Lecture 14
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

System in contact with a heat reservoir

We consider a small system A_1 characterized by E_1, V_1 and N_1 in thermal interaction with a heat reservoir A_2 characterized by E_2, V_2 and N_1 in thermal interaction such that $A_1 \ll A_2$, A_1 has hence fewer degrees of freedom than A_2.

$$E_2 \gg E_1 \qquad N_1 = \text{const.}$$
$$N_2 \gg N_1 \qquad N_2 = \text{const.}$$

with

$$E_1 + E_2 = E = \text{const.}$$
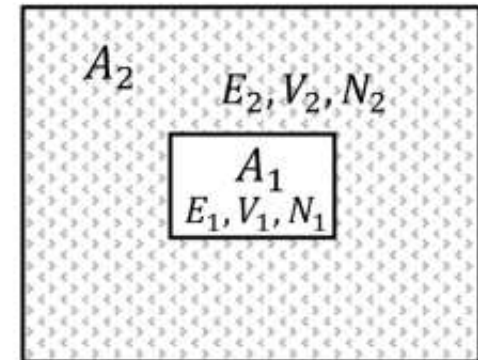
Both systems are in thermal equilibrium at temperature T. The wall between them allows interchange of heat but not of particles. The system A_1 may be any relatively small macroscopic system such as, for instance, a bottle of water in a lake, while the lake acts as the heat reservoir A_2.

Distribution of energy states	The question we want to answer is the following:
	"Under equilibrium conditions, what is the probability of finding the small system A_1 in any particular microstate α of energy E_α? In other words, what is the distribution function $\rho = \rho(E_\alpha)$ of the system A_1?"

We note that the energy E_1 is not fixed, only the total energy $E = E_1 + E_2$ of the combined system.

Canonical Ensemble
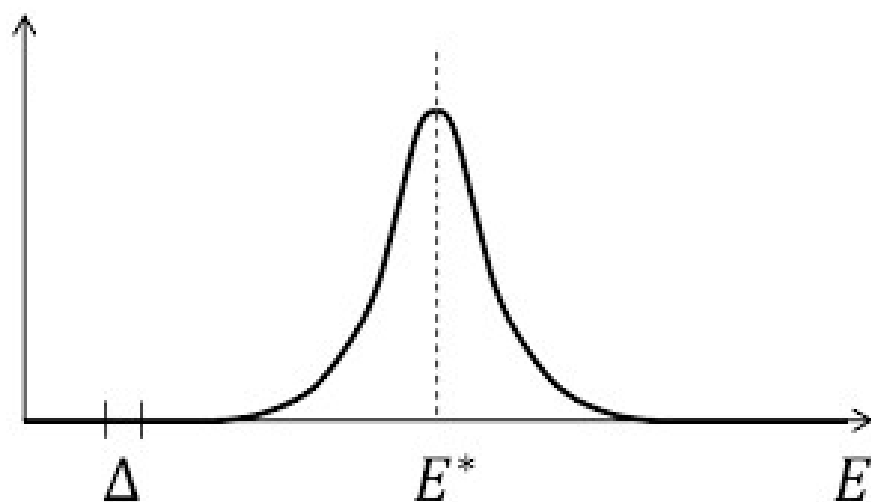
Example :— N distinguishable, non interacting spin-$\frac{1}{2}$ particles,
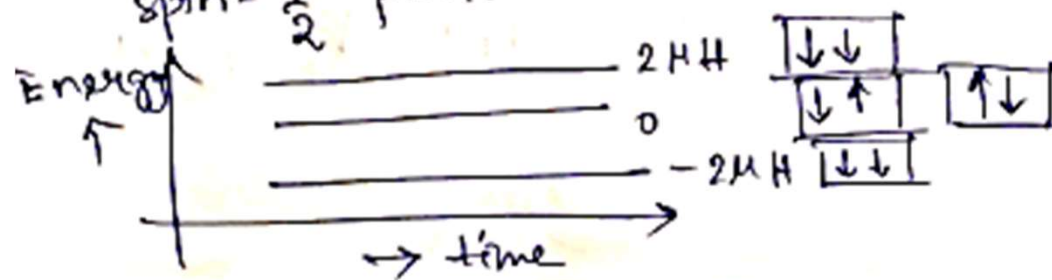
E_i	$\Pi(E_i)$
$\overline{E} - \Delta E$	1
$\overline{E}$	2
$\overline{E} + \Delta E$	1

Pre-requisite Methods: Max Term Method and Lagrange Multiplier Method

Maximum term method :—

It says that under appropriate conditions the logarithm of a summation is essentially equal to the logarithm of the maximum term in summation.

$$S = \sum_{i=1}^{M} T_i \quad (T_i > 0)$$

$$\Rightarrow \quad T_{max} \leq S_1 \leq M \, T_{max}$$

$$\Rightarrow \quad \ln T_{max} \leq \ln S \leq \ln T_{max} + \ln M$$

In statistical mechanics T_{max} will be $O(e^M)$ or $O(10^M)$

$\ln M$ is negligible.

$$\hookrightarrow \ln S = \ln T_{max}$$

Numerical Example:

$$S = e^2 + e^5 + e^{10}.$$

Clearly, e^{10} dominates the sum.

Compute exactly:

$$S = e^2 + e^5 + e^{10} \approx 7.39 + 148.4 + 22026.5 = 22182.3.$$

Now:

$$\ln S = \ln(22182.3) \approx 10.004.$$

Compare with the largest term:

$$\ln(e^{10}) = 10.$$

Method of Lagrange multipliers

Suppose you want to **maximize or minimize** a function

$$f(x, y, z)$$

subject to a **constraint**

$$g(x, y, z) = 0.$$

The key idea is:

At the optimum point, the **gradient of f** is **parallel** to the **gradient of g**.

That is,

$$\nabla f = \lambda \nabla g$$

where λ is the **Lagrange multiplier**.

Steps

1. **Write the Lagrangian function:**

$$\mathcal{L}(x, y, z, \lambda) = f(x, y, z) - \lambda[g(x, y, z)]$$

2. **Set partial derivatives to zero:**

$$\frac{\partial \mathcal{L}}{\partial x} = 0, \quad \frac{\partial \mathcal{L}}{\partial y} = 0, \quad \frac{\partial \mathcal{L}}{\partial z} = 0, \quad \frac{\partial \mathcal{L}}{\partial \lambda} = 0$$

3. **Solve the resulting equations** to get x, y, z, and λ.

Example

Minimize $f(x, y) = x^2 + y^2$ subject to $x + y = 1$.

1. Lagrangian:

$$\mathcal{L}(x, y, \lambda) = x^2 + y^2 - \lambda(x + y - 1)$$

2. Derivatives:

$$2x - \lambda = 0, \quad 2y - \lambda = 0, \quad x + y - 1 = 0$$

3. Solving → $x = y = 0.5, \lambda = 1$.

✅ Minimum at $(0.5, 0.5)$.

Consider an ensemble made up of M members, each with N molecules. Let M_i be the number of member systems that have energy ε_i so that,

$$M = \sum_i M_i$$

$$E_{tot} = \sum_i M_i \varepsilon_i$$

These two are the constraints that we have.

Now we want to find the average energy (and other properties) $\langle E \rangle$. This means that we need to know the probability of the occurance of each quantum state i. We know that for this particular ensemble (i.e collection of systems) the probability of observing a system in state i is,

$$P_i = \frac{M_i}{M} \longrightarrow \text{Just for (ith) one ensemble.}$$

$\underline{\qquad \circledast}$

of systems) the probability of observing a system in state i is,

$$P_i = \frac{M_i}{M} \longrightarrow \text{just for (ith) one ensemble.}$$

—Ⓧ

There are many many possible ensembles. In other word, think of making many copies of the ensemble or think of letting the ensemble evolve in time and then making new observations. we want to calculate the average number of system in state i for many ensembles. Let this be $\langle M_i \rangle$. Since principle of equal a priori probability applies, each state with same energy is equally likely. Hence we need a combination of ways that a particular system can occure. That is, we need to find out all possible arrangement. The way to find $\langle M_i \rangle$ is to use the multinomial distribution,

$$\Gamma(M_1, M_2, \ldots) = \frac{M!}{\prod_i M_i!} \qquad \text{where } M = \sum M_i$$

Ⓘ

Probability of finding $\langle M_i \rangle = P_i = \dfrac{\langle M_i \rangle}{M}$

where $\langle M_i \rangle = \dfrac{\sum\limits_{M} M_i \, \Gamma(M)}{\sum\limits_{M} \Gamma(M)}$

$$= \dfrac{\sum\limits_{M} M_i \, \dfrac{M!}{\prod_i M_i!}}{\sum\limits_{M} \dfrac{M!}{\prod_i M_i!}}$$

We can not possibly write down all the terms in this equation, so we want to simplify the expression by replacing the sum over all distributions by the most probable distribution Γ^*.

$$\langle M_i \rangle = \dfrac{\sum\limits_{M} M_i \, \Gamma(M)}{\sum\limits_{M} \Gamma(M)} = \dfrac{M_i^* \, \Gamma^*}{\Gamma^*} = M_i^* \qquad \begin{bmatrix} \text{As } M \text{ is very very} \\ \text{large, we used} \\ \text{the Maximum} \\ \text{term method.} \end{bmatrix}$$

Where m_i^* is the maximum term method in Γ^*.

Now we have two goal:

(i) we want to find M_i^* (Most probable member configuration)

(ii) & $P_i = \dfrac{M_i^*}{M}$ [probability of getting most probable member configuration]

Subject to constraints, $M = \sum M_i$

$$E = E_{tot} = \sum M_i E_i.$$

Thus, we applied maximum term method.

For convenience, we maximize $\ln\Gamma$ rather than Γ.

Using Lagrange's multipliers α & β to form a new function F.

$$F = \ln\Gamma + \alpha\left[M - \sum_i M_i\right] + \beta\left[E - \sum_i E_i M_i\right] \qquad \left[\Gamma = \frac{M!}{\prod M_i!}\right]$$

$$= \ln M! - \sum_i \ln M_i + \alpha\left[M - \sum_i M_i\right]$$

$$+ \beta\left[E - \sum_i E_i M_i\right]$$

Starling Approximation

Recall Lecture 5

$$= M\ln M - M - \sum_i \left(M_i \ln M_i - M_i \right) + \alpha \left[M - \sum_i M_i \right]$$
$$+ \beta \left[E - \sum_i E_i M_i \right]$$

Now we need to maximize F, with respect to M_i and find for what value of $M_i = M_i^*$ F will be maximum.

$$\left(\frac{\partial F}{\partial M_i} \right)_{M_i = M_i^*} = - \ln M_i - M_i \frac{1}{M_i} + \alpha(-1) + \beta(-E_i) + 1$$

$$= - \ln M_i - 1 - \alpha - \beta E_i + 1$$

$$= - \ln M_i - \alpha - \beta E_i$$

$$\left. \frac{\partial F}{\partial M_i} \right|_{M_i^*} = - \ln M_i^* - \alpha - \beta E_i = 0$$

$$\Rightarrow \ln M_i^* = - \alpha - \beta E_i$$

$$M_i^* = \exp(-\alpha) \exp(-\beta E_i)$$
$$\downarrow$$

This gives us the most probable distribution.

Evaluation of the undetermined multipliers, α and β

$$M_i^* = \exp(-\alpha) \exp(-\beta\varepsilon_i)$$

Lets Sum on both sides,

$$\sum M_i^* = \exp(-\alpha) \sum \exp(-\beta\varepsilon_i)$$

$$M = \exp(-\alpha) \sum_i \exp(-\beta\varepsilon_i)$$

$$\Rightarrow \quad \exp(-\alpha) = \frac{M}{\sum\limits_i \exp(-\beta\varepsilon_i)}$$

putting this in the definition of p in (*) equⁿ, we get,

$$P_i = \frac{M_i^*}{M}$$

$$= \frac{1}{M} \cdot \frac{M}{\sum_i \exp(-\beta\varepsilon_i)} \exp(-\beta\varepsilon_i)$$

$$= \frac{\exp(-\beta\varepsilon_i)}{\sum_i \exp(-\beta\varepsilon_i)}$$

$$P_i = \frac{\exp(-\beta\varepsilon_i)}{Q}$$

where,

$$\boxed{Q = \sum_i \exp(-\beta\varepsilon_i)}$$

$$\boxed{\beta = \frac{1}{K_B T}}$$

K_B = Boltzmann constant.

⇓

Canonical partition function.

Relationship between Canonical partition Function & thermodynamic Functions.

Shannon's entropy formulae from information theory

$$S = -K_B \sum_i p_i \ln p_i$$

In case of microcanomical ensemble when all micro-states are equally probable,

$$S = K_B N_E \frac{1}{N_E} \ln \Gamma$$

$$S = K_B \ln \Gamma$$

We are now in a position to summerize the basic statistical mechanical equations that can be used to calculate the thermodynamic properties of a closed isothermal system. In first place, the probability that the system is in any particular energy state E_i is

$$P_i(N,V,T) = \frac{e^{-E_i(N,V)/K_B T}}{Q(N,V,T)}$$

$$P_i(N,V,T) = \frac{e^{-E_i(N,V)/k_BT}}{Q(N,V,T)}$$

where, $Q(N,V,T) = \sum e^{-E_i(N,V)/k_BT}$

$$S = -k_B \sum_j p_j \ln p_j$$

$$= -k_B \sum_i \frac{e^{-E_i/k_BT}}{Q}\left[-\frac{E_i}{k_BT} - \ln Q\right]$$

$$S = \frac{1}{T}\frac{\sum E_i e^{-E_i/k_BT}}{Q} + k_B \ln Q$$

$$S = \frac{\bar{E}}{T} + k_B \ln Q$$

Now $\quad A = E - TS$

$$S = \frac{E}{T} - \frac{A}{T}$$

Comparing these equations for entropy, we get,

$$A = -k_B T \ln \varphi$$

$$\boxed{A = -k_B T \ln \varphi (N, V, T)}$$

$$dA = -SdT - pdV + \sum_i \mu_i dN$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_{N,V} = k_B T \left(\frac{\partial \ln \varphi}{\partial T}\right)_{V,N} + k \ln \varphi$$

$$p = -\left(\frac{\partial A}{\partial V}\right)_{T,N} = k_B T \left(\frac{\partial \ln \varphi}{\partial V}\right)_{T,N}$$

$$E = A + TS = -k_B \ln \varphi + k_B T^2 \left(\frac{\partial \ln \varphi}{\partial T}\right) + k_B \ln \varphi$$

$$= k_B T^2 \left(\frac{\partial \ln \varphi}{\partial T}\right)_{V,N}$$

$$\mu_i = \left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_{\alpha \neq i}} = -k_B T \ln \left(\frac{\partial \ln \varphi}{\partial N_i}\right)_{T,V,N_{\alpha \neq i}}$$

Implication:

$$F = -k_B T \ln Q = -k_B T \ln \left(\frac{e^{-\beta E_i}}{P_i}\right)$$

$$F = -k_B T \left(-\beta E_i - \ln P_i\right)$$

$$F = E_i - k_B T \ln P_i.$$

This shows that **at a given configuration (microstate)**, the *Helmholtz free energy* associated with that configuration is proportional to the **logarithm of its probability**.

Huge Implication in Free Energy Calculation from Molecular Simulations