MSE-421
Exercise session 2

20.03.2025

The canonical ensemble

Microcanonical Ensemble

N, V, E fixed

$$P_\nu \propto \begin{cases} 1 & \text{if } E_\nu = E \\ 0 & \text{if } E_\nu \neq E \end{cases}$$

$$P_\nu = \begin{cases} \frac{1}{\Omega} & \text{if } E_\nu = E \\ 0 & \text{if } E_\nu \neq E \end{cases}$$

Canonical Ensemble

N, V, T fixed

$$P_\nu \propto e^{-\beta E_\nu}$$

$$P_\nu = \frac{e^{-\beta E_\nu}}{Q}$$

The canonical partition function

Q, it is the normalization constant for canonical probabilities

Discrete (quantum)

$$Q = \sum_{\boldsymbol{\nu}} e^{-\beta E_{\boldsymbol{\nu}}}$$

Continuous (classical)

$$Q = \iint e^{-\beta E(\boldsymbol{p},\boldsymbol{q})} d\boldsymbol{p}\, d\boldsymbol{q}$$

A useful fact: if 1 and 2 are non-interacting: $Q_{12} = Q_1 Q_2$

The canonical partition function

It contains all the thermodynamic information about the system

$$\langle E \rangle = -\frac{\partial \ln Q}{\partial \beta}$$

$$Var(E) = \frac{\partial^2 \ln Q}{\partial \beta^2}$$

→

Both scale as the system size N, hence the relative magnitude of fluctuations $\sqrt{Var(E)}/\langle E \rangle$ scales as $N^{-\frac{1}{2}}$.

Thermodynamic potential $A = -k_B T \ln Q$

Gibbs entropy

A new definition of entropy

$$S = -k_B \sum_{\nu} P_\nu \ln P_\nu$$

- Same form as information entropy (Shannon)
- Consistent with Boltzmann definition in the NVE ensemble
- Also applicable to non-equilibrium systems

Deriving more ensembles

We derived the NVT, μVT and NpT ensembles with the "maxent" principle

- Maximize $S = -k_B \sum_\nu P_\nu \ln P_\nu$ w.r.t. all P_ν with constraints
- Use one Lagrange multiplier for each constraint
- Constant T: impose a well-defined $\langle E \rangle$
- Constant μ: impose a well-defined $\langle N \rangle$
- Constant p: impose a well-defined $\langle V \rangle$