Advanced Thermodynamics and Molecular Simulations
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Lecture - 15
Definition of Temperature; Third Law of Thermodynamics

Hello, all of you. So in the last lecture, we have been discussing the canonical ensemble that is the NVT ensemble and we determined how we can find properties such as average energy, average pressure using the canonical ensemble.

So in today's lecture, I will discuss like how the temperature is defined using the zeroth law of thermodynamics, what is the origin of that if we think in terms of the canonical ensemble. So essentially what we have been talking about is that in the canonical ensemble you have systems which are having same number of molecules, volume and temperature and there are 'A' such systems in the ensemble.

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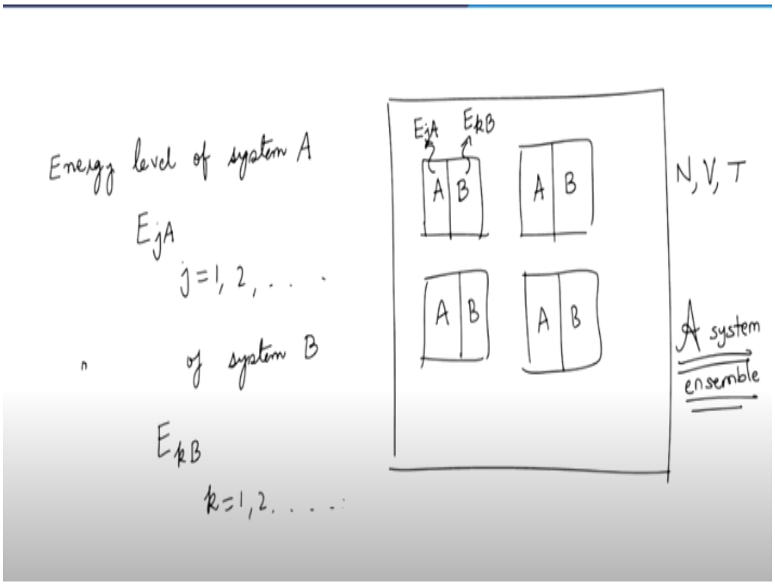

So in order to define temperature, what we do is, we first assume that there is not one system, but two systems which are in a state of thermodynamic equilibrium that is to say that, inside the ensemble, you have systems 'A' and 'B' which are in close contact by close contact, I mean they can exchange energy, but they cannot exchange the molecules between them. So they are in a state of thermal equilibrium so as to speak, they can exchange energies, they can have same temperatures eventually, once they reach equilibrium but the number of molecules in A number of molecules in B are constant for the ensemble. So if I assume that in that case, now again I have ‘A’ systems in the ensemble, but in each of these ‘A’ systems, you have system ‘A’ and system ‘B’ in close contact.

So essentially now we can talk about the energies of the system ‘A’ and the energies of the system ‘B’ and just like we had different possible energy levels of system in the last example we have done, in this case again you will have different energy levels, but different for system ‘A’ and system ‘B’, right. So essentially you will have energy level of system ‘A’ that are E_jA where j refers to different possible energy levels. And similarly, energy level of system B are E_kB, k = 1, 2 and so on.

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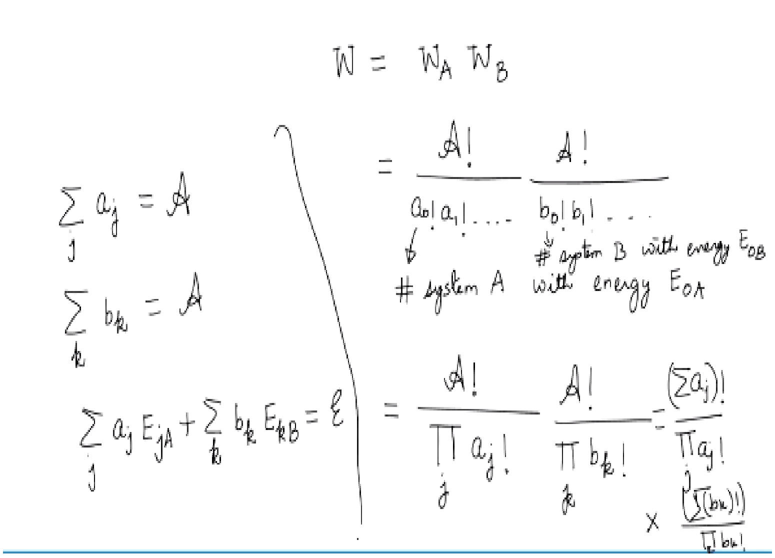

So if I am now interested in writing the number of ways of distribution for this particular ensemble, the number of ways are equal to the number of ways in which I can distribute the energies in the ‘A’ systems multiplied by the number of ways in which I can distribute energy in the ‘B’ systems and since ‘A’ and ‘B’ are always in close contact, the total number of ‘A’ systems is equal to total number of ‘B’ systems. So we can write this as-

$$W = W_A W_B$$

$$= \frac{A!}{a_0!\, a_1! \ldots\ldots} \frac{A!}{b_0!\, b_1! \ldots\ldots}$$

So a_0 refers to the number of systems 'A' with energy E_0A, a_1 is the number of systems with energy E_1A. Similarly, b_0 is the number of system 'B' with energy E_0B. And we can have b_1 as the number of systems 'B' systems with the energy E_1B and so on.

So now just like I wrote for the last example, in here as well, we can write this A as-

$$W = \frac{A!}{\prod_j a_j!}\, x \,\frac{A!}{\prod_k b_k!} = \frac{\left(\sum a_j\right)!}{\prod_j a_j!}\, x\, \frac{\left(\sum b_k\right)!}{\prod_k b_k!}$$

Keep in mind that both the numerators are the same, but since I am taking care of constraints separately, therefore I have replaced the numerator with the summation, right. So even if we do not do that, we get the same result but just to be rigorous, it is always a good idea to think of it in this particular way.

So now there are certain constraints here. And the constraints are-

$$\sum_j a_j = A$$

And,

$$\sum_k b_k = A$$

But now when I look at the energies, now we have to add the energy of 'A' and 'B' because they can exchange energies although they cannot exchange molecules, they can still exchange energy. So if I talk about energy of 'A' and 'B' in close contact, that we can write something like this-

$$\sum_j a_j E_j A + \sum_k b_k E_{kB} = \epsilon$$

As the entire ensemble can be again thought as an isolated system. So total energy for the entire ensemble can still be assumed to be constant that I am representing as capital ϵ.

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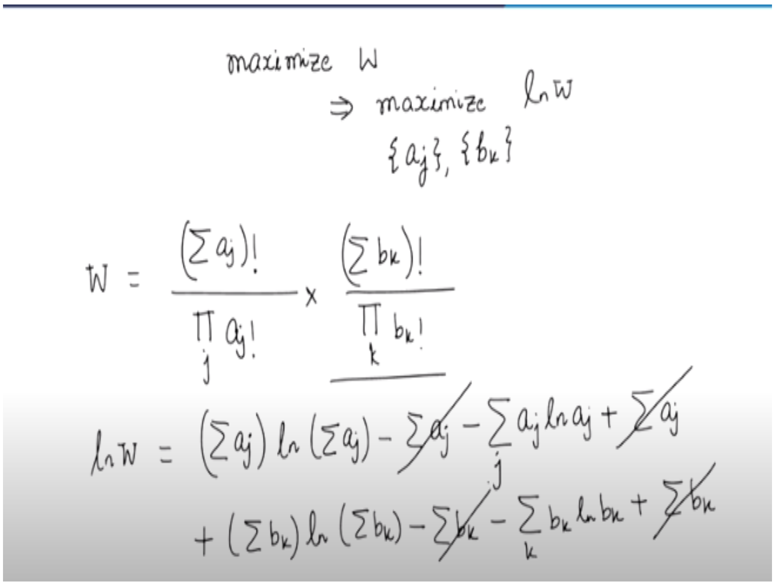

So now I want to maximize W that essentially is equivalent of maximizing ln W. But now the variables that we have are both the a_j values and the b_k values, actually the distribution of them in the ensemble. So now since W is equal to-

$$W = \frac{(\sum a_j)!}{\prod_j a_j} \; x \; \frac{(\sum b_k)!}{\prod_k b_k}$$

We can again use the Stirling approximation and then the ln W will be summation over a_j. Keep in mind that whenever I write summation over a_j, the index is j whenever I write summation over b_k, the index happens to be k. So it is-

$$\begin{aligned}\ln W = &\left(\sum a_j\right)\ln\left(\sum a_j\right) \\ &- \sum a_j \\ &- \sum_j a_j \ln a_j + \sum a_j \\ &+ \left(\sum b_k\right)\ln\left(\sum b_k\right) - \sum b_k - \sum_k b_k \ln b_k + \sum b_k\end{aligned}$$

Again, we will have the cancellation and therefore, we can write ln W as-

$$\ln W = \left(\sum a_j\right)\ln(\sum a_j) - \sum a_j \ln a_j + \left(\sum b_k\right)\ln\left(\sum b_k\right) - \sum b_k \ln b_k$$

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$$\ln W = \left(\sum a_j\right) \ln\left(\sum a_j\right) - \sum a_j \ln a_j + \left(\sum b_k\right) \ln\left(\sum b_k\right) - \sum b_k \ln b_k$$

$$g_1 \equiv \sum a_j - A = 0$$

$$g_2 = \sum b_k - A = 0$$

$$g_3 = \sum a_j E_{jA} + \sum b_k E_{kB} - E = 0$$

$$\{a_j\}, \{b_k\} \equiv \{a_0, a_1, \ldots, b_0, b_1, \ldots\}$$

$$\frac{\partial \ln W}{\partial a_j} - \lambda_1 \frac{\partial g_1}{\partial a_j} - \lambda_2 \frac{\partial g_2}{\partial a_j} - \lambda_3 \frac{\partial g_3}{\partial a_j} = 0 \quad \forall a_j$$

$$\frac{\partial \ln W}{\partial b_k} - \lambda_1 \frac{\partial g_1}{\partial b_k} - \lambda_2 \frac{\partial g_2}{\partial b_k} - \lambda_3 \frac{\partial g_3}{\partial b_k} = 0 \quad \forall k$$

And then we have certain constraints here that we have written i.e.-

$$g_1 \equiv \sum a_j - A = 0$$

$$g_2 \equiv \sum b_k - A = 0$$

$$g_3 \equiv \sum a_j E_{jA} + \sum b_k E_{KB} - E = 0$$

So now if I do the minimization, the minimization has to be done with both a_j and b_k variable. However, keep in mind that the constraints that are there are defined for both the variables together, right. So we did not think of them as two separate types of variable and therefore, we should think of two different constraints, because in the constraints, since the variables come together, we should think of both a_j and b_j as forming a list of variable. So whatever minimization that we are doing, in that the constraints will have the same Lagrange multiplier right.

So if it is not very clear, you can think of this as equivalent of variables a_0, a_1 and so on. And b_0, b_1 and so on. Mathematically speaking a_0, a_1 and b_0, b_1 are still the variables of the same equation although they refer to different systems in the particular example, but mathematically speaking, there is no difference between the ‘a’ variables and the ‘b’ variables. So therefore, the corresponding Lagrange multipliers for the constraints are going to be the same. So that means, that I can write the maximization problem as-

$$\frac{\partial \ln W}{\partial a_j} - \lambda_1 \frac{\partial g_1}{\partial a_j} - \lambda_2 \frac{\partial g_2}{\partial a_j} - \lambda_3 \frac{\partial g_3}{\partial a_j} = 0$$

for all values of a_j.

And similarly, we can write for b_k. And the point remember is the Lagrange multiplier has to be the same because as I said, we can combine the two variables together and they become the variable for the entire equation, right. So there is no difference between the variables as such. So we should not have different Lagrange multipliers for the same constraints that is particularly important for the last one because in here both aj and b_k come together. So this then becomes the same thing but with respect to b_k for all values of b_k.

$$\frac{\partial \, ln \, W}{\partial b_k} - \lambda_1 \frac{\partial g_1}{\partial b_k} - \lambda_2 \frac{\partial g_2}{\partial b_k} - \lambda_3 \frac{\partial g_3}{\partial b_k} = 0$$

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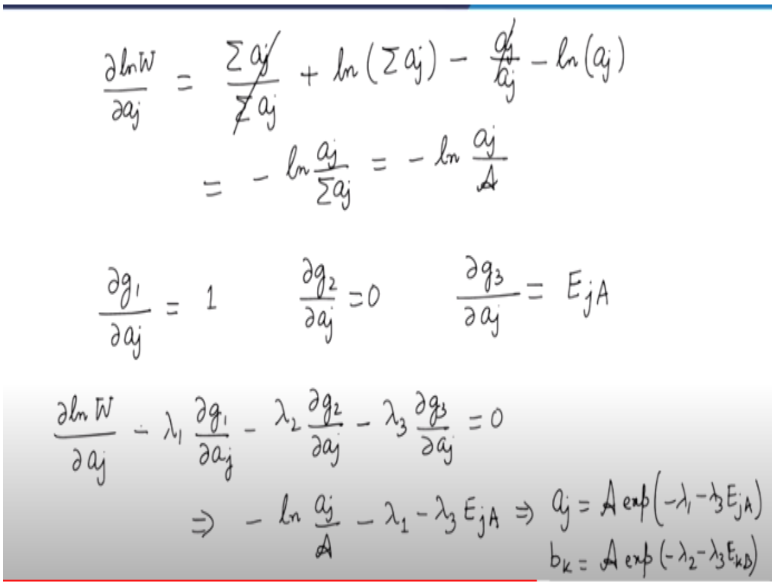

So now I can write the equation as-

$$\frac{\partial \ln W}{\partial a_j} = \frac{\sum a_j}{\sum a_j} + \ln\left(\sum a_j\right) - \frac{a_j}{a_j} - \ln(a_j)$$

And then we have terms containing b_k in the equation which will not have any derivative with respect to a_j. And therefore, those terms will not appear. So therefore, we will have cancellations here. This is equal to-

$$\frac{\partial \ln W}{\partial a_j} = -\ln \frac{a_j}{\sum a_j} = -\ln \frac{a_j}{A}$$

So now,

$$\frac{\partial g_1}{\partial a_j} = 1, \frac{\partial g_2}{\partial a_j} = 0 \; and \; \frac{\partial g_3}{\partial a_j} = E_j A$$

So therefore, I can write the maximization problem as-

$$\frac{\partial \ln W}{\partial a_j} - \lambda_1 \frac{\partial g_1}{\partial a_j} - \lambda_2 \frac{\partial g_2}{\partial a_j} - \lambda_3 \frac{\partial g_3}{\partial a_j} = 0$$

Therefore,

$$-\ln \frac{a_j}{A} - \lambda_1 - \lambda_3 - E_j A$$

And it gives me-

$$a_j = A \exp\left(-\lambda_1 - \lambda_3 E_{jA}\right)$$

If I do the same stuff for the variables b_k the equation we will have is-

$$b_k = A \exp(-\lambda_2 - \lambda_3 E_{kB}$$

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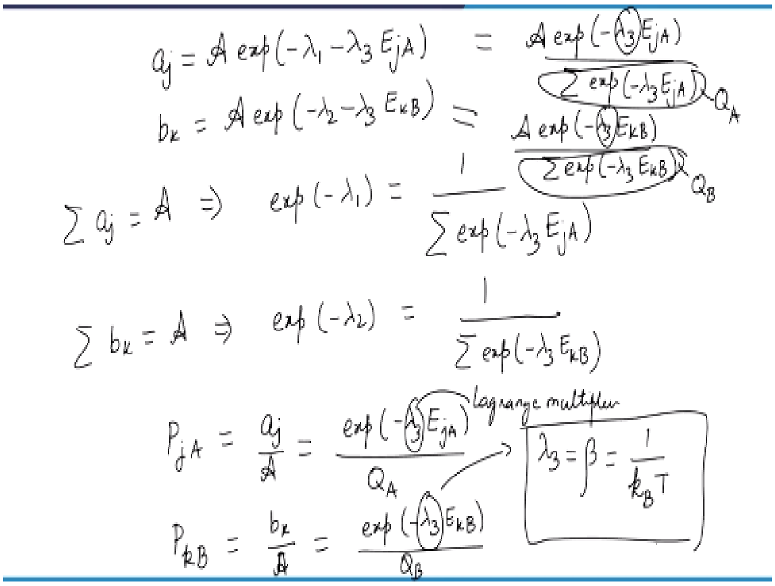

Now let us look at these two equations. So we have found-

$$a_j = A \exp\left(-\lambda_1 - \lambda_3 E_{jA}\right)$$

$$b_k = A \exp(-\lambda_2 - \lambda_3 E_{kB}$$

Let us first use the constraints. So summation over a_j is equal to A this gives me the value-

$$\sum a_j = A$$

This gives me-

$$\exp(-\lambda_1) = \frac{1}{\left(\sum \exp(-\lambda_3 E_j A\right)}$$

And,

$$\sum b_k = A$$

And this gives me-

$$\exp(-\lambda_2) = \frac{1}{(\sum \exp(-\lambda_3 E_{KB})}$$

So if I look at this particular expression here, we notice something that this Lagrange multiplier is the same in both these equations, right. And the denominator is similar to the partition function we defined earlier. But now the partition function is different for systems 'A' and for systems 'B'. The other way to think about it is we can define the probability for a system 'A' to have energy E_jA something like-

$$P_{jA} = \frac{a_j}{A} = \frac{\exp\left(-\lambda_3 E_{jA}\right)}{Q_A}$$

And,

$$P_{KB} = \frac{b_k}{A} = \frac{\exp(-\lambda_3 E_{kB})}{Q_B}$$

So although the probability of having the state E_j and for systems 'A' and probability of having state E_{kB} for systems 'B', they are themselves different, but both of them are essentially proportional to something like the Boltzmann factor we had that is exponential of minus of something and that something contains the same factor λ3. So therefore, whenever the systems are in a close contact, there is something that is common between the system and that something in this case is the Lagrange multiplier λ3, which is same in both these cases. It turns out that we can identify this λ3 as β that is equal to 1 over k_B T. And this exactly is the statement of the zeroth law of thermodynamics.

So whenever two systems are in close contact, there has to be something that is common between the two systems and that something relates to the temperature. This is the definition of temperature, whenever there are two systems in close contact, there has to be a quantity called temperature that will be same when the systems come in a state of thermal equilibrium and that is the definition of the β variable in thermodynamics.

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$$P_{jA} = \frac{\exp(-\beta E_{jA})}{Q_A}$$

$$P_{kB} = \frac{\exp(-\beta E_{kB})}{Q_B}$$

$P_{jk} \equiv$ system A has energy E_{jA} and system B has energy E_{kB}

$$= P_{jA} P_{kB}$$

$$= \frac{\exp[-\beta(E_{jA} + E_{kB}]}{Q_A Q_B}$$

So therefore, we can now write finally,-

$$P_{jA} = \frac{\exp\left(-\beta E_{jA}\right)}{Q_A}$$

$$P_{kB} = \frac{\exp(-\beta E_{kB})}{Q_B}$$

And naturally whenever we talk about this probabilities, we are talking about two systems in close contact. So the probability should be of the system ‘A’ having some energy and system ‘B’ having some energy. So what is more relevant here is a probability of the form P_{jk} that means, that the system A has energy E_{jA} and system ‘B’ has energy E_{kB} and that is equal to-

$$P_{jk} = P_{jA} x P_{kB}$$

$$= \frac{\exp\left[-\beta(E_{jA} + E_{kB})\right]}{Q_A Q_B}$$

So this completes the derivation of temperature. There is another way to look at the same problem that we will discuss in the next lecture.