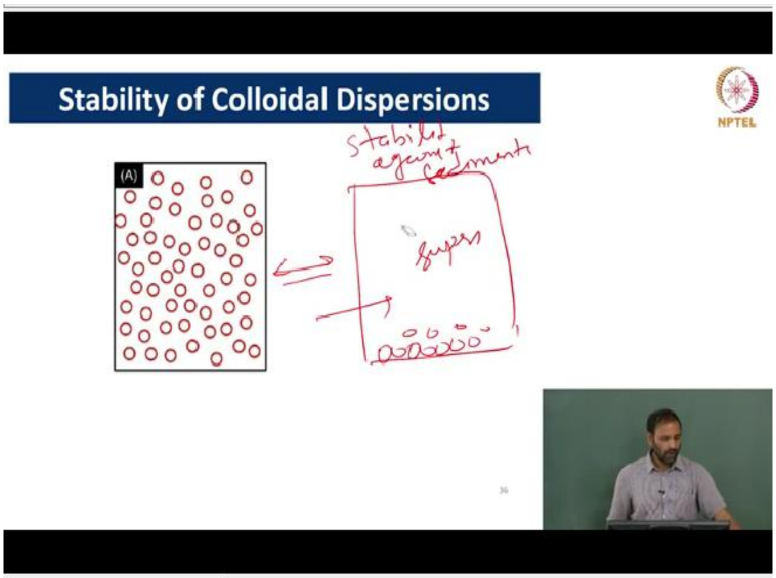
Colloids and Surfaces

Prof. Basavaraj Madivala Gurappa
Department of Chemical Engineering
Indian Institute of Technology-Madras

Lecture-03
Stability in Colloids

(Refer Slide Time: 00:14)

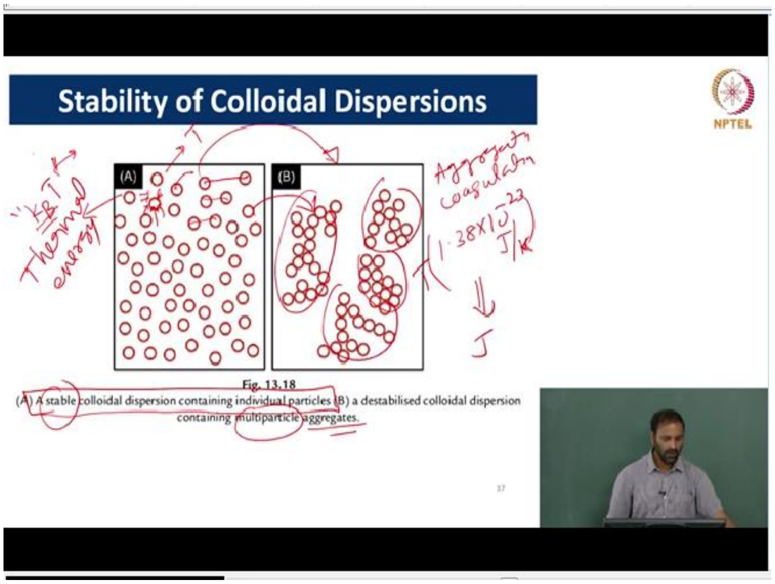


Stability of Colloidal Dispersions

So, we will talk a little bit about stability of colloidal dispersions okay. So, what do you understand if I say that the colloidal dispersions are stable, any thoughts, some thoughts. So, we can think about a table stability has in 2 different ways right. As I mentioned already, I can think about something called as stability against sedimentation right.

It means I have the same dispersion if I leave it for a while everything goes here right, they all settle down. But typically, I said that such a thing will only happen if you are working with what are called as colloidal or suspensions right okay. Typically, this will happen when you are working with suspensions, where the particles are larger in size. And because you work with very small particles, it is assumed that the gravity does not play a role okay.

(Refer Slide Time: 01:38)



Stability of Colloidal Dispersions

Fig. 13.18

(A) A stable colloidal dispersion containing individual particles (B) a destabilised colloidal dispersion containing multiparticle aggregates.

However, what could happen is this right. What you are looking at is 2 pictures. Picture A, where you have a stable colloidal dispersion really not defined what is stability. But I am saying that it is stable because all the particles are in their individual state, okay they are having being in the fluid okay. However, we know that because the particles are very, very small in size, they have a high surface area right, which makes them prone to what is called as aggregation okay.

Again people used term called aggregation, coagulation okay and things like that okay. So, what do you have here is an example where you have form, what is called as an aggregate, which contains multiple particles okay. So, why do you think things will go from this state to this state, or can you think about ways by which things can go from this to this state okay. So, the answer that I get is that if the interaction between the 2 particles okay is more favorable than the interaction between the particle and the fluid okay.

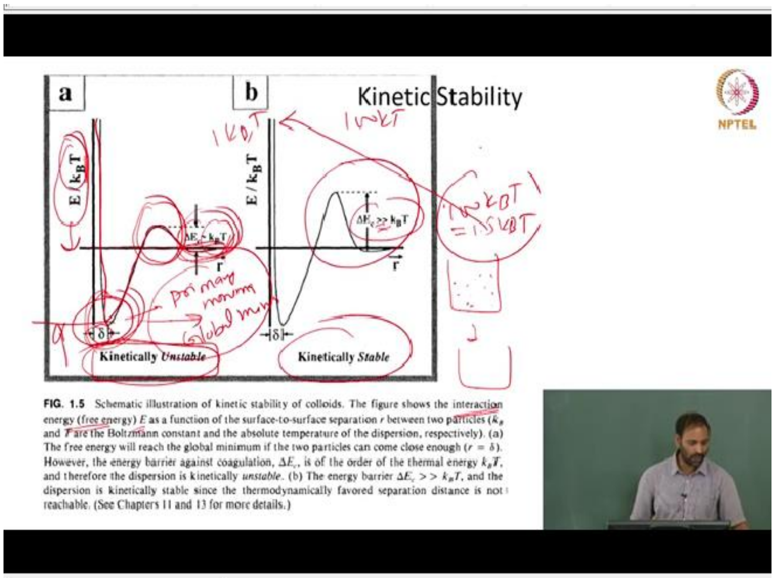
Yeah so you can think about along those lines. Now, okay we can again spend a little bit of time talking about interactions in the next few lectures. So, what will happen is this right. So, if you have particles in a fluid, you know that these particles are not stationary right. They are being continuously hit by the solvent molecules in which the particles are dispersed. That means for every particle there are a lot of solvent molecules which are hitting okay.

They are hitting everywhere okay, because of which the particles can move around okay. So, whenever you take a dispersion okay and if you say that I have this dispersion at a temperature T okay, so the energy that the particles have okay. It is given by what is called as $k_B T$ or the thermal energy okay. This k_B is what is called a Boltzmann constant okay, which has a value of 1.38×10^{-23} joules / Kelvin okay.

That multiplied by the temperature will give you a unit joule which is a unit of energy right. Therefore, the moment you have any fluid or a colloidal dispersion at some temperature T invariably all the molecules, as well as the particles in the fluid have this terminology $k_B T$ okay. Now, you can ask a question as to what now I am drawing these particles very far apart right. The sufficiently far apart what can bring the particles close to each other with this thermal energy right.

The thermal fluctuation they are moving around okay when they are moving around they could approach another particle okay, when they approach another particles the particles may either attract or repel okay that depends on the type of the particle that you are trying to deal with okay.

(Refer Slide Time: 05:54)



Kinetic Stability

FIG. 1.5 Schematic illustration of kinetic stability of colloids. The figure shows the interaction energy (free energy) E as a function of the surface-to-surface separation r between two particles (k_B and T are the Boltzmann constant and the absolute temperature of the dispersion, respectively). (a) The free energy will reach the global minimum if the two particles can come close enough ($r = \delta$). However, the energy barrier against coagulation, ΔE_c, is of the order of the thermal energy $k_B T$, and therefore the dispersion is kinetically *unstable*. (b) The energy barrier $\Delta E_c >> k_B T$, and the dispersion is kinetically stable since the thermodynamically favored separation distance is not reachable. (See Chapters 11 and 13 for more details.)

Now here is an example okay where. So, what do you have is some energy. In this case it is called as its interaction energy okay or also called as a free energy okay, that is this and you will see in colloids literature that whenever people talk about interaction energy, you always scale with $k_B T$ okay. The reason is this right, when you do interaction energy calculations I said that the Boltzmann constant is 10 power - 23 right.

Now, if I multiply that by, you know like, say if the temperature is 300 right. This energy will be of the order of 10^{-21} right. So, when you do calculations, when you get numbers which are 10^{-21} joules. So, you may say that look you know is too low, you know, reading is not important okay. So, just to get a feel for the numbers that you get out of such calculations, you typically always scale the interaction energy with thermal energy.

So, that I can compare and say, hey, the interaction energy that we are obtaining, it is one times $k_B T$, 2 times $k_B T$, 10 times $k_B T$ something like that okay. Therefore, you will always see that people who do interaction energy calculation they always scale the interaction energy with the thermal energy. So, what is plotted here is this interaction energy okay, as a function of separation distance.

That is plotted on the x axis okay. So, the way to think about is interaction energy is it is the energy with which the particles attract or repel given whatever distance they are at okay. So, if you look at this, lets trace this plot okay, that is your x axis okay. So, the interaction energy goes something like that, you know, right. So, people typically talk about this minima that you have is what is called as a primary minima okay or also called as a global minima okay.

This is what is called as a secondary minima okay. Now, what you have here is a, a barrier okay. So, in order for the particles to approach and reach this primary minima the global minima, they have to cross this energy barrier okay. Now, if the energy barrier that you have okay, if it is of the order of $k_B T$ okay because the particles, already have a thermal energy and that thermal energy in fact is $k_B T$.

If the energy barrier is also of the order of $k_B T$, what can happen is, these particles can easily cross the energy barrier. And then they can come and reach this global minima state where the particles can form aggregates like this okay. Now, once the particles form such aggregates, which are essentially at a very small separation distance right, this is delta, this is a separation distance okay, that corresponds to, you know, this global minima okay.

So, once they reach that place they are aggregated, it is very difficult to separate them out okay, you can do sonication. Of course this again depends on how, what is this you know the minima is right, what is the location of the minima, the location of the minima is really, really large. That means, it is practically impossible to separate these particles once they aggregate.

However, if you know this minima is of the order of maybe few times k_BT, then sonication or anything you know may be able to rip them apart okay. So, therefore, so if you have cases where the energy scale associated with this barrier is of the order of thermal energy. Such dispersions are said to be what is called as kinetically unstable, because the kinetic energy that the particle posses, because of the thermal energy.

It is good enough to overcome the barrier and then make it go from this state to this state, okay such, you know, a process or such a you know case is referred to as a case where you have dispersions, which are kinetically unstable okay. On the other hand, you could have a case where the energy okay, which corresponds to this barrier, it could be much, much larger than k_BT okay, when I say much, much larger than k_BT, it could be, you know, 100 times k_BT or you know, several orders of magnitude larger than k_BT okay.

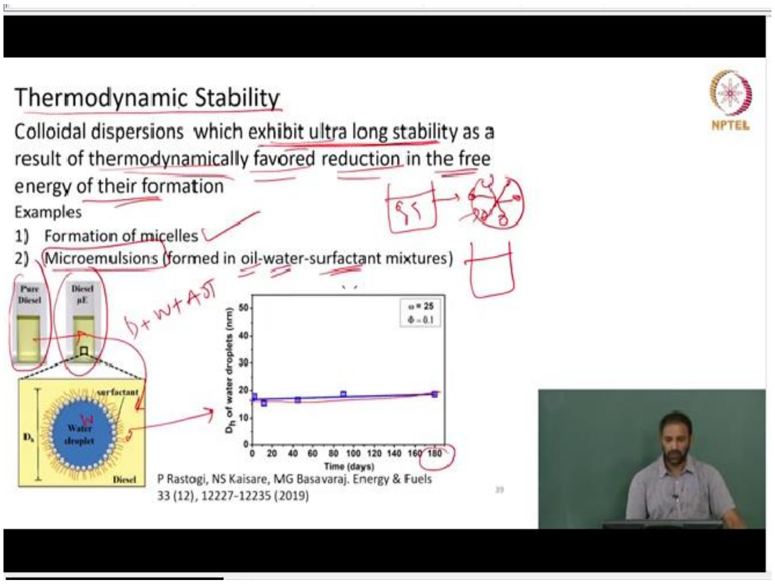
Such dispersions are set to be kinetically stable okay, that means there is an energy barrier associated with the particles being in a dispersed state and a destabilized state okay, if the height of this energy barrier is of the order of k_BT, then the dispersions are kinetically unstable. If the height of this energy barrier is much, much larger than k_BT then such dispersions are kinetically stable okay.

Yeah so any questions with this okay. Now, one can ask it yeah, yeah. Yes. Yeah, so first stable collides also everything depends on this energy, right. So, if I have a stable dispersion okay, I could have. So, again stability is a very relative term right. When I say stable you know I could have a dispersion of particles okay, homogeneous dispersion.

You know it may be stable for a day. You know, but if you wait for a few days you know, things may, you know coagulate okay, so everything depends on so what will happen is this right. So, the particles are moving around because of Brownian motion, they approach each other. Now, if okay let me put it this way. So, what you can do is I can play with this energy barrier right, I can play with this energy barrier.

Now say that I have dispersion where this energy barrier is like say 1.5 k_BT okay. Now, you could ask a question as to look something where the energy barrier is 1.5 k_BT, is it highly stable. No right because you know, so, of course, if you look at one times k_BT and 1.5 times they are comparable okay. Of course, if I talk about 1 k_BT and 100 k_BT. There are 2 orders of magnitude larger therefore definitely such colloids will exhibit a better stability okay. So, I will come back and answer you a question.

(Refer Slide Time: 13:55)



Thermodynamic Stability

Colloidal dispersions which exhibit ultra long stability as a result of thermodynamically favored reduction in the free energy of their formation

Examples

1) Formation of micelles
2) Microemulsions (formed in oil-water-surfactant mixtures)

P Rastogi, NS Kaisare, MG Basavaraj. Energy & Fuels 33 (12), 12227-12235 (2019)

Before that I want to talk a little bit about something called as a thermodynamic stability okay. So, these are dispersions, which exhibit, what is called as ultra long stability. Because such a colloidal dispersions are formed, because of what is called as a thermodynamically favored reduction in the free energy of their formation okay. I talked about the formation of micelles right. So when you start with, you know fluid and start adding surfactants.

I said that they form micelles right, the formation of micelles is a process where there is a overall reduction in the free energy of the entire system. Therefore, okay such association colloids in water. They do exhibit ultra-long stability that means I take a dispersion of micelles, keep it for years and years. You know if you, if things do not change if the temperature does not change. If the solution conditions do not change, they continue to exist as micelles okay.

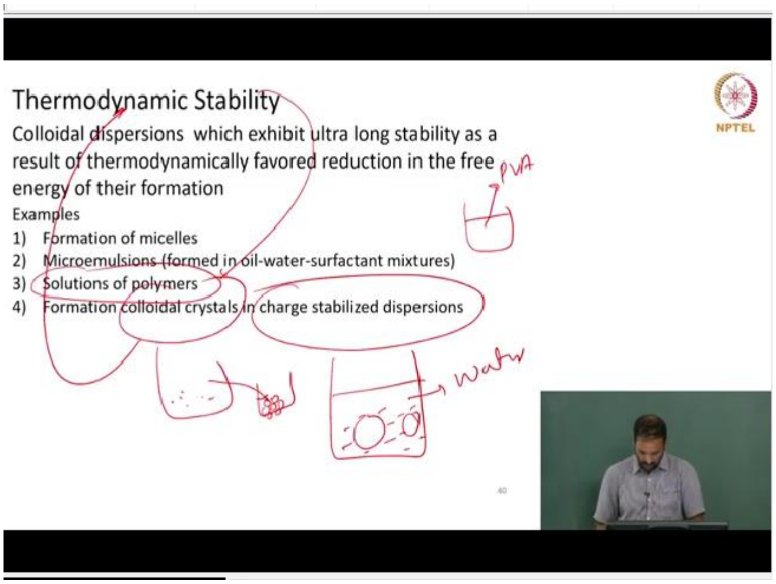
Another example is what is called as a micro emulsions okay, which are typically formed when you have oil, water and surfactant. What you are looking at is some example from our lab. This is a pure diesel, you know, a fuel that people use right. And then, this is diesel micro emulsion. This has diesel plus water plus a surfactant called AOT okay. If you look, macroscopically you do not see anything right.

You know it is very difficult to say that look I have water in there okay, it has some amount of water and some surfactant but it looks very transparent okay. That is because it contains very tiny reverse micelles okay. So, the micelles are you know something that I said, right, reverse micelles will have water inside, add an oil outside and the surfactant molecules are arranged something like this.

Now, if we look at the size of the dispersed phase okay, that is these micelles reverse micelles in water in oil, you look at the size right, this is measured as a function of time 180 days that is 6 months okay, tactically there is almost no change okay. However, if you take a dispersion of kinetically stable colloids okay. You could also have a case where there are kinetically stable colloids, which are available in the market, which do exhibit a shelf life of years if you want okay.

But however, I cannot say that such colloids are infinitely stable or they are stable forever okay, because, you know, at some point, you know the thermal energy is going to overtake and they are going to aggregate.

(Refer Slide Time: 17:05)



Thermodynamic Stability

Colloidal dispersions which exhibit ultra long stability as a result of thermodynamically favored reduction in the free energy of their formation

Examples

1) Formation of micelles
2) Microemulsions (formed in oil-water-surfactant mixtures)
3) Solutions of polymers
4) Formation colloidal crystals in charge stabilized dispersions

So, these are 2 examples of what are called as thermodynamically stable colloids, the other examples of thermodynamically stable colloids are solutions of polymers okay. I can take water, put a polymer like PVA or polyvinyl alcohol, you know make a solution you know keep it for you know we do not see any changes to that size or no aggregates, no aggregation, right. So, final example of thermodynamic stable state one to achieve is cases where you work with charge stabilized colloids.

Now I said that when I say charge stabilized colloids you should imagine that I have a dispersion, say the continuous phase is water and a dispersed phase is particles and the particles have some charge okay. That is a charge stabilize dispersion okay. In such a case, what you will have is, there is a high energy barrier for them to aggregate and they are actually an example of kinetically stable colloids.

Because they have an energy barrier much larger than k_BT for their aggregation okay, however when you have a large collection of such particles in the fluid, what will happen is they exhibit a crystal state okay. I was showing you some images, the other day right. So, these particles they formed what is called a crystalline state where, you know, they are closely packed periodic arrangement okay.

And such crystals again are an example of thermodynamically stable states, because again, their formation leads to reduction in their free energy okay. So, that is something about the stability, maybe I will stop here. And then we will look a little bit about some properties of colloidal dispersion in the next class okay. Yeah, Thanks.