PolCoPUS
Prof. Abhijit P Deshpande
Department of Chemical Engineering
Indian Institute of Technology, Madras

Lecture No -61
Diffusion in polymers

Hello, welcome to the course on polymers after having spent significant amount of time learning about single macromolecules, we started looking at different states of macromolecules thereby getting to know the structure of macromolecular systems. Subsequently we looked at properties, we looked at electrical and mechanical properties and viscoelasticity in great detail and in this week we are looking at introduction of polymers with other materials.

And in this particular lecture, we will look at the phenomenon of diffusion in macromolecular systems and the focus will remain on conceptual framework.

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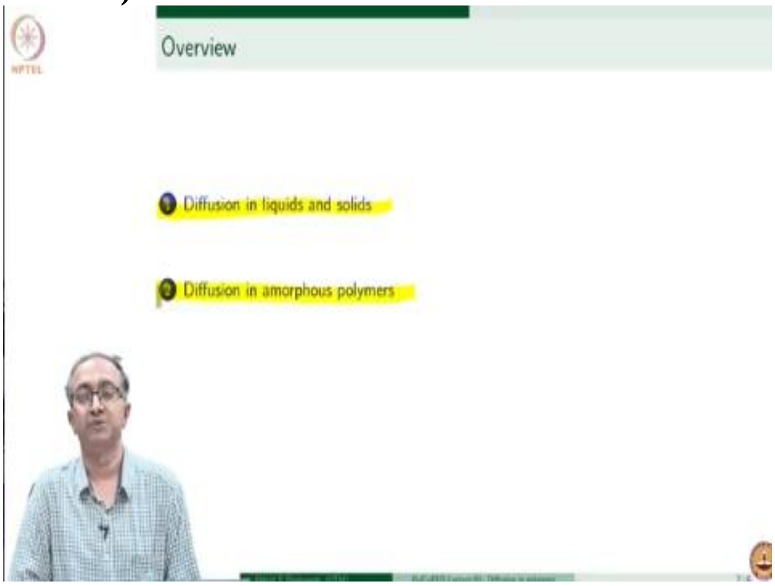

Overview

- Diffusion in liquids and solids
- Diffusion in amorphous polymers

So we will review first the diffusion as it happens in liquids and solids, because macromolecular systems have behavior which is similar to both and we will finish the lecture by looking at diffusion in amorphous polymers and will end by posing questions related to how might be the diffusion in case of semicrystalline polymers?

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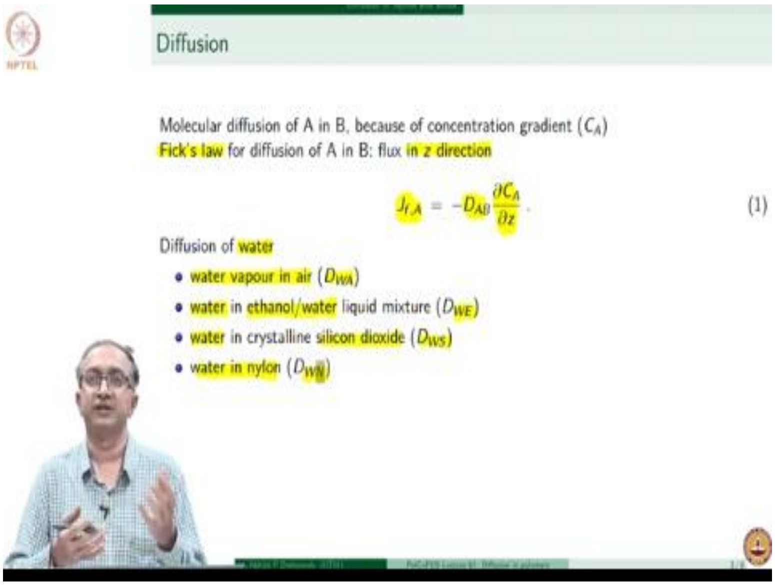

Diffusion

Molecular diffusion of A in B, because of concentration gradient (C_A)

Fick's law for diffusion of A in B: flux in z direction

$$J_{f,A} = -D_{AB}\frac{\partial C_A}{\partial z}. \qquad (1)$$

Diffusion of water

- water vapour in air (D_{WA})
- water in ethanol/water liquid mixture (D_{WE})
- water in crystalline silicon dioxide (D_{WS})
- water in nylon (D_{WN})

So diffusion is a phenomenon which is due to the gradient of chemical potential and the simplest form of diffusion basically, when we have a mixture of multiple components given that their chemical potentials can vary as a function of position diffusion happens and therefore we need a way to describe, how much will a species or a component migrate because of this chemical potential gradient and Fick's law is a one way which draws analogy from Fourier law of heat conduction.

And tries to state the mass flux in terms of a concentration gradient. So Fourier's law you recall is heat flux related to temperature gradient, so therefore this is very similar and similar to conductivity we have the coefficient which is called the diffusion coefficient or diffusivity and diffusivity is since we are talking about multi-component mixture, diffusivity refers to the component which is diffusing as well as the surrounding components which are its neighbors.

So D_{AB} is diffusivity of A or diffusion coefficient of A in B and like heat flux vector mass flux of a J of A is also a vector, but we are looking at a simplistic picture in which there is a concentration gradient only in one direction and therefore flux of A is also there in one direction. So if the gradient is high then the flux will be high and this is something which we know from common experience that if lot of perfume is applied then it diffuses quite fast and we come to smell of it more quickly.

While if less perfume will be applied it takes a little longer for us to sense it and smell it, so given that diffusion of let us say water it depends on where and what molecules are we talking about. So water vapour in air for example is one diffusivity this is gas phase diffusivity of water, so water is also as water vapour and the surrounding molecules of oxygen, nitrogen in air are also there.

On the other hand, we could also have let us say an ethanol water liquid mixture and we could again talk of water diffusivity, so in this case it is water and ethanol mixture in which water molecules are diffusing and therefore the diffusivity will depend on the interactions between water and ethanol. We can talk in solid let us say a crystalline silicon oxide and then we will have the diffusivity of water in quartz, let us say or silicon oxide.

We could also then talk in for this course purpose what will be of interest to know diffusivity of water in a polymer like nylon and so each of these is a different phase, there are different set of interactions between water and the surrounding molecules and since we are talking about potential chemical potential of each species interactions between these different molecules make a huge influence on how is the diffusion coefficient different.

Generally diffusion coefficient is highest in gas phase, then in liquid phase and then its lower in solid phase and it is understandable because there is more molecular motion possible in gas phase mean free path is much larger and therefore molecular interactions are also much less in case of gas phase compared to solid phase.

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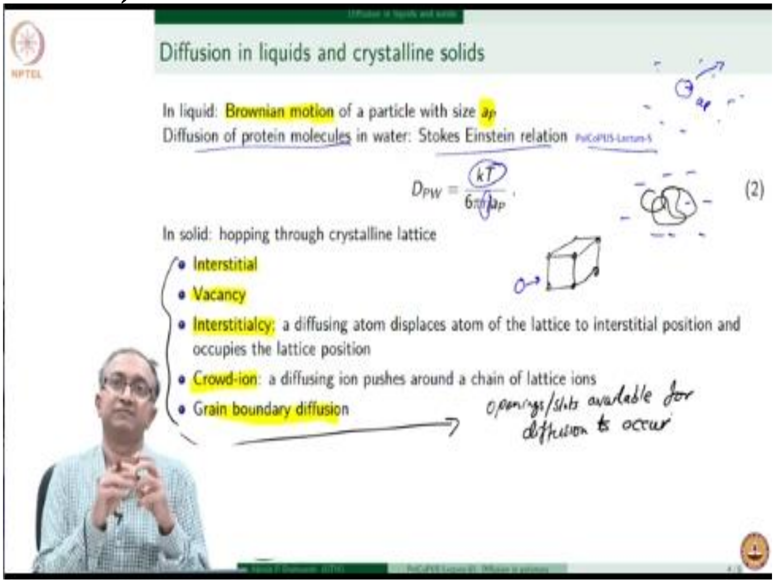

Diffusion in liquids and crystalline solids

In liquid: Brownian motion of a particle with size a_p

Diffusion of protein molecules in water: Stokes Einstein relation PolCoPUS-Lecture-5

$$D_{PW} = \frac{kT}{6\pi\mu a_p} \quad (2)$$

In solid: hopping through crystalline lattice

- Interstitial
- Vacancy
- Interstitialcy: a diffusing atom displaces atom of the lattice to interstitial position and occupies the lattice position
- Crowd-ion: a diffusing ion pushes around a chain of lattice ions
- Grain boundary diffusion

openings/slits available for diffusion to occur

So with this preliminary understanding let us do a review of what it is when a species diffuses either in case of liquids or solids. So in case of liquids it is pretty much determined like a Brownian motion, so we have a particle of size a_p. So let us say there is some particle with size ap and so this is interacting with surrounding molecules and so how much will this diffuse and what is the rate of diffusion will depend on its diffusivity and that is defined.

For example in lecture 5 we have looked at the diffusion coefficient of protein and so for such things where there is a large protein which is diffusing in an aqueous water based solution, the diffusion coefficient of protein in such case can be written in terms of a Stokes Einstein relation, which is based on the theory of Brownian motion and so it is inversely proportional to the medium viscosity and its directly proportional to the thermal energy which is available.

And so based on these things you can see that there is a temperature dependence, however what we will see is in case of solids and polymers we will find very different nature of temperature dependence. In case of solids what we have is a lattice and especially a crystalline solid we have a lattice and there are atoms which are occupying let us say this is a simple cubic structure and so the diffusing species will again have to basically diffuse through this crystalline lattice.

And so what are the possible ways in which such a species can move in a crystalline lattice and it can move only if there are some interstitial spaces between these atoms which are occupying a lattice or if there are defects such as vacancies and so there are these different mechanisms such as interstitialcy or crowd-ion or when there are multiple grains polycrystalline material as we discussed.

Then there will be grain boundaries which are quite significant and there can be diffusion there. So these different mechanisms lead to diffusion of a small molecule in a crystalline lattice and if you look at this description what we have basically is a certain number of such spots which are available. So these kind of mechanisms what they define is let us say the openings or slots available for diffusion to occur.

So there may be a certain density of these slots which are available and so if the number of these slots are very high and their distances are less than the diffusion can happen.

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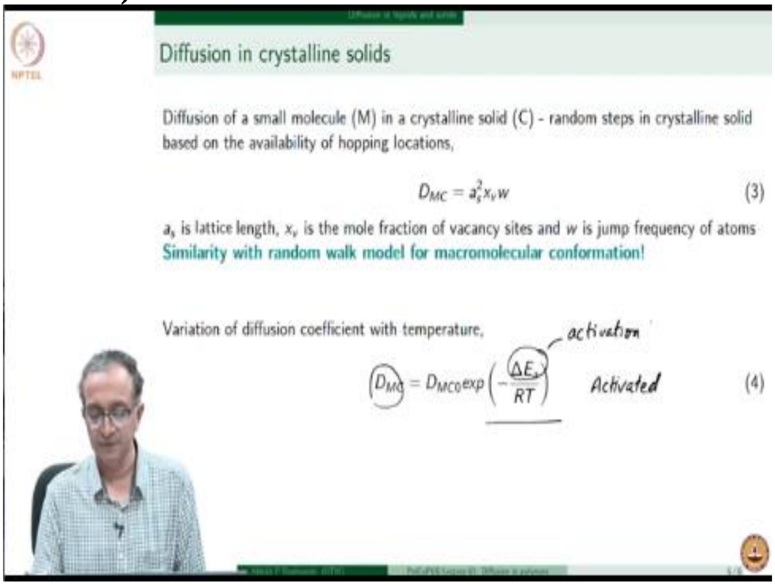

Diffusion in crystalline solids

Diffusion of a small molecule (M) in a crystalline solid (C) - random steps in crystalline solid based on the availability of hopping locations,

$$D_{MC} = a_s^2 x_v w \qquad (3)$$

a_s is lattice length, x_v is the mole fraction of vacancy sites and w is jump frequency of atoms

Similarity with random walk model for macromolecular conformation!

Variation of diffusion coefficient with temperature,

$$\boxed{D_{MC}} = D_{MC0} \exp\left(-\frac{\overset{\text{activation}}{\boxed{\Delta E_a}}}{RT}\right) \quad \text{Activated} \qquad (4)$$

And so we can look at this problem in terms of diffusion of a small molecule in a crystalline solid and it is like saying that you have all these different slots available and then the diffusing species can jump to this slot or this slot and from here it can jump to this slot or it can jump to this slot and so this is very similar to a random walk problem that we have discussed earlier. So it can take random steps in crystalline solid based on availability of hopping location or the slots as I talked about them.

And so diffusion coefficient in this case then depends on the number of such steps you can take and the size of the step. So therefore a_s is the size of the step and x_v is the basically mole fraction of the vacancy site and this is the jump frequency. So x_v into W gives us the idea of the number of such jumps which are possible and so this is very similar to N into a^2, the end to end distance measurement that we had got.

Expression for end to end distance in case of a macromolecule, so therefore this random walk for a diffusing species is very similar to a macromolecular conformation case that we saw earlier. So based on this description there is a barrier energy associated with this hopping and because of that this is an activated process and so diffusion at any temperature will basically be dependent on some activation energy barrier.

And then Arhenius dependence is what is expected, so this is the case very different compared to diffusion in liquids, where we saw the Stokes Einstein relation.

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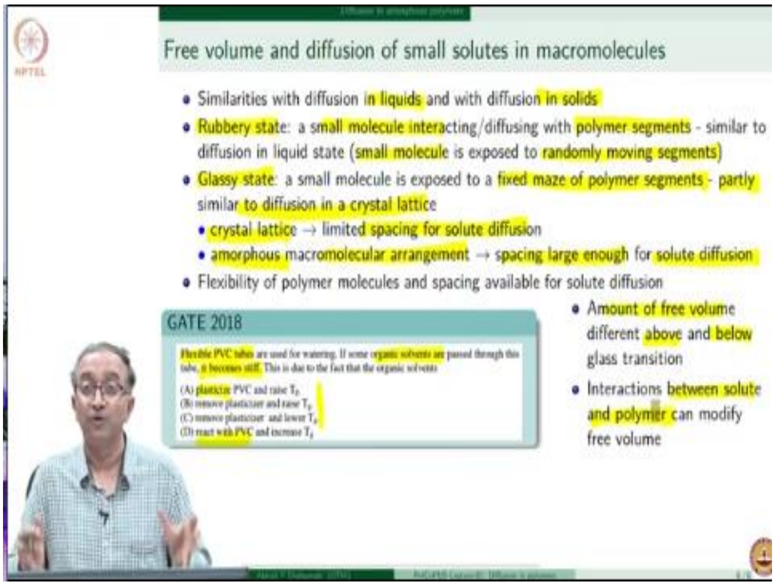

Free volume and diffusion of small solutes in macromolecules

- Similarities with diffusion in liquids and with diffusion in solids
- Rubbery state: a small molecule interacting/diffusing with polymer segments - similar to diffusion in liquid state (small molecule is exposed to randomly moving segments)
- Glassy state: a small molecule is exposed to a fixed maze of polymer segments - partly similar to diffusion in a crystal lattice
  - crystal lattice → limited spacing for solute diffusion
  - amorphous macromolecular arrangement → spacing large enough for solute diffusion
- Flexibility of polymer molecules and spacing available for solute diffusion

GATE 2018

Flexible PVC tubes are used for watering. If some organic solvents are passed through this tube, it becomes stiff. This is due to the fact that the organic solvents

(A) plasticize PVC and raise T_g
(B) remove plasticizer and raise T_g
(C) remove plasticizer and lower T_g
(D) react with PVC and increase T_g

- Amount of free volume different above and below glass transition
- Interactions between solute and polymer can modify free volume

So what is it in terms of diffusion in macromolecules? So macromolecular system have similarities both with liquid and diffusion in solids. So we have some elements of diffusion in liquids and some elements of diffusion in solids, in case of rubbery state a small molecule is basically diffusing where there are these polymer segments but the polymer segments themselves are moving around.

So this is like diffusion in a liquid state, so for example if water is diffusing in ethanol, ethanol molecule stem cells are moving about and then water is diffusing. So similarly let us say if we have a styrene monomer in polystyrene, then styrene is moving around in polystyrene but polystyrene is in a rubbery state. So the conformations of macromolecule polystyrene are continuously changing.

And so this interaction dynamic interaction between the diffusing molecule and the background molecule can happen. So therefore the small molecule is exposed to randomly moving segments of the macromolecule. On the other hand if you look at glassy state, then the glassy state will encounter only the fixed segments of macromolecule. So this is almost like diffusion in solid but difference being in crystalline solid there were the arrangement of host atoms and molecules was a crystalline lattice.

But here there will be random arrangements of macromolecule. So that is why this is partly similar to diffusion in crystalline lattice. Crystal lattice of course there is a limited spacing in case of amorphous macromolecular arrangement spacing is large enough for solute diffusion, because the arrangements are random and generally the space which is large enough in case of amorphous molecules by the way I would again remind you that the densities of amorphous materials are always less than densities of crystalline material.

And so that again points to the fact that spacing between macromolecules is larger in case of amorphous molecules. So what we have is the availability of free volume and this free volume determines the rate at which diffusing molecule can hop around, as opposed to a crystalline lattice where because of the specific lattice arrangement of atoms and molecules the free volume availability is defined already because of lattice.

So let us give you a thought regarding how diffusion is important is let us look at this question where there is a flexible tube of polyvinyl chloride which we use quite often as garden hose and if at all instead of passing water if we allow organic solvent to flow through it, the observation is that it becomes stiff. So its modulus increases is the appearance of it, so then what is it due to? So what is the phenomenon which is happening?

So clearly it is to do with looks like plasticizer. There are 3 options which talk about plasticizer, there is also an option which talks about some reaction with PVC so where is diffusion involved in all of this. Can you think of that and what is happening when this organic solvent is contacting the PVC pipe? So think about it, while we discuss the phenomenon of diffusion in little more detail.

So the amount of free volume determines how a molecule can diffuse through a macromolecule, of course this free volume is very different above and below glass transition. So diffusion coefficient in rubber is going to be much higher than diffusion coefficient in glassy state and the other feature is also the fact that the diffusing molecule and macromolecule can interact with each other.

So for example if there is dry nylon, the macromolecular network in amorphous state will have a certain free volume and there will be frozen macromolecules. But once water starts diffusing in what water can do is it can plasticize the nylon macromolecules and then nylon macromolecules can start changing conformations and so the interaction between water which hydrogen bonds with amide bonds of nylon can induce macromolecular segmental flexibility in case of nylon.

And therefore the free volume changes and so as water is coming in it is in fact changing the background or the lattice which is around it or the host macro molecules which are around it and so therefore it can have very different diffusion coefficient because of these interactions.

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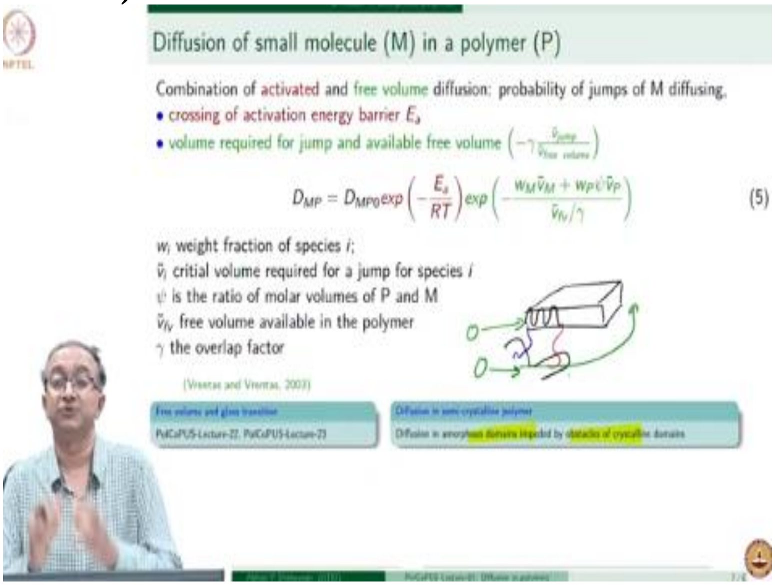

Diffusion of small molecule (M) in a polymer (P)

Combination of activated and free volume diffusion: probability of jumps of M diffusing.

- crossing of activation energy barrier E_a
- volume required for jump and available free volume $\left(-\gamma \frac{\bar{v}_{jump}}{\bar{v}_{free\ volume}}\right)$

$$D_{MP} = D_{MP0} exp\left(-\frac{E_a}{RT}\right) exp\left(-\frac{w_M \bar{v}_M + w_P \psi \bar{v}_P}{\bar{v}_{fv}/\gamma}\right) \quad (5)$$

w_i weight fraction of species i;
$\bar{v}_i$ critial volume required for a jump for species i
ψ is the ratio of molar volumes of P and M
$\bar{v}_{fv}$ free volume available in the polymer
γ the overlap factor

(Vrentas and Vrentas, 2003)

Free volume and glass transition
PolCoPUS-Lecture-22, PolCoPUS-Lecture-23

Diffusion in semi-crystalline polymer
Diffusion in amorphous domains impeded by obstacles of crystalline domains

So let us look at in terms of conceptually how do we frame what is the dependence of diffusion coefficient on let us say temperature? We understand that as temperature will increase diffusion coefficient will increase and then there will be a step change at class transition, because with associated with glass transition is a drastic change in segmental mobility and as segmental mobility is very high in case of rubbers we will observe high diffusion coefficient for rubbers.

So in case of macromolecule the diffusion of a small molecule let us say M in a polymer P is a combination of both activated and free volume diffusion. So we saw that for a crystalline lattice it was only an activated process, in case of a macromolecule we suspect that free volume will play an important role especially in case of the amorphous polymers and how their random arrangements are.

And so the probability of M diffusing depends on some activation energy barrier, but it also depends on what is the available free volume. So this free volume can be estimated based on whatever is the volume required for jump, as opposed to the free volume which is there and so this is an example of an expression which can be used to describe and what you can see is there is an activated part and then there is a so this is the activated part and then there is a free volume part.

So under what condition the activated part will be operational think about it. Similarly under what condition the free volume part will be operational think about it. So generally what we have are the free volume which is available, the ratio of the molar volumes of the molecule which is diffusing and also the weight fraction of whatever is the molecule which is diffusing with respect to whatever is the background macromolecule.

So in general we need to pay lot of attention to the glassy state and rubbery state and their descriptions and this is we have already discussed in great detail in lectures 22 and 23. Now having seen this picture a question that we can ask is what happens in case diffusion is happening in a semi crystalline material? So in case of semicrystalline material what we have is let us say a lamella of crystalline material and then of course surrounding this is the amorphous state.

And so we can possibly have the combination of crystalline state and amorphous state and now in this if there is a small molecule which is diffusing how does it diffuse in this and how does it diffuse in this? So you can clearly see that depending on the size of the molecule it may not be able to diffuse through the crystalline lamella, but it may be able to diffuse through the amorphous region where free volume availability is always much larger.

So this is almost as if there is the diffusion in amorphous polymer but which is impeded because there are some obstacles, so the crystalline portions act as obstacles and so therefore diffusion will have to happen where the diffusion diffusing molecule has to travel around in the amorphous domain by avoiding the crystalline domains. So there are impediments posed by the crystalline domains.

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Answers

GATE question on Slide Number 6 : Answer B

Absorption and Leaching: PolCoPUS-Lecture-81

So with this picture, I hope you can see that because of the plasticizer when it comes out into the organic solvent we have the effect that since plasticizer is coming out the glass transition temperature therefore will increase and because of that the material which was in the rubbery state now will become in more glassy state and therefore it becomes rigid and in this not only diffusion is happening but the overall important phenomena of leaching is also happening.

So leaching is a process by which a small molecule goes from a solid state to a liquid state, so in this case organic solvent is flowing through the PVC pipe the plasticizer is in the PVC which is the solid like material and then this plasticizer has to diffuse within the polymer then has to leach out to the organic solvent and then again it has to diffuse and get flown along with the organic solvent.

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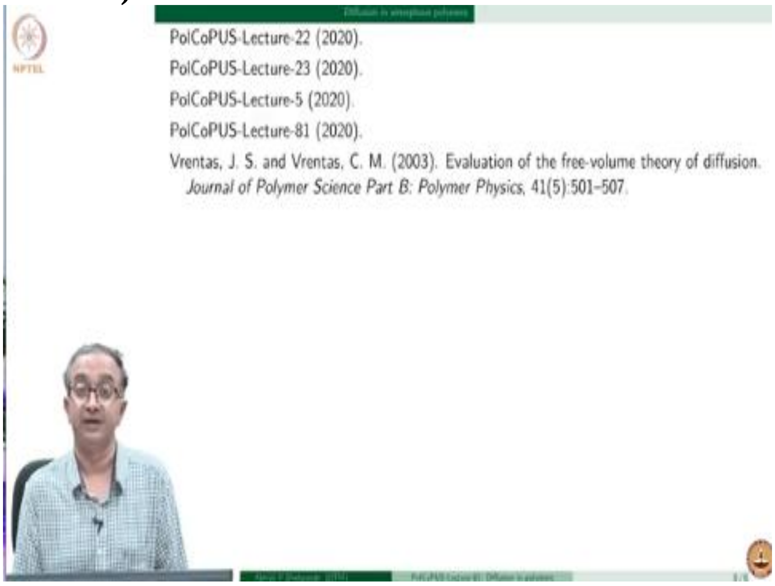

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PolCoPUS-Lecture-23 (2020).

PolCoPUS-Lecture-5 (2020).

PolCoPUS-Lecture-81 (2020).

Vrentas, J. S. and Vrentas, C. M. (2003). Evaluation of the free-volume theory of diffusion. *Journal of Polymer Science Part B: Polymer Physics*, 41(5):501–507.

So there are these aspects of absorption and leaching we will discuss in the 81st lecture. So with this will come to close this lecture, thank you.