

Foundations of Computational Materials Modelling
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Lecture 17
Introduction to Statistical Mechanics-2

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$\Omega^0 = \Omega^1(E_1) \times \Omega^2(E_2) = \Omega^0(E_1, E_2)$
 Maximize $\Omega^0(E_1, E_2)$ subject to constraint that $E^0 = E_1 + E_2$
 $\bar{\Omega}^0 = \Omega^1(E_1) \times \Omega^2(E_2) + \lambda (E^0 - E_1 - E_2)$
 $\frac{\partial \bar{\Omega}^0}{\partial E_1} = \frac{\partial \Omega^1}{\partial E_1} - \lambda = 0$; $\frac{\partial \bar{\Omega}^0}{\partial E_2} = \frac{\partial \Omega^2}{\partial E_2} - \lambda = 0$
 $\frac{\partial \ln \Omega^1}{\partial E_1} = \frac{\partial \ln \Omega^2}{\partial E_2}$
 $\beta_1 = \beta_2$
 $dU = Tds$
 $\left(\frac{\partial S}{\partial U}\right)_{N,V} = \frac{1}{T}$; $\frac{1}{T_1} = \frac{1}{T_2}$; $T_1 = T_2$
 $\left(\frac{\partial S_1}{\partial E^1}\right)_{N_1, V_1} = \frac{1}{T}$; $\left(\frac{\partial S_2}{\partial E^2}\right)_{N_2, V_2} = \frac{1}{T}$

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Or see if we can invoke some equality and drop parallelism between our microscopic way of approaching things and our macroscopic knowledge of classical thermodynamics. So, the number of complexions. So, at any instant of time during the process of, so once I remove this or make the central display it as, you know as something that will allow the exchange of energy E1 is gradually going to change and E2 is also gradually going to change, they are going to exchange energies E1 and E2 are gradually.

However, at any instant of time E_1 plus E_2 is going to be equal to E naught simply because of the fact that this entire thing is an isolated system? So, it is possible for us to write E naught minus E_1 as well. Now, the composite system A_1 plus A_2 which I will call us A naught, can have can be now, how many different ways can at any instant of time you can achieve it in E_1 times E_2 different ways.

$$E_1 + E_2 = E^0$$

The composite system such that A_1 is in energy E_1 and A_2 is in energy E_2 is nothing can be in Ω_1 , E_1 times Ω_2 E_2 different ways at any instant of time so many different possibilities are existing for them to actually have this energy E_1 have this energy E_2 , the composite system both of them together.

$$\Omega^0 = \Omega^1(E_1) \times \Omega^2(E_2) = \Omega^0(E_1, E_2)$$

The obviously this Ω naught is a function of say E_1 . So, the question that we asked now is when will this energy transfer stop? Or what will be the value of E_1 at which no more or E_1 or E_2 at which no more energy exchange between the two is going to take place? So, we make one assertion. This is probably the only assertion that we will make without explicitly proving.

We say that, once equilibrium is reached, the value of Ω naught is the maximum. Once equilibrium is reached, the number of ways in which the system can actually arrange itself is the one which has the maximum value and therefore, the probability that you will see it in that system is the highest.

Consequently, our problem reduces to that of a maximization of maximization problem, where we have to maximize Ω naught with respect to the variables E_1 and E_2 subject to the constraint that E naught is equal to E_1 plus E_2 . So, how will you achieve my functions which have constraints, you have you heard of Lagrange multiplier method. So, we will use exactly the same thing.

So, we will form a composite function Ω naught bar which is nothing but Ω_1 , E_1 times Ω_2 E_2 plus λ times E naught minus E_1 minus E_2 , we need to extremize

this. So, extremizing this with respect to the variables E_1 and E_2 . So what happens when we so when we want extremize, we have to differentiate this entire function with respect to E_1 equal to zero and then with respect to E_2 and then equal to 0, what do we get?

$$\bar{\Omega} = \Omega^1(E_1) \times \Omega^2(E_2) + \lambda (E - E_1 - E_2).$$

We get $\frac{\partial \bar{\Omega}}{\partial E_1}$ with respect to E_1 and that would mean $\frac{\partial \Omega^1}{\partial E_1} \times \Omega^2 - \lambda = 0$ and $\frac{\partial \bar{\Omega}}{\partial E_2}$ with respect to E_2 will be $\frac{\partial \Omega^2}{\partial E_2} \times \Omega^1 - \lambda = 0$. Now, these two equations are telling you that $\frac{\partial \Omega^1}{\partial E_1} \times \Omega^2$ is actually equal to $\frac{\partial \Omega^2}{\partial E_2} \times \Omega^1$.

$$\frac{\partial \bar{\Omega}}{\partial E_1} = \frac{\partial \Omega^1}{\partial E_1} \times \Omega^2 - \lambda = 0$$

So, if you do a little bit of algebra, this turns out to be $\frac{\partial \ln \Omega^1}{\partial E_1}$ is equal to $\frac{\partial \ln \Omega^2}{\partial E_2}$ and during this process remember, we have kept the number of species and the volume in each thing constant. So, we made an assertion without proof, we said that the energy exchange between the two systems will take place until this is a maximum value.

$$\frac{\partial \Omega^1 \Omega^2}{\partial E_1} = \frac{\partial \Omega^2 \Omega^1}{\partial E_2}$$

$$\left. \frac{\partial \ln \Omega^1}{\partial E_1} \right|_{N_1, V_1} = \left. \frac{\partial \ln \Omega^2}{\partial E_2} \right|_{N_2, V_2}$$

So, once this has reached the maximum value, there will be a E_1 bar and the corresponding E_2 bar which is equal to E bar minus E_1 bar that each of the subsystems will have and

once that E_1 bar and E_2 bar have reached then no more energy transfer will take place, but the condition for you to find that E_1 bar and E_2 bar is this.

So we call this beta 1 and this is beta 2 we just calling it by different names beta 1 and beta 2. Is this okay until now until so far? Now, in order to basically understand what this is, we need actually thermodynamics to draw the parallelism between statistically we are we are obviously trying to obtain expressions for classical thermodynamic quantities from statistical mechanics.

$$\beta_1 = \beta_2$$

So, we cannot do away with thermodynamics, we have to use result of thermodynamics to draw the parallelism. So, when you write the first law we just wrote this the beginning of the class. So, we said that du is equal to Tds because I am going to keep my volume constant. So, $\frac{dS}{du}$ by du at constant N, V turns out to be $\frac{1}{T}$ at equilibrium I will have $\frac{1}{T_1}$ equal to $\frac{1}{T_2}$ or T_1 equal to T_2 correct yes or no? at equilibrium, Yes.

Now, look at look at this expression here and look at this expression here. This is $\frac{dS}{d \ln \Omega}$ by dE , this is $\frac{dS}{du}$ and in this case u is nothing but E , that is the internal energy of the system. So, $\frac{dS}{d \ln \Omega}$ by dE N_1, V_1 will be equal to $\frac{1}{T_1}$ and $\frac{dS}{d \ln \Omega}$ by dE N_2, V_2 will be equal to $\frac{1}{T_2}$ from thermodynamics.

$$du = Tds$$

$$\left(\frac{\partial S}{\partial u} \right)_{N, V} = \frac{1}{T} \quad \left(\frac{1}{T_1} = \frac{1}{T_2} \right)$$

(or) $T_1 = T_2$

Therefore, from this expression and this expression we are kind of tempted to write the following $\frac{dS}{d \ln \Omega}$ is equal to $\frac{1}{\beta}$ by looking at this expression right here, which is equal to β_1 or β $\frac{d \ln \Omega}{dE}$ is basically β .

So, it belongs to one system one than it is beta 1 if it belongs to system two then it is beta, beta 2.

And similarly, $\frac{\partial S}{\partial E}$ is $\frac{1}{T}$. So, I am just removing the suffixes 1 here. Because it can be any arbitrary system as long as N and V are constant. So, $\frac{\partial S}{\partial \ln \Omega}$ is $\frac{1}{\beta T}$ and this has to be what a constant. Now, what Boltzmann did was this is where Boltzmann left it, this was written down by Boltzmann, and basically he thought that since this approach is kind of correcting something at classical thermodynamics level and the microscopic nature of the system, this has to be some sort of a universal constant.

$$\left(\frac{\partial S}{\partial \ln \Omega} \right)_{N, V} = \frac{1}{\beta T}$$

Later on Planck came and said, S is equal to $k \ln \Omega$ and then if you did this, $\frac{\partial S}{\partial \ln \Omega}$, you would get the Boltzmann constant K. So, this $\frac{1}{\beta T}$ happens to be a universal constant, we call it the Boltzmann's constant. So, right now, if you see we have an expression for the macroscopic thermodynamic quantity in terms of this number of complexions Ω , which has got nothing to do with thermodynamics.

$$S = k \ln \Omega$$

$$\left(\frac{\partial S}{\partial \ln \Omega} \right) = k$$

It has total number of ways you can arrange something. So, S is equal to $K \log \Omega$ is one such statistical mechanical expression, which connects the microscopic quantity to the

macroscopic thermodynamic property of the system. We can now do this for different cases, which I will do in the next class.

So, this in this case we did not so, this kind of shows you what beta and temperature seems seem to have a similar meaning or similar effect. So, beta might be true when you are talking about the thermodynamics of the system using the microstate approach whereas temperature has a meaning of equality when you are taking the classical thermodynamic approach.

So, beta and T are related through just one constant which is the Boltzmann's constant. Now, the next job is to see what will happen if you actually allow this central system or whatever this thing that is allowing the exchange of energy to not only exchange energy but in addition to that also move.

So, if you allow it to move, then what should be the conditions for equilibrium P1 should be equal to P2. In addition to that, if you are also following the condition for them to exchange the particle numbers, then what should be the condition the chemical potentials and the both ends the exchange of species will happen until μ_1 is equal to μ_2 .

So, we will see how these quantities also are coming from just this omega or the microscopic or a term that is related more to the microscopic nature basically the number of complexions that you can have. Once we do that, we will go on to discuss how this omega comes about and what is it, how big how large it is, and things like that now, how we can compute it for some simple systems.

So, the basic spirit is this, once you know this omega, then you can also find things like Gibbs free energy, Helmholtz free energy and all these energies and all your properties of the system are in some way only derivatives of these quantities.

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$$E(-)$$

$$G(-)$$

$$\frac{\partial G}{\partial \epsilon_{ij}} = P_{ij}$$



So, if you are able to represent, say strain, in terms of microscopic quantities and you are able to represent the Gibbs free energy in terms of these microscopic quantities or the number of complexions, then $\frac{\partial G}{\partial \epsilon_{ij}}$ strain will give you some stress. So, we will see later that all these things that come here how strain or Gibbs free energy is represented in terms of the microscopic quantities will be in terms of the positions and the velocities of all the atoms that the system is comprised of all.

Helmholtz free energy etcetera everything will be related only to those things. So, we are not yet discussed how ω is obtained, but we will do that and show you that ω depends on these microscopic quantities, which is basically the position and a moment of all the atoms.