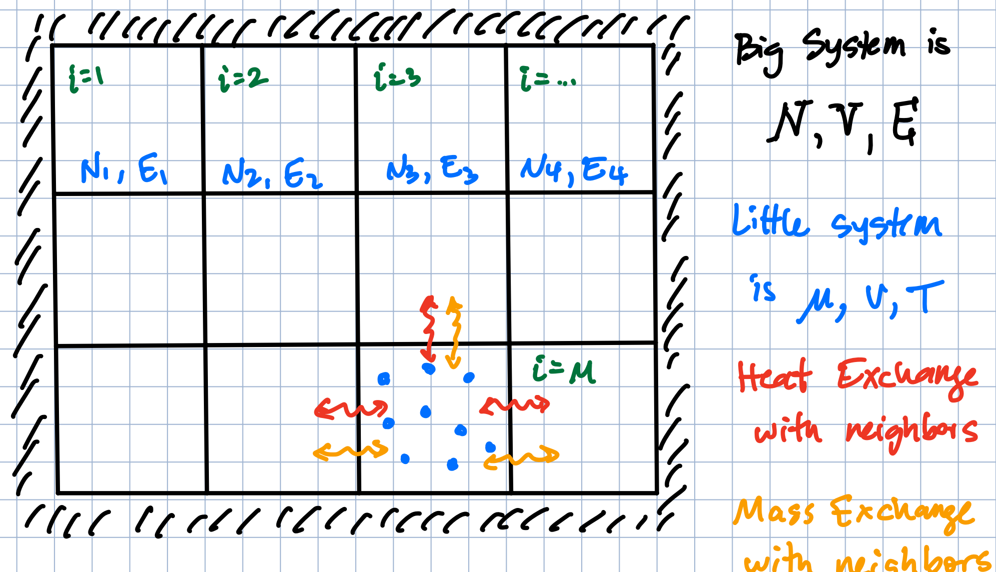
Lecture 19 – The Grand Canonical Ensemble

A. Grand Canonical Probability Density

We saw that we could define the microcanonical (NVE) ensemble and get thermodynamics, and we can define the canonical (NVT) ensemble to get thermodynamics. Are there other ensembles? Yes! The ensemble with constant μVT, where μ is the chemical potential is the Grand canonical ensemble. Note that μ is the thermodynamic conjugate variable to N. As before, there is no reason why we have more/less information with either N or μ.

We can construct a μVT-ensemble in a way that is similar to how we obtained an NVT ensemble from an NVE ensemble.



- Now, both the energy and number of molecules in each bin can vary: N_i, E_i
- The occupation number can now make a 2D matrix:

$$m_{jk} = \sum_{i=1}^{M} \delta(E_i - E_j)\,\delta(N_i - N_k) \qquad \delta(E_i - E_j) = \begin{cases} 1 & \text{if } E_i = E_j \\ 0 & \text{otherwise} \end{cases}$$

M: Total # of ensembles

$$\delta(N_i - N_k) = \begin{cases} 1 & \text{if } N_i = N_k \\ 0 & \text{otherwise} \end{cases}$$

$j \in \{1, J\}$, J: # of energy levels $\underline{\underline{m}} = m_{jk}$ = matrix of occupation #'s in the ensemble.

$k \in \{1, K\}$, K: # of particles (possible)

Similar to before, we want to find the probability mass function

$$P_{\mu V T} = \frac{\langle m_{jk} \rangle}{M}$$

Using the now-familiar logic, we know that the number of ways we can arrange the occupation of particles and energy is going to be almost certainly the maximum.

$$\langle m_{jk} \rangle \approx m_{jk}^{*} \quad \leftarrow \text{most likely distribution}$$

$$P_{\mu V T} = \frac{m_{kj}^{*}}{M}$$

To find the most probable distribution, we are going to maximize the # of ways of distributing both energy and mass subject to the NVE constraints.

$$W(\underline{\underline{m}}) = \frac{M!}{\prod_{j=1}^{J} \prod_{k=1}^{K} m_{jk}!} \qquad \sum_{j=1}^{J} \sum_{k=1}^{K} m_{jk} = M$$

$$\sum_{j=1}^{J} \sum_{k=1}^{K} m_{jk} E_j = \mathcal{E} \qquad \sum_{j=1}^{J} \sum_{k=1}^{K} m_{jk} N_k = \mathcal{N}$$

Accordingly we define

$$f(m_{jk}) = \ln W(m_{jk}) - \alpha \left[\sum_j \sum_k m_{jk} - M \right]$$
$$- \beta \left[\sum_j \sum_k m_{jk} E_j - \mathcal{E} \right] - \gamma \left[\sum_j \sum_k m_{jk} N_k - \mathcal{N} \right]$$

And we seek the solution to

$$\left.\frac{df}{dm_{jk}}\right|_{m_{jk}^*} = 0$$

$$\frac{df}{dm_{jk}} = \underbrace{\frac{d}{dm_{jk}}(\ln W)}_{1} - \underbrace{\frac{d}{dm_{jk}}\left[\sum_j \sum_k m_{jk} - M\right]}_{2}$$
$$- \underbrace{\frac{d}{dm_{jk}}\left[\sum_j \sum_k m_{jk} E_j - E\right]}_{3} - \underbrace{\frac{d}{dm_{jk}}\left[\sum_j \sum_k m_{jk} N_k - N\right]}_{4}$$

1) $$\frac{d}{dm_{jk}}(\ln W) = \frac{d}{dm_{jk}}\left[\ln\left(\frac{M!}{\prod_j \prod_k m_{jk}!}\right)\right]$$
$$= \frac{d}{dm_{jk}}\left[\cancel{\ln M!} - \sum_j \sum_k \ln m_{jk}!\right]$$

$\ln m_{jk}! = m_{jk} \ln m_{jk} - m_{jk}$

$$= \frac{d}{dm_{jk}}\left[-\sum_j \sum_k m_{jk} \ln m_{jk} - m_{jk}\right]$$

only one survives. (note the abuse of notation of dummy vars j, k)

$$= -\frac{d}{dm_{jk}}\left(m_{jk} \ln m_{jk} - m_{jk}\right)$$
$$= -\ln m_{jk} - m_{jk} \cdot \frac{1}{m_{jk}} + 1 = -\ln m_{jk}$$

2) $$\frac{d}{dm_{jk}}\left[\underbrace{\sum_j \sum_k m_{jk}}_{\text{only 1 survives}} - \underbrace{M}_{0}\right] = \frac{d}{dm_{jk}}(m_{jk}) = 1$$

3) $$\frac{d}{dm_{jk}}\left[\underbrace{\sum_j \sum_k m_{jk} E_j}_{\text{only 1 survives}} - \underbrace{E}_{0}\right] = \frac{d}{dm_{jk}}(m_{jk} E_j) = E_j$$

4) $$\frac{d}{dm_{jk}}\left[\underbrace{\sum_j \sum_k m_{jk} N_k}_{\text{only 1 survives}} - \underbrace{N}_{0}\right] = \frac{d}{dm_{jk}}(m_{jk} N_k) = N_k$$

Putting it all together gives

$$\frac{df}{dm_{jk}} = -\ln m_{jk}^* - \alpha - \beta E_j - \gamma N_k = 0$$

$$\ln m_{jk}^* = -\alpha - \beta E_j - \gamma N_k$$

$$\boxed{m_{jk}^* = e^{-\alpha} e^{-\beta E_j} e^{-\gamma N_k}}$$

most likely distribution for grand canonical ensemble

The probability mass function is

$$P = \frac{m_{jk}^*}{M} = \frac{e^{-\alpha} e^{-\beta E_j} e^{-\gamma N_k}}{M}$$

We can solve for α in terms of M using the fact that

$$\sum_j \sum_k P = 1 \longrightarrow \sum_j \sum_k e^{-\alpha} e^{-\beta E_j} e^{-\gamma N_k} \frac{1}{M} = 1$$

$\leftarrow$ no N or j dependence.

$$e^{-\alpha} \sum_j \sum_k e^{-\beta E_j} e^{-\gamma N_k} = M \quad \leftarrow \text{sub into P}$$

$$P = \frac{\cancel{e^{-\alpha}} e^{-\beta E_j} e^{-\gamma N_k}}{\cancel{e^{-\alpha}} \sum_j \sum_k e^{-\beta E_j} e^{-\gamma N_k}}$$

$$\boxed{P_{\mu V T} = \frac{e^{-\beta E_j} e^{-\gamma N_k}}{\sum_j \sum_k e^{-\beta E_j} e^{-\gamma N_k}}}$$

PMF for the Grand Canonical ensemble.

What are β and γ? We will get this in the next section.

But (spoiler alert) $\beta = 1/k_B T$ and $\gamma = -\mu/k_B T$

The denominator is the Grand (Canonical) Partition function

$$\Xi(\mu, V, T) = \sum_j \sum_k e^{-\beta E_j} e^{-\gamma N_k}$$

Ξ: capital xi (ξ)

Sometimes caligraphic $\mathcal{Z}$

$$= \sum_k Q(N_k, V, T)\, e^{-\gamma N_k}$$

note the similarity with how we wrote Q in terms of Ω.

How are these expressed in continuum/classical statistical mechanics?

$$\boxed{\Xi = \sum_{N=0}^{\infty} \frac{e^{\beta\mu N}}{h^{3N} N!} \int_\Gamma e^{-\beta H_N(\underline{x})}\, d\underline{x}}$$

$\sum_k \to \sum_{N=0}^{\infty}$, $\sum_j \to \int d\underline{x}$

$\gamma = -\beta\mu$, $E_j \to H(\underline{x})$, $N_k \to N$

$H(\underline{x})$ depends on N

$$\Xi = \Xi(\mu, V, T) = \sum_{N=0}^{\infty} \frac{z^N}{h^{3N} N!} \int_\Gamma e^{-\beta H_N(\underline{x})}\, d\underline{x} = \sum_{N=0}^{\infty} \frac{z^N}{h^{3N} N!} Q_N$$

$z = e^{\beta\mu}$ fugacity or activity $\qquad \beta = 1/k_B T$

What about the probability density?

$$\rho(\underline{x}) = \frac{e^{\beta\mu N} e^{-\beta H(\underline{x})}}{\sum_{N=0}^{\infty} e^{\beta\mu N} \int_\Gamma e^{-\beta H(\underline{x})}\, d\underline{x}}$$

not as common b/c it is missing the corrections for overcounting in numerator and denominator

$$\boxed{\tilde{\rho}(\underline{x}) = \frac{1}{\Xi} \exp\left[-\beta H(\underline{x}) + \beta\mu N\right]}$$

Probability density for classical μVT ensemble

B. Connecting GCE to Thermodynamics

To connect the GCE to thermodynamics, we need the Gibbs entropy formula,

$$S = -k_B \langle \ln \tilde{\rho} \rangle$$

$$= -k_B \sum_{N=0}^{\infty} \frac{1}{h^{3N} N!} \int_\Gamma \tilde{\rho}(\underline{x}) \ln \tilde{\rho}(\underline{x})\, d\underline{x} \qquad \tilde{\rho}(\underline{x}) = \frac{e^{-\beta H + \beta\mu N}}{\Xi}$$

$$S = -k_B \sum_{N=0}^{\infty} \frac{1}{h^{3N} N!} \int_\Gamma \tilde{\rho}(\underline{x}) \ln\left(\frac{1}{\Xi} e^{-\beta H + \beta\mu N}\right) d\underline{x}$$

$$= -k_B \sum_{N=0}^{\infty} \frac{1}{h^{3N} N!} \int_\Gamma \left[\tilde{\rho}(\underline{x}) \ln \frac{1}{\Xi} + \tilde{\rho}(\underline{x}) \ln e^{-\beta H + \beta\mu N}\right] d\underline{x}$$

$$= -k_B \ln \frac{1}{\Xi} \underbrace{\sum_{N=0}^{\infty} \frac{1}{h^{3N} N!} \int_\Gamma \tilde{\rho}(\underline{x})\, d\underline{x}}_{1}$$

$$- \underbrace{k_B \beta}_{1/k_BT} \sum_{N=0}^{\infty} \frac{1}{h^{3N} N!} \underbrace{\int_\Gamma (-H + \mu N)\, \tilde{\rho}(\underline{x})\, d\underline{x}}_{\langle -H + \mu N \rangle}$$

$$= k_B \ln \Xi + \frac{1}{T} \underbrace{\langle H \rangle}_{U} - \frac{\mu}{T} \underbrace{\langle N \rangle}_{N}$$

$$\boxed{S = k_B \ln \Xi + \frac{U}{T} - \frac{\mu N}{T}}$$ Entropy in GCE

There is a more compact way.

$A = U - TS$ Helmholtz Free Energy

$\Phi = A - \mu N$ Grand Potential

$$A = U - T\left[k_B \ln \Xi + \frac{U}{T} - \frac{\mu N}{T}\right] = \cancel{U} - k_B T \ln \Xi - \cancel{U} + \mu N$$

$$\boxed{A = -k_B T \ln \Xi + \mu N}$$ Helmholtz Free Energy in GCE

$\Phi = A - \mu N$

$\Phi = -k_B T \ln \Xi + \mu N - \mu N$

$$\boxed{\Phi = -k_B T \ln \Xi}$$ Key Relationship for GCE!

$\Phi = \Phi(\mu, V, T)$

What is the Grand potential Φ?

$\Phi = A - \mu N \qquad G = \mu N \qquad G = A + PV$

$\Phi = A - G = -PV$!

So, we can then write

$$\boxed{PV = k_B T \ln \Xi}$$ Grand canonical relation for thermodynamics.

$\Xi = \Xi(\mu, V, T)$

easy to get PVT E.O.S.