Z is multiplicative

The partition function of multiple uncorrelated systems in contact with the same heat bath is the product of the partition functions of individual systems.

$$Z = \sum_{jk} e^{-\beta(E_j^{(A)} + E_k^{(B)})} = \sum_{jk} e^{-\beta E_j^{(A)}} e^{-\beta E_k^{(B)}}$$

$$= \left(\sum_j e^{-\beta E_j^{(A)}}\right)\left(\sum_k e^{-\beta E_k^{(B)}}\right) = Z_A Z_B$$

Notations Single-particle partition function Z_1

N-particle partition function $Z_N = \frac{Z_1^N}{N!}$

If particles are indistinguishable $\to N!$

One of the consequence is that the free energy is additive.

$$F = -k_B T \ln Z = -k_B T \ln\left(Z^{(A)} Z^{(B)}\right) = F_A + F_B$$

Equipartition Theorem

Let x_j be any component of $\mu = (\vec{q}, \vec{p})$. (That is, it can be any position or momentum component)

Expectation value

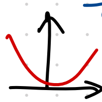
$$\left\langle x_j \frac{\partial H}{\partial x_k} \right\rangle = \frac{1}{Z} \int d\Gamma \, x_j \frac{\partial H}{\partial x_k} e^{-\beta H(\mu)}, \qquad d\Gamma = \prod_{j=1}^{N} d^3q_j \, d^3p_j$$

Notice that

$$\frac{\partial}{\partial x_k}\left[\frac{1}{\beta} e^{-\beta H(\mu)}\right] = -\frac{\partial H}{\partial x_k} e^{-\beta H(\mu)}$$

So I can perform the integration by parts on the numerator; if we define $\overline{d\Gamma_k}$ to be the integration measure but without the coordinate dx_k, then

$$\int d\Gamma \, x_j \frac{\partial H}{\partial x_k} e^{-\beta H} = \left[-x_j \frac{\partial H}{\partial x_k} e^{-\beta H} \Big|_{-\infty}^{\infty} + \frac{1}{\beta} \int dx_k \cancelto{\delta_{jk}}{\frac{\partial x_j}{\partial x_k}} e^{-\beta H} \right] \overline{d\Gamma_k}$$

If the Hamiltonian is harmonic , then $H(\infty) = H(-\infty) = \infty$ and the first term vanishes. Consequently,

$$\left\langle x_j \frac{\partial H}{\partial x_k} \right\rangle = \frac{1}{\beta} \delta_{jk} \frac{\cancel{\int d\Gamma \, e^{-\beta H}}}{\cancel{Z}} = \boxed{\delta_{jk} k_B T}$$

Review

The task of statistical mechanics is to assign probabilities to different microstates given our knowledge of the macrostate.

Microcanonical

$$p_{E,\vec{x},N}(\mu) = \frac{1}{\Omega(E,\vec{x},N)} \cdot \begin{cases} 1 & \text{if } H(\mu)=E, \\ 0 & \text{otherwise.} \end{cases}$$

$$\frac{S}{k_B} = -\langle \ln p \rangle = \ln \Omega$$

Identify partial derivatives of S with thermodynamic quantities

$$\boxed{dS = \frac{dE + P\,dV - \mu\,dN}{T}} \iff dE = T\,dS - P\,dV + \mu\,dN$$

Canonical $E \to T$

$$p_{T,\vec{x},N}(\mu) = \frac{e^{-\beta H(\mu)}}{Z} \quad \begin{cases} Z = \sum_{\mu} e^{-\beta H(\mu)} \\ \beta = \frac{1}{k_B T} \end{cases}$$

Minimize to find the most probable config.

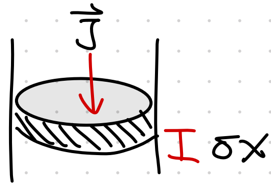
$$p(E) = \frac{e^{-\beta E}}{Z}\,\Omega(E) = \frac{e^{-\beta E + S/k_B}}{Z} = \frac{e^{\overbrace{-\beta(E-TS)}}}{Z}$$

$$\frac{S}{k_B} = -\langle \ln p \rangle = \frac{\langle E \rangle}{k_B T} + \ln Z$$

$$\therefore \boxed{-k_B T \ln Z = U - TS =: F} \quad \text{(Helmholtz free energy)}$$

$$dF = \cancel{T\,dS} - P\,dV + \mu\,dN - \cancel{T\,dS} - S\,dT = \boxed{-S\,dT - P\,dV + \mu\,dN}$$

Gibbs canonical $V \mapsto P$



Energy $H(\mu) - \vec{J}\cdot\vec{x} = H(\mu) + PV$

$$p_{T,P,N}(\mu) = \frac{e^{-\beta[H(\mu)+PV]}}{\mathcal{Z}}, \qquad \mathcal{Z} = \sum_{\mu} e^{-\beta[H(\mu)+PV]}$$

$$\frac{S}{k_B} = -\langle \ln p \rangle = \frac{\langle H \rangle + PV}{k_B T} + \ln \mathcal{Z}$$

$$\boxed{-k_B T \ln \mathcal{Z} = U - TS + PV =: G}$$ (Gibbs free energy)

$$dG = dF + d(PV) = -SdT - \cancel{PdV} + \mu dN + \cancel{PdV} + VdP$$

$$= \boxed{-SdT + VdP + \mu dN}$$

Grand canonical $N \mapsto \mu$

Energy $H(\mu) - \mu N$

$$p_{T,V,\mu}(\mu) = \frac{e^{-\beta(H-\mu N)}}{\mathcal{Q}}, \qquad \mathcal{Q} = \sum_{\mu} e^{-\beta(H-\mu N)}$$

Sorry for using the same symbols

$$\frac{S}{k_B} = \langle -\ln p \rangle = \frac{\langle H \rangle - \mu N}{k_B T} + \ln \mathcal{Q}$$

$$\boxed{-k_B T \ln \mathcal{Q} = U + TS - \mu N =: \Phi}$$ (Grand potential)

$$d\Phi = dF - d(\mu N) = -SdT - PdV + \cancel{\mu dN} - \cancel{\mu dN} - N d\mu$$

$$= \boxed{-SdT - PdV - Nd\mu}$$