# **CEN 207 Physical Chemistry**

### Text book:

Atkins' Physical Chemistry, Peter Atkins, Julio de Paula, James Keeler, 11<sup>th</sup> Edition, Oxford University Press.

### **Reference books**

- . Physical Chemistry, Robert J. Silbey, Robert A. Alberty, Moungi G. Bawendi
- . Physical Chemistry, Ira N. Levine

In the kinetic theory of gases (which is sometimes called the kinetic-molecular theory, KMT) it is assumed that the only contribution to the energy of the gas is from the kinetic energies of the molecules.

### The model assumptions:

- i. The gas consists of molecules of mass **m** ceaseless random motion obeying the laws of classical mechanics.
- ii. The size of the molecules is negligible, in the sense that their diameters are much smaller than the average distance travelled between collisions; they are "point-like".
- iii. The molecules interact only through brief elastical collisions. (An elastical collision is a collision in which the total translational kinetic energy of the molecules is conserved).

**Pressure and molecular speeds**: using the kinetic model to derive an expression for the pressure of a gas.

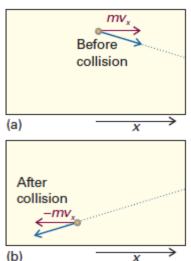
#### The calculation of the change in momentum:

m: particle mass;

v<sub>x</sub>: a component of velocity is parallel to the x-axis

Linear momentum: mv<sub>x</sub> (before collision) Linear momentum: -mv<sub>x</sub> (after collision)

The x-component of momentum therefore changes by  $\underline{2mv}_{x}$  (y and z components are unchanged. Many molecules collide with the wall in an interval  $\Delta t$  (for total change of momentum x the number of molecules)



distance  $(v_x \Delta t)$  along with the x-axis to strike the wall.

A: the area of the wall

V: the volume  $(A*v_x\Delta t)$  all the particles reach the wall (if they are travelling towars it)

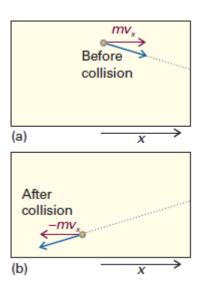
The number density of particles: nN<sub>A</sub>/V

n: the total amount of molecules,

N<sub>A</sub>: Avogadro's constant

V: the container of volume

It follows that the number of molecules in the volume  $(A^*v_x\Delta t)$  is  $(nN_A/V) \times (A^*v_x\Delta t)$ 



The total momentum change:

$$Momentum\ change = \frac{nN_A A v_x \Delta t}{2V} * 2mv_x = \frac{n\widetilde{mN_A} A v_x^2 \Delta t}{V} = \frac{nMA v_x^2 \Delta t}{V}$$

#### Calculate the force

Momentum change is divided by the interval  $\Delta t$  during which it occurs, is

Rate of change of momentum = 
$$\frac{nMAv_x^2}{V}$$

Rate of change of momentum = Force (according to Newton's second law of motion).

### **Calculate the pressure**

$$Pressure = \frac{nM\langle v_x^2 \rangle}{V} \; \; ; \; \langle v_x^2 \rangle = \frac{1}{3} \langle v^2 \rangle$$

 $v_{rms} = \langle v^2 \rangle^{1/2}$  Root-mean-square speed (definition)

So it can be written for the pressure as

$$\langle v_{\chi}^2 \rangle = \frac{1}{3} \langle v^2 \rangle = \frac{1}{3} v_{rms}^2$$

to give

$$pV = \frac{1}{3}nMv_{rms}^2$$

Relation between pressure and volume [KMT]

**pV= constant** (at constant temperature) which is the content of Boyle's law. The right-hand side of the equation is equal to **nRT** (pV=nRT).