

Lecture 15

CH-4114

Molecular Simulation

“Everything that living things do can be understood in terms of the jigglings and wigglings of atoms.”

- Richard P. Feynman

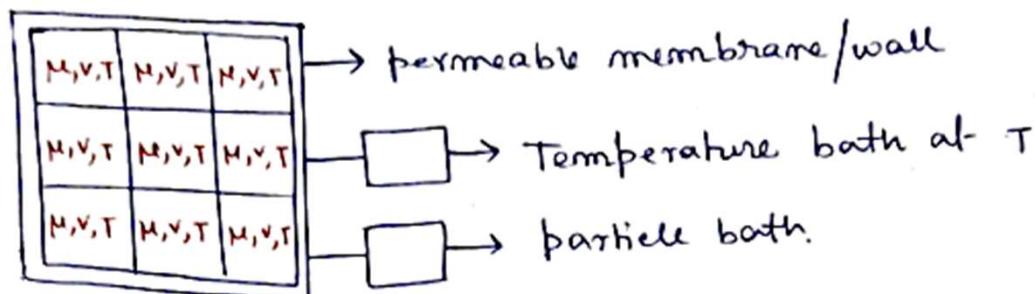
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Handling Simulations of Different Ensembles
+
Fluctuation and Response Function

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 $\{n_{Nj}\}$, the set of occupation numbers. 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:

$$\sum_N \sum_j M_{Nj} = M \quad (1)$$

$$\sum_N \sum_j M_{Nj} E_{Nj} = E \quad (2)$$

$$\sum_N \sum_j M_{Nj} N = N \quad (3)$$

M = Total number of members/systems in the ensemble.

E = total energy of the ensemble.

N = 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 Γ subject to appropriate constraints completely dominates all other. 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 α is easily determined in terms of other parameters. we sum both the sides.

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

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

\Downarrow

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

$$\boxed{\sum_N \sum_j e^{-\beta E_{Nj}(v)} e^{-\gamma N}}$$



$$\boxed{H(v, \beta, \gamma)}$$

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

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

$$b_j(N, v, T, \mu) = \frac{e^{MN/k_B T} e^{-E_j(N, v)/k_B T}}{H}$$

Using Shannon's entropy formula:-

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

Now Gibbs energy,

$$G = H - TS$$

$$MN = E + PV - TS$$

$$S = \frac{E}{T} + \frac{MN}{T} + \frac{PV}{T}$$

$$\frac{PV}{T} > k_B \ln H$$

Fluctuations and Response Functions

cause and effect relation:

Effect	Cause	
ST	$\frac{1}{C_P} S\theta$	$\theta =$ heat is supplied, we see change in temperature.
SV	$-k S P$	$P =$ pressure applied, we see change in volume.
SM	$\chi S H$	$H =$ 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 ^m)
Enthalpy (at constant pressure) [H]	c_p (specific heat at constant pressure)
volume [v]	Isothermal Compressibility (K)
Number density [N]	"
Magnetization [M]	Magnetic Susceptibility [x]
polarization or total dipole moment.	Dielectric constant [ϵ] ①

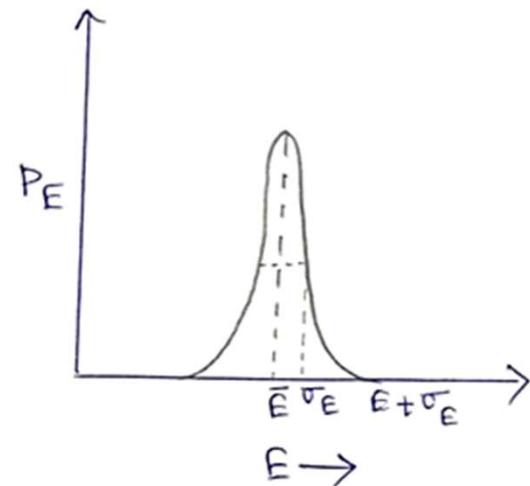
	C_v	Liquid	Gases
Ice (-5°C)	2.1		
Al	0.89	water 4.184	Hydrogen 14.32
Iron(Fe)	0.45	Ethanol 2.48	Helium 5.23
Cu	0.39	Liq N ₂ 2.04	steam (110°C) 1.97
Au	0.13	Benzene 1.72	Nitrogen 1.04
		Mercury 0.14	Oxygen 0.91

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 $K_B T$) due to H-bond. The modes at 200 cm^{-1} (HIS excitation) and 585 cm^{-1} (libra-

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

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

\Downarrow
Root mean square
deviation



$$\overline{(E - \bar{E})^2} = \overline{E^2 - 2E\bar{E} + (\bar{E})^2}$$

$$= \overline{E^2} - (\bar{E})^2$$

where

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

This is necessarily a positive quantity.

Now if we differentiate,

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

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

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

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

$$= k_B T^2 C_V$$

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

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

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

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

$$\frac{v_E}{\bar{E}} = \frac{(kT c_V)^{1/2}}{\bar{E}}$$

v_E^2 or $c_V \sim O(NK)$
 $\bar{E} \sim O(NKT)$

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

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

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

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

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

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

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

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

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,

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

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

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

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

Fluctuation formula of compressibility:

The average volume can be written as,

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

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

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

$$= - \bar{v}_v^2 \times \beta$$

$$-k_B T \frac{d\langle v \rangle}{dp} = \bar{v}_v^2$$

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

$$= - \overline{v}^2 \alpha \beta$$

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

But compressibility is given by

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

$$k_B T V K_T = \overline{v}^2$$

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

Important Application:

Fluctuation formula for number of particles:-

$$\overline{\sigma_N}^2 = \frac{\bar{N}^2 K_B T K}{V}$$

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

An interesting application of the fluctuation formulae:-

is scattering of light by the atmosphere:-

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

σ_ϵ → Variance of ϵ where ϵ is dielectric constant
 when light of intensity I_0 is incident on a region
 of volume V with dielectric ϵ , the intensity of light
 scattered at an angle θ at a distance R , this is called
 Rayleigh scattering. The dielectric constant ϵ is related

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 to the density by the so-called Clausius-Mossotti equⁿ.

$$\frac{\epsilon - 1}{\epsilon + 2} = Ag$$

If we calculate σ_{ϵ}^2 in terms of σ_p^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.