**Polymer Reaction Engineering**
Prof. Shishir Sinha
Department of Chemical Engineering
Indian Institute of Technology – Roorkee

Lecture - 47
Population Balance Modelling Other Techniques - I

Welcome to the new lecture of population balance modelling. Now, population balance modelling is a very important concept in any kind of polymerization reaction. And this is also very useful for predicting the behaviour of In-situ polymerization and further developed polymers which may be produced in due course of any polymerization process. Basically, it deals with the various kind of chain development of chain monomer behaviour within this polymer mass.
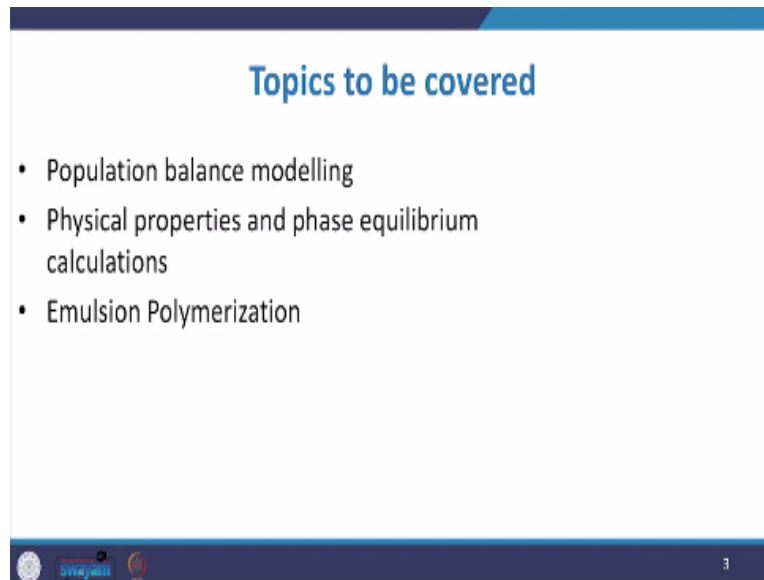
So, we will start this population balance modelling in this particular sub chapter. Now, before we start this thing, let us have a brief look about that what we discussed previously. We discussed about the heterogeneous polymerization.

(Refer Slide Time: 01:12)
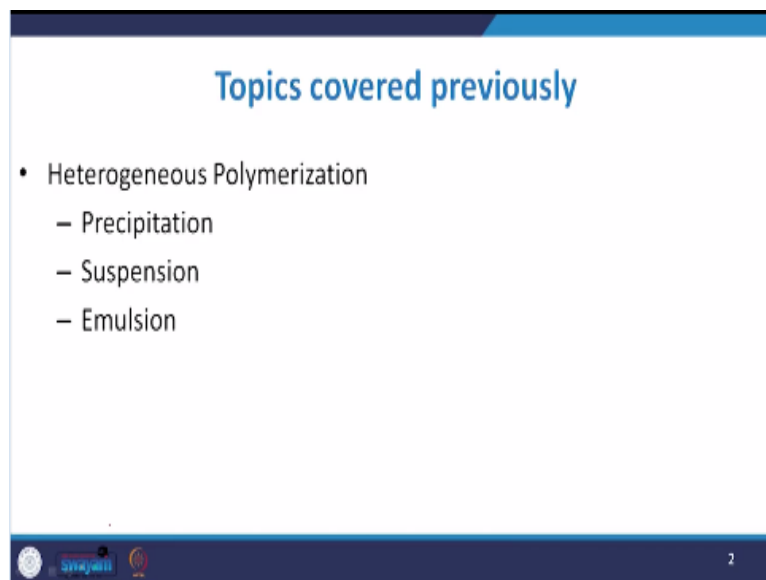
Apart from this under the subhead of heterogeneous polymerization, we discussed the precipitation concept of suspension polymerization and discuss a brief about the emulsion polymerization. Now, emulsion polymerization is a very vast segment in which with the help of emulsion be used to form the polymerization process and we will seek the help of this emulsion polymerization concept in this particular chapter.

(Refer Slide Time: 01:48)

So, we are going to cover the population balance modelling in this chapter. Apart from this, we will discuss about the various calculations attributed to the physical properties and phase equilibrium. Both these things are a very important concept in polymerization step and then we will discuss all these things with the help of the emulsion polymerization concept. Now, let us have a look about the concept of population balance modelling.

Now, population balance modelling is widely used approach to describe the growth of a polymer chains. It also explains the concept of chain agglomeration and breakage. Now, before we proceed further, let us have a look about this particular concept as we know that when whatever method we follow for the polymerization process, it consists of development of chains within the polymer mass, within the reaction mass.

So, whenever we talk about this, the control of these chains are extremely important. Now, control parameter also attributed to the molecular weight distribution. As we know that the molecular weight distribution plays a very vital role in predicting the property of polymer, sometimes, it is attributed to the viscosity; sometimes, it is attributed to the glass transition temperature.

So, it plays a very vital role in deciding the final outcome of the polymer. So, whenever we discuss this particular approach, then our point of focus should be like this that what is the fate comply of those chains being developed into reaction mass. When we carry out any kind of polymerization reaction in a reactor, then my focus of attention would be that how many
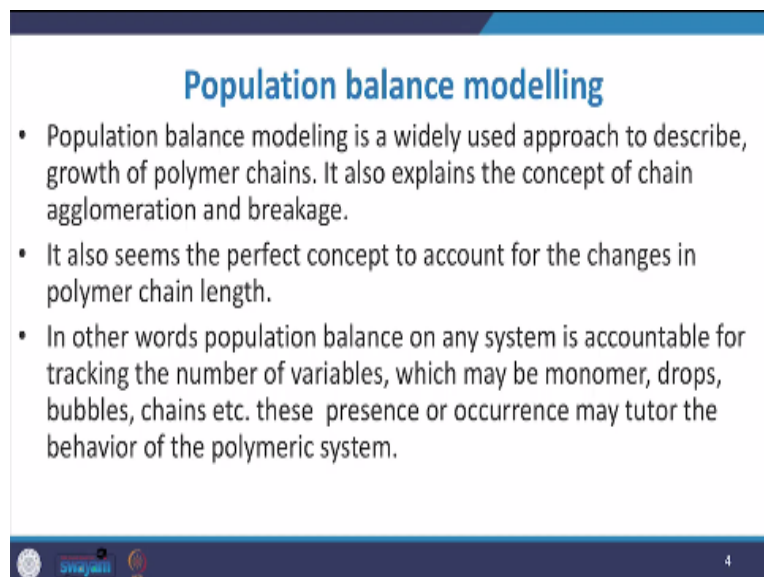
monomers are participating, what is the fate of chains, what is the length of those chains, what is molecular weight of those chains, so etcetera.

So, there are so many things should come into our mind. So, that is why whenever we wish to predict the behaviour of final outcome, maybe the polymer, maybe the polymeric system etcetera. So, population balance modelling comes into the picture. So, see, it also seems the perfect concept of accounting for the changes in the polymer chain length. So, whenever we talk about the molecular weight distribution, then polymer chain length, they play a very vital role in deciding the fate of those polymer, those molecular weight distribution.

So, slight change in the length of a polymer chain, slight change in other aspects of those chains may adversely or favourably affect the molecular weight distribution. And moreover, you see that these polymer chains are sometimes overlapped each other or entangled with each other. So, whenever we deal with the bulky chains, then sometimes the movement of those chains would be restricted because of the higher molecules weight or higher weight.

So, it ultimately affects the final property of the polymer. So, therefore, in view of this, one may be interested that what is going on within the reaction mass and what are those polymer chains affect; how these polymer chains are affecting those polymer mass. So, based on this the population balance modelling, it came into the existence for the help of the predicting the behaviour of polymerization process in totality.

(Refer Slide Time: 05:40)

Population balance modelling

- Population balance modeling is a widely used approach to describe, growth of polymer chains. It also explains the concept of chain agglomeration and breakage.
- It also seems the perfect concept to account for the changes in polymer chain length.
- In other words population balance on any system is accountable for tracking the number of variables, which may be monomer, drops, bubbles, chains etc. these presence or occurrence may tutor the behavior of the polymeric system.

So, in other words, we must say that the population balance on any system is usually accountable for tracking the number of variables. Now, you see there are so many variables present in the reaction mass; one may be the monomer; sometimes, it may be that drops; sometimes, it may be with respect to the bubble; sometimes, it may be with respect to the chains; sometimes, it may be with respect to the catalytic behaviour.

So, there are so many variables are associated with the polymerization reaction and you know that these presents are occurrence; this may alter the behaviour of polymeric system. So, that is why keeping count of these variables, these different parameters etcetera, those who are directly affecting the behaviour of polymerization, directly affecting the final outcome of the polymer product, the population balance modelling is extremely important.

Now, question arises, what is the basic genesis of this population balance modelling? Now, this usually follow the dynamic evolution of particle size distribution, sometimes, referred as PSD in a particular process. So, see, this is, you can correlate that one single monomer may attach with another monomer to give you two monomer join together and then the series of these monomer when joined together, they will form the polymer chain.

So, by this way, there is a dynamic evaluation of various chains. Similarly, this is the dynamic evaluation of the particle size distribution. So, a population balance approach is commonly employed to predict the behaviour of those dynamic evaluation concept in any kind of particle size distribution.

(Refer Slide Time: 07:38)

The distribution of the particle is usually considered to be continuous in the volume domain and it is usually described by the number density function n(v,t); usually it is a function of v and t. Now, you see in this particular figure where there are 2 types of agglomeration is, agglomerations are presented. Here, this is one mass and other is collision. Now, there are 2 concepts. One is that either a directly collide with this particular mass and this is the unsuccessful collision.

Now, once it is a successful collision, then there are again 2 options with respect to this primary agglomeration. It may successfully collide and it may attach to the surface of this particular particle. And similarly, it may have another option that it may have a successful collision. So, this is the; you see that this is the single layer of primary particle via primary agglomeration and whenever it may, you may have a sufficient number of other particles, then there may be a chance of multi layer formation while the secondary agglomeration.

So, by this way, you can predict and you can see that there is a evolution; there is a successive evolution of different type of particle sized.

Thus, n(v,t)dv represents the number of particles per unit volume within the differential volume set (v,v+dv).

For the dynamic particle particular system, the rate of change of number density function with respect to time and volume is usually calculated by different non-linear integral differential population balance equation. So, let us have a look about those differential population balance equation.

(Refer Slide Time: 09:50)

So, this is the mathematical representation of this population balance;

$$\frac{\partial[(n,v,t)]}{\partial t} = \int_v^{v_{max}} \beta(u,v)u(u)g(u)n(u,t)du + \int_{v_{min}}^v k(v-u,u)n(v-u,t)n(u,t)du -$$

$$n(v,t)g(v) - n(v,t)\int_{v_{min}}^{v_{max}} k(v,u)n(u,t)du \dots (1)$$

- The first term on the right-hand side of the equation represents the generation of droplets in the size range (v, v+dv) due to drop breakage.
- β(u, v) is a daughter drop breakage function, accounting for the probability that a drop of volume v is formed via the breakage of a drop of volume u.

(Refer Slide Time: 12:33)
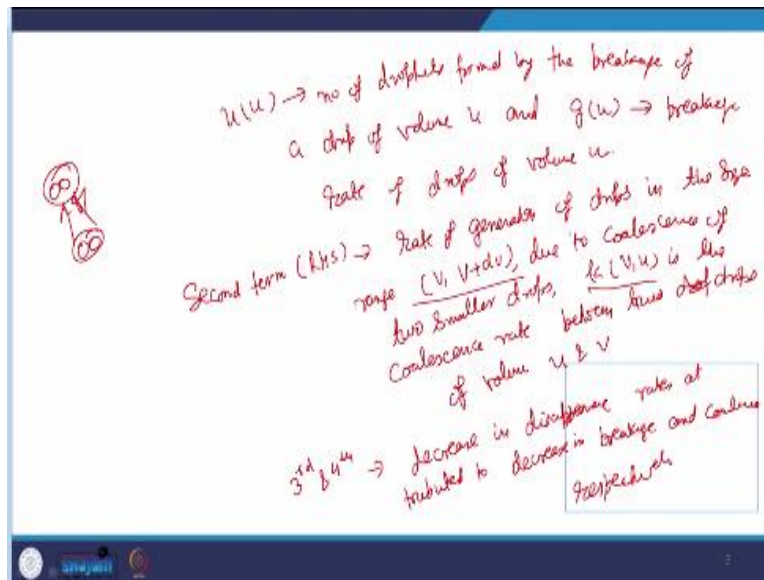
- The function u(u) denotes the number of droplets formed by the breakage of a drop of volume u and g (u) is the breakage rate of drops of volume u.
- The second term on the right-hand side of the equation describes the rate of generation of drops in the size range (v, v + dv) due to the coalescence of two smaller drops, k(v, u) is the coalescence rate between two drops of volume v and u.
- Third and fourth words reflect the decrease in disappearance rates attributed to the dec rease in breakage and coalescence, respectively.

This particular concept is again very important in view of this that sometimes, there is a formation as well as there is a dissociation of all these chains. So, sometimes, it may appear that due to this particular concept, you are having the utmost attention towards this population balance modelling.

(Refer Slide Time: 16:00)
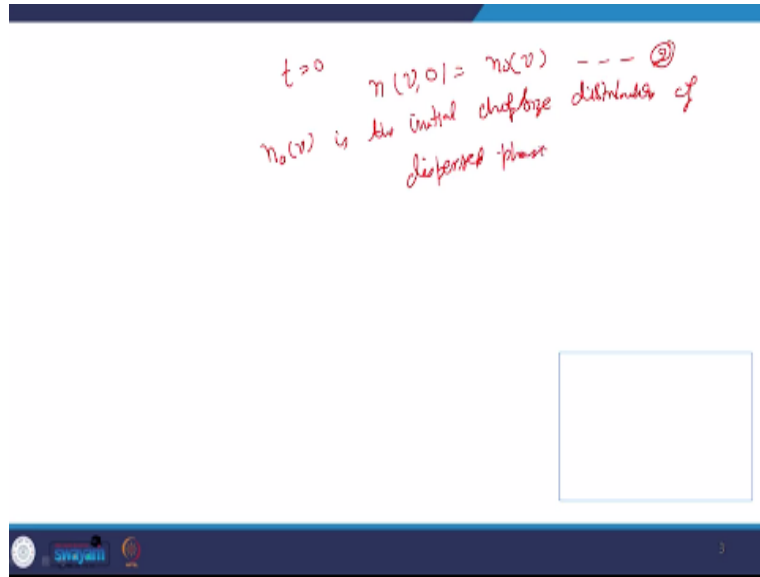
- Equation (1) will satisfy the following initial condition at t = 0:

$$n(v, 0) = n_0(v)\ldots\ldots(2)$$

- Where, $n_0(v)$ is the initial drop size distribution of the dispersed phase.

When we talk about the dispersed phase that means, the emulsion polymerization, it comes into the existence.

Now, let us have a brief outlook that the concept of drop breakage process.

The drop breakage in the turbulent flow field can be caused by the viscous shear force by the turbulent pressure fluctuation and by the relative velocity fluctuation.

So, sometimes in the polymeric system, you need to incorporate these type of approaches to enhance the rate of polymerization. So, that is why this particular approach is sometimes extremely useful and if you recall that during the emulsion or suspension polymerization process, then we discussed agitation and the flow rate both play a very vital role in deciding the fate and deciding the number and size of the polymeric chain being developed in due course of time. As a drop breakage happens due to the viscous shear force, the monomer droplet is the first elongate into two fluid lumps system divided by a liquid card.

(Refer Slide Time: 18:02)
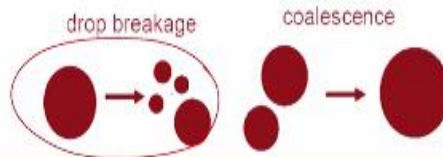
You can see that this is the concept of a drop breakage; there is a big drop and it can be backed into the small, small particles and sometimes these small particles may go for the coalescence to give you the bigger one.

(Refer Slide Time: 18:14)

So, let us have this particular concept related to the breakage. So, there are thorough breakage. Now, sometimes the deformed monomer droplets, they split into 2 nearly equal sized droplets and corresponding to fluid lumps and a series of smaller droplets corresponding to the liquid threads. So, this is considered as a thorough breakage. So, the genesis of this thorough breakage is that splitting into two nearly to equal size of drops. Another is the erosive breakage.

So, when the relative velocity of this particle is similar to that needed to make a drop slightly unstable. A number of tiny droplets, they are separated from the original one like we discussed

in this figure. So, this drop breakage condition is sometimes referred to as erosive breakage. Now, it is considered to be the dominant mechanism of low coalescence system and that exhibit a characteristic by modality in the particle size distribution.

So, that is why this particular concept is extremely important while discussing when drop size breakage and equally important in emulsion polymerization as well as the suspension polymerization. Now, if you recall in the suspension polymerization, we are more and more concerned towards the formation of small drop at early stage. So, when you perform the agitation, then this type of a concept plays a very vital role in deciding the final outcome of those polymers product.

(Refer Slide Time: 20:09)
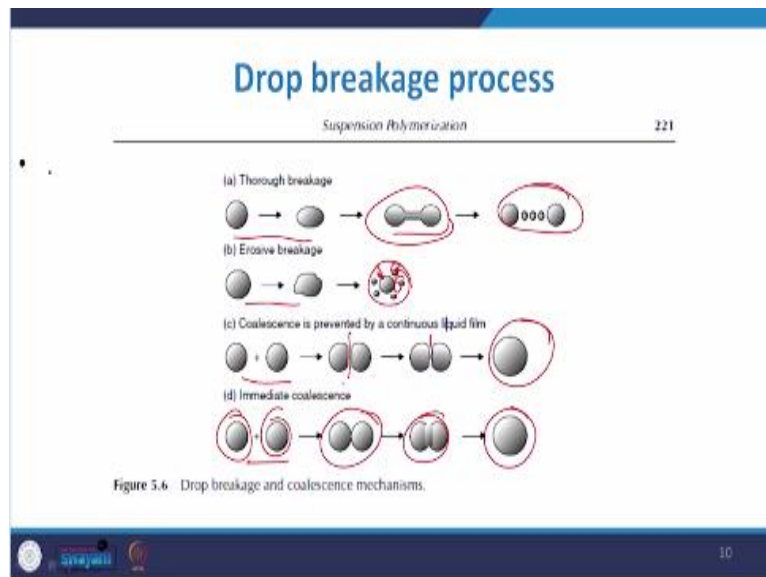
Let us have the things related to the suspension polymerization. Now, here you see that the thorough breakage, where you see that this drop is bred into to nearly equal sized of drops. When we talk about the erosive breakage, then you see that there are dissimilar type of things happened in this approach, you may see there are small, small particles drops and then a bigger one. Sometimes, this, we discussed that the coalescence is provided by the continuous liquid film.
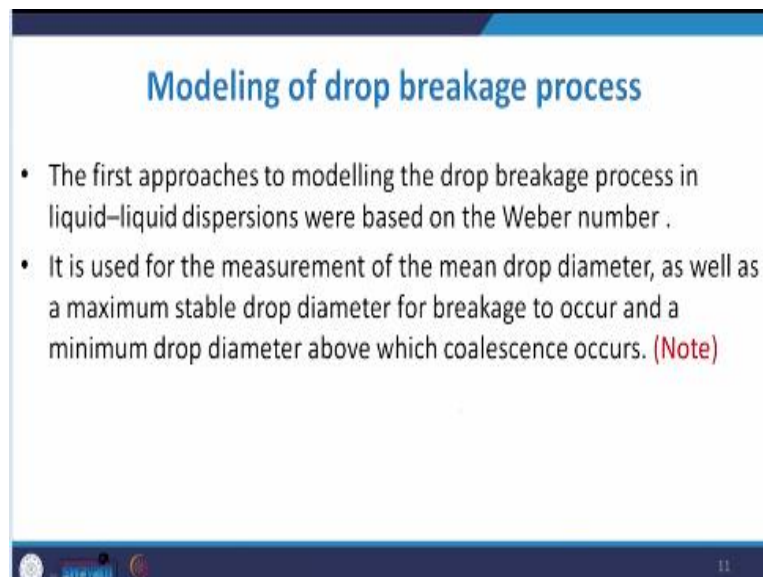
So, sometimes, this particular approach is like this, you may have see that here is the formation of a film and thereafter, you may experience the bigger one or bigger drop size in the suspension polymerization. Similarly, if we see sometimes, we may see that immediate coalescence now, immediate coalescence is that two equal sized drops. They are combined together to form this one and then over the period of time, they may form this type of bigger drop.

When we talk about the suspension polymerization, this type of approach is sometimes very trivial one because sometimes, it may promote the formation of agglomeration thereby the highly viscous polymer gel within the reactor system and that may create a future problem and sometimes, it may create the problem of damage to the reactor or sometimes, the damage to the impellers of agitators etcetera.

So, this type of things should be addressed clearly when we discuss this drop breakage process under the head of suspension polymerization. So, when we talk about the modelling of these that drop breakage process within the head of polymerization process. The first approaches to modelling the drop breakage process in liquid-liquid dispersion, this was based by the Weber number.

Now, it is used for the measurement of mean drop diameter, you see that we discussed a lot of different sizes of drops in this particular slide.
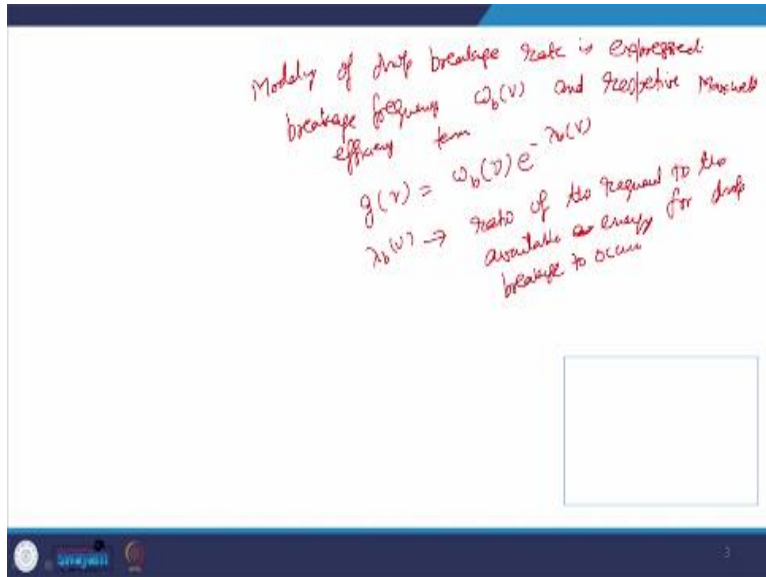
(Refer Slide Time: 22:28)

So, it is used to measure the mean drop diameter as well as the maximum stable drop diameter for breakage to occur and minimum drop diameter above which coalescence occur. So, this particular approach is extremely important while discussing the things. Now, let us have a look about the modelling concept of this drop breakage process.
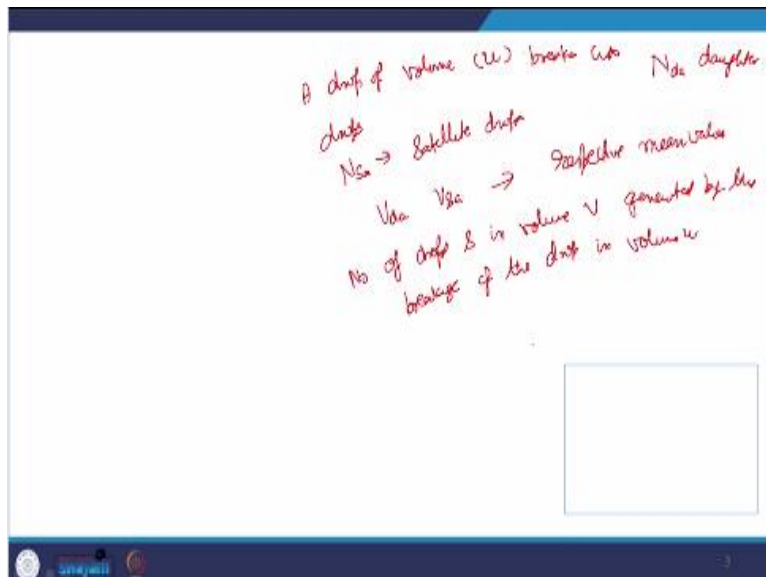
(Refer Slide Time: 22:58)

- The modeling of drop breakage rate is expressed in terms of a breakage frequency, $\omega_b(v)$, and a respective Maxwell efficiency term:

$$g(v) = w_b(v)e^{-\lambda_b(v)}$$

where $\lambda_b(v)$ is the ratio of the required to the available energy for drop breakage to occur.

(Refer Slide Time: 24:43)

Assume that a drop of volume u breaks up into N_{da} daughter drops and N_{sa} satellite drops and the daughter and satellite drops are normally distributed about their respective mean values, v_{da} and v_{sa}.

The following expression can then be derived for the number of drops in volume v generated by the breakage of the drop in volume u:
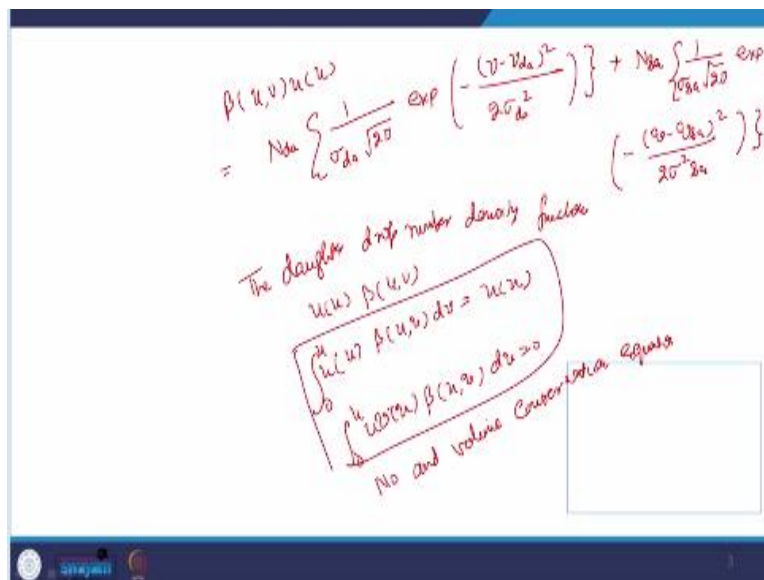
$$\beta(u,v)u(u) = N_{da}\left\{\frac{1}{\sigma_{da}\sqrt{2\pi}}\exp\left(-\frac{(v-v_{da})^2}{2\sigma_{da}^2}\right)\right\} + N_{sa}\left\{\frac{1}{\sigma_{sa}\sqrt{2\pi}}\exp\left(-\frac{(v-v_{sa})^2}{2\sigma_{sa}^2}\right)\right\}$$

- The daughter drop number density function, $u(u)\beta(u,v)$, should satisfy the following number and volume conservation equations:
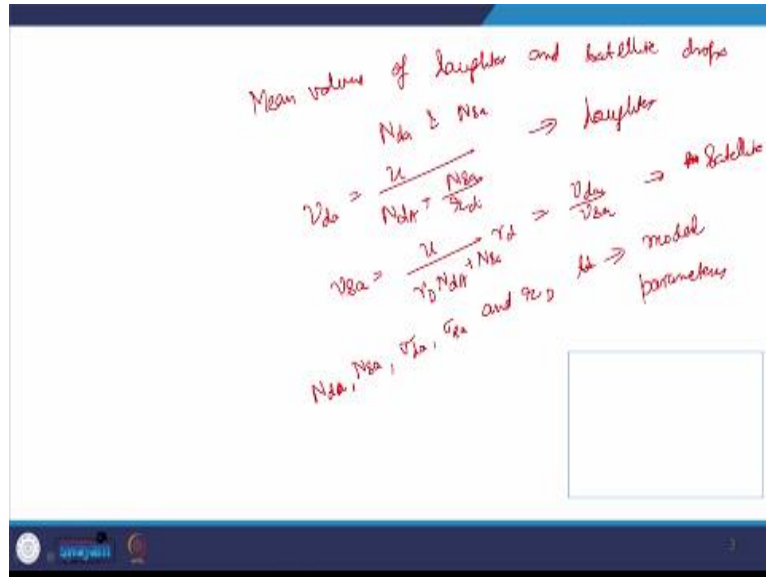
$$\int_0^u u(u)\beta(u,v)dv = u(u)$$

$$\int_0^u vu(u)\beta(u,v)dv = u$$

So, these are the number and volume conservation equations and these equations are quite useful for further calculation.

the mean volumes of daughter and satellite drops, formed by the breakage of a drop of volume u in terms of N_{da} and N_{sa}

$$v_{da} = \frac{u}{N_{da} + \dfrac{N_{sa}}{r_D}}$$

$$v_{sa} = \frac{u}{r_D N_{da} + N_{sa}} \quad r_D = v_{da}/v_{sa}$$

where N_{da}, N_{sa}, σ_{da}, σ_{sa} and r_D are model parameters. So, by this way, we can start this modelling of those parameters.

If you recall that in this discuss, first, we formed the 2 drops and then the coalescence of these two drops in turbulent fluid flow field.

Two different mechanisms have been postulated in the open literature to describe the coalescence of two drops in a turbulent flow field.

The first believes that after the initial collision of two drops, a continuous phase liquid film is stuck between the two drops, which stops them from coalescing.

(Refer Slide Time: 31:01)

Now, this is the small ones, they coalesce, then there is a formation of a small thin film in between these 2 drops. So, thereby, this prohibits or inhibits the formation of a coalescence. Now, due to the presence of attractive force draining the liquid film can occur leading to drop coalescence.

(Refer Slide Time: 31:24)

Due to the presence of attractive forces, draining of the liquid film can occur leading to drop coalescence.

If the kinetic energy of the triggered drop oscillations is greater than the energy of the adhesion between the drops, the drop link is interrupted until the liquid film is fully drained. So, that the coalescence may form in due course of time and you may experience the bigger sized drop.

The second concept attributed that coalescence process implies that the instantaneous coalescence happen as the relative velocity of two colliding species decreases at the moment of collision reaches the critical value. So, whenever these two are combining together, relative velocity decreases and thereby, they form this one. So, it is just like this and this one. So, this means that the drops will coalesce if energy of coalescence is greater than the total drop surface energy. So, these two things are very crucial.

Now, sometimes, when we need to express the things, so, the drop coalescence rate, it can be expressed in terms of coalescence frequencies sometimes, referred as omega b v u and a Maxwell efficiency term which we described earlier.

(Refer Slide Time: 32:59)

The **drop coalescence rate** can be expressed in terms of a collision frequency, $\omega_b(v, u)$, and a Maxwell efficiency term:

$$k(v,\ u)\ =\ \omega_c(v,\ u)e\big({-}\lambda c(v,u)\big)$$

where $\lambda_c(v, u)$ is the ratio of the required to the available energy for drop coalescence to occur.

 (Refer Slide Time: 33:23)

References

❖ G. Odian, Principles of Polymerization, Fourth Edition, John Wiley & Sons, Inc., (2004), ISBN:9780471478751 | DOI:10.1002/047147875X

❖ J.M. Asua, Polymer Reaction Engineering, Blackwell Publishing, (2007), ISBN: 978-1-4051-4442-1

❖ M. Szwarc, Marcel Van Beylen (auth.) - Ionic Polymerization and Living Polymers, Springer Netherlands, (1993)

❖ Werner Pauer - Polymer Reaction Engineering of Dispersed Systems_ Volume I, Springer International Publishing, (2018)

❖ Klaus-Dieter Hungenberg, Michael Wulkow - Modeling and Simulation in Polymer Reaction Engineering- A Modular Approach, Wiley (2018)

❖ Sajid Iqbal and Sharif Ahmad, Recent development in hybrid conducting polymers: Synthesis, applications and future prospects, Journal of Industrial and Engineering Chemistry, 60 (2018), 53-84

So, in this particular lecture, we discussed about the concept of population balance and its efficacy in predicting the behaviour of various particles or various chains being developing the polymerization process. We discussed about the drop coalescence process, we discussed about the various concepts of formation of a drop and then adjoining and the formation of the agglomerates in these drop coalescence process.

In the next lecture, we will discuss about the physical properties and the phase equilibrium concept related to the polymerization system. Thank you very much.