Basic Statistical Mechanics
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Lecture - 16
Fluctuations and Response Function Part 1

This was the one which was worked out by Einstein and which is this many many things he did, I know he did the Brownian motion and Brownian diffusion but this was the thing which was done somewhat later and it is a brilliant way that he started. Somehow he got into his idea to study the probability of a fluctuation and he introduced the concept that at system at equilibrium in the homogeneous state.

It has two independent thermodynamic variables and he worked out with and it played a very important role in the later hydrodynamics. That for example, he took temperature and pressure and worked it out and this that situation isothermal, isobaric is the best way to do hydrodynamics and he also do entropy and volume these fluctuations and then he found out the probability of fluctuation.

The way he did that, he constructed a fluctuation and got the work done to this, create that fluctuation and from there he did the probability of fluctuation. Now why do we talk of fluctuation?

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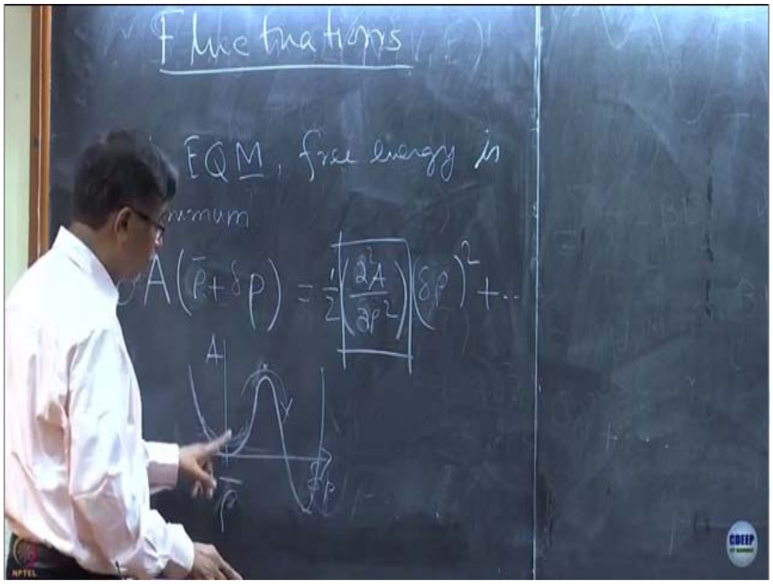

And what is the reason? We know that at equilibrium free energy is minimum. So, now if the free energy is minimum, then, if I expand free energy as a function of say density and I say, my density undergoes a fluctuation around the equilibrium fluctuation. So, free energy is $A(\overline{\rho}+\delta\rho)=A_0(\overline{\rho})+\left(\frac{\partial A}{\partial\rho}\right)(\delta\rho)+\frac{1}{2}\left(\frac{\partial^2 A}{\partial\rho^2}\right)(\delta\rho)^2+......$, then the way one writes is that free energy A0 at equilibrium rho average.

Now the first derivative of free energy with respect to density goes on like that. Now this quantity which is the derivative because the free energy is minimum these goes to 0. So then I have and I make the delta change in free energy as a delta rho then this also goes out. Then I can write as a first term of this Taylor expansion as, so this will be the partial derivative other things get fixed.

Now then we can say that if I want to have a fluctuation that fluctuation has this cost in free energy. That means to a small enough fluctuation my free energy surface is harmonic. This is rho average. Is it clear? Is it very trivial logic? But at the same time this is very profound**.** So these are the then we call this quantity as the force constant of the fluctuation. So you immediately see that this is the quantity which must be positive so that there is a cost of free energy.

Then if as in phase transitional chemical reactions, if there is a barrier and then there is another state here, then to small we say to small fluctuations this is stable but to a large fluctuations this goes over there. When it reaches there these derivative becomes negative now. So either it has to once it reaches there it has to come back there or come there. So the equilibrium between in the two such state characters by minimum is determined by the difference in this.

But dynamics is profoundly dependent by the oscillations here and the curvature there. Now we do not want to talk of dynamics instead we want to talk about these quantity. So this is the chapter you can read where talked of all the fluctuations. So basic idea is that what are these fluctuations are the most important quantity because this is the, determines the response, the second derivative determines the response of the system to your fluctuation. How?

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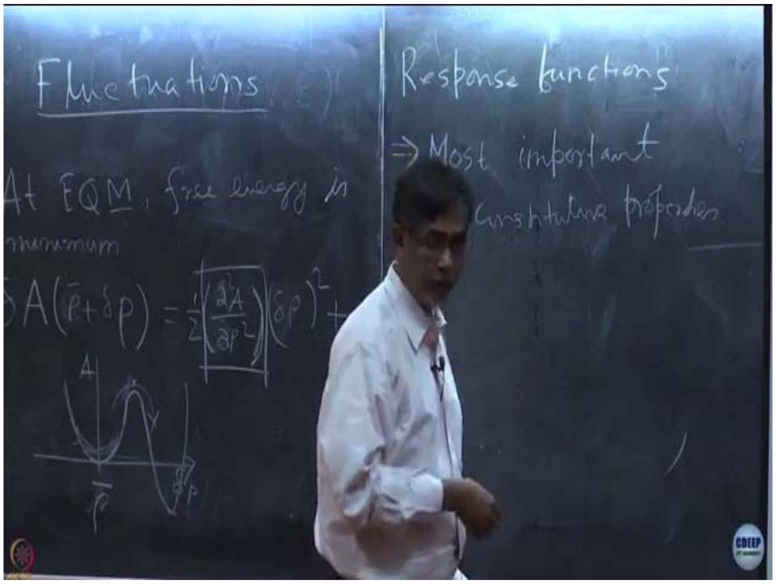

That is called the linear response or response functions and this response functions are the most important properties of a system like when we brought the rock from the moon**,** other than the density the first thing they calculate is the specific heat. Actually whenever you go to many museums, they will write down the specific heat of that below and the conductivity. Those properties conductivity, specific heat are the response functions. Why? Because if you;

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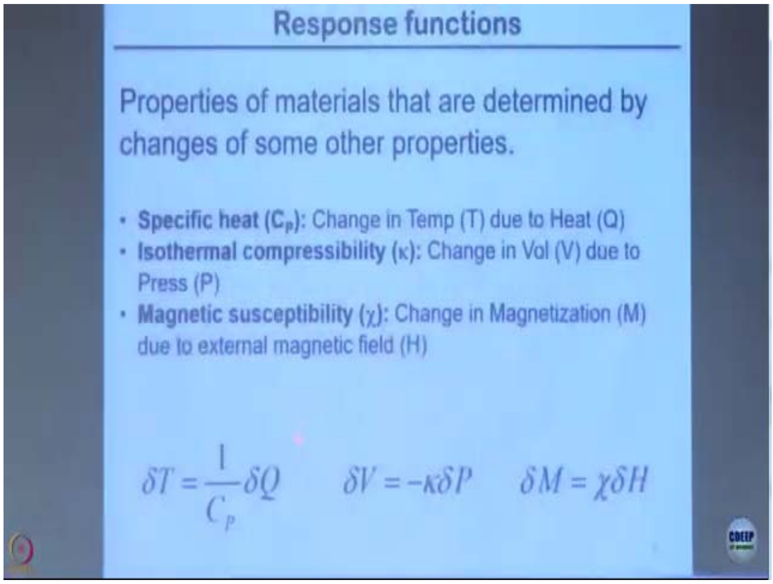

Response functions

Properties of materials that are determined by changes of some other properties.

- **Specific heat (C_p):** Change in Temp (T) due to Heat (Q)
- **Isothermal compressibility (κ):** Change in Vol (V) due to Press (P)
- **Magnetic susceptibility (χ):** Change in Magnetization (M) due to external magnetic field (H)

$$\delta T = \frac{1}{C_p}\delta Q \qquad \delta V = -\kappa \delta P \qquad \delta M = \chi \delta H$$

So now as I am telling you from the morning that these are very important. If I change, if I want to change temperature by delta T then I have to give a amount of heat delta Q and so this is the relation. Cp if you bring it here, then $\delta Q / \delta T$ is the Cp. So specific heat is the amount of heat needed to change the temperature by 1 degree that is what you have started in the 8th grade at least we started in 8th grade.

Compressibility now I bring here, $\delta V / \delta P$ is the compressibility. That means unit pressure, the pressure needed to change volume everything by unit and this is the magnetic susceptibility χ. It is connected to the polarization of the magnetization created in the system by applying this amount of external field. So every case we are applying an external perturbation, here we are giving an amount of heat.

Here we are giving an amount of pressure and here we are giving an external magnetic field. On the left-hand side we are having the response of the system and then these constant coefficients are the one which gives the response, the magnitude of the response. Near phase transition these response functions all diverge then a very small amount of perturbation, create a huge response. Specific heat goes to infinity remember the lambda curve compressibility goes to 0 in gas liquid transition with an compressively so then and these also diverges.

So, stability condition of a system both mechanical this gives you the mechanical stability and these you give the thermodynamic stability. Both these stabilities are connected with these quantities. So whenever we talk of a system is stable or non stable there is set of stability conditions which is discussed in my book in a little later I will hope to get in that. So I hope I have impressed sufficient amount on you to tell the importance of these response functions.

They are the most important constitutive properties of the system most important constitutive properties of the system. So and the once whenever any matter is new things are created these are the first properties that one measures to characterize the system okay. Now so my next comment and very important comment too is that these are the quantities these response functions. In addition also and this is the most fundamental relation one of the things.

In my book first time, I have the chapter 6, I had fluctuations and I said realization of the promises. Later my students said they notice that that is bit too much but the whole statistical mechanics is quite a formidable structure as we have seen, you have to go quite a bit before you start getting the results which is somewhat different from quantum mechanics. Because you start with running this equation which is also postulate and then you start getting results which are connected to spectroscopy really together quickly.

Not in statistical mechanics here, you will get a huge amount of results but you have to plow through certain amount of things. You have to understand systematically how, just going to partition function is itself as this process and but then at the end of the day much of these are, for example if you are going to do soft method, you are going to do phase transition, you are going to do polymer liquid crystals everything is nothing but statistical mechanics.

So, you are going to put this extra the nucleation everything, you are going to put this but at the end of the day you are stunning phenomena. So you have again I am telling one thing in chemistry the way we do quantum we do not study phenomena rarely we study phenomena. We study numbers which are then connected to spectroscopically. So there is a huge difference the way these two disciplines work.

You go to a quantum chemistry conference here at this India they hardly talk of they talk of formalisms. They talk of second decimal place sometimes. But they do not talk of any phenomena. So, their main delight is the publication in Jacks and Angewandte okay. Now so the important thing at these quantities here my point I am going to make most important point are essentially these second derivatives of free energy.

Specific heat with respect to temperature, this one is with respect to density on number or volume and susceptibility is with respect to these external field. So these quantity density, temperature, magnetization sorry these are external control parameter. We will introduce a term called order parameter, little later okay. So to summarize, this part that these important things specific heat, compressibility these things are the second derivatives of free energy.

First derivative is 0 and you can easily see why? Because if I give a small amount of heat or small change I put a little bit of pressure then since it is in a minimum how much it is going to displace is determined by this quantity and then which is given by this which is a swing constant. Is that a harmonic surface, it is a spring constant. This is an extremely important because these trivial apparently trivial things are basis of theory of Landau's theory of phase transition.

It is a wonderful theory that we do. After this we will do monatomic gas, then we do diatomic, then we will jump a little bit, we will do both Einstein later we will go to Meyer's your interacting system, then you go to Landau theory. So I will do a little bit back and forth kind of thing I will not follow the textbook completely. Now we write a textbook you are kind of constrained by the kind of established by McQuarrie or all other people. So I am going to now do the next part.

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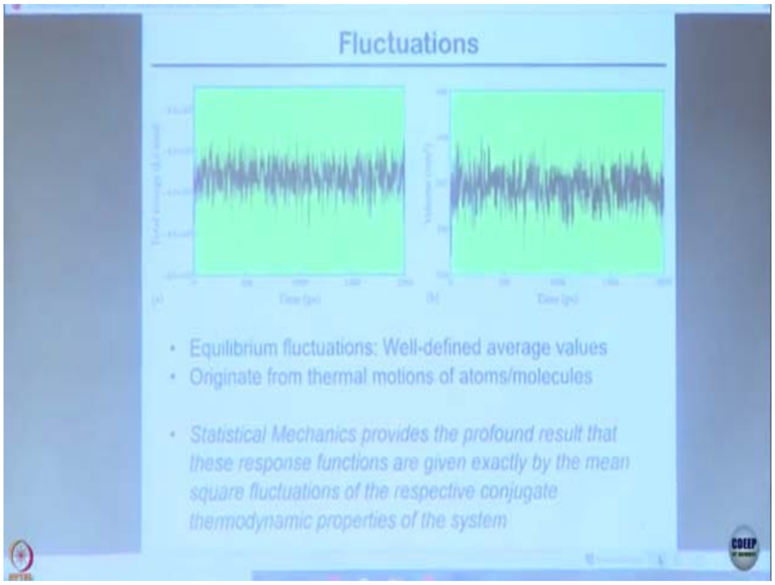

Fluctuations

- Equilibrium fluctuations: Well-defined average values
- Originate from thermal motions of atoms/molecules

- *Statistical Mechanics provides the profound result that these response functions are given exactly by the mean square fluctuations of the respective conjugate thermodynamic properties of the system*

So this quantity is a very interesting quantity now. How do I get that? This is the another very important response that if I study this thing even at equilibrium, even in the absence of an external perturbation is the most important thing the particles are moving. This is a very important language, which our Ryogo Kubo introduced, called the natural motion of the system. The system is undergoing continuous the thermal motion.

That thermal motion gives you diffusion dynamics that gives you resistivity that also give you specific heat. Now I am making this far-reaching observation that these fluctuations contain the information of specific heat and isothermal compressibility. So natural motion of the system determines and I am telling you I cannot overemphasize this so important. Here my student has done these fluctuations in total energy where simulation and volume.

And you can see it is as I was telling in the morning they continuously fluctuate. They are just natural system. Remember Castellon gave a wonderful example of Castellon said....ok...

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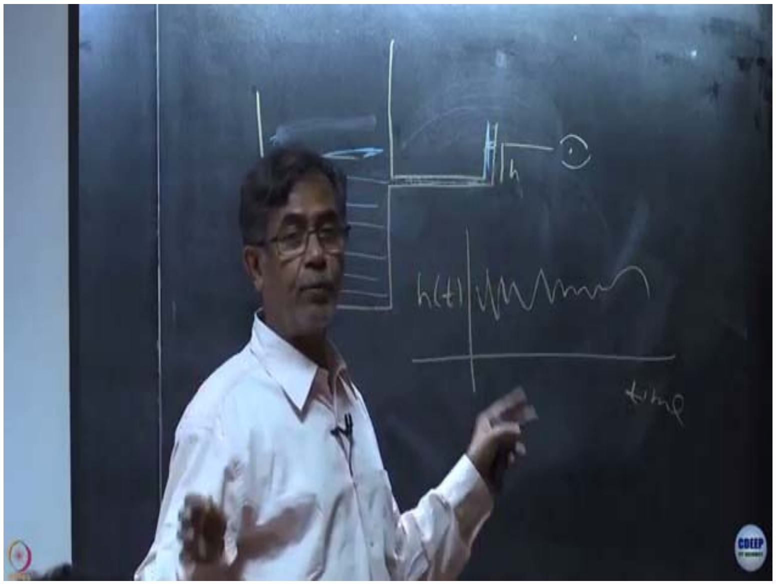

I now, and I have put some colored liquid here which will now go into here and say this is the up to this so same level here the earlier discussed but I make this pipe is very narrow. So this many scars is visible in a microscope. So now I look at it through a microscope. I am an wonderful artist as you can figure out. So now these height, I call this height h and now I plot that from h as a function of time.

I will find that this continuous velocity without anything it is at equilibrium with the atmosphere. So the reason is that there is a natural motion of the system you know. So the way that is the nature's way or the system's way to interact with the external pressure. Everything is at equilibrium. So I am in completely equilibrium but my system is undergoing these fluctuations. It is very very important to realize that this is a natural fluctuation.

So equilibrium fluctuatuation defines average values originate from thermal motion of atoms or molecules. This from my book; statistical mechanics provides the profound result that these response function that I am discussed here in three thing are given exactly by mean square fluctuations of the respective conjugate thermodynamic properties. So, I am going to now tell you what is the specific heat, how do we calculate specific heat and what is the microscopic definition and microscopic meaning of the specific heat.

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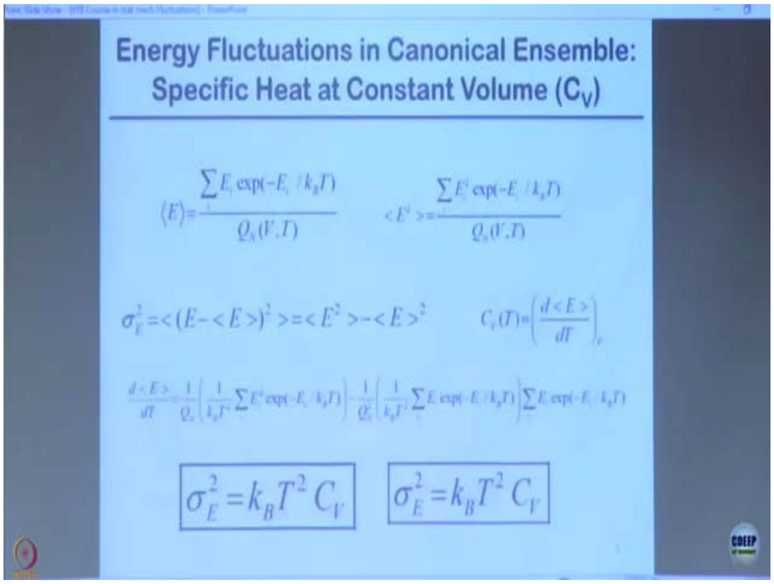

Energy Fluctuations in Canonical Ensemble: Specific Heat at Constant Volume (C_V)

$$\langle E\rangle = \frac{\sum_i E_i \exp(-E_i/k_BT)}{Q_N(V,T)} \qquad <E^2> = \frac{\sum_i E_i^2 \exp(-E_i/k_BT)}{Q_N(V,T)}$$

$$\sigma_E^2 = <(E-<E>)^2> = <E^2> - <E>^2 \qquad C_V(T) = \left(\frac{d<E>}{dT}\right)_V$$

$$\frac{d<E>}{dT} = \frac{1}{Q_N}\left(\frac{1}{k_BT^2}\sum_i E_i^2 \exp(-E_i/k_BT)\right) - \frac{1}{Q_N^2}\left(\frac{1}{k_BT^2}\sum_i E_i \exp(-E_i/k_BT)\right)\sum_i E_i \exp(-E_i/k_BT)$$

$$\boxed{\sigma_E^2 = k_BT^2 C_V} \qquad \boxed{\sigma_E^2 = k_BT^2 C_V}$$

And so this is the way we remember dE/dT is this specific heat. So I do the dE/dT , I go to this dE/dT, I do I bring one E so it becomes E^2. Another term comes from here but $Q = \sum_i \frac{e^{E_i}}{k_BT}$. So that brings it so Q right? So take a derivative it will become 1 over Q square because it is in denominator and then I take the derivative it brings Ei out and there is one Ei before here. So same thing Ei by KBT **s**o this become a square.

Now D square but it has Q denominator so I put the Q inside and complete this square so that thing is just average energy square. These quantity on the other hand is this E square K_BT square when by a it is K_BT square both the two places and then 1 over QN. So this quantity is nothing but E square okay. So I have E square minus average E square exactly so specific heat is then this quantity.

So that is why the relation that E square this is specific heat CV 1 over K_BT square in both the two cases I bring it upstairs so I get K_BT square CV and this square is this quantity on the left hand side. So specific heat is nothing but mean square fluctuation of energy ie $C_V = \frac{1}{k_BT^2}\sigma_E{}^2$. This is very simple thing that is what I wrote in my book I had the original title that realization of promises. This is really such wonderful result, which nobody anticipated.

That did specific heat is nothing but mean square energy fluctuation is that as I said I cannot overemphasize the beauty and the importance of this relation okay.

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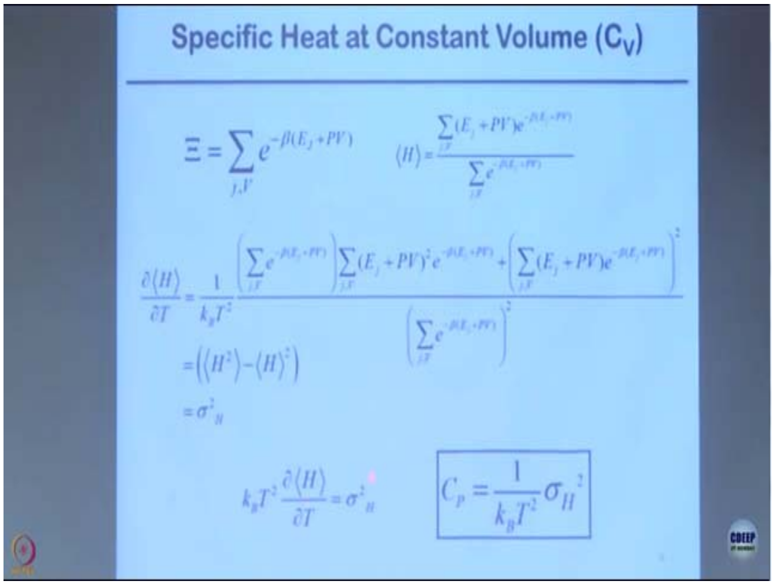

Specific Heat at Constant Volume (C_V)

$$\Xi = \sum_{j,V} e^{-\beta(E_j+PV)} \qquad \langle H \rangle = \frac{\sum_{j,V}(E_j+PV)e^{-\beta(E_j+PV)}}{\sum_{j,V} e^{-\beta(E_j+PV)}}$$

$$\frac{\partial\langle H\rangle}{\partial T} = \frac{1}{k_B T^2}\frac{\left(\sum_{j,V} e^{-\beta(E_j+PV)}\right)\sum_{j,V}(E_j+PV)^2 e^{-\beta(E_j+PV)} + \left(\sum_{j,V}(E_j+PV)e^{-\beta(E_j+PV)}\right)^2}{\left(\sum_{j,V} e^{-\beta(E_j+PV)}\right)^2}$$

$$= \left(\langle H^2\rangle - \langle H\rangle^2\right)$$

$$= \sigma^2_H$$

$$k_B T^2 \frac{\partial\langle H\rangle}{\partial T} = \sigma^2_H \qquad \boxed{C_P = \frac{1}{k_B T^2}\sigma_H{}^2}$$

Now I that I did is specific heat at constant volume. Now I want to do specific heat at constant pressure. Specific heat at constant pressure will come from our NPT Ensemble and H then it become E + P V. We discussed in the morning and then you can exactly play the same game and you find out that the specific heat at constant pressure is again mean square fluctuation in the enthalpy. That is Cp.

Cp and Cv can be quite different. Experimentally we work with Cp but Cv is the one theoreticians work with that reason is that the other one much in canonical ensemble is easier and that is what we do all the time canonical ensemble.

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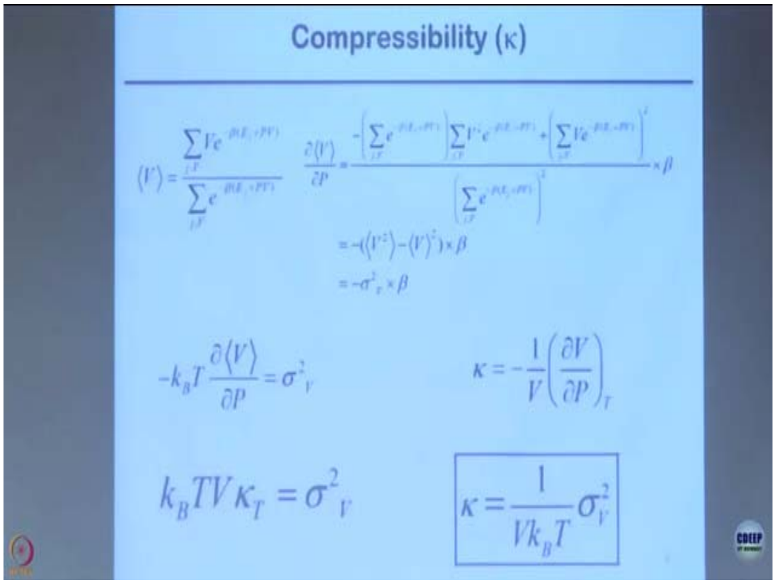

Compressibility (κ)

$$\langle V\rangle = \frac{\sum_{i,V} V e^{-\beta(E_i+PV)}}{\sum_{i,V} e^{-\beta(E_i+PV)}} \qquad \frac{\partial\langle V\rangle}{\partial P} = \frac{-\left(\sum_{i,V} e^{-\beta(E_i+PV)}\right)\sum_{i,V} V^2 e^{-\beta(E_i+PV)} + \left(\sum_{i,V} V e^{-\beta(E_i+PV)}\right)^2}{\left(\sum_{i,V} e^{-\beta(E_i+PV)}\right)^2}\times\beta$$

$$= -(\langle V^2\rangle - \langle V\rangle^2)\times\beta$$

$$= -\sigma^2{}_V \times\beta$$

$$-k_B T\frac{\partial\langle V\rangle}{\partial P} = \sigma^2{}_V \qquad \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$k_B T V\kappa_T = \sigma^2{}_V \qquad \boxed{\kappa = \frac{1}{Vk_BT}\sigma_V^2}$$

Now I go into compressibility. Again the same thing, I go to the NPT ensemble and I again do the V square delta V and you know $\left(\frac{\partial V}{\partial P}\right)$, here $\left(\frac{\partial V}{\partial P}\right)$ I do here by P and P here brings out to V square. So I get V square - delta V square which is the mean square fluctuation then $\left(\frac{\partial V}{\partial P}\right)$ is the mean square fluctuation in volume and this is my compressibility. So I get the relation is that the isothermal compressibility is nothing but sigma V square ie

compressibility is given by

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T ,$$

So,

$$k_B T V\kappa_T = \sigma^2{}_V$$

$$\boxed{\kappa = \frac{1}{Vk_BT}\sigma_V^2}$$

Or here is the Euilmen relation. Important thing is that isothermal compressibility is given by mean square volume fluctuation. So that is why this was given here this is the mean square energy fluctuation this the mean square volume fluctuation. These are real simulations of I believe of water. There is reason to talk of water and I will talk about water in the context in a little bit in a greater detail. So compressibility we have done specific heat we have done.

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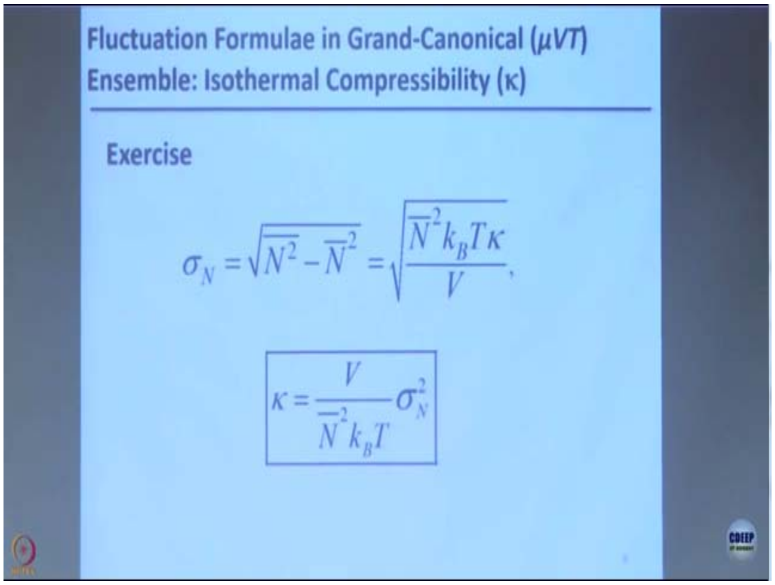

Fluctuation Formulae in Grand-Canonical (μVT) Ensemble: Isothermal Compressibility (κ)

Exercise

$$\sigma_N = \sqrt{\overline{N^2} - \overline{N}^2} = \sqrt{\frac{\overline{N}^2 k_B T \kappa}{V}},$$

$$\boxed{\kappa = \frac{V}{\overline{N}^2 k_B T}\sigma_N^2}$$

We have not done I so this is an exercise that you can easily do. This you have to do in the grand canonical. Grant canonical you have to consider you can do exactly the same game you play, you know but in the grand canonical remember that we are screwing it up little bit having the same notation but grand canonical you do you can do the number fluctuation right? And now you can write the compressibility isothermal compressor as a derivative.

We see it is DV then you write $\left(\frac{\partial V}{\partial P}\right)$ and replace V by density N by V and say I want the number fluctuation not the volume to fluctuate. Then you will get $\left(\frac{\partial E}{\partial N}\right)$ that means I have here in density I have N instead of volume and these will be if you work it out you will be able to get this result the isothermal compressibility is the final value is the same. You can calculate in the grand canonical, you can calculate isobaric ensemble.

Two different things two different way we calculate that. If we want to calculate in canonical ensemble then I just do the volume fluctuation. Sorry if I do NPT ensemble I do the volume fluctuation because you know canonical ensemble volume is fixed does not fluctuate. But in isothermal isobaric NPT ensemble volume fluctuates. From that fluctuation I can get the mean square fluctuation and that gives the compressibility.

But if I consider that as I told you we discussed this is difficult to do in a computer simulation. The end that is the unread Gibbs ensemble.

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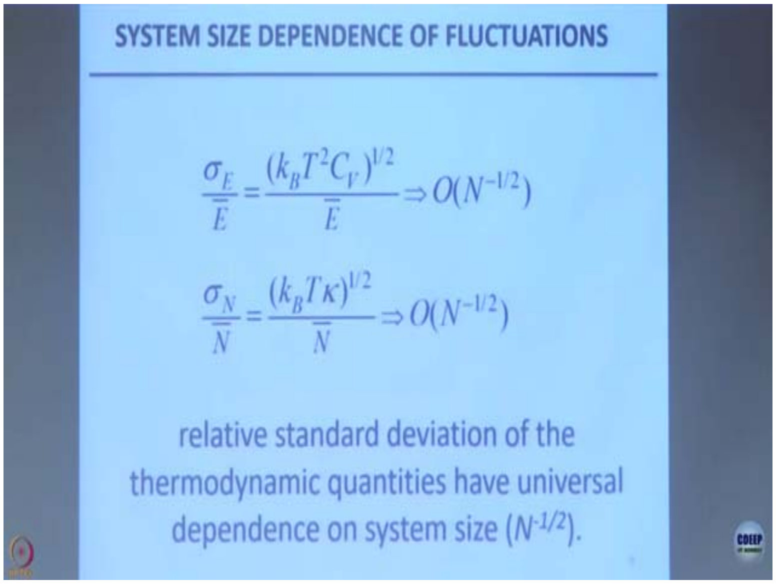

SYSTEM SIZE DEPENDENCE OF FLUCTUATIONS

$$\frac{\sigma_E}{\overline{E}} = \frac{(k_B T^2 C_V)^{1/2}}{\overline{E}} \Rightarrow O(N^{-1/2})$$

$$\frac{\sigma_N}{\overline{N}} = \frac{(k_B T \kappa)^{1/2}}{\overline{N}} \Rightarrow O(N^{-1/2})$$

relative standard deviation of the thermodynamic quantities have universal dependence on system size ($N^{-1/2}$).

And that is the eye path that I am not going to go into because I am not very clear myself about it. So the one of the questions that was raised why different ensembles have the same result? The reason is the following.

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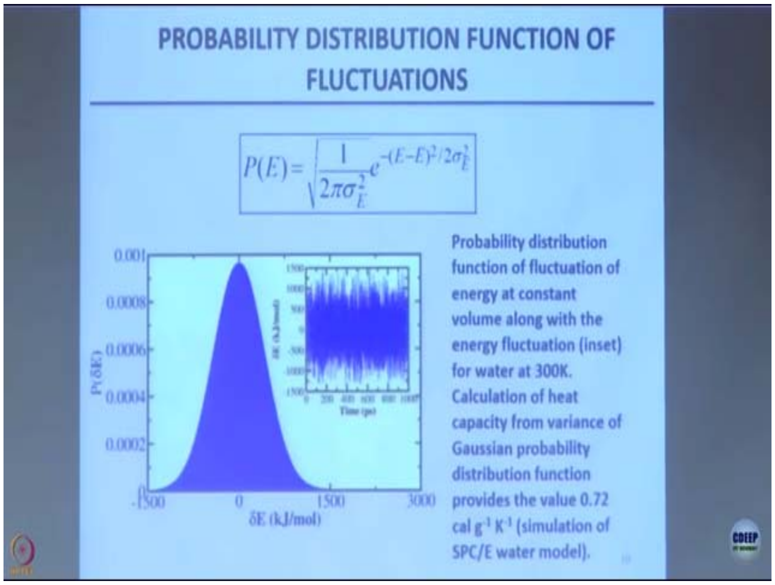

PROBABILITY DISTRIBUTION FUNCTION OF FLUCTUATIONS

$$\boxed{P(E) = \sqrt{\frac{1}{2\pi\sigma_E^2}}\, e^{-(E-\overline{E})^2/2\sigma_E^2}}$$

Probability distribution function of fluctuation of energy at constant volume along with the energy fluctuation (inset) for water at 300K. Calculation of heat capacity from variance of Gaussian probability distribution function provides the value 0.72 cal g^{-1} K^{-1} (simulation of SPC/E water model).

Let me see if I, I have the graph here; The reason is the following that now let us see the relative fluctuation. So, sigma E square this is the width and these also a question that was asked we will come to that answer both the two questions.

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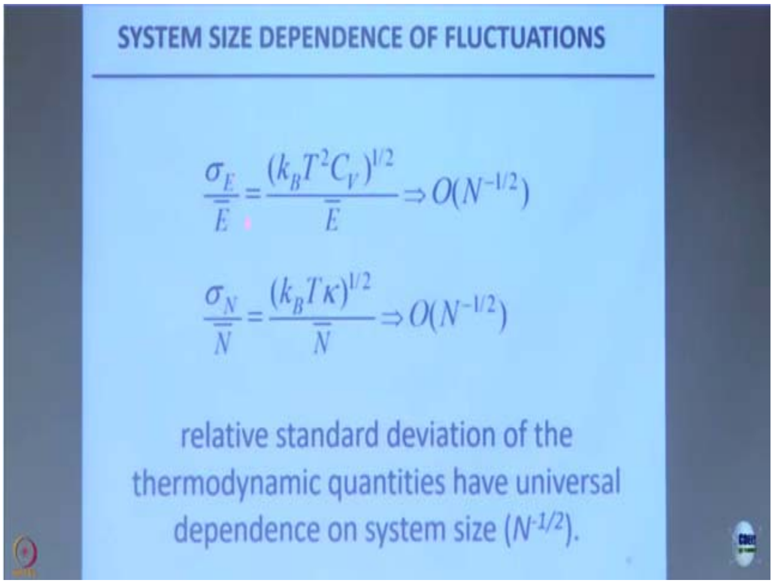

SYSTEM SIZE DEPENDENCE OF FLUCTUATIONS

$$\frac{\sigma_E}{\overline{E}} = \frac{(k_B T^2 C_V)^{1/2}}{\overline{E}} \Rightarrow O(N^{-1/2})$$

$$\frac{\sigma_N}{\overline{N}} = \frac{(k_B T \kappa)^{1/2}}{\overline{N}} \Rightarrow O(N^{-1/2})$$

relative standard deviation of the thermodynamic quantities have universal dependence on system size ($N^{-1/2}$).

So remember when we do we always talk we need to talk of the relative value. Why you have to consider relative value? That because you cannot compare 100 to 1000 and you cannot compare 1000 to 10000. Say we want to describe the distribution of salary in a concern. Then what you have to do? You have to find out the maximum salary now the concern to concern the maximum salary is changing.

If you want to study the dispersion if you better scale by that make that equal to 1 and then say how the dispersion goes. Here also so this is the relative fluctuation that we need to look into. And relative fluctuation then sigma E square. Sigma E square is Cv KBT square i.e. $\boxed{\sigma_E^2 = k_B T^2 C_V}$. So sigma is $\boxed{\sigma_E = \sqrt{k_B T^2 C_V}}$. I divide by then the energy these scales as N because this is the average energy there is an extensive property.

These scales as N to the power half. The specific heat is also an extensive property. So we have root over N by N. So it scales as 1 over root N that is true everywhere so the scaling of fluctuations. So now if I want to compare the results of canonical and grand canonical or canonical and isothermal isobaric ensemble, then the results will be the same when the fluctuations are small.

So the fluctuations are these things that is moving around here. When N goes to infinity these fluctuations relative fluctuations become very very small then it goes to 0. The fluctuations go to 0 as 1 over root N. This is the reason why whatever ensemble you study you get the same result. This also intimately related with the stability conditions that we will discuss later.