Classical Physics
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Lecture No. # 30

We have got to a stage where we have defined a few critical exponents and I mentioned that in mean field theory. These exponents have well determined values such as magnetization exponent data was equal to half. The susceptibility exponent gamma was equal to one and the critical isotherm was equal to delta was equal to three in Mean field theory. Of course once you go beyond mean field theory these exponents change, but it is a very non trivial problem to go one step beyond Mean field theory and we will not quite do that in this course. But I would like to point out to you, how lambda arrived originally at these exponents in general framework and this idea was rigorous it is as follows, it is motive was slightly different.

It is motive was to understand what sort of structural phase transitions? You could have in a crystal so; you will solidify the liquid which goes into some crystalline phase as you lower the temperature. You control the temperature and the pressure for instance, it turns out that a given crystalline structure undergoes a phase transition to some other structure and so, on. And there is a huge variety of these structures, so this idea was to find out based on symmetry considerations. What possible phase transitions could occur for a given crystal structure as you change the pressure and temperature. This required conditions of group theory and crystallography, which we have not done in this course.

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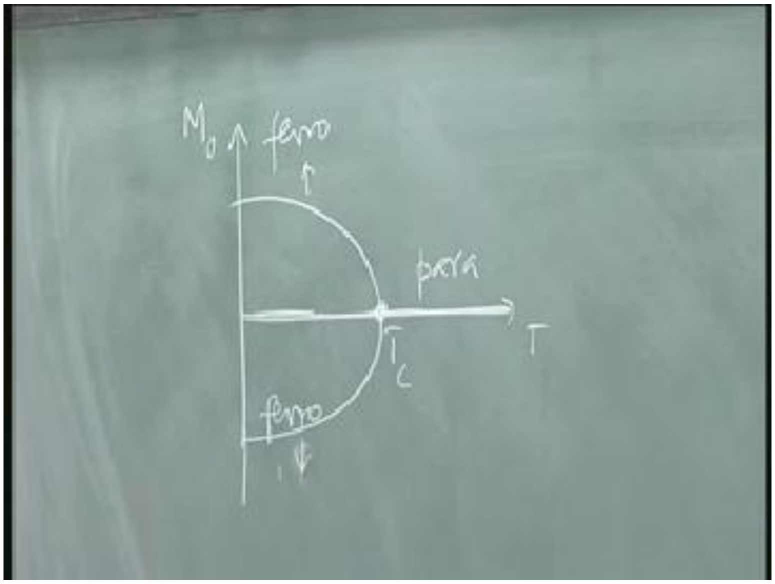

So, I will skip that, but I will point out what the elementary theory? That he gave was to start with for the magnetic phase transition and the idea was very simple. This point was that if you took the temperature versus, the magnetization diagram. And I plot the spontaneous magnetization for instance then in the Para to Ferro transition. You have a Para phase with zero spontaneous magnetization and at the Curie temperature or critical temperature. You have the phase transition into two one of two branches. This corresponds to Ferro up down for instance, this is Ferro up this is also Ferro magnetic phase. This is the Para magnetic phase and this was the phase diagram in T plane and you had similar diagrams. You will have corresponding diagrams M versus H graph or the H versus T.

Now, how do you acquire this? How does this happen? How does this kind of phase transition happen? This point was for every phase transition, you identify a quantity called an order parameter, because in the high temperature phase you have disordered. The magnetic moments are all aligned at random, on the other hand in the Ferro up or down phase.

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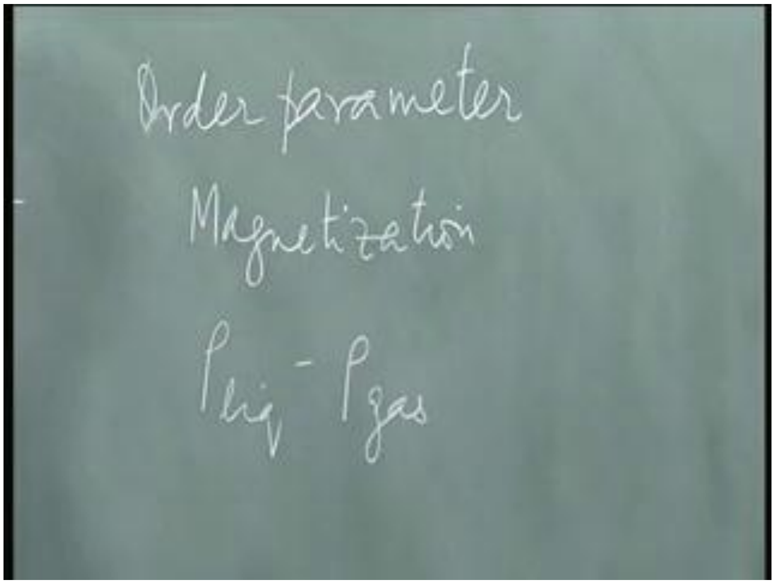
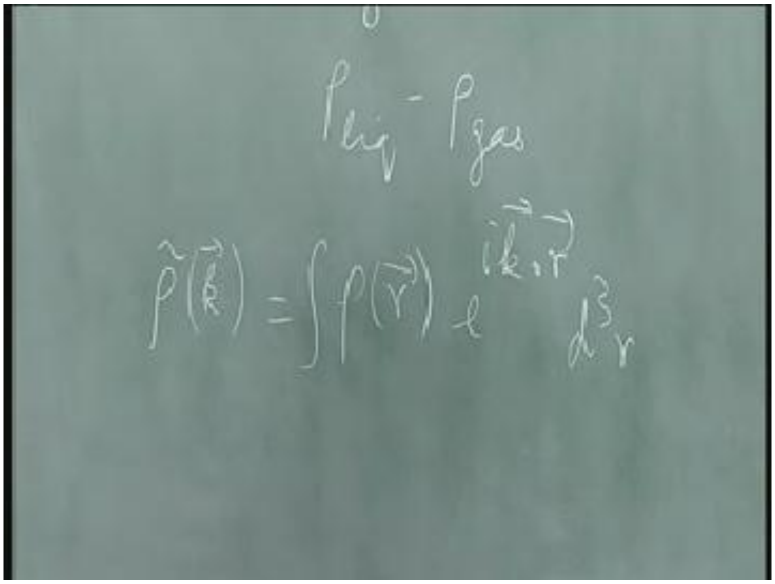


Order parameter

Magnetization

$\rho_{liq} - \rho_{gas}$



$\rho_{liq} - \rho_{gas}$

$$\tilde{\rho}(\vec{k}) = \int \rho(\vec{r})\, e^{i\vec{k}\cdot\vec{r}}\, d^3r$$

They are all aligned up or down on the average and therefore, you define a quantity called the order parameter. You identify a quantity called the ordered parameter for a given phase transition and he chose the order parameter. In such a way that above transition temperature the order parameter to zero and below it is non zero some value, which is what happens in this transition?

The order parameter for the case of magnetic phase transitions Para to Ferro magnetic for example, is the magnetization. We will see in another example of this ordered parameter and that is the liquid gas phase transition. What would you think is the order parameter for liquid and gas the analog of the magnetization; we know the analog of the magnetization is a volume. So, in this case the order parameter would be the difference in volume between specific volumes or densities. For instance between the liquid and gas phase above the critical temperature there is no difference. So, this is zero, but below the critical temperature the density difference between the liquid and gas is non zero.

So, we could say density difference r o liquid minus r o gas magnetization is an extensive quantity. I can define magnetization per unit atom or per unit volume, but then it is an intensive volume. What would you say is the order parameter so; important thing in phase transition is to identify the order parameter. What would you say is the order parameter, for the substance undergoing the phase transition from liquid to the solid to a crystalline phase? You cannot say volume difference as negligible completely negligible and sometimes it goes the other way also, but a solid is a crystalline solid has a long range order. On the other hand the liquid does not it is isotropic.

So, it does not so, you need something, which distinguishes between these two phases based on the fact. That the solid has crystalline order and the liquid does not have this entropy.

Good. Guess entropy, but that is not an order parameter, for technical reasons the entropy is not the order parameter. Now, think physically some physical measurable quantity some quantities, which can observe is the order parameter. It is not a trivial one so, what could it be in a very crude way? Let me say the following while it is true, that the density of the solid and the density of the liquid are almost the same compressible. One of them is ordered arrangement other is a disordered arrangement. So, whatever order parameter you choose must take into account this fact that the atoms are sitting in a regular array, in the crystalline phase and a disordered in the liquid phase.

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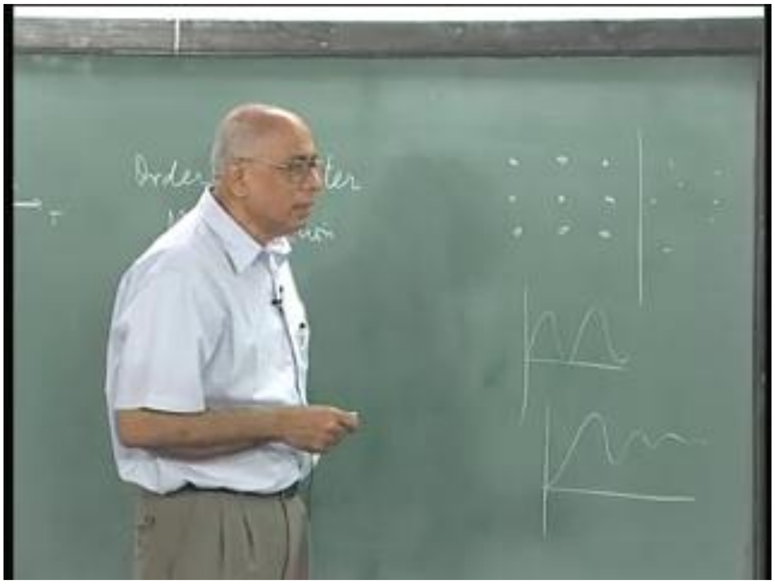

So, what happens is the following if you had? For example, just for a schematic thing in the crystalline phase you had things arranged in some regular array of this kind in the liquid phase. This approximately the same density these fellows would be arranged in a disordered way compared to this. How would you detect? This you would look at nearest neighbors, you would define order parameter based on what is the probability? If I have an atom here, I have an atom at a fixed distance away from it and of course I have to do this in different directions. This is the probability I may write it in the case of a solid this thing called the function, would actually go up and down. Because this atom here, there is nothing in between and it goes and so on.

So, there is a peak at that point and then there is a trough in between and a peak again so, on. So, roughly speaking you would have kind of periodic pattern. On the other hand for a liquid, we just have something more or less in a liquid. Also I would expect this to happen, I would expect that it would start to up and wiggle a couple of times and then do this, because it is short range order. So, there is certainly a problem that we can one lattice distance, we have another one and after that it becomes in a gas. On the other hand it is none of these things, first of all it is larger distance the mean distance and then the probability becomes essentially uniform.

So, some subtle order parameter of this kind has to be brought for the case of liquid and the order parameter. For the crystalline phase transition would be to take the density r o, which is the function of the position. Because it changes at atomic level it changes density changes and then the fact that it is periodic in a certain sense would be reflected how do you find periods? What you do to a function to find it is periodic or not I have to do it, but what is the mathematical function to see? If a function has one or more periods what would I do to a function? I suspect some hidden periodicity in a function, what would I do Fourier transform?

I do a Fourier transform and then I find out, which amplitudes would be right that will give me all the reasons the spatial.

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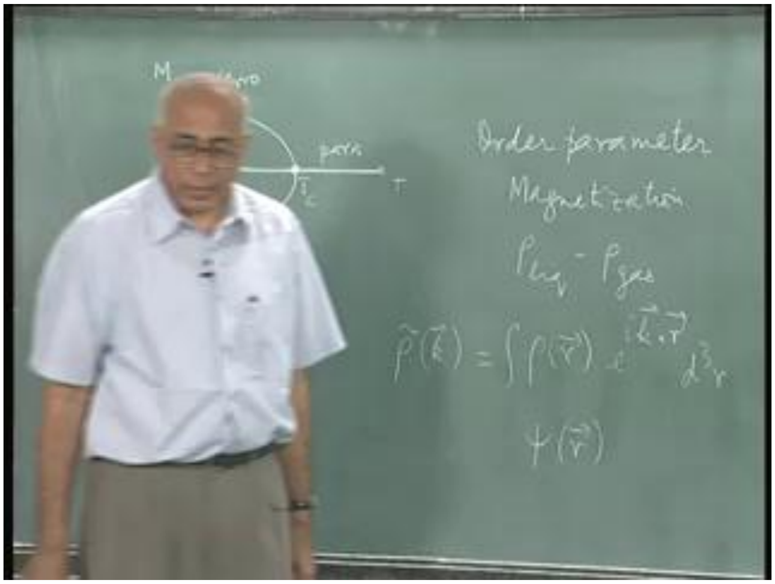

So, in fact what you should do is to take? This quantity to e to the power k dot r integrates over r here and this is equal to r o of k the Fourier transform o the density. This quantity would have certain directions in k it would have peaks in other directions it would have ups and so on. So, the properties of this the set of Fourier amplitudes r o tilde of k corresponding to a crystalline case, that would uniquely determine. What kind of crystalline order it is? So, that is the order parameter like this and in the isotropic phase. This order parameter could not have any special direction single direction could be constant.

So, this is the kind of order parameter you use for this crystalline phase it is not entirely trivial. If you looked at super fluid helium becomes super fluid at 4 Kelvin in the next course, we will talk about little bit of quantum statistics. Then I will mention like super fluid, what happens to helium? There it is a liquid it is isotropic. So, you cannot have this as the order parameter on the other hand. When it becomes super fluid the large fractions of the atom are in the so, called fluid phase, which means they form a single quantum state called the condensed state and in this quantum state there is long range core relations coherence of this medium. You have an order parameter, which is the wave function of the condenser.

The quantum mechanical wave function and that wave function zero in the disordered phase, but in the normal liquid phase, but in the super fluid phase, there is a non zero condensing wave function. Therefore, as you know quantum mechanical wave function zhi is a complex number, which is the order parameter. So, you can have order parameters, which are complex both the real and imaginary parts would have the physical meanings or the modulus. The amplitude argument would have physical meanings and that kind of thing zhi r for super fluid helium would be the order parameter and so on. Depending upon the phase transitions, you can have all kinds of order parameters.

You have complex numbers, you have Fourier amplitude, you can have scalars, you can have a vector like magnetization. You could have tenses in any other situations and so, on. So, depending upon the phase you can define a order parameter and that is the basic quantity, which you have to look at? Now, lambda was inside was to say that the free energy near a critical point is a function, of this order parameter and in general it is some asymptotic series some kind of power series.

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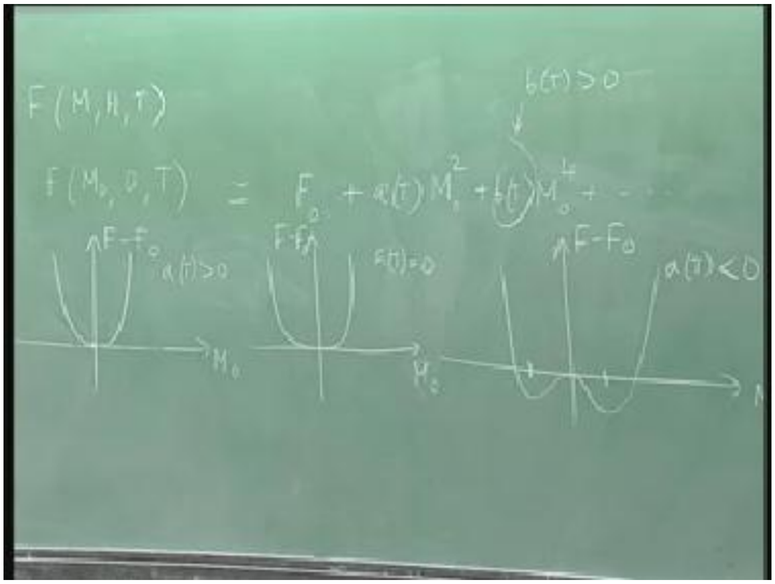

So, he started off by saying he want to explain the thing like, that you assume that the free energy is the function of M H and T. We would like to see they are spontaneous magnetization, so as the idea was …

Let us look at F of M naught this is zero of course and T switch off the field and ask what does this free energy look like? And this point was that this is in the vicinity of the critical point. This is approximately equal to some F naught, let me just call it F naught plus a power series in this M naught what kind of power series can you have?

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Of course for generic power series it is of the form alpha A one write this some c one times M naught plus some c two times M naught square plus c three times M naught cube plus dot dot dot. In general, where these coefficients are functions of T, because I am focusing, on the dependence on M naught. Then make the assumption, that there is power series of this kind and all the coefficients will be functions of the temperature. Then you can rule out various terms here by symmetry arguments first of all in the absence of the field, I do not expect the sign of m naught to be important. I expect whatever M naught. You have also an up, you have also a symmetry would have a down. So, that this quantity cannot have a linear term of this kind to be of that kind and in standard location, you write this as the form some a one times M square plus a times M square say plus b times M four plus etcetera. Typically and then of course this is a function of temperature.

Of course, you put an external field and you have a non zero field, then there would be a term proportional to M naught multiplied by the field itself linear in field. Then of course this symmetry is gone. Therefore, you can distinguish between up and down therefore, you have a term which goes like H times M naught linear in nature M naught could be interested in this spontaneous magnetization. So, the H times M missing just M naught square plus M naught four and so on. Now, what does this graph like this? What does a function like this? Look like if we plot it. Let me plot the function of M naught, let me plot F minus F naught, this fellow is just a constant so, let me move it.

Then there are three possibilities one if a is positive, b is positive zero and b is positive, a is negative and b is positive. Similar set of graphs b negative. Let us look at these terms and since we are looking at it near the critical point. They are not pretty small for the moment avoid this term and take the coefficient of this term to positive, which is what definition? Then what does this free energy look like? The graph was a positive a of temperature a of T greater than zero is a parabola to start with, but then it becomes much steeper curve looks like this, with a single minimum at the point. On the other hand the graph for m naught F minus F naught for a of T less than zero, looks like an inverted parabola. Near the origin, but then of course eventually the b term takes over and it has something like this.

Assuming always that b of T is greater than 0, and since this is a potential thermodynamic potential. I want stable equilibrium I take b to be positive so, it points upwards mind you this is only valid in the immediate vicinity. What is it at a equal to zero? This is M naught a of T identically zero and this is F minus F naught and what you have is a very flat curve? So, it is clear. That as a of T goes from positive values to negative values, the free energy function undergoes this change of shape and it is immediately obvious that a of T is greater than zero. There is one single stable thermal equilibrium state at M naught equal to zero and if a of T is negative. There are two stable states corresponding to this and this value while this state in between becomes unstable now, that is all. It is as simple as that the next thing to ask is what would a of T be a of T passes through zero in the vicinity of a equal to T c? So, it must start with dependence on T minus T c.

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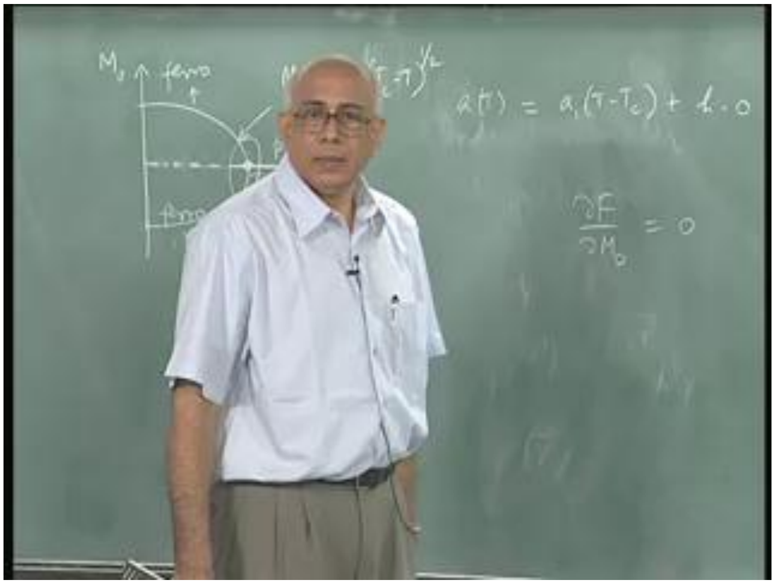

So, a of T is equal to some a one T minus T c plus higher orders of this kind. Then the job is done as T crosses T c a of T goes to zero and it passes through, this set of configurations and that gives us the phase transition. You start with m naught equal to 0 that is our minimum in the paramagnetic phase and then as you lower the temperature across T c. You have got two roots here and here, which correspond to the two minima. There while the root in between becomes unstable and you have a bifurcation a stable point becomes to a stable equilibrium point. In the essence of dynamics becomes now two stable point and the in between one becomes stable.

This kind of thing is called a pitch fort bifurcation and this is the bifurcation diagram all that remains is to find what is the dependence? What kind of singularity do you have here? How does this root depend on T minus T c, the answer is simple because you know that in equilibrium delta F over delta M naught is 0. That is the extreme end of potential and if I do that the roots that I get. So, let us make simple by putting a two here and put a 4 so, that you can differentiate 2s and 4s. Then this implies the first case that M naught a plus b M naught cube equal to 0. So, that is the thing and then a b greater than zero implies the only root is M naught equal to 0.

If a is less than 0 and b is greater than 0, you have two roots at m naught equal to plus or minus square root of minus a modulus a and that immediately tells you that this region M naught plus T c minus T. So, you produce the exponent half now, the reason it happened is generic the reason is happened, because in a generic power series our first argument was by symmetry the absence of the field the odd terms are absent. This guy is a constant I remove it. So, generically typically unless there are strange accidents there would be it would start with the square term move on to the fourth order term and that immediately produces by the square root. Of course you could have one specific problem, where it starts with the sixth order term and the next term is the tenth order term accidents it would happen.

Generically, this is what would happen? And this was the idea for explaining how a second order phase transition occurs? A continuous phase transition the important thing is the word continuous as you come along here. It continuously takes of the order parameter takes off continuously. Below the critical point, there is a discontinuous jump, but at the critical point it is the second order for continuous terms and this is the mechanism. There are other mechanisms, but this is a typical most characteristic method of all. Now, this could happen in many ways we have a very simple situation here, but it could have very complex ways, very different ways.

For instance, if you had more than one variable or you had complex number then things, could happen in a slightly different way. You would have for example, the same thing you did with the complex number like in super fluid helium to get, what would happen? You have something, which goes like in the modulus; you have in the modulus, because the energy is real. And then you would have a thing, which says that mod s i square plus b mod s i power 4, this is F proportional here. Of course now you could solve to find modulus s i has non-trivial roots s i itself is a complex number. So, what would the shape change in the shape of the potential do?

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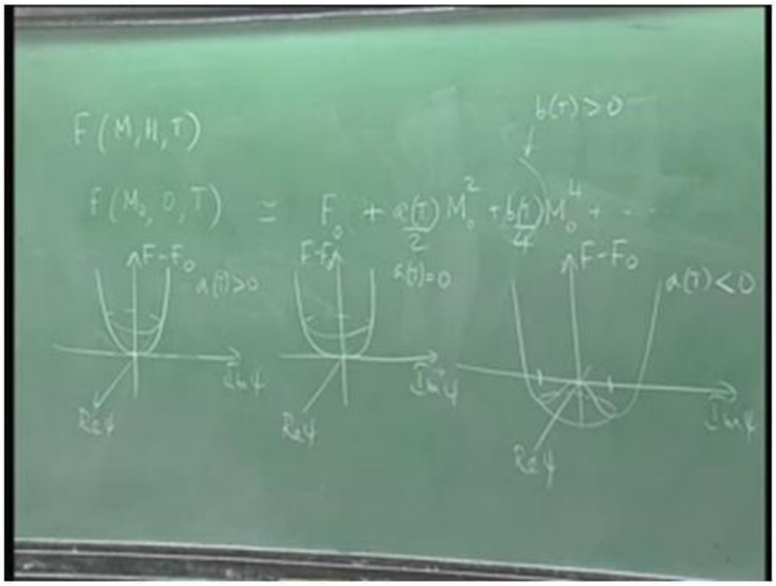

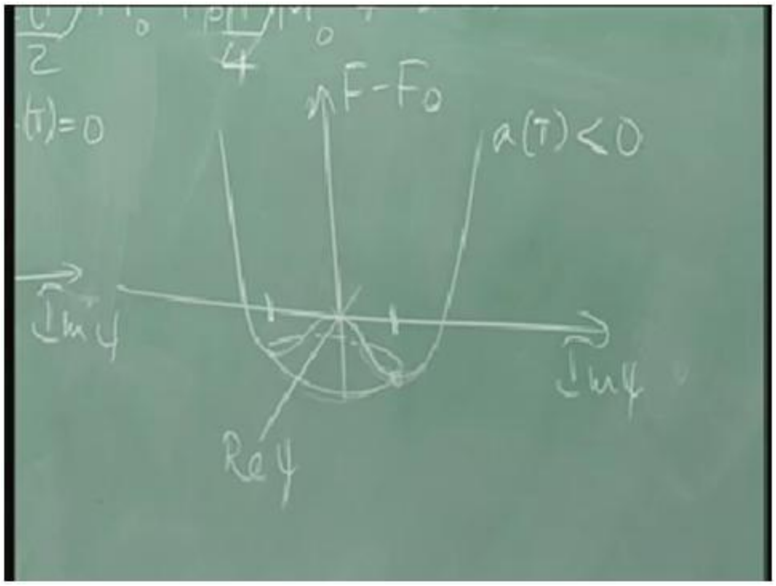

It would look like in that case, I must plot s i 1 and s i 2, the real and imaginary parts perpendicular and plot F as a function of s i 1 and s i 2 and then this guy here would be really like a bowl. Imagine the other axis coming out here so, I could say real s i 1 and imaginary s i and it would look like this. And it would become extremely flat bowl this side at the critical point and below the critical point it would have very different shape s i and this one really look like. You have what is called the shape of Mexican hat potential, but it would look like the bottom of the bottle, which you have. The rim and you have the minimum and the center of the bottle, you have minimum slope of there.

So, water goes to the other end. So, that is very interesting, because this ways the number of equilibrium points is actually infinity, whereas earlier you had the left or right. Now, you have anywhere in the bottom of this rim, this system could fall into any. One of these things and then you see it is energetically does not cost you anything to move from here to there.

Imagine by putting a ball bearing ring at the bottom of the bottle, it does not stay in the middle. It goes to the rim, but now tangentially you can move this without changing the potential energy. Radically, it is going to cost you energy it will go up and down, radial oscillations are expensive energy, because you are trying to go closer to the centre of the gravity from it in this potential. It is going to cost you energy to lift this particle down here, in this situation of neutral equilibrium. You can move around without any cosmic energy at all that has profound implications, because the symmetry has broken. In this case is a continuous symmetry as course of discrete symmetry, in the case of let me say the plus or minus values and that also implies. That the system can fall into one of these guys, these minima and you can wonder mechanically.

Does the theory of phase transitions involve we mentioned about quantum mechanics as well n max is perfectly large system. This tangling does not happen and the symmetry remains closed. Then you have what is called spontaneous breakdown of symmetry? On the other hand all these states are connected to each other by the existence of more, which causes zero. They are called goldstone moles and there are physical examples of it in condensed matter physics spin waves and Ferro magnets at Ferro temperatures phonons and crystals acoustic phonons. They are all examples of such nodes, which cost energy as the wavelength goes to infinity, the wave number goes to zero, and the energy also goes to zero.

I will talk about these aspects and we have to do little more of quantum statistics, because that is very important interesting subject, but just to point out my intention was just to point out here. That there is a basic difference between the way the symmetry gets broken the discrete symmetry and would depend on this aspect as well. So, much for second order phase transition continuous phase transition, we could have. Can I give a similar theory for a discontinuous phase transition, the first order phase transition and the answer is yes. A similar picture can be given except it is slightly different, you can do it in several ways, and here is one possible mode.

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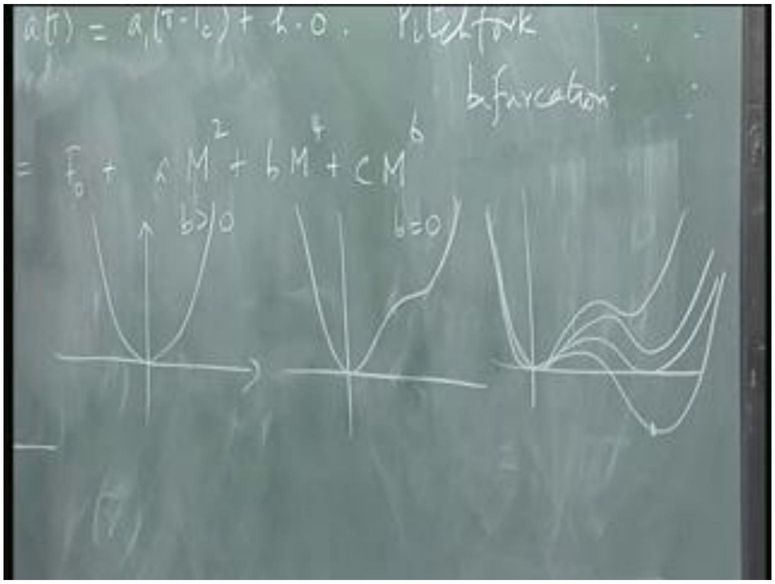

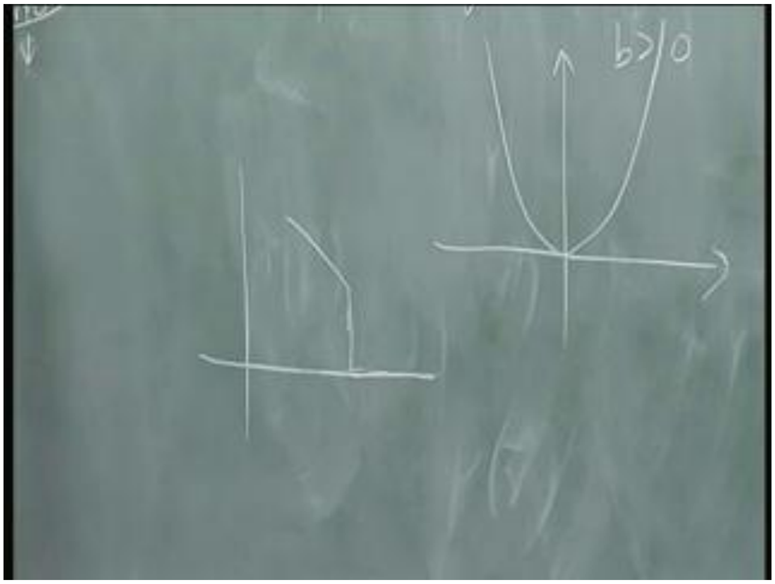

So, if you want a free energy it goes like, let me use continually for M for the order parameter. If it goes like some constant plus, let us say a M square plus b M four plus c M six retaining, once again symmetry. Then you can produce a discontinuous transition by mechanism, I can show you, but you could also produce this by putting a cubic term in it by making a single term. By taking the symmetry without breaking, the symmetry, the things like this. You could produce such a shape by now looking at what happens to the minimum? This guy is minimum, if a, b, c are all positive, but if b changes sign at some point. Then this potential goes over into something, where you have a minimum? And then the inflection point develops.

This is at d equal to zero, this is b positive and as you decrease p makes it more and more negative, and this guy remains like this, but a maximum and minimum develops. And then on the same figure as you keep decreasing b this minimum keeps coming down, then comes a stage at certain temperature. When the minimum is equal the two minima are equal and the next stage it does this. And now what is happened is? This minimum has become meta stable and it is possible. There is a local minimum and that becomes the global minimum and this is moves it, but it is done. So, discontinuously so, if you plot this, there is a function of temperature or whatever it kept on having zero and all of a sudden it jumped to a positive value and then it went on.

So, the order parameter would jump discontinuously, if you have this kind of unfolding so, that is a mechanism for producing the discontinuous phase transition, where the order parameter jumps? There are other several other mechanisms, but this again is a very generic way of doing this. Many structural phase transitions, where there is actually discontinuity, there is a latent heat every time there is a discontinuity some latent heat. They are described by such mechanisms by such land out so, this in a nut shell is the original land of theory, it is undergone a large number of modifications. First and most important was the fact, which we talked about thermodynamic equilibrium and the phases are homogeneous.

You know in a phase transition at the phase transition point, there are very many strange things going on and the real way to look at it is what happens to correlation functions? For instance when you have a transition from a magnet, that is magnetized upwards, magnetized downwards. As you cross the transition point originally, there are lots of islands of up magnetic moments and a few down magnetic moments. So, the average is up total average is up, and then this gradually changes. The islands are up shrink at the expense of the islands of the down and eventually you have islands of the down taking over.

So, correlation functions become very important, in these phase transitions and therefore, some information has to be put in into this free energy. On this spatial variation of the order parameter and the modifications are done the original modification was due to Ginsburg.

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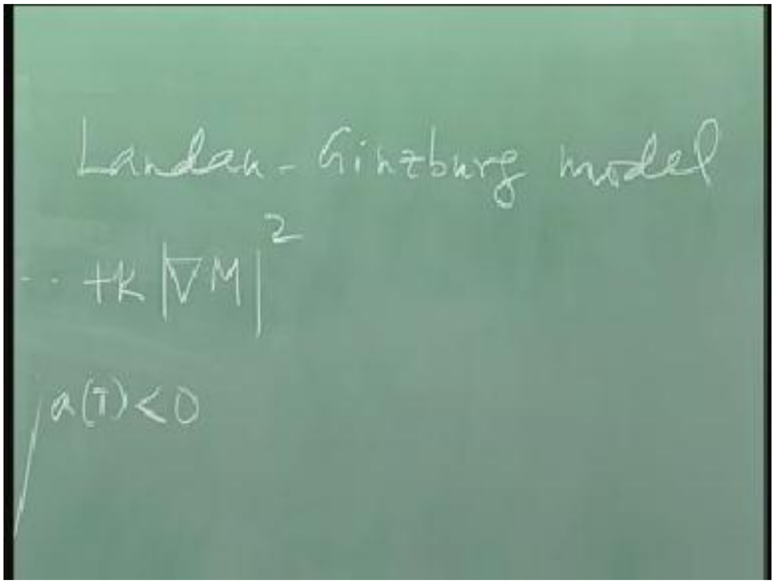

It is now called the Landau Ginsburg model and the idea was put a term here, which says that it is going to cost energy, in order to have a change in the magnetization from point to point. And typically what would this do? What sort of energy we would have? Here it would depend on the gradient of M and since it has to be a scalar of this form. So, some k times delta M that is the leading contribution.

Now, you can talk about what happens in correlation function itself? So, this is something I want to get into here to point out that, such modifications completely empirical to start with. But they are very generic, very typical and this is what done in real systems? As, I mentioned earlier, this is the very starting point of the theory of phase transitions great deal. We understand equilibrium transitions, but I will not go into that course. What I would like to do next is backtrack, a little bit. Since, I left that out and spend just a few minutes on thermodynamic identities, thermodynamic relations and so, on. We, go back. What happened?

It is not zero.

No, I am not saying it is zero at all, there is no end. It says the solid liquid distance line does not end at a critical point and the reason is if it. Did you could go continuously symmetric phase, isotropic phase, the liquid phase to one, where you have discrete symmetry? The crystalline phase, this is not possible. So, it does not end, anywhere the order parameter for the solid is a set of Fourier amplitudes of the density, which is to be distinguished from the density of the liquid, which is what less homogeneous? So, the fact is you have a function, which is essentially a constant, and you have a function, which is periodic and it is this distance that is measured in the Fourier amplitude. It is not that anything goes to zero the density of the liquid is of course.

Let me just mention that the factors on, which the phase transitions depend the factors on, which critical exponents depend and so, on. Is something like the following, they would depend on the nature of the order parameter. So, that it is a scalar vector tensile, the number of components of the order parameter; it would depend on the dimensionality of the system. The spatial dimensionality are you talking about one dimensional or two dimensional or three dimensional system, because you could have system, where the ordering is essentially two dimensions. You could have systems, where the interactions are primarily in a plane and not in three dimensions in three dimensions like graphite. The inter planar action is very small and most of the things is happening, most of the binding things happening in plane, which is why graphite gets into planes?

There could also be magnetic systems, where the magnetic items are all lined up in chains and therefore one dimensional. So, critical exponents sensitively depend on the number of spatial dimensions effective, spatial dimensionality the number of components of the order parameter 50. They would also depend on whether the symmetry is broken in the transition or not what kind of symmetry is broken? That is a discrete symmetry or a continuous symmetry. So, now we have a pretty good understanding of all these factors, the roles of all these factors, there are systems. Where you have no phase transition at all in a model below a certain dimensionality, which is called the lower critical dimensionality?

There are phase transitions, but they are explainable by mean field theory above a certain dimensionality and that is called the upper critical dimensionality. So, the main aim of the game it is business is to look at all these factors and then ask what the lower critical dimensionality is.

What is the upper critical dimensionality? Interesting enough it turns out most of the phase transitions. Most of the systems the lower critical dimensionality is two may be very often and the upper critical dimensionality is four and of course we live in three dimensions. So, by mathematically you would say mean field theory is valid from four upwards, in reality you have to deal with the fact, that you are not with three dimensions.

So, that is why you need this theory of very normalization, there is also a fact that the reason why? The order is destroyed above a certain temperature is due to thermal fluctuations, but there are also quantum fluctuations. Which we have not taken into account at all and even at absolute zero, there are still quantum fluctuations. So, it could be it is possible that the system, which goes into an ordered phase breaking. Certain symmetry could now have order restored due to either thermal or a combination of both and one has to worry about that. It is a very right field modern field, modern field for quantum phase transitions.

These are phase transitions that occurred at absolute zero of temperature genuine phase transitions occur in various kinds of condensed matter. As we approach absolute zero and it is of interest then to look at such systems and they are highly quantum mechanical. So, we will not get into any of these complications, here some of them. I have mentioned subsequent, let me now turn back to some thermodynamic identities in particular, I mentioned that I would show you a small trick, which would enable you to do most of this thermodynamic identities.

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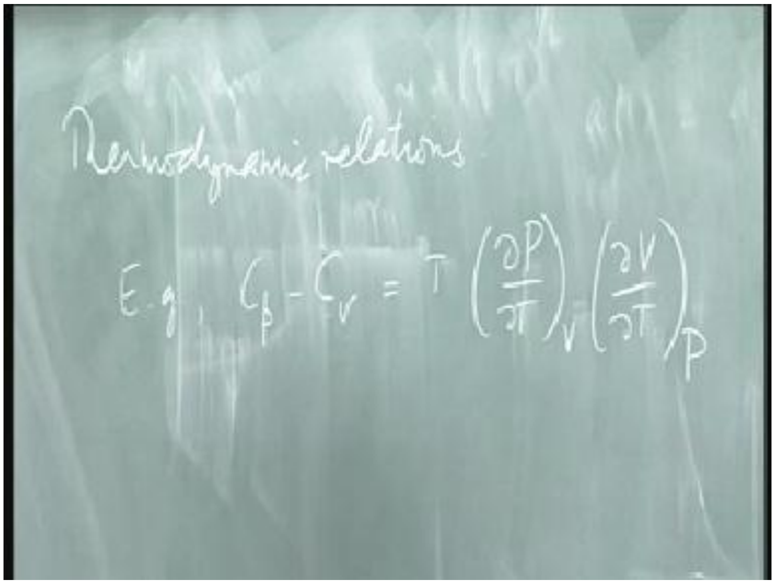

Thermodynamic relations

$$\text{E.g.,}\quad C_p - C_v = T\left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial V}{\partial T}\right)_P$$

For example, there are relations like thermodynamic relation one of them was mentioned in the quiz. Like example we had c p minus c v equal to T delta P over delta T at constant V delta V over delta T at constant P. The question asked was whether, this is only valid for ideal gas, where c p minus c v is r. You can easily verify it is true or it is true in general and the answer. Of course is this is the general statement and there is nothing to do whether it is a statement, whether it is an ideal gas or not it is true for all fluids. Now, how do you derive these relations? There is a cheap way of doing this of course a little bit of manipulation is involved always, but then you always tend to forget this precisely.

What step has to be used? The way in which many of these things come out automatically is a mathematical trick and so, therefore let me do it here.

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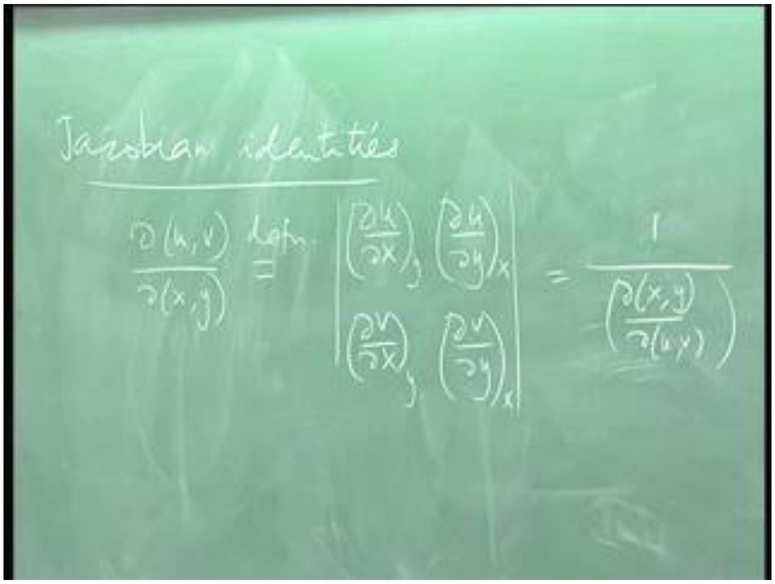

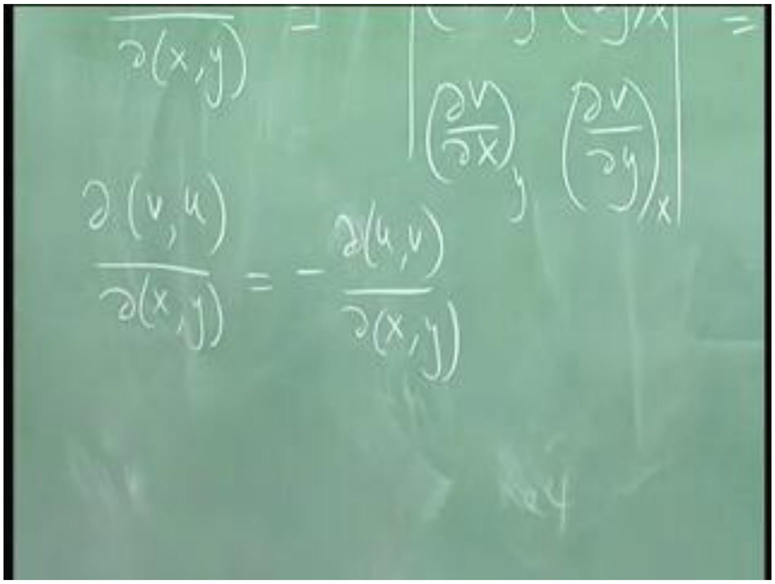

Let me mention this has to go with Jacobians identities; it is pompous trying to be simple calculus. And has to do with the following you recall that, if you have two functions u and v of two variables x and y. I define this Jacobian as this matrix determinant, it is delta u by delta x delta u delta y delta v over delta x and this by the way stands for keeping the other guy in the denominator constant, that is the definition. This much we know. Now, it turns out that, this is also equal to one over delta x y over delta u v the reciprocal.

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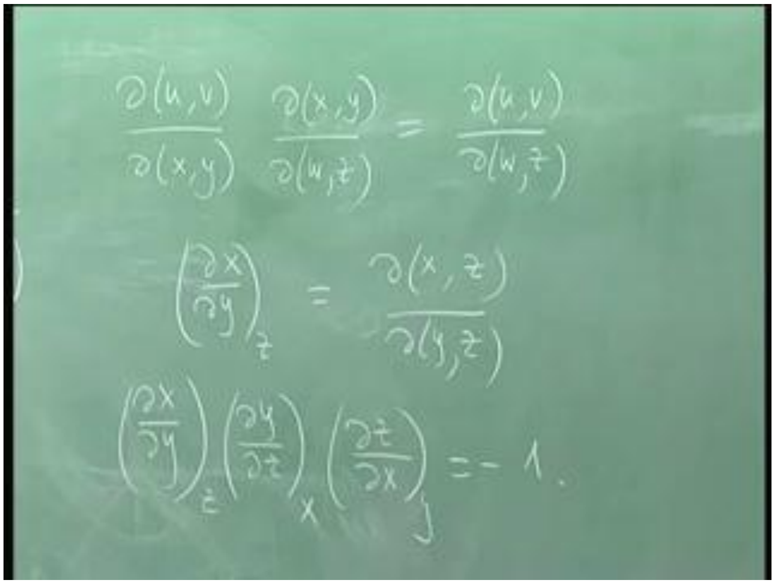

$$\frac{\partial(u,v)}{\partial(x,y)}\,\frac{\partial(x,y)}{\partial(w,z)} = \frac{\partial(u,v)}{\partial(w,z)}$$

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{\partial(x,z)}{\partial(y,z)}$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1.$$

So, if you took the numerator to be the independent variables in the denominator variables could be independent. Then the Jacobian is just the reciprocal. Then it is also clear, that delta v u over delta x y equal to minus delta. Then they have this interesting property delta u v over delta x y delta x y over say w z two other variables, it is equal to delta u v over delta w z. So, you can always insert so, two factors in between and they cancel out. And the most interesting of all the most useful in practice is utterly trivial delta x over delta y keeping z constant. This happens very often p v and t, one of them is kept constant is also the same as and this is trivial x z over delta y z by definition. Because, delta z over, delta z is one and delta z over y is 0, because they are independent variables.

So, you can always insert this variable in between so, that helps you to write down to work out all. These sorts of ideas look for the answer and put this required factor in by the way, you know. There is also this other identity for partial derivatives, which is delta x over delta y at constant z, delta y over delta z by constant x, delta z over delta x at constant y is equal to minus y. By the way you can establish with that using this. So, this is essentially all you need.

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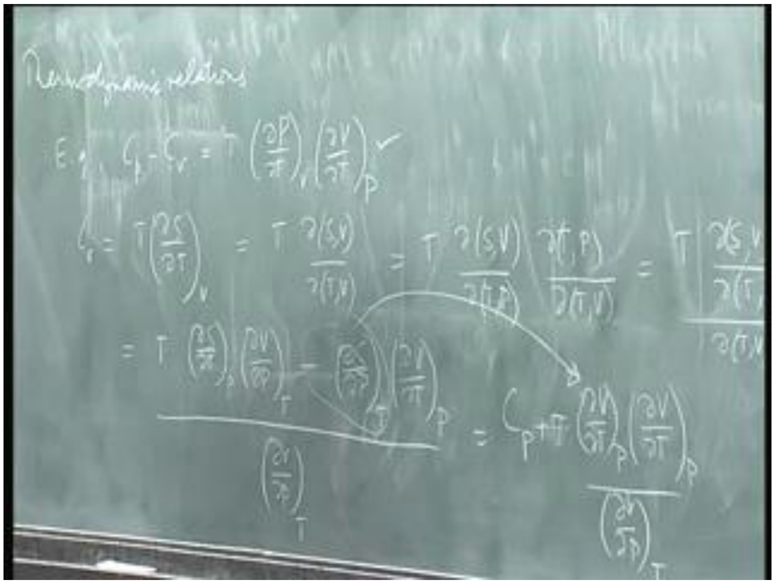

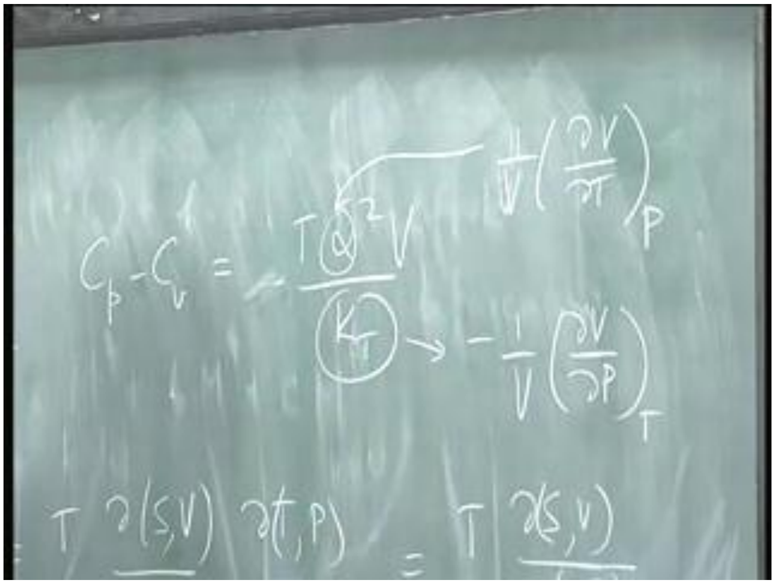

For example, I promise I do not do this top of my head, by I start with t v C v and this is equal to T delta s over delta T at constant. That is the definition d q over d T at constant V T delta s delta T constant V and the first thing is to write this as T delta s v over delta T V by that identity.

I can always put this, and then of course I would like to have c p coming somewhere, which means I must have delta t p instead of t v. So, I write this as T delta S V over T V. So, you can do close your eyes and do these things so, this is equal to T delta S V over delta T P divided by delta

T V divided by it is supposed to be written as T times. Now, let us get serious this is delta S over delta T at constant pressure delta V by delta P at constant temperature minus, the cos terms delta S by delta P at constant temperature delta V over delta T at constant pressure. That is the numerator and I divide. I can get rid of this T here so, it is just delta v over delta p at constant temperature and obligingly this cancels out and you get T delta S over delta at P.

So, that is C p so, I have already got the left hand side equal to C p minus, these three guys, but now I start using Maxwell relations. What is delta S over delta P at constant temperature? It is equal to plus delta V over delta T at constant pressure divided by delta V over delta P. This is the Maxwell relation minus, this guy is equal to that times T and we are done, because by that statement there that minus one, the ratio of these guys is going to be just delta P over delta T at constant volume. So, this relation is established it is true. So, the whole game the crucial step was this right in this by putting this in and then changing this V to P by using those identities. And that is it after that so, all the thermodynamic identities. You see can all be written down by the way this number can also be written in another form. You play with a little bit I do not remember, this relation now.

You can also presumably write this as C p minus C v equal to … I do not remember the sign here, but there is another famous relation, which says it is the ratio of the thermal expansion may be there is a T. Also I do not remember T alpha, T alpha square, alpha square V over the isothermal compressibility, I do not remember this. There is a minus sign here, the minus sign. This is by the way this we know, this is minus one over V delta, V over delta P at constant temperature and this guy here. Alpha is a coefficient of thermal expansion, which is delta V over delta T at constant pressure one over V. So, it is the coefficient of thermal expansion, you play with this I mean with this term can also be written as in that form etcetera.

Completely general relation, but that set of relations is extremely useful in establishing. Once that is realized then there is no need to memorize separately each of these identities. So, the Jacobian identities along with Euler’s theorem for homogenous functions, these two play very big role in all these manipulations. Most of these identities, most of these relations in one form or the other, there are many directions, in which we can go now. It is not immediately clear to me, which particular one. We should choose, because our time is limited each of them sort of leads into a subject by itself. Is there anything I left out?

You think I should talk about anything at all, any fundamental thing I left out. I have done so far, which you think to be explained something. I said, I will talk about it later and did not get back to such as the origin. I will talk about groups, when we do symmetries. We are going to do that so, we will talk about the rotation rule and similar groups of various kinds, but anything in phase transitions anything at all pardon me. I said, I derived the central limit theorem from a random walk, yes this is true. Let me see there is a simple way of doing, this trying to think simple way of doing this. All right I am not sure, if I write down to the last factor, but let us do it.

Let us do this so, let me call it the continuum limit of a random walk my statement was the following.

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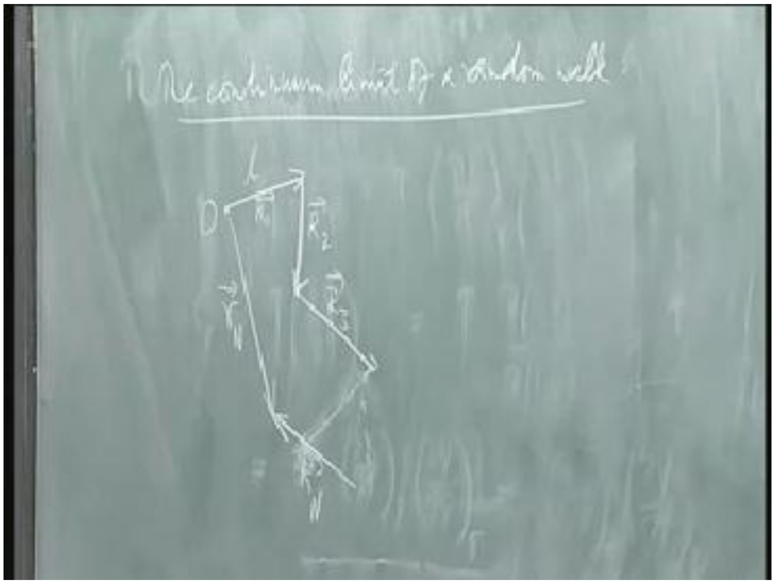

I said that, if you took random walk namely a person who takes step at random in various directions at fixed intervals of time. Then the end to end distance that it travels after certain time given an amount of time is proportional on the average to the square root of the kind. So, let me quickly do this and show you how this comes about? And find out what the actual probability distribution of the end to end distances? So, that is our target and the idea is you start at some point arbitrary origin in three dimensional spaces.

For example, then you take a step in this direction and the length of the step is l, it is fixed. That is the simplest assumption to start with and then I take a second step in a random direction all together a third step and a fourth step and so on. The question asked is if I start with the origin here and I call this R 1, this is R 2; this is R 3 and so on. Let us say after lot of steps, I end up with R sub n and I want to know what is the distribution of this vector r v? All directions equally probable, if it is on a plane then everything on a plane equally probable in one dimension, it becomes trivial. Then I can go back and forth then it becomes very trivial that is fine.

Then I do not need any vectors or anything I simply say, I take a step to the right or to the left and everything is in terms of scalar. Now, I want to do in arbitrary number of dimensions and you will see that this argument is independent of how many dimensions I have made? So, whether it is two or three or four or one, it does not matter. You are going to get the same answer.

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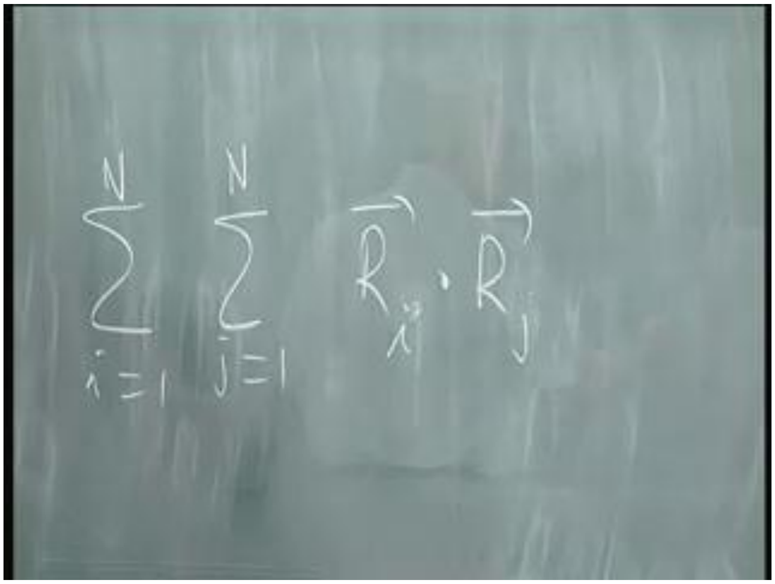
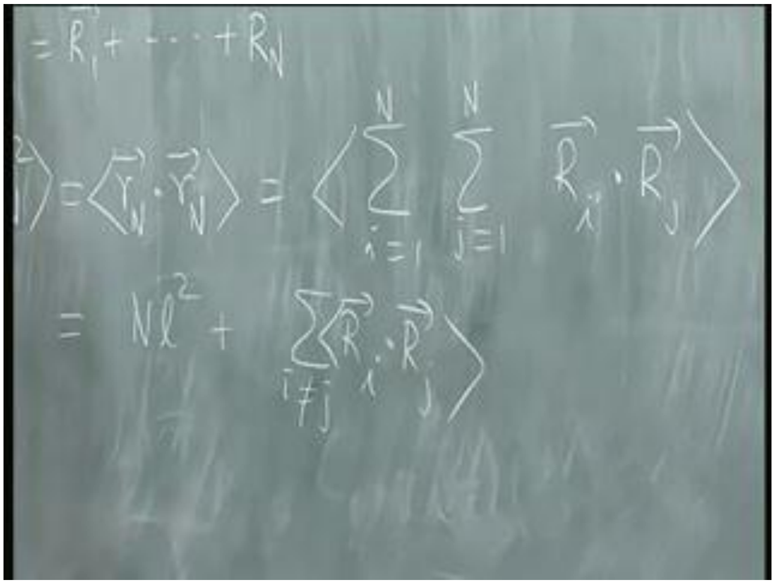


$$\sum_{i=1}^{N} \sum_{j=1}^{N} \vec{R}_i \cdot \vec{R}_j$$



$$= \vec{R}_1 + \cdots + R_N$$

$$\langle r_N^2 \rangle = \langle \vec{r}_N \cdot \vec{r}_N \rangle = \left\langle \sum_{i=1}^{N} \sum_{j=1}^{N} \vec{R}_i \cdot \vec{R}_j \right\rangle$$

$$= N\ell^2 + \sum_{i \neq j} \langle \vec{R}_i \cdot \vec{R}_j \rangle$$

So I would like to know what the probability distribution of this vector r n is which is r 1 plus etcetera up to r n, before we find the probability distribution. Let us find the mean square distance or root mean square distance and that of course, you immediately see is r n square is equal to r n dot r n. That is equal to summation i equal to one to n summation j equal to one to n r i dot r j in this fashion. I would like to have the average value of it over all possible random walks over all possible configurations.

So, that is the average value here and that is equal to two kinds of terms one of them is when i is equal to j, then of course you got r i dot r i whole square, but that is equal to l square there are n of these terms. So, we have n l square plus i naught equal to j r i dot r j average value. Since the average value of the sum is the, sum of the average values, since they are linear operations. They commute therefore, I put the average inside, but r i dot r j is l square cosine of the angle between the two.

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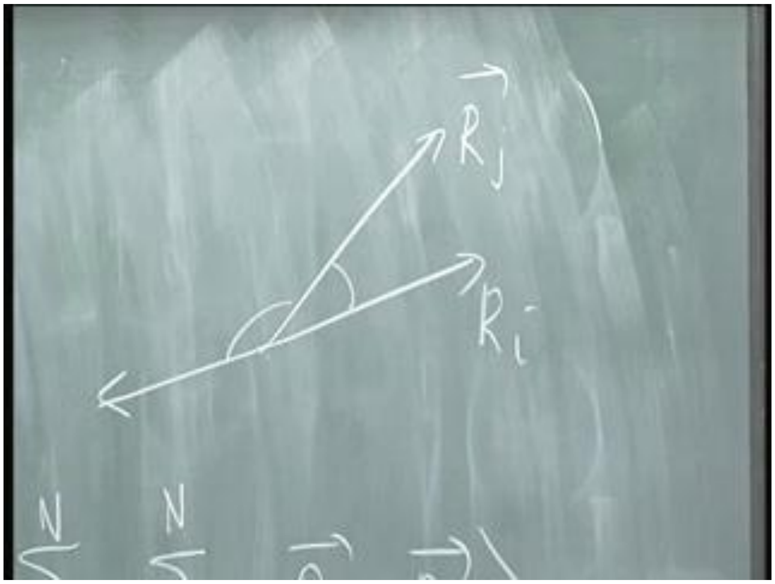

And as you can see very trivially the cosine of the angle, here is r i and here is r j the cosine of the angle between the two is this, but there is a opposite configuration, where r i could look in this direction equally probable and then the cosine of the angle is this, which is the minus the original cosine and therefore, on average this is 0 that immediately says r n square is equal to l times square root of n.

The root mean square displacement is proportional to the square root of the number of steps. If I take steps at constant rate it is proportional to the square root of the time very simple, but what it required was the assumption? That all these capital R’s are independent random variables. So, that I could average over them separately, if they are co related, and then it is no longer true. If it should so, happen that every time I take a step in the forward direction and the next step it is correlated to the previous one. And says I am more biased to go in the forward direction, backward then this is not true completely wrong or if I pass a rule saying that I should take these steps. In such a way that I never return to my starting point or never visit a starting point, where I have visited before. Then this is not true, but it is completely uncorrelated random walk simple random walk.

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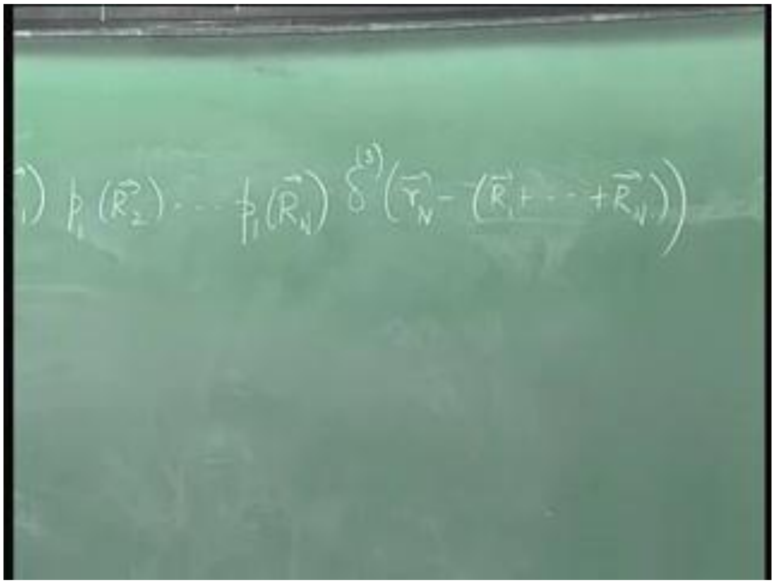
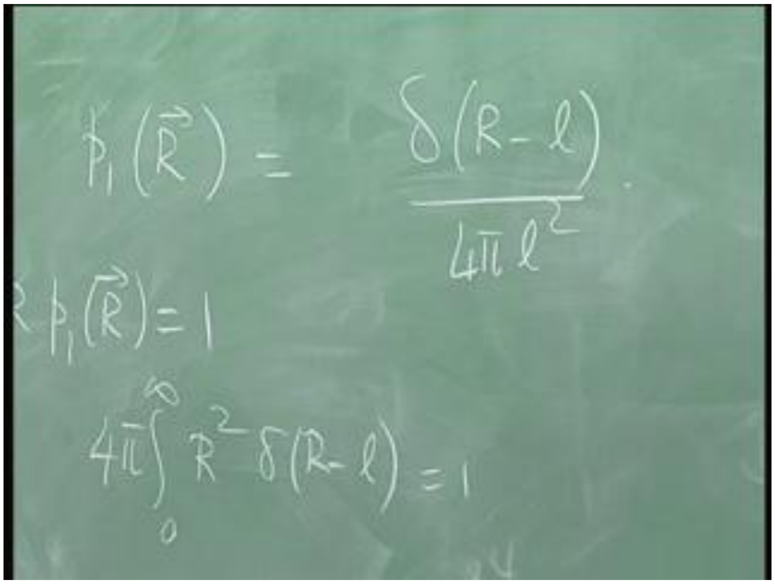


$$) \; p_1(\vec{R}_2) \cdots p_1(\vec{R}_N) \, \delta^{(3)}\left(\vec{r}_N - (\vec{R}_1 + \cdots + \vec{R}_N)\right)$$



$$p_1(\vec{R}) = \frac{\delta(R-l)}{4\pi l^2}.$$

$$R\,p_1(\vec{R}) = 1$$

$$4\pi\int_0^\infty R^2\,\delta(R-l) = 1$$

Now I ask what the probability distribution of this vector is. So, let us ask what is the probability density rather p of r? Or this equal to this is not a trivial statement. What you have to do is to ask integrate over all possibilities r 1 to r n and then compute this. So, this is equal to integral d 3 r 1, and d 3 r n over all directions possible directions. The probability that you will make density let me call it one step probability, that it is r 1 p 1 of r 2 p 1 of r n. This is the probability of a single step that it is in a particular direction and it is the same thing for all the steps. So, I just multiply all these guys together, but I have to put a constraint, there saying finally a delta function of r minus r 1 plus etcetera up to r n. Let me just call that's the probability distribution.

So, there is a delta function by the way this is a three dimensional delta function, each component of this vector must be the same to the current component, There so, you can just put delta. Now, the next task is to find out what is this guy? What is p 1 of r 1? So, what is p 1 of a vector r? What is this equal to it must be a normalized probability density? If I integrate over all directions, I should get unity and I also have the constraint, that the magnitude of this capital R must be equal to l. The length of the step it is clear that this is equal to a delta function of r minus l zero for all other lengths, but the direction is completely arbitrary totally arbitrary. Therefore, as far as the density is concerned it is 1 divided by the solid angle and I want to integrate over.

So, I want to make sure that integral d 3 r p 1 of r equal to 1, if I do this in polar coordinates and this fellow depends only on magnitude r here. Then you are going to get the statement, which says that integral r square delta of r minus l from 0 to infinity and then you integrate over angles you get a 4 pi. This guy must be equal to 1 so, it immediately tells you that the normalization. Constant for this guy is just this integral here, which is 4 pi l square and it has right dimensions, because it is a probability density in three dimensional spaces.

So, therefore it must have dimensions one over length cubed, one over l square is one over length square and the delta function provides one more length in the denominator. So, this is the normalized density and that is what we are going to put in here? All you have to do is to put that in here, but now you are on to a bit of trouble. What do? I do with this, I can adjust to one integration r n, but that is not going to help. I would like to factor this whole thing. So, what is the trick what should you do? I want to convert that delta function. What should I do? Say that again how do I split that delta function into factors? It is a product of three delta functions for the three Cartesian components, but that is not going to help very much.

What do? I do, I have n variables n is arbitrary number, I am going to take it to infinity and I am going to sum like this, but I want to convert it into a product. And then what will it do? It will finally give me an n minus 1 integral and I have a huge number of them characteristic function. That is on the right track. Yes, I could find the Fourier transform of this, but in easier ways equivalent to it is to write that delta function in a Fourier representation.

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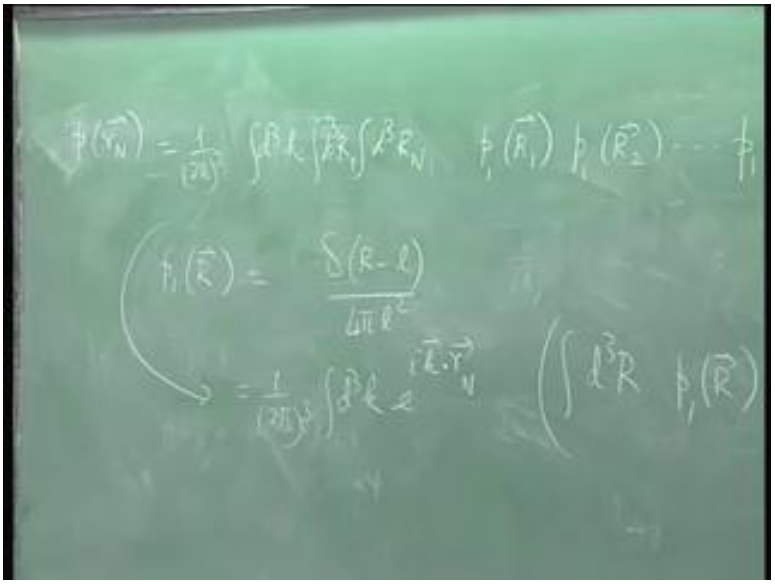

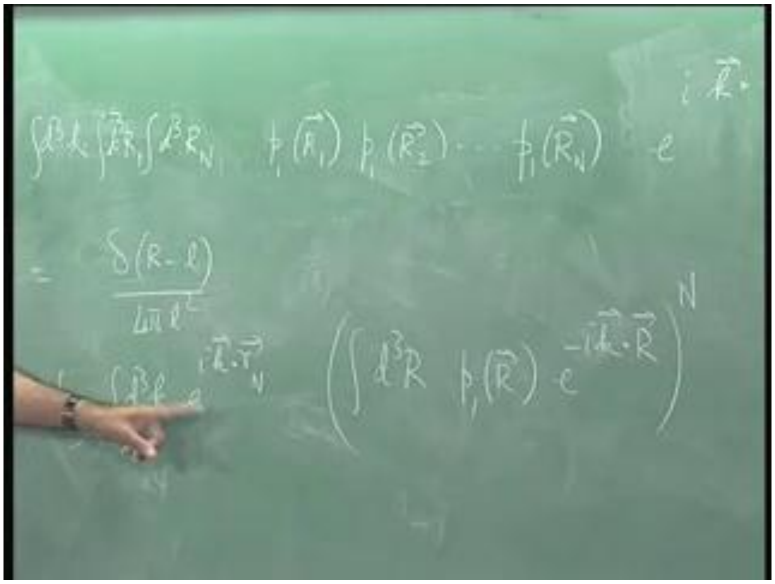

You know this is true? You know that minus infinity to infinity d k e to the power i k x 1 over 2 pi equal to delta of x. We know that and if I do this in three dimensions then it is 1 over 2 pi cube integral d to the e to the power i k dot, r is delta of r delta three of r.

So, that is all, I have to do. Once I do that, this is also equal to let me do that step right there so, I erase this and write that as 1 over 2 pi whole cube integral d 3 k. Let us put that d 3 k, in the beginning d 3 r 1 and so, on e to the power k dot r equal to minus i k dot r 1 all the way to minus i k dot r n. So, you see we factored it, but at the expense of adding one more integration and then matter becomes extremely simple. Because this is equal to immediately 1 over 2 pi whole cube integral d 3 k e to the i k dot r n. And then an integration d 3 r p n e of r e to the minus k dot r and that is just raised to the power n, because all these integrals are exactly the same apart from change of dummy variable.

I just have to find the nth power of this integral and then to the Fourier transform of that and that gives me p of r. So, this is in fact the characteristic whatever is inside, but what is this? I put this in out here and then what do I get?

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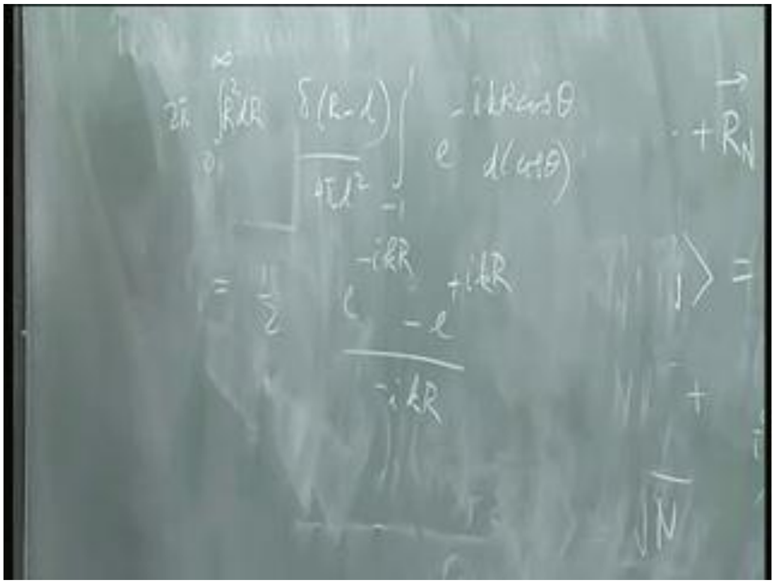

So, let me do that and perhaps stop and know the time integral d 3 r delta of r minus l over 4 pi l square and then you have e to the power minus i k dot r and I have to raise this to the power n. Now it is clear that the answer depends on vector k, but it cannot depend on the direction of k. Because I can actually rotate this is a scalar, this is a scalar. So, the whole thing is invariant under rotations and therefore, I can choose any direction. I like for the polar axis, I choose the direction of k and the moment.

I do that this integral becomes e to the minus i k r cos theta no free dependence. This d 3 r gives me a 2 pi from the free integral zero to infinity r square dr. And then integral minus 1 to 1 d cos theta, that is the polar. So, that gives me the factor 2 pi is going to cancel out that does not matter, we will leave this. This is 2 pi by the way this 4 pi 1 over 2, that this guy against this and then r square dr. There is a delta function here; there is l square obligingly here. So, this integral is gone. This factor cancels neatly against, that it is gone. You are left with just this and you have to integrate this from minus 1 to plus 1 so, this is equal to half. Then e to the power minus i k r minus e to the power plus i k over minus i k r, this is equal to minus 2 i sine k r, i should have done this first.

So, the minus goes the 2 i goes this fellow, goes this guy goes and then k r, when i integrate with delta r that gives me k l over delta. So, the whole thing reduces to this integral sine k l by k l that is it. So, it is the inverse Fourier transform of sine k l over l, what kind of functions that sine k l over k l? It is a sink function. So, now you can see, this is a fraction. This guy is a fraction and as n goes to infinity, this will go to 0 unless l also goes to 0 and how will l go to 0? How should it go to 0, in order to have non trivial thing the sine k l is like k l.

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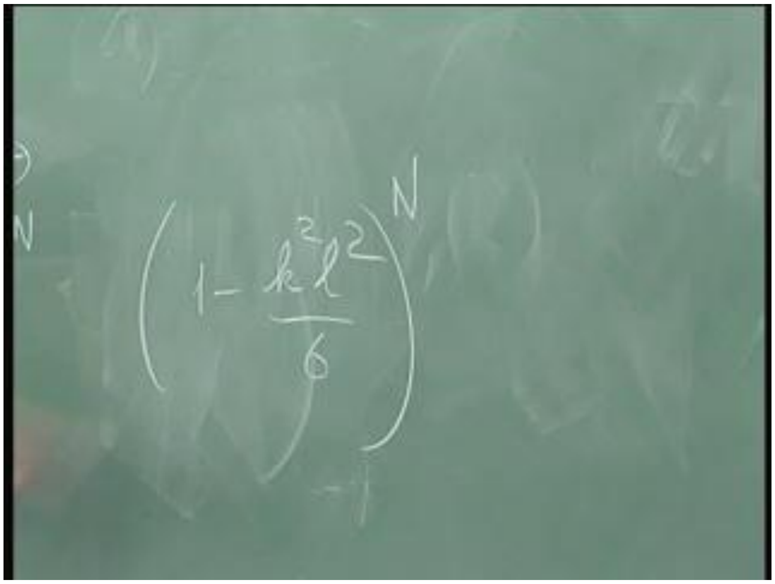
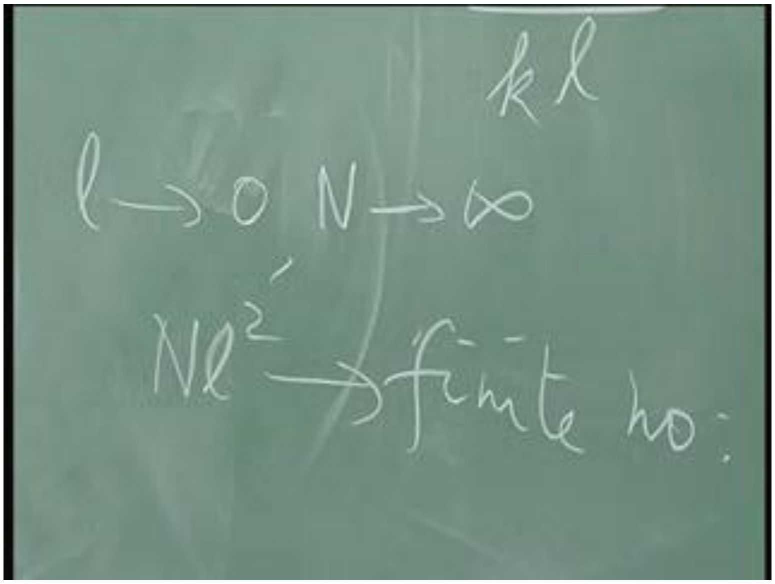


$$\left(1-\frac{k^2 l^2}{6}\right)^N$$



kl

$l \to 0 \quad N \to \infty$

$Nl^2 \to$ finite no:

So, sine k l over k l is 1 minus k square, l square over 3 over 6, 3 factorial. So, you could essentially retain just that here, when l becomes very small 1 minus k square, l square over 6 to the power n and I want to have this as a finite limit. n is going to go to infinity, l is going to go to 0 under what circumstances does? It have a limit, we know that 1 minus x over n to the power n. When n goes to infinity is e to the minus x, that is the only limit that is non trivial. So, it is immediately clear. That you must have l go to 0, n go to infinity such that n l square goes to finite. So, call it some d or something like that and if you did that it goes like e to the minus d k square, but then this is a Gaussian in k. This fellow is a Fourier transform and we know Fourier transform is Gaussian r square, which is a Gaussian.

So, that is how a random walk goes into a solution of a diffusion equation. I did this in a hurry, but apart from some factors we are almost there the crucial input is this. Now, the interesting thing is you do not need this actually, it does not matter. All these steps could be different probability distributions. They could have different lengths, but the variants must be finite mean and variance must be finite then it is still a Gaussian. So, that is the robust part of the central limit theorem. So, you could have steps completely random directions, completely random lengths and they are completely uncorrelated provided the variance of each step is finite. You still have a Gaussian; you need not take the steps at fixed intervals of time.

You could take them at random interval completely uncorrelated by Poisson process and you would still get a Gaussian completely. So, it is a very strong and robust result, but this is the simplest. This was done first by this great mathematician Markov, this is called Markovian flights. So, he is one who established that right in the beginning long ago and then there is absolute classic, which you must look at, which is Chandrasekar’s article in modern physics detailed reference to it later. So, that is how you from a random walk the solution of a diffusion equation.