# Lecture 3

Thursday, September 14, 2023 11:33

## Maxwell- Boltzmann Distribution cont'd

$$f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}$$

$$\langle v^n\rangle = \int_0^\infty v^n f(v)\,dv$$

$\times v^2$

$$\langle v^2\rangle = \int_0^\infty v^2 f(v)\,dv$$

$$\langle v^2\rangle = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\int_0^\infty v^4 e^{-Mv^2/2RT}\,dv$$

$$\boxed{\int_0^\infty x^4 e^{-kx^2}\,dx = \frac{3}{8k^2}\left(\frac{\pi}{k}\right)^{\frac{1}{2}}}$$

integral table

$$\langle v^2\rangle = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\cdot\frac{3}{8}\cdot\left(\frac{M}{2RT}\right)^{-2}$$

$$\cdot\,\pi^{\frac{1}{2}}\left(\frac{M}{2RT}\right)^{-\frac{1}{2}} \qquad \left[k = \frac{M}{2RT}\right]$$

$$\langle v^2\rangle = \frac{3}{8}\cdot\left(\frac{M}{2RT}\right)^{-5/2}\cdot 4\cancel{\pi^{3/2}}\left(\frac{M}{2\cancel{\pi}RT}\right)^{3/2}$$

$$\langle v^2\rangle = \frac{3}{2}\cdot\frac{2RT}{M} = \boxed{\frac{3RT}{M}}$$

$$\boxed{v_{rms} = \langle v^2\rangle^{\frac{1}{2}} = \left(\frac{3RT}{M}\right)^{\frac{1}{2}}}$$

$$pV = \frac{1}{3} n M v_{rms}^{2}$$

$$pV = \frac{1}{\cancel{3}} n \cancel{M}\left[\frac{\cancel{3}RT}{\cancel{M}}\right]$$

$$\boxed{pV = nRT}$$

perfect gas equation from KMT!

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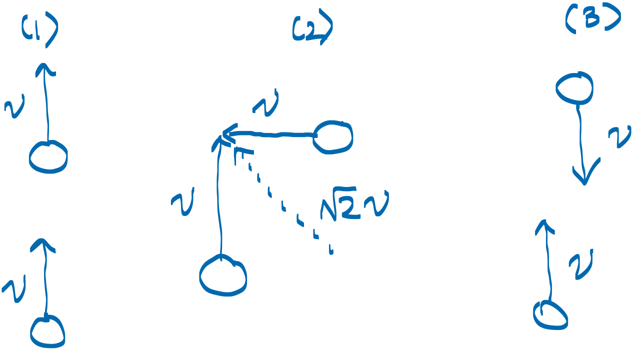
Mean relative speed $v_{rel}$ : the mean speed with which one molecule approaches another of the same kind

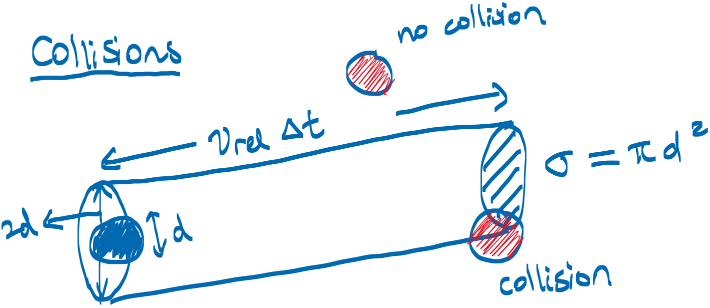
$$v_{rel} = \sqrt{2}\, v_{mean}$$



$v_{rel} = 0$ $v_{rel} = \sqrt{2}v$ $v_{rel} = 2v$

$$v_{rel} = \left(\frac{8k_BT}{\pi\mu}\right)^{\frac{1}{2}}, \quad \mu = \frac{m_A m_B}{m_A + m_B}$$

## Collisions



volume : $v_{rel}\Delta t\,\sigma$ $\mathcal{N} = \frac{N}{V}$ (number density)

number of particles within volume :

$\mathcal{N} v_{rel} \Delta t\, \sigma$

collision frequency z : $\mathcal{N} \sigma v_{rel}$

$$\mathcal{N} = \frac{N}{V} = \frac{nN_A}{V} = \frac{nN_A}{nRT/p} = \frac{pN_A}{RT} = \frac{p}{k_BT}$$

$$\boxed{z = \frac{v_{rel}\sigma p}{k_BT}}$$

## The mean free path

$\lambda$ : average distance a molecule travels between collisions

$z$: frequency $\quad$ time $= \frac{1}{z}$

distance : $\frac{1}{z} v_{rel}$ $\quad$ $\lambda = \frac{v_{rel}}{z}$

$$\boxed{\lambda = \frac{k_B T}{\sigma p}}$$

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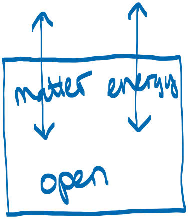
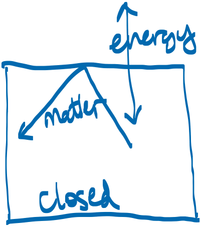
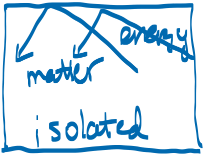
## Topic 2A: The Internal Energy



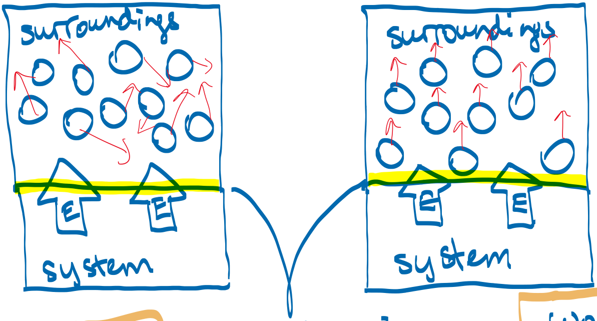




work & heat

**work** is done to achieve motion against an opposing force; e.g. the process of raising a weight against the pull of gravity

**energy**: the capacity of a system to do work when the energy changes as a result of a temperature difference between the system and its surroundings, this energy has been transferred as heat



heat (random)

diathermic barrier; allows transfer of energy as heat

work (organized)

The internal energy, $U$ : total energy of a system

$U$ is a state function ; does not depend on path $\Delta U = U_f - U_i$

## The First Law of Thermodynamics

Heat and work are equivalent ways of changing the internal energy of a system.

"You can't win." (perpetual motion machine of the first kind does not exist)

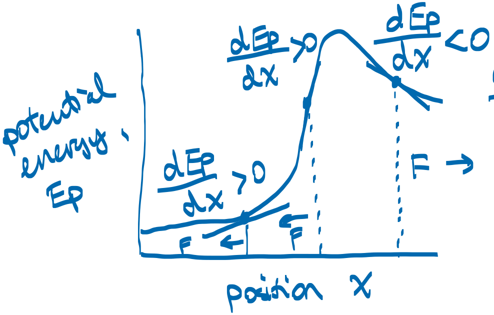
"You can't get something for nothing."

The internal energy of an isolated system is constant.

$$\boxed{\Delta U = q + w}$$

q : heat

w : work



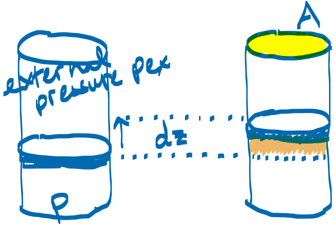
$$\underline{dw = -\vec{F} \cdot d\vec{s}}$$

$$dE_p = -F_x\, dx$$

$$F_x = -\frac{dE_p}{dx}$$

$$dU = dq + dw$$

## Expansion work



$$dV = A \cdot dz$$

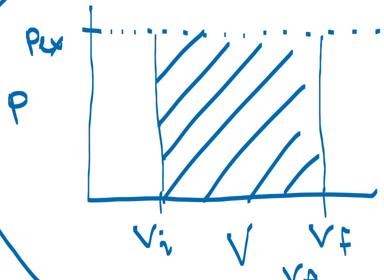
$$dw = -|\vec{F}|\, dz$$

$$dw = -|p_{ex} \cdot \boxed{A| \; dz}$$

$$dw = -p_{ex}\, dV$$

$$\int_i^f dw = -\int_{V_i}^{V_f} p_{ex}\, dV$$

$$w = -\int_{V_i}^{V_f} p_{ex}\, dV$$



area $= p_{ex} \Delta V$

total work

$$w = -p_{ex} \int_{V_i}^{V_f} dV$$

$$= -p_{ex}(V_f - V_i)$$

$$\boxed{w = -p_{ex} \Delta V}$$

expansion work against constant external pressure

2A → 2A.4 (heat transactions)