

Last lecture:

$$\overline{K}_{\text{trans}} = \frac{3}{2} kT$$

Connection between temp & kinetic energy

- We derived this for an ideal gas of "point particles"

In reality, a molecule's total energy comes from more than just $\overline{K}_{\text{trans}}$

- rotational

$$K_{\text{rot}} = \frac{1}{2} I \omega_x^2, \frac{1}{2} I \omega_y^2, \dots$$

$$K_{\text{vib}} = \frac{1}{2} k_s x^2$$



- Call these forms of energy degrees of freedom

Equipartition Thm

At temp T , each quadratic component of a particle's energy is (on avg) $\frac{1}{2} kT$

For a monoatomic molecule:

$$E = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 \quad (3 \text{ dof})$$

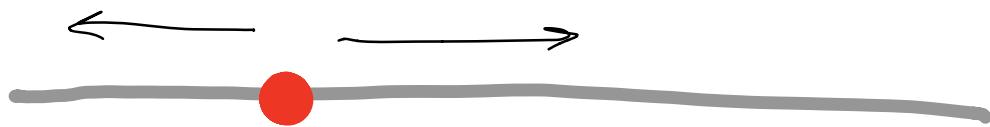
$$\bar{E} = \frac{1}{2}kT + \frac{1}{2}kT + \frac{1}{2}kT$$

$$\bar{E} = \frac{3}{2}kT$$

What is a degree of freedom?

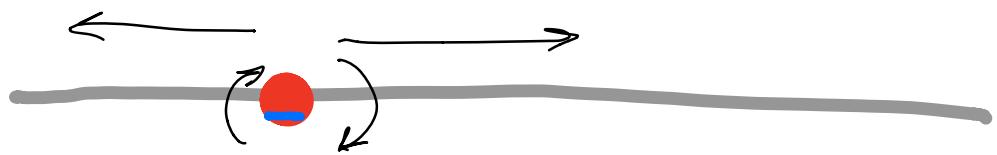
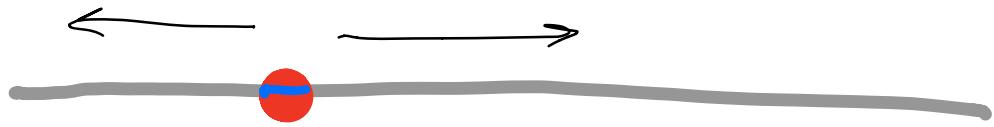
"How many numbers to describe an object's motion?"

Ex: Bead on a thread



- only need 1 coordinate : 1 dof
- For 8 beads, dof = 8

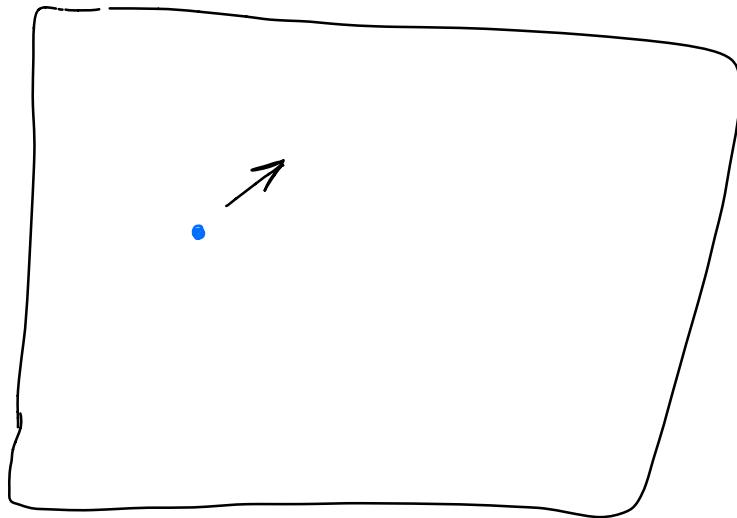
Now let the beads rotate



$$\text{dof} = 2$$

for 13 such beads, dof = 26

- Go back to the ideal gas



How many coordinates do we need?

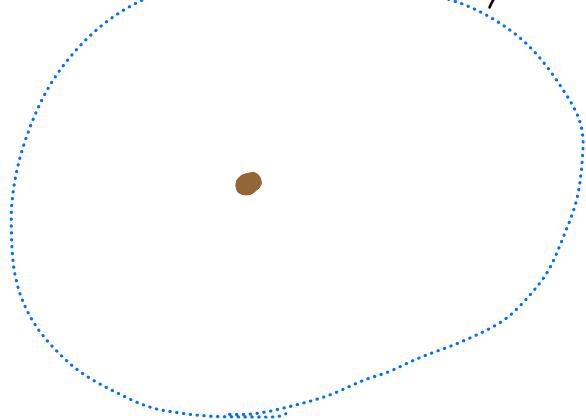
Translational motion: x, y, z (v_x, v_y, v_z)

Rotational? No. Why?

What does it mean to rotate an atom?

Let's say it's Hydrogen

- Spherical symmetry



- rotation can't change anything
- QMically, it doesn't exist

- Another way: We are modeling these particles as points, how do you rotate a point?

So because $f = 3$

$$U_{th} = 3 \left(\frac{1}{2} kT \right) = \frac{3}{2} kT$$

if we have N many molecules

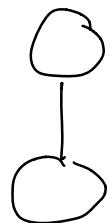
$$U_{th} = \frac{3}{2} N kT$$

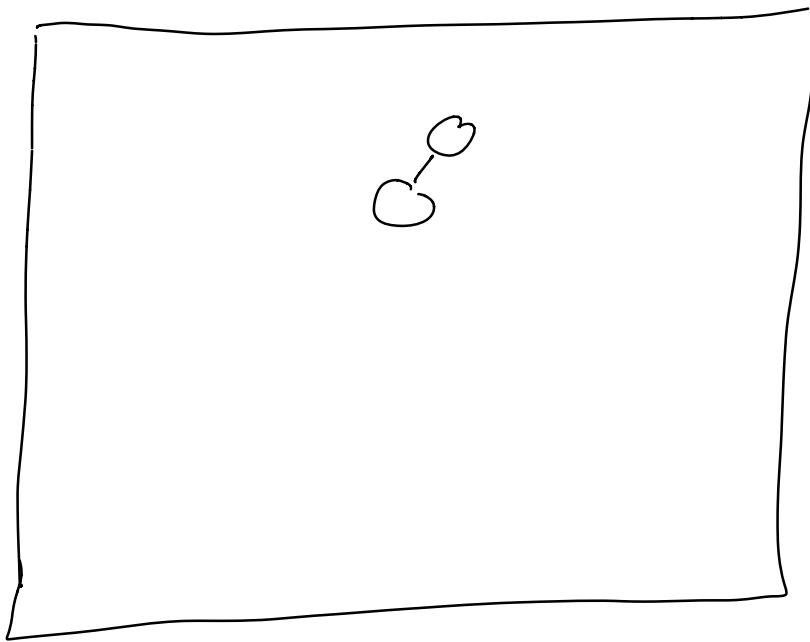
In general:

$$U_{th} = N \cdot f \cdot \frac{1}{2} kT$$

What about a diatomic gas?

N_2





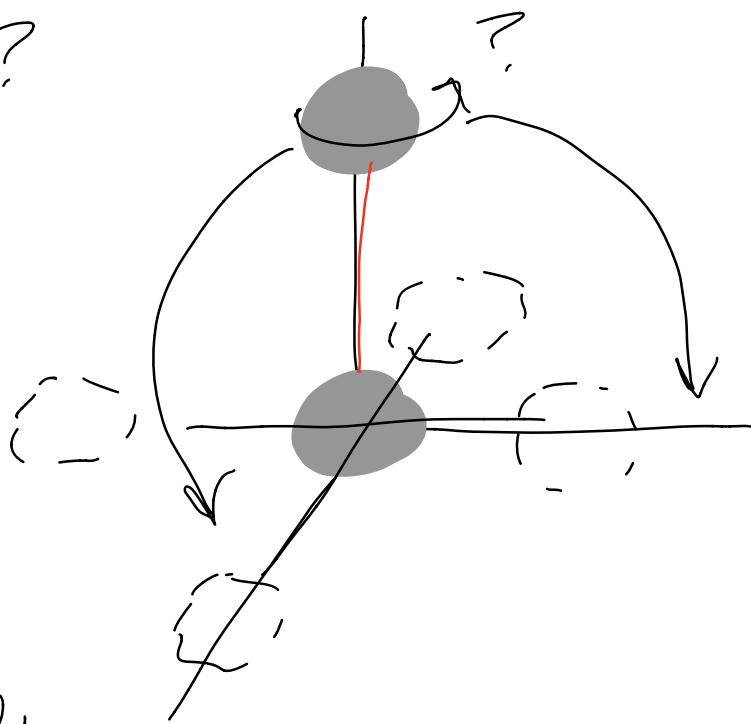
How many dof?

translational: 3

rotational: 2

rotations about
axis of symmetry
don't count

vibrational?



vibrational?



- In principle, yes, (z)

- In practice, no

Energy transfer in collisions \leftarrow (energy
of
molecular
bond)

"Frozen Out"

Dintrinsic: 3 trans + 2 rot = 5

$$U_{th} = N \cdot f \cdot \frac{1}{2} kT$$

$$U_{th} = \frac{5}{2} N kT$$

Will discuss + prove later:

For now

$$U_{th} = N f \left(\frac{1}{2} kT \right)$$

monoatomic

$$U_{th} = \sum N kT$$

diatomic

$$U_{th} = \frac{5}{2} N kT$$

Pause + ask questions

- I have a gas @ room temp
(20°C). I now double the temp.

What is the new temp, in $^{\circ}\text{C}$?

$$20\text{ C} = 293\text{ K}$$

$$T_2 = 586\text{ K}$$

$$586\text{ K} - 273\text{ K} = 313^{\circ}\text{C}$$

$$T = 313^{\circ}\text{C}$$

In a room at 30°C , I grab a molecule at random. What temperature is it most likely at?

- Doesn't make sense



Thermodynamics deals with the movement of energy

(two boxes w/ different temps)

- Broadly speaking: 2 types of energy transfer

Heat, Work

Heat: spontaneous energy flow

Ex: Thermal energy from
higher to lower T
(radiation, sun, etc.)

Spontaneous: Not caused by any external
"agent"

Work:

- Any other transfer of energy
- Push on a piston
- Stir a cup of coffee
- Caused by external agent

If a system has energy U , any change
in U

$$\Delta U = Q + W$$

\mathcal{I}^{st} Law of Thermo
(Really just energy cons)

$$\Delta U = Q + W$$

W : Work done ON a system

If a gas expands and moves a piston,
the gas does + work on the piston

But $W = W_{\text{piston on gas}}$ is negative

Q : heat entering the system

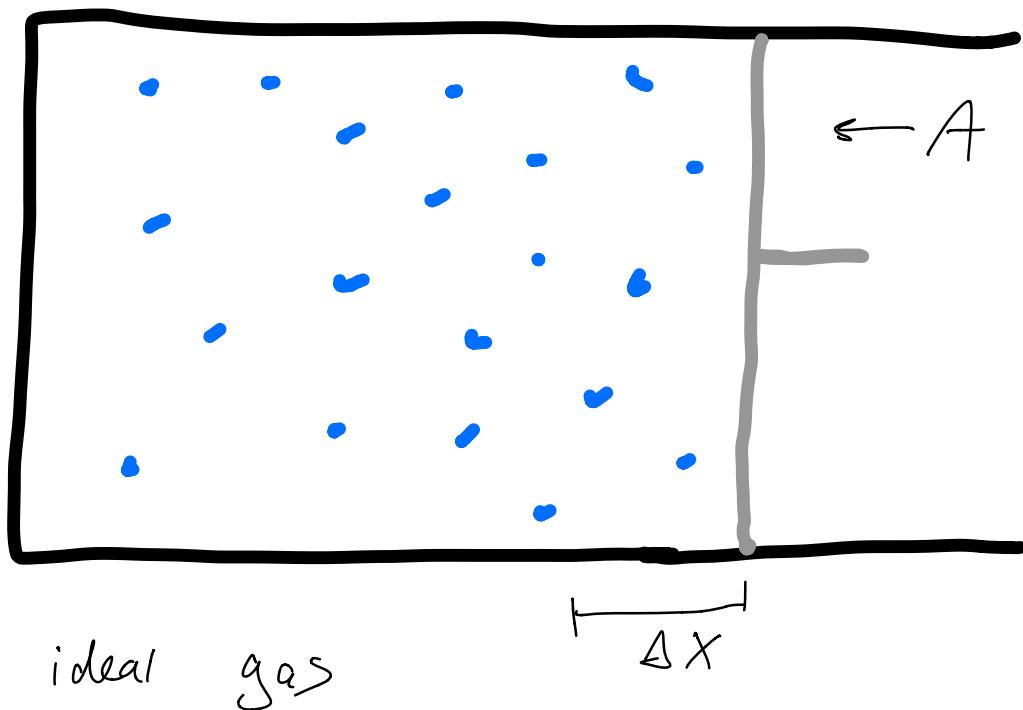
- Conduction (transfer via direct contact)

- Convection (transfer via gas motion)

- Radiation (transfer via light)

Work Done on a gas:

Compression work



$$PV = NkT$$

Push on piston w force F until piston moves
by ΔX

Work done on gas: $W = F \Delta X$

$$F = PA$$

$$W = PA \Delta x$$

Δx is the amount by which V_{gas}
decreased, $- \Delta V$

$$W = -P \Delta V \quad (\text{Expansion} \Rightarrow \text{energy leaves gas})$$

Done quasi statically

Strictly speaking, only true for
infinitesimal changes in V , or for
const pressure

Better

$$W = - \int_{V_i}^{V_f} P(V) dV$$

Compressing an ideal gas

If we do it slowly:

- Gas will equilibrate w/ surroundings (heat)
no temp change
"so thermal"

Quickly: No time for heat flow out of system,
temperature will increase
"adiabatic"

First: the isotherm

$$W = - \int_{V_i}^{V_f} P dV$$

$$PV = NkT$$

$$P = \frac{NkT}{V}$$

N, T const

$$W = -NkT \int_{V_i}^{V_f} \frac{1}{V} dV = NkT \left(\ln V_f - \ln V_i \right) \\ = NkT \ln \left(\frac{V_f}{V_i} \right)$$

isotherm

$$W = NkT \ln\left(\frac{V_i}{V_f}\right)$$

if $V_i > V_f$ (compression)

then $W > 0$

Q: How much does the energy of the gas increase?

A: 0

For an ideal gas

$$U = \frac{1}{2} N F k T$$

$$\Delta T = 0, \Delta N = 0$$

$$\Delta U = 0$$

If $\Delta U = 0$, then Q must be < 0

$$\Delta U = Q + W$$

$$Q = \Delta U - W \\ = -W$$

$$Q = NkT \ln \left(\frac{V_f}{V_i} \right)$$

For compression ($V_f < V_i$) $Q < 0$

