

## Heat Capacity Summary for Ideal Gases:

$C_v = (3/2) R$ , KE change only. **Note,  $C_v$  independent of T.**

$C_p = (3/2) R + R$ , KE change + work. **Also Independent of T**

$$C_p/C_v = [(5/2)R]/[(3/2)R] = 5/3$$

$$C_p/C_v = 1.67$$

Find for monatomic ideal gases such as He, Xe, Ar, Kr, Ne

$$C_p/C_v = 1.67$$

**For diatomics and polyatomics find  $C_p/C_v < 1.67!$**

Since work argument above

$P(V_2 - V_1) = RT$  is simple and holds for all gases,

This suggests  $KE > (3/2)RT$  for diatomics,

This would make  $C_p/C_v < 1.67$

A possible solution:

**Equipartition Theorem:** This is a very general law which states that for a molecule or atom:

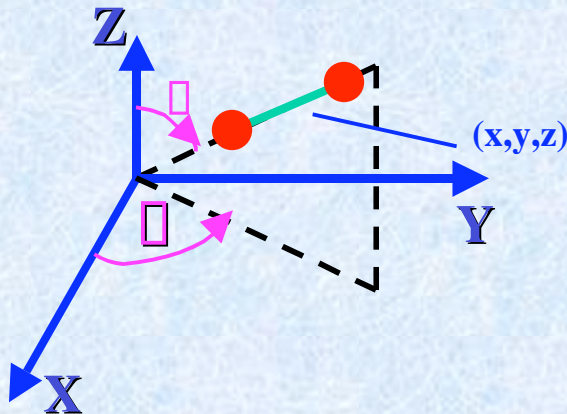
**$KE = (1/2)kT$  (or  $1/2 RT$  on a mole basis) per degree of freedom.**

**A degree of freedom is a coordinate needed to describe position of a molecule in space.**

**Example: A point has 3 degrees of freedom because it requires three coordinates to describe its position: (x, y, z).**

**Thus  $KE = 3 \left[ \frac{1}{2} kT \right] = \frac{3}{2} kT$  as for a monatomic gas**

**A diatomic molecule is a line (2 points connected by a chemical bond). It requires 5 coordinates to describe its position: x, y, z,  $\theta$ ,  $\phi$**



$$KE = 5 \left[ \frac{1}{2} kT \right] = \frac{5}{2} kT$$

**(Extra KE comes from Rotation of diatomic molecule!)**

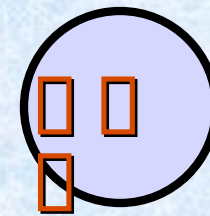


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# Collision Frequency and Mean Free Path

Real gases consist of particles of finite size that bump into each other.

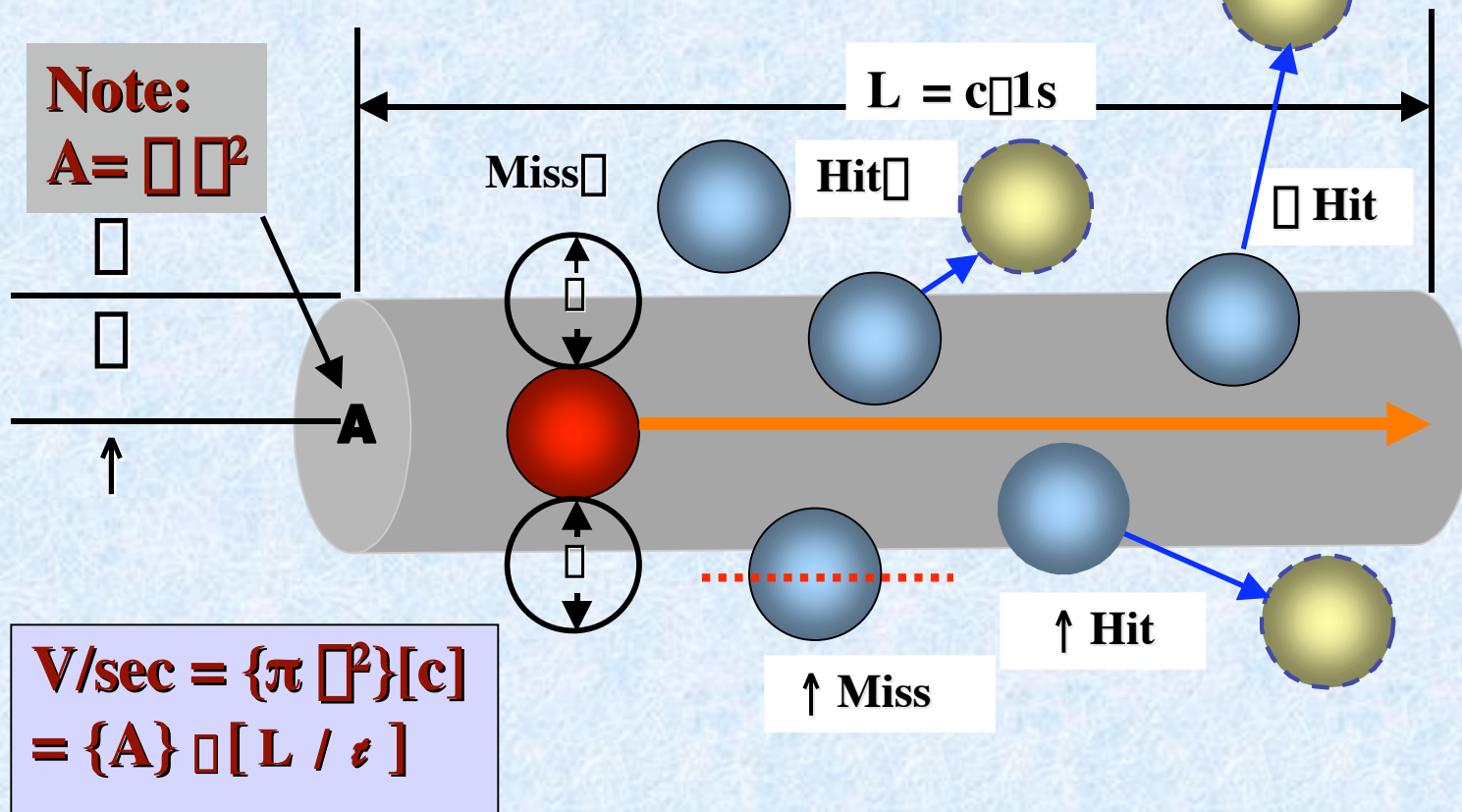
Let gas molecules be spheres of radius  $r$   
or diameter  $2r = d$ .



Focus on one molecule (say a **red** one) flying through a background of other molecules (say blue ones).

Make the simplifying assumption that only the **red** one is moving. (Will fix later.)

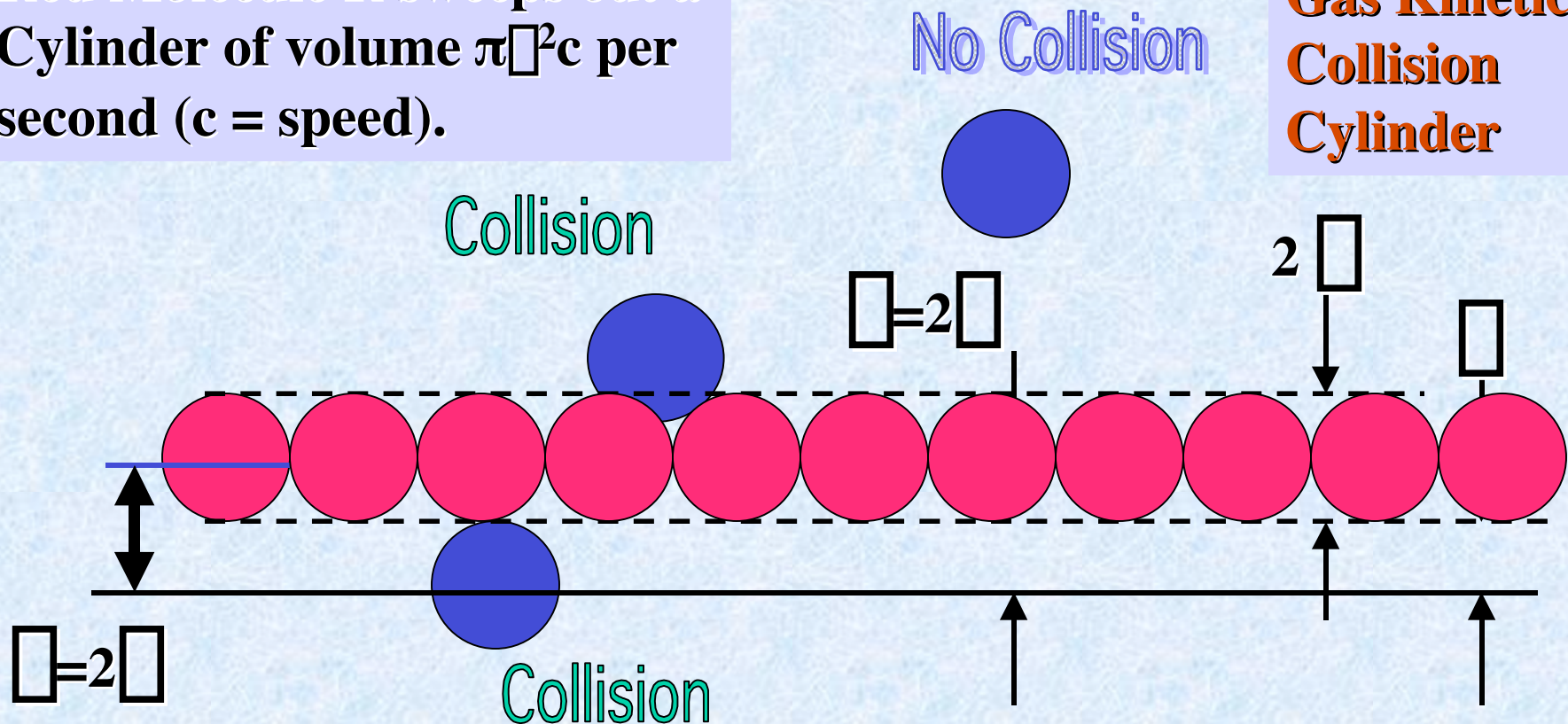
# Gas Kinetic Collision Cylinder



The red molecule sweeps out a cylinder of volume  $\pi r^2 c$  in one second. It will collide with any molecules **whose centers** lie within the cylinder. Note that the (collision) cylinder radius is the diameter  $r$  of the molecule **NOT** its radius  $r/2$ !

Red Molecule R sweeps out a Cylinder of volume  $\pi r^2 c$  per second ( $c = \text{speed}$ ).

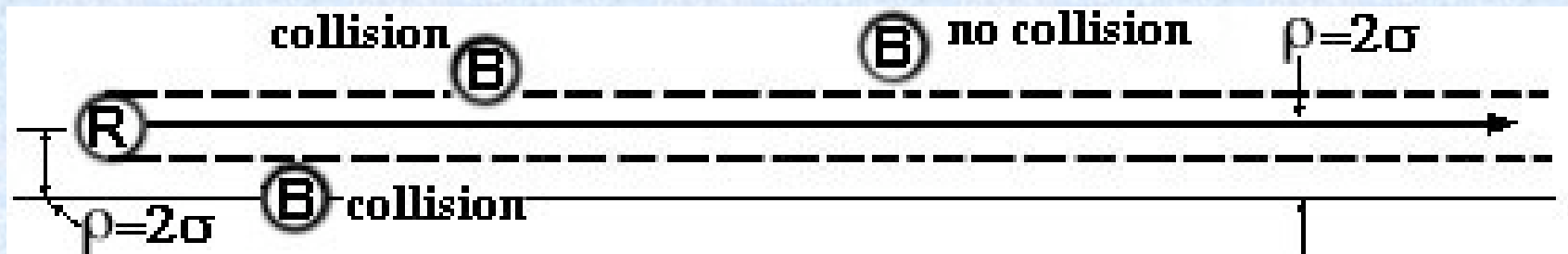
Gas Kinetic Collision Cylinder



If another molecule has some part in this volume,  $V_c = \pi(\lambda)^2 c$ , it will suffer a collision with the red molecule.



Make the simplifying assumption that only the **red** one is moving. (Will fix later.)



On average the collision frequency  $z$  will be:

$z = [\text{volume swept out per second}] \times [\text{molecules per unit volume}]$

$$z = \pi \sigma^2 c \left[ \frac{N}{V} \right]$$



$$z = \sigma n^2 c \quad (N/V)$$

Assumes volume swept out is independent of whether collisions occur (not a bad assumption in most cases)

**Mean Free Path = average distance traveled between collisions:**

$$c = \frac{\text{distance}}{\text{sec}}, \quad z = \frac{\text{collisions}}{\text{sec}}$$

$$\lambda = \text{mean free path}, \quad \lambda = \frac{c}{z}$$

$$\lambda = 1/[\sigma n^2(N/V)]$$

Some typical numbers: STP:  $6.02 \times 10^{23}$  molecules / 22.4 liters

$$\frac{N}{V} = 2.69 \times 10^{19} \text{ molecule / cm}^3; \quad \sigma \approx 3.5 \text{ \AA};$$

$$\pi \sigma^2 = 38.5 \times 10^{-16} \text{ cm}^2; \quad c = 4 \times 10^4 \text{ cm / sec.}$$

$$P = 1 \text{ atm} \quad \square$$

$$z = 4.14 \times 10^9 \text{ sec}^{-1} (P = 1 \text{ atm})$$

$$P = 1 \text{ Torr} \quad \square$$

$$z = 5.45 \times 10^6 \text{ sec}^{-1} (P = 1/760 \text{ atm})$$

$$\lambda(P = 1 \text{ atm}) =$$

$$\frac{4 \times 10^4 \text{ cm / sec}}{4.14 \times 10^9 \text{ collisions / sec}} = 9.7 \times 10^{-6} \text{ cm / collision} \quad (P = 1 \text{ atm})$$

$\lambda \gg \sigma$ , [ $\sigma \approx 3.5 \times 10^{-8} \text{ cm}$ ], consistent with our initial assumption from the Kinetic Theory of gases!

$$\lambda(P = 1 \text{ Torr}) =$$

$$\frac{4 \times 10^4 \text{ cm / sec}}{5.45 \times 10^6 \text{ collisions / sec}} = 7.3 \times 10^{-3} \text{ cm / collision} \quad (P = 1/760 \text{ atm})$$

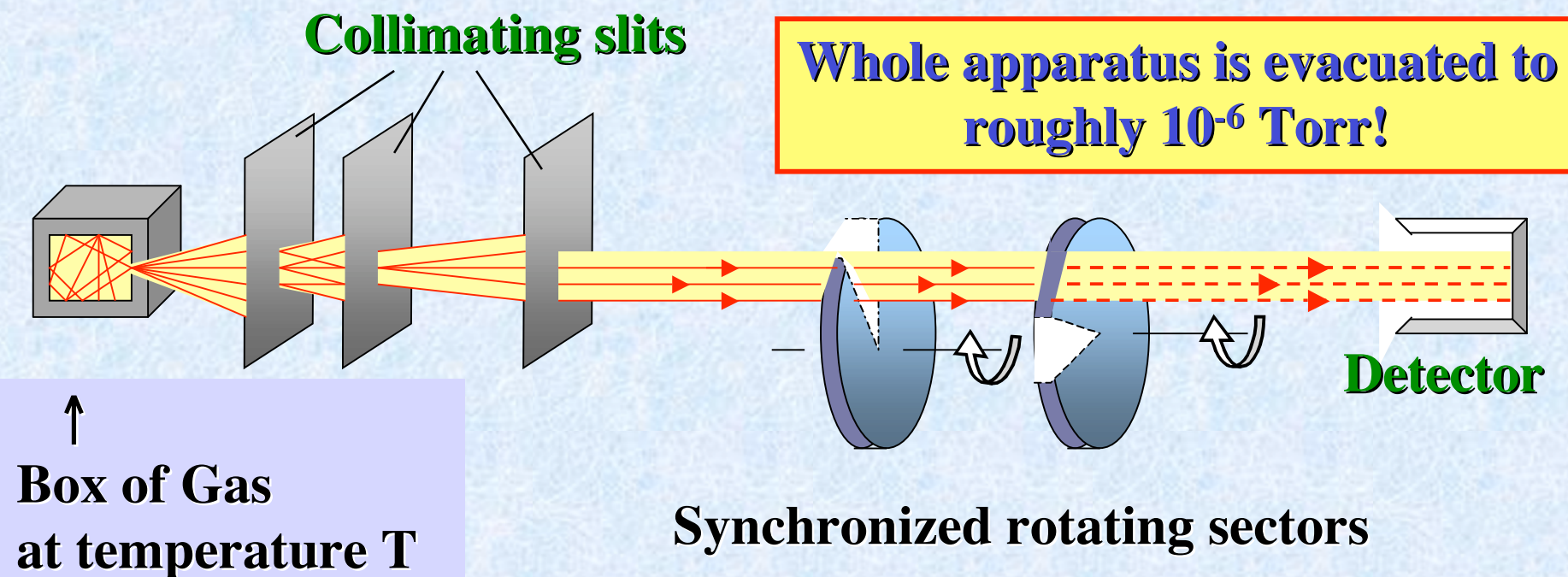
# **Distribution of Molecular Speeds**

**Real gases do not have a single fixed speed. Rather molecules have speeds that vary giving a **speed distribution**.**

**This distribution can be measured in a laboratory (done at Columbia by Polykarp Kusch) or derived from theoretical principles.**



## Molecular Beam Apparatus for Determining Molecular Speeds



**A device similar to this was used by Professor Polykarp Kusch (Columbia Physics Nobel Laureate) to measure the speed distribution of molecules. Only those molecules with the correct speed can pass through **both** rotating sectors and reach the detector, where they are counted. By changing the rate of rotation of the sectors, the speed distribution can be determined.**

# Maxwell-Boltzmann Speed Distribution

$$\left(\frac{\Delta N}{N}\right) = 4 \left[\frac{m}{2\pi kT}\right]^{3/2} e^{-[(1/2)mc^2/kT]} (c^2)\Delta c$$

where  $c$  is no longer a constant but can take any value  $0 \leq c \leq \infty$ .

$\Delta c$  is some small interval of  $c$ .  $k$  = Boltzmann constant,

$T$  = Kelvin temperature,  $m$  = atomic mass,

$\Delta N$  is the number of molecules in the range  $c$  to  $c + \Delta c$  and

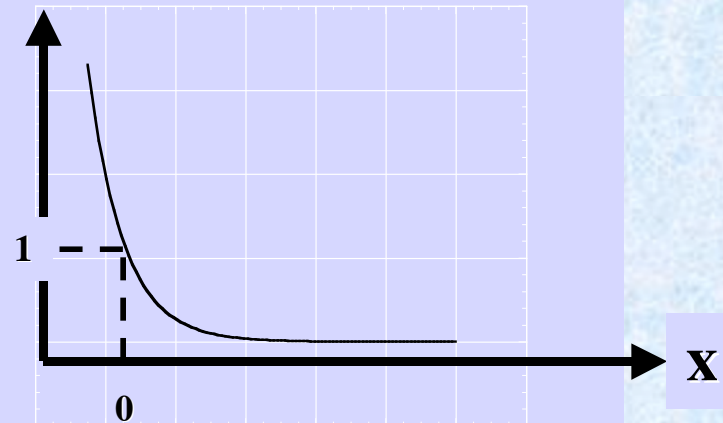
$N$  = Total # of molecules.

$\Delta N/N$  is the fraction of molecules with speed in the range  $c$  to  $c + \Delta c$

Look at exponential behavior:

$$x = (1/2)mc^2/kT$$

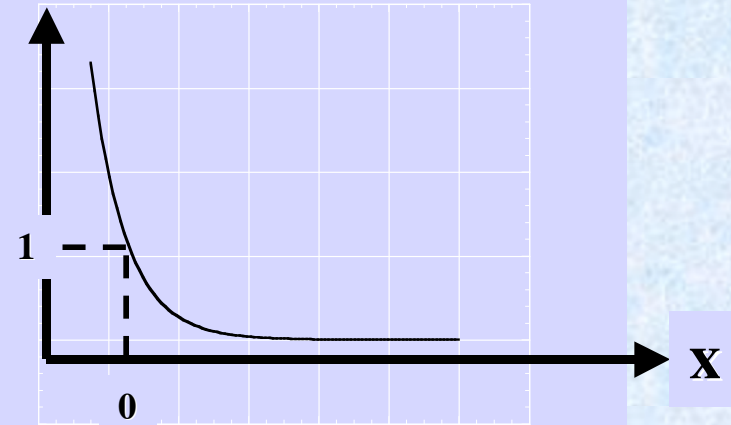
$$y = e^{-x}$$



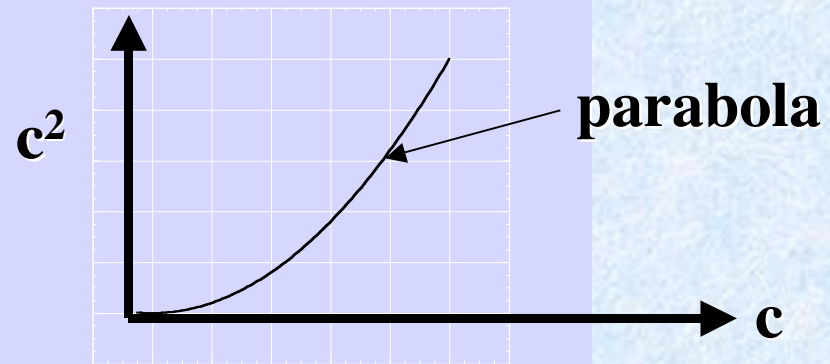
For our case  $x = (1/2) mc^2/kT = \epsilon/kT$ , where  $\epsilon = \text{K.E.}$

Exponential **decreases** probability of finding molecules with, large  $c^2$  ( $\epsilon$ ).

$$y = e^{-x}$$



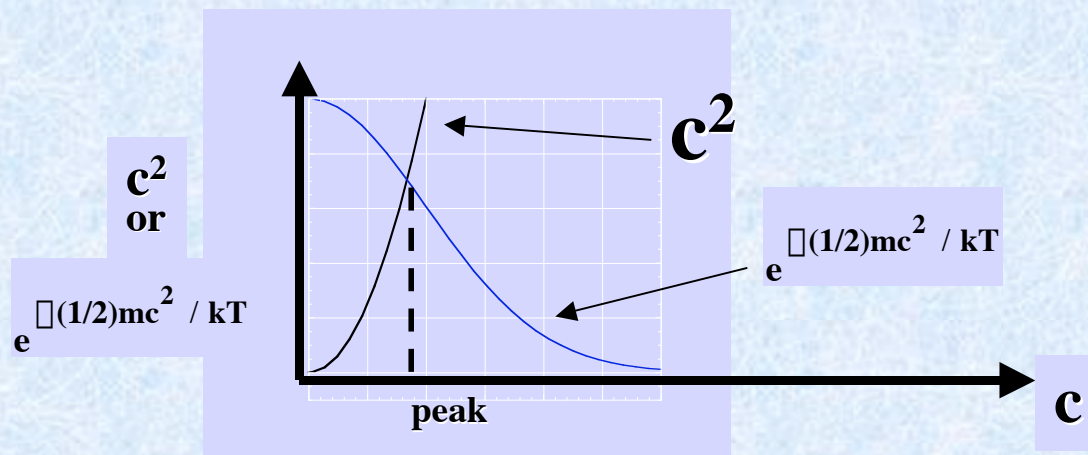
Note also, however, that  $\Delta N / N \sim c^2$  (or  $\epsilon$ ). This part of the distribution **grows** with energy or ( $c^2$ )





**Maxwell-Boltzmann Distribution is a competition between these two effects: decreasing exponential, growing  $c^2$  term**

**[This is actually an energy versus entropy effect!]**

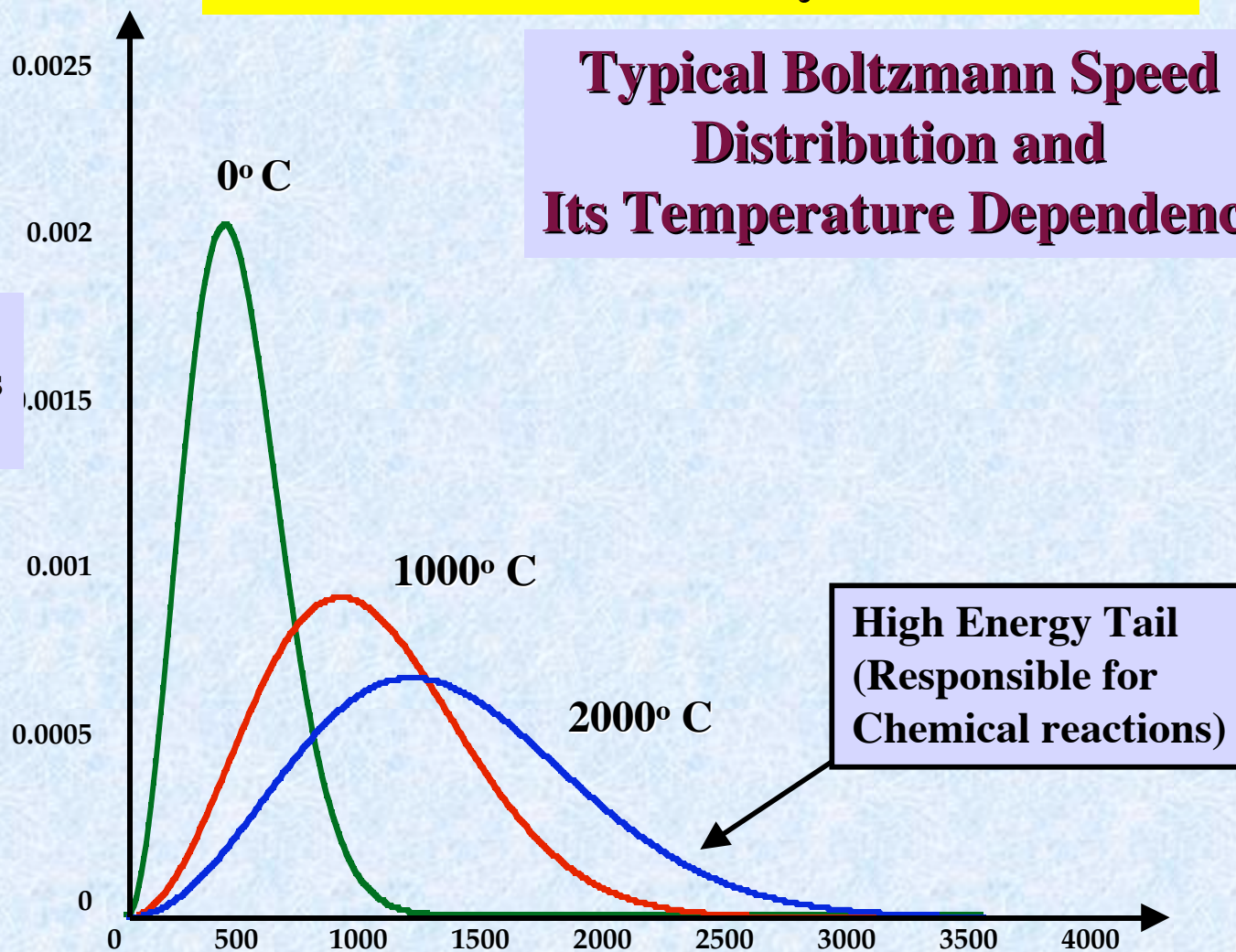


$$\left(\frac{\Delta N}{N}\right) = 4 \left[ \frac{m}{2\pi kT} \right]^{3/2} e^{-[(1/2)mc^2/kT]} (c^2)\Delta c$$

[Hold  $\Delta c$  constant at say  $c = 0.001$  m/s]

**Typical Boltzmann Speed Distribution and Its Temperature Dependence**

**Fractional # of Molecules ( $\Delta N/N$ )**



**Speed,  $c$  (m/s)**

We can see from the Boltzmann distribution, that the assumption of a single speed in the Kinetic Theory is over simplified!

In fact there are three kinds of average or characteristic speeds that we can identify from the Boltzmann distribution:

1) The Root Mean Square Speed:

$$c_{\text{rms}} = (3RT/M)^{1/2}$$

If  $N$  is the total number of atoms,  $c_1$  is the speed of atom 1, and  $c_2$  the speed of atom 2, etc.:

$$c_{\text{rms}} = [(1/N)(c_1^2 + c_2^2 + c_3^2 + \dots)]^{1/2}$$

2) The Average Speed:

$$c_{\text{avge}} = (8RT/\pi M)^{1/2}$$

$$c_{\text{avge}} = [(1/N)(c_1 + c_2 + c_3 + \dots)]$$

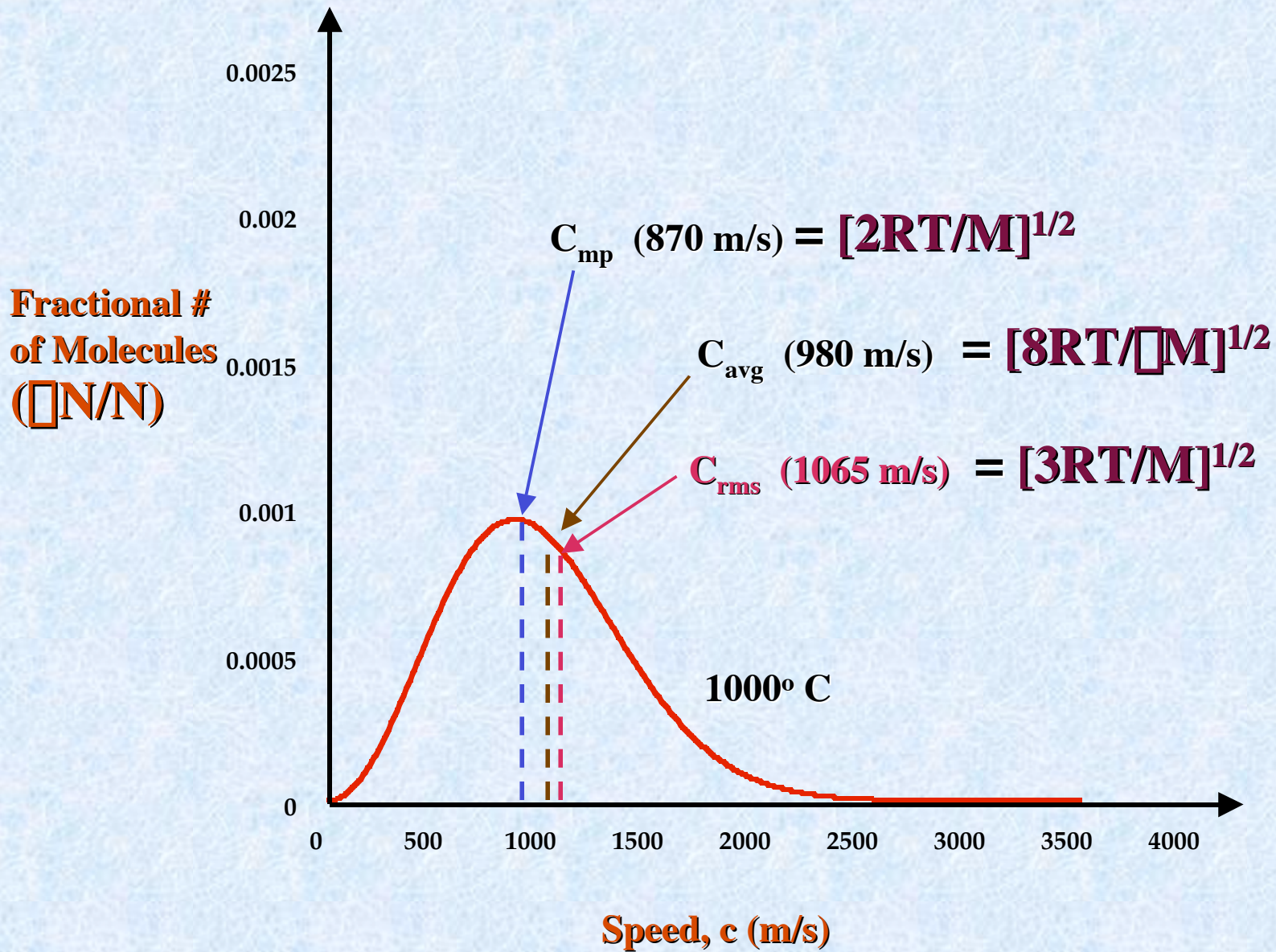
3) The Most Probable Speed:

$$c_{\text{mp}} = (2RT/M)^{1/2}$$

$c_{\text{mp}}$  is the value of  $c$  that gives  $(\square N/N)$  in the Boltzmann distribution its largest value.



# Boltzmann Speed Distribution for Nitrogen

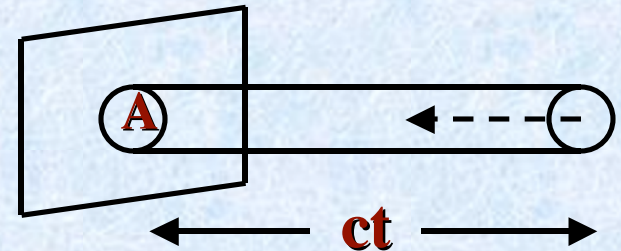


## Cleaning Up Some Details

A number of simplifying assumptions that we have made in deriving the Kinetic Theory of Gases cause small errors in the formulas for wall collision frequency, collision frequency ( $z$ ), mean free path ( $\lambda$ ), and the meaning of  $c$ , the speed:

1) # impacts / sec =  $I =$

$$((1/6)(N / V)(Ac t)) / t = [(1/6)(N / V)(Ac)]$$



The assumption that all atoms move only perpendicular to the walls of the vessel is obviously an over simplification.

Correcting for this only changes the (1/6) to (1/4):

$$\text{Correct \# impacts / sec} = I_{\text{corr}} = [(1/4)(N / V)(Ac)]$$

2) For the collision frequency,  $z$ , the correct formula is

$$z = (2)^{1/2} (N/V) \sigma^2 c$$

The  $(2)^{1/2}$  error here arises from the fact that we assumed only one particle (**red**) was moving while the others (**blue**) stood still.

In reality, of course, all the atoms are moving.

3) Even though the formula for wall collisions used in deriving the pressure was incorrect, the pressure formula is correct!

$$pV = (2/3) N [(1/2) mc^2]$$

This is because of offsetting errors made in deriving the wall collision rate,  $I$ , and the momentum change per impact,  $2mc$ .



A final question that arises concerns which  $c$ ,  $c_{\text{avge}}$ ,  $c_{\text{rms}}$ , or  $c_{\text{mp}}$  is the correct one to use in the formulas for wall collision rates ( $I$ ), molecule collision rates ( $z$ ), mean free path ( $\lambda$ ) and pressure ( $p$ ).

Basically, any property that scales as  $c^2$ , uses  $c_{\text{rms}}$ , while any property that scales as  $c$  uses  $c_{\text{avge}}$ .

For  $p$  the correct form of  $c$  is  $c_{\text{rms}}$  while for  $I$ , or  $z$  considered as independent quantities,  $c_{\text{avge}}$  is correct.

Since  $\lambda$  is the ratio of two quantities depending linearly on  $c$ ,  
 $\lambda = c_{\text{avge}}/z$ , where  $z = (2)^{1/2}(N/V)\lambda c_{\text{avge}}$

$$\lambda = c_{\text{avge}} / \{ (2)^{1/2} (N/V) \lambda c_{\text{avge}} \}$$

$$\lambda = 1 / \{ (2)^{1/2} (N/V) \lambda \}$$

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