Transport Processes I: Heat and Mass Transfer

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Lecture – 14
Conservation equations and constitutive relations

Welcome to this 14th lecture is this series on transport processes; we were getting to the important part of the course that is how are we describing transport processes.

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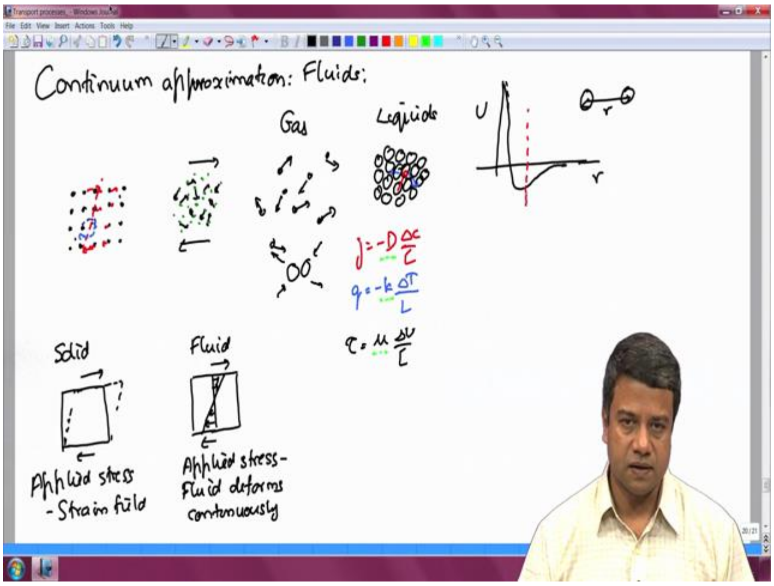

Last class I had first discussed the distinction between solids and fluids and between liquids and gases. In solids from a mechanical point of view if you apply a stress, the solid will deform and then stop, it will stop at the point where the restoring force is equal to the applied force, whereas in fluids if you deform the fluid it will if you apply a stress it will deform continuously and at a microscopic level this distinction arises because in the case of solids all molecules have their equilibrium positions about which they vibrate and any deformation of the solid will result in displacement of molecules from their equilibrium positions and of course, if they are displaced from equilibrium, there is going to be a restoring force. And when that restoring force is equal to the applied force the solid will stop moving; whereas in fluids the molecules do not have any equilibrium positions, they are randomly fluctuating throughout the fluid, each molecule can sample the entire fluid volume and because of that there is no restoring force and therefore, the fluid is going to deform continuously.

Fluids of course, are further distinguished into liquids and gases, gases the distance between molecules is much larger than the molecular diameter in liquids, the distance is comparable to the molecular diameter. So, this actually makes a difference in the mode of interaction. In gases it is primarily due to instantaneous collisions because the molecules just move distance is large compared to the diameter between successive interactions.

Whereas in liquids, each molecule is interacting simultaneously with all of its neighboring molecules that does make a difference as far as the density the coefficient of diffusion are concerned; however, there is no difference in the form of the constitutive relation. The constitutive relation for liquids and gases are identical, only the values of these coefficients change. So, in this course we will deal primarily with liquids and gases and we will make no distinction as far as the formulation is concerned between liquids and gases only the numerical values of the coefficients will change.

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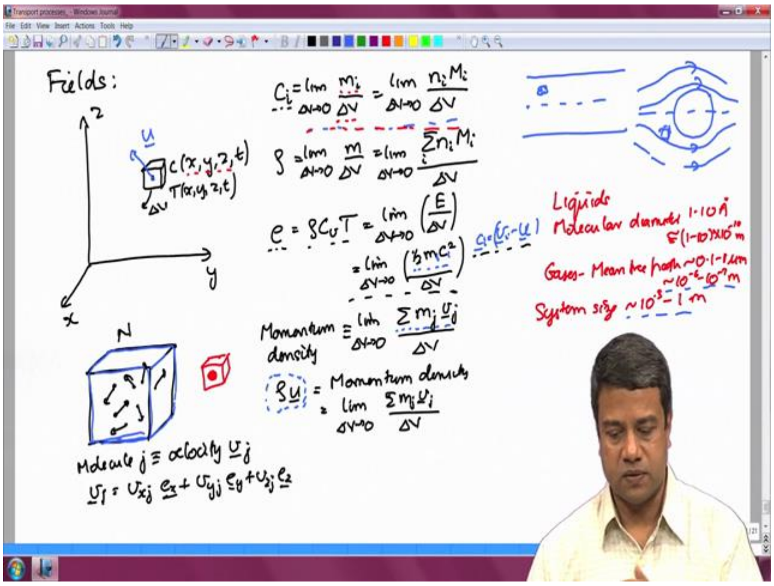

Fields:

$C_i = \lim_{\Delta V \to 0} \frac{m_i}{\Delta V} = \lim_{\Delta V \to 0} \frac{n_i M_i}{\Delta V}$

$\rho = \lim_{\Delta V \to 0} \frac{m}{\Delta V} = \lim_{\Delta V \to 0} \frac{\sum_i n_i M_i}{\Delta V}$

$e = \rho C_v T = \lim_{\Delta V \to 0} \left(\frac{E}{\Delta V}\right) = \lim_{\Delta V \to 0} \left(\frac{\frac{1}{2} m c^2}{\Delta V}\right)$ $\quad \underline{c} = (\underline{v}_i - \underline{u})$

Momentum density $\equiv \lim_{\Delta V \to 0} \frac{\sum m_j \underline{v}_j}{\Delta V}$

$\rho \underline{u}$ = Momentum density $= \lim_{\Delta V \to 0} \frac{\sum m_j \underline{v}_i}{\Delta V}$

Molecule $j \equiv$ velocity $\underline{v}_j$

$\underline{v}_j = v_{xj} \underline{e}_x + v_{yj} \underline{e}_y + v_{zj} \underline{e}_z$

Liquids

Molecular diameter 1-10 Å $= (1-10) \times 10^{-10}$ m

Gases- Mean free path $\sim 0.1-1\,\mu m$ $\sim 10^{-6}-10^{-7}$ m

System size $\sim 10^{-3} - 1$ m

Now, how are we going to analyze the systems? So, in the case of the flow in a pipe for example, or the mass transfer form a spherical particle for example, what we going to do is that in the fluid volume we are going to define fields of the concentration momentum and temperature, we have continuously varying functions in space and in time, they could vary in time as well. So, they are in general functions of the three coordinates as well as time. So, their functions they vary in the three special directions and they vary in time as well.

Now, this fields you are defined at each point within the system. How are these related to the properties of the molecule sensors? I had defined for you previously the concentration field. In order to find out the concentration of a particular species within the flow, what you do is you take the total mass of that species, the concentration as I said is defined at one particular location, you construct a small volume around that location, find out the total mass of the molecules of species i within that location and divided by the volume. In the limit of course, if you construct any volume the concentration will depend upon the volume whether its center at this location and what shape it has and so on; however, in the limit as the goes to zero, this ratio is going to assume a unique value; as the volume goes to zero the mass goes to zero, but the ratio of these two is unique and that is defined as a concentration at that particular location within the fluid.

Similar the mean velocity at a given location; the velocity is a vector it has three components, not to find out the mean velocity at the location we define it through the momentum density. We take a differential volume and calculate: what is the total momentum of all the molecules within that volume, divided by the volume to get the momentum density. I should note that the momentum is a vector, the molecular velocity is a vector, therefore, you have to add the vector in any particular direction it could be either positive or negative, you have to add up all of those and get the total momentum goes in the differential volume divided by the volume itself to get what is the momentum density and through that you defines the momentum density is equal to the mass density times the mean velocity and through that you get the mean velocity. So, the mean velocity is defined through the momentum density.

Even though the molecules have a nonzero fluctuating velocity, the fluid velocity itself could be zero; in a stationary fluid the fluid velocity is zero, but the molecular velocities are not because the molecular velocities at a given location all cancel out in order to give you a net zero fluid momentum density, for a net zero fluid velocity. Similarly the energy density is defined through the thermal energy of the molecules, if molecules had only translational degrees of freedom; the thermal energy is equal to half m c square, where c is equal to the difference between the molecular velocity and the fluid mean velocity.

So, first of all you have to find out what is the fluid fluctuating velocity at each location. That fluid fluctuating velocity is the difference between the molecular velocity and I am sorry; you have to first find out what is the molecular fluctuating velocity at each location. That molecule of fluctuating velocity is the difference between the molecular velocity and the fluid mean velocity, you subtract that out that gives you the fluctuating velocity of each molecule, then you sum up the fluctuating velocity of each molecule times the mass of each molecule and then you take the limit as delta V goes to 0, within this volume the ratio of those two is actually will be defined as rho C v times T, case of mono atomic molecules C v will be 3 by 2 because you have 3 degrees of freedom. This translational thermal energy is can be defined as rho c v t for mono atomic molecules because there are only translations decrees of freedom. In the case of diatomic of polyatomic molecules, there are rotational as well as vibrational degrees of freedom as well, all of the energies in all of those degrees of freedom are added up for each molecule, summed over all the molecules within that volume and divided by the volume, in the limit as the volume goes to zero, this is equal to rho c b t for the internal energy the molecules.

So, that basically gives you the definitions of the density, the mean velocity and the temperature concentrations and so on; however, one has to be careful in how one a place these definitions, I said you take the limit of the volume going to zero, but when you take the limit of the volume going to zero in a volume like this of course, if the volume itself is large compared to the molecular scale, the distance between the molecules in a gas or the molecular diameter in a liquid then you will have a large number of molecules within this volume and one can sensibly define averages.

However if your volume becomes smaller and smaller, such that the volume becomes comparable to the molecular size, in that case you might have one molecule in there, you might have zero molecules in there and when the volume becomes comparable to the molecular size you can no longer define average quantities because the average will be fluctuating rapidly in space and time, it will depend upon whether within this volume there was a molecule at that instant or not and therefore, you do not have a sufficiently large sample of molecules in order to be able to make a sensible statistical average therefore, the volume that we choose has to be much larger than the molecular diameter or the mean free path in a gas, you cannot apply this continuum description when the volume becomes much smaller then are comparable to the molecular dimensions of the molecular mean free path.

You have to have a volume that is sufficiently large that it does contain a large number of molecules. So, at every instant in time even if whether one molecule leaves that comes in it does not make that much difference to the quantity that is being defined the average concentration the momentum or the energy. So, it is important that the molecular sizes that the volume be large compared to the molecular size; however, to have a sensible definition a continuum sensible continuum definition, it is also necessary that this volume has to be much smaller than whatever a system that are analyzing. So, we are analyzing the pipe flow for example, I should be able to define a volume that is much smaller than the diameter of the pipe, otherwise it does not make sense to define a field which has a value at every point, you can define a field only if the volume or which you are averaging is much smaller than the size of the pipe.

Similarly, for the flow around particle, it was a flow around the particle the volume that I defined has to be much smaller than the volume around the particle. If I define a volume that is large, then that will average over variations in the concentration in the vicinity of this particle or within the cross section of this pipe therefore, you need to have an intermediate scaled intermediate between the system than scale the pipe diameter the particle radius of the radius the impeller in the case of the stirring in a tank and so on. You need have an intermediate size which is intermediate between that large system size and the molecular scales, only then does it make sense to define continued fields as I have done in this case.

In this intermediate range you can define a size, the size of the differential volume that is small compared to the system size, but still much larger than the molecular size. So, that each volume contains many molecules, so that one can sensibly define average quantities within that differential volume, but it is still small enough that it captures the variations in the properties in the system, that is be much smaller than the system size so that it captures the variations in properties in the system is only this intermediate range that we can use a continuum approximation.

For that of course, the system size has to be sufficiently large compared to molecular sizes, you cannot for example, use this continuum description in systems whose size itself is comparable to the molecular sizes. Fortunately for us molecular sizes are sufficiently small that this continuum approximation is valid for most systems that we consider for example, in liquids the molecular diameter is of the order of 1 to 10 angstrom, which is about 1 to 10 into 10 powers minus 10 meters. So, the system size is actually molecular sizes are actually at the order of 10 power minus 10 meters.

In the case of gases the mean free path is of the order of 0.1 to 1 microns micrometers, this is about 10 power minus 6 to 10 power minus 7 meters. In the case of gases the mean free path is much larger I told you that the distance between collisions is much larger than the molecular diameter and therefore, it is about 10 to 100 times the molecular diameter in this case and because of this for systems that we consider normally in our everyday life system size, that system sizes are typically a server of one millimeter 10 power minus 3 to about 1 meters or even larger in the case of large tanks it could be even larger.

But we rarely consider systems which are less than a millimeter unless we are considering very specific applications such as micro fluidics and you can see that between these two; between this one and this, that is a sufficiently large range of length scales that it makes sense to define intermediate scale, that is approximately the geometric average of these two, in such a way that we can define a volume that is small compared to the macroscopic scale was still very large compared to the molecular scales and it was in this intermediate regime that the continuum approximation is valid, it cannot be used in cases where the molecular scale and the system size are approximately the same.

However most of our applications are in the range where the system size is much larger than the molecule scale and therefore, we can usefully make use of this continuum approximation. Now once we have defined this continuum field, what do we do? We write down equations which are basically conservation equations.

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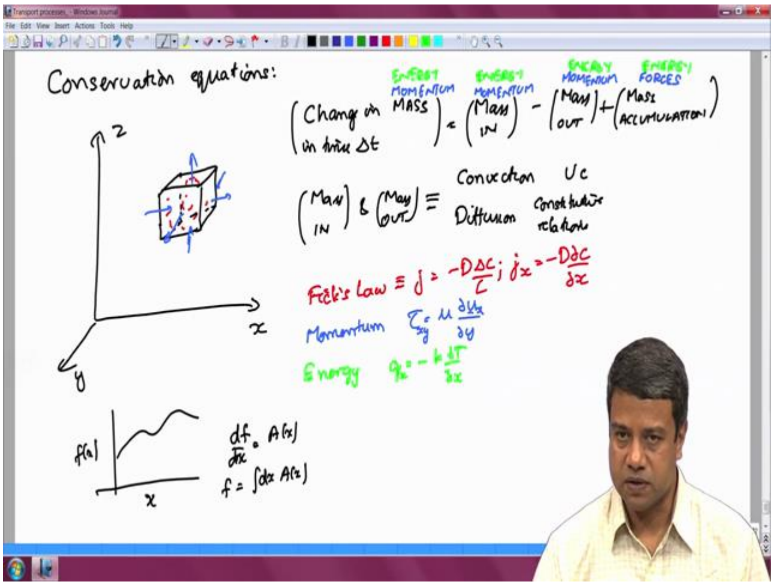

What the conservation equation will tell you is that, for each differential volume within the flow, total mass has to be conserved, mass is always conserved unless speeds are close to the speed of light for example, total mass has to be considered cannot be converted into energy, total momentum has to be conserved the rate of change of momentum has to be equal to the sum of the applied forces, and the thermal energy has to be conserved provided that there is no inter conversion between thermal and mechanical energy. In case that is inter conversion, the rate of change of thermal energy is equal to the rate at which mechanical energy is converted into thermal energy. So, for each of these you will right balance equations, change in mass in time delta t; the change in mass within a time delta t is going to be equal to mass in minus mass out, plus any mass accumulation. If the mass is accumulated due to a reaction for example, you will have a mass accumulation term; if mass is consumed in the reaction this term will be negative. So, let us see only difference.

So, what is saying is that the change in mass within this differential volume of some species equal to the mass coming in minus mass going out, plus the accumulation or depletion. Now the mass coming in and the mass going out to this differential volume, it goes through the surfaces coming in and going out is to the surfaces of this differential volume. So, therefore, you are writing your balance between the rate of changes mass within this volume, to what is coming in and going out. Coming in and going out take place due to two reasons, one is due to convection and the other is due to diffusion.

These are both surface terms, they are proportional to the surface area is calling whatever mask comes in and goes out from portion to the surface area of this volume; it will change in mass portion to the volume itself. The convection I told you of mass for example, is U c equal to U times the concentration. So, if you know the fluid velocity at that point at these surfaces you know how much is coming in and how much is going out, later on the fluid velocity as well as the concentration on the different surfaces. For the diffusion you have to find out what is the mass coming in and going out due to the fluid fluctuating velocity. I am sorry the molecular fluctuating velocities; that is determined by what are called constitutive relations and you have seen that through diffusion it is Fick’s law.

That is how we have written it so far, except that now considering differential volumes you have to write this as a gradient, a derivative concentration with respect to coordinate. So, rather than writing it this way and write the vector flux, the flux in one particular direction let us say the x direction coordinate system here. I will write the flux in the x direction as minus d times the variation of concentration with respect to the x coordinate. So, this is the way that I will write the flux in this particular case. So, therefore, I have to put in the convection and the diffusion contributions to the mass in and mass out and use those in order to get an equation for the change in mass in the time delta t based upon the mass distribution throughout the volume. Note that the convection term just contains the concentration at that location itself whereas, the diffusion term contains the derivative of the concentration, it contains the spatial variations of the concentration.

Therefore the change in mass in a time delta t can be written as the time derivative and these convection and diffusion terms will contain spatial derivatives. So, we will end up with a partial differential equation for the concentration field; exact same principle applies for momentum, momentum in, momentum out and the other hand mass accumulation I will have the sum of forces on that system.

Once again momentum transports there are two effects: convection and diffusion. Diffusion is given by the constitutive relation, which is the equation for the stress, this is the shear stress tau x y, I will come and specify this for you in the next lecture more precisely, but it is the analysis exact between mass and momentum and the same thing for energy and here it is energy accumulation and for energy I have the constitutive relation and so on in the other directions as well.

So, this is a fundamental equation fundamental balance equation, which contains a convection term and the diffusion term. Both of these depend upon the current distribution of mass momentum or energy throughout this entire volume. So, when I write this down I will get a partial differential equation, which contains variations in time as well as variations in space that equation is valid at each location within the flow. Now from this equation I have to now determine what is the concentration temperature or velocity field; that field is determined by integrating this equation just as for example, if you had the equation for some function f of x is a function of x and he had some function, you are given a differential equation d f by d x is equal to sum function A of x.

You can now integrate this to find out what is function a f equal to integral d x, A of x. Similarly you can do it if you have a second order differential equation and so on. These are all ordinary differential equations because this function f depends only upon x, in this case what we will get a partial differential equations this equation depends upon time as well as spatial locations therefore, I have to go through an integration process to find out what is the concentration at each location within the domain by an integration process, which involves the application of boundary conditions as well because when you have do an integration you get constants of integration, in this particular case they would not be constant because we are working in a multi dimensional space therefore, you get some functions which are to be determined from the boundary conditions.

So, it is in three spatial dimensions and time dimension, the differential equation is analogous to what you would have in one dimension, except that you have multiple directions here; however, the solution is not the same there is no general way to solve these equations in order to get an exact solution in the case of partial differential equations. In fact, if the equation is linear, you are guaranteed there is a solution; is the equation is non-linear, there is no guarantee that the solution even exists.

And this is where physical insight comes in, the solution of these equations requires a physical understanding of the processes and an understanding of what approximations we can use in different parameter regimes in order to simplify the problem and thereby get a solution.

So, rather than trying to get an exact solution for each differential equation each configuration, you will try to simplify the problem based upon physical understanding in order to get a simplified equation then solve this not to get the concentration fields and from that determine the average fluxes. The physical understanding: what are the important processes can we scale the equations in determine this convection more important? Is diffusion more important? In case diffusion is more important can we formulate methods for solving the diffusion equation; that we can get a solution in cases where convection is not important; in cases where convection is more important, can we formulate a solution which does include connection primarily, but as I told you close to surfaces transport across surfaces that should take place to diffusion, these effects have to be incorporated in order to get a solution of the equation and from that to be able to get that the correlations for the dependent fluxes the average fluxes.

So, that will be the theme of the rest of course, how do we use? First of all formulate these differential equations which give us the balances, how can we simplify these in specific regimes in order to get solutions which are valid in those regimes, it is important to realize that all of these correlations are based upon approximations, they work in certain regime, the reason they work is because in those regimes we can make specific approximations which will enable us to simplify the problem sufficiently that we can get an analytical solution in that regime. So, we will build up our physical insight in order to be able to solve these equations in specific configurations and from that get the kind of correlations which are used in order to predict; what are the average fluxes in all of these transport processes.

So, before we go on to actually analyzing formulating with the essential equation, in the next couple of lectures I will talk about diffusion. Diffusion transport due to molecular velocity fluctuations, how does diffusion arise and why do you get the kinds of constitutive relations that I have written down here from the molecular velocity fluctuation? So, molecular diffusion of mass momentum and energy and the estimation of the diffusion coefficients will be the subject of the next couple of lectures, before we go on to formulating conservation equations when looking at methods based upon physical insight in order to solve these conservation equations. I will start with diffusion in the next lecture, I will see you then.