MATH327: Statistical Physics

Tuesday, 27 February 2024

55 15 85

Something to consider

Systems governed by the canonical ensemble can have different internal energy E_i for each micro-state ω_i.

In the very special case that all micro-states have the same energy E, will we observe behaviour similar to the micro-canonical ensemble?

Recap

Micro-canonical temperature and heat exchange

Canonical ensemble – fix T via thermal reservoir

$$\Omega_{tot} = \Omega \otimes \Omega_{res} \quad \text{micro-canonical}$$

Replica trick: Suppose Ω_{res} is $\underbrace{R-1}_{\gg 1}$ copies of Ω

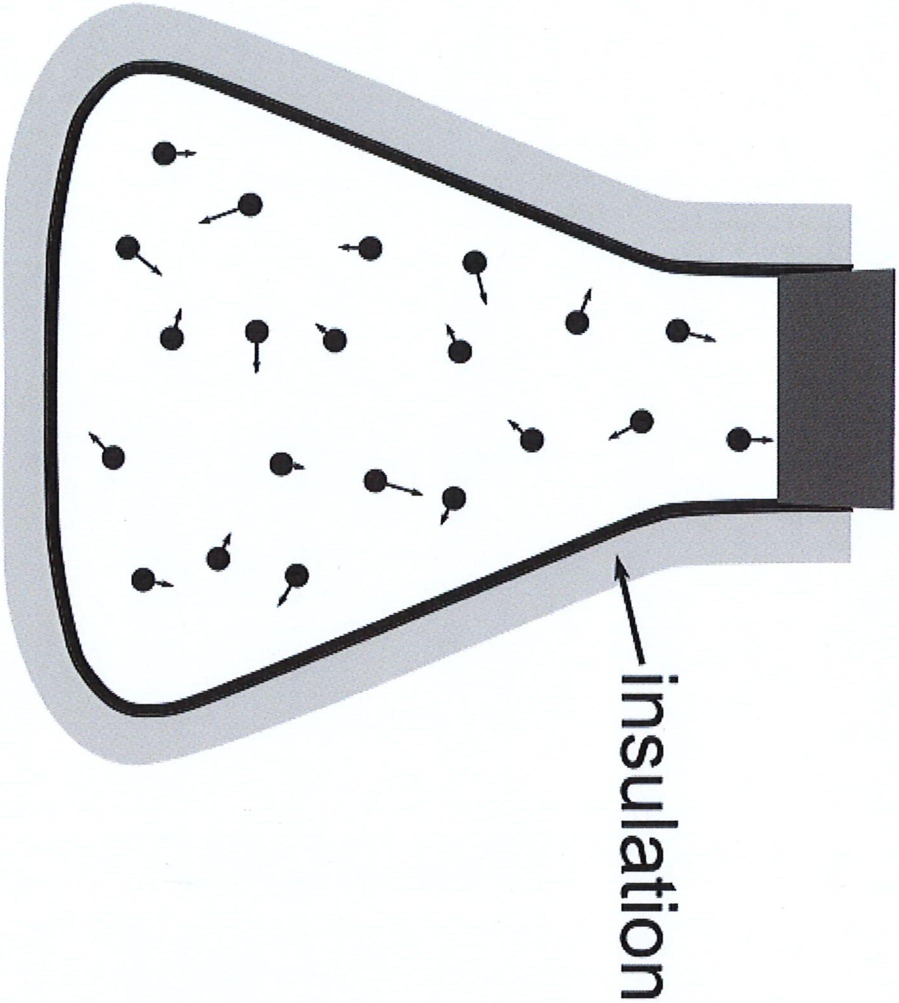
Number of micro-states $M_{tot} = \dfrac{R!}{n_1!\, n_2!\, n_3! \cdots n_M!}$

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

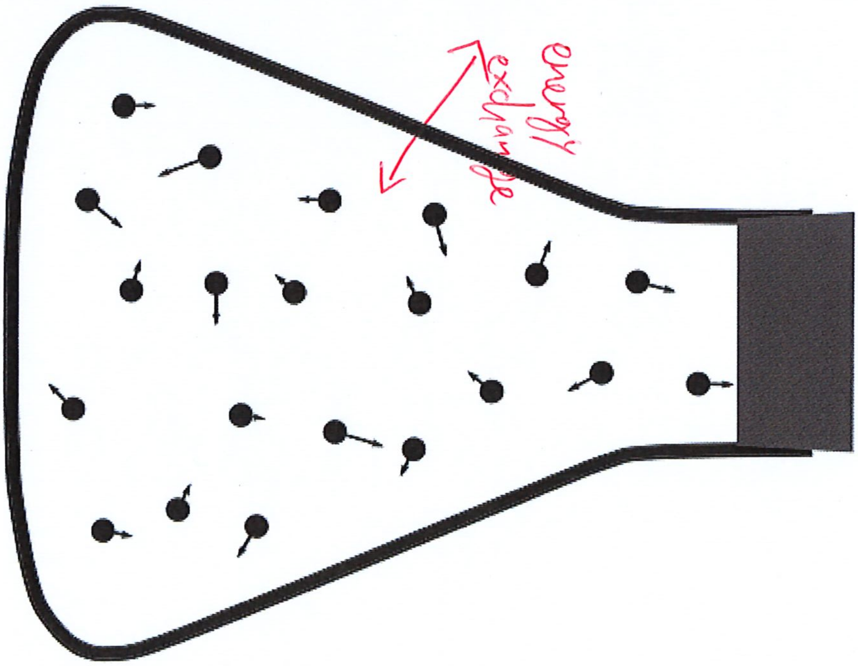
Assume all $n_i \gg 1$ and approx. $\log(n!) \approx n\log n - n$

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

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



Microcanonical
(const. N E)



Canonical
(const. N T)

Maximize entropy with constraints $\sum_i p_i = 1$

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

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

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

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

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

page 44

Impose constraints

$$\sum_i p_i = 1 = \frac{1}{Z}\sum_i e^{-\beta E_i} \quad \rightarrow \quad Z(\beta) = \sum_i e^{-\beta E_i}$$

partition function

(fundamental)

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

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

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

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

page 45

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

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

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

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

We have derived the <u>Gibbs distribution</u>

$$p_i = \frac{1}{Z} \underbrace{e^{-E_i/T}}_{\text{Boltzmann factor}} \qquad Z = \sum_i e^{-E_i/T} \qquad \frac{1}{T} = \beta$$

p_i are probability system Ω adopts micro-state ω_i with energy E_i

(Equal $E_i \rightarrow$ equal p_i)

Reservoir unknowable apart from fixing T

Derived quantities

Expectation value of internal energy

page 47

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

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

$$\underbrace{c_V}_{\text{Heat capacity}} = \frac{\partial}{\partial T} \langle E \rangle \geq 0$$

(HW: Fluctuation-response)

Higher temperature $\rightarrow$ larger internal energy

Entropy

$$\boxed{\begin{aligned} S &= -\sum_i p_i \log p_i = -\sum_i p_i \log\left(\frac{1}{Z} e^{-\beta E_i}\right) \\ &= \log Z + \beta \sum_i p_i E_i = \log Z + \frac{\langle E \rangle}{T} \\ \langle E \rangle &= T \cdot S - T \log Z = T \cdot S + F \end{aligned}}$$

page 48

<u>Helmholtz free energy</u>

$$F(T) = -T \log Z$$

$$Z = e^{-F/T}$$

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