III. Results for Classical Ideal Gas

Assumption: You know the conditions (assumptions) while real gases behave as an ideal gas

(supported experimentally, e.g. gas thermometers)

p, V, T, N

↖ # particles (atoms, molecules)

Here, we list the key results

must note!

↓

a very special situation (not general)

▪ $\boxed{U = \frac{3}{2} NkT \quad (1)}$ (ideal gas: U depends on T only)

[for a mole: $N_A k \equiv R$ (gas constant), $U = \frac{3}{2} RT$ (one mole)]

U consists of k.e. of particles only (ignore particle-particle interaction p.e.)

⇒ $\boxed{\text{T (or kT)} \approx \text{kinetic energy per particle (ideal gas)}}$

Equation of State

Connects state variables

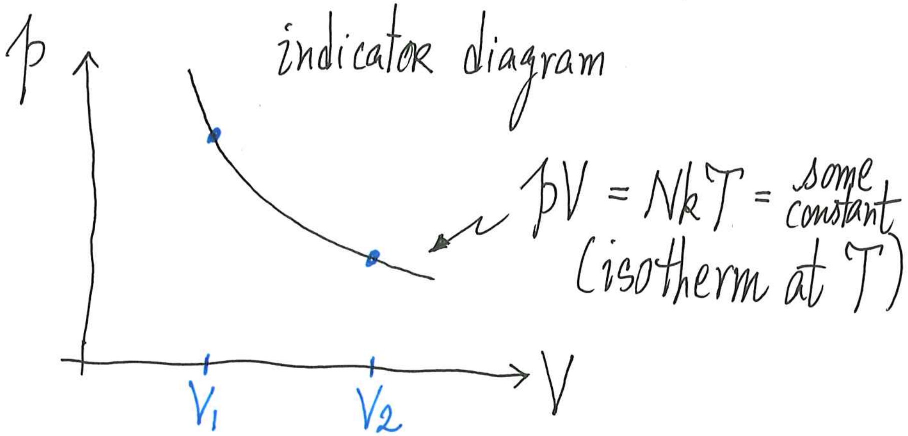
$$\boxed{pV = NkT}^{+} \quad (2)$$

Referring to system in equilibrium with well-defined $p, V, T, (N)$

[one mole: $pv = RT$]
$\uparrow$ molar volume

A. Isothermal Processes and Isotherms (T = constant process)

$$pV = \text{constant} = NkT$$



Recall: If we consider an isothermal (and reversible) process of expansion from V_1 to V_2, then we can
(i) draw the path on indicator diagram,
(ii) use $\int_{\text{path}}(-p\,dV)$ for Work done On system

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[+] Experimentally based (Charles, Boyce, Joule). In statistical mechanics, we want to DERIVE it from the Hamiltonian describing an ideal gas. and also derive $U = \frac{3}{2}NkT$.

Isothermal (slowly done) expansion

Work done ON system $= -\int_{V_1}^{V_2} p\,dV = -\int_{V_1}^{V_2} NkT\frac{dV}{V} = -NkT\ln\left(\frac{V_2}{V_1}\right)$

bigger

negative

smaller

$$\therefore \boxed{\text{Work done by ideal gas in isothermal expansion from } V_1 \text{ to } V_2 = NkT\ln\left(\frac{V_2}{V_1}\right)} \quad (3)$$

Physics: Work done by ideal gas during isothermal expansion

⇒ used up some energy

Simplicity of ideal gas allows us to think about the physics easily!

But isothermal (T constant) ⇒ $U = \frac{3}{2}NkT$ kept constant

1st law $\Delta U = 0$ ($\because T$ constant)

$\Rightarrow Q = -W =$ Work Done BY system $= NkT\ln\left(\frac{V_2}{V_2}\right) > 0$ into system (4)

take in this Q to compensate for work done and keeping U fixed!

$$\boxed{\begin{array}{l}\text{Work done } \underline{\text{ON}} \text{ ideal gas in isothermal} \\ \quad \text{compression from } V_2 \text{ to } V_1\end{array} = NkT\ln\left(\frac{V_2}{V_1}\right)} \quad (4) \quad (>0)$$

↳ To keep T (thus U) constant, need to take same amount of Q <u>OUT</u> of the system.

B. Heat Capacities

- $$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}Nk \quad (5)$$

[Note: Gas particle with NO internal structure, i.e. ● ✓ <u>Not</u> ●–● × diatomic molecule]

- $$H = U + pV = \frac{3}{2}NkT + pV = \frac{3}{2}pV + pV = \frac{5}{2}pV = \frac{5}{2}NkT$$

$$\therefore C_p = \left(\frac{\partial H}{\partial T}\right)_p = \frac{5}{2}Nk = \frac{3}{2}Nk + Nk = C_V + Nk \quad (6)$$

(so $C_p > C_V$ as expected)

[<u>one mole</u>: $c_p = c_V + R$]

and $\boxed{c_V = \frac{3}{2}R, \text{ thus } c_p = \frac{5}{2}R \quad \text{(molar heat capacities)}}$ (7)

"Ideal Gas" is real stuff!

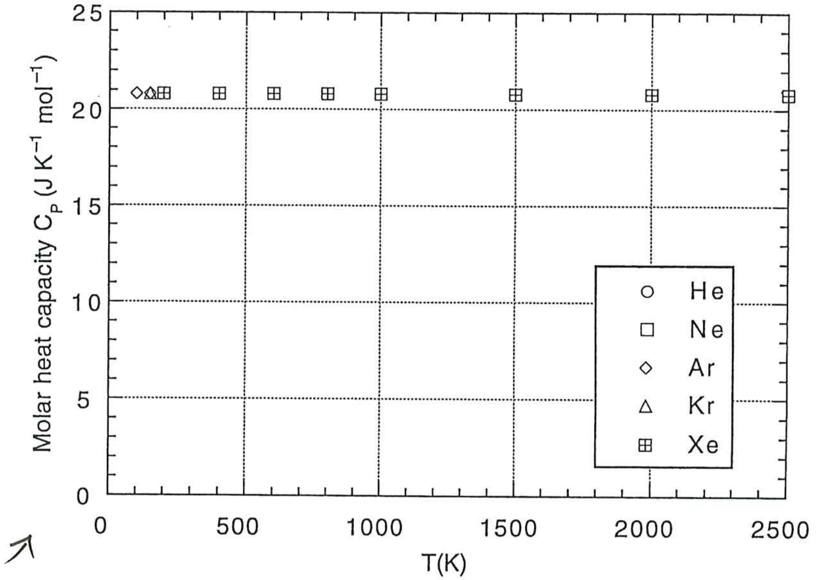
C_p (molar) ($J\,K^{-1}\,mol^{-1}$)

Monatomic noble gases

T(K)	He	Ne	Ar	Kr	Xe
50	—	—	24.8	25.1	25.1
100	—	—	20.8	31.6	28.2
150	—	—	20.8	20.8	33.6
200	—	—	20.8	20.8	20.8
298.15	20.786	20.786	20.786	20.786	20.786
400	20.8	20.8	20.8	20.8	20.8
600	20.8	20.8	20.8	20.8	20.8
800	20.8	20.8	20.8	20.8	20.8
1000	20.8	20.8	20.8	20.8	20.8
1500	20.8	20.8	20.8	20.8	20.8
2000	20.8	20.8	20.8	20.8	20.8
2500	20.8	20.8	20.8	20.8	20.8

not in gas phase

The heat capacity of monatomic gases C_P versus absolute temperature. Data for temperatures less than the boiling point are not plotted. Notice that at the resolution of the measurement, the gases have the same heat capacity across a temperature variation of over an order of magnitude.



Taken from de Podesta, "Understanding the properties of matter".

R = Gas constant = 8.3145 $J\,K^{-1}\,mol^{-1}$

$C_p \underset{\text{ideal gas}}{=} \frac{5}{2}R = 20.78625\ J\,K^{-1}\,mol^{-1}$ [worked very well against data]

A signal on more physics in Diatomic Gases (O_2, N_2, …)

C_p (molar) ($J\,K^{-1}mol^{-1}$)

increasing temperature ↓

T(K)	H_2	O_2	N_2	F_2	Cl_2	Br_2	I_2
50	—	46.1	41.5	—	29.2	33.3	35.8
100	—	29.1	29.1	—	42.3	43.6	45.6
150	—	29.1	29.1	—	51.0	49.2	49.6
200	—	29.1	29.1	—	54.2	53.8	51.5
400	29.2	30.1	29.2	33.0	35.3	36.7	80.3
600	29.3	32.1	30.1	35.2	36.6	37.3	37.6
800	29.6	33.7	31.4	36.3	37.2	37.5	37.8
1000	30.2	34.9	32.7	37.0	37.5	37.7	37.9
1500	32.3	36.6	34.9	37.9	38.0	38.0	38.2
2000	34.3	37.8	36.0	38.4	38.3	38.2	38.5
2500	36.0	38.9	36.0	38.8	38.6	38.5	38.8

Not in gas phases

Taken from de Podesta, "Understanding the properties of matter"

$C_p \neq \underbrace{\frac{5}{2}R}_{\sim 20.8\ J\,K^{-1}mol^{-1}}$ as for monatomic gases

What is "29.2"? "$20.8 + \underbrace{8.3}_{R}$"?

What is "37.x"? "20.8 + 8.3 + 8.3"?

Something more about diatomic gases

rotate vibrate

["internal degrees"]

Define $\boxed{\gamma \equiv \frac{C_p}{C_V}}$ (8) [we know $\gamma > 1$ in general]

- ideal gas (not general) $\gamma_{\text{ideal gas}} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3} = 1.667$ (9)

Data of γ for Gases [from de Podesta, "Understanding the properties of Matter"]

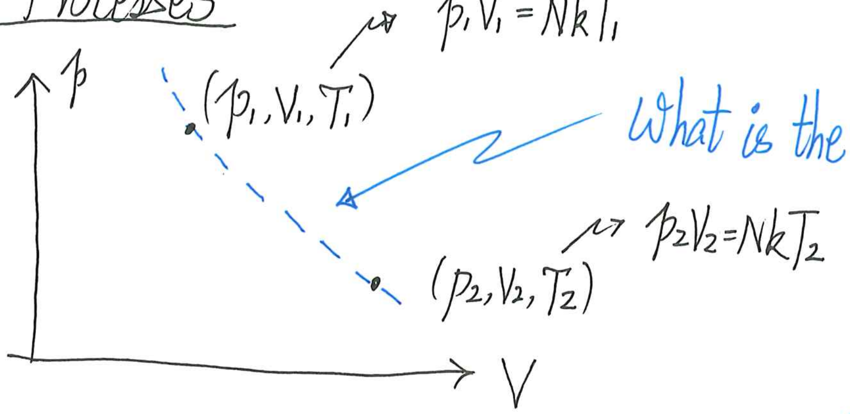
Gas	T(°C)	T(K)	γ
Monatomic gases			
He	0.0	273.20	1.630
Ar	0.0	273.20	1.667
Ne	19.0	292.20	1.642
Kr	19.0	292.20	1.689
Xe	19.0	292.20	1.666
Hg	310.0	583.20	1.666
All the above results are close to 1.66			
Diatomic gases			
H_2	10.0	283.20	1.407
N_2	20.0	293.20	1.401
O_2	10.0	283.20	1.400
CO	1800.0	2073.2	1.297
NO	—	—	1.394
Most of the above results are close to 1.4			

Gas	T(°C)	T(K)	γ
Triatomic gases			
O_3	—	—	1.290
H_20	100.0	373.20	1.334
CO_2	10.0	283.20	1.300
CO_2	300.0	573.20	1.220
CO_2	500.0	773.20	1.200
NH_3	—	—	1.336
N_20	—	—	1.324
H_2S	—	—	1.340
CS_2	—	—	1.239
SO_2	20.0	293.20	1.260
SO_2	500.0	773.20	1.200
All the above results are close to 1.3			
Polyatomic gases			
CH_4	—	—	1.313
C_2H_6	—	—	1.220
C_3H_8	—	—	1.130
C_2H_2	—	—	1.260
C_2H_4	—	—	1.264
C_6H_6	20.0	293.20	1.400
C_6H_6	99.7	372.90	1.105
$CHCl_3$	30.0	303.20	1.110
$CHCl_3$	99.8	373.00	1.150
CCl_4	—	—	1.130
The above results are between 1.1 and 1.4			

"—" (temperature ≈ 0°C - 20°C)

C. Adiabatic Processes

Question:

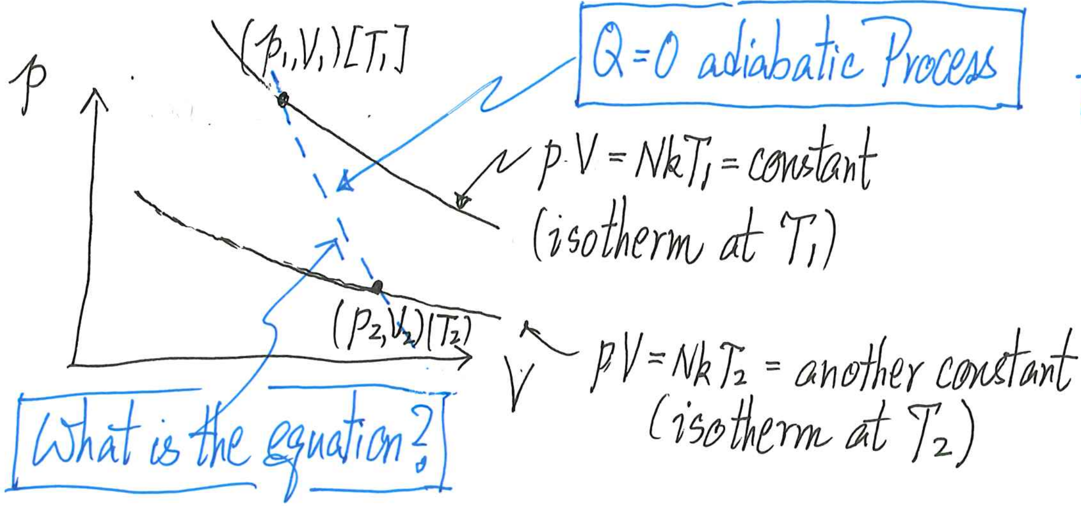


What is the equation for the curve on the indicator diagram when the process is carried out as a adiabatic reversible process?

Adiabatic $\Rightarrow Q = 0$; 1st law $dU = -p\,dV$

Ideal gas has $U(T)$ only, there is work done by system "$p\,dV$" for adiabatic expansion $\Rightarrow$ drop in U (by dU) $\Rightarrow$ drop in temperature (by dT)

this is why $T_2 < T_1$



$Q=0$ adiabatic Process

What is the equation?

there are many more isotherms for $T_1 < T < T_2$

Physical Sense: $\underbrace{\text{Adiabatic curve}}_{\text{it cuts across many isotherms between } T_1 \text{ and } T_2}$ is steeper than the isotherms

Answer:

$$dU = \text{đ}Q - p\,dV = -p\,dV \qquad [\text{đ}Q = 0]$$

$$\Rightarrow dU + p\,dV = 0$$

(general)

ideal gas: (one mole) $U = \frac{3}{2} N_A kT$, $dU = \frac{3}{2} N_A k\,dT$

$$= \frac{3}{2} R\,dT$$

$$= C_v\,dT$$

$pV = RT$

1 mole ideal gas

$$C_v\,dT + \frac{RT}{V}\,dV = 0 \qquad (10)$$

Physics: $\frac{RT}{V}\,dV = -C_v\,dT$

adiabatic expansion gives $dT < 0$ (drop in temperature, as U is spent on work done)

[Make sense!]

$$\therefore \quad \frac{C_v}{R}\frac{dT}{T} + \frac{dV}{V} = 0$$

eq. of state used

[integrate from state ① to state ② (path already specified $\text{đ}Q = 0$, reversibility used)]

$$\frac{C_V}{R}\ln T\Big|_{T_1}^{T_2} + \ln V\Big|_{V_1}^{V_2} = 0 \Rightarrow \frac{C_V}{R}\ln\left(\frac{T_2}{T_1}\right) + \ln\left(\frac{V_2}{V_1}\right) = 0$$

$$\Rightarrow \ln\left[\left(\frac{T_2}{T_1}\right)^{\frac{C_V}{R}}\left(\frac{V_2}{V_1}\right)\right] = 0$$

$$\therefore \left(\frac{T_2}{T_1}\right)^{\frac{C_V}{R}}\left(\frac{V_2}{V_1}\right) = 1$$

[Physics: Expansion $V_2 > V$, $\frac{V_2}{V_1} > 1$

$\therefore \left(\frac{T_2}{T_1}\right)^{\frac{C_V}{R}} < 1$ OR $T_2 < T_1$ (temperature drops)]

(now given quantitatively)

(ideal gas used: $C_V = \frac{3}{2}R$, $\frac{C_V}{R} = \frac{3}{2}$)

$$\Rightarrow T_1^{\frac{C_V}{R}} V_1 = T_2^{\frac{C_V}{R}} V_2$$

$$\therefore \boxed{T^{\frac{C_V}{R}} V = \text{constant}} \quad (11)$$

[governing curve in T-V diagram for adiabatic process of ideal gas]

Next, turn this into curve in p-V diagram (easy: use $\underbrace{pV = RT}_{\text{true for all equil. states}}$)

$$\left(\frac{pV}{R}\right)^{\frac{C_V}{R}} V = \overset{\text{a constant}}{C'}$$

$$p^{\frac{C_V}{R}} V^{\frac{C_V}{R}+1} = RC' = \overset{\text{also a constant}}{C''}$$

$$p^{\frac{C_V}{R}} V^{\frac{C_V+R}{R}} = C''$$

$$\left(\frac{\text{ideal gas}}{C_V + R = C_p}\right)$$

$$p^{\frac{C_V}{R}} V^{\frac{C_p}{R}} = C''$$

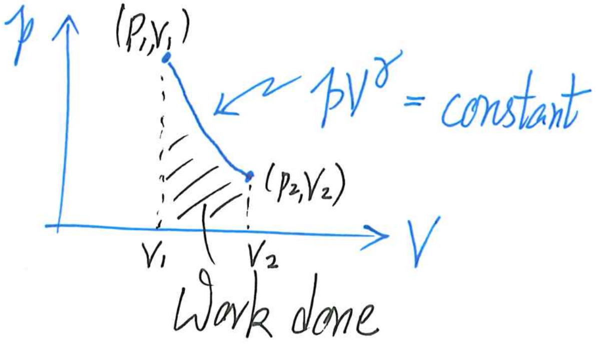
$$p V^{\frac{C_p}{C_V}} = C \leftarrow \text{just another constant} \qquad \left(\gamma \equiv \frac{C_p}{C_V}\right)$$

$$\Rightarrow \boxed{pV^{\gamma} = \text{constant}} \quad (12)$$

← this is the curve on the p-V diagram for adiabatic processes (ideal gas)

↖ it is steeper than the isotherms given by $pV = \underbrace{\text{constant}}_{\text{determined by } T}$ $(\gamma > 1)$ as expected

Adiabatic Expansion



Work Done BY system

$$= \int_{V_1}^{V_2} p(V)\,dV \qquad \left(pV^\gamma = C \Rightarrow p = CV^{-\gamma}\right)$$

$$= C\int_{V_1}^{V_2} V^{-\gamma}\,dV = \frac{C}{1-\gamma}\left[V_2^{1-\gamma} - V_1^{1-\gamma}\right] \quad (13a)$$

(Done!)

$$= \frac{1}{1-\gamma}\left[P_2V_2^\gamma V_2^{1-\gamma} - P_1V_1^\gamma V_1^{1-\gamma}\right]$$

both on curve

$$\left(P_1V_1^\gamma = C = P_2V_2^\gamma\right)$$

$$= \frac{1}{1-\gamma}\left[P_2V_2 - P_1V_1\right]$$

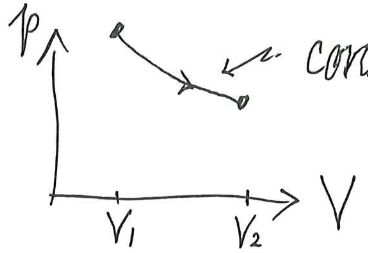
$$\Rightarrow \boxed{W_{\substack{\text{by system}\\ \text{(adiabatic)}}} = \frac{P_1V_1 - P_2V_2}{\gamma - 1}} \quad (13)$$

(this should be positive)

Reminder: $Q_{\text{adibatic}} = 0$ (thus U drops by $W_{\text{by system}}$)

E. Summary

Reversible Isothermal expansion

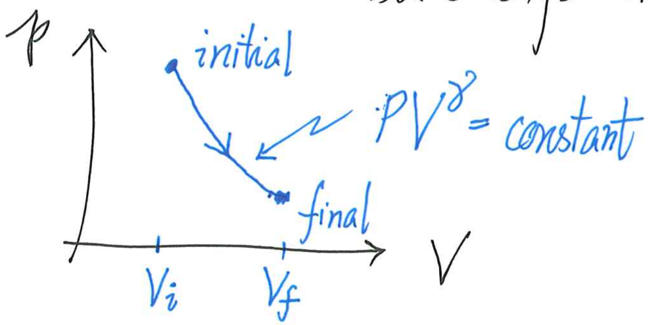


$$W_{\text{by system}} = RT\ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta U = 0 \quad (\because U(T) \text{ for ideal gas})$$

$$Q_{\text{into system}} = RT\ln\left(\frac{V_2}{V_1}\right)$$

Reversible adiabatic expansion



$$W_{\text{by system}} = \frac{p_iV_i - p_fV_f}{\gamma - 1}, \quad \gamma = \frac{C_p}{C_v} = \frac{5}{3}$$

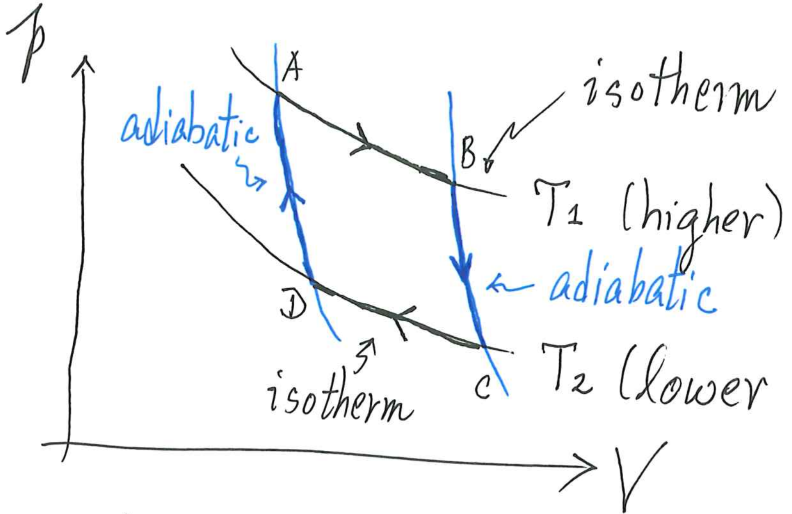
monatomic

$$Q = 0$$

ΔU drops by amount of $W_{\text{by system}}$

F. What for?

Ready to study reversible cycle



$$\underbrace{A \to B \to C \to D}_{\text{a cycle}} \to A \to B \to C \to D \to \cdots$$

Can write down

- $W_{\text{by system}}$ ($W_{\text{on system}}$)
- Q_{in} (Q_{out})
- ΔU

for every steps $(\underbrace{A \to B}_{\text{isothermal}}, \overbrace{B \to C}^{\text{adiabatic}}, \underbrace{C \to D}_{\text{isothermal}}, \overbrace{D \to A}^{\text{adiabatic}})$

Done!

Remarks : What is the creature called "Classical Ideal Gas" ?

- Every entity (particles (e.g. electrons, protons), atoms, molecules) is either a boson or a fermion (Quantum Mechanics)
  $\Rightarrow$ Should there only be gases of bosons and gases of fermions?
- Under what conditions can QM effect be ignored?
- $pV = NkT$ has no indication of condensation to a liquid
  [How to describe gas to liquid transition? What is missing?]

Final Comment

- Ideal Gas [Nice, simple, quantities can easily be calculated & considered physically]
- Ideal Gas [Results are <u>NOT</u> general, don't extend them too far, e.g. $U=U(T)$ not true usually!]

Appendix: Layman's "Kinetic Theory of Gas"

- Why $U = \frac{3}{2} NkT$ for $\underbrace{\text{classical ideal gas}}_{\text{no inter-particle interaction (except collisions)}}$?

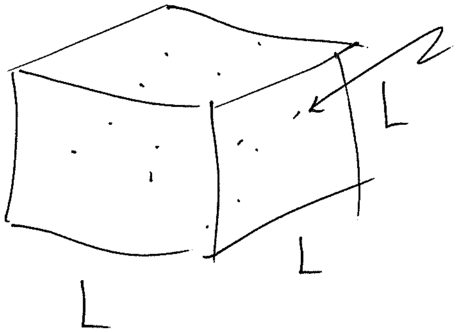
U = Total kinetic energy of particles $\cancel{U(\vec{r}_1 - \vec{r}_2)}$

Kinetic Theory of Gas

- accept that there are particles (atoms, thus microscopic)
- follow particle's dynamics on an averaged way

Formally, derive Maxwell's distribution of molecular speeds and then obtain average k.e. per particle

But here we will do something far simpler (based on the "principles" of "make sense" & "What else can it be?")



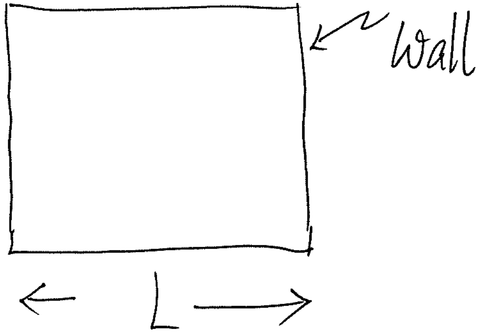
N particles moving around in every possible direction, collide, hit the walls and bounce back, ∘∘∘
($N \sim 10^{23}$ for a small cube)

How about this?

- Particles just move along x, y, z directions

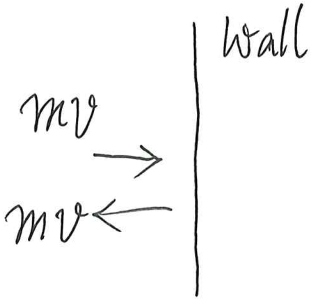
  $\frac{N}{3}$ of them along each direction (e.g. x-direction, left-right)

- There is a representative speed v (or rougher - they all move with v)



$\frac{2L}{v}$ = time to travel and hit wall on RHS (one particle)

$\frac{v}{2L}$ = # times a particle hits wall in one second



Change of momentum per hit = 2mv (one particle)

change of momentum per second $= 2mv\cdot\frac{v}{2L}$ (one particle)

$$\text{Force} = 2mv\cdot\frac{v}{2L}$$ (due to one particle)

$$\underset{\text{due to one particle}}{\text{Pressure}} = 2mv\cdot\frac{v}{2L}\left(\frac{1}{\underset{\substack{\uparrow\\ \text{Area}}}{L^2}}\right) = \frac{2mv^2}{2V}$$

$V = L^3 = \text{Volume}$

N/3 particles together

$$\text{Pressure } P = \frac{N}{3}\cdot\frac{mv^2}{V} \Rightarrow PV = \frac{N}{3}mv^2 = \frac{2}{3}\overbrace{N\cdot\left(\frac{1}{2}mv^2\right)}^{\substack{U\,(\text{Total K.E.})\\ \parallel}}$$

$$\therefore PV = \frac{2}{3}U \quad \text{OR} \quad \boxed{U = \frac{3}{2}pV = \frac{3}{2}NkT}$$ Done! (1)

Q: Can you trace the origin of that "3" and that "2"?

$$U = \text{Total k.e.} = N\cdot\underbrace{\left(\frac{1}{2}mv^2\right)}_{\substack{\text{typical k.e.}\\ \text{of a particle}}} = N\cdot\left(\frac{3}{2}kT\right)$$

∴ Temperature (or kT) is associated with the average kinetic energy due to the random motion of molecules in a system

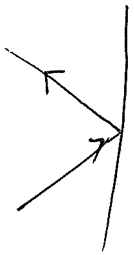
Copied from HKDSE Physics Curriculum & Assessment Guide!

- You may say that particles move in $\underbrace{E, S, W, N, NE, NW, SW, SE}_{8 \text{ directions}}$

and $N/8$ in each direction

OR even finer divisions

Then you need to resolve component



You will get the same answer!