Mathematical Modelling and Simulation of Chemical Engineering Process
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Lecture 03
Constitutive Relations

Hello everyone, welcome to the third lecture of Mathematical modelling and simulation of Chemical Engineering Process. Today we are going to talk about some of the constitutive relations used mostly in the transport phenomena and also in thermodynamics.

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So, first I mean the key concept that we are going to cover in this lecture today will be related to Momentum or the as you know the Fluid flow, energy and the Mass transport phenomena and we will talk about also related to the thermodynamics and different Thermo dynamical concepts.

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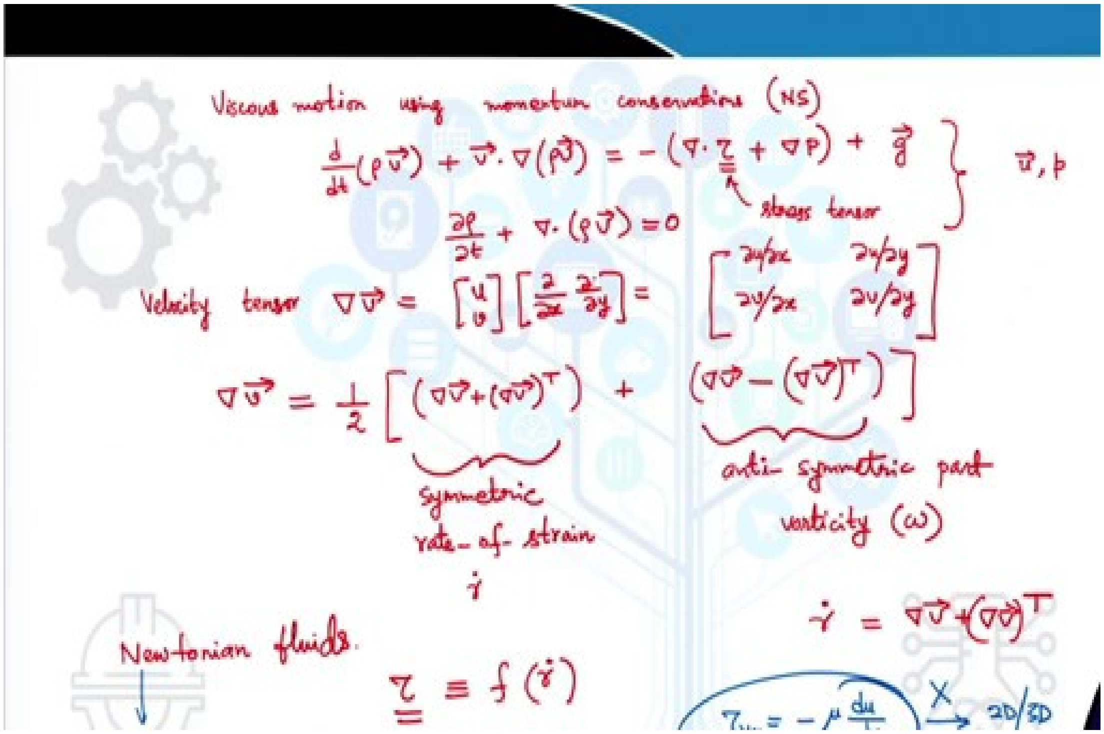

Now, first let us begin with the fluid flow all of you are aware of the viscous motion concepts using momentum conservation. So, let me just write this conservation equation first, which is essentially nothing but the Navier-Stokes equation in the most generalized and the conservative form. So, it is the Navier-Stokes equation.

So, let me just write down first and then we take it from there. So, this up arrow denotes the vectors. So, please note that I write this equation in terms of the conservative form that is the reason why the density is taken inside the derivatives and along with this also you have the continuity equation. So, this is a tensor, this is the stress tensor. So, together these 2 equations can be used to solve for the velocity field and the pressure in the system.

So, these are generally the unknowns. So, this Navier-Stokes equation can have 3 components for 3 directions of the velocity. So, there are 3 unknowns as well as the pressure is also unknown. So, you have the component momentum equations and the continuity equation, together they constitute a closed system where the number of equations and the number of unknowns are same.

Now, next important concept is the velocity tensor. And from there we will take forward what we mean by the stress tensor. So, velocity tensor grad V is generally written as, let us say I am writing this in terms for the 2-dimension case, you can also write down in terms of the 3-dimensional case also, in terms of cylindrical and spherical coordinates also.

So, this is what we mean by the velocity tensor. It can also be written down as the components of symmetric and anti-symmetric part in this way. This is the symmetric part where it is generally represented as the rate of strain, represented commonly by Gamma dot and this is the anti symmetric part and generally known as the vorticity to the problem.

Now, please note, it is a very important part and pay attention to this, that for Newtonian fluids this stress tensor Tau is a function of the strain rate, Gamma dot. So, what is this Gamma dot? So, Gamma dot is grad V plus grad V transpose. So, this is the strain rate and please note that the conventional idea we are used to seeing that, what we generally know by, you know these Newtonian fluids this, that something like this Tau yx is equal to minus Mu du by dy this idea is not valid for 2 dimensional or 3 dimensional cases, and it is over generalization of the stress tensor.

So, the best way of writing the stress tensor or the stress components (then you can talk about the you know the stress components in different direction) the stress components is writing as a function of the strain rate, as the Gamma dot. So, this is how we generally write for generalized fluid in the particularly for the case of the Newtonian fluids. This is, so, this Tau is a function or a direct function of the Gamma dot. So, we will talk about this more.

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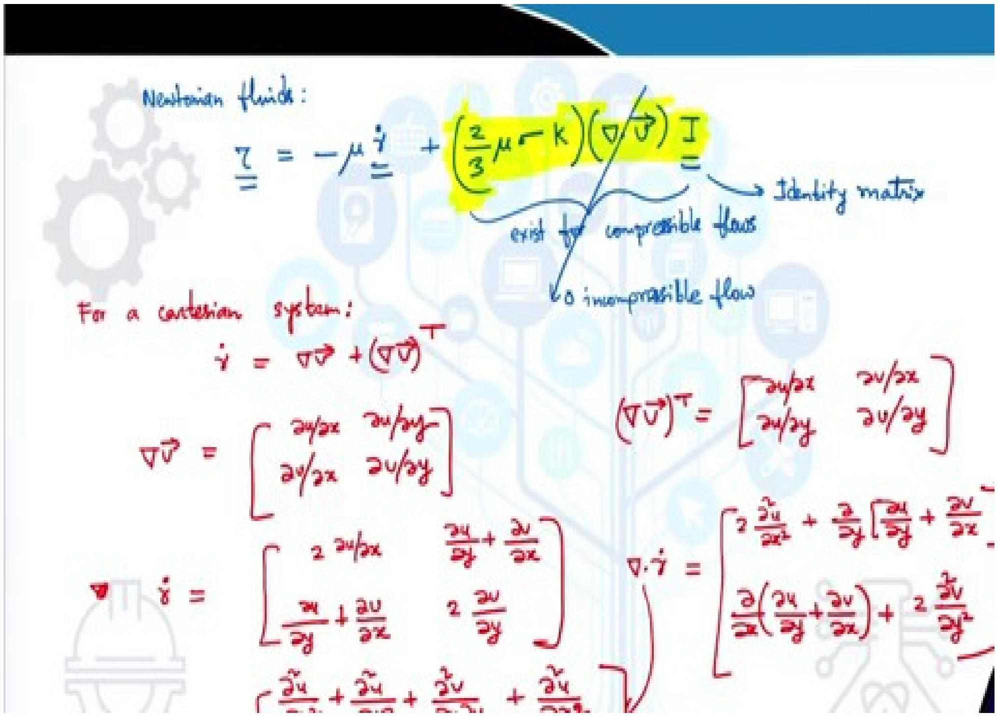
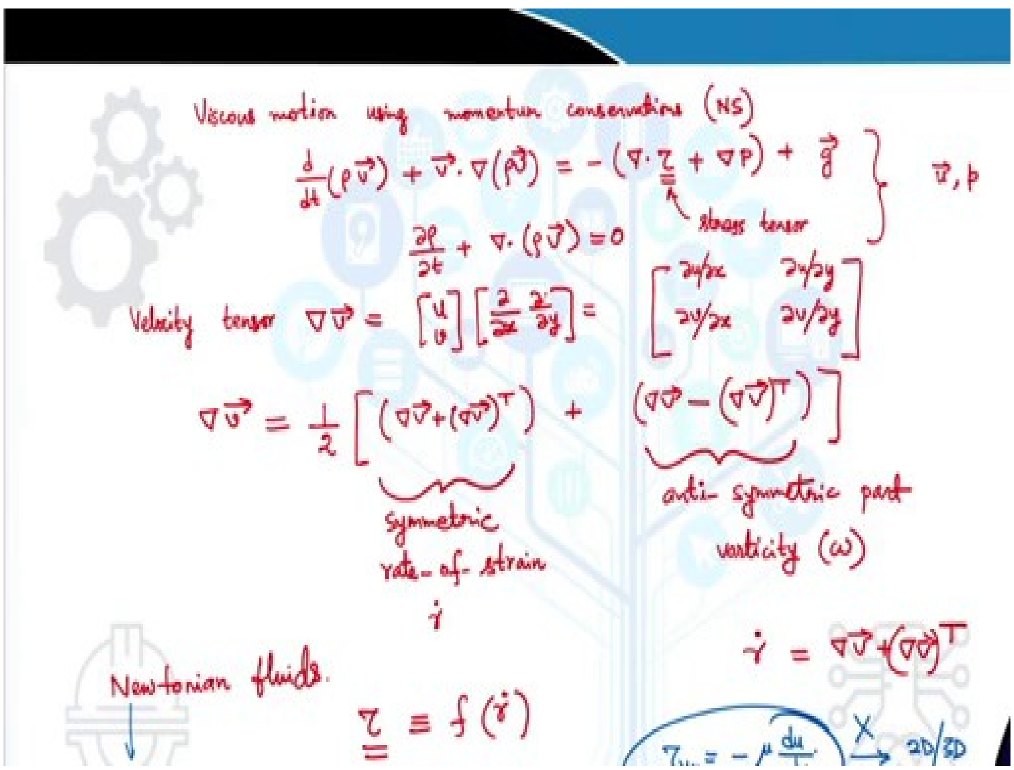
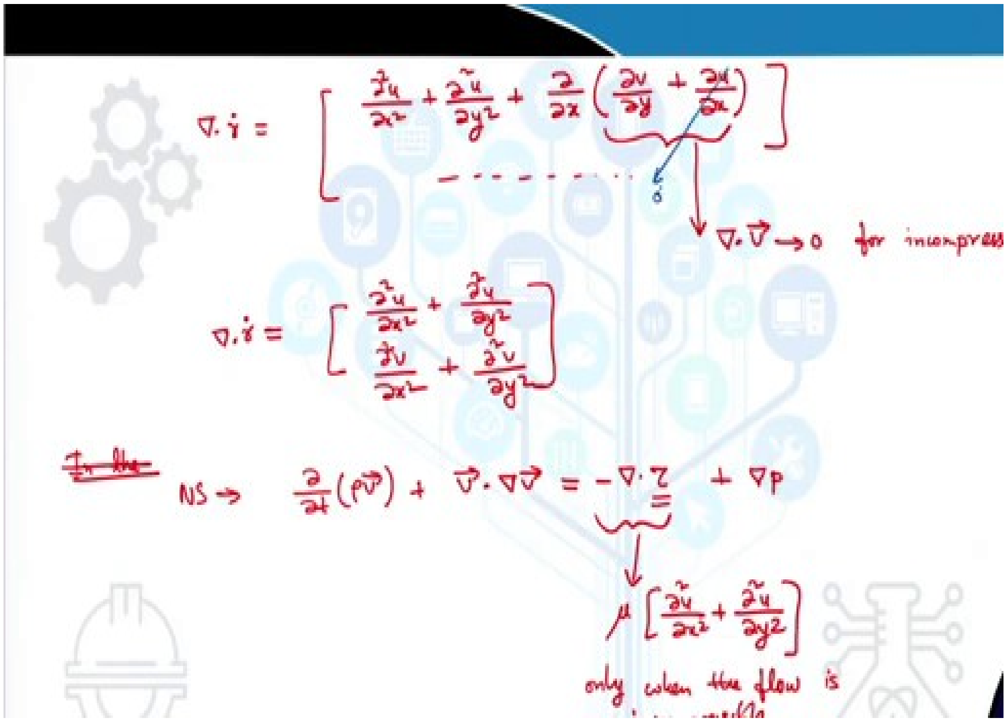

Newtonian fluids:
$\underline{\underline{\tau}} = -\mu \underline{\underline{\dot{\gamma}}} + \left(\frac{2}{3}\mu - k\right)(\nabla\cdot\vec{v})\,\underline{\underline{I}}$
Identity matrix
exist for compressible flows
0 incompressible flow
For a cartesian system:
$\dot{\gamma} = \nabla\vec{v} + (\nabla\vec{v})^T$
$\nabla\vec{v} = \begin{bmatrix} \partial u/\partial x & \partial u/\partial y \\ \partial v/\partial x & \partial v/\partial y \end{bmatrix}$
$(\nabla\vec{v})^T = \begin{bmatrix} \partial u/\partial x & \partial v/\partial x \\ \partial u/\partial y & \partial v/\partial y \end{bmatrix}$
$\dot{\gamma} = \begin{bmatrix} 2\,\partial u/\partial x & \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \\ \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} & 2\frac{\partial v}{\partial y} \end{bmatrix}$
$\nabla\cdot\dot{\gamma} = \begin{bmatrix} 2\frac{\partial^2 u}{\partial x^2} + \frac{\partial}{\partial y}\left[\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x}\right] \\ \frac{\partial}{\partial x}\left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x}\right) + 2\frac{\partial^2 v}{\partial y^2} \end{bmatrix}$


Viscous motion using momentum conservation (NS)
$\frac{\partial}{\partial t}(\rho\vec{v}) + \vec{v}\cdot\nabla(\rho\vec{v}) = -(\nabla\cdot\underline{\underline{\tau}} + \nabla p) + \vec{g}$
stress tensor
$\frac{\partial\rho}{\partial t} + \nabla\cdot(\rho\vec{v}) = 0$
$\vec{v}, p$
Velocity tensor $\nabla\vec{v} = \begin{bmatrix} u \\ v \end{bmatrix}\begin{bmatrix} \frac{\partial}{\partial x} & \frac{\partial}{\partial y} \end{bmatrix} = \begin{bmatrix} \partial u/\partial x & \partial u/\partial y \\ \partial v/\partial x & \partial v/\partial y \end{bmatrix}$
$\nabla\vec{v} = \frac{1}{2}\left[(\nabla\vec{v} + (\nabla\vec{v})^T) + (\nabla\vec{v} - (\nabla\vec{v})^T)\right]$
symmetric
rate-of-strain
$\dot{\gamma}$
anti-symmetric part
vorticity (ω)
$\dot{\gamma} = \nabla\vec{v} + (\nabla\vec{v})^T$
Newtonian fluids.
$\underline{\underline{\tau}} \equiv f(\dot{\gamma})$
2D/3D



So, for Newtonian fluids the generalized expression is that the stress tensor is equal to minus Mu Gamma dot and this is known as a tensor. So, this is a tensor equation where I am writing down and this is another component that is generally present in the case of compressive flows and this is the identity matrix, where only the diagonal components are unity and rest are 0.

So, this is how we generally write a stress tensor in this case and please note that in the case of compressible system, there is an additional component for the Newtonian fluids. So, this is you know, this exist for compressible flows. So, now trying to simplify the process and trying to write the system for a Cartesian coordinate, Cartesian system Gamma dot is equal to grad V plus grad V transpose.

So, you can directly get, so, let us just work out the, this gradient matrix. So, grad V, I have already written down, I will write it once again du by dx, dv by dy and the transpose of this is. So, now you try to do, try to write the strain rate matrix isn't it. So, we write this Gamma dot. I hope all of you are following it. It's plain algebra now, and if I try to write grad dot Gamma dot because that is what ultimately you are going to get, when you do, try to bring this into the Navier-Stokes equation. You are getting to plus Del Del y of Del u Del y plus Del v, Del x, plus, something like this and this further can be written down as.

Similarly, you can write the second row. Now you can observe clearly that this thing, what we get d2 u by dx square plus v2, this third component I can do this slight rearrangement assuming the second component will be there and this part as you can clearly understand is nothing but now, this is equal to 0 for incompressible flow.

So, with this you can, you write down that your, this Gamma dot will be equal to. Similarly, the next one would be in terms of the V. So, from the Navier-Stokes which does not write more and but let me help you to write that. Please note 2 things here that the Navier-Stokes equation: essentially the stress tensor part, this part gets converted to Mu into d 2 u, dx2 plus.

So, this is converted only when the flow is in incompressible and not always. There are 2 parts: one is that this component is you know converted to so, this component is converted to 0 because of the incompressibility condition and also the Newtonian this part, this part is converted to 0, for incompressible case.

So, only when the fluid is incompressible, flow is incompressible, you can essentially have this, you know this, this divergence of the stress tensor to be equal to d2u dx squared plus d2u /dy2 and not always so, that does not come. So, this d2u/dx2 and d2u/dy2 does not come from this approximation and that is only true for the case of 1 dimension, but it does not is not true. So, using this you cannot establish the near you know this momentum conservation equation in the 2 or in the 3- dimension. So, this is a very important thing that I wanted to highlight. Of course, you can also work out keeping the, you know these additional terms like these additional terms in this case. You can also work out keeping these additional terms, you can also work out that what would be the stress essentially the stress tensor for the system that is something as an exercise I leave it for. What is the velocity tensor is going to look like? keeping the additional terms due to the compressible nature of the flow.

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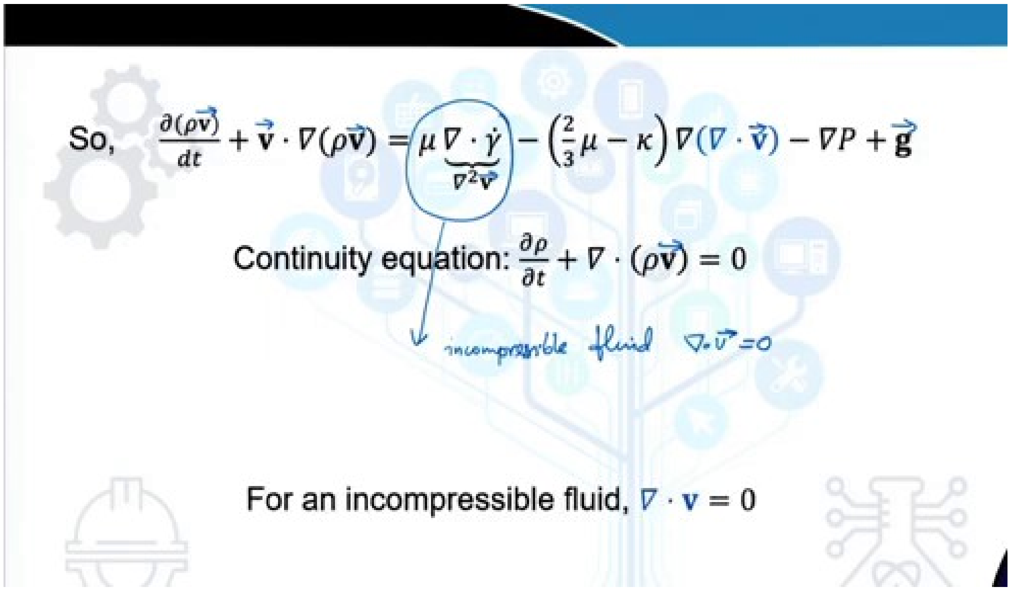

So, with this let us let me try to summarize that for the viscous motion this part or the stress part essentially the stress part to the equation converted to grad square u, only in the case of incompressible fluid. So, that is an important observation and a thing to remember, and it is not true always.

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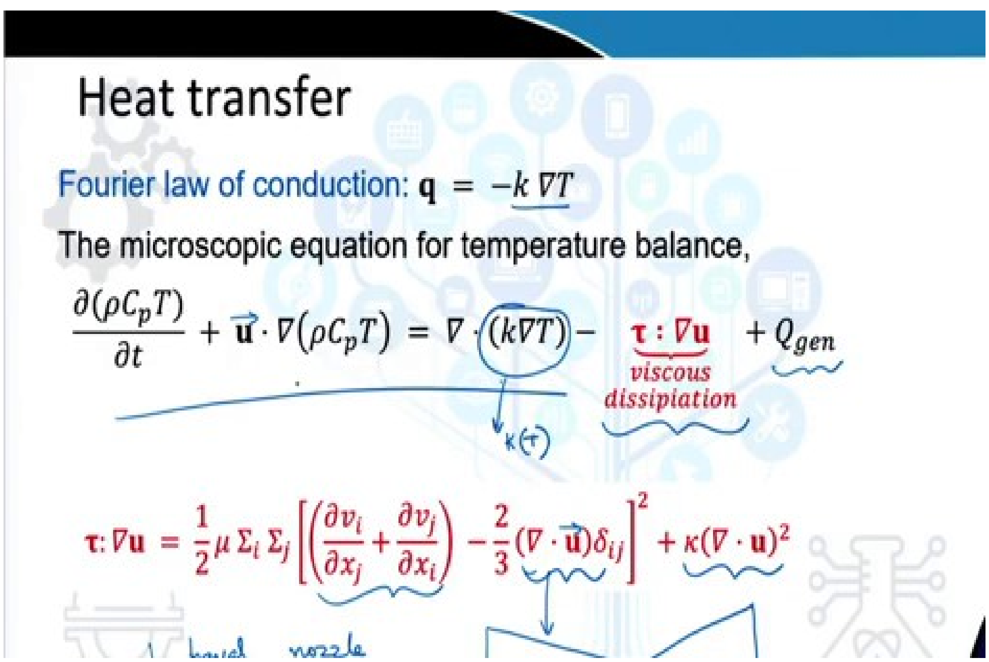

Moving to heat transfer, all of us are aware of the Fourier law of heat conduction and we know that in this case: in the case of the Fourier heat conduction the heat flux is given as k x grad T and from this equation or the energy burn, energy balance you can write the generalized equation for the case of heat transfer and please note here I have intentionally written down this k to be inside the gradient because it is possible that the thermal conductivity (and it is likely the case that the thermal conductivity) is a function of temperature.

Similarly, density, specific heat capacity can also be functions of temperature and that is the reason why they are kept inside the derivative. So, this is the most conservative form. There is an additional term which is given by the viscous dissipation and this is true generally for the case of highly viscous fluids or polymeric fluids in the, in systems and you can see that there is an additional heat component which is mostly produced due to the friction between the different layers in the fluid, and this viscous dissipation is an additional term to the energy balance and there could be additional you know a source of energies into this problem.

So, this viscous dissipation is generally important when we have compressible flows. You can see that this is a part due to the compressible nature of the flow. So, this part exists only when we have compressible flows in the system, and it is found that these components – the second term in this viscous dissipation, or the component with respect to the divergence of the velocity field is comparatively dominant over the first component. And this is what we generally mean, generally comes in the picture, when we talk about the compressible nature of the flow and that is where viscous dissipation also starts to become more prominent.

So, this is 1 term when there is also another term of the viscous dissipation. So, in this context, I must also enlighten you about what is known as the de Laval nozzle. So, a de Laval nozzle is a convergence-divergence nozzle which is constructed to get supersonic flow.

So, in the case of you know when the Mach number to the problem or Mach number tothe system is, is high or the system is in the compressible nature or is in the subsonic regime or when the Mach number is generally exceeds 0.3, I encourage all of you to look into the Wikipedia page of this de Laval nozzle and really understand more from the thermodynamic concepts that if the flow or the Mach number of the system is in the subsonic range or greater than 0.33 in fact. Using a converging nozzle, it is not possible to accelerate our flow. Generally by the principle of this conservation or the area conservation or the continuity you will see that the flow becomes more in accelerates when it passes through a nozzle because the area shrinks and the flow rate unit increases for the mass balance but this is true only when the flow is not in the you know sonic range when the Mach number is greater than 0.33 and it is proven that and based on this idea of the de Laval nozzle came into the picture that the flow in this nozzle is decelerating in nature.

So, it is not possible to accelerate a flow using a converging nozzle in the case of Mach number better than 0.3. So, and that is why it is this de Laval nozzle is constructed and the design is such that you have a converging section, so, that you reach Mach number close to the subsonic range and then you have an expanding zone or a diverging zone, which will further accelerate it.

So, this de Laval nozzle is an interesting engineering design used to construct are used to obtain these supersonic flows or to accelerate a flow. Next, I would like to talk about the some of the important mass transfer concepts particularly related to diffusion.

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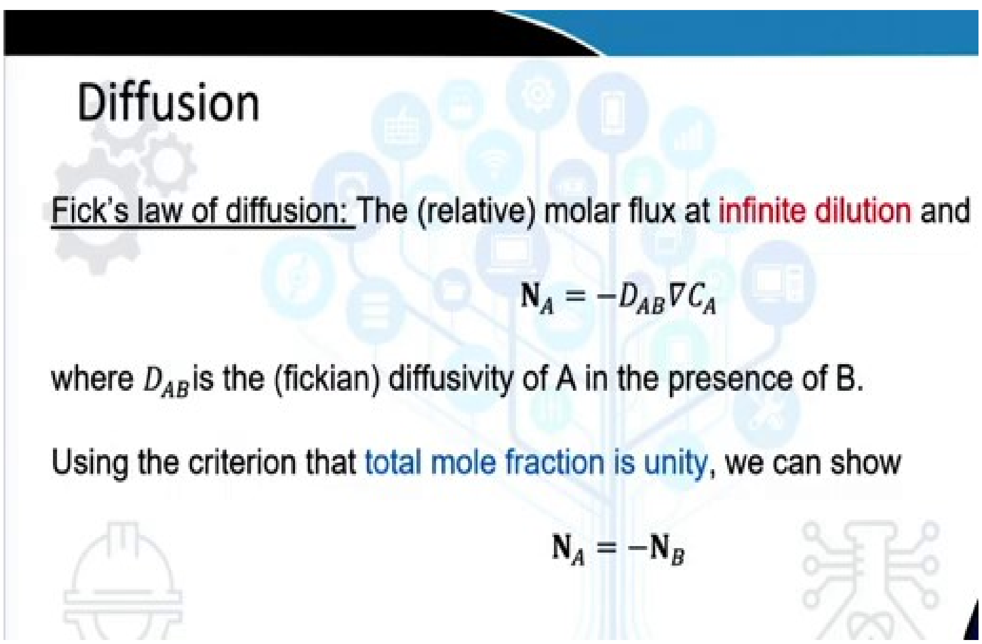

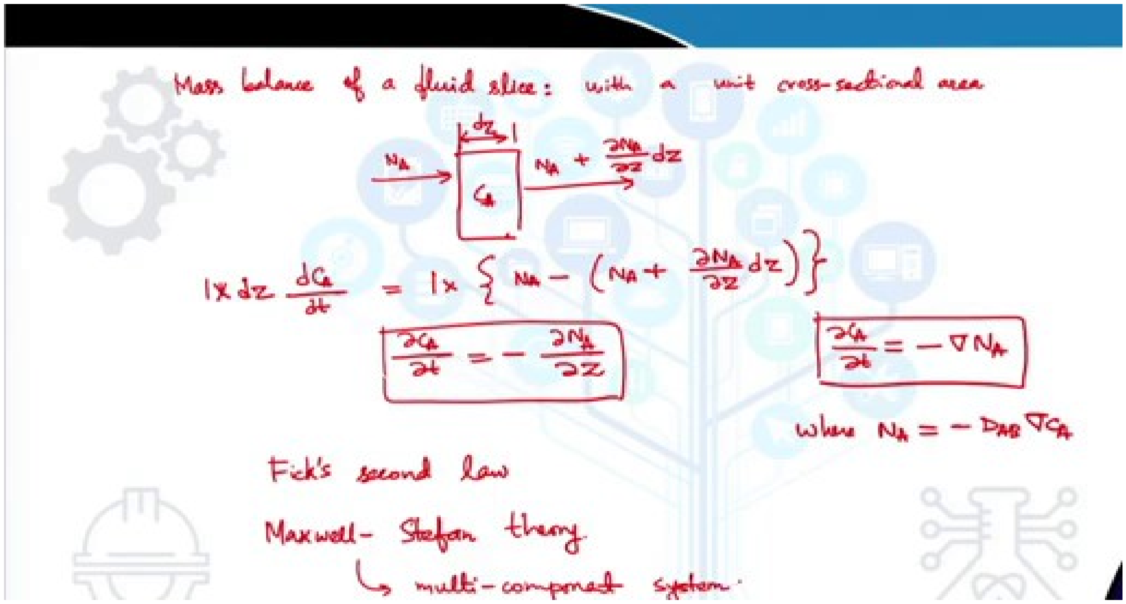

So, let me just proceed. So, all of us are aware of the Fick's law of diffusion which tells that the molar flux is proportional to the concentration gradient. The two important conditions on this Fick's law, essentially the Fick's first law of diffusion is that the system should have in finite dilution; it is generally applicable for Fick's law of diffusion and you consider the system to be in steady state.

So, there is also unsteady version of the Fick's law, but this is the generalized Fick's law and it tells you that the total mole fraction should be unity. So, you can say that always this flux of A, if it is a binary system is equal to the negative of flux B and it is an infinite dilution and at steady state.

So, let us try to write down the mass balance of a fluid element, size with unit cross sectional area. Let us say cross sectional area is dz. Flux is NA, that is in and NA plus the flux out. So, we are trying to achieve the if you know, the idea of the Fick's second law essentially and so, what we can write, we can write a mass balance how do we write dCA dt.

So, 1 into dz… So, in many places, you will find that diffusive flux is written in terms of JA. So, please do not get confused here we write I mean JA is equivalent to NA here, because in many cases or in many books also you will find that and JA is used to write diffusive flux and NA is used to write total flux to the problem. But in this case, we choose NA to be the diffusive flux.

So, this is the, (you know) this 1 dimensional (you know) unsteady version of the Fick's law. NA is of course, the flux of the component A in the z direction. So, the generalized setting of this Fick's law and unsteady Fick's law is minus grad NA, where NA is generally, written as NA is written as this plus where, NA from the Fick's first law you have minus D_{AB} grad CA sorry, why I wrote minus it should be, should be minus I wrote plus.

So, this is the Fick's second law. Now, let me try to explain or let me try to (you know) discuss what are the assumptions in this Fick's law. Of course, 1 assumption is the case of the infinite dilution; then you have generally it is valid for binary systems; then, it is true when you have a stagnant medium, when generally molecular convection does not play a big role or you do not consider any molecular movements or Brownian motion in the system affecting the distribution of the concentration.

So, these are some of the important assumptions in the Fick's law based on which based on which, an upgraded version or a more generalized version known as the Maxwell Stefan's theory or this model is developed and this can, to some extent you know account for all the limitations that are involved in the Fick's law. And you will also note that the Maxwell Stefan's theory is very well suited for multi-component system.

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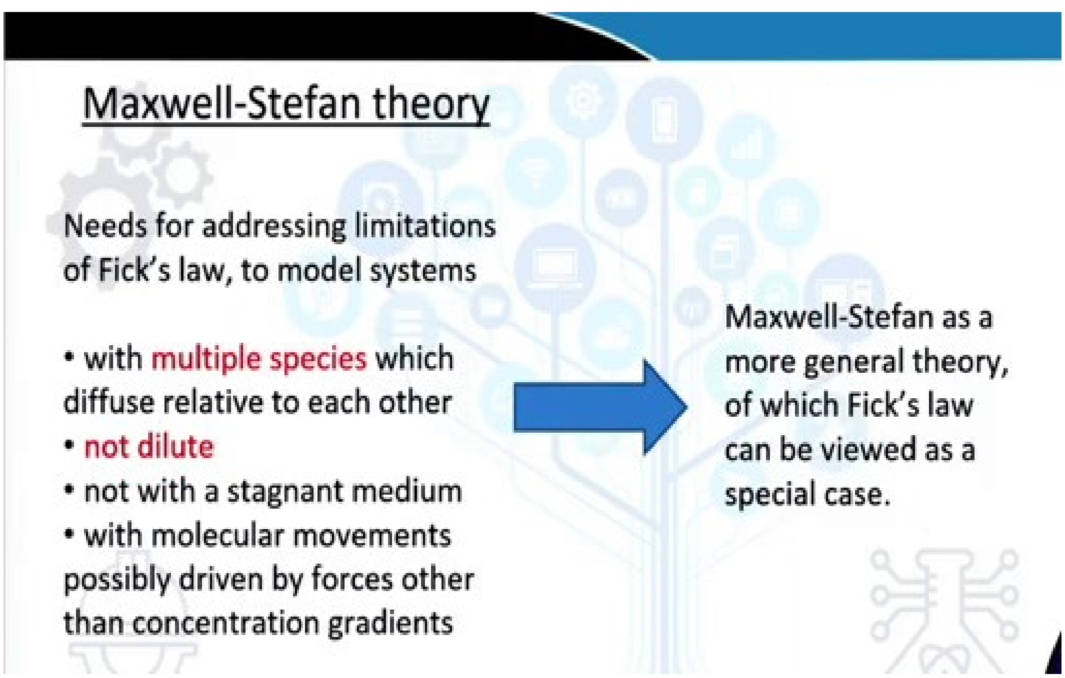

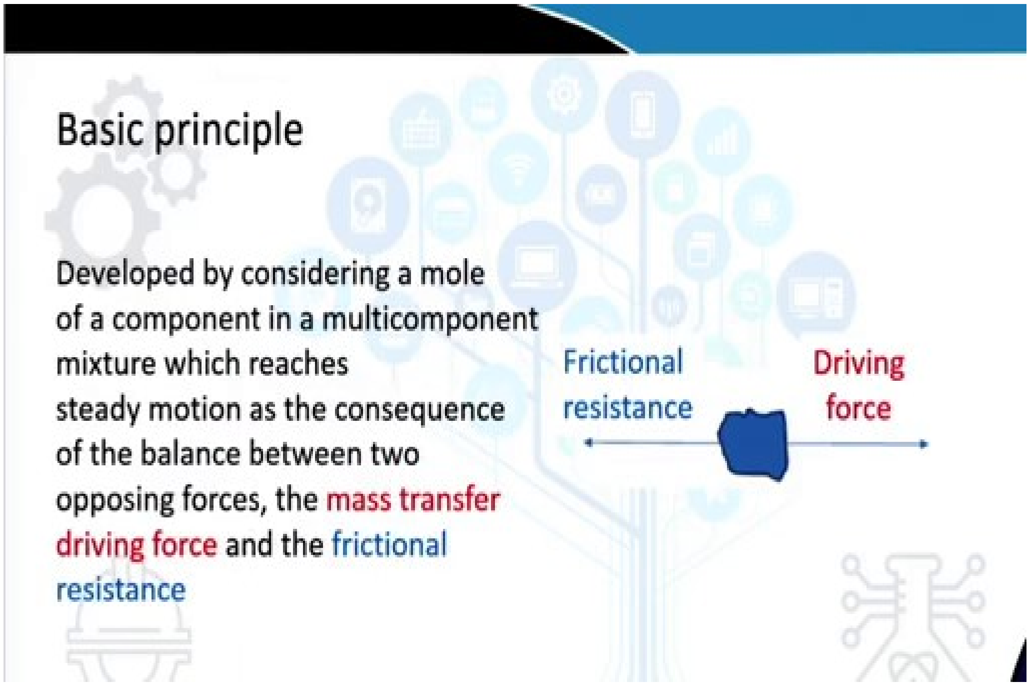

So, what is this Maxwell-Stefan's theory: It is it is a generalized systems and here you do not have these limitations with respect to the (you know) multiple species that need not to be binary system; need not to be dilute, infinitely dilute; and the presence of the other component of the concentration of the other component can also be accounted for very nicely; and you will also see that the condition of the stagnant medium is not invoked in the Maxwell-Stefan's theory.

The basic principle is developed by considering that at steady state, at a molecular level steady state, I would say that there is a balance of the driving force and the frictional resistance. So, what is this frictional resistance? The frictional resistance comes due to the relative motion of a particular molecule with respect to another molecule. We will of course, elaborate on this and what do we mean by the driving force?

So, the driving force is the gradient of the chemical potential, that is the classical definition of the driving force. So, with this I mean (considering this) we will try to you know elaborate from the thermodynamics that how this theory of the Stefan's Maxwell can be established and you will see that under the limiting cases or with imposing the specific conditions like this dilute system, binary system, infinite, the stagnant medium, and all. The Stefan's-Maxwell theory can also be simplified to obtain the Fick's law of diffusion.

So, with this I would like to conclude for this lecture and let me just tell you a quick recap on whatever we learned today, it is related to the different (you know) transport equations for the momentum conservation. Then we also talked about the heat transfer. And now we are trying to work out on the diffusion and how the assumptions behind the Fick's law can be eliminated with the help of a more generalized theory something that we are possibly going to talk about in the next class. Thank you for your attention. Hope you liked it.