Introduction to Polymer Physics
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Lecture-38
Brownian Motion- III

Welcome in the last class we have discussed the Brownian motion and we have been discussing the displacement correlation function and velocity correlation function. So, I want to just conclude that discussion in this lecture and then we will talk about then we will talk about the Brownian motion of a free particle setting ground again for the discussion of polymer solutions, so, just to recall the discussion regarding the velocity and auto correlation function what we had derived-

$$\langle \acute{x}_i(t)\acute{x}_j(0)\rangle$$

so this is what my velocity correlation function is again just to reiterate the velocity really mean the rate of any change of any property not really only the position it can be any property. The rate of change is what I call velocity just like the language that is been used here, velocity correlation function which I can write as half of the second derivative of the displacement correlation function. It is-

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

The x_i and x_j can be so x_i and x_j is the change in position along X and Y direction so this would the first term would then be change in X second term will be change in Y and on the left hand side we would have the velocity in X multiplied by the velocity in Y it can also be for example position and say dipole moment so position let us say X coordinate can be my x_i and the dipole moment can be my x_j and again we can use this relation so we can interchange this x_i and x_j for any property that we are we are looking at.

So, we can also write this particular relation in integral form if I simply integrate this twice what we should get is a displacement correlation function as an integral over the velocity correlation function. We can write this as-

$$2\int_0^t dt_1 \int_0^{t_1} dt_2 \langle \dot{x}_i(t)\dot{x}_j(0)\rangle = \langle (x_i(t)-x_i(0))(x_j(t)-x_j(0))\rangle$$

So, I can relate the displacement correlation function to velocity correlation function in either of these two ways either in differential form or integral form and both of them works and we will use that correlation functions later in the class. So, before that I want to now talk about a slightly different concept and we will come back to the idea of correlation functions eventually and these concepts that I have covered so far will be useful in what we will discuss. So, so now I want to talk about the Brownian motion of a free particle purely from the perspective that we are used to.

We will start from what we typically use in a macroscopic description and then using that we want to establish what should be the case in a macroscopic description of Brownian motion and this therefore will set the ground for like what we will discuss in the case of polymers later.

So, we discuss the Brownian motion of a free particle and the system. Let us say you have some vessel, the vessel shape and size and everything is inconsequential here. The key point is that it contains some solvent and just one particle a solute particle that is moving in the solution that is why we call it a free particle. So, it has a particle that is moving in a solvent. The solvent can be much smaller compared to the solute particle.

So, if I think of the motion of this particle, the particle is large enough we already have said that the Brownian motion is insignificant that is the velocity of the particle due to thermal fluctuations is very limited. In this case since I have taken just one solute particle it is not undergoing any collision with any of the solute particles because they are not present the only thermal motions it is getting is because of collisions from solvent molecules.

So, if I really zoom in there what I would see is we have this solute particle surrounded by solvent molecules which are bumping into it of course not all of them. They are bumping into it and because it was bumping it is getting some thermal motion or fluctuation in its motion and the solute also can have some motion ‘V’ that of again can change in direction with time because at every moment it is experiencing a different configuration of water molecules around it or different orientation of water molecules around it or different momentum of water molecules around it. So, the collisions it experiences at every time is different and therefore the motion of solute molecule can be somewhat fluctuating in nature.

Again as I was telling in the case of the Brownian motion discussion in very beginning of the last couple of lectures that although it appear to be random it is not quite random although we will use a random function to represent it. If we really can solve the equation of motion of all the solute and solvent molecules in the system in principle we can get a fully deterministic solution. The only thing is that it is computationally very intensive to do and of course that is the idea that we do in the molecular dynamics that we can do for smaller systems. So, if we cannot do that then we can do some math and that math turn out to be known out to be quite simple but yet very useful.

So, the solute molecule is surrounded by solvents and as I have already said if solute molecule is large enough then in that case we know how to characterize the motion of the solute molecule we have relations like say Stokes law that tells me that the force acting on the particle or the drag force acting on the solute particle is equal to some constant ζ multiplied by v. So,

$$F_{drag} = -\zeta v$$

This is in the limit of very low flows and it is referred as a Stokes drag. Of course we are going to no flow situation in a movement but let us just start with the case when it has some drag because of this and then this ζ is referred as friction coefficient and for a spherical particle of radius ‘a’ in liquid of viscosity μ we have this Stokes relation ζ = 6▯▯ηa.

If it is not a spherical we can have some other value of ζ but that is not really very important the main thing is that the solute motion will be resisted by the presence of the drag that is due to the solvent molecules in the in the system. Now of course there can be other force that can give rise to a net motion but let us say we are looking at equilibrium then the other force is absent. Then the only force for macroscopic particle is the drag force we have not yet talked about the thermal forces yet. But apart from the thermal force we only have a drag force. If there was some external force then that would have caused the motion but let us imagine that there is no external force we are at equilibrium.

So at equilibrium then, assuming that we do not consider the thermal forces yet we have this relation-

$$m\frac{dv}{dt}=-\zeta v$$

It is true for large particles when effect of thermal fluctuation when neglected. So, by the way how large is too large and we have already done some scaling in fact if it is like greater than one millimeter it is already very large particle only when we go to say a micron range then the thermal motion become appreciable otherwise the drag force is all that is acting on the system.

So, if you are having difficulty looking at how the solute molecule can be moving if there was no force acting on it you can assume that let us see the motion was occurring in the previous time the force was being applied and then at time $t = 0$ we stopped that force and now the only force acting is the drag force. So, we may have started with a velocity that may have been due to a previous motion but now that velocity that external force is absent and we only have the drag force acting. So, if you only have the drag force acting and if I solve this equation what I would get is-

$$v=v_0\exp\left(\frac{-t}{\tau_v}\right)$$

Here $\tau_v=\frac{m}{\zeta}$ and v_0 is my initial velocity. It means is if I start with a velocity of say v_0 it would rapidly decay to 0 with time t by an exponential kind of a decay and the system will cease to move.

So, for a large particle this is indeed the case the system will cease to move and then there is no motion but if the particles are like now smaller in the micron range then something else should be present in this equation to make the motion happen. The motion that we attribute to the collisions it is experiencing from solvent molecules you must have a term in the equation of motion that should give rise to that fluctuating motion that is occurring because of the collisions from solvent molecules.

So, one way to do that is apart from the drag force we also include some other force that is a function of time and that force will keep on moving the system even when the drag force the velocity is goes to small value then also this force will always exist that will lead to that kind of a motion that we have. So for small particles we have-

$$m\frac{dv}{dt}=-\zeta v+F_r(t)$$

ζv is always dissipative f_r is not a dissipative force this is a force that is giving rise to the fluctuating kind of a motion that you see in the actual system.

So, for small particles say 10 micron but in any way this is really something that you have to do the math for every diameter thinking of like Brownian motion below say 10 micron I would say it will be appreciable. The lower we go it will be more and more appreciable but if we go to say nanometer range we will not be able to observe it and then we do not call it a Brownian motion we simply call it a thermal motion let us say for at molecular level we do not call the motion of molecules due to collision as a Brownian motion we simply call it a thermal motion.

The Brownian motion we attribute in the limit when we can see through a naked eye or through the microscope some random motion of the molecules because that is how it was observed originally by Robert Brown. Now we can include this random force F_r (t) but we do not know what that force should be, but we know something for sure that this force should not have a net directionality because let us say if the force is always in the horizontal direction and always to the right then this will lead to the motion of the sphere to the right then this would be same as an external force the whole notion of Brownian motion is based on the idea that the molecule fluctuate around its position because of the frequent collisions the forces are not really constant and they do not apply in just one direction they should be able to change directions.

So, one attribute we can think of having is this force must have a mean value of 0 if I take an average over time or if I do an ensemble average over many, many particles in the system. It means-

$$\langle F_r(t)\rangle = 0$$

Now if the mean value is 0 then how do we characterize the strength of the force, the strength we characterize using again the idea of the autocorrelation function we have discussed. So although the force has a mean value of 0 it does not mean the force does not exist at any particular time it can have say fluctuations around 0 and we can talk of the strength of the force by looking at the correlation between point's t and t' . So-

$$\langle F_r(t) F_r(t')\rangle \neq 0$$

Now the question is non 0 means what we like ultimately it does not provide an answer of what that value should be and one of the good approximations can be that we represent using a δ function because eventually when t becomes t' then it becomes F_r (t^2) and that clearly is a large value and the correlations must decay at long times because after some time the system will lose its memory. So, these correlations will not exist permanently after certain time scale the correlations must die out and therefore we can approximate possibly by a δ function not really the force but the correlation of the forces.

$$\langle F_r(t) F_r(t')\rangle = A\delta(t-t')$$

Now the question is like how do we how do we get this quantity A and that is what we can do now. So, we want to get the value of A, until so far we have assumed that the force we do not know what F_r (t) is but the mean value is 0 and the correlation value is given by this particular function.

So, now we want to get the magnitude of A and to get that we want to use the definition that we started with that comes from equipartition that the square averaged of the average of the squares of the velocity must be equal to k_BT by m again in owning the pre-factors and using that we can then get the expression of A.

$$\langle v(t)^2 \rangle = \frac{k_B T}{m}$$

So, what we want is we want to start from here-

$$m\frac{dv}{dt} = -\zeta v + F_r(t)$$

then try to use this relation to get the expression of A so in here I want to ultimately write not in terms of $F_r(t)$ but in terms of $F_r(t)$ $F_r($ t' $)$ because the relation we have assumed is for $F_r(t)$ $F_r($ t' $)$.

$$\frac{dv}{dt} + \frac{\zeta}{m} v = \frac{F_r(t)}{m} = ¿ e^{\frac{t}{\tau_v}} \frac{dv}{dt} + \left(\frac{\zeta}{m}\right) v e^{\frac{t}{\tau_v}} = e^{t/\tau_v} \frac{F_r(t)}{m}$$

By using linearity ODE we get-

$$\frac{d}{dt}\left(e^{\frac{t}{\tau_v}} v\right) = \frac{F_r(t)}{m} e^{\frac{xt}{\tau_v}}$$

So, we will start from this particular point in the next lecture and then get the expression of A that we had in our relation we have assumed for the autocorrelation of $F_r(t)$ that is a random function that we have introduced to characterize the Brownian motion of the free particle.

So, with that I conclude this lecture, thank you.