Statistical Thermodynamics for Engineers
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Lecture 01
Introduction to Statistical Thermodynamics

Welcome to the first lecture of this course Statistical Thermodynamics for Engineers. So, this will be the first lecture of the series. So, after 60 lectures that we are going to provide. So, initially as we start, let us look at the bigger question first that, what is statistical thermodynamics? Now, at this point in your career probably you have always dealt with macroscopic systems. Now, these macroscopic systems could be you know from an scientific or engineering viewpoint, this could be like your piston cylinder arrangement or your gas turbines or whatever device that you can think of.

So, in all those cases, you have analysed the problem using certain methods, which in this case are the thermodynamic methods. So, analysis of macroscopic systems usually will involve you know conservation equations, the field equations, thermodynamics and stuff like that. Now, if it is for example, it uses principles from classical mechanics, it also uses principles from electromagnetism and it uses principles from thermodynamics.

So, this is how all systems have been analysed, all macroscopic systems are usually analyst. So, we are going to deal in this particular course with systems which are of thermally origin, thermal systems. So, for example, gas turbines one such terminal systems, because these thermal systems will utilize thermodynamics, fluid mechanics, heat transfer, etc. So, here heat exchangers everything comes under these thermal systems.

So, in order to understand this, understand the classical thermodynamics, you should also recall that classical thermodynamics is inherently little limited sometimes to explain the simplest thermodynamics behaviour of a system or say it can be gaseous system, it can be liquid or it can be solid whatever it is.

So, if you do not consider the microscopic part of such a system, you cannot adequately, that means atoms and the molecules if you are not able to handle them or treat them well enough it will be, it will be almost hard to understand the full extent of thermodynamic properties, what is thermodynamic equilibrium? So, long and so forth.

So, for example, if we ask the question that what is the influence of temperature on transport properties such as viscosity or thermal conductivity, you need to know that how temperature actually influences these kinds of properties in what ways. So, this elementary viewpoint is what will be covered in the statistical thermodynamics course.

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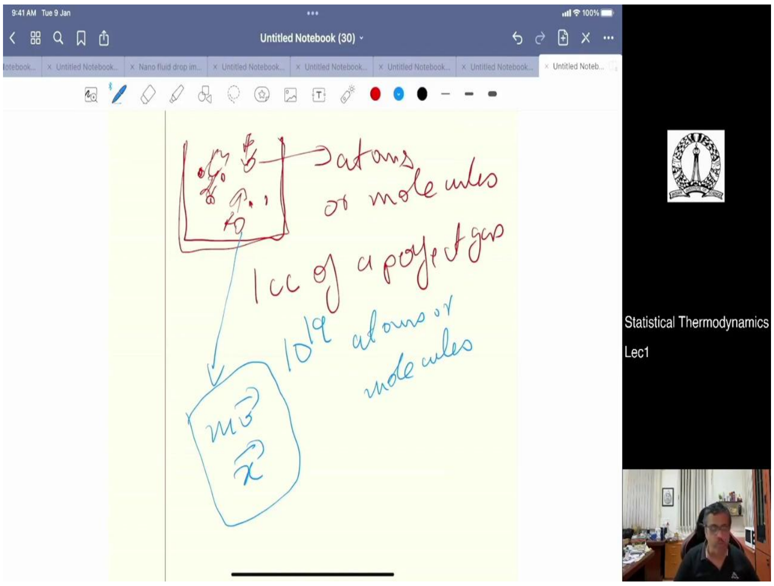

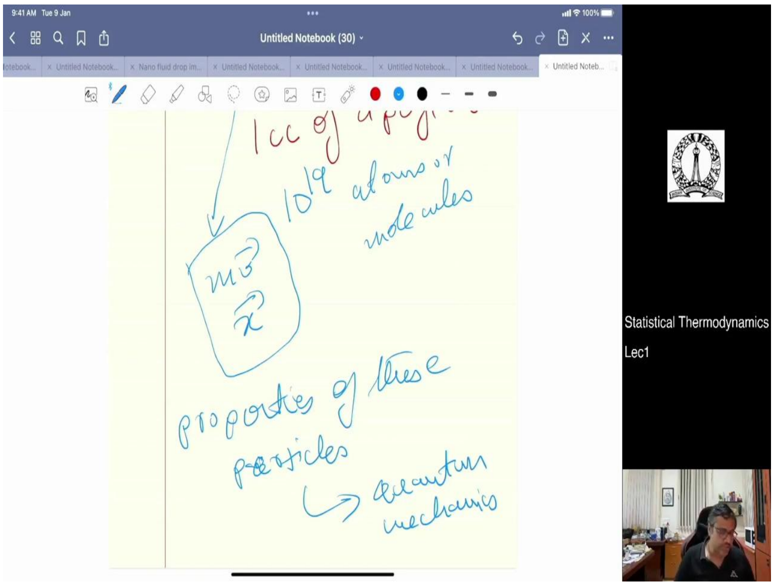

Now, any particular system thermodynamics system is composed of atoms and molecules, so atoms and molecules, so, if you look at the particular page, you will be able to get a good thing. So, let us take any system it is composed of, you know these are your atoms or molecules, that we will call it where, now these atoms and molecules they all move around as you know, move around in different directions, if they are placed in a container, this is like a container, for example.

Now, even the simplest of a system, see if you take 1 CC of a perfect gas that contains 10 to the power of 19 atoms or molecules. So, book keeping becomes a very difficult task because you are dealing with a huge number of particles. And not only you are dealing with a huge number of particles, in order to describe this particular phenomena, you have to know the position and the momentum of each of these particle.

So, you need to know what is momentum and what is the position of these particles. If you know these then you can evolve how these particles actually move and essentially you would be able to describe macroscopic thermodynamics system. Now, the properties of these individual particles can be only obtained through Quantum

Mechanics. So, if you look at if you ask the question, how about the properties of these particles. So, they come from quantum mechanics, which most of us are familiar with that what quantum mechanics is, so, they come from they have their origin in quantum mechanics.

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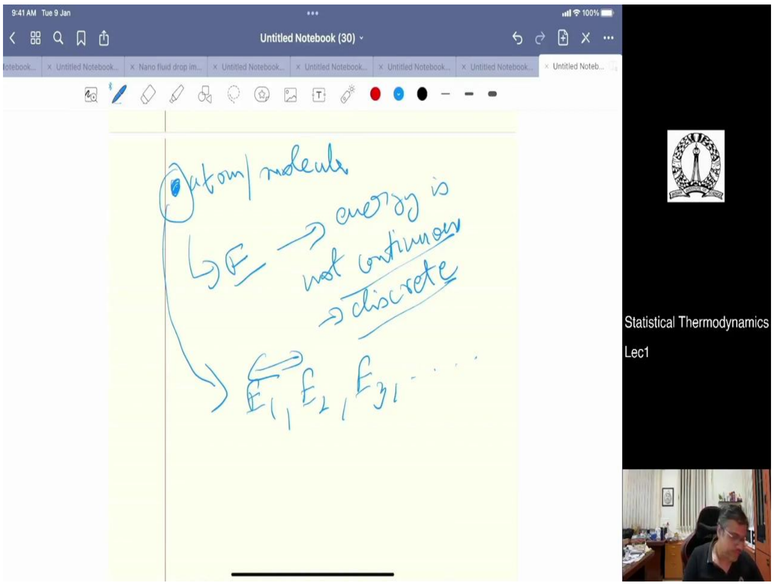

Atom/molecule

E → energy is not continuous

→ discrete

E1, E2, E3, ...

Now, one of the most important results when you deal with a quantum mechanical system is that, the energy of any single atom or molecule, say this is an atom or a molecule, if this is the atom or a molecule, then the energy E of this atom or the molecule is not continuous but discrete. So, the energy E is not continuous and essentially it is discrete in nature, that is the very basic tenant of the quantum mechanics.

Now, because they are distinct in the, they are discrete in nature it is discrete, because of the reason that these atoms or the molecules, they only can have certain distinct energy values. So, they cannot have all energy values, they only can have discrete energy, distinct energy values. So, this atom or the molecule they can have energy say E1, E2, E3 and stuff like that, but not continuous that between E1 and E2 they cannot have some kind of an energy say, which is 1.5 E1.

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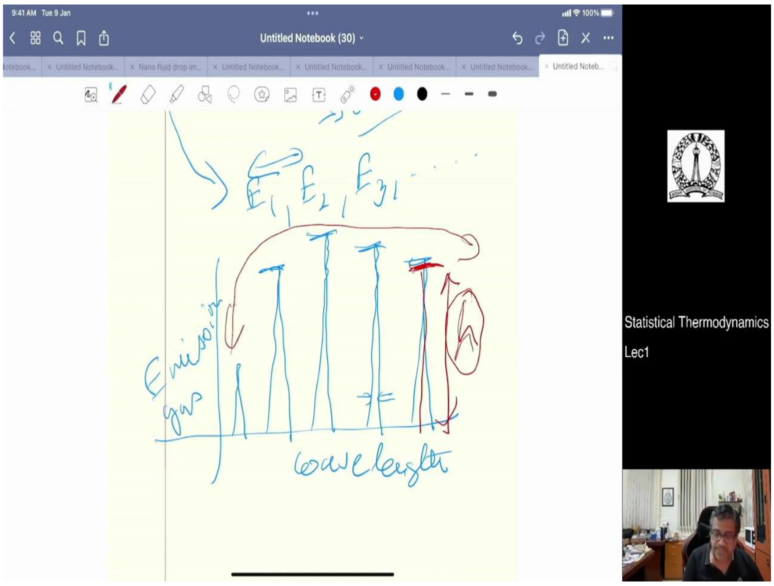

So, based on this if you just plot the spectrum, say you take an emission signature from a gas, and this is a wavelength. So, you have basically you are monitoring that how this energy actually varies, you will find that the spectrum is composed of stuff like that very narrow, or very discrete lines, these lines do have a little bit of a finite width, which will cover that how that width actually comes from.

So, for example, this is the discrete changes the energy that is stored by an atom or a molecule. So, the height of each of this line, if we take a look at the height, this is the height of each of this line. So, the height of each of this line basically reflect the number of particles that are causing that emission signal. So, it is basically more the height, more are the number of particles which actually has that particular energy.

So, that that is how the number of particles is actually related to a height of this emission signature. So, the point of view of classical… or statistical thermodynamics is that a number of relative particles can only be determined by what we call some kind of thing called probability theory. But we will come to that a little later, but as we can understand that in quantum mechanics, all the spectrum that you see over here they are discrete and the height is related to the number of atoms or particles or atoms molecules which are essentially particles, number of particles that are causing sharp change in the height.

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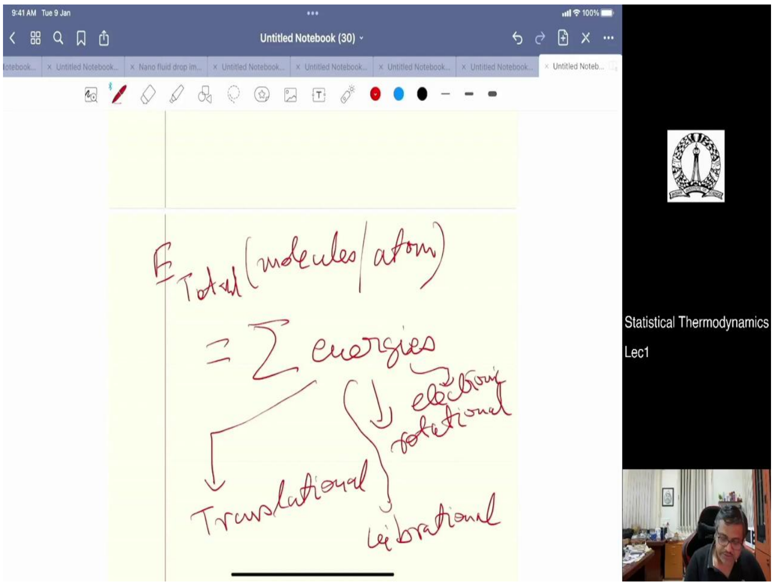


E_{Total} (molecules / atom)

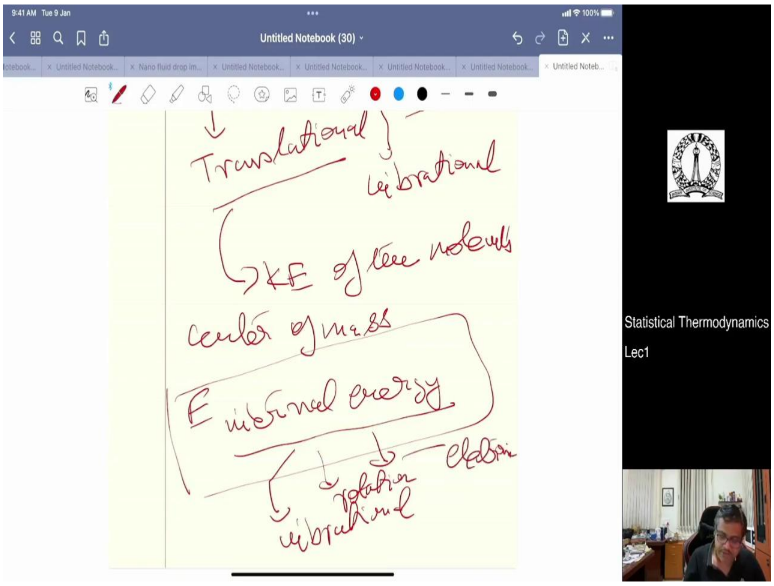
$= \sum$ energies

Translational

electronic

rotational

vibrational



Translational

vibrational

→ KE of the molecules

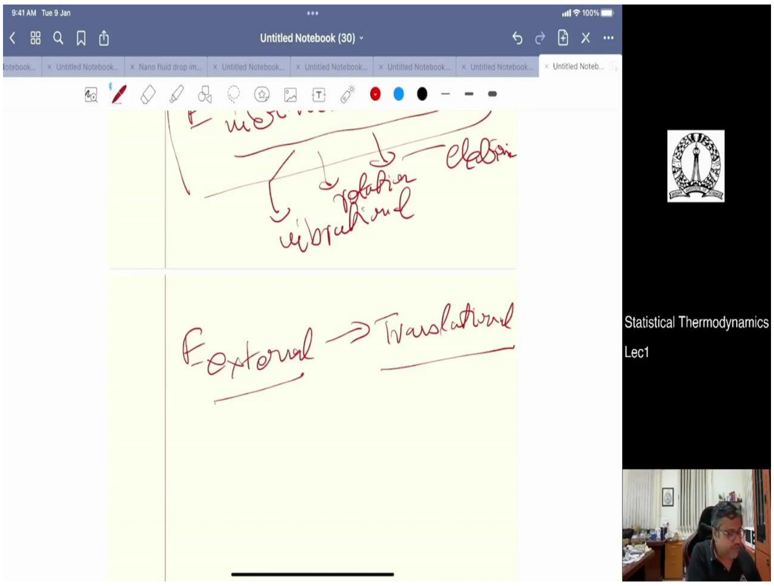
center of mass

E internal energy

vibrational

rotation

elec spin



vibrational

rotation

elec spin

$E_{external}$ → Translational

Now, the total energy of a (())(08:57) this is the total energy of a single say molecule or atom whatever? And be taken as the sum total of the energies, caused by what we call translational mode. We will come to what these means in a second, translational of course, that is rotation, there is vibrational and there is of course electronic.

So, these are the sources of energy. So, that is what is a translational energy, translational energy is nothing but a kinetic energy of the molecules centre of mass. So, the kinetic energy of the molecule centre of mass is basically,what is called the translational mode of energy.

Now, the other sources for example, rotational, if I take rotational now, what will be rotational? Rotational basically describes the energy that is stored by the molecular rotation, the molecular rotation, the energy that is stored by the molecular rotation is what actually determines the rotational mode of energy, the vibrational mode is a energy that is stored by the vibrational bonds that holds the molecules and the electronic mode is basically the energy that is stored by the motion of electrons within the molecules.

So, you can understand So, each of this mode is very distinct, translational mode is nothing but the kinetic energy of the molecules, the vibrational mode is basically the bond the vibration of the bond of the molecules, then rotational is the rotation of the molecule across different accesses and electronic is basically the energy that is stored by the electrons to decrease motion around that the energy that is stored when electrons in the molecule.

So, as you can understand that by combining all these energies is what actually gives you the total energy or the total internal energy (())(11:27) is energy is internal energy. So, internal energy basically is of course the usually we say that this is the vibrational plus rotational plus electronic.

Whereas, the external mode is termed is basically the translational mode that is how these things are differentiated just for bookkeeping purposes as much. So, the external is basically the translation because this involves bulk motion, I guess it cannot indeed the rotational (())(12:14) to its own states. So, what can we can do is that by combining predictions from quantum mechanics with experimental data that is obtained via spectroscopy, it turns out that we can evaluate what will be the contribution from each of this mode later on, when we actually you know, do a little bit of work on absorption spectroscopy and similar type of spectroscopy it needs, you will know exactly what I mean.

So, you can combine what we call you know measurements from spectroscopic measurements combined with quantum mechanics, we can actually evaluate what are the contributions from each mode and therefore, we can determine the microscopic properties of this individual molecules. So, such properties actually include bond distances for example, the rotational or vibrational frequencies, the translational or electronic energies, etc etc.

And then by employing statistical methods, we can average this across all particles to calculate the macroscopic properties. So, you understand from quantum mechanical calculations, we understand what are the contributions of the different modes, the vibrational or rotational electronic translational and then by using statistical methods, we basically average it across the entire system, which is basically composed of millions and millions of atoms and then that will lead us to a final macroscopic properties, the macroscopic properties, which is what we learn in our classical thermodynamics.

So, temperature, internal energy, entropy these will be some of the properties that we can actually understand from these statistical methods.

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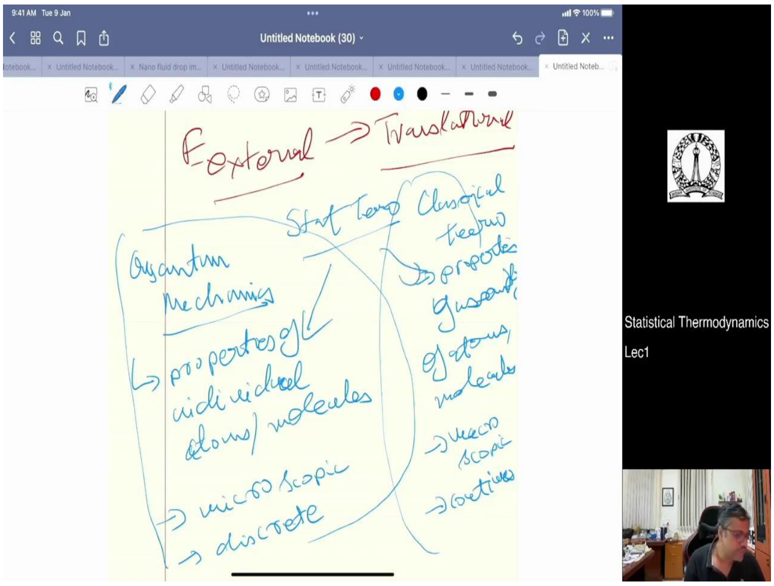

So, let us look at particular figure as a roadmap of what we are supposed to do. So, on one side you have quantum mechanics. So, what does quantum mechanics do? Quantum mechanics looks at the you know the properties of individual atoms slash molecules. It is microscopic of course, it is microscopic and it is discrete. So, these are all hallmarks of quantum mechanics calculation.

Then on this side you have classical thermodynamics, so classical thermodynamics which basically looks into the properties of an ensemble, of an assembly basically, ensemble actually has a different connotation. Assembly, properties or assembly of atoms or molecules. So, you are not concerned about you know, individual atoms or molecules anymore, this is the other end of the spectrum. And it is macroscopic obviously, because these are properties that you can see, you can measure, you can feel and they are continuous usually they are continuous. So, the bridge between these two is provided by the statistical thermodynamics. So, stat thermo acts as a bridge between these two.

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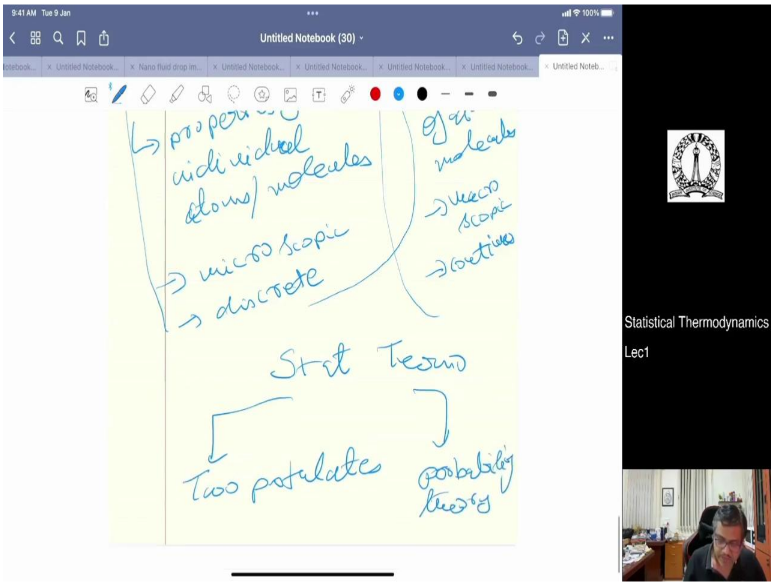

So, how it does is basically there are two we were going to see that stat thermo has got two postulates which we are going to see in a second postulates, and it banks on probability theory, that means, we have to learn a little bit of probability. So, as you can see, so, this is the roadmap. So, as we can see that the framework for statistical thermodynamics can be divided into three conceptual themes.

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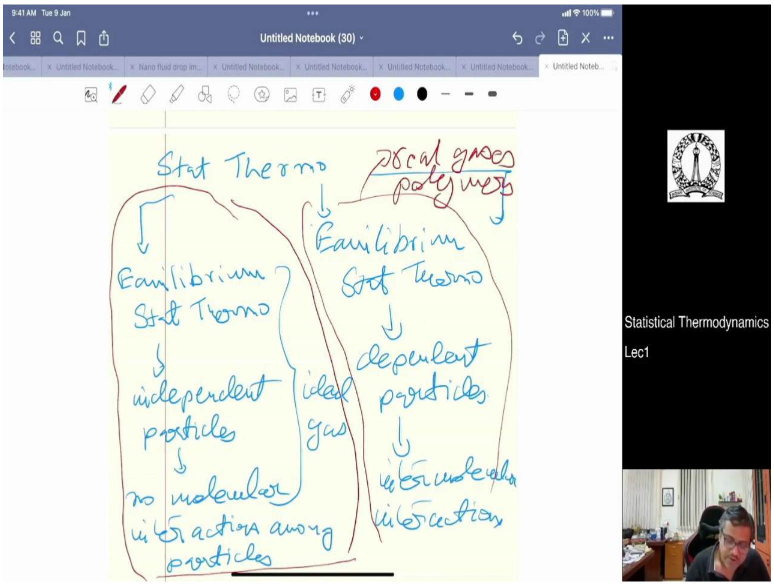

So, stat thermo will have three conceptual themes that we can kind of go through them one by one the first is equilibrium, equilibrium stat thermo. So, that equilibrium stat thermo will focus on independent particles. So, by independent particles we mean that there is no molecule interactions, molecular interactions among particles of interest, so there is no molecular interaction between the two, between the particles of interest.

So, this is equilibrium stat thermo, then of course, the second one so, examples of this will be like for example, ideal gas in also pure crystalline metal blackbody radiation etc these are all part of this, the second one is called the second one after it is also called as equilibrium statistical thermodynamics. This is also equilibrium stat thermo, but this comes with a catch, the catch is that now the particles are dependent.

So, by dependent particles moment we say that these are dependent particles. So, dependent particles essentially mean that now, there will be interactions among the particles. So, there will be intramolecular interactions. So, there will be intermolecular interactions in this case, where we are dealing with dependent particles. So, these are for example, real gases, polymers these are all examples of these real gases for example gases, polymers, so, these are will be all part of this second part.

So, now that we know that this intermolecular traction becomes very, interactions becomes very important at higher densities at which the particles are close together, they are brought close together and because there is a lot of mathematical difficulties now, because the macroscopic properties now will require a lot of semi empirical type of calculations.

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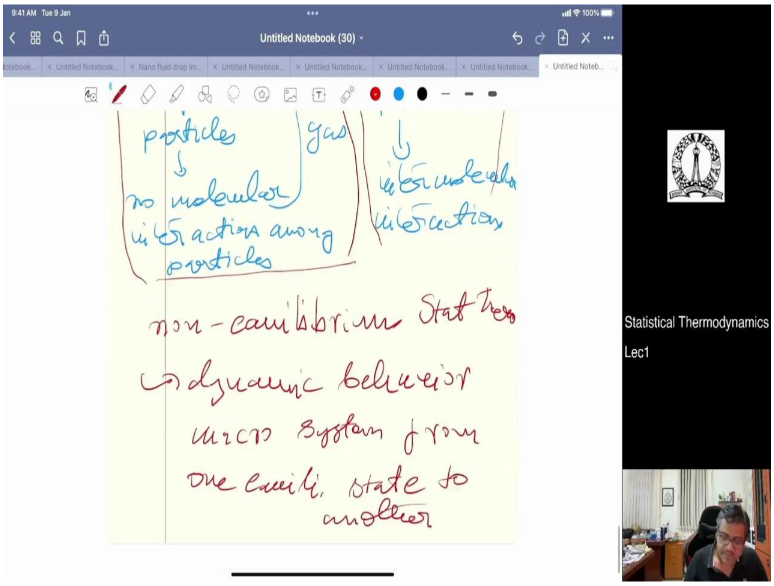

particles → no molecular interaction among particles

gas

↓ intermolecular interaction

non-equilibrium Stat Thero

↳ dynamic behavior micro System from One equili. state to another

The third conceptual theme is called non-equilibrium. Remember the word non-equilibrium stat thermo, now this is a little dicey because here we are concerned with the dynamic behaviour that happens in our system ships from different equilibrium stats. So, so the dynamic behaviour, so, this is basically the dynamic behaviour, behaviour of a system when it of macroscopic system basically, microsystem when it goes from one state from one equilibrium state to another.

So, this arises. So, well there are different ways to analyse it there are time correlation methods, which deals with non-equilibrium thermodynamics, but in this particular thing we are going to look at basically dynamic processes that can be linked with the kinetic theory of gases, kinetic theory basically… So, we can get some deeper understanding of fluid mechanics and heat transfer and molecular diffusion, which basically is the dynamic behaviour of a system as it goes from one equilibrium state to another.

So, with all these things keeping all this phenomenon in mind, all this drama basically, all this drama and all these things, you would be actually able to calculate from atomic and molecular properties, the thermodynamic properties of real systems. So, from atoms and molecules all the way up to the thermodynamics, thermodynamic properties of ideal gases, real gases and metals and all these things, you can actually calculate using this.

So, the idea over here is that statistical thermodynamics now, therefore, we have to look into a probability part, we have to learn a little bit of probability before we go on and start evaluating the tenor… the behaviour of these kinds of systems. And so, basic probability that comes with maths that you may have studied in your undergraduate or basically in your school days, we are going to do a rehash of those.

And before we get into this (())(22:11) before we move on and try to understand the dynamic behaviour, and how we can best analyse these kind of systems. So, in a nutshell, what we have covered in the first lecture is basically, we have all this dealt with macroscopic systems and macroscopic systems, we have been, I mean, we have all looked up the properties of such systems, we know what is the internal energy entropy, all these things, we have looked at thermodynamic tables, stuff like that, but we were never really you know, clear that how those properties actually evolves, what was the origin of those properties, that we were never certain and because we were never certain about those, the understanding of those insights was not there.

So, therefore, we have to deal with microscopic systems, understand what is happening at the microscopic level. And once we understand what is happening at the microscopic level, you will be able to get a very clear idea that what how that can be translated to the macroscopic level. So, the second thing that we learned is that in thermodynamics system is composed of atoms and molecules.

So, there are even a 1CC of a gas ideal gas which is very dilute in nature will have 10 to the power 19 atoms or molecules is a huge number, huge amount of bookkeeping and you need to know the position you need to know the momentum all these particles, you do not need to know the properties of these particles. So, the properties of these particles comes from your quantum mechanical calculations.

And all the main feature of the quantum mechanics is that the energy of these particles are discrete, because this is what we are going to use later, energies are discrete, they are not continuous, because each particle can only have certain distinct energy levels, it cannot have any energy that you want. As a result of that, as a result of that, we come to the concept that these energies are basically quantized.

So, when you deal with a single particle atom or molecule, you will find that they will have these energies like translation, rotation, vibration, and electronics out of that, except translation all the other three are considered to be internal modes, whereas, translation is considered to be an external mode. So, all these energies are somehow related to how this atoms and molecules actually is. And that comes from your quantum mechanical calculations.

So, using like, sometimes you use quantum mechanical calculations with this, with spectroscopy measurements, to get an idea of what these systems actually are, how these systems, what are the properties of these systems? And then use statistical tools now, to average it across a whole lot of particles and then find out macroscopic properties.

And as we learned that a classification of statistical thermodynamics is also important, most of the time when dealing with equilibrium statistical thermodynamics, it can be based on independent particles that means, the particles that moves around without seeing each other that happens in the case of ideal gas or in the dilute limit, but on the other hand, it can be dependent particles in that case, you need to know the intramolecular interactions between particles.

And thirdly, it can be non-equilibrium thermodynamics, where you actually are concerned about the dynamic behaviour of a system as it migrates from one equilibrium state to another and this is where your fluid mechanics, heat transfer all these things comes into the picture. So, this is the excitement, this is what it is and this is how, how the how statistical thermodynamics can actually help engineers to find out what will be the next step forward.

So, based on this we are going to learn in the next class, look at the probabilities that what are the probabilistic, what are the probability and statistics basically, we are going to look into probability and statistics. And once we go into probability in statistics, we will introduce concepts like what is the mutually exclusive event, what is equally likely events and all those things and once we understand those, it will be much easier for us to know the next few steps that how, how statistical power thermodynamics is based on this probability and statistics. So, this will be the topic of the first lecture.

So, and as a matter of fact, we are prescribing the book of Normand M. Laurendeau, as was shown in the introductory video. So, the Normand Laurendeau course can be actually looked up and you know, that book is what we are going to follow pretty rigorously throughout this particular course, and we will assign homework problems and assignments, which we need to do and turn up, turn them in, so, that we can get an idea, there will be exercises should be given at regular intervals. So, that is a part of the course curriculum.

And we have already in the introductory video, if you look at it carefully, we have already covered now, how the… what are the, what is the syllabus? What is the motivation for studying this particular course, by this time you already know a little bit of this already. So, we will take a look at all of those in the next class. So, this is where we end the first lecture and we will see the next lecture which will be on probability and statistics. Thank you so much.