MATH327: Statistical Physics

Friday, 15 March 2024

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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 and plan

PV diagrams represent processes (including adiabats and isotherms)

Combine into therm. cycles

Grand-canonical ensemble

Carnot cycle (1824) – do work by moving heat

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

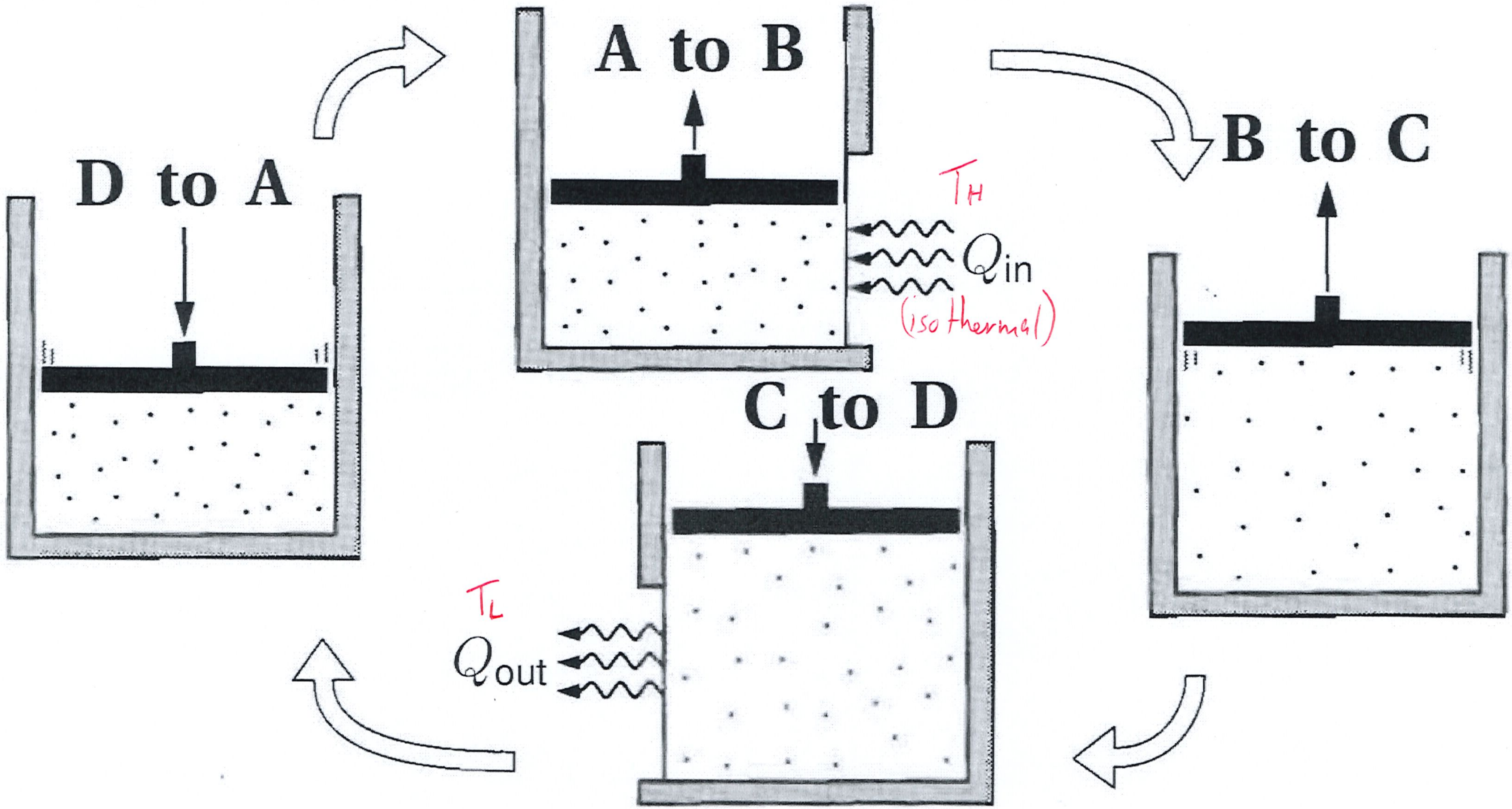
slow isothermal and then fast adiabatic expansion

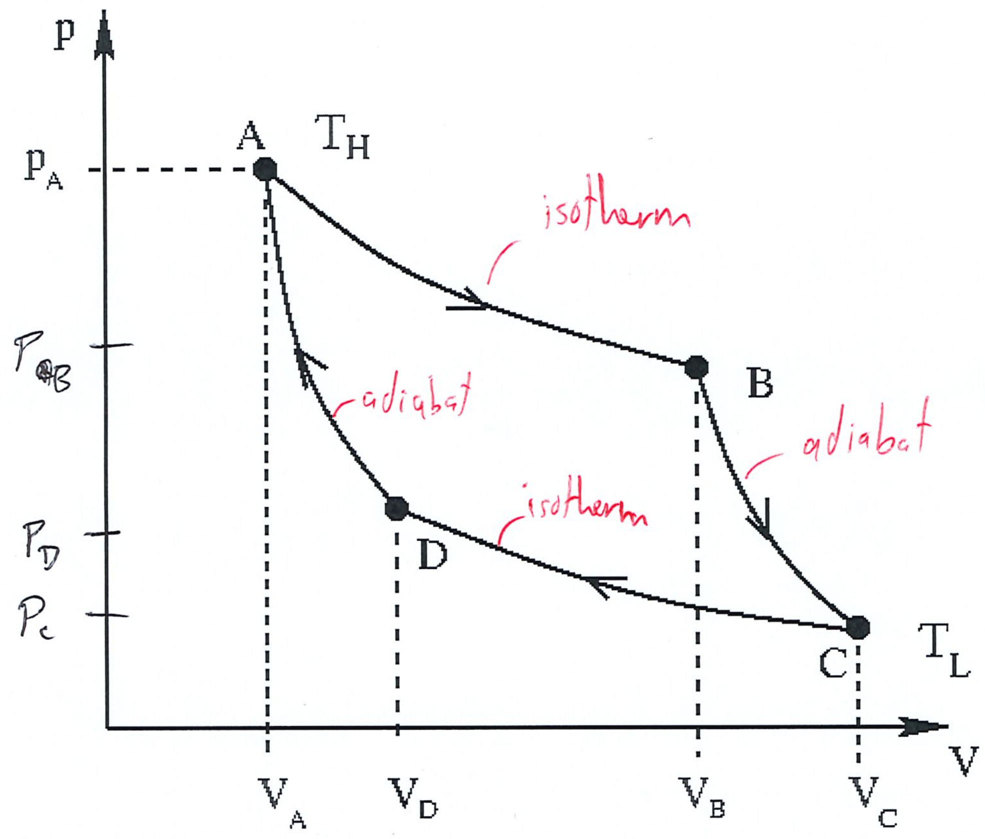
" " compression

Check cycle self-consistent

Starting with $\{N, P_A, \overset{T_H}{V_A}\}$, choose $\{V_B, V_C\}$

find consistent $\{P_D, \underset{T_L}{V_D}\}$


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


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

Determine points B, C, D

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

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

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2) $B \to C$

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

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

$$N = \frac{P_A V_A}{T_H} = \frac{P_C V_C}{T_L} \;\to\; P_C = \left(\frac{V_A}{V_C}\right)\left(\frac{T_L}{T_H}\right) P_A$$

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

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

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

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

constant ratios: $\dfrac{V_A}{V_D} = \dfrac{V_B}{V_C} \qquad \dfrac{V_A}{V_B} = \dfrac{V_D}{V_C}$

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

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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 sign

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

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

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

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

Efficiency $\quad \eta = \dfrac{W_{done}}{Q_{in}} = \dfrac{W_{out} - W_{in}}{Q_{in}}$

Net work done by interation vs. total input heat

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

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

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

So $0 < \eta \leq 1$ "can't win"

Example: Carnot cycle

Check work and heat for each process

1) $A \rightarrow B$

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

$\searrow W_{out}$

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

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

$\searrow Q_{in}$

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

$$\Delta \langle E \rangle_{BC} = W_{BC} = \frac{3}{2} N (T_L - T_H)$$
$$= \frac{3}{2} N T_H \left(\frac{T_L}{T_H} - 1 \right)$$
$$= \frac{3}{2} P_A V_A \left(\left(\frac{V_B}{V_C} \right)^{2/3} - 1 \right) < 0 \quad \hookrightarrow W_{out}$$

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3) $C \to D$

$$W_{CD} = -\int_{V_C}^{V_D} \frac{N T_L}{V} dV = P_A V_A \left(\frac{T_L}{T_H} \right) \log\left(\frac{V_C}{V_D} \right)$$
$$= P_A V_A \left(\frac{V_B}{V_C} \right)^{2/3} \log\left(\frac{V_B}{V_A} \right) > 0 \quad \hookrightarrow W_{in}$$

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

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

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

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

$$W_{out} = -W_{AB} - W_{BC} > 0$$
$$W_{in} = W_{CD} + W_{DA} > 0$$
$$Q_{in} = Q_{AB} = -W_{AB} > 0$$

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

Check $\quad 0 < \eta < 1$

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

General results

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

(no heat flow to do work)

2) Larger $\frac{T_H}{T_L} \to$ more efficient

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

$Q = T\,dS$

to cold

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

from hot res.

After each iteration, same S_A in system

ΔS_{in} removed from hot res.

ΔS_{out} added to cold res.

$$\Delta S = \Delta S_{out} - \Delta S_{in} \geq 0 \quad \text{by second law}$$

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

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

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

"can't break even"

Carnot cycle gives max. possible η

Not used because too slow!

<u>Refrigerator</u>: Reverse cycle - put in work to remove heat from cold res.

Coefficient of permance (COP)

$$\frac{Q_{in}}{W_{in} - W_{out}} = \frac{Q_{in}}{Q_{out} - Q_{in}} = \frac{1}{\frac{Q_{out}}{Q_{in}} - 1}$$

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

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

Second law $\quad \frac{Q_{out}}{Q_{in}} \geq \frac{T_H}{T_L}$

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

Typical COP $\sim 5-6$, maximized by Carnot cycle

<u>Grand-canonical ensemble</u>

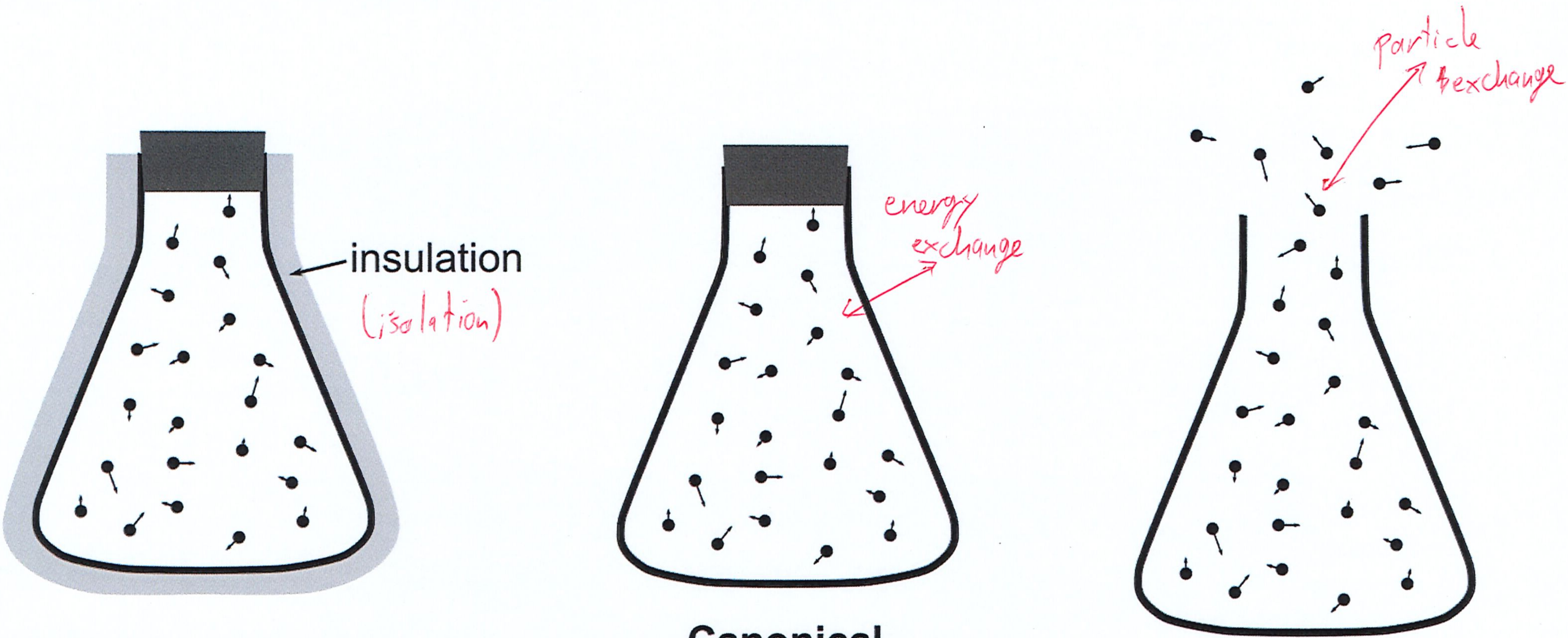
Allow <u>both</u> heat and particle exchange with particle res.
fix T what else?

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

Analogously <u>chemical potential</u> is $\mu = -T \left.\frac{\partial S}{\partial N}\right|_E$

The grand-canonical ensemble
is characterized by fixed T and μ
through energy and particle exchange with particle res.

commons.wikimedia.org/wiki/File:Statistical_Ensembles.png



Microcanonical (const. N E)

Canonical (const. N T)

Grand Canonical (const. μ T)

$\mu = -T \left.\frac{\partial S}{\partial N}\right|_E$ is intensive with dimension of energy (and T)

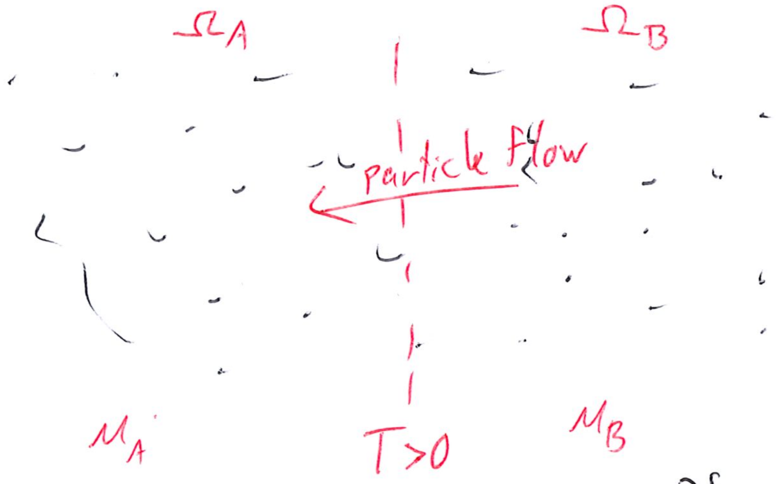
For $T > 0$ "natural" system

more particles → more entropy (even with fixed E)

$$\left.\frac{\partial S}{\partial N}\right|_E > 0 \rightarrow \mu < 0$$

Sign is choice to aid intuition

Consider particle flow with $\mu_A < \mu_B < 0$



same $\rightarrow \frac{\partial S_A}{\partial N_A} > \frac{\partial S_B}{\partial N_B} > 0$

Particle flow $\Delta N_A = -\Delta N_B$

$$\Delta S = \Delta S_A + \Delta S_B = \frac{\partial S_A}{\partial N_A}\Delta N_A + \frac{\partial S_B}{\partial N_B}\Delta N_B \geq 0 \quad (2^{nd} \text{ law})$$

$$\Delta N_A \left[\frac{\partial S_A}{\partial N_A} - \frac{\partial S_B}{\partial N_B}\right] \geq 0 \rightarrow \Delta N_A \geq 0$$

Particles flow from Ω_B (larger μ)

to Ω_A (smaller μ – more negative)

(same as heat flow w/ temperature)