Mon 13 Mar

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Recap

Canonical ensemble → partition function

→ ideal gases

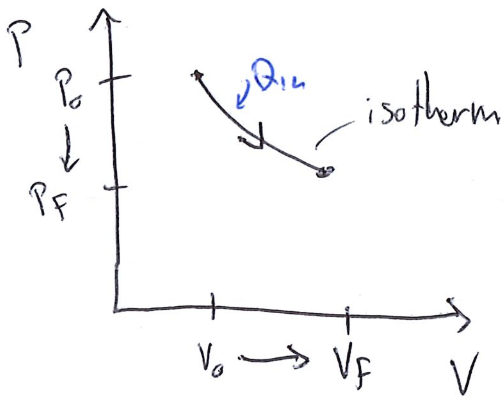
→ engines / refrigerators (therm. cycles)

$$\langle E\rangle = \frac{3}{2}NT \qquad S \propto VT^{3/2}$$

$$PV = NT$$

$$d\langle E\rangle = TdS - PdV = \underline{Q} + W$$

PV diagram capture (changing) macro-state



state ~ point

process ~ line

cycle ~ closed path

Example: Isothermal expansion

Fixed T → slow for heat exchange

$$T = \frac{P_0 V_0}{N} = \frac{P_f V_f}{N} \rightarrow P_f = \left(\frac{V_0}{V_f}\right) P_0 < P_0$$

$$\Delta P = P_f - P_0 = P_0\left(\frac{V_0}{V_f} - 1\right) < 0$$

$$E_i \propto \frac{\hbar^2\pi^2}{2mL^2} \rightarrow \langle E\rangle = \frac{3}{2}NT \text{ decreases} \rightarrow \text{heat in}$$

$L^2 \sim V^{2/3}$

Crossing isotherms:

Same $\frac{PV}{N} = T$ → same isotherm

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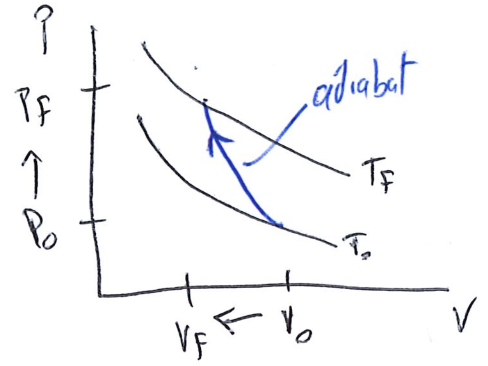

Example:

Adiabatic compression (fast) $\quad Q = 0 = T\,dS$

Changes temperature connecting two isotherms

$$V_0 T_0^{3/2} = V_F T_F^{3/2} \rightarrow T_F = \left(\frac{V_0}{V_F}\right)^{2/3} T_0 > 1$$

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

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

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

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Carnot cycle

Two reservoirs: hot (T_H) and cold (T_L)

Is cycle self-consistent?

Given initial $\{V_A, P_A, N\}$, plus V_B & V_C.

must find correct V_D to close cycle

1) $A \rightarrow B \quad T_B = T_H = \frac{P_A V_A}{N}$

$$P_B = \frac{N T_H}{V_B} = \frac{N}{V_B}\left(\frac{P_A V_A}{N}\right) = \left(\frac{V_A}{V_B}\right) P_A$$

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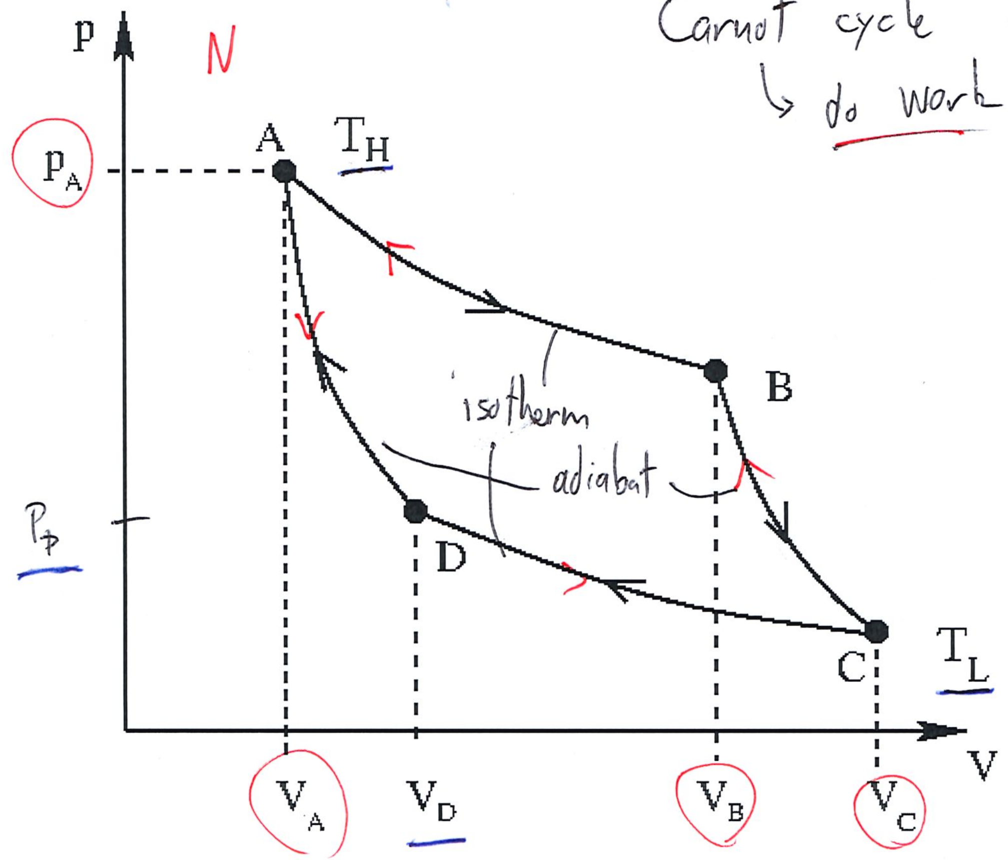
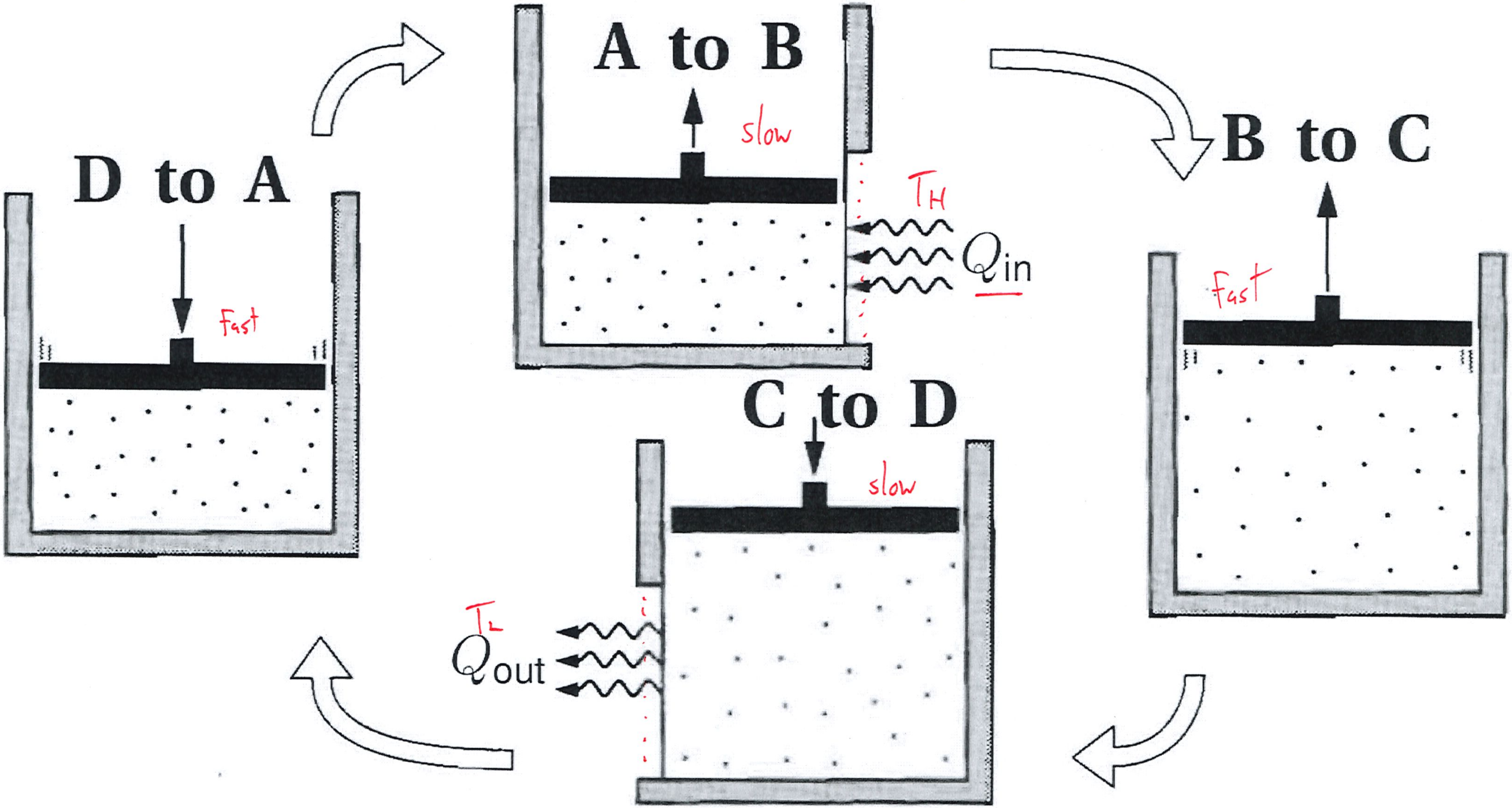
Carnot cycle 1824
↳ do work





A to B
slow
T_H
Q_{in}
B to C
fast
C to D
slow
T_L
Q_{out}
D to A
fast

2) $B \to C$

$$S_B = S_C \rightarrow V_B T_H^{3/2} = V_C T_L^{3/2}$$

$$\underline{T_L = \left(\frac{V_B}{V_C}\right)^{2/3} T_H} = \frac{P_A \cancel{V_A}}{N}\left(\frac{V_B}{V_C}\right)^{2/3} < T_H$$

$$N = \frac{P_A V_A}{T_H} = \frac{P_C V_C}{T_L}$$

page 76 $\quad P_C = \left(\frac{V_A}{V_C}\right)\left(\frac{T_L}{T_H}\right) P_A = \left(\frac{V_A}{V_C}\right)\left(\frac{V_B}{V_C}\right)^{2/3} P_A < P_A$

3) $C \to D$ $\quad T_D = T_L$

$D \to A$

$$S_D = S_A \rightarrow V_D T_L^{3/2} = V_A T_H^{3/2}$$

$$V_D = \left(\frac{T_H}{T_L}\right)^{3/2} V_A = \left(\frac{V_C}{V_B}\right) V_A > V_A$$

$$\frac{V_A}{V_D} = \frac{V_B}{V_C} \quad // \quad \frac{V_A}{V_B} = \frac{V_D}{V_C}$$

matching stages

Finally

page 76 $\quad P_D = \frac{N T_L}{V_D} = N\left(\frac{\cancel{V_A} V_B}{\cancel{V_A} V_C}\right)\left(\frac{V_B}{V_C}\right)^{2/3} \frac{P_A \cancel{V_A}}{\cancel{N}} = \left(\frac{V_B}{V_C}\right)^{5/3} P_A < P_A$

Self-consistency gives $\{P_B, P_C, T_L, P_D, V_D\}$ fixed from $\{N, P_A, V_A, V_B, V_C\}$

The point: Move heat to do work

how much? how much?

Convenience definitions:

Work <u>on</u> system $\qquad W_{in} = W = -\int P dV > 0$

Work <u>by</u> system $\qquad W_{out} = -W = \int P dV > 0$

Heat into system $\qquad Q_{in} = Q = \int T dS > 0$

Heat out of system $\qquad Q_{out} = -Q = -\int T dS > 0$

<u>Efficiency</u>

$$\eta = \frac{W_{done}}{Q_{in}} = \frac{W_{out} - W_{in}}{Q_{in}}$$

<u>net</u> work done by each iteration per unit heat

Engine $\rightarrow$ $\eta > 0$ (does work)

First law: $\Delta\langle E\rangle = Q_{in} - Q_{out} + W_{in} - W_{out} = 0$

$$W_{out} - W_{in} = Q_{in} - \underbrace{Q_{out}}_{\text{waste heat}} \leq Q_{in}$$

$$0 < \eta \leq 1$$

Fraction of heat the engine can convert to work

(can't win)

Carnot cycle efficiency

1) $A \rightarrow B$

$$W_{AB} = -\int_{V_A}^{V_B} P(V)\, dV = -\int_{V_A}^{V_B} \frac{NT_H}{V} dV$$

$$= -NT_H \log\left(\frac{V_B}{V_A}\right) = P_A V_A \log\left(\frac{V_A}{V_B}\right) < 0$$

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$\hookrightarrow W_{out}$

$$\Delta\langle E\rangle_{AB} = \frac{3}{2} N (\Delta T)_{AB} = 0 = Q_{AB} + W_{AB}$$

$$Q_{AB} = -W_{AB} > 0 \rightarrow Q_{in}$$

2) $B \to C$ $\quad Q_{BC} = 0$

$$\boxed{\begin{aligned} \Delta\langle E\rangle_{BC} = W_{BC} &= \tfrac{3}{2}N(T_L - T_H) = \tfrac{3}{2}NT_H\left(\frac{T_L}{T_H} - 1\right) \\ &= \tfrac{3}{2}P_AV_A\left[\left(\frac{V_B}{V_C}\right)^{2/3} - 1\right] < 0 \to W_{out} \end{aligned}}$$

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3) $C \to D$

$$W_{CD} = -\int_{V_C}^{V_D} \frac{NT_L}{V}\,dV = P_AV_A\left(\frac{T_L}{T_H}\right)\log\left(\frac{V_C}{V_D}\right)$$

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$$= P_AV_A\left(\frac{V_B}{V_C}\right)^{2/3}\log\left(\frac{V_B}{V_A}\right) > 0 \to W_{in}$$

$$Q_{CD} = -W_{CD} < 0 \to Q_{out}$$

4) $D \to A$ $\quad Q_{DA} = 0$

$$\Delta\langle E\rangle_{DA} = W_{DA} = \tfrac{3}{2}N(T_H - T_L) = -W_{BC} > 0 \to W_{in}$$

$$\eta = \frac{W_{out} - W_{in}}{Q_{in}} = \frac{-W_{AB} - \cancel{W_{BC}} - W_{CD} - \cancel{W_{DA}}}{-W_{AB}} = 1 + \frac{W_{CD}}{W_{AB}}$$

$$W_{out} = -W_{AB} - W_{BC} > 0$$

$$W_{in} = W_{CD} + W_{DA} > 0$$

$$Q_{in} = Q_{AB} = -W_{AB} > 0$$

$$\eta = 1 + \frac{\cancel{P_A}V_A\left(\frac{T_L}{T_H}\right)\log\left(\frac{V_B}{V_A}\right)}{\cancel{P_A}V_A\log\left(\frac{V_A}{V_B}\right)} = 1 - \frac{T_L}{T_H} \qquad T_L < T_H$$

Check $\quad 0 < \eta < 1$

$\dfrac{T_L}{T_H} \to 1$ $\qquad\qquad$ $\dfrac{T_L}{T_H} \to 0$

single isotherm $\qquad\qquad$ absolute zero

infinitely hot

General results

$\frac{T_L}{T_H} \to 1$ always means $\eta \to 0$
No heat flow to do work

Larger T_H vs. T_L $\to$ more efficient

$Q = T\,dS$

First law: $W_{out} - W_{in} = Q_{in} - Q_{out}$

$$\eta = \frac{Q_{in} - Q_{out}}{Q_{in}} = 1 - \frac{\overset{\text{to cold res}}{Q_{out}}}{\underset{\text{from hot res.}}{Q_{in}}} = 1 - \frac{T_L \Delta S_{out}}{T_H \Delta S_{in}}$$

After each iteration, same S_A in system
ΔS_{out} added to cold res.
ΔS_{in} removed from hot res.

Second law: $\Delta S = \Delta S_{out} - \Delta S_{in} \geq 0$

$$\frac{\Delta S_{out}}{\Delta S_{in}} \geq 1 \qquad \frac{Q_{out}}{Q_{in}} \geq \frac{T_L}{T_H}$$

$$\to \eta \leq 1 - \frac{T_L}{T_H} < 1$$

Maximum efficiency $\eta < 1 \to$ can't break even

Carnot cycle gives max. possible η
Not used... too slow!

Reverse Carnot cycle $\to$ put in work to remove heat from cold res.

$\to$ Refrigerator

Coefficient of performance: $\dfrac{Q_{in}}{W_{in} - W_{out}} = \dfrac{Q_{in}}{Q_{out} - Q_{in}} = \dfrac{1}{\frac{Q_{out}}{Q_{in}} - 1}$

$Q_{in} = T_L \Delta S_{in}$

$Q_{out} = T_H \Delta S_{out}$

Second law $\rightarrow$ $\dfrac{Q_{out}}{Q_{in}} \geq \dfrac{T_H}{T_L}$

$\rightarrow COP \leq \dfrac{1}{\frac{T_H}{T_L} - 1} = \dfrac{T_L}{T_H - T_L}$

Typical COP ~ 5–6

(maximized by Carnot cycle)

Grand-canonical ensemble

Micro-canonical directly conserve energy & particle #
complete isolation

Canonical instead fix temperature via thermal reservoir

Now allow both heat & particle exchange
via particle reservoir

What is fixed due to particle exchange?

Recall $\dfrac{1}{T} = \left.\dfrac{\partial S}{\partial E}\right|_N$

Swap $E \leftrightarrow N$ to define chemical potential

$$\mu = -T \left.\frac{\partial S}{\partial N}\right|_E$$

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