NVE $\rightarrow$ NVT ensemble review

$$\frac{dS}{k_B} = d\ln\Omega = \beta dE + \beta P dV - \beta\mu dN = dy^{(0)}$$

$$d\ln Q = -E d\beta + \beta P dV - \beta\mu dN = dy^{(1)}$$

$$y^{(1)} = \frac{S}{k_B} - \beta E = \frac{TS - E}{k_B T} = -\frac{A}{k_B T} = -\beta A$$

$y^{(0)} = S/k_B = \ln\Omega$

Variables (fixed)	derivatives (fluctuate)
E	$\beta = 1/k_B T$
V	βP
N	$-\beta\mu$

$y^{(1)} = -\beta A = \ln Q$

Variables (fixed)	derivatives (fluctuate)
β	$-E$
V	βP
N	$-\beta\mu$

$$\mathcal{P}_m = \frac{1}{\Omega} \qquad\qquad \mathcal{P}_m = \frac{\exp(-\beta E_m)}{Q}$$

One can generalize this to any Legendre transformation of $y^{(0)}$. E.g.,

Isothermal - Isobaric Ensemble (NPT)

$$y^{(2)} = y^{(0)} - x_1\xi_1 - x_2\xi_2 \qquad \mathcal{P}_m = \frac{\exp(-x_1\xi_1 - x_2\xi_2)}{\Delta}$$

$$\Delta = \sum_{\text{all states}} \exp(-x_1\xi_1 - x_2\xi_2) \qquad \ln\Delta = y^{(2)}$$

Δ : partition function for NPT ensemble

Substitute: $$y^{(2)} = \frac{S}{k_B} - \beta E - \beta P V = -\frac{G}{k_B T} = \ln\Delta$$

$$\Delta = \sum_{\text{all } V_m} \sum_{\substack{\text{all } m \\ \text{at } N,V}} \exp(-\beta E_m - \beta P V_m) = \sum_{\text{all } V_m} e^{-\beta P V_m} Q(N, V_m, T)$$

$$= \sum_V \sum_E e^{-\beta E - \beta P V} \Omega(E, V, N)$$

Extending Table of variables + derivatives from previous page

$$y^{(2)} = -\beta G = \ln \Delta$$

Variables	Derivatives
β	$-E$
βP	$-V$
N	$-\beta\mu$

$$\therefore \quad \langle V \rangle = -\left.\frac{\partial \ln \Delta}{\partial \beta P}\right)_{\beta, N} = -k_B T \left.\frac{\partial \ln \Delta}{\partial P}\right)_{T, N}$$

The NPT ensemble is commonly used in simulations [volume fluctuates to sample appropriate states]

Grand Canonical Ensemble : μVT

This is still a second-order transform, but starting from a different ordering of variables:

$$y^{(0)} = S/k_B = \ln \Omega$$

var.	der.
E	β
N	$-\beta\mu$
V	βP

$$y^{(2)} = \ln \Xi = \frac{S}{k_B} - \beta E + \beta\mu N$$

var.	der.
β	$-E$
$-\beta\mu$	$-N$
V	βP

which thermodynamic potential corresponds to $\ln \Xi$ (as $N \to \infty$) ?

$$\ln \Xi = \frac{TS - E + \mu N}{k_B T} = \frac{PV}{k_B T}$$

$\Leftarrow$ not named previously, but valid for (μ, V, T) variables

Relationship between Ξ and $\langle N \rangle$:

$$\left[\frac{\partial \ln \Xi}{\partial(-\beta\mu)}\right]_{\beta, V} = -\langle N \rangle \Rightarrow k_B T \left.\frac{\partial \ln \Xi}{\partial \mu}\right)_{T,V} = \langle N \rangle$$

Probabilities of microstates: $P_m = \dfrac{\exp(-\beta E_m + \beta\mu N_m)}{\Xi(\ ,\mu, V)}$

The grand canonical partition function Ξ can be related to other partition functions:

$$\Xi(T,\mu,V) = \sum_{N_m=0}^{\infty} \sum_{\substack{\text{all states } j \\ \text{at } N_m, V}} \exp(-\beta E_j + \beta\mu N_m) =$$

$$= \underbrace{\sum_{N_m=0}^{\infty} e^{\beta\mu N_m} Q(N_m, V, T)}_{A} = \sum_{N_m=0}^{\infty} \sum_{E_j} e^{\beta\mu N_m - \beta E_j} \Omega(N_m, E_j, V)$$

A can also be expressed as $\Xi = \sum_{N=0}^{\infty} \lambda^N Q(N,V,T)$

where $\lambda = \exp(\beta\mu) \Rightarrow \mu = k_B T \ln\lambda$

[What is λ in classical thermodynamics?]

For Classical systems, we have derived the relationship:

$$Q(N,V,T) = \frac{Z(N,V,T)}{\Lambda^{3N} N!}$$ where $Z = \int \cdots \int e^{-\beta U(\vec{r}^N)} d\vec{r}^N$ is the configurational integral

$$\therefore \ \Xi(\mu, V, T) = \sum_{N=0}^{\infty} \frac{\lambda^N Z(T,V,N)}{\Lambda(T)^{3N} N!} =$$

$$= 1 + \frac{\lambda Z(T,V,N=1)}{\Lambda(T)^3} + \frac{\lambda^2 Z(T,V,N=2)}{\Lambda(T)^6\ 2!} + \cdots$$

This last expression in terms of configurational integrals of increasing order forms the basis for virial expansions of thermodynamic properties.

Example 19.3

Grand Canonical partition function for an ideal monoatomic gas

$$Z(T,V,N) = \int \cdots \int e^{0}\, d\vec{r}^{\,N} = V^N$$

Substituting for $\Xi(\mu,V,T) = \sum_{N=0}^{\infty} \frac{\lambda^N V^N}{\Lambda^{3N} N!} =$

$$= \sum_{N=0}^{\infty} \left(\frac{\lambda V}{\Lambda^3}\right)^N \cdot \frac{1}{N!}$$

Taylor expansion of exponential around $x=0$.

$$e^x = e^0 + e^0 \cdot x + \frac{1}{2!} e^0 x^2 + \cdots = \sum_{n=0}^{\infty} \frac{x^N}{N!}$$

Setting $x = \lambda V / \Lambda^3$ we get $\Xi(\mu,V,T) = \exp\left[\frac{\lambda V}{\Lambda(T)^3}\right]$

Since $\ln \Xi = \frac{PV}{k_B T} \Rightarrow \frac{\lambda \cancel{V}}{\Lambda^3} = \frac{P\cancel{V}}{k_B T} \Rightarrow$

$$\Rightarrow \exp(\beta\mu) = \beta P \Lambda^3 \Rightarrow \mu = k_B T \ln P + \mu^0(T)$$

The Grand Canonical Ensemble is also widely used in Simulations (Grand Canonical Monte Carlo) which need to sample different N's by adding particles at random locations, or deleting particles

Gibbs Entropy formula

A famous expression for the entropy S is due to Gibbs: - valid in any ensemble:

$$S = -k_B \sum_m \mathcal{P}_m \ln \mathcal{P}_m$$

m: microstates

$\mathcal{P}_m$: probability of m

[Compare to Boltzmann's $S = k_B \ln \Omega$, consistent since there are Ω states w/ $\mathcal{P}_m = \frac{1}{\Omega}$]

Proof? $$\mathcal{P}_m = \frac{\exp(-x_1 \xi_1 - x_2 \xi_2 - \cdots x_K \xi_K)}{\Upsilon}$$

(partition function, $\sum_m \exp(-x_1\xi_1 - \cdots - x_K \xi_K)$)

$$\sum_m \mathcal{P}_m \ln \mathcal{P}_m = \sum_m \mathcal{P}_m \left[-x_1 \xi_1 - x_2 \xi_2 - \cdots x_K \xi_K - \ln \Upsilon \right]$$

In this ensemble, $\xi_1, \xi_2 \ldots \xi_K$ are constant:

$$\therefore \sum_m \mathcal{P}_m \ln \mathcal{P}_m = -\xi_1 \sum_m \mathcal{P}_m x_1 - \xi_2 \sum_m \mathcal{P}_m x_2 - \cdots - \xi_K \sum_m \mathcal{P}_m x_K - \ln \Upsilon$$

$$= -\xi_1 \langle x_1 \rangle - \xi_2 \langle x_2 \rangle - \cdots \xi_K \langle x_K \rangle - \ln \Upsilon$$

but - $$y^{(K)} = \ln \Upsilon = \frac{S}{k_B} - \xi_1 x_1 - \xi_2 x_2 - \cdots - \xi_K x_K$$

At thermodynamic limit, $\langle x_i \rangle$ is the same as x_i

$$\sum_m \mathcal{P}_m \ln \mathcal{P}_m = -\frac{S}{k_B} \quad \text{QED}$$