Advanced Thermodynamics and Molecular Simulations
Prof. Prateek Kumar Jha
Department of Chemical Engineering
Indian Institute of Technology-Roorkee

Lecture - 01
Introduction to the Course

Hello, all of you. So a very warm welcome to this course on Advanced Thermodynamics and Molecular Simulations. Myself, Dr. Prateek Kumar Jha. I am a faculty in the Department of Chemical Engineering at IIT Roorkee and in today's lecture, I will introduce you to this particular course and talk about the outline and what we will cover in this course and then, I will touch upon the motivation for studying this course and thermodynamics in general.

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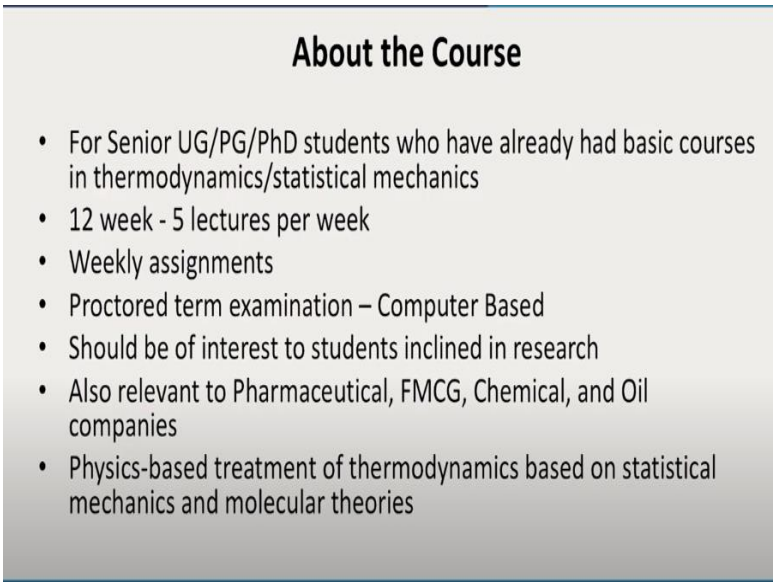

So as you probably have seen this course is for senior undergrads and post grad and PhD students in chemical engineering and other disciplines who has done some basic course in thermodynamics or statistical mechanics. For chemical engineering students you should have done either one or two courses in your first or second year and other students may have done also in your undergrad curriculum.

So this course is going to be of 12 weeks. We will have five lectures per week. I will give you weekly assignments and then we will have a proctored end-term examination.

This course should be of particularly interest to those who are interested in research. But this would also be useful to people working in industry or interested in going towards industry jobs, particularly in the area of pharmaceuticals, FMCG, chemical and oil companies. So the basic goal of this course is to develop a physics based treatment of thermodynamics. If you have done a course on thermodynamics in your second year, that was more applied I would say, where the focus was on how thermodynamics is applied. Unlike that course, this course is going to start from molecular level principles and try to get to the point on what is the molecular basis of the thermodynamic concepts that you have already covered.

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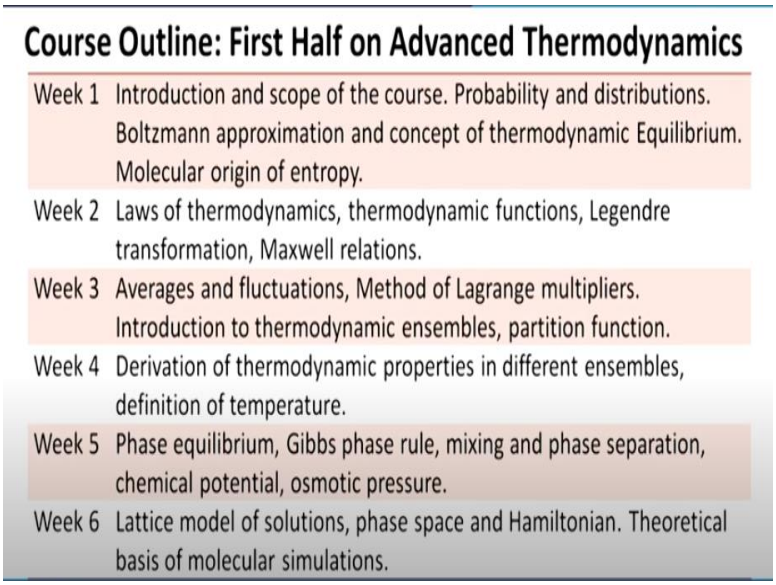

So here is the course outline. We will start with the introduction to the course and as you can see, the first half of the course is going to be on thermodynamics, I would say statistical mechanics and the second half is going to be what I call molecular simulations. So I will start with the introduction. We talk about probability distributions, we talk about the Boltzmann approximation, we come to the concept of thermodynamic equilibrium, but again trying to explain what is the molecular basis of that what is the molecular origin of entropy.

In the second week, we come to the laws of thermodynamics and show that how they are a natural outcome of molecular level principles. We talk about thermodynamic

functions, Legendre transformations and derive Maxwell relations that you have already had in undergrad, but now we are providing a molecular basis or molecular pathway to derive that equation.

Then in the next week, we will talk about the averages and fluctuations. We use the method of Lagrange multipliers. So we discuss that and then we discuss the idea of thermodynamic ensembles and the idea of partition function that is where we come to the regime of statistical mechanics and then I will tell you how to derive properties of thermodynamics in different ensembles and how do we define temperature using these kind of principles.

Then we come to the idea of phase equilibrium, we talk about mixing and phase separation, we talk about the Gibbs phase rule, we talk about the molecular origin of chemical potential and osmotic pressure and after that, we will come to the thermodynamics of solutions. We will talk about the lattice model of solutions. We talk about the idea of phase space, the idea of Hamiltonian and that will pretty much set the ground for the theoretical basis for the molecular simulations that is going to be covered in the next half of the course.

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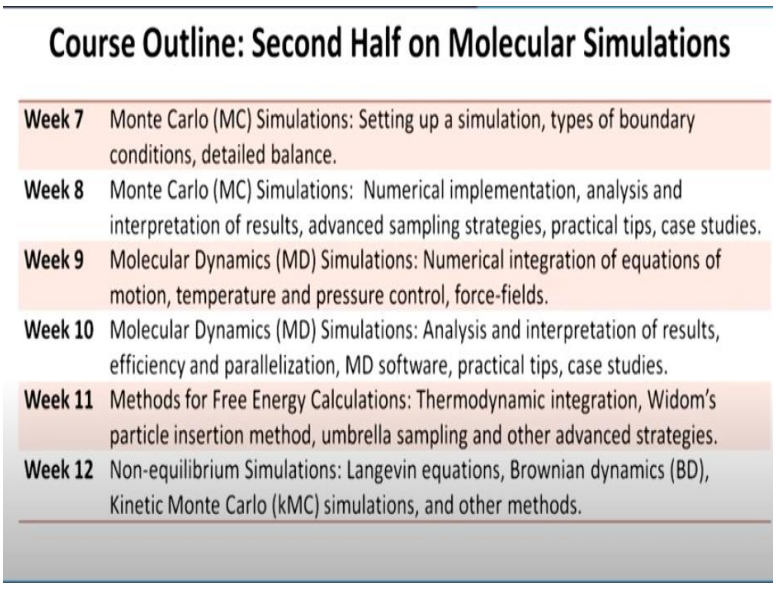

So in the molecular simulation part, we will start with the Monte Carlo simulations and we discuss how do we set up a simulation, what are the boundary conditions, how are they implemented? What is the idea of detailed balance? Then we come to the

implementation of Monte Carlo simulations. How do we analyze and interpret the results? What are some advanced strategies in sampling and then we discuss some practical tips of Monte Carlo simulations and I will discuss or go through some of the case studies in the area of Monte Carlo simulations.

After that, we will cover the molecular dynamics simulations. We talk about the numerical integration of equations of motion, the idea of temperature and pressure control, the concept of force-fields. Then again we will discuss how do we analyze and interpret results in a molecular dynamics simulations. How can I make our codes more efficient by the by using parallel computers. We talk about the software's that are used in molecular dynamics simulations and again we will end with practical tips and case studies on molecular dynamics.

And then in the last two weeks, we come to some advanced topics. Although the main focus is around Monte Carlo and molecular dynamics we will cover some advanced topics in the last two weeks, particularly we discuss free energy calculations, the concept of thermodynamic integration, the concept of Widom's particle insertion that is used to compute chemical potentials, the idea of umbrella sampling and other advanced strategies.

And finally, in the last week, we cover non-equilibrium simulations whatever we have covered so far will be the equilibrium simulations. But now we come to the non-equilibrium simulations. We talk about briefly Langevin equations, the Brownian dynamics and Kinetic Monte Carlo simulations and some other methods that I will briefly touch upon. So that is the broad course overview and these are the reference books that you may like to follow, although I will try to make my lectures self sufficient, but if you want any additional reading, these are the books I will recommend the ones in bold are our recommended selection, particularly the first one by Hanson is the one that is I would say at a very basic level book that can help you understand the molecular principles that drive chemical thermodynamics and the second one by Mcquarrie is a classical book on statistical mechanics and then the last three books are on molecular simulations. I will particularly recommend the book by Tildesley which I will follow, which is on computer simulation of liquids. But the book of Frenkel is also quite popular and quite nice.

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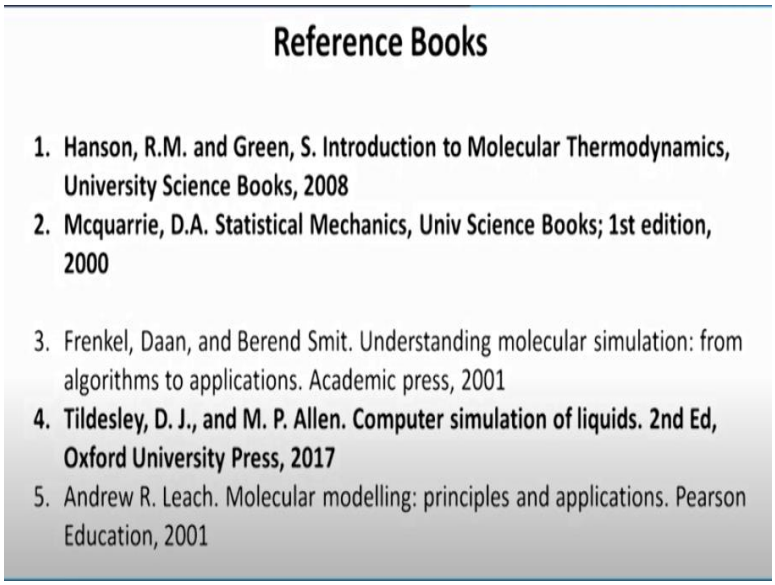

With this let us now come to why do we study thermodynamics in general and why do we do this course, right. So as you probably know we study thermodynamics because thermodynamics is the one that drives chemical processes whether we talk about mass transfer by diffusion, whether we talk about chemical reactions, whether we talk about separations, thermodynamics drives all these processes and therefore, for example, if I want to design a reactor or design a separation column, thermodynamics does play a very important role but thermodynamics really goes much more beyond chemical engineering the I would say that thermodynamics is the one that drives the universe

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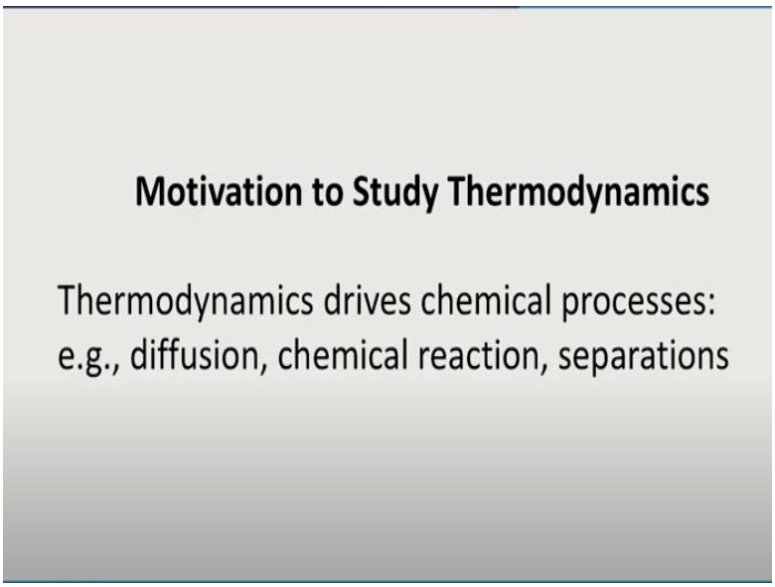

But before coming to that, let us let me quickly recap the basic laws of thermodynamics. We will come to that again in the course, but just to set a ground for those who are coming with this background, this will serve as a quick recap of how much we know in thermodynamics. So in thermodynamics, we talk about basically four laws. We start with what is called the 0th law of thermodynamics.

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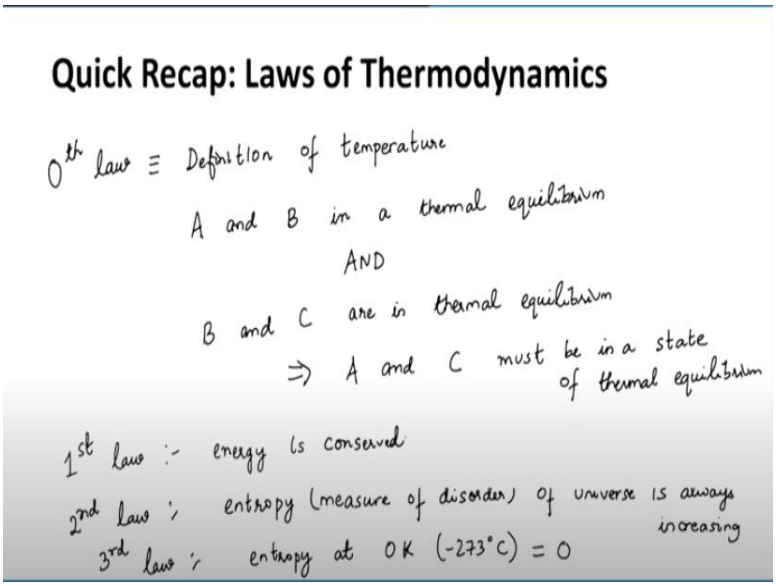

And 0^{th} law essentially is the definition of temperature although the actual statement of the law is somewhat I would say more complicated at first glance, but this is what gives rise to the idea of temperature. What do we say in 0^{th} law, if for example we have two systems A and B in a state of thermal equilibrium and B happens to be in thermal equilibrium with another system C, then as per the 0^{th} law of thermodynamics, A and C must be in a state of thermal equilibrium. And you may already see why it give rise to the notion of temperature. So there must be some property that is common between A and B and that happens to be common also between B and C and that property is the one that we call a temperature. So temperature defines in some way the thermal state of a substance and if the temperatures of two systems are the same, we call them in a state of thermal equilibrium.

So then there is the first law of thermodynamics, which essentially if you think about it is simply a conservation of energy, right. So it says that energy is conserved. So if I

supply energy to a system, it may either be manifested in the form of a heat or it can be manifested in the form of work, right. So these are the two ways the energy can be manifested and that is the first law of thermodynamics and energy has to be conserved, whatever energy we put in, that must go either in heat or in terms of work. Then there are second and third law of thermodynamics, which are not about energy they talk about a property called entropy that is defined as a measure of disorder and as you will see, we will spend extensive amount of time in this particular course, talking about what exactly entropy is, and how do we characterize entropy of a substance. But the second law says that entropy of universe is always increasing and the third law says that the entropy at 0 Kelvin that is -273 degrees Celsius, a condition that will be extremely difficult to realize, if not impossible, but that is used in the definition that is why we measure temperature in Kelvins that entropy happens to be 0.

So third law essentially sets the reference of entropy, the entropy must be 0 at 0 Kelvin. All the disorder should vanish at 0 Kelvin. And the second law says that the entropy of universe is always increasing.

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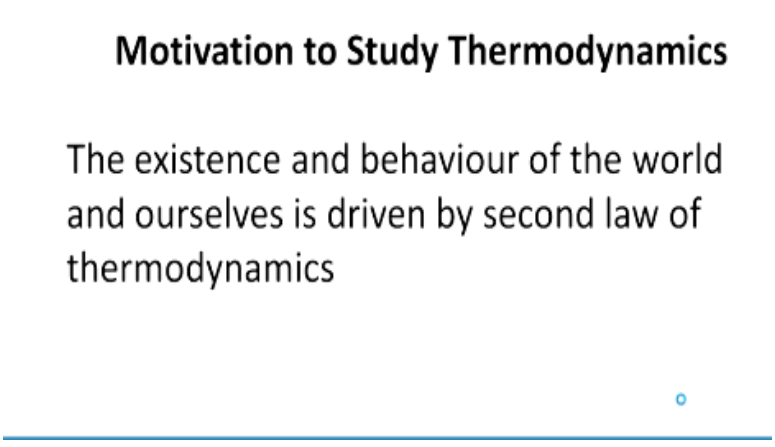

So with these ideas, what one can claim is that the existence and behavior of the world and actually ourselves is driven by the second law of thermodynamics. It happens to be the most important law not really in thermodynamics, but also in nature, right. So why I am saying that?

The reason why I am saying that is if I look at any other equation in physics, be it the equation of motion, be it the Schrödinger equation, be it some other equation, all these equations, do not really differentiate between the sign of time that means the direction of time, right. So if for example, a car has moved in this particular direction, the car may also move in that particular direction. I can simply put a - T in the equation and I can get the result for the opposite direction of time. The equations do not differentiate between time in the positive direction that is the future and time in the past direction that is the past.

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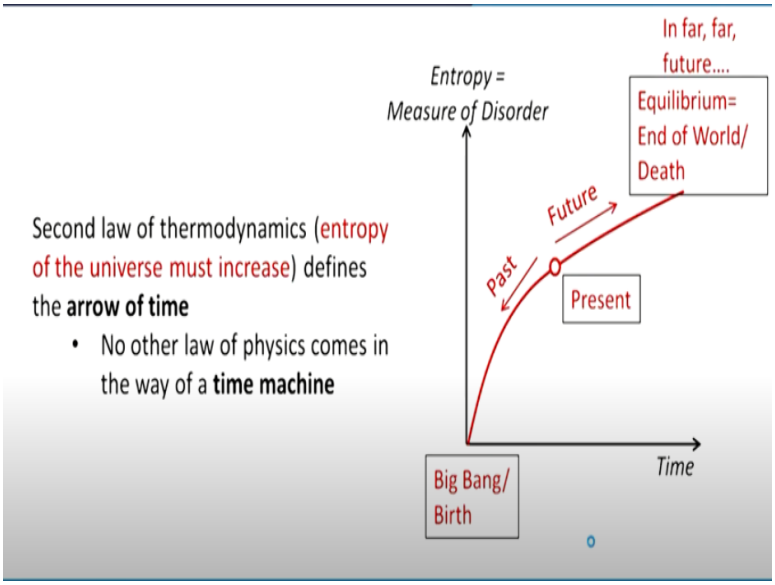

However, the second law of thermodynamics what it says is that the entropy of the universe must always increase. What this pretty much tells is that I cannot go back in time, because going back in time would mean that I am going to a state of lower entropy and that cannot really happen, right. So it is the second law of thermodynamics, that essentially limits us from basically making a time machine that essentially defines what I what we call the arrow of time.

So where we are in the present that corresponds to a certain state of entropy, future corresponds to higher entropy, past corresponds to lower entropy. If we go back in the past when the Big Bang happened, the Big Bang, as you may recall, the Big Bang was a state of very dense system, everything was close together and that was when the disorder was the least. And that is when the entropy was very small and as after the

Big Bang, the nature started getting organized, we are having more and more disorder and more and more entropy actually, as you will see, disorder is not a very correct word to characterize entropy, we will come to that in this course. But the main point is that the entropy is going to increase.

So if I go in the far far future, that will be a state of equilibrium of the universe and that equilibrium state will correspond to the case where the disorder is maximum, right and as you may imagine, if there is disorder is maximum means no order in the world. And that is probably when the universe will end.

The similar actually applies also to our own being here, what is our state of equilibrium, when we are dead, that is when we do not perform any function that is the most possible disordered state we can go towards. So our life is actually going towards the equilibrium and life is actually basically driven by entropy as much the universe is driven by entropy.

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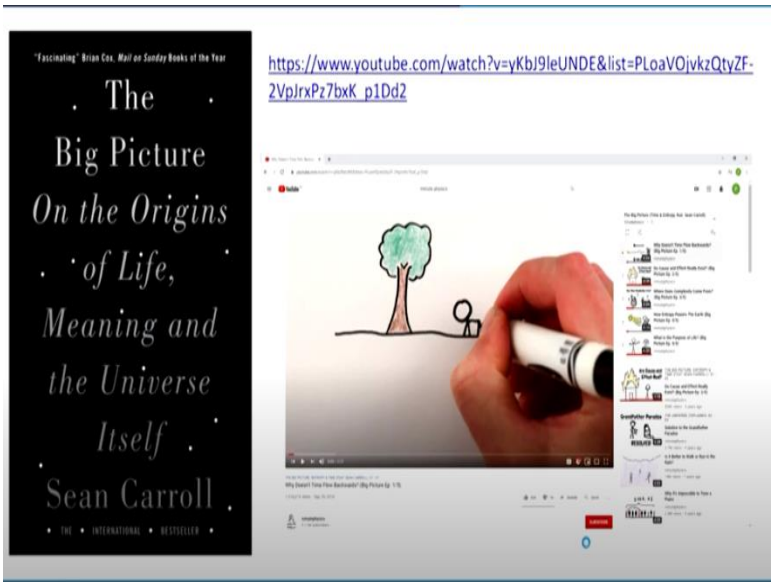

So with this particular motivation, you can read more about this, I will recommend you a very excellent reading this is a nonfiction reading, not recommended not for this particular course but in general, this book Big Picture by Sean Carroll, if you do not have time to read the book, at least watch this four or five very small videos on YouTube, that will basically motivate towards why do we study thermodynamics in general and as you will realize, that it is not just about description of chemical

processes or description of some particular phenomena in chemical engineering, thermodynamics actually applies to much more things that then we could have imagined in the world.

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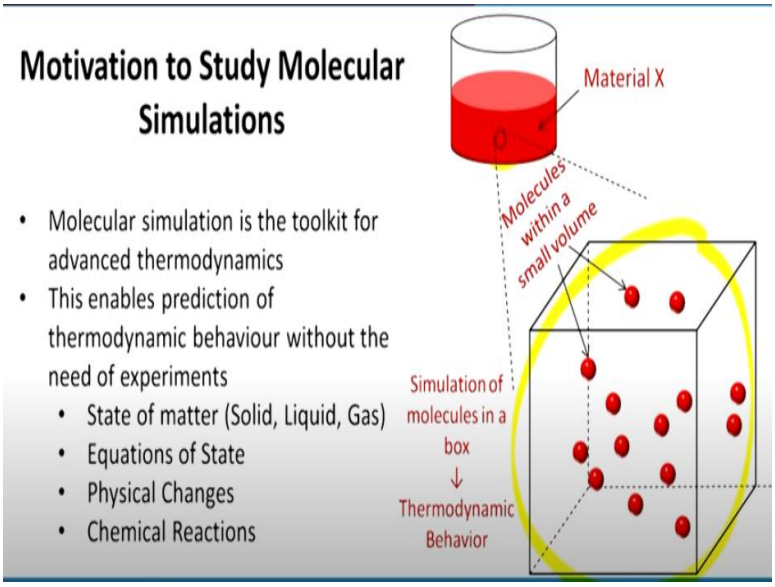

So the next part of the course is on molecular simulations and here is why we study that. So molecular simulations essentially provide a toolkit for thermodynamics and the way it happens is that, if you recall in your chemical engineering thermodynamics course, or any other course you may have taken, you must have heard of the idea of equation of state.

Let us say for ideal gas, it is PV = nRT that becomes the input to the thermodynamic model we are using, right. So in this particular course, I will try to argue that we can actually derive the equation of the state by using the idea of molecular simulations, right. And the way it is going to work is that, if I look at any particular system, it is actually composed of molecules so as you can see, if I look at any material x right here, ultimately this material is going to be composed of molecules. So what I am doing right here is that I am representing a system of molecules that basically is like a small cross section of the material itself and molecular simulations we simulate that and we basically get the equation of state or we get the thermodynamic behavior of the system. So essentially, molecular simulation serves as the toolkit for the thermodynamics and this way, we can predict the behavior of any substance without

even knowing the equation of state we are going to derive the equation of state by using molecular simulations.

So just to briefly tell you about the power of molecular simulation just let me touch upon various example that you may have come across. This is a very famous virus, the COVID-19 virus and this virus essentially is SARS CoV-2 and the challenge that the world faced is like how to find the cure of this particular virus?

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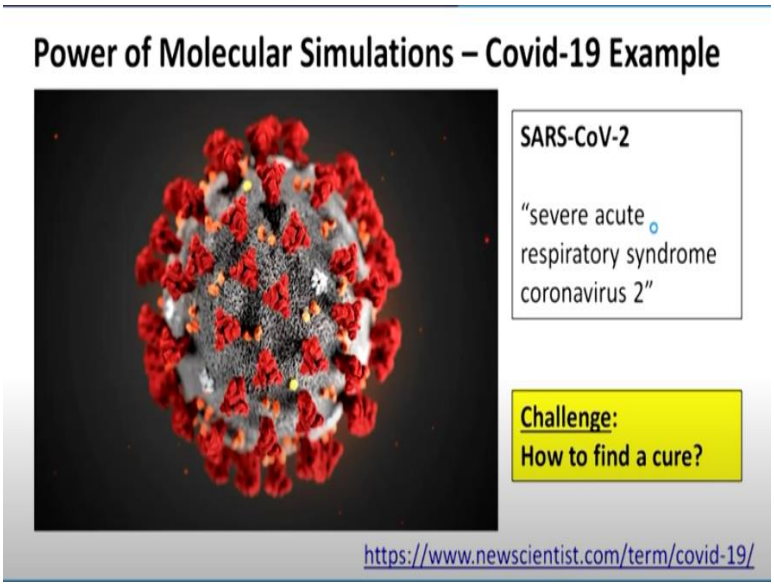

How do we develop a vaccine? And ultimately, molecular simulations can help in there and how will it do that is that if I look at this particular virus, ultimately it is going to be a molecule, right and this is how the molecule looks like it has various types of proteins, right? The most important protein for the point of view of attacking that virus are these spike proteins that you see this read beautiful guys in here so this spike proteins actually are very complicated molecules they look like something like that, right.

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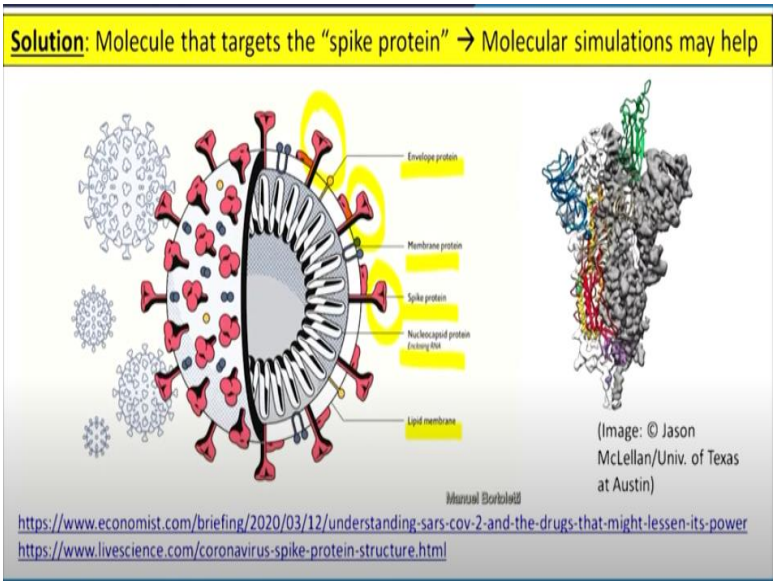

So ultimately, if I want to find the cure of this virus, we need to find a molecule that attacks these spike proteins, right? So somehow, that vaccine molecule or whatever should be compatible with this particular molecule, or it should do some kind of an action on this kind of molecule.

So therefore, if I want to essentially find a cure, I can simulate a variety of molecules that are potential cure of this with this particular molecule and find its compatibility. The same thing we can do in the experiments. But the problem is that we need to do experiments for millions of different types of chemicals in the world and that is, of course going to be much more time consuming than doing it on a computer. So actually, the use of molecular simulations can accelerate the development of vaccines and so applies to every other material in the world nowadays. If I want to develop a new drug, molecular simulations can come handy in finding the drugs which are most promising. Of course, we may have to do experiments later, but we do not have to do experiments for all possible candidates.

Let us say for example, if you have a million candidate, then I can do the simulations and find the 100 or 1000 most promising candidates, which are essentially molecules that are compatible or that they perform some action on the drug in question. And so it does apply to every other material that we are trying to develop.

So with this background, I hope I have convinced you that the thermodynamics is really something that is very important, both as a chemical engineer and in general and therefore you should be motivated enough for this course.

In the next lecture, I will start going into the details of like what molecular principles drive thermodynamics.

Thank you so much. See you in the next class.