Advanced NMR Techniques in Solution and Solid-State
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Module-31
T1 Relaxation Concepts and Measurements
Lecture – 31

Welcome all of you. In the last class we started discussing about relaxation time. Of course before that we discussed something about various other things like pulse phases, receiver phases, and pulse field gradient everything. Afterwards I jumped into relaxation. I explained to you what is the relaxation phenomena; for example, you take the sample outside and put it in a magnetic field. You know that in the absence of magnetic field the spins are randomly oriented there was no preferential alignment of the spins. As soon as we put the sample in a magnetic field, immediately after the sample is put, we have what is called as saturation state. That is a state wherein both these energy levels for spin of system are are equally occupied. There is no population difference, that situation is called as saturation condition. So, immediately after we put the sample you have a saturation condition. But give some time then spins will develop some polarization, in the sense it so happens more spins gets aligned along the direction of the magnetic field than opposing it. Of course, then we brought in the probabilities of spin going from alpha to beta and beta to alpha states.

And we worked out mathematically and showed that if that is the situation, mathematically this cannot happen. If I take N alpha and N beta are the number of spins in alpha and beta states, we did mathematical calculation and showed that somehow this was not agreeing with our assumption, because there is always some magnetization developed where the spins are preferentially aligned along the direction of the magnetic field.

More spins are in the direction of the magnetic field than opposing it, so there is some magnetization. So, we understood this by taking into account not the spin population of N alpha and N beta states, but the deviation from equilibrium; then we arrived at the expression, then the expression what we got it is, how after certain time the magnetization grows along Z axis. It requires a time that time constant is called T1.

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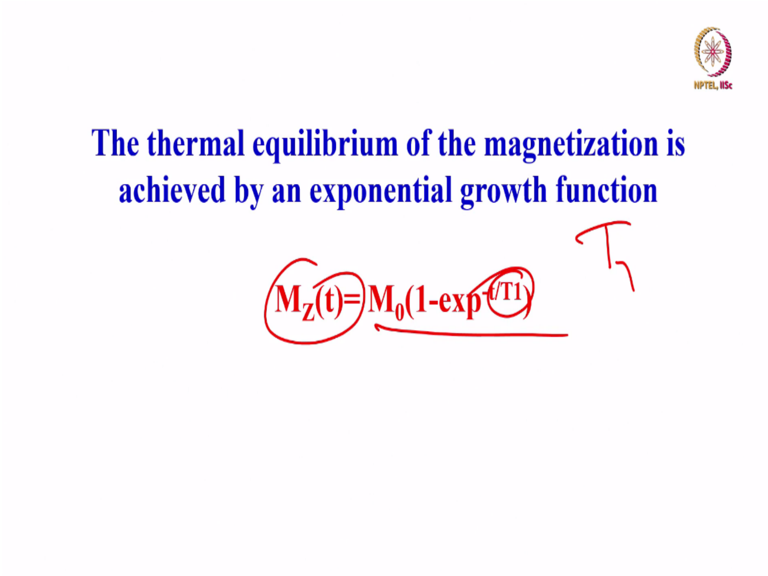

We arrived at this exponential function. This exponential function is the one which is given as Mz t = M0 into 1 – exponential – t/T1 and T1 is actually this one. This is the time constant called spin lattice relaxation time, it is the time that is required for the growth of magnetization along this Z axis.

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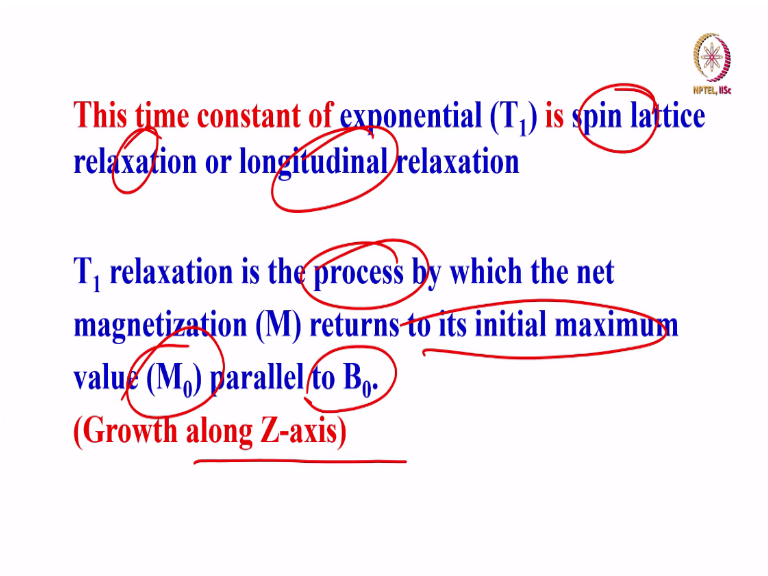

This is also called spin lattice relaxation or longitudinal relaxation also. There are certain synonymous for it. So, what is the meaning of T1, we understood. It is a relaxation process by which the net magnetization returns to its initial maximum value, growth along Z axis. This can happen as soon as we put the sample in a magnetic field or you disturb this thermal equilibrium magnetization by applying a radio frequency pulse.

And then it has to come back to equilibrium position; equilibrium condition. That means it has to attain its original value called M0 which is parallel to B0 and this growth along Z axis is what is called time which is required for that, it is called spin lattice relaxation time and this phenomena is called relaxation along the Z axis. That is called spin lattice relaxation.

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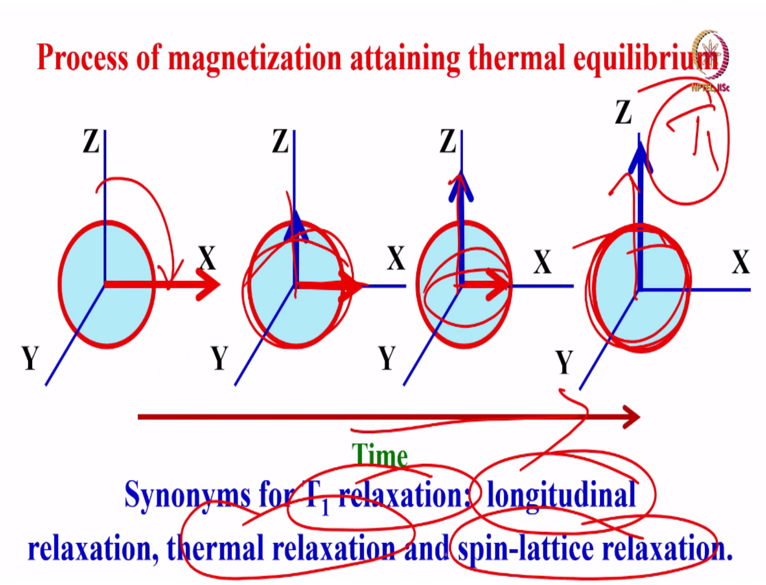

Pictorially in the vector diagram I showed like this. Immediately after the 90 degree pulse magnetization is brought to X or Y axis by 90 degree pulse. Immediately then there is a statistical phase coherence; all the spin vectors are aligned along this axis, but with time what happens the spin start dephasing in the XY plane; I will come to that later, that is called another type of relaxation.

And then simultaneously it starts growing along Z axis; This decreases in the XY plane start growing along the Z axis. It so happens after a certain amount of time which is called T1 the magnetization in the XY plane will be completely dephased; and there is a complete growth of magnetization along Z axis, which is called T1. This happens as a function of time this is what we understood.

And there are certain synonymous for this I told you it is called T1 relaxation, the longitudinal relaxation also called thermal relaxation and spin lattice relaxation. These are the synonymous which you find them in various textbooks of NMR. I just wanted to give you some of the synonymous, please remember these things.

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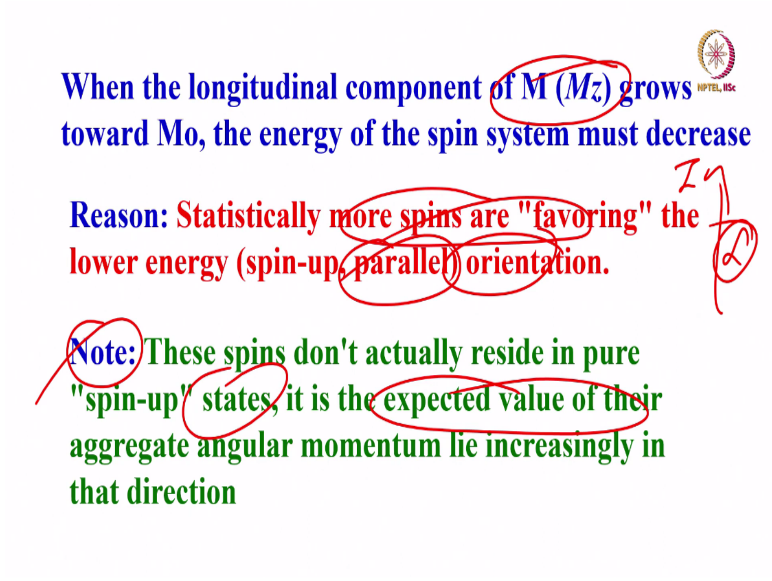

Now longitudinal magnetization M grows towards M0, what will happen, the energy of the system is decreasing, because as you know somehow when there is a preferential alignment along Mz, the energy of the system has to decrease. It can happen even when you apply radio frequency pulse also. Apply a rf pulse you are disturbing a spin system, giving energy by external RF. Now the energy of the system must decrease.

The reason why it has to lose energy because statistically there are more spins favoring the lower energy orientation. That is spin up or parallel orientation or in the direction of the magnetic field which is along Z axis. So, this is the reason. Statistically; not that all spins will align statistically more spins are favoring the orientation along the Z axis; it is a parallel orientation; that is the reason why system has to lose energy.

Energy must decrease for Mz to grow along Z axis. But one thing I wanted to caution you here. Note these spins do not actually reside in the spin up states. I am telling you it is only a statistical average. It is only the expected value of their aggregate angular momentum lie increasingly in the direction of Z axis; or in the direction of the magnetic field. Not that all spins suddenly align along the direction of magnetic field.

Statistically, it so happens that is preferentially more spins actually will try to orient along the direction of the magnetic field, this is a caution. Do not be under the impression spins are aligned means, all along Z axis. No, there is also orientation in the direction opposite to magnetic field; there is a preferential excess of magnetization, excess spins in the direction of magnetic field.

This we have been discussing even from the first lecture itself in this course and also in the previous course.

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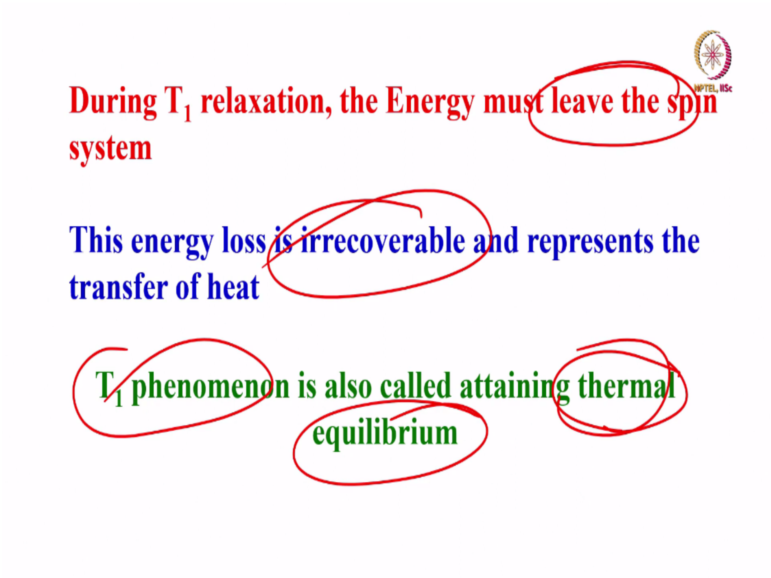

Now when I say during this T1 relaxation spin system must lose the energy. It has to leave the energy from the spin system. It will go out of the spin system. And when it leaves it is irrecoverable loss. It transfers to the system; where it goes we will discuss. The energy loss is irrecoverable and it represents transfer of heat, it gives to the surroundings in the form of heat. That is the way the spin system loses energy to the system.

And that is the reason why in some books we say T1 phenomenon is also called attaining thermal equilibrium; that mean system is attaining thermal equilibrium means because it had more energy, it will leave energy to the surroundings. After losing the energy it will come back to Z axis; this loss of energy is not recoverable. It is an irrecoverable loss of energy, and the way it loses the energy is in the form of heat. That is why it is called attaining thermal equilibrium.

These are the terminologies which were very often used in NMR you must remember why it is called thermal equilibrium is because of this.

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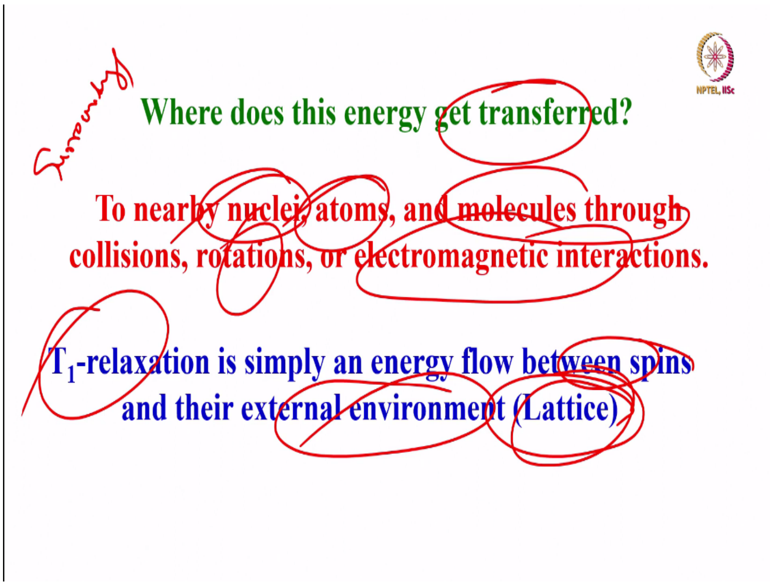

Now you may ask me a question, okay, the system is losing energy, fine I understand. But where does this energy gets transferred, where does it go, how does the system absorbs this energy which is lost by the spin system. This energy has to be transferred somewhere; and it gives its energy to other system. It could be nearby nuclei, it would be nearby atoms and also molecules through collisions, rotations or electromagnetic interactions, varieties of interactions can be there.

Somehow it gives energy to surroundings. In general, you can call it as gives its energy to surroundings. That is how the system gives energy in the form of heat to the system, in the form of collision of molecules, rotation, giving some sort of motion for It; or some electromagnetic interaction. Or in other words, simply understand T1 is the relaxation, it is simply an energy flow between spins and the external environment, other than the spins of your interest.

In the molecules let us say you are concentrating on the protons. The protons spins, you are worried about relaxation of proton spins. Apart from the spins of the your interest that is protons, everything surrounding it which is called as external environment, we call by a collective word called lattice. It gives its energy to lattice. Please do not get confused with the crystal lattice, that is different.

In the rigid system we can talk about crystal lattice. But here it is a colloquial world which is used as a lattice, in the sense everything surrounding the nuclear spin of our interest; entire surroundings of the system for which the spins are going to lose the energy; or give the energy to them is called lattice. That is why it is called spin lattice relaxation. Spins are giving this energy to the lattice, and then relaxing; that is why it is called spin lattice relaxation. please remember this.

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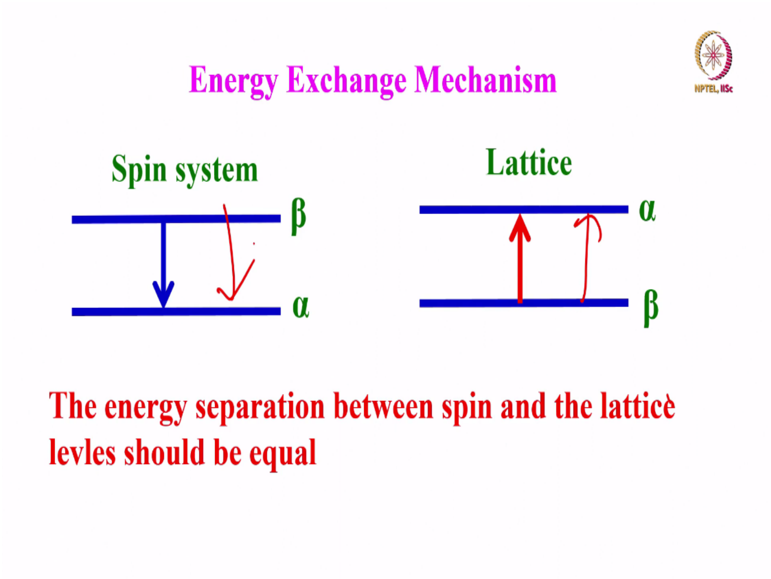

Now how does exchange phenomena takes place? See when the exchange takes place there must be some sort of a resonance; and let us see how does the energy exchange phenomena mechanism is there; we will understand. Let us consider the spin system and also consider the lattice. The spin system has energy states alpha and beta, we know that we are considering this spin half nuclei which has two energy states alpha and beta.

I know what is energy separation, I can express in terms of frequency, that also you know. Now, the system has to give energy to the lattice, from a perturbed state; that means the energy is already in the beta states. Somehow energy is already in the beta state. It has to give its energy to the lattice and come down to alpha state, it is a stable state it has to come from disturbed state to stable state. That is from beta state the spins have to come to alpha state.

If that has to happen it has to give the energy to the lattice, you should have the lattice system with identical energy separation. It is in not spin system, it is lattice now. We can think of lattice as different energy levels, which can be called as alpha and beta; again it is colloquial not spin states alpha and beta. I will call it lattice energy levels as alpha and beta; so that this energy separation between alpha and beta of the spin system must exactly match with the energy separation for the lattice system.

This lattice energy separation delta E must be equal to this thing, for example delta E of lattice should be equal to delta E of the spin system. It has to match, only then what will happen, the spins in the excited state when it matches gives energy to the lattice and comes down. When it comes down, what will happen? The lattice will absorb energy and this will go up.

It goes to the excited state; see when the spins are coming down here, it is lattice is going up it is gaining energy. Here the spins are losing energy; when the spins are losing energy, lattice is gaining energy here. See it is gaining energy while the spins are losing energy. Only if this can happen, only if the energy states between spin system and lattice agree with each other, if it matches. These two-energy separations must be equal.

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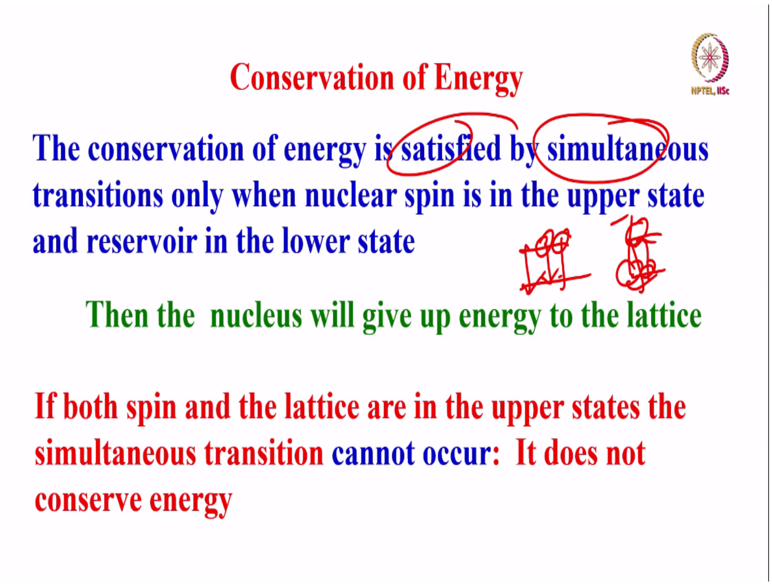

And then we call it as conservation of energy, energy is conserved. If the conservation of energy is satisfied then there is a simultaneous transitions of spins from the nuclear upper state and the reservoir in the lower states. What happens I mean you go back here and there is a simultaneous transition of the spins from the upper state and spins from the lattice reservoir state.

So, this is what happens; reservoir lower state gain energy and go the upper state. The spins in upper state lose energy and come to the ground state. This is what happens; then nuclear spins will give energy to the lattice. You understand what I am trying to say. From the energy there is a separation between spins and the lattice, the spins in the excited state or in upper state come down; simultaneously lattice absorb energy and go to the excited state that is what happens.

Now you may ask me a question why not spins and lattice both are in the upper states; simultaneously transition cannot occur? why not this will come here and this will also come here. No, it will not conserve the energy; that transition cannot occur for that transition to occur energy conservation will not be satisfied. So, as a consequence only the spins from the upper energy state will come to ground state, that is the lower energy state. Simultaneously lattice will gain energy and go from lower energy state to higher energy state.

This has to happen for the conservation of energy. Please remember if both spins and lattice are in the upper states, there is no conservation of energy and that type of transition simultaneously cannot happen.

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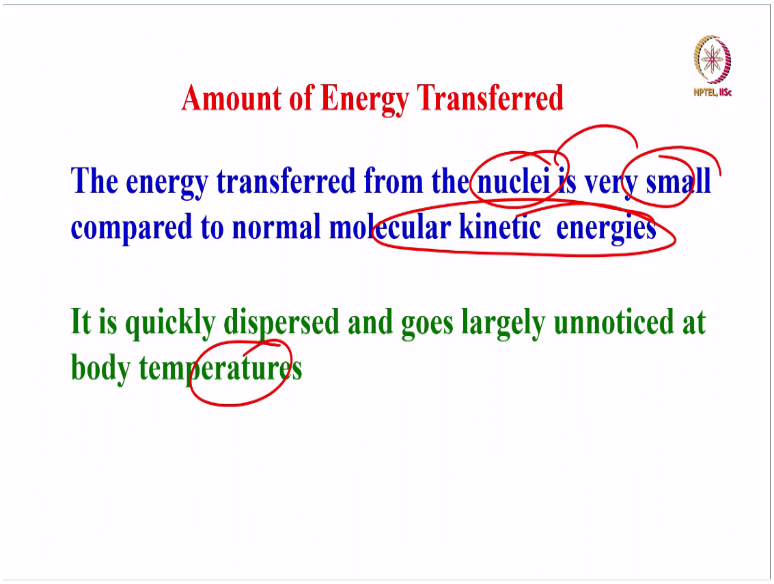

Now okay energy is transferred, I agree. How much energy is transferred to the lattice? Is it the huge amount of energy? The energy transferred to the nuclei is very small compared to molecular kinetic energy. There is always a kinetic energy of the system, where molecular motions are going on, there will be natural thermal agitation. It is much, much smaller than that.

The energy transferred from the nuclear to the lattice is much, much smaller than the kinetic energy of the system; so it quickly get dispersed. And largely goes unnoticed at the body temperatures, at the room temperature, it largely goes unnoticed to all. That means imagine a situation, it is like telling there is a big reservoir, big river, huge river is there and it is at some temperature; the reservoir water is at some temperature.

Now I am going to take a hot bucket of water; a bucket of water which is very, very hot. I will transfer, I will pour that hot water into the river. The river is so huge and this will not raise the temperature of the reservoir, that is river; this one bucket of hot water cannot increase the temperature of the entire river. Exactly similar to that, this energy quickly get dispersed among the lattice; among the surroundings and it largely get unnoticed at all. That is what happens. This is a very small energy compared to kinetic energy of this system.

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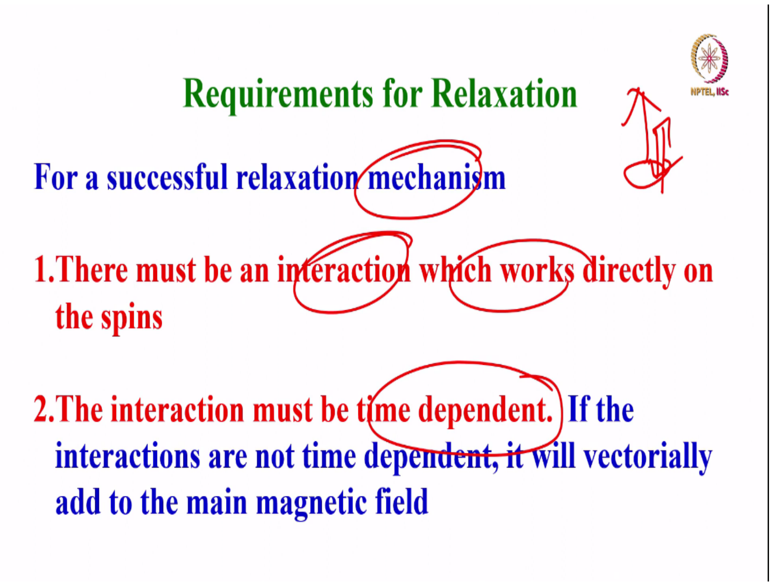

Now we can see the requirements for the relaxation. We understood spins will relax and give the energy to the lattice, the amount of energy also we know, it is very small and it quickly dispersed; and it gives energy in the form of a heat. And we also understood it is a small amount of heat compared to the kinetic energy of the system, I understand. Now when can such a situation occur? how can the spins relax? what is the way it has to transfer the heat.

There are certain requirements for it, it cannot just like that, the spins can transfer the energy to the lattice. A spin system has to successfully relax, We require the spins to relax, if spins do not relax you cannot do another experiment. The spins has to relax go back to Z axis so that again you can pulse and you can collect the signal. This is a repetitive phenomena you can keep on doing the experiments.

So, spins has to go back has to relax and attain thermal equilibrium. For such a successful relaxation mechanism there are certain requirements. One or two conditions, I will tell you. There must been interaction which works directly on the spin system, the interaction must work on the spins, that is type of interaction and secondly interaction must be time dependent it cannot be static.

If the interactions are not time dependent, what will happen it will only vectorially add to the magnetic field. The interaction should be in such a way, it should perturb the spin system. Let us say magnitude field is along this axis; with a static magnetic field it will simply add to the magnetic field or if it is opposite ,subtract to the magnetic field. It will vectoriallly add to the main magnetic field.

It does not help you. For the spins to relax the main condition is the interactions must be time dependent; and not only that it should work directly on the spin system. These are the two important conditions for a successful relaxation mechanism.

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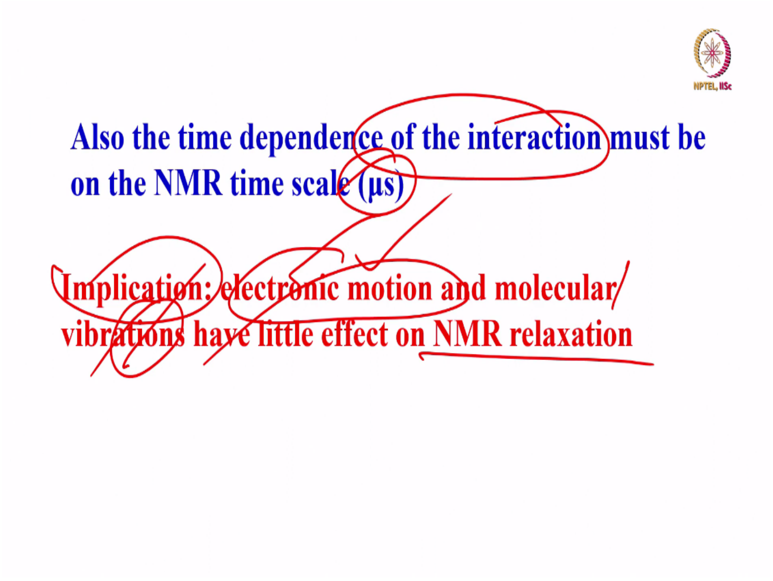

And what is this time dependent interaction, what is the interaction time. See you can talk in terms of microsecond, millisecond like that. It should be NMR time scale, remember NMR time scale is microseconds. So it should be of that order; the interaction between the spins and the surroundings must be of the order of microsecond, at the NMR timescale. If the interaction takes place, let us say for seconds or much shorter than that or much larger than that, it will not perturb the spin system.

It must be in the NMR time scale. The interaction has to be in the NMR time scale. The implication now, what do we understand from that? You consider there are various motion present in the molecule. There could be an electronic motion, there could be vibrational motion, all those things. In addition to thermal motion, like agitation, like random fluctuations everything would be there. But important thing is you should know electronic motion and molecular vibrations do not affect NMR relaxation.

They have very, very little effect on the NMR relaxation. These things contribute negligibly or almost nothing it contributes as far as the relaxation of the nuclear spins are concerned. For NMR relaxation electronic motions and molecular vibrations have little affect.

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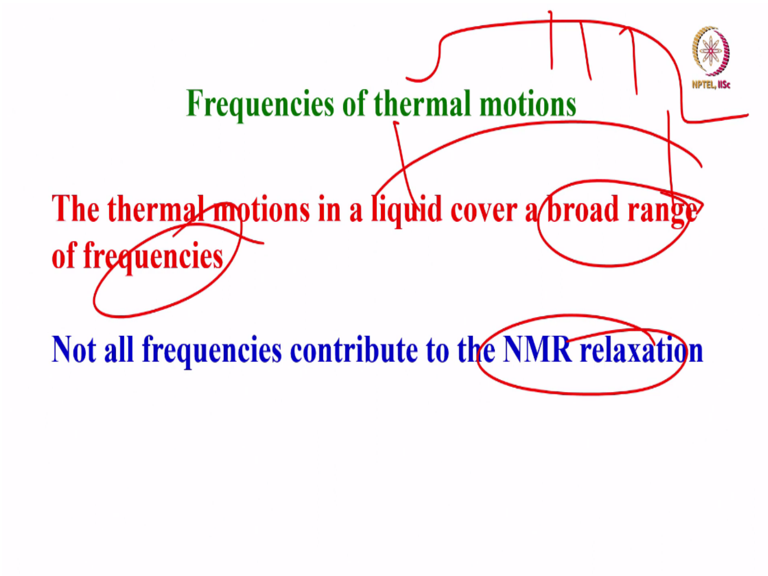

Then what is that which is required? what are the thermal motions that are required? The frequencies of the thermal motions should be of the order of Larmor frequency. Larmor frequency at which the spins resonate. The interaction frequency, the energy of interaction should be of that order, it should be thermal motional frequency should cover the broad range of frequencies so that it will contribute to NMR spins relaxations.

It should cover broad range, not one monochromatic frequency or single frequency. It should have a wide range of frequencies. If we consider such wide range of frequencies, several thermal motions you can think of in a liquid, where you can have not one frequency, but over a wide range of frequency. Then it can induce relaxation. It can contribute to NMR spin relaxation. But of course, when I take the wide range of frequencies like this so many frequencies are there in this broad frequency band. Not all of them will contribute; only certain frequencies which matches will contribute for NMR spin relaxation.

The frequency of these should match for the energy separation of the nuclear spins, such that interaction energy should aid the relaxation; that should be of that order. So, all frequencies in the broad range will not aid in the relaxation phenomena. Please remember thermal motions are required in the liquids there are thermal motion which cover broad range of frequencies only selected few frequencies add in the NMR relaxation.

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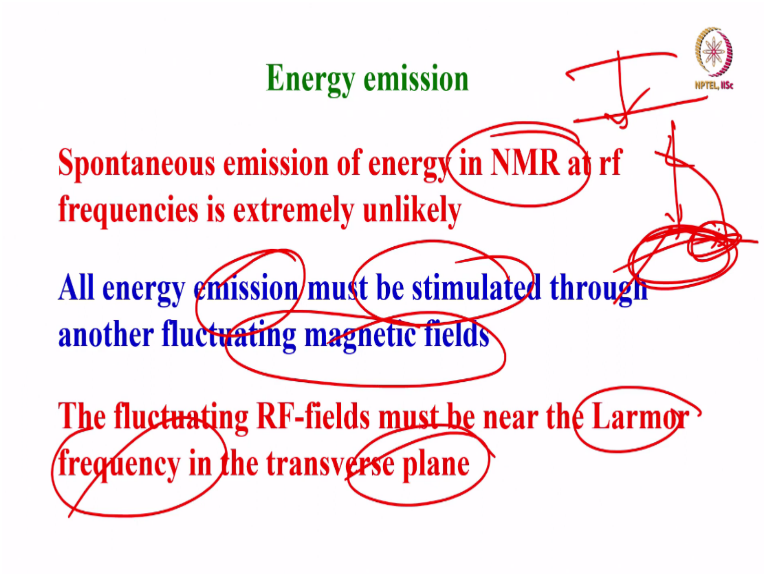

So, now we will talk about the energy emission; How does the energy emission takes place and everything. Of course, as we already discussed with energy levels, the spins in the upper energy state comes to the lower energy state simultaneously lattice ow from lower energy state to higher state, that is what we discussed. There is no doubt about it.

But how does the spins which are in upper state will come to ground state? who will induce the transition? can there be a spontaneous emission of energy? can the spins in the excited state spontaneously come down to the lower energy state? A spontaneous emission in the NMR frequency range is quite unlikely. In the radio frequency range spontaneous emission is very unlikely because it goes by the cube of frequencies, so it is not possible.

So, any transition, any energy emission of the spin system between two energy states; from upper to a lower energy state; if the spins have to come down while emitting energy, it must be stimulated through other fluctuating magnetic fields. So, the stimulation comes by another fluctuating magnetic field. Please remember that, all the energy emissions in NMR must be stimulated.

Spontaneous emission of energy is very unlikely. And the stimulation comes by other fluctuating magnetic fields. So, this fluctuating magnetic field must be generated. When the fluctuating magnetic fields are generated that will stimulate emission of energy. Please understand the concept, now slowly I am moving step by step. We understood the energy emission is there and energy emission is from spin system to lattice.

But the reason for emission is not spontaneous and it has to be stimulated; the stimulated emission comes because of the fluctuating magnetic fields at the site of the nucleus; that is another thing. The fluctuating RF field again must be at the Larmor frequency, in the transverse plane, because spins are already in this transverse plane. If those spins have to give energy to the lattice and go back to Z axis ; it must be at the Larmor frequency.

Only then the interaction of fluctuating RF fields, that is generated, if they are at the Larmor frequency in the traverse plane, then spins will stimulate these spins to emit radiation. The fluctuating field that is generated in the transverse plane must be in the Larmor frequency range. This is important point one should remember this.

Now you ask me okay there is a fluctuating field, that is there, that is a source for stimulated emission; this fluctuating fields that is generated in the transverse plane at the site of nucleus, But how do these fluctuating fields are generate? that is the next question. You understand the concept, spins require fluctuating magnetic fields at the Larmor frequency in the transverse plane for emission of the energy, to interact with the spins, so that spins can lose energy and a stimulated emission can takes place, and give its energy to the lattice.

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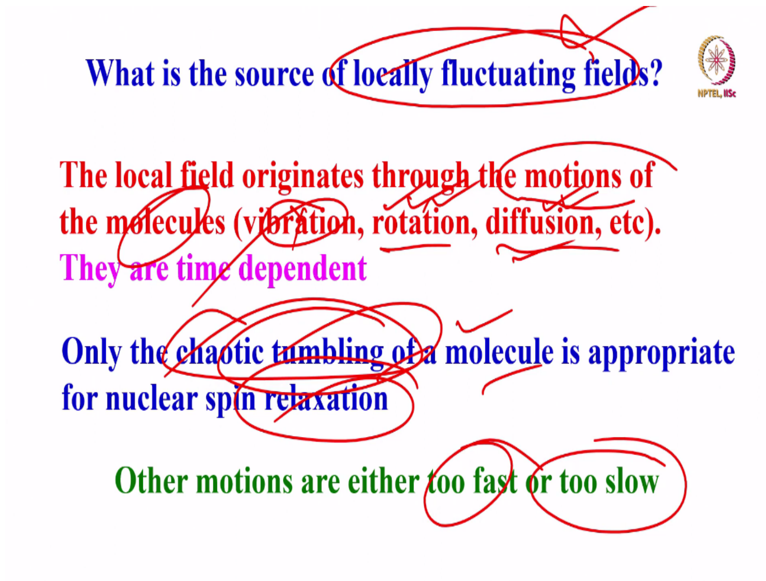

But the question is what is source of this fluctuating magnetic fields in the transverse plane? something there must be some phenomena which generates this fluctuating fields. And these fluctuating fields originates because of motions of the molecules. These motions I said I told you this has least effect, and it comes because of rotation, diffusion, molecule this you can ignore. There are various types of motions, but mostly the rotation motion of the molecule, diffusion and some thermal agitation, random fluctuations, these all are responsible for that. Remember the sources of the local magnetic field originates because of motions of the molecules, because of rotation, diffusion and random motions. All those things are responsible and they must be time dependent.

It cannot be all the time same rotational frequency, and same diffusion frequency. Molecules could be continuously undergoing diffusion or continuous rotation and it keeps on changing. It should be time dependent field; that is important. If that happens then the local fluctuating fields at the Larmor frequency responsible for stimulated emission of the energy takes place; you got the point now.

This stimulated emission comes because of the fluctuating magnetic fields generated in the transverse plane at the Larmor frequency. And the source of the fluctuating magnetic fields are the motions of the molecules; especially rotational motion, molecular caotic motions or diffusion or some random fluctuations. All these are necessary, there could be many; all are responsible for the spins to create local magnetic field.

And all of them are time dependent; very important. I told you already if they are not time dependent it will vectorially add to the main magnetic field, that does not help us. So, now only the chaotic tumbling motions of the molecules are appropriate for spin relaxation. Varieties of motions are there molecular motions, but please remember chaotic tumbling motions of the molecules is appropriate for spin relaxation, nuclear spin relaxation; because that can generate fluctuating fields at the Larmor frequency.

The chaotic tumbling motion, random motion, random fluctuating motion of the molecules create a fluctuating field that is appropriate for nuclear spin relaxation. Please remember that one. Various molecular motions are there, especially this chaotic tumbling motion is important. Other motions could be present like vibration or electronic transition, etcetera they are either too fast or too slow and it will not contribute for the relaxation, you get the point now. Fluctuating molecular motions is the source of fluctuating magnetic fields, we understood how it gets generated.

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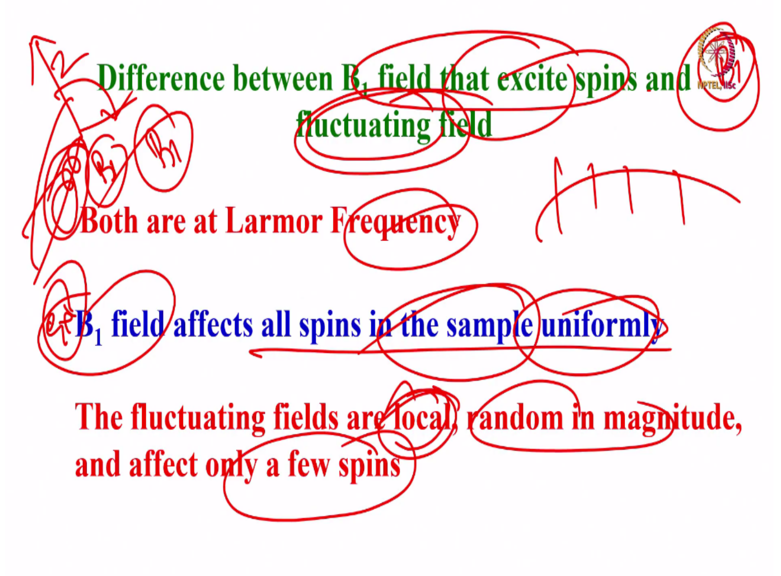

Now very interesting question will come. So far, I was telling you we have generated a fluctuating magnetic fields at the Larmor frequency, that must be B1 field. Simulative or RF field which you apply externally to till the thermal magnetization, which is a thermal equilibrium to the X Y plane is a B1 field. That is also at Larmor frequency. Remember I told you, see there is alignment of the magnetization in thermal equilibrium along the Z axis.

It is an equilibrium magnetization, is perfectly aligned, there is no motion. Now what I am going to do is, I will send a RF pulse in a direction perpendicular to it and then bring the magnetization to another axis; and this RF we are going to apply, B1 field, is at the Larmor frequency. That we have been discussing in the very first class. But now also I tell you the fluctuating magnetic fields that is generated in the transverse plane because of the random chaotic tumbling motion of the molecules is also B1, that also at Larmor frequency.

Now we have two interesting situations we have got. External field applied at Larmor frequency and the fluctuating magnetic field generated in the transverse plane B1 is also at Larmor frequency. Then what is the difference? That is the next question; both are at Larmor frequency, but the difference is one thing you should know the B1 field, external B1 field I should say, affects all the spins uniformly.

It excites the spins in the sample, uniformly it excites. For example there are so many spins are there, so many transitions frequencies are present in a system. If you analyze the spectrum there may be so many frequencies present, but then all the spins are uniformly excited. It affects all the spins and then collect the FID and do a Fourier transformation. So, the B1 field RF field which applied externally affects all the spins uniformly in the sample; whereas the fluctuating fields are local, random in magnitude and affects only few spins. Very important thing.

See that is the important point. If there are several nuclear spins in a molecule, take a structure of a molecule; different protons are there in different chemical environment, but as you go ahead we will see that, different spins will have a different relaxation time T1. That is because spins will relax differently, and then as a consequence for them to relax, the random fluctuating fields are also not same, they are different.

The magnetic field generated locally at the site of different spins are different, so it does not affect all the spins uniformly, it affects only few spins; this is the main difference. If external RF affects all the spins uniformly, whereas the fluctuating magnetic field generated in a transverse plane also at Larmor frequency affects only a few spins. This is the main difference.

So, now the time is up we will come back and understand much about these things. So, I am going to stop here, but please remember one thing what I was telling you today we were discussing about the relaxation phenomenon especially the spin lattice relaxation I discussed with you and told you what is lattice, this lattice is not like a crystal lattice, not a rigid system. In the solution state anything other than the spins of your observation is called a lattice.

Any surrounding spins of interest is called a lattice and then energy of the spins will give energy to the lattice; the way it gives energy is in the form of heat, extremely small amount of energy less than the kinetic energy and quickly get dispersed at the body temperature. Its effect is less noticeable, not even noticeable, I told you. I gave you an example of a big river or a big ocean put one bucket of hot water to the ocean, the temperature will not rise it may rise by one-tenth of milli degree or micro degrees; very small effect, it is not going to be felt at all.

Similarly the energy which is going to be lost by the spin system to the lattice is largely goes unnoticed and quickly dispersed in the lattice system; that is what is going to happen. And then we also understood for efficient relaxation phenomena we require a fluctuating magnetic fields. It is a stimulated emission, the stimulated emission happens because of the fluctuating magnetic field, this is generated by to chaotic tumbling motions of the nuclear spins, or system. Common motions like electronic or vibrational have least affect on the spontaneous emission. The spontaneous emission is not possible here, only stimulate emission. So, the chaotic motion should be time dependent, which is at the Larmor frequency in the transverse plane affects the spins. Then only the spins will lose energy, that is the stimulated. Actually these are the things which cause random fluctuating fields, causes spin to lose energy and we saw the difference between the random fluctuating field and external RF field both at the Larmor frequency.

But the external RF field will affect all the spins uniformly, whereas the fluctuating magnetic field in the transverse plane affect only few spins. And different spins will be affected with different fluctuating fields. So, with this I will stop here, we will come back in the next class and then continue further and understand more about the concepts of this T1 relaxation and also T2 relaxation. Thank you