MATH327: StatMech and Thermo

Tuesday, 17 February 2026

57 91 82

Something to consider

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

How would such systems behave in the very special case that all micro-states have the same energy E?

Recap

Micro-canonical temperature, heat exchange

Canonical ensemble

Replica trick

Occupation prob. $p_i = \frac{n_i}{R}$ for $\omega_i \in \Omega$

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

Today

Maximize entropy $\to$ partition function

Derive energy, heat capacity, free energy, ...

Maximize energy with constraints $\sum_i p_i = 1$

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

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

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

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

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

page 44

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

partition function

What is β? Relate to T via entropy

$$\boxed{\begin{aligned} S_{tot} &= -R \sum_i p_i \log p_i = -R \sum_i p_i \log\left(\frac{1}{Z} e^{-\beta E_i}\right) \\ &= +R \log Z + R\beta \sum_i E_i p_i \\ &= R \log Z + \beta E_{tot} \end{aligned}}$$

page 45

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

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

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

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

We have derived the Gibbs distribution

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

p_i are prob. that system Ω adopts micro-state w_j with energy E_i

Reservoir unknowable apart from fixing T ✓

Internal energy no longer conserved

Predict its expectation value

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

page 47

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

$\frac{\partial}{\partial T}\langle E\rangle = C_V \geq 0 \rightarrow$ higher T increases internal energy

Heat capacity

$$\boxed{\begin{aligned}&\text{Entropy } S = -\sum_i p_i \log p_i = -\sum_i p_i \log\left(\frac{1}{Z}e^{-\beta E_i}\right) \\ &\text{(not } S_{tot}\text{)} \quad = \log Z + \beta \sum_i E_i p_i = \log Z + \frac{\langle E\rangle}{T} \\ &\langle E\rangle = T\cdot S - T\log Z = T\cdot S + F\end{aligned}}$$

page 48

Helmholtz Free energy

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

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

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