

Introduction to Polymer Physics
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Lecture-18

Flory Theory for Bad Solvent, Self-Similarity and Fractal Nature of Polymers

In the last class we have discussed the Flory theory for good solvent and we have been able to derive the scaling law for the self-avoiding walk that is essentially R that that we can think of as-

$$SAW = R \sqrt{\langle R_g^2 \rangle}$$

$$R \propto M^{\frac{3}{5}} \nu^{\frac{1}{5}}$$

If I now I extend the idea to bad solvent case there is a problem and the problem is we also had $\nu^{1/5}$ there and the ν can be negative in the bad solvent case and is negative in the bad solvent case and so we give get like an imaginary value of R which is not possible and then what we said is we have to go back to the real expansion and keep in mind that three body interaction that we have ignored for the good solvent will become important for the bad solvent case. So you must include that and now I will show you like how does it counter particular problem and how do we get scaling law for the bad solvent case.

So we are doing the Flory theory for the bad solvent or poor solvent. So we again do the approximation that we made earlier that the total energy is additive we can add the elastic energy and interaction energy, but now in the interaction energy term. If you recall from what we derive the real expansion,

$$U = U_{elastic} + U_i$$

$$U_i = \int d\vec{r} \left[\frac{1}{2} \nu k_B T c(\vec{r})^2 + \frac{1}{6} w k_B T c(\vec{r})^3 \dots \dots \right]$$

U_i

In the earlier case we only considered the first term and now we will consider both first and second term, I will see like what difference it makes, the earlier one was for v higher than 0 and now we do it for v less than 0. We have given argument that there be more three body interaction with the change is collapsed simply because the number of contacts as equal to the collapse chain.

We again make the other approximations that we have made that is my elastic energy we take it to be same as that we have got for an ideal chain and we still assume that the concentration C can be approximated as a uniform concentration where we ignore the connectivity of polymers segments-

$$U_{elastic} \frac{R^2}{M b^2}$$

$$c(\vec{r}) \approx \tilde{c} = \frac{M}{R^3}$$

If I include the U_{int} scales we get-

$$U_{\tilde{c}} = k_B T \left[R^3 v \left(\frac{M}{R^3} \right)^2 + w R^3 \left(\frac{M}{R^3} \right)^3 \right] + k_B T \left[v \frac{M^2}{R^3} + \frac{w M^3}{R^6} \right]$$

$$U = k_B T \left[\frac{R^2}{M b^2} + v \frac{M^2}{R^3} + w \frac{M^3}{R^6} \right]$$

So in totality what we now have is the total energy of chain is sum of the elastic energy and the two body terms and 3-body terms. So now you play trick here and the trick is that M is very higher than 1 and that we already assume that the chain is very long. Ok, but also happens in the case of a collapse chain is R is very small.

So if I look at the first term here the first term will be very small compared to the other two terms simply because it has M in the denominator a large quantity in denominator others have in the numerator and also it has R in the numerator R is small others have R in the denominator and so we can essentially drop the first term from here that we can do for the for the bad solvent case. Essentially now the competition which was earlier for the good solvent case between the elastic

energy and 2-body interaction is now the competition between the two body interaction and three body interaction for the bad solvent case.

So now you can note few things here, the first thing the first term is negative because v is less than 0 and of course M & R are positive. We don't yet know about the sign of w we have to think

of like what should be its sign that we can get by looking at the $\frac{\partial U}{\partial R} = 0$ that is the energy minimization condition that we have used earlier.

So let us do the same thing we did earlier keeping in mind that now the V is negative. So this gives me-

$$\frac{-vM^2}{R^4} - \frac{wM^3}{R^7} = 0$$

$$R^3 \frac{w}{v} \cdot M$$

We have taken v to be less than 0 that means w also has to be so, in this case what we get is R^3 is minus of this, so if v is less than 0 then to make this R positive w has to be higher than 0. That is a requirement that the three-body term the coefficient must be positive, if the 2-bodies term coefficient is negative. Ok, if this is not true then in that case we will not get a positive value of R , so it must be true by this kind of a scaling theory idea it turns out that indeed is the case if I do a more rigorous derivation.

So if we keep that in mind then we get-

$$R \left(\frac{-w}{v} \right)^{\frac{1}{3}} M^{\frac{1}{3}}$$

Therefore, $R \propto M^{\frac{1}{3}} \wedge R^2 \propto M^{\left(\frac{2}{3}\right)}$ so again now comparing to the ideal chain which was r-squared scaling as $M^{2/3}$, $2/3$ is less than 1 the chain is more collapsed compared to the ideal chain and of course the self-avoiding walk (SAW) what we have discussed earlier.

So to summarise what we have discussed for the good solvent and bad solvent case and also including the ideal chain we have derived earlier. We can write R in general to be like scaling like m to the power a coefficient μ or M scaling like-

$$R \propto M^{\nu} \vee M \propto R^{1/\nu}$$

Where, $\nu=1/2$ for random walk (ideal chain), $\nu=3/5$ for self-avoiding walk (swollen chain) and $\nu=1/3$ for collapsed chain.

We can also talk in terms of ν and temperature to the first case is realised when $\nu=0$. The second case is for ν higher than 0. The third case is for ν less than 0. So the first case is for $T = \theta$, the second case is for T higher than θ and third case is for T less than θ , θ being the temperature where ideal change behaviour is established.

So now I want to take somewhat the detour from here and talk about some other behaviour of polymer chains and will come back to this particular scaling law that we have derived. And see how exactly it tells something about the structure of the polymer. Ok, before we go into that I want to take a smaller detour and talk about something that is known as self-similarity and something as known as fractal nature of polymers. So let us talk about to other 2 features of a polymer chain that it shares with many other objects So they are subjects of their own will be very briefly describe about this features. The first one is self-similarity and second one is fractal nature.

So what self-similarity means if I zoom in into a polymer chain that is undergoing is an ideal thing like behaviour like a random walk or self-avoiding walk or collapse chain irrespective of like what condition that changes if I zoom into it I will essentially see the same type of object

because the number of segments are anyway huge that means that if we look at large polymer chain like this and if I say zoom into a particular region here I will still see the same thing same kind of a polymer chain. Again if I zoom into here I will still see the same kind of a chain, right don't go really by the scale here. So we can change the resolution of our camera, the way of looking into and will look at the same kind of structure at all scales and this happened because M is very large, there is another way to think about it. If I think of say a freely jointed chain model containing say 10000 segments compared to the case of a freely jointed chain model saying 100 segments or 50 segments, they both look identical and so similar scaling behaviour ok. So the scaling behaviour the way we look at the chain does not really change no matter how we for what resolution we look into through the camera. This is the feature that is unique to polymer chains and some other object that they possess it is not present in everything else you think of like let us say if I zoom into a sphere or just. So if I zoom in their let say if we have a disc if I zoom in there may be I will focus on a particular order of the disc and I will see maybe an structure that does not look like a disc anymore and if I zoom in further I will see something else you can look at a particular edge for example the of the disc the same thing we can extend to any other say anything regular shape if I am zooming in I am looking at a particular corner or else or some part or some portion of the chain and they will look very different than compared to the original shape that we started with. This is what makes polymers different way they have what is known as a self-similarity that is independent of scale independent of where I look into it.

The only ideas that the number of segments has to be very large of course if I go to the level of $M=1$ then that in that case we will look at the molecular conformations of carbons and level of course with different than compared to the case that we see larger values of M Provided M is large enough we will look at the polymer chain as a Gaussian or the self-avoiding random walk and it will be somewhat independent of the scale and resolution. That's one feature that very unique to the polymer chains and some other objects.

The other feature is if I look at the number of units or the number of atoms or particles present in the system distance R from a particular point that shows very particular scaling than compared to

regular objects we are used to see. So if I look at the number of say particles or constituents or segments at certain distance R and let us call this as N of R , then if I have a one dimensional object like a rod then the more distance I cover the more particles I will see in the object and I can really say that the number will go like R . ok. So think of it like the rod is built up of segments like and if I count these segments then the longer distance I look the more particle or segments I will see and it is simply proportional that the number proportional to the distance I am looking at.

If I look at 2D object let's say if I look at a circle and I start from the origin and if I look at objects at a distance R , now you can very well expect that the number of things we will see proportional to the area. In this case in proportion to the length for one dimension, for 2D is proportion to the area and so the number will go like R^2 , other way to think about it is in the one dimension case I can think of a line density and if I multiply the line density with the length then we get the number of segments for unit. In the case of 2D we can think of a surface density that is we have to multiply the surface density with the area to get the number of units or objects or particles. Similarly for 3D let us say we have a sphere the number of segments go like R^3 so in general what we can say is for solid objects:

$$n(R) \propto R^d$$

Where, d is the dimensionality.

Now if I look at the polymer chain this behaviour is not observed because we have just derived the previous class the scaling laws for the good solvent case and we just discuss the scaling laws for the bad solvent case and essentially this n of R correspond to our M in the scaling law and if I look at that we have got R going like M^{ν} , so M that is equivalent of (n of R) is going like R to the power $1/\nu$ which is not the same as the dimension that we are working with.

For example so the ideal chain in any dimension and this we have shown using a description of a drunkard walk in one dimension we are going left and right. Then still we got R going like

square root of M , then we did the case of two dimensional walk on a lattice we still got the same scale in law we can do it for any dimension lattice we still got the things scaling law. So for an ideal chain of any dimension v . $1/v$ is simply equal to 2 become v is equal to $1/2$ ok.

So what we can then say for objects that do not have $n(R)$ going like R to the power d with the dimension that we are working in they are called a fractal, and in general they follow some other scaling that we can call the fractal dimension.

So now the fractal dimension of the course is $1/v$ for the models we have discussed. So it is equal to 2 for an ideal chain it is equal to $5/3$ for self-avoiding walk, it equal to 3 for the collapse chain which at least for the 3D case it equal to the d , that is the first two can be considered the fractal to be more specific the ideal chain in 3D can be considered a fractal, an ideal chain in 2D has the $df=d$ in that case we can consider it has not been effective.

So this is the idea we will build upon so before we go further into it just like we have done for the ideal change case we looked at one dimension, two dimensions and in general z dimension walk for a lattice. Let us see how the Flory theory helps us when we are trying to do scaling law for general d dimensional walk.

So I will discuss that in the next class, so thank you.

