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Lecture No. # 11 Large Systems and Statistical Mechanics

Hello, welcome to this 11th lecture in this physics of materials lecture series, in the past few classes, we have develop the Drude model; and examined in what ways it is successful, in what prediction its successful, and also we have identify some of its weaknesses. Specifically, in the last class we spent a time looking at several of the values, associated the kinds of numbers, associated with the Drude model in terms of what prediction it makes, and how those numbers come about and so on.

And so every put on lot of numbers, and for example we recognize that the specifically the electronic mean square velocity, is being under predicted by a factor of 100, and the specific heat at constant volume is being over predicted by a factor of 100's. So, these are, when you come down to values these are two places to critical places, where the Drude model seems to have some difficulty giving as a prediction. So, we finished of saying that, we need to examine the kinds of assumptions that have wanted to the Drude model, the basic underlying theory that hides behind the Drude model.

To see exactly at what stage we have made a mistake or the model has made a mistake, and from their try to, and based on that finding, and based on that understanding we can than see, if there is a manner of creating refined model, so to speak. This is of course, we done in the past ages going over this process, as we rediscover this whole process, as we go through the journey again. So, this is the basic idea, and so today what we will do is, we will examine our system, the kind of system that we are dealing with, will examine at in greater detail.

Let us look at, what is the approach that would make sense for the kind of a system, what are typical ways in which such system are handled when you look at the literature, or look at the textbooks and so on. And from their, we will in fact, we were look at we will develop this general idea of statistical mechanics, so by time with done with this class, we would we will have mention this area of study, and then also at least briefly understood what it is all about, so this is what we are going to do.

We will touch upon different aspects of how were approaching this work, and what a some new answers associated with it, as we go for it through this class. So, they will all add up eventually at each add given point in time, each as an independent piece of information which eventually adds up, so you have to take it in that spirit and the follow the discussion as we go along. So, let us examiner system, and also keep in mind that will also see, how people go about handling such systems and therefore, I will start their.

Specifically, I want to draw your attention to one detail, which you will stumble upon as a look through a various textbooks, but it may not be immediately apparent to you why it is so, so I would like to take speak to take a movement to explain that you, before we get started with our discussion. So, the point I wish to make is, if you look at the kind of analysis we have done, especially say the kinetic theory of case kind of analysis, you will find there are approaches to handling these kinds of systems, which you will see in say chemistry books, you will see in metallurgy books, you will also seen physics books.

So, especially where we are you know bordering on the thermodynamics of the system, in terms of discussion; you will find that all this books have discussion to relate to large systems, so to speak. So, it may be the system may not be exactly the same, it may different systems in each case, but large system meaning a system containing huge number of particles, so that is the basic frame work of the system that, we are dealing with.

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What you will find is in a typical chemistry book or in a typical chemical engineering book, you are likely to find that, the systems are discussed, and analyzed, under conditions of constant temperature and pressure. Constant temperature, and Constant pressure, this is the kind of experimental condition, under which the systems are analyzed and discussed, in most books in chemical engineering, chemistry and so on, so this is what you will see.

If you look at books in metallurgical engineering, you will find that in fact, often again same metallurgical thermodynamics, if you look at it you will again find that the same constant temperature and pressure are used, so this is chemistry (No audio from 05:06 to 05:18) (Refer Slide Time: 05:06) and generalizing here. So, it is not that in as a face this I will highlight that, once again I am doing some bit of generalization, but generally speaking, this is what you look at.

In metallurgical engineering, you will also see the same kind of constant temperature and constant pressure (No audio from 05:32 to 05:43), but more especially the pressure will often be one atmosphere. So, not just is the pressure constant, it is constant at one atmosphere typically, this is all generalization whatever I am describing to you, I mean at there are lots of exception to this, but in general you will find this to be the case.

Now, if you come in to physics, so in physics kind of books, you will find constant temperature and constant volume in physics. So, books that are essentially trying to describe, the kinds of system that were dealing with; if they are some physics background, aimed at physics students, you will often find constant temperature, constant volume being used. If it is aimed at chemistry and chemical engineering students, often it will be constant temperature and pressure that is use; and if it is aimed at metallurgical engineering students, it will still be constant temperature and pressure typically, but over and above that constant pressure will be one atmosphere.

So, the reason for this something as is as follows, if you look at chemistry and chemical engineering, often the the discussion is based on experimental findings, and analysis of those experimental findings; and trying to create new situations, where they can some specific compounds and so on. So, for example, if they were looking at you know, if you looking at refining oil, and how you would separate the various fractions, all those kinds of discussions, are situations where you have to you have a physical system, that you actually have to directly handle, and you have to put experimental controls on it.

So, when you talk of a physical system, and you want to actually put experimental controls on it, constant temperature and constant pressure are much easier to impose on a system, from an experimental perspective. You can apply constant pressure very easily on more systems; you can generate experiment where the pressure is constant quit easily in in most cases. So, therefore, from an experimental perspective, constant pressure is is the approach to take, which makes the process convenient, so this is what is being done in most of chemistry, and chemical engineering, so that is the that is why this is being process.

In metallurgical engineering, you are often talking of solid metals, you are talking of liquid melts and so on, and that is typically open to open to some atmosphere in fact, if you talking of solid object, it may be even open to air, so to speak. So, at that point in time, in the general pressure that the system is spacing is one atmosphere, so we we looking at large melts and so on, so it becomes it difficult to pressurize the system. So, therefore, the it is just left to phase the atmospheric pressure, so that is the general situation.

So, again it is an experimental system, in the sense that there is a physical system, you can actually see the system, you can see what is going on in the process, subject to some you know some safety requirements, but basically you can see the process, it is

something that is physical occurring. And therefore, an experimental limitation is what is being reflected, in the form of the temperature and pressure, being chosen as the parameters that you will hold constant for the system, as you try to study the system, so that this what is being that.

And in the metallurgical systems sense the since, it is typically handling looking up or facing at one atmosphere pressure from from a natural atmosphere around us; you end up finding one atmosphere, it could be like this. In fact, there are diagrams, where the assumption is already one atmosphere, so many many of the phase diagrams that you will see, associated with metallurgical engineering systems; you will only see temperature and composition, in that phase diagram, in most often.

You can generated other other conditions also, but typically you will see temperature verses composition, and the assumption is that the or it will be stated somewhere of course, that the diagram has been made at one atmosphere. So, you could have done it some other pressure, if you had wanted to, but in general it is going to be done at one atmosphere. So, large amount of the data base, that you will come across in metallurgical engineering will be temperature constant temperature, constant pressure as with pressure being one atmosphere.

So, that leads us with the physics approach, so our question therefore, **is** if all of these people to ten to stick to constant temperature and constant pressure, why would the physicist choose constant temperature, constant volume instead. So, by the way in all this discussion, the underlying idea is that, when you when you try to steady the system, certain number of parameters, you have to hold constant and within that frame work is where you steady the system. So, only then the system reaches equilibrium, and you are able to steady that system.

So, and in generally it turns out that you need to hold at least two parameters constants, so this is why it is temperature and pressure, and in this case it is temperature and volume. The reason is in in the typical physics book physic book typically that you take, the discussion is about theoretical frame work, for the process that you are dealing with, so theoretical frame work for the concept that you are dealing with, for the process that you are trying to a describe and so on.

So, now, for theoretical understanding or to develop a module or to develop equation for the system, it is very important to know, what the energy levels available in the system. So, that becomes a very important consideration, you should be able to say clearly that these are the energy level that is available within the system. Once you know the energy levels, then you can do further theoretical calculations, and theoretical consideration can put into place, to see how those systems how those energy levels are felt and therefore, say something about the system.

So, it is very fundamental that you should know, what are the energy levels you should be able to say that, what happens which is something we will get back to much later in our course, several classes down the line, we will we will look at it in greater detail. But, the basic idea is that, when we have constant volume system, when the volume is constant the energy levels have identifiable. So, it is if the volume where not constant, if the volume change from from movement to movement, the energy levels also keep changing, the allowed energy levels keep changing.

So, therefore, from if you want to develop a theoretical frame work or theoretical understanding of the system, order of develop a theory for the system, constant volume becomes very important; because, a constant volume ensures that your understand, what are they energy levels within the system. And once you understand that you can then go about filling it up in various ways, and then saying something about the system.

Therefore, from theoretical perspective, when you want make calculations that reflect the theory behind how the system is working, you end up having to choose constant temperature and constant volume, as the defining characteristic of the system, within which you are actually developing the frame work. So, so therefore, this is the difference you see between the kind of information, and discussion that you will see in books, in chemistry, chemical engineering, metallurgical engineering and then physics.

Now, just two more comments I will add on this before we proceed, the first thing the most important thing I would saying at this stage is that, this does not mean there talking of something totally different, it is not, so we are actually looking at a system, which shows it is the to described it something like this. You have some kind of surface, which contains all the properties of the system reflected in some kind of surface, we are just looking at if a looking at it from the perspective of chemical engineering or chemistry or

metallurgical engineering, you are looking at one point term the surface. You are if a looking at it from the physics perspective of constant volume, we are looking at an other point on the on that same surface.

But, you still describing the same surface, that is the way it looks at it, you are still describing the same system, the same surface you are just looking at it from two different perspectives. So, the finals the final set of things that you will say about the system, should end up being the same; it is as simple as you know looking a mountain from one side or from another side, that is it; it is a same mountain, so you are going to say the same thing about the same mountain. So, or you may give some you understanding to the mountain principally, there is no disputing the fact that you are talking of the same thing.

So, therefore, theses to approaches, even though there is using different variables and holding them, putting constrain on different variables, they are essentially talking of the same system, and they will end up giving use a same description. I mean the end of the day your final results or not going to be diametrically opposite or different in any fundamental sense, because that they have chosen this. So, so that is that is the thing that I want to high light, also the second thing which I want highlight, which I also just mention little while earlier, but I will state it again here.

What I have told you our generalizations, so there are exception, so **I** there is no reason to give that what I have sided is exactly the way, you will always see it in every book that you take up. Largely this is true, this is largely true and the reasons have given you are basically reasons like this is the case, there are going to be exception, but that is how it is, so this is what it is. So, right now our discussions are on the physics of the material, and as we as you already experienced from a previous classes, our initiatives to develop theoretical understanding of the system right.

So, therefore, our discussion tends to have the same constant temperature, constant volume as the defining frame work, these are the constraints of placed on the system, and within the extent of the constraints, we describe the system, fine. So, we will leave this I leave this thought with you for the movement, I just wanted a bring it up now because, as we proceed into some of the other discussions, this is some were hidden in that discussion. It is not a stated of front at every stage in that discussion, this is hidden somewhere in the discussion, much later in one of the later classes, it is like an stand out.

But, I just want it highlight it now, so that at least you aware, why that this is there somewhere in the, are rather than being surprised pried the later stage, so this is there in the background, that it is constant approach constant module, so I will leave it here, we will come back to this at a little later stage. Now, we will come back to discussing are immediate topic, so to speak which of course, is that the Drude module succeed in some places, in failed in some places.

So, we will look at some of the parameters that are associated with the kind of system, we are dealing with and then, in that process we will try to go forward, and see what is that detail that we are interested in identify.

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The first thing is that the system that we are dealing with is a very large system, so we have gone through this calculation repeatedly, just to give you an idea 1 meter cube of a material is going to have about 10 power 28 atoms or free electrons per unit volume. So, 10 power 28 atoms of 10 power 28 free electrons per unit volume, is what 1 meter cube of the system has of this is very large number. So, this is I mean it is immediately apparent it is a large number, but many case it will become much more apparent you, as we proceed through the class, that it is a very large number.

As it is it is clear that it is a large number, but relative to what is a question, so which is what we will look at, so the first thing is we deal with large system with the large system and we are trying to say something we are trying to say something about this large system, we want to get some feel for what is this large system doing, how will it respond and different circumstances, so this is the main sort of issue here, that it is a large system. The other thing is we are our discussion especially, when we spoke about the Drude module, and a did various of calculations, our discussions at some point revolve around energy (No audio from 18:30 to 18:42) or discussion revolve surround energy associated with the system.

And how that energy behaves, I mean in other words when we talk of specifically therefore, how is that what is happening, when you try to raise the energy or lower the energy and so on. So, should there are two thing, again to immediately link up to what we just is discussed, please not that we are top of energy, so immediately this need for that constant volume gets linked up here, so with what our we discussed. But, we will see it most specifically little later, as as as a concept this is varied is getting linked up, that we have energy associated with the system as are primary consideration plus that it is a theoretical calculation, those are the two things that we look at.

So, we want no energy associated with the system, and that is the case for a very large system, so what we want to see is that, what we want what we want to understand of this situation where that were dealing with, is that when you look at an energy associated with the system, ultimately it is the energy, when you in our take a system in heated or put it some term; even let us say it is an room temperature. Now, the idea that it is are that temperature is something that is that convey is the fact, that all the constitute of that material actually, have that energy or an average have that energy.

The average energy associated with the all the constituents of the system, the that is held there will be the same that will correspond to this temperature of that system, at that large energy of that large system, so this is what we are looking at. So, now, when you look at a large system, and you want say something associated with the energy of the system, what should immediately standout as a concern or as an issue, is that it is not possible for us, it is not physically feasible for us, to actually know the exact correct information about each of those 10 power 28 atoms or 10 power 28 electrons.

It is simply not physically feasible, for us to identify all the details of the 10 power 28 atoms, and then on the basis of all the details we just some them up, if necessary or you take the average of them if necessary and so on; so that is physically not possible. So, we

need an approach (No audio from 20:57 to 21:51), so we need an approach that enables has to make statements about the system as a whole, without knowing every single detail of the system. So, that is the basic problem that were dealing with or the challenge that were dealing with, we need to have an approach that enables as to make some overall statements about the system, which are correct and consistent about that system.

But, that approach should not require us to know every single detail of every one of those 10 power 28 atoms. So, as this as the system unfolds, it should automatically give us the averages that we are looking at, the average behavior of the system should begin to stand out.

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So, this general approach that we are looking at is what is referring to as statistical mechanics (No audio from: 22:38 to 22:49), so this general approach that were looking at which will give us some overall idea of the system, without requiring us to have all the intricate details of every single particle that present with a system; that overall approach is refer to us statistical mechanics. So, what we will do in the rest to the class is, I will lead you from a very small system forward, and then let see if the understanding of a very small system or a few very small systems.

We look at two other three very small system, will see if that understanding from those two or three small systems, gives us some indication of where we can had with the very large system. And what kind of generalization we can pull together for a very large system, and that generalization that we can pull together is this statistical mechanics is this field of statistical mechanics, so that is what we will do. So, what we will do is, we will look at for this purpose in thermodynamics, they talk of what is called a macro state and a microstate, so let say we have constant temperature, constant volume and total energy is fixed at some value, which I will call say 3 E.

So, 3 E is the total energy I am just arbitrarily putting this number down, so that we can run through an example, so 3 E is the total energy of the system, and you have it is a constant temperature, constant volume and total energy is fixed. So, we will look at 3 examples of small systems, which could be placed under these constraints, and we will say we will see what is what the general statement is, we can make about such systems.

So, let me just say that, let say that the system because, it as constant volume and as I said we will discuss that later, because it as constant volume it as fixed energy levels is is a statement will just arbitrary make for the moment. And we will say the those energy levels are 0 E 2 E and 3 E, so these are energy levels, so this is energy so this is energy. So, these are energy levels that are available in the system, because it is a because of the constants that have been placed on the system; we will look at three possible small system and see how they can handle these constraints.

The constant volume and temperature have already resulted in the total energy, and the energy levels and total energy value is 3 E, so all this constraints are now placed here, we will look at a possibility that the system consist of just two particles, let say it has 3 particles, and we will look at case where it as four particles. So, will look just three possible cases, two particles, three particles and four particles being present in the system, and these are the energy levels available to that system fine.

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So, let us look at this lets take to two particles will put this energy levels back here, so this is 0, E, 2 E, 3 E, incidentally I also want to draw your attention to one additional detail here, the fact that it is constant temperature, constant volume and the total energy is 3 E that combination is referred to as a macro state for the system. So, that combination that overall combination for the system is that macro state, now we can arrange these two particles, let say we are now only going to discuss two particles; the two particles can be arrange in various different ways within this energy levels, to be consistent with this overall macro state.

Each way in which you can arrange those two particles, becomes called a, gives to be called as a microstate, so we will what I am going to put down there, will be two different microstate, which are consistent with the same macro state. So, for example, we have two particles, and we know that we need a total energy of 3 E, so what a what are the options one option is, you have a particle at 3 E and the other particle sitting at 0, this is one option available to you, so this is particle, so these are the particles.

So, this is at one is at 0, one is at 3 E, the other possibility is that one particles it say 2 E, and the other particles it is at E, so this is one possibility. So, this would become considered as a one microstate, where you have one particles setting at 3 E, one particle setting at 0, this is a other microstate where one particle is set 2 E, and another particle is set E. So, this is this is the thing, if you swap this particle, say it does not matter this is

still the same microstate, if we similarly you swap to this is two particles, it does not matter, it is a same microstate. So, so this is the in the in the sense we at least it is a difference situation, but it is a same state, I mean same microstate it what I am saying. So, now what are the ways in which you can accomplish this, basically if you look at the if you put it down in terms of factorials, which we will just do for the for the moment.

There are two particles, so you put accomplish this into 2 factorial ways of which, there is one particle of one kind in 3, in the say one particle of the same kind in 0, so we would say 2 factorial by 1 factorial by 1 factorial. For now, we just assume that this is this is correct, when we look at alternate possibilities the details of this kind of an analysis will come out, but simply if we take two particles, and you have this energy levels, this is the way in which could accomplish this.

So, so in other words, so you could do this in two ways, which is which is fine, you could either have and incidentally this particles, we will also call them, when we do it like this, when we do this kind of an analysis, when we approach the problem the way will we are doing it, what is true about those particles is that they are identical, but distinguishable. So, they are identical particles, but we are able to distinguish between them, that are why when you take this particle and put it up there, and you swap them down.

You swap these two particles around, we call it an other state, I mean all at is we count it as two possibilities, so it is a same microstate, but there are two ways in which you can arrival this microstate. So, therefore, they this is done in two ways, the same will be true here you can do this the same way 2 factorial by 1 factorial 1 by 1 factorial, so this can also be accomplished in two ways, so both this arrangements accomplish in two ways; given the over riding definition that the particles are identical, but distinguishable.

So, right now I am putting some terms down, which are actually very important terms, when we say identical and distinguishable, there is they mean something very specific, at this moment I will just leave it like this, we will because are focus is on the calculation. A little further down may be in a class or two, may been couple of classes form now, we will actually come back to discussing what is meant by identical, what is meant by distinguishable and also why it is so important, why is that right now, they adjust to descriptive terms, I mean does not seen like any great term out there.

Identical, distinguishable are not do not immediately come across something great relevance, but for the purpose of our discussion in fact, for the theories that we develop you will you will very surprise to find that this the this pair of words is extremely crucial for the body of material that we are study. So, when when we find that the Drude module fails, it will fail because of something that is related to the this two words, and the alternate modules that they will pick up, which will actually do well, will again have to do with of the fundamental reason why they will be doing well, will have to do with how they are handling two terms, how what do this terms represent in those system, in those modules.

So, right now these are just two words, I will leave them here for now because that is not the purpose of immediate discussion; will come back to it later. In fact into classes we will back at this this two terms. So, for the moment it is enough that will find this discussion we find there identical particle. So, this is same microstate as if you were to reverse it, so you will call them we will therefore, treat them as being under the same microstate, but they are distinguishable.

Therefore, if you shift that one down and shift this one up there it is counted as second possibility as two ways in which you can accomplish this microstate right. So, both of them are consistent with this description. So, you have two ways to do this, two ways to do that. So, if you randomly look at the system you randomly take a snap shot of the system, there is 50 percent probability that the system is sitting in this condition. And there is 50 percent probability and it sitting in this condition, because you have 2 and 2 that is it, there is no no specific preference and so on.

So, there are this a 50 percent chance, that you will you will the macro state of the system the macros state of the system is fixed there is no change in the macro state. The macro state is everything that i just describe constant temperature, constant volume and total energy being 3 E, so that is all fixed. So, So, that is fixed but, which microstate you will find it in will you find the particles being at E and 2 E or will you find it 0 and 3 E those are the two possibilities that you have.

And since both of them have can be arrange arrived at there is say basically same number of ways in which you accomplish both of them, as a 50 percent chance you will see it in this microstate and 50 percent chance that you will see, that microstate all right.

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So, also put it down as a ratio 1 is to 1 is what we are looking at 1 is to 1 1 is to 1 is the ratio of the chances that you will find it in this state or the others fine. Now, the same system, same macro state we will look at if we have what will happen if we actually have three particles in the system, so we will do that. So, we will look at now the same system, same macro state with three particles and see what what the possibilities are.

So, same thing will have written the energy levels down here 0 E 2 E and 3 E, now we have three particles available in our system, so we will say three particle system. So, what other possibilities we can once again we can have two of the particles sitting at 0, which I represent by these 2 points. And in which case one particles its at e i am sorry one particles it is 3 E, so you have two particles sitting at 0 and one particle sitting at 3 that is one way in which you can get a total energy of 3 E.

Next possibility is that you have one particle at 2 E, one particle at E and one particle at 0, that is one way in which, which you can accomplish this 3 E being a total energy. And the third possibilities all the 3 particles are sitting at E, so these are three possibilities that you have. So, this one possibility, this is another possibility and this is third possibility they. So, these are three different microstates corresponding to the same macro state that is the two uses are terminology that is what we are looking at fine.

So, now how many ways a can be accomplish this, this and this (Refer Slide Time: 35:26) is the question that we can we need ask our self, so if you look at it here, this is

three factorial there are three particles, so you select them in three factorial ways, in which in one place we have only one particle. So, one factorial there and in this energy level there are two two particles, so there is two factorial base in which you can re arrange them and still be the same.

So, just swapping them around in the same energy level does not count, so that is why it ends up it this. So, if you look at this works out to three, in three ways we can accomplish this right. So, and you can also see effectively it means one particle here, you can move the next particle there or the third particle there, so that is way which would do it. Now, if you look at this arrangement, there are three ways in which you can pick this particle, there are two ways in which you can pick this particle, there are only one way in which you can pick this particle.

If **if** you want look at that way or if you want put it down in this notation, you have essentially 3 factorial by **1** factorial 1 factorial and 1 factorial. So, that is essentially three factorial that is says same thing as 3 2 and 1 that is that is what i just described you three ways you can pick this, two ways you can pick this, one way can pick this. So, therefore, this **this** works out there are 6 ways in which you can make put this particles here **right**.

So, there are six possible ways in which you can keep rearranging this particles, such that each is different arrangements is unique, because the particles are distinguishable they are identical but, they are distinguishable. So, moving this particle up in energy level and moving that particle down in energy level is considered as the new way in which you can accomplish the same microstate. Whereas, here they are of the same energy level therefore, swapping them does not count that is the only difference. So, so, this is the thing there is 6 ways in in which you can accomplish this.

Now all the three particles are sitting at the same energy level there is only one way you can do it, because there are only three particles, if all of them sitting at the same energy level there is no further arrangement that you can do. Because, they are at the same energy level even if the distinguishable just rotating them around at the same energy level makes no difference; the system is still in the same state. So, this is this microstate can be arrived at in only one way.

So, or if you want in put in down in factorial analysis it is simply 3 factorial by 3 factorial, because 3 are there in the same energy level, so this occurs 1. So, with three

particles we find that this macro state of the system can be accomplished using three different microstates as supposed to 2 different microstate's that we saw there. And in among this microstate, we find that one of the microstates can be arrived at 3 times in three different ways, the other microstate can be arrived at in 6 different ways and the microstate can be arrived at only 1, in one in one form.

So, if you want to put it down as percentages, if you take a snapshot of the system, and we will say that in all these cases in our discussion, upfront there is no preference for a for a given microstate, it is a completely random system, it only has this overall constraint placed on it. So, at a given moment it could be any one of this microstate equally happily, so there is nothing that upfront tells the system that, do not know you should stick to this microstate that is not the way it is.

Only the overall constraint placed on the system, which define the macro state are actually valid, within it within that as long as the system is consistent with the microstate it is equally possible, that it is at that state. So, now that that only leave us with the possibility of the fact that one of the microstate can be arrived at in many many many different ways therefore, you are more likely to see the system in that, particular microstate, if you take a snapshot of the system, which is basically what we are looking at here.

If you randomly look at the system, and assume that any one of these state is equally probable, then 30 percent of the time you will find that, it is in a it is in this microstate because, it is available to us 3 times 30 percent, it is going to be available here 60 percent it will be available here, and 10 percent it will be available here. So, 10 percent of the time you will find it in this microstate, 60 percent of the time you will find it in this microstate, and 30 percent of the time find it in the this microstate. If you wish to take a ratio again, you will find this is now one especially, we we will take a ratio of only the top two, because that gives us that is information that is more useful to us.

So, if you look at the top two, it is 1 is to 2, that most two probable cases, if I want to look at with respect to 10 it is going to be even larger, so it is 1 is to 6 is to whatever 3 1 is to 1 is to 3, between if you want you can put that also it is 1 is to I am sorry 3 is to 6 is to 1. So, 1 is to 6 is to 3 amongst the top two that is 1 is to 2, so in other words in this discussion, we find that the microstates are not equally probable, there is one microstate

that is more probable, because it is at 60 percent, so so there is a microstate that is more probable, and that is twice as probable as the next next most probable microstate.

So, this is the most probable microstate, this is the next most probable microstate, this is the least probable microstate; the most probable microstate is twice as probable, as the next most probable state right (Refer Slide Time: 40:34). So, moving from two particles, when we move to three particles, first of all we find that the probability of occurrence of a microstate now begins to differ; we find that each of the microstate has a different probability of existence. And on top of it, we find that there is one microstate, which is distinctly more probable than the other microstates.

In fact, even now we find that this microstate is actually more probable than the other two microstates combine, but that is something we will look at as a next step, but more importantly this is twice as probable as the next most probable state. So, you just go one more step, we will take four particles and then we will make some generalizations.

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So, same system we will take same energy levels 0, E, 2 E and 3 E we will say there are four particles available to us, so four particle system right, and the same considerations in terms of the macro system, macro state. So, what do we have, we can have one state where you have one particle here, and three sitting here, this is one way in which you can accomplish 3 E, another possibility is you have a particle at 2 E, one particle at E and two particles at 0. The third possibility is you have three particles at E, and one particle

at 0, so these are three possible arrangements given the, these are the only three possible arrangements that you can think of, you cannot have more than one particle in 2 E because, then the energy of the system is more than the 3 E limit that you have.

So, you can never have two particles there or two particles here, maximum you can have this one particle and then, that leaves you with the other systems again other energy levels again, if you have one particle here you can only have one here almost, you cannot have anything more and then, if you have three this is what you will have. So, these are the only ways in which you can arrive at the system, subject to the constraints that we have. Now, let us look at the number of ways this microstate can be accomplished, since you have only one here, and three here essentially, it is 4 factorial by 3 by 1 factorial times 3 factorial, so there is essentially 4 ways.

And even otherwise, you can see you have one and you have three, so you can rotate them around each particle can be brought up here once, so therefore, and there are four particles therefore, there are 4 ways in which you can do this done. So, same thing we will do here, this will come out to 4 factorial divided by 1 factorial 1 factorial and 2 factorial right, so this is simply 4 into 3 that is 12. So, there are 12 ways in which you can accomplish this microstate, and if you come to the last one it is actually sort of an inverse of this, in terms of the number of ways, the in terms of the way the arrangement.

Here, we have three at the higher energy level, one at the lower energy level, but in terms of number of ways in which you can accomplish it is the same there you can rotate this energy level around 4 times. So, again you will have the same thing 4 factorial by 3 factorial times 1 factorial, so again you will accomplish this 4 times yeah, as I mentioned you know this this one can be rotated around. So, you can get one by one out here, the others will go back there, so we have 4 is to 12 is to 4 right.

So, if you put down as a probability, so if you actually count them up this is out of this will work out to out of 20, so in terms of percentages this is 60 percent, this is 20 percent and this is 20 percent, same comment will hold as before, that is each individual microstate is equally probable. So, simply because, this microstate can be arrived at in 12 different ways, at given instant if you just randomly look at the system, there is a great of chance that it will be in this microstate; that is all we are talking, that is all we are saying, and in terms of a ratio this is 1 is to 3 is to 1 right.

So, we have now looked at this we have looked at a very small system, and we have gradually added particles to it, we started with two particles, then we made it three particles, and we made it four particles. What we find is as the particles; number of particles in the system increase, one concept that begins to arrive or immediately arrives is that, the microstates are now no longer equally probable; there is one microstate that seems to be more probable, than the rest of them. So, so there is a more probable microstate, so that begins to stand out in the system, and we also find that in general, the tendency is that, the more probable microstate.

The probability associated with it seems to go up or at least in relation to the other microstates that are available. Reason being, when we first added with two particles, the ratio between the two possible microstates was 1 is to 1, then we made it a three particle system, the most probable microstate was twice as probable as the next most probable state. When you put four particles in, it became three times as probable as the next more probable state, so 1 is to 1 became 2 is to 1 became 3 is to 1 fine, so this is what we are saying in the simplified set of examples, that we have taken.

So, I am not saying if you exactly go about this add one more particle it will it will proceed exactly precisely, the way in which I have described it, but the general trend is will going to hold. The general trend is going to be that, as you add more and more particles to your system, the more most probable state will become more and more probable. So, please remember that, these are all like one particle, two particle, three particle I mean sorry two particle, three particle, and four particle system, that we looked at, we started the class by highlighting the fact, that the system that we talking of have 10 power 28 particles.

So, that is the huge number, that is so many orders of magnitude, 28 order magnitude away from what we are talking of here, so the comparison in scale is like huge, there is no I mean, it is just completely out of scale with respect to what we have discussed here. So, what is seen is that, when you go to such very large numbers of particles in a system, this small trend that we have seen here, the small trend that we have seen here, which is that there is microstate, which is more probable than the other microstates, and since we getting more and more probable, that small trend that we have seen is amplified in a very huge way (Refer Slide Time: 47:22).

So, what happens there is that, we ham bunch of microstates, whole bunch of microstates that are possible for the system, but there is one microstate which is the most probable microstate, but the number of ways in which you can arrive at that microstate is very very significantly higher than even the next most probable microstate.

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So, we will put that down (No audio from 47:55 to 48:58), so this statement is this, as the number of particles in the system increases, the most probable microstate of the system becomes more probable than all of the other microstates combine. So, this is the very important statement, and it is very relevant with respect to the fact that the number of particles has increased. So, only under those constraints, we spoke about one of two particles, three particles, and four particles, from there we have made leap 10 power 28 particles.

When we move from such a small system of two, three, and four particles 10 power 28 particles, the most probable microstate, the all the other concepts are still the same, that there is an overall macro state and corresponding to those that macro state, you can have several several microstates. The most probable microstate, will be one where its probability of occurrence, will be way higher than all of the other microstates combined, I just showed that the most probable microstate is twice as probable as the next most probable the next most micro probable the next micro probable the next m

microstate, so we are only talking of factor of 2 and factor of 3 with respect to the immediately next most probable microstate in this in the examples that we considered.

I am saying that when you move it up to 10 power 28 particles, you reach a state, you reach a situation where the most probable microstate completely swarms the probability of all of the other microstates combined, not just the second one alone; I am saying the second, third, fourth, fifth possible microstates, you combine all of them, their probability of occurrence will be tiny compare to the probability of occurrence, with the most probable microstate. So, you can also you can also sort of imagine, this you may ask how that happens and all that, why we have shown, while I have shown you a small trend and so on.

Please note that in all these cases, we are talking of factorials, so on top of the on the numerator, we may have all of the particles in the system, say N f N f factorial you may have right, and in the bottom you have several factorials, which are also very large numbers, so you will have whatever n 1 factorial n 2 factorial and so on. This is again I am just generalizing to give you give you hold on where this issue might come up with, so when we talking of very large numbers, if one of these factorials disappears, and everything else stays common between the various situations, that you are considering.

Just the disappearance of 1 1 factorial simply, because it is a huge huge number we change the ratio of this, with respect to the immediately next probable system by many many many orders of magnitude. So, so that is where this issue comes up from, this is that is the crux of this idea, and that is where this issue, the situation arises where that whereas the number of particles increases the most probable microstate of the system. Becomes more probable, than all of the other microstates please remember, this it is all of the other microstates combined not just the second most probable microstate, all of the other microstates combined.

So, statistical mechanics is a field of study, where it looks at this situation and it says that the equilibrium state of a system is the most probable state of the system that is the basic idea of statistical mechanics. It says equilibrium state of the system equilibrium state of the system is the most probable state, I want again emphasize that there are other states, other possible states, it is simply that the most probable state is almost like you know 99.99 percent chance that you will find it, or even more 99.999 percent chance that you will find it in the most probable state. Therefore, for all practical purposes that is the equilibrium state of the, you go at any given point in time, you try and look at the system, that is the that is the state you will find the system.

So, the equilibrium state is the most probable state, and statistical mechanics is works on this principle, it looks at large systems where, because of the nature of the system the equilibrium state is the most probable state. And statistical mechanics provides with all the tools of getting you the properties of the most probable state, so this is the general idea. So, it is with this theme of this concept in in mind that I would like to halt this class, and just reemphasize that as we go forward, we will look at we will look at the system again or the system that we have dealt with again.

Except that we will now introduce the concept of statistical mechanics into that system, and try to identify the most probable state of our system, which which is what we used and therefore, try to understand the properties of the system; on the basis of our recognizing what is the most probable state of the system and therefore, the equilibrium state of the system. When we are able to do that we find, that we can extract information about properties of the system, without knowing the details of every single particle within the system; and that is the basic goal of our analysis.

Because, once we do that we can say something about the V square values, mean square velocities values in the system, we can say something about the specific heat of the at constant volume of the system, as for the whole system without knowing the details of the every single particle. And therefore, we are now able to actually make some scientific statements, about why the CVE value has ended up as what at what it has ended up with and what why the v square value has ended up at, what it has ended up with.

And therefore, have a good understanding as to where the errors of the Drude model come from, and that would then lead us to the next step which is how we would go about improving on the model. So, with this we will halt, we will take it up next class, keeping in mind statistical mechanics will now become the tool, that we will use to look at our system, thank you.