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## Recap

Mixing entropy and irreversibility from dist'ability

Control parameters – H, T, V, ...

## Today

Equation of state → thermodynamic cycles

Starting with pressure $P = -\left.\frac{\partial \langle E \rangle}{\partial V}\right|_S$

change volume (new) with fixed entropy (isentropic)

Ideal gas $S_D, S_I$ depend on $\frac{V}{\lambda_{th}^3} \propto VT^{3/2}$

$\therefore$ constant entropy $\rightarrow VT^{3/2} = c^{3/2} \rightarrow T = cV^{-2/3}$

$$\langle E \rangle = \frac{3}{2}NT = \frac{3c}{2}\frac{N}{V^{2/3}}$$

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$$\boxed{P = -\frac{3c}{\cancel{2}} N \left( \frac{-\cancel{2}}{\cancel{3}} \frac{V^{-2/3}}{V} \right) = \frac{N}{V}\left(cV^{-2/3}\right) = \frac{NT}{V}}$$

$PV = NT$ is ideal gas law

Equation of state (EoS)

thermodynamic macro-state

Relate macroscopic properties

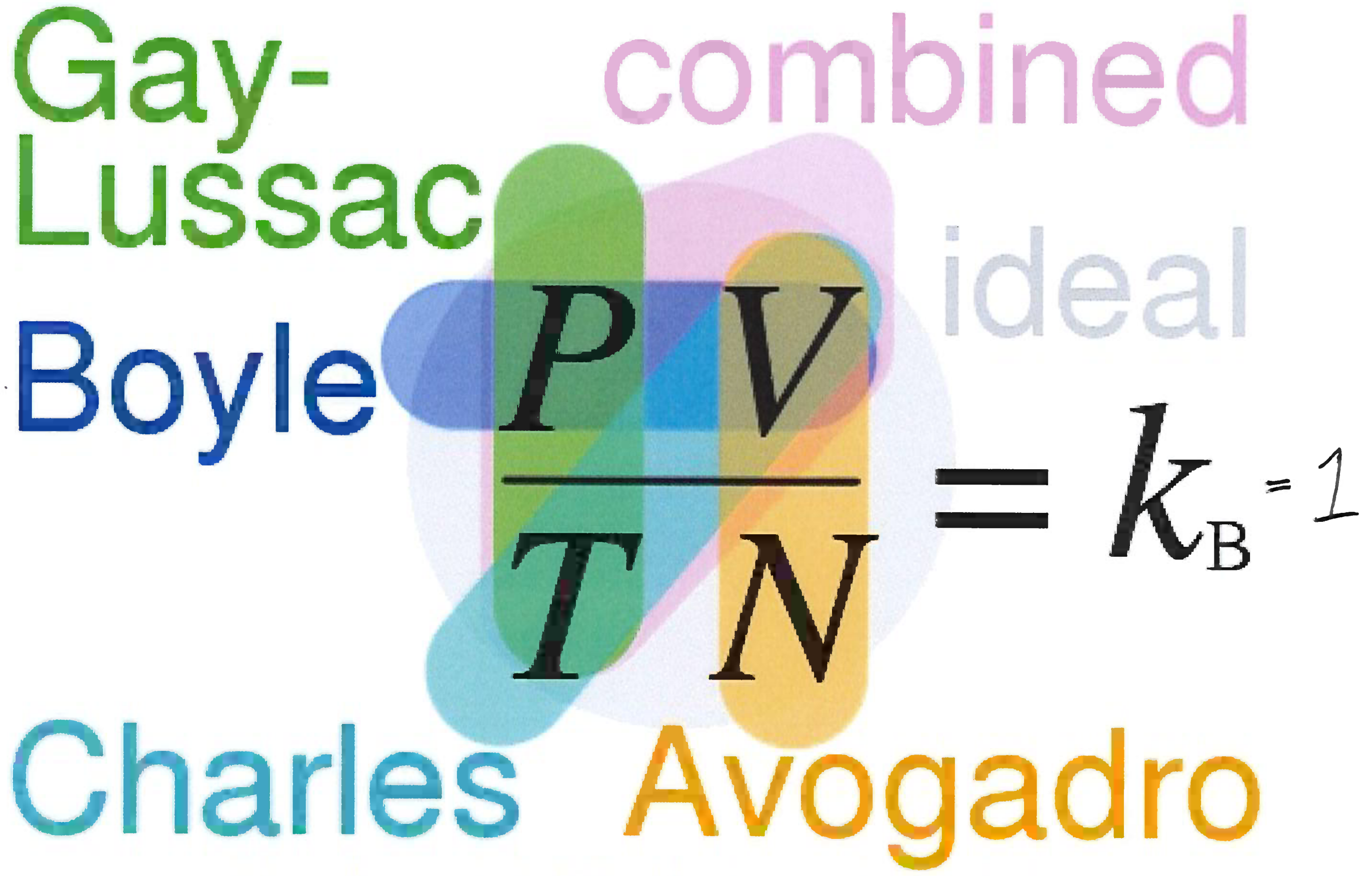
$P, V, N, T, E, S, \ldots$

Historically empirical observations

followed by math'ical explanation

Robert Boyle (1660s) – change pressure with fixed $T, N$

Find $PV = \text{const.}$ → "Boyle's law"



$$\frac{PV}{TN} = k_B = 1$$

commons.wikimedia.org/wiki/File:Ideal_gas_law_relationships.svg

Fix $N, P$

$$\frac{V}{T} = \text{const.}$$

"Charles's law"
1787

fix $N, V$

$$\frac{P}{T} = \text{const}$$

"Gay-Lussac's law"
1802

Fix $P, T$

$$\frac{V}{N} = \text{const.}$$

"Avogadro's law"
1812

Combined into ideal gas law in 1830s

Derived from stat mech in 1850s

Mutual reinforcement of scientific progress
& Industrial Revolution
↖ including <u>engines</u>

Pressure related to mechanic process

<u>Work</u> done by force $\vec{F}$
displacing object by $d\vec{r}$
changing energy by $dE$

Infinitesimal $W = dE = \vec{F} \cdot d\vec{r}$

$$\rightarrow \quad W = \Delta E = E_f - E_0 = \int_{r_0}^{r_f} \vec{F} \cdot d\vec{r} \qquad \text{(line integral)}$$

<u>Example</u>: Object falling due to gravity, $\vec{F} = (0, 0, -mg)$

Start at rest, $E_0 = 0$ at height $h$

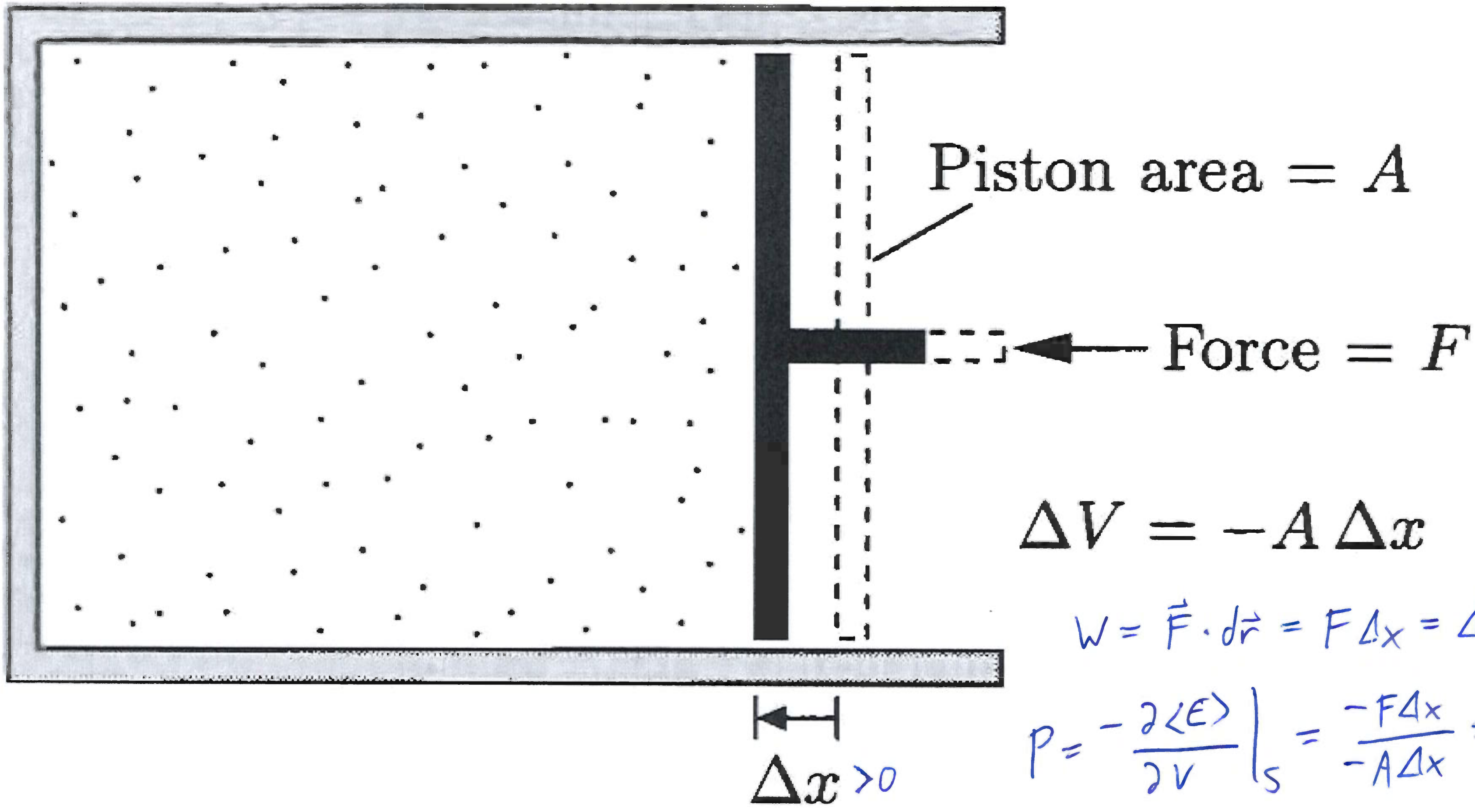
Final $E_f = W = \int \vec{F} \cdot d\vec{r} = -mg \int_h^0 dz = mgh > 0$ ✓

$$\frac{p_z^2}{2m} = mgh \rightarrow p_z = -m\sqrt{2gh}$$

$N \gg 1$: Work is change in internal energy
due to force that changes volume

<u>Example</u>: Piston

→ Pressure is force per unit area
on surface of container holding gas



$$\Delta V = -A\,\Delta x$$

$$W = \vec{F} \cdot d\vec{r} = F\Delta x = \Delta\langle E\rangle$$

$$P = -\left.\frac{\partial\langle E\rangle}{\partial V}\right|_S = \frac{-F\Delta x}{-A\Delta x} = \frac{F}{A} > 0$$

Assuming constant entropy, $\Delta\langle E\rangle = -P\Delta V = W$

$\langle E\rangle$ can also change by changing entropy

$\therefore \Delta\langle E\rangle = W + \text{more}$

Even if entropy changes, $W = -P\,dV$ is general

$$\rightarrow W = -\int_{V_0}^{V_f} P(V)\,dV$$

$\frac{NT}{V}$ from ideal gas law

$W > 0$ is work done <u>on gas</u> by surroundings raising $\langle E\rangle$

$W < 0$ is work done <u>by gas</u> on surroundings ~~raising~~ lowering $\langle E\rangle$

Can change $\langle E\rangle = \frac{3}{2}NT$ with constant volume

$W=0$

$d\langle E\rangle = \frac{3}{2}N\,dT \neq 0$

Entropy must change

$S = N\log(T^{3/2}) + T\text{-indep.} = \frac{3}{2}N\log T + T\text{-indep}$

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$$\boxed{dS = \frac{3}{2}N\left(\frac{dT}{T}\right) = \frac{d\langle E\rangle}{T} \neq 0}$$

<u>Heat</u> is change in $\langle E\rangle$ with constant $V$

$d\langle E\rangle = Q = T\,dS$

$$\rightarrow Q = \int_{S_0}^{S_f} T(S)\,dS$$

assuming $S(T)$ invertible

Assume entropy not created (or destroyed) (reversible)

Like energy, $dS \neq 0$ flows between system and surroundings

Adiabatic process changes $\langle E \rangle$ with $Q = 0$

Adiabatic + reversible → isentropic, $dS = 0$

Fast – no time for heat flow

Other extreme: isothermal process~~es~~ changes $\langle E \rangle$ with Fixed $T$

Slow – all possible heat flow to/from reservoir

Real processes in between – usually closer to adiabatic

Invert $S(T, V) \rightarrow T(S, V) \propto \langle E \rangle (S, V)$

Taylor expansion

$$\langle E \rangle (S, V) = \langle E \rangle (S_0, V_0) + (S - S_0) \left. \frac{\partial \langle E \rangle}{\partial S} \right|_V + (V - V_0) \left. \frac{\partial \langle E \rangle}{\partial V} \right|_S + \ldots$$

$$\rightarrow d\langle E \rangle = dS \left( \frac{1}{T} \right)^{-1} + dV(-P)$$

$$= T\,dS - P\,dV = Q + W$$

Generalized first law: Any change in internal energy matched by heat flow to/from surroundings and work done on/by surroundings

Other key ideal gas equations

$\langle E \rangle = \frac{3}{2} NT$

$PV = NT$ (EoS)

$S$ function of $VT^{3/2}$

Sequence of processes that return to initial macro-state $(P, V, T, E, S, \ldots)$

→ thermodynamic cycle can be repeated

to do work

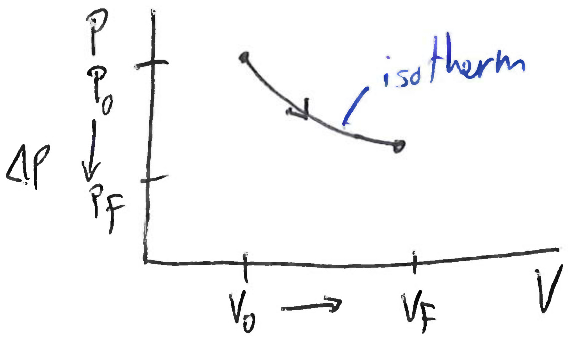
transfer heat

...

$N$ fixed → $P$ and $V$ specify macro-state

$T = \frac{PV}{N}$, $\langle E \rangle = \frac{3}{2} PV$, $S$ func. of $V\left(\frac{PV}{N}\right)^{3/2}$

Represent macro-state as point in <u>PV diagram</u>



processes ⟷ line

cycles ⟷ closed paths

<u>Example:</u> Isothermal expansion (slow)

$$\boxed{\text{Fixed } T = \frac{P_0 V_0}{\cancel{N}} = \frac{P_F V_F}{\cancel{N}} \to P_F = \left(\frac{V_0}{V_F}\right) P_0 < P_0 \qquad \Delta P = \left[\frac{V_0}{V_F} - 1\right] P_0 < 0}$$ ✓

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$$W = -\int_{V_0}^{V_F} P(V)\, dV < 0$$

would decrease $\langle E \rangle = \frac{3}{2} NT$

Need incoming heat $Q > 0$ to keep $T$ and $\langle E \rangle$ constant

What if two isotherms cross?

$$\boxed{\text{Same } \frac{PV}{N} = T \to \text{same isotherm}}$$

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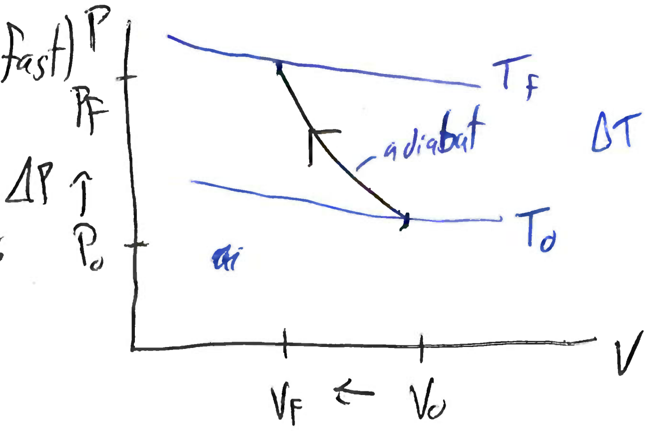
Distinct isotherm with $T_i \neq T_j$ never cross

<u>Example:</u> Adiabatic compression (fast)

$Q = 0$ → Temperature changes

connect different isotherms



Constant entropy: $V_0 T_0^{3/2} = V_F T_F^{3/2}$

$$\rightarrow \quad T_F = \left(\frac{V_0}{V_F}\right)^{2/3} T_0 > T_0$$

$$\Delta T = \left[\left(\frac{V_0}{V_F}\right)^{2/3} - 1\right] \frac{P_0 V_0}{N} > 0$$

$$V_0 \left(\frac{P_0 V_0}{\cancel{N}}\right)^{3/2} = V_F \left(\frac{P_F V_F}{\cancel{N}}\right)^{3/2} \longrightarrow P_F = \left(\frac{V_0}{V_F}\right)^{5/3} P_0 > P_0$$

$$\Delta P = \left[\left(\frac{V_0}{V_F}\right)^{5/3} - 1\right] P_0 > 0$$

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