

## Kinetic theory of gas.

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1. It's a classical model of the thermodynamic behaviour of gases (typically ideal gas)
2. The model assumes large number of identical microscopic particles (atoms, molecules) which are in rapid constant and random motion
3. The size of the particles are assumed to be much smaller than their interatomic distances.
4. The particles undergo random elastic collisions between themselves and with the enclosing walls.
5. The basic version of the model describes ideal gas and consider no other interaction between the particles.
6. The number of particles are so large that a statistical treatment of the problem is justified. This is called the thermodynamic limit.
7. collisions between the particles are strictly binary. There is no three-body or higher-order interactions.
8. The collisions no forces on each other i.e., no potential energy term.
9. The kinetic theory of gas explains the macroscopic properties of gases such as ~~volume~~ pressure, viscosity, thermal conductivity, mass diffusivity, etc.

## Some standard integrals

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$$\boxed{\Gamma(n)} \equiv \int_0^{\infty} e^{-x} x^{n-1} dx \quad \left\{ \begin{array}{l} n \text{ is } \text{not integer} \\ \text{and } \text{not any} \\ \text{number.} \end{array} \right.$$

This is called gamma function.

$$\Gamma(n) = (n-1)! \quad \text{For } n \text{ is a positive integer}$$

In general:

$$\Gamma(n) = (n-1) \Gamma(n-1)$$

$\boxed{I(n)}$

$$I(n) \equiv \int_0^{\infty} e^{-\alpha x^2} x^n dx \quad \text{where } n \geq 0$$

$$I(n) = \frac{1}{2} \Gamma\left(\frac{n+1}{2}\right) \alpha^{-(n+1)/2}$$

$$I(0) = \frac{1}{2} \Gamma\left(\frac{1}{2}\right) \alpha^{-1/2} = \frac{1}{2} \sqrt{\pi} \alpha^{-1/2}$$

$$I(1) = \frac{1}{2} \Gamma(1) \alpha^{-1} = \frac{1}{2} \alpha^{-1}$$

$$I(2) = \frac{1}{2} \Gamma\left(\frac{3}{2}\right) \alpha^{-3/2} = \frac{1}{2} \cdot \frac{1}{2} \Gamma\left(\frac{1}{2}\right) \alpha^{-3/2} = \frac{1}{4} \sqrt{\pi} \alpha^{-3/2}$$

## The Boltzmann factor ( $e^{-\beta E_r}$ )

Consider the system A is in contact with a heat reservoir A', where  $A \ll A'$ .

The energy of the combined system A & A' is constant in some range of energy ( $E^{(0)}$  and  $E^{(0)} + \delta E$ ).

$$A \rightarrow E_r, \quad A' \rightarrow E'$$
$$A + A' = A^{(0)} \rightarrow [E^{(0)} \rightarrow E^{(0)} + \delta E]$$

$$\therefore E_r + E' = E^{(0)} \quad \left\{ \begin{array}{l} \text{The system A in the} \\ \text{microstate } r \text{ has energy} \\ E_r \text{ which can exchange} \\ \text{energy with } E'. \end{array} \right.$$
$$\Rightarrow E' = (E^{(0)} - E_r)$$

▣ The probability ( $P_r$ ) of occurrence in the ensemble of situation where A is in the state r is given by the number of all microstates accessible to  $A^{(0)}$ ,

$$\therefore P_r = c' \Omega'(E^{(0)} - E_r) \quad ; \quad \Omega' = \text{No of all microstates}$$

Since  $E_r \ll E^{(0)}$ , we can write

$$\ln \Omega'(E^{(0)} - E_r) = \ln \Omega'(E^{(0)}) - \left[ \frac{\partial \ln \Omega'}{\partial E'} \right]_0 E_r \dots$$

$$\approx \ln \Omega'(E^{(0)}) - \frac{\partial \ln \Omega'}{\partial E'} \bigg|_0 E_r$$

$$= \ln \Omega'(E^{(0)}) - \beta E_r$$

$$\therefore P_r = c' \Omega'(E^{(0)}) e^{-\beta E_r}$$

$$\boxed{P_r = c e^{-\beta E_r}}$$

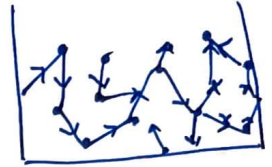
Probability of finding the system A in the microstate r within energy  $E_r$  within a range of energy ( $\delta E$ ).



## Kinetic theory of gas

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- The state of a particle in the container can be specified by specifying that the position ( $\vec{r}$ ) of the particle lies in the range  $\vec{r}$  to  $\vec{r} + d\vec{r}$  i.e., in the volume element  $d^3\vec{r} = dx dy dz$



- And by specifying its momentum ( $\vec{p}$ ) in the range  $\vec{p}$  to  $\vec{p} + d\vec{p}$ .

$\therefore$  Probability of finding the particle in the range ( $\vec{r}$  to  $\vec{r} + d\vec{r}$ ) and ( $\vec{p}$  to  $\vec{p} + d\vec{p}$ ) is

$$P(\vec{r}, \vec{p}) d^3\vec{r} d^3\vec{p} \propto e^{-\beta \tilde{p}/2m} d^3\vec{r} d^3\vec{p}$$

- Since  $\vec{v} = \vec{p}/m$ , we can re-express the above relation in terms of  $\vec{v}$  and  $\vec{r}$ .

- Since the above expression is a probability, if we multiply it by the total no. of particle, it gives the mean number of particles in this position and momentum range.

Let's say  $N$  = total no. of particle

$$\therefore N P(\vec{r}, \vec{p}) d^3\vec{r} d^3\vec{p} = f(\vec{r}, \vec{v}) d^3\vec{r} d^3\vec{v}$$

which is the mean number particles with position between  $\vec{r}$  and  $\vec{r} + d\vec{r}$  and velocity between  $\vec{v}$  and  $\vec{v} + d\vec{v}$

$$\therefore f(\vec{r}, \vec{v}) d^3\vec{r} d^3\vec{v} = C e^{-\beta m \tilde{v}/2} d^3\vec{r} d^3\vec{v}$$

Therefore, 
$$\int_{\vec{r}} \int_{\vec{v}} f(\vec{r}, \vec{v}) d^3\vec{r} d^3\vec{v} = N$$

$$\therefore c \int_{\vec{r}} \int_{\vec{v}} e^{-\beta m \tilde{v}^2/2} d^3 \vec{r} d^3 \vec{v} = N$$

Since the integrand does not depend on  $\vec{r}$ , we get

$$c v \int_{\vec{v}} e^{-\beta m \tilde{v}^2/2} d^3 \vec{v} = N$$

$$\Rightarrow c v \left( \frac{2\pi k_B T}{m} \right)^{3/2} = N$$

$$\therefore c = \frac{N}{V} \left( \frac{m}{2\pi k_B T} \right)^{3/2} = n \left( \frac{m}{2\pi k_B T} \right)^{3/2}$$

$$\beta = \frac{1}{k_B T}$$

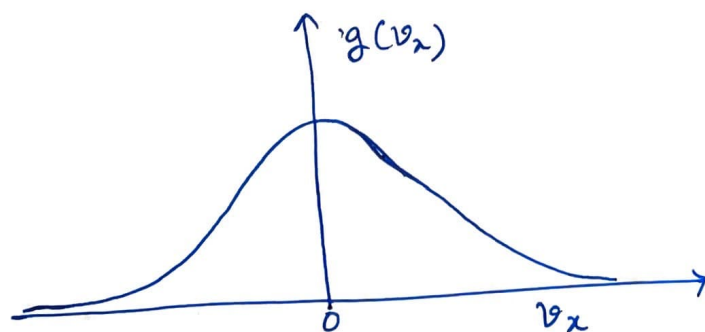
$k_B = \text{Boltzmann constant}$

$$\therefore f(\vec{v}) d^3 \vec{r} d^3 \vec{v} = n \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{m \tilde{v}^2}{2 k_B T}} d^3 \vec{r} d^3 \vec{v}$$

This is Maxwell velocity distribution.

- If we divide the above expression by  $d^3 \vec{r}$ , we get  $f(\vec{v}) d^3 \vec{v} = n \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{m \tilde{v}^2}{2 k_B T}} d^3 \vec{v}$

This is the mean number of molecules per unit volume with velocity in the range  $\vec{v}$  and  $\vec{v} + d\vec{v}$ .



- Distribution of velocity component: we can define

$$g(v_x) dv_x = \int_{v_y} \int_{v_z} f(\vec{v}) d\vec{v}$$

This is the mean number of molecules per unit volume with  $v_x$  in the range between  $\vec{v}_x$  and  $\vec{v}_x + d\vec{v}_x$ .

$$\begin{aligned}
 g(v_x) dv_x &= n \left( \frac{m}{2\pi k_B T} \right)^{3/2} \int_{v_y} \int_{v_z} e^{-\frac{m}{2k_B T} (v_x^2 + v_y^2 + v_z^2)} dv_y dv_z \\
 &= n \left( \frac{m}{2\pi k_B T} \right)^{3/2} \int_{v_y} e^{-\frac{m v_y^2}{2k_B T}} dv_y \int_{v_z} e^{-\frac{m v_z^2}{2k_B T}} dv_z e^{-\frac{m v_x^2}{2k_B T}} dv_x \\
 &= n \left( \frac{m}{2\pi k_B T} \right)^{3/2} \left( \frac{2\pi k_B T}{m} \right)^{1/2} \left( \frac{2\pi k_B T}{m} \right)^{1/2} e^{-\frac{m v_x^2}{2k_B T}} dv_x \\
 &= n \left( \frac{m}{2\pi k_B T} \right)^{1/2} e^{-\frac{m v_x^2}{2k_B T}} dv_x
 \end{aligned}$$

$$\therefore g(v_x) dv_x = n \left( \frac{m}{2\pi k_B T} \right)^{1/2} e^{-\frac{m v_x^2}{2k_B T}} dv_x$$

$$\int_{-\infty}^{\infty} g(v_x) dv_x = n$$

▣ Mean velocity distribution

$$\langle v_x \rangle = \frac{1}{n} \int_{-\infty}^{\infty} v_x g(v_x) dv_x = 0$$

$$\langle v_x^2 \rangle = \frac{1}{n} \int_{-\infty}^{\infty} v_x^2 g(v_x) dv_x$$

$$= \frac{2 \times \frac{1}{n} \times \frac{1}{2} \Gamma\left(\frac{1}{2}\right) \left(\frac{m}{2k_B T}\right)^{-1}}{n}$$

$$= \frac{2k_B T}{m} \times \frac{1}{n}$$

$$= \frac{1}{n} \times n \times \left( \frac{m}{2\pi k_B T} \right)^{1/2} \frac{1}{2} \Gamma\left(\frac{3}{2}\right) \left( \frac{m}{2k_B T} \right)^{-3/2}$$

$$= \left( \frac{m}{2\pi k_B T} \right)^{1/2} \frac{1}{2} \cdot \frac{1}{2} \sqrt{\pi} \left( \frac{m}{2k_B T} \right)^{-3/2}$$

$$= \frac{1}{4} \times \frac{2k_B T}{m} = \frac{k_B T}{m}$$

- This result can be directly obtained using the equipartition theorem  $\left\langle \frac{1}{2} m v_x^2 \right\rangle = \frac{1}{2} k_B T$