MATH327: StatMech and Thermo

Tuesday, 10 March 2026

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Something to consider

Recall $\left.\frac{\partial S}{\partial E}\right|_N$ gives the inverse temperature in the micro-canonical ensemble.

How can we interpret $\left.\frac{\partial S}{\partial N}\right|_E$?

Recap

Therm. cycles

PV diagrams

Carnot cycle

Engine efficiency $\quad 0 < \eta \leq 1 - \frac{T_L}{T_H} < 1$

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

Today

Fridges & heat pumps

Grand-canonical ensemble — chemical potential

Reverse cycle — put in work to move heat

Remove Q_{in} from cold res. — refrigerator

Add Q_{out} to hot res. — heat pump

Coefficient of performance

For fridge, $COP = \dfrac{Q_{in}}{W_{in} - W_{out}} = \dfrac{Q_{in}}{Q_{out} - Q_{in}} = \dfrac{1}{Q_{out}/Q_{in} - 1}$

Now $\left.\begin{aligned} Q_{in} &= T_L \Delta S_{in} \\ Q_{out} &= T_H \Delta S_{out} \end{aligned}\right\}$ $\dfrac{Q_{out}}{Q_{in}} = \dfrac{T_H \Delta S_{out}}{T_L \Delta S_{in}} \geq \dfrac{T_H}{T_L}$

by second law

$$COP \leq \frac{1}{T_H/T_L - 1} = \frac{T_L}{T_H - T_L} > 0$$

For heat pump $COP = \dfrac{Q_{out}}{W_{in} - W_{out}} = \dfrac{1}{1 - \frac{Q_{in}}{Q_{out}}}$

$$\frac{Q_{in}}{Q_{out}} \leq \frac{T_L}{T_H} \rightarrow COP \leq \frac{1}{1 - T_L/T_H} = \frac{T_H}{T_H - T_L} > 0$$

Typical COP ~5 for fridge, ~3 for heat pump

Carnot cycle maximizes for fixed $T_H - T_L$

Smaller $T_H - T_L$ helps but may not be wanted!

Grand-canonical ensemble

Allow <u>both</u> heat and particles exchange with reservoir

$\underbrace{\text{heat}}_{\text{fix } T}$ ... $\underbrace{\text{particles}}_{\text{what else?}}$

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

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

The <u>grand-canonical</u> ensemble

is characterized by fixed T and μ

through energy and particle exchange with <u>particle</u> reservoir

$\mu = -T \left.\frac{\partial S}{\partial N}\right|_E$ is intensive, same dims as E or T

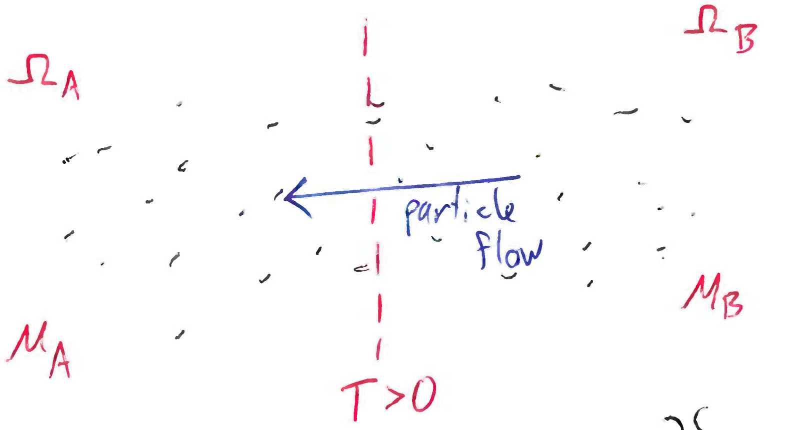
For $T>0$ "natural" systems

more particles $\rightarrow$ 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 $\mu_A < \mu_B < 0$



(indist'able)

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

$\Delta N_A = -\Delta N_B$

$$\Delta S = \Delta S_A + \Delta S_B = \frac{\partial S_A}{\partial N_A}\Delta N_A + \frac{\partial S_B}{\partial N_B}\Delta N_B \geq 0 \quad \text{by second law}$$

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

Particles flow from larger (Ω_B) to smaller μ (Ω_A)

like heat flow and T

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