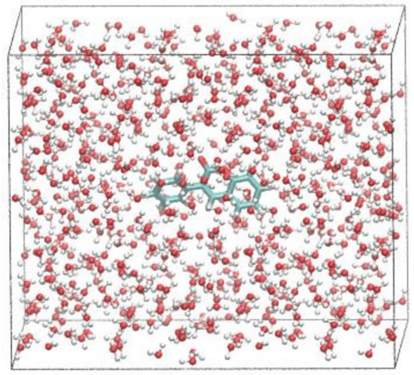
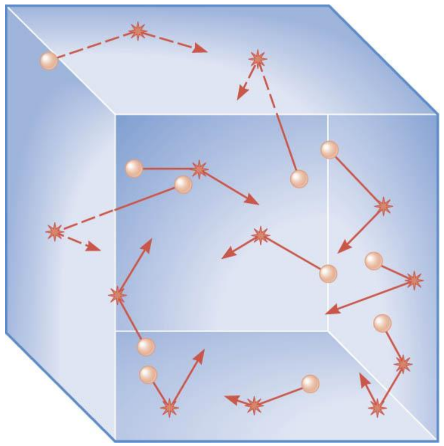
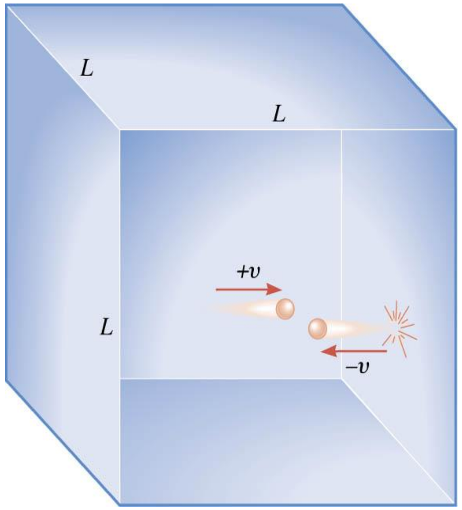
From macroscopic to microscopic scales…

- Normal Thermodynamics measures "macroscopic" properties of a system
- A the microscopic levels the concepts remain but their interpretation is different
  - Internal energy: Kinetic energy of molecules + Interactions between components
  - Pressure: Collisions with system walls
  - Temperature: Kinetic energy of molecules
  - …
- Distribution of properties is not uniform
  - Molecules are in different states with different populations and energies
  - Any measure is always an average of those states
- Kinetic gas theory and Statistical thermodynamics are used to understand the microscopic scales



Kinetic theory of gases to understand microscopic levels



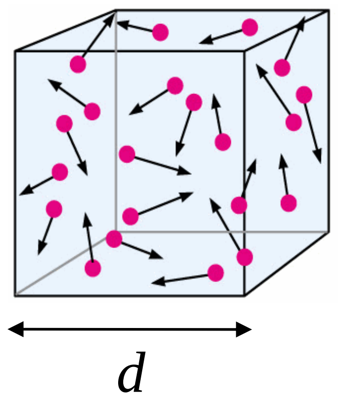


- The pressure that a gas exerts is caused by the collisions of its molecules with the walls of the container.
- A single gas particle is shown colliding elastically with the right wall of the container and rebounding from it.

- Assumptions
  - The number of molecules is large and identical
  - The average separation between molecules is large
  - Molecules moves randomly
  - Molecules obeys Newton’s Law
  - Molecules collide elastically with each other and with the wall

Determination of pressure

- Pressure: Results from collisions of molecules on the surface



The molecule perform an elastic collision with the wall of the box.

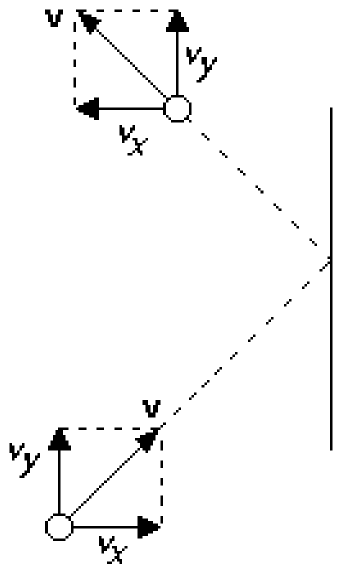
$$v_x(\text{inicial}) = -v_x(\text{final})$$

$$\Delta p_x = -mv_x - (mv_x) = -2\,mv_x$$

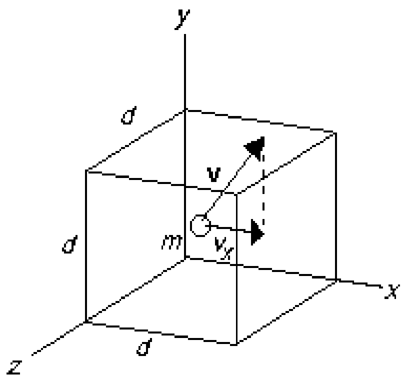
$$F_{\text{wall}} = -F_{\text{molecule}} \qquad F_{\text{wall,x}}\Delta t = -\Delta p_x = 2\,mv_x$$

$$F_{\text{wall,x}} = \frac{2mv_x}{\Delta t} = \frac{2mv_x}{2d/v_x} = \frac{mv_x^2}{d}$$

Max distance run by molecules which collide with one wall is 2d then
$\Delta t = 2d/v_x$



Counting all molecules $\quad F_x = \frac{m}{d}\left(v_{x1}^2 + v_{x2}^2 + \cdots\right) = \frac{N\,m}{d}\overline{v_x^2}$

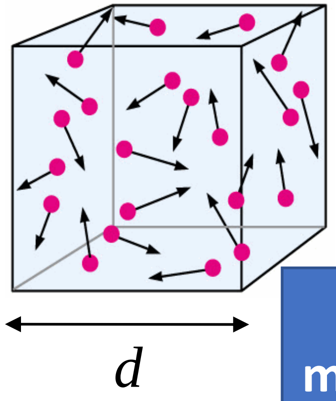


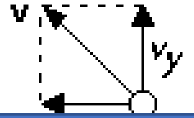
Counting all directions (all are equivalent) $\quad \overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} = 3\overline{v_x^2}$

$$F = \frac{N}{3}\left(\frac{m\overline{v^2}}{d}\right) \qquad P = \frac{F}{A} = \frac{F}{d^2} = \frac{1}{3}\left(\frac{N}{d^3}m\overline{v^2}\right) = \frac{\mathbf{1}}{\mathbf{3}}\left(\frac{\boldsymbol{N}}{\boldsymbol{V}}\right)\mathbf{m}\overline{\boldsymbol{v}^{\mathbf{2}}} = \frac{\mathbf{2}}{\mathbf{3}}\left(\frac{\boldsymbol{N}}{\boldsymbol{V}}\right)\left(\frac{\mathbf{1}}{\mathbf{2}}\mathbf{m}\overline{\boldsymbol{v}^{\mathbf{2}}}\right)$$

Determination of pressure

- Pressure: Results from collisions of molecules on the surface





The molecule perform an elastic collision with the wall of the box.

$$v_x(\text{inicial}) = -v_x(\text{final})$$

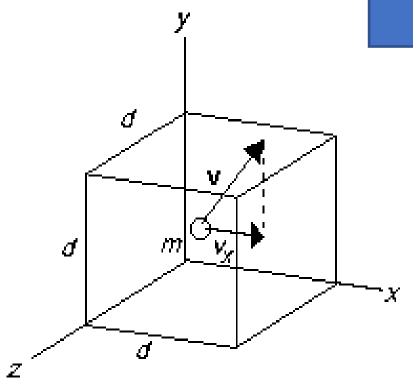
$$\Delta p_x = -mv_x - (mv_x) = -2\, mv_x$$

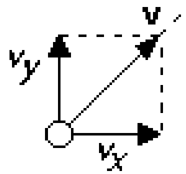
$$F \quad \Delta t = -\Delta p \; = 2\, mv$$

Max distance run by molecules which collide with one wall is

$2d/v_x$

This results shows that the pressure is proportional to the **number of molecules per volume** unit and to the **average translational kinetic energy** of molecules.





Counting all molecules $\quad F_x = \frac{m}{d}\left(v_{x1}^2 + v_{x2}^2 + \cdots\right) = \frac{N\,m}{d}\overline{v_x^2}$

Counting all directions (all are equivalent) $\quad \overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} = 3\overline{v_x^2}$

$$F = \frac{N}{3}\left(\frac{m\overline{v^2}}{d}\right) \qquad P = \frac{F}{A} = \frac{F}{d^2} = \frac{1}{3}\left(\frac{N}{d^3}m\overline{v^2}\right) = \frac{\mathbf{1}}{\mathbf{3}}\left(\frac{\boldsymbol{N}}{\boldsymbol{V}}\right)\mathbf{m}\overline{\boldsymbol{v}^2} = \frac{\mathbf{2}}{\mathbf{3}}\left(\frac{\boldsymbol{N}}{\boldsymbol{V}}\right)\left(\frac{\mathbf{1}}{\mathbf{2}}\mathbf{m}\overline{\boldsymbol{v}^2}\right)$$

Microscopic Temperature

$k_B = R/N_A$

$k_B = 1.3806 \cdot 10^{-23}$ J/K
R = 8.314 J / (K mol)
R = 1.987 Kcal / (K mol)
$N_A = 6.022 \cdot 10^{23}$ mol^{-1}

- Temperature has no microscopic meaning, but from

$$PV = \frac{2}{3} N \left(\frac{1}{2} m \overline{v^2} \right)$$

Comparing with the ideal gas equation (expressed in "molecules" instead of "mols" R → k_B) :

$$PV = N k_B T$$

$$T = \frac{2}{3k_B} \left(\frac{1}{2} m \overline{v^2} \right)$$

"Microscopic temperature" is a measure of the kinetic energy

$$\left(\frac{1}{2} m \overline{v^2} \right) = \frac{3}{2} k_B T \qquad v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3RT}{M}}$$

Examples of some velocities (rms)

Gas	Molecular mass (g/mol)	v_{rms} at 20ºC (m/s)
H_2	2.02	1902
He	4.0	1352
H_2O	18	637
Ne	20.1	603
N_2 or CO	28	511
NO	30	494
CO_2	44	408

Sound velocity: 340 m/s

How are molecules distributed?

- The Boltzmann distribution is a probability distribution that gives the probability of a certain state as a function of that state's energy and temperature of the system to which the distribution is applied.
  It is given as

State populations are proportional to e^{-E_i/k_BT}

$$p_i = \frac{e^{-E_i/k_BT}}{\sum_{j=1}^{M} e^{-E_j/k_BT}}$$

where *p* is the probability of state *i*, *E* the energy of state *i*, *k* the Boltzmann constant, *T* the temperature of the system and *M* is the number of all states accessible to the system

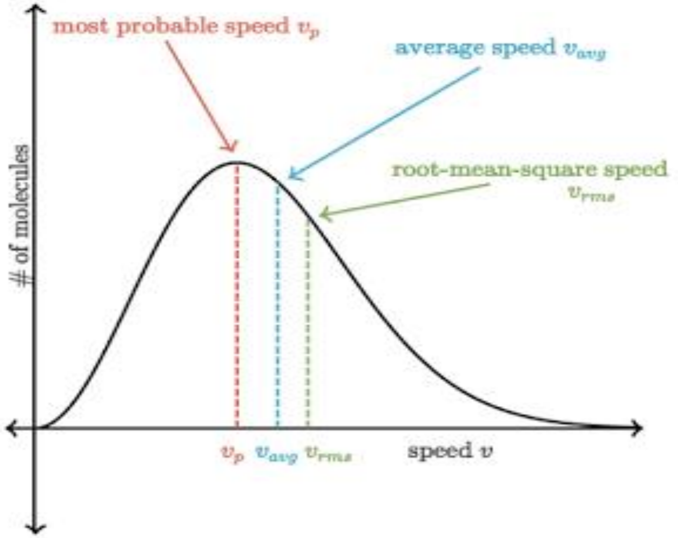
- Boltzmann distribution corresponds to the maximum probability (hence the maximum Entropy!!)
- Population ratios can be calculated as $\frac{N_j}{N_i} = \frac{p_j}{p_i} = e^{-\Delta E_{ij}/k_BT}$

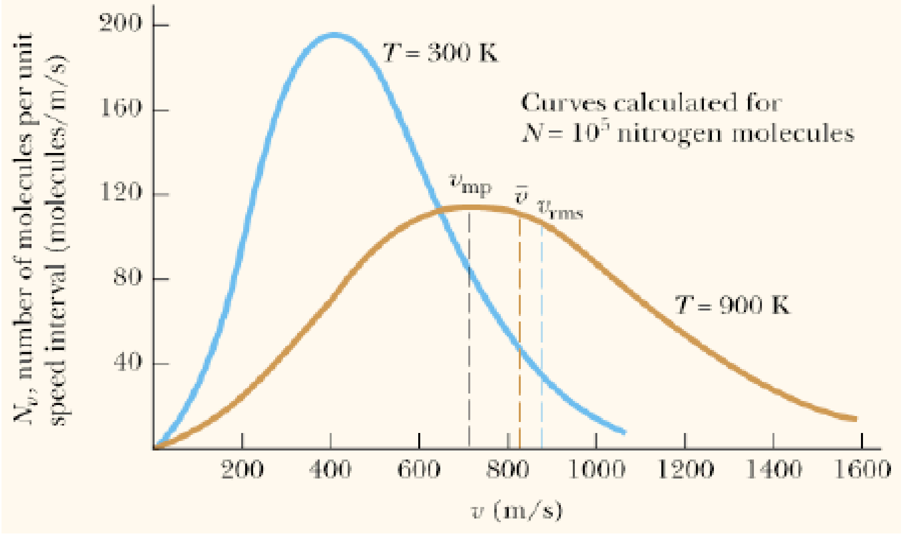
How are velocities distributed?

- Velocities follow the Maxwell-Boltzmann distribution

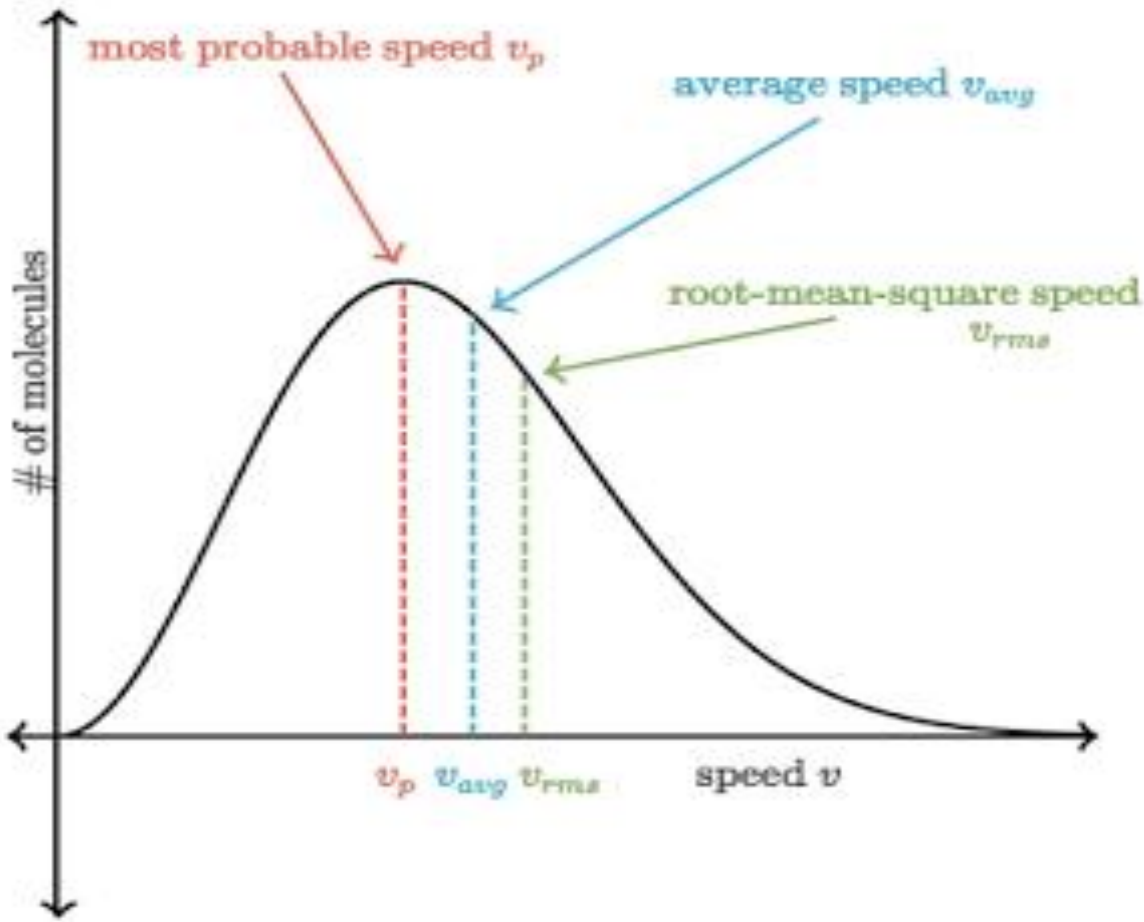
$$f(v) = \sqrt{\left(\frac{m}{2\pi kT}\right)^3} 4\pi v^2 e^{-\frac{mv^2}{2kT}}$$

- The Maxwell-Boltzmann distribution shows that the molecular velocities depend on mass and temperature.
- For a given temperature, the fraction of velocities greater than a reference value increase with the reduction of the mass.
- This explain why light molecules, as hydrogen and helium, escape easily from the atmosphere. Heaviest molecules as nitrogen and oxygen are retained





How are velocities distributed?



escape easily from the atmosphere. Heaviest molecules as nitrogen and oxygen are retained