Physics of Functional Materials and Devices
Prof. Amreesh Chandra
Department of Physics
Indian Institute of Technology Kharagpur

Lecture – 19, Week 5
Phase and phase transitions

Welcome back to the course on physics of functional materials and devices. This is the second lecture of week 5. Let us continue our discussion on materials and how do they change their properties as we move from one thermodynamical parameter condition to the other. What do I mean by that? I mean as you change the value of the thermodynamical parameter which you are considering, be it be temperature, be it be pressure, be it be volume or be it be entropy, what happens to the properties of the materials? Do they remain same or do they change? And if they change, what are the reasons why these changes are observed and what this change is called? So, in today's lecture what we will do? We will start our discussion from phase and phase transitions and you will find that these transitions are linked to the change in thermodynamical parameters. And there are various types of phase transitions. So, if there are various types of phase transitions, what you need to do? You need to classify a group of similar type of phase transitions in one heading or under one heading and that would lead to various types or classifications of phase transitions.

Two major classification strategies which we will discuss today would be on Erenfest or Baeuger classifications of phase transitions. Then we will understand the kinetics of phase transitions. What are the driving forces for these phase transitions to actually take place and what are the consequences? What have we seen till now? We have seen that there are materials which can be synthesized. So, you can have various types of materials which you can synthesize.

So, these materials can be synthesized. Their properties can be tuned. And how are you going to change the properties? You are going to change these properties by changing the structure or any of the thermodynamical parameters. And you can then move from one distinct form of the material to the other without changing its chemical formula. For example, if you have a tetragonal phase of $\mathbf{ABO_3}$ structure, this is what we had discussed in the previous lecture.

If you have a tetragonal phase of an $\mathbf{ABO_3}$ structure, you can move from a tetragonal phase to a cubic phase of an ABO_3 structure. The chemical unit or the molecular formula remains the same. It is only the crystal structure which changes. You can go, for example, from tetragonal p4mm space group to a cubic like unit cell with pm3m space group. So, there is a rearrangement of atomic positions.

So, you can see that rearrangement of atomic positions can lead to changes in the physio chemical properties of these materials. So, till now we have seen that transformations occur when there are changes in the structure of the materials. The structure modifications can occur as a function of composition or as a function of particle size or grain size or as a function of the unit cell which is being obtained after a certain temperature range. So, composition change, what do we mean by composition change? For example, barium titanate is a well known ABO_3 structure. It is a well known **ABO_3** perovskite.

Suppose you use a dopant to modify this material. For example, you say you have $Ba_{1-x}Sr_xTiO_3$, where x can be 0 or it can be 1 or it can take any value between 0 and 1. So, x defines the composition. For example, if x is equal to 0.5, then what it will mean? It would mean that you have barium 0.5, strontium 0.5, **TiO_3,** but the addition of the concentration of barium and strontium will still give you 1. So, certain Wyckoff positions in the unit cell are going to be occupied by the barium atoms and the rest would be occupied by the strontium atom, but the overall unit cell would still remain an **ABO_3** type structure where the A sites are being occupied by the combination of barium and strontium atoms. That is what is meant by compositional changes. You have seen that as you move from one synthesis route to the other, you can get different types of particle sizes.

You can have materials which have particle size of 1 micron or you can go to as low as 10 nanometers or 1 nanometer. You can go to nanomaterials of the same material. So, nano size of the same material. You can have nanoparticles of barium titanate or you can have the bulk particles of barium titanate. So, as you move from larger size particles to smaller size particles, the properties change and that is what is meant by change in the particle size or grain sizes.

And as you move from one crystal structure to the other, then also you see modifications. As I said, the structural changes occur as a result of rearrangement of atoms in the material. This can happen as a function of chemical reactions or you can induce some phase transformation. You move from one phase to the other or you can induce changes or rearrangement of atoms by diffusion. Diffusion means migration of certain entities from the region of higher concentration to lower concentration.

So, you move from one region to the other and the overall arrangement within the lattice or the material changes and hence you will see certain modification in the properties. Let us understand the phase transformations which we are talking about. Many a times it is difficult to explain the term phase. If you want to have a broad definition of phase, phase is defined as state of matter that is uniform throughout in the chemical composition and physical state. What do we mean? Phase means you are talking about a state of matter which is chemically homogeneous, physically distinct and mechanically separable.

Means, the chemical composition throughout that material would remain the same. That is, if you have the building block of, let us take the same example of barium type net, the building block is what? Is an $\mathbf{ABO_3}$ unit cell that is the molecular formula. So, wherever you go from one place in the material to the other, to the third, to the fourth and you travel along the whole material, you will find that the chemical composition will still define that the building blocks are remaining as $\mathbf{ABO_3}$ that is barium, titanium and oxygen. That is what is meant by chemical composition. So, throughout you will have the same chemical composition.

Physically distinct means, if you have the arrangements where the atoms are placed in a way that they form a unit cell which is tetragonal and then you form a unit cell which is forming a cubic. So, you can distinguish between the two sets of unit cell quite clearly that defines the physically distinct state for the material. And if you have the capacities, then you can always differentiate or separate out particles of different sizes and that will give you the term mechanically separable. So, either you can define phase as a state which is chemically homogeneous, physically distinct and mechanically separable or you can define a phase of a substance in the form of a matter that is uniform throughout in chemical composition and physical state. The most common which we have been seeing is the solid, liquid and gaseous phases.

Let us also see and talk about some other phases which also exist. It is not always solid, liquid and gas. You have plasma phase. What is this phase? This is a phase where a gas is completely or partially ionized. Because of this ionization, you have strong electrical interactions between the adjacent charged particles and this is more prominent in dense plasmas which means that there would be strong electrical fields.

The particle motion in these plasma gives rise to currents and results in magnetic fields. And examples of natural plasma include sun, lightning or even neon lights. There are other types of phases which can occur. That for example, a magnetic phase. What is a magnetic phase? As the name suggests, this would be a phase where the magnetic moments of the atoms or molecules that are forming the material are aligned in a particular direction.

So, you have heard about ferromagnetism, ferrimagnetism, antiferromagnetism, paramagnetism. So, you have different forms or phase of magnetic state or alignment of atoms in these magnetic materials. For example, you can have ferromagnetism in iron or you can have ferrimagnetism in magnetite. Similarly, you can also now define quantum phase. This is a phase where quantum states of particles in a system are correlated in a particular way.

There are various examples. For example, Bose Einstein kernel state. What is that? It is a state of matter that occurs at very low temperatures. Or you can talk about superconducting states where materials lose all of their electrical resistance. And then you can also go and talk about quantum phase transitions.

So, let us start with phase transition. A phase transition is what? It is a spontaneous conversion of one phase into the other. It occurs at a characteristic temperature for a given pressure or it can also occur at a given pressure for fixed temperature. So, you can change either temperature or pressure while keeping the other fixed and you will see certain phase transition. Why I am talking about temperature and pressure? Because these are the two thermodynamical parameters which are routinely changed to observe phase transformation in the functional materials which we are talking in this course.

Associated with the term phase transition, there are certain terminologies which you will hear routinely. The first one is the phase diagram. The phase diagram basically defines the regions of pressure and temperature at which its various phases are thermodynamically stable. And the second term is phase boundary. It is the line separating the regions particularly showing the values of p and t at which the two phases coexist in an equilibrium.

Let us take a simple example of the phase diagram of water. So, this is the y-axis showing pressure and temperature axis in the x. So, you will find that there are regions in which water will form solid like structures, then you have a liquid phase and then you have a vapor phase. So, if you have pressure for example, below p1 and temperature between t3 and t0. So, which phase of water will you get? You will get a vapor phase of water.

Similarly, if you have pressure which is more than p1 and temperature which is less than t3. So, somewhere in this region what will you get? You will get a solid phase. So, that is what we mean and these are the solid lines are defining the phase boundaries. And at the phase boundaries the two phases coexist. But you will see that in the phase diagram of water there is a point where all the three phases can exist and they are in equilibrium that is called the triple point.

So, this is what is now mentioned in text and you will see what we have seen we have discussed about the melting curve, the vaporization curve. But please remember what are we emphasizing by this discussion? You will stabilize in a phase where the Gibbs free energy would be lower than the phases where the material is not going into. So, the basic criteria that you will stabilize in a phase in a phase that would give you the minimum Gibbs free energy. You can clearly see that phase transformations can occur by varying pressure and temperature conditions and you can move from one phase to the other. Some other important terms of course, transition temperature is the first amongst them.

This would be the temperature at which two phases are in equilibrium and the Gibbs energy is minimized at constant pressure. So, you will see there is a triple point is the transition temperature where all the three phases of water are in equilibrium. So, you have a transition temperature which should be well understood. Then you have a critical temperature. This is the point where the vaporization curve and the melting curve meet.

This is called the critical point. Above this, water can only exist as a super critical fluid. So, beyond the critical point what you will see? You will find that water will only exist as a super critical fluid. So, $\mathbf{T_0}$ is the critical temperature for water which was shown in the previous curve. So, what happens to the thermodynamical parameters which we introduced in the previous lecture whenever there is a phase transformation? What happens to enthalpy? The enthalpy of the system changes during a phase transformation. Why? Because you can either absorb energy or release energy as you move from one phase to the other.

What will happen to entropy? Entropy can also change during a phase transition. Why? Because you are changing the randomness or disorder of the system. As you go from one atomic arrangement to the other, what have you changed? You have changed the disorder of the system and obviously the entropy would change near the phase transformation temperature. What happens to pressure and volume? When you move from one phase to the other, you cross a transition temperature. The pressure and volume of this material which is transforming from one phase to the other can also change and this would be due to the different densities and compressibility of different phases.

For example, the volume of water increases when it freezes into ice because the solid phase is less dense than the liquid phase. What is happening to the temperature? During a phase transformation, please remember the temperature of the system remains constant. Why? Because the heat energy is absorbed or released. So, absorbed or released without a change in temperature. This is because energy is being used to change the state of the substance rather than increase its temperature.

So, if you have for example, the same arrangement of atoms, a cubic arrangement and then you move to a unit cell clearly which has a tetragonal type arrangement. So, you are moving from C to T as a function of temperature. Now, this transformation or rearrangement in atoms or displacement of atoms from the earlier mean position would happen because of what? Because you are giving temperature to the system, this is being absorbed by the atoms and as they vibrate, they need to occupy a new location, so that they can again minimize their Gibbs free energy. So, the temperature absorbed and drives this movement of atom from the earlier mean position to a new mean position. So, there would be no increase in temperature because that energy is being absorbed by the material to undergo this transformation from one mean position to the other.

Classification of phase transitions are basically based on two broad mechanisms; one was given by Ehrenfest and the other by Baeuger. Let us start with Erenfest classification of phase transitions. And what we have seen? We have seen that there are various types of phase transitions. We have talked about solid to solid, we have talked about conducting to superconducting or there would be slightly more uncommon, but routinely observed is fluid to super fluid transitions, but what you are seeing is that the whole concept is based on the minimization of Gibbs free energy. So, let us consider that you transform from phase A to phase B.

So, you transform from phase A to phase B. What are we saying? We are saying that you have change in Gibbs free energy when you move from phase A to phase B. So, delta G B by delta P at a given temperature and minus delta G A by delta P at the same temperature is basically what? Change in the volume in the two phases. So, v B minus v A that is the change in the volume near the transition. Similarly, you can write about the entropy, you will get delta S transition.

These are non-zero for melting and vaporization. It follows that for such transitions, the slopes of Gibbs energy plotted against either pressure or temperature are different on either sides of the transition temperature or pressure. So, in other words, the first derivative of the chemical potentials we have seen in the previous lecture, what are the chemical potentials? The enthalpy, the Gibbs free energy, the Helmholtz energy. We have seen that these chemical potentials with respect to pressure or temperature will show a discontinuous change near the transition. So, the first derivative of the chemical potential with respect to temperature or pressure will show a discontinuous change near the transition temperature. Based on these postulates, you have the order of phase transitions.

So, you have first order phase transitions. It means a transition for which the first derivative of the Gibbs energy with respect to temperature is discontinuous. During this phase transition, the temperature of the substance remains constant until the transition is complete. Beyond that, you will see there would be increase in temperature. And we have seen why temperature will remain the same at the transition temperature because the energy is being absorbed by the material to undergo rearrangement. This temperature is called the transition temperature or melting point for a solid liquid transition or a boiling point for a liquid to gas type transition.

Examples of first order phase transitions include melting of ice, boiling of water, condensation of steam and you can have materials like perovskite materials undergoing phase transitions which are of first order. And what will happen to the corresponding thermodynamic parameters? You will see a discontinuous change in volume in the V-T diagram or you will see a discontinuous change in the entropy versus T diagram or a similar discontinuity in the entropy versus T diagram. So, you can see that there is a discontinuous change near the phase transitions. So, what is happening? V, S or H are changing by a finite amount for a infinitesimal change of temperature. So, there is nearly no change of temperature, but there is a large change in the values of volume entropy or enthalpy.

That is what is meant by first order phase transitions. So,this is clear from the three curves. Then came the second order phase transitions. For this, the first derivative of the Gibbs energy with respect to the temperature is continuous. The first derivative is now continuous, but the second derivative is discontinuous and that is defining the second order phase transitions. So, what is basically happening? You will see a change in slope near the phase transition, but it would be nearly continuous change, but you would not see a drastic or dramatic change at the phase transitions if the material is going through a second order phase transition.

So, the Gibbs energy as heat capacity becomes discontinuous, but not infinite. Infinite means much much larger from one side of the region to the other region. So, there are materials which show this kind of second order phase transitions. For example, ferromagnetic or paramagnetic state in materials like iron or transition from superfluid to normal fluid in liquid helium or transitions from normal metal to superconductors.

There are also lambda type transitions. In lambda transitions, you will get heat capacities which are changing by large amounts on either side of the temperature at which the transition is occurring. So, these kinds of transitions include order disorder transitions in alloys, onset of ferromagnetism or fluid to superfluid transition in liquid helium. So, if you see the lambda transitions, what are we meaning? We are meaning that the shape of the curve has the form of the Greek letter lambda. So, you have a lambda type transition. You can see them in alloys, you can see in materials which are transforming from ferromagnetic state to a paramagnetic state or they are going from a normal liquid to a superfluid state.

The second classification is based on Biot-Guerre classifications of phase transitions. These are based on the changes in the symmetry that occurs during the transition. So, you are now going to consider the changes in symmetry. If you have a continuous symmetry change that is type 1 type phase transition. In this type of transition, the symmetry of the crystal remains the same, but the shape of the unit cell changes.

So, the symmetry remains the same, but the shape of the unit cell changes. This type of transition is also known as Displacive transition as it involves small displacements of atoms within the crystal lattice. An example of a continuous symmetry change is the transition in quartz from its low temperature alpha form to its high temperature beta form. The second way of classifying the phase transition is the discontinuous symmetry change or type 2 kind of transitions. In this type of transition what would happen? Here the symmetry of the crystal changes abruptly with no intermediate structure between the initial and the final phase.

And these kinds of transitions are also known as order disorder transitions as it involves a rearrangement of the atoms within the crystal lattice. So, what is happening in Displacive transitions? You are having small displacements of the atoms, but in case of order disorder transitions what is happening? You are talking a rearrangement of atoms. Obviously, these are two different phenomena which are occurring. An example of discontinuous symmetry change is a transition of the mineral Pyroxene from its low temperature monoclinic form to its high temperature orthorhombic form.

Many of you would not even have heard about Pyroxene. Let me take an example of barium titanate once again because that is what I took in the previous slides. So,if you look into this material, a very well-known ferroelectric material, piezoelectric material, it is being used in solid state memories, it is being used in sensors, it is being used in electrochemical sensors, it is being used for dielectric in capacitors. So, you have a large range of application for the same material, a perfect example for a functional material. If you look into its performance or changes which occur in this material as a function of temperature, you will find that as you come from high temperature. So,let us say you come from high temperature side and then you cool down.

Then at 130 degrees, the material at high temperature had a cubic symmetry. At 130 $\circ$C, this material transforms to a tetragonal like unit cell. At 5 degrees, So, if you go from 130 to 5 and then go on cooling, So, 5 $\circ$C. What happens? This material transforms to orthorhombic. You go on cooling a material, then at approximately minus 90 $\circ$C, the material transforms to rhombohedral.

So, you can see the same material, it remains the molecular formula remains barium titanate, $BaTiO_3$. But as a function of temperature, you can see that there are significant changes in the symmetry of the material as well as the unit cell. So, you can go from cubic to tetragonal to orthorhombic to rhombohedral type materials. So, you have this kind of order disorder transitions taking place in these materials. And obviously as you go from one unit cell to the other, the properties of these materials change and hence the range of applications can be tuned depending upon the temperature regime in which you want to apply this material.

You have an intermediate symmetry change type phase transition. In this type, of transition the symmetry of the crystal changes through one or more intermediate structures before reaching the final phase. This type of transition is also known as a modulated or composite transition because it involves combination of continuous and discontinuous changes. Typical examples are in minerals, let us say muscovite where you have a low temperature monoclinic form to its high temperature hexagonal form and there is a region in between where these structures can coexist. You can have the kinetics of phase transitions where you will find the transformation is driven by the concept that is called as nucleation and it is the same concept which we discussed during the synthesis of material and why the material should actually stabilize where the volume energy overtakes the surface energy term.

So, concept remains the same. First there is a system which has well defined order but as you change the temperature there is a region within this material where a small seed will form but because of this region which is surrounded by much dominant primary phase the seed may get dissolved again in this whole surrounding but as you go on giving energy to the seed, the seed will form and stabilize at one point that is the nucleation of the second phase. As you give more energy to this nucleated side it will start to grow and there would be a point as a function of increasing or decreasing temperature where this growing seed will start overtaking the parent phase. So, what will happen? Beyond the transition temperature the material will then be dominated by the side which initially nucleated then had a growth and finally it overtook the parent phase. So, what happens? You have nucleation where a new phase or structure forms in the system where seeds or nuclei act as the template for the second phase to grow.

It involves what? So, it can involve clusters or aggregates of atoms. These will build the next structure. Once this seed is nucleated that means it is stable then growth will proceed until the equilibrium is attained. So, what will happen in this condition? The system would move from a relatively unstable state or supersaturated state to a more stable state by overcoming the barrier which is known as nucleation barrier. As you have understood by now what is the driving force to drive this nucleation process till now, we are talking about temperature. There are two types of conditions which you can encounter those can be supercooling or superheating.

Supercooling nucleation refers to the nucleation process that occurs when a liquid is cooled below is its normal freezing point without actually solidifying. In other words, it involves the formation of a solid phase from a supercooled liquid. In comparison superheating typically refers to the process of heating a substance above its boiling point without undergoing a phase transition into the gaseous phase. Examples are heating water in clean container in a microwave oven can result in super heating. So, there are two broad classifications of nuclear nucleation processes they are heterogeneous nucleation or homogeneous nucleation.

You have already seen about the homogeneous and heterogeneous nucleation during the synthesis protocols but let me quickly revise them. Heterogeneous nucleation is a process in which formation of a new phase or structure occurs at the interface between the two phases or grain boundaries. In this the presence of nucleation site or substrate provides a surface for the nucleation to occur more easily compared to the homogeneous nucleation. So, you can have cavitation processes linked to bubble formation, you can have heterogeneous catalysis metal electro deposition or superconducting conductivity where these kind of nucleations take place. In comparison what is happening in homogeneous nucleation where the new phase or structure occurs within a homogeneous or uniform material.

There is no foreign nucleation sites. So, you are not growing a material on a substrate. The growth is within a material that is the basic difference. It is typically characterized by higher energy barrier compared to a heterogeneous nucleation and these processes are quite common in polymerization, crystallization, precipitation reactions or cosmic inflations. You have seen in today's lecture that transformations can occur through chemical reactions, phase transformations or diffusion. You have also understood that during phase transformation there are changes in thermodynamical quantities or parameters.

You have been introduced with the various classifications of phase transformations and the driving force which leads to the phase to transform from A to B that is the initial to a new final phase and that what we have discussed today is temperature. But similar concepts can be extended to pressure and you will find that lot of people are working on pressure dependent phase transitions in materials and those type of materials also have large number of applications. These are the books which you can refer to for getting more details about the topics that we discussed today and I thank you once again for attending lecture 2 of week 5.