MATH327: Statistical Physics

Monday, 20 February 2023

121145

Something to consider

A micro-canonical system can't exchange energy with its surroundings.

How can we observe a system without exchanging energy with it?

Recap

Micro-canonical ensemble

Thermodynamic equilibrium (dynamic)

Maximizing entropy $S = -\sum_i p_i \log p_i$

$\to \log M$

(Second Law)

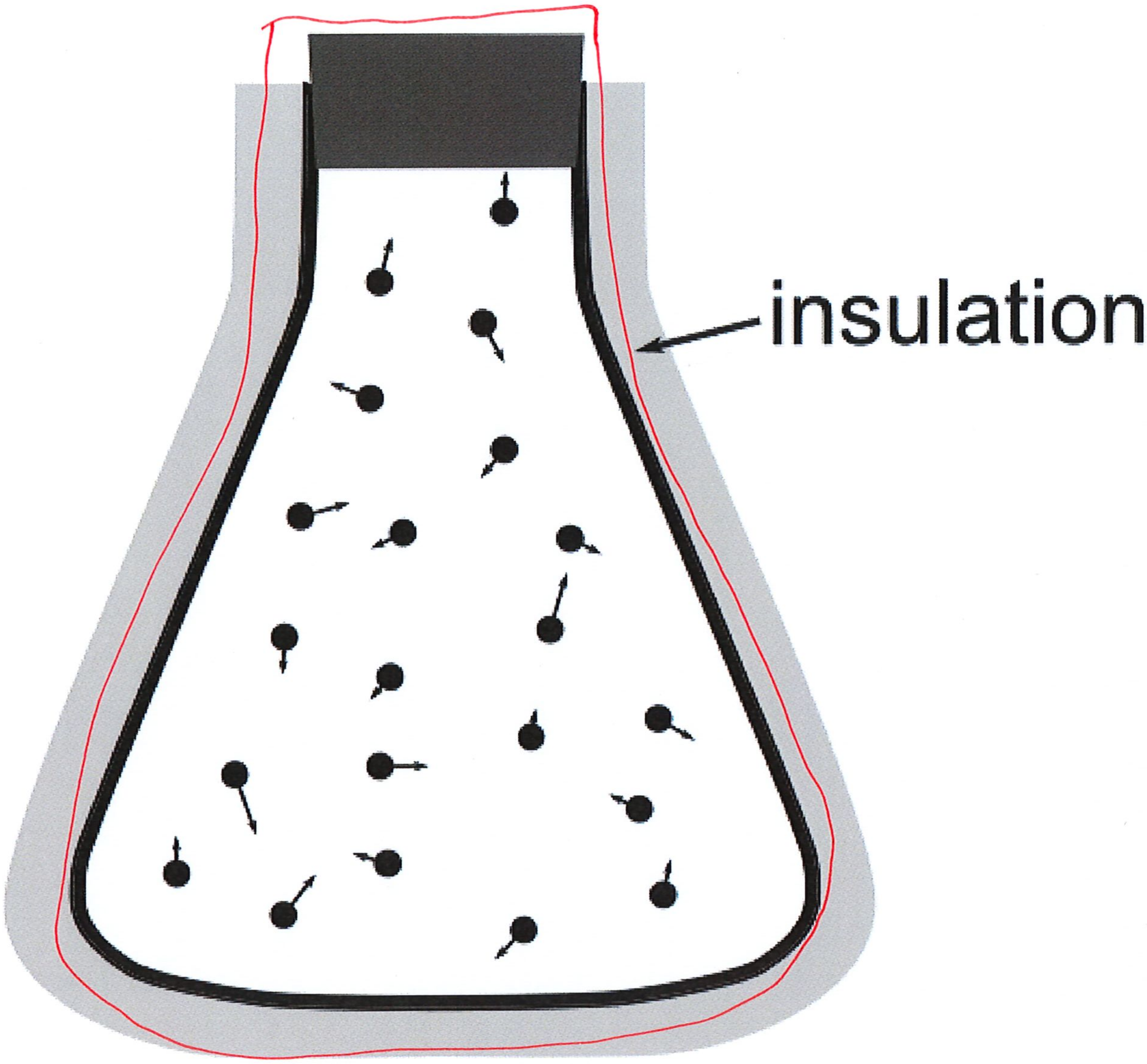
Plan

Temperature & heat exchange

Canonical ensemble

Partition function

Heat capacity



Microcanonical
(const. N E)

Temperature

Derived quantity should be stable in equil.

→ function of conserved quantities $T(E,N)$

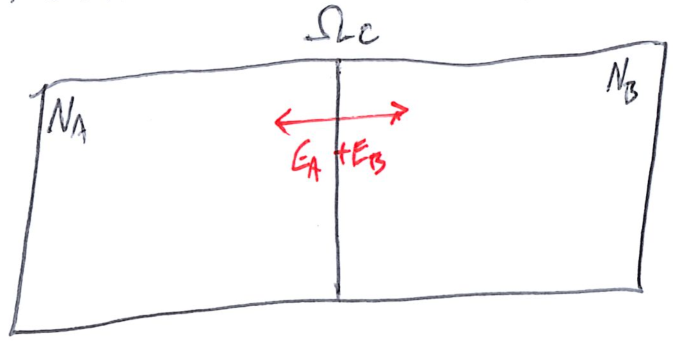
Define $$\frac{1}{T} = \frac{\partial S}{\partial E}\bigg|_N = \frac{\partial}{\partial E} \log M \bigg|_N$$

Adding energy → large increase in entropy means small temperature

Heat exchange

1) Two isolated micro-canonical systems

2) Put in thermal contact → equilibrate to $T_c > 0$



3) Re-isolate the two subsystems

Expect energy flow from hotter to colder system

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

$$\underset{(1)}{S(E_A) + S(E_B)} \leq \underset{(2)}{S(E_A + E_B)} \leq \underset{(3)}{S(E_A') + S(E_B')}$$

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

Taylor expansion

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

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$$\cancel{S(E_A)} + \cancel{S(E_B)} \leq \cancel{S(E_A)} + \frac{\Delta E_A}{T_A} + \cancel{S(E_B)} + \frac{\Delta E_B}{T_B}$$

$$\frac{\Delta E_A}{T_A} - \frac{\Delta E_A}{T_B} \geq 0$$

$$\left(\frac{1}{T_A} - \frac{1}{T_B}\right)\Delta E_A \geq 0$$

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

Energy flows from hotter system Ω_A
to colder system Ω_B

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

Same " Ω_B
Ω_A

$T_A = T_B \rightarrow \Delta E = 0$

Canonical ensemble

Complete isolation unrealistic

Instead consider canonical ensemble
characterized by fixed temperature T
and conserved particle # N

Fix temperature by thermal contact
with thermal reservoir ("heat bath")

System + reservoir remains micro-canonical

$$\Omega \otimes \Omega_{res} = \Omega_{tot}$$

$$E_{tot} = E + E_{res} \quad \text{conserved}$$

$\uparrow$ fluctuate without changing (intensive) T

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

$\rightarrow$ 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.

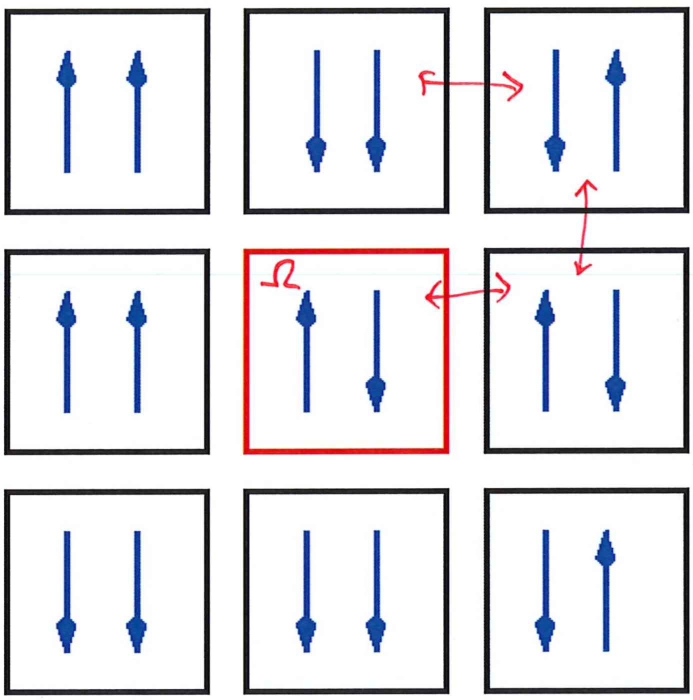
$$E_{tot} = E + E_{res} = \sum_{r=1}^{R} E_r$$

Let E_i be (non-conserved) energy of micro-state ω_i of Ω

Occupation number n_i is # of replicas adopt ω_i

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

$$\sum_i \frac{n_i}{R} = \sum_i p_i = 1 \quad \leftarrow \text{occupation probability}$$



w_i	n_i
↑↑	2
↑↓	2
↓↑	2
↓↓	3

$\sum_i n_i = 9 = R$ ✓

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

What is the temperature? $\frac{1}{T} = \frac{\partial S_{tot}}{\partial E_{tot}}\Big|_{N_{tot}} = \frac{\partial}{\partial E_{tot}} \log M_{tot}\Big|_N$

M_{tot} counts ways of arranging R replicas into $\{n_i\}$ occupation #s

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

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

Assume all $n_i \gg 1$ to apply Stirling's formula

$$S_{tot} \approx R\log R - \cancel{R} - \sum_i (n_i \log n_i - \cancel{n_i})$$
$$= \cancel{R\log R} - R\sum_i p_i(\log p_i + \cancel{\log R})$$
$$= -R\sum_i p_i \log p_i$$

$n_i = p_i R$

$\sum p_i = 1$

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Thermodynamic equilibrium $\longleftrightarrow$ maximized entropy conserving probability and E_{tot}

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

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

$$p_k = \exp\left[-\left(1-\frac{\alpha}{R}\right) - \beta E_k\right] = \frac{\exp(-\beta E_k)}{\exp\left(1-\frac{\alpha}{R}\right)}$$

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$$= \frac{1}{Z} e^{-\beta E_k}$$

Impose constraints

$$1 = \sum_i p_i = \frac{1}{Z} \sum_i e^{-\beta E_i}$$

$$Z(\beta) = \sum_i e^{-\beta E_i}$$ partition function

$$E_{tot} = R \sum_i p_i E_i$$

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

$$= R \log Z + R\beta \sum_i p_i E_i$$

$$= R \log Z + \beta E_{tot}$$

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$$\frac{1}{T} = \frac{\partial S}{\partial E} = \beta + E \frac{\partial \beta}{\partial E} + \frac{R}{Z} \frac{\partial Z}{\partial \beta} \frac{\partial \beta}{\partial E}$$

$$\frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{1}{Z} \sum_i \frac{\partial}{\partial \beta} e^{-\beta E_i} = \frac{-1}{Z} \sum_i E_i e^{-\beta E_i}$$

$$= -\sum_i p_i E_i = \frac{-E_{tot}}{R}$$

$$\frac{1}{T} = \beta + E \cancel{\frac{\partial \beta}{\partial E}} + \cancel{R\left(\frac{-E}{R}\right) \frac{\partial \beta}{\partial E}}$$

$$T = 1/\beta$$

We have derived the Gibbs distribution in therm. equil.

$$p_i = \frac{1}{Z} e^{-E_i/T} \qquad Z = \sum_i e^{-E_i/T} \qquad \frac{1}{T} = \beta$$

Boltzmann factor

Interpret p_i as probability system Ω adopt micro-state w_i with energy E_i (non-conserved)

Reservoir unknowable except for fixing temperature T

Derived quantities

Expectation value of internal energy

$$\langle E\rangle(T) = \sum_{i=1}^{M} E_i\, p_i = \frac{1}{Z}\sum_i E_i\, e^{-\beta E_i} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}$$

$$= -\frac{\partial}{\partial \beta}\log Z$$

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How does energy $\langle E\rangle$ depend on T?

Heat capacity $\quad C_V = \frac{\partial}{\partial T}\langle E\rangle \geq 0$

$\sim (E_i - \langle E\rangle)^2$ Fluctuation-response relation

Higher temperature $\rightarrow$ larger internal energy

Entropy $S = -\sum_i p_i \log p_i = -\sum_i p_i \log\left(\frac{1}{Z} e^{-\beta E_i}\right)$

$$= \log Z + \beta \sum_i p_i E_i = \log Z + \frac{\langle E\rangle}{T}$$

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$$\langle E\rangle = T\cdot S - T\log Z = T\cdot S + F$$

Helmholtz free energy $\quad F(T) = -T\log Z(T)$

Rearranging, $\quad Z = e^{-F/T}$

$$p_i = \frac{1}{Z}e^{-E_i/T} = e^{(F-E_i)/T}$$

Derivatives of $F(T)$ related to $\langle E \rangle(T)$ and $S(T)$

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \log Z = \frac{\partial}{\partial \beta}\left(\frac{F}{T}\right) = \frac{\partial T}{\partial \beta} \frac{\partial}{\partial T}\left(\frac{F}{T}\right)$$

$$= \frac{-1}{\beta^2} \frac{\partial}{\partial T}\left(\frac{F}{T}\right) = -T^2 \frac{\partial}{\partial T}\left(\frac{F}{T}\right)$$

Similarly $\frac{\partial}{\partial T} F = \frac{\partial}{\partial T}\left(-T \log Z\right) = -\log Z - T \frac{\partial}{\partial T} \log Z$

$$= -\log Z - \frac{\langle E \rangle}{T} = -S$$

$$S = -\frac{\partial}{\partial T} F$$

$$= \frac{\langle E \rangle - F}{T}$$