Introduction to Polymer Physics

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Lecture-19
Derivation of Fractal Dimension, Concentration Regimes and Overlap Concentration

In the last class we have discussed about the Flory theory for the good solvent case and the bad solvent case and we have got this scaling relations and then towards the end I discuss about the self-similarity of the polymer chains and the fractal nature and we said that the number of segments at a distance R does not go like R^d, as for a solid object d being the dimension we are working in so if it is like a solid rod or a disk or a sphere you basically have the proportion the scaling relation for the number of segments at a distance R within a distance R to be like R^d.

In the case the polymer chain it is not true we can have m going like R to the some other power df is not equal to d and if that is the case we call this fractal, so we have done this briefly for the free dimensional case. So what I will do now I will do Flory theory analysis for a general d dimensional walks for different cases. So you already did for ideal thing we have done the one-dimensional drunkard walk 2-D walk on a lattice and the three dimensional or general z dimensional walk and we have found that this given relation is unchanged. So now you will do it for the case of the self-avoiding walk and the collapse chain that we see in the good solvent case and bad solvent case. So and then we see like how the fractal dimension of these walks depend on the dimensionality.

So let's get started with the self-avoiding walk in d dimensions that we get from Flory theory. Again the Flory theory basically refers to the idea that the contributions of energy are additive and then we take the elastic energy as that of an ideal chain the excluded volume energy with take it as of a segment gas where concentrations are uniform, and not all theories of both had done by Flory himself but this basic assumptions are what is referred as Flory theory in literature

So let us look at the self-avoiding walk for the case of V higher than 0. If you recall we look at the competition between the elastic energy and two body interaction assuming that the higher order interactions in concentrations are smaller compared to the two body interactions and essentially for the elastic energy we are using the relation we derived-

$$M \quad R^{df} \wedge df \neq d$$

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

$$\int \text{¿} = \int d\vec{r} \frac{v}{2} k_B T c(\vec{r})^2$$
$$U_{\text{¿}}$$

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

We assume that the concentration is uniform in the volume, so now the analogous quantity of volume in two dimension would be the area in one dimension will be the length. In general we are interested in the number of segments in R^d because R^d is the relevant volume or surface area of the length depending on the dimensionality we are interested.

So now,

$$\int \text{¿} \quad R^d v k_B T \left(\frac{M}{R^d}\right)^2 \quad v k_B T \frac{M^2}{R^d}$$
$$U_{\text{¿}}$$

$$\int \text{¿} \quad k_B T \left[\frac{R^2}{M b^2} + \frac{v M^2}{R^d}\right]$$
$$U = U_{elastic} + U_{\text{¿}}$$

Now I will again use the same idea that we have used for three dimensional case, we take the minimization of this u to get the size.

$$\frac{\partial U}{\partial R}=0$$

$$\frac{R}{M b^2} \quad \frac{vd\, M^2}{R^{(d+1)}}=0$$

$$R^{d+2} \quad v\, M^3$$

$$R \quad v^{\frac{1}{d+2}} M^{\frac{3}{d+2}}$$

So, now since the fractal dimension df is defined in this particular way what we get from here is-

$$d_f=\frac{d+2}{3}$$

In case of 1-D $d_f=1,$ So in this case it behaves like a solid object and you can see why this is a case because imagine a walk in one dimension that is self-avoiding what it means if you remember the drunkard walk idea that the drunkard can only walk either to the left or to the right in all the steps as every time he makes the opposite move it will lead to an overlap. So essentially in this case what we recover is a relation we derive for a rod, so the distance travelled by the drunkard will be scaling like the number of steps ok. So in this case it is not a fractal.

However if we have 2D then we get d_f=4/3 this is fractal. So I can see in 2D we do not need to be like avoid any direction we can move in both X and Y is still avoiding overlap. This for example contains steps which are both in the X and Y directions and both in positive and negative directions, but still it is self-avoiding because there are no overlaps of steps. So this is fractal and for 3D of course d_f=5/3.

Since we are departing from the Euclidian idea of dimension, a fractal dimension like a fraction really so it is very difficult to think in terms of an actual dimension that were used to see with is not a one dimensional space or two dimensional space of 3 dimensional space. So the derivations we are doing are for an arbitrary dimension d so we can plug in d=4, 5, 6 whatever we want to the assumptions made in the model will still hold in that particular case if we want to depart from the Euclidian idea of dimension.

So let us see like how it happens in the case of the poor solvent collapsed chain that is when v is less than 0. So in this case we assume that the elastic energy is less than the two body interaction and we also noted that we have to include a three body interaction just to make sure that R does not end up becoming imaginary and we will make the same assumption here. So u can be approximated by simply the excluded volume part which again by virial expansion is-

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

$$U \approx U_{¿}$$

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

$$R^d\left[v k_B T\frac{M^2}{R^{2d}} + w k_B T\frac{M^3}{R^{3d}}\right]$$

$$k_B T\left[v\frac{M^2}{R^d} + w\frac{M^3}{R^{2d}}\right]$$

So again we will make the same exemption about the minimization of energy to get the R, so we have,

$$\frac{\partial U}{\partial R} = 0$$

$$\frac{-dv M^2}{R^{d+1}} - \frac{2dw M^3}{R^{2d+1}} = 0$$

$$R^d \quad M$$

So again this is not a fractal, so just like we have derived for three dimensional case we can show in general that for the collapsed chain case that is the poor solvent when v is less than 0 the polymer chain is not fractal, it has a scaling of same like a solid object. So, we only referred to the scaling law for this R or M we do not talk about structure the object of course the polymer chain even in a collapsed state will have a different structure compared to say metal ball, will come to that later. All we are saying is a scaling law behave similarly to a solid object, so the relation that we have derived is the scaling relation can also be useful in other cases, so one particular example is the case when we think beyond a single chain in the system.

So if you think of the actual experiment you do not have this one chain, you have an ensemble of things present in the system. So only in the very dilute limit, that is for very low polymer concentrations we can imagine that polymer chains are far off from each other and each of them are following say whatever statistics we are assuming.

So let us say if we assume the random walk statistics that we assume that it is an ideal chain. So in that case it will remain an ideal chain only if we consider that there is no interaction between different chains in the system, so only when they are like far off in the volume they can show that scaling law for the ideal chain for each of in this case each of them will show scaling law for ideal chain if I assume that the system is θ solvent or $v=0$.

However if I increase the polymer concentration eventually what will happen is these polymer chains will start to come together. Ok, And once they start coming together they get like entangled with each other ok, so closest analogy one can think of is like a noodle, ok, so every chain in the in the system will be like a noodle piece but then as they come together they get entangled and in that case the polymer chain behaviour is affected by the other polymer chains in the system.

So the overlap will start to happen at particular concentration which we can imagine in this following way. What we can imagine is can imagine that there will be a situation where the polymer chains are sufficiently close together if not overlapping at certain concentration and the after this point if I go to even higher concentrations then the polymer chains will start to overlap and then what we have is essentially arrangement where you cannot differentiate where one chain in did started like what you see in noodle. As you raise the concentration polymer concentration you see that in the very beginning it is in an range that is referred as a dilute solution and then in between when did just start to overlap it is referred as some semi dilute condition and then at even higher value we have a concentrated solution and of course if I further raise the polymer concentration we have a limit when the system only contains the polymer it has no solvent. So that will correspond to what is known as polymer melt i.e. no solvent available for very little solvent present.

So let us say that there is some concentration let's say C* which we call the overlap concentration where this happens then for C less then C* star we are in the dilute range and for C higher than C* we are in the concentrated range. So now when it starts to overlap we can imagine that every chain is contained in a volume and we can represent the volume by say a sphere and then those volumes are just touching each other and there is no empty space in between those volumes but anyway there must be some polymer chain also here and so on, such that within that small volume there is only one polymer change content that's theoretical way to look at the overlap but it helps is it helps us to find the overlap concentration ok, these guys are often referred as a blob, where the blob may have different meaning in different context but the idea is the show some kind of a confinement of a polymer chain on the segments for polymer chain within a certain volume.

So at overlap concentration blobs touch each other. And in that case we can think of that the polymer concentration in the entire beaker or whatever volume by looking at is the same as the polymer concentration inside those blobs. So there is one way to see that will it say if I also think of like putting a blob here then for dilute case we can see that inside the blogs the concentration will be higher, but if I look at say here or here any other empty space concentrations are very small. But once we go to the semi dilute regime then in that case the blobs occupy the entire beaker there is no vacant space left for the concentration inside the Blob becomes the concentration in the overall volume and this helps us to find the overlap concentration.

So and we know what concentration inside the blob is it is-

$$C^{¿}\ \frac{M}{R^3}$$

You know this scaling law for R with M so let us say for the ideal chain case R is going like $M^{½}$. So we can say C* goes like $M^{-0.5}$. We can extend the idea also for the self -avoiding walk and the collapsed chain. So in general R is like M^{v} so C* is M^{1-3v} which is $M^{-0.5}$ for ideal chain, $M^{1-9/5}$ that is -0.8 for self-avoiding walk and it is simply 1 for a collapsed chain.

Now you can see that since entanglements will start to occur beyond the same the semi dilute concentration. And the concentration at which the semi dilute concentration is achieved or semi-dilute regime is achieved given like $M^{-0.5}$ and $M^{-0.8}$ for the ideal and self-avoiding walk cases and we assume that M is much higher than 1 what is turn what it means is at very low concentration itself because it going lot like 1/m and M it is already high. So even at a very low concentration for example 1 mill molar or below we start to see overlap of polymer chains. The polymer chains start getting entangled other way to think about is although we have developed the scaling models for dilute solution, they can be very difficult to realise in the concentration ranges we typically are used to that will happen at very small concentrations.

However if the chain is collapsed anyway it is occupying very small volume so the blobs will also be small. So the condition when blobs touch each other and fill the entire space will take a higher concentration to reach and that explains why entanglement will take longer time to happen in the collapsed chain case or in bad solvent than compared to the case when we are in a good solvent or θ solvent.

So where we are now going is going towards the behaviour of multiple chains all the models we have done was for the single chain. So now we are going towards multiple chain what will also show eventually in this course is we can start doing a thermodynamic kind of models or derive equations of states of polymer chains for polymeric systems just like we do for other liquids and solids and we will come back to this point later.

So I want to stop here and will start with this in the next class thank you.