

Assume a molecule makes many round trips before colliding with another molecule

time between collisions with one wall

$$\Delta t = \frac{2L}{v_x}$$

impulse per collision: $\Delta p = m(v_x - (-v_x)) = 2mv_x$

one molecule :

$$P = \frac{F_x}{A} = \frac{\Delta p / \Delta t}{A} = \frac{mv_x^2}{AL}$$

N molecules :

$$PV = Nm\overline{v_x^2} = NkT$$

KE for
x-motion : $KE = N \frac{1}{2} m \overline{v_x^2} = N \frac{1}{2} kT$

all 3 directions $KE = N \left(\underbrace{\frac{1}{2} m \overline{v_x^2}}_{\frac{1}{2} kT} + \underbrace{\frac{1}{2} m \overline{v_y^2}}_{\frac{1}{2} kT} + \underbrace{\frac{1}{2} m \overline{v_z^2}}_{\frac{1}{2} kT} \right) = 3N \frac{1}{2} kT$

special case of Equipartition Theorem

at thermal equilibrium, each quadratic contribution to energy (Degree of freedom) will have an avg of $\frac{1}{2} kT$ energy

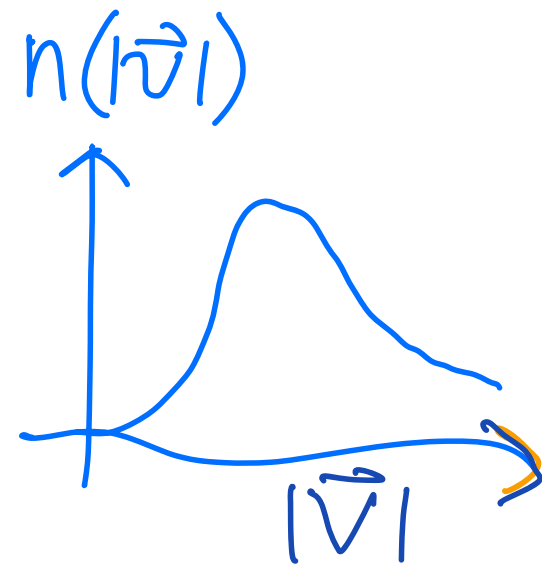
$$KE_{\text{trans}} = 3N \frac{1}{2} kT = N \frac{1}{2} m \overline{v^2}$$

$$v^2 = \vec{v} \cdot \vec{v}$$

$$\frac{3}{2} kT = \frac{1}{2} m \overline{v^2}$$

$$v_{\text{RMS}} = \sqrt{\overline{v^2}} = \sqrt{3kT/m}$$

$$v_{\text{RMS}} = \sqrt{\overline{v^2}} \neq \overline{|\vec{v}|}$$



Equipartition Theorem

$$U_{\text{thermal}} = N * f * \frac{1}{2} kT$$

of particles

of degrees of freedom

quadratic meaning the energy depends on square of a coord or momentum.

$$E = \sum_{n=1}^N \left(\frac{p_{x,n}^2}{2m} + \frac{p_{y,n}^2}{2m} + \frac{p_{z,n}^2}{2m} \right) \left. \vphantom{\sum} \right\} \text{only translation}$$

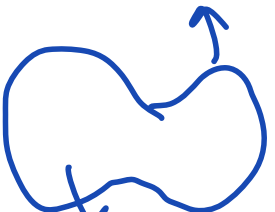
$$E = \sum_{n=1}^N \left(\frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} + \frac{1}{2} m \omega^2 x^2 + \frac{1}{2} m \omega^2 y^2 + \frac{1}{2} m \omega^2 z^2 \right)$$

6 DoF per particle. Each particle moves in 3D in a harmonic oscillator potential.

system has $6N$ DoF

average: $U_{\text{thermal}} = 6N \times \frac{1}{2} kT$ "spring const"

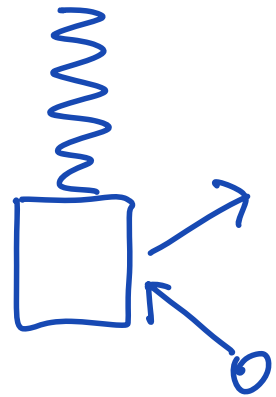
add to E : vibration  N_2 $\frac{1}{2} k \Delta x^2$

rotate:  $2 \times \frac{1}{2} I \omega^2$

Equipartition Theorem is CLASSICAL

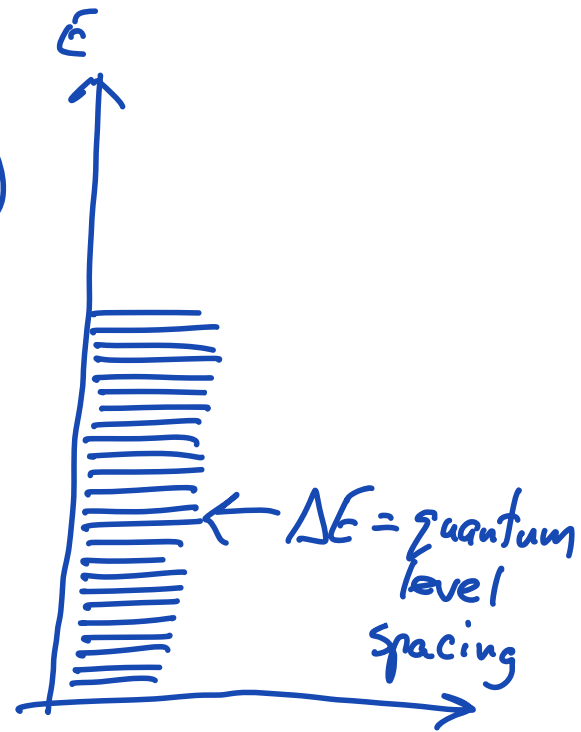
Requires: $kT \gg \Delta E$

1D harmonic oscillator: $E_{osc} = \hbar\omega (n + 1/2)$



air molecule with $E \sim kT$
can change E_{osc} by $\sim kT$

if $kT \gg \Delta E$
the ΔE steps don't
matter.



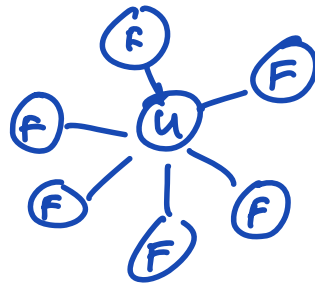
$kT \lesssim \Delta E$: ΔE matters, energy steps important, not continuous energy
NOT CLASSICAL. E.P.T. does not apply

$kT \gg \Delta E$: can't see energy steps, energy look classical. E.P.T. OK

U-235 ← fissionable

U-238 ← not fissionable

Gaseous Diffusion: separate U-235 by exploiting fact that $UF_6(235)$ molecules move faster than $UF_6(238)$



Uranium Hexafluoride, UF_6 , a gas

U-238:

$$v_{RMS} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3(8.31 \text{ J/mol}\cdot\text{K})(300 \text{ K})}{0.352 \text{ kg/mol}}} = 145.8 \frac{\text{m}}{\text{s}}$$

molar mass
= mass per mol

$$v_{RMS}(UF_6, 235) = 146.4 \frac{\text{m}}{\text{s}}$$

U-238 is only
0.6 m/s slower!

★ Should be 19 ★

$$M_F = 19 \text{ g/mol}$$

$$M(UF_6, 235) = 349 \text{ g/mole}$$

$$M_{U-235} = 235 \text{ g/mol} \quad \left. \vphantom{M_{U-235}} \right\} M(UF_6, 238) = 352 \text{ g/mol}$$