Rheology of Complex Materials
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Lecture - 62
Microscopic models for rheology

So, in this segment of the course we are looking at Microscopic models for Rheology and to begin with we are looking at some key statistical mechanics concepts.

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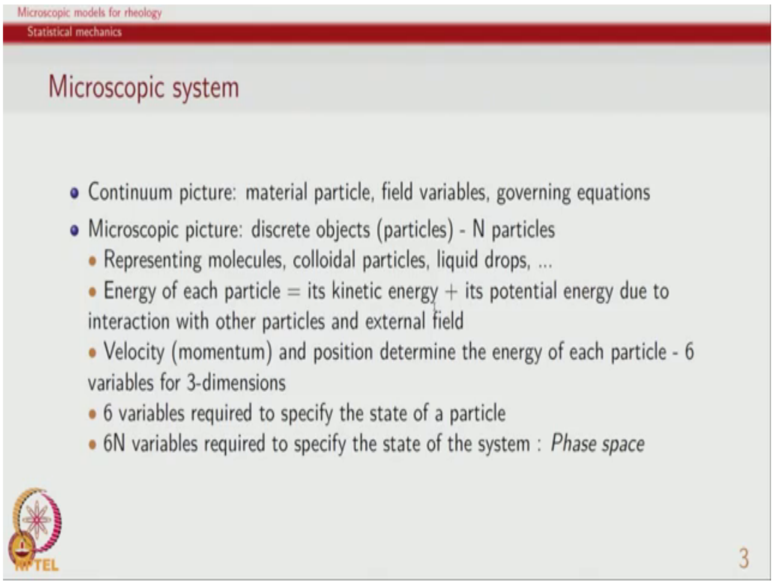

Microscopic models for rheology
Statistical mechanics

Microscopic system

- Continuum picture: material particle, field variables, governing equations
- Microscopic picture: discrete objects (particles) - N particles
  - Representing molecules, colloidal particles, liquid drops, ...
  - Energy of each particle = its kinetic energy + its potential energy due to interaction with other particles and external field
  - Velocity (momentum) and position determine the energy of each particle - 6 variables for 3-dimensions
  - 6 variables required to specify the state of a particle
  - 6N variables required to specify the state of the system : *Phase space*

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We already saw that how the microscopic system is made up of capital N particles.

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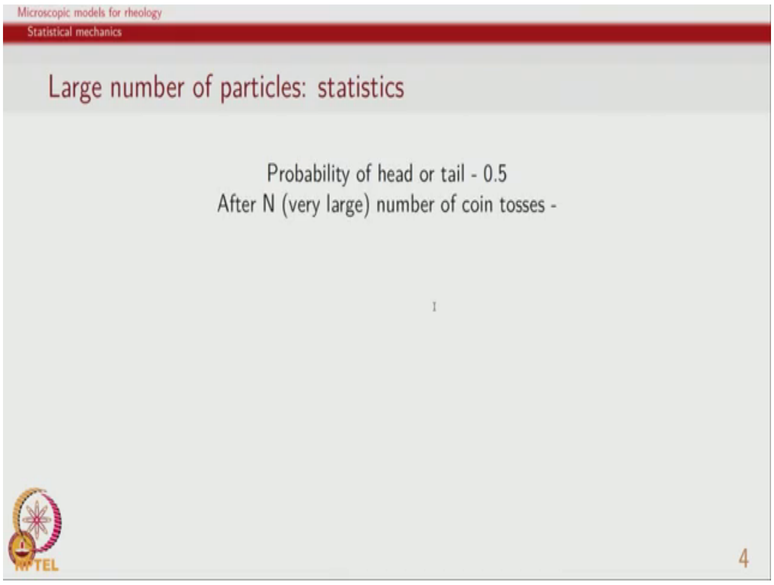

Microscopic models for rheology
Statistical mechanics

Large number of particles: statistics

Probability of head or tail - 0.5
After N (very large) number of coin tosses -

And the behavior of large numbers is very useful tool in terms of getting the bulk properties, in terms of the average behaviour. And so, the overall governing system for this n particle system could be written in terms of a governing equation for each and every particle.

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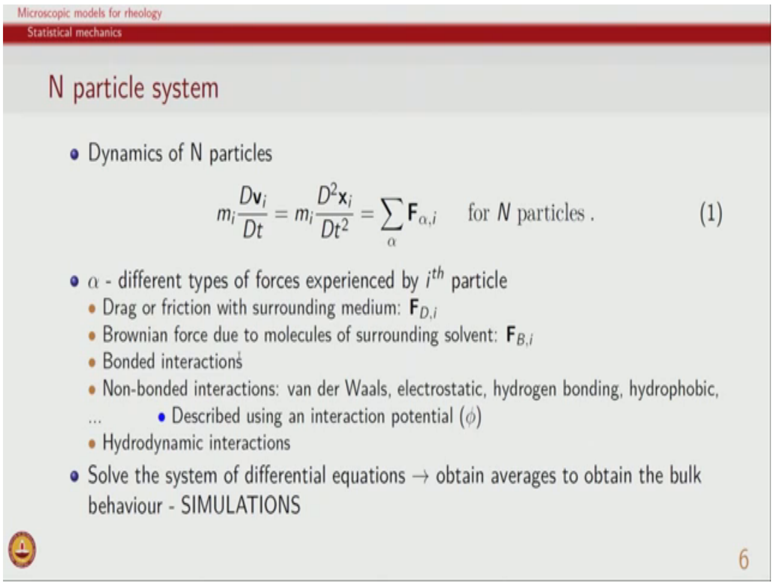

Microscopic models for rheology
Statistical mechanics

N particle system

- Dynamics of N particles

$$m_i \frac{D\mathbf{v}_i}{Dt} = m_i \frac{D^2\mathbf{x}_i}{Dt^2} = \sum_{\alpha} \mathbf{F}_{\alpha,i} \quad \text{for } N \text{ particles} . \tag{1}$$

- α - different types of forces experienced by i^{th} particle
  - Drag or friction with surrounding medium: $\mathbf{F}_{D,i}$
  - Brownian force due to molecules of surrounding solvent: $\mathbf{F}_{B,i}$
  - Bonded interactions
  - Non-bonded interactions: van der Waals, electrostatic, hydrogen bonding, hydrophobic, ...
    - Described using an interaction potential (ϕ)
  - Hydrodynamic interactions
- Solve the system of differential equations → obtain averages to obtain the bulk behaviour - SIMULATIONS

And so, the Newton’s second law of motion states that mass into acceleration for each and every particle is related to sum of all forces. And so, the forces could be as we discussed in the previous class, the drag and friction with the surrounding medium, where we use stokes law, we could also have the surrounding medium act on the particles as a Brownian force.

So, when we have a motion of a Brownian particle, a particle which is there in air which is randomly moving about the motion is due to the air molecules impinging, and interacting with this particle on random and therefore, it acquires a path which appears to be random to us. So, therefore, this is called the Brownian force and this is one of the forces which could be acting on the particles of course, some of the particles could be bonded to each other, when we are looking at polymer molecules for example, we have several monomers, which are covalently bonded together and so, what we have is a set of interactions between these particles which are bonded interactions.

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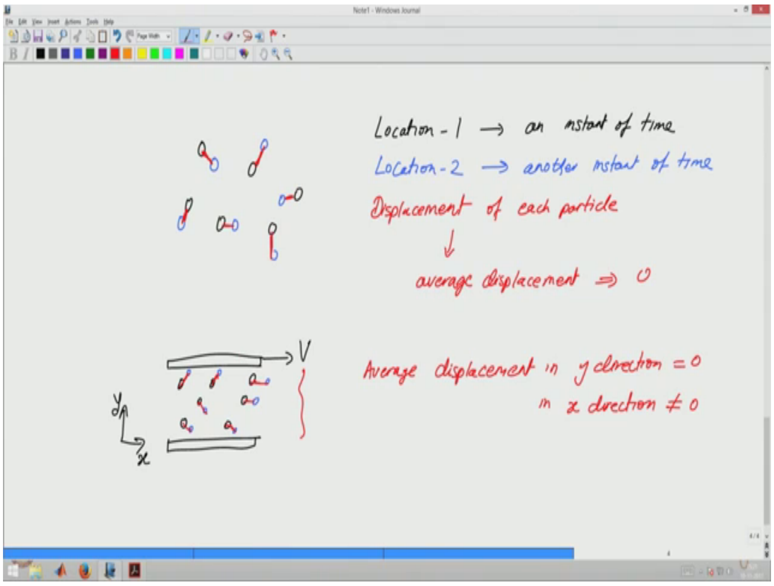

Location - 1 → an instant of time

Location - 2 → another instant of time

Displacement of each particle

↓

average displacement ⇒ 0

Average displacement in y direction = 0

in x direction ≠ 0

So, whenever we have a system where we look at the isolated particles.

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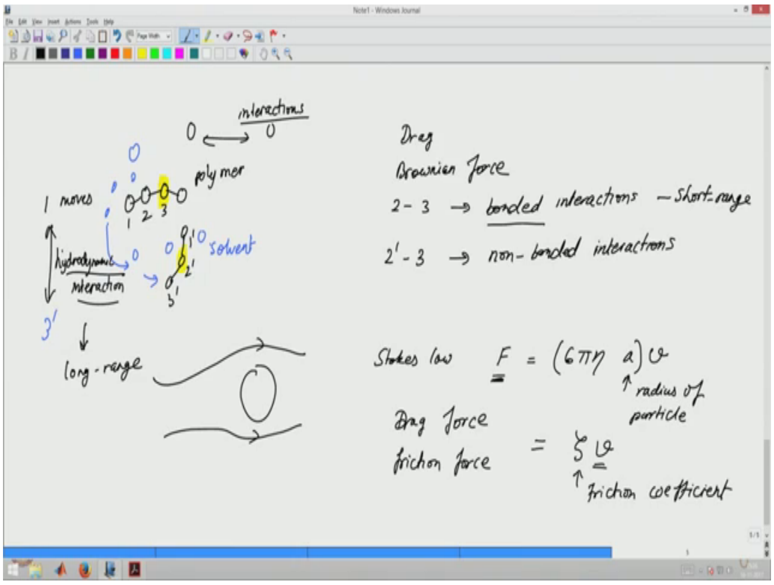

Drag

Brownian force

2 - 3 → bonded interactions – short-range

2' - 3 → non-bonded interactions

Stokes law $F = (6\pi\eta\ a)v$

radius of particle

Drag force

friction force $= \xi v$

friction coefficient

So, between the particles there are always interactions. So, if we now have a hypothesis that we have the monomer, which is bonded to another monomer, and so this becomes then a depiction of polymer and, this polymer could be interacting with the solvent so, the interaction with the solvent could be in terms of drag as we said earlier, it could be in terms of a Brownian force, we could also have the bonded interaction.

So, therefore, the bead the 2 and 3 will interact through bond, but let say if there is another polymer which is in the and lets number those as 1 dash 2 dash 3 dash. So, then the interaction between 2 dash and 3, so the molecule which is this molecule and this particle and this particle, then it will be non bonded interaction. So, therefore, we have both bonded and non bonded interaction, we have in this case polymer solution the interaction between the particles and the surrounding medium, which could be a solvent medium.

And so, generally the bonded and the non bonded interactions are described using an interaction potential phi and, then we would also have hydrodynamic interactions the simplest hydrodynamic interaction that we have seen is drag or a friction, in which case each particle surrounds with the is a interacting with the solvent and this of course, we have seen generally in stokes law, where a fluid is flowing around a particle. And we know that in this case the force is related to 6 pi eta mu a where a is the radius of the particle, and so one can think of the overall coefficient here as describing the friction of the so, we can describe this drag force. So, drag force or the friction force can be described as a friction coefficient higher the friction coefficient the more will be the force felt at higher velocity of course, also we have more force. So, this is one example of hydrodynamic interaction, where the particle and the surrounding medium only interacts, but we also have a situation where let us say in this case bead 1 moves or the particle 1 moves.

Because, of this the solvents which are surrounding one will also move and because, these solvents are moving they will also interact with the other solvents which are surrounding 3 prime. So, therefore, 1 and 3 prime will interact through what is called hydrodynamic interactions and what we can see is some of the bonded interactions for example, is a short range interaction because, only neighbour interact with each other hydrodynamic interaction on the other hand is going to be a long range interaction because, particles which are not close to each other can also interact with each other through hydrodynamic interaction.

So, therefore, in general for a polymeric or a colloidal system these are the types of interactions which would be there, and so each and every microscopic system we will have to specify, which of the microscopic mechanisms and which are the interactions present. And then we will be able to write such a governing equation for all the capital n particles and of course, the one way to solve the problem is to just solve these differential equations.

And once we get the solutions for example, we get the solution for where at 1 instant of time where all particles are, or we get the solution for the position of the particle, then by averaging out we can know what exactly is the configuration of the overall system, or what is the physical arrangement of the particles in the overall system. So, this is usually done in simulations, where we take these simultaneous governing equations and solve them numerically and simulate the overall particle system.

For our course purposes for Rheology we will attempt, the other approach where we try to take the governing equations and, use the idea of distribution function and to use definitions of averaging and statistical averages to try to arrive at a set of governing equations, which are valid for the bulk scale, but they are derived from microscopic scale and, then average to obtain the properties at the bulk scale.

One example of this we have encountered from our school time onwards which is called kinetic theory of gases. In kinetic theory of gases also we have again a capital n particle system and at the microscopic scale each every molecule or particle is supposed to be randomly moving about. And when we do kinetic theory of gases we obtain the overall average response at the bulk scale for example, we know that the internal energy of an ideal gas is related to the overall kinetic energy of individual particles and, when we obtain the mean square velocity, we can obtain the internal energy.

So, internal energy which is a bulk variable can be obtained based on the definitions of microscopic velocities. So, similarly we will need to do kinetic theory for many of the microscopic systems that are of relevance to rheology. So, an example of that we will see in terms of polymer kinetic theory to obtain the relation between stress and strain and strain rate for a polymer solution system.

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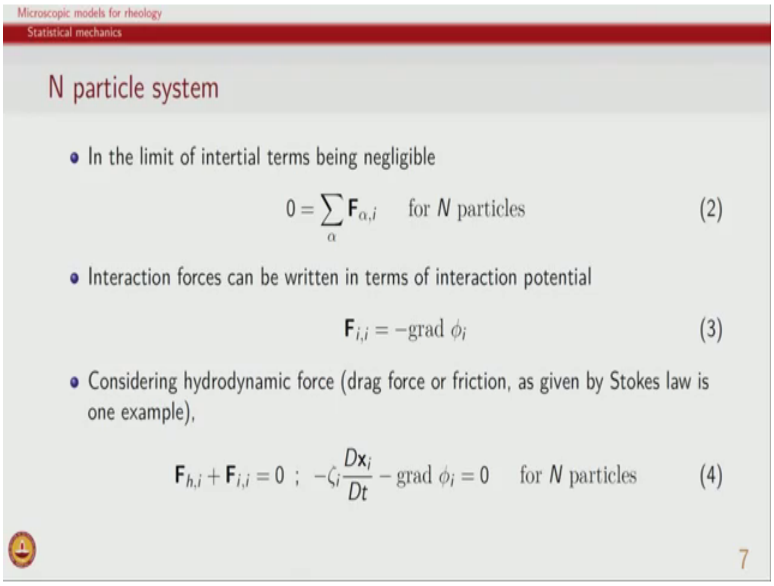

Microscopic models for rheology
Statistical mechanics

N particle system

- In the limit of intertial terms being negligible

$$0 = \sum_{\alpha} \mathbf{F}_{\alpha,i} \quad \text{for } N \text{ particles} \qquad (2)$$

- Interaction forces can be written in terms of interaction potential

$$\mathbf{F}_{i,i} = -\text{grad}\,\phi_i \qquad (3)$$

- Considering hydrodynamic force (drag force or friction, as given by Stokes law is one example),

$$\mathbf{F}_{h,i} + \mathbf{F}_{i,i} = 0\ ;\ -\zeta_i \frac{D\mathbf{x}_i}{Dt} - \text{grad}\,\phi_i = 0 \quad \text{for } N \text{ particles} \qquad (4)$$

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So, in order to think about the overall kinetic theory, we will look at some of the simplifications that can be possible. So, if we look at a system n particle system where the inertial terms are negligible, then the overall statement is related to basically all the forces will sum to 0, what we mean when we say that the inertial terms are negligible it implies that the velocities of the particles are not changing, or the overall distribution of velocities is given when let say there were no forces also of interaction. So, whatever was the equilibrium case, even if we make the material flow the overall velocity distribution does not get affected and therefore, we will not solve problems related to change in the velocity.

And therefore, we can ignore the inertial terms, we also have the scenario where some of these forces will lead to strong dissipation and, as long as those dissipation forces are significant we can ignore the inertial terms in these equations. The overall interaction forces can be written in terms of an interaction potential. And this is again similar to what we know in terms of potential energy in gravitational case.

So, the gravitational force is related to the gradient of potential energy by gradient we need, we mean how much does the potential change. So, 2 points which are of course, potential energy is higher potential energy is lower. So, the change in potential energy between these two points tells us that there will be a gravitational force in the direction of the gradient of the potential energy.

And so, if we look at the governing equation now, in a case where there is only hydrodynamic force and let us assume that that let us is given by the drag force or friction and, we only have an interaction which is based on the phi i then the overall governing equation will be the hydrodynamic interaction force and, then the forces of interaction and given that we were only considering friction between the particle of interest and the surrounding medium, we have the friction coefficient into the velocity as we saw earlier and, the gradient of phi which describes the force of interactions.

So, the governing equations for all the particles is simplified, and it says that hydrodynamic force or drag is balanced by the overall interaction force.

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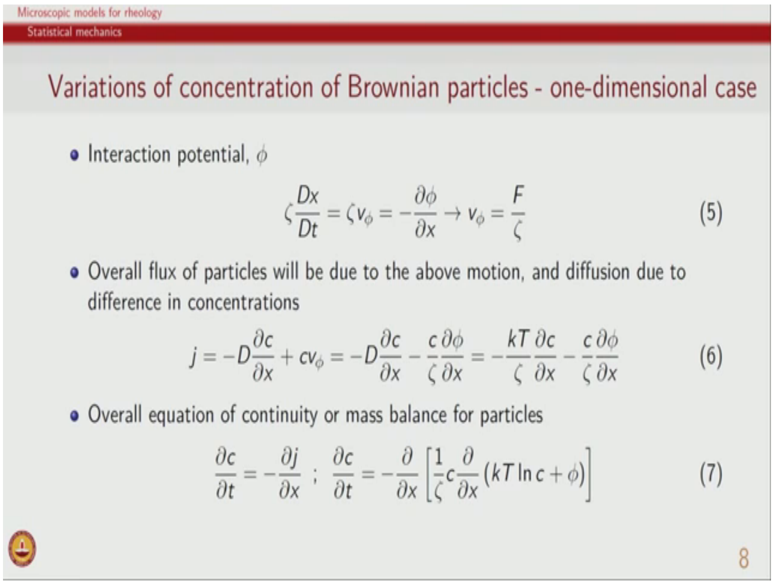

Microscopic models for rheology
Statistical mechanics

Variations of concentration of Brownian particles - one-dimensional case

- Interaction potential, ϕ

$$\zeta \frac{Dx}{Dt} = \zeta v_\phi = -\frac{\partial \phi}{\partial x} \to v_\phi = \frac{F}{\zeta} \qquad (5)$$

- Overall flux of particles will be due to the above motion, and diffusion due to difference in concentrations

$$j = -D\frac{\partial c}{\partial x} + c v_\phi = -D\frac{\partial c}{\partial x} - \frac{c}{\zeta}\frac{\partial \phi}{\partial x} = -\frac{kT}{\zeta}\frac{\partial c}{\partial x} - \frac{c}{\zeta}\frac{\partial \phi}{\partial x} \qquad (6)$$

- Overall equation of continuity or mass balance for particles

$$\frac{\partial c}{\partial t} = -\frac{\partial j}{\partial x} \; ; \; \frac{\partial c}{\partial t} = -\frac{\partial}{\partial x}\left[\frac{1}{\zeta} c \frac{\partial}{\partial x}\left(kT \ln c + \phi\right)\right] \qquad (7)$$

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Now we can look at much more simpler case also, let us look at a set of Brownian particles and what we have is a system in which the particles can move about randomly.

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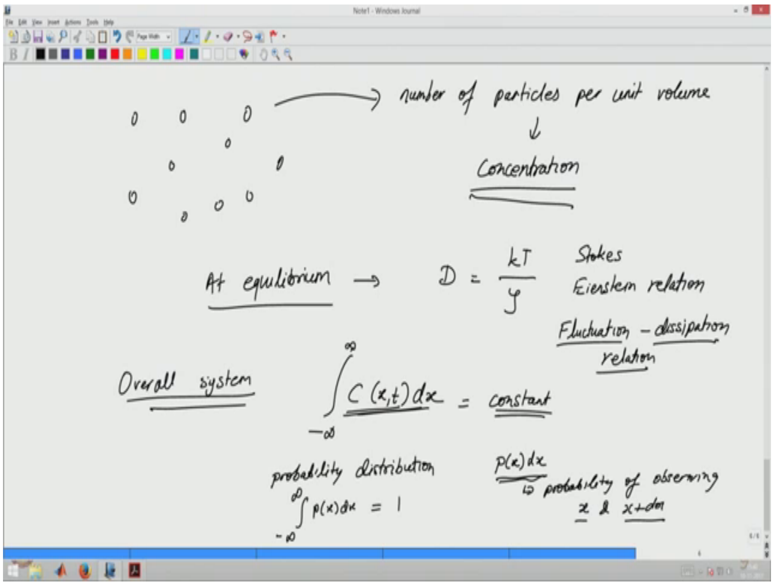

→ number of particles per unit volume
↓
Concentration

At equilibrium → $D = \frac{kT}{\zeta}$ Stokes Einstein relation

Fluctuation – dissipation relation

Overall system $\int_{-\infty}^{\infty} C(x,t)\,dx = \text{constant}$

probability distribution $\int_{-\infty}^{\infty} p(x)\,dx = 1$

$p(x)dx$ is probability of observing x & $x+dx$

And since they are moving about randomly we could define a variable of the number of particles per unit volume as its concentration. And generally the particle motion in such a scenario will be due to 2 factors, if there is any interaction here that interaction will force the particles to move, or because the concentration itself is high or low at some points particles may move from high concentration to lower concentration. So, generally when we talk of how these particles move, 1 reason could be is the fact that they are due to some interaction in a force field and, then the force divided by the friction coefficient which in case of stokes law is just 6 pi eta into a will define the overall velocity. So, the particles move because, of the presence of interaction and interaction right, now we are dealing with only a simple case.

So, we say that there is one type of interaction which is described by an interaction potential phi and, the force associated with this interaction potential is F. And remember that F is just gradient of phi since we are looking at a 1-dimensional case it is del phi by del X. Now so, the overall mole flux which is due to the external field or the interactions, or and also due to diffusion because concentration is different, then there will be a diffusion flux based on the diffusivity.

So, the overall flux of particles will be the diffusion flux times, the current which is or the flux which is set up due to the forces of interaction. And so we can rewrite in terms of V phi in terms of the force of interaction and therefore, in terms of the potential of interaction as follows and at equilibrium of course, what we will have is this overall the flux will go to 0 based on that we can in fact, derive the relationship between the friction coefficient and the so, at equilibrium and the friction coefficient.

So, the diffusivity is related to the friction coefficient and this is called the stokes Einstein relation. So, diffusivity whenever there is a concentration difference diffusivity because of diffusivity, there will be a flux cost and again concentration will become uniform. And whenever there is a diffusion happening there is a friction being exchanged between the moving particles and the surrounding medium.

So, basically both of these phenomena was, are related to each other and, this is also called the fluctuation dissipation relation. So, the diffusion happens because of the overall fluctuations in the concentration field and, the opposing force is dissipation in terms of the friction that is encountered, and these two are related to each other. So, using this relation we can then substitute for D in terms of k T by the friction coefficient and the overall flux therefore, is a diffusion flux times the flux due to interactions.

Now, the overall mass balance given that the overall number of particles remains the same, the statement is that if particles disappear from one particular position, they will appear somewhere else. So, the rate of change of concentration at any given location, as a function of time is related to what is the gradient in the current. So, this is a statement of equation of continuity for the number of particles and, by substituting the overall flux in this relation, we can obtain an equation for how does the concentration change as a function of time and position in this case.

So, we have in this case a partial differential equation, we are looking at a one dimensional case we are looking at location in physical space. So therefore, X here is the physical dimension c is the number of particles and phi is the interaction potential. So, we can see that for this simple case of concentration of particles which are moving about randomly, we can describe the evolution of concentration using this expression.

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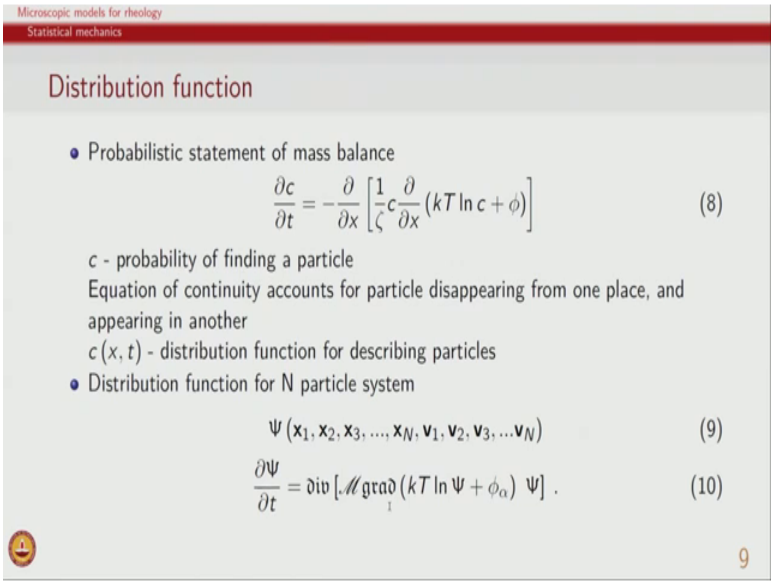

Microscopic models for rheology

Statistical mechanics

Distribution function

- Probabilistic statement of mass balance

$$\frac{\partial c}{\partial t} = -\frac{\partial}{\partial x}\left[\frac{1}{\zeta} c \frac{\partial}{\partial x}(kT \ln c + \phi)\right] \tag{8}$$

c - probability of finding a particle

Equation of continuity accounts for particle disappearing from one place, and appearing in another

$c(x, t)$ - distribution function for describing particles

- Distribution function for N particle system

$$\Psi\left(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \ldots, \mathbf{x}_N, \mathbf{v}_1, \mathbf{v}_2, \mathbf{v}_3, \ldots \mathbf{v}_N\right) \tag{9}$$

$$\frac{\partial \Psi}{\partial t} = \mathfrak{div}\left[\mathscr{M} \underset{1}{\mathfrak{grad}}\left(kT \ln \Psi + \phi_\alpha\right) \ \Psi\right] . \tag{10}$$

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So, we can also make a probabilistic statement of the same mass balance the c which is the concentration per unit volume of the particles, we could interpret that as probability of finding a particle. So, we can take any volume element in the overall system of interest and, we count the number of particles which are there, and that is nothing, but concentration. So, so we could ask the question as to what is the probability of finding particles in a given volume. So, the c also indicates the probability.

And so, this equation of continuity therefore, accounts for the probability changing as a function of time. And position and the statement that is being made is that when concentration when it reduces in one place it happens because, there is an overall flux which is being set up. Similarly the probability distribution changes because, there is an overall evolution in the system because, probability is changing from one location to the other location. So, therefore we could think of the c which is a function of X and time in this case X is the physical location and time.

So, it is the distribution function for describing the particles. So, we could interpret it as a concentration which changes from position and time, we could think of it as a probability distribution function which describes what is the probability of finding a particle at location X and location time and of course, when we do this for the overall system we know that. So, if we do this from minus infinity to plus infinity which means the overall system then this is a constant value because, the overall number of particles do not change and so, this is again very similar that if we have a probability distribution. .

And this we usually learn in our earlier statistics courses that if P x is the probability density or probability distribution P x dx is the probability of observing between x and x plus dx and, we know that when you do the overall probability from minus infinity to plus infinity this is normalized. So, the overall probability of observing any value of x is of course 1. And observing value of x between x and x plus dx is given by this P x dx. So, similarly this concentration variable could also be interpreted as a dense distribution function, and that is what we do for describing the state of the system in a phase space. So, as we described earlier phase space is 6 n dimensional spaces.

So, we have position of each and every particle and velocity of each and every particle. So, there are 6 n such variables because each of them is vector. So, N into 3 N into 3 so, we have 6 n variables and so, we could describe the system behaviour by describing how does this distribution function evolve, just the way here we describe the concentration of the particles and the configuration of the overall system by looking at how c evolves as a function of time.

So, in this case also how psi which is the distribution function evolves as a function of time is related to the divergence which is like the spatial derivative here gradient, which is again the spatial derivative here the m here is some measure of mobility zeta is the friction factor. So, 1 over zeta is mobility. So, therefore, this is some measure of mobility and again psi and c are again involved, so by analogy you can see that a governing equation which was written to account for how does probability and the concentration of particles change, a similar equation can be written for probability of observing a state of the overall system, given that the state of the overall system depends on individual particles and their states, the overall distribution function is a function of 6 N variables.

So, the evolution that happens of psi is happens in 6 N dimensional space and this evolution equation describe this gradient and divergence in that phase space. So, of course, this is much more complicated than a simple diffusion equation that we have seen earlier because, here we deal with three-dimensional and physical space this is phase space.

So, we will only deal with a simpler case, and so you know in the next few sets of lectures, what we will see is how do we simplify using this equation the overall response of a microscopic system which this which is describing a polymer system. So, the polymer system will be described using a bead spring chain model and, so the basic idea of beaks bead spring chain model is the following.

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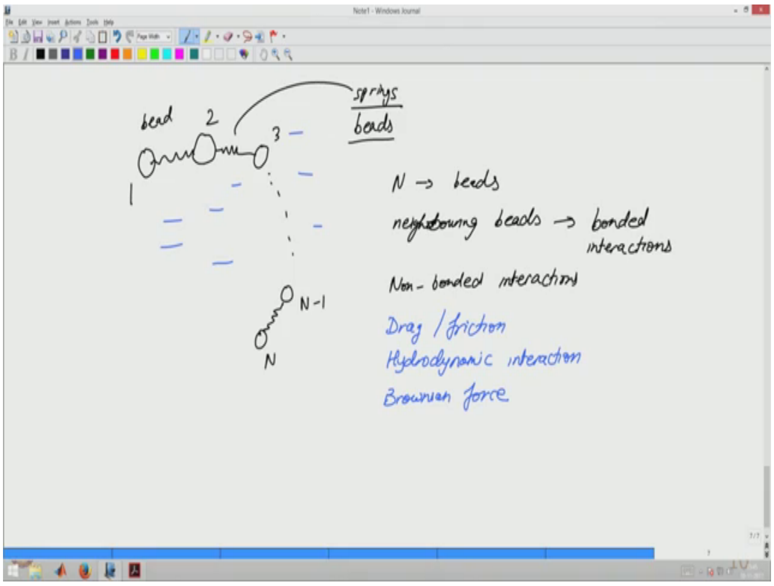

N → beads

neighbouring beads → bonded interactions

Non-bonded interaction

Drag / friction

Hydrodynamic interaction

Brownian force

That we have the polymer being depicted using beads and the beads are connected to each other through springs, and so we have beads several beads and so, N minus 1 and N. So, we have beads and we have springs and, we will see that this bead spring chain a chain which is found with beads and spring is a very effective model to describe. So, in this case again the capital N particles that we are talking about are N beads. And so the neigh boring beads are interacting with each other using bonded interactions, neighbouring beads are interacting with bonded interactions. And of course, there are non bonded interactions also present; we will also have the solvent in the system.

So, therefore, there will be drag or friction and hydrodynamic interaction and the solvent molecules would also be interacting with beads with a random Brownian force. So, now the task for us will be to set up the overall governing equation for such a microscopic model and, then to simplify it with the theoretical tools required to analyze the distribution function for such a system.