MATH327: StatMech and Thermo

Thursday, 5 March 2026

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Something to consider

You may have heard that the first and second laws of thermodynamics rule out the existence of perpetual-motion machines.

How can we see this at play in thermodynamic cycles?

Recap

Work and heat $\rightarrow$ $d\langle E\rangle = Q + W = T\,dS - P\,dV$

Adiabatic vs. isothermal processes

Today

Thermodynamic cycles $\rightarrow$ Carnot cycle and efficiency

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

Can repeat to do work or transfer heat

Other key ideal gas equations:

EoS: $PV = NT$ $\qquad$ S func. of $VT^{3/2}$

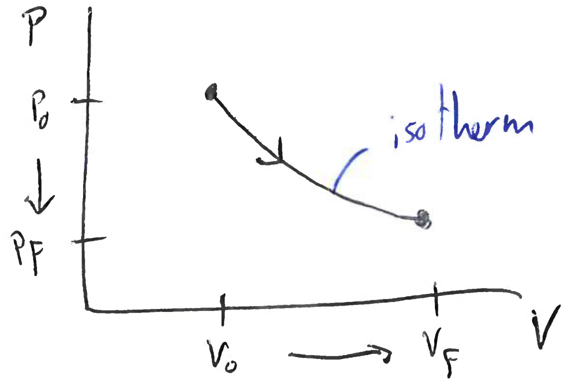
$\langle E\rangle = \frac{3}{2}NT$

N fixed $\rightarrow$ P and V specify macro-state

$T = \frac{PV}{N}$ $\qquad$ $\langle E\rangle = \frac{3}{2}PV$

S func of $V\left(\frac{PV}{N}\right)^{3/2}$

Represent macro-state as point in PV diagram



processes $\leftrightarrow$ line

cycles $\leftrightarrow$ closed paths

Example: Isothermal expansion (slow)

Fixed $T = \frac{P_0 V_0}{\cancel{N}} = \frac{P_F V_F}{\cancel{N}} \longrightarrow P_F = \left(\frac{V_0}{V_F}\right) P_0 < P_0$

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

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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?

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

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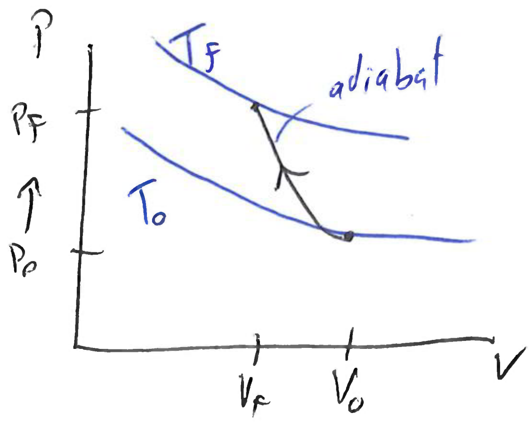
Distinct isotherms with $T_i \neq T_j$ never cross

Example:

Adiabatic compression (Fast)

$Q = 0 \rightarrow$ temperature changes

connect different isotherms



Constant entropy: $V_0 T_0^{3/2} = V_f T_f^{3/2}$

$$T_f = \left(\frac{V_0}{V_f}\right)^{2/3} T_0 > T_0$$

$$\Delta T = \left[\left(\frac{V_0}{V_f}\right)^{2/3} - 1\right] T_0 > 0$$

$$= \left[\left(\frac{V_0}{V_f}\right)^{2/3} - 1\right] \frac{P_0 V_0}{N}$$

$$V_0 \left(\frac{P_0 V_0}{\cancel{N}}\right)^{3/2} = V_f \left(\frac{P_f V_f}{\cancel{N}}\right)^{3/2}$$

$$\rightarrow P_f = \left(\frac{V_0}{V_f}\right)^{5/3} P_0 > P_0$$

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

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<u>Carnot cycle</u> (1824): Do ~~and~~ work by moving heat

Two reservoirs: hot T_H and cold $T_L < T_H$

Slow isothermal expansion then fast expansion

" compression " compression

Check cycle self-consistent

Start with $\{N, P_A, V_A\} \rightarrow T_H$, choose V_B and V_C

Find consistent $\{P_D, V_D\} \rightarrow T_L$

Determine points B, C, D

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1) $A \rightarrow B$ $\quad T_B = T_H = \frac{P_A V_A}{N} \longrightarrow \boxed{P_B = \left(\frac{V_A}{V_B}\right) P_A}$ ✓

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

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

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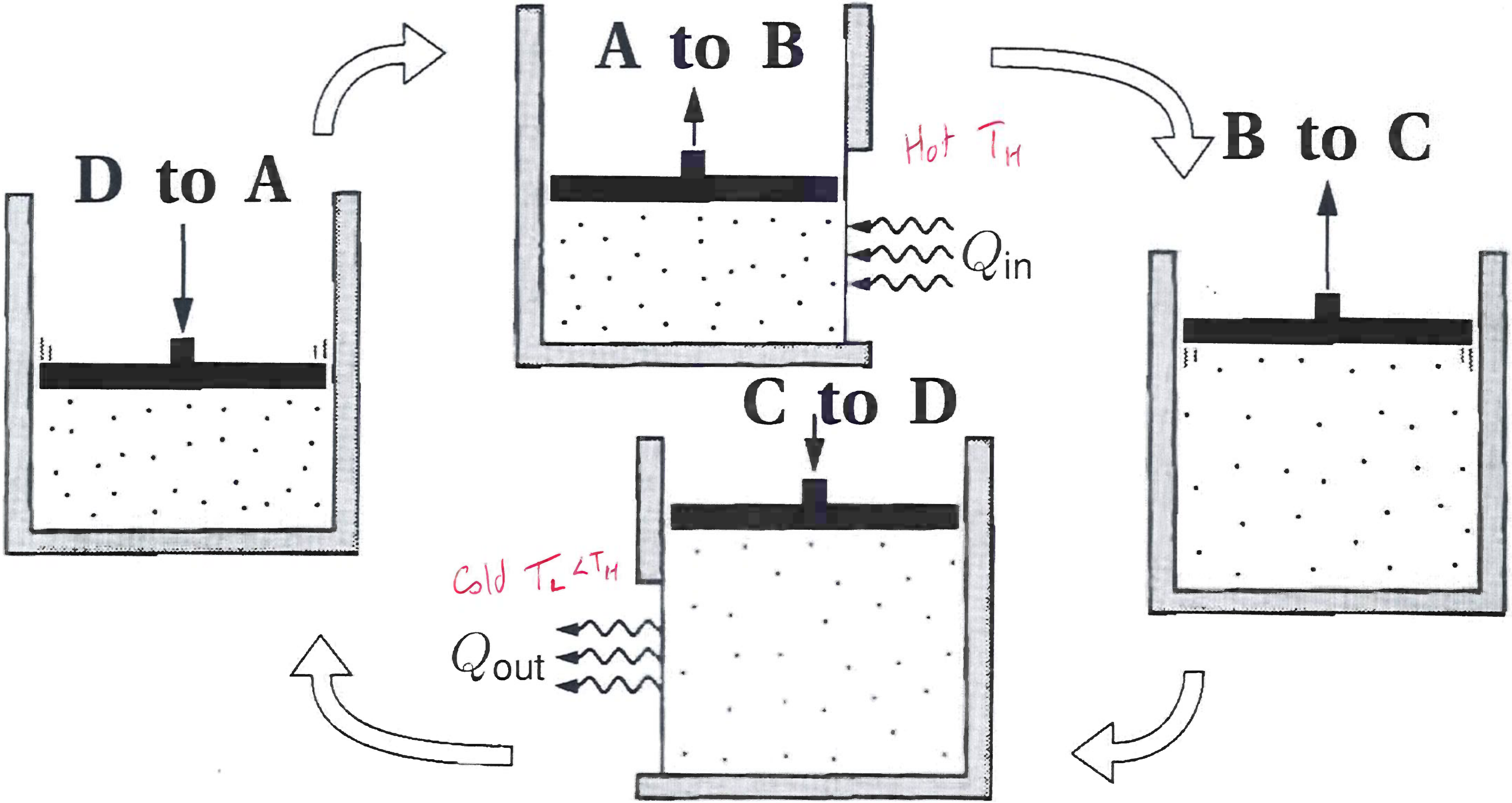
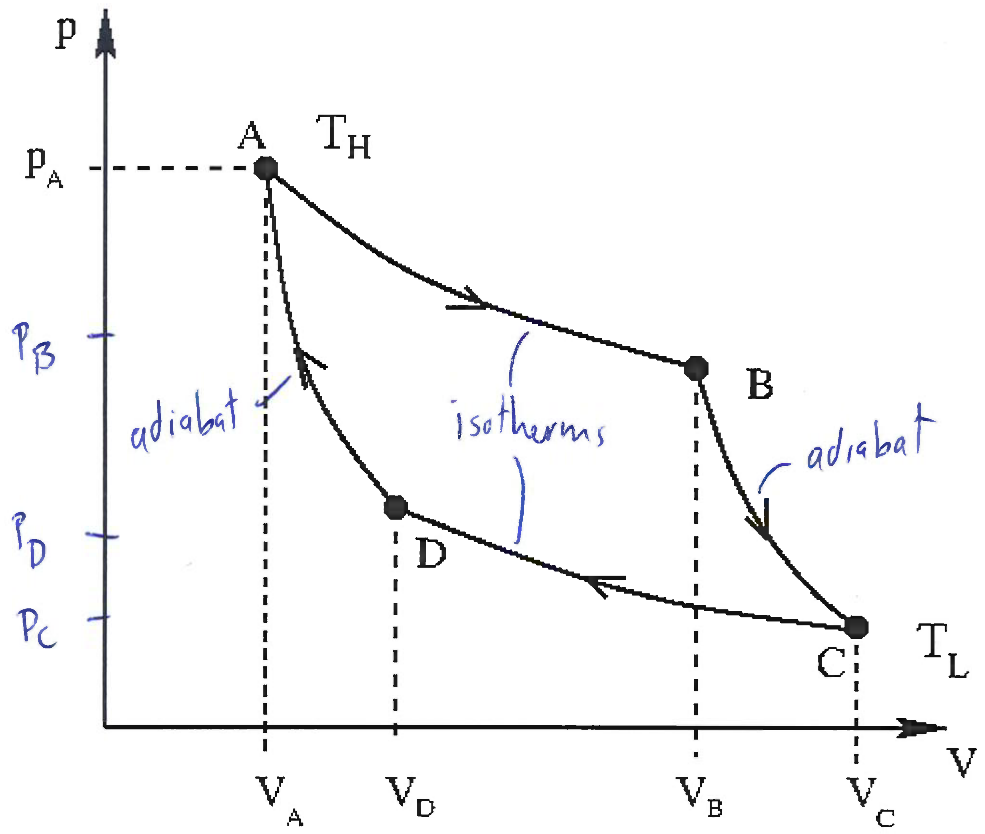

A to B
Hot T_H
Q_{in}
B to C
C to D
Cold $T_L < T_H$
Q_{out}
D to A


p
V
A
T_H
B
C
T_L
D
p_A
p_B
p_D
p_C
V_A
V_D
V_B
V_C
adiabat
isotherms
adiabat

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$$P_C = \frac{NT_L}{V_C} = \left(\frac{V_A}{V_C}\right)\left(\frac{V_B}{V_C}\right)^{2/3} P_A < P_A$$

3) $C \to D$ and $D \to A$

$T_D = T_L$

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

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

Constant ratios: $\dfrac{V_A}{V_D} = \dfrac{V_B}{V_C}$ (adiabats) $\qquad \dfrac{V_A}{V_B} = \dfrac{V_D}{V_C}$ (isotherms)

Finally $P_D = \dfrac{NT_L}{V_D} = \cancel{N}\left(\dfrac{V_B}{\cancel{V_A} V_C}\right)\left(\dfrac{V_B}{V_C}\right)^{2/3} \dfrac{P_A \cancel{V_A}}{\cancel{N}} = \left(\dfrac{V_B}{V_C}\right)^{5/3} P_A$

$$= \left(\frac{V_A}{V_D}\right)^{5/3} P_A < P_A$$

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$\therefore \{N, P_A, V_A, V_B, V_C\}$ fix $\{P_B, T_L, P_C, V_D, P_D\}$

$\rightarrow$ self-consistent ✓

The point: Do work by moving heat

how much? how much?

Notation to help keep track of signs

Work on system $\quad W_{in} = W = -\int P dV \geq 0$

Work by system $\quad W_{out} = -W = \int P dV \geq 0$

Heat into system $\quad Q_{in} = Q = \int T dS \geq 0$

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

Efficiency

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

Net $\oint$ work done by ~~the~~ each iteration vs. total input heat

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

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

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

So $0 < \eta \leq 1$ – "can't win"

Example: Carnot cycle

Check work and heat for each processes

1) $A \rightarrow B$

$$\boxed{\begin{aligned} W_{AB} &= -\int_{V_A}^{V_B} \frac{N T_H}{V}\, dV = -N T_H \log\left(\frac{V_B}{V_A}\right) \\ &= P_A V_A \log\left(\frac{V_A}{V_B}\right) < 0 \rightarrow W_{out} \end{aligned}}$$

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

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

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

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

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3) $C \to D$

$$W_{CD} = -\int_{V_C}^{V_B} \frac{NT_L}{V}\, dV = P_A V_A \left(\frac{T_L}{T_H}\right) \log\left(\frac{V_C}{V_D}\right) > 0$$

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$$\left(\frac{V_B}{V_C}\right)^{2/3} \to W_{in}$$

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

4) $D \to A$

$$Q_{DA} = 0$$

$$W_{DA} = \frac{3}{2} N (T_H - T_L) = -W_{BC} > 0 \to W_{in}$$

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

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

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

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

$T_L < T_H$

$$\eta = 1 + \frac{\cancel{P_A V_A} \left(\frac{V_B}{V_C}\right)^{2/3} \log\left(\frac{V_B}{V_A}\right)}{\cancel{P_A V_A} \log\left(\frac{V_A}{V_B}\right)} = 1 - \left(\frac{V_B}{V_C}\right)^{2/3} = 1 - \frac{T_L}{T_H}$$

$\therefore\ 0 < \eta < 1$ ✓

$\frac{T_L}{T_H} \to 1$ single isotherm

$\frac{T_L}{T_H} \to 0$ abs. zero or infinitely hot

General results

1) $\frac{T_L}{T_H} \to 1$ always mean $\eta \to 0$

No heat flow to do work

2) More efficient as $\dfrac{T_H}{T_L}$ increases

3) Recall $W_{out} - W_{in} = Q_{in} - Q_{out}$ from first law

to cold res.

$$\eta = \frac{Q_{in} - Q_{out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}} \qquad Q = T\,dS$$

from hot res.

$$= 1 - \frac{T_L \Delta S_{out}}{T_H \Delta S_{in}}$$

After each iteration, same S_A in system

ΔS_{in} removed from hot res.

ΔS_{out} added to cold res.

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

$$\frac{\Delta S_{out}}{\Delta S_{in}} \geq 1$$

$$\frac{Q_{out}/T_L}{Q_{in}/T_H} \geq 1 \rightarrow \frac{Q_{out}}{Q_{in}} \geq \frac{T_L}{T_H} > 0$$

∴ for any therm. cycle

$$\eta = 1 - \frac{Q_{out}}{Q_{in}} \leq 1 - \frac{T_L}{T_H} < 1$$

"can't break even"

Carnot cycle gives max possible η

Not used – too slow!