Bio - Microelectomechanical Systems

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Module No. # 01

Lecture No. # 30

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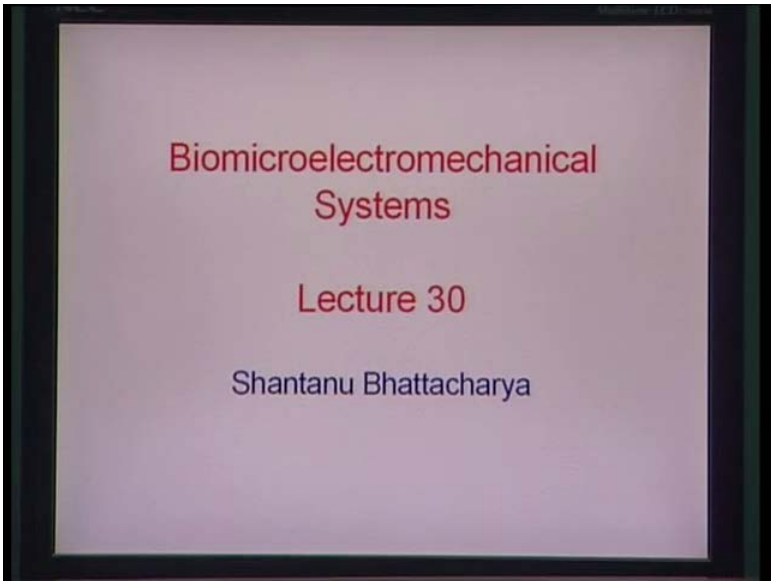

Biomicroelectromechanical Systems

Lecture 30

Shantanu Bhattacharya

Hello and welcome back to this 30th lecture of Biomicroelectromechanical Systems.

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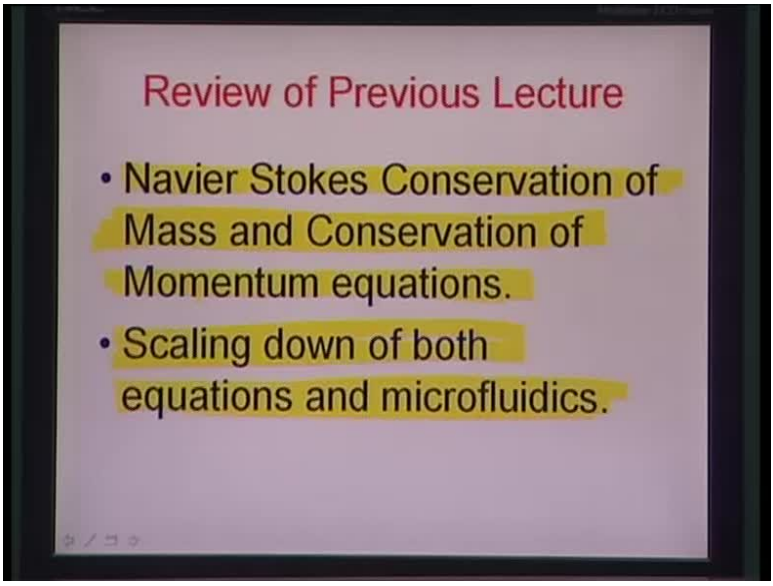

Review of Previous Lecture

- Navier Stokes Conservation of Mass and Conservation of Momentum equations.
- Scaling down of both equations and microfluidics.

Just quickly preview what we did last time. We talked about these famous Navier-Stokes Conservation of mass and Conservation of momentum equations, tried to derive them from the elementary control volume concept and then actually tried to go ahead and scale down both of these equations and tried to figure out how they apply to microfluidics.

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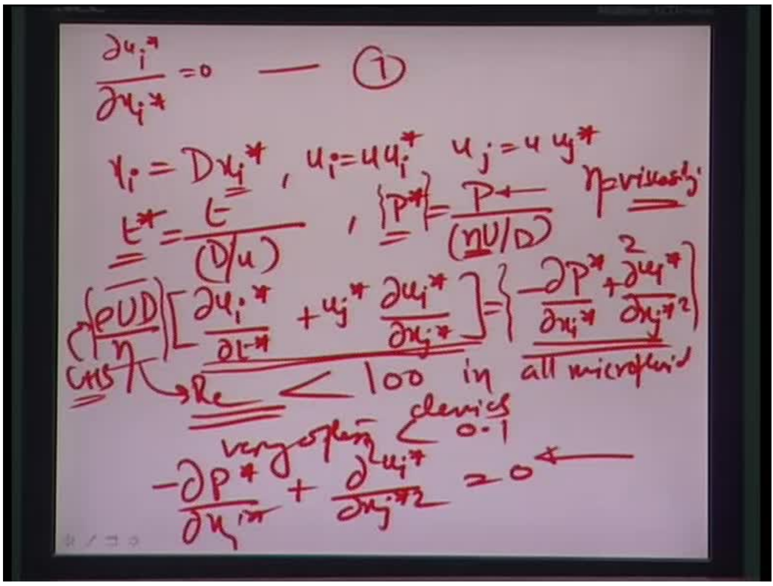

$\frac{\partial u_i^*}{\partial x_i^*} = 0$ — ①

$x_i = D x_i^*$, $u_i = U u_i^*$, $u_j = U u_j^*$

$t^* = \frac{t}{(D/U)}$, $\{P^*\} = \frac{P}{(\eta U/D)}$ η = viscosity

$\left(\frac{\rho U D}{\eta}\right)\left[\frac{\partial u_i^*}{\partial t^*} + u_j^* \frac{\partial u_i^*}{\partial x_j^*}\right] = \left\{-\frac{\partial P^*}{\partial x_i^*} + \frac{\partial^2 u_i^*}{\partial x_j^{*2}}\right\}$

LHS → Re < 100 in all microfluidic devices

very often < 0.1

$-\frac{\partial P^*}{\partial x_i^*} + \frac{\partial^2 u_i^*}{\partial x_j^{*2}} = 0$ ←

Let us actually go ahead and just reiterate a little bit of what the conclusions were out of the scaling down. We tried to first take the conservation of momentum equation and the scale down version of this equation came out to be dui star by dxi star equals 0. and this essentially indicated and Let me just reiterate the way these expressions came into picture. xi would be related to a scaled distance at that particular scale times of xi star, the xi star is a dimensionless number. Similarly, ui and uj both were equated to a scaled velocity at that particular scale, times of ui star and same scale velocity times of uj star respectively.

Also, we saw that the time star of the non-dimensional quantity in time in this particular scale would be represented as the original time divided by the distance by u, the velocity and the pressure star which is again a non-dimensional quantity in pressure in this particular scale was represented by the term P - this is the absolute value of pressure divided by eta U by D. As we all know, eta is the viscosity and it is actually scale independent. So, it remains constant even if you go to the micron scale; you have to assume though that the equations are that of continuity equations or continuously maintained for the viscosity to be independent of time and constant property associated with the medium.

So, because our micro flows are mostly in this domain where the continuum is still assumed and all the modeling is done using the continuity equations, it is almost always obvious to assume the viscosity to be constant at that particular scale. Therefore, the pressure star that means P star which is essentially the dimensionless number in the Navier-Stokes equation would be represented as P the absolute value of the pressure divided by nU by D and so we derived at the second equation the conservation of momentum equation and we figured out that rho U D by eta times of del ui star by del t star plus uj star times of del ui star divided by del xj star would be equal to minus del P star by del xi star plus del 2 ui star divided by or del x with respect to del xj star square.

Which means that This essentially is Reynolds number Re and this we found out last time while scaling down and Re is more or less, less than 100 in all microfluidic devices, very often less than 0.1. It almost always gives you an opportunity to write down minus del P star by del xi star, the right hand side of this particular equation, plus del 2 ui star divided by del xj star square equal to 0 because the left hand side here is essentially dominated by the lesser magnitude of the Reynolds number. (Refer Slide Time: 04:30) So, irrespective of whatever this quantity here is, the overall size of the quantity in the LHS because of the low value of Reynolds number is very small in comparison to this quantity inside the brackets.

So, because it is overall negligible, we can assume this RHS part of the equation to be equal to 0. What are our conclusions from this particular statement? One conclusion which comes out is that at this particular scale, the momentum equation becomes time independent. Therefore, it is obvious to assume that if suppose you have 2 or 3 flows which are introduced into a same micro channel and we assume low value of Reynolds number, due to which the left hand side of this continuity equation or momentum equation becomes 0, the obvious conclusion would be that the pressure driven flow - number 1 and number 2 is that it is time independent. Therefore, if you could actually run past both these different types of flows from the outlet end back into the inlet end or you reverse the flows in time, they should be able to emanate as original inlets to the particular channel.

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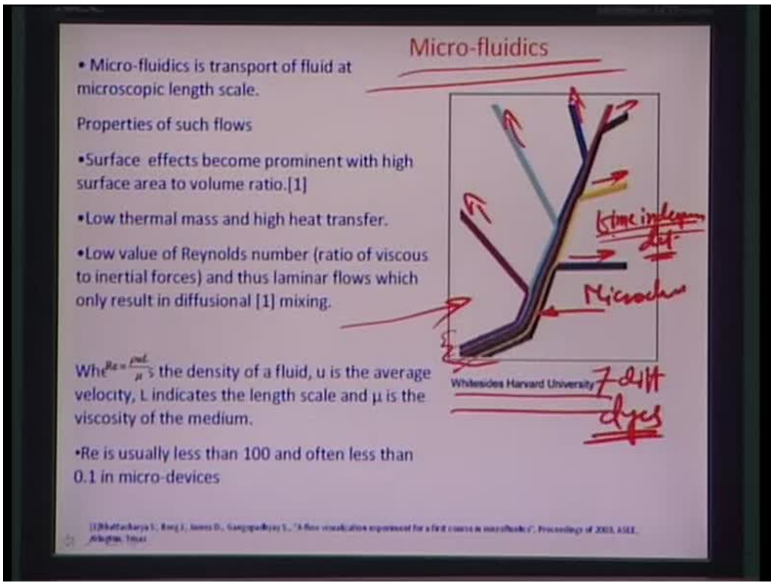

Micro-fluidics

- Micro-fluidics is transport of fluid at microscopic length scale.

Properties of such flows

- Surface effects become prominent with high surface area to volume ratio.[1]
- Low thermal mass and high heat transfer.
- Low value of Reynolds number (ratio of viscous to inertial forces) and thus laminar flows which only result in diffusional [1] mixing.

Where $Re = \frac{\rho u L}{\mu}$, ρ is the density of a fluid, u is the average velocity, L indicates the length scale and μ is the viscosity of the medium.

- Re is usually less than 100 and often less than 0.1 in micro-devices

This is illustrated in this particular example here. If you see again I would just like to reiterate that this slide was shown before. That in microfluidics very often there are situations like this here where you are seeing that you have these different dyes which are flowing into this particular channel; you have about 1, 2, 3, 4, 5, 6, 7 different dies here.

As you see, as this flow happens past this micro channel here and goes for a certain distance. We are able to extract the dyes independent in the same cover as they were introduced originally at the other ends. Therefore, it is really the momentum equation is really time independent assuming that this were to be true and this actually is a simulation result done by the Whitesides group at Harvard. If you assume these flows to be flowing in the reverse direction then you should be able to get these flows out as independent dyes or as independent colours.

This is in fact, the essence of the scaled down form of the momentum equation in this particular scale. The domain of microfluidics therefore, is a very novel and interesting domain wherein it is a really very hard for flows laid out together without any diffusional effects to mix.

However, because of this particular deliberation that has been just shown in the last slide and the time independence of the momentum equation all the mixing which happens at the micron scale takes place because of a concentration gradient and is diffusional in nature.

Basically, that gives us a feel that it may be impossible sometimes to flow two fluids together in a micro channel and mix them, if the 2 flows have equal concentrations and there is no concentration gradient which is established between the flows; that is number 1. Number 2 is that it becomes a very interesting paradigm in microfluidics to design intelligent systems which could be actually, suppose there is also existence of diffusion in the parallel flows so which could be actually promoting diffusion and reducing the diffusion time in a manner that it becomes lesser than the residence time of the flows and the flows start mixing. So, these are 2 interesting paradigms in microfluidics.

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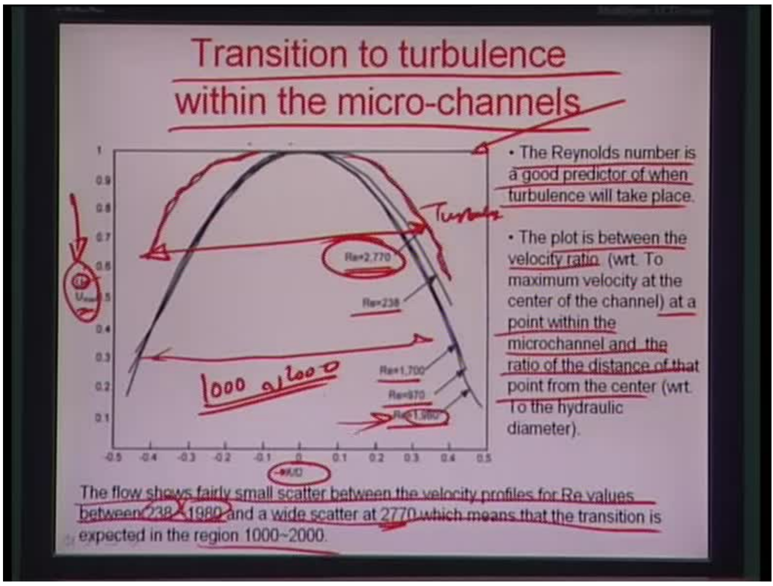

Transition to turbulence within the micro-channels

- The Reynolds number is a good predictor of when turbulence will take place.
- The plot is between the velocity ratio (wrt. To maximum velocity at the center of the channel) at a point within the microchannel and the ratio of the distance of that point from the center (wrt. To the hydraulic diameter).

The flow shows fairly small scatter between the velocity profiles for Re values between 238 – 1980 and a wide scatter at 2770 which means that the transition is expected in the region 1000~2000.

So, I would like to go ahead and actually see some of the effects of Reynolds numbers on the different flows particularly within micro channels and I call this slide, transition to turbulence within the micro channels. If you see here, there are different Reynolds number values at which we plotted the U by U maximum, which is essentially the velocity at a certain position divided by velocity at the center which is the maximum velocity and this is plotted with respect to x by D, x is the position at which the local velocity is u and D is essential the diameter of the particular channel.

As we see here, the Reynolds number definitely is a very good predictor of when the turbulence will take place. The plot is between the velocity ratio at a point within the micro channel and the ratio of the distance of that point from the center. Conclusions from this are that if you see this particular plot here, it is basically at a very high Reynolds number value, 2770 that you see a fairly a large scatter in the velocity. Therefore, you can see that you know the if you see this scatter can be also represented by this span of the parabola, an inverted parabola. and so if The span is much more in this case as compared to the low Reynolds number cases from 238 to almost 1980 when the scatter is not that high and which also shows that probably at 2770, there is a transition or between 2770 and 1980, there is definitely a transition into the turbulent zone.

Therefore, there is no control really on U after this higher Reynolds number value is reached whereas, at a lower Reynolds number value there is still some control and you can really say that the flows have not yet turned into a eddies or vortices or it has not really turned into turbulent flows and that is what this graph would indicate. Therefore, the flows shows fairly small scatter between the velocity profiles for Re values between 238 and 1980 and a wide scatter at 2770 which means that the transition is expected in the region 1000 to 2000.

Which is also true otherwise that there is a transition definitely between Reynolds number 1000 and 2000 whether it is the macroscopic counterpart or the micro channel.

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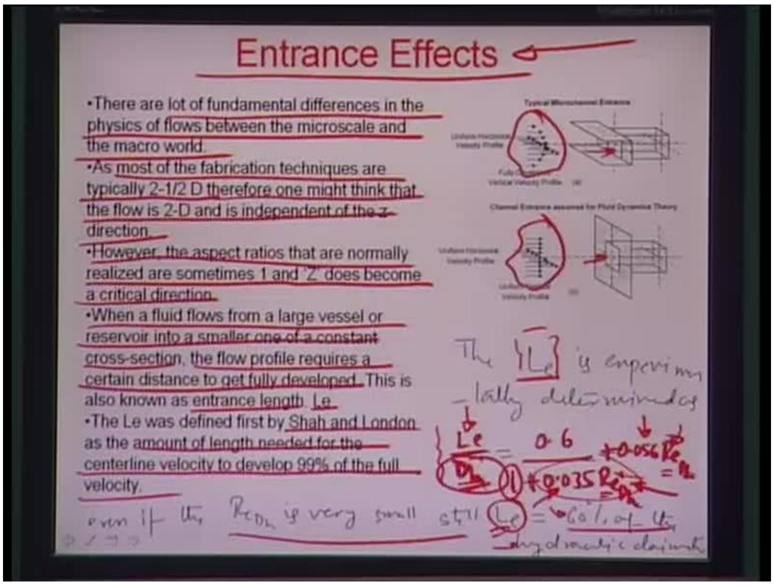

Entrance Effects

- There are lot of fundamental differences in the physics of flows between the microscale and the macro world.
- As most of the fabrication techniques are typically 2-1/2 D therefore one might think that the flow is 2-D and is independent of the z-direction.
- However, the aspect ratios that are normally realized are sometimes 1 and 'Z' does become a critical direction.
- When a fluid flows from a large vessel or reservoir into a smaller one of a constant cross-section, the flow profile requires a certain distance to get fully developed. This is also known as entrance length Le.
- The Le was defined first by Shah and London as the amount of length needed for the centerline velocity to develop 99% of the full velocity.

The {Le} is experimentally determined as

$$\frac{L_e}{D_h} = \frac{0.6}{1 + 0.035\,Re_{D_h}} + 0.056\,Re_{D_h}$$

even if the Re_{D_h} is very small still L_e = 60% of the hydraulic diameter

One more interesting paradigm to be evaluated in microfluidics is related to the effects which can come at the entrance of a micro channel. As we know that as a channel is approached by flow of a constant velocity and pressure driven flow at the moment after the flow enters the channels, there is always some time which the flow takes to get fully developed where this parabolic profile of the flow gets created within the micro channel.

Now, in cases with in channel In cases of micro channels though this length which is also known as the entrance length where the flow profile or whatever the flow profile takes to get developed fully really also is a kind of function of the Reynolds number and it is very critical to design micro channels by assuming what really would be the entrance length over and above which the flow is fully developed within the micro channel.

Let us explain this even by saying that there are a lot of fundamental differences in the physics of flows between micro and macro scales and most of the fabrication techniques as you know are typically two and half D. Therefore, one might think that the flow 2-D is independent of the of the Z direction. However, the aspect ratios that are normally realized are sometimes 1 and Z becomes a critical direction for these kinds of flows.

When a fluid flows from a large vessel or reservoir into a small one of a constant cross section which means the velocity of approach of this particular flow is almost constant as this approaches this small channel here. The flow takes or the flow profile requires a certain distance to get fully developed. So, this is also known as the entrance length. Various people have tried to experimentally and otherwise calculate what this entrance length would be and the best experiment that was proposed by Shah and London was that the amount of length needed for centerline velocity to develop 99 percent of the full velocity is actually given by this expression here. (Refer Slide Time: 13:37) Le, Le is the entrance length divided by Dh, Dh is the diameter of the particular channel is equal to 0.6 divided by 1 plus 0.035 Re Reynolds number of that particular diameter or cross section and plus 0.056 Re Reynolds number at that particular cross-section.

So, entrance length is then a function of the Reynolds number very critically and also the cross section diameter of that particular micro channel. Le is normally about 60 percent of the hydraulic diameter in case the Reynolds number is low because then there is the 1 is prominent over this term 0.035 Reynolds number or 0.056 Reynolds number.

However, in cases where this Reynolds number becomes a little bigger, the entrance length effects are felt more properly. This is the hydraulic diameter cross-section diameter or the hydraulic diameter. In cases where the Reynolds number becomes little bigger, the contribution from this term and this term is significantly enhanced and therefore, the entrance length becomes less than 60 percent of the hydraulic diameter.

What does it mean really? It means that suppose in case of a micro channel, when the Reynolds number is comparatively low at the entrance length has significant amount in terms of 60 percent of the hydraulic diameter as opposed to macro scale where Re is more and this is much lesser than 60 percent.

So, this shows that whenever you want to design micro channel, you almost have to be careful always about selecting the entrance length before the perturbations or structures that you would like to create within the micro channel to cause certain physical phenomena would start to be placed. You need to wait up till the whole entrance length which is needed for developing the flow fully is traversed before the flow can get into region were significant differences can be made to it by changing the physical form or shape of the micro channel. So definitely, entrance effects are very critical as far as microfluidics is concerned.

So, this brings us to an end of the theoretical analysis that was needed to understand microfluidics. I would like to go ahead now today and try to get into a little more different area as to what would happen really if the continuum assumptions failed and then would be talking about things which are more related to inter molecular forces. Scaling from microns to nanometers it is very important that we consider altogether different approach which is not driven by continuity and which is more driven by inter molecular forces between the molecules which are present in a very small nanometer cube size probably control volume.

After looking into that aspect really, I would like to go ahead and start with the topics of the actual technology that microfluidics can be put to and that can be directly applied to as in BIOMEMS wherein we would start realizing these active devices like Microvalves, Micromixers, Micropumps, etcetera. The idea is that after we demonstrate all these on a fundamental level we will go ahead and assemble these units together on a single BIOMEMS platform which would do something useful and important.

So, the last part of the course would be probably dedicated to reviewing some of the papers and articles which have been in this area where these small fundamental concepts are introduced and integrated together to form integrated systems which would do total chemical analysis.

Let us actually go ahead and see what happens when the scale changes to a little bit lower and as I told you before in one of my earlier lectures that continuum assumptions fail beyond a certain scale. Let us say for example, if you have a small control volume which is about 1 nanometer cube in dimensions and you assume or you try to find out what is the density or velocity of molecules which are within this 1 nanometer cube.

There is a tendency of the molecules to rush past the boundaries of these very randomly with time resulting in a change in density with time or may be a change in viscosity with time. So, all these properties which were assumed to be averaged out properties as in case of continuum mechanics or continuum fluid mechanics would actually boil down to a time dependent property when you go to this particular scale. Therefore, whatever the presumption Navier-Stokes equations made in assuming that the density is constant, the flow is incompressible or even if the velocity is really only dependent on space and even if it is dependent on time, it does not change at a certain instant of time.

These assumptions were made in order to derive the Navier-Stokes equations. However, that is not true at that small scale of 1 nanometer cube or so. Therefore, inter molecular forces would play a major role there in order to figure out what is going on in terms of interactions between the molecules etcetera.

Intermolecular Forces.

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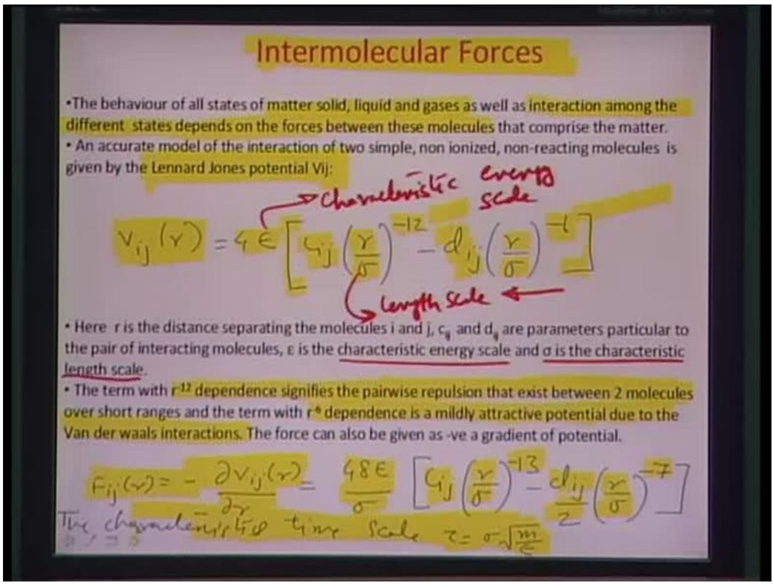

Intermolecular Forces

- The behaviour of all states of matter solid, liquid and gases as well as interaction among the different states depends on the forces between these molecules that comprise the matter.
- An accurate model of the interaction of two simple, non ionized, non-reacting molecules is given by the Lennard Jones potential Vij:

Characteristic energy scale

$$V_{ij}(r) = 4\epsilon\left[c_{ij}\left(\frac{r}{\sigma}\right)^{-12} - d_{ij}\left(\frac{r}{\sigma}\right)^{-6}\right]$$

length scale

- Here r is the distance separating the molecules i and j, c_{ij} and d_{ij} are parameters particular to the pair of interacting molecules, ε is the characteristic energy scale and σ is the characteristic length scale.
- The term with r^{12} dependence signifies the pairwise repulsion that exist between 2 molecules over short ranges and the term with r^{6} dependence is a mildly attractive potential due to the Van der waals interactions. The force can also be given as -ve a gradient of potential.

$$F_{ij}(r) = -\frac{\partial V_{ij}(r)}{\partial r} = \frac{48\epsilon}{\sigma}\left[c_{ij}\left(\frac{r}{\sigma}\right)^{-13} - \frac{d_{ij}}{2}\left(\frac{r}{\sigma}\right)^{-7}\right]$$

The characteristic time scale $\tau = \sigma\sqrt{\frac{m}{\epsilon}}$

.

What are Intermolecular Forces? If you look at the different states of matter you can really categorize matter into solids, liquids and gases. These are all based on the interaction among the different states depending on the forces between molecules of these particular states which comprise the matter.

These interaction forces can be very well explained by a model of potential energy of two such molecular systems which are close by at a distance r and this is also known as the Lennard Jones potential model. It is a non-dimensional equation and we have scaled down factors there. You have a skill factor for distance between let us say 2 molecular systems and so without going into the details of derivation of such an equation I would just like to illustrate because most of the stimulation work which is at this nanometrics scale as far as fluidics is concerned is more using this model of Lennard Jones potential.

Let us say, you have two systems i and j and that means 2 molecular systems of this particular notation and they are separated by a distance r. So, the potential that would happen between 2 of these i and j systems is equal to 4 epsilon cij r by sigma to the power minus 12 minus dij r by sigma to the power of minus 6.

(Refer Slide Time: 21:32) Let me just go ahead and explain what all these different terms are. Epsilon is essentially the scaled energy; this is the scaled energy, the characteristic energy scale we call it, characteristic energy scale. Sigma is the characteristic distance scale or the length scale; this is the length scale.

By now, you are probably familiar because we did a scaling down in the Navier-Stokes equation of conservation of momentum. You probably are aware of what these different scales mean. It is characteristic distance or characteristic energy value at the scale at which all these different forces or potentials are considered.

r by sigma is a non-dimensional term. Similarly, dij by epsilon again is a non-dimensional term because it is a comparison of the potential with respect to an energy scale that means a value of energy at that particular scale in which all these experiments or all these equations is being used for studying the intermolecular behaviour.

What is more interesting here is that there are 2 different terms and dependencies on r by sigma. 1 is to the power of minus 12 and another is to the power of minus 6. This minus 12 term would signify the pairwise repulsion that exists between 2 molecules and this repulsion as you all know are because of inter-electronic repulsion between the 2 molecular systems. There are orbitals which contain electrons which has a probability of having an electron or having bunch of electrons.

When 2 of such molecular systems come close by, there is repulsion between the electrons on both these systems which would cause them to have a positive potential. It takes some work for getting them any closer than the characteristic distance r in which they are placed. So, that is what the r minus 12 dependence would signify and then there is r minus 6 dependence which is a mildly attractive potential and this is due to Van der waals interaction forces.

So, what are really Van der waals forces? They are basically attractions formulated between 2 such molecular systems between the electrons on one and the nucleus on the other and similarly, the electrons on the other and the nucleus on the first one. That is what Van der waals interaction forces are and they are principally attractive in nature. However, they are very weak forces because the attraction between the nucleus on the first and the electron on the second has to go through an electronic layer. I mean it has to shield by electronic layer it is shielded by electronic layer which is in between. Therefore, r by sigma to the power minus 6 dependency is a pretty much weak force in comparison to the minus 12 dependency, which is a strong force.

Therefore, we can easily say that the potential is contributed by the pairwise repulsion and the pairwise attraction given by these 2 terms here - minus 12 and minus 6. Also what is interesting for me to tell you is that as you know force between these 2 systems i and j is also represented by a negative gradient of the potential between the 2 systems.

We can calculate Fij the force as minus dVij by dr where r is the intermolecular distance between these 2 molecular systems. Fij(r) essentially is minus dVij(r) by dr and if I actually differentiate this Vij term here with respect to r, we get 46 epsilon by sigma cij r by sigma to the power of minus 13 which is a pairwise repulsion force probably and minus dij by 2 r by sigma to the power of minus 7 which is the pairwise Van der waals attraction force.

In this particular scale, I can also assume that the corresponding timescale would be represented by this quantity here sigma root over m by epsilon, m by epsilon again is mass per unit energy which has the dimensions of square of velocity and a typical characteristic velocity at this scale could be represented by the mass at this scale divided by the energy at this particular scale.

Therefore, under root the mass per unit energy gives you the velocity scale and dividing the distance sigma by the velocity scale would give you an indication of the timescale - what kind of times or characteristic times would exist in this particular scale.

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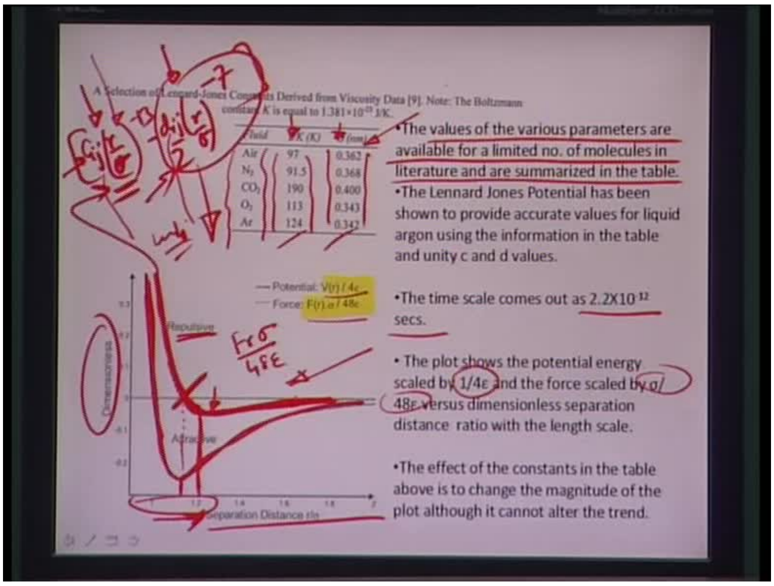

A Selection of Lennard-Jones Constants Derived from Viscosity Data [9]. Note: The Boltzmann constant K is equal to 1.381×10^{-23} J/K.

Fluid	ε/K (K)	σ (nm)
Air	97	0.362
N_2	91.5	0.368
CO_2	190	0.400
O_2	113	0.343
Ar	124	0.342

- The values of the various parameters are available for a limited no. of molecules in literature and are summarized in the table.
- The Lennard Jones Potential has been shown to provide accurate values for liquid argon using the information in the table and unity c and d values.
- The time scale comes out as 2.2×10^{-12} secs.
- The plot shows the potential energy scaled by $1/4\varepsilon$ and the force scaled by $\sigma/48\varepsilon$ versus dimensionless separation distance ratio with the length scale.
- The effect of the constants in the table above is to change the magnitude of the plot although it cannot alter the trend.

What is also interesting here is that if you really plot the dimensionless parameters V(r) by 4 epsilon and F(r) by 48 epsilon times sigma which is, if you just see back in this equation nothing, but this whole dimensional term in one case, the force divided by 48 epsilon sigma and this whole dimensional term on another case which is Vij, the potential function divided by 4 epsilon.

These are 2 non-dimensional terms and what is interesting here to find out is that there are 2 curves which come out. One is for the potential function and of course, these dimensionless numbers are plotted with respect to the separation distance r by sigma. So, what we find out here is that the behaviour in both the cases are pretty much similar except the fact that the force value has a more deeper well in comparison to as of the potential value has much more deeper well in comparison to the force value here.

What is also interesting here is to note that beyond a certain distance, let us say this particular distance where it really has the peak point, the forces try to gain prominence of the Van der waals attraction. So, this region here is the repulsive force. If you have to see the dimensionless quantity in this particular example F(r) sigma by 48 epsilon is continuously going down which means that if you look at the dimensionless quantity here which is let us say cij r by sigma to the power of minus 13 minus dij by 2 r by sigma to the power of minus 7. This going down would signify that this term here, the second term here is starting to dominate and which means that this is the pairwise repulsion this is the pairwise attraction - the Van der waals attraction.

So, the Van der waals attraction is continuously dominating or it is trying to dominate, but it is being superposed by a higher value of r by sigma when it is below the certain separation distance. After it crosses certain characteristic separation distance, this component here really predominates which is actually this point here, where the pairwise attraction becomes more than the pairwise repulsion after which again there is a slow prominence or a slow gain of the first term where it asymptotically goes all the way to 0.

If you draw the potential function, it also shows similar behaviour and the point where the forces have really changed from being perfectly repulsive to slightly attractive here. The potential function is actually dipping down to its minima at that particular point where there are probably close to 0 forces. There are no forces of any attraction or repulsion and the attraction, repulsion is kind of balanced each other and both the terms in the dimensionless quantity are equal to each other.

So, if you really look at these Lennard Jones functions in the case of diatomic gases particularly or in case of certain gaseous states, the values of various parameters available for a limited number of molecules have only been studied and summarized and specially they have been done so more for gases wherein you can find out the characteristic energy scale per unit, Boltzmann constant and also the characteristics distance scale. Mind you, there are only a few systems in the world which have been really modelled and studied for finding out these different energy scales or distance scales etcetera.

Some of them are illustrated here in the table like for example, in case of air, the energy scale would be typically energy scale per unit Boltzmann constant k would typically be equal to about 97 kelvin, for N2 nitrogen it would be about 91.5, CO2 it is 190, oxygen it is 113, Air 124, so and so forth and in terms of distance scale in nanometer range, the air molecules have probably a characteristic distance of 0.362 which goes all the way to about 0.342 for Argon.

These have been of course, calculated by assuming cij and dij parameters to be both unity. That is how these values have been really calculated. The timescale for these kinds of energy and distance scales come out to be about 2.2 picoseconds. These are some of the characteristic dimensions which are available at the domestic scale that we are talking about. The plot again here as you are seeing here has been shown only for these few systems. What is interesting here what I did not discuss before is that it is basically the potential energy scaled by a factor of 1 by 4 epsilon and the force scaled by sigma by 4 epsilon.

The effects of these constants in the table above here really is to not change the basic characteristic, but to actually shift it by adding a dc bias. So, the whole curve can shift up and down if these characteristic parameters epsilon by k and sigma would change without really changing the behaviour or the trend that the dimensionless number would follow with respect to r by sigma. So, that is all about Lennard Jones potential models.

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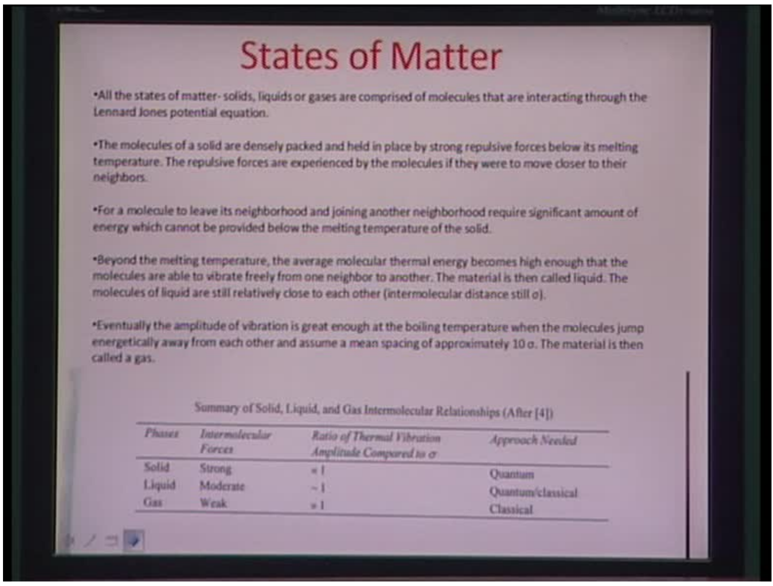

States of Matter

- All the states of matter- solids, liquids or gases are comprised of molecules that are interacting through the Lennard Jones potential equation.
- The molecules of a solid are densely packed and held in place by strong repulsive forces below its melting temperature. The repulsive forces are experienced by the molecules if they were to move closer to their neighbors.
- For a molecule to leave its neighborhood and joining another neighborhood require significant amount of energy which cannot be provided below the melting temperature of the solid.
- Beyond the melting temperature, the average molecular thermal energy becomes high enough that the molecules are able to vibrate freely from one neighbor to another. The material is then called liquid. The molecules of liquid are still relatively close to each other (intermolecular distance still σ).
- Eventually the amplitude of vibration is great enough at the boiling temperature when the molecules jump energetically away from each other and assume a mean spacing of approximately 10 σ. The material is then called a gas.

Summary of Solid, Liquid, and Gas Intermolecular Relationships (After [4])

Phases	*Intermolecular Forces*	*Ratio of Thermal Vibration Amplitude Compared to σ*	*Approach Needed*
Solid	Strong	$\ll 1$	Quantum
Liquid	Moderate	~ 1	Quantum/classical
Gas	Weak	$\gg 1$	Classical

If you look at the states of matters, what are the differences in terms of forces? In a solid, we can assume all the molecules being densely packed and held by strong repulsive forces. The pairwise repulsion is very high in some solids and as a result of which putting a particular atom from its position out of that is highly difficult because it is being repelled from all these sides by equal amount of high repulsive forces. So, it remains in its state very firmly bound in where it is without really being able to get liberated from that particular state.

So, moving an atom from one neighbourhood to another becomes an immense problem. For a molecule to kind of leave its neighbourhood and join another neighbourhood you would need to provide energy to the system and this energy would be in terms of thermal energy. If you have bond vibrations which are happening between these molecular system, after a while the kinetic energy of the molecules would be sufficient enough for it to leave one neighbourhood to another and that is also known as the melting temperature or the melting point of the particular solid where the molecules are just about capable to move between neighbourhoods and it has sufficient amount of kinetic energy for doing that.

Beyond the melting temperature of course, the average molecular thermal energy becomes high enough so that the molecules are able to vibrate freely, go over large distances and you know between one neighbourhood to another. If the distance that they are traversing of distance scale that they are traversing is till stigma they are also called liquid state material.

But then if the distance becomes almost an order of magnitude more like about 10 sigma or so, they are known as gaseous states. In that kind of a situation where the inter molecular distances are more than about 10 sigma, sigma being the distance scale in the solid state, these are essentially then known as the boiling temperature and the species are known as gaseous species.

In a nutshell, there are 3 different configurations to look at. Solid state, the atoms are firmly bound, there are huge amount of repulsive forces to an atom in its pocket from all its neighbours and movement between neighbourhoods becomes an impossibility. In a liquid state just about when kinetic energy is applied and it has been able to lift to a state where the atom can from move from one neighbourhood to another; the distances moved is still about same range sigma, but the movement just becomes possible is known as liquid state or the melting point of the material. At a point when this sigma increases to about 10 sigma or so and there is total decontrol on the molecule from its current location, it reaches the boiling point, it is known as a gas phase.

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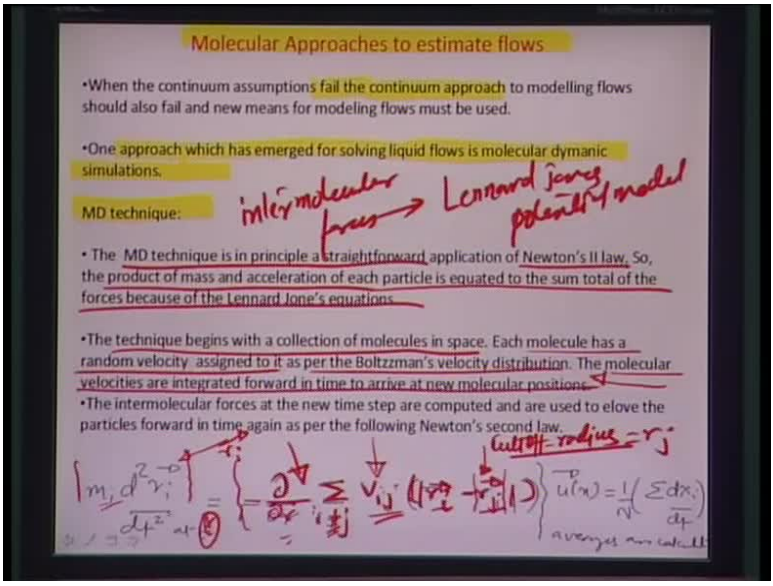

Molecular Approaches to estimate flows

- When the continuum assumptions fail the continuum approach to modelling flows should also fail and new means for modeling flows must be used.
- One approach which has emerged for solving liquid flows is molecular dymanic simulations.

MD technique:

intermolecular forces → Lennard Jones potential model

- The MD technique is in principle a straightforward application of Newton's II law. So, the product of mass and acceleration of each particle is equated to the sum total of the forces because of the Lennard Jone's equations
- The technique begins with a collection of molecules in space. Each molecule has a random velocity assigned to it as per the Boltzzman's velocity distribution. The molecular velocities are integrated forward in time to arrive at new molecular positions.
- The intermolecular forces at the new time step are computed and are used to elove the particles forward in time again as per the following Newton's second law.

cutoff radius = r_j

$$m_i \frac{d^2 \vec{r}_i}{dt^2} \text{ at } t = \left\{ -\frac{\partial}{\partial r} \sum_{i \neq j} V_{ij}\left(|\vec{r}_i - \vec{r}_j|\right) \right\} \quad \bar{u}(x) = \frac{1}{N}\left(\sum \frac{dx_i}{dt}\right)$$

averages are calculated

Therefore with this kind of a concept in mind, let us actually look at what happens when the continuum fails. We would like to do this - the molecular approaches to estimate flows particularly when there is failure of the continuum approach and so the only other approach which probably emerges for solving liquid flows is called molecular dynamic simulation which talks about all these inter molecular forces as I have been telling before - inter molecular forces and which can be established from the Lennard Jones potential model.

The MD technique is in principle very straightforward and is an application of this Newton's second law. What is Newton's second law? The product of mass and acceleration is equal to the total amount of force that a particular system should have. The same can be translated into molecular systems as well.

However, we have to somehow ascertain how to find the acceleration of this kind of a molecular system and we already know that from Lennard Jones potential. We can find out the average force between 2 molecular systems i and j separated by a distance of r. That is what we are doing here, the product of mass and acceleration of each particle is equated to the sum total of forces because of Lennard Jones equations and the technique really begins with collection of molecules in space. Each molecule has a random velocity assigned to it as per the Boltzmann velocity distribution and the molecular velocities are integrated forward in time to arrive at the new molecular positions.

If you see the Intermolecular Forces really which are equated to mi d2 ri by dt2 at time t, let us say time instance t is equal to minus d by dr, a negative gradient of potential, Lennard Jones potential. sigma i not equal to j and these are that systems all systems of the likes i and all systems of the likes j that 2 molecule systems between which there is a force of attraction and repulsion.

So, it is the negative gradient with respect to r of Vij and here the assumptions that we use to simplify is that if you consider a molecular system, it is a huge amount or huge number of molecules. 1 mole as you know is about 10 to the power of 23 molecules. Therefore, if suppose you are talking about a certain radius or if you are talking about a molecule system where there are 1000s of these molecules which are inter playing and there are inter molecular forces between these 1000s of molecules, there would be a tendency of the computations to go extensively at a very high rate and at sometimes so essentially the whole idea that you know in a molecular system like this.

If you have 1 molecule surrounded by 1000s or actually millions of molecules, there are intermolecular forces between this 1 molecule of interest and its neighbourhood which comprises of millions of such forces and it makes the whole system computationally extensive and the solutions may not converge with time and there may be issues related to more number of computations.

To solve this problem, you really need to consider an effective radius within which you can consider the interactions. It is called the cut off rate radius. If radius is exceeded or the radius goes beyond the cut off radius, we assume that the molecular forces arising out of molecules which are outside this cut off radius is 0. You terminate the calculations at a certain intermolecular distance beyond which we assume that the distances are too large for the forces to be really effective in the overall calculation.

Therefore, this Lennard Jones function really changes into Vij ri minus rj, vector rj is essentially the vector radius where there would be a forced cut off. This is the cutting radius or cut-off radius. Any point below this would be effectively considered in the calculation is here. It is kind of a truncated solution. Truncated solution of the force between the radius with cut off radius of let us say rj in this particular case is given by minus d by dr of sigma i not equal to j, that means these are 2 different molecular systems, Vij ri minus rj mod.

This is equated to by the Newton's second law mi del2 ri vector by dt2. This is the acceleration at time t and the forward integration of this twice successively would give you the new position vector ri from which you would again recalculate this. Consider it is a criterion to define new cut off radius. Therefore, from position to position you can have a very good estimate of the velocity, the position vectors and the acceleration vectors of these individual particles based on this force, change of momentum approximation.

Therefore, the averages of velocities, let us say, are calculated by if you have a knowledge of all positions by the forward time integration and you want to find the x velocity. All the x positions, the d by dxi by dt, you make a sigma of all these and calculate an average velocity, an average density, an average of other properties, etcetera Mind you because these positions are changing with time, these quantities would also be changing with time. Even though continuum assumption is not really validated in this particular case, the averages keep on varying based on the interactions - the molecular interactions in that small control volume.

Therefore, these are very appropriate, very accurate technique to simulate the motional properties of fluids at the nanometer scale; these are called molecular dynamic simulations. In fact, such simulations can be used to study lot of properties like combustion, fluid mechanics in general, then lot of surface-based interactions with charged molecules or interactions between different charged molecules in a system, so on and so forth. They are very useful as a technique to predict the position vectors, velocity average properties, etcetera time variant essentially.

So, this gives you an estimate of how from continuum to a scale where continuum does not hold you could to change your approach to get the different solutions. Now, I would like to go more towards the application side and describe these different kind applications of these micro scale fluidic techniques into realizing engineering products like Microvalves, Micromixers, Micropumps etcetera.

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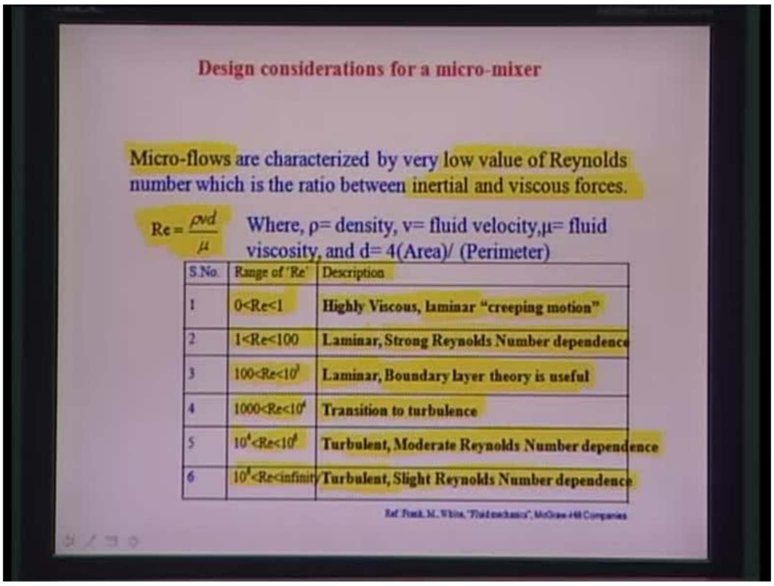

Design considerations for a micro-mixer

Micro-flows are characterized by very low value of Reynolds number which is the ratio between inertial and viscous forces.

$Re = \frac{\rho v d}{\mu}$ Where, ρ= density, v= fluid velocity,μ= fluid viscosity, and d= 4(Area)/ (Perimeter)

S.No.	Range of 'Re'	Description
1	$0<Re<1$	Highly Viscous, laminar "creeping motion"
2	$1<Re<100$	Laminar, Strong Reynolds Number dependence
3	$100<Re<10^3$	Laminar, Boundary layer theory is useful
4	$1000<Re<10^4$	Transition to turbulence
5	$10^4<Re<10^6$	Turbulent, Moderate Reynolds Number dependence
6	$10^6<Re<$infinity	Turbulent, Slight Reynolds Number dependence

Ref Frank M. White, "Fluid mechanics", McGraw-Hill Companies

Let us study these one by one. I would like to first start by looking at Micromixers. If you look at really the characterization of micro flows, the first property which comes out as we have seen earlier is the low value of Reynolds number. Of course, it is the ratio between inertial and viscous forces again. You can mathematically define it as rho vd by mu, rho is the density, v is velocity, d is the dimension at that particular scale and mu is the viscosity of the medium.

The way you calculate d in Reynolds number is essentially four times area by parameter and it is also known as the hydraulic diameter of particular section. Based on the different ranges that this Reynolds number kind of comes into ranges of values you could categorize flows into many types.

This table here illustrates the corresponding range of Reynolds numbers with the description of the flow. You are looking Re between 0 and 1 which is mostly the case in the microfluidics. The flows are highly viscous, they are highly laminar and they are as if they execute creeping motion as they are moving in a very tightly packed, close pack channel or creeping in a closed pack channel without really interfering much into each other's path; the molecules move in perfect streamlines parallel to each other.

For Reynolds number of 1 to 100, the flow still remains very laminar and there is of course, a very strong dependency on the Reynolds number in this particular scale.

Suddenly, the flow properties may demonstrate or change in behaviour with very minute change in Reynolds number.

If you go slightly above and consider the Reynolds number between 100 and 1000, the flows again are very laminar, they have not yet changed the genes. However, here in this particular range you could really have a very good boundary layer which is formulated. If you may recall boundary layer again is the layer which is separating the fully developed flow from the flow which is made up of these; the flow which is actually having shear stress or predominated by shear. Therefore, this boundary between the fully developed part and the sheared part of the flow is what laminar boundary layer rapidly is and this boundary layer formulates whenever very close to a fixed surface maybe a channel or some kind of flat plate or flow over a surface.

So, essentially this Reynolds number range of 100 to 1000 would inculcate a prominent boundary layer and here most of the theorizing of boundary layer is very useful. If you change the Reynolds number a little bit from 1000 plus all the way to about 10000, there is a slow transition which takes place in the flow from laminar to turbulence, but then this is really a transition. You have instances where the flow is slightly laminar or instances where the flow is turbulent and is slowly changing the behaviour. After a certain value let us say 10 to the power 4 or so on up to about 10 to the power 6, the flow becomes fully turbulent.

Of course, in this particular range there is some Reynolds dependence which happens particularly from 10 to the power 4 to 10 to the power 5 Reynolds number. Beyond which all the way up to infinity not only flow is turbulent, but it is having very less dependency on the Reynolds number and that is probably because the flow really gets defined by the local eddies and vortices more than the overall bulk flow. That is essentially what these different categories of flows are with respect to different values of the Reynolds numbers.

What I would like to reiterate here is that as I told you before in the 1 to 100 case or even less than one case as is mostly the case in all the microfluidics devices, the mixing behaviour or the mass transport between the mixing inter layers and typically is not really dependent on the momentum of the flows. There are no eddies or no vortices which would cause mass transport between the 2 mixing inter layers just by virtue of motion.

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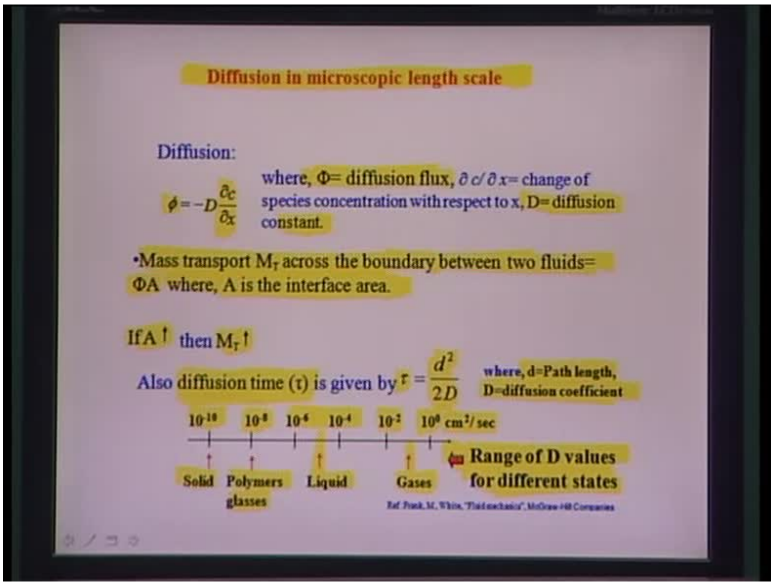

Diffusion in microscopic length scale

Diffusion:

$\phi = -D\frac{\partial c}{\partial x}$ where, Φ= diffusion flux, $\partial c/\partial x$= change of species concentration with respect to x, D= diffusion constant.

- Mass transport M_T across the boundary between two fluids= ΦA where, A is the interface area.

If A ↑ then M_T ↑

Also diffusion time (τ) is given by $\tau = \frac{d^2}{2D}$ where, d=Path length, D=diffusion coefficient

Range of D values for different states

Ref. Frank M. White, "Fluid mechanics", McGraw-Hill Companies

You need something else to drive the flow up and down a particular direction and what could be more appropriate than a concentration gradient. Therefore, the diffusion approximation comes into picture. Most of the micro scale flow mixing takes place probably by diffusion. If you look at the diffusion equations really, the diffusion flux because of the existence of this concentration gradient here dc by dx, they are proportionate to each other. Diffusion flux is proportional to the negative gradient of concentration with respect to the perpendicular distance.

The proportionality constant really is D here, the diffusion constant which can be varied for different states of the matter. For example, diffusion constant is very low if you consider solid. You see this scale below here, diffusion constant is in the range of about 10 to the power minus 10 in case of solids; in case of polymers and glasses this constant increases a little bit about 10 to power minus 8, but still is very low. Mostly liquids have a diffusion constant in the range of 10 to the power of 6 to minus 4 in this particular region and therefore, it is of some significance, the diffusion is of some significance as for as liquid is concerned.

But in case of gases, this constant is very high. It is about 10 to the power minus 2 to 1 centimeter square per second. Therefore, you have to be very careful about the diffusion as you go to gas flows. However, most microfluidics being single phase and mostly liquid dominated, the diffusion constants that we will be considering in all our calculations are in the range of about 10 to the power of minus 6 to minus 4.

The mass transport Mt across the boundary between 2 fluids is also equal to the flux times of the area of interface between the 2 mixing fluids. You have let us say 2 fluids running parallel and there interfacial area is A and flux is 5. The amount of mass transport Mt really is equal to 5 times A, 5 being the mass transport per unit area or the flux of mass per unit area. Therefore, interfacial area in such cases becomes highly prominent especially when mixing is concerned. If you have somehow a mechanism wherein you can accommodate 2 flows over a larger amount of area, automatically their mass transport would be more. Sometimes it becomes architectural promising to design micro-mixers where this area of interface between the 2 flows is increased resulting in some mass transport.

So, if area is more, then the mass transport Mt is more. Also of special significance is an equation which I am not going to prove here though, but then I just borrowed it from normal diffusion kinetics and here it talks about the time of diffusion. The time of diffusion is essentially equal to d square by 2D, d being the path length over which the 2 flows are going for which they are diffusing at the end or throughout as they are going with respect to each other and big D here is the diffusion coefficient.

If you have a length L of channel over which these 2 flows are mixing and going as they move along the length L is nothing, but the path Ll the path d or path length d. If the length is more, then in that case the time of diffusion tau is automatically more. This length is essentially the cross sectional length when we are talking about 2 flows which are going in a particular channel of the cross sectional length L.

So, it almost makes sense to assume here that the time of diffusion will reduce, if the d value that is the cross-sectional length value 2 flows is reduced. If I am able to somehow create shorter laminas of these flows and thus the cross sectional length of the flow reduces by division of d into let us say n where n in the number of laminas. Then automatically the time or diffusion reduces as the square of the reduction in the d and it is very important understanding that one must have in order to design what you call passive micro-mixers, where the whole idea is how the diffusion length can be split up into smaller values so that time of diffusion would reduce.

The whole essence of microfluidic structures or microfluidic architectures is how the time, where these 2 flows have been introduced from one side and side within the chip is going to be more than the time that the fluidics take to diffuse into each other. At the end of the day when it emerges out from the other side of the chip they are fully mixed.

So, range d values for different states are indicated here in this particular illustration and that is a little bit of fundamentals of how mixing would take place at the microscopic length scale.

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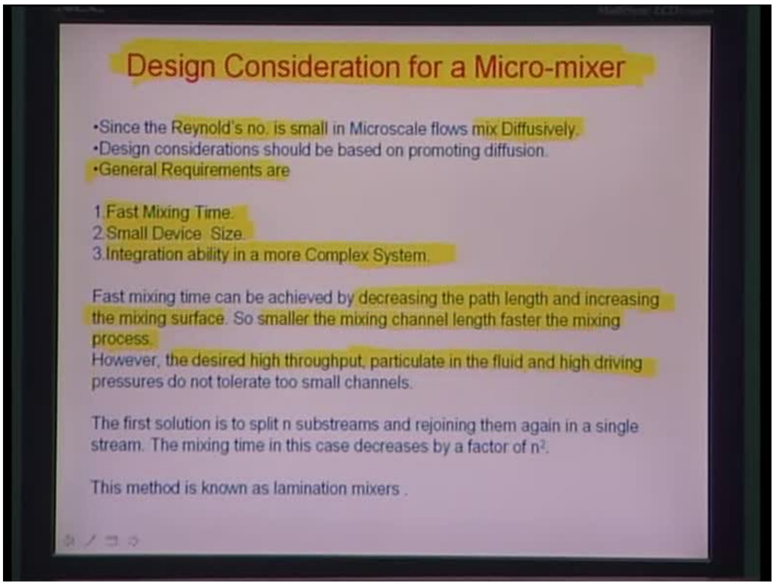

Design Consideration for a Micro-mixer

- Since the Reynold's no. is small in Microscale flows mix Diffusively.
- Design considerations should be based on promoting diffusion.
- General Requirements are

1. Fast Mixing Time.
2. Small Device Size.
3. Integration ability in a more Complex System.

Fast mixing time can be achieved by decreasing the path length and increasing the mixing surface. So smaller the mixing channel length faster the mixing process.
However, the desired high throughput, particulate in the fluid and high driving pressures do not tolerate too small channels.

The first solution is to split n substreams and rejoining them again in a single stream. The mixing time in this case decreases by a factor of n^2.

This method is known as lamination mixers .

What really would be considered when we talk about design of micro-mixers? The number one problem that we are left with this is a small value of the Reynolds number and therefore, the diffusive mixing. Design considerations should be definitely based on somehow enable to promote a diffusion between 2 layers and essentially which means faster mixing time, general requirements, a small device size and also you should have integration ability particularly complex systems with the overall setup. Fast mixing time again can be achieved by, as I told you before, decreasing the path length. The path length means the cross sectional path, the path that diffusion happens along and is perpendicular to the direction of the actual flow of these fluids and you can also have more accurate or better mixing and faster mixing by increasing the interfacial area between the two or more mixing streams.

So, smaller the mixing channel length faster would be the mixing process. However, the desired high throughput, particulate infield and high driving pressures do not tolerate too small channels; that is the unfortunate part. Most of the flows in microfluidics as you know are pressure driven and are therefore, too small channel would have too high resistance and therefore, the yield at the end of the channel of the flow would be so small that it is very negligible.

So, you have do design something wherein you can still be able to get substantial amount of throughput, but at the same time the mixing can be faster. Therefore, lamination is something that comes into picture automatically that means, you split up let us say 2 streams of 2 different dyes or 2 different colors which you want to mix into multiple streams stacking with each other. If you have n such splits, what would happen is that you have one stream with a diffusion length d or cross sectional length or 2 streams going into a cross sectional length L or d, which is also the diffusion length and in another instance after n splitting, the cross sectional is simply reduced by d by n.

We are going to investigate this a little bit further as we do mixer designing. Therefore, the first solution really is to split n sub streams and rejoining them again in a single stream so that the mixing time reduces by a factor of n square. This basically is the principle of lamination mixers.

So, this brings us to an end of this particular lecture. We have a take-home message that mixing essentially is diffusional, it is dependent on the interfacial area, it is dependent on the diffusion length, time of diffusion essentially has to be kind of lesser than the time of residence for the flow to be effectively mixing with each other and overall requirements of the micro-mixers should be it has a faster mixing time, small device size, integration ability particularly in a higher order complex system. We will consider these aspects in little more detail in the next lecture. Thank you.