Thermodynamics of Fluid Phase Equilibria
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Lecture – 34
Introduction to Statistical Mechanics

Welcome back, in this lecture I will go through the introduction of statistical mechanics.

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So, the statistical mechanics basically used for various different purposes. Ah from the point of view of prediction of the property the statistical mechanics is used pertaining to the modeling, and the prediction of the properties of materials. Ah from the structure of the atoms and molecules which comprise the material? So, what we are interested is basically making use of the stat mech to generate the probability distribution of the energies of the atoms and molecules. And these averages over this distribution of the probability distributions are what a experiments measure ok. This is something which is the core of the stat mech usage in predicting materials.

So, let us first look at an example of the type of problem we wish to solve, and then we will introduce the basic concept of stat mech.

So, let us consider this 2-dimensional model of 4 bead polymer chain ok. So, this is a 4-bead polymer chain of different conformation. So, we can categorize this conformation into ah 2 types one is a open conformation; which is basically the first excited macrostate. And the second is the closed conformation which is a ground state so, the close and this is open ok.
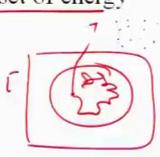
And then what is our goal is to compute the probability distribution of know the 4-bead chain occupying these 2 conformation. That is the fraction of the molecules that are in each conformation. So, will come back come to in details of what is macrostate and microstates so forth in next few slides ok.

So, let me just first go through the basic definition of various different terminology, which we use in statistical mechanics so, will start with the energy levels ok.

So, in this we will be assume that each system, this is a molecular system or atom a system has a well define set of energy levels that the system can occupy ok. And the ground state will be the state having the lowest energy. States of higher energy will be called excited states. We often use terminology such as microstate and macrostate. So, what are microstates? A microstate is a snapshot of the system ok. When you measure system property you measure averages over multiple microstate.

So, if we talk about a phase space which basically is a combination of various different positions and the momentum ok. So, each point represent in a phase space some unique position a moment of the particle. So, when you freeze them for moment then you basically generate a configuration ok, or the snapshot of the system. So, in general the system may move like this ok, and you are taking an average over this. So, you are taking an you are measuring the system property averages of this multiple macrostate and thus you obtain a property or you know in the measurement and that is what typically the experiments ah outcomes are.

So, we make use of the microstate, but by collection of microstates property we obtain a single properties. For example, it could be an average of energy it could be an average of density depending on what is a state variable. Now in addition to microstate we also

make use of terminology called macrostate. Macrostate is defined by one or more thermodynamic property of the system that is total energy or number of particle n; that means, when you are fixing thermodynamic property E and v this would lead to a macrostate ok. A macrostate can have many different microstates. The relation between macrostate and microstate is that of one to many ok; that means, for given macrostate, that is for given that is a total energy fix number of particle, and fixed they are in general numerous microstate that satisfied the macrostate conditions; that means, there could be a many macrostate having a total energy E number of particle n, and our constant volume for example.
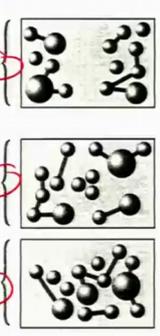
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Bit more complex system we can consider.

The system we typically analyze can be more complex than the 4 bead polymer chain models. So, in realistic system the polymer chains could be a many beads, but this is a very simple model. Ah for our illustration in general, the energy of a system is given by intramolecular energies of the molecules which includes translation rotation vibration etcetera and the intermolecular interaction between in interaction between molecules such as 2 body or 3 body or higher body interaction between molecules.

So, if you consider many different snapshot of a system such as this which is shown here ok, there could be many energy levels E 1 to E 2 and E j depending on the arrangement of the particles. So now, in our nomenclature is j, represents the energy of one particular

conformational system, no matter how complex it is ok. And if we collect this various different properties, then the average of this energy level would be given as some weighted average over this individual energy levels to obtained average energy and the question is basically what is wi that is a weight of individual energy, this is something which we are going to learn very quickly.

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Let us consider how to derive this wi the weight .So, let us consider a system having n particle of single type so; that means, they have same type of .So, there is no mixture of system there is of same type. And what we are considering in this that the system containing n particle has T different microstate with energy levels varying from E 1 to E T in this form ok. Now these energy levels are defined by the physics of the system ok, and the problem that you are you want to solve.

At this point we will simply will accept that the energy level exists. And we do not concern ourselves with how to compute the energy level of a system; in general information about the energy level is deduced from quantum mechanics or from a microscopic model ok. So, quantum mechanics means you are doing a very detailed solving strategy equations to solve energy levels, or if they say a simple model could be a you know hard sphere and other models which we can which will have a get a feeling on the later part of this course.

So, what is our objective our objective as I said we can our objective is basically to compute the probability of a given state that the system has or; that means, the probability that a system in each microstate j. So, once we have pj we should be able to calculate many different properties. So, in order to appreciate this, what we are going to do is we will work at a constant TVN ok, this is microscopic parameter. And for TVN or nvt we know that at equilibrium the Helmholtz free energy would be minimum ok; that means, dF is equal to du minus TdS should be 0 at minimum ok.

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Now we have already discussed this how to find out the maximum probability, ah the probability or equilibrium within the constraints. So, we have earlier in the lecture we are derived the maximization of a entropy with certain constraints. We will be trying to use this LaGrange multiplier concept in this lecture as well. So, what is the entropy we have already know known? This we have already done this exercise earlier. So, we can make use of this expression of entropy in the differential form which is this. What we are going to postulate for you? Because we have to get this expression.

So, dS of course, we can calculate from the probability what about du. We can consider du to be d of average and energy E; which will be average of all microscopic energies minus TdS ok. So, this is what we are going to do here dS of course, in terms of dp we have written here, and u is now an average of ve we can write as summation the probability of each macro state multiplied by E j ok. So, j is equal to 1 to T t has a

number of macrostates with that is what we said earlier that that the system has T different macrostates with different energy levels.

Now, having said that now you can take the derivative of u, which will be in this case. Now this one important thing is that we have E j dp. So, p is a variable with respect to j's, but what about dE now is is energy level variable. Ah like the macro scopic energy u the microscopic energy E j depends only on v and n. So, E is a basically function of v and n. Unlike you the energy level E do not depend on the entropy or temperature ok. So, E actually depends only on the system ok, this that comes directly from the quantum mechanics. It says that well for a given system you have a fixed energy levels. And what what varies with temperature is basically the population of this energy level, not the energy level itself.

So, the energy level do not depend on the temperature, but the population of the energy level depends on the temperature.

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So, with this, we can simply say that at a constant V N, this is going to be 0, in other word we can write d average differential value of the average energy is simply E dp ok. So, that means, this part goes to 0. Now given this n dS we can now replace this in the final expression ok, which is so you have this expression, and this expression, this you can plug in in dF.

Now, this is to minimize; that means, this is a basically the function which we are trying to minimize. We also need to understand that we have a constraint; constraint is of course, this this is done this is something which we have done it earlier also. Now we have to minimize this function subject to the constraint here. So, we are going to put alpha times dp equal to 0.

So, here we have introduce the langrage multiply alpha, and if you want to minimize f we are going to now plug in this expression dF is equal to du d of average E which is this comes here multiplied by dp. And minus TdS which is this, plus this alpha times dp here ok. This is the basic to the function which we have to minimize which using the LaGrange multiplier, and this within the brace within the bracket this must be 0.

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Based on that we can calculate your this expression from here we get an expression for pj, star indicates that this is the probability corresponding to the minimum value of f.

Now, in order to get rid of alpha we make use of the fact that we can divide this as by we normalize it by summation pj, which should be one. And this is what we have done here ok. So, this we can get rid of this because alpha is a constant, what remains is a function this which is E to power minus E j divided by KT and divided by summation of E to a minus E j by KT. And this we have done we have said that summation of this factor Boltzmann factor is nothing but partition function Q ok, and this expression which is relates to the to the Boltzmann factor of corresponding to the energy level or j divided by

the partition function is called Boltzmann distribution function, or sometimes or this is also called Boltzmann distribution law.

So, this is the derivation based on the earlier exercises which we have done. Now we are going to make use of it to understand a few things ok.

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The Boltzmann Distribution Law

Boltzmann Distribution Law
- Where Q is the *partition function*

$$Q = \sum_{j=1}^{t} e^{-E_j/kT}$$ ✓

- The relative populations of two microstates i and j at equilibrium are given by

$$\frac{p_i^*}{p_j^*} = e^{-(E_i-E_j)/kT} \;=\; \frac{e^{-E_i/kT}/Q}{e^{-E_j/kT}/Q}$$

$$\frac{p_i}{p_j} > 1 \qquad E_i < E_j$$

- The Boltzmann distribution says that more particles will have low energies and fewer particles will have high energies
- Why? There are more arrangements of the system that way

This is something which we have already defined that Q is a partition function, which is simply sum of the Boltzmann factor correspond to different energy levels. So, one can make use of this expression to understand relative population of 2 microstates. Let us assume that this is we are concern of microstate i and j. And if we divide pi star divided by pij this is going to be E to the minus E i minus E j divided by KT. This comes directly from the fact that we can write this as minus E i by KT divided by Q E minus E j divided by KT divided by Q, Q gets cancelled and then you can realize to get this expression.

Now, what it this expression tells you? This expression tells you that, more particle will have low energies and fewer particles will have higher energies ok. Now because p i by pj if it is greater than one, it is indicates that E i is less than E j ok. So, that is what it would tell you. Because it means basically E j is a at higher level, and E i is at lower level. So, but why is that? Why this is the case? Because if you can redo this exercise of arrangement, as we have done earlier, this will allow more number of arrangement of the system and this way.
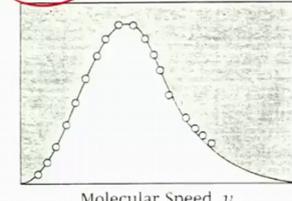
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Example: The Maxwell-Boltzmann Distribution

According to the kinetic theory, gases and liquids can be regarded as Newtonian particles having mass m, velocity v, and kinetic energy ε, where

$$\varepsilon(v) = \frac{1}{2}mv^2$$

Determine the distribution of velocities at temperature T

$v \cdot p(v)$

Molecular Speed, v

Now, using this Maxwell distribution we can also calculate the probability distribution of the velocities, or the distribution of the velocity this is sometime call Maxwell Boltzmann distribution. So, according to the kinetic energy theory, gases and liquid can be regarded as Newtonian particles having mass m velocity v and kinetic energy epsilon; where the kinetic energy is given in this form ok. So, if you would like to calculate the distribution of velocity at temperature T , this is the distribution this follows the Maxwell distribution model. And using these we can make use of various different things for example, this can be connected to the temperature. And you can try to solve various different expect using this expressions here ok.

So, we can find out the probability pv also based on this you can make use of the energy levels to find out the velocity or the probability velocities also ok using simple the Maxwell distributions here. So, I am not going into details here, just wanted to tell you about the origin of the relations with the Maxwell Boltzmann distribution, where these expressions are commonly used to connect with the temperature ok.

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So, let me come back again to the partition function. So, what does the partition function tells you? So, partition function now provides a connection between the macroscopic thermodynamic property and a microscopic models. It is a sum of Boltzmann factor that specify how particles are partitioned through throughout the accessible states. So, let us assume that the ground state is 0, in that case the partition function can be written in this form and resuming T energy levels. So, it would be 1 plus E to power minus E 2 by KT and so forth until E to power minus E T by KT.

So, the partition function accounts for the number of states that are effectively accessible to a system at a given temperature. So, these the T levels energy levels, but initiates if we consider the energy levels energies of different levels with respect to the ground energy it tells you that that this is basically the sum of possible effect sum of ah effective accessibility. So, this 1 plus the Boltzmann factor to access energy level 2 Boltzmann factor to access energy level 3 and forth.

So, it is simply the particles, the probability how they are partition throughout the accessible state that is what it tells you. And now this is certainly dependent on the temperature. So, if you write the temperature T goes to 0, or T goes to infinity, you can clearly see what will be there the partition function of such a limiting case.

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Which we can now understand so, if you if you considering at the high temperature of course, all of them is going to be either the Boltzmann factor E to power j by KT, this factor is going to be 0; which essentially means E to power which means basically E to power minus E j by KT goes to one. In that case Q goes to T, because Q is going to be some of this factor ok. There is going to be T and in that case the probability for accessing a state j it will be simply 1 by T.

So, that means, all the states will be equally populated as you know that is what the idea is ok, from here. If you consider low temperature then E to power j KT is going to be ah is approaches towards infinity, in that case, all the particles will occupy only the ground level as shown in this case probability of one the ground state will be one, and the probability all other state other than the ground state would be 0 in that case Q is going to be just one. That is what it is here ok. There will be only one possible level accessible level.

So, essentially tells you that temperature is the only driving force by which you can populate the energy levels ok, and the Q represent basically the effective number of the levels which are getting accessible ok.

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What Does a Partition Function Tell You?

Density of States

- In macroscopic systems, the number of microstates is vary large
- Therefore, it is often useful to work with macrostates instead of microstates
- The *density of states* $W(E)$ is the number of microstates in a given macrostate
- If $W(E) > 1$, an energy level is called *degenerate*
- Let's say the system has energy levels $l = 1, 2, \ldots, l_{max}$
- The partition function can now be expressed in terms of a sum over energy levels

$$Q = \sum_{l=1}^{l_{max}} W(E_l) e^{-E_l/kT}$$

$$Q = \sum_{l=1}^{\Xi} e^{-E_l/kT}$$

- The probability that a system is in energy level l is

$$p_l = Q^{-1} W(E_l) e^{-E_l/kT}$$

$$P_L = \frac{W(E_l) e^{-E_l/kT}}{Q}$$

- You are free to choose whether to focus on micro or macrostates

Let me further extend this exercise, and now let me define density of state. In macroscopic system the number of microstates are very large. Therefore, many times it is easy to work with the macrostate instead of microstate ok. So, the density of state is the basically the number of microstate in a given macrostate.

So, if w the density of state is greater than 1, we call it the energy levels are called degenerate. So, let us assume that the system has energy level from one to l max. Then the partition function where we wrote simply Q is equal to summation here, where i is equal to all possible states. Now you can rewrite this expression in terms of some of energy levels. Where, w is basically the number of degenerate states cross point to energy levels.

Now, in that case the probability of the system in energy level l, now we are not talking about energy ah system in the in a specific macrostate. Here we are saying that the probability that a given system is energy level l, who is going to be written like this pl is w of E l multiplied by energy the Boltzmann factor of that particular energy level divided by Q ok. This would be the probability of accessing a or system is basically in a certain energy level l ok. Now in general you can choose both ways, you can use it in terms of microstate or in terms of macrostates so that is pretty much up to you what to decide.

So, let me just try to explain this understanding, and try to solve a simple example which is a 4-bead polymer chain, which we started with this lecture, as an objective to solve. Here you have 2 possible energy states, or 2 possible states here one is basically open state, and the other one is a closed. In case of a closed case you have one confirmation, in case of open system or open ah microstate we have 4 possible confirmation, having the same energy epsilon 0. And other one we are considered to be 0 as a ground state.

Now, what is we have to find is basically we have to find the probabilities here. So, we can consider first the partition function. So, what is the partition function? So, partition function is basically sum of all possible you know energy levels, in terms of either I can write it in this way energy levels, and E to a minus E l by KT. Or I can write overall microstate ok. So, so, here if I use it here so, it is going to be E to power minus epsilon 0 by KT. Because there are 4 of them becomes 4 plus E to power minus 0 by KT for the case of ground 0. So, that means, we have Q is 1 plus 4 E to power minus epsilon 0 by KT.

So, you can use it either this way or you can use either in this way, both will yield the same expression ok. Now if the next question would be that what is the probability of the system is basically in a compact set that would be E to power minus 0 by KT divided by Q. Or 1 by Q what about for the open system? This will be 4 E to power minus epsilon

by KT divided by Q. Now you can use this and actually plot, because you have the handle or you have the expression Q in terms of T's so, you can plot it also.

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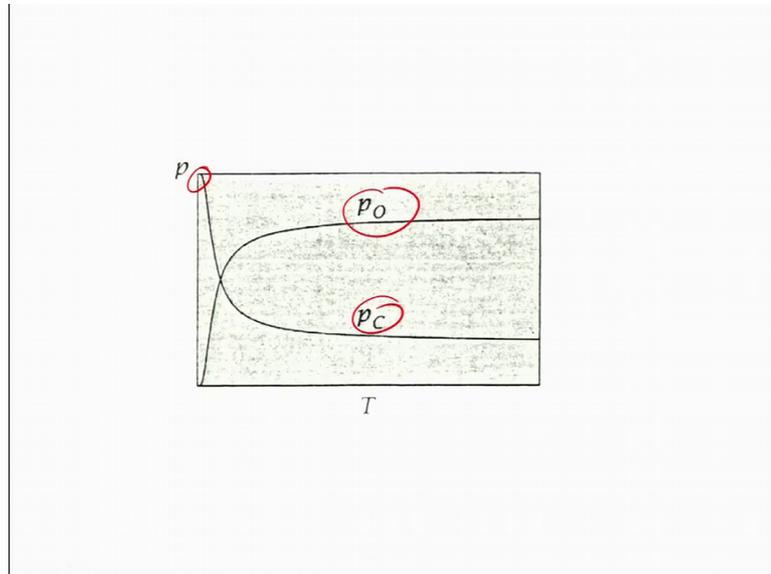
And this is the expression which will come out; where it will clearly show you that the compact state preferred at low temperature where the probability increases closer to 1, and open state is preferred at a very high temperature ok. Where the probability increases, and the probability of comparison decreases at high temperature.

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You can continue this exercise also for 6 bead polymer chains which I will leave you for you to try at your home ok. So, now this is a very simple ah introduction of statistical mechanics, we will see you in the next lecture.