Module 25 - Lecture 10

Free path length and Mechanism of transfer

So, we continue further on the lecture, that we are doing on our printing, here we will see, the mechanism of transfer and because it is just like a gas, when you work, in this transfer. So, there is a concept of free path length, how much path is available, before a molecule of a dye, which is in a vapor, from goes and strikes another one. So, then you strike things happen, differently. So, that's what something which will work around. In the case of, the disperse dyes as such, when we die or print, we are looking at the possibility, of Some of the dye, dis solving, in whatever little water that you have? Then it goes into molecular form and then goes the surface and then diffuses, in this case we are expecting there is no Solution, there is only air and a vapor. So, it will vaporize and the molecules will be in the vapor form and then they have to traverse, a path and go, to the fiber. So, this is what we hopefully? Be able to explain and that’s the way we can look at the, mechanism of transfer.

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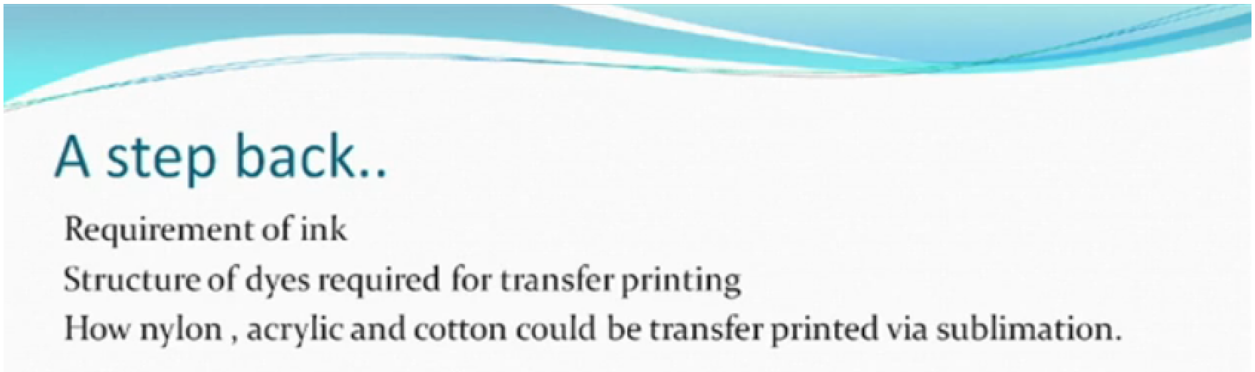

A step back..

Requirement of ink

Structure of dyes required for transfer printing

How nylon , acrylic and cotton could be transfer printed via sublimation.

So, stepping back we understood that there is a requirement of ink, it would have Some Solvent, which is relevant, to the technology, there may be a binder, which will be relevant for fixing and also, various types of dyes, can be used for transfer printing, dispersed of course and various other fibers, nylon, acrylic, cotton also could be transfer printed via, sublimation printing .So, the moment we are still, on sublimation, transfer printing, not on any other transfer. So, we go to the, mechanism of transfer.

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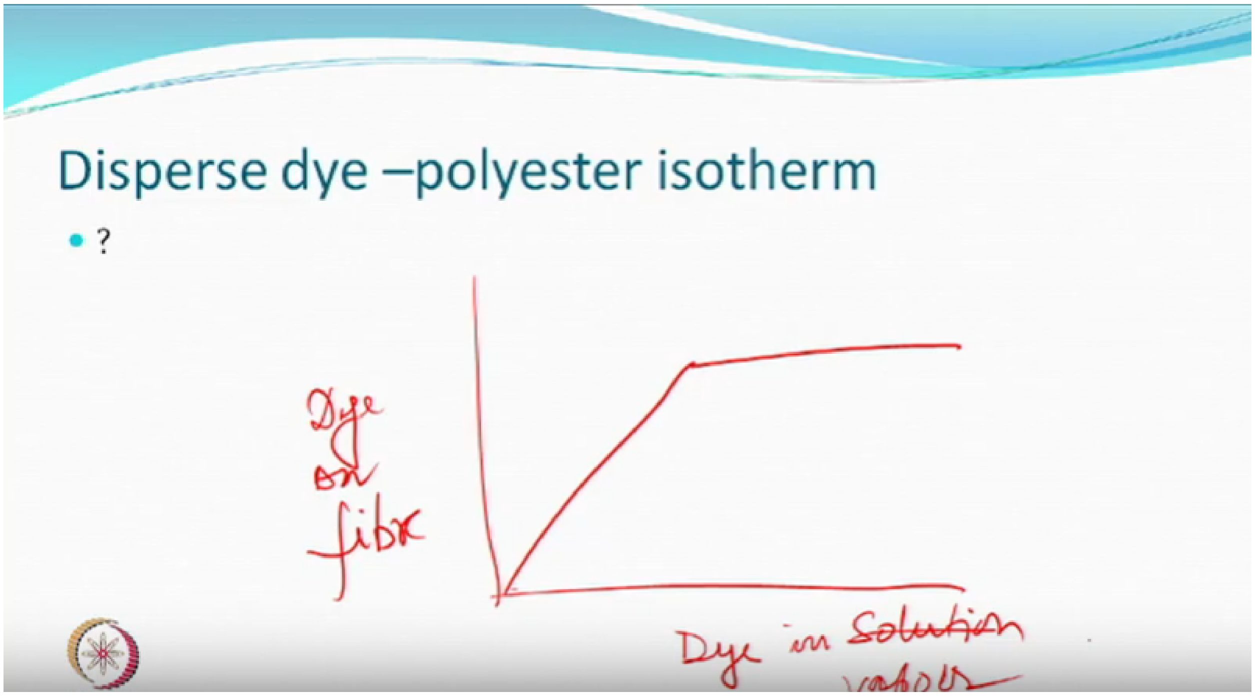

Disperse dye –polyester isotherm

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So, we know on the dispersed dye, polyester, isotherm. It follows Solid Solution, this should be valid here as well, it doesn't matter whether the dye, is going through a Solution or going from vapor form, instead of Solution, we'll be talking about dye, in the surrounding environment. So, what are you expecting is? The dye is going to vaporize, from paper, not just paper but, we expect the dye is only on a layer, of ink it is not inside the paper, it’s outside but, it's in Solid form, after we heat, it is going to go into the vapor from. So, instead of you talking about let us say, dye in Solution, you may say, dye available in vapor, form the concentration of a dye, in the vapor that would become important and I own fiber of course. So, there'll be an equilibrium, established and this, would of course, change because the concentration of a dye in a vapor can change and what how will it change? It can change because of temperature. So, it is doesn't mean that if Something, is subliming at 190 degree centigrade, will not sublime at 200, were two temperatures are different, the respectability of the five fabric and fiber also different and the vapor, pressure had a different temperature is also different. So, the moment you come to guess. Now, you're looking at vapor pressure, higher vapor pressure means, obviously there is a molecules have higher kinetic energy and they would be going for one end to the other end and trying to strike Something and so, if they strike early, obviously they are on the surface, once they are on the surface, affinity forces will start working and because, temperature the fabric holes is high, then if studying them.

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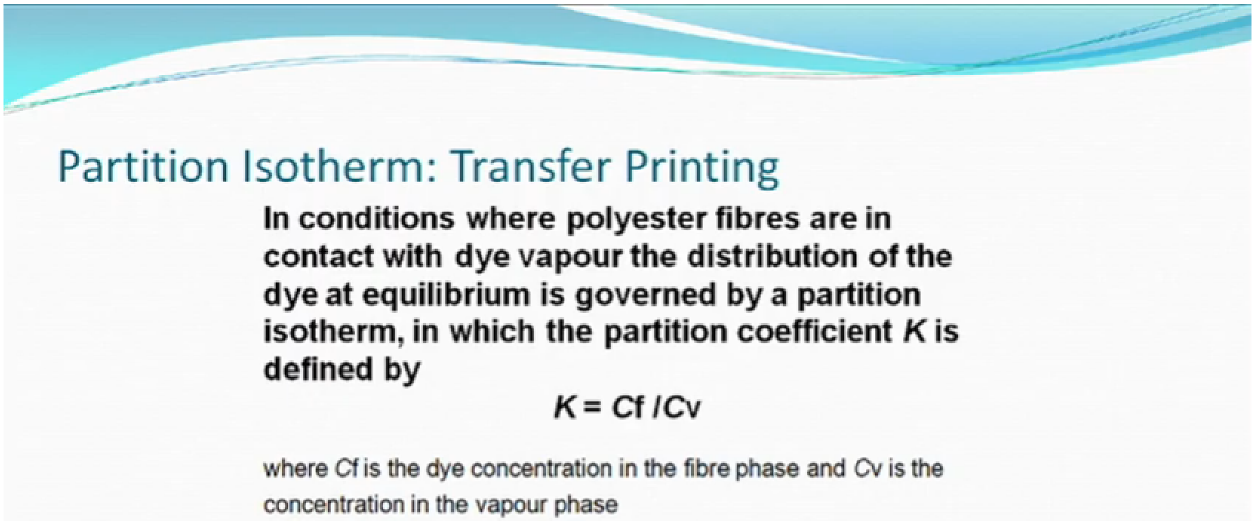

Partition Isotherm: Transfer Printing

In conditions where polyester fibres are in contact with dye vapour the distribution of the dye at equilibrium is governed by a partition isotherm, in which the partition coefficient K is defined by

$$K = Cf / Cv$$

where Cf is the dye concentration in the fibre phase and Cv is the concentration in the vapour phase

So, conditions where the polyester fibers and want with dye, vapor. Right? The distribution of dye at equilibrium is again governed by the same partition isotherm, in which the coefficient could be defined in the same manner. Where the concentration CF, is the concentration, on the fiber and CV, is the concentration, of the dye, in the vapor phase. We are not talking, about how much dye, was present in the ink on the paper, is very difficult to find the correlation there. So, we are only interested in the dye which is in the vapor form. So, all we have to do is, ensure that there is enough, concentration of the dye in the vapor, just before we have learnt that the amount, of dye which is actually going to be, on the vapor, in the vapor, would depend on his molecular weight, like it there like it was, dependent on Solubility, of the dye, in the case of aqua system, here it is dependent on how much is the concentration in the vapor and this obviously, has Something to do with the sublimation transfer, sublimation which means the molecule, the structure of the molecule and therefore is a complex process and this is as you have seen, a small change, in intra and Inter molecular harden bonding, can produce a large change as so, the concentrations are going to be there and therefore you definitely, will be much more careful, when you select a dye, mix the two die together or three dies together or different colors, which you choose, from different parts, of the design, should have similar transfer rates.
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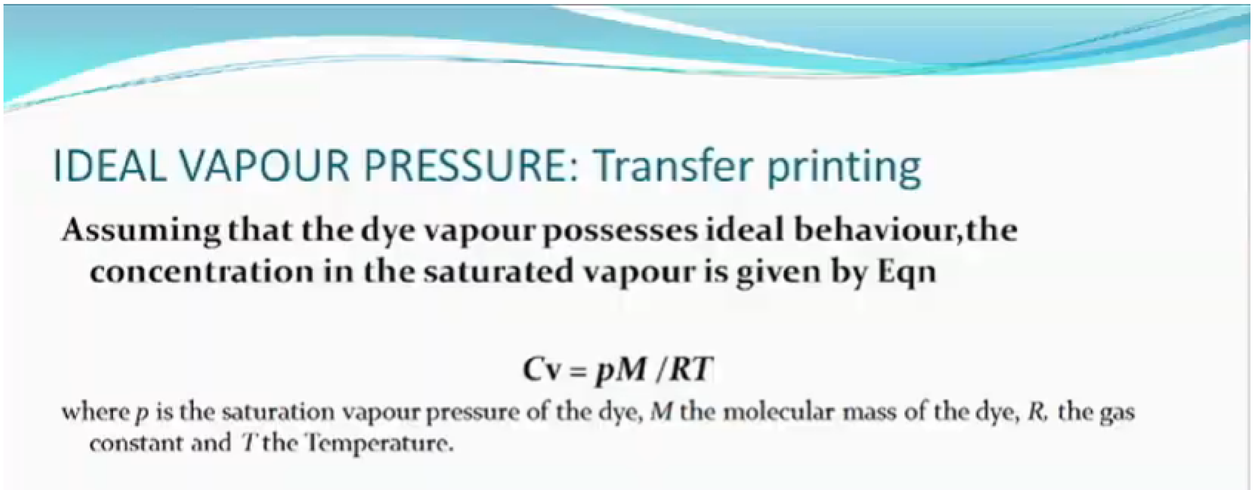

IDEAL VAPOUR PRESSURE: Transfer printing

Assuming that the dye vapour possesses ideal behaviour,the concentration in the saturated vapour is given by Eqn

$$Cv = pM / RT$$

where p is the saturation vapour pressure of the dye, M the molecular mass of the dye, R, the gas constant and T the Temperature.

So, ideal gas. Okay? So, nothing is ideal in this world. But, assuming that, it has an ideal behavior, then the concentration of a dye, would be related to P, which is the vapor pressure saturation, vapor pressure, M the molecular mass of the dye. So, if the concentration is in moles the different story and RN, is the gas constant and T is the temperature, if suppose somebody gives you a numerical problem, the only thing you have to, understand is, that the units must be compatible, numbers always look compatible. Right? But, if the units are not then you will get order differences in the results. Right? So, whenever you have to Solve any numerical you should be, concerned about what units are we talking about. So, simple relationship, the concentration of the dye in the vapor form, will be related to, the partial pressure or the saturation vapor pressure, that obviously you know independent, indirectly dependent on the, rate at which this can be evaporated, sublimation rate, the molecular mass, it's a gas therefore R and T are becoming important the T remember, is going to bean absolute temperature and not degree centigrade. Right? All Right? So, before we go further let's look at this.

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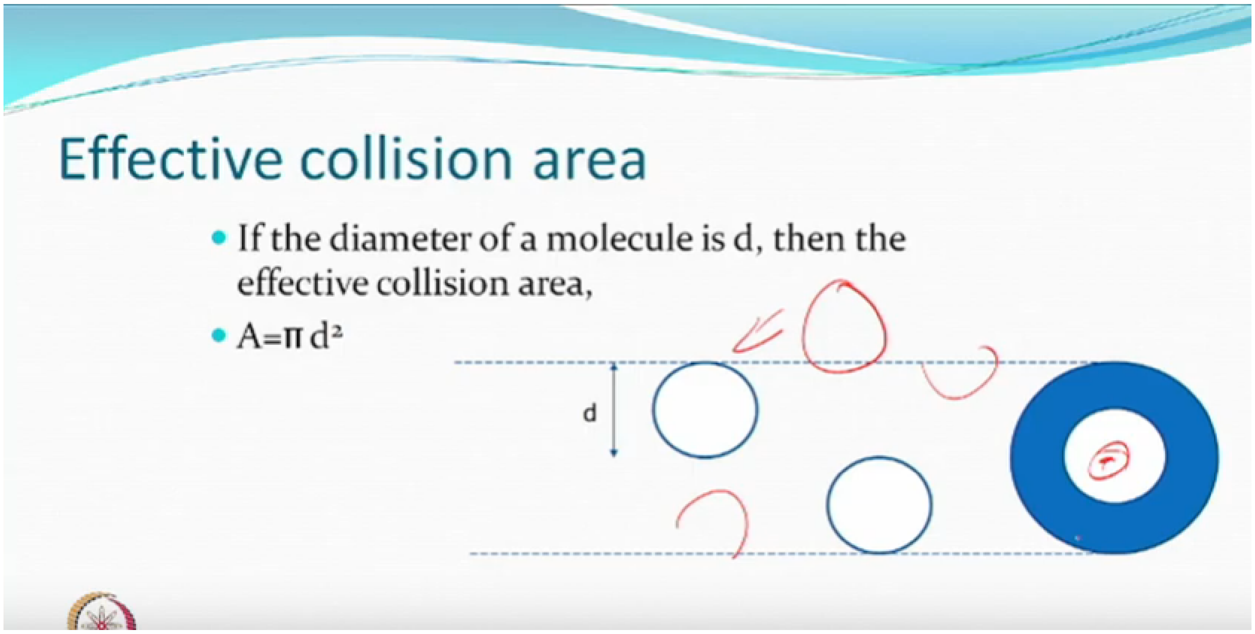

Effective collision area

- If the diameter of a molecule is d, then the effective collision area,
- $A=\pi d^2$

So, let's say this is a molecule of a dye being represented by some size. So, you have assize for molecule and this molecule is. Now, in the vapor form and have is rushing everywhere. So, the probability, that anything which comes in its path, it will contact. So, it is not is going to contact only, the fiber, fiber is much, far off when it starts in the vapor from, from the surface of the ink, layer fiber is very, very far off, in between there are a lot of molecules, of the dye itself, it can Sort of this is a simplistic view, simplistic in the sense give them all the, molecules which are in the vapor of the same size, they represent spherical and so, they can they move as a particle, from one to the other or the molecule and it can strike and what looks strike ? If the distance, it can strike if the diameter of this particle let's say is, B then it can traverse, a kind of a path which is, a to D, let's say a cylinder moving and then the molecule goes from this side, can strike here, can strike there, if other particle is within the thing, how many particles, are there within this range. So, the area of this particular thing, is if you consider PI d square. Right? D becomes the radius

of the larger, pipe shall we hit this a pipe, theoretical pipe. So, if it is in the center, the molecule will be here, but doesn't have to be always in the center, it can be anywhere. So, this is molecule is the same or something similar molecule, if the distance of this is more than 2 D, more than 2 D, then this particle may be here, it may pass through without touching. So, it may not strike, if the distance is like this, therefore it is bound to touch, whether, it is here, it is there. So, this is, the thing that they say let us, theoretically say what will happen, if this is the pipe where this is moving. So, within the 2 D range, definitely anything that comes, it will strike. We are assuming that all the particles, because of our Newton's law, will move in straight line, till they strike something else, in the strike they can change. So, they have a velocity and a direction of the sleep, they're moving in particular direction and this direction need not be, in one direction, they can go in anywhere, because they are free, the movement of particle or a molecule is out, of the particle vapor is then is free, the kinetic energy does not say, go only in X Direction, y direction, unless and until you create such situations, you create a vacuum on one side, then they would obviously get tendency, to go in one direction. But, forget about that. So, it's going to move, when it moves from one end to the other end, I'll keep on coming, in contact with particles and when the interaction is there. So, what people would like to know, how much is the free, path likely to be there, where it just moves without hindrance, it's not possible, theoretically but, if suppose the path length, is just, that starts from the ink and reaches, the fiber surface and no one, has come in between. It's not happening, because molecule is too small, you understand ever greater the number, of agate rows number, think about those numbers, very small molecules**.** So, many of them, all over the place and therefore you talk about concentration build up.
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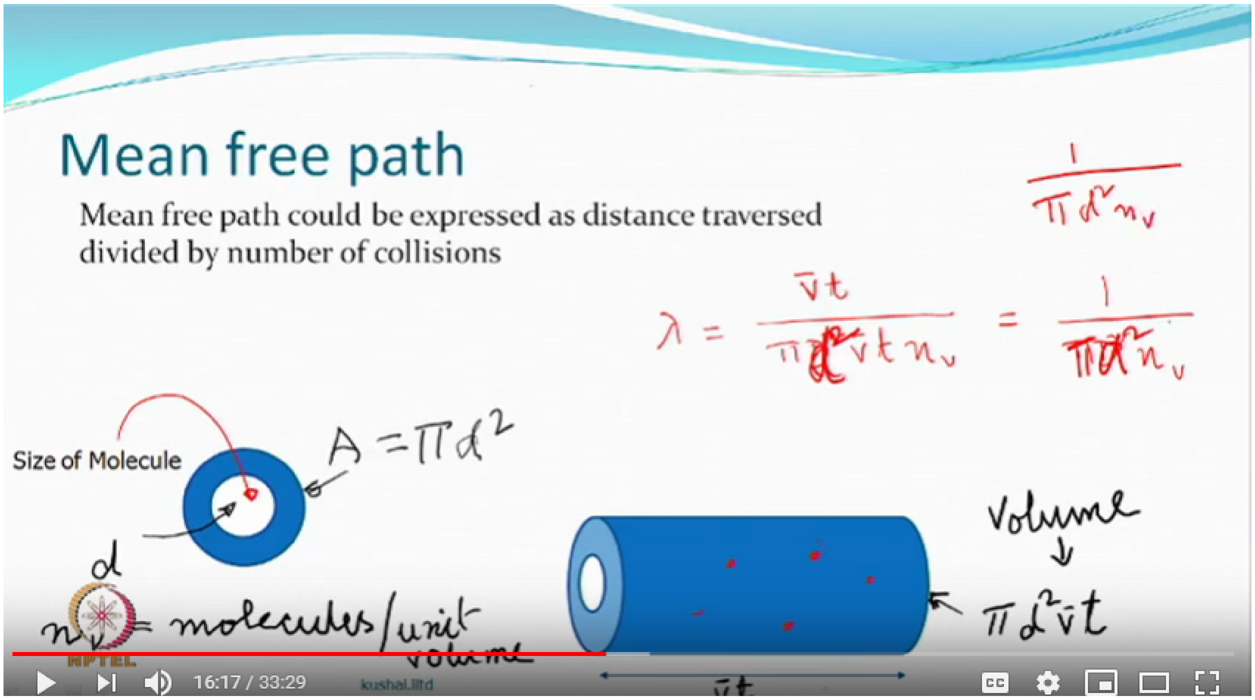

Mean free path

Mean free path could be expressed as distance traversed divided by number of collisions

$$\frac{1}{\pi d^2 n_v}$$

$$\lambda = \frac{\bar{v}t}{\pi d^2 \bar{v} t n_v} = \frac{1}{\pi d^2 n_v}$$

$A = \pi d^2$

n_v = molecules/unit volume

Volume ↓ $\pi d^2 \bar{v} t$

So, as we said the area assumed, virtual pipe, in which there may be so, many molecules and they would go from one end to another end let us say, of the pipe, in between they would probably connect with many other molecules also so, the time taken. Al right? So, mean free path could be expressed, as the distance traversed, divided by the number of such collisions that would also, mean that there have to be, how many molecules per unit volume? Something like that is available. So, the volume of this, virtual cylinder can be, phi d square, V Bar, is an average velocity, which is traveling, average means we are not hoping or we are hoping that some, particle or some molecule, from one end has reached the other end and some of them could actually go, absolutely out also. Right? So, whatever, we looking at some those who, pass through in one direction, whichever the direction and went around. So, in this virtual. So, called, ‘Cylindrical Path’ you would have, the volume is there and so, if n V, which is the number of molecules, within that So-called, ‘Unit Volume’. Then the lambda, is therefore distance divided by, the number of possible, collisions and which means, this is 1 by PI d square, I'm Sorry, I have used D Sometimes, capital let me just make all of them small, maybe it’s not working. So, let me just make this, is small D and this is also small D. Okay? Right? So, PI d square, average velocity V bar, number of molecules, are the ones which are going to decide, that the lambda will be, therefore if we write it again, is 1 over, PI D Square and n V, is that ok. So, it is dependent on the size of the molecule and dependent on the number of molecules.

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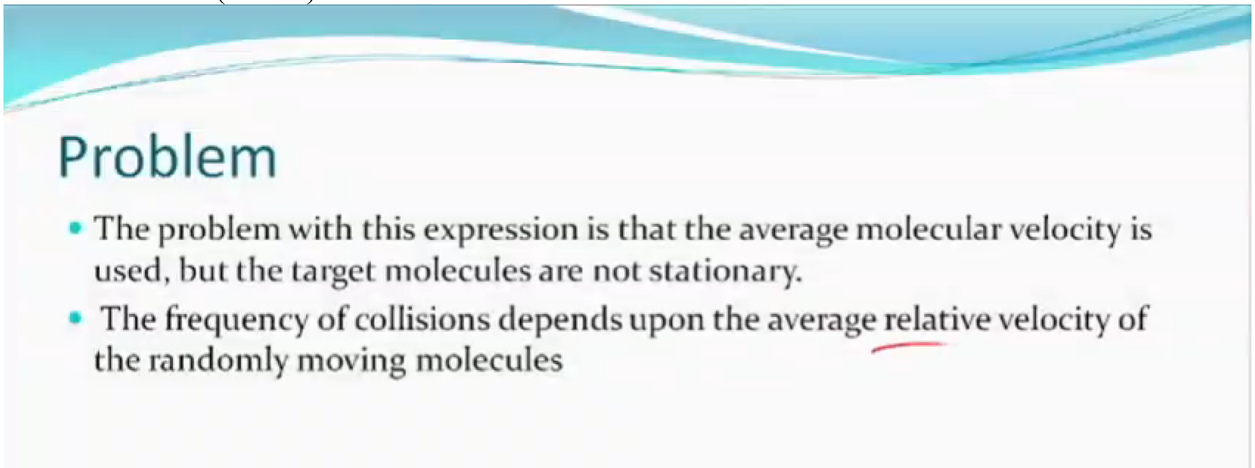

Problem

- The problem with this expression is that the average molecular velocity is used, but the target molecules are not stationary.
- The frequency of collisions depends upon the average relative velocity of the randomly moving molecules

The problem is that the average molecular velocity is being used, in this expression but, it is not that the molecule which is going to strike, are stationary, they are also moving, none of the molecules is just stationary, it has a velocity, in which every direction is going, was going it can still strike and therefore the collision, will depend on the average relative velocity, of randomly moving molecules and not just an average velocity but, average relative velocity.

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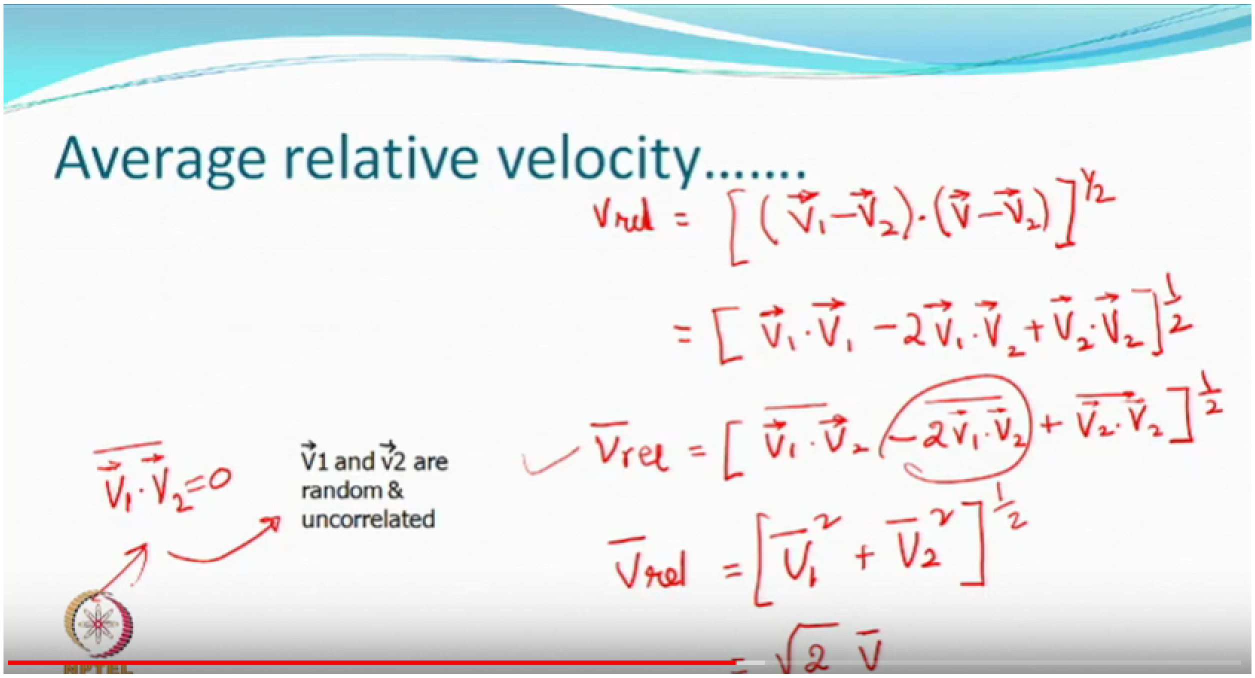

Average relative velocity.......

$$V_{rel} = \left[(\vec{V}_1-\vec{V}_2)\cdot(\vec{V}-\vec{V}_2)\right]^{1/2}$$

$$= \left[\vec{V}_1\cdot\vec{V}_1 - 2\vec{V}_1\cdot\vec{V}_2 + \vec{V}_2\cdot\vec{V}_2\right]^{\frac{1}{2}}$$

$$✓\ \bar{V}_{rel} = \left[\overline{\vec{V}_1\cdot\vec{V}_2}\ \boxed{\overline{-2\vec{V}_1\cdot\vec{V}_2}} + \overline{\vec{V}_2\cdot\vec{V}_2}\right]^{\frac{1}{2}}$$

$$\bar{V}_{rel} = \left[\bar{V}_1^2 + \bar{V}_2^2\right]^{\frac{1}{2}}$$

$$= \sqrt{2}\,\bar{V}$$

$$\overline{\vec{V}_1\cdot\vec{V}_2} = 0$$

$\vec{V}1$ and $\vec{V}2$ are random & uncorrelated

So, you have to find a relative velocity. So, how do you find the average relative velocity and what do you mean by that that one is moving with a V one, velocity the direction also is same as seen it is one single particle. So, as the direction of the it's a vector quantity. So, you're showing as a, vector V one, other is moving with the vector velocity V 2. But, when they, worry around one way or the other, let's say one is moving in this, the relative velocity, therefore would be V 1minus, V 2. Al right? And so and there will be so many, relative velocities also, you strike can go somewhere else and all those kind of things. So, you work about average relative velocity, how do we calculate that? So, a relative velocity, is like a dot product of the differences, of one and the other, square of that, the multiply and then let's take the square root and if you do that, you get terms like this, because all of them are also moving. So, all these terms will also, can be averaged out. So, this shows that the average velocity will be V velocity which is a vector, V 2 vector, then minus2 V 1 vector, V 2 vector and V 2 and V 2vector and then square root of that. Now, that becomes, mean average. Now, what we get, is the average velocity, will not have, this term which will be equal to zero, because they are moving randomly, in their products, on an average everywhere, if you look at it they will become zero, one moving base, the other moving that, something with this. But, V 1 square obviously will be there and V 2 square will be there, then average of those, products and then you take the square root and therefore relative velocity, is not just V average but, a root 2 of, V average and that becomes a change and that you make that change, for a single molecule that is in the whole thing, there is a single molecule, then you can use this term, rather than the other term

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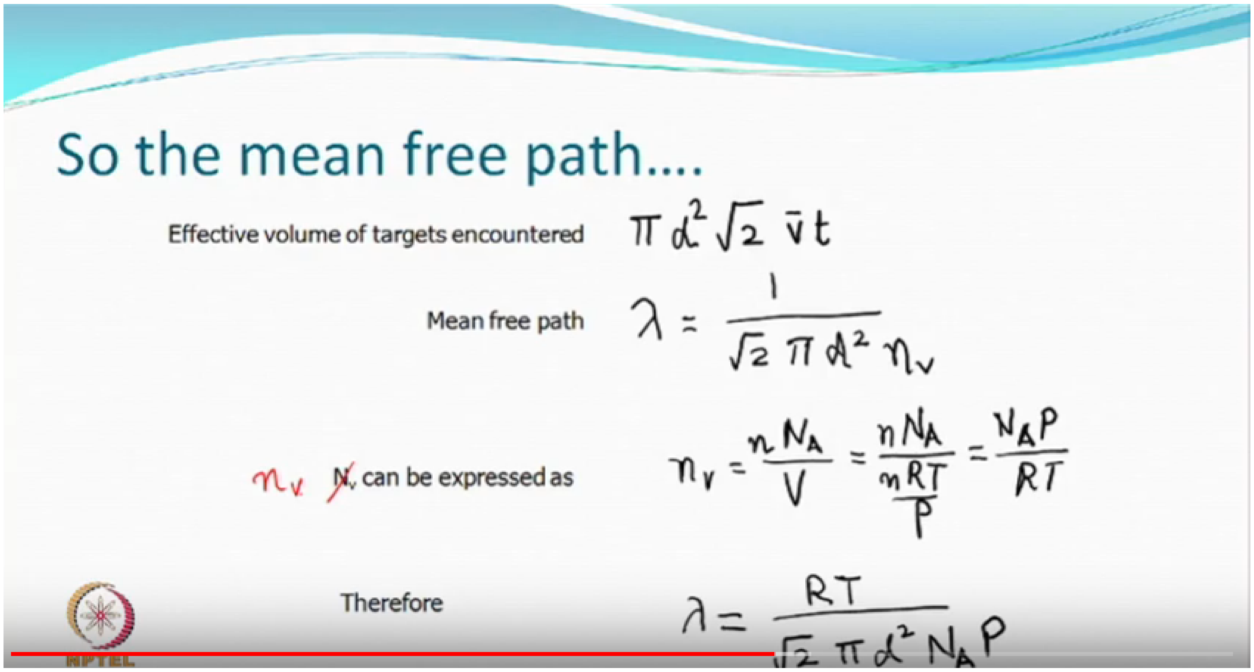

So the mean free path....

Effective volume of targets encountered $\pi d^2 \sqrt{2}\,\bar{v}\,t$

Mean free path $\lambda = \frac{1}{\sqrt{2}\,\pi d^2 n_v}$

n_v ~~N~~, can be expressed as $n_v = \frac{n N_A}{V} = \frac{n N_A}{\frac{nRT}{P}} = \frac{N_A P}{RT}$

Therefore $\lambda = \frac{RT}{\sqrt{2}\,\pi d^2 N_A P}$

And therefore the lambda, which is the mean free path, would be 1 over root 2, phi d square and the number of molecules in that unit volume. Okay? If we again say that n can be the number, the moles and plus ever get rose number N a is, Avogadro's number and then, the whole number NV, N V can be expressed as, capital n a which is they have a Avogadro's number, the pressure which is the saturated vapor pressure, RN t and so, the free path length will also depend on the temperature, it depends on the pressure. Right? So, if pressure is high, path length will be less and the dependent on the D of course. So, this is how, one can roughly, say well this is the way I can consider this will be the path length, interesting.

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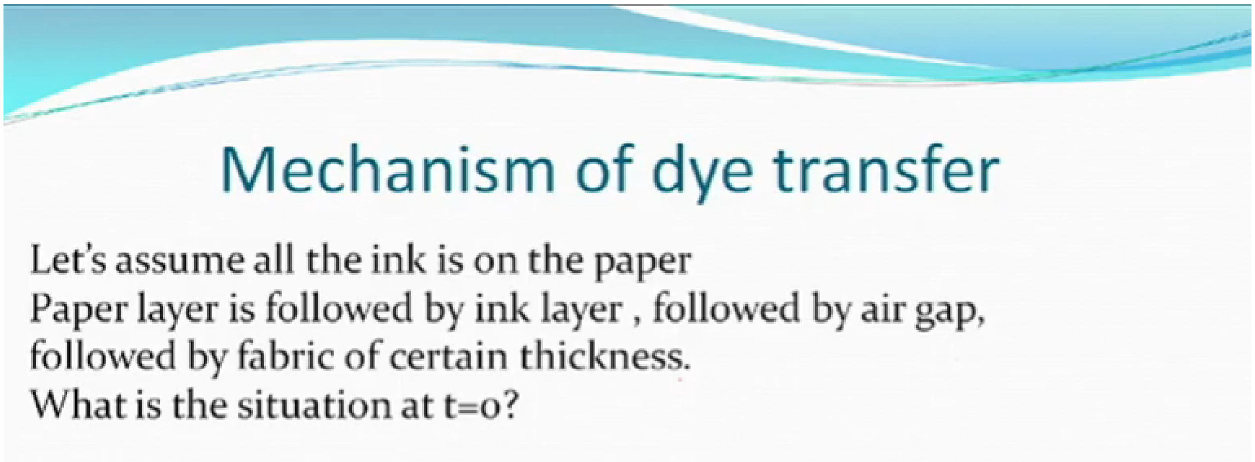

Mechanism of dye transfer

Let's assume all the ink is on the paper
Paper layer is followed by ink layer , followed by air gap, followed by fabric of certain thickness.
What is the situation at t=o?

So, let's assume, that all the ink is on the paper.

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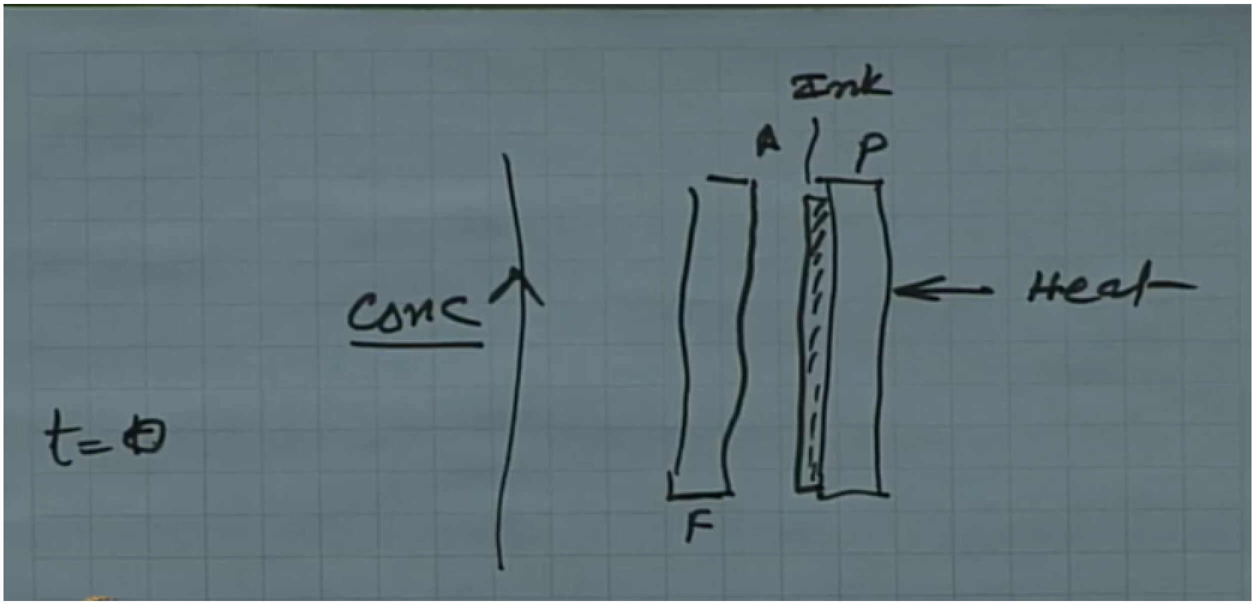

The paper also, has some thickness, then now what is there is let's say this is called, ‘Ink Layer’. Then there may be some gap, which is the air gap and then there is a fabric on the other side, which is the fabric. Now, if you assume this interesting way to look at it is, that they will consider this as the, axis which is representing concentration. So, at a given time, T is equal to zero, all the dye, is here, in the ink layer. So, maximum concentration is there, the concentration of a dye, in the fiber is zero. So, there is a gap, there is a distance and we hope that in the paper layer, whichever there is no dye, concentration. So, this is what is there so, we have, ink on the paper, paper layer is followed by the ink layer, then there is a air gap, followed by fabric, of a certain thickness. Okay? So this is what we expect to happen? This is the situation, what will happen is with time, when you apply heat, then some vapor formation will be there and once the vapor formation takes place, then the concentration of the ink, in the ink layer, will go down. Okay? And in the others it will start increasing. Okay? Let's say we work.

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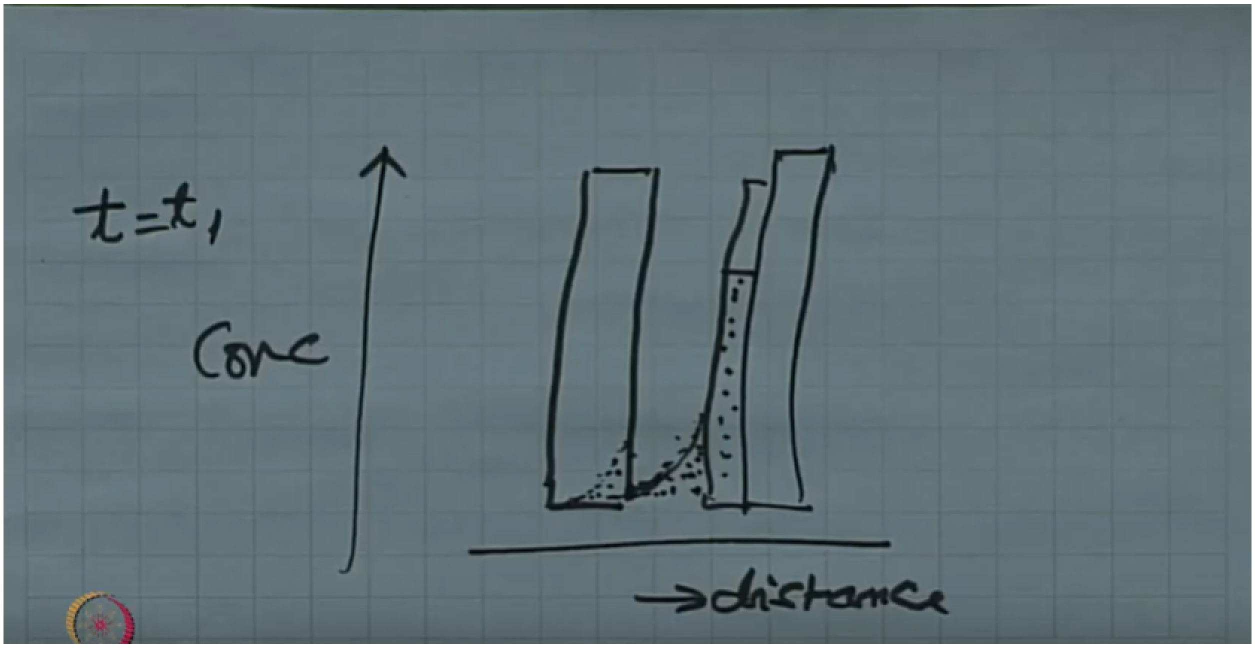

Same situation, paper thickness remains same, the thickness remains same. But, the concentration of ink, let us say goes down, at say, time T is equal to some timet1.It'll go down, concentrations go down. So, this is remember I were talking about concentration on this side. So, where will the dye go? This is the fiber and there's the gap. So, dye will come on this side, if you measure let's say this is, the distance, molecule has to cover a distance. So, we say, maybe this concentration profile is something like this, that there is a dye which comes out, in the air, but near, the ink layer the concentration is more, near the fabric surface the concentration maybe less. But, by the time if we look at, for whatever thing, some dye has come into the fiber also.

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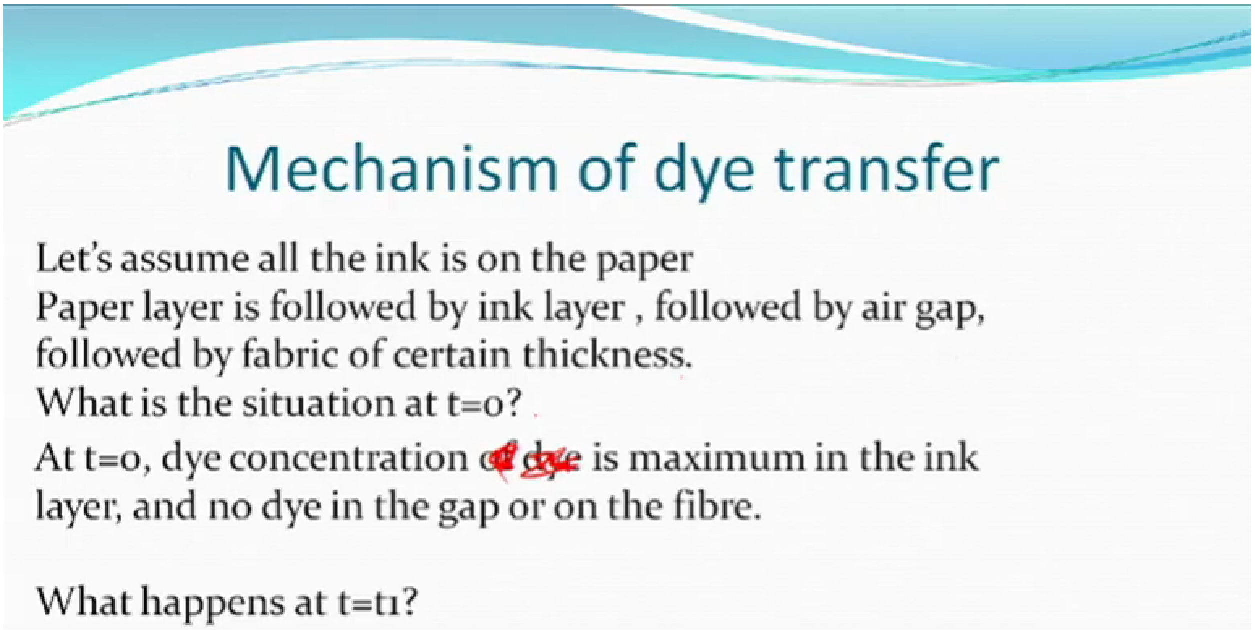

Mechanism of dye transfer

Let's assume all the ink is on the paper

Paper layer is followed by ink layer , followed by air gap, followed by fabric of certain thickness.

What is the situation at t=o?

At t=o, dye concentration ~~of dye~~ is maximum in the ink layer, and no dye in the gap or on the fibre.

What happens at t=t1?

So, at T is equal tot0, dye concentration, is maximum in the ink. Right? That's what we say? Is maximum in the ink, the dye concentration is maximum in the ink and no dye, I was in the gap or in the fiber, at T is equal to t1.
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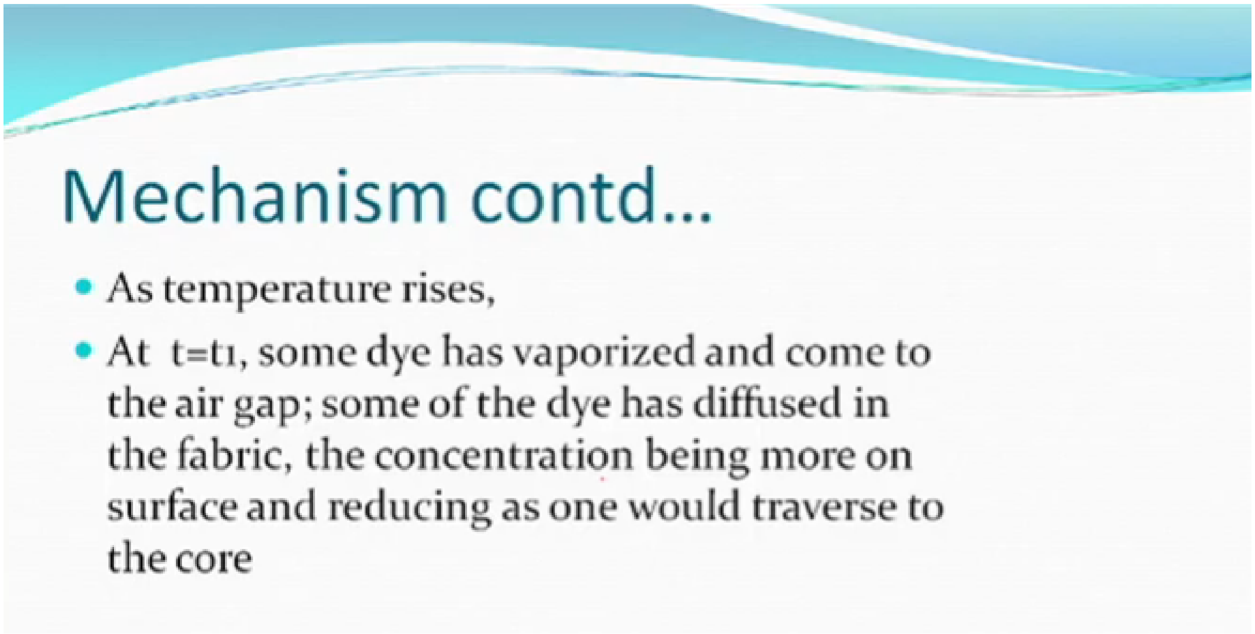

Mechanism contd…

- As temperature rises,
- At t=t1, some dye has vaporized and come to the air gap; some of the dye has diffused in the fabric, the concentration being more on surface and reducing as one would traverse to the core

And the temperature rises, some dye has vaporized, has come to the air gap, some who died has diffused in the fiber, the concentration being more on the surface and reducing as one would Traverse to the core the fiber. So, this is what we said that the concentration will be more, on the surface of the fiber, as you go inside the fiber, the concentration of dye will be less, something similar is here.
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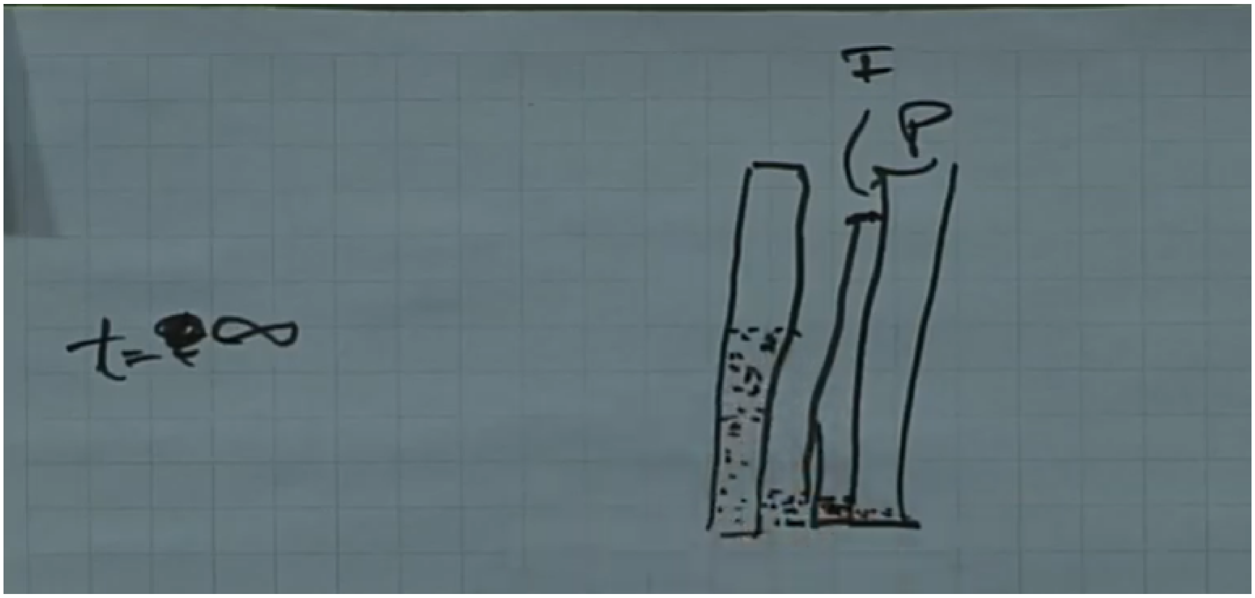

When we go to a time, again the paper and the ink layer, if everything is nice, good amount of dye may have gone, the concentration in the ink layer, would go down, in the air, there may be some concentration. But, at an equilibrium, on the fiber we hope that the concentration not only has risen. But, is probably uniformly distributed, when at time is equal to infinity, that's the equilibrium, possibly some dye may diffuse, also in the paper. Al right? So, you have very less, amount of ink remaining and the ink layer, it cannot be0 in the vapor. But, most of the dye, may have reached where it was supposed to reach and this is how, one can describe. So, at T is equal to infinity, what happens?

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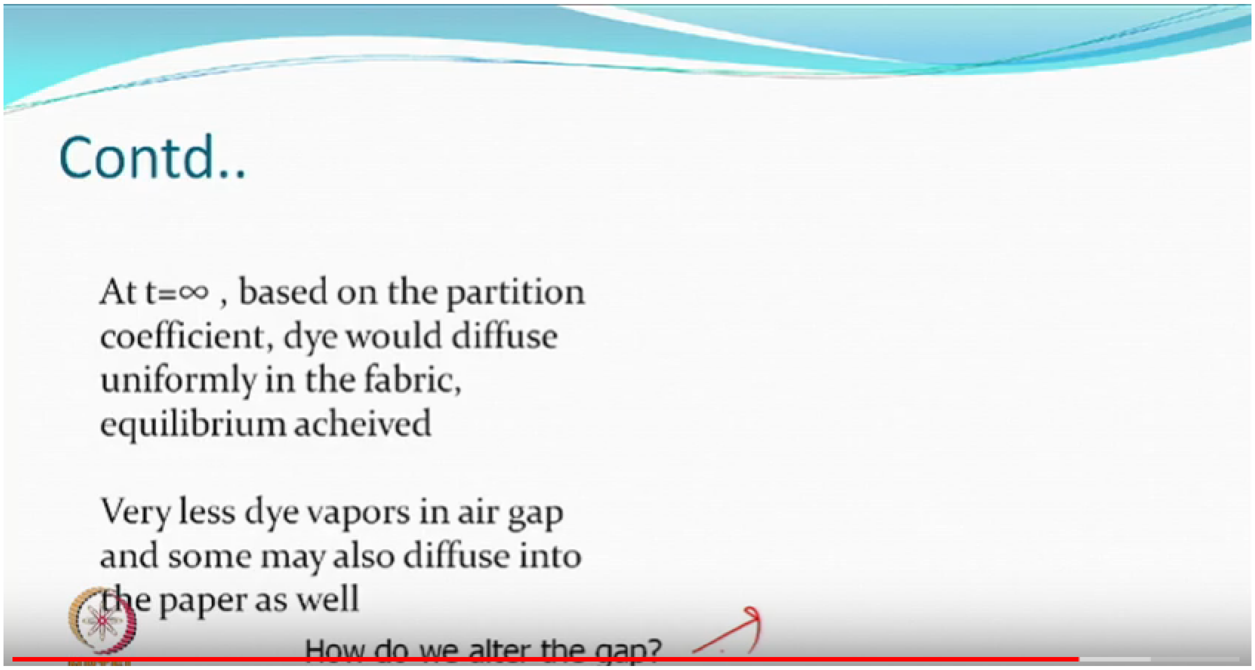

Contd..

At t=∞ , based on the partition coefficient, dye would diffuse uniformly in the fabric, equilibrium acheived

Very less dye vapors in air gap and some may also diffuse into the paper as well

How do we alter the gap?

At T is equal infinity based on the partition coefficient. Now, this is air all that affinity, forces, would be working, the molecule, molecular size, the temperature, will working, we hope that dye, would diffuse uniformly, in the fabric at the as the equilibrium is achieved and very, less dye vapors in the air gap and some may also, diffuse into the paper as well. Right? So, this is a general way of describing the same thing which we tried to describe in the solution and the fiber surface. So, the gap is important how, do we all to the gap, well we apply pressure, if you apply more and more pressure, the gap will be less, that means the chances of this transfer, to the fabric will be quicker and other diffusions here and there also will be less and so, will be in our own interest, to reduce the gap, because the gap would mean there is air, it is not a vacuum, the molecule is not traveling through the vacuum, if there is air, there are other molecules also, then the whole equation becomes very complex, a large molecule, in a small molecule, hitting each other what is happening and things like that. So, any air particle is it additional resistance, to motion. So, it is not just distance to be traveled. But, you will be encountering many other kind of particles, molecules which will also, hinder, the motion the gap reduction means pressure.

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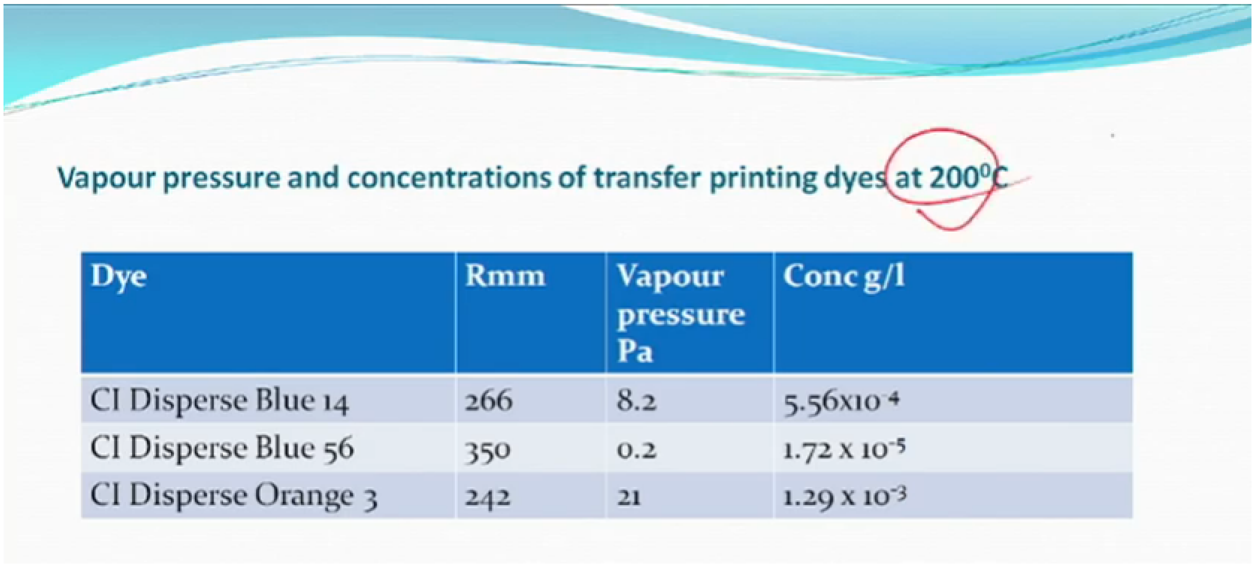

Vapour pressure and concentrations of transfer printing dyes at 200^{0}C

Dye	Rmm	Vapour pressure Pa	Conc g/l
CI Disperse Blue 14	266	8.2	$5.56\text{x}10^{-4}$
CI Disperse Blue 56	350	0.2	$1.72 \text{ x } 10^{-5}$
CI Disperse Orange 3	242	21	$1.29 \text{ x } 10^{-3}$

Some examples, before we close you see, just taken some example, where the molecular weight is, similar and where the molecular weight is different. So, the diamond fractures, are defining, these pressures etcetera, at a temperature 200 degree centigrade. Right? So, they say well, this is the thing sublimation will take place, most of people were using. So, all the properties will be available measured, at this temperature, at 200 degree centigrade. So, what do we see? We see that there is something dispersed blue, with 266 as a molecular weight, at this temperatures got some vapor pressure and based on whatever, thing we have the amount the concentration of this is somewhere around 10 raise to minus 4, remember we were talking about concentrations of grams per liter and so on. So, forth and now, we are talking about less, concentrations. But, it still work, sat 350 molecular weight of one of the other dive is blue 56, the vapor pressure, is very low and the concentration expected is 10 days to minus 5 and when you have another dive, which is 242 vapor pressure, is 21 and the concentrations and they don't tends to minus 3. Right? Often in editor. So, we are obviously, looking at very, less amount of molecules, because they're really molecules and not particles and they are ready to go wherever, they want to go. But, the difference is quite large you know? – 3 2- 4 - -5 and this is where one should appreciate that unless and until you choose, your dyes correctly, then you will be getting whatever you see on a paper, what you see on fabric, will be very different, the shade will be changed. If this is the kind of order. So, this order is quite a lot of difference order and one can always say, why this is happening? But, this is again the molecular structures that you have, the auxochromes that you have fixed up, the hydrogen bonding that they make, etcetera, etcetera. I think with this, as far as today is concerned, we can stop.

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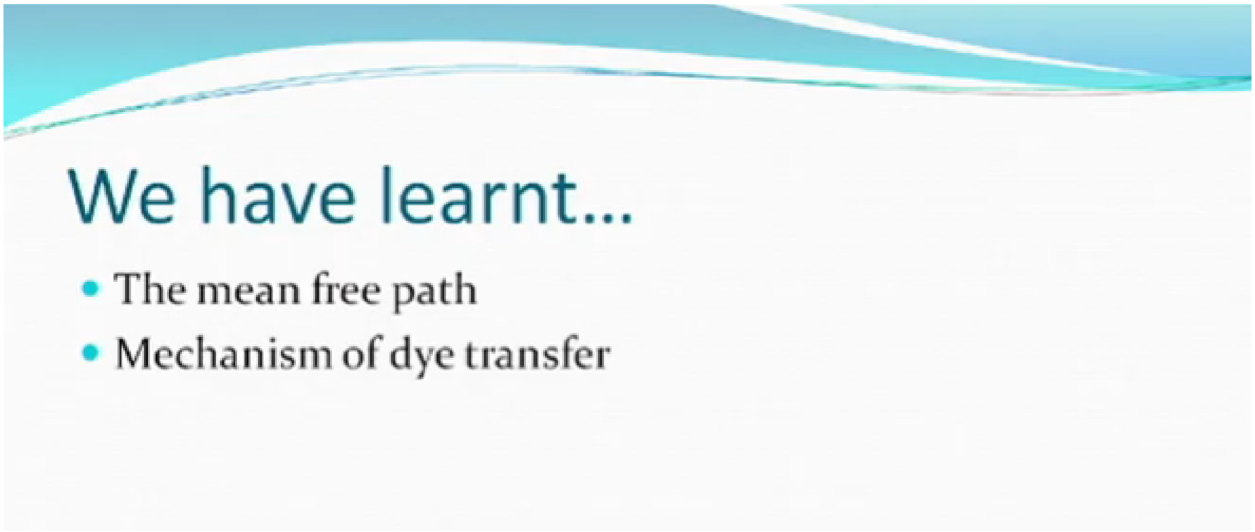

We have learnt...

- The mean free path
- Mechanism of dye transfer

So, we have understood what does the mean free path, of a at least, for a single molecule moving around in an ideal gas environment and the mechanism of transfer, of the dye from the vapor form to the fabric. Thank you.