Molecular Arrangements and States of Polymers

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Lecture – 20
Interactions

Hello, welcome to this course on polymers. In this course, we have focused not only on the molecular picture; we are looking at the bulk response as well as engineering applications and one of the most underlying features related to the overall response of material is related to molecular interactions. So, in this lecture, we will briefly summarize what are these molecular interactions and how they have an influence on properties or applications will be discussed throughout the course. And so, in this third week, we are looking at molecular arrangements and the solid states of polymer and the transition from liquid like states to solid like states. And in this particular lecture, the focus will be on learning the concepts related to interactions.

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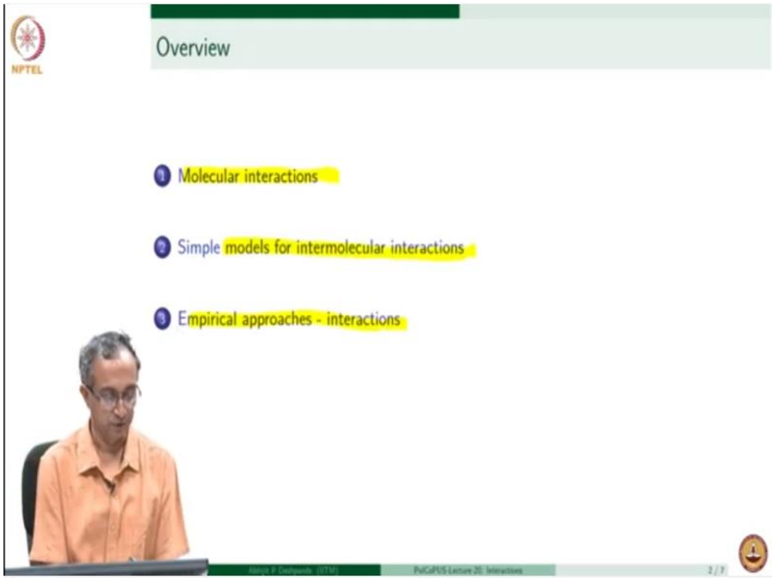

Overview

1. Molecular interactions
2. Simple models for intermolecular interactions
3. Empirical approaches - interactions

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And we will do this by first quickly looking at what are the set of molecular interactions. The quantitative understanding is reached if we look at simple models and in this course, we may not use many of these models, but the concept behind these models are very useful for us to think in terms of bulk response of materials also. And many times the molecular level information can be complex to understand or maybe more complex to arrive at quick decision making set of guidelines, we use empirical or semi empirical approaches. So, even though we know that the underlying interactions are at the molecular level, we may form an empirical or semi empirical formulation, which can give us quick decision making capabilities. So, we will look at couple of examples of this approach which are used in polymers.

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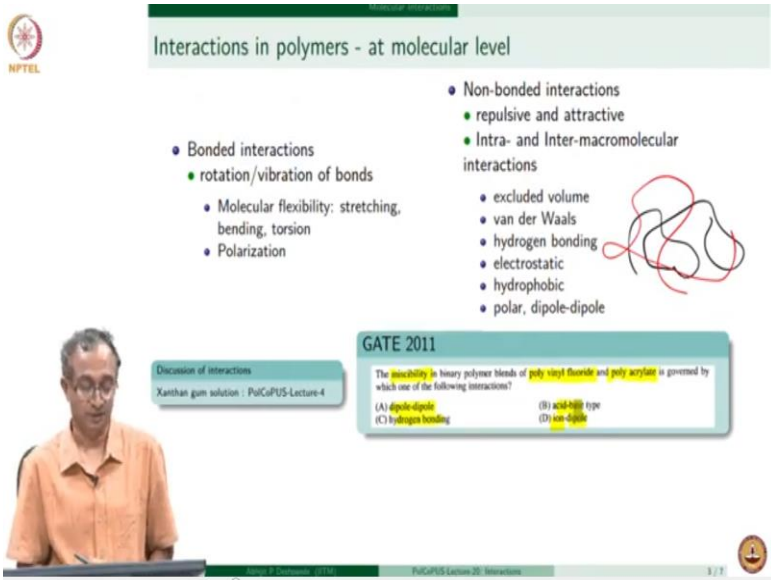

Molecular interactions

Interactions in polymers - at molecular level

- Bonded interactions
  - rotation/vibration of bonds
    - Molecular flexibility: stretching, bending, torsion
    - Polarization
- Non-bonded interactions
  - repulsive and attractive
  - Intra- and Inter-macromolecular interactions
    - excluded volume
    - van der Waals
    - hydrogen bonding
    - electrostatic
    - hydrophobic
    - polar, dipole-dipole

Discussion of interactions

Xanthan gum solution : PolCoPUS-Lecture-4

GATE 2011

The miscibility in binary polymer blends of poly vinyl fluoride and poly acrylate is governed by which one of the following interactions?

(A) dipole-dipole (B) acid-base type
(C) hydrogen bonding (D) ion-dipole

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So, when we look at interactions for macromolecules at the molecular level, we can look at the interactions which are due to bonds which are there, covalent bonds. And we've seen that these covalent bonds are either carbon-carbon or carbon-oxygen or carbon-sulphur and silicon-oxygen. So, depending on the nature of macromolecule, we can have a variety of these bonds. And so, rotation vibration of these bonds leads to one set of interactions and these are of course, between neighboring atoms. So, the two atoms which are bonded to each other can react this way. So, when we have let us say one atom and another atom and they are bonded then what happens is, there is a vibration possible in different dimensions. And then, if we have let us say a set of these atoms, then also there is bending possible and so, all of these features are related to bond.

And an important aspect of these bond and how the their position is, there rotation is also is related to the polarization of the material because many of these bonds will have a polarity which means a partial charge separation where there will be a plus and minus charge separation and across this bond and so, there are there is polarity present and what happens to this polarity as a function of the rotation and vibration on bonds will be of great interest when we are looking at the dielectric properties or electrical properties of these macromolecules.

On the other hand, when we look at non-bonded interactions, they could be both repulsive and attractive. And in case of macromolecules, what is very crucial is we have interactions within a macromolecule itself, because macromolecule is such a long giant object, there are different parts of same macromolecules which interact with each other.

And so, you could have intra-molecular or inter macromolecule. So, therefore, if there is another macromolecule present then of course, you can again have interactions between these different macromolecules also. And what are the examples? We have already seen, when we looked at expanded chain that we have same molecule, same space cannot be occupied by two different parts of the macromolecule or two different macromolecule. This gave us to the model which was we called expanded chain and there is Van der Waals attraction, so, excluded volume is an example of repulsion Van der Waals will lead to attraction and of course, there are several other interactions that we are familiar with whether hydrogen bonding or hydrophobic interactions, we can have charged charge interactions which we call electrostatic or we could have interactions between the polar bonds or dipoles, which are available in the sample.

And why all of this is important is highlighted in this question related to whether two polymers can mix and if at all they mix why do they mix? So, here we are talking about a polymer poly vinyl fluoride and another polymer polyacrylate and the question is, these two are miscible, which means, if we mix if we make polyacrylate, if we make pol yvinyl fluoride and mix them together, there is a molecular mixing.

So, the two polymers will in fact interact with each other and mix. So, the question is what is the nature of interaction which leads to this miscibility? So, is the interaction because there is acid on one polymer and base on another polymer? Is it because both the polymers can do hydrogen bonding and therefore, interact with each other? Do they have dipoles and therefore, the dipoles can interact favorably and lead to favorable interactions? Or is it because one has an ion and another has a dipole?

So, I would suggest looking at polyacrylate and polyvinyl fluoride structures and try to spot whether you can see if there is a presence of polarity? Is there an ion? Is there a dipole? And then try to answer this question.

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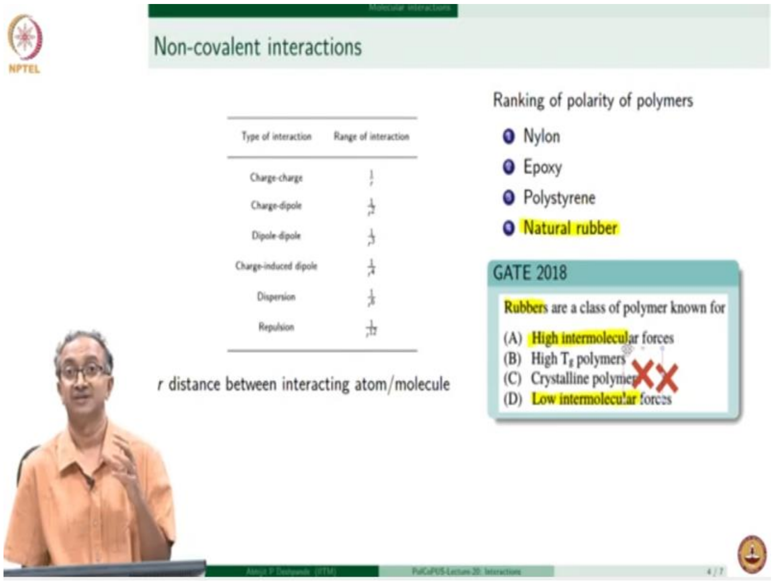

Molecular interactions

Non-covalent interactions

Type of interaction	Range of interaction
Charge-charge	$\frac{1}{r}$
Charge-dipole	$\frac{1}{r^2}$
Dipole-dipole	$\frac{1}{r^3}$
Charge-induced dipole	$\frac{1}{r^4}$
Dispersion	$\frac{1}{r^6}$
Repulsion	$\frac{1}{r^{12}}$

r distance between interacting atom/molecule

Ranking of polarity of polymers

1. Nylon
2. Epoxy
3. Polystyrene
4. Natural rubber

GATE 2018

Rubbers are a class of polymer known for

(A) High intermolecular forces
(B) High T_g polymers
(C) Crystalline polymers
(D) Low intermolecular forces

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We will go ahead and look at some of the specifics of these different types of non-bonded interactions. And what we notice is they are acting over a range of distances. Here, if let's say r is the distance between the two atoms or molecules, which are interacting many of these have a very different range. So, if you look at the interaction as a function of r, they have very different interaction. So, for example, 1 over r to the power 12 will be something like this, while 1 over r will be very gradual. So, some of them are long distance interaction. So, even if atoms and molecules are far apart, they can feel the force of attraction. Just to remind you that derivative of this is nothing but force and all of you remember that charge-charge interaction potential is 1 over r, but the force is 1 over r squared, because its derivative with respect to r.

And, so, given that there are these different ranges over these interactions are present, macromolecular behavior depends very strongly on which of these interactions are present in a material. Of course, these interactions could also be between a macromolecule and the surrounding solvent or a diluent or a monomer, whatever may be the small molecule present along with the macromolecule.

Just to let you think a little bit more on this as an exercise, what you can do is look at these 4 polymers and try to justify why is the rank of polarity given in this way. So, why is nylon ranked as much higher polarity compared to natural rubber? So, again you can go and look at the formula and you can quickly spot, what are the bonds, what are the groups, which are responsible for polarity? One general guideline is that whenever hetero atoms are present nitrogen, oxygen that immediately leads to polarity. Nitrogen. So, therefore, you can try to see whether which of these have that. Aromatic group versus a methyl or alkyl groups again has very different levels of polarity.

So, a generic understanding of what a macromolecule is and what set of interactions are there helps us in understanding what the behavior is. For example, when I have discussed the behavior of nylon and I highlighted that whether moisture is there or not, the commercial companies will always give you a nylon properties dry and under some conditioned sample and so that is because nylon because of its polarity can absorb a lot of water. So, therefore, the behavior of nylon is apparent based on our understanding of what are the nature of interactions that are present.

Just to highlight given that we have placed so much emphasis on the interactions, and of course, in this ranking list, natural rubber is the lowest in terms of polarity and any of these stronger interactions present there. This is a question that rubbers are a class of polymers which are known for high intermolecular forces or low intermolecular forces. Just to give you a hint that these, the middle two are not the answers. It is not the high Tg and it’s not the crystallinity in rubber. So are their intermolecular forces very high in rubber? Or they are low in rubber? Just ponder over this fact.

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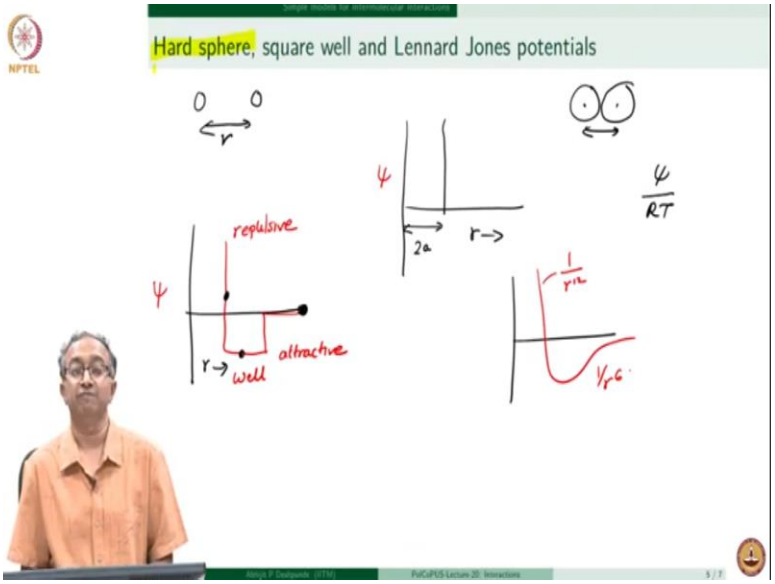

Hard sphere, square well and Lennard Jones potentials

And just to give a get a quantitative feel for the interactions, what we saw is examples of how interaction changes as a function of distance between two entities and so, r is the distance and we look at the interaction. So, for example, excluded volume interaction, if we were to look at, one way to look at it is if this is a molecule and this is another molecule, they can come close and touch each other and as soon as they touch each other, they cannot go any further. So, this is called hard sphere. And if you look at the interaction for hard sphere, it is just an interaction where up to some distance. So, what is this distance related to this distance? So, if a is the radius of spheres, then this will be 2a. So, the idea of hard sphere model is that there is no interaction at all. So, this is like two balls or two carrom coins.

When they are away from each other, even if they as soon as they touch only there is an interaction and that is repulsive interaction, they cannot really get any closer. So, that is a hard sphere model. When we include some attraction, the square well potential is so it includes a repulsion and an attraction. Just go back and try to think in terms of how this interaction potential is repulsive or attractive, whether it is positive or negative. And so, this part of interaction indicates repulsion while this part of so, we have what is called an attractive well. And so, if molecules have distance *r*, then and if they are somewhere this is the distance then what happens is no interaction is felt. If they are this is the distance then they will attract each other, if the distance approaches this then they will repel each other.
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Now, why does this happen? I mean, so, why should if attraction is there, why should the material the two atoms and molecules repel or go apart? Remember that with all of this there is always presence of thermal energy. And so, quite often what happens to these atoms and molecules and how they are distributed with respect to each other will depend on the relative ratio between the interaction energy which is present and the thermal energy which is present.

And of course, the most common example of such interaction is Lennard Jones, which also includes both repulsive and attractive and this is a very strong repulsive force which is indicated as 1 over *r* 12. And then the attractive force is indicated as 1 over *r* 6. So, based on this you can just look at the expression for the Lennard Jones potential and the force which is felt by two sets of atoms and molecules which feel Lennard Jones potential. So, this is all at the scale of macromolecule or molecular level.

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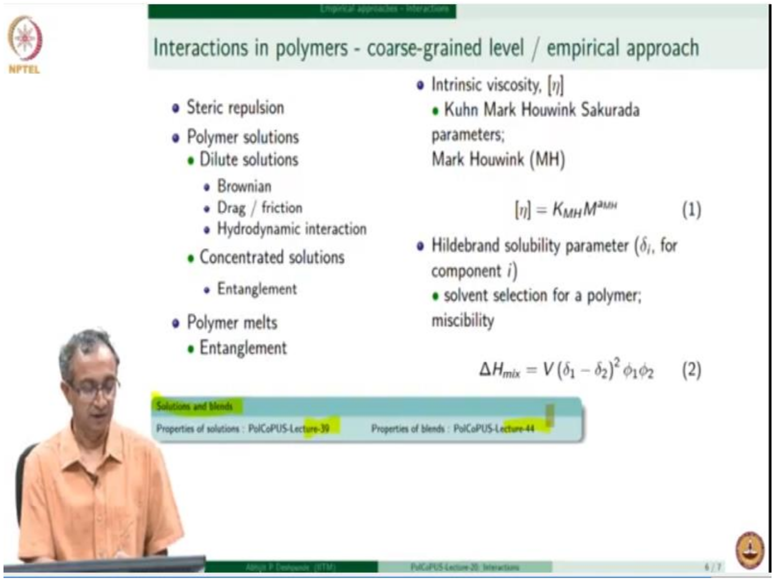

Empirical approaches - Interactions

Interactions in polymers - coarse-grained level / empirical approach

- Steric repulsion
- Polymer solutions
  - Dilute solutions
    - Brownian
    - Drag / friction
    - Hydrodynamic interaction
  - Concentrated solutions
    - Entanglement
- Polymer melts
  - Entanglement

- Intrinsic viscosity, $[\eta]$
  - Kuhn Mark Houwink Sakurada parameters; Mark Houwink (MH)

$$[\eta] = K_{MH} M^{a_{MH}} \qquad (1)$$

- Hildebrand solubility parameter (δ_i, for component i)
  - solvent selection for a polymer; miscibility

$$\Delta H_{mix} = V(\delta_1 - \delta_2)^2 \phi_1 \phi_2 \qquad (2)$$

Solutions and blends

Properties of solutions : PolCoPUS-Lecture-39 Properties of blends : PolCoPUS-Lecture-44

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Now, many times it is helpful to look at broader scales, because in the end, we are interested in bulk response. At the bulk scale what we can do is coarse grain or make averaging of some of these interactions and talk up them on a coarse grained level. So, one example of coarse graining is to say that there is a steric repulsion. So, if we have macromolecular chain and let’s say it has a very bulky group, what we can do is instead of looking at each individual atom which is present in this bulky group; we can say that the two bulky groups actually are sterically hindering each other. While we are analyzing crystallization behavior of such macromolecule or while we are looking at orientation in such macromolecule, we can look at what happens to you to say a steric hindrance or steric repulsion.

So, in this case, we do a coarse graining and look at a broader picture. Similar such things are possible let's say in case of polymer solution, when we say that the macromolecule is flipping back and forth because of Brownian force. How is this Brownian force present? Because there is also surrounding solvent molecules and then there is interaction between polymer and solvent, and so, in this thermal mass of solution which is present the macromolecule keeps on flipping back and forth. So, it experiences a Brownian force. Similarly, we could also talk in terms of the atoms of solvent and atoms of and molecules of macromolecule face friction with respect to each other. So, if let's say we have solvent present in the system, and now, if we are shearing this particular macromolecule, so that some part of macromolecule has to move faster because we have put them in the shearing, then what happens is there is a relative friction between the solvent and the macromolecule and that we can call a drag between macromolecule in solvent.

Similarly, if this part of the macromolecule moves, it will move the solvent around it and because of the solvent which moves then what happens is this part of macromolecule also feels the motion of the solvent. So, therefore, this is called a hydrodynamic interaction. So, these are all interactions not at the molecular scale, but at a higher scale and at the coarse grained scale. If we have concentrated solutions, in which case there are other sets of macromolecules present, then what we will also have are entanglements between different macromolecules. And similarly, in case of polymer melt also entanglements are present. So, depending on the situation molecular interactions or coarse grain interactions may be helpful for us to analyze the bulk response. Even further, if we want to look at some quick engineering decision making and design decisions, then we may also adopt different approaches and two such approaches are based on viscosity measurement, and also based on what is called the solubility parameter measurement.

So, we will have chance later on to define this intrinsic viscosity. It is a useful measure to try to capture what is the interaction between a macromolecule and the solvent and it is called intrinsic viscosity, because we are trying to ask the question that what will be the modification to viscosity if I add exceedingly small amount of Polymer. So, in fact this intrinsic viscosity if you go and look at the definition, the concentration of polymer tends to 0.

If I just add very small amount of polymers to a solvent, what does that do to the solution? And the answer is based on the interactions which happened between the macromolecule and the solvent and this is captured using an empirical correlation called Mark Houwink equation and which basically captures, how does the intrinsic viscosity depend on the molar mass of the polymer and the K and ***a*** depend on a specific polymer solvent system.

$$[\eta] = K_{MH} M^{\boldsymbol{a}_{MH}}$$

So, anytime we are interested in a polymer solvent system and its behavior, we can just look up K and ***a*** from the handbooks and textbooks and references and then get an idea about what is the interaction. Similarly, there is also concept of solubility parameter, which is denoted using delta i for ith component and this is useful for a solvent selection or looking at miscibility in systems and we will again when we discuss blends and solution, we will see that the enthalpy of mixing can be related to how different the solubility parameter for component 1 and component 2. So, if let us say delta 1 is equal to delta 2, then there is no enthalpy of mixing and then we will see that miscibility will be more likely. So, therefore, we will have much more chance to look at these empirical approaches when we discuss polymer solutions and blends in a couple of future lectures.

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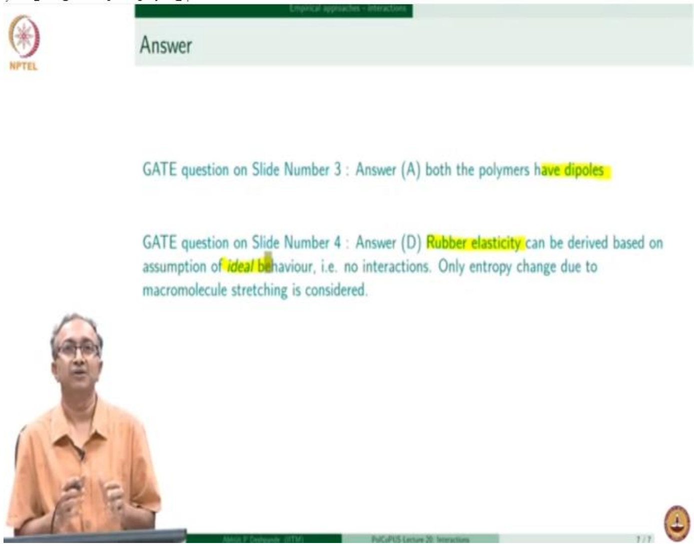

Answer

GATE question on Slide Number 3 : Answer (A) both the polymers have dipoles

GATE question on Slide Number 4 : Answer (D) Rubber elasticity can be derived based on assumption of *ideal* behaviour, i.e. no interactions. Only entropy change due to macromolecule stretching is considered.

And with this, we will close this lecture on interactions, where we did a brief survey of molecular interactions, coarse grained interactions and also empirical approaches to account for interactions. And if you go and look at the polymers and if you did the search related to what is the molecular structure, you can identify the dipoles which are present on both vinyl fluoride as well as acrylate, and interactions may not always be the deciding factor for a given material for a specific question.

And so rubber elasticity, how much will rubber extend as a function of force on it can be answered using a model, which is ideal where we ignore the interactions and only look at entropic variations. Free Energy is combination of internal energy and entropic contributions. And so, internal energy and enthalpy contributions can be ignored, while analyzing rubber elasticity. So, therefore, rubber is an example, especially while addressing its elasticity properties, where interaction between molecules are only present in the form of macromolecule being able to stretch and contract. Therefore, it’s entropic variation alone can explain many of its mechanical behavior. So therefore, this is a very interesting example, to remind us that what is important and what is not important will depend on what is the material and what is the question we are asking. So, with this, let’s pause here, and we will continue our journey with the next lecture. Thank you.