MATH327: StatMech and Thermo

Monday, 10 March 2025

36 32 73

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

Ideal gas law

Therm. cycles – key eqs, PV diagrams

adiabats & isotherms

Today

Carnot cycle – efficiency

1824: do work by moving heat

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

Slow isothermal and then fast adiabatic expansion

" " compression

Check cycle self-consistent

Start with $\{N, P_A, V_A\} \to T_H$, choose V_B & V_C

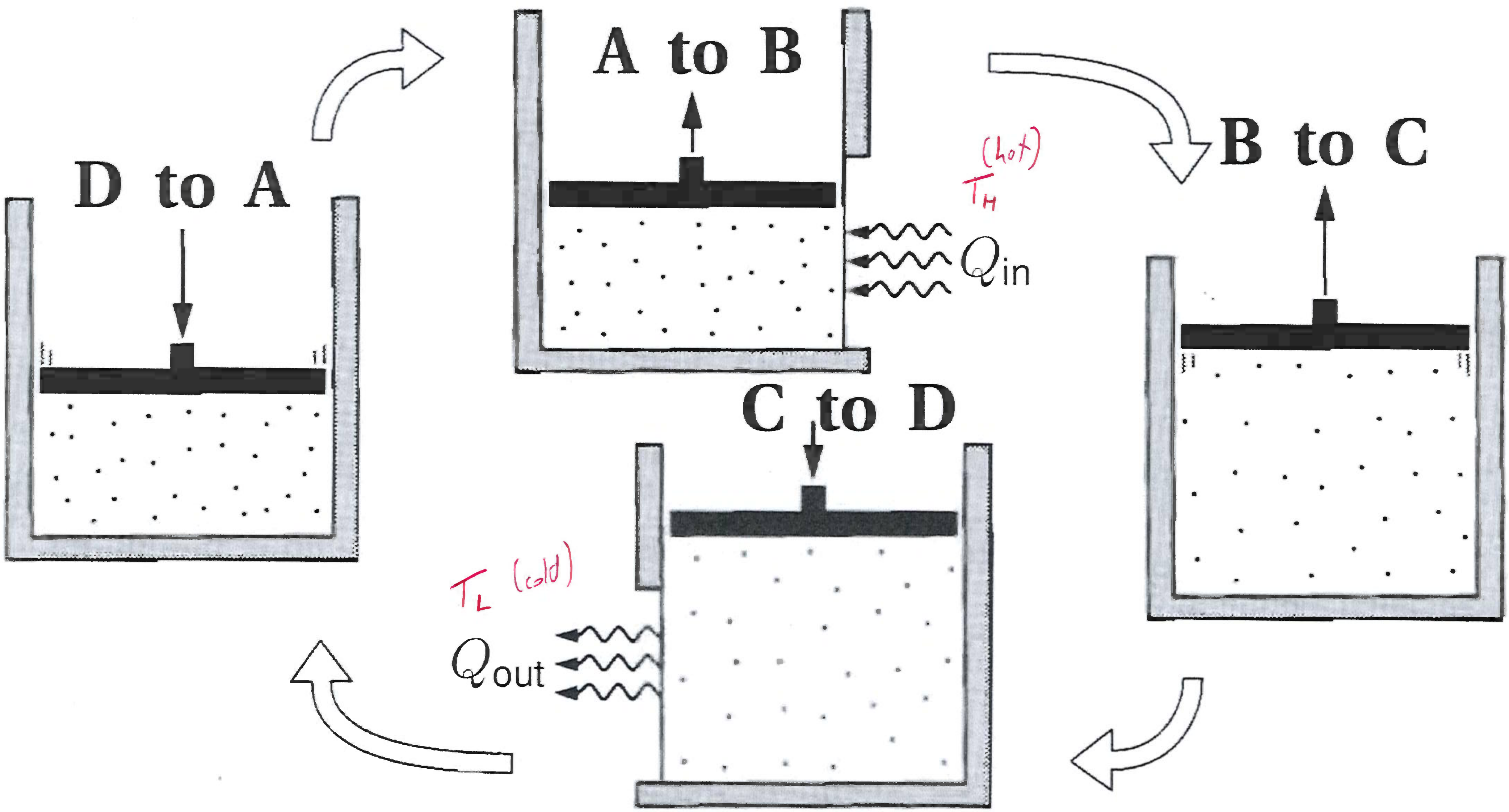
Find consistent $\{P_D, V_D\} \to T_L$

Determine points B, C, D

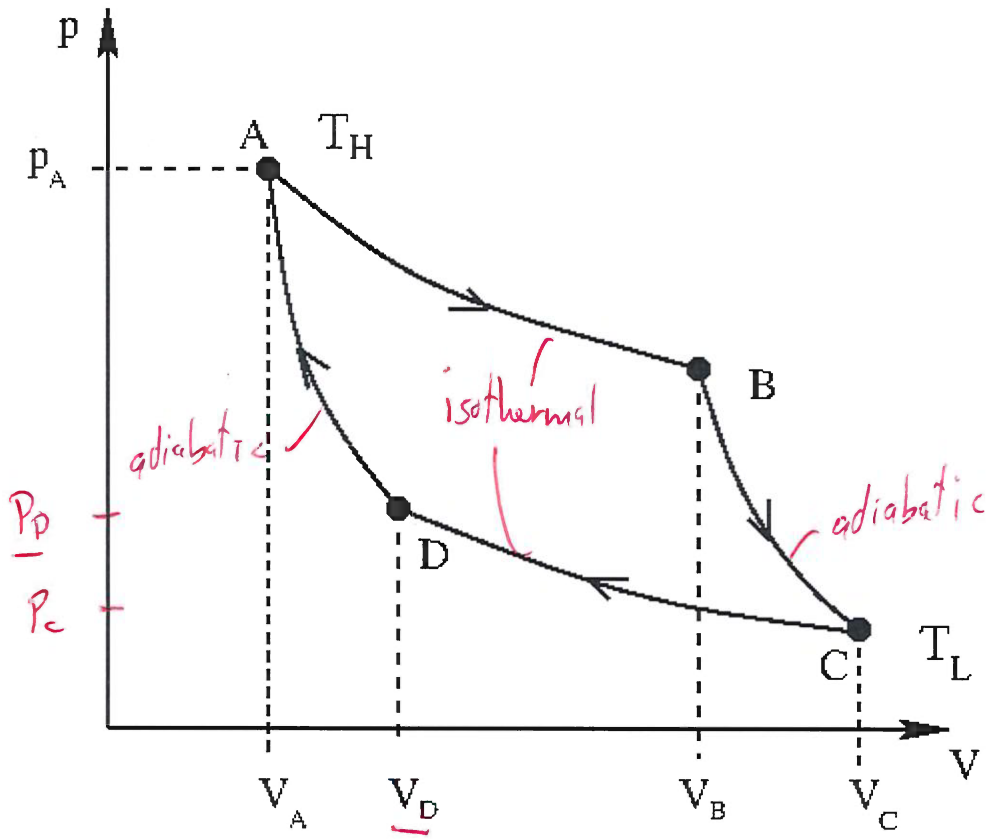
1) $A \to B$: $T_B = T_H = \dfrac{P_A V_A}{N}$

page 75

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



D to A
A to B
T_H (hot)
Q_{in}
B to C
C to D
T_L (cold)
Q_{out}



p
p_A
A
T_H
B
C
T_L
D
isothermal
adiabatic
adiabatic
p_D
p_C
V
V_A
V_D
V_B
V_C

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

$$T_L = \left(\frac{V_B}{V_C}\right)^{2/3} T_H < T_H \quad ✓$$

page 76

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

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

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

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

Constant ratios: $\frac{V_D}{V_A} = \frac{V_C}{V_B} \qquad \frac{V_D}{V_C} = \frac{V_A}{V_B}$

Finally $P_D = \frac{N T_L}{V_D} = \cancel{N}\left(\frac{V_B}{V_C}\right)^{2/3} \frac{P_A \cancel{V_A}}{\cancel{N}} \left(\frac{V_B}{V_C}\right) \frac{1}{\cancel{V_A}}$

page 76 $\qquad = \left(\frac{V_B}{V_C}\right)^{5/3} P_A < P_A$

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

$\to$ self-consistent ✓

The point: Do work by moving heat

how much? how much?

Notation to help keep track of signs

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

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

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

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

Efficiency

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

Net work done by each iteration vs. total input heat

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

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

$$W_{out} - W_{in} = Q_{in} - \underline{Q_{out}} \leq Q_{in}$$

So $0 < \eta \leq 1$ — "can't win"

Example: Carnot cycle

Check work and heat for each process

1) $A \rightarrow B$

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

page 77

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

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

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

$$\Delta\langle E\rangle_{BC} = W_{BC} = \frac{3}{2} N (T_L - T_H)$$

$$= \frac{3}{2} N T_H \left(\frac{T_L}{T_H} - 1\right)$$

$$= \frac{3}{2} P_A V_A \left[\left(\frac{V_B}{V_C}\right)^{2/3} - 1\right] < 0$$

page 77 $\qquad \rightarrow W_{out}$