Fundamentals of Particle and Fluid Solid Processing
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Lecture - 56
Colloids and nanoparticles

Hello everyone, and welcome back to the class of Fundamentals of Particle and Fluid Solid Processing. So, we have covered a lot of content in this course and now finally, we will be talking about the colloids and the nanoparticles; a special section of these particles. Now these are of huge importance nowadays because they are the cornerstone of some cutting edge research that is currently going on.

And also this concept or the details on these nanoparticles will help us to understand a certain extent of the phenomena that we have considered in the previous sections. For examples why the particles are cohesive in nature, the fine particles are cohesive in nature typically or difficult to flow and what can be done to separate them.

So, if we go into the details of these fundamentals of colloids and nanoparticles, then this will shade some light on the mechanisms or the fundamentals of fine particles that eventually we have handled.

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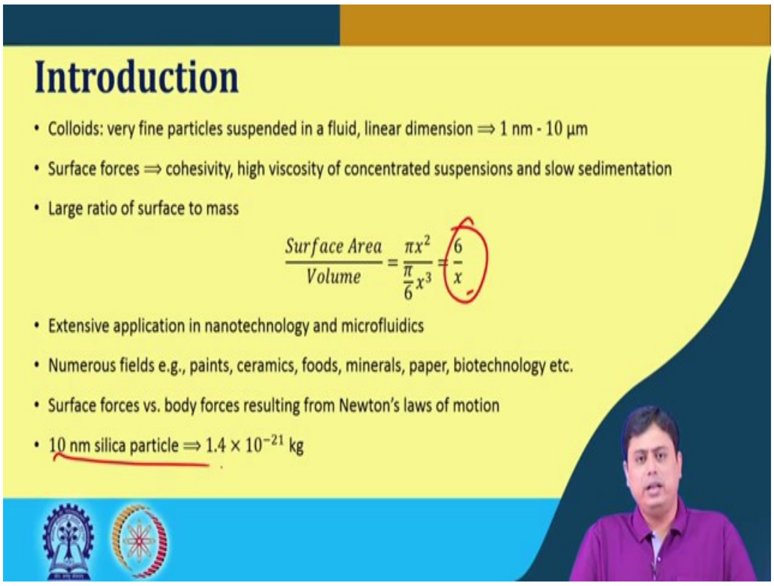

Introduction

- Colloids: very fine particles suspended in a fluid, linear dimension ⇒ 1 nm - 10 μm
- Surface forces ⇒ cohesivity, high viscosity of concentrated suspensions and slow sedimentation
- Large ratio of surface to mass

$$\frac{Surface\ Area}{Volume} = \frac{\pi x^2}{\frac{\pi}{6}x^3} = \frac{6}{x}$$

- Extensive application in nanotechnology and microfluidics
- Numerous fields e.g., paints, ceramics, foods, minerals, paper, biotechnology etc.
- Surface forces vs. body forces resulting from Newton's laws of motion
- 10 nm silica particle ⇒ 1.4×10^{-21} kg

Now, colloids are typically a very fine particles that are suspended in a fluid and have one or more linear dimensions of around 1 nm - 10 µm or even lesser than that. So, we can understand the magnitude of the length or the linear dimension we are talking about now we have come down to the nanometer range. Now these fine particles we will interchangeably using here as the fine particles and when these are suspended in liquid or the colloids.

Now, in this case what becomes a critical factor is the surface forces, because these small particles if we look at their mass these are of very very small amount of mass. Now, these surface forces that are the reason of being fine particles as cohesive in nature.

The we can it can exhibit the behavior of high viscosity of concentrated suspension and it also results in very slow sedimentation. And that is why we spoke about sedimentation in some external field like the centrifugal field and etc, because by gravity separations this kind of fine particles cannot be set separated this remains suspended for a longer time.

Now the reason the surface forces are important because it provides this fine particles provides a very large ratio of surface to mass. Now, the mass and the volume is related with the density; now for a fixed density of the particle or the bulk density or the say the material density of the particle.

Large ratio of surface to mass

$$\frac{Surface\ Area}{Volume} = \frac{\pi x^2}{\frac{\pi}{6} x^3} = \frac{6}{x}$$

So, if the particle size which is the x the diameter of the particle it goes down or decreases we can see that the surface area per unit volume increases.

Now, these actually have a lot of implications in several research areas like the nanotechnology microfluidics and all these cutting as research areas. So, also it finds widespread applications this fine or the nanoparticles or the colloids in paints, ceramics, food, mineral, paper, biotechnological industries.

Now the reason we are talking about the surface force is that this has a very very small amount of mass for example, this over 10 nm of silica particle has a weight or the mass of in the order of 1.4×10^{-21} kg. So; that means, the body force on these small particles are virtually insignificant, because the body force results from the Newton's law of motion, ok.

So, this relative dominance of the surface force on the smaller particles is actually makes it difficult to understand. Because, the surface forces are not only the, I mean it comes from several electromagnetic forces it depends on the surface property, material property, the intervening fluid property etcetera; whereas, the body force is relatively easier to understand. And that is why we will see in this section in a bit details that what are the surface force that actually dictates this behavior of the fine particles or the colloids.

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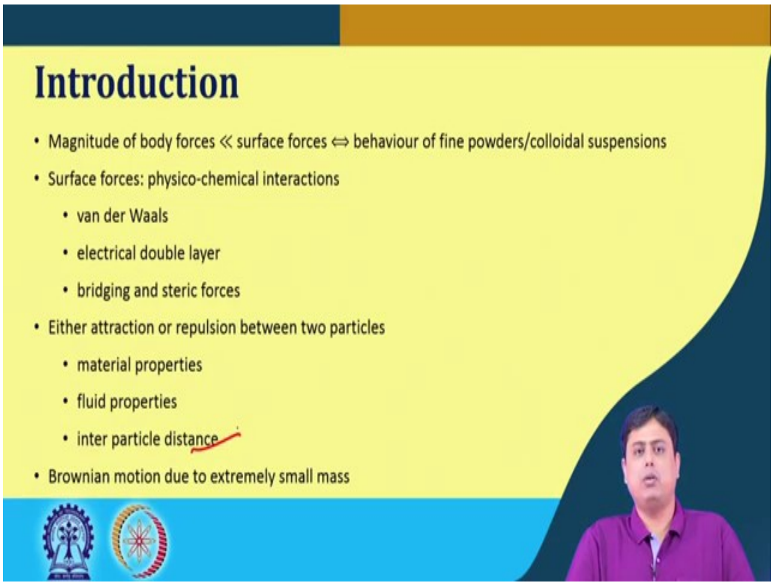

Introduction

- Magnitude of body forces ≪ surface forces ⟺ behaviour of fine powders/colloidal suspensions
- Surface forces: physico-chemical interactions
    - van der Waals
    - electrical double layer
    - bridging and steric forces
- Either attraction or repulsion between two particles
    - material properties
    - fluid properties
    - inter particle distance
- Brownian motion due to extremely small mass

Now, as I am repeatedly mentioning this magnitude of body force is much much lesser than the surface force and that dictates the behavior of this nanopowders or the colloid suspensions. Now, this surface forces are the physicochemical at interactions between two molecules or two atoms, and the examples of the surface forces are the van der waal forces, electrical double layer, bridging and steric forces etcetera. These forces can be attractive and the summation of these forces can be attractive or repulsive and that actually dictates that whether the particles the two different particles will be coming together or it will be a repulsive in nature so, that they will be kept away at a certain distance.

Now, this thing as I mentioned depends on the material property, fluid property and the other most important is the inter particle distance, the distance between the two particles. So, we can easily remember the coulomb interaction, the coulomb chart, the coulombs law for the two such charged materials; now we will be coming in to that, ok.

Now before that, this another feature or another effect of this very small amount of mass of these fine particles or the nanoparticles that has implication is that the Brownian motion of those particles. Because these now are so fine or so small and very miniscule in mass that it behaves as if a somewhat like molecules and then easily diffuse into the liquid.

So, there are random motions of these particles which we typically know as the Brownian motion.

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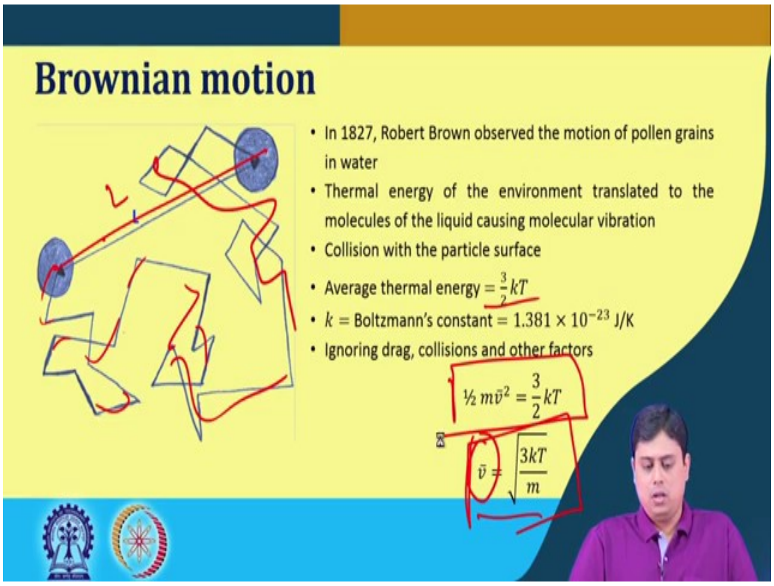

Brownian motion

- In 1827, Robert Brown observed the motion of pollen grains in water
- Thermal energy of the environment translated to the molecules of the liquid causing molecular vibration
- Collision with the particle surface
- Average thermal energy = $\frac{3}{2}kT$
- k = Boltzmann's constant = 1.381×10^{-23} J/K
- Ignoring drag, collisions and other factors

$$\boxed{\tfrac{1}{2} m\bar{v}^2 = \frac{3}{2}kT}$$

$$\boxed{\bar{v} = \sqrt{\frac{3kT}{m}}}$$

Now, in Brownian motion this in 1827 was observed by Robert Brown after which after whom this name has been mentioned is the Brownian motion is that, the motion of he observed the motion of pollen grains in water and these are this such kind of random walk has been named after that. So, what happens is there that the neighbor thermal energy or the surrounding thermal energy is basically translated to the molecules of the liquid that causes its molecular vibration.

Now, as the molecular vibration happens, it collides with each other of those liquid molecules and also with the surfaces of the suspended particles; suspended fine particles. So, this collision results into this random motion of this particles and a simple let us say the kinetic model can help us that what would be the average velocity of these particles.

So, if we assume that the all thermal this thermal energy is being converted to this molecular vibration. So, neglecting all other forces or ignoring drag forces collisions and other factor, we can equate

Average thermal energy ¿ $\frac{3}{2}kT$

where k is the Boltzmann's constant and T is the temperature in Kelvin that with the kinetic energy of the particle with a average velocity. By equating these two expression of these two term, this can give us this average velocity of the particle.

Ignoring drag, collisions and other factors

$$½\, m\acute{v}^2=\frac{3}{2}kT$$

$$\acute{v}=\sqrt{\frac{3kT}{m}}$$

Now, from this expression we can understand that with changing temperature this velocity will be influenced, or if we increase the temperature the velocity will increase the Brownian and motion will be more rapid or random. If we decrease the mass of the particle the velocity will be higher. So, this expression tell this simple thing and it is useful to understand this phenomena; that as the particles becoming smaller and smaller the mass goes down and as the mass goes down it has a higher average velocity during this Brownian motion.

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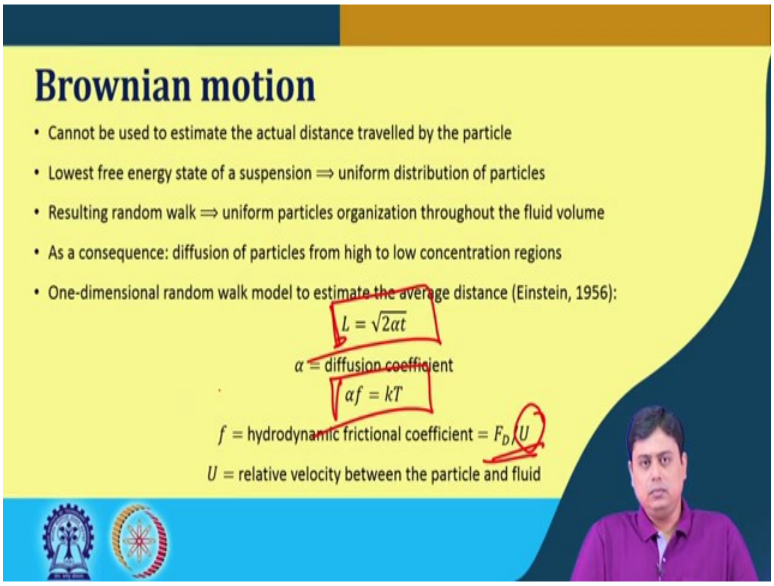

Brownian motion

- Cannot be used to estimate the actual distance travelled by the particle
- Lowest free energy state of a suspension ⟹ uniform distribution of particles
- Resulting random walk ⟹ uniform particles organization throughout the fluid volume
- As a consequence: diffusion of particles from high to low concentration regions
- One-dimensional random walk model to estimate the average distance (Einstein, 1956):

$$\boxed{L = \sqrt{2\alpha t}}$$

α = diffusion coefficient

$$\boxed{\alpha f = kT}$$

f = hydrodynamic frictional coefficient = F_D/U

U = relative velocity between the particle and fluid

Now such simple analysis cannot be used to estimate the actual distance traveled by the particle, because the actual distance travel say these between these two particles is L. But, it is it does not just come across that length it goes through like this zig zag path this random path this is a random structure random path, it can follow any random path. So, the actual distance that is travels cannot be calculated by this velocity.

So, now if a solution say or a suspension is stable then in thermodynamics by principle it has to be in its lowest free energy state of a suspension and; that means, the particles will be uniformly distributed throughout the suspension. So, this Brownian motion basically a mechanism by which this resulting random walk; generates a uniform profile inside the or in the suspension. So, that the particles can organize themselves throughout the fluid volume in order to be in the lowest free energy state. So, as a consequence diffusion of particle happens from high to low concentration region.

Now, in order to estimate the length it travels Einstein proposed a one-dimensional random walk model, which says that this length that it travels is $L=\sqrt{2\alpha t}$ where α is a diffusion coefficient of the particles. He further developed a relation between hydrodynamic drag or the hydrodynamic frictional drag with this α which is the diffusion coefficient, and that is proposed in this manner that $\alpha f = kT$, where f is the hydrodynamic frictional coefficient which is F_D/U is equals to Boltzmann constant multiplied by the temperature in Kelvin. Now, this u in this expression is the relative velocity between the particle and the fluid.

So, it provides us this expression provides us an estimate that how much length this particles will travel.

Now, with this say in the creeping flow we know this f value from the Stoke’s law or the expression of f from Stoke’s law which is

$$f = 3\pi x\mu$$

where x is the diameter of the particle, μ is the viscosity of the suspension. Which means, we have

$$\alpha = kT/3\pi x\mu$$

which implies that the length Lthat it travels is of this expression

$$L = \sqrt{\frac{2kT}{3\pi x\mu}t}$$

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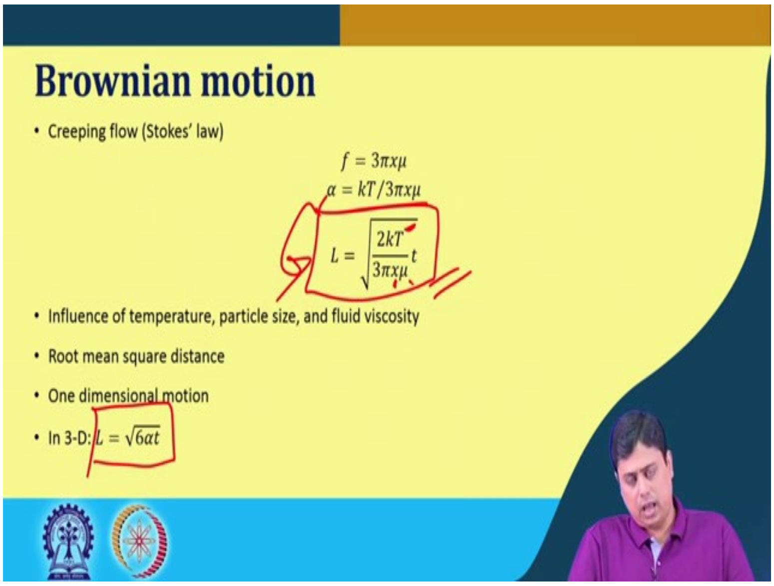

Brownian motion

- Creeping flow (Stokes’ law)

$$f = 3\pi x\mu$$

$$\alpha = kT/3\pi x\mu$$

$$\boxed{L = \sqrt{\frac{2kT}{3\pi x\mu}t}}$$

- Influence of temperature, particle size, and fluid viscosity
- Root mean square distance
- One dimensional motion
- In 3-D: $\boxed{L = \sqrt{6\alpha t}}$

This expression shows that this length it travels is dependent on the temperature, particle size and fluid viscosity. It also shows that this time and the length it travels is related with the root square relation square root relation. This length or the average length was also called the root mean square distance. It is indeed one-dimensional motion, but in reality this is the three dimension motion of the particles, but the reason this expression is important or has implication is that, in sedimentation say that is our concern, because we want to separate say the solid particle. So, our main objective is on the solid particles or the fine particles.

So, during sedimentation the motion of this particle is considered as one-dimensional that is in the direction of the gravity. And, but in that time, during that period it is not in the other two orthogonal directions. So,, that is basically the reason that this expression has important, but in 3-D analogous relation can be developed and that has this $L=\sqrt{6\alpha t}$.

So; that means, we have understood that why this Brownian motion happens how to estimate the length how much it travels a certain particle in one-dimensional random walk model and what are the dependent parameters, that which parameters influences this length that it travels or it is average velocity.

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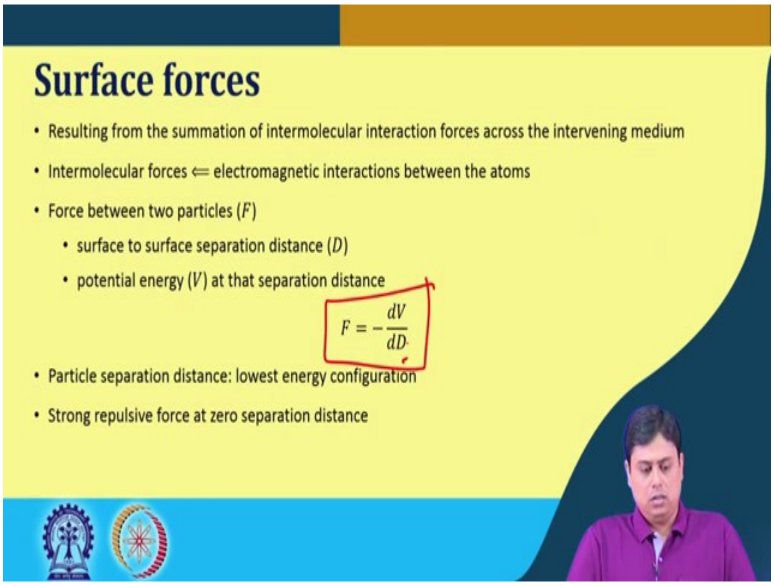

Surface forces

- Resulting from the summation of intermolecular interaction forces across the intervening medium
- Intermolecular forces ⇐ electromagnetic interactions between the atoms
- Force between two particles (F)
  - surface to surface separation distance (D)
  - potential energy (V) at that separation distance

$$\boxed{F = -\frac{dV}{dD}}$$

- Particle separation distance: lowest energy configuration
- Strong repulsive force at zero separation distance

Now, the surface forces that occur, this surface forces are basically resulting from summation of intermolecular interaction forces across the intervening medium. Now, this intermolecular forces comes from the electromagnetic interactions between the atoms.

So, generally a force between two particles is dependent on the surface to surface separation distance and the potential energy at that separation distance. And the relation between these three is this expression, that the force is $F=\frac{-dV}{dD}$, V is the potential energy and this D stands for the separation distance.

Now, this particles are in suspension it always try to attain the lowest energy configuration by thermal dynamics. So, the particle separation distance would be when there is nothing to do with any other external forces, it will try to achieve the lowest energy configuration state.

Now; that means, there is a equilibrium distance between the two particles and when we try to make them very closer there is a strong repulsive force at zero separation distance; that means, when they are in contact, ok. Then they have are if we try to penetrate say one surface with another there is a strong repulsive force at that distance, and that is the reason that in one certain space there can be just only one molecule. So, the force profile and the energy profile typically looks like this kind of profile.

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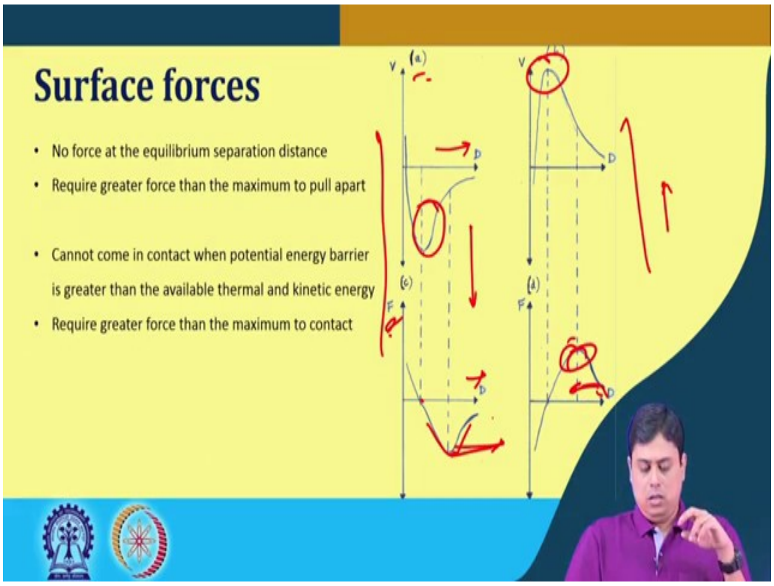

Surface forces

- No force at the equilibrium separation distance
- Require greater force than the maximum to pull apart
- Cannot come in contact when potential energy barrier is greater than the available thermal and kinetic energy
- Require greater force than the maximum to contact

Now, typically what happens that this first one is the energy versus the separation distance interaction energy versus the separation distance, and this one the corresponding force and the separation distance. So, usual I mean usually the convention is that when this energy or the force is in the negative it is the attractive force, and when it is in the positive values it is the repulsive one. So, this happens when the interaction is there and this happens when the repulsion is there.

So, here we can see that there is no force at equilibrium separation distance, which is at the minimum energy state. Now; so, which means now if we try to make them further closer there is a huge repulsive force that acts in between the two particles. And when they are separated at a longer or a larger distance there is a very weak attraction there. And if we try to make them closer or even try to take them apart then we require a greater force than the maximum to pull them apart. We require a force higher than this to separate them to a greater distance.

Now, in case when there is repulsion; the interaction is repulsive they cannot come in contact because of this potential energy barrier which is greater than the available thermal or the kinetic energy of the surrounding. So, it requires a greater force to overcome this in order to make them in contact. So, the particles when there is attractive in nature, they stay in this energy way; minimum energy way. If we try to separate them we require a higher force than this one then a maximum want to pull them apart.

The particles interact; so, the particle interactions are repulsive in nature we try to contact them, then what happens we require we required to overcome a certain potential barrier or we require a greater force than the maximum to keep them in contact.

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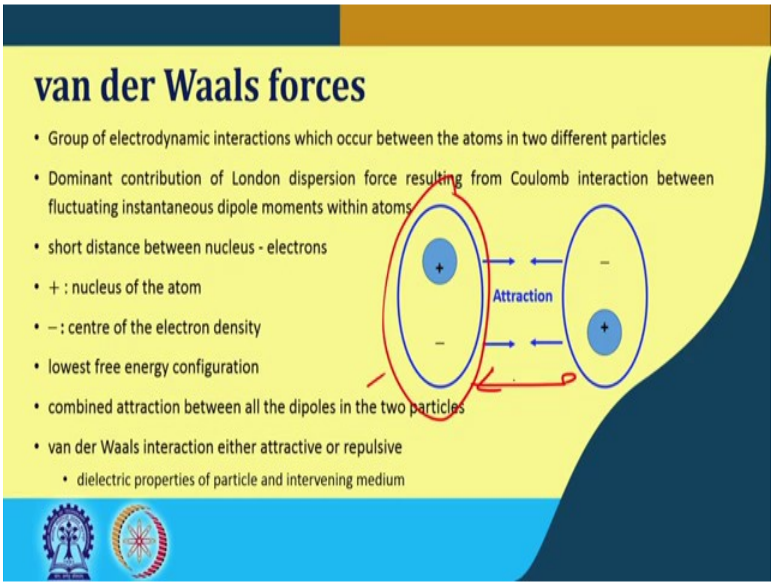

van der Waals forces

- Group of electrodynamic interactions which occur between the atoms in two different particles
- Dominant contribution of London dispersion force resulting from Coulomb interaction between fluctuating instantaneous dipole moments within atoms
- short distance between nucleus - electrons
- + : nucleus of the atom
- – : centre of the electron density
- lowest free energy configuration
- combined attraction between all the dipoles in the two particles
- van der Waals interaction either attractive or repulsive
  - dielectric properties of particle and intervening medium

Now, the one of the major surface forces that we introduced earlier or we have seen this earlier is the van der Waals forces. We have discussed this, but for the sake of coherency lets again see this part, but in a bit detailed. So, this van der Waal forces are the group of electro dynamic interactions which occur between the atoms in two different particles.

Now, it consists of several surface forces like or the electromagnetic forces of the electro dynamic forces like (Refer Time: 24:18) London dispersion forces, and the dominant contribution of London dispersion force that results from the coulomb interaction between fluctuating instantaneous dipole moments within the atom. So, London dispersion is basically the dominant contributor to this van der Waal forces.

Now, this coulomb interaction between fluctuating instantaneous dipole moments within the atoms how it happens; so, let us consider a scenario that we have a molecule now there is a very short distance between the nucleus and the electrons of any atoms. Now in that case see that nucleus that is say positive charged around which the electrons are orbiting are revolving. Now, this electron or the electron clouds as it rotates around this nucleus, it creates a electron density across or around this nucleus.

Now, what happens in that case this in order to be in a minimum energy state this say one particle or the one atom would be in such configuration, where this plus sign designates the nucleus of the atom and negative sign is the center of this electron density.

So, now since this electron density is shifting with time at any instant in time continuously these would try to adjust its lowest configuration mode, lowest energy state mode. Similarly this will happen or this actually is called the dipole moment; now, these dipole moments will occur in all the elements of this particle. Now, these will try to accommodate themselves or rearrange themselves in order to be in sync.

Now, if the two atoms or say the particles are positively charged or say the same charge of same charge of the same material rather; now, if those two are same material then what will happen this kind of configuration would result, in order to maintain its electro neutrality. So, this would be the lowest free energy configuration and this combined interaction between all the particles in the all the dipoles in the two particles will create a attraction overall attraction.

So, this van der Waal interaction can be attractive or repulsive in nature depending on the dielectric properties of the particle and the intervening media. When there is this usually the can the people understand the van der Waals interaction is attractive in nature between certain cases, in rare case in fact, this can be repulsive in nature as well. But, it is strength or the magnitude depends on the dielectric property of the particle and the intervening medium.

So, if we just summarize what we have seen is that we have seen the Brownian motion of the particle, the surface force its nature between the two particles and one of the major surface forces is the van der Waal force why it occurs. The mechanism of dipole moment and its attraction that is what we have discussed today. We will go into this in further details in the coming classes till then.

Thank you for your attention.