Basic Statistical Mechanics
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Lecture - 61
Conclusion

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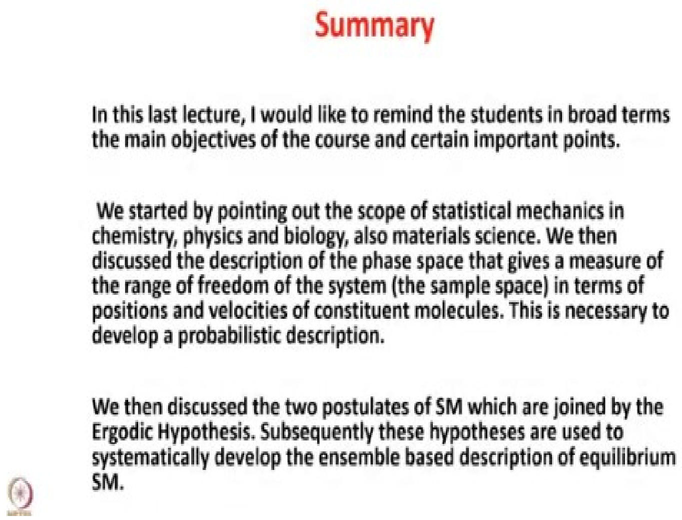

Summary

In this last lecture, I would like to remind the students in broad terms the main objectives of the course and certain important points.

We started by pointing out the scope of statistical mechanics in chemistry, physics and biology, also materials science. We then discussed the description of the phase space that gives a measure of the range of freedom of the system (the sample space) in terms of positions and velocities of constituent molecules. This is necessary to develop a probabilistic description.

We then discussed the two postulates of SM which are joined by the Ergodic Hypothesis. Subsequently these hypotheses are used to systematically develop the ensemble based description of equilibrium SM.

Welcome back to the final class on statistical mechanics. This will be a summary lecture while you would like to take the student the subjects covered in this rather long course on statistical mechanics. In this last of summary lecture, I would like to remind the students the basic objectives of the course and certain important points. If you look back, we started by pointing out the scope of statistical mechanics. There is a lecture called “why we study statistical mechanics.”

There I tried to point out the huge scope of the subject in physics, chemistry, biology and also material science particularly in chemistry and biology this is an extremely important subject. Here it is becoming important in material science also in the synthesis of new materials. After the preliminaries we tried to formulate the subject. I pointed out that they are actually two theoretical subjects who made your theoretical discipline in our entire arsenal: one is quantum mechanics and other is statistical mechanics.

Both use a substantial amount of mathematics and based on physics like, Newton's laws of motion and Schrodinger equation. So quantum mechanics provides you about the microscopic world about the energy levels about the wave function and very intimately connected to spectroscopy. On the other hand, statistical mechanics deals with many body. The phenomena the properties that appear because of interactions of many molecules, like a glass of water.

The properties of a glass of water is not the property of one individual water molecule. It is a sum of total of properties, one water molecule does not have the solvation properties does not have its flow or many other things that we know and associated with water. So the keyword is the interaction among this water molecules. It is not just water we can have ethanol, we can have methyl sulfoxide and argon many of metals, liquid metals. There is a huge number of these systems.

All around us including our body where the uniqueness of each system and the properties comes not from the constituents but also from the interaction. Interactions is the term determined by the nature of the molecules and atoms given the interaction potential. The duty or responsibility of statistical mechanics is to explain the properties like how in water aqueous. Other wonderful properties, for example, why boils $100^o C$, why it freezes into ice at $0^o C$, why water and ethanol form such a wonderful mixture. Innumerable such things that around us which statistical mechanics set how to explain. In this huge work, one goes to develop the substantial formalism which we discussed. We showed that how set with this huge task their forefathers like, Boltzmann and Gibbs they formulated two postulates.

Postulate one and postulate two: one is equal priority probability and the other is the ensemble average. Before that came the introduction of the concept of ensembles that huge I discussed at great length that is millions and billions of the mental replica of the original system. So that we can talk of probability distribution that was only when you assume that each system is in a different microscopic state, which are equally likely.

So it is equal a priori probability. However, the averages that we real world at the time average is a munch of the time. So time average is equal to ensemble average and that postulate is the second postulate. I also discussed how these two postulates are connected by the hypothesis that is called Ergodic hypothesis. With these two postulates and one hypothesis say the statistical mechanics it is how to explain the first number of observed phenomena.

It is amazing that how such simple and fairly innocuous postulate can lead you to explain why water freezes at $0^{o}C$ at ambient pressure.

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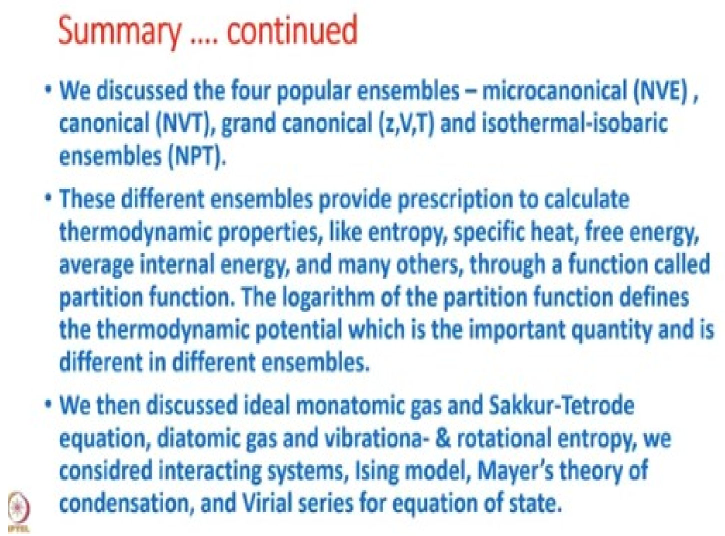

Summary .... continued

- We discussed the four popular ensembles – microcanonical (NVE) , canonical (NVT), grand canonical (z,V,T) and isothermal-isobaric ensembles (NPT).
- These different ensembles provide prescription to calculate thermodynamic properties, like entropy, specific heat, free energy, average internal energy, and many others, through a function called partition function. The logarithm of the partition function defines the thermodynamic potential which is the important quantity and is different in different ensembles.
- We then discussed ideal monatomic gas and Sakkur-Tetrode equation, diatomic gas and vibrationa- & rotational entropy, we considred interacting systems, Ising model, Mayer's theory of condensation, and Virial series for equation of state.

First, we discussed the concept of ensembles and that they will start with the microcanonical ensemble which is called NVE. Then there are four ensembles. We discussed like, from microcanonical to canonical, canonical to grandcanonical and then isothermal and Isobaric. Microcanonical is NVE, canonical NVT, grandcanonical is fugacity volume temperature and the isothermal isobaric ensemble is NPT.

So as you clearly see these different ensembles serve different purposes because often our experimental systems are different conditions. Almost neighbour in NVE because we cannot control energy because our systems are always in interacting with surrounding. We cannot fully control the volume though it is little more than energy. Number N also many times molecules are getting exchanged to surrounding media like a glass of water.

So these may we need the different ensembles to treat different experimental conditions. Also there is a very fundamental theoretical reason that doing calculations or theory in microcanonical ensemble is rather difficult. We set out with these four different ensembles to calculate a thermodynamics properties like entropy, specific heat, free energy, average internal energy, radial distribution function etc.

All of them go through one rout that is the partition function. The partition function is essentially weight of that particular state of the system like given by saying NVE. Then partition function gives me what is the weight of that and that weight has to be maximized much of the time. Longer the partition function defines what is called the thermodynamic potential. We discussed in detail like logarithmic of the canonical partition function is the free energy. Lowering of the microcanonical partition function is the entropy and this is then the first states describing thermodynamics from statistical mechanics which is one of the major goals. After formulation of the expression for the partition function we did several wonderful calculations, we calculate entropy, Sakkur-Tetrode equation for entropy which is the diatomic gas and vibrational-rotational entropy.

These are for ideal gas, where molecules do not interact with each other but just they are many of them together even with non-interacting limited, some wonderful properties like Sakkur-Tetrode equation, vibrational-rotational which can actually be experimentally derived in many cases, not in a completely but you know 90% or so in dilute gas, for example, is a good model of the ideal gas you know certain approximations then we did interacting systems.

We did Ising model which is a system of spins and we did the Mayer's theory of condensation, and from Mayer's theory, so wonderful fairly sophisticated theory to tell you how in the presence of intermolecular interaction you go around calculating the partition function, calculating the pressure and equation of state. Ultimately, we show how from Mayer's theory you get the well-known Virial series. The Virial series was derived in 19th century mid 19th century.

First Virial coefficient, second Virial coefficients, third Virial coefficient all those things were done and measured long time ago. When Mayer's theory was done then the expression second virial coefficient and third virial coefficient in terms of intermolecular potential allows to use the experimental result to construct intermolecular potential.

And this is actually some kind of a fitting to experimental data, but at the end you find a very important quantity. Which is not just it which was introduced from imagination that two molecules interact, but we had no way to know what is the interaction potential between it. This Mayer's theory and the expression for virial coefficients allowed us mapped and get the intermolecular potential. This is a big game, now which is called the force field.

So these virial coefficient first time and for example that two argon atoms interact through something like Lenard-Jones potential that came out and the parameters of the Lenard-Jones potential came out from this, a theoretical expression write by Mayer for the viral coefficients.

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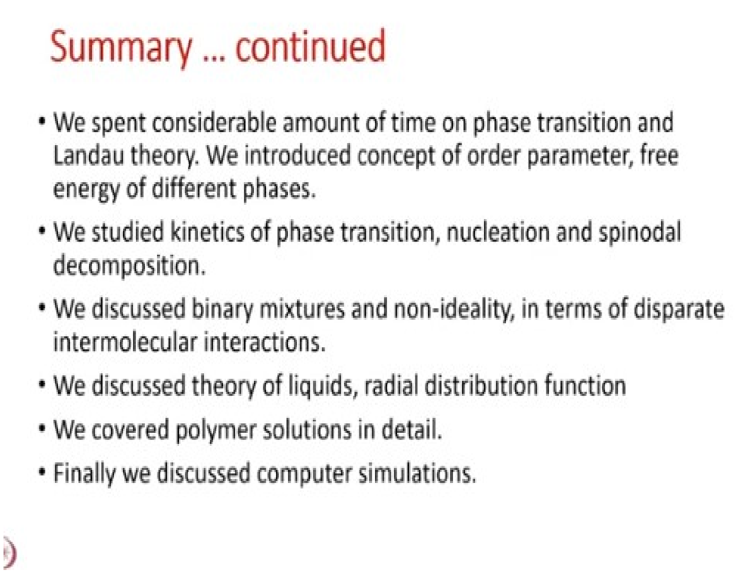

Summary ... continued

- We spent considerable amount of time on phase transition and Landau theory. We introduced concept of order parameter, free energy of different phases.
- We studied kinetics of phase transition, nucleation and spinodal decomposition.
- We discussed binary mixtures and non-ideality, in terms of disparate intermolecular interactions.
- We discussed theory of liquids, radial distribution function
- We covered polymer solutions in detail.
- Finally we discussed computer simulations.

Continuing that, we spend a lot of time on phase transition to different solid phases form. How condensation takes place. So Mayer's theory told us how intermolecular interactions to be included, but that there is a very difficult theory which was further developed later two clusters for other things. There is a simpler and more direct approach to understand many aspects of phase transition the universality of phase transition.

Without going through intermolecular potential that is called Landau Theory of phase transition. So we discuss about the theory of Landau theory which is the free energy expansion in terms of the order parameter. We introduced the concept order parameter, free energy as a function of order parameter. Different phases at different free energy and what is the basic structure. After we studied the phase transition of thermodynamics of phase transition like the discontinuity at the phase transition. We discuss first order of phase transition. We discuss second order phase transition that is called Ehrenfest classification and how Landau theory kind of unifies these different things into a beautiful scheme based on free energy. We then subsequently studied the kinetics of phase transition should. We study nucleation or spinodal decomposition.

These are wonderful subjects and they are very useful because the nucleation is something raindrops falling, ice forming, all around us or now that the ice melting. So nucleation is very important these spinodal decomposition on the other hand, is a theory of pattern formation how beautiful patterns form in nature and this is also a part of kinetics of phase transition.

Then now we went on and we studied binary mixture. Binary mixtures is a wonderful subject where you studied in undergraduate physical chemistry in great detail and also in bio- physical chemistry, that how binary mixtures two liquids a and b mixed we had to add new properties and that property is extremely useful in a chemical industry and also in biology. So one needed to understand in terms of intermolecular interactions how these unique properties and the composition dependent of the property so binary mixtures.

How much a or how much b we mix to get this property. That also prescription given by statistical mechanics and lot of work has been done on the along that line and we discussed that. Then you want you to describe the three lectures, we found on theory of liquids, radial distribution functions and extreme important called function called $g(r)$, which describes many properties of the liquid.

Then we covered in detail, again three lectures on polymer solutions, polymer thermodynamics, Flory’s theory, sol-gel transition. We discussed the Flory-Hugginstheory. We discussed how polymer collapse takes place. We discussed how while polymers in solution would solvent are swollen. The interaction effective interaction between monomers or get it solvent molecules.

We discussed polymer in great detail finally in two lectures we discussed computer simulations which is extremely important because you could not do many of the complex interactions. We cannot do statistical mechanics and these are very important subjects that we dealt with. We went through huge number of subjects. We did quite a bit of theory to quite a bit of mathematics.

And, however, as I was saying, when I real molecules we are as I mentioned in the lecture interactions are quite complex. So we cannot do them through analytical work, even Mayer's theory you found out difficulties pushed through Mayer's theory. So the field was suffering, but at the same time in the 1960's computers came in and this statistical mechanics again could go ahead because they could not treat those complex interactions using the principles of statistical mechanics by computer simulations. Molecule dynamics and Monte Carlo simulation they are all based on principles of statistical mechanics that one should not forget that. But so computer simulation doing the people doing that kind of computer simulations are actually at the statistical mechanics but instead of doing analytically pen and paper and pencil they we cannot do complete.