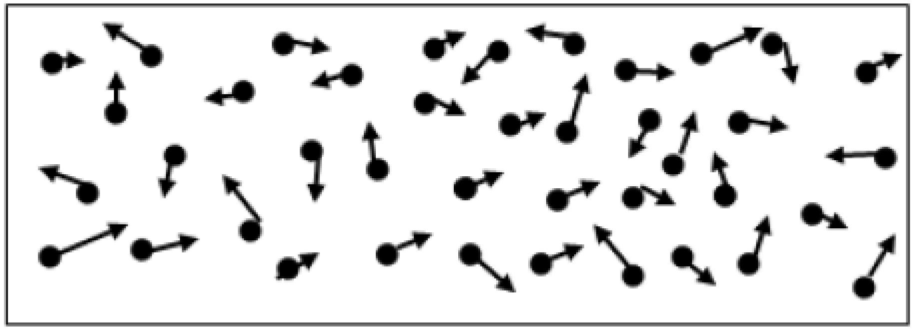
## THERMAL & STATISTICAL PHYSICS
## SSP3133

# MAXWELL-BOLTZMANN DISTRIBUTION

- DR WAN NURULHUDA WAN SHAMSURI
  - Acknowledgement : PROFESSOR DR RAMLI ABU HASSAN

***-a description of the statistical distribution of the energies of the molecules of a classical gas.***

**-James Clerk Maxwell in 1859** --on the basis of probabilistic arguments, and gave **the distribution of velocities** among the molecules of a gas.



-Maxwell's finding was generalized (1871) by a German physicist, Ludwig Boltzmann

-of a particular chemical, compound or element

  -All the molecules have the same mass

  -their kinetic energy is only dependent on the speed of the particles.

$$\text{Kinetic Energy} = ½mv^2$$

-Moving molecules, the speed v --from very slow to very fast particles

Most of the particles: at a **speed close to the average v**.

The probability of a small system in thermal equilibrium with reservoir occupying state S, with energy $E_S$

$$P_S = Ae^{-\beta E}$$

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

Where

$E_S$ is the energy of the particle
k is the Boltzman's constant = $8.617 \times 10^{-5}$ eV/K
T is the temperature
A is the normalization constant

$e^{-\beta E}$ : Boltzmann factor

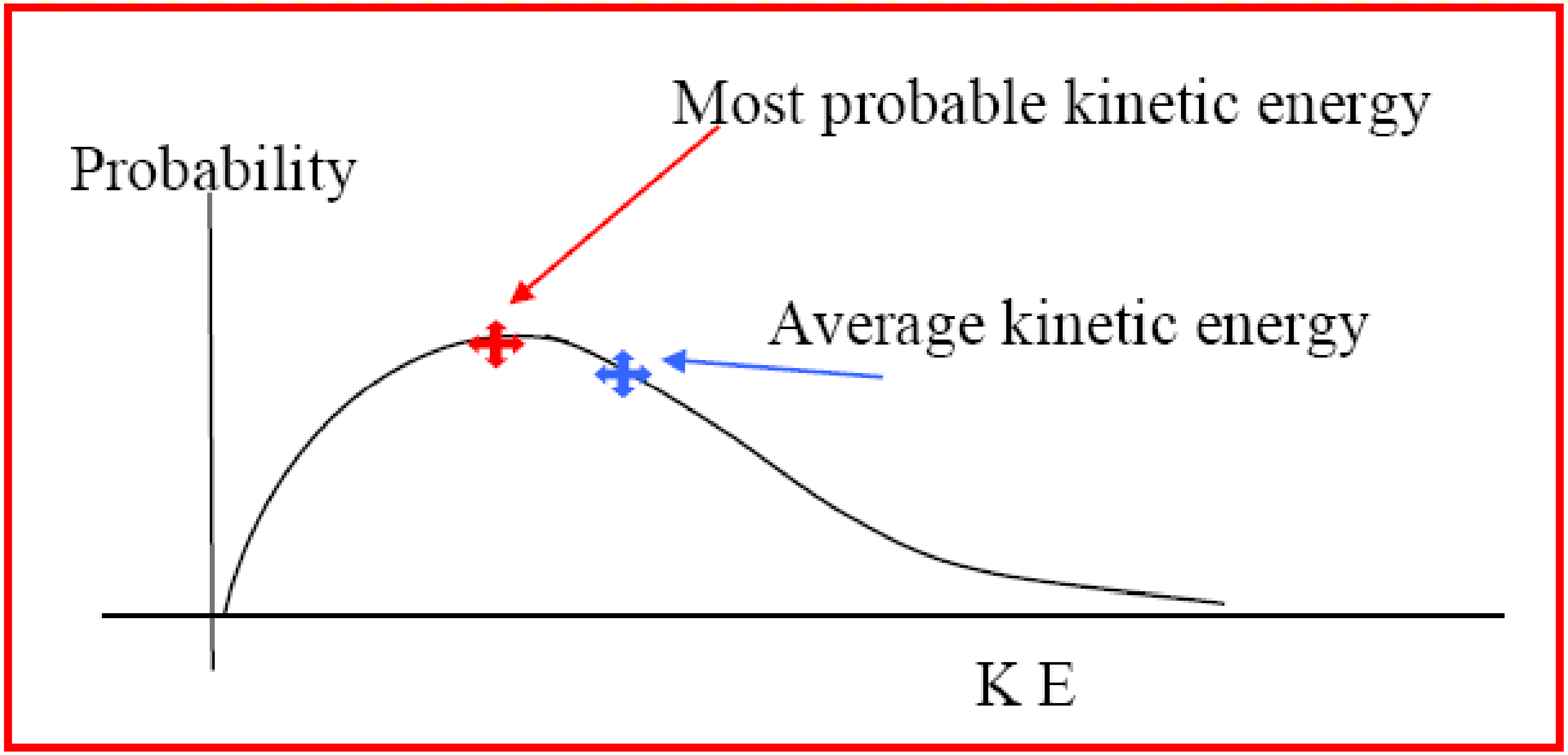
# The Maxwell speed distribution

Statistics -distribution of kinetic energies in a large collection of particles

Maxwell and Boltzmann- plotting the **fraction** of molecules in a container with a given kinetic energy versus kinetic energy.

Or

Plot **the probability** that gas molecules will have a given kinetic energy versus kinetic energy.


Most probable kinetic energy
Probability
Average kinetic energy
K E

From equipartition theorem, for an ideal gas

$$\bar{\varepsilon} = \frac{3}{2}kT \quad , \quad \text{but} \quad \bar{\varepsilon} = \frac{1}{2}mv^{2}$$

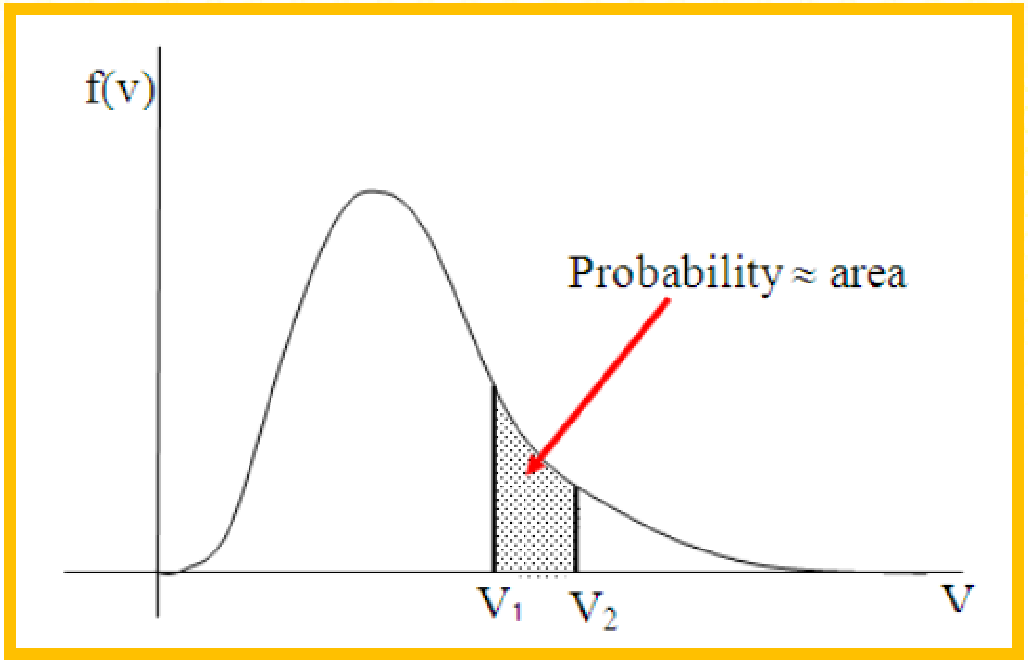
$v^2 = 3kT/m$ , $v_{rms} = \sqrt{(3kT/m)}$ ……..average speed

-interested to know the real speed

-if $P_v$: probability a molecule moving with velocity v
$P_v = 0$ … speed vary continuously

-But some speeds are more probable than others

-Can present the relative probabilities of speed by graph



-the most probable speed when the graph is highest

-the probability the speed between $v_1$ and $v_2$ is equaled to area under the graph

$$P_{v1,v2} = \int_{v1}^{v2} f(v)dv$$

$$P_{v1,v2} = \int_{v1}^{v2} f(v)\,dv$$

For $v_2 - v_1$ small, f(v) almost unchanged

$$P_{v,v+dv} = f(v)\,dv$$

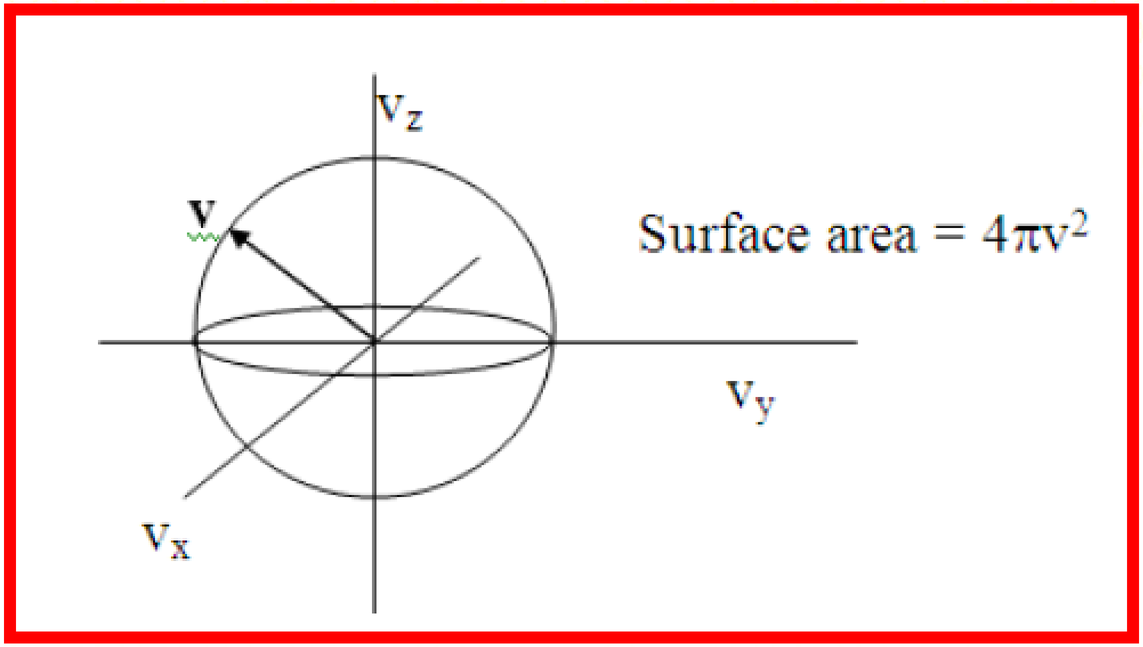
f(v): the height of the graph
-is called distribution function

f(v) ∝ (probab. of a molecule with velocity **v**)

∝ (number of vector **v** corresponding to v)

(probab. of a molecule with velocity **v**) $\propto e^{-E/kT} = e^{-mv^2/2kT}$

-every point on the surface of sphere radius v, is speed which can be associated with velocity vectors



Surface area = $4\pi v^2$

(number of vector **v** corresponding to v) $\propto 4\pi\, v^2$

Probab. of a molecule with velocity **v**

$$f(v) = C(4\pi v^2)e^{-mv^2/2kT}$$

Total probability = 1

$$1 = \int_0^\infty f(v)dv = C4\pi\int_0^\infty v^2 e^{-mv^2/2kT}dv$$

note: take x = v√(m/2kT)

$$1 = C4\pi\left(\frac{2kT}{m}\right)^{3/2}\int_0^\infty x^2 e^{-x^2}dx$$

$$note: \int_0^\infty x^2 e^{-x^2}dx = \frac{\sqrt{\pi}}{4}$$

$$C = \left(\frac{m}{2\pi kT}\right)^{3/2}$$

$$f(v) = \left(\frac{m}{2\pi kT}\right)^{3/2} (4\pi v^2) e^{-mv^2/2kT}$$

Or

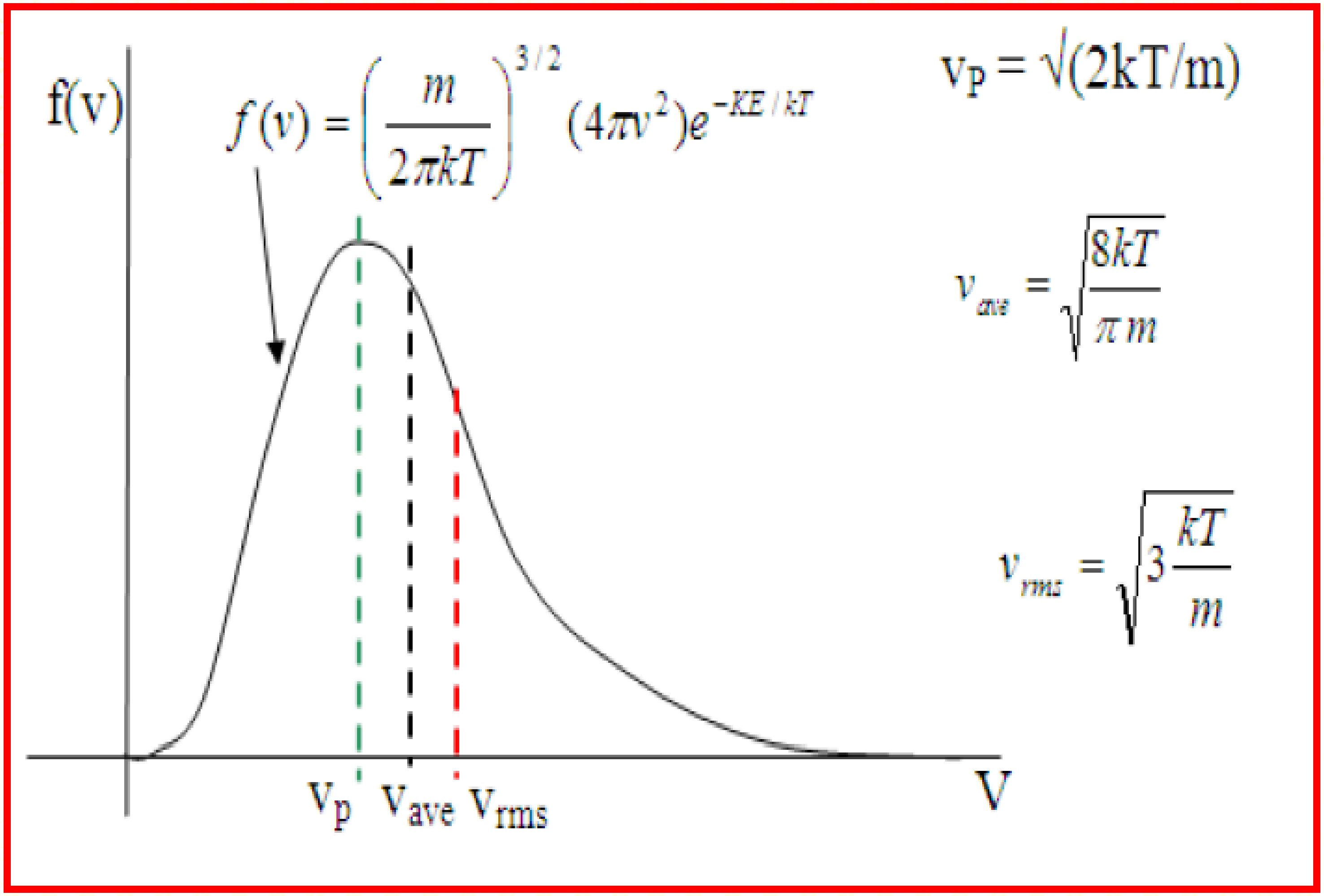
$$f(v) = \left(\frac{m}{2\pi kT}\right)^{3/2} (4\pi v^2) e^{-KE/kT}$$

……Maxwell distribution

……. when $\frac{d}{dv} f(v) = 0$

$v_{max} = \sqrt{(2kT/m)}$

Average speed $\bar{v} = \sqrt{\frac{8kT}{\pi m}}$

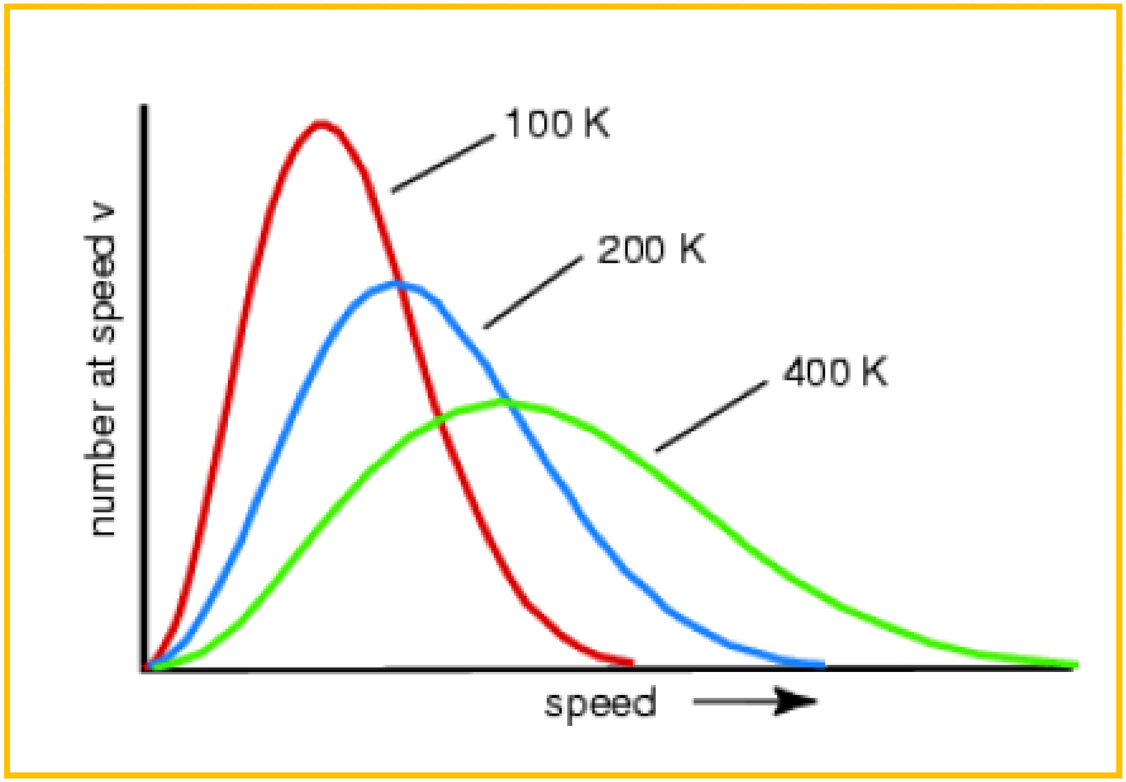


$$f(v) = \left(\frac{m}{2\pi kT}\right)^{3/2}(4\pi v^2)e^{-KE/kT}$$

$$v_P = \sqrt{(2kT/m)}$$

$$v_{ave} = \sqrt{\frac{8kT}{\pi m}}$$

$$v_{rms} = \sqrt{3\frac{kT}{m}}$$

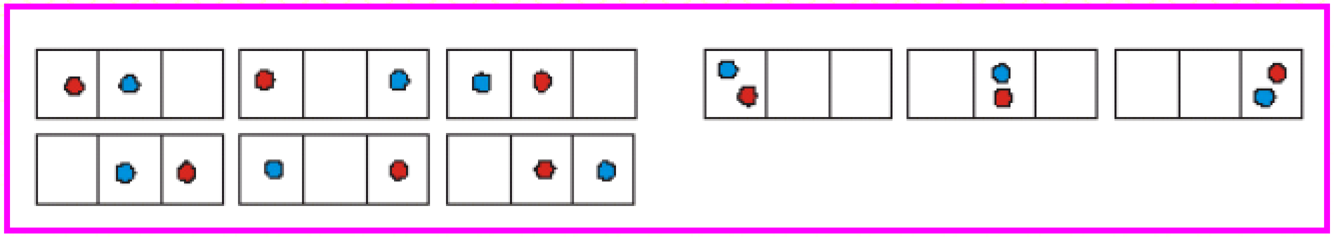


Points to note:

- No molecules at zero energy
- Few molecules at high energy
- No maximum energy value

Note:

# Maxwell-Boltzmann Distribution
Case-1: putting two balls into 3 different boxes



Total number of particles, N = 18

2 balls in separate boxes:

States, 6 with number of particles, $n_i$ =12

$$\frac{n_i}{N} = \frac{12}{18}$$

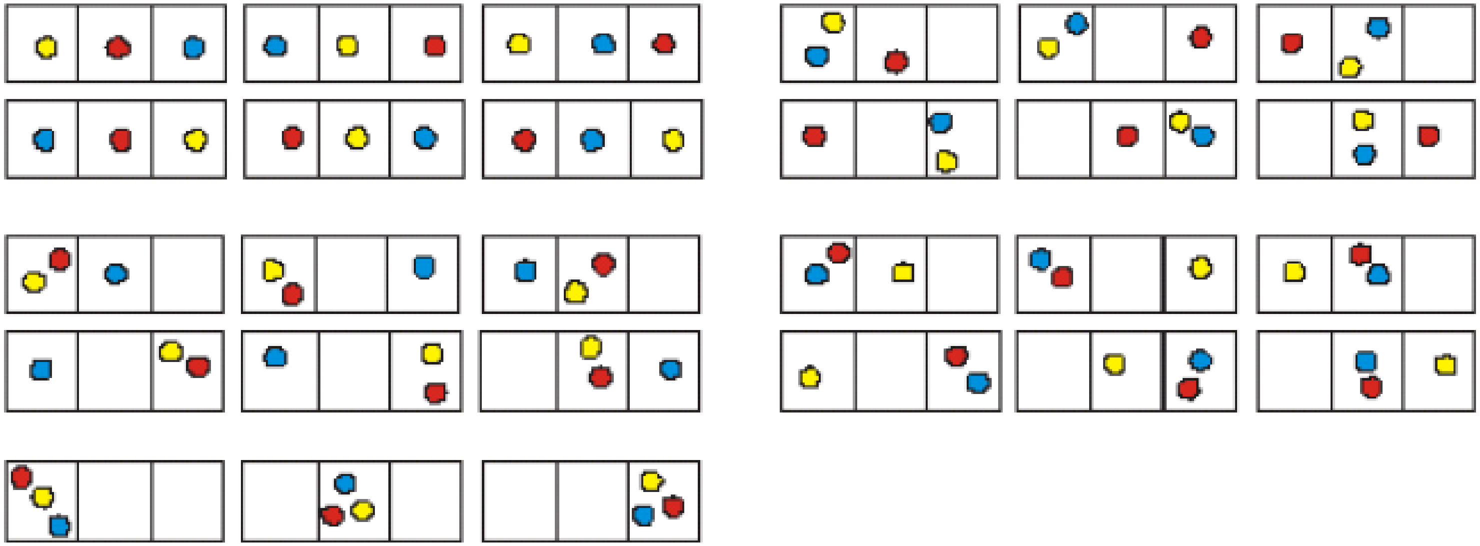
2 balls in one box:

States, 3 with number of particles, $n_i$ = 6

$$\frac{n_i}{N} = \frac{6}{18}$$

Note: $N = \sum N_i = 12 + 6 = 18$

# Case 2: putting 3 balls into 3 different boxes



Total number of particles, N = 81

Total no of accessible states?

# Total no of accessible states?

3 balls in one box:

States, 3 with number of particles, $n_i = 9$

$$\frac{n_i}{N} = \frac{9}{81}$$

2 balls in one box and 1 ball in separate box:

States, 18 with number of particles, $n_i = 54$

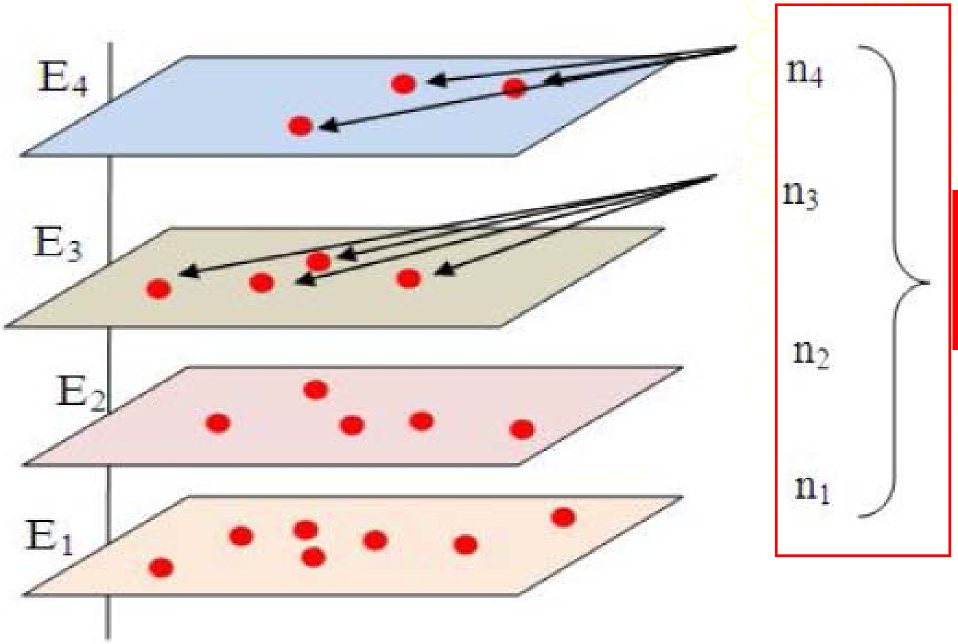
$$\frac{n_i}{N} = \frac{54}{81}$$

3 balls in separate boxes:

States, 6 with number of particles, $n_i = 18$

$$\frac{n_i}{N} = \frac{18}{81}$$

Note: $N = \sum N_i = 9+54 + 18 = 81$



$$N = n_1 + n_2 + n_3 + n_4$$

As number, N become larger (example; N ~around $10^{23}$)

$$\frac{n_i}{N} = \frac{e^{-E_i / kT}}{\sum e - E_i / kT}$$

$n_i$: number of molecules in the ith energy state
N: total number of molecules
$E_i$: energy of the ith energy state
K: Boltzmann's constant
R: gas constant
$R = kN_A$

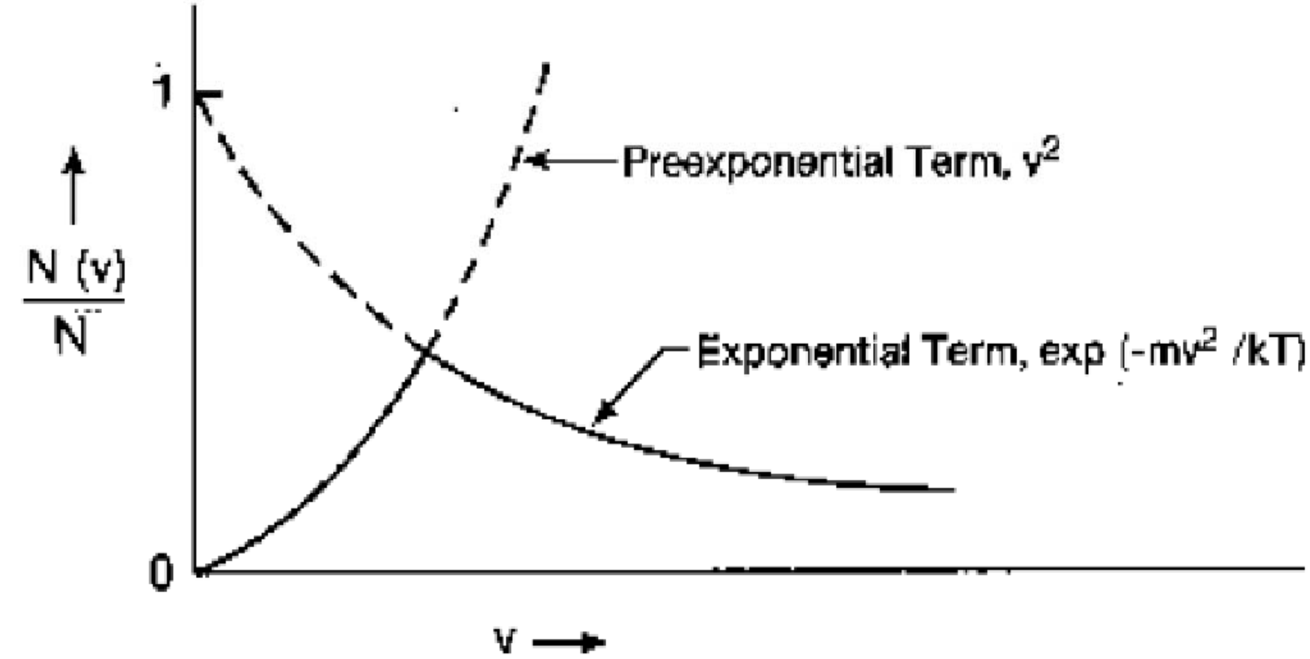
But $E_i = ½\, mV_i^2$

$$\frac{n(v_i)}{N} = \frac{e^{-\frac{mv^2}{2kT}}}{\sum e^{-\frac{mv^2}{2kT}}}$$

$n(v_i)$: number of particles with velocity $v_i$

N : total number of particles

$$\frac{n(v_i)}{N} = F(v_i) = \left(\frac{m}{2\pi kT}\right)^{3/2} (4\pi v^2) e^{-mv^2/2kT}$$



# Maxwell-Boltzmann distribution function

$$n_v = 4\pi N \left( \frac{m}{2\pi kT} \right)^{3/2} v^2 \exp\left( -\frac{mv^2}{2kT} \right)$$

$n_v$ number of particles with velocity v

Let $E = \frac{1}{2}mv^2$ & $dE = mvdv$ & $n_E dE = n_v dv$

Where, $n_E$ – number of particles with energy E

TO WRITE MAXWELL-BOLTZMANN DISTRIBUTION FUNCTION:

$$n_E = \frac{2}{\pi^{1/2}} N \left(\frac{1}{kT}\right)^{3/2} E^{1/2} \exp(-\frac{E}{kT})$$

$$\frac{n_E}{N} = F(E_i) = \frac{2}{\pi^{1/2}} \left(\frac{1}{kT}\right)^{3/2} E^{1/2} \exp(-\frac{E}{kT}) \quad (*)$$

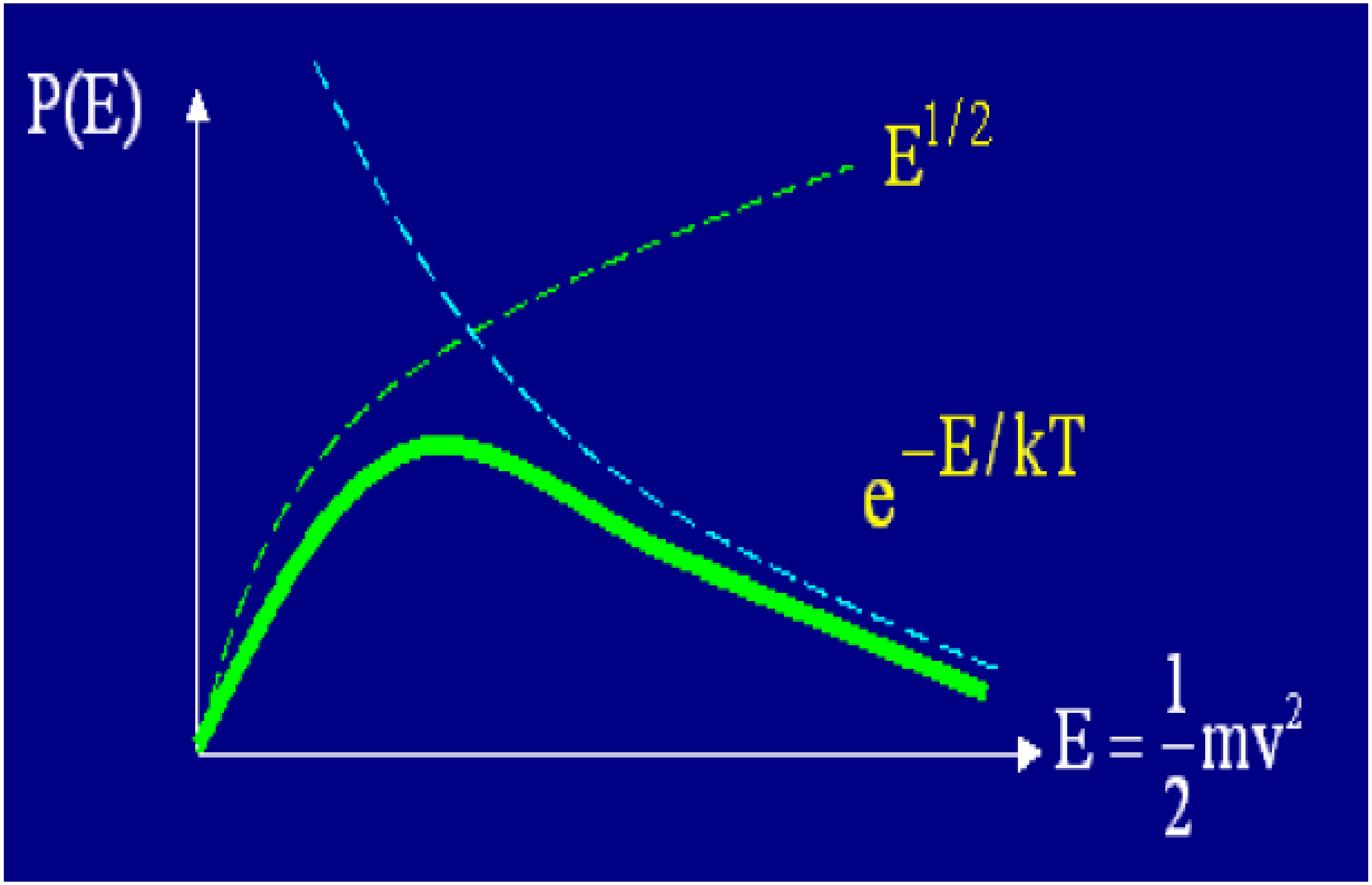
The probability of finding particle with energy E

$$P(E) = \int_{E1}^{E2} f(E)dE$$

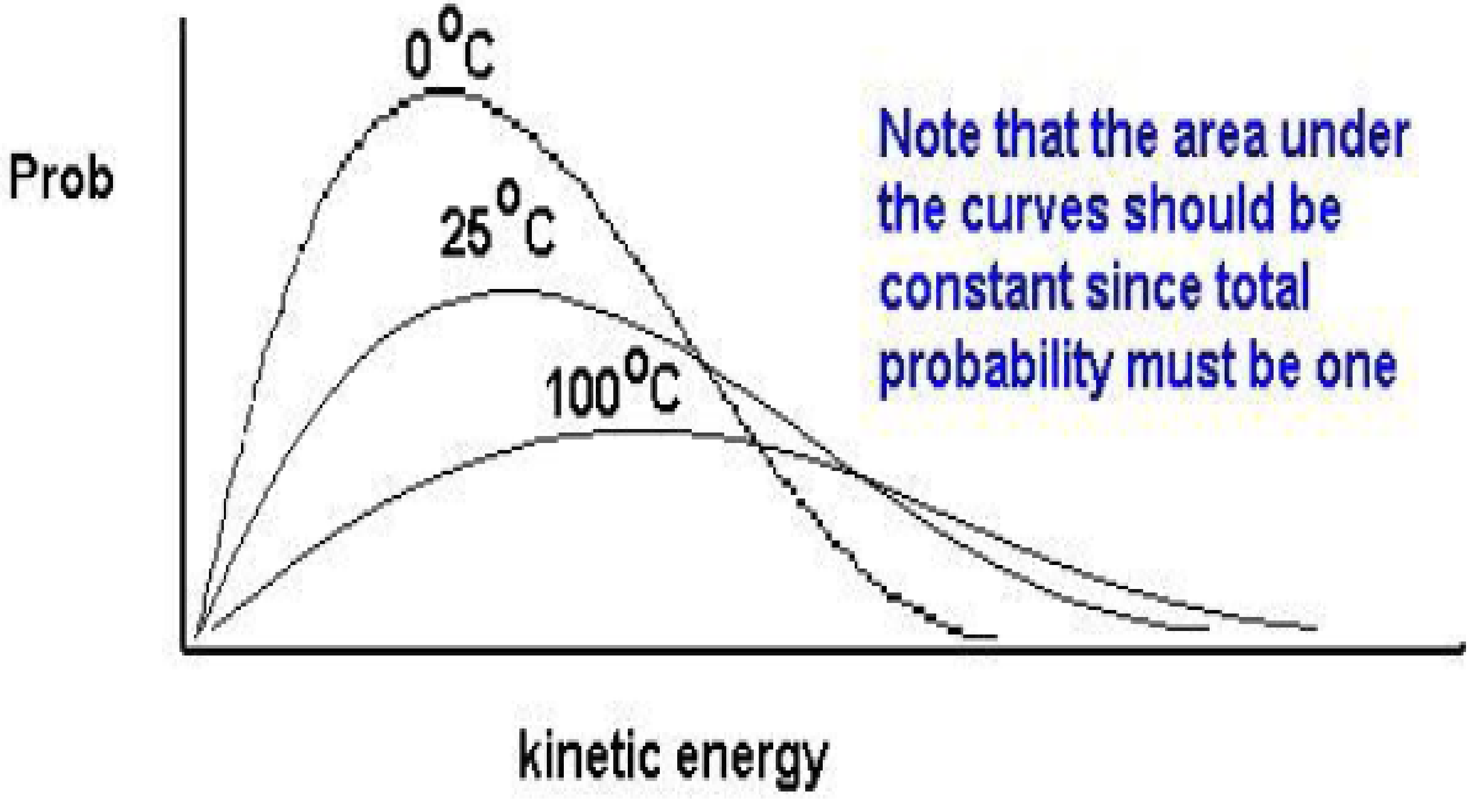
$$\frac{n_E}{N} = F(E_i) = \frac{2}{\pi^{1/2}}\left(\frac{1}{kT}\right)^{3/2} E^{1/2}\exp(-\frac{E}{kT}) \quad (*)$$

Eq (*) can be written as,

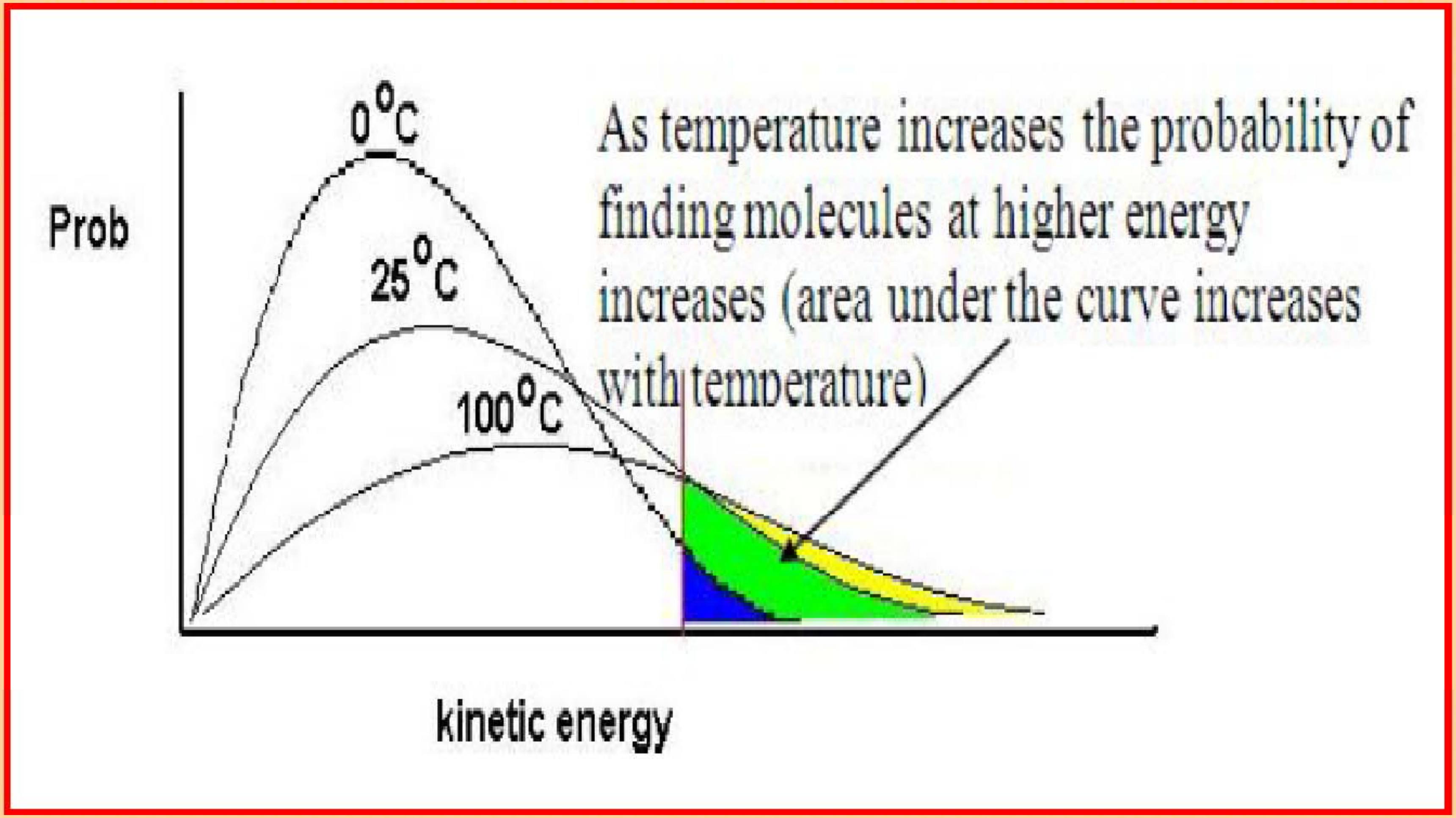
$$P(E) = CE^{1/2} e^{-E/kT}$$


P(E)
$E^{1/2}$
$e^{-E/kT}$
$E = \frac{1}{2}mv^2$

# Effect of temperature



Note that the area under the curves should be constant since total probability must be one



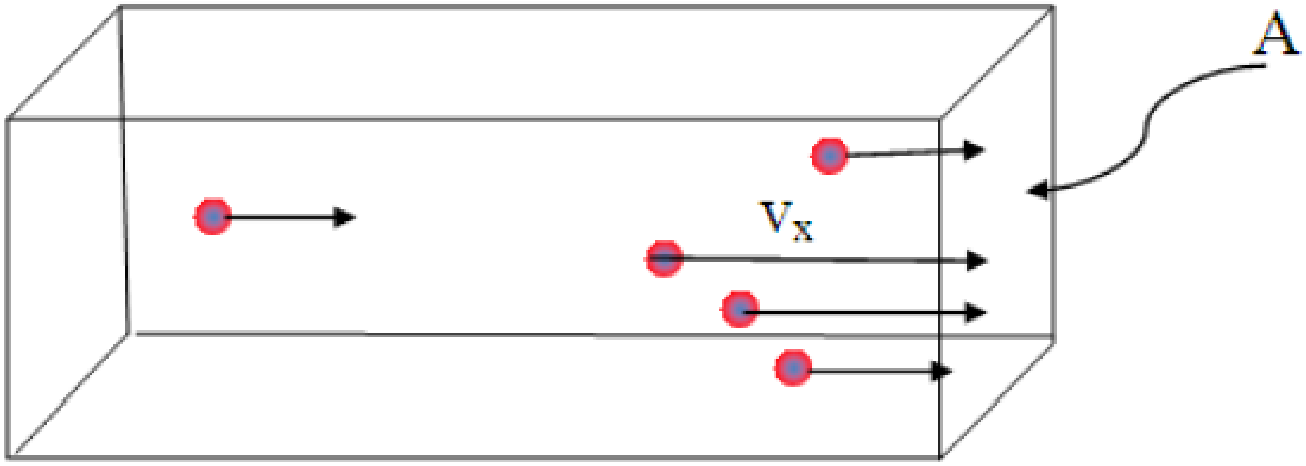
As temperature increases the probability of finding molecules at higher energy increases (area under the curve increases with temperature)

The Maxwell-Boltzmann probability distribution functions…...
to determine the speeds of molecules.

-determining a statistical representation which will accurately predict the velocities of particles in a given sample

-restrict to an ideal or hard-sphere gas in which there are no intermolecular interactions

-examine the number of collisions of gas exerts on a planar boundary surface, perpendicular to the x-axis.



$$N = \rho_N A \Delta t \sum v_x f(v_x)$$

N: number of collisions,

$\rho_N$: density of particles,

A: area of the surface,

$\Delta t$: time duration in which the particles are allowed to collide.

But $v_x t$: distance along the x-axis,

$A(v_x t)$: volume.

The change in momentum of the molecules as they hit the wall

$$\Delta p = N 2 m v_x = 2 m \rho_N A \Delta t \sum_{v_x > 0} v_x^2 f(v_x)$$

Pressure is related to momentum

$$P = \frac{\Delta p}{A \Delta t} = 2 m \rho_N \sum_{v_x > 0} v_x^2 f(v_x)$$

Gas is assumed to be stationary

The sum of all velocities above zero is equal to half the sum of all the velocities from negative to positive infinity. Pressure

$$P = 2m\rho_N \sum_{v_x>0} v_x^2 f(v_x) = 2m\rho_N \frac{1}{2} \sum_{v_x=-\infty}^{v_x=+\infty} v_x^2 f(v_x)$$

Assumed ideal gas

$$\frac{nRT}{V} = m\rho_N \sum_{v_x} v_x^2 f(v_x)$$

or

$$\frac{nRT}{V} = m\rho_N \langle v_x^2 \rangle$$

# The mean-square speed of the molecules

$$\frac{nRT}{V} = m\frac{N}{V}\left\langle v_x^2 \right\rangle$$

$$nRT = mN\left\langle v_x^2 \right\rangle$$

In terms of the number of moles and Avogadro's number:

$$\mathrm{nRT} = \mathrm{mnN_A}\left\langle \mathrm{v_x^2} \right\rangle$$

$$\left\langle \mathrm{v_x^2} \right\rangle = \frac{\mathrm{RT}}{\mathrm{M}}$$

M: molecular weight.

For three dimensions,

$$\left\langle v^2 \right\rangle = \left\langle v_x^2 \right\rangle + \left\langle v_y^2 \right\rangle + \left\langle v_z^2 \right\rangle = 3\left\langle v_x^2 \right\rangle$$

Consequently:

$$\langle v^2 \rangle = \frac{3RT}{M} \quad and \quad v_{rms} = \sqrt{\frac{3RT}{M}}$$

$V_{rms}$: the root-mean-square speed

Constants

$$k_b = \frac{R}{N_A}, \quad and \quad M = \frac{M}{N_A}$$

$$\langle v^2 \rangle = \frac{3k_bT}{m}$$

$k_b$: Boltzmann constant ($1.38 \times 10^{-23}$ J/K).

Kinetic energy

$$\langle E \rangle = \frac{m\langle v^2 \rangle}{2} = \frac{m}{2}\left(\frac{3k_bT}{m}\right) = \frac{3k_bT}{2}$$

The mean kinetic energy of an *ideal* gas is dependent only on its temperature.

to derive a function which could relate several state variables of a gas to produce a distribution of speeds for the molecules of which the gas consists.

One begins by creating a distribution function g,

$$g(v)dv = f(v_x)f(v_y)f(v_z)dv_x dv_y dv_z$$

To derive some information from this equation,

take the derivative of g with respect to a coordinate variable, $v_x$ in this case, and then using the chain rule:

$$\frac{\partial g}{\partial v_x} = \frac{dg}{dv}\frac{\partial v}{\partial v_x} = \frac{dg}{dv}\frac{\partial}{\partial v_x}\sqrt{v_x^2 + v_y^2 + v_z^2}$$

the derivative on the right side

$$\frac{\partial g}{\partial v_x} = \frac{dg}{dv}\frac{v_x}{v}$$

Dividing by $v_x$:

$$\frac{1}{v_x}\frac{\partial g}{\partial v_x} = \frac{1}{v}\frac{dg}{dv}$$

the expression for g

$$\frac{1}{v_x}\frac{\partial}{\partial v_x}(f(v_x)f(v_y)f(v_z)) = \frac{1}{v}\frac{dg}{dv}$$

Taking the derivative with respect to v$_x$,

$$\frac{f(v_y)f(v_z)}{v_x}\frac{\partial f(v_x)}{\partial v_x} = \frac{1}{v}\frac{dg}{dv}$$

$$\frac{f(v_x)f(v_z)}{v_y}\frac{\partial f(v_y)}{\partial v_y} = \frac{1}{v}\frac{dg}{dv}$$

And:

$$\frac{f(v_x)f(v_y)}{v_z}\frac{\partial f(v_z)}{\partial v_z}=\frac{1}{v}\frac{dg}{dv}$$

can equate the left hand side of each equation with some constant, let say -k

$$\frac{f(v_y)f(v_z)}{v_x}\frac{\partial f(v_x)}{\partial v_x}=-k$$

Dividing the above eq simultaneously by g

$$\frac{1}{f(v_x)v_x}\frac{\partial f(v_x)}{\partial v_x}=-k$$

or

$$\frac{\partial f(v_x)}{f(v_x)} = -kv_x \partial v_x$$

integrating:

$$f(v_x) = Ce^{-kv_x^2/2}$$

C is the integrating constant

the integral of the distribution over the entire region of space it encompasses must be unity.

$$1 = \int_{-\infty}^{\infty} f(v_x) dv_x = C \int_{-\infty}^{\infty} e^{-kv_x^2/2} dv_x$$

using numerical tables or from integral tables

$$1 = N\sqrt{\frac{2\pi}{k}} \quad \text{or} \quad C = \sqrt{\frac{k}{2\pi}}$$

The function f is therefore:

$$f(v_x) = \sqrt{\frac{k}{2\pi}} e^{-kv_x^2/2}$$

the value of k

$$g(v) = f(v_x)\,f(v_y)\,f(v_z)$$

$$g(v) = \left(\frac{k}{2\pi}\right)^{3/2} e^{-kv_x^2/2}\,e^{-kv_y^2/2}\,e^{-kv_z^2/2}$$

Using the mean kinetic energy of an ideal and the distribution g:

$$\langle E\rangle = \frac{2mk^{3/2}}{2(2\pi)^{3/2}} \int_{-\infty}^{\infty} e^{-kv_x^2/2} dv_x \int_{-\infty}^{\infty} e^{-kv_y^2/2} dv_y \int_{-\infty}^{\infty} e^{-kv_z^2/2} dv_z$$

Simplifying:

$$\langle E\rangle = \frac{2mk^{3/2}}{2(2\pi)^{3/2}} \frac{2\pi}{k} \int_{-\infty}^{\infty} v_x^2 e^{-kv_x^2/2} dv_x$$

cannot be solved in closed form.

Use table

$$\langle E\rangle = \frac{3mk^{1/2}}{2(2\pi)^{1/2}}\frac{(2\pi)^{1/2}}{k^{3/2}}$$

or

$$\langle E\rangle = \frac{3m}{2k}$$

$$k = \frac{m}{k_b T}$$

$$\frac{3k_b T}{2} = \frac{3m}{2k}$$

# the velocity distribution f :

$$f(v_x) = \left(\frac{m}{2\pi k_b T}\right)^{1/2} e^{-mv_x^2/2k_bT}$$

# THE END….

REFERENCES:

1. REAF, F : “Fundamentals Of  Statistical And Thermal Physics”, McGraw-Hill.

2. KITTEL & KROMER: “Thermal Physics”, W.H. Freeman & Company.