_j \dots Q_i \dots Q_N)$$

Then if i and j are in the same state $\psi = 0$. Then i and j cannot have the same quantum numbers (Pauli's exclusion principle).

$\longrightarrow$ Fermi-Dirac's statistics

Example: gas made of 2 particles A and B with 3 possible quantum states:

M - B (9 states)

1	2	3
AB	–	–
–	AB	–
–	–	AB
A	B	–
B	A	–
–	A	B
–	B	A
A	–	B
B	–	A

B - E : $A \equiv B$

1	2	3
AA	–	–
–	AA	–
–	–	AA
A	A	–
A	–	A
–	A	A

6 states

F-D : $A \equiv B$

1	2	3
A	A	–
A	–	A
–	A	A

3 states

Probability of Double occupancy of a state:

M - B B - E F - D

$\frac{3}{9} = \frac{1}{3}$ $\frac{3}{6} = \frac{1}{2}$ $\frac{0}{3} = 0$

The statistics affects the outcome.

Maxwell-Boltzmann's statistics:

$$Z = \sum_R e^{-\beta(n_1 \varepsilon_1 + n_2 \varepsilon_2 + \cdots)}$$

R: all possible states

n_i: all possible fillings of state i

constrain: $\sum_r n_r = N$ canonical

$$\frac{N!}{n_1!\, n_2! \cdots}$$

# of ways in which N distinguishable particle can be put in a configuration $\{n_1, n_2, \ldots\}$

In our example $N = 2$ $i = 1, 2, 3$

$$\frac{N!}{n_1!\, n_2!\, n_3!}$$

Double occupancy.

$$\frac{2!}{2!\,0!\,0!} = 1$$ for double occupancy AB

single occupancy:

$$\frac{2!}{1!\,1!\,0!} = 2$$

A B —
B A —

Then

$$Z = \sum_{n_1, n_2, \dots} \frac{N!}{n_1!\, n_2! \cdots} e^{-\beta(n_1 \varepsilon_1 + n_2 \varepsilon_2 + \dots)} =$$

n_i ranges from 0 to N but $\sum_i n_i = N$.

$$= \sum_{n_1, \dots} \frac{N!}{n_1!\, n_2! \cdots} \left(e^{-\beta \varepsilon_1}\right)^{n_1} \left(e^{-\beta \varepsilon_2}\right)^{n_2} \cdots\cdots =$$

$$(x_1 + x_2 + \dots + x_p)^n = \sum \frac{n!}{n_1!\, n_2! \cdots n_p!} x^{n_1} x^{n_2} \cdots x^{n_p}$$

$$= \left(e^{-\beta \varepsilon_1} + e^{-\beta \varepsilon_2} + \dots\right)^N = \left(\sum_r e^{-\beta \varepsilon_r}\right)^N =$$

$$\sum_{n_i} n_i = n$$

$$= Z_0^N \quad (1)$$

Then $\ln Z = N \ln Z_0 = N \ln \left(\sum_r e^{-\beta \varepsilon_r} \right)$

(We already had this result for the classical ideal gas).

But:

$$\bar{n}_s = \frac{\sum_R n_s e^{-\beta(n_1 \varepsilon_1 + \cdots)}}{\sum_R e^{-\beta(n_1 \varepsilon_1 + \cdots)}} = \frac{1}{Z} \sum_R \left(-\frac{1}{\beta} \frac{\partial}{\partial \varepsilon_s} \right) e^{-\beta(n_1 \varepsilon_1 + \cdots)}$$

$$= -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \varepsilon_s} \quad \left(\tfrac{1}{2}\right)$$

Then using ① in ②:

$$\bar{n}_s = -\frac{1}{\beta}\frac{\partial}{\partial \varepsilon_s} N \ln \sum_r e^{-\beta\varepsilon_r} =$$

$$= -\frac{1}{\beta} N (-\beta) \frac{e^{-\beta\varepsilon_s}}{\sum_r e^{-\beta\varepsilon_r}} = \frac{N\, e^{-\beta\varepsilon_s}}{\sum_r e^{-\beta\varepsilon_r}}$$

Maxwell-Boltzmann's distribution.

Photons: $S=1$ (bosons)

N is undefined $\to$ no constrain on N. canonical

$$Z = \sum_R e^{-\beta n_r \varepsilon_r} = \left(\sum_{n_1=0}^{\infty} e^{-\beta n_1 \varepsilon_1}\right)\left(\sum_{n_2=0}^{\infty} e^{-\beta n_2 \varepsilon_2}\right)$$

$$\dots = \prod_r \underbrace{\sum_{n_r=0}^{\infty} e^{-\beta n_r \varepsilon_r}}_{\text{geometric series}} = \prod_r \frac{1}{1-e^{-\beta\varepsilon_r}}$$

$$\sum_{i=0}^{\infty} x^i = \frac{1}{1-x}$$

$$\therefore \ln Z = -\sum_r \ln\left(1-e^{-\beta\varepsilon_r}\right)$$

Now

$$\boxed{\bar{n}_s} = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \varepsilon_s} = -\frac{1}{\beta}\frac{\partial\left(-\sum_r \ln\left(1-e^{-\beta\varepsilon_r}\right)\right)}{\partial \varepsilon_s} =$$

$$= +\frac{1}{\cancel{\beta}}\frac{\left(+\cancel{\beta}\, e^{-\beta\varepsilon_s}\right)}{1-e^{-\beta\varepsilon_s}} = \boxed{\frac{1}{e^{\beta\varepsilon_s}-1}}$$

Planck's distribution.

Bose - Einstein: N is fixed $\underbrace{\sum_r n_r = N}_{\text{constraint}}$.

Using the constraint as a Lagrange multiplier simplifies the problem. So we will work in the grand-canonical formalism.

Notice that $Z(N')$ increases with N'
and $e^{-\alpha N'}$ decreases with N'

So $e^{-\alpha N'} Z(N')$ is going to have a sharp peak at $N = \tilde{N}$.

Then we write

increases with N'

due to sharp peak

$$\mathcal{Z} = \sum_{N'=0}^{\infty} Z(N')\, e^{-\alpha N'} \cong$$

decreases with N'

$$\cong Z(N)\, e^{-\alpha N}\, \Delta^* N'$$