Basic Statistical Mechanics
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Lecture - 02
Thermodynamics

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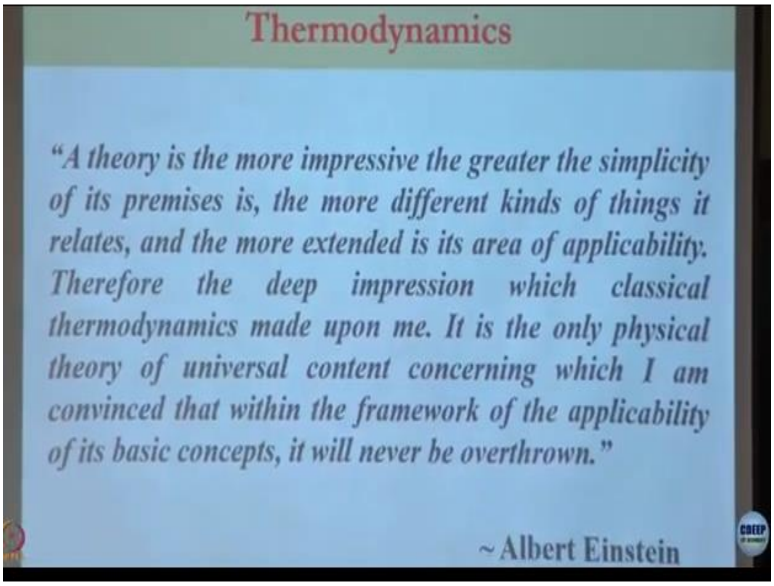

Thermodynamics

"A theory is the more impressive the greater the simplicity of its premises is, the more different kinds of things it relates, and the more extended is its area of applicability. Therefore the deep impression which classical thermodynamics made upon me. It is the only physical theory of universal content concerning which I am convinced that within the framework of the applicability of its basic concepts, it will never be overthrown."

~ Albert Einstein

Now, whenever we do statistical mechanics we always go through thermodynamics. However, we do not need to go through thermodynamics actually. As I said I can develop an alternative way or approach to statistical mechanics but the standard thing of doing it through thermodynamics has a merit. The merit is that it allows you to go and discuss some of the things that statistical mechanics actually do.

One of the main merits of statistical mechanics is that it calculates the thermodynamic properties. It calculates the entropy. It can give you the free energy. That is the main merit of statistical mechanics.

Other than that Einstein wrote many things about thermodynamics. He wanted to say that the only thing that will remain if the world is getting destroyed in a capsule to alien is thermodynamics, the only thing that you should send is thermodynamics or one thing that will survive is thermodynamics. It will never be overthrown. Now, I will spend a little time on thermodynamics and the reason is that again I will tell it little bit differently. I will tell it the way I looked at it. So it is very important to realize when did thermodynamics start.

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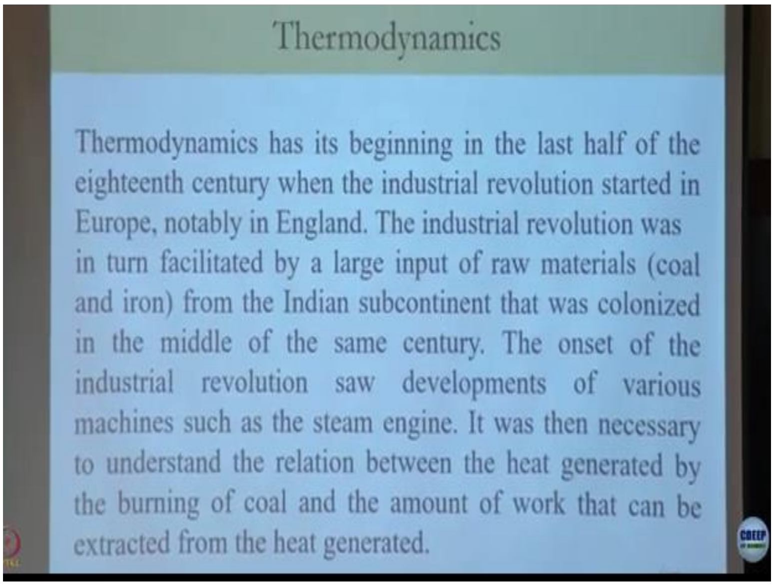

Thermodynamics

Thermodynamics has its beginning in the last half of the eighteenth century when the industrial revolution started in Europe, notably in England. The industrial revolution was in turn facilitated by a large input of raw materials (coal and iron) from the Indian subcontinent that was colonized in the middle of the same century. The onset of the industrial revolution saw developments of various machines such as the steam engine. It was then necessary to understand the relation between the heat generated by the burning of coal and the amount of work that can be extracted from the heat generated.

As I tell you again and again if you take interest in the history of evolution you will find it is much more interesting in whatever work that you are doing because you will be able to relate a little bit. Thermodynamics started with the Industrial Revolution. Why did it start with the Industrial Revolution? Because India played a very important role in this industrial revolution. Around 1757, the British then, the first thing they started was to take away the coal.

Though England already had enough coal but they also had steel. Those days there was huge thirst for the raw material and India provided a huge amount of raw material. There was a man, you might know, Raja Ram Mohan Roy who was considered the first Renaissance man in India. Raja Ram Mohan Roy made a fantastic calculation about the money British was taking away. Does anybody know of that amount?

He figured out those days by this raw material and everything how much money British were taking away. Even those days you have few million pounds per week and all in all now the calculation is that British took away 45 trillion dollars. It is important that suddenly enormous amount of coal-steel went to England, the same happened to France also which equally efficiently robbed Africa.

Coming back to thermodynamics … steam engine came and so there was now the necessity to have an efficient engine and that is where thermodynamics play a role. I am telling you again and again one very important thing that everything is very practical. Thermodynamics was done completely because of this. Boyle was travelling in a steamship and he is the one who formulated the first law.

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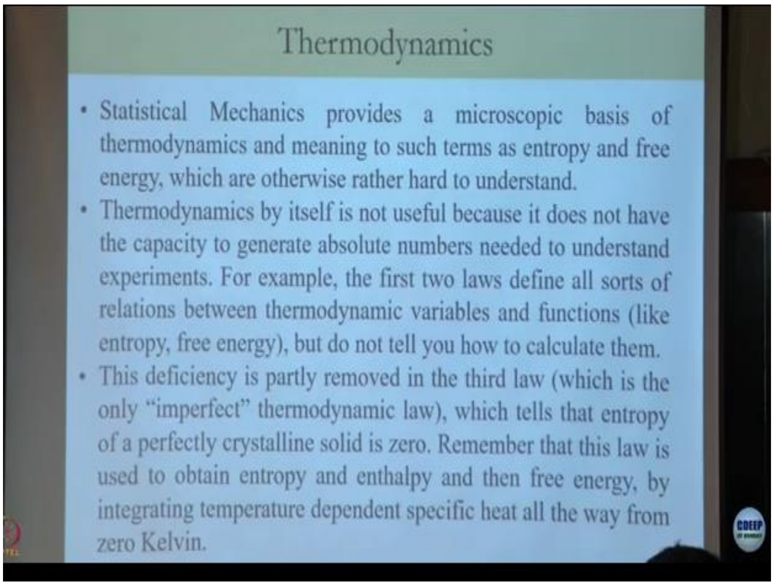

Thermodynamics

- Statistical Mechanics provides a microscopic basis of thermodynamics and meaning to such terms as entropy and free energy, which are otherwise rather hard to understand.
- Thermodynamics by itself is not useful because it does not have the capacity to generate absolute numbers needed to understand experiments. For example, the first two laws define all sorts of relations between thermodynamic variables and functions (like entropy, free energy), but do not tell you how to calculate them.
- This deficiency is partly removed in the third law (which is the only "imperfect" thermodynamic law), which tells that entropy of a perfectly crystalline solid is zero. Remember that this law is used to obtain entropy and enthalpy and then free energy, by integrating temperature dependent specific heat all the way from zero Kelvin.

So quickly go through; as I say statistical mechanics provides a microscopic basis of thermodynamics in terms of atoms and molecules. When I say microscopic basis I say atoms and molecules and they are interacting. They have an interaction potential. Boltzmann gave the meaning of entropy. There are other definitions of the entropy. As I told you Einstein gave the meaning to specific heat. All these come from statistical mechanics.

Thermodynamics limitations: all of you know or some of you know that it does not provide numbers because it provides changes, that all of us know $\Delta G = \Delta H - T\Delta S$, but it does not tell you how to calculate except you have to go when they had to calculate free energy that is what Planck and Nernst introduced the third law.

Then third law combines specific heat; temperature dependence specific gives you enthalpy and entropy. So that was an imperfect law and why it was that? That one understands from Boltzmann equation, $S = k_B \ln \omega$, but those days people did not know that. I will quickly go through thermodynamics and tell you something rather interesting about thermodynamics.

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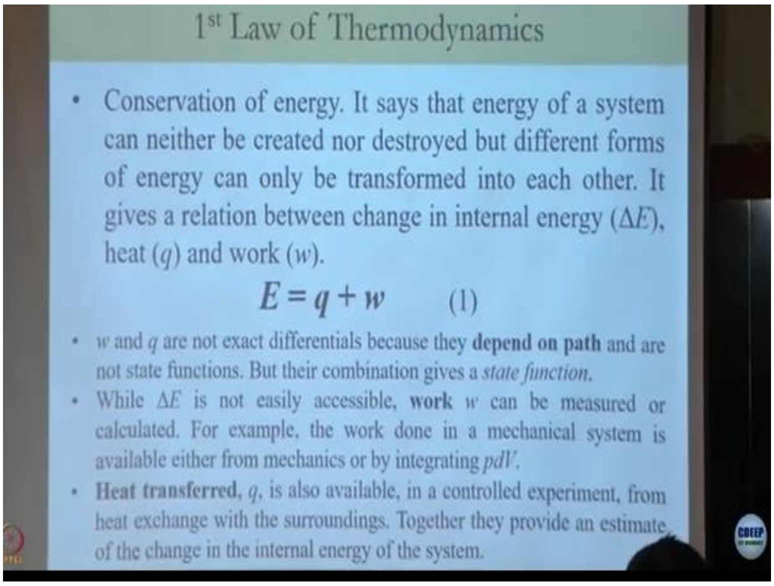

1st Law of Thermodynamics

- Conservation of energy. It says that energy of a system can neither be created nor destroyed but different forms of energy can only be transformed into each other. It gives a relation between change in internal energy (ΔE), heat (q) and work (w).

$$E = q + w \qquad (1)$$

- w and q are not exact differentials because they **depend on path** and are not state functions. But their combination gives a *state function*.
- While ΔE is not easily accessible, **work** w can be measured or calculated. For example, the work done in a mechanical system is available either from mechanics or by integrating pdV.
- **Heat transferred**, q, is also available, in a controlled experiment, from heat exchange with the surroundings. Together they provide an estimate of the change in the internal energy of the system.

Again I am not going to do a full course on thermodynamics that is beyond the scope. Many Statistical Mechanics books have one very long chapter on thermodynamics. I always thought that was not the right thing because I am going to here study statistical mechanics. Students should learn something new. Statistical mechanics gives me the values of thermodynamic quantities that is an important input that makes sense.

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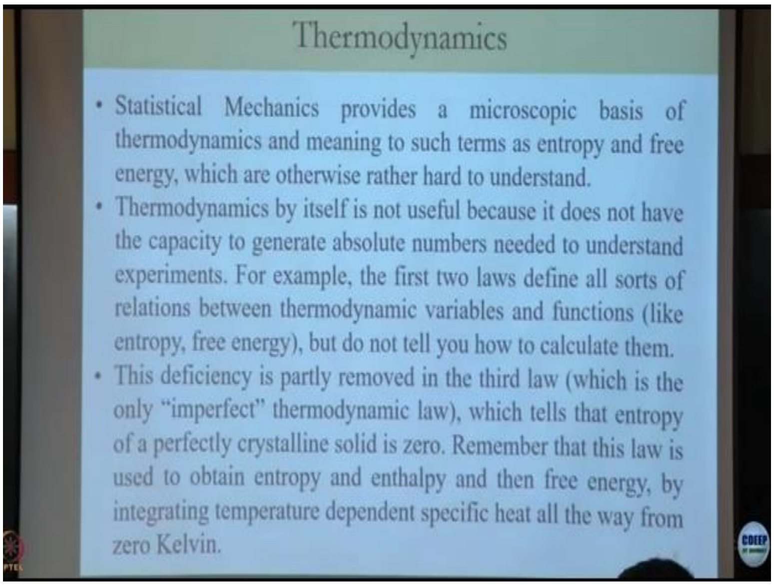

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Let us quickly go through the laws. So you know, $\Delta E = q + w$, q is the heat. So if you are going from one state to another state then internal energy changes ΔE and this ΔE is a state function (a function of the state does not depend on the path) but these two heat and work depends on the path. Now, this is a very interesting law, change of internal energy sum of two path functions.

So it is a constraint. I am interested actually in a steam engine. I think that you guys have not seen this old steam engine, we travelled on this railway. Usually, there are two guys in the engine section and one putting coal into the fire and boiler and all these things water going and that was the force turning over the engine. So in all these things, heat was generating the work.

But one important thing is that it is not easy to calculate the accessible work. There are certain problems. But the major problem is that, this is one equation but we have two unknowns. You know I want to have a relation between q and w but this equation gives other than that q and w; I can vary any way I want but I do not know anything more than that but they have to be together, they have to be conserved. So, one equation, two unknown.

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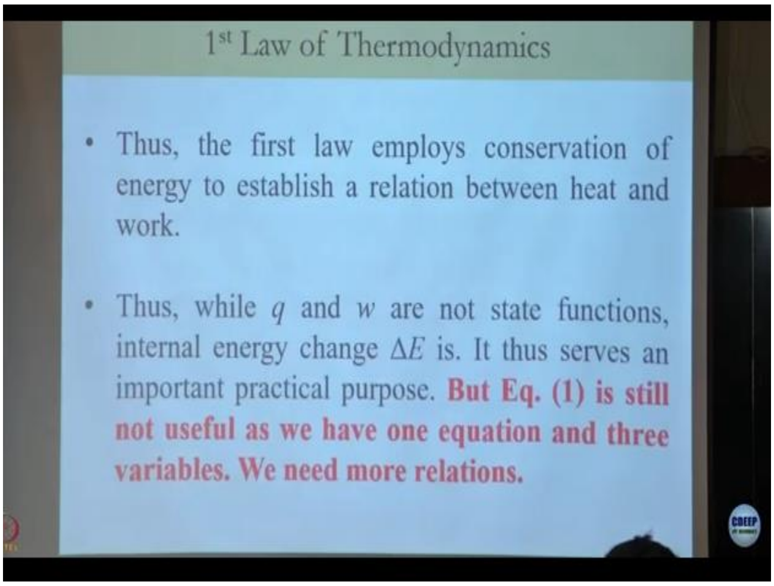

1st Law of Thermodynamics

- Thus, the first law employs conservation of energy to establish a relation between heat and work.
- Thus, while q and w are not state functions, internal energy change ΔE is. It thus serves an important practical purpose. **But Eq. (1) is still not useful as we have one equation and three variables. We need more relations.**

This equation is not useful as you have 1 equation and 3 variables. ΔE, say I can measure but they are still I have 2 things. So this is very important limitation of the first law of thermodynamics that it does not let you do anything. So important thing is that I want to have the relation between q and w; that then took a long time; that is the one, that whole generation of scientists did. Carnot engine and all these things were just to get a relation between q and w.

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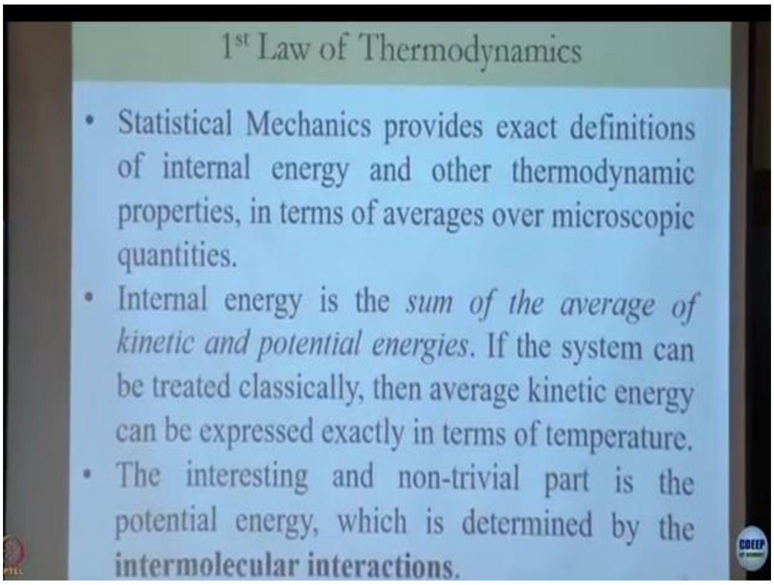

1st Law of Thermodynamics

- Statistical Mechanics provides exact definitions of internal energy and other thermodynamic properties, in terms of averages over microscopic quantities.
- Internal energy is the *sum of the average of kinetic and potential energies*. If the system can be treated classically, then average kinetic energy can be expressed exactly in terms of temperature.
- The interesting and non-trivial part is the potential energy, which is determined by the **intermolecular interactions**.

So, well, Statistical Mechanics provides exact definitions, that is not too important right now. We have to do in terms of intermolecular interactions. Internal energy is the sum of kinetic and potential energies. So, Statistical Mechanics gives you certain tips into these quantities like what is energy! It does not tell you about q and w.

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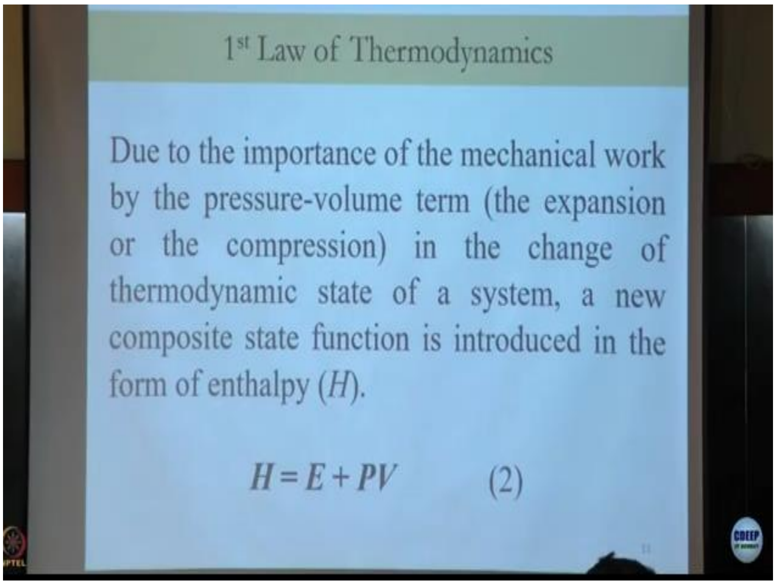

1st Law of Thermodynamics

Due to the importance of the mechanical work by the pressure-volume term (the expansion or the compression) in the change of thermodynamic state of a system, a new composite state function is introduced in the form of enthalpy (H).

$$H = E + PV \qquad (2)$$

I will come back to that. One thing we separate out is enthalpy because there is mechanical work which is thermodynamics. We introduced the enthalpy, $H = E + PV$.

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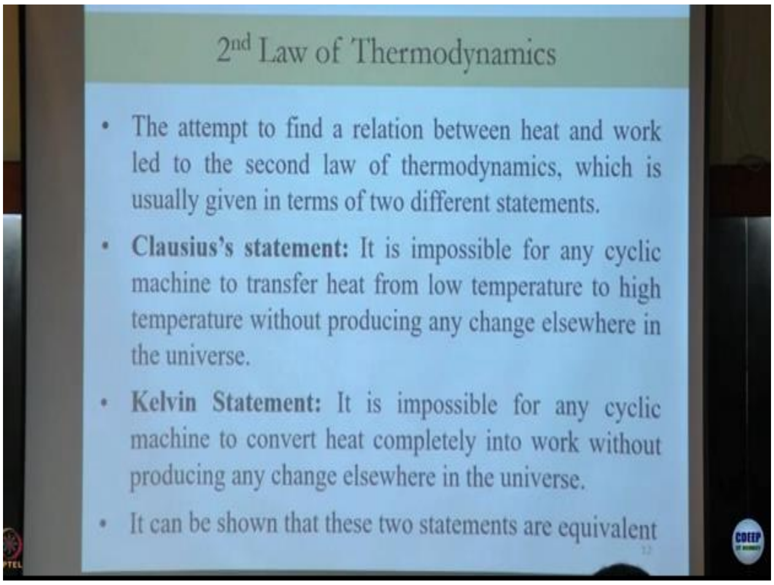

2nd Law of Thermodynamics

- The attempt to find a relation between heat and work led to the second law of thermodynamics, which is usually given in terms of two different statements.
- **Clausius's statement:** It is impossible for any cyclic machine to transfer heat from low temperature to high temperature without producing any change elsewhere in the universe.
- **Kelvin Statement:** It is impossible for any cyclic machine to convert heat completely into work without producing any change elsewhere in the universe.
- It can be shown that these two statements are equivalent

I will come back to intermolecular interaction that was a digression and I do not want to do that right now. So I continue with the second law of thermodynamics. Whole idea of Clausius, Clapeyron, Thomson and all these people where to find the relation between heat (q) and work(w) and there are several statements like Clausius statement, Kelvin statement etc. See they are trying to find a relation between heat and work.

Clausius statement: "it is impossible for any cyclic machine to transfer heat from low temperature to high temperature without producing any changes elsewhere in the universe." Kelvin statement: "it is impossible for any cyclic machine to convert heat completely into work without producing any changes elsewhere in the universe." That was the dream to convert heat completely into work. So all of these are statements of negation. You know all of these things, you have done at least five times as I am telling you.

So these statements are equivalent as all of you know but all of them are statements of what you cannot do. But then what we can do? One thing that everybody was interested in how to find the maximum amount of work out of the heat. I have ΔE conserved. Now, I want a relation between q and w which satisfies that particular way of doing which Maxwell did. In those days, in the Industrial Revolution, there is tremendous work done on the efficiency and you know the efficient of Carnot engine.

It was very practical. They wanted to increase the efficiency of a steam engine and steam engine was there everywhere like in train, in ships.

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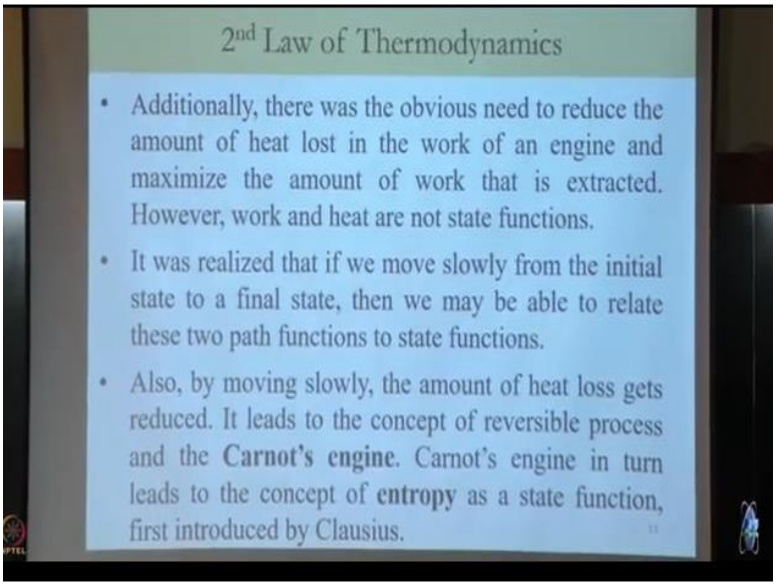

2nd Law of Thermodynamics

- Additionally, there was the obvious need to reduce the amount of heat lost in the work of an engine and maximize the amount of work that is extracted. However, work and heat are not state functions.
- It was realized that if we move slowly from the initial state to a final state, then we may be able to relate these two path functions to state functions.
- Also, by moving slowly, the amount of heat loss gets reduced. It leads to the concept of reversible process and the **Carnot's engine**. Carnot's engine in turn leads to the concept of **entropy** as a state function, first introduced by Clausius.

Then what the one thing they realized that, well, they cannot find a relation between heat and work because both are path functions. But if they go so slowly from one state to other state, then they will be able to do something. That means if they think, they picked you to move so slowly (that is the reversible path), you can go from one state to other state and along the path, in such case, Carnot showed that I can introduce the entropy.

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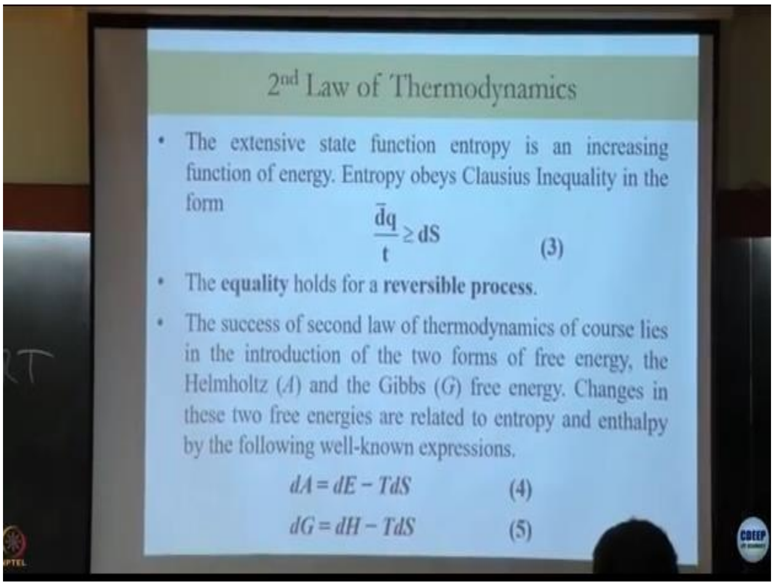

2nd Law of Thermodynamics

- The extensive state function entropy is an increasing function of energy. Entropy obeys Clausius Inequality in the form

$$\frac{đq}{t} \geq dS \qquad (3)$$

- The **equality** holds for a **reversible process**.
- The success of second law of thermodynamics of course lies in the introduction of the two forms of free energy, the Helmholtz (A) and the Gibbs (G) free energy. Changes in these two free energies are related to entropy and enthalpy by the following well-known expressions.

$$dA = dE - TdS \qquad (4)$$

$$dG = dH - TdS \qquad (5)$$

So this is the thing all of you know that $\frac{đq}{T} \geq dS$. This is the Clausius inequality. So important thing here is the equality $\frac{đq_{rev}}{T} = dS$ and this equality holds for reversible process.

The equality is the one that then allows us to derive all the free energy. Now why free energy is so important; can anybody tell me why free energy is so important?

Why so much work? Carnot Engine, two three chapters of thermodynamics and at the end of the day we get the free energy, why so much attempt was made to get the free energy? Absolutely, this is the energy free to work. So the part that we cannot do anything is entropy. Now you understand the whole second law, so much work by so many smart people was done to derive an equation of this kind under different conditions.

So the two new things, somewhat new things, that I have told you (a) the first law gives you relation between work and heat but it is one equation, two unknown and so I need a relation between *q* and *w* and then (b) there is huge amount of work went into all these smart people in Europe try to get the relation. They cannot do it if it is irreversible because it is arbitrary.

But if you go infinitely slowly by going from one equilibrium state to another equilibrium state to another equilibrium state, piece together then you get what is Clausius equality part of the inequality. Inequality part is not too useful other than sometimes in irreversible thermodynamics but not in equilibrium thermodynamics. In equilibrium thermodynamics, it is the equality part that is important and that ultimately leads you to these things.

And this is the energy change, this is the one that is getting lost and so this is the one that is free to do work. Now I have an upper bound of the efficiency because now I know how much work I can extract from the internal energy. So this is just one free energy surface that I will talk later.

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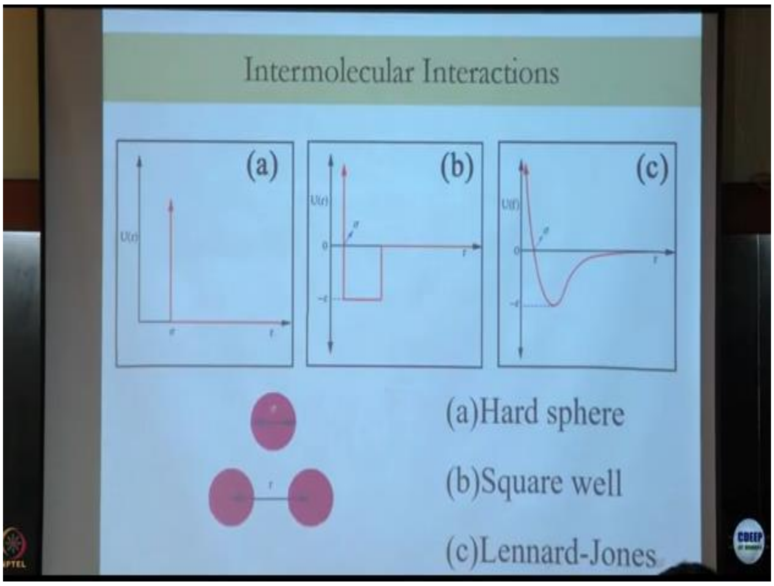

Intermolecular Interactions

(a)Hard sphere

(b)Square well

(c)Lennard-Jones

Let me go back one important thing of statistical mechanics that is what started with Van der Waals and Boltzmann, not that much by Maxwell, that the two particles interact. So intermolecular interaction plays an essential role in our understanding because in both physics and chemistry (particularly in chemistry) we want to think of two molecules that are interacting, so that all the properties whether specific heat or the density or any dielectric constant or conductivity, all those are determined by the intermolecular interactions.

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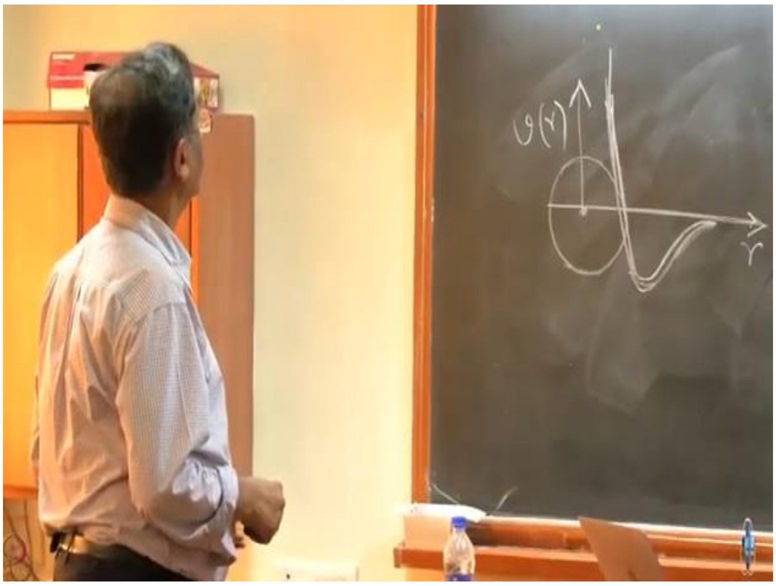

That means two molecules are coming together. When there is one molecule I put it at the centre of my coordinate system then I bring one more molecule and that is the interaction. When the overlap here, then there is a large repulsion. So basic part then and then , there is an attraction because of electronic fluctuations of wavefunctions that we are not going to go into. So this is the separation between two particles and this is what is called intermolecular interaction.

So then this whole idea of statistical mechanics is that if I give you this intermolecular interaction, starting from this intermolecular interaction can you give us everything else? Can you give us this specific heat? Can you give us the phase transitions? Can you tell us why water freezes into ice at zero degree centigrade and goes into vapour at 100 degree centigrade? So all these things, which statistical mechanics claims, was the dream of Boltzmann that starting with a bare potential one can get all the properties.

There are three things given here, this is the one that I drew here is called Lenard-Jones. This is a hard sphere of the billiard model, there is no interaction till they touch and when they touch potential goes to infinity. Another one which people sometimes use is this, called square well; that means there is an attraction, then 0 and then the harsh repulsive potential. Interestingly such a simple potential, one of the simplest possible potential describes liquid to crystal transition fairly accurately.

And that captures the essence of freezing, however, surprising that may appear to you. This is the one and these two would describe gas to liquid, liquid to crystal many, many other things. For example, if I want to do water then for water there will be somewhat more complex potential.

So now think of the following that we have done little bit of thermodynamics. First law that is essentially formulated by Boyle; Second law by many people, give it to entropy and free energy. We have our agenda fixed and well there is not one agenda. There are many agenda, one of them is that how can I calculate the properties of a matter and to start with the property calculation of properties of matter. If I want to calculate entropy from the first principle, I want to calculate the specific heat, I want to calculate say conductivity or isothermal compressibility or a phase transition. What is the latent heat of freezing? What is it latent of evaporation? I want to calculate, what is the binary property of water and ethanol? And why there is a eutectic point at 95% of the water-ethanol mixture. When we add little DMSO to Lysozyme, why its cells walls break; breaking of C-O bond in Lysozyme bond get accelerated by a factor of 3? Why protein folds to its structure negative state?

So Statistical Mechanics has this agenda, the grand agenda, that you give me this interaction potential and I give you answers to all the questions. That is the basic idea of Statistical Mechanics and it can be broadly divided into two parts equilibrium a non-equilibrium. What we are going to say in the beginning is equilibrium Statistical Mechanics because if you do not do equilibrium Statistical Mechanics, you would not be able to do non-equilibrium Statistical Mechanics.

You need to know how particles interact just like Gibbs did; gave away the path of Boltzmann because he realized equilibrium is much simpler or rather there is a simpler way to do the equilibrium Statistical Mechanics. So that is the vision and brilliant understanding of Willard Gibbs. By that time of Willard Gibbs and by the time of Boltzmann and of course Einstein they already had this agenda. They knew that you give me an interaction potential then the idea was that how simple it can be?

It turned out, as I told, gas to liquid cannot be explained by that, but liquid to crystal can be explained by these very simple potentials. There are many potentials which can explain both gas to liquid and liquid to crystal. Now, how do you get the interaction potential? I can give you a flow chart that is you start from quantum mechanics and quantum mechanics gives you the interaction potential. Once you get the interaction potential, then you get all the properties from the interaction potential.

I am not really lying to you and I am not bragging. I am not saying but that is really the agenda and promise of statistical mechanics which has been largely fulfilled. This realization of the promises but it took more than a hundred years, particularly advances of computer simulation. Because many of the equations which Boltzmann could not do, or Gibbs could not do, we can do it with computer simulations.

Now, of course, you know you always have to do analytical work because these analytical models tell you how to go, then you do more complex things. So again to formulate, starting from Boltzmann who introduced intermolecular potential, Boltzmann considered this potential. In his case, it was a hard disk or hard-sphere, billiard model, only two of them he considered.

He could not consider three as I said even now three-body problem is unsolved analytically. Now, I think I will stop here today the interaction potential business and then subsequently we will start from the Statistical Mechanics, as in Quantum Mechanics we start with Schrodinger equation, in Statistical Mechanics we need certain postulates.

There are two postulates of Statistical Mechanics. As Einstein repeatedly said that the simplicity of a theory is based on how few assumptions you can make and then how far you can go! The Statistical Mechanics, with a goal that starting with an intermolecular potential to go to thermodynamic properties or realistic properties, builds only on two postulates and one hypothesis. In the next class, we will do it.

What I have done today, gave the history and did the thermodynamics. In the next class, I will start with the postulates of Statistical Mechanics. One of the postulates was done by Boltzmann which is the time average second postulate was done by Willard Gibbs which is the ensemble and these two combined with the help of hypothesis and that leads to the development.

So the way it happens is that you have the postulates and the hypothesis that allow you to go definition of certain quantities called partition functions which immediately gives you thermodynamic properties. So after that, we will do certain simple models just like in Quantum Mechanics, like we do particle in a box, we do ideal gas, we will do harmonic oscillator.

Just like in Quantum Mechanics we do harmonic oscillator, here we will also do harmonic oscillators. That you will see. We will go to the Sackur-Tetrode equation and many equations which is still used today. Then you do rigid rotator same you do in quantum mechanics, we do in statistical mechanics the rigid rotator. So you will find that the certain things, the step-by-step things of Statistical Mechanics parallel Quantum Mechanics.

And the step by step thing was done by Schrodinger in the quantum mechanics. It was Willard Gibbs who did all these things for Statistical Mechanics. And in the process, you will see again we will derive ideal gas law, we will be deriving something like Van der Waals but now with an intermolecular potential. Van der Waals had an imperfect and incomplete intermolecular potential but we will now be able to do in a more complete way.

So now I think I will stop here today but I will take some questions……
No this is one, you know, pure equilibrium means you do not go anywhere. Pure equilibrium means you stay there. So here you are making infinitely small changes, you are making so small change that you can talk like the concept of virtual work you do, a very small amount of thing and you say that I can apply equilibrium principle.

So you are not at equilibrium. You are inducing a change but change is done such a small step that you can say okay I am going from A1 to A2 but I can now talk of thermodynamics, I can talk of equilibrium principles inducing the small change. So it is like that you going from one to next and you do by infinitesimal change. Now you the next step you are doing from say step 1 to 2, then step 2 to 3, all of them piece together give you it which is not equilibrium but is reversible.

So if you do a reversible change then I think I do not have any control anymore. If I will go for a big jump or finite jump from one state to other state, then all I have is that relation; go back to your first law and you have an inequality but inequality does not help you because it is ill-defined.

So you strive to get the quality. It was derived in classical mechanics we have this virtual work. We do very small amount of work but then we use thermodynamic principle to get that. So it is exactly that somewhat funny concept that you are doing in infinite change slowly to that unique path which is the reversible path. It is confusing all the way.

It is what Carnot showed by this reversible path that you can show $\frac{đq_{rev}}{T}$ is independent of path. There is a beautiful proof and the only place where such a good proof is given is in Castellan where he showed that you can piece together these and get a state function. So the whole idea is that $\frac{đq_{rev}}{T}$ is a state function for the universal path that is the Carnot engine.

And then Carnot engine again I have to do the thermodynamics which I do not want to do but when Carnot engine was that next proof came that $\frac{đq_{rev}}{T}$ over a cyclic path.