Thermodynamics for Biological Systems: Classical and Statistical Aspects
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Lecture - 2
Review contd.,

Welcome! Let us continue with our review of some principles in Thermodynamics that we started in the previous lecture.

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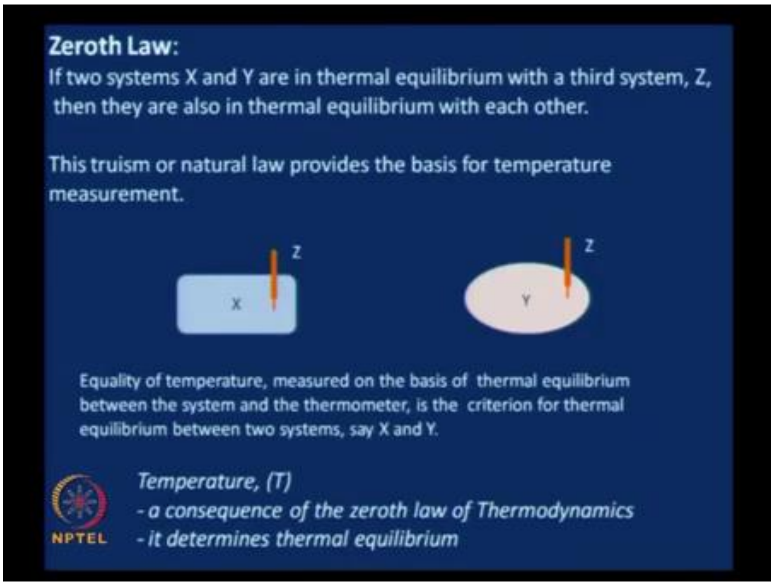

Zeroth Law:
If two systems X and Y are in thermal equilibrium with a third system, Z, then they are also in thermal equilibrium with each other.

This truism or natural law provides the basis for temperature measurement.

Equality of temperature, measured on the basis of thermal equilibrium between the system and the thermometer, is the criterion for thermal equilibrium between two systems, say X and Y.

Temperature, (T)
- a consequence of the zeroth law of Thermodynamics
- it determines thermal equilibrium

Now, let us look at the three laws that you would have already studied – the three laws of Thermodynamics. The zeroth law first. The zeroth law states that if two systems, let us say X and Y, are in thermal equilibrium with a third system Z, then they are also in thermal equilibrium with each other. A very simple statement. And, it is actually a truism – we need not go about proving it by other means. To repeat, there are two systems, let them … let us call them X and Y. If they are in thermal equilibrium with the third system, let us say Z, then they are also in thermal equilibrium with each other.

This zeroth law actually, provides the basis for temperature measurement. As it is shown here, this is the substance X or system X, this is the system Y, and they are individually in thermal equilibrium with this Z here. The Z is the thermometer, which is used to measure the temperature of X or of Y. If X is in thermal equilibrium with Z and Y is also in thermal equilibrium with Z, then X and Y are in thermal equilibrium with each other.

Let us consider the condition that, we just said; X in thermal equilibrium with Z and Y in thermal equilibrium with Z – which means that the reading on thermometer would be the same. And therefore, the equality of temperature measured on the basis of thermal equilibrium between the system and the thermometer is the criterion for thermal equilibrium between the two systems say, X and Y. Therefore, temperature T can be considered as a consequence of the zeroth law of Thermodynamics. And, it is the one that determines thermal equilibrium.

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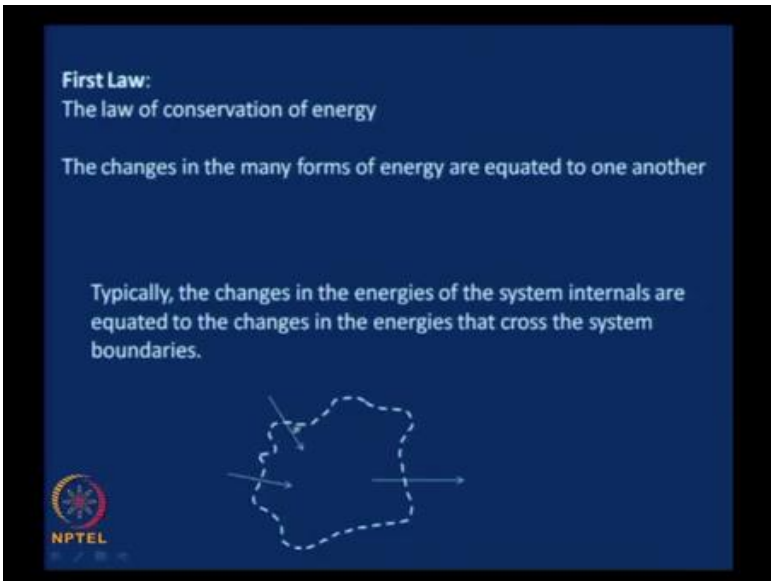

First Law:
The law of conservation of energy

The changes in the many forms of energy are equated to one another

Typically, the changes in the energies of the system internals are equated to the changes in the energies that cross the system boundaries.

Now, let us look at first law. The first law is nothing but the law of conservation of energy. The changes in many forms of energy are essentially equated to one another in the first law. It is nothing more to first law. Typically, the changes in the energies of the system parts are equated to each other. For example, the changes in the energies of the system internals are equated to the changes in the energies of the system that cross the system boundaries. This is the system that is indicated by the dotted line here. The energies that cross the system boundaries - these two are coming in and this is going out, and so on. The changes in energy inside the system are related to the changes that cross the system boundaries.

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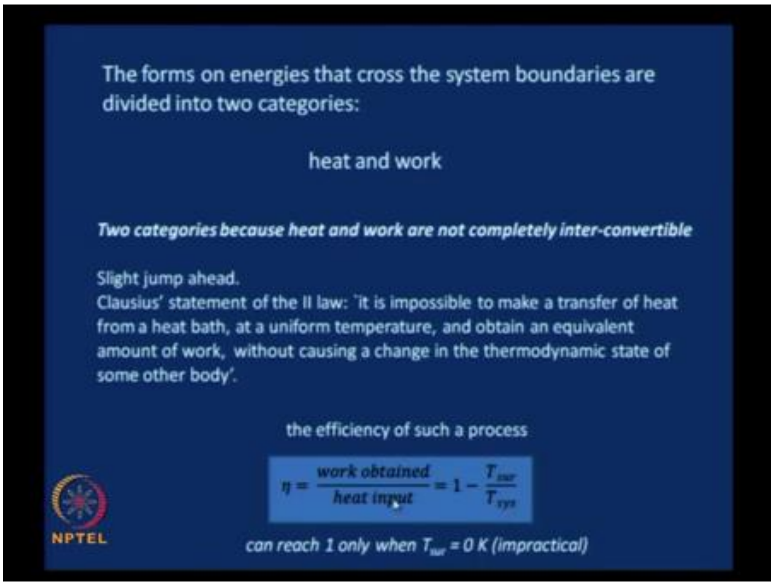

The forms on energies that cross the system boundaries are divided into two categories:

heat and work

Two categories because heat and work are not completely inter-convertible

Slight jump ahead.
Clausius' statement of the II law: 'it is impossible to make a transfer of heat from a heat bath, at a uniform temperature, and obtain an equivalent amount of work, without causing a change in the thermodynamic state of some other body'.

the efficiency of such a process

$$\boxed{\eta = \frac{\textit{work obtained}}{\textit{heat input}} = 1 - \frac{T_{sur}}{T_{sys}}}$$

can reach 1 only when $T_{sur} = 0$ K (impractical)

There are two forms of energies that cross the system boundaries. Or, the forms of energies that cross the system boundaries are actually divided into two categories: heat and work. Why do we need to divide these into two categories, heat and work? It is, essentially because heat and work are not completely inter-convertible. They are… you cannot convert heat into work completely. And therefore, you need to consider them as two separate entities. To understand this a little better, let us likely jump ahead. We are going to look at this later. But, since this is the review, you would have already looked at it, we can jump ahead to understand this a little better. The Clausius statement of the second law is as follows: "it is impossible to make a transfer of heat from a heat bath at uniform temperature, and obtain an equivalent amount of work, without causing a change in the thermodynamic state of some other body". That is the complete statement of the second law. Let me read it again to get across a little better. It is impossible to make a transfer of heat from a heat bath at the uniform temperature and obtain an equivalent amount of work, without causing a change in the thermodynamic state of some other body. The efficiency of such a process is given by (work obtained)/ (heat input). And, you would already seen in the previous classes that can be related to 1 minus the ratio of the surroundings temperature to the system temperature.

The efficiency can reach 1, only when the surroundings temperature is 0 Kelvin. If you recall, these temperatures are in Kelvin. And, reaching 0 kelvin is impractical. And therefore, it is impossible to completely convert heat into work. And, that is the reason we need to consider them as two separate quantities.

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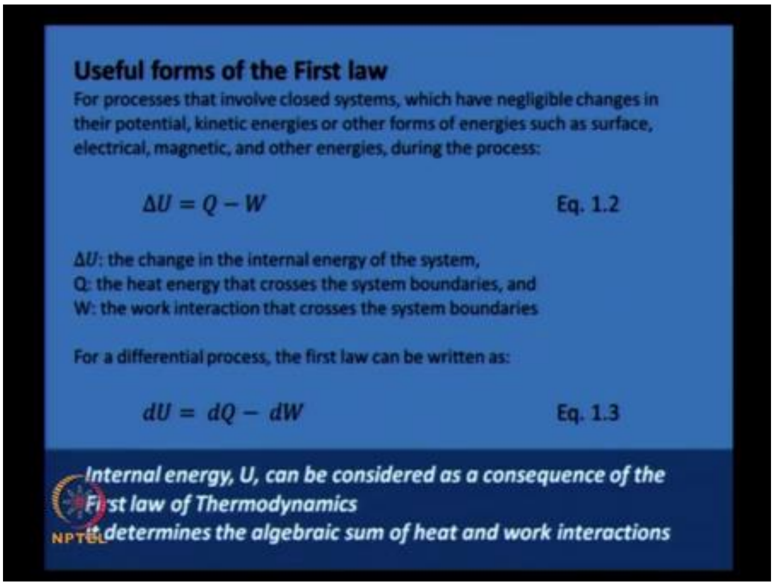

Useful forms of the First law

For processes that involve closed systems, which have negligible changes in their potential, kinetic energies or other forms of energies such as surface, electrical, magnetic, and other energies, during the process:

$$\Delta U = Q - W \qquad \text{Eq. 1.2}$$

ΔU: the change in the internal energy of the system,
Q: the heat energy that crosses the system boundaries, and
W: the work interaction that crosses the system boundaries

For a differential process, the first law can be written as:

$$dU = dQ - dW \qquad \text{Eq. 1.3}$$

Internal energy, U, can be considered as a consequence of the First law of Thermodynamics
It determines the algebraic sum of heat and work interactions

The useful form of the first law, for us at least, is to begin with, when it is applied to closed system. For a closed system, when there are negligible changes in other kinds of energies, such as potential energies, kinetic energies, surface energies, magnetic energies and other kinds of energies, then you can relate the change in the internal energy (delta U) to the heat interaction across the system boundaries and the work interaction across the system boundaries.

$$\Delta U = Q - W$$

is a useful statement of the first law for us. This ΔU is a change that occurs inside the system, Q and W are the energy interactions across the system boundaries. What happens inside is being related to what crosses in the system boundaries. For a differential process, we can write the first law as

$$dU = dQ - dW$$

where these d represent the differentials. Therefore, internal energy, U, can be considered as a consequence of the first law of Thermodynamics. It essentially determines the algebraic sum of the heat and work interactions in a process or heat and work interactions for a system.

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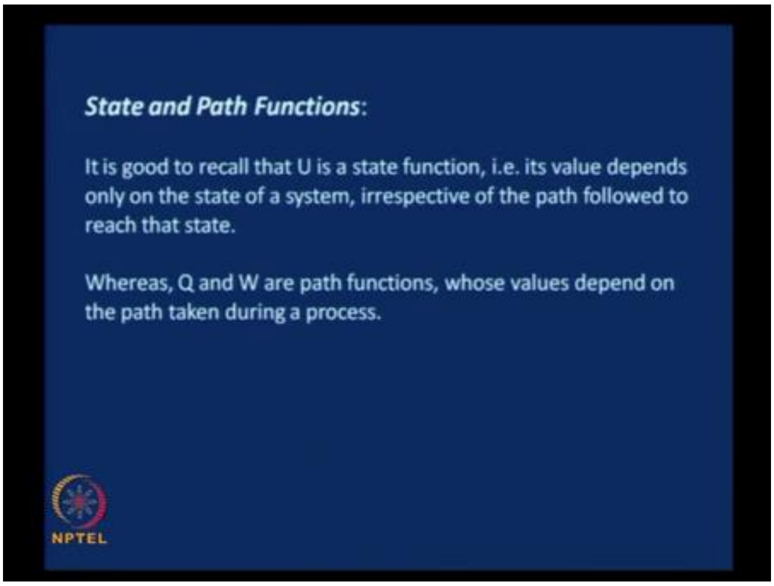

State and Path Functions:

It is good to recall that U is a state function, i.e. its value depends only on the state of a system, irrespective of the path followed to reach that state.

Whereas, Q and W are path functions, whose values depend on the path taken during a process.

We also need to understand, what state and path functions are, very clearly. You would have learnt that the internal energy is a state function. In other words, its value depends only on the state of the system, irrespective of the path followed to reach that state. For example, if the system is undergoing a process from state 1 to state 2, whether the path of the processes one way or the other way, and so on and so forth. By path, we mean the set of intensive variables changing and so on and so forth. Whether, the path is one or the other, as long as it is a state function, the value of that function depends only on the state of the system. The value of internal energy at state 1 would be the same and the value of internal energy at state 2 would be the same; irrespective of the path taken to reach 2 from 1.

Whereas, the heat interaction across a system boundary and the work interaction across a system boundary are path functions, whose values depend on the path taken during the process. This is a very important concept. In fact, we will be visiting this again and again. And, at an appropriate time, I will tell you an important aspect of this, which helps us significantly in developing relationships in Thermodynamics.

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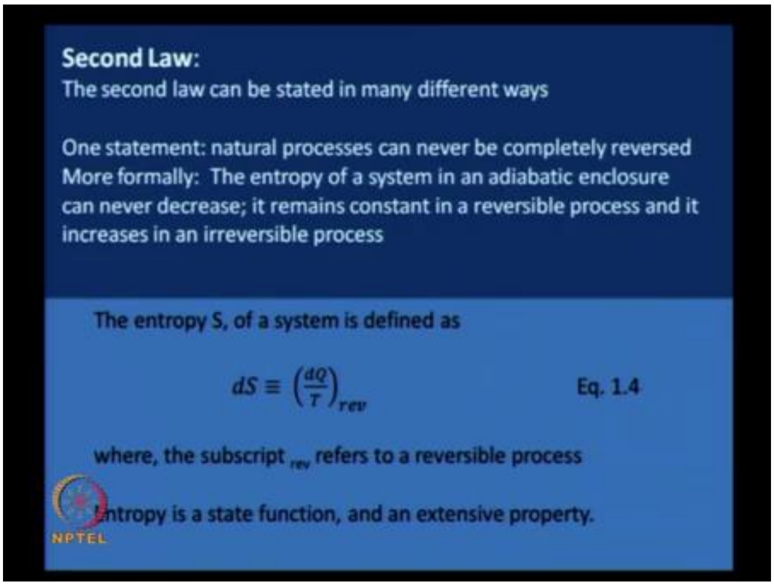

Second Law:
The second law can be stated in many different ways

One statement: natural processes can never be completely reversed
More formally: The entropy of a system in an adiabatic enclosure can never decrease; it remains constant in a reversible process and it increases in an irreversible process

The entropy S, of a system is defined as

$$dS \equiv \left(\frac{dQ}{T}\right)_{rev} \qquad \text{Eq. 1.4}$$

where, the subscript $_{rev}$ refers to a reversible process

Entropy is a state function, and an extensive property.

Now, let us look at second law. The second law can be stated in many different ways. And, one of the statements is as follows. Natural processes can never be completely reversed; is, one way of stating it. More formally, the entropy of a system in an adiabatic enclosure can never decrease; it remains constant in a reversible process and it increases in an irreversible process. That is another formal way of stating it. The entropy of the system, as you would know already is defined as

$dS = \frac{dQ}{T}$ in a reversible process.

As you know Q is a path function. If dQ reversible by T is a way of stating … is a way of defining entropy dS.

Entropy is a state function, and is an extensive property. State function depends only on the state of the system and not on the path taken to reach the system. Extensive property means that, more the amount of the material there, higher the value of the property.

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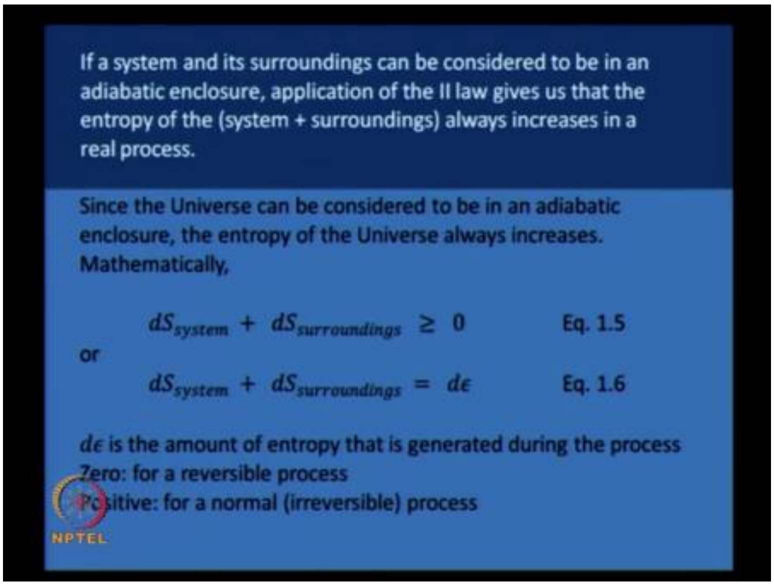

If a system and its surroundings can be considered to be in an adiabatic enclosure, application of the II law gives us that the entropy of the (system + surroundings) always increases in a real process.

Since the Universe can be considered to be in an adiabatic enclosure, the entropy of the Universe always increases. Mathematically,

$$dS_{system} + dS_{surroundings} \geq 0 \qquad \text{Eq. 1.5}$$

or

$$dS_{system} + dS_{surroundings} = d\epsilon \qquad \text{Eq. 1.6}$$

$d\epsilon$ is the amount of entropy that is generated during the process
Zero: for a reversible process
Positive: for a normal (irreversible) process

If a system and its surroundings can be considered to be in an adiabatic enclosure, very important, please note this; if the system and its surroundings can be considered to be in an adiabatic enclosure, application of the second law gives us that the entropy of the system of both the system and the surroundings, always increases in a real process.

Now, the universe itself can be taken to be in an adiabatic enclosure; because universe contains everything. It is nothing beyond the universe. So, the whole thing can be considered to be in an adiabatic enclosure, which means there is no heat interaction. For the universe as a whole, the entropy of the universe always increases. You can state this mathematically as the changes in entropy of the system plus the changes in entropy of its surroundings should always be greater than or equal to 0. And, if you want to replace this by an equality, we say that the change in entropy of the system, dS of the system and dS of the surroundings equals d epsilon. d epsilon is the amount of entropy that is generated during the process. It is, of course 0 for a reversible process. As we know, as we saw earlier, the definition of reversible process is positive for a normal or an irreversible process.

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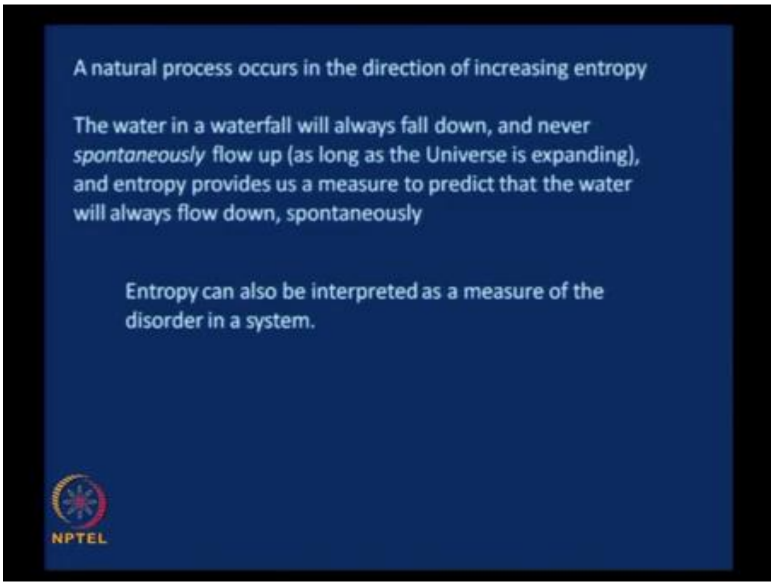

A natural process occurs in the direction of increasing entropy

The water in a waterfall will always fall down, and never *spontaneously* flow up (as long as the Universe is expanding), and entropy provides us a measure to predict that the water will always flow down, spontaneously

Entropy can also be interpreted as a measure of the disorder in a system.

A natural process occurs in the direction of increasing entropy. We have already seen that, if you take the entire universe as a system, the entropy of the system has to increase. Further, as long as we have an expanding universe, the natural process will always happen in the direction of increasing entropy. The water in a water fall will always fall down and never spontaneously flow up, and the entropy provides us a measure to predict whether the water will flow down – to tell that, the water will flow down spontaneously. Always flow down spontaneously.

Entropy can also be interpreted as a measure of the disorder in the system. It is a concept; order, disorder. Order: everything nice and packed, and so on and so forth. Disorder: not so packed, random not so ordered.

The biological cell as we all know is highly organised. There are many processes taking place in it, but the biological cell itself is highly organised. Is that does that biological cell contradict the second law?

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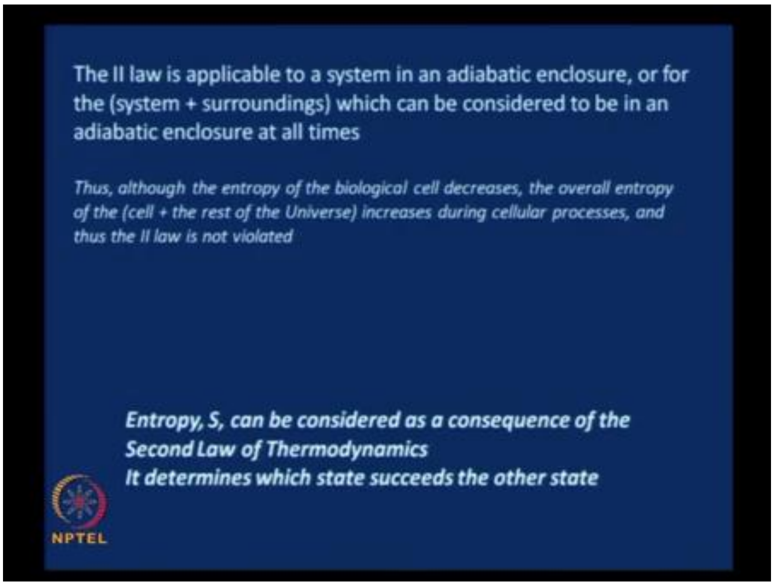

The II law is applicable to a system in an adiabatic enclosure, or for the (system + surroundings) which can be considered to be in an adiabatic enclosure at all times

Thus, although the entropy of the biological cell decreases, the overall entropy of the (cell + the rest of the Universe) increases during cellular processes, and thus the II law is not violated

Entropy, S, can be considered as a consequence of the Second Law of Thermodynamics
It determines which state succeeds the other state

The answer is it does not.

So far, we have not come across something that violates second law. That is because of the following reason. The second law is applicable to a system in an adiabatic enclosure, or for … if you take the system and surroundings as a whole, which can be considered in an adiabatic enclosure at all times. Therefore, although the biological … the entropy of the biological cell decreases as employed in the higher order in a biological system, the overall entropy of the cell and the rest of the universe, increases during a cellular process. And therefore, the second law is not violated.

Entropy S; entropy as indicated by the letter S, denoted by the letter S, can be considered as a consequence of the second law of Thermodynamics. It determines which state succeeds the other state.

Now let us look at what Continuum means. We said that a Continuum is essential for the application of classical Thermodynamics, and therefore let us see what actually Continuum means.

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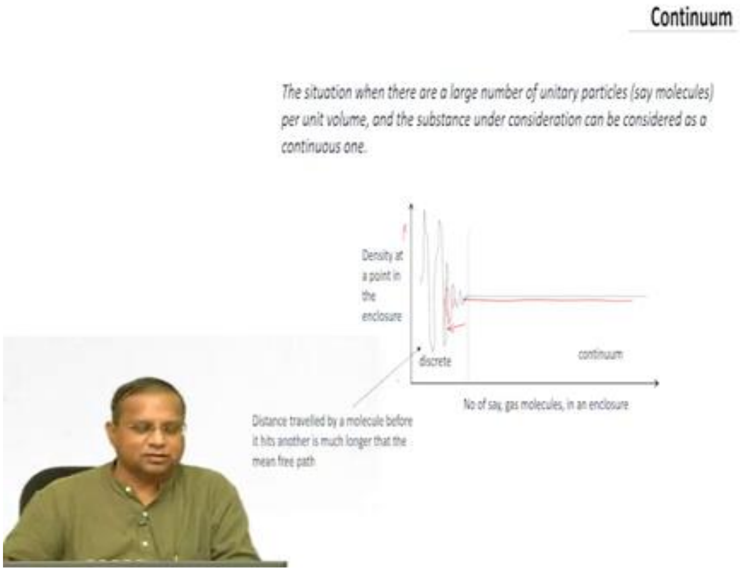
Continuum

The situation when there are a large number of unitary particles (say molecules) per unit volume, and the substance under consideration can be considered as a continuous one.

Distance travelled by a molecule before it hits another is much longer that the mean free path

The Continuum is a situation when there are large numbers of unitary particles. They could be molecules say, per unit volume, and the substance under consideration can be considered as a continuous one. That is saying it in words, but what does it actually mean? It is something like this: If you look at the plot of density, it is the density here … given here … and this is the density at a point in an enclosure that is containing a gas, let us say. And, let us say this X-axis gives you the number of gas molecules in the enclosure.

When the number of gas molecules are large, and we are measuring the density at a point, then the gas is said to be a normal gas; properties are dependent on pressure, temperature, and so on. Therefore, you expect the density of gas to be reasonably constant. That is this region here. And by doing this I mean we are reducing the number of molecules in the enclosure as we go from here to here, say by pumping out through vacuum pump, or something like that.

When we reach a certain point, the density at that point is going to start to vary, because the mean free path of the gas molecules is not going to be representative of the normal gas conditions. The number of molecules have become so small per say, unit volume that the mean free path and other aspects are not going to be appropriate to consider it as the continuous gas. And, therefore the density at the point is going to vary significantly, and the variation is going to go up and up as you go … as you reduce the number of molecules more and more in the curriculum. The number of gas molecules actually going to go on reducing in the enclosure … less and less number of molecules in the enclosure. The … this part where, let us say, the properties are continuous, the mean free path is appropriate as given in a normal gas so and so forth. The mean free path is the distance travelled by the molecules before an average collision. This is the region where the Continuum is applicable or this is the Continuum region.

This is the region where the classical thermodynamics is applicable. Classical Thermodynamics is not applicable in this region where the principle of continuum is not applicable. However the statistical thermodynamics is applicable to the entire region and that part will be taken up in the last ten hours of this course by Professor Sanjb Senapati.

I think this is good enough a … review …

Just to make it formal, distance travelled by a molecule before it hits another molecule – that is the mean free path – is much longer than the standard mean free path of the gas. And, that is what happens in this region where you need statistical thermodynamics. And Statistical Thermodynamics principles are highly useful in analysing, understanding interactions between biological molecules, DNA, proteins, and so on and so forth. That is the reason why it is important to know this at an undergraduate level.

I think this information is … whatever we have covered over the past 2 lectures … is good enough as a review of the background information. When we begin with the next lecture we will get into the actual material for this course.