Introduction to Polymer Physics
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Lecture-37
Brownian Motion- II

Welcome in the last class we started discussing the Brownian motion and so far we have discussed what Brownian motion is and how do we characterize the magnitude of fluctuations by using correlation functions- the autocorrelation and cross correlation.

So, now I will take it further the discussion that we started so what we said is the autocorrelation function is an even function by the time translational invariance that was like only the difference between the two point time points is important not the origin of time and what we also said is due to scientist name Onsager the same property also holds for a cross correlation function. So, just to recall-

$$C_{ii}(t)=C_{ii}(-t)$$

$$C_{ij}(t)=C_{ij}(-t)$$

$$C_{ii}(t)=\langle \Delta x_i(t)\Delta x_i(0)\rangle$$

$$C_{ij}(t)=\langle \Delta x_i(t)\Delta x_j(0)\rangle$$

Both of them essentially fluctuate around a mean value $\acute{x}_i$ so Δx_i is the deviation from the mean value with time.

So, now there is a detail here that is not really of much concern to us but it must be stated that although the first one is quite general the second one only applies to two properties that depend on positions and momentum of particle this is true for the dipole movement that depends on the position of particles. It is actually true for many properties that only depends on position and momentum. It is not true for other properties that we typically do not care about in polymer physics but you can read about the cases where this relation is not true.

So, now what this evenness of these functions, so I am doing like Ct versus t it is true for both, C_{ii} or C_{ij} it tells me that if I say go forward in time or if I go backward in time I would essentially see the same behavior that is to say that if I have say a video playing and if I do like reverse the video I play it like in the backward direction I would see the same things happening right that is of course not true for actual video because if some things happen in some direction in the forward direction we will see things happening in opposite direction. So, let us say a person dies in the video you cannot go back because you will not have a death occurring in the backward direction right. So, but it is only true it will be true when the system which is equilibrium because at equilibrium the rate of forward processes become same as the rate of backward processes that is at equilibrium it does not matter if I am going in the positive time or if I am going in the negative time.

Now this very concept has a much philosophical I would say philosophical significance in terms of how we view life. For example when we view life we always think about time that time is passing and we are going from here to there and time for us only goes in one direction we cannot go back in time we cannot do a time travel in the backward direction and this is true because we are not in a state of equilibrium. If we are in a state of equilibrium then we could be it could be possible for us to go in the minus time and actually thermodynamics present a limitation that prevents time travel in the first place because since things have a tendency to go to equilibrium we cannot really go back in the opposite direction because in one direction we are going towards equilibrium in opposite direction we are going away from equilibrium and only the direction towards the equilibrium is favored not the direction opposite from the equilibrium only when we reach equilibrium we can say that now the time is immaterial that for us of course the time when we die because then we are nested of equilibrium and no time travel is any way meaningless.

So, this really explains our understanding of forward and backward processes. So, with time we can have forward processes backward processes once we have reached equilibrium then the rate of both the forward and backward processes become equal and now it does not matter if I go in + t or – t. In fact if you think of like all the laws of nature it is only the thermodynamics the tendency of system going to equilibrium that poses a limitation to go to –t because in every other equation let us say Newton's laws of motion with no problem I can put a -t instead of t and the equation is still valid right. So, we can think of a car going in this direction or car coming backward there is no contradiction if I put t = -t in the laws of motion. Only in thermodynamics we have to decide upon a direction of time and that determination is by the tendency of system to go towards equilibrium and that is why we say that once we have attained the equilibrium state then it does not matter then we can go in + t or - t and this particular principle that I am discussing is what is known as a time reversal symmetry that applies for fluctuations at equilibrium.

A video being played will look the same in the forward or backward direction you can think of a system at equilibrium where it must show these two strong properties that we have discussed time translation invariance and time reversal symmetry they are better ways to characterize equilibrium then say for example to look at a property that is being constant because a system can be in some sort of in a steady state for example let us say water is flowing in a pipeline this is not an equilibrium system water is moving at a velocity V properties are indeed constant the density of water the velocity of water and so on but it does not satisfy the time transnational and time reversal symmetry if we go back in time or if I change the origin of time that particular behavior will not be the same it will depend on the origin it will depend on the direction of the time and so on.

So, only the systems which are at equilibrium which are at thermodynamic equilibrium so as to speak will satisfy these two relations and that is why they become very critical to our understanding of Brownian motion occurring at equilibrium.

So, now if I start thinking in terms of this time reversal symmetry now we can see why the cross correlation function has to be even because if I start from time reversal symmetry then-

$$\langle \Delta x_i(t) \Delta x_j(0) \rangle = \langle \Delta x_i(-t) \Delta x_j(0) \rangle$$

And then my time translational invariance which anyway holds true for both autocorrelation and cross correlation function this has to be equal to-

$$\langle \Delta x_i(0)\Delta x_j(-t)\rangle = \langle \Delta x_i(0)\Delta x_j(t)\rangle$$

Now it turns out that instead of looking at just the autocorrelation or cost correlation in terms of the deviation from a mean value it is sometimes more convenient to talk in terms of displacements instead of the deviation from a mean. Let us say if I am looking at the position of a particular particle in the system. Now there is a mean position but the mean position can be like anywhere in the system the mean position is not really constant for different particle in the system what we can specify is the initial position and talk about displacements from that position and in that sense we can define the displacement correlation function and which will become useful to us in what we will do next.

So, let me also define what is known as displacement correlation function which can be-

$$\langle (x_i(t)-x_i(0))(x_j(t)-x_j(0))\rangle$$

So, although I talk about displacement it should not always be in terms of like only the length displacement does not have like a meaning in terms of dimension it can also mean for example change in any property from an origin of time how much the property has changed and that change is what I call displacement.

So, this I can also write in terms of deltas because the mean values anyway will cancel out. So, this will also be equal to-

$$¿\langle (\Delta x_i(t)-\Delta x_i(0))(\Delta x_j(t)-\Delta x_j(0))\rangle$$

So if I expand this thing what I get is-

$$¿\langle \Delta x_i(t)\Delta x_j(t)\rangle + \langle \Delta x_i(0)\Delta x_j(0)\rangle - \langle \Delta x_i(t)\Delta x_j(0)\rangle - \langle \Delta x_i(0)\Delta x_j(t)\rangle$$

Now in this case the first two terms are same by the time translational invariance. Since both of them are separated by 0 t - t is 0 and 0 - 0 is 0 and the last two terms are also same by time reversal symmetry, so t - 0 is opposite of - t so 0 -t is - t actually we use both time reversal symmetry and time translation invariance to get the second result. So, what I get then is-

$$2\left[\langle \Delta x_i(0)\Delta x_j(0)\rangle - \langle \Delta x_i(t)\Delta x_j(0)\rangle\right]$$

So, now just like we can have a displacement correlation function. We can also talk about something like a velocity correlation function that would characterize the rate of change of position instead of positions themselves again keep in mind that the system is still at equilibrium and we are talking about the motions because of fluctuations not really a bulk velocity for the system at non equilibrium, in this case equilibrium is still holding.

So, we can also define the velocity correlation function, again the velocity is the rate of change of any property with time not really only the position with time the velocity is defined in a more general sense. So, maybe I will put the velocity under quotes just like the displacement just to characterize that it is for any property not really only for the change in position. So, this I can define as-

$$\langle \dot{x}_i(t)\dot{x}_j(t')\rangle$$

that is the velocity correlation for i and j at time t and t'. We have not yet said that this will also satisfy the time translational invariance so we have written in terms of t and t'. So, now and dot represents the time derivative. So, now this I can write as-

$$\langle \dot{x}_i(t)\dot{x}_j(t')\rangle = \left\langle \frac{\partial}{\partial t}\Delta x_i(t)\frac{\partial}{\partial t'}\Delta x_j(t')\right\rangle$$

So, now this I can write as the change in Δx_i with time and the change in Δx_j where we have t' now and I can move the derivatives outside this would be-

$$¿\frac{\partial^2}{\partial t\,\partial t'}\langle \Delta x_i(t)\Delta x_j(t')\rangle$$

Now the first thing I can do is I can write $\langle \Delta x_i(t) \Delta x_j(t') \rangle$ as $\Delta x_i(t-t') \Delta x_j(0)$ this comes by virtue of the time translational invariance and then we can note that now we have a function that is some function of t - t' So, what it means is if I do the derivative with respect to t' this would be minus of the derivative with respect to t just because the function is of t - t' so the derivative with t' should be minus off derivative a with respect to t. So, this would be I can write this as something like-

$$¿-\frac{\partial^2}{\partial t^2} \langle \Delta x_i(t-t') \Delta x_j(0) \rangle$$

So, now I can express the velocity correlation function in terms of the cross correlation functions of the positions or again the positions can really mean the actual value of whatever property we are looking at and then using that we can go ahead and connect to the displacement correlation function and that is what we will do now. So, now what we can write from the previous thing is-

$$\langle \acute{x}_i(t) \acute{x}_j(0) \rangle = \frac{-\partial^2}{\partial t^2} \langle \Delta x_i(t-t') \Delta x_j(0) \rangle$$

And we already know the displacement correlation function-

$$\langle (x_i(t)-x_i(0))(x_j(t)-x_j(0)) \rangle = 2[\langle \Delta x_i(0) \Delta x_j(0) \rangle - \langle \Delta x_i(t) \Delta x_j(0) \rangle]$$

So, if I take a second derivative with respect to time on both the sides. I get-

$$\frac{\partial^2}{\partial t^2} \langle (x_i(t)-x_i(0))(x_j(t)-x_j(0)) \rangle = -2 \frac{\partial^2}{\partial t^2} \langle \Delta x_i(t) \Delta x_j(0) \rangle$$

This is the velocity correlation function that we have derived. So, what it means is I can write this as-

$$\langle \acute{x}_i(t) \acute{x}_j(0) \rangle = \frac{1}{2} \frac{\partial^2}{\partial t^2} \langle (x_i(t)-x_i(0))(x_j(t)-x_j(0)) \rangle$$

This means we can write the velocity correlation function as half of the secondary second derivative with respect to time of the displacement correlation function.

So, far we have been like setting up the language to discuss the Brownian motion and we will extend that of course to polymers in the classes that we come later. So, in the next lecture I will start from this particular this particular point and take the discussion further regarding the Brownian motion of the systems in general and of course we then take it to polymeric systems with that I conclude here, thank you.