## Introduction to Polymer Physics Dr. Prateek Kumar Jha Department of Chemical Engineering Indian Institute of Technology-Roorkee

## Lecture-40 Brownian Motion- V

Welcome in the last class we have been discussing the velocity correlation function for the purpose of deriving what we said as Einstein relation for diffusivity and so far we have found the velocity correlation function again for Brownian motion of a free particle as the following-

$$\langle v(t)v(t')\rangle = \frac{k_BT}{m} \exp\left(\frac{-|t-t'|}{\tau_v}\right)$$

This function is even that is it is same for negative times and positive times and so it satisfies the relation we have earlier established for the well for the autocorrelation.

So, now if I want to take it further ultimately I said that I will relate the displacement correlation function with this velocity correlation function because from displacement correlation function we can get the mean square displacement and then we can get the relation for the diffusivity and that is what we will do it now. So, we have earlier derived-

$$\left\langle \left(x\left(t\right)-x\left(0\right)\right)^{2}\right\rangle = 2\int_{0}^{t} dt_{1} \int_{0}^{t_{1}} dt_{2} \left\langle v\left(t_{2}\right)v\left(0\right)\right\rangle$$
  
Here,  $\left\langle v\left(t_{2}\right)v\left(0\right)\right\rangle = \frac{k_{B}T}{m} e^{\frac{-t_{2}}{\tau_{v}}}$   
 $\left.\frac{2k_{B}T}{m} \int_{0}^{t} dt_{1} \left[\frac{e^{-\left(\frac{t_{2}}{\tau_{v}}\right)}}{\frac{-1}{\tau_{v}}}\right]_{0}^{t_{1}}$ 

Now there is a small detail here or the assumption that we make and the assumption is like if I look at the  $\tau_v$ ,  $\tau_v$  is m/ $\zeta$  this is some sort of a time scale that characterizes the diffusion if

that time scale is very small compared actually  $\tau_v$  is the time scale that is characterizes the time scale of dissipation to be more specific because we are dividing the mass by the friction coefficient that we had.

So, if this time scale is very small compared to the time scale we are interested in or the time scale of diffusion that is to say if t2 is much higher than  $\tau_v$  which is not so much of a bad assumption because  $\tau_v$  is typically of the order of say 10 nanoseconds or a smaller and we may be interested in the times may be like in microseconds or milliseconds or seconds those times will be very high compared to the  $\tau_v$ .

So, in that case we make use of the fact that ultimately the integrand here is an exponential function that would decay with time and so of course at  $t_2 = 0$  it is = 1 but at  $t_2 = t_1$  it is already a very small number. So, even if I change the upper limit to say infinity that would not really change the result by a lot but it would simplify our analysis quite a bit right, and that is only true when this  $t_2$  and  $t_1$ ,  $t_1$  to be more specific in this case is much higher than  $t_1$ .

Actually if the idea of like dummy variables confuses all we need to care about is what the time scale that we want to study for the diffusion problem and what is the time scale we get from m by  $\zeta$  and as long as the time scale we want to a study for diffusion problem is much higher than that  $\tau_v$  then in that case we can make this particular approximation that I can change the upper limit from t<sub>1</sub> to infinity because in any case that would make very small numerical error and it would be a great simplification in what we will do next. So, that is what I will do here so now the upper limit goes to 0 and we only have the lower limit so that is then it is-

$$\langle (\mathbf{x}(t) - \mathbf{x}(0)) \rangle = \frac{2k_BT}{m} \cdot \frac{m}{\zeta} \int_0^t dt_1 = \frac{2k_BT}{\tau} t$$

So, what we therefore get is my mean square displacement is equal to this-

$$\langle (\mathbf{x}(t) - \mathbf{x}(0))^2 \rangle = 2 \left( \frac{k_B T}{\zeta} \right) t$$

And if I associate this quantity that we get as my diffusion coefficient then this becomes-

$$\langle (x(t)-x(0))^2 \rangle = 2 \left( \frac{k_B T}{\zeta} \right) t = 2 D t$$

This makes perfect sense because now D is a ratio of the mean square displacement with the time and that is what we have begun where from because we said that the D has a unit of meter square per second it characterizes the mean square displacement the particle undergoes and so on.

There are two points to be made here the first point is of course we have done it in only one dimension. If I am doing in say a general 2 dimension or a 3 dimension in this case only change we will see in the d dimension is we will have the factor D there-

$$\langle (\mathbf{x}(t) - \mathbf{x}(0))^2 \rangle = 2 \, dDt$$

1

So, for example in 3D this is = 6 Dt into 2D this is = 4 Dt and so on.

The second point is let us say I want to compare this behavior with say the mean square displacement if for a normal rectilinear motion when things are moving in a particular direction without experiencing collision. So, in that case we know that the distance traveled should be proportional to the time and x should be equal to something like vt + some initial value for a rectilinear motion. So, in that case what we do get is  $(x-x_0)^2$  would simply be proportional to  $t^2$ .

For Rectilinear Motion,

 $x \propto t$  $x = vt + x_0$  $(x-x_0) \propto t^2$ 

So, if you think of a motion that is like a rectilinear motion or motion of a projectile for example in that case we see mean square displacement goes like  $t^2$ . In the case when there is a diffusive motion where motion is because of the collisions we get from surrounding molecules then the mean square displacement goes like t that is basically square root of the result that we had for the

case of t linear motion this is what is called a diffusive motion so if the mean square displacement is proportional to t that is what I will call a diffusive motion.

If we have some deviation from this particular power law we will see we will call it a non diffusive kind of motion or non fickian kind of diffusion and so on right so the whole notion that the mean square displacement should go like t was given by the Einstein and it still serves as the basis of how we understand diffusion.

So, now I want to take discussion it bit further so far we have been talking about Brownian motion of a free particle of course a polymer is first of all a large molecule and we typically represent a polymer by say segments connected together by some sort of bonds and therefore if I want to represent the Brownian motion of a polymer chain it is probably better that we talk about Brownian motion of the individual segments of the polymer chain.

If I now look at a polymer chain and we can think of any model but let us say we think about a bead spring model then we have beads connected by springs and all these beads are then surrounded by water molecules and they are all undergoing some sort of Brownian motion right. So of course we could have said that I would represent the polymer motion by simply assuming that this entire polymer chain is some sort of an effective shape object and think of the Brownian motion as the motion of this object as a result of solvent collisions okay. So, although the model right here is not bad because still it captures the effect of like solvent collisions. It does not capture the internal motion of polymer segments, the polymer segments will also have some internal motion that is the whole reason why polymer can take multiple confirmations and those confirmations can also be because of the Brownian motion of the individual segments that behavior is not captured if I treat the polymer chain as a single entity so it is better off if we treat a polymer chain as composed of these beads.

This is not really a problem if I think of for example say a metal ball so in that case the internal motion of metal atoms is not important we will see a net motion of metal ball although metal ball really has to be very small for Brownian motion to be of any significance but the internal motion

of the atoms inside the ball will not be of much significance. But in this case of polymer chains since the molecule since the segments can rearrange themselves and we can have various confirmations those confirmations also result from this kind of Brownian motion and though for therefore we should think of Brownian motion in the case of a polymer chain in terms of the motion of these individual segments or beads that is the first point.

The second point is if I now look at this polymer chain in motion because of say the Brownian motion the solvent collisions are not the only force acting on every bead. Now what you will have is every bead let us say if I look at this particular bead here then this bead is interacting with the two neighboring beads by the two springs that connects them. So, if I move this bead by little bit even other beads will get affected and that is how we include it in front of any spring. So, if I let us say pull one guy other guys will also experience some force and respond to that kind of emotion. So, we also have to have some way to incorporate that spring force in addition to the force due to thermal motions that is not the drag force the drag force is because of solvent molecules in the system. The thermal motions are also because of solvent molecules in the system 1 is bigger dissipative in nature and other has a fluctuation type of nature but this force that a spring force is internal to the system. It is between the 2 beads in the polymer chain or 2 segments in the polymer chain and this is some sort of an external force acting on each of these beads.

So, therefore the way we will develop the model of a polymer chain if you first discuss how the Brownian motion changes in the presence of an external field because every bead is experiencing an external field that is my spring force and then we will using that equation we will then describe the Brownian motion for a bead ring model of a polymer chain.

So, let us first talk about the Brownian motion in an external field and let us say for the time being take the same problem that we started with a free particle that is undergoing a Brownian motion the only thing is that now there is also an external field acting on it. You still have a free particle but now we also think that the external field is acting on the system and then we can generalize that for the case of a polymer chain. This can be for example is be a scenario where we have an electric field being applied on the system. Now of course that system would not be in equilibrium but nowhere in the description of the Brownian motion the equation of motion have we assumed the equilibrium nature. The equilibrium nature comes much later and we talk about for example the correlation functions and so on. The Brownian motion equation the equation of motion itself is applicable also in that scenario but then when we do the case of a polymer chains then those as I have just said the spring forces are not really external to the system they are internal to the system. And therefore the polymer chain can very much in equilibrium I will do it is experiencing some spring forces between the segments those forces still are present but they are not external to the system it only sets the ground. This model only touch the ground for the description of polymer models that we will we will do.

So, in this case we still have, so let us say if I look in one dimension, so we still have the two terms that we had discussed in addition to that we now also have a force term that is simply a gradient of the external field-

$$m\dot{x} = -\zeta \,\dot{x} + F_r(t) - \frac{\partial U}{\partial x}$$

So, in this case again if the  $\tau_v$  is much smaller than the time scale under consideration here, the  $\tau_v$  is my m/ $\zeta$ . So, if m/ $\zeta$  is very small what it means is my inertial term is very small compared to my drag term because m is small and  $\zeta$  is higher would give me a smaller value for m/ $\zeta$ . So, in this case I can drop m  $\dot{x}$  that is my inertial term that is not a bad approximation in many cases as long as either the mass is very small or the friction is high enough in that case we can drop the inertial term and we have-

$$-\zeta x + F_r(t) - \frac{\partial U}{\partial x} = 0$$

And so we have-

$$\frac{dx}{dt} = \frac{-1}{\zeta} \frac{\partial U}{\partial x} + \left(\frac{F_r(t)}{\zeta}\right)$$

So this particular quantity  $\frac{F_r(t)}{\zeta}$  will have units of velocity because we have a velocity here so, I would call it as the random velocity that we impose because anyway  $\zeta$  is a constant here.

And then I have a term coming from the external field that is present in the system. So, now this  $v_r(t)$  satisfies similar relations as  $F_r(t)$  does.

$$\langle \mathbf{v}_r(t) \rangle = 0$$
  
 $\langle \mathbf{v}_r(t) \mathbf{v}_r(t') \rangle = 2D \,\delta(t - t')$   
 $D = \frac{2k_B T}{\zeta} = diffusion coefficient$ 

So,  $\langle V_r(t) V_r(t') \rangle = 2D\delta(t-t')$ 

So this becomes the equation of Brownian motion in the presence of an external field U. So, let us take an example let us say that thisU follows some functional form. For example if u is-

$$U(X) = \frac{1}{2} k x^2$$

You can see where we are going because ultimately these are the kinds of forces which apply in a polymer chain. But now we are applying them on single solute particle in solution. So, in this case-

1)

$$\frac{\partial U}{\partial x} = -kx$$
  
$$\frac{dx}{dt} = \frac{k}{\zeta} x + v_r(t)$$
  
$$v_r(t) = 0 \text{ so , } \langle v_r(t) v_r(t') \rangle = 2D\delta(t - t)$$

So, we will start from this particular point the Brownian motion of a free particle in external field that we have derived today and we will use it to discuss the Brownian motion of a bead spring model of a polymer chain in a solution by a simple extension of what we have done in this particular lecture.

Thank you