Rheology of Complex Materials
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Lecture - 61
Microscopic models for rheology

So in the course on rheology we have discussed several times the microstructure of complex materials and we have seen that the microstructure plays a crucial role in determining the rheological response and we always try to understand the overall rheological response by trying to relate to whatever maybe the microscopic mechanisms.

And in the last two-three decades there has been significant progress in trying to make models for rheology based on the microscopic picture itself. Given that microstructure has such a relevant role and such a crucial role to play in determining rheology. It becomes more insightful if we can develop a model at the microscopic scale. We decide what are the dominant mechanisms, which contribute at the microscopic scale and then we have to have tools to then take the microscopic picture to the bulk scale, so that we can get the rheological response.

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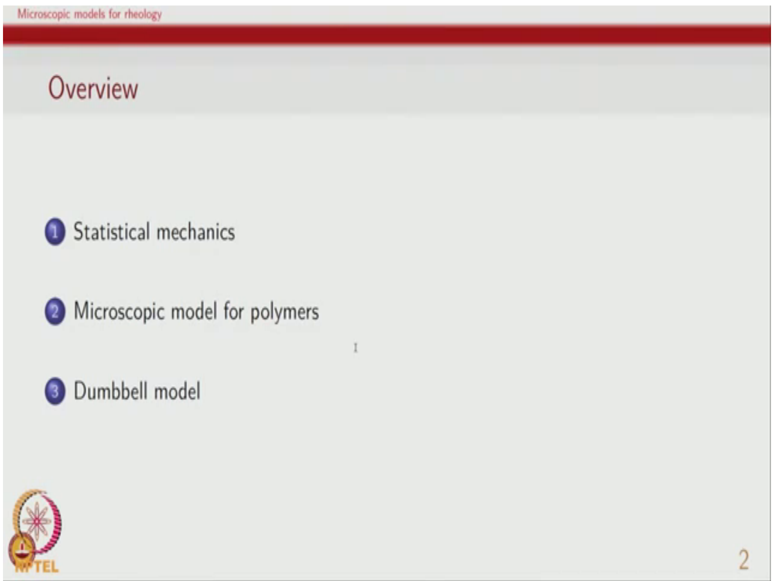

And so, in this segment of the course we will discuss the microscopic models for rheology. Specifically what we will do is initially just review some key concepts of statistical mechanics. Going from the microscopic scale to the rheological response we require tools of statistical mechanics. So that we can average the behaviour which is observed at microscopic scale to obtain the bulk response. We will discuss some aspects of microscopic models that are available to describe the polymer behaviour and then specifically we will look at one simple model which is called the Dumbbell model and we will see that how based on the microscopic mechanisms that we incorporate in the Dumbbell model we get a response which can be map back to the bulk rheological response for which we have already discussed in the course.

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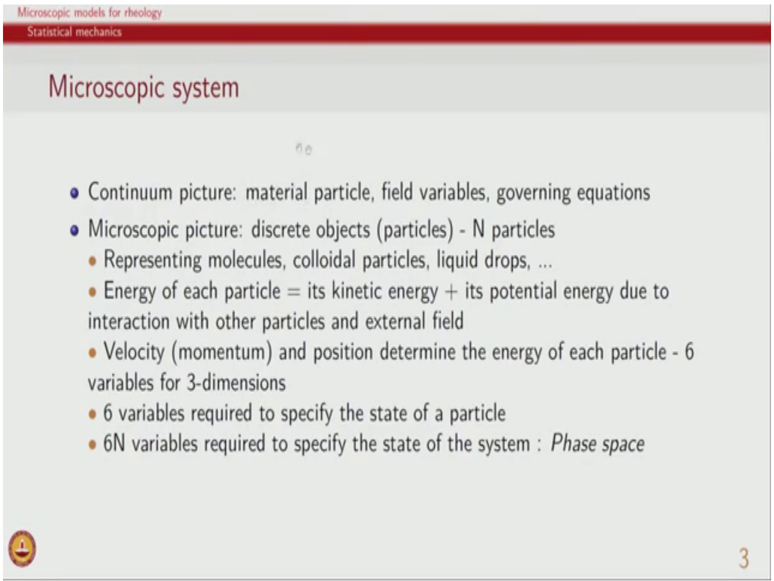

So, beginning with the overall idea we discussed continuum picture throughout the course. When we said Continuum picture we said that the continuum is made up of material particles. And these material particles were uncountably infinite basically between any two particles there are again infinite sets of particles. And because of the continuity of the field variables that describe the material point particles and the attribute, field variables or the attributes for several material particles we can then describe the overall relations between field variables using governing equations.

And we saw that for rheometry the mass balance and the linear momentum balance or equation of continuity in equation of motion were the two governing equations which can be used to solve all problems related to rheology.

And so when we look at Microscopic picture we recognise that matter is made up of discrete objects. So, therefore we built in our model the discreteness of the objects. And again they are referred to as particles, but these particles could represent one of several things. For example, the particles could represent atoms, they could represent subatomic particles like electrons and protons the particles could also represent molecules or they could also represent the drops and colloidal particles for a multiphase system. So, therefore particle in this sense is a generic description of the basic building block of matter and the key idea here is that we have discrete set of objects.

So, in general we will talk of the material being described using let us say N particles. And so what these N particles do and how do they interact with each other or with surrounding will determine how the overall microscopic picture is defined. So, energy of the each of the particle will be very important in terms of description of the system and at the microscopic scale since a particle moves about it has a velocity and based on its velocity it will have a kinetic energy. And given that the particle moves about and it interacts with the other particles.

It interacts with the surrounding medium. It also may interact with a field such as electric field or gravitational field which is imposed on the overall system. So, therefore there is a potential energy associated with each and every particle. And so the overall energy of these particles can be thought of at the microscopic scale being defined based on the kinetic energy and the potential energy of these particles. And so the velocity and position therefore determine the energy of each particle. Velocity directly determines the kinetic energy itself. When we know the position of each and every particle we know how they are interacting with each other.

We know, what is the relationship between position and the interaction with an external field such as; gravitational field. For example, when we generally use the word potential energy in school and earlier we are only talking about gravitational potential. And so when the distance changes the potential energy changes and therefore, we can talk about how the potential energy changes can be related to what is the gravitational force. So similarly in each case in the N particle system given that we have multiple particles how they are spaced with respect to each other will determine the overall potential energy.

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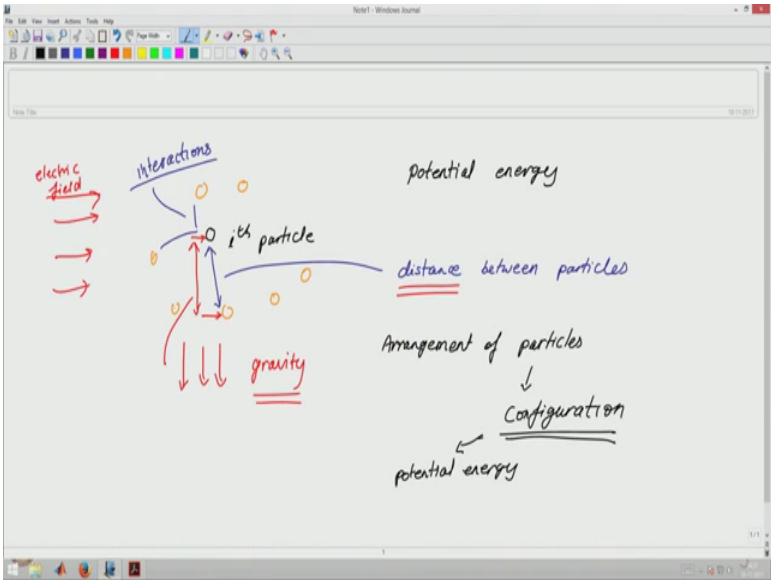

So, we have let us say a particle which we will choose to call ith particle and surrounding this we will have several other particles. And so what we have are interactions between these particles. So, these are all various interactions that can take place. And so our interest is in defining the overall potential energy based on these interactions. And the potential energy will be determined based on the distance between particles.

Similarly, if there is an external field which is being imposed for example, it could be an electric field or we could have an external field which is let us say gravity. Then in that case again the relative position of each and every particle with respect to so the position of this particle and the position of this particle and the distance again will determine what is the influence of the gravitational field. And so in general distance between particles is very important. The overall arrangement of these N particles is also called the configuration. So therefore, the arrangement of particles in 3-dimensional space is called the configuration.

So therefore configuration is very important in determining the potential energy. Because configuration which implies the difference between various interacting particles will determine how much is the interaction energy between these interesting particle. And so velocity of the particle will determine the kinetic energy and the configuration will determine the potential energy.

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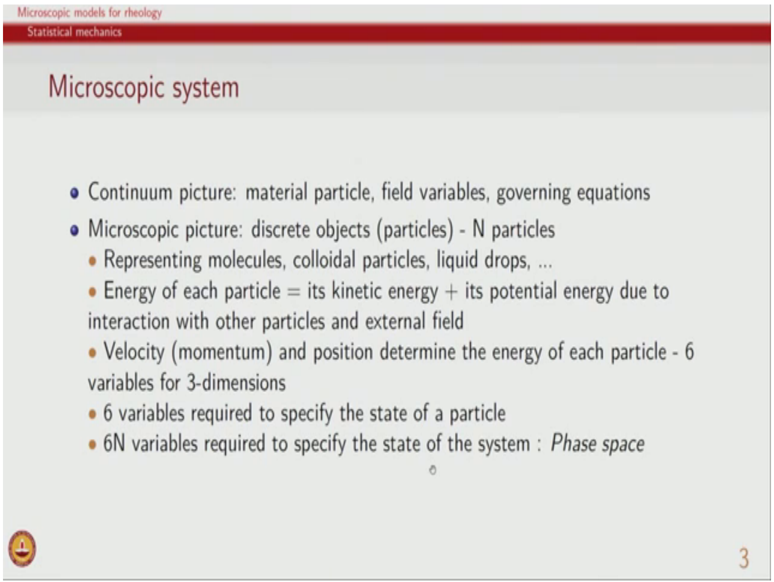

So, therefore to specify the overall microscopic state of each and every particle we will need to define its velocity and its position. Now, velocity itself is vector position also is a vector. And in if you are describing them using a 3-dimensional space then we require 3 velocity components and 3 position components. But basically we required 6 variables 3 components of velocity and 3 components of position to describe the state of one particular particle. Similarly if we describe the state of all such particles then we would have completely specified the configurational space of the particles as well as we would have described the overall velocity of each and every particle.

So, in general to describe the N particle system we need 6N variables. 6 variables are required to specify state of one given particle. 6 times capital N variables will be required to specify the state of the system. So, you can see that the number of variables that have to be specified are exceedingly large. Remember we are trying to use these particles in the microscopic picture to represent molecules and colloidal particles and drops and so on.

And our aim is to actually use this microscopic picture to represent the material properties at the bulk scale. And we know that large number of molecules or particles and drops will make up the bulk of the material. We know for example, that Avogadro's number 10 to the power 23 molecules are involved in one mole of material.

Similarly, when we take a small drop of ink the number of colloidal particles there is exceedingly large 10 to the power 6, 10 to the power 8 per unit volume. So therefore, we are talking about extremely large number of particles, with generally make up the microscopic system. And therefore the number of variables which are required to specify the state of the overall system is exceedingly large. We talk of this specification of state of the system in terms of phase space. So, just the way we have 3-dimensional space and which describe physical space.

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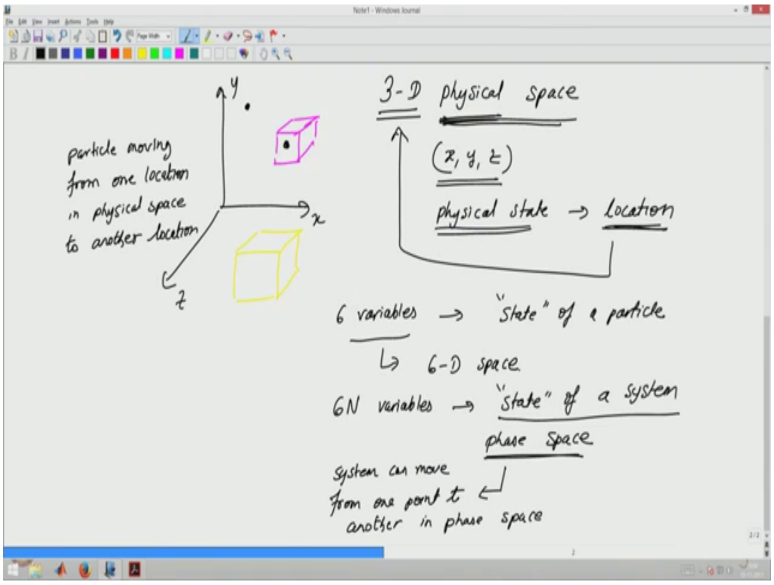

For example we could talk of let us say rectangular coordinate system which is the 3-dimensional physical space. And I could ask the question that if I am looking at let say position of a particle in this. So, I would say that the position of the particle can be specified by specifying the three coordinate systems x y z. And I could ask questions related to for example, whether the particle is in some hypothetical control volume. I could ask the question also that, what is the probability of observing; the particle in this volume, compared to let us say some other volume which is much larger. So, this is all the description in 3-dimensional physical space and we required three variables and therefore, this is a 3-D space.

Now what we have seen is for a overall particle we required 6 variables to describe the state of the system. Since in this case we are only describing the system using a physical state which means location. We require only 3-D space. But if we have 6 variables to specify the state of a particle we will require a 6-D space. And therefore, the 6N variables which are required to describe the state of a system is called phase space . So, at this point what is helpful for us to know is the following that it is specify position we require only three variables. Then we are trying to specify state of a system we require 6N variables and unless we are able to specify the 6N variables we cannot specify the state of the system. Just the way here also if you just specify x and y there is a whole lot of possibilities of z in fact infinite possibility just specifying x and y cannot specify the position of the particle.

Similarly, when we specify the state of the system we will need to specify all the variables that are required to be specified and these 6N variables are of course velocities and positions. Now you could ask similar question that for example, if this particle disappears from this position and appears in another position then what we say is the particles has changed the physical state or it has changed its location. Similarly in the phase space a system can be depicted as a point and then it can move from one point to another point in the phase space.

So system can move from one point to another in phase space. So, this is very analogous to the particle moving from one location in physical space to another location. So therefore we can see that there is an analogous description which is being used to describe physical space which we have all very comfortable with and we have solved many problems related to description of physical space and motion of objects in physical space. We have to imagine now a similar phase space in which the evolution of system takes place. When we say evolution of a system takes place we imply that system moves from one particular state to another state through series of in between states and so this is called the evolution of the system.

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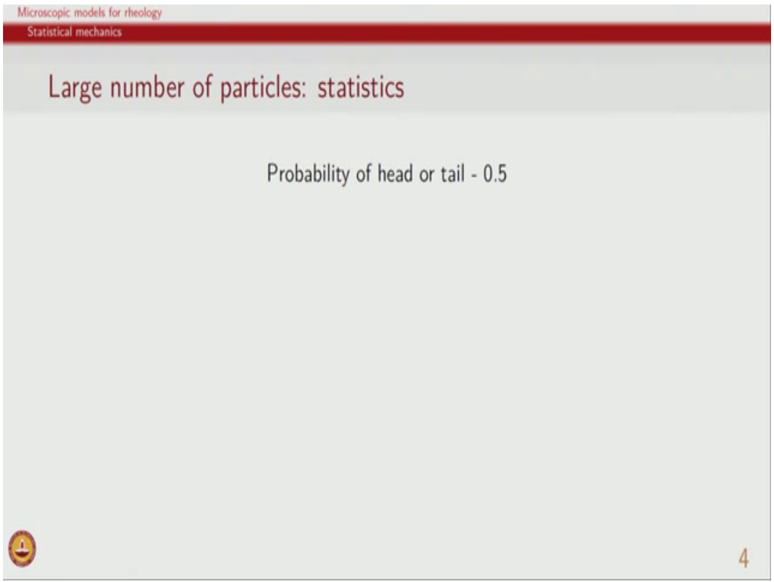

So now looking at the fact that there are very large number of particles we are necessarily requesters statistical measures to define various quantities which are related to the system. Given that the number of particles is very large. The specification of each and every particle is required. However, the description of the bulk behaviour need not be related to the properties of each and every particle, but it is related on average to what the particles are doing.

So, to understand this feature one interesting observation that we make is the fact that what happens when there are very large numbers involved. And we could not think of the phenomena of large numbers by just looking at coin experiment. When we toss a coin whether it is head or tail, the probability is just half. Now if I throw 2 tosses of coins then what happens is the probability of all heads.

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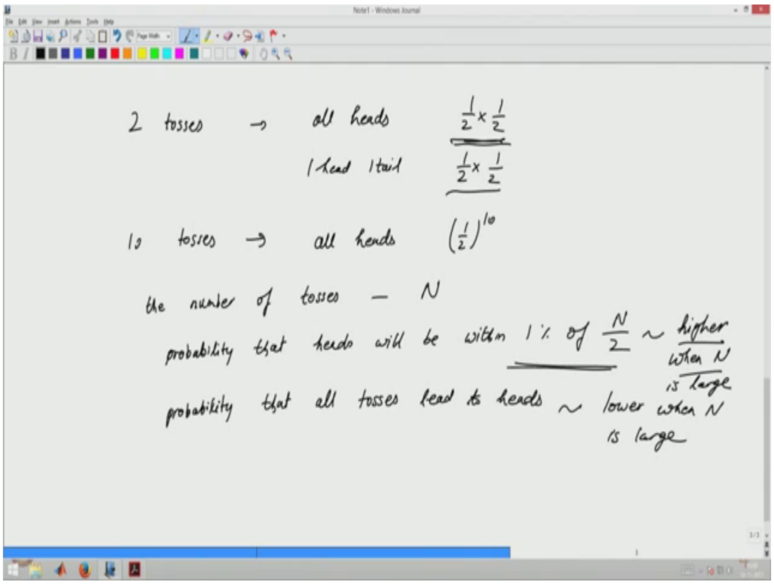

So if I have 2 tosses probability of all heads is 1 by 2 into 1 by 2. Similarly probability of 1 head 1 tail is also half. And so the probability that in 2 tosses I will get both of them as heads or both of them a tails or 1 head 1 tail. Now all of these are equivalent. So, this is not a big difference between all of them being heads or all of one of them being head and one of them being tail. But if I do 10 such tosses, then the probability of all of them being heads is half into 10 to the power 10. So this now an exceedingly small number, what happens is when we do large number of trials then we can quite often say that the number of tosses, if let us say in this case if number of tosses is , the probability that heads will be within 1 percent of N by 2.

So, if I throw 100 tosses, if I throw do, the coin toss experiment 100 times 49 to 51 of them are heads. This probability is going to be higher and higher when N is larger. So, this probability is higher when N is larger. We saw that this probability is quite as significant but not equal. It is equivalent to obtaining heads and tails but as we go on we will see that the probability that where 1 percent of N by 2 will be higher and higher. Similarly the probability that all tosses lead to heads, this probability will be lower and lower when N is larger and larger. Again we saw that all tosses leading to heads the probability was significant but it will be lower and lower.

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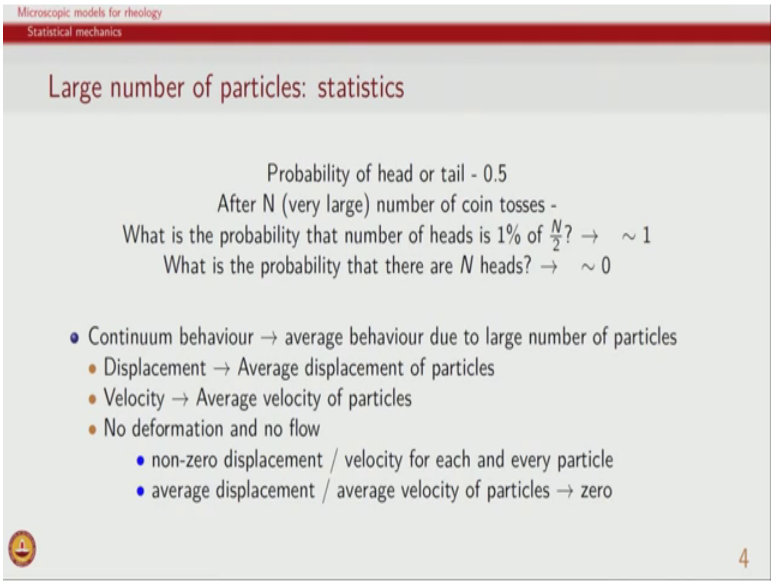

So the fact that large number of N is involved in the microscopic system of our description, this helps in terms of defining statistics which are relatively easy to deal with. So, if you have N very large number of coin tosses we can generally say that the probability that the number of heads is between 1 percent of N by 2 is almost close to 1. So, therefore we can generally assume that if there are large number of trials we will get 50 percent heads and 50 percent tails.

And similarly the probability that all of them are heads such probabilities can be since its exceedingly small such events can be discounted. And when capital N becomes 100, 200 even with such number itself we can get the statements or that are mentioned here to be true. So therefore large numbers whenever they are involved the statistics quickly convert to what is the expected or most likely scenario.

So, in case of this coin toss experiment the fact that half of them will be heads and half of them will be tails will be the expected scenario and that is what we are most likely to observe in any trial as long as capital N is large. So, given this overall behaviour of large numbers it helps us in describing the Continuum behaviour as an average of behaviour which is at the microscopic scale based on large number of particles. So all the particles they move about, they interact with each other, they interact with external fields and based on their displacement we could also talk of what is the average displacement at the bulk scale.

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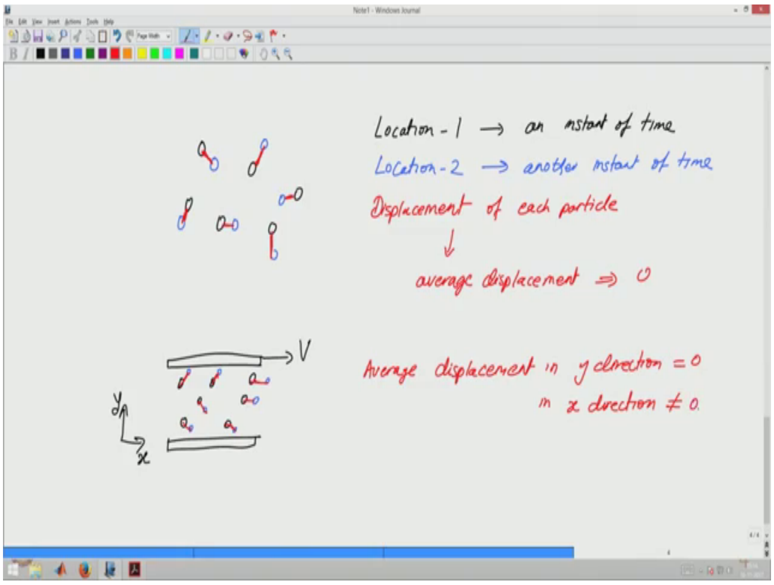

So for example, in the microscopic state if we have the picture that we have a particle and these few sets of particle. If let us say the overall fluid is stationary then we know that for example if I take a jar of water and overall the water as a fluid is stationary. We still know that water molecules are moving about. So, when we are trying to build the microscopic model for water what we will do is we will say particles which are moving about. So, if I take a snapshot after a instant of time what I will see as that the same particles would have moved in a different location. So, the particles which were in location 1 at one instance of time, an instant of time have moved to another location another instant of time.

Now, if I look at the displacement of each and every particle, so I can look at what each and every particle has displaced by. I can see in this case that this is one displacement, this is another displacement, this is another displacement and if I have such large number of particles and if I find the average. So displacement of each particle and if I now find the average displacement this will go to 0 because it is a stationary fluid and particles are going in random directions.

So, clearly in this is what happens is the displacement of each and every particle is definitely not 0, but the average displacement is 0. In our course what we will deal with is rheological rheometric flows. So, for example we may have a simple shear flow in which case we have the top plate moving with certain velocities. And in this case again we have let us say a certain particles and they occupy certain location again at one instant of time.

Now, when we look at the same set of particles in another instant of time, what we will generally see is the fact that on average each of them get displaced with some. So, in all cases if you try to resolve the displacement in y direction and displacement in x direction what we will see is average displacement in y direction will be 0 and the average displacement in x direction will not be 0. So therefore what we can see is whatever is the behaviour of the particles at the microscopic scale, in this case the behaviour is being described using displacement as a variable, the average displacement can be used at a bulk scale.

Similarly if you have a velocity of these particles then the average velocity of all the particles can describe the bulk velocity. Again for a stationary jar of water the velocity of each and every particle which is representing let us say the molecules of water will be non zero since molecules are moving about. However when we calculate the average velocity that is going to be 0 because the overall particle overall fluid is stationery if we now subject the same fluid to a shear field such as given here. Then in this case we will again have an average displacement of particles which is over and above the random displacement which comes about because of microscopic interactions which happened between different particles.

So, variables which are at the microscopic scale can be averaged to give us the bulk response. Now when we have no deformation and no full will have nonzero displacement and velocity for each and every particle. But we will have average displacement and average velocity of particle to be zero.

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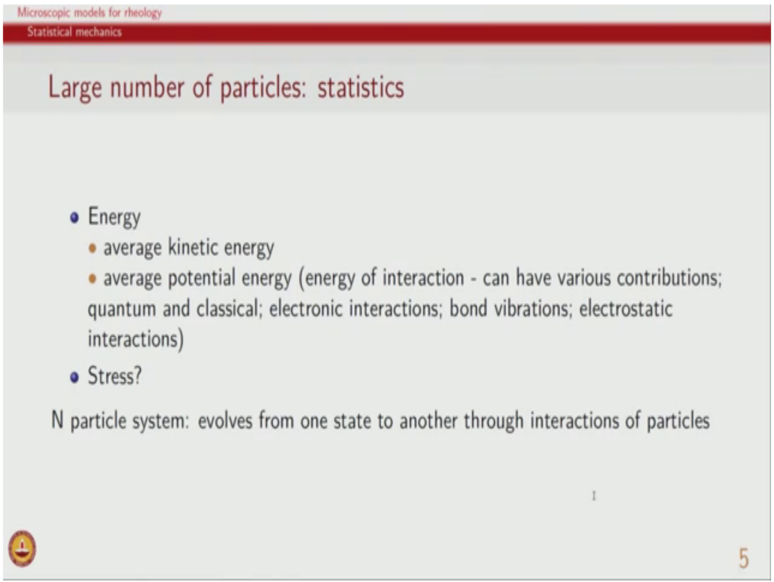

Now when we look at some other variables for example energy so, we discussed already that each and every particle has velocity and therefore kinetic energy. Similarly each and every particle has a potential energy because it is interacting with other particles, it interacting with external fields and many of these interactions can be classified in several ways. For example, there could be quantum contributions which are related to electronics interaction it which are related to bond vibrations and so on. There could also be classical interactions in the sense interaction between two charges which are electrostatic interaction.

So, therefore depending on the nature of interactions and depending on the interactions that are important for the system of interest we have an average potential energy which can be described at the bulk scale also depending on how each and every particle interact with each other and that is average to give us the bulk potential energy. Now similar question arises given that in rheology we have discussed stress, strain and strain rates. Since velocities and displacement can be averaged out to give us the bulk displacement and bulk velocity those are easy to calculate.

What is meant by stress at the bulk scale? Given that at the microscopic scale each and every particle is interacting through these energy we will make a hypothesis of forces which are experienced by each and every particle. And based on the presence of these forces and how the forces are exchanged across a hypothetical surface in the material we will define stress. So, one of the object one of the key learning in this segment of the course will be as to learn what is the microscopic interpretation of stress. .

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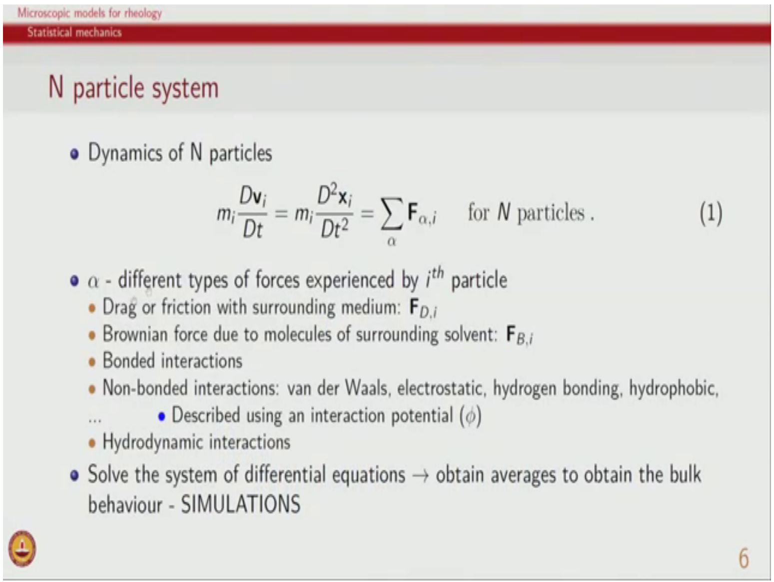

And so the N particle system basically we have said evolves from one state to the other and its evolution is based on dynamics of each and every particle. So, for all capital N particles we can write a governing equation and this case this is nothing, but a linear momentum balance or Newton's second law which say that mass into acceleration is equal to sum of all the forces on it.

Now, the forces that each and every particle experiences is could be different types. It could be the drag or friction which is experienced based on surrounding medium. So, quite often we use Stokes law kind of expression to describe the drag force that is being experienced by a single particle. So, each and every particle has several forces which it experiences.

So, in the next segment of the course we will first discuss some of these forces that are encountered by the particles and then we will look at how do we try to simplify some ways in which we can analyse the system more easily.