MATH327: Statistical Physics

Friday, 23 February 2024

38 51 75

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

Micro-canonical ensemble — conserve E, N

Entropy $S = -\sum_i p_i \log p_i$ & second law

Maximize → thermodynamic equilibrium (p_i equal in M-C case)

Plan

Temperature

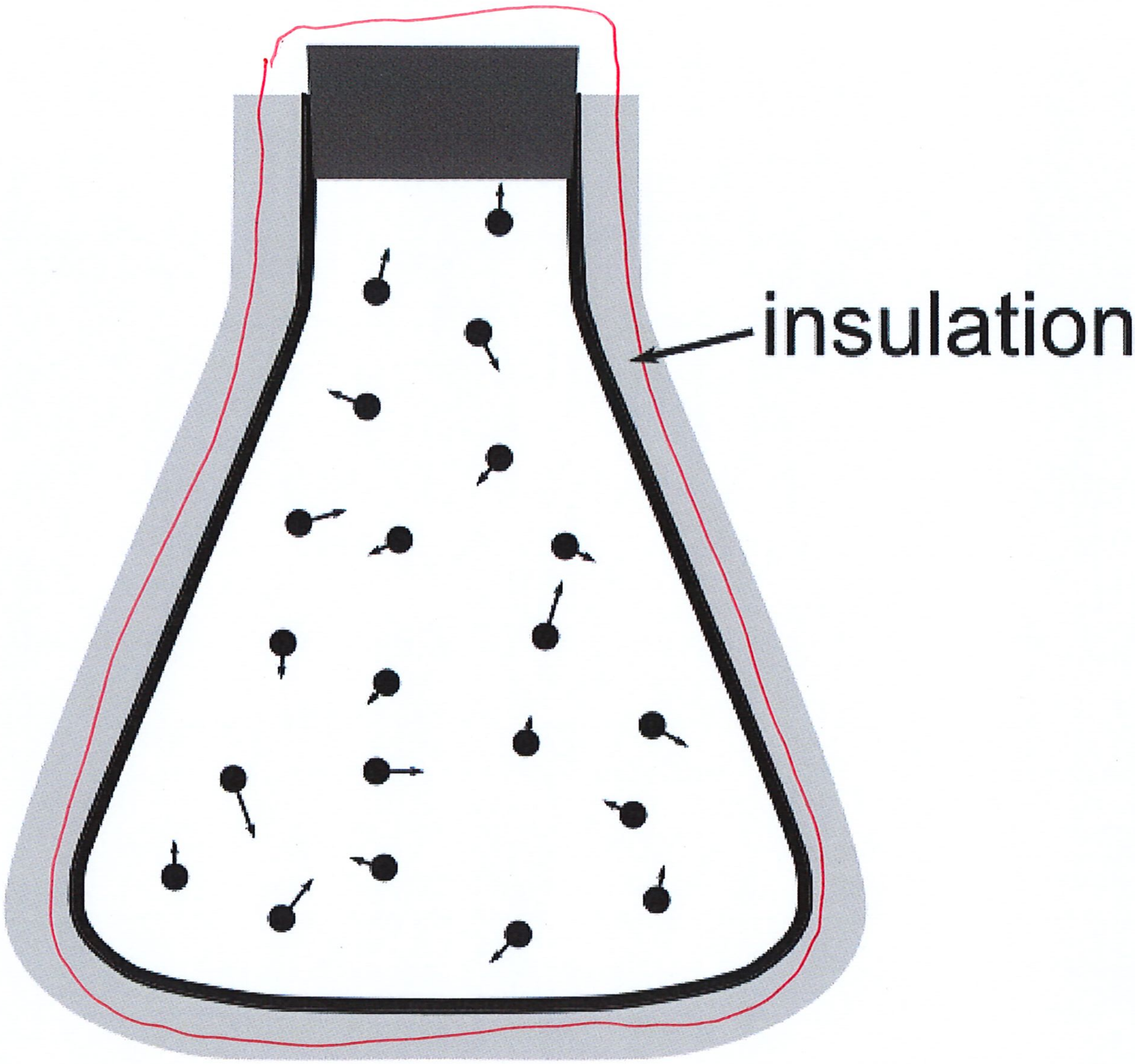
Spin system

Heat exchange

Canonical ensemble

Partition function

Heat capacity



Microcanonical
(const. N E)

Temperature – another derived quantity

$T(E,N)$ (in therm. equil.)

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_N = \left.\frac{\partial}{\partial E} \log M\right|_N \qquad \text{for micro-states}$$

Add energy $\rightarrow$ large increase in entropy

$\Updownarrow$

small temperature & vice versa

Example: Spin system $\quad E = -H(2n_+ - N)$

Different (conserved) E means different n_+, M, S, T

Lowest energy: H $\uparrow\uparrow\uparrow\cdots\uparrow$ $\quad n_+ = N \quad n_- = 0$

$E_0 = -NH \qquad M(E_0) = 1 = \binom{N}{0}$

Next-lowest energy: H $\uparrow\uparrow\uparrow\cdots\downarrow\uparrow$ $\quad n_+ = N-1 \quad n_- = 1$

$\uparrow\downarrow\uparrow\cdots\uparrow\uparrow \qquad E_1 = -H(N-1) + H = -(N-2)H$

page 35

$M(E_1) = N = \binom{N}{1}$

In general $M(E_{n_-}) = \binom{N}{n_-} = \frac{N!}{n_-!\, n_+!} = \binom{N}{n_+}$

For T, need derivative of $S = \log M$

need $\{n_+, n_-\}$ in terms of $\{E, N\}$

need differentiable approx. to $n_+!$, $N!$

System is random walk in energy space

Each spin in "step" of $\pm H$ in $E \rightarrow \pm 1$ in $x = \frac{-E}{H} = 2n_+ - N$

$\rightarrow$ simple one-dim'l example with $p = q = \frac{1}{2}$ $\qquad H > 0$

All 2^N walks (spin configs) equally likely

$$M(E_n) = 2^N P_{n_+} \qquad P_{n_+} = \frac{1}{2^N}\binom{N}{n_+}$$

Approx. P_{n_+} from CLT, $N \gg 1$

$$p(x) \approx \frac{1}{\sqrt{2\pi N \sigma^2}} \exp\left(\frac{-(x-N\mu)^2}{2N\sigma^2}\right) = \frac{1}{\sqrt{2\pi N}} \exp\left(\frac{-x^2}{2N}\right)$$

$\mu = 2p - 1 = 0$

$\sigma^2 = 4pq = 1$

Integrate distribution using constant approx,

$$P_{n_+} = p(2n_+ - N)\underbrace{\Delta n_+}_{1} = \frac{1}{\sqrt{2\pi N}} \exp\left(\frac{-E^2}{2NH^2}\right)$$

So $M(E) \approx \dfrac{2^N}{\sqrt{2\pi N}} \exp\left(\dfrac{-E^2}{2NH^2}\right)$

$$\boxed{\frac{1}{T} = \frac{\partial}{\partial E} \log M = \frac{\partial}{\partial E}\left(\frac{-E^2}{2NH^2} + E\text{-indep.}\right) = \frac{-E}{NH^2}}$$ page 36

Temperature $T = \dfrac{-NH^2}{E}$ for $N \gg 1$, $H > 0$

Unusual features:

T diverges if $E \to 0$ $(n_+ \approx n_-)$

T negative if $E > 0$ $(n_+ < n_-)$

Adding energy reduces # of micro-states

Definition: <u>Natural</u> systems have $T > 0$ (in this case $E < 0$, $n_+ > n_-$)

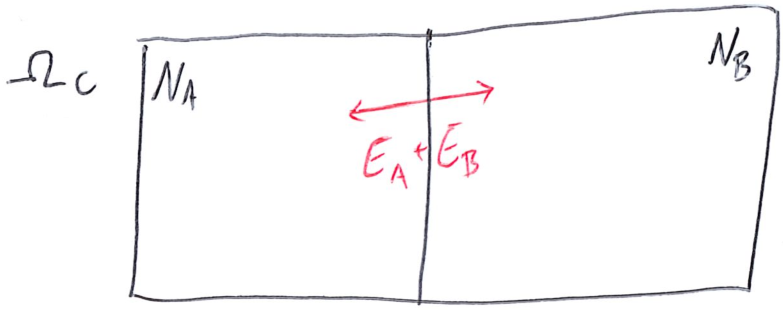
Minimum natural $T_{min} = H$ for $E_0 = -NH$ $n_- = 0$

adding energy increases temperature

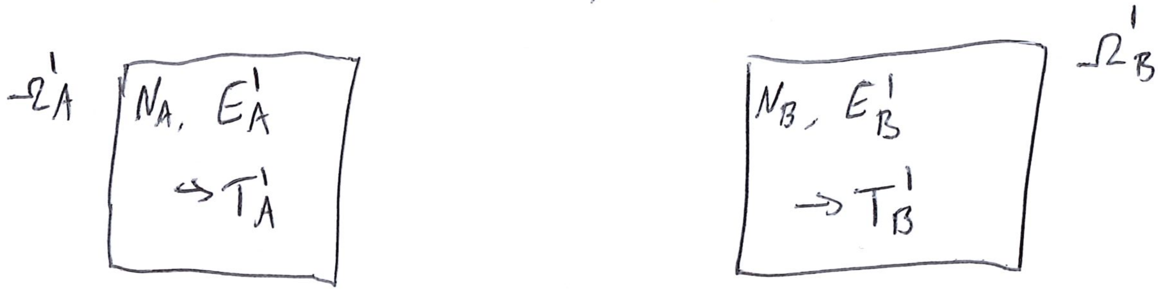
More general heat exchange – formal definition gives physically senible behaviour

1) Two isolated micro-canonical subsystems

2) Put in thermal contact, equilibrate to T_C



3) Re-isolate the two subsystems



Expect energy flow from hotter to colder system – check

Let $E'_s = E_s + \Delta E_s$ $\qquad \Delta E_A = -\Delta E_B$

Taylor expand

$$
\begin{aligned}
S(E'_s) &= S(E_s + \Delta E_s) \\
&= S(E_s) + \left.\frac{\partial S}{\partial E}\right|_{E_s} \Delta E_s + \mathcal{O}(\Delta E_s^2) \\
&\simeq S(E_s) + \frac{\Delta E_s}{T_s}
\end{aligned}
$$

page 38

Second law: $S(E_A) + S(E_B) \leq S(E_A + E_B) \leq S(E_A') + S_B(E_B')$

$$\boxed{\begin{aligned} &\cancel{S(E_A)} + \cancel{S(E_B)} \leq \cancel{S(E_A)} + \frac{\Delta E_A}{T_A} + \cancel{S(E_B)} + \frac{\Delta E_B}{T_B} \\ &\frac{\Delta E_A}{T_A} - \frac{\Delta E_A}{T_B} \geq 0 \qquad \Delta E_A \left(\frac{1}{T_A} - \frac{1}{T_B}\right) \geq 0 \end{aligned}}$$

page 39

$T_A > T_B \rightarrow \Delta E_A < 0$

Energy flow from hotter Ω_A (lower T_A') to colder Ω_B (higher T_B')

$T_A < T_B \rightarrow \Delta E_A > 0$ 〃 Ω_B 〃 Ω_A

Special case $T_A = T_B \rightarrow \Delta E = 0$ $T_s' = T_s$

Complete isolation unrealistic

More useful: <u>Canonical ensemble</u> characterized by fixed temperature T and conserved particle # N

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

System + reservoir remains 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

Replica trick

Ansatz: Let Ω_{res} be $R-1 \gg 1$ replicas of Ω
all in thermal contact & therm. equil.

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

Let E_i be (non-conserved) energy of micro-state $w_i \in \Omega$

Occupation number n_i is # of replicas adopting w_i

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

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

p_i: occupation probability

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

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

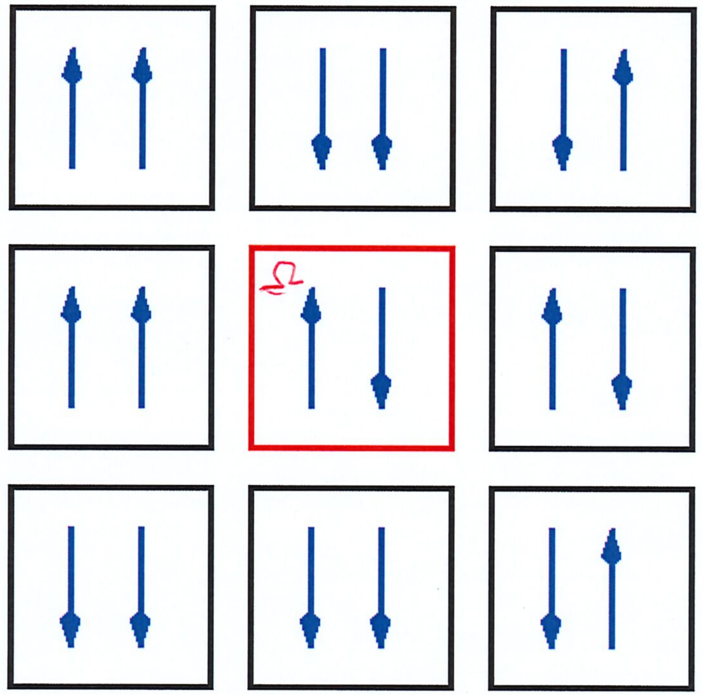
M_{tot} counts ways of arranging R replica into set $\{n_i\}$

$$M_{tot} = \binom{R}{n_1}\binom{R-n_1}{n_2}\binom{R-n_1-n_2}{n_3}\cdots$$

$$= \left(\frac{R!}{n_1!\,\cancel{(R-n_1)!}}\right)\left(\frac{\cancel{(R-n_1)!}}{n_2!\,\cancel{(R-n_1-n_2)!}}\right)\left(\frac{\cancel{(R-n_1-n_2)!}}{n_3!\,(R-n_1-n_2-n_3)!}\right)\cdots$$

$$= \frac{R!}{n_1!\,n_2!\,n_3!\cdots n_M!}$$

$R=9$



w_i	n_i
$\uparrow\uparrow$	2
$\uparrow\downarrow$	2
$\downarrow\uparrow$	2
$\downarrow\downarrow$	3

Sum: $9 = R$ ✓

page 42