MATH327: StatMech and Thermo

Monday, 17 February 2025

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Something to consider

A micro-canonical system has to be isolated from the rest of the world to ensure its internal energy is conserved.

How can we arrange to observe a system while still obeying conservation of energy (the first law)?

Recap

Second law $\rightarrow$ generalized therm. equil.

Temperature in micro-canonical ens.

Spin system

Heat exchange

Today

Canonical ensemble

Replica trick

Complete isolation required by micro-canonical ensemble is unrealistic

More practical: Canonical ensemble characterized by fixed temperature T and conserved particle # N

T fixed by thermal contact with large external reservoir ("heat bath")

System + reservoir remain micro-canonical

$\Omega \otimes \Omega_{res} = \Omega_{tot}$ with conserved $E_{tot} = E + E_{res}$

E can fluctuate without changing intensive T

Need to show details of Ω_{res} don't matter

$\rightarrow$ can consider Ω on its own

Sensible ansatz for Ω_{res} from <u>replica trick</u>

Let Ω_{res} be $R-1 \gg 1$ replicas of Ω

all in thermal contact & therm. equil.

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

Micro-state $w_i \in \Omega$ has non-conserved E_i $\quad i = 1, \ldots, M$

<u>Occupation number</u> n_i is # of replicas adopting w_i

$$\sum_{i=1}^{M} n_i = R \qquad \sum_{i=1}^{M} n_i E_i = E_{tot}$$

$$\sum_i \frac{n_i}{R} = 1 = \sum_i p_i$$

$\nwarrow$ occupation probability

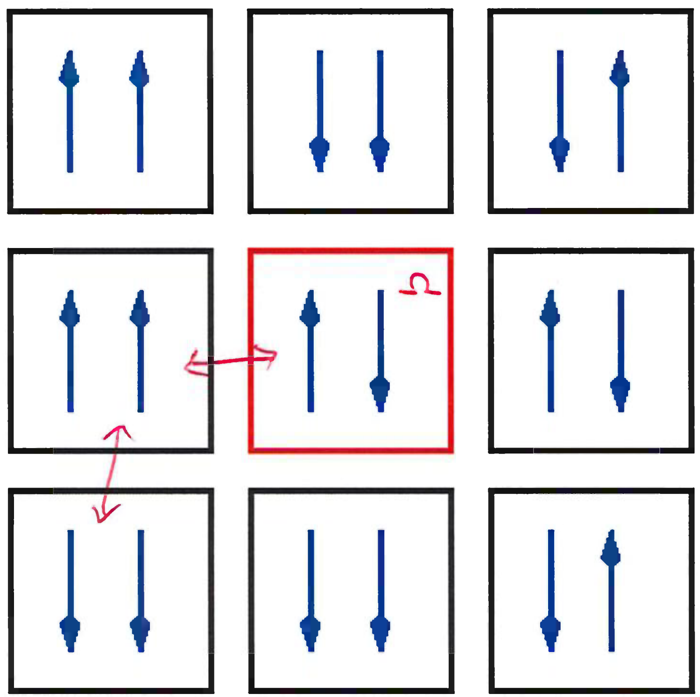
System + reservoir Ω_{tot} fully specified by $\{n_i\}$ or $\{p_i\}$

It has $\displaystyle \frac{1}{T} = \left.\frac{\partial S_{tot}}{\partial E_{tot}}\right|_{N_{tot}} = \left.\frac{\partial}{\partial E_{tot}} \log M_{tot}\right|_{N_{tot}}$

M_{tot} counts ways of arranging R replicas in set $\{n_i\}$

$$\boxed{\begin{aligned} M_{tot} &= \binom{R}{n_1}\binom{R-n_1}{n_2}\binom{R-n_1-n_2}{n_3}\cdots \\ &= \left(\frac{R!}{n_1!\,\cancel{(R-n_1)!}}\right)\left(\frac{\cancel{(R-n_1)!}}{n_2!\,\cancel{(R-n_1-n_2)!}}\right)\left(\frac{(R-\cancel{n_1-n_2})!}{n_3!\,(R-n_1-n_2-n_3)!}\right)\cdots \\ &= \frac{R!}{n_1!\,n_2!\,n_3!\cdots n_M!} \end{aligned}}$$

$R=9$



w_i	n_i
↑↑	2
↑↓	2
↓↑	2
↓↓	3
	$9=R$

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Entropy $S_{tot} = \log M_{tot} = \log(R!) - \sum_{i=1}^{m} \log(n_i!)$

Assume all $n_i \gg 1$ and approx. $\log(n!) \approx n\log n - n$

$n_i = p_i R$

$$\boxed{\begin{aligned} S_{tot} &\approx R\log R \cancel{-R} - \sum_i (n_i \log n_i \cancel{- n_i}) \\ &= \cancel{R\log R} - R\sum_i p_i(\log p_i + \cancel{\log R}) = -R\sum_i p_i \log p_i \end{aligned}}$$

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Preview: Must be maximal since in therm. equil.

Maximize entropy S_{tot} with constraints