**Advanced NMR Techniques in Solution and Solid - State**
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**Module-30**
**Relaxation Phenomenon**
**Lecture - 30**

Welcome all of you, since last couple of classes we discussed varieties of topics especially about evolution of the chemical shifts, pulse phase, receiver phase evolution of coupling constants how it evolves during on resonance or off resonance conditions, all those things we discussed a lot. And then afterwards we also discuss some advanced topics like coherence pathway selection; what is your coherence order? How do, you do the phase cycling by selecting a particular coherence path way? So, these were all very, very important. We can select a particular coherence pathway by using phase cycling; we took number of examples and understood what is phase cycling and then the same thing can also be done by what are called gradients, pulse field gradients. We discussed a lot about what is pulse field gradient how we can dephase the signal by applying gradients.

What happened to the nuclear spins precession when we apply gradient; from the center of the coil, above upper half and lower half; the precessing is faster above, other is slower. We also know by applying strong gradient, you will ensure that size thickness become narrow and narrow. Finally it so happens there is a continuous distribution, spins over the entire sample volume will experience different Larmor frequency all through; there will be will complete dephasing and you do not get any signal at all.

We also understood that the dephased signal can also be rephased. And number of applications we understood. We can use gradients to select a particular coherence pathway of my choice, both in the homonuclear case and also in heteronuclear case. Only thing is we need to calculate what is the phase acquired along the Z gradient, because of the G1 and G2 in the case of homonuclear case, which depends upon the coherent order you have chosen.

If the coherent order chosen before the application of pulse is P1 and the other is P2, based on this we can find out the phase acquired. And this total phase acquired by both the gradients should be equal to 0 for the refocusing condition. Use that and we can find out the gradient ratio; same thing we can do for the heteronuclear case. In the case of hetero-nuclear now there are 2 things which we have to understand; if there are gradients G1 and G2, then depending upon how the phase is acquired by I spin and S spin during G1 and also the phase acquired by S spin during G2 we have to consider. And then find out what is the total phase acquired. And you apply the refocusing condition get the G1, G2 ratio, then you can select the particular pathway. We also understood how we can utilize the gradients for various other applications including 180 gradient pulse imperfections, purge gradient as homospoil to remove the transverse magnetization for clean selective excitation, for a cleaner selective inversion; all those things we understood. So, I think you have got a hang up some of these topics which will be quite handy when you are designing the NMR experiments. Next, we will go into another topic which is used to obtain the information about the dynamics of the molecules. For example, if you get the NMR parameter like chemical shifts, coupling constants, dipolar couplings, all those things they give the static information of the molecule like molecule structure and conformation.

What if I want the dynamic information of the molecule, what if there is a motion going on? if molecule is undergoing some motion, etcetera. I can use another parameter called relaxation parameter; I can get to find out what is the relaxation which gives you some more information about dynamics of the molecules. So, there is something very interesting, which is another important parameter in NMR, which is also useful in various applications. So, we will try to understand what is this relaxation phenomenon, how we can measure them? So, we will start with a simple thing like this.

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**Perturb equilibrium distributions of spins by rf pulses**

First, in all the experiments, the 1D experiments we observed, we perturb the equilibrium magnetization, where the spins are distributed equally, in equilibrium along Z axis, by rf pulse. What is going to happen? when you perturb the spins in equilibrium by rf pulse?

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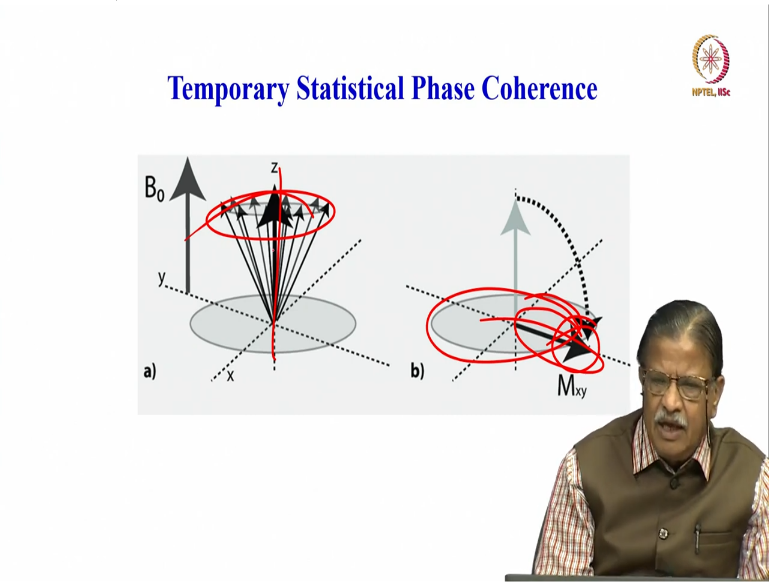


Then you are going to bring the magnetization to perpendicular axis, whether x axis or y axis does not matter, that is not important thing now. So, what is going to happen instantaneously as soon as you bring the magnetization to x axis, there will be a phase coherence, temporary there is a statistical phase coherence. All the nuclear spins will be aligned along a particular axis. But then what happens? this phase coherence will get disturbed and after some time the nuclear spins start undergoing decoherence.

And at the same time they will start go back along z axis. This is a phenomena which happens. The spins will get completed dephased here and then afterwards it will go back. Firstly, it was along z axis where there was no coherence and then you bring them to coherence here by applying 90 pulse.

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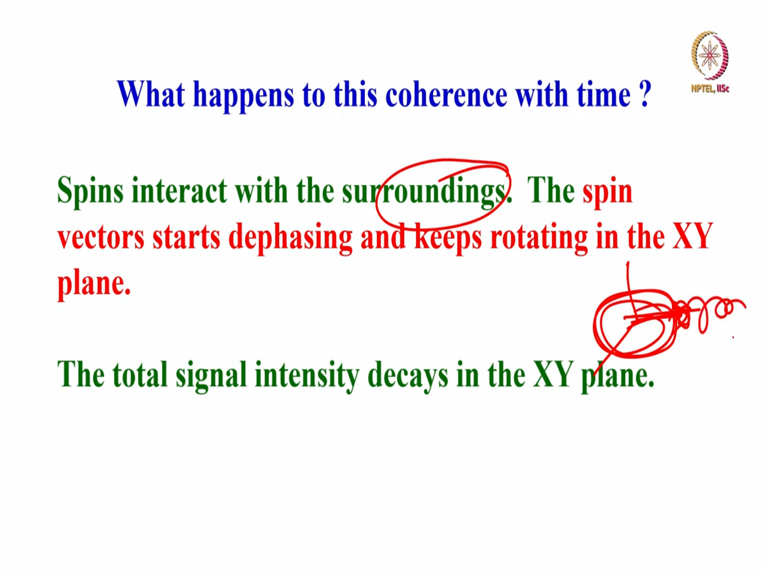


This coherence, as I said, interact to the surroundings and the spin vectors start dephasing and keep rotating in the XY plane; in the XY plane keep rotating. Initially as soon as the magnetization is brought to the X axis there is a statistical phase coherence instantaneously and you get maximum signal. With time there is a dephasing going on, the signal intensity along this axis keeps coming down. If you have a receiver coil here, you do get detect less signal; so the total signal it is start decaying in the XY plane.

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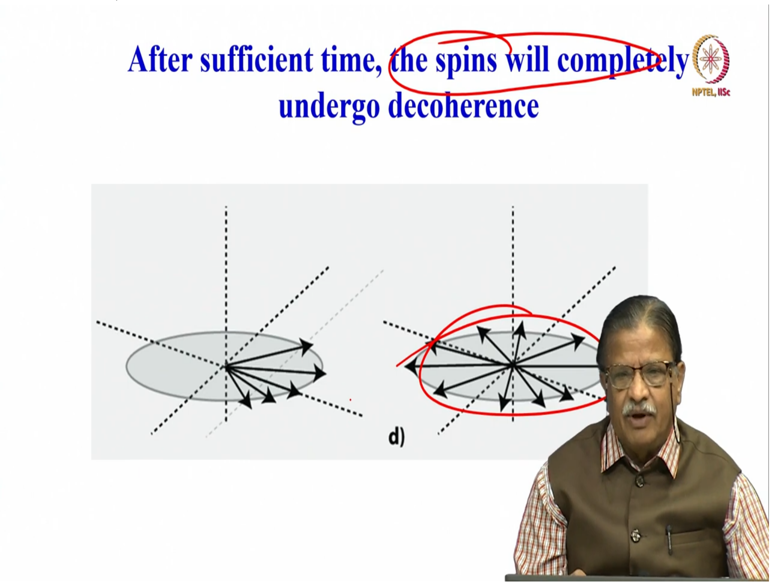


And you wait for a long time, sufficiently long time. After sufficiently long time the spins will completely undergo decoherence; there is no coherence at all. That means you will not see any signal in the XY plane. If you put a receiver there you do not get any signal; zero signal you are going to get. This is what happens. There is complete decoherence and you do not see any signal.

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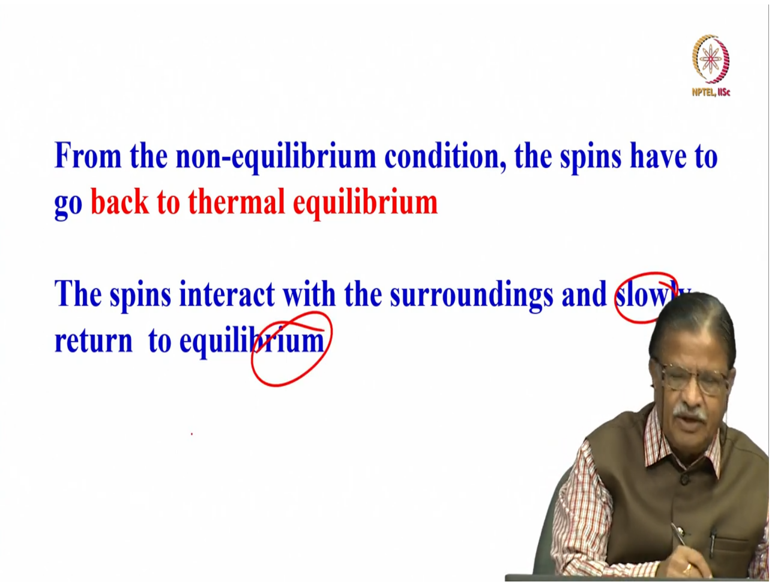


Also what is going to happen to this? you apply a radiofrequency pulse bring the magnetization from Z axis to XY plane, and do the experiment. But then if you want to do the signal averaging you should have the magnetization back again at Z axis, to apply another pulse. The magnetization has to come back, whether you want it or not, what will happen is the magnetization which was disturbed from the equilibrium position, from equilibrium condition bring it to non-equilibrium state. Now the spins will go back to thermal equilibrium. They again interact with the surroundings and then slowly they return to equilibrium condition.

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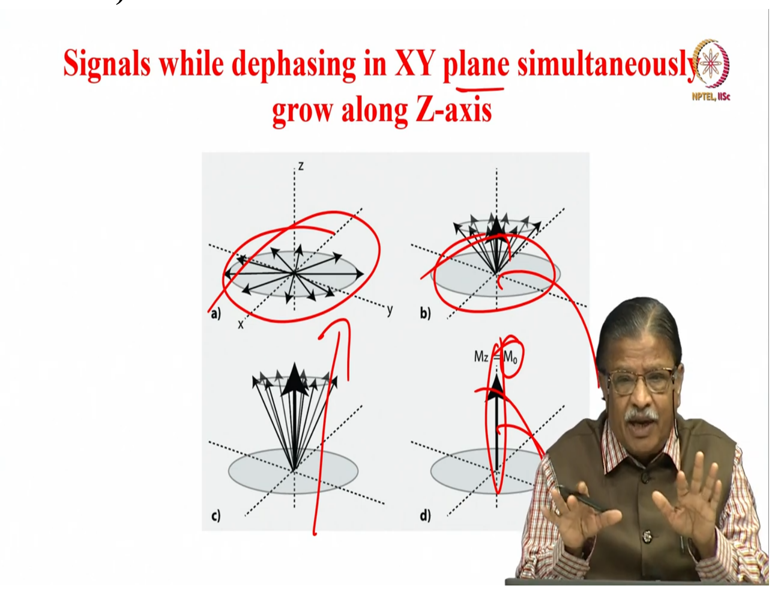


So, now we have understood 2 phenomena; one, there is a decoherence in the XY plane. At the same time when undergoing decoherence at the same time, the magnetization start going back to Z axis. So the initial magnetization was M0 initially, that is the Z magnetization. After decoherence once you bring the magnetization to x axis, there wont be any magnetization along Z axis. Now because of decoherence there won't be any magnetization in the XY plane and magnetization starts going back to Z axis.

And after some time 2 things will happen. There is a complete decoherence in the XY plane; there is no magnetization and complete recovery of the magnetization to Z axis. These are 2 independent phenomena, but happening simultaneously. They are happening simultaneously but they are 2 independent phenomena.

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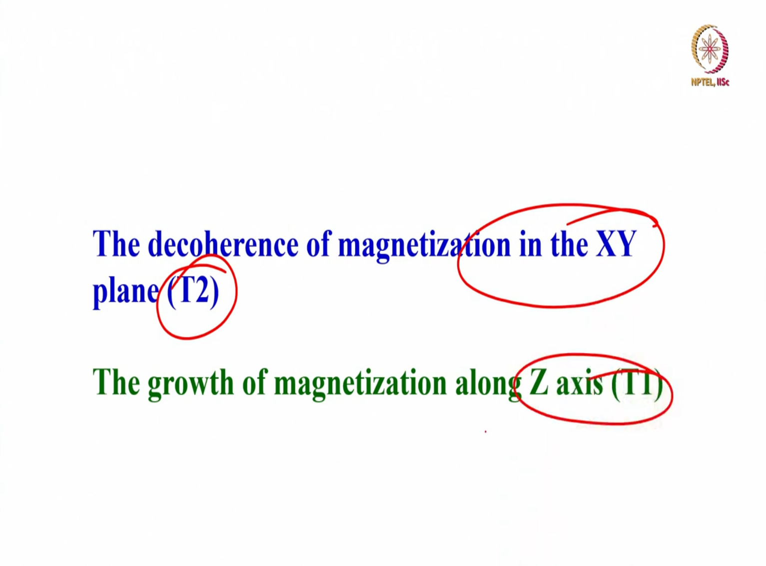


So, these 2 are referred to as two relaxation phenomena. The decoherence of the magnetization in the XY plane is called T2 relaxation; it is called spin-spin relaxation and growth along Z axis is called T1 relaxation, called spin lattice relaxation. So, the processes that bring the magnetization to the thermal equilibrium is a relaxation phenomena. So, when the magnetization gets disturbed it goes back to the Z axis, spins will experience these 2 phenomena; decoherence in the XY plane and a growth along the Z axis; both are simultaneously happening.

What are these phenomena? how they are happening? OK, it is is enough if I say these are the two relaxation phenomena; magnetization is decayed in the XY plane and it has grown along Z axis. One is a spin- spin relaxation, and other is the spin lattice relaxation. These are the 2 concepts, but 2 terms. But we have to understand more about how it happens. What is the concept of relaxation?

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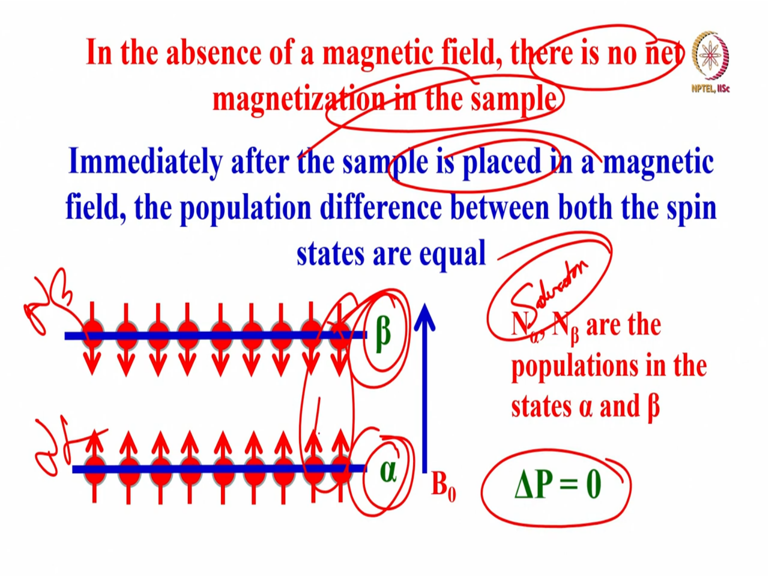


We will start with the same way, assuming that I have a sample which is outside the magnet. I will not put the sample in the NMR magnet. I have taken a sample of NMR tube, but put it outside. In the absence of the magnetic field, there is no net magnetization in the sample. There is no net magnetization because there is a random distribution. Now I am going to put the sample in a magnetic field. Immediately after I put the sample what is the population between different energy states?

If I consider I have two spin states. I am not waiting even for a millisecond or microsecond; immediately after putting the sample in the magnetic field I look at the population difference. Both alpha and beta states have equal population; there is no difference in spin population at all. What is this condition called? This a condition called saturation; we have discussed earlier in the previous course. If you can make the spins states become equally populated, this is a condition called saturation; you can do that. So, now I have not done anything, taken the sample and put it inside the magnetic field. Immediately after that I looked at the population; they are equal and they are saturated. So, what is the population difference between these two. I call this an alpha state and this beta state. The number of spins in the alpha state is called N alpha number of spins in the beta state I call it as N beta.

Now what is the difference in the population, delta P, it is 0. Remember this delta P is do not get confused the previous one where I was talking about difference phase coherence, the selection of the coherence path way; that is different. This is population difference delta P = 0.

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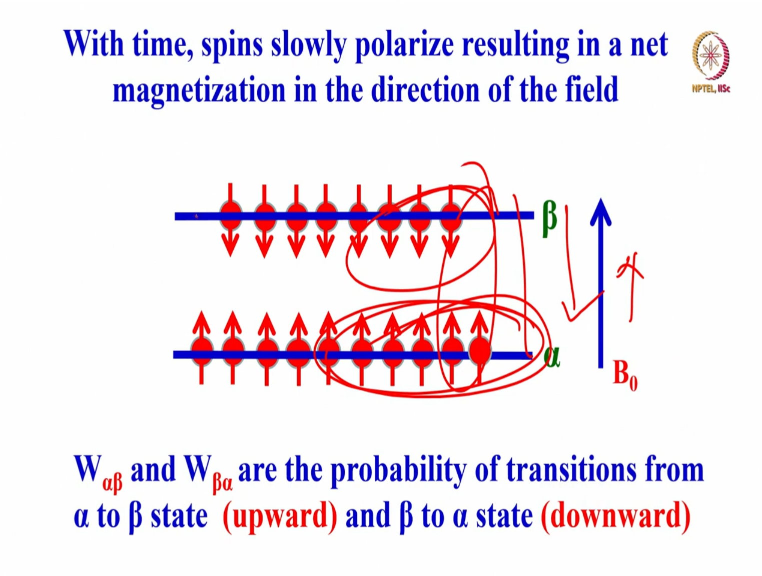


Wait for some time, do not do anything put the sample immediately there is no magnetization there is saturation condition, population difference is 0; then wait without doing anything for some time. Slowly the spins starts polarizing along the magnetic field direction, they come to Z axis; automatically get polarized, they get polarized in such a way, it generates population difference between alpha and beta states.

Now you see there are more spins in the direction of the field than opposing it. This what we discussed, this is because the Boltzmann population, we have know that. So, this there is a time required for spins to attain thermal equilibrium. When they attain thermal equilibrium you will see the more spins are there in the direction the field than opposing it. So, population difference has been obtained. It takes some time.

Now how does the population the difference occur? How the spins from here went there; how the spins from here came down. Now we will discuss 2 things. I consider W alpha beta and W beta alpha are the 2 transition probabilities of the transitions from spin alpha to beta and beta to alpha. The alpha to beta is upward transition from here to here I will considers W alpha beta and spins coming from here to here I consider as W beta alpha, it is a downward.

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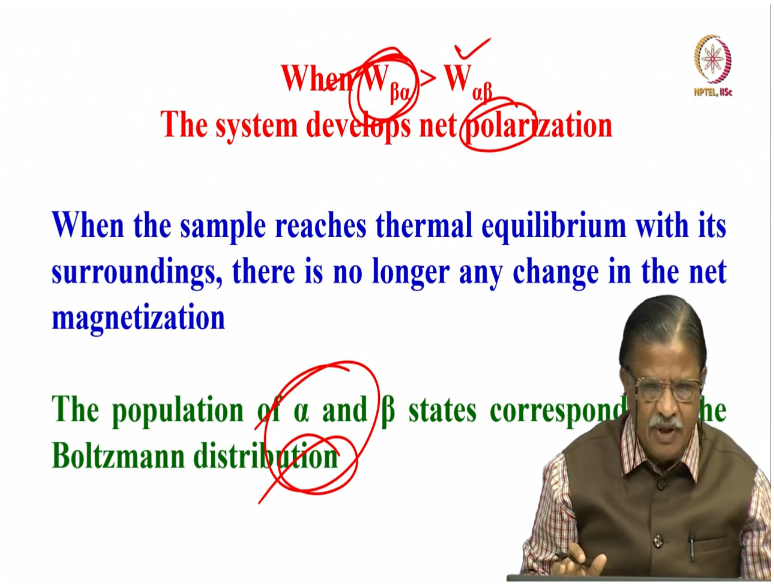


It is some simple basic conceptual understanding; Ofcourse, there is an advanced theory of understanding concept of relaxation and everything. For the benefit of the participants here that is not essential, but only understand the concept here. Now when this situation will happen? when there is a maximum population here in the alpha state? population difference will become more when beta to alpha becomes more ,when W beta alpha, the transition probability from beta state to alpha states becomes larger than the alpha beta state, the spins can simultaneously go from alpha to beta, beta to alpha. But when this transition probability is larger there are more spins in the alpha state. That is more spins are aligned along the Z axis. Then only system will develop net polarization, that is important. So, this is the condition required for the spins to develop net polarization, net magnetization what you call, When the sample reaches thermal equilibrium, wait for some time; that time is of the order of seconds to millisecond depending upon the sample. It attains thermal equilibrium, afterwards no change in the population at all. There would not be any change in the population difference, it remains same. And that population difference you can calculate after some time that corresponds to what is called Boltzmann distribution formula, which we calculated long back.

So, it takes some time, all I said is do not do anything; take the sample put it in a magnetic field, wait for some time. Instantaneously there is a saturation situation, where the population difference is not there, but after sometime it population difference, the possibility it can happen because there is more probability of spin coming from beta to alpha, which is much more than going from alpha to beta. If that can happen there is net polarization; that is what I am telling you. And after some time there would not be change; it remains same.

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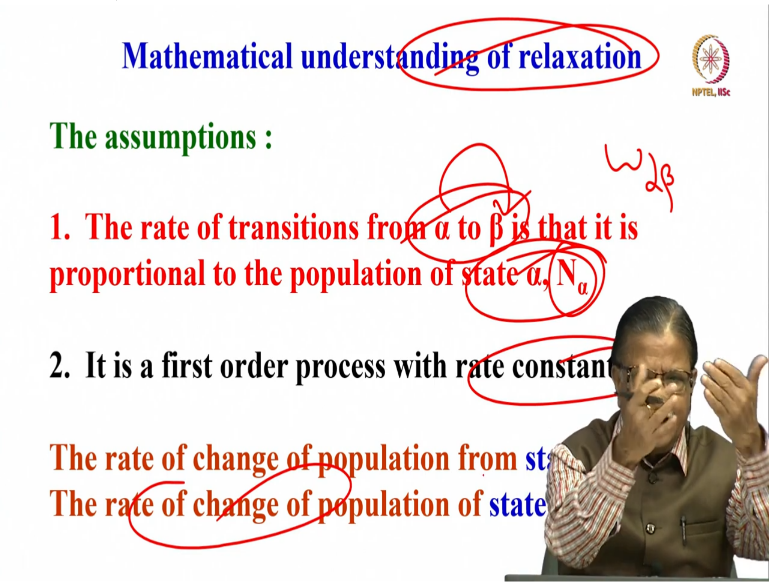


We will understand this phenomena mathematically, in a very, very elementary basic mathematics, very elementary. I am not talking about advanced theories of this relaxation. One of the assumption I do some is the rate of transition from alpha to beta is proportional to population of the state alpha; when there are more spins the rate will become more; the rate of transition from alpha to beta that is W alpha beta is proportional to N alpha.

Similarly, the first order process is with the rate constant W; it is the first order process the rate constant is W. The rate of change of population from from alpha state is W alpha beta; change of the population from alpha, from alpha it has to go to beta; that I consider as rate of alpha beta. Similarly the rate of population change from beta I will call it is beta alpha, from beta it has to go to alpha; from alpha state population has to go to beta. I consider as W alpha beta from beta it has to come to alpha I consider as W beta alpha.

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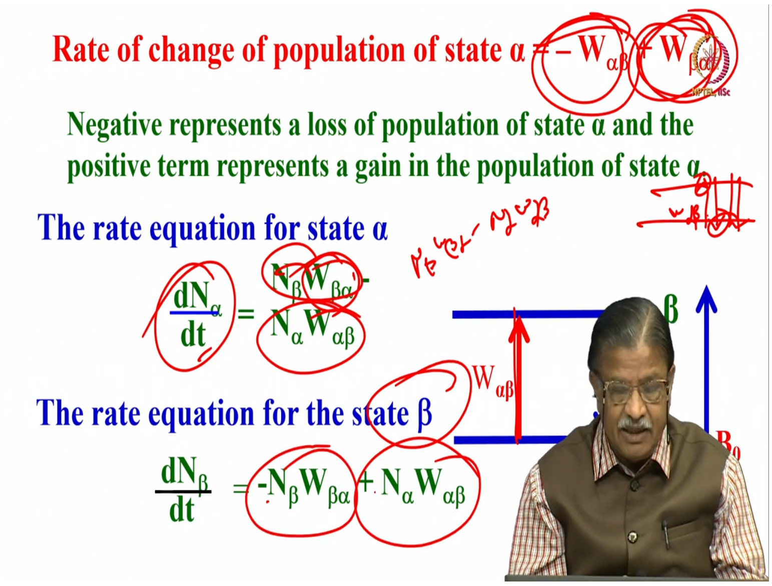


Now if I consider, there is a possibility that simultaneously everything is going on; from the alpha states to beta state the spins are going up, the spins are also coming down from beta to alpha, both are happening. Now let from alpha to beta W alpha beta is there, from here the probability of spins going from here to alpha to beta W alpha beta, I will call it negative, I call it a minus alpha beta.

Why? Because I am losing these spins from alpha to beta, it is going out so I call it negative. Now another thing what is happening is the spins are also coming from beta to alpha; there I am adding up, there is incoming population, spins are coming to alpha state that is why I call it as plus. The total change of population of the spin state alpha if you consider, how much population change is going on, some are going out some are coming in. So, this is considered as alpha = - W alpha beta plus W beta alpha. This is going out this is a loss and this is a gain. That is what is happening. And now consider a situation like this; spins are going from alpha to beta is W alpha beta is W beta alpha. Now I can find out what from the rate equation what is the rate of change of this population? This is a simple differential equation, I can do that I can find out.

Then number of spins in the alpha state can be given by the simple equation dN alpha / dt = N beta, N beta is the number of spins in beta state minus the probability of beta to alpha into this one, minus N alpha multipled by alpha beta. This is the ; this is rate equation for alpha state. The same thing for the rate equation for beta state, it goes in the reverse way negative for this and positive for this.

Here in the previous example N beta W beta alpha minus an alpha W alpha beta, but here minus beta plus alpha that is what is the only thing happening because in both the case one case there is a gain other cases other times there is loss. Same thing happened for the beta state also. So, this is the rate of change of population for both the spin states.

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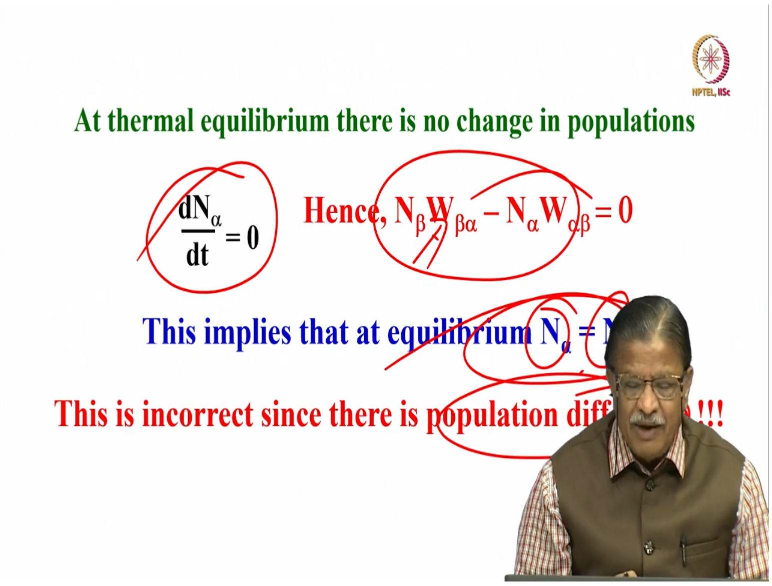


Now when we are at thermal equilibrium, I told you after some time, put the sample in a magnetic field keep quite do not do anything, there is the thermal equilibrium, meaning there is no change in the populations. That means dN alpha / dt should be equal to 0. With time there is no change. So, in my condition I had to put this as 0, correct, this is what the rate of change in the population, taking the probability into account. That is what I worked out; simple equation I wrote you know, they are phenomenological equations.

Now this implies I will make sure then N alpha should be equal to N beta, correct this, from this equation you can understand. So, that means there is no net gain in the population at all. It is not understandable. We know there is a net population along the Z axis, that is equilibrium population that we are detecting always in NMR; but according to this equation N alpha = N beta; the saturation state after some time, so this is incorrect.

So, there is a population difference, however, according to this, there is no population difference; it is wrong. So, my assumption is wrong, something is wrong in my equation or in my understanding.

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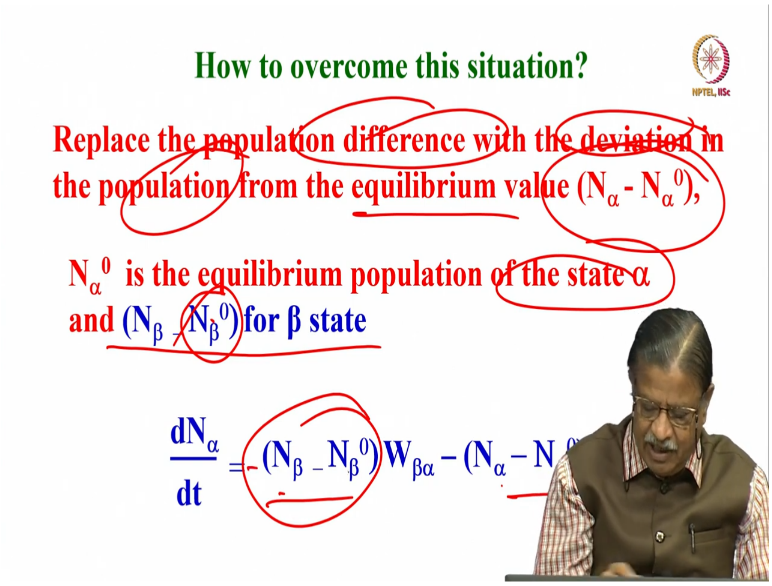


So, what we do? how do we overcome this situation? instead of replacing the population difference what we do is, we find out deviation from the equilibrium population. We do not call it is a population difference, but deviation of the population from an equilibrium value, equilibrium value is N alpha - N alpha 0; N alpha 0 is the population at the equilibrium state. And then if similarly, if you consider for the beta state it is N beta - N beta 0; that is N beta 0 is the population in the beta state in equilibrium.

So, now deviation of this population from the equilibrium we consider, let us see what happens. We do not consider population difference; we can see the deviation of the population from the equilibrium. Then simple, instead of N alpha and N beta which we were using earlier put the deviation now; not N alpha or N beta; but N beta - N beta 0, N alpha - N alpha 0 for N alpha; for N beta dN / dt same thing, you have to work it out this becomes negative this becomes positive; that we have solved here.

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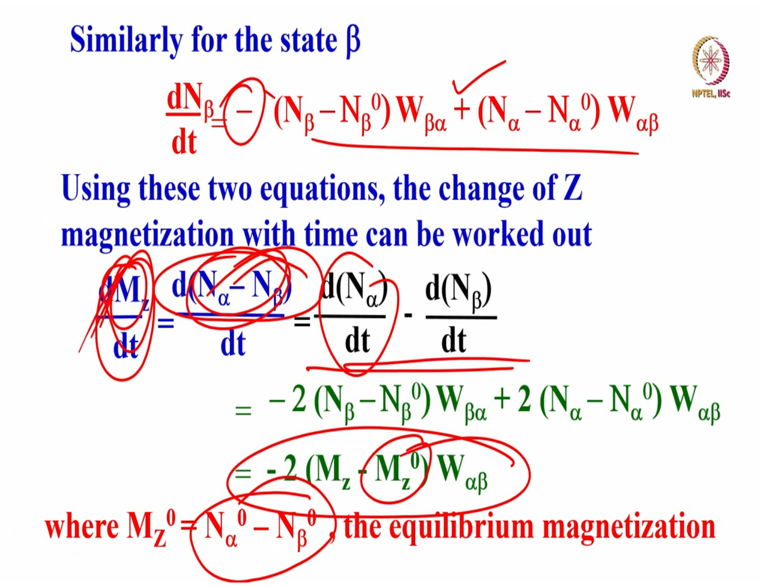


Similarly for the beta state it is like this, now this is negative this becomes positive both equations we have written; are we right now? Let us work out using these 2 equations; the change of Z magnetism with time we can work out, we will work out let us see what happens. We work out what is dM z / dt. The dM z / dt is nothing but d of N alpha - N beta / dt is the change in the population between two states.

Now this you can expand, it is like this. it can be dN alpha / dt - dN beta / dt there is no doubt about it, it is very simple. What I did is my equilibrium magnetization I took, that is the difference of the spin population. And then the change of Z magnetization I considered, and then what is the rate of change? We found out of Mz; we substituted this and just expanded this. Now we know what is the d N alpha / dt, we worked out here.

What is dN beta / dt we know; substitute all those things here. And do some jugglery, in the sense, rearrange the terms, it is a simple high school arithmetic, you do that. Then this is what you are going to get, minus 2 M z - M z 0 into W alpha beta. Now what is M z 0? M z 0 we have called it as N alpha 0 - N beta 0; it is the equilibrium magnetization; difference between alpha and beta states in equilibrium. There is a net magnetization that should be non 0; there should M 0 in equilibrium. So that is called as M0 as N alpha 0 - N beta 0.

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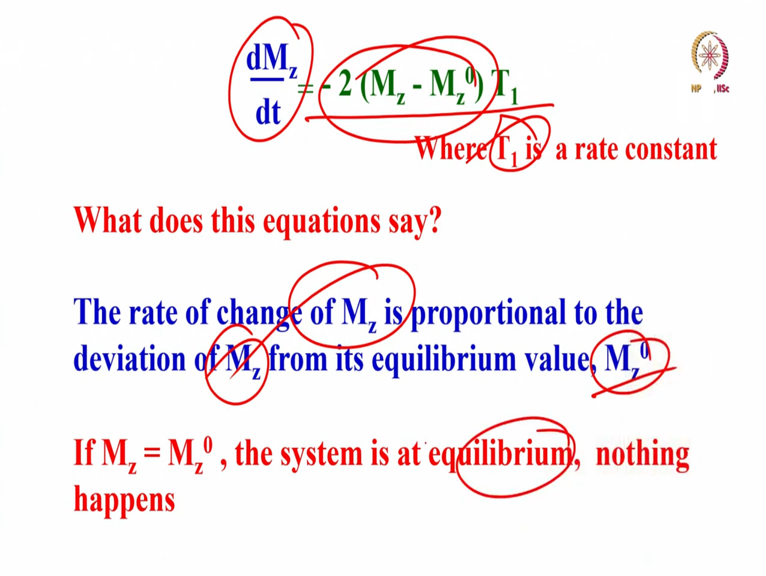


No if you put it here, dM z / dt it turns out to be this. Now I have put T1 as a rate constant. I have put T1 from this equation, instead of this I am going to put this T1 as a rate constant. So, what does this equation tell you now? It is a simple arithmetic we did, and arrived at the equations, what does it say? The rate of change of Mz is proportional to the deviation from the equilibrium magnetization Mz 0.

What is the deviation? Deviation of Mz from which equilibrium magnetization is what you are going to see. The rate of change of Mz is the deviation of Mz from its equilibrium value. Now if Mz = M0 the state is at equilibrium. We have attained thermal equilibrium, what will happen? If you put the Mz = M0 nothing will happen.

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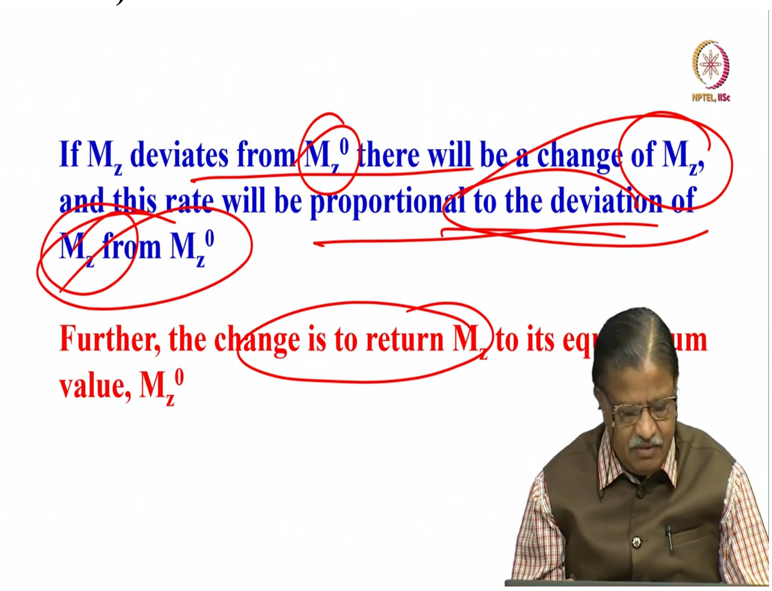


So, Mz deviates from M0 but there will be a change of Mz. Iif Mz = M0 here no change, equation is 0. If M z deviates from M0; not equal to Mz, is not equal to Mz0. If there is a change then rate the population also deviates. The rate equation tells me the proportion of the deviation of Mz from Mz 0. Or in simple terms remember, if Mz deviate from M0 there will be a change of Mz.

And this rate of change will be proportional to the deviation of Mz from M0. Earlier was different, when Mz 0 = M z it there is no change, but Mz when it deviates from Mz 0 there will be change of MZ and this rate will be proportional to the deviation of Mz from Mz 0. This is whatyou should understand. Further change of return to Mz that is to its equilibrium value Mz 0.

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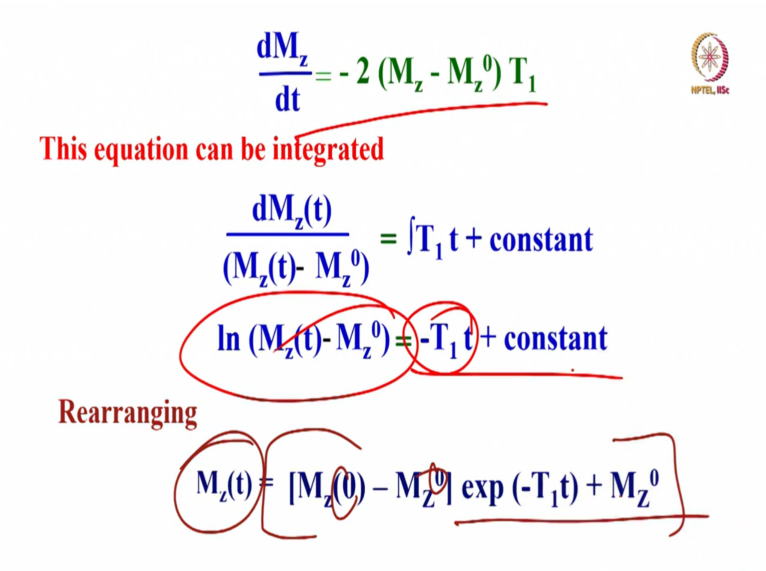


So, now dM z / dt; if it is like this, you can integrate this equation, very simple. When I integrate this equation this turns out to be this thing, I take logarithm, simple calculus you can do, then it turns out to minus T1 /t into T1 /t plus constant rearrange the terms; simple equation. This is high school mathematics, you do Mz t = Mz 0 - Mz time t = 0; and then exponential minus T1 t + Mz 0 some equation you workout.

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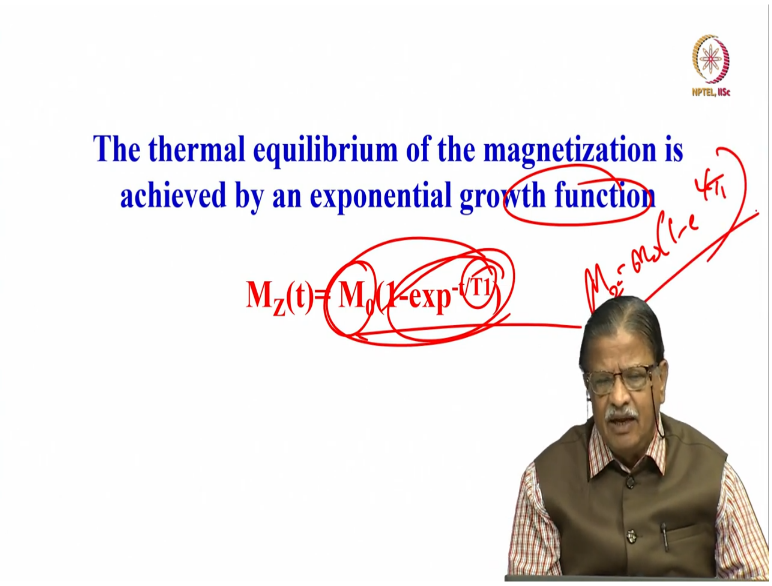


The thermal equilibrium with the magnetization is achieved, by an exponential growth function. The thermal equilibrium is achieved not simply by a linear function it is obtained by an exponentially growth function, because 1 minus something is there. So, Mz t as a function of time if you calculate Mz t turns out to be M0 into 1 - exponential - t/T1 so, there is a growth function.

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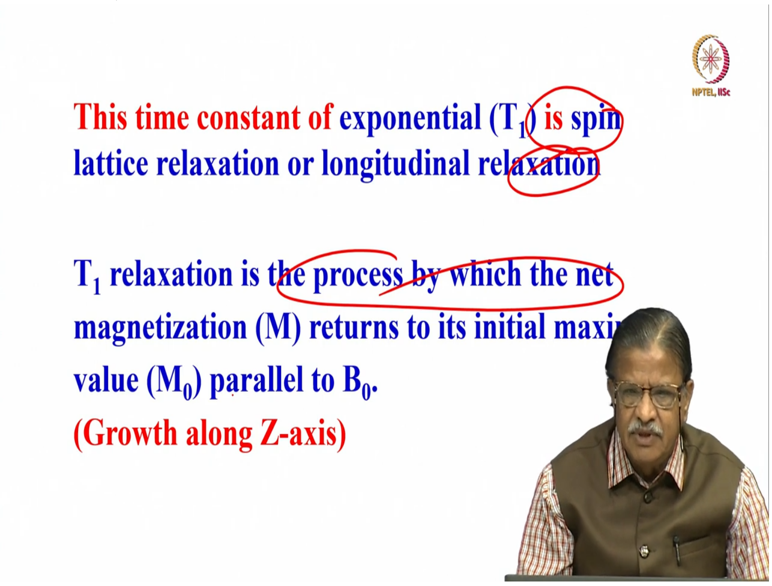


So, the time constant of the exponential T1 is called spin lattice relaxation. The time constant here in this equation which is the time required for the spins to grow along Z axis is called spin lattice relaxation. So, T1 relaxation is a process by which the net magnetization M returns towards initial maximum value; what is the initial maximum value? M0; that is the thermal equilibrium value.

So, the net magnetizations M will come back to M0 after some time, that time is called T1. It is the relaxation time, this results in growth of magnetization along Z axis. You simply understand what we did is a simple equation, we did this and rearranged something we got exponential minus T1/t. So, this is what we are going to get.

Remember this is Mz = M0 into 1 - e to the power of t / T1. This is the equation which governs or which tells me about thermal equilibrium magnetization achieved by an exponential growth. And this is T1 relaxation process which causes the net magnetization to return to initial maximum value; and this phenomenon is called spin lattice relaxation; and the time required for the spin to attain this thermal equilibrium is called spin lattice relaxation time.

It is also called T1; it is also called longitudinal relaxation time; is also called longitudinal relaxation; growth of magnetisation along z axis' spin lattice relaxation' attaining thermal equilibrium. All these are the terminologies that are normally used. But remember T1 is relaxation time, it is spin lattice relaxation time.

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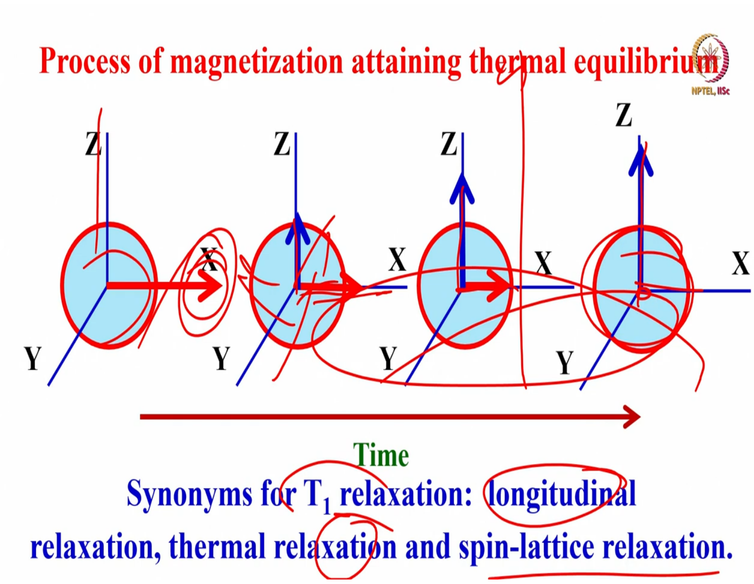


The process can be diagrammatically given like this. Initially the magnetization is brought to X axis. Of course, I am not showing the decoherence, there is also decoherence simultaneously going on, do not ever be under the impression that there is no decoherence. The decoherence is shown here by the reduction in the signal intensity. In principle I should have written all your vectors here. Since it was too much of a work I did not do it.

But I am showing the total magnetization, because of decoherence it is coming down here in the x axis. So, initially full magnetization, instantaneously there is a phase coherence, and then there is no magnetization along Z axis. By the time this start dephasing here, this intensity comes down, this goes up. So, see red will be coming down and blue is going up. Finally red becomes 0 and there is a complete growth.  The entire magnetization will come back. This is the way the magnetization attains thermal equilibrium. It decays in the XY plane; and grows along Z axis as a function of time. And synonyms for this are T1 relaxation, longitudinal relaxation, thermal relaxation, spin lattice relaxation; these are the terminologies which are used you know, various things. So, more what about these things we can discuss. Now the time is up, I just wanted to tell us today about what is spin lattice relaxation.

Please remember relaxation phenomena,  phenomenologically we tried to work out, what is the growth factor. And we know it is the exponential function which is responsible for attaining thermal equilibrium; and diagrammatically we know what happened to the the equilibrium magnetization when it is disturbed brought to X axis or Y, axis after some time, decoherence starts in the XY plane, slowly grows along Z axis .  After some time there will be complete decoherence along the XY plane and then magnetization completely grow along Z axis. And this phenomena is called spin lattice relaxation time. There are a lot more to understand about these phenomena; we will come back and discuss in the next class. So, I am going to stop here. Today we have understood more about relaxation phenomena, starting with the phenomenological equation we tried to understand a lot of things; what is relaxation? What are the transition probabilities? Why if we do not take into account the deviation from equilibrium it does not help us. So, finally there must be a net magnetization developed in equilibrium according to Boltzmann population. So, all these phenomena conceptually we are trying to understand. We will continue further understanding from next class. Thank you.