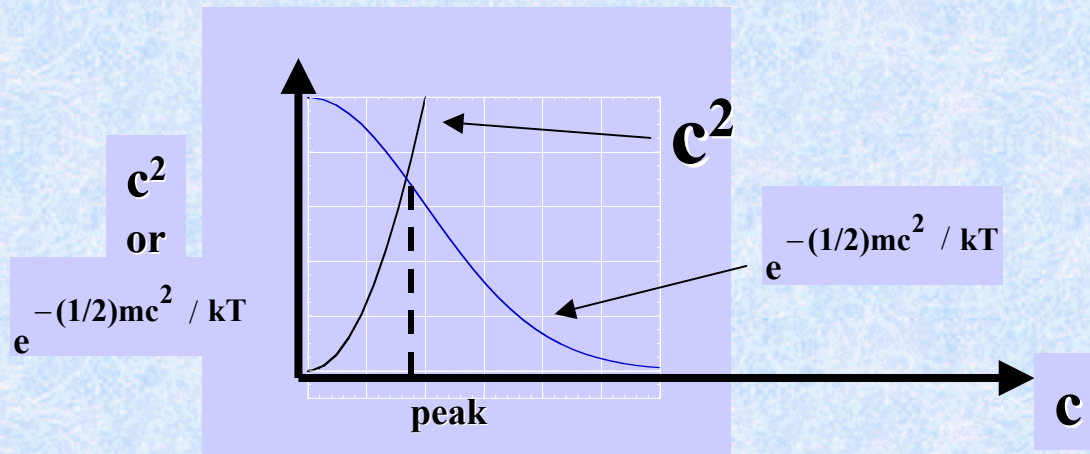**Maxwell-Boltzmann Distribution is a competition between these two effects: decreasing exponential, growing c^2 term**

[This is actually an energy versus entropy effect!]
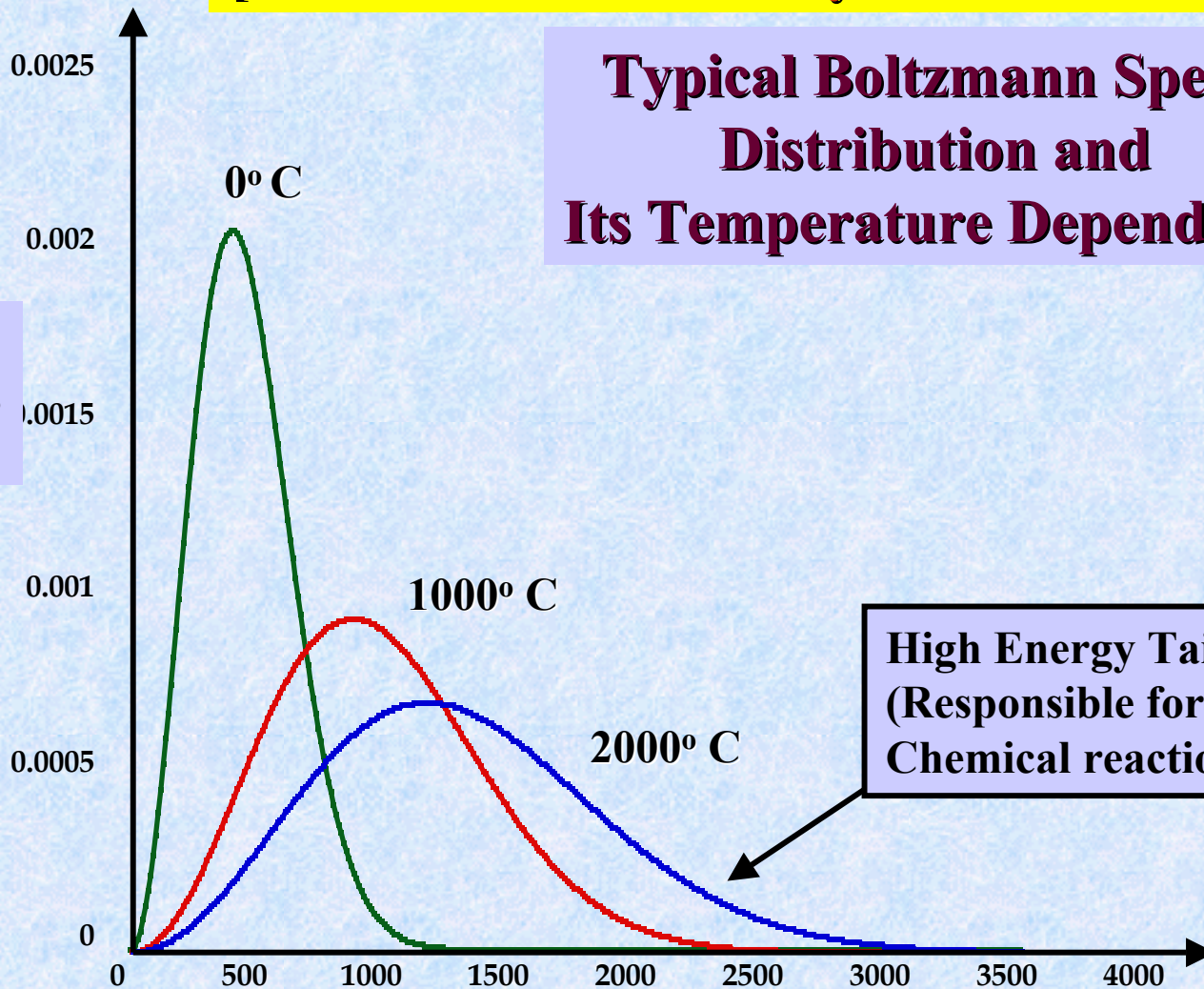
$$(\Delta N/N) = 4\pi[m/(2\pi kT)]^{3/2} \; e^{-[(1/2)mc^2/kT]} \; (c^2)\Delta c$$

[Hold Δc constant at say c = 0.001 m/s]

Typical Boltzmann Speed Distribution and Its Temperature Dependence

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

0° C

1000° C

2000° C

High Energy Tail (Responsible for Chemical reactions)

0.0025

0.002

0.0015

0.001

0.0005

0

0   500   1000   1500   2000   2500   3000   3500   4000

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:

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

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.:

$$c_{rms} = [(1/N)(c_1^2 + c_2^2 + c_3^2 + \ldots\ldots)]^{1/2}$$
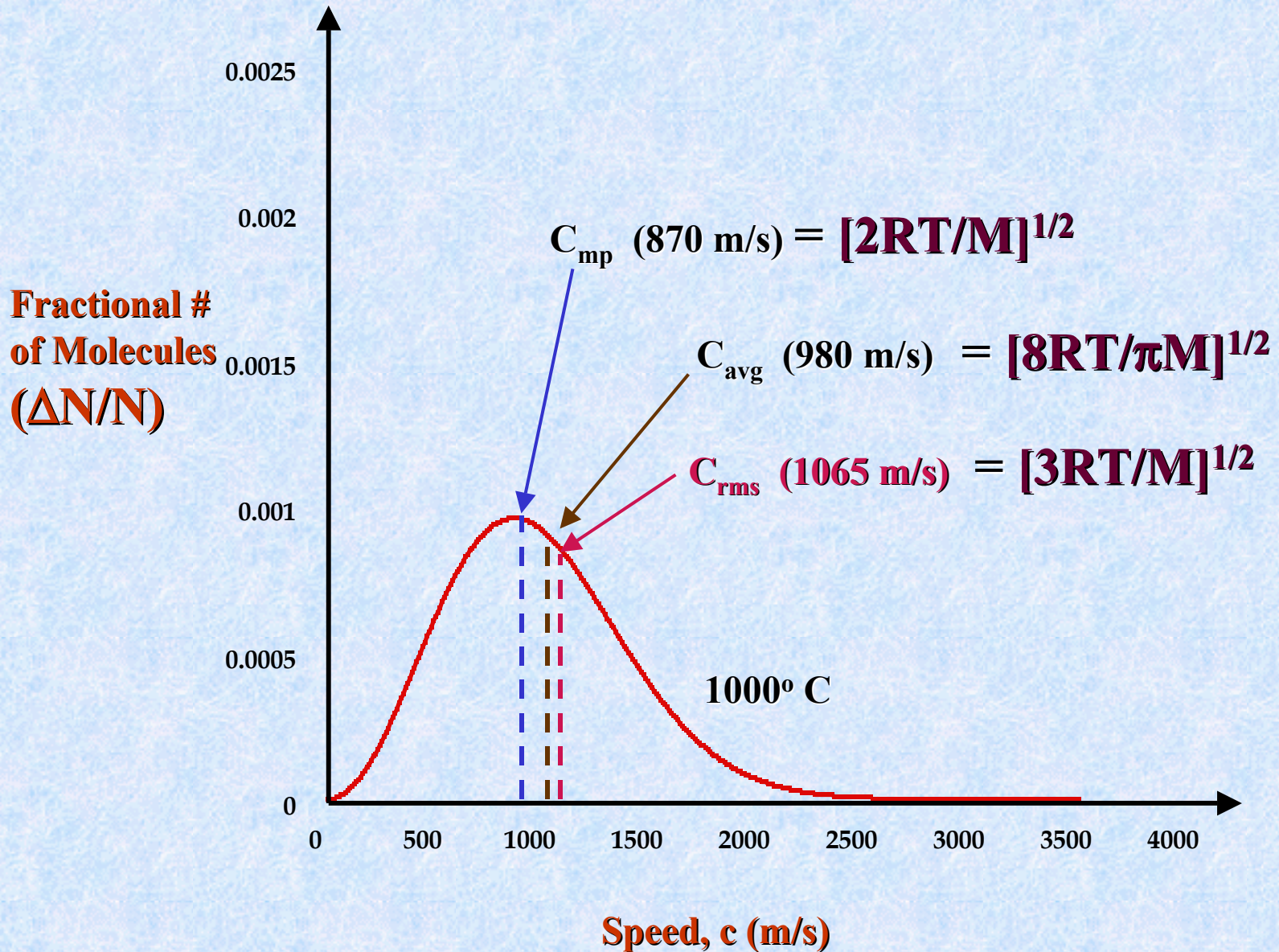
2) The Average Speed:

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

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

3) The Most Probable Speed:

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

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

Boltzmann Speed Distribution for Nitrogen

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

C_{mp} (870 m/s) = $[2RT/M]^{1/2}$

C_{avg} (980 m/s) = $[8RT/\pi M]^{1/2}$

C_{rms} (1065 m/s) = $[3RT/M]^{1/2}$

1000° C

0.0025

0.002

0.0015

0.001

0.0005

0

0   500   1000   1500   2000   2500   3000   3500   4000
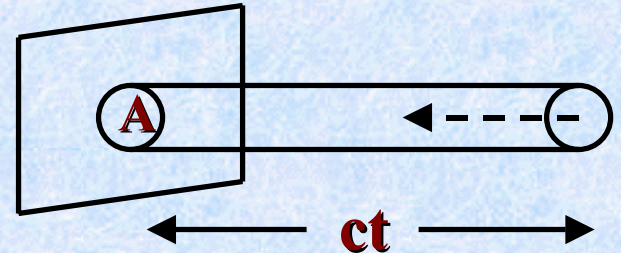
Speed, c (m/s)

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 (λ), 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):

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

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

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

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_{avge}, c_{rms}, or c_{mp} is the correct one to use in the formulas for wall collision rates (I), molecule collision rates (z), mean free path (λ) and pressure (p).

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

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

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

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

$$\lambda = 1/\{(2)^{1/2}(N/V)\pi \rho^2\}$$
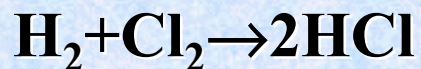
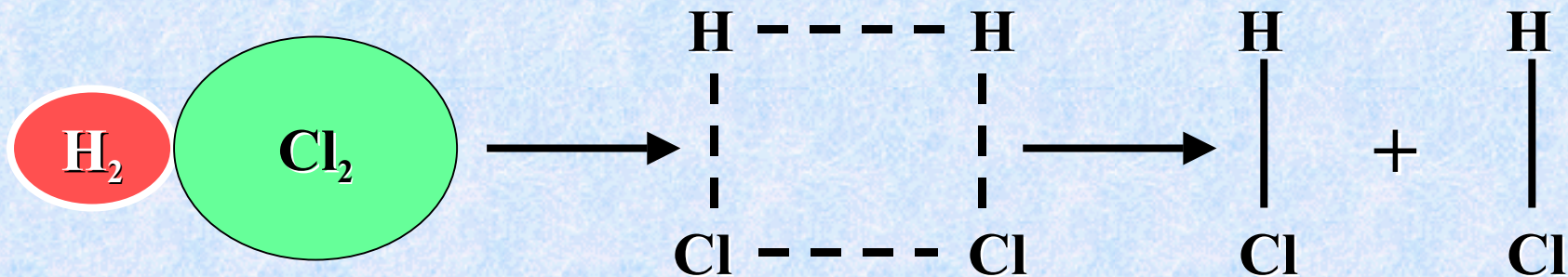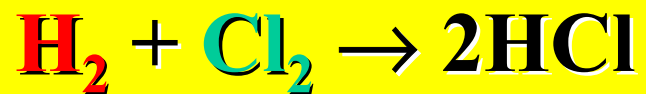# Bonus * Bonus * Bonus * Bonus * Bonus * Bonus

Chemical Kinetics

The Binary Collision Model

Reaction requires the "collision" of two molecules to occur

For Example, in the reaction
$$H_2 + Cl_2 \rightarrow 2HCl$$

Must actually have a hydrogen molecule bump into a chlorine molecule to have chemistry occur. Reaction during such a collision might look like the following picture:

Collision Frequency

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

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

Assume first that the red molecule has a constant speed C and the green ones are standing still.

The red molecule sweeps out a "collision volume" per second of $V_c = \pi(\sigma_{AB})^2 C$, where σ_{AB} is the sum of the radii of the red and green molecules (treated as spheres).
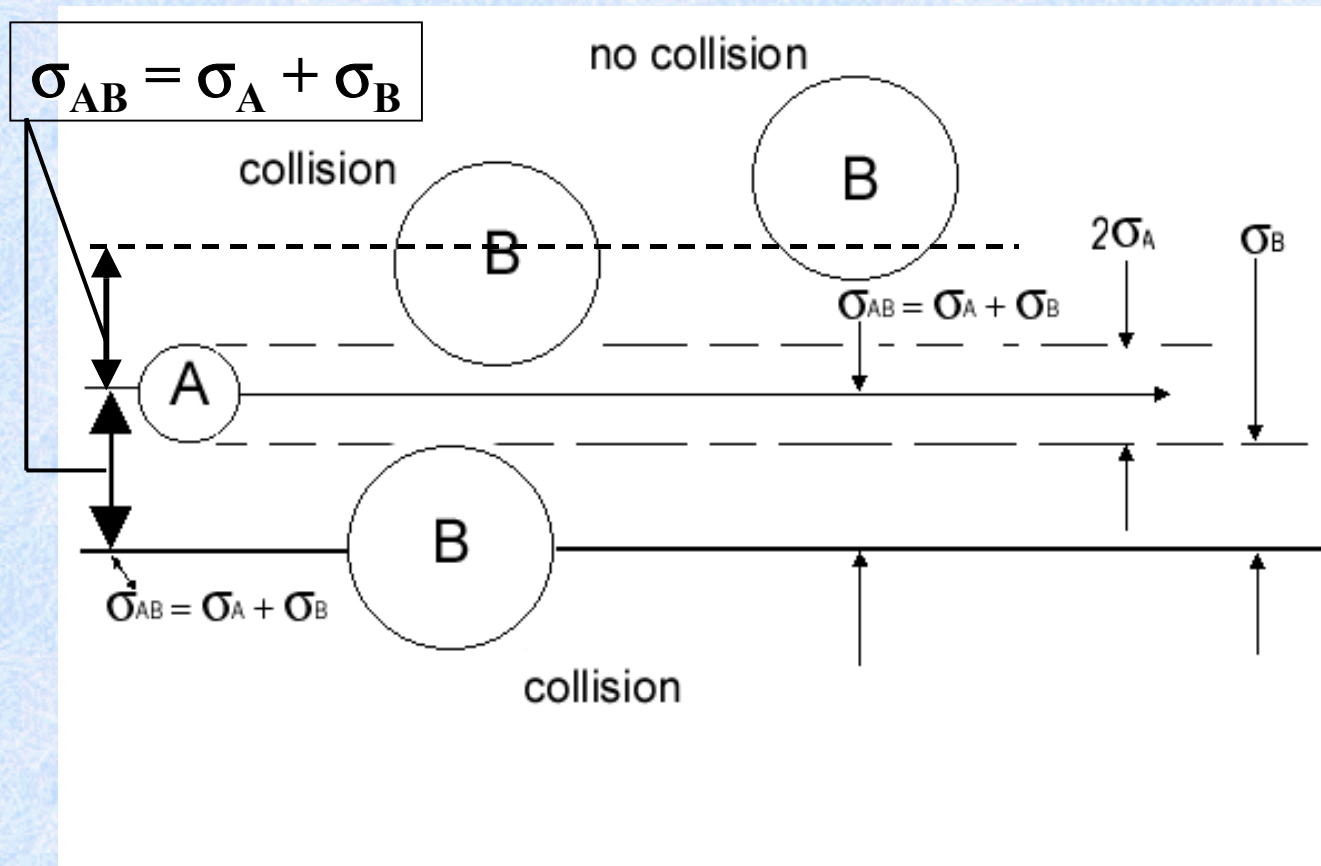
$$V_c = \pi(\sigma_{AB})^2 C$$

No Collision

Collision

$$2\sigma_A$$

$$\sigma_{AB} = \sigma_A + \sigma_B$$

$$\sigma_B$$

$$\sigma_{AB} = \sigma_A + \sigma_B$$
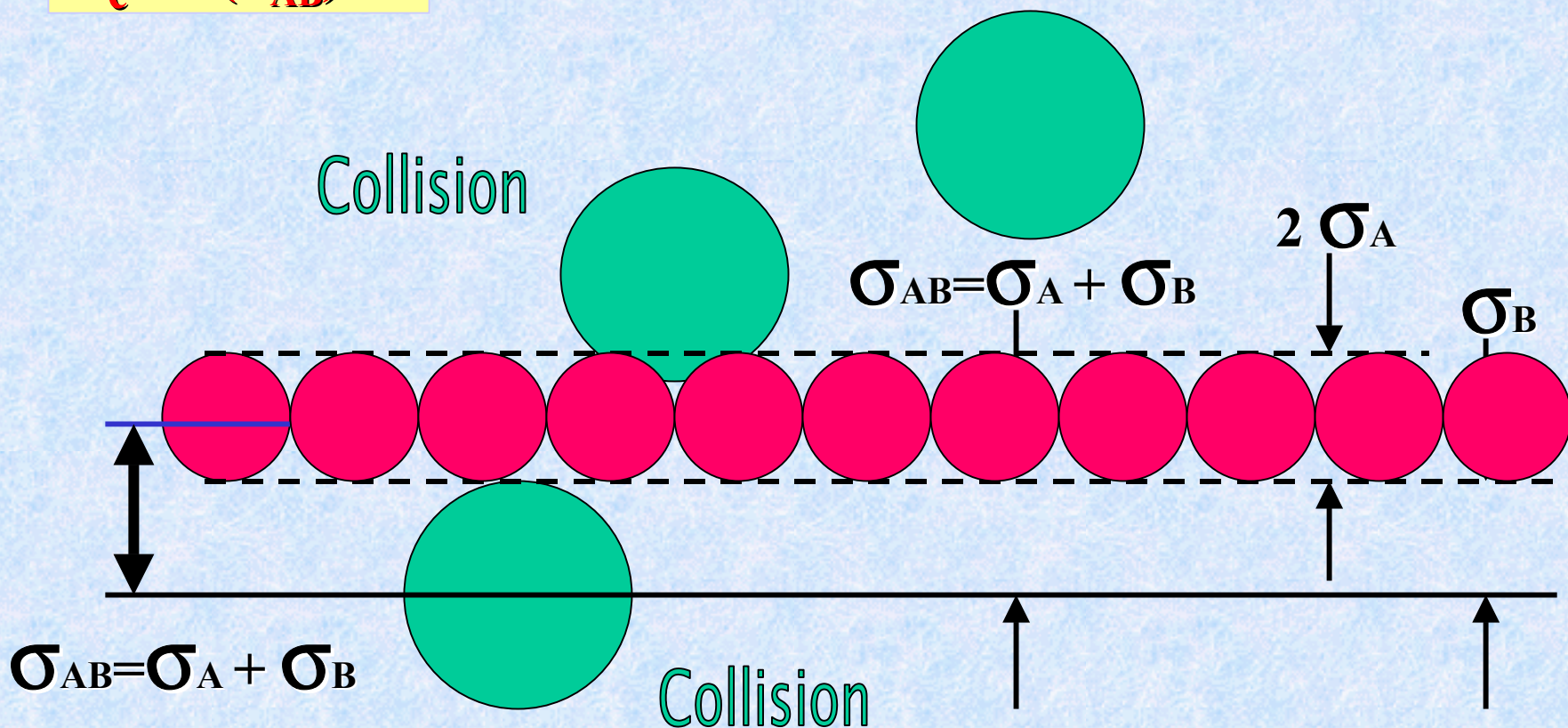
Collision

If a green molecule has some piece in this volume→Collision!

Average collision frequency, z = [volume swept out per second by a red A] x [number of green B molecules per unit volume] = [π(σ_AB)² C] x [N_B/V]

$\sigma_{AB} = \sigma_A + \sigma_B$

$(\sigma_{AB})^2$ is called the collision <u>cross section</u>

σ_A is the radius of molecule A, σ_B the radius of B

$z = [\pi(\sigma_{AB})^2 C] \times [N_B/V]$. (Collisions of one A with all B's.)

There is one subtlety. In deriving z, we assumed the red molecule flew through a cloud of motionless green ones at a speed of C.

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

To correct for this we need only replace C (the "constant" speed of a single molecule) by $\langle u_{rel} \rangle$

$\langle u_{rel} \rangle$ is the mean speed of molecule A with respect to molecule B.

$$\langle u_{rel} \rangle = [(8/\pi)\,(kT/\mu)]^{1/2}$$

Where $\mu = m_A\, m_B/(m_A + m_B)$

μ is called the <u>reduced mass</u> and can be thought of as a kind of (geometric) average of the masses of A,B.

Note that μ has units of mass (gm, kg) and its value approaches m_B if $m_A \gg m_B$