Basic Statistical Mechanics

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Lecture - 17
Fluctuations and Response Function Part 2

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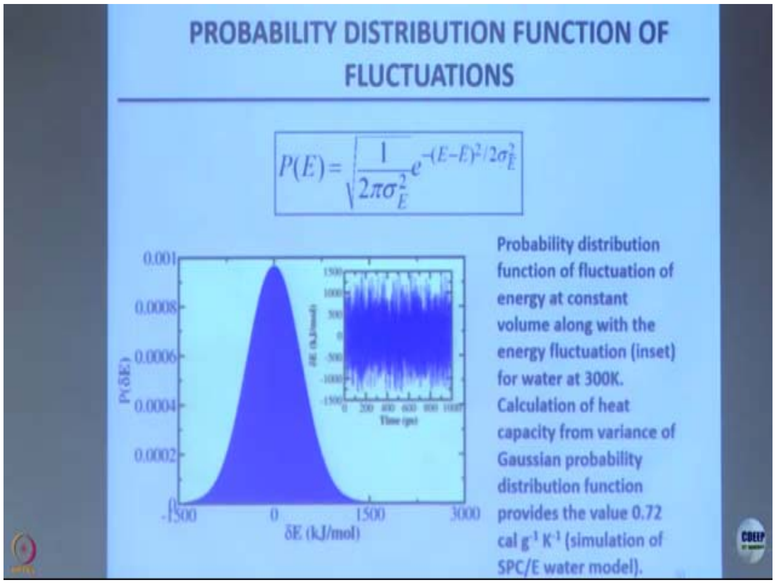

PROBABILITY DISTRIBUTION FUNCTION OF FLUCTUATIONS

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

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).

So this is the, we have done that this is given as energy. So fluctuations in energy, when you plot that low and be old it is a very good Gaussian, amazingly good Gaussian, another surprise of nature. And then the width of that fluctuation is the specific heat, and that is this spring constant in my, so why it becomes Gaussian? There are two reasons of that and I will give fuzzy mathematical then the physical or both can be considered mathematical.

But before I go into that look at this functional form, why now remember <E> is the value at the minimum and that is a macroscopic quantity that the average energy of the system. So system must be minimum with respect to the average energy. So I now fist derivative will go to 0. So the second derivative will be this quantity which is the Sigma square is this specific heat. So this is the reason why these one of the explanations is that the total energy of the system or the fluctuation in total energy is Gaussian.

There was the question asked I think yesterday or day before yesterday and this is the answer to that question. Second important explanation that comes from a very profound theory of probability that I described I think in my third lecture and I did my book also I describe that quite a bit, that is called central limit theorem. Central limit theorem says that if your total observable makes the X, capital X is a sum of a large number of small parts. And if there is a weak correlation, correlation is allowed, the correlation but the weak correlation between them, then this sum is the Gaussian. This is called central limit theorem which is an exceedingly important part of statistical mechanics and I think I have discussed it a couple of times in my book and I think in my third lecture we discussed it and this is what Rajarshi keeps complaining that how many times we teach the students;

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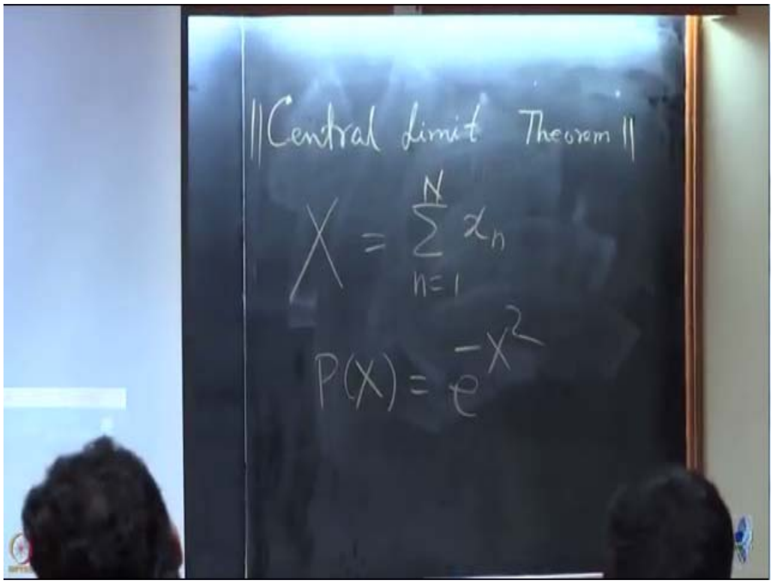

||Central limit Theorem||

$$X = \sum_{n=1}^{N} x_n$$

$$P(X) = e^{-X^2}$$

The students forget but these things should not forget. There is a strong law, there is a weak law and I told you mathematicians are not given this was also the person who worked on it theory of errors and all these things goes back to Gauss. Gauss I think had one of the proofs long long time ago. I think Gauss was after Shakespeare, I think somewhere 1600 around that time a little later than 1600, I used to know all these things but forgetting.

So then central limit theorem says if I have something X which is sum over x_n, n is large number and then x_n are weakly correlated. Then the P(X) an amazing theorem, just amazing theorem. That this is the central limit theorem, perhaps the almost and I told you my mathematicians are not given to give big names. We chemists and physicists, we just mutilate and insult the English language. But they have a very rarely one thing like fundamental theorem or algebra. Whole algebra is based on that theorem, whole complex analysis. This is the whole much of probability theories based on this central limit theory.

The center limit theorem says that this is Gaussian. One of the ways you can do that which take up any book of probability, they will do in terms of binomial theorem. Toss a coin or take it dice, then you will find the sum will become go on adding 3, 6 with, if you are throwing a dice and then you find that is Gaussian. Now all of you, who do molecular dynamics are Monte Carlo simulation use this at very early stage of your simulation.

Now tell me where, not quite Bhava, use sample from a Gaussian distribution. How do you create the Gaussian distribution? You take random numbers equal I seek, call random numbers, add the random numbers. You know if you do not use a package like our days, we used to there us a function photon called rand, but we used to write our own code usually as because we are always pseudo random number and the not Gaussian correlation. We used to do it ourselves by doing a, you can play around little bit and make it much better.

And sometimes we use the assembler language and to make it more uncorrelated. However, one important thing you should do it yourself, you call a random number, call it on dual times, add them up, you find this some. All it takes is 12, so I do not need to go to infinity. Strictly speaking it has to be large but in real world just 12, gives it Gaussian. This is one of the reason many many things in observed properties in nature are Gaussian.

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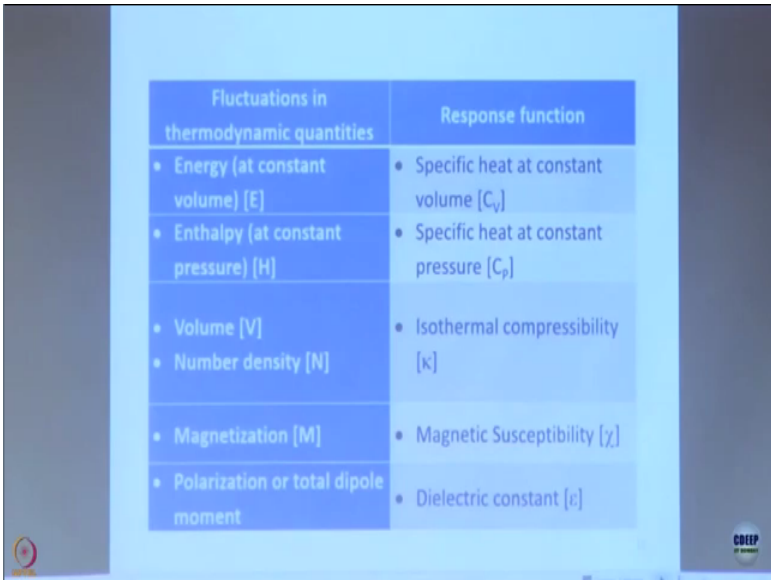

Fluctuations in thermodynamic quantities	Response function
• Energy (at constant volume) [E]	• Specific heat at constant volume [C_V]
• Enthalpy (at constant pressure) [H]	• Specific heat at constant pressure [C_P]
• Volume [V] • Number density [N]	• Isothermal compressibility [κ]
• Magnetization [M]	• Magnetic Susceptibility [χ]
• Polarization or total dipole moment	• Dielectric constant [ε]

So then here is a table actually by student Mary today, very quickly from the book but, here energy at constant volume, then C_v response function. So see the thermodynamic one, so there are actually three things one should have add here; one is the perturbation, one is the fluctuation and one is the response function. I probably have done perturbation, response function then microscopic interpretation. This as I told you it is a profound result of statistical mechanics.

Perhaps one of the most, I will not say the most but one of the most profound result of statistical mechanics and this is amazing that it tells you what is specific heat. Then Cp is that of enthalpy, then volume and number density give you isothermal compressibility and you have to work in different ensembles to get that. NPT will give you volume fluctuation and grand canonical will give you number fluctuation.

These listen carefully, these comes from NPT, isothermal isobaric, these comes from grand canonical ensemble. You can calculate the fluctuations that give you both give you isothermal compressibility and they give you exactly same results. You can do the simulation A in one ensemble and other ensemble you will find they are exactly the same. Magnetization is the external magnetic field. Magnetization is the response and this is the my response function.

Then I put an external electric field. This is the response polarization and these are response function directive constant. So all the time experiment is measuring directive constant without really doing what the hell they are doing. But it is the theoreticians are responsibility to understand these things and that has happened, that Is the way it has happened. Experimentalist much of the time need to work extremely hard to get a result;

They really have not much time for this theory and all these things and you will find there a kind of disregard for us which is painful but that is the way it is.

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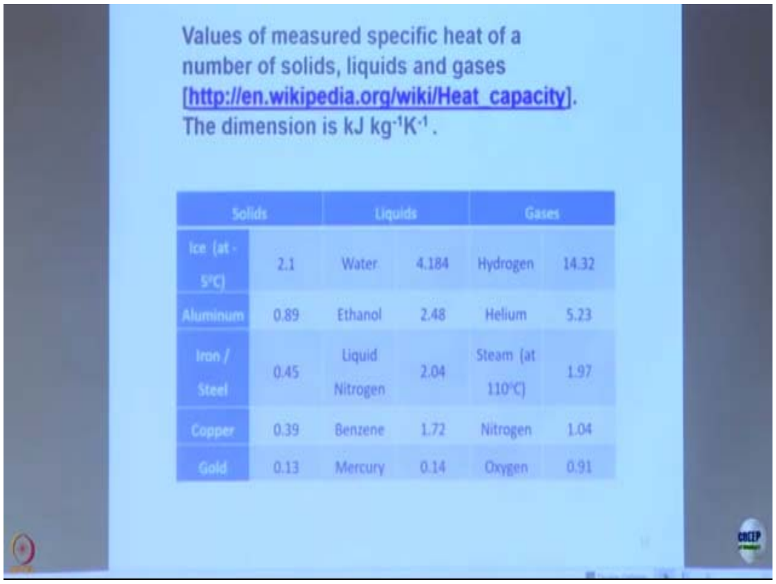

Values of measured specific heat of a number of solids, liquids and gases [http://en.wikipedia.org/wiki/Heat_capacity]. The dimension is kJ $kg^{-1}K^{-1}$.

Solids		Liquids		Gases	
Ice (at -5°C)	2.1	Water	4.184	Hydrogen	14.32
Aluminum	0.89	Ethanol	2.48	Helium	5.23
Iron / Steel	0.45	Liquid Nitrogen	2.04	Steam (at 110°C)	1.97
Copper	0.39	Benzene	1.72	Nitrogen	1.04
Gold	0.13	Mercury	0.14	Oxygen	0.91

So now there are certain very interesting result that I want to tell you and that you should know. Here is this specific heat ice, then these are solids, ice, aluminum. Look at this, now you expect solid to have less fluctuations and that specific to be same less, that indeed, there is less. Now look at the things liquid, look at that, Ethanol is so much bigger but water has almost twice this specific heat. Why? I come to that.

Liquid nitrogen, this one benzene, these benzenes so much bigger than water but, much small. Mercury is really has much less specific heat. Hydrogen partly because this is an anomaly, because they are the ortho para equilibrium. As a result of that there were very large fluctuations. Helium has quantum effects in it which allows it to really explore much larger energy fluctuations.

But look at that, as you would expect this is less, this somewhat more and where this is little bit more. So there now it is a standard questions we asked, why has water specific heat is that of more than twice of benzene which is bigger than water and also bigger than ethanol? So this is a question I am now asking you, explain why water has such large specific heat? And that is very good for you otherwise, you would die of fever.

You know our body, we are very lucky that large, water has large specific because 70% of our body is water. Otherwise your protein, if the temperature some comes outside your protein would become temperature of the body will rise then your protein will become unfolded and you would die. Now you need to tell me why and how water has such a large specific heat? Right, it is due to hydrogen bond.

There is a bit more than that, this is a good beginning. Hydrogen bond for if hydrogen bond not there then water would not be liquid first of all but this only tripling 18. Much much heavier things are gas but, water because hydrogen bonding. So it is hydrogen bonding but what next? Ethanol also has hydrogen bonding, do not forget that. Ethanol has, ethanol forms three hydrogen bonding, two through oxygen one through hydrogen.

Water forms how many hydrogen bonds? Four, four hydrogen bonding. Still answer is not there, come on. That you are saying these is the semantics, you are just putting the same thing in words. I will not, we will not be able to waste too much time here. That the reason is that, because of hydrogen bond there lot of excitations in this system. There is if we do the normal mode analysis.

That means you can freeze water or take the temperature out and then do a normal mode analysis, means you calculate the density of states or you can even take water little what temperature and do the velocity time correlation function and do a Fourier transform that will gives you the oscillations and as it peak you will find water has three pronounced peaks, one is about 50 centimeter inverse that is because of rattling.

But there is this peak at 20 centimeter inverse which is hydrogen bond excitation. Now tell me what is one k_BT? Thermal energy how much in centimeter inverse? 300 Kelvin how much? 206

centimeter inverse. One $k_B T$ is 206 and you might look surprised but that is what it is. So one $k_B T$, 300 Kelvin is 206 centimeter inverse. Hydrogen bond excitation, the network is vibrating like that.

That is a Raman active mode, that is 206 centimeter inverse. Then there is a libration which is about 600 centimeter inverse. So water because of the hydrogen bond it has all these collective excitations. So when you pool raise the temperature, then all these excitations get populated. So before temperature goes up, you need to populate them and as a result of that kind of extensive nature not in ethanol because they ethyl groups in hydrophobic.

So there is a local order but this kind of extensive high network what we call hydrogen bond network, that is so peculiar of water, that is not there. So this is a beautiful slide that I think I will give it to them to put it on the book.

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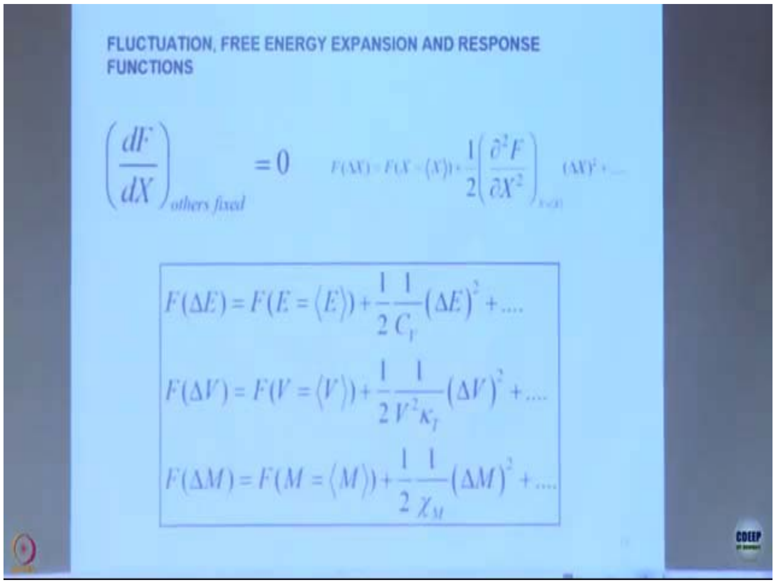

FLUCTUATION, FREE ENERGY EXPANSION AND RESPONSE FUNCTIONS

$$\left(\frac{dF}{dX}\right)_{\text{others fixed}} = 0 \qquad F(\Delta X) = F(X = \langle X\rangle) + \frac{1}{2}\left(\frac{\partial^2 F}{\partial X^2}\right)_{X=\langle X\rangle}(\Delta X)^2 + \ldots$$

$$F(\Delta E) = F(E = \langle E\rangle) + \frac{1}{2}\frac{1}{C_V}(\Delta E)^2 + \ldots$$

$$F(\Delta V) = F(V = \langle V\rangle) + \frac{1}{2}\frac{1}{V^2\kappa_T}(\Delta V)^2 + \ldots$$

$$F(\Delta M) = F(M = \langle M\rangle) + \frac{1}{2}\frac{1}{\chi_M}(\Delta M)^2 + \ldots$$

So now these, what I have been talking, free energy expansion and the response functions. This because of the minimum or a quantity X is either pressure or my, then this is 0 but, then the expansion becomes that in free energy and these are the expansions in energy fluctuation is a specific heat volume fluctuation compressibility and the if I have the fluctuations in the system is the magnetic susceptibility.

So what is the important these free energy expansions, who free energy second derivative are these response functions. Those are the same functions that give you, that tell you how much is system going to react and I gave in the example of water is essential for you and your body that water has large specific heat, otherwise you die off. And exactly that have these quantities are the ones which are most important constitutive properties of a material. They are the ones which measure it in the very beginning.

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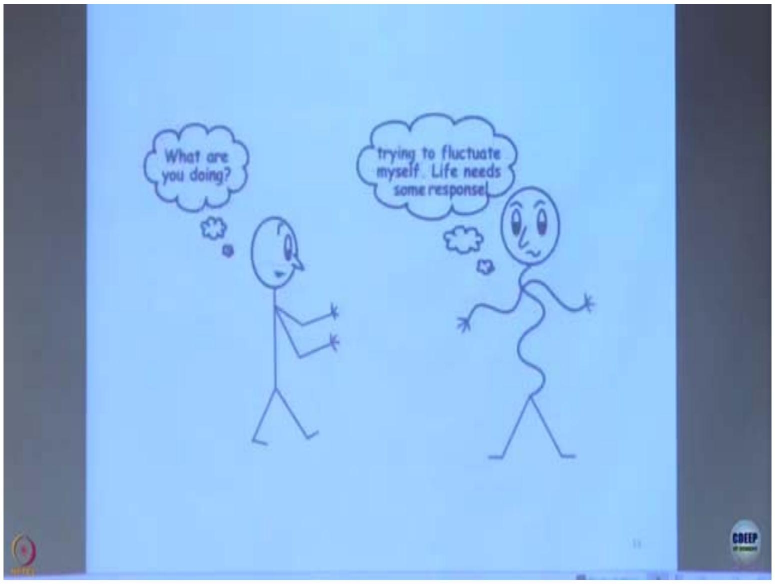

This is the end. So there my students are fond of cartoon. So they are, they say that I am trying to fluctuate because it is sudden life must have some responsibility. So they are not great cartoons but in statistical mechanics such a difficult subject is good to have some cartoon then no cartoon.

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So this is a picture of Einstein I really like. So we now, this is the chapter which you have to read and again the same kind of things that I have been talking here, that how the same thing repeating again and the equations from there. But, there are lot of very nice things that are discussed here and quite a detail because this is my favorite chapter. So energy fluctuation specific heat the derivation is given here is a little better than what is given here.

You can see the derivation in full glory. Sequence is little different from what I told you there, then the fluctuation in other response functions, full derivation is given here. And this both grand canonical and NPT ensemble and then. There are some very nice system size dependence on fluctuations that we just discussed.

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Yes, no nonlinear phase transition**,** all free energy is minimum with respect to all thermodynamic properties. Whatever you choose as Einstein showed there are two independent values, so you have to be like me, if you look Einstein's statistical physics there somewhere around chapter I think a Landau series, the old second edition that I studied somewhere in after after 30 or 40. Around that, he had this, Landau has this chapter fluctuations and there.

He discusses this that the Einstein chose selected two independent variables entropy and volume. And as I told you paramo also discuss pressure and temperature Landau because that is connection with the hydrodynamics and discussing very important experimental results which can also be through entropy and volume but it is get very complicated. Pressure and temperature is a better variable, the Rayleigh Brillouin spectra, the three peeks that is explained by hydrodynamics.

So it is minimum, only thing you have to make sure that you have the two independent variables, do not take two dependent variables then you screwed up. Only near a phase transition this spring constant just goes. That is why it is like here, so long I am here I am stable but when I am come here it is no longer stable. That exactly happens in phase transition the system falls out of the clif and it forms out of the cliff this quantity just becomes like that flat.

Do we call is softening very important term in physics, softening of course? Absolutely, I do not know why you are confused. Really has to be minimum otherwise it is not stable, it has to be cage them, that is why I am talking of spring constant. Let us take a spring, do that, the spring comes back right. So you are applying a force spring getting elongated, who determined? I could have put that also that I give a force elongation is L that is the omega square X.

So that has to, you know this is a good question but you have to think and make yourself believe because these are the fundamental and exact results. That I told you in book I had I wish I kept it that is really testing a very significant result from statistical mechanics. Explaining your high school thermodynamics and physics is coming from this chapter. We do not question it, but we should actually think about it because it is just too fundamental to ignore, rest there is a point of doing science, this is really beautiful.

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So this is same thing I discussed, this probability distributions. And now going back to different ensemble microcanonical, grand canonical ensemble in the maximum means now omega has to be maximum. And then partition function has to, I told you partition function is the quantity that is maximum and I explained in the morning why partition function is maximum. Partition function is maximum because E to the power minus C by $k_B T$ as I said.

Or omega is that particular state is selected which has the maximum number of microscopic states. And then this is what we discussed there is a question actually one of you asked why it is Gaussian? This is the reason why it is Gaussian little bit fundamental level and the distribution of specific heat and thermal conductivity all these things we discussed. So but I would strongly recommend you take a look into this book, this my book because I do not think there is any other book that has discussed this in so beautifully except I think Pathria statistical physics;

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But then he does not connected to this water specific heat and the kind of things we physical chemistry or chemist deal with, that is not their cup of tea. They will go to liquid metals and not interesting as I said mercury is specific heat point, how much, 0.2. Solids less we get it so small except when they go to phase transition this specific heat diverges, order disorder transition. Order disorder tends in aluminum and manganese.

And there goes all order disorder transition but that because you have this multiple ways to arrange things in different energy. So, a binary alloy undergoes the spectacular phase transition. Anything else? We will next class Monday we will start with the applications of the partition function and describe in some way and getting some very, very important results which are even to be used in drug design or all kinds of thermal dynamic power thing.

Packages from NIH and other people use what will be really it is I never knew that in drug design we use this circuit tested equation which is right with more atomic gas, ideal monatomic gas.