Introduction to Polymer Physics
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Lecture-36
Brownian Motion- I

Welcome, so far in the course we have discussed about the behavior of single polymer chains and the random walk models in that context and then we started looking at the behavior of a polymer solution or a polymer melt that contains many, many of the polymer chains in a solution and in that context we have been developing the lattice models from where we can look at the mixing and phase separation behavior of polymer solutions and also to polymer melts and so on.

So now we will start looking at a different aspect of the motion of the polymer molecules we will first discuss the motions at equilibrium that we call the Brownian motion. We already had discussed diffusion earlier a bit so, Brownian motion the after the concept is I would say similar to diffusion or same as diffusion and once we discussed that the Brownian motion in general we will then apply to the models of polymer chains that we have discussed the particularly the bead spring model and what we will develop is then called the Rouse model that is used to find the diffusion coefficient of polymer chains and after we have finished doing the Brownian motions in the next couple of weeks we can go on and talk about the behavior under non equilibrium cases the behavior under flow and that goes in the subject of Physiology.

So, let us first begin with the concept of Brownian motion I am again as I have been doing I will first discuss the concept in general for any system and then we can extend the idea to a polymer solution and see like how the models turn out to be. So, if you think of like what the origin of Brownian motion is ultimately it is a result of the thermal fluctuations but even before that if we start thinking of like what does the motion of molecule entail at a molecular level what do we mean by the motion of molecules. So, for example if we have some molecules which are present in a beaker or any volume how will these molecules move?

Let us say if I apply a force on the beaker the force will not result in the collective motion of all the molecules in the same direction that is if I apply say a force in this direction it would not be that all the molecules would start moving in the direction of the force as we normally think in the case of like macroscopic system. Let us say if we have a block I apply a force the block moves in the direction of force applied but if I look at the molecules within the block they do not quite move in the direction of the force they actually have what is known as some diffusive motion and some convective motion of course if I take an average over many, many of those molecules what we call a fluid packet in the case of fluid mechanics then we can assign an average velocity that would be in the direction of flow direction of the force applied but individual molecules will actually be having somewhat erratic kind of movement and such erratic movement are even present when the force is not being applied so even if you have say a stationary beaker particularly liquid containing different molecules which I am drawing by circles here even when the force is equal to 0 even if it is a static or in a state of equilibrium it is not that the molecules are not moving molecules do indeed move but the motion of molecules are in different directions which we refer to as diffusion or Brownian motion and only when an additional force is applied if the F is higher than 0 then we also have an additional convection net occur because on an average the molecule tend to move in the direction of the force.

So, the first thing to note here is when we talk about the motion of molecules it is very different compared to the motion of macroscopic objects that we have been used to seeing and the reason why it is different because the motion at the molecular level is dictated by the kinetic theory or the temperature of the system and I would saw in a moment that why we do not care about that when we go to a macroscopic system.

So, if you recall from high school the definition of temperature- the temperature of a system is actually a result of the kinetic energy of the molecules and there is an equipartition principle that basically relates the kinetic energy to the temperature I am not worrying about the pre factors here the pre-factors vary depending on whether the molecule is mono atomic, diatomic and so on but in general the kinetic energy scales like k_BT.

$$m\langle v^2\rangle \quad k_B T$$

Where k_B is the Boltzmann constant and T is an absolute temperature in Kelvin and the Boltzmann constant is of the order of 10^{-23} in SI units actually it is Joule per Kelvin because this has a unit of energy and this is in Kelvin, so k_B has to be in Joule per Kelvin SI units and temperature typically is of the order of 100 like 300 Kelvin is a room temperature. We typically do not go very high in the case of a liquid but we can go see 500 Kelvin 600 Kelvin and so on all of them we can say are of an order of magnitude of 100.

So, if we then find the mean square velocity of molecules this goes like-

$$\langle v^2\rangle = \frac{k_B T}{m} \, so, v = \sqrt{\frac{k_B T}{m}}$$

Now let us try plugging in numbers here and try to see like how much this velocity is for particles of different size or molecules of different size. So, let us say we know that the density of water is 1 gm/cm^3 and so if I have say a block of 1 centimeter in each direction a cubic block. It will have a volume 1cm^3 and therefore a mass of 1cm^3 multiplied by 1gm/cm^3 that is 1 gram that is 10^{-3} kg in SI units and if I now compute the temperature that would be again there are pre-factors here of the order of 1 but k_B goes like 10^{-23} temperature goes like 100 and mass in this case is 10^{-3}. So, this gives me 10^{-18} in SI units that is meter per second 10^{-9} meter per second or 1 nanometer per second.

So, if you have a 1 centimeter by 1 centimeter by 1 centimeter cubed block because of temperature this would be moving at a velocity of 1 nanometer per second and the direction of velocity will keep on changing with time with time because there is no external force being applied on the system it is purely by diffusion and diffusion can take place in different directions because other molecules come and collide on different occasions from different sides and that is what is giving rise to the velocity that we see. So, 1 nanometer per second of velocity for a 1cm^3

block is almost negligible provided also that it is not always in the same direction it keeps on changing direction.

So that is what the reason why we do not observe any sort of Brownian motion for large blocks and if I think of say ourselves we are much longer than 1cc so our velocity is because of Brownian motion will be even smaller and we can barely observe that.

But if we really go to smaller systems let us say now we look at a block that is 1 micron each, now the velocity is 1 micron cube and 1 micron is 10^{-4} centimeter. So, it is 10^{-12} cm^3. So, now the mass will be 10^{-12} kg and if I now look at the velocity it is going to be 10^{-23} into 100 / 10^{-12} and this would be something like 10^{-9} which is of the order of 10^{-5} meter per second which would roughly be like 10 micron per second. So, now if I have a 1 micron block that is moving by a velocity of say 10 micron per second or let us say when 1 micron per second for the lower estimate then this velocity is quite significant because that now the block or the molecule that is a 1 micron size is moving at a velocity such that you can appreciably see the movement because the amount of movement you can get in one second is comparable to or larger than the size of the block itself.

So, this is the phenomena that intrigued a botanist Robert Brown back I would say more than 100 years ago and he saw like things we are moving even when there was no external force being applied in the system and this is what we refer to as a Brownian motion because of his name but essentially the Brownian motion is simply a result of thermal fluctuations which in turn comes from the collision of molecules in the system and it is always present for a small systems whether we can see that by our naked eye depends first on how big the movement is from compared to the size of the system and second how good our microscope is because of course if I go to smaller molecules we would not be able to see that under a microscope because their size is very less.

So, this is the velocity the molecules have even at equilibrium even when it is not experiencing any external force and these velocities give rise to what we know as the phenomena of diffusion and we already have discussed diffusion in the class. The diffusion is still applied in the non-equilibrium cases things intend to move from a high chemical potential to a low chemical potential but the diffusion also exists for systems at equilibrium the when we have we do not have a real concentration gradient as such because at the molecular level the molecules still are undergoing collisions which are giving rise to this motion especially in the case of a liquid and a gas for a solid it is rather difficult to visualize and these effects are typically negligible although unless the temperature is 0 Kelvin we always have thermal energy in the system and thermal energy always is because of the collisions of molecules that are present in the system.

So, now if I think of this kind of a movement happening at equilibrium where each of the molecules are moving in different directions. The first thing we can of course note that the average velocity of the molecules need to be 0 because there is net no net movement in any direction that is the reason why we used a mean square velocities in the previous derivation that we just did because the squares do add up but the actual velocities they cancel and so if I look at any of the properties of this system now those properties also should depend on the this individual motion of each of the molecules and how they collide with each other each other and so on and since the collisions themselves are although deterministic because ultimately if I know where the collisions are occurring I can solve the Newton's laws of motion I can get the position of particles and so on but since the number of molecules in the system is huge it is very difficult to keep track of all the individual molecule in the system what we then see is the properties of system tend to fluctuate because at any given time the configuration of molecules and the velocity of molecules are not constant they are continuously changing and different configurations mean different orientation of molecules, different velocity of molecules which give rise to fluctuations in the properties of the system that we see even at equilibrium.

It would appear to us that any quantity that we look like tend to fluctuate around some mean value let us call it $\acute{X}_i$ but I want to note again here that the fluctuations are not random although you will see that I will use a random function to characterize the fluctuation purely for mathematical regions fluctuations are not random they are simply a result of the fact that molecules have different velocities at different times because of the frequent collisions it is having with other molecules in the system.

So, in principle it is fully deterministic if we can solve equations of motion of all molecules. So, over the time but we should see if this molecule let us say it is start going in this way undergoes a collision changes direction undergoes collisions again, again it has certain trajectory similarly other molecules will also undergo collisions change directions will have certain trajectory and if we can really do solve the equation of motion we can get the trajectory of all the molecules and this is what essentially what we do in a molecular dynamics simulation the only limitation is it is for very small system.

Let’s say simulation walks of the order of 10 nanometer by 10 nanometer but nanometer for larger systems will have molecules in millions of molecules and it is very difficult to keep track of trajectories of all the molecules and do that and there is an easier approximate way that tells me about the behavior of the system assuming that the fluctuations are somewhat random purely again in mathematical terms I want to emphasize this point over an over that the process is not random but we use a random function to characterize the process and the final outcomes are somewhat such that they make physical sense.

So, if we do see a property it sole fluctuations like this and then of course the mean values is what we typically are interested in but to characterize the magnitude of these fluctuations because those magnitude are actually are a result of the Brownian motion. We will use what is known as correlation functions that characterizes the magnitude of fluctuations not the average value property right. So, we will use correlation functions and there are two different correlations functions I will use to characterize the magnitude of Brownian motion.

One we call an autocorrelation function and other we call a cross correlation function and for both of these it is preferable that instead of looking at the actual value of the property what we look at is some sort of deviation from the mean value. Let us say mean value we have already computed or we know from experiment. We take the deviation from the mean value and this characterizes the amount of fluctuation at a given time. So, autocorrelation function is defined as-

$$Autocorrelation\,Function\,C_{ii}(t,t')=\langle \Delta x_i(t)\,\Delta x_i(t')\rangle$$

It characterizes the magnitudes of fluctuations at two different time point time points and how are they correlated. If it is completely a random process then the deviation we have at any time and any time else this would be completely uncorrelated. So, let us say if I am doing a coin toss experiment each of the event is completely independent of the other but if I think in terms of the Brownian motion the immediate events are correlated and even the events after are correlated because the particle is undergoing trajectory. The new position of particle of course depends on the old position. Of course the correlation may decay with time but the correlation is always present in the system because it is not that each of at each time correspond to random events each time correspond to a progression in the time that is a result of trajectory of the molecule or particle we are looking at.

The cross correlation function is essentially the same stuff except that it is defined for two different properties let us call it-

$$Cross-Corelation\,Function\,C_{ij}(t,t')=\langle \Delta x_i(t)\,\Delta x_j(t')\rangle\,here\,i\neq j$$

Now there are two interesting properties that do apply in equilibrium and I will discuss both these properties in some detail here which are I would say very essential to describe systems at equilibrium. These properties must hold for a system at equilibrium and they are very essential not only for the polymer physics course we are discussing but the general description of many phenomena. One of that is what is known as the time translational invariance and what it tells me if I look at the correlation between two times points which are separated by say some Δt and if I look at the correlation between two other time points that are again separated by Δt those two correlations will be identical that is to say the origin of time is not important only the difference between the two times contribute to the correlation function. In other words-

$$C_{ii}(t,t')=C_{ii}(t-t',0)$$

$$\langle \Delta x_i(t)\Delta x_i(t')\rangle = \langle \Delta x_i(t-t')\Delta x_i(0)\rangle$$

The origin of time is immaterial. So, if I am looking at and this must be the case at equilibrium because let us say if I want to start doing an experiment on an equilibrium system that is my beaker. I cannot understand the system properly if the autocorrelation is like time dependent because I can start the experiment at any time, so let us say I start the experiment now and measured the autocorrelation for a time interval of 1 hour that tells me the strength of Brownian motion in that system at for 1 hour time and let us say I go back home and come, come, come tomorrow and start doing experiment again after 24 hours has elapsed but again looking at now and one hour after I should not be getting different results because the system is in equilibrium. If that would be true then of course the system behavior will keep on changing with time which is not the case because in equilibrium we say the system behavior at least in thermodynamic sense is constant.

So, the magnitude of Brownian motion also has to be constant so the origin of time must be immaterial for the system to be in equilibrium of course it would not be true if the system is in non-equilibrium. If for example in we start with a solution here and tomorrow I come and the solution has for example sedimentented Now we have a different system that we had from what we had earlier and of course we should get a different value in this case because the system I had yesterday and system I have today are not the same but once the system has attained equilibrium after that it should not matter when do I start my experiment only the time duration should be important and that is why this is a very important relation that actually characterizes the equilibrium behavior of any system and this has great consequence in the understanding of equilibrium processes in general because now we are not looking at the mean value.

So, it can be for example that the mean value of any property yesterday and the mean value today is same but by some coincidence but if this particular principle is not applying if the correlations are changing with time we can we cannot say that the system is attained equilibrium the constancy of the mean value can be because of an experimental error because there is a small change that we cannot notice by how we are measuring it. The constancy of the correlation function for a given time duration is what is that is most essential for the system to be at equilibrium.

So, if I now go by the time testing invariance I can also establish that-

$$C_{ii}(t)=\langle\Delta x_i(t)\Delta x_i(0)\rangle \textit{ gives by time translational invariance } \langle\Delta x_i(0)\Delta x_i(-t)\rangle=\langle\Delta x_i(-t)\Delta x_i(0)\rangle=C_{ii}(-t)$$

It means the autocorrelation must be an even function. So, if I do plot the autocorrelation function it should have the same value for positive time and negative time there should be a mirror symmetry around t = 0.

It is difficult to derive it for a cross correlation function by the same means that we just did but there is a scientist named on Onsager who showed that the cross correlation function is also even that is C_{ij} (t) is also equal to C_{ij} (- t) again by the physical intuition I have given you in the very beginning if I do the experiment now if I do an experiment 1 hour later this should hold true but he mathematically derived it for a cross correlation function I am not going in the derivation here.

So, we will start from this point in the next class but please note that the cross correlation function also must show mirror symmetry around t = 0.

With that I conclude here, thank you.