MATH327: StatMech and Thermo

Wednesday, 12 March 2025

95 06 66

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

Carnot cycle

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

First law: $0 < \eta \leq 1$ "can't win"

Today

Therm. cycle wrap-up

Grand-canonical ensemble

Carnot cycle efficiency

Last time: $W_{AB} = P_A V_A \log\left(\frac{V_A}{V_B}\right) < 0 \rightarrow W_{out}$

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

$$Q_{BC} = 0$$

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

3) $C \to D$

$$\boxed{\begin{aligned} W_{CD} &= -\int_{V_C}^{V_D} \frac{NT_L}{V}\, dV = P_A V_A \left(\frac{T_L}{T_H}\right) \log\left(\frac{V_C}{V_D}\right) \\ &= P_A V_A \left(\frac{V_B}{V_C}\right)^{2/3} \log\left(\frac{V_B}{V_A}\right) > 0 \to W_{in} \end{aligned}}$$

page 78

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

4) $D \to A$

$$Q_{DA} = 0$$

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

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

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

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

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

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

So $0 < \eta < 1$

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

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

abs. zero or infinitely hot

General results

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

No heat flow to do work

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

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

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

to cold res

from hot res.

$Q = T\,dS$

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

After each iteration, same S_A in system

ΔS_{in} removed from hot res.

ΔS_{out} added to cold res.

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

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

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

$\therefore$ 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!

Reverse cycle - put in work to remove heat from cold res.

$\rightarrow$ refrigerator

Coefficient of performance (COP)

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

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

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

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

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

fix T ... what else?

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

$$-T \left.\frac{\partial S}{\partial N}\right|_E = \mu \quad \text{is } \underline{\text{chemical potential}}$$

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

is characterized by fixed T and μ

through energy and particle exchange with <u>particle</u> res.

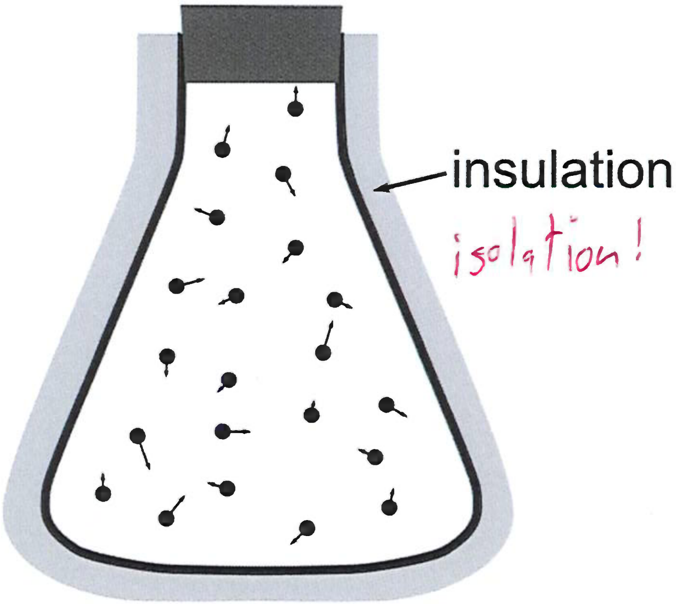
$\mu = -T \left.\frac{\partial S}{\partial N}\right|_E$ is intensive, dimensions of E & T

For $T > 0$ "natural" systems

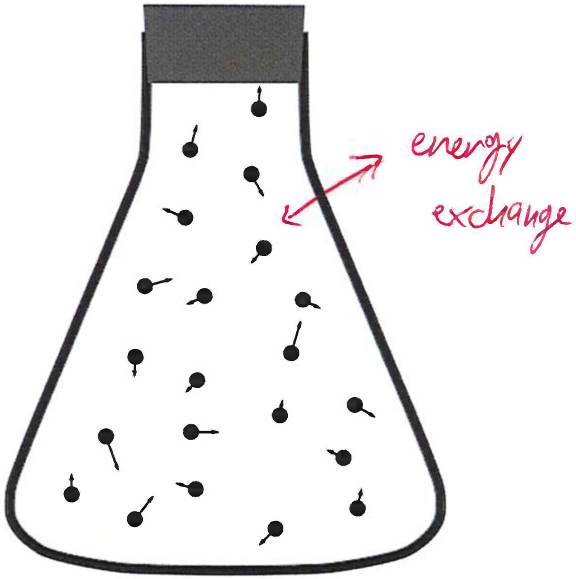
more particles → more entropy even with fixed E

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

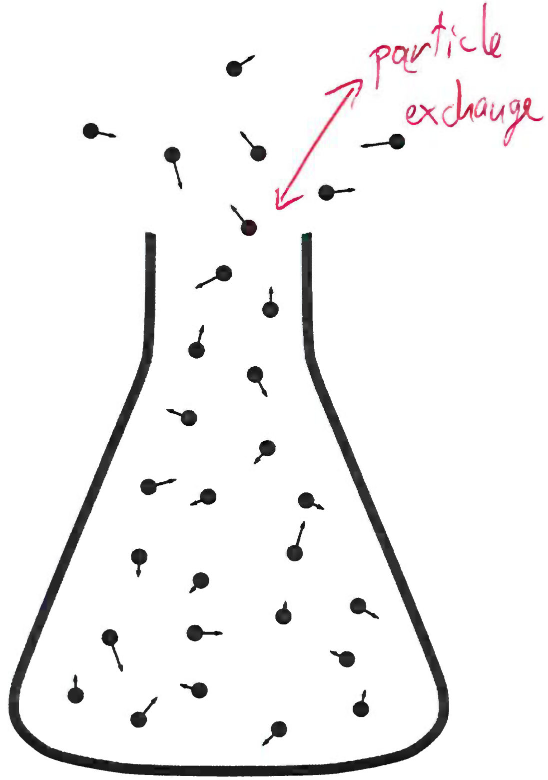
commons.wikimedia.org/wiki/File:Statistical_Ensembles.png



Microcanonical
(const. N E)



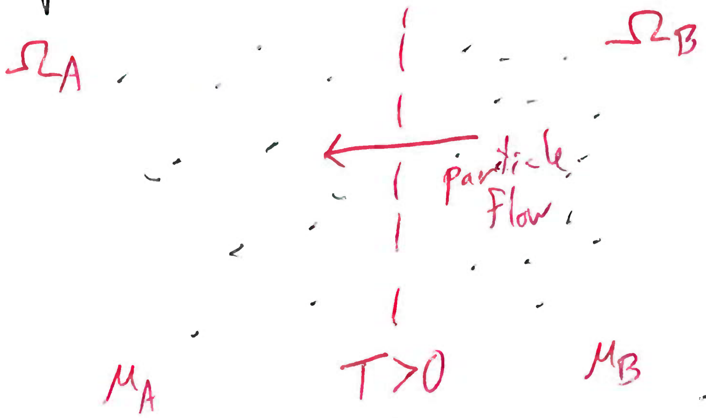
Canonical
(const. N T)



Grand Canonical
(const. μ T)

Sign in choice to aid intuition

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



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

$\Delta N_A = -\Delta N_B$

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

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

Particles flow from larger μ (Ω_B)

to smaller μ (Ω_A)

like heat flow and T

N_i and E_i depend on micro-state w_i

Want p_i free from dependence on reservoir

Adapt replica trick

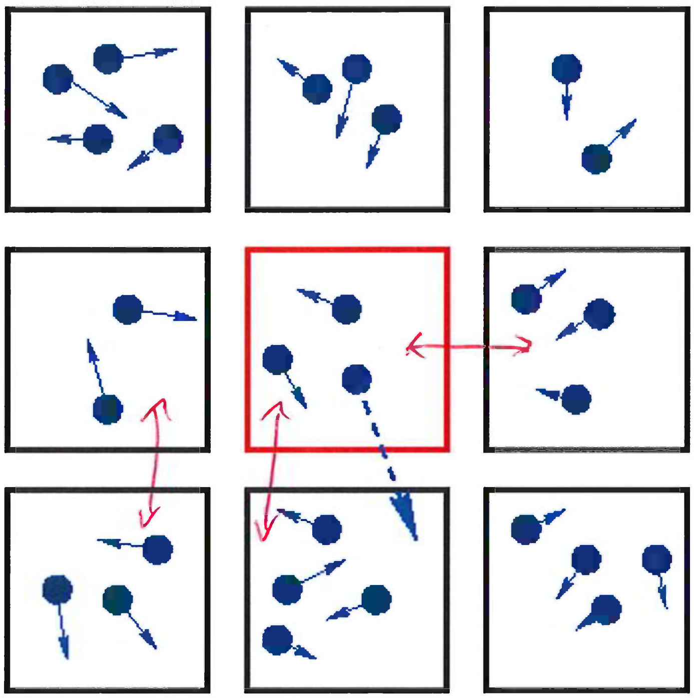
$$E_{tot} = E + E_{res} = \sum_{r=1}^{R} E_r$$

$$N_{tot} = N + N_{res} = \sum_r N_r$$

Ω has M micro-states $w_i = w_1, w_2 \cdots w_M$

with energy E_i and N_i indist'able particle

$\Omega_{tot} = \Omega \otimes \Omega_{res} \rightarrow R$ copies of Ω



Recall occupation numbers n_i

replicas in w_i

and probabilities $p_i = n_i / R$

$$\sum_{i=1}^{M} n_i = R$$

$$\sum_i p_i = 1$$

$$E_{tot} = \sum_i n_i E_i \qquad N_{tot} = \sum_i n_i N_i = R \sum_i p_i N_i$$

Compute (intensive) T and μ of micro-canonical Ω_{tot}

Need therm. equil. $\rightarrow$ maximizing S_{tot} with constraints

Same $\quad M_{tot} = \binom{R}{n_1}\binom{R-n_1}{n_2} \cdots = \dfrac{R!}{n_1! \, n_2! \cdots n_M!}$

$n_i \gg 1$

$$S_{tot} = -R \sum_i p_i \log p_i$$

Another Lagrange multiplier

$$\bar{S} = -R \sum_i p_i \log p_i + \alpha\left(\sum_i p_i - 1\right) - \beta\left(R \sum_i p_i E_i - E_{tot}\right) + \gamma\left(R \sum_i p_i N_i - N_{tot}\right)$$

$$\frac{\partial \bar{S}}{\partial p_k} = 0 = -R\left(\log p_k + 1\right) + \alpha - \beta R E_k + \gamma R N_k$$

$$\log p_k = -1 + \frac{\alpha}{R} - \beta E_k + \gamma N_k$$

$$p_k = \frac{\exp(-\beta E_k + \gamma N_k)}{\exp\left(1 - \frac{\alpha}{R}\right)} = \frac{1}{Z_g} e^{-\beta E_k + \gamma N_k}$$

page 63

Impose constraints

$$1 = \sum_i p_i = \frac{1}{Z_g} \sum_i e^{-\beta E_i + \gamma N_i}$$

$$Z_g = \sum_i e^{-\beta E_i + \gamma N_i} = Z_g(\beta, \gamma)$$

grand-canonical partition function

page 84

T and μ come from entropy

$$S_{tot} = -R \sum_i p_i \log\left(\frac{1}{Z_g} e^{-\beta E_i + \gamma N_i}\right)$$

$$= -R \sum_i p_i \left(-\log Z_g - \beta E_i + \gamma N_i\right)$$

$$= R \log Z_g + \beta E_{tot} - \gamma N_{tot}$$

page 84

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_N = R\left(\frac{\partial \beta}{\partial E}\frac{\partial}{\partial \beta}\log Z_g + \frac{\partial \gamma}{\partial E}\frac{\partial}{\partial \gamma}\log Z_g\right) + \beta + E\frac{\partial \beta}{\partial E} - N\frac{\partial \gamma}{\partial E}$$

1) $\displaystyle \frac{1}{Z_g}\sum_i \frac{\partial}{\partial \beta} e^{-\beta E_i + \gamma N_i} = \frac{1}{Z_g}\sum_i (-E_i) e^{-\beta E_i + \gamma N_i} = -\sum_i p_i E_i = \frac{-E}{R}$

2) $\displaystyle \frac{1}{Z_g}\sum_i \frac{\partial}{\partial \gamma} e^{-\beta E_i + \gamma N_i} = \sum_i p_i N_i = \frac{N}{R}$

$$\frac{1}{T} = -E\cancel{\frac{\partial \beta}{\partial E}} + N\cancel{\frac{\partial \gamma}{\partial E}} + \beta + E\cancel{\frac{\partial \beta}{\partial E}} - N\cancel{\frac{\partial \gamma}{\partial E}} = \beta \quad \checkmark$$

page 85

Similarly $\displaystyle -\frac{\mu}{T} = \left.\frac{\partial S}{\partial N}\right|_E = R\left(\cancel{\frac{\partial \beta}{\partial N}\left(\frac{-E}{R}\right)} + \cancel{\frac{\partial \gamma}{\partial N}\left(\frac{N}{R}\right)}\right) + E\cancel{\frac{\partial \beta}{\partial N}} - \gamma - N\cancel{\frac{\partial \gamma}{\partial N}}$

So $\displaystyle \gamma = \frac{\mu}{T}$

page 85

Putting things together, we have derived the micro-state probabilities

$$P_i = \frac{1}{Z_g} e^{-E_i/T + \mu N_i/T} = \frac{1}{Z_g} e^{-\beta(E_i - \mu N_i)}$$

$$Z_g(T, \mu) = \sum_i e^{-(E_i - \mu N_i)/T}$$

Both E_i and N_i Fluctuate

Reservoir unknowable apart from fixing T and μ

~~Predict~~

Preview: From Z_g predict

entropy $S(T, \mu)$

internal energy $\langle E \rangle (T, \mu)$

particle number $\langle N \rangle (T, \mu)$