Introduction to Polymer Physics
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Lecture-21
Order-Disorder Transition

Welcome, so we have been discussing about the polymers size and structure in the previous few weeks and we have discuss several models to look at the size of a polymer and lately we discussed like how to characterize the polymer chain. So today we will start discussing about the structure as we have suggested earlier that one of the aspect is like how ordered or disordered the polymer system is and we talk about polymers in general not like a single chain but it can be like a solution of polymers which can be concentrated containing many chains. So we will first take a detour talk about order and disorder in general then I will discuss experimentally how do we characterize order and then I will come back to the theory of behind it or how theoretically we can describe order and then finally will come back to the polymer physics and say like how does we apply those concepts in the polymer systems.

So let us start with the description of order and disorder what do we mean by order- So one way to start thinking about what you mean by order is to start thinking in terms of like how the molecules in the solid or liquid and gas are arranged. How does the distribution of molecules in a volume changes when I go from one phase or one state of matter to other state of matter. So if we know from the ideal gas theory you know that there is no interaction between molecules.

So in a gas the arrangement of molecules are pretty random actually in fact to the ideal gas they can also overlap because we assume the ideal gas to be a collection of point particles. So in that sense we do not really assign any kind of size to the molecules. If I start thinking in a thermodynamic way of course at molecular level one can question that what does the overlap mean so on but in a thermodynamic description it is often better think of gases as like molecules which are like point particles and non-interacting.

It really means is if I start looking from any particular molecule in the gas phase and at any particular distance or distance vector from the molecule it is equally likely to find the molecule at 1 distance and other distance that means that the probability of finding a molecule is independent of distance, this because we have assumed the gases to be either non interacting set of molecules or at most of weakly interacting set, that is what we do for the real gases but what you mean is the probability to find a another molecule at a distance vector 'r' is independent of distance anywhere we go we will have equal probability of finding a molecule then they will say there is no order in the system. So we assume that gas is in what is known as a disordered state. Another way to think of it is in terms of entropy. So in the gas we assume entropy is very high and entropy characterizes disorder. So it means that we have a disorder collection of particle if I start from one molecule I can find another molecule anywhere in the volume with equal probability.

As soon we go to a liquid phase this is no longer true because as we discussed a water molecule tend to form on an average 3 hydrogen bonds with its neighbouring water molecules. Although these 3 hydrogen bonding partners need not be permanent so water molecules can switch a hydrogen bonding partner for a different hydrogen bonding partner, but in general what we have said is on an average a water molecule is participating in three hydrogen bonds so each of the oxygen is hydrogen bonded to one of the hydrogens of other water molecules and the same is true for the hydrogens, and of course the water molecules can switch partners as we said so the next water molecule can come here and this hydrogen bond can go away and a new hydrogen bond can form.

It means at slightly mesoscopic level is if I look at water now then close to any particular molecule in the system there are 3 hydrogen bonds which means that at distances very close to water molecule at small values of r there is some sort of order. Why do I say it some order and not more order the reason is that the water molecules which are nearby they are connected by a hydrogen bond and hydrogen bond itself is very weak so what it means is of course these 3 water molecules are connected to the water molecule in the middle, but then can really wiggle around in their positions as long as they remain close to the water molecule in position. That means that it to the positions of the partners are not fixed but the distances have to be within a range such that it can form hydrogen bonds and the one estimate is around 0.3 or 0.4 nanometre is a typical distance where hydrogen bonds form. So it has to be within that particular distance but there is no particular direction where the other water molecule will be. That is why I would say it has some order unlike the gas molecule where there were no interactions ideal gas even for the real gases the interactions is very weak. In this case of liquid it is still not so strong and it is still weak but much stronger than what we have in the gas.

Now let’s see what will happen in the case of solid however and if I start thinking in terms of say crystals there we have a repeating pattern of molecules. Let us say for example if I think of sodium chloride crystal then you will have an arrangement in solid, something of this sort-

$-¿$
$+¿Cl^{¿}$
$-¿Na^{¿}$
$+¿Cl^{¿}$
$-¿Na^{¿}$
$+¿Cl^{¿}$
$Na^{¿}$

$-¿$
$+¿Cl^{¿}$
$-¿Na^{¿}$
$+¿Cl^{¿}$
$-¿Na^{¿}$
$+¿Cl^{¿}$
$Na^{¿}$

As the positive ions and cations attract the negative ions are anions and so they tend to form a repeating pattern in the bulk what we see is a crystal like crystal structure and what this amount to is repeating pattern of molecules. So now unlike the gas of course there is much more order the molecules are strongly interacting in this case and of course unlike a liquid as well where the order was limited to very small range that is for the first near neighbour we have like hydrogen bond interactions but they also can be pretty much anywhere as long as they remain close to the water molecule.

Now in this case if I look at any particular molecule in a crystal the other molecules cannot be just anywhere else they have to be at specific discrete distances for a perfect crystal that means that we can find the molecules A apart then 2A apart then 3A apart and this is an example of a cubic crystal. If we have different crystal and we will have different arrangements. Similarly along all the axis along the diagonals also we can apply some geometry and see that the distance of the molecules are fixed they can be either the unit cell length or some geometric factor multiplied by the unit cell.

So in this case both for small and large 'r' we have order what I will call henceforth is liquid the order is somewhat short range and in here the order is long ranged and this gives us a way to look at the order and disorder in a material.

So again if I go from a gas to solid the order increases and if I go from gas to solid the entropy decreases and this makes perfect sense because entropy is a measure of disorder. So when we are doing a polymer chain we defined the disorder in a slightly different way we said that the number of possible conformations of a polymer chain are large that means that polymers have high entropy. So that is perfectly in line with what we are discussing here because the molecules in the gas can pretty much be anywhere so there are many system confirmation corresponding to a given density and temperature.

Similarly for the liquid there are many possible confirmation with but lesser than what we have for the gas and in solid we have even lesser number of confirmation because the molecules must form some kind of a repeating pattern and they cannot occupy any position in the space they have to be at certain discrete distances from the neighbouring molecules and this extends to the second neighbouring cell third neighbouring cell and so on. So that is why we call a long range long range order.

So we can say few things about the order and disorders I will make some statements and I will give some physical justification for that and then once we apply these ideas to polymers these concepts can make more sense eventually and also when we discuss that.

So first statement is the order to disorder transition occur with an increase in temperature. In fact order to disorder transition also known in physics as phase transition, not essentially we mean is if I think of water if I go to very small temperatures what we have is ice and ice is of course rather ordered if I raise temperature eventually it becomes liquid water which is as lesser order but still somewhat ordered compared to a gas and then if I further raise temperature I get water vapour that is almost no order.

So not only in the case of this distinct phase transition from a solid to liquid to gas as in the case shown here it can also happen if I look within a phase that means if I look at water at 20 degree Celsius compare to water that 60 degree Celsius compared to water at 80 degree Celsius. They are all liquids but if I look into it the order is decreasing as we raise temperature. This is because the hydrogen bonding decreases. So when I said on an average 3 hydrogen bond that is typically at the room temperature as we raise temperature it can become two and half and two and so on and so eventually at very high temperatures we will have lesson number of hydrogen bond than compared to lower temperature.

So although in a distinct manner we cannot see a macroscopic phase separation happening but the order is changing with the temperature. Similarly if I look at say a crystal at 0 kelvin that is -273 degree Celsius. That is when we have the perfect crystal where the molecules are only present at discrete positions, if I raise temperature let us say crystal at 0 degree Celsius and crystal at 25 degree Celsius. They will be less ordered that means that we will have small vehicles around each of the positions of the molecules, the molecules will have certain vibration around their position resulting in a decrease in the in the order. So again order decreases and molecule vibrations increases.

So ultimately the game is happening because of the change in the entropy as we raise temperature entropy is increasing and entropy always favours a disordered state. Ok. So what this means is we can think of only the 0 kelvin as the point where entropy does not have any effect then we have a perfect order going to the ideal crystal behaviour or perfect crystal behavior I just described earlier as soon as the temperatures become higher than zero kelvin the molecular vibrations start to appear at room temperature they are quite significant although it remains the crystal more ordered compared to a liquid counterpart but still it is less ordered than compared to the 0 kelvin crystal.

Similarly once it becomes water there is first a big order to disorder transition as soon as the crystal dissolves and become a liquid there is a huge change in the in the order it becomes highly disordered because there is a latent heat that is essentially released from there and after that again there are small changes in the order the order is decreasing as we raise temperature again we have a distinct jump at the boiling point and that is when it becomes a vapour. So we can think in terms of two ways of order disorder transition one is the one that is discontinuous in some sense or macroscopic that is when the ice has become water or water becomes vapour and other that is happening with a continuous change in temperature.
So the next statement I am going to make is somewhat related that is order disorder transition occur because of a competition between enthalpy and entropy. So if you look at the energy of the system it has two parts, it has enthalpy part and entropy part. This is the part that is coming from all interactions within the system,

$$G = H - TS$$

Here 'G' is by the way is the Gibbs free energy and 'S' is coming purely from entropy or disorder, now this explains since temperature is in kelvin here that if I go to 0 Kelvin we do not have any entropy term as we go to higher and higher temperatures we have a significant entropy term and so the entropy becomes more and more dominant as we go towards more and more disordered state basically is a restatement of what we have said earlier.

Now third statement I am going to make is that the order can be measured using the average probability of finding another molecule at distance $\vec{r}$ from molecule, this quantity is what we will referred to as a pair distribution function or pair correlation function and we refer to as something called g of ($\vec{r}$¿ . this goes back to the idea we started with the for the case of a gas we said that no matter where I go I will find the same probability of finding another molecules from any given molecule at any distance. As we go to a liquid we start to have some sort of an order every water molecule have some neighbours which are connected by hydrogen bonds but that does not extend to long rangers and in the case of a solid we do have a longer range order this extends to long distance.

So basically the way turns out is if I look at g of ($\vec{r}$¿ versus $\vec{r}$ and I can look in terms of absolute value, at least for the case of a for the gas is a constant for an ideal gas for real gas it is not a constant but it is still close to ideal gas behaviour. If I look at a liquid again we talk in terms of an absolute $\vec{r}$ value because as I said the neighbouring water molecules can be at a particular distance but they can be at any direction because they can orient themselves differently while maintaining the same distance order distance range that is required for hydrogen bond. So we get something of this particular sort what this means is at very short distances we do have interaction that give rise to some sort of a peek at small distances but eventually it really dies off because at long range we do not have any order.

It is also important that we started form 0 here or the origin here and the reason is in the case of an ideal gas we do allow for the overlap of molecules. The molecules can overlap because they are assumed to be like point particles, we do not make that assumption for liquid and for the reasons will discuss eventually for the liquid these overlaps are penalised they are assumed to have a certain size and because of that we always start from 0 and come back to this point as we go in the course.

So and then if I look at this for a liquid and then if I look at a crystal now we can no longer talk in terms of absolute values of r because now there are discrete positions along directions where the molecules are present. So let us say for example if I start from here I find the molecule here it is X and Y another here at distances A but if I go along the diagonal I will find the first molecule at root 2A where A is unit length. The next molecule will come at 2A distance along the x 2A along the y, but 2 root 2A along diagonal and this by the way is a simple cubic crystal the actual distances will change, if I go for different crystal symmetry like body centred cubic for a face centred cubicOk. But what this essentially amount to is there are only certain positions which are allowed and everywhere else this is equal to 0 because we cannot find a molecule in between 0-A only we can find at a and similarly between A-2A. In the case of simple cubic we cannot find any molecule you only find at root 2A, similarly for root 2A to A and so on extend this idea, but there are only particular position where we do see molecule. So this is called crystal actually a perfect crystal to be precise that we look at.

Now there can be departure from this behaviour so if for example think of crystals at room temperature they will not be quite like what they used to be them still has peaks but now the peaks are somewhat broader that allows for vibration round those positions. Similarly for the case of liquid this is one of the ideal cases we can think off but for the real liquid it can be having more than one peak. Similarly for the ideal gas this the behaviour for real gases it can show some behaviour that is not quite a straight line, but close to a gas.

So this also has some analogy in terms of states of matter that is we do not always have something that is an ideal gas or liquid we can have things in between that shows certain characteristics of liquid and certain characteristics of gas. Similarly we can have things between liquid and solid that shows some certain characteristics of a liquid and certain of the solid and so with this g of r we can essentially talk not only in terms of whether the molecule or the system of molecules is forming a solid liquid or gas. But we can talk in terms of how much solid like the molecule is how much liquid like the molecule is and how much gas like molecule is.

For example if we have a polymer gel it is between liquid and solid, we can talk about how much liquid it is and how much solid it is and what happens if I change for example certain parameter that say the amount of solvent contained in there and how the liquid like part and solid like part will change as a function of the quantity I am changing. We will come back to this the basic idea is this particular type of measure will help us characterise the actual amount of order present in the material and characterize whether it is akin to a gas liquid or solid and if not then if it is in between those 2 then how much of liquid it is, how much of solid it is, or how much gas it is, where exactly it fall in the spectrum of the phases that we can obtain.

The next statement I am going to make the order disorder transition can be macroscopically observed what it means is by naked eye in the formal language in certain cases. Let’s say going from ice to water I can see the melting happening similarly water to water vapour. I can see the boiling happening in a microscopic setting we can see by the naked eye.

In other cases where I cannot see using naked eye then I can see may be using optical microscope, so then we say it is a microscopic observation and then as we are going to discuss is in some cases even the microscope will not give you a very high resolution the normal optical microscope and then we can use the idea of scattering.

So and finally related to the statement 5 I am putting here is the Fourier transform of g of r is related to something known as structure function which I will call something like g of q and I will discuss that in next class found using scattering.

So this is all we had regarding the order disorder transition we have made certain statements regarding this transition before that we have discussed what order and disorder means. So in the next class I will start talking about scattering in more detail and tell you how exactly we see that within an experimental setting.

Thank you.