Ch 1b Lecture 10
January 29th, 2013

Next few lectures – Moving toward chemical reactivity, we'll start with the gaseous state.

Today: The kinetic theory of gases.

Reading: OGC Chapter 9, esp. sections 9.5, 9.8.

Objective:

Understand the origins of the IDEAL GAS LAW

IDEAL GAS LAW: $PV = nRT$

P = Pressure
V = Volume
n = # moles
R = ideal gas constant
= 8.314 Joules Kelvin^{-1} Mol^{-1}
T = Temperature

The Ideal Gas Law - first written in 1834 by Emil Clapeyron *(shown here relaxing at home)*

The Kinetic Theory of Ideal Gases - Assumptions

1. An ideal gas consists of discrete particles ***(could be molecules or atoms).***
2. The particles are far apart and occupy zero volume.
3. The particles are in constant motion – ***Newtonian type physics describes those motions***

The Kinetic Theory of Ideal Gases - Assumptions

1. An ideal gas consists of discrete particles ***(could be molecules or atoms).***
2. The particles are far apart and occupy zero volume.
3. The particles are in constant motion – ***Newtonian type physics describes those motions***
4. The particles couldn't care less about each other or the container that holds them ***(no attractive forces).***
5. The particles do collide with one another and the sides of the container.
6. Energy is conserved. ***A particle may gain energy if another loses an equal amount***.

A few things to remember:

$k_B T$ = an energy –
each degree of freedom in a particle contains ½ $k_B T$ of energy (3/2 $k_B T$ total – WHY??)

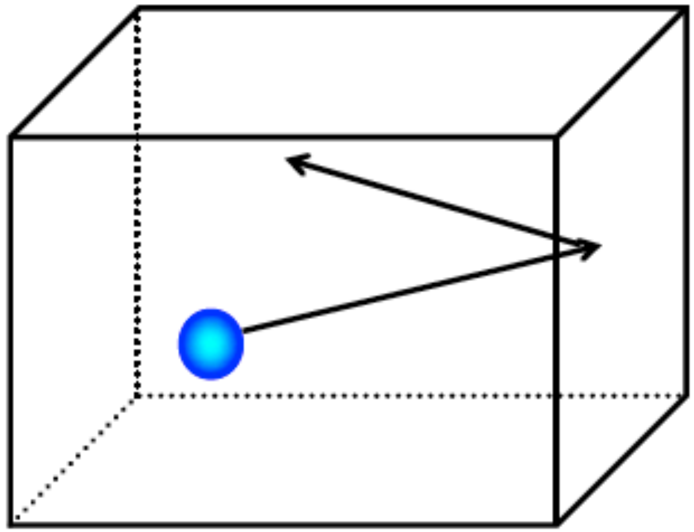
Momentum = mv = (mass)(velocity)

d(mv)/dt = a Force = $\Delta p/\Delta T$ *(**p** = momentum)*

Force/Area, or Force per unit Area = Pressure

h = 6.626e-34 J·s (kg m^2 s^{-1}) = Planck's constant
k_B = 1.381e-23 J·K^{-1} T = temperature (in K)

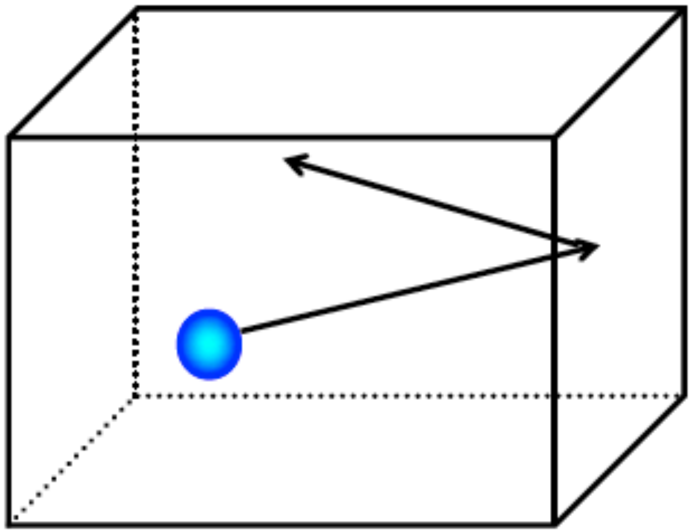
Particle of mass m striking a wall within a container.



With the below assumptions, what does the above picture imply?

Redacted Assumptions	
Particles move	Particles collide
Energy is conserved	Newtonian physics is good.

What is momentum change upon collision?



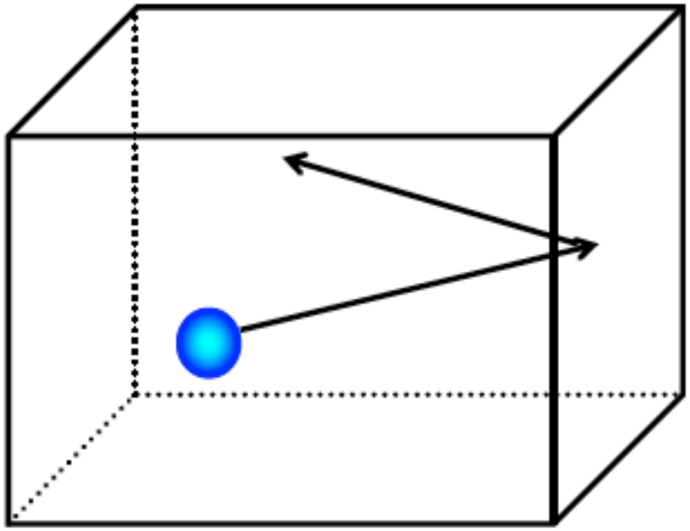
Particle has momentum (p) = mass × velocity (= mv_x) before striking wall
(moving in x-direction) = $-mv_x$ after striking wall

$$\Delta p = 2m\Delta v = 2m|v_x|$$

Redacted Assumptions

The particles move
They collide (with walls)
Energy is conserved
Newtonian physics is good.

How about per unit time?



$$\Delta p = 2m\Delta v = 2m|v_x|$$

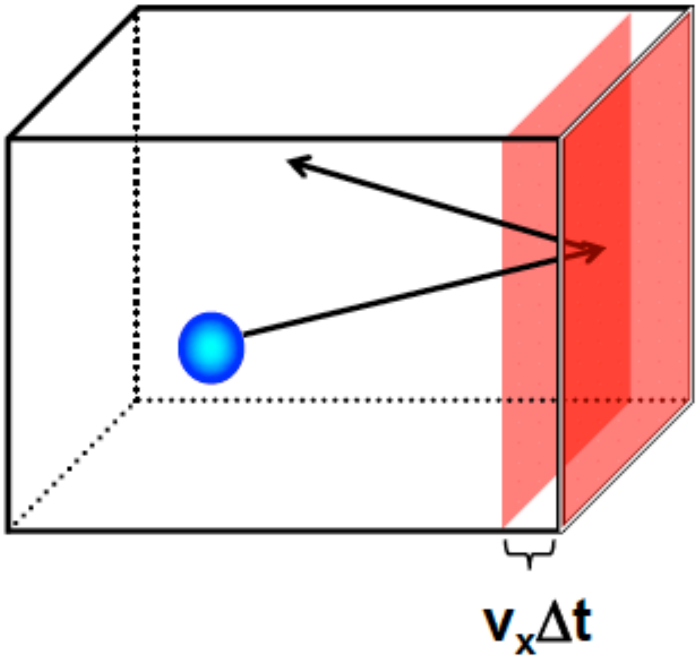
Unit time = Δt

Distance particle travels in $\Delta t = |v_x|\Delta t$

Redacted Assumptions

The particles move	**They collide**
Energy is conserved	**Newtonian physics is good.**

Volume containing all striking particles



$\Delta p = 2m\Delta v = 2m|v_x|$

Wall area = A

Distance particle travels $\Delta t = |v_x|\Delta t$

$|v_x|A\Delta t =$ a Volume element containing all particles that *might* strike the wall within Δt

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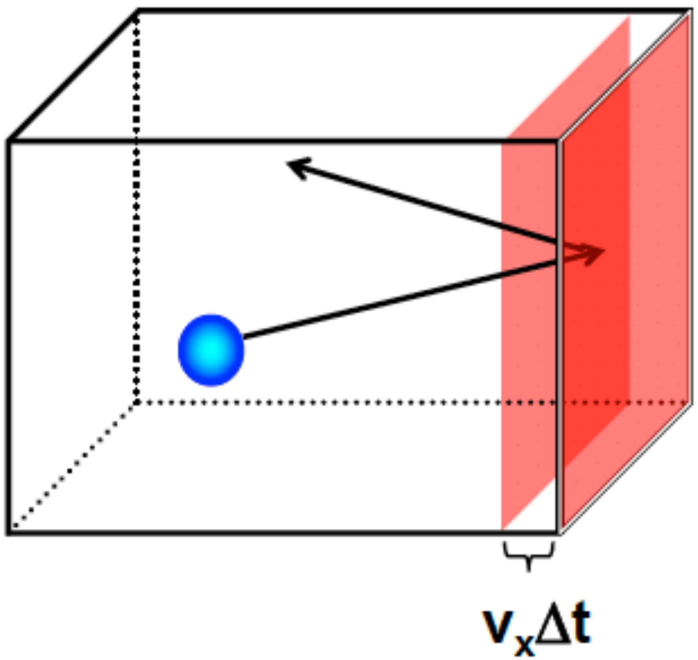
particles per volume strike wall per unit time?



$\Delta p = 2m\Delta v = 2m|v_x|$

Wall area = A

Distance particle travels $\Delta t = |v_x|\Delta t$

$V = |v_x|A\Delta t =$ contains all particles that *might* strike wall within Δt

Define the # particles/unit Volume as η

Then, there exist $\eta|v_x|A\Delta t$ particles of interest

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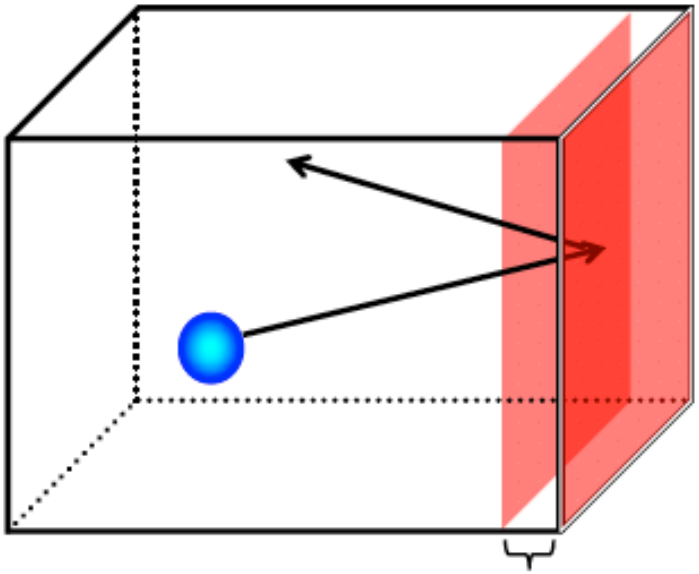
particles per volume strike wall per unit time?



$v_x \Delta t$

$\eta |v_x| A \Delta t$

= # of particles of interest

½ have a v_x $\xrightarrow{+v_x}$

And ½ have a v_x $\xleftarrow{-v_x}$

So…

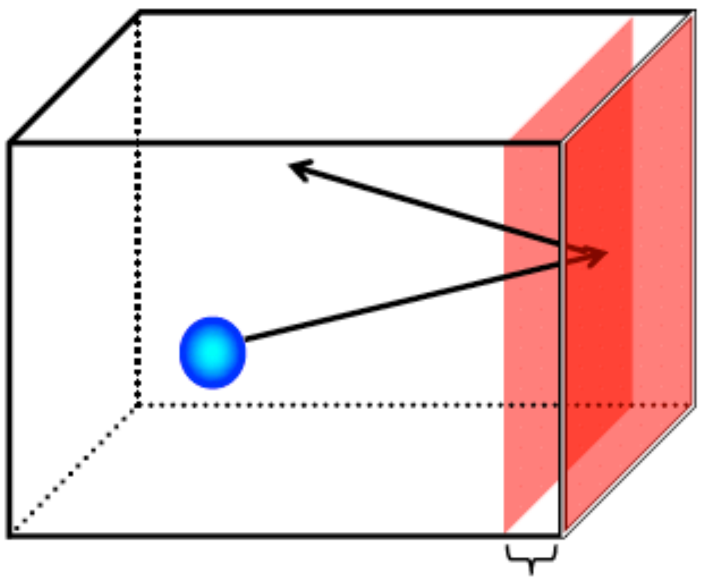
$\frac{1}{2} \eta |v_x| A \Delta t$

molecules strike wall in given unit of time

Redacted Assumptions

The particles move	**They collide**
Energy is conserved	**Newtonian physics is good.**

Total momentum change per unit time



$v_x \Delta t$

$\frac{1}{2}\,\eta |v_x| A \Delta t$

= # particles striking wall per unit time

Total momentum change = $\frac{1}{2}\,\eta A |v_x| \Delta t \cdot 2m|v_x| = \eta A m v_x^2 \Delta t$

= (# particles)· (momentum change per particle)

Redacted Assumptions

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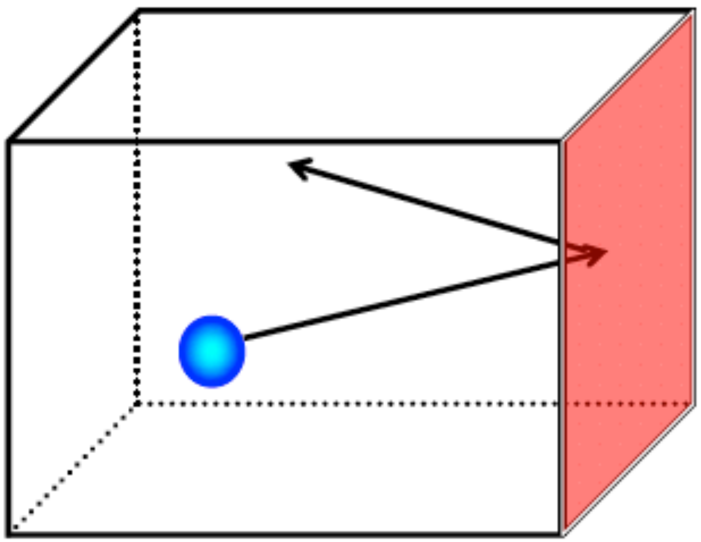
Newtonian physics is good.

Force from all of those particle striking events?



Total momentum change

$= \Delta p = \eta A m v_x^2 \Delta t$

According to Newton – the time derivative of momentum is a force

$\Delta p / \Delta t = \eta A m v_x^2 = \text{Force}$

Redacted Assumptions

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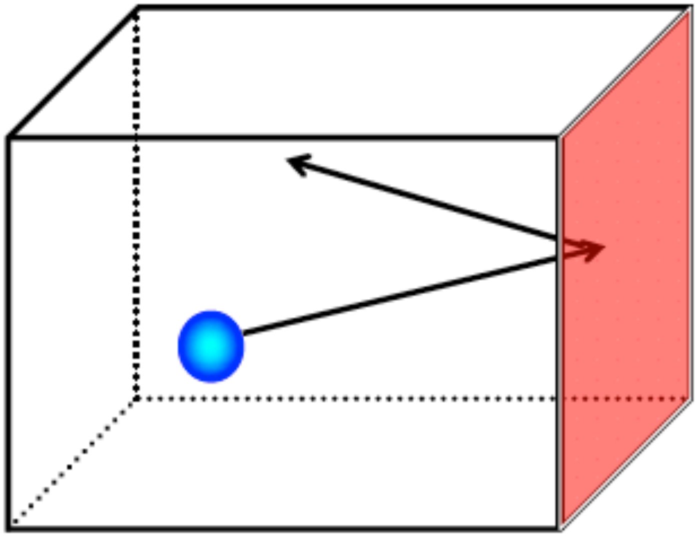
Converting Force to Pressure



Total momentum change

$= \Delta p = \eta A m v_x^2 \Delta t$

According to Newton – the time derivative of momentum is a force

$\Delta p/\Delta t = \eta A m v_x^2 = \text{Force}$

And … force per unit Area = Pressure

$$\eta m v_x^2 = \text{Pressure} = \text{Force}/A$$

Redacted Assumptions

The particles move	They collide
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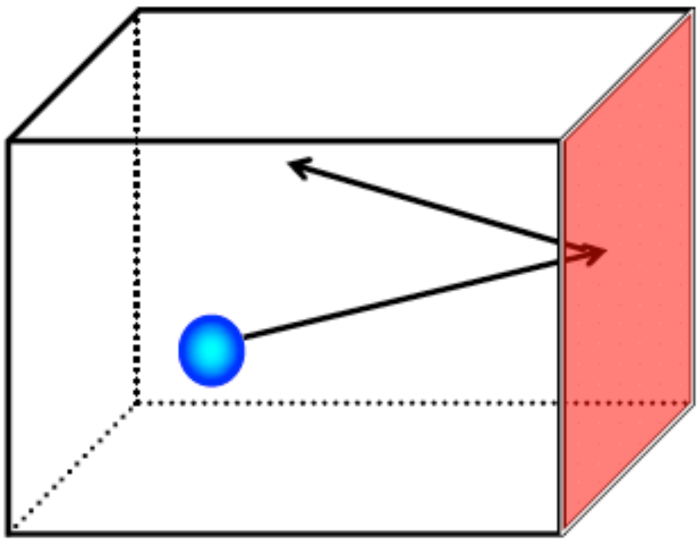
Generalizing pressure for all particle velocities



$\eta m v_x^2$ = Pressure on 1 wall

Measured Pressure reflects the average velocity = $<v_x^2>$

The magnitude of velocity is speed =

$$<v^2> = <v_x^2> + <v_y^2> + <v_z^2> = 3<v_x^2> = c^2$$

= mean square speed.

Redacted Assumptions

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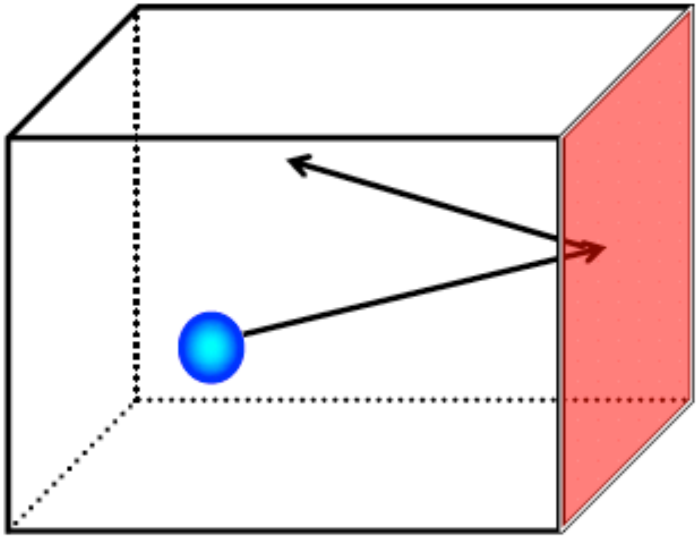
Newtonian physics is good.

Generalizing pressure for all particle velocities



$\eta m v_x^2$ = P on 1 wall

$3\langle v_x^2 \rangle = c^2$ = mean square speed

Substituting

$$P_{total} = 1/3 \eta m c^2$$

Redacted Assumptions

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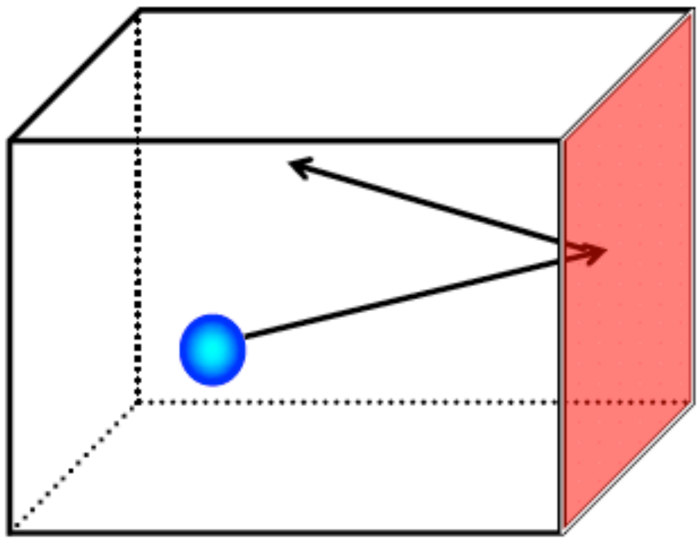
Moving towards the Ideal Gas Law..



$$P_{total} = 1/3\eta mc^2$$

η (= particle density) = N/V where (N = total # particles in chamber)

N = nL, where n = # moles; L = Avogadro's number

Then $P = 1/3(nL/V)mc^2$ or $PV = 1/3\ nLmc^2$

Redacted Assumptions

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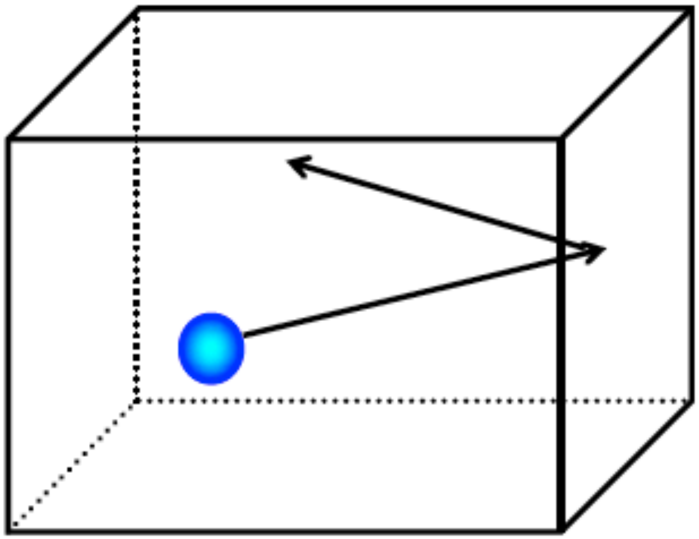
Moving towards the Ideal Gas Law..



$$PV = 1/3\ nLmc^2$$

Just for the hell of it –
divide each side of the above equality by 2

$$½\ PV = 1/3\ \ nL[½\ mc^2]$$

$$= 1/3\ nL\ \times \text{avg. kinetic energy per particle}$$

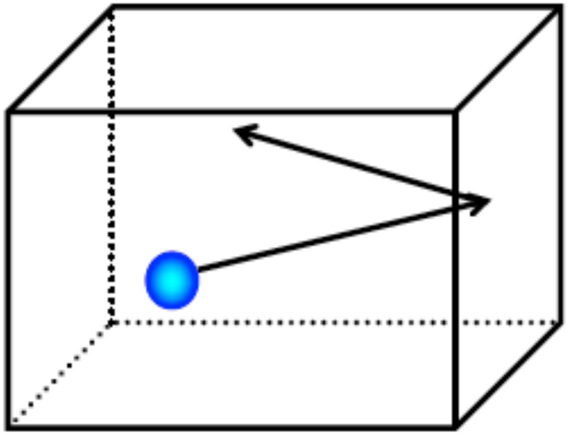
Since Kinetic Energy = $½\ mv^2$

Redacted Assumptions

The particles move
Energy is conserved

They collide
Newtonian physics is good.

Here we need Ludvig Boltzmann



$\frac{1}{2}$ PV = 1/3 nL[$\frac{1}{2}$ mc^2]

= 1/3 nL × avg. kinetic energy per particle

Ludvig Boltzmann

Boltzmann showed that each translational degree of freedom *(there are 3 (why?))* from a particle contributes

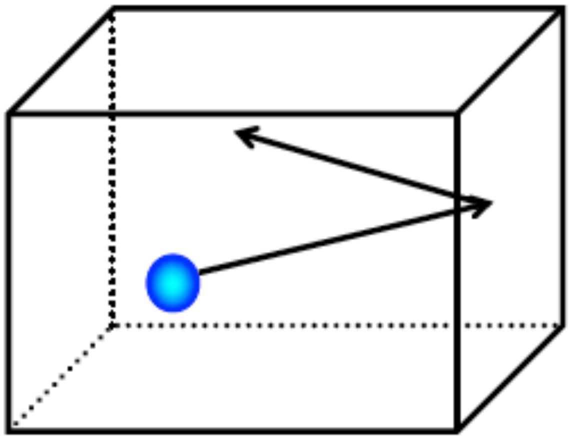
$\frac{1}{2}$ k_BT kinetic energy

yielding

3/2k_BT kinetic energy·particle^{-1}

So … 3/2 k_BT = $\frac{1}{2}$ mc^2

THE IDEAL GAS LAW!!



$\frac{1}{2}$ PV = 1/3 nL[$\frac{1}{2}$ mc^2]

= 1/3 nL × avg. kinetic energy per particle

Since 3/2 $k_BT = \frac{1}{2} mc^2$

$\frac{1}{2}$ PV = (1/3) (3/2) nL k_BT or $\boxed{PV = nLk_BT = nRT}$

since $R = k_B \cdot L$

L = Avagadro's #

Thus, velocity distributions are key!

Maxwell

Let's look a bit closer…

For a generalized Boltzmann distribution,

$$f(E) = Ae^{-E/kT}$$

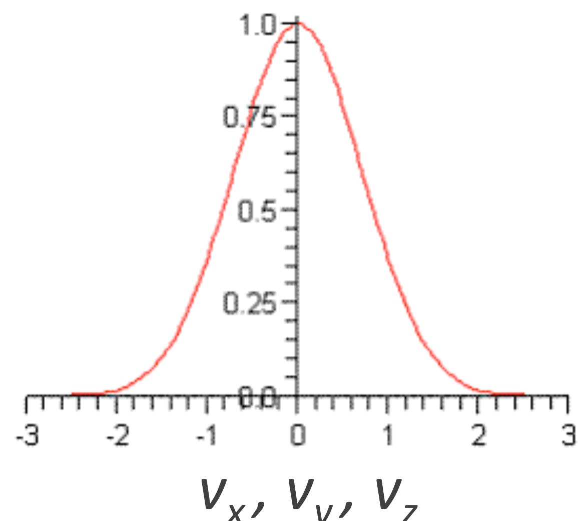
where A serves to normalize things.

If we only worry about kinetic energy,

$$f(v_z)dv_z = A \exp(-mv_z^2/2kT)\, dv_z$$

$$\int_0^\infty e^{-ax^2}\, dx = \frac{1}{2}\sqrt{\frac{\pi}{a}}$$

$$f(v_z) = \sqrt{\frac{m}{2\pi kT}}\, e^{\frac{-mv_z^2}{2kT}}$$



Full velocity distrbution:

$$F(v_x, v_y, v_z) = f(v_x)f(v_y)f(v_z)$$

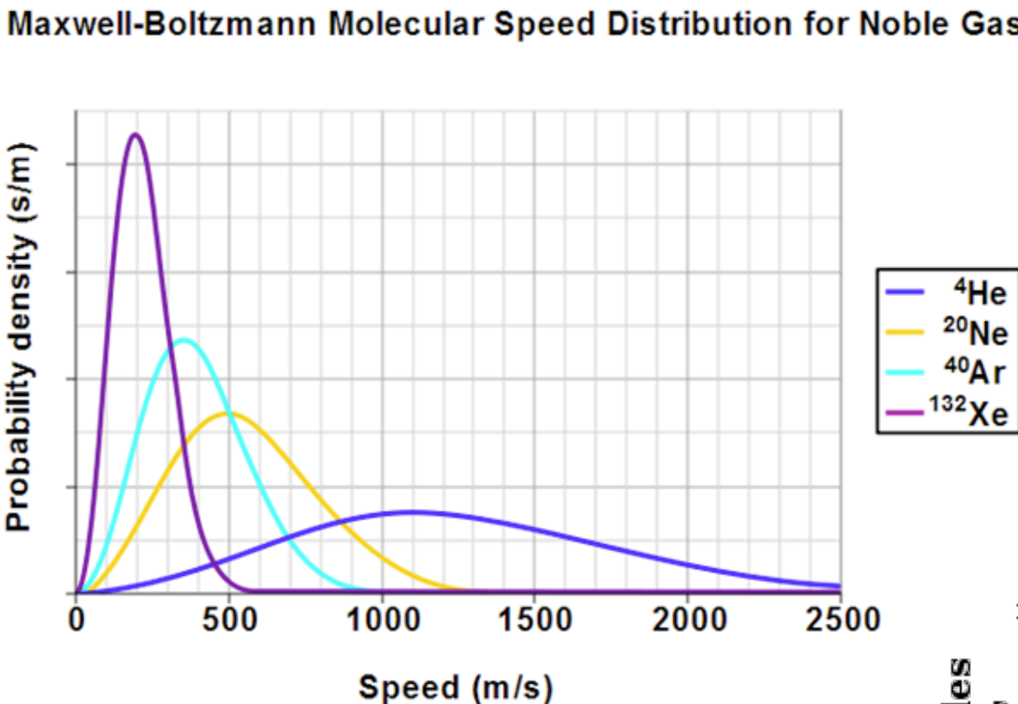
and

$$½(mv^2)_{avg} = ½(mv_x^{\ 2})_{avg} + ½(mv_y^{\ 2})_{avg} + ½(mv_z^{\ 2})_{avg}$$

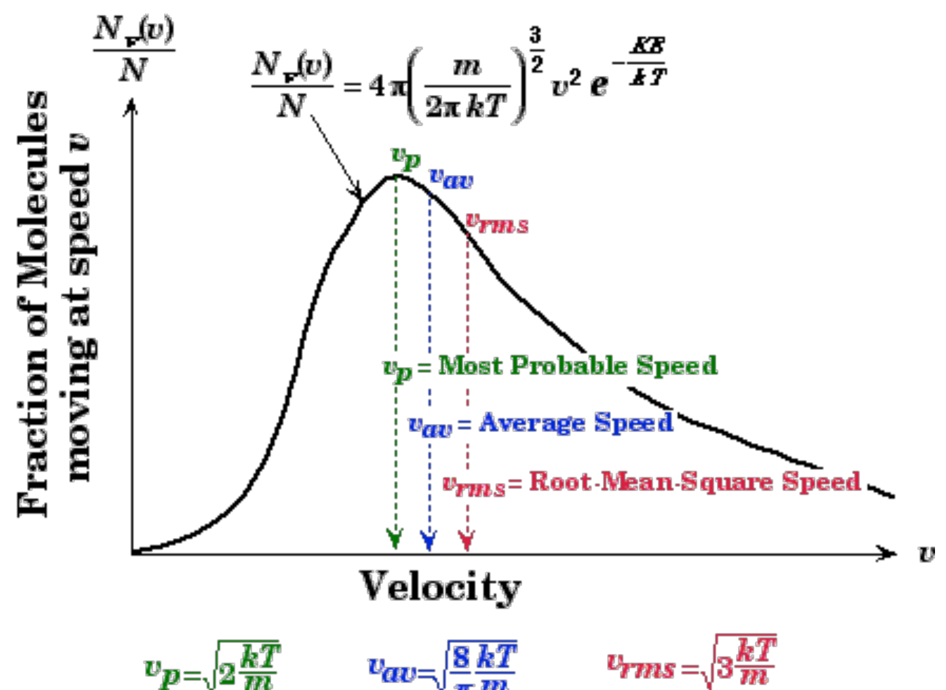
Thus, to get the *molecular speed* (call it u) distribution, we need to multiply F(v) by the number of molecules with speeds between u and u+du. This involves the volume of the spherical shell across the interval, or $4\pi u^2 du$, to give:

$$f(u)du = 4\pi(m/2\pi kT)^{3/2}\, u^2 \exp(-mu^2/2kT)\, du$$

Molecular Speed Distributions:



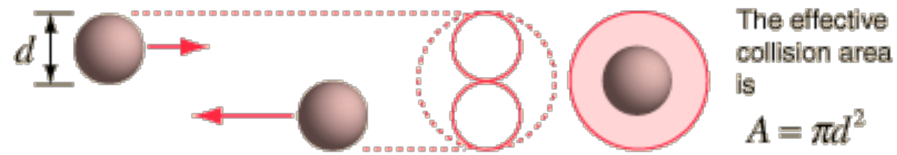
Here at room temp., clearly depends on mass as it should. The sound speed is roughly $c_{sound}^2 \sim RT/M$ (331 m/s in air).



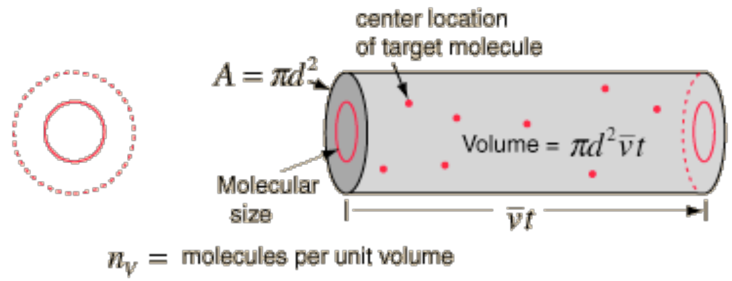
Can define numerous speeds: Most probable, average, rms, etc. (so c^2=int(u^2f(u))du = 3kT/m, which we saw on p. 19)

Mean Free Path:

Consider molecules of diameter *d*:



The gas density is *η*, let's have stationary targets for now:



$$\text{Mean free path estimate} = \frac{\overset{\text{Distance traveled}}{\bar{v}t}}{\underbrace{\pi d^2 \bar{v} t}_{\text{Volume of interaction}}\; \underbrace{n_V}_{\text{Number of molecules per unit volume}}} = \overset{\text{Mean distance per collision}}{\frac{1}{\pi d^2 n_V}}$$

For actual gases, the average relative velocity is sqrt(2) the average velocity, so M.F.P. $\lambda = (\sqrt{2}\, \pi d^2 \eta)^{-1}$

For CO_2 at STP, λ~ 56 nm.

Collisional Rates:

- The maximum rate at which a chemical reaction can occur is the rate of collisions between partners.
- For a single component gas, the rate, in s^{-1}, would just be the average molecular velocity times the mean free path just calculated, or:

$$Z_1 = v_{avg}/\lambda = (8kT/\pi m)^{1/2} \bullet \sqrt{2}\pi d^2\eta \qquad s^{-1}$$

$$Z_1 = v_{avg}/\lambda = 4\eta d^2 \bullet (\pi kT/m)^{1/2} \qquad s^{-1}$$

$$Z_1 = v_{avg}/\lambda = 4\eta d^2 \bullet (\pi RT/M)^{1/2} \qquad s^{-1}$$

For CO_2 at STP, $Z_1 \sim 3 \times 10^9\ s^{-1}$.