

# Lecture 15

## CH-4114

### Molecular Simulation

**“Everything that living things do can be understood in terms of the jiggings and wiggings of atoms.”**

**- Richard P. Feynman**

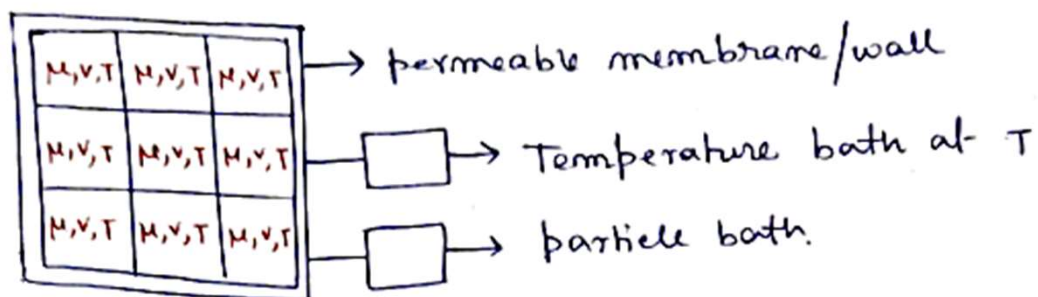
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# Handling Simulations of Different Ensembles + Fluctuation and Response Function

## Grand Canonical Ensemble

### Framework



We must specify here the quantum state of each system but also the number of molecules in each system. For each value of  $N$  has a particular set of energy levels associated with it, so we first specify  $N$  and then  $j$ . The set of occupation number  $\{M_{N,j}\}$  is a distribution. By equal a priori probability postulate, we assume that all states associated with all possible distributions have equal probabilities of occurrence in the ensemble. Each possible distribution must satisfy the following three conditions:

$$\sum_N \sum_j M_{Nj} = M \quad (1) \quad M = \text{Total number of members/ systems in the ensemble.}$$

$$\sum_N \sum_j M_{Nj} E_{Nj} = E \quad (2) \quad E = \text{total energy of the ensemble.}$$

$$\sum_N \sum_j M_{Nj} N = N \quad (3) \quad N = \text{Total number of molecules.}$$

For any possible distribution, the number of states is given by,

$$\Gamma(\{M_{Nj}\}) = \frac{M!}{\prod_N \prod_j M_{Nj}!} \quad (4)$$

As in the canonical ensemble, the distribution that maximizes  $\Gamma$  subject to appropriate constraints completely dominates all others. Thus we maximize (4) under the constraints of equation (1) to (3) and we get:

$$M_{Nj}^* = e^{-\alpha} e^{-\beta E_{Nj}} e^{-\gamma N}$$

As before  $\alpha$  is easily determined in terms of other parameters. we sum both the sides.

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$$\sum_N \sum_j M_{Nj}^* = \exp(-\alpha) \sum_N \sum_j e^{-\beta E_{Nj}(v)} e^{-\gamma N} = M$$

$$p_j = \frac{M_{Nj}^*}{M} = \frac{e^{-\beta E_{Nj}(v)} e^{-\gamma N}}{\sum_N \sum_j e^{-\beta E_{Nj}(v)} e^{-\gamma N}} \Rightarrow \boxed{p_j(v, \beta, \gamma)}$$

$\Downarrow$

$$p_{Nj}(v, \beta, \gamma)$$

grand canonical partition function.

$p_{Nj}(v, \beta, \gamma)$  is probability that any randomly chosen system contains  $N$  molecules and be in the  $j$ th

One can prove that

$$\beta = \frac{1}{k_B T} ; \quad \gamma = -\frac{\mu}{k_B T}$$

$$p_j(N, v, T, \mu) = \frac{e^{\mu N / k_B T} e^{-E_j(N, v) / k_B T}}{\boxed{\Omega}}$$

Using Shannon's entropy formula:-

$$\begin{aligned}
 S &= -k_B \sum_j b_j \ln b_j \\
 &= -k_B \frac{\sum_N \sum_j e^{MN/k_B T} e^{-E_j(N,N)/k_B T}}{\boxed{H}} \times \left[ \frac{NM}{k_B T} - \frac{E_j(N,N)}{k_B T} - \ln \boxed{H} \right] \\
 &= -\frac{\bar{N}\mu}{T} + \frac{\bar{E}}{T} + k_B \ln \boxed{H}
 \end{aligned}$$

Now Gibbs energy,

$$G = H - TS$$

$$\mu N = E + PV - TS$$

$$S = \frac{E}{T} + \frac{\mu N}{T} + \frac{PV}{T}$$

$$\frac{PV}{T} = k_B \ln \boxed{H}$$

## Fluctuations and Response Functions

☑ Cause and effect relation:

Effect	Cause	
ST	$\frac{1}{c_p} \Delta Q$	$Q$ = Heat is supplied, we see change in temperature.
SV	$-k \Delta P$	$P$ = pressure applied, we see change in volume.
SM	$\chi \Delta H$	$H$ = We apply external magnetic field, we see change in magnetization.

These are all response of materials to external perturbation. These important properties are known as response functions.

Relation between fluctuation in thermodynamic quantity and response function.

<u>Fluctuation in therm. quantity</u>	<u>Response Function</u>
Energy (at constant volume) [E]	$c_v$ (specific heat at constant vol <sup>m</sup> )
Enthalpy (at constant pressure) [H]	$c_p$ (specific heat at constant pressure)
Volume [V]	Isothermal Compressibility ( $\kappa$ )
Number density [N]	"
Magnetization [M]	Magnetic Susceptibility [ $\chi$ ]
polarization or total dipole moment.	Dielectric constant [ $\epsilon$ ] ①

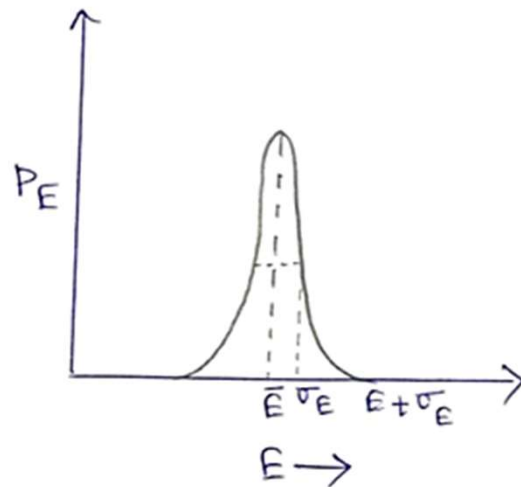
Ice ( $-5^{\circ}\text{C}$ )		Liquid	Gases
Al	0.89	water	Hydrogen
Iron(Fe)	0.45	Ethanol	Helium
Cu	0.39	Liq $\text{N}_2$	Steam ( $110^{\circ}\text{C}$ )
Au	0.13	Benzene	Nitrogen
		Mercury	Oxygen

The  $C_v$  of water shows to be the best liquid for holding heat. It is best for transferring. To increase the temperature of liquid water we need to break hydrogen bonds. In terms of fluctuation of specific heat water has broad energy distribution again related to H-bond. The reason for high value of specific heat of water is due to the existence of energy modes of relatively low frequency (of the order of  $\text{KBT}$ ) due to H-bond. The modes at  $200\text{ cm}^{-1}$  (H<sub>2</sub> excitation) and  $585\text{ cm}^{-1}$  (libra-

For canonical Ensemble  $(N, V, T)$  the dispersion or spread is characterized by standard deviation  $\sigma_E$ .

$$\sigma_E = \left[ \overline{(E - \bar{E})^2} \right]^{1/2}$$

⇓  
Root mean square deviation



$$\begin{aligned} \overline{(E - \bar{E})^2} &= \overline{E^2 - 2E\bar{E} + (\bar{E})^2} \\ &= \overline{E^2} - (\bar{E})^2 \end{aligned}$$

⇓

This is necessarily a positive quantity.

where

$$\bar{E} = \frac{\sum E_j(N, V) e^{-E_j(N, V)/k_B T}}{\mathcal{Q}}$$

Now if we differentiate,

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$$\bar{E} \sum_j e^{-E_j(N,V)/k_B T} = \sum_j E_j(N,V) e^{-E_j(N,V)/k_B T}$$

$$\left(\frac{\partial \bar{E}}{\partial T}\right)_{N,V} + \frac{\bar{E}}{k_B T^2} \sum_j E_j e^{-E_j(N,V)/k_B T} = \frac{1}{k_B T^2} \sum_j E_j^2 e^{-E_j/k_B T}$$

$$\left(\frac{\partial \bar{E}}{\partial T}\right)_{N,V} = \frac{\bar{E}^2}{k_B T^2} - \frac{(\bar{E})^2}{k_B T^2}$$

$$\overline{E^2} - (\bar{E})^2 = (E - \bar{E})^2 = \sigma_E^2 = k_B T^2 \left(\frac{\partial \bar{E}}{\partial T}\right)_{N,V}$$

$$= k_B T^2 C_V$$

$$C_V = \frac{\sigma_E^2}{k_B T^2}$$

for ideal gas we can write the average kinetic energy of particle as,

$$\bar{E}_K = \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} NKT$$

$$C_V = \left( \frac{\partial E}{\partial T} \right)_V = \frac{3}{2} NK$$

$$\frac{\sigma_E}{\bar{E}} = \frac{(KTC_V)^{1/2}}{\bar{E}}$$

$$= O(N^{-1/2})$$

$$\sigma_E^2 \text{ or } C_V \sim O(NK)$$

$$\bar{E} \sim O(NKT)$$

$$* \quad C_V = \left( \frac{\partial E}{\partial T} \right)_V = \frac{3}{2} NK$$

$$C_P = \left( \frac{\partial E}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial T} \right)_P$$

$$C_P = \frac{3}{2} NK + P \frac{\partial}{\partial T} \left( \frac{NKT}{P} \right)_P$$

$$= \frac{3}{2} NK + NK$$

$$= \frac{5}{2} NK$$

### Fluctuation Formula for specific heat ( $c_p$ ):

Fluctuation in enthalpy & volume in isothermal-isobaric ensemble (NPT) can be respectively related to  $c_p$ .

The partition function of the system can be written

$$\Xi = \sum_{j,v} e^{-\beta(E_j + Pv)}$$

Now the average enthalpy can be written as,

$$\langle H \rangle = \frac{\sum_{j,v} (E_j + Pv) e^{-\beta(E_j + Pv)}}{\sum_{j,v} e^{-\beta(E_j + Pv)}}$$

Differentiating w.r.t T we get,

$$\frac{\partial \langle H \rangle}{\partial T} = \frac{1}{k_B T^2} \frac{\left( \sum_{j,v} e^{-\beta(E_j + P v)} \right) \sum_{j,v} (E_j + P v)^2 e^{-\beta(E_j + P v)} + \left( \sum_{j,v} (E_j + P v) e^{-\beta(E_j + P v)} \right)^2}{\left[ \sum_{j,v} e^{-\beta(E_j + P v)} \right]^2}$$

$$= \left[ \langle H^2 \rangle - \langle H \rangle^2 \right]$$

$$= \frac{1}{k_B T^2} \sigma_H^2$$

$$c_p = \frac{\sigma_H^2}{k_B T^2}$$

### Fluctuation formula of compressibility:

The average volume can be written as,

$$\langle v \rangle = \frac{\sum_{j,v} v e^{-\beta(E_j + Pv)}}{\sum_{j,v} e^{-\beta(E_j + Pv)}}$$

$$\frac{\partial \langle v \rangle}{\partial \beta} = \frac{-\left(\sum_{j,v} e^{-\beta(E_j + Pv)}\right) \sum_{j,v} v^2 e^{-\beta(E_j + Pv)} + \left(\sum_{j,v} v e^{-\beta(E_j + Pv)}\right)^2}{\left(\sum_{j,v} e^{-\beta(E_j + Pv)}\right)^2} \times \beta$$

$$= -[\langle v^2 \rangle - \langle v \rangle^2] \times \beta$$

$$= -\sigma_v^2 \times \beta$$

$$-k_B T \frac{\partial \langle v \rangle}{\partial P} = \sigma_v^2$$

$$= -[\langle v^2 \rangle - \langle v \rangle^2] \alpha \beta$$

$$= -\sigma_v^2 \alpha \beta$$

$$-k_B T \frac{\partial \langle v \rangle}{\partial p} = \sigma_v^2$$

But- compressibility is given by

$$K_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T$$

$$k_B T V K_T = \sigma_v^2$$

$$K_T = \frac{1}{V k_B T} \sigma_v^2$$

### Important Application:

Fluctuation formula for number of particles:—

$$\sigma_N^2 = \frac{\bar{N}^2 k_B T K}{V}$$
$$\frac{\sigma_N}{\bar{N}} = \left( \frac{k_B T K}{V} \right)^{1/2}$$

An interesting application of the fluctuation formulae:—  
is scattering of light by the atmosphere:—

$$\frac{I(\theta)}{I_0} = \frac{\pi^2 V^2 \sigma_\epsilon^2}{2\lambda^4} = \frac{(1 + \cos^2 \theta)}{R^2}$$

$\sigma_\epsilon \rightarrow$  variance of  $\epsilon$  where  $\epsilon$  is dielectric constant  
when light of intensity  $I_0$  is incident on a region  
of volume  $V$  with dielectric  $\epsilon$ , the intensity of light  
scattered at an angle  $\theta$  at a distance  $R$ , this is called  
Rayleigh scattering. The dielectric constant  $\epsilon$  is related

$\sigma_E \rightarrow$  variance of  $\epsilon$  where  $\epsilon$  is dielectric constant when light of intensity  $I_0$  is incident on a region of volume  $V$  with dielectric  $\epsilon$ , the intensity of light scattered at an angle  $\theta$  at a distance  $R$ , this is called Rayleigh scattering. The dielectric constant  $\epsilon$  is related to the density by the so-called Clausius-Mossotti equ<sup>n</sup>.

$$\frac{\epsilon - 1}{\epsilon + 2} = A\rho$$

If we calculate  $\sigma_E^2$  in terms of  $\sigma_\rho^2$  we find,

$$\begin{aligned} \frac{I(\theta)}{I_0} &= \int \frac{I(\theta)}{I_0} R^2 \sin\theta \, d\theta \, d\phi \\ &= \frac{8\pi^3}{27\lambda^4} K_B T K (\epsilon - 1)^2 (\epsilon + 2)^2 V \end{aligned}$$

This equation shows that the blue colour of sky is due to fluctuations in the density of the atmosphere. Blue scatter more than red and hence sky appears blue due to the combined effect of density fluctuation and Rayleigh scattering.