Introduction to Polymer Physics
Prof. Dr. Prateek Kumar Jha
Department for Chemical Engineering
Indian Institute of Technology-Roorkee

Lecture-22
Scattering experiments, Pair Correlation Function

In the last class we have discussed about the order and disorder transitions, order for transitions. So now I will talk about a way to characterize the order and disorder in the experimental setting and as we have already pointed out in the last lecture it is known as scattering. So we will briefly discuss the scattering theory what is known as the Bragg's law that is one of the simplest descriptions of scattering and then I will not derive the complete expressions for the actual result from the setup but I will discuss at a qualitative level what does that mean and how does that relate to the pair distribution function that we have discussed earlier.

The fundamental basis of scattering experiment is the fact that the light when I say light it can be any type of light like UV light, visible light it can even refer to an x-ray or some other kind of a light source but all these kind of lights will have some particle in nature and some wave nature. So essentially just to remind you something about the waves, waves do possess something known as a wavelength that characterizes some sort of length scale of the fluctuations of the of the wave and that is related to something known as a wave number that is called ‘k’.

$$\lambda = \frac{2\pi}{k}$$

This is the one-dimensional sort of a wave. We can generalize to a 3 dimension then we have instead of a λ we have λX λy, λz and essentially will also have a wave vector in place of wave number. This is the real one is called wave number, for a general case will have for a wave vector and essentially what we do in any scattering experiment is let us say we have a sample then we send a light to a certain wave vector that light is then diffracted or scattered and we get a new wave vector and this tell me the magnitude of the obstacle the sample presents to the light source.

The game is between a wave interacting with a particle obstacle depending on how big the obstacle is or how does the obstacle will change the amount of the scattering that we can receive and the amount of scattering essentially is given like something of the order of k’-k. I can reproduce a k using the triangle rule this particular vector become my k’ –k . So we can see if I add k with k‘-k I get the vector k prime.

So that is essential idea of scattering and now will see like how does the scattering give you a different result in the case of solid, liquid and gas. So solid as I said has a repeating pattern of repeating arrangement of molecules. So in a very simple kind of thinking or a simple kind of an experiment we can approximate the crystal nature or the solid nature as a set of infinite planes that we have in the assorted. So let’s say if I looking at fcc crystal I like see a series of 100 or 111 planes depending on how I am cutting it across the solid and each of these planes then in general will have some kind of scattering pattern and this is what we will discuss and this is what becomes the basis of what is known as the Bragg's law.

We will talk about the Bragg's law and the assumption is we are considering the solid to be a set of infinite planes because we think of bulk solid it will indeed have these different planes coming in and then a light source comes in and it is scattered by each of these planes. We have a k and k‘. Now in practice many things are happening.

When the light source comes in hit this infinite set of parallel planes but essentially what matters is how many of them have constructive interference and we only we look at the final result after the constructive interference, destructive interferences will basically cancel out and I am not really going in details here but the basic idea is that we are looking at the superposition of all the constructive interference.

So then if I look at say 2 adjacent planes means let us say i and i+1. And if I look at the scatter through them then if I look at these 2 they differ in the length of the path by these small, this is the length difference that we see between the two waves and scatter between two adjacent planes. Ok, and this is what I will referred to a different in path length. So this may be coming at an angle θ then of course leaves so of course this light also goes to other the planes. So, the net scatter can be something like 2θ and this distance can be‘d’ that is the distance between 2 place, so we have a d here, so we have another θ in between so essentially this particular quantity become dsinθ here and dsinθ there, so different in path length becomes 2d of sinθ and this is equal to n times λ where n is an integer and λ is a wavelength of the fluctuation that we have in the system in the light source.

So I am not really completely deriving it but essential ideas that we have a series of planes and scatter through each of them will give rise to differences in path length but those differences will be integer multiple of the λ of the lights source. So now what this means is-

$$d = \frac{\lambda}{2 \sin \theta}$$

This is the distance between two planes. So that basically means that if I do not know the ‘d’ to begin with and if I know the wavelength of light if I know the scattering angle this I can get from experiment I can get the periodicity of the solid by means of doing this scattering experiment.

$$Difference \in path\, length = 2D \sin \theta = n\lambda$$

So this is the basic idea of scattering experiment that I can do a scatter I can know wavelength of light to start with and I can measure the scattering angle θ and then I can get the periodicity of the surface but then if I have other kinds of solid arrangements this particular approximation we have made of infinite set of parallel planes will not work but the basic essence that we can get the periodicity or we can get information about the order through the measuring of scattering angle and through measuring of the wavelength of a light source continue to work, but it also means if I want to look at structures with a certain periodicity I have to choose the light source of a certain wavelength. For example if this λ value is very small I can look at smaller values of d. On the other hand if λ values are large I can only get larger values of d. So depending on the light source the resolution into which we can go will change and that’s the reason why we have many kinds of scattering experiment available.

We can do electronic scattering, we can do x-ray scattering, we can do of course visible light scattering, ultraviolet scattering and so on. Since they possess different wavelength they essentially are applicable to different length scales that we are interested in. ok. So with this background and without actually deriving the expressions I will present what does the scattering experiment gives you and then we relate back to the theoretical description of the pair distribution function that we have discussed earlier.

So scattering experiment essentially gives you what is known as a structure function-

$$I(\vec{q})=\left\langle \sum_{\alpha\alpha'} e^{i\vec{q}\cdot\left(\vec{x}_{\alpha}-\vec{x}'_{\alpha}\right)} \right\rangle$$

So α and α' are indices over all particles in the system which may referred to molecules or segments depending on the length scales the light source can resolve. So now we can see the I($\vec{q}$) is extensive since we are adding all the possible indices.

If the number of particles increase we will have a higher values of I($\vec{q}$). So we want to have a measure that is independent of the number of particles let's call the number of particles to be 'n'. So we can define an intensive measure that is known as structure factor and in literature there are two ways it is define- in one way we divide by the number of particles and in other way we divide by the volume of the system. In both the cases, since the volume also scales like the number of particles we do get an intensive quantity.

$$Structure\ Factor=S(\vec{q})=\frac{I(\vec{q})}{N}\vee S(\vec{q})=\frac{I(\vec{q})}{V}$$

$$\tilde{S}=S\frac{N}{V}$$

If you looking at any particular literature on the structure factor order scattering then see how exactly they are normalising it, is it by N or by V but both of them are n related.

So now so that the structure factor is basically a Fourier transform of what is known as number density correlation function that in turn is related to the pair distribution function as will discuss.

So, before this I will define the number density- which is similar to the concentration that we have derived when we are doing virial expansion essentially we want where interested in the numbers per unit volume so we can add up δ functions for every particles at a particular position x and since δ function has unit of 1 /volume we do get a number density. So essentially it is-

$$Number\ Density = n(\vec{x}) = \sum_{\alpha} \delta(\vec{x} - \vec{x}_{\alpha})$$

If the particle is at x I will add 1, if a particle is not a x I will add 0 and after summing it over we divide by the volume and we get the number density at a particular location x.

So if I take an ensemble average of the number density-

$$\langle n(\vec{x}) \rangle = \langle n \rangle = \frac{N}{V}$$

We should get the number by volume only for a homogenous system like a liquid the molecules can essentially take up any position of course in a particular confirmation molecules are only at particular position. If I take an ensemble average what we will find is that the number density gives me a number that is simply n/V that is the average density of system number per unit volume. This is not true if we have a solid because in a solid there are only particular position in space where the molecules can be they cannot be anywhere. If I take an ensemble average still you will see there are vacancies in between where the number density essentially remain 0. So only for homogenous systems we can make this particular approximation.

For solid this is a periodic function-

$$\langle n(\vec{x}) \rangle$$

So if I find number density at certain distances we get the same value. Similarly if I find the number densities so again we always see a vacancy that means that if I do ensemble I should get a periodic function which will repeat after certain values of x.

So now I can define number density correlation function- this is written as-

$$C_{nn}(\vec{x}_1,\vec{x}_2)=\langle n(\vec{x}_1)n(\vec{x}_2)\rangle=\left\langle\sum_{\alpha\alpha'}\delta(\vec{x}_1-\vec{x}_\alpha)\delta(\vec{x}_2-\vec{x}'_\alpha)\right\rangle$$

That means what is the probability effectively that if particle is at x1 another particle will be at x2 although we will normalise this probability later but this is what it is. So we look at the case where one particle is at x1 in you want to know where what is the probability where another particle is at x2 thus we define 2 delta functions 1 for x1 and another for x2.

So now if I Fourier transform this particular correlation function, let us see what do us get-

$$\mathit{Fourier\ Transform\ of}\ C_{nn}(\vec{x}_1,\vec{x}_2)=\int e^{-i\vec{q}\cdot(\vec{x}_1-\vec{x}_2)}\langle n(\vec{x}_1)n(\vec{x}_2)\rangle d\vec{x}_1 d\vec{x}_2$$

You can see it is an extension of Fourier transform in one dimension if you are not used to Fourier transform in three dimensions.

So now I can move this thing inside for this let us use the expression that I have just discussed. So now I will move this in and you know that if I integrate a δ function over the entire volume and I multiply the δ function with a function-

$$¿\left\langle\sum_{\alpha}e^{-i\vec{q}\cdot\vec{x}_\alpha}\sum_{\alpha'}e^{+i\vec{q}\cdot\vec{x}_{\alpha'}}\right\rangle$$

$$¿\left\langle\left(\sum_{\alpha}e^{-i\vec{q}\cdot\vec{x}_\alpha}\right)\left(\sum_{\alpha}e^{-(-i\vec{q}\cdot\vec{x}_{\alpha'})}\right)\right\rangle$$

$$\langle n(\vec{q})n(-\vec{q})\rangle$$

So essentially what we can conclude from here is if I Fourier transform the number density correlation function what essentially I do get is my structure function. Because this is what get after I get the fully transformation ok. So this a gives me I (q). So now we have a perfect relation we can theoretically get the number density correlation function or through by simulation we can get that quantity and I will fully transform that and I will get the structure function that I can then get by experiment and then we have one way to compare the theory with experiments, there is a catch however the catch is that the inverse is not possible let's say that you do an experiment and you do get I(q). I cannot back calculate the number density correlation function. Because the inverse Fourier transform turns out to be difficult than compared to the direct Fourier transform.

So we can do for certain cases particularly if we have like homogenous isotropic fluid in that case inverse Fourier transform can be possible. But in general we can easily get I of (q) by structure function by Fourier transforming our number density correlation function but we cannot to the experimental I(q) inverse Fourier transform and get back the theoretical value. This remains the challenge it is called the inverse problem in mathematics.

So I will stop with this in next class we will discuss what is known as the pair distribution function which will essentially be a function of this number density correlation function and from there we will go to the discussion of the particle simulations especially the Monte Carlo simulations of polymers and then we will see how we can use those simulation to get number density correlation function for the pair distribution function that we discuss. So that you can have a systematic way of looking at the structure of polymer systems.

Thank you.