Basic Statistical Mechanics
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Lecture – 37
Comments on Some Important Concepts of Statistical Mechanics

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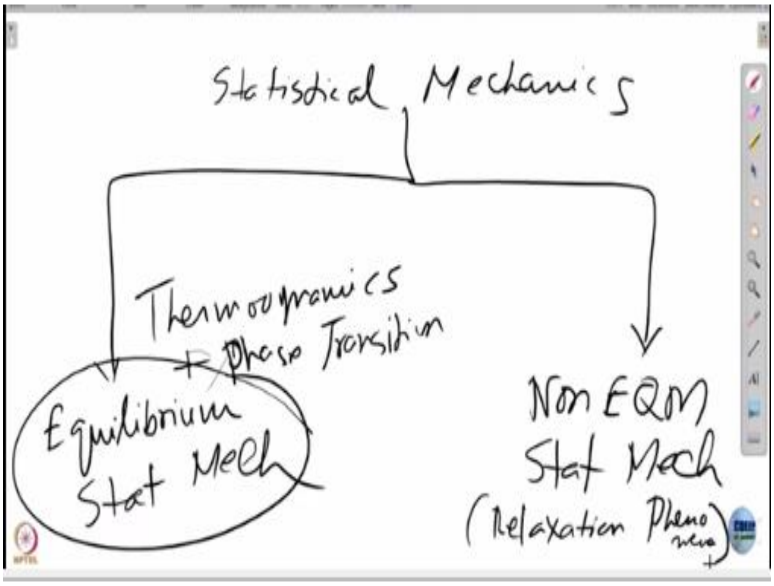

Welcome back, good morning, in this course of statistical mechanics, we are dealing with equilibrium phenomena, so just a brief reminder that statistical mechanics is broadly divided into 2; one is equilibrium statistical mechanics, another is non-equilibrium; non-equilibrium stat mech, this is the one that we deal with the thermodynamics and very, very important part, thermodynamic properties and also the phase transition.

Here, we do relaxation phenomena, chemical kinetics and then time dependent processes, now in these; so we are dealing with in this equilibrium statistical mechanics and we already started with the basic postulates and the hypotheses and with that, we went to construct the methodology which was built on the failure of; well, failure in a very essence, he succeeded a lot.

But he failed to develop a theory of kinetic theory of matter or those days used to be called heat and the reason was that Boltzmann tried to go all the way by starting a time dependent phenomena. So, what Boltzmann was trying to develop was a theory of non-equilibrium or time dependent phenomenon, non-equilibrium statistical mechanics and then he landed in the difficulty that the hierarchy.

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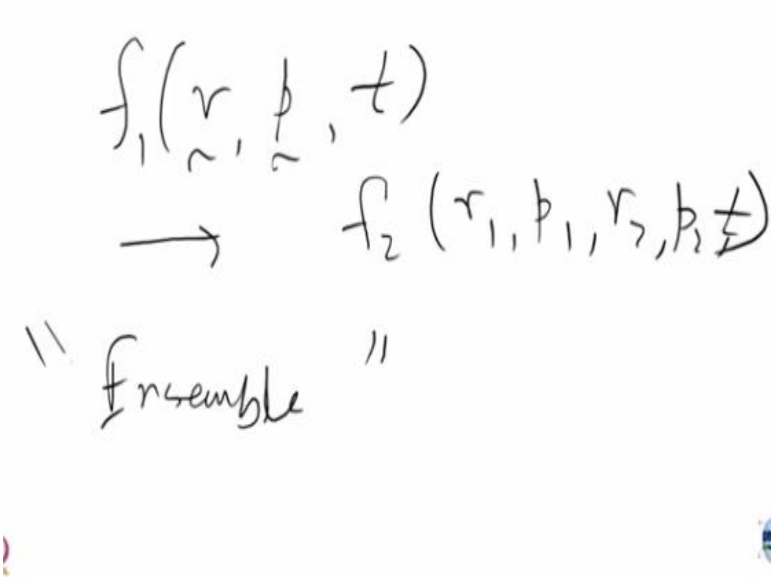

$$f_1(\underset{\sim}{r}, \underset{\sim}{p}, t)$$

$$\longrightarrow f_2(r_1, p_1, r_2, p_2, t)$$

"Ensemble"

I discuss a hierarchy that he taught it with single particle distributions and then that he tried to develop a distribution for position of a single particle in position and momentum but he found that gets connected to 2 particle distribution, then he made it approximation which called molecular chaos and that landed him into lot of difficulty but anyway that this project did not work out.

Then, however Willard Gibbs sitting there at the Yale University in New Haven, he had a brilliant idea, he realized that this approach will not work, so he went on to develop the what is the modern equilibrium statistical mechanics, he realized that to do an equilibrium stat mech, we do not need to know the trajectory, we do not know the detailed dynamics because thermodynamic properties are independent of time but it was the concept of ensemble is the one of the most, most brilliant idea that a mankind has come up with is somewhat less given credit to.

But he then said okay, I can thought of doing equilibrium statistical mechanics, I need to do a probability distribution but probability distribution mean how; I need to consider particles in the system is in different microscopic states, how do I; now create these microscopic states without going Boltzmann way, then he created a mental replica and the basic idea is that the number of microscopic states is so huge that the systems, the mental replica of my original system all inside in different microscopic states.

So, now he came up with these 2 postulates you know, ensemble average equal to time average, so now the macroscopic thermodynamic properties of the system are the average of the systems of the ensemble and each system is residing in a different microscopic state. So, as if Boltzmann trajectory is going through all these systems but however, he now had to after making the ensemble average or time average, he has to make sure the system really indeed goes through all that, that is what and you were to talk of a distribution.

So, all the microscopic states at constant energy, they are equally probable that is the assumption, second postulate and then you have to say okay, my system must go through all these things and the Boltzmann trajectory as I was saying a minute before and that is the Ergodic hypothesis okay, so that is started then we went to micro canonical ensemble and micro canonical partition function which is the entropy actually, partition function omega, make a number of microscopic states.

And thermodynamic potential; each ensemble comes with a partition function and each partition function comes with thermodynamic potential and from the thermodynamic potential we can calculate the thermodynamic properties. In micro canonical ensemble, NV ensemble we have already discussed, omega; total number of microscopic states is the partition function and entropy is $S = k_B \ln \omega$, that is why k_B the term Boltzmann constant comes.

Because the Boltzmann is the one who introduced it, so that is the micro canonical partition function, now that of course becomes very difficult and also not practical because systems are not in constant energy, you can have constant volume but an even number but energy is always fluctuating because we cannot isolate systems. So, then Boltzmann; gives with another brilliant thing introduced the canonical ensemble, where now the particles, the systems; particles in the system is allowed to exchange energy with the surrounding.

So, the energy is not conserved but energy is replaced by conjugate variable which is the temperature, so the ensemble has now constant number, constant volume, constant temperature, so NVT and that gives rise to the canonical ensemble and the canonical partition function which is denoted by Q and the logarithmic of the Q, $-k_BTlnQ$ gives Helmoltz free energy.

And as we discussed that is the advantage of these Helmoltz free energy is that I can get equation of state like pressure by a volume derivative of free energy, entropy by temperature derivative of the free energy and then specific heat by the temperature derivative of entropy, so these are just very beautifully flows that it was kind of fortunate that in NVT, we get that. We are not that fortunate we want to NPT because NPT, the thermodynamic potential and partition functions are not that helpful, they are still useful quantities.

Equilibrium statistical mechanics however, one very important thing of in addition to this thermodynamics which we get from ensemble, the important thing is the phase transition that is one of the real mandate of statistical mechanics is to describe the phase transition because phase transition as I described is an amazingly beautiful thing and is also really, really very, very striking.

Because you are changing a control parameter by infinitesimally small amount and you are getting a huge change and we said that is the definition of phase transition that control parameter is changed by an infinitesimal amount but the S is changed by huge amount.

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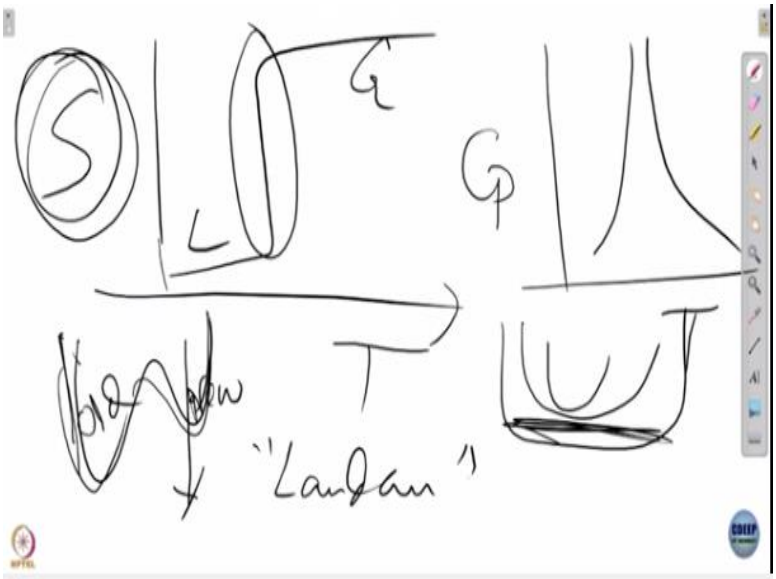

So, it is like this that I can; entropy against temperature, then this is the way if this is the liquid, this the gas, so look at the sharpness, so all the derivatives diverge in a; these are first order phase transition, or first derivative of the free energy, he describes that Ehrenfest classification. The first derivative of free energy this continuous give you the first order phase transition.

But in the second derivative of the free energy like specific heat acts funny, then we call that a second order phase transition and this particular is a continuous type, second order; 2 kinds of second order phase transition that we need, this is the gas liquid or order, disorder or magnetic, ferromagnetic paramagnetic transition. Superconducting transition is the Ehrenfest, really jump discontinuity, like this kind of discontinuity in the second derivative that is the resistance or resistivity, okay.

So, these are the basic elemental things of phase transitions, the definition of what is the phase transition, then we want to know why and how and why does a phase transition take place and then we come up with the thermodynamic logic okay, phase transition takes place because we have a another minima appear, so these in first order phase transition that another minimum appears and that minimum now becomes deeper as a lower temperature.

And this old phase is gets replaced by the new phase, so these are free energy description on y, now in this case this free energy becomes flatter and flatter and we get huge fluctuations on a flat; this surface those fluctuation does not cost any energy and that is the way this was described. This description all these came by in terms of Landau, so Landau introduced the kind of free energy landscape picture of phase transition.

And this then led to the Landau theory of phase transition, the definition of order parameter and many, many other beautiful things and we learned how to talk of free energy expansion in order parameter, we learn to calculate the changes in entropy from this theory and we learn to change these; how to describe these kind of divergence, the Landau theory is not a perfect theory, it took a lot of time for people to correct it almost 40 years but people did correct it and we have a much more complete theory of phase transition.

Now, so the Landau theory which describes a free energy in terms of things as I told you was a parallel almost parallel with the other theory which was developed more quantitatively from physical chemists perspective, so it was more specialized but more quantitative, so that was the Mayer’s theory.

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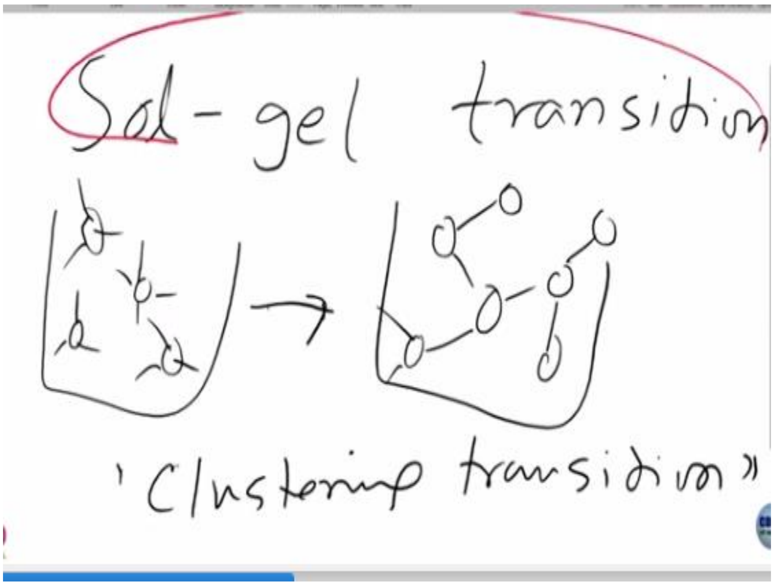

So, Mayer theory described that how gas can go into liquid and how you can develop the Virial series, so and the picture that may have developed and this beautiful that we get it the definition of Virial, so this was almost last century, the Virial series was introduced or something like that in the beginning of 1900 or so, however we did not know what is the second Virial coefficient, third Virial coefficient, Mayer's theory to give us an analytical expression in terms of intermolecular interaction and that is just beautiful.

Because that I discussed last class, we have the intermolecular interactions, B_2 we can measure experimentally because this is just nothing but P versus ρ and this is ideal gas, this goes like that, so I know these, so I can now have an expression for B_2 in terms of intermolecular interaction U(r), then I can put that and play around with that and I can get a potential and that was the first force field that was developed as I described once before, so it is an extremely important theory.

One more success of Mayer's theory is that Mayer's theory gave us a picture, a physical picture how a gas can go into liquid and that was used in many other things like in lattice theories and many other cases. It is very, very important to appreciate the continuity and the appreciate the flow of development of a subject, the historical perspective. Now, Mayer's theory then told us that okay, there is suddenly large clusters appears in the system and we know that this is not perfectly a physical cluster.

Because this everything is very mathematically defined, it does not; the real chemical bond lasting for a long time not there, they are mathematical definition in terms of Mayer function f that we described but it is nevertheless tells you how a big picture appears. Now, before I go to the next thing in a Mayer's theory there are 2 more things that we must discuss and not in great detail but in a semi-quantitative level.

One is this sol gel transition, these are very common phenomena that when you have a sol and you have polymers and then you have here these, you have the polymers which functionality 3 or 4, then when you increase the concentration or lower the temperature though it is not true thermodynamics, then what happened that it, they form a gel phase. How do I know they form a gel phase?

The viscosity diverges, so sol gel transition is a clustering transition, large clusters appears, there is a very weak thermodynamic signature, this sol gel transition is a very common phase transition usually, subject of polymer physics and polymer science though it is not done that well in polymer thing but this is very important in the industrial context in industrial chemistry, the formation of a gel.

We routinely form gel not like just a gelatin that you eat as a dessert but in many, many industrial functions, we form sol gel transition, rubber can be considered as the formation by this kind of chemical process where sulphur acts as the vulcanization on different carbon groups, okay. So, then what is the essence of sol gel transition, how do I describe sol gel transition; qualitatively, I will then describe how it is done quantitatively.

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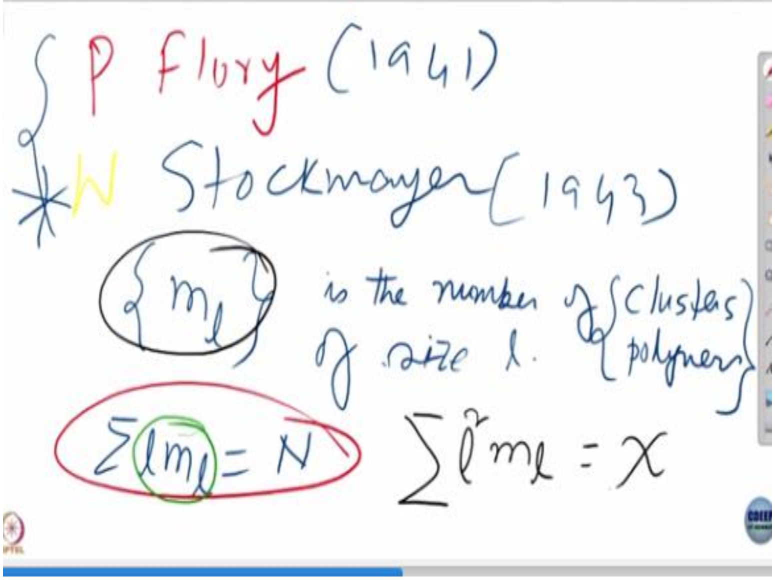

P Flory (1941)

W Stockmayer (1943)

$\{m_l\}$ is the number of {clusters / polymers} of size l.

$\sum l m_l = N$ $\quad \sum l^2 m_l = X$

So, this is the very, very interesting, the theory that was developed for sol gel transition was done by 2 people at the same time, 1 person is Paul Flory and who is consider as the father of polymer physics and it was also done at the same time by Walter Stockmayer, these I think 1943, I think this is little before, 1941 but both of them consider okay, this is not really a thermodynamic transition, it is a clustering transitions.

And these are real clusters now, chemical bonds are forming okay that you are bringing a monomer which is a functionality 3 or 4 and they are connected together to form a branch sometime, there are rings also but the huge branch that is forming, so suddenly, so there is again a phase transition because suddenly at some point, the clusters becoming infinite, so how do I describe that?

Both of them came out with identical description and I will describe the Stockmayer's one because that follows Joseph mayer's treatment and Stockmayer was a student of Joseph mayer. So, now they consider both of them, let me consider m_l, exactly the way we did Mayer, m_l is the number of clusters or polymers of size l, there now there are N number of monomers.

So, I have a condition $lm_l = N$, now lm_l these quantity then these quantity is number of monomers in a cluster of size l is lm_l, okay. Then, there is one more quantity both of them consider which is a very interesting quantity which is l^2 ml, so this is second moment, so m_l is a distribution, this is the first moment and this is the second moment and let me call that a susceptibility.

Now, what the way Stockmayer went about doing it is a very interesting, Stockmayer now consider exactly what Mayer did, that I give you that at a given time my system at a given extent of reaction that means, certain amount of reaction has taken place, then the that this ml has formed, how many ways now I can distribute monomer into a polymer.

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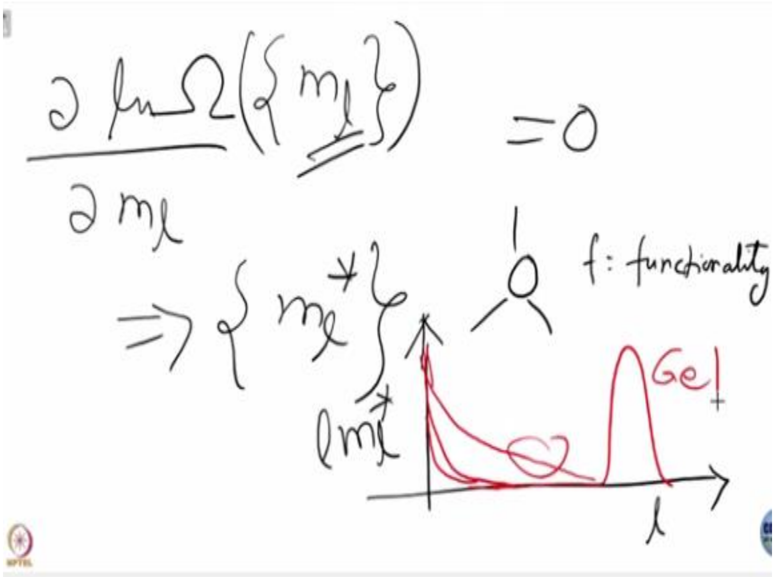

So, then he went around doing again the same way Mayer did that how many ways, I can form ω out of a m_l, number of clusters, then what Stockmayer went around doing; he maximizes these quantity these d ml with respect to ml, ln, he maximizes and found out the most probability distribution exactly the way Mayer did in, there is a non-trivial calculation just Mayer had a non-trivial calculation of finding the; which led to the partition function.

Here in non-trivial calculation to calculating that if each of my monomer has a functionality f, then how do I calculate omega that is the crux of a very, very difficult calculation. Once you do that calculation and you can find out the distribution ml star, then he found that if I now plot lm_l star which is the same I discussed that when the system of large size, the most probability distribution is same as the average l.

Then one finds that I plot it against l, then before the; say I am increasing the density and putting more and more monomer in my box and they are solved but certainly a critical density is reached and then the huge cluster appears. So, now this is now will be given like this at a low density, it will be mostly monomer may be few dimer, then I am going on increasing, then there are this kind of tail appears.

Then these actually comes down; number of monomer comes down and when there is nothing in between the intermediate population disappears because they become a large, so this is the gel phase. The analysis I am not doing in great detail but this is almost because one can go into doing a very detailed job that is not necessary in this course but one need to know that the sol-gel transition formulated in a Stockmayer way is exactly same as a Mayer's theory of condensation.

So, then one can calculate the viscosity of the system in a polymer, when you do polymer we will do that in more detail these kind of things but here I just want to bring it to the attention to these.

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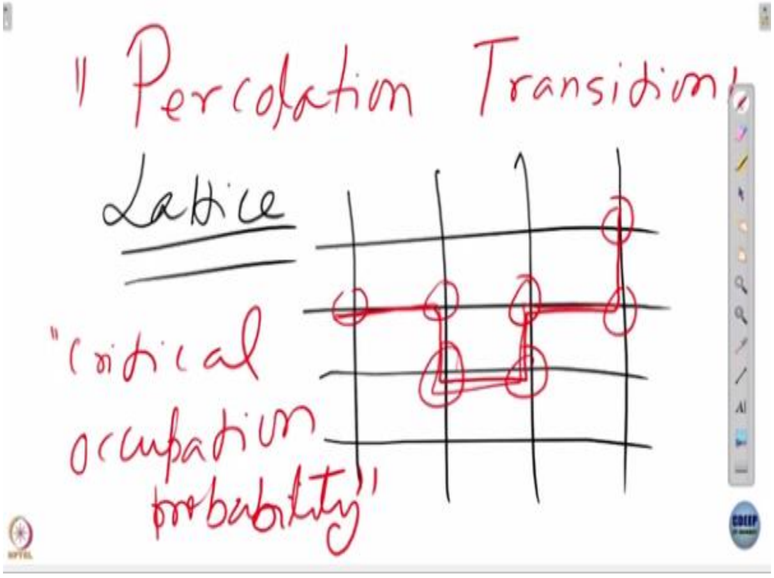

And one more transition which are very similar and then I will describe a few quantitative aspects of that which is the percolation, this you might have heard a lot, this is essentially same as this sol gel transition but the difference is that percolation transition is in solid state physics and we consider almost always on lattice. So, basically you have a lattice, I will briefly describe what is the percolation transition, then 1 or 2 quantitative aspects.

Sol gel transition and percolation transition are essentially the same from the point of view of phase transition though they are very different systems, as I told you this is one of the greatness of the universality of phase transition that you do first order phase transition of; once I say it is a first order phase transition, I immediately it comes to my mind okay, then this transition will have a first derivative discontinuous jump discontinuity, then I will have a latent heat, I will have a volume change.

And these are the properties, I say second order phase transition, I know okay specific heat will diverge, so first order phase transition of many different materials and just amazing universality that we and I will talk a little bit of the universality little bit now before we go to the thing that all these things will be done a little bit more detail later but right now, percolation transition is in solid state physics, it comes in the conductivity problem.

Basically, when you have 2 kinds of spaces in the system; one is a conducting, another is a non-conducting and you have disperse them in micro crystallites in a lattice phase gold nano particles and that is with another carbon nanoparticle maybe binary mixture of the 2. Now, one of them contact current, other does not, that does not, so when you have very low density of the conducting one, then there is no conduction, no current goes through that this is a very important industrial or practical thing.

However, when you have the conducting one, which has certain concentration, then suddenly you find the current comes in and so the way it happens is that these guys, they have to form a chain, so it has to form a connected cluster, so when this connected cluster is form, it forms a path and current flows in this path, so this is the percolation transition. Percolation transition then again forms a sudden appearance of a connected cluster. So, both percolation and sol gel transition are; there is a something called the critical occupation probability, what is the these red ones, they have to be certain number.

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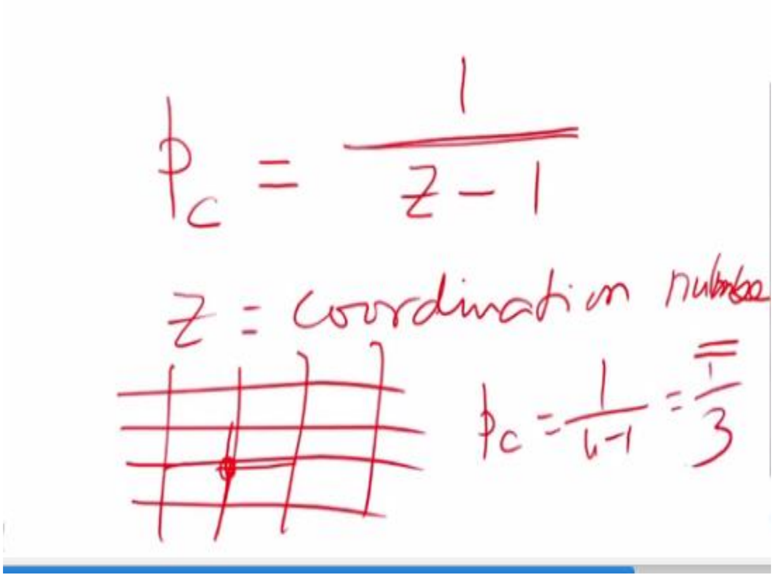

And that number goes by critical percolation is given as $p_c = \frac{1}{z-1}$, z is the coordination number, so when for example, you can imagine that in a 2 dimension lattice, square lattice where z is 4, there z is 4, your percolation probability is 1/(4-1) is 1/3, so these space is now the; these red ones now has to be 33%, when it reaches 33%, before 33% it is again completely dramatic and sudden, even at 30% you see that there are disconnected clusters, an intermediate sized disconnected clusters.

But as soon as you reach the within 0.01% of the 1/3 these clusters suddenly appear, so it has both these and sol gel transition has all these things, these kind of expressions also there exist 1 for a sol gel transition, there also we described in terms of this quantity l square; l square ml and l square ml describe again diverges with a at a given concentration of the monomers.

So, in sudden sense they have the characteristics of a phase transition both sol gel transition and percolation but both of them are clustering transition both of them has to do with appearance of large clusters, both of them has the second moment source divergence, this l square ml quantity these shows divergence and like these divergence is happens with exponent something will we will talk later and there I will discuss a percolation little bit in more detail and the derivation of these things little bit more detail.

But I do not want to go into these things but to know that these description of sol gel transition and percolation transition are very similar to the Mayer's theory of condensation and in certain sense, all 3 can be considered as a; is the appearance of a gigantic molecule, the appearance of a gigantic molecule that happens at a certain critical concentration of the monomer and they do not have the very weak thermodynamic signatures.

Thermodynamics you do not see much but you see their properties like in sol gel transition is the viscosity that diverges, in a percolation you suddenly in the lattice you see the current, current starts flowing, percolation also used very much in the flow of water in the sand boxes or in the sand where there are the conductivity is to be made for water to flow, so these are very, very similar things and quite universality.

And I cannot go into very detail of these things right now, instead we will now go on to do something different but before that a little bit more of a statistician that I want to just review and then go over to that. So, these are the; so we have done first order phase transition and first order phase transition and second order phase transition they are universal and we have not talked of any specific systems.

Similarly, in sol gel transition and percolation they are clustering transition in the Mayer sense and we have not described in detail any particular system and though some examples, I will be given they are given in my book and we will probably do a little bit later.

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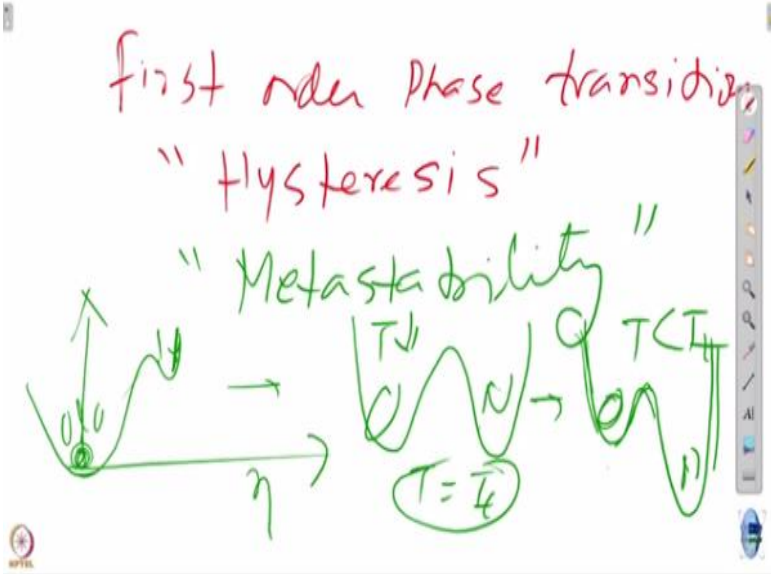

Before we go into something completely different, I just want to do one thing that when we do first order phase transition, I discuss a one thing which is called hysteresis and this I also called this is same as meta stability and I also told from Landau theory; Landau’s free energy surface it means that we have free energy landscape, if I plot against the order parameters eta, then this is; if this is the minimum, then something else large there.

So, when I go then further then these becomes this, then it becomes, so this is the metastable phase, this is the stable phase, when I lower the temperature, then so temperature going down and but this is T equal to transition temperature T_t and these temperatures below the transition temperature, so this is the old and this is the new; old and new. Now, new is more stable path, the minimum at old remains and that means the system can even trapped.

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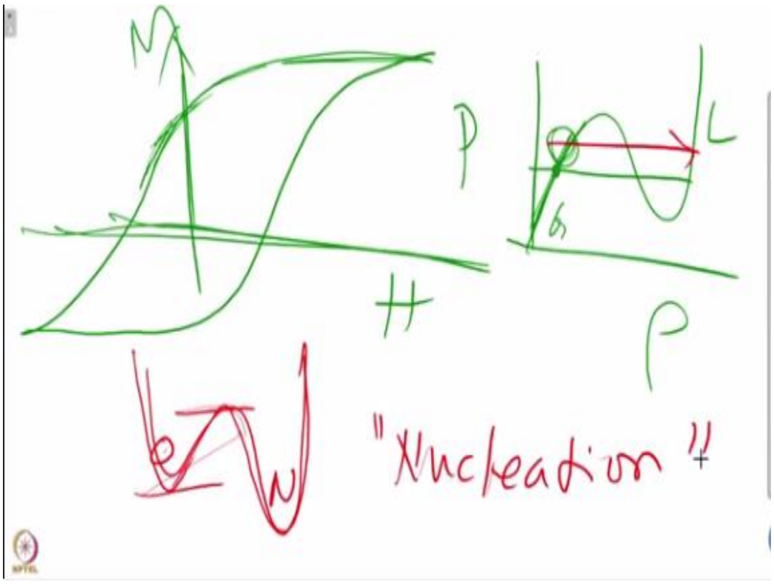

And this we see when you do hysteresis, we plot H against magnetization M, we have a large H, so it is now when it comes back, it does not go, so even though I have switched the field, spins remain up, magnetisation even positive and these we know in pressure versus density, this is Van der Waals loop, the exactly same thing, this is beautiful actually, this analogy between magnetic system and the gas liquid system is one of the most wonderful thing.

Because we gain tremendously by comparing one with the other, so here this is called a hysteresis or meta stability here, so when I pressure against density this is the Maxwell, so beyond this point it should go over to liquid but it does not, in the experiment not just in Van der Waals theory, in experiments these continues to stay and then an explosive transformation to metastable gas, this is the metastable gas that goes over to liquid.

It just then goes like this bang with a bang, it goes transferred to that, so this is the essence of first order phase transition is the meta stability, now why meta stability happens; the meta stability happens because once you have this kind of free energy but the system which is trapped in the old phase, the barrier is the thermodynamic system, this is a thermodynamic barrier, there is a huge barrier, no way this system can cross this barrier.

So, well there is a way but in bulk transformation of the old to new is not possible, the way it is done is another beautiful thing that we will do next in the next class that is nucleation, so this is the end of this particular lecture and so I discuss to you just I revised the sol gel transition and percolation transition and I did not go into very detail but there are the similar thing Mayer's theory that mean the large clusters appear in the system.

And the method that is done; sol gel transition was done by a Walter Stockmayer is same, exactly same as Stockmayer; as Mayer and percolation done in a more detail quantity by somewhat later in the context of more of a critical phenomena and that is still critical phenomena, is best understood in terms of the percolation that we will do in a later class and I I want to describe the mean, I said the percolation probability was z-1, exactly similar thing is there in 1-α; α is the extent of reaction and in sol gel transition.

So, the extent of reaction when certain; which is given by the total number of bonds form actually $(2n-m)/nm$ that is the extent of reaction and your critical thing is happens when extent of reaction reaches certain value which is matches with that of percolation, it is a very similar thing that means, the second moment diverges with the exponent minus 1 but I do not want to talk of exponent right now, I will talk when I do the critical phenomena.

But both have the signatures of phase transition in the cluster plane both so very weak thermodynamic anomaly and almost no thermodynamic anomaly, you cannot detect them that the percolation transition has taken place with thermodynamics, you detect them by doing dynamics but there is something very fundamental change in the nature and organization of the system has taken place and that is this appearance of the large gigantic cluster same as gas liquid transition. So, we stop here now and we will start with nucleation in the next class.