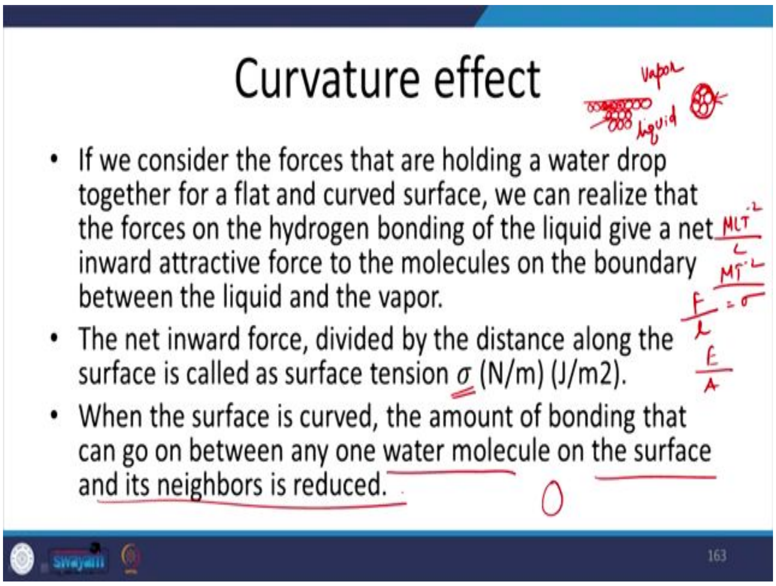
Introduction to Atmospheric and Space Sciences
Prof. M. V. Sunil Krishna
Department of Physics
Indian Institute of Technology, Roorkee

Lecture – 37
Droplet Growth and Curvature Effect

Hello dear students. So, far we have discussed the formation of cloud, how the cloud condensation nuclei are important for the formation of cloud droplets and what happens when this cloud droplet ones forms and travels within the cloud, what kind of physical effects can take place right. We have also seen what are the various different types of precipitation; precipitation in the form of liquid water, precipitation in the form of solid ice so many things.

So, now where we want to understand the diffusional growth of a liquid droplet. How a small cloud droplet which is a result of the condensation grows to be the size of a rain droplet, what are the physical processes? Now in order to be able to understand these things mathematically. We should consider two very important effects which are called as curvature effect and dissolute effect.

(Refer Slide Time: 01:30)



Curvature effects is important in the sense that the rain droplet is a spherical in shape and being spherical in shape will affect how the saturation vapor pressure changes with respect to plane surface of water right. Now just imagine if we consider forces that are holding the water drop together for a flat and curved surface. So, we wanted to understand what will happen if you have a plane surface of water and if you have a curved surface of water.

So, what is the force that holds the molecules, various so many molecules on the surface of this plane surface or inside a droplet. So, if we consider the forces that are holding a water drop together. So, there is some amount of force which is holding this water drop together. So, it is not breaking apart, it is together in the sense it is a single entity for a flat surface. We can realize that the forces on the hydrogen bonding of the liquid given net inward attractive force to the molecules on the boundary between the liquid and the vapor.

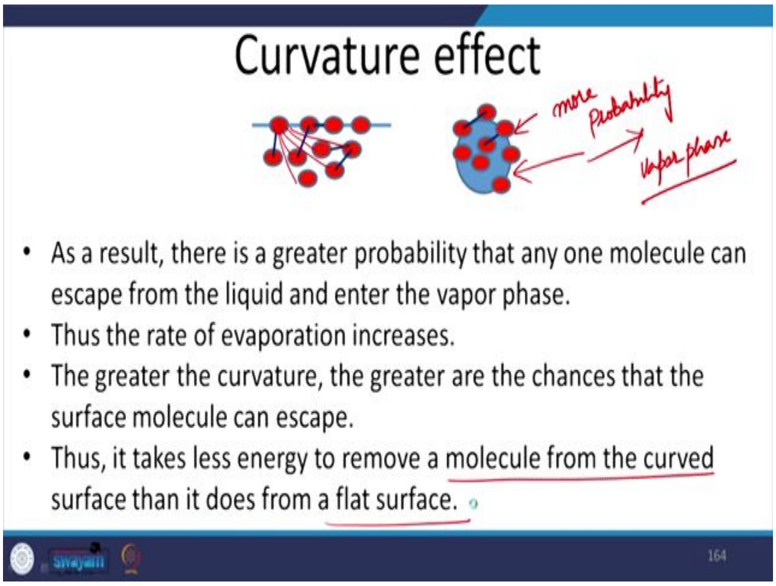
So, this is the boundary which separates the vapor and the liquid. So, the idea is that. So, we have all these molecules which are attracted by their neighbors and so on and so forth. So, the net force of attraction felt by a single molecule due to all other molecule is what keeps this molecule within the liquid and does not allow this molecule to evaporate or to leave the liquid surface right.

Now, the net inward force; so now, we want to understand what will be the net inward force will it be larger over a molecule if it is plane surface of water or it will be larger if it is a liquid droplet ok. So, the net inward force divided by the distance. Let us say this is force per distance let us say is called as the surface tension which actually holds them holds the droplet together right. Or surface tension can also be defined as energy per unit area.

So, this is the surface tension right. So, the net inward force divided by the distance along the surface is called as the surface tension sigma. When the surface is curved, let us say if the surface is kind of curved, what happens? The amount of bonding the amount of force that can be felt by a given molecule due to all it is surroundings or due to all it is neighbors will be less. The amount of bonding that can be go on between one water molecule on the surface and it is neighbors is reduced, that is what the idea is.

So, if you form a droplet, any given molecule on the surface when evaporate contributes to the vapor pressure, will experience less amount of force from its neighbors. So, it has more tendency that this molecule can escape and form a vapor go into the vapor phase right. So, this picture indicates the effect.

(Refer Slide Time: 04:52)

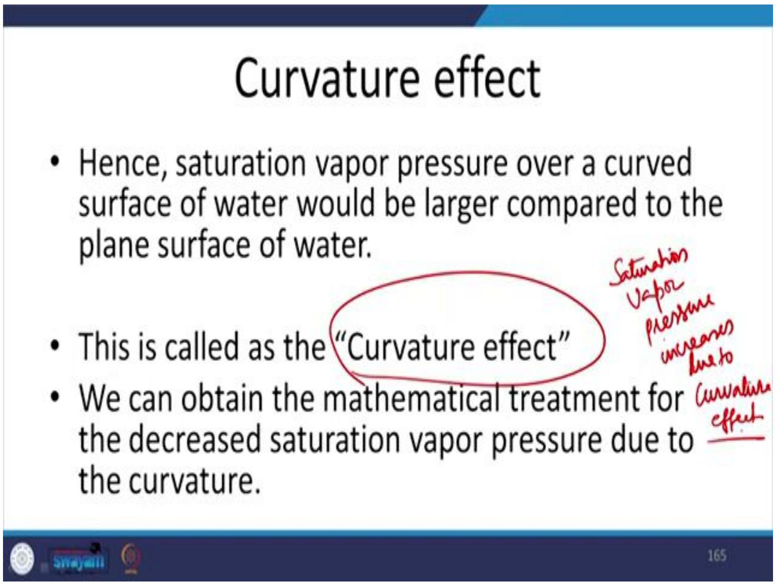


So, what you see here is that this molecule, let us say is bound by all these small forces with all these molecules, long range or whatever. But the thing is so this molecule overall is experiencing more amount of force due to the other molecules, but when you take the liquid to be in the form of a droplet and not in the bulk or not in the plane surface you see that each molecule at any given time is of course, experiencing lesser force.

So, as a result there is a greater probability that any one molecule can escape from the liquid and enter the vapor phase right, the molecule that is on the droplet. So, this has the more probability to escape and enter into the vapor phase. So, vapor phase more evaporation happens you will realize the saturation to be achieved much faster that is the basic idea. So, that is the rate of evaporation will increase from a droplet, the greater the curvature.

So, if you imagine a huge or larger droplet; obviously, the greater are the chances that the surface molecule can not escape. Thus it takes less energy to remove a molecule from the curved surface than it does for a flat surface right. So, the point is evident now right.

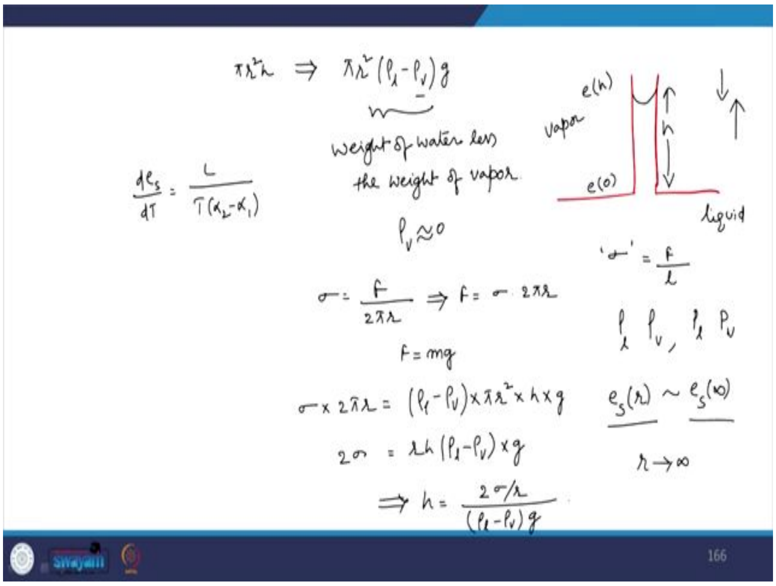
(Refer Slide Time: 06:15)



So, hence the saturation vapor pressure over a curved surface of water would be larger compared to plane surface of water. Why is it larger? Because of the larger evaporation rate, the saturation vapor pressure where evaporation is equal to condensation. We cannot comment on the condensation, but given that we have droplets we can surely say that evaporation is larger. So, saturation vapor pressure will also be larger right. So, this effect which comes into picture when you have the water in the form of a droplet is called as the curvature.

So, curvature effect is eventually the increase in the saturation vapor pressure due to the water present in in the form of a droplet, in the shape of a droplets. So, one thing we can surely say they say that saturation vapor pressure, saturation vapor pressure increases due to the curvature effect ok, this is the conclusion. Now we can obtain a mathematical treatment for the decreased saturation vapor pressure due to the curvature. Let us see how we can obtain a mathematical treatment for that.

(Refer Slide Time: 07:48)



Let us consider a small tube of radius r from which we have removed the air and it is now in a liquid surface, it is immersed in a liquid surface. So, what will happen is so, with time, as the time progresses water will enter into this tube and there will be some amount of; some amount of evaporation and ultimately equilibrium value is achieved.

So, the tube stands in the water and water has rise into a height h. So, water will rise to a height h. Let us say so, with time as the evaporation happens. So, it will rise to a height h. So, this is the meniscus. So, the meniscus is curved right. Now let us say the sigma is the surface tension that is force per unit length along the surface right. And let us say that rho l is the density of liquid and rho w. So, rho l is the density of the liquid or water rho v is the density of vapor.

Similarly, P l is the pressure of the liquid or water, P v is the pressure of the vapor right. Now what is the volume of liquid? Now what we are trying to do is we are trying to see how this saturation vapor pressure over a curved surface e s of r. So, what is the e s of r? e s of r is the saturation vapor pressure. Now we see that we are indicating vapor pressures with a small e, we have put a subscript of s indicating saturation and r indicating saturation vapor pressure over a curved surface.

We want to find out how e s of r changes or relates to saturation vapor pressure over infinity. So, the idea is for a plain surface of water the radius can be considered as infinity. So, we want to see how the saturation vapor pressure changes with respect to saturation vapor pressure over plain surface of water. Now let us say to be able to do that we want to find out what is the height up to which this will rise to be able to balance the forces of let us say gravity and the pressure gradient.

So, this height will tell us how we can achieve this objective right. Now let us say the volume of the column of water, volume of the column of water is pi r square h. And it is weight and so, if this is the volume the weight is pi r square rho l minus rho v into g. Where g is the acceleration due to gravity, this is the weight of the water, less the water weight of the water vapor it displaces.

So, this is weight of water less the weight of vapor because we have a minus right. So, since the density of vapor is negligible in comparison to the density of water. We can any how replace or consider rho v to be approximately equal to 0 in comparison to rho l. So, now, the weight must be balanced by the force created by the surface tension in the meniscus of the tube.

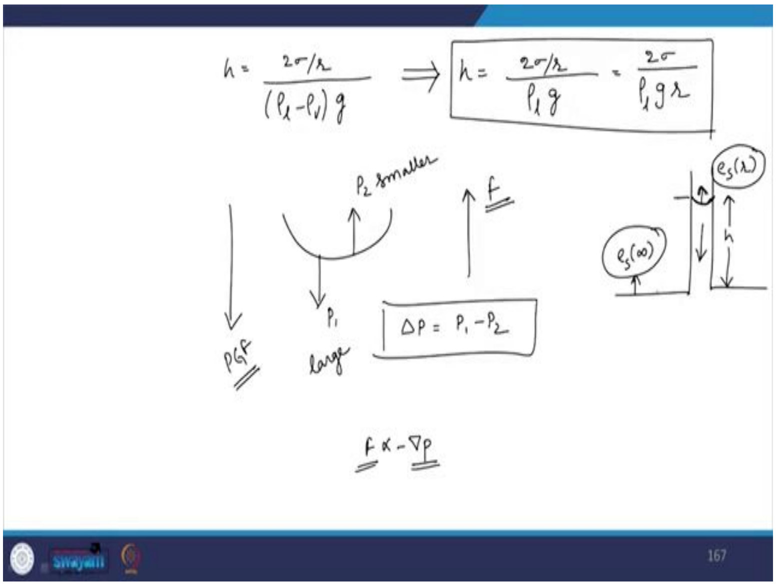
So, this weight that is trying to come down must be balanced by the surface tension in the meniscus of the tube. Now, so, the surface tension is, surface tension is force by two pi r. So, the force that we are talking about is sigma times 2 pi r. So, let us say here at the bottom here this is the liquid phase and this is the gas or vapor phase. Let us say the surface is e 0, the vapor pressure at the surface is e 0 where at the surface so and the vapor pressure at the height of the meniscus is e h ok.

Now, we know that the, if we consider the temperature. So, the saturation vapor pressure can be simply written in terms of specific volumes and the latent heat. So, which gives the equilibrium saturation vapor pressure variation with respect to the temperature right. So, now, let us say sigma is the surface energy per unit area or force per unit surface length. The force balance is so, how can you write the force balance this force has to be equal to mg.

So, surface tension is the force per unit length or interfacial energy per unit area of the liquid vapor interface. So, the weight must be balanced by the force created by the surface tension in the meniscus right. So, if you write this equality between the forces, these two forces must balance each other. So, sigma times 2 pi r, force on the left hand side is rho l minus rho v times pi r square times h times g.

So, which is 2 sigma is equals to r h times rho l minus rho v times g. So, where we can write h is equals to. So, when these two forces balance each other, we will realize the height of the meniscus as rho l minus rho v times g. So, if we neglect the density of vapor with respect to the density of the water let us say.

(Refer Slide Time: 14:17)



So, we can write we have written h is equals to 2 sigma by r divided by rho l minus rho v times g. We neglect this expression reduces to h is equals to 2 sigma by r divided by rho l times g or 2 sigma by rho l g r. So, what is r? r is the radius of the petal curvature with which the meniscus is being made sigma is the surface tension or force per unit surface length and or surface energy per unit area rho l is the density of the liquid g is the acceleration due to gravity right.

So, this is a very important expression. So, if you put a capillary tube in the liquid. this height the height of the meniscus where the weight is balanced by the surface energy per unit area or the surface tension, the force due to surface tension this height is given as this we were trying to achieve, how the saturation vapor pressure changes. So, we can simply say that the saturation vapor pressure here is e s of r and here is not sorry, so, it is e s, e s of infinity it is. So, it is e s of infinity here and here it is e s of r.

We want to find out how e s of r depends on e s of infinity, that is it, that is the objective. So, we can say that this gives the height at which the upward pressure due to the Laplace pressure associated with the surface tension is balanced by the downward force due to hydrostatic pressure which is assumed in the column of the liquid. So, this downward pressure is due to the column of the liquid the upward pressure.

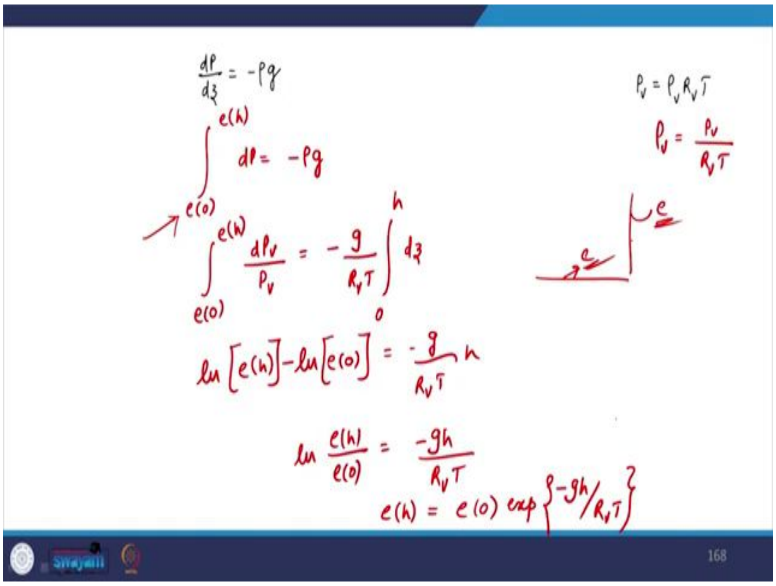
So, if you keep it why is not that the liquid is not coming out of the capillary tube. It is why should the liquid rise to this particular height? Why should it rise in the first place if it rises why is it constant at a particular height, why is it not above or why is it not below is the question. So, the simplest answer for that is that this meniscus is maintained by a force balance; that means, there is a force which is acting downwards and this force is countered by a force which is acting upwards right.

So, the Laplace pressure is the pressure difference between the inward and the outside of a curved surface. So, if you take a curved surface; the pressure difference so, let us say you have a pressure like this and you have a pressure like this. Let us call this as P 1 and let us call this as P 2.

So, the Laplace pressure is delta P is a difference of the inward and outward pressure. Now when this pressure balances itself with respect to the downward hydrostatic pressure then you have a meniscus right. So, basically, so the idea is these two forces balance each other and we will be able to write an equation for the force balance. So, if in this case what you see is; P 1 is larger and P 2 is of course, smaller.

So, the pressure gradient is obviously is in this direction right. So, this is a pressure gradient is in this direction. So, the net direction of force should obviously be in this direction. So, pressure gradient force because F is proportional to minus del p. So, whatever the gradient the force should act in the opposite direction. So, this is the force right. So, this force should now be balanced because if this is the force the entire column of the fluid should rise indefinitely and come out of the tube it never happens. So, this force must now be balanced by the gravity right.

(Refer Slide Time: 18:29)



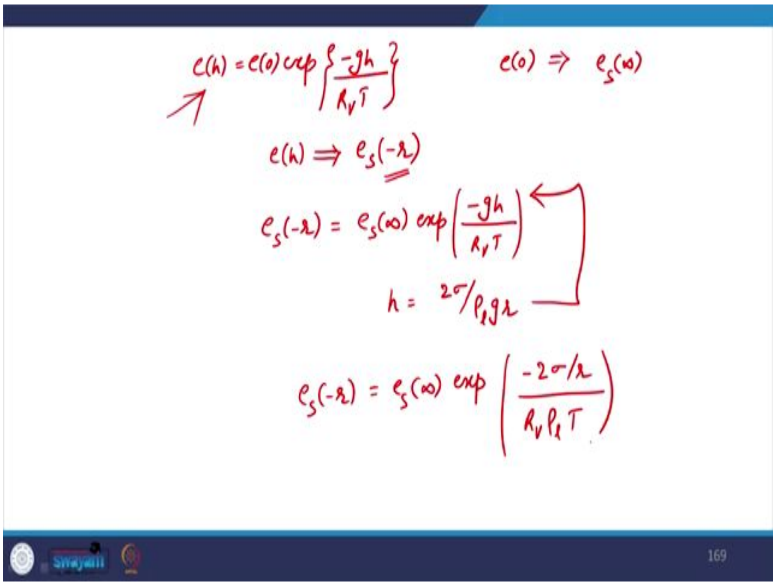
So, let us say so, we will use the hydrostatic equilibrium, hydrostatic equilibrium means dP over dz is minus rho g. So, for the vapor phase we can write the ideal gas as P v is rho v, R v T right. So, we can write the ideal gas for the vapor phase as this right. So, now, let us say now we want to understand how the pressure changes with respect to height or how the so, on the difference of vapor pressure at a height h compare to the vapor pressure in the water at the base of the tube is approximately equal to the negative of the weight of the vapor over a height h ok.

So, if it is the case then, so then we can integrate this equation from let us say vapor pressures at the surface to vapor pressure and the height h is dP is equals to minus rho g right. And from this expression we can write rho v is equals to Pv by R v T. So, if you carry out this we can write integral e of 0 to e of h d P v over P v is equals to minus g by R v T integral 0 to h correspondence between the pressure and the height right.

So, we can write lon of e of h minus lon e of 0 is minus g by R v T times h or lon of e of h divided by e of 0 is equals to minus g h divided by R v T. So, the vapor pressure at a height h is equals to in comparison to the vapor pressure at the base of the tube is equals to e of 0 exponential minus gh divided by R v T right.

So, I hope you are getting this. So, we have started the so, we know we just wanted to find out how the vapor pressure here is can be related to the vapor pressure here right. So, this gives the variation of vapor.

(Refer Slide Time: 21:07)



So, e of h is equals to e of 0 times exponential minus g h divided by R v T. This is what gives the variation of the vapor pressure with respect to height. Now what is missing here we do not have the information of the radius of the curvature because this can be just a height, but until unless you put the at what radius of curvature things change.

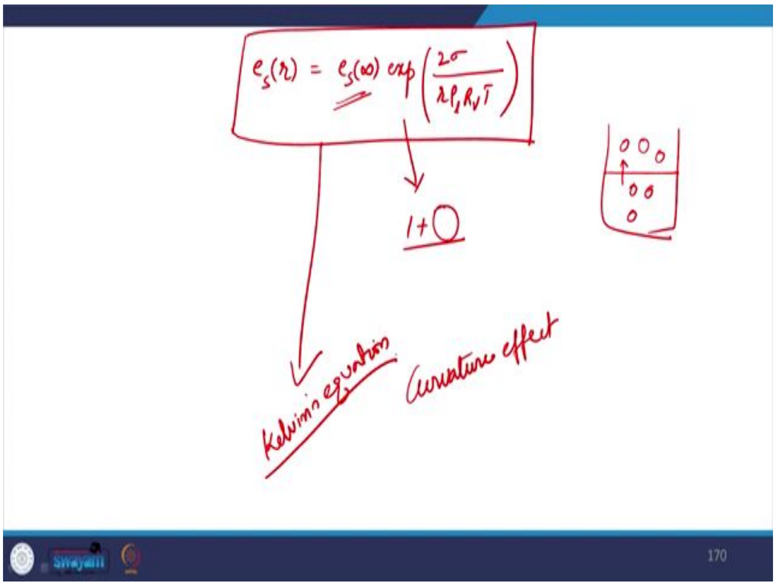
So, since the system is in equilibrium, the vapor pressure of the plane surface that is e of 0 is the equilibrium saturation vapor pressure which we will write as e of 0 is the vapor pressure at saturation with respect to plane surface of water right. So, e if it is in equilibrium. So, this is at an instant, now we write it as e s of infinity. So, we assume that there is an equilibrium and if the equilibrium is persistent, we will write this as e s of infinite ok.

So, this saturation vapor pressure over the surface of water where the radius of curvature is infinite right. So, again the system is in equilibrium, if the system is in equilibrium the vapor pressure at a height h should be horizontally uniform right. The vapor pressure at a height h must be equal to the saturation vapor pressure over the surface of meniscus which we write as. So, e of h can be written as e s saturation at equilibrium at minus r. Why is minus r? Minus r to indicate the negative radius of curvature of the meniscus the type of meniscus that we have taken.

So, we can rewrite this expression as e s of minus r is e s of infinity times exponential minus gh divided by R v T. Now from the earlier derivation we have already seen the height of the meniscus where the forces balance each other was 2 sigma by rho l g r right. Now you can use this in this expression and we can write e s of minus r is e s of infinite times exponential minus 2 sigma by r divided by R v rho l times T.

So, exponent is the ratio of Laplace pressure to the pressure, the vapor would leave let us say if it has the density of liquid. So, if the radius if the radius of curvature we just have to have a plus in this expression where. So, we can write a generalized expression for the saturation vapor pressure with respect to plane surface of water.

(Refer Slide Time: 24:00)



So, e s of r with a positive radius of curvature is the saturation vapor pressure over the droplet is equal to e s of infinity over a plane surface of water times exponential 2 sigma by r rho l R v T.

The saturation vapor pressure over a curved surface or say droplet would be larger in comparison to the plane surface of water, this expression itself. So, this is kind of 1 plus something right. So that means, that anything will be more than the plane surface of water. So, saturation vapor pressure over a droplet and droplet surface will be larger in comparison to the saturation vapor pressure that you can achieve if you have a plane surface of water.

So, this is the basic idea right. So, in which direction we have a vapor phase. So, in this vapor phase if there is pure surface of water we have to understand how the saturation vapor pressure changes. If you have droplets in this let us say then how the vapor pressure changes now all right. So, this is the basic understanding of curvature effect and this equation is very famously known as the Kelvin's equation.

Now, in the formation of the droplet there are two things that come into picture. One; we cannot take it to be a plane surface of water because it is curved surface, the other thing is that because, it so happens that when the droplets are falling because we cannot constitute a homogeneous nucleation because homogeneous nucleation will demand 400 to 500 percent of the relative humidity where the water will automatically by itself come together and form droplets.

We will never experience such a kind of situation. What it means is that the moment it encounters LCL hugely aerosol particles are available. So, it means that you are adding something to the water. So, we have to understand what happens if you add something to the water, what happens to it is vapor pressure will it increase or decrease, what happens to the saturation will the saturation be achieved easier or will the saturation be achieved later let us say .

So, this is the basic idea. So, we will summarize here saying that. So, this is the curvature effect which says that due to the fact that the droplets are in the curved or in the form of a sphere, the saturation vapor pressure will increase because of the ease with which you can detach a molecule from the droplet and make it into the vapor phase right.

So, we will stop here. We will continue this discussion by understanding what is the solute effect and how we can derive an expression how the vapor pressure changes in the presence of a solute in comparison to pure phase. So, you have a diluted phase, you have a mixed phase where you have some foreign particles inside the droplet which are trying to change the vapor pressures or the saturation vapor pressure right. So, we will continue this discussion in the next class.