Introduction to Polymer Physics
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Lecture-39
Brownian Motion- IV

Welcome in the last lecture we have been discussing the Brownian motion of free particle and we have been able to write the equation for the Brownian motion of free particle and we defined a random function that takes care of thermal fluctuations. The effect of thermal fluctuations on the motion and we have been working on the pre-factor of the random function we have defined and today I will take it further and derive the expression for the prefactor and then take the discussion further regarding the Brownian motion of free particle.

So, just to recap what we said if the particle is small enough then I can write the equation of motion as the usual term that we get from Stokes equation that is the acceleration is equal to the drag force that is in the presence of no external force on the system and the effects of fluctuations are incorporated by using this random force term F_r (t).

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

We have a solute particle that is being surrounded by tiny solvent molecules and in fact there is only one solid particle present in the solvent that is why we call it the Brownian motion of a free particle. And then we have established that since the thermal fluctuations can give rise to motion in different directions at different times if there is no external force acting on the system.

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

We have some conditions on the function that I include, the random function, again I want to emphasize here that the random function I have included is only for the purpose of capturing the effect of the solvent collisions with the solute by no means we are saying that the system is a stochastic in nature. We are making the approximation just because we cannot solve for trajectories of all the solute and solvent molecules in the system. This assumption kind of takes care of the qualitative effect the solvent collisions have but this by no means tells that the system itself is a stochastic system is fully deterministic. This equation works to describe the motion of solute.

We said that assuming that the correlations in that random force decay fastly, very fast with time we can represent using a δ function and we want to get the prefactor A in the equation and to get the prefactor A. We get-

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

Now using the relation for the mean square displacement mean square velocity –

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

We derived the expression-

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

So, let us take it further, so now if I integrate this equation I get-

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

Here $\tau_v = \frac{m}{\zeta}$ the ratio of mass and friction coefficient. So, now I can write this expression as-

$$v(t) = e^{\frac{t}{\tau_v}} \int_{-\infty}^{t} \frac{e^{\frac{-t}{\tau_v}}}{m} F_r(t')\, dt'$$

So, I will choose a dummy variable here and I will integrate this with dt' and this has to be multiplied with a prefactor e to the power t by τ_v and for the limits I will start from - infinity to t because at t = - infinity you can say the prefactor becomes 0. So, the velocity goes to 0 we cannot take the velocity to be 0 at origin of time t = 0, because solute is undergoing motion but far before in the time we can set it equal to 0 because the exponential itself in the prefactor becomes 0. So, now I can write this expression as so I can move the exponential t by τ_v inside the integral because we have a t' variable inside there is no t here. So, now we have we have-

$$v(t)=\frac{1}{m}\int_{-\infty}^{t} e^{-\left(\frac{t-t'}{\tau_v}\right)} F_r(t')\,dt'$$

So, now if you want to get the velocity square averaged basically we are doing-

$$\langle v^2(t)\rangle=\langle v(t)\,v(t)\rangle$$

Now we have to be slightly careful here because if I multiply these two velocities they are both integrals from - infinity to + t but they can have different dummy variables because we can possibly have cross terms between those dummy variables. So, now this would be-

$$\langle v^2(t)\rangle=\langle v(t)\,v(t)\rangle=\frac{1}{m^2}\left\langle \int_{-\infty}^{t} d t_1 e^{-\left(\frac{t-t_1}{\tau_v}\right)} F_r(t_1)\int_{-\infty}^{t} d t_2 e^{-\left(\frac{t-t_2}{\tau_v}\right)} F_r(t_2)\right\rangle$$

Here I have defined t1 and t2 as the dummy variables the first term is v_t, the second term is also v_t I have simply used different variables t1 and t2 because there is a possibility to have cross terms here.

Now we can move the integrals outside and move the ensemble average inside and then we have this-

$$\text{¿}\frac{1}{m^2}\int_{-\infty}^{t} d t_1 \int_{-\infty}^{t} d t_2 e^{-\left(\frac{t-t_1}{\tau_v}\right)} e^{-\left(\frac{t-t_2}{\tau_v}\right)} \langle F_r(t_1) F_r(t_2)\rangle$$

Now the ensemble average of Fr (t_1), F_r (t_2) product is assumed to be the A δ (t_1 - t_2) by what we have assumed earlier. So, I can say integrate over t_2 first and that integration because we have a delta function here would simply imply that I would replace the t_2 by t_1 in the equation and the integral sign will go. Now we have-

$$\langle (v(t)^2)\rangle=\frac{A}{m^2}\int_{-\infty}^{t} d t_1 e^{-2\left(\frac{t-t_1}{\tau_v}\right)}$$

$$¿\frac{A}{m^2}\left[\frac{e^{-2\left(\frac{t-t_1}{\tau_v}\right)}}{\frac{2}{\tau_v}}\right]_{\infty}^{t}=\frac{A\tau_v}{2m^2}$$

So if I now put in the value for τ_v we get-

$$\frac{A\zeta\tau_v}{2m^2}=\frac{Am}{2\zeta m^2}=\frac{A}{2\zeta m}$$

This has to be equated to $k_B T$ by m which means m cancels out here. So we get-

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

Therefore,

$$A=2\zeta k_B T$$

Now this particular relation is an outcome of more general theorem that is known as fluctuation dissipation theorem and this comes because if I look at A, A signifies the strength of the fluctuations because it is a pre factor that appears in the correlation function for the random force we have defined so this is a magnitude of fluctuation. On the other hand ζ comes from the drag force and this is a usual dissipative force that is acting because of the friction present in the system so this is a magnitude of dissipation. So, essentially what the fraction the fluctuation dissipation theorem states is the magnitude of fluctuation is related to the magnitude of dissipation in the system they are not really completely decoupled both of them have to be related.

So, if for example the dissipation is high the fluctuation would also be high if dissipation is low fluctuation would also be low. For example dissipation would be low in the case of for example a low viscosity liquid in that case the fluctuation also has to be low right and it does not come naturally if I think in terms of like pure intuitively but it is beautifully derived if I start from the approximation that we have made and this is not quite an approximation because of the kinetic energy of course should be because of the thermal energy present in the system that is $k_B T$ and from there we can see a direct relation between the fluctuation and dissipation in the system.

So, with this if I want to go back here now we know what A is so, A is now $2\zeta k_B T$, so I can write this relation as-

$$\langle F_r(t) F_r(t') \rangle = 2\zeta k_B T \delta(t-t')$$

Now we have a fully stated problem so we know we have the equation of motion we know what properties the function F_r (t), should satisfy the only thing we do not know is what the F_r (t), should be what functional form should it have and here we use the idea of the central limit theorem that we have discussed earlier. So, from that theorem we can say that all the stochastic distribution would anyway go to Gaussian distribution for large value of samples. So, therefore we can assume that F_r (t) is a Gaussian function satisfying the two relations we have established.

This actually is the basis of what is known as a Brownian dynamic simulations. The advantage here is like let us say if I am looking at a motion of a solute molecule I will not care about the motion of solvent molecules their effect on the system is taken care of by the ζ and also F_r (t) because ultimately the random force also depends on the dissipative force as we get from the fluctuation dissipation theorem. So, this is like a fully stated problem that we solve in what is known as a Brownian dynamics simulation.

So, I will not discuss much about the simulations now I will take the theory a bit further and see like what else we can do with the relations that we have derived. It may become somewhat complicated but there is a lot of meaning into in what we can get and then we can extend that idea to the case of a polymer model that we have discussed earlier the bead spring model. So, the next thing I am going to derive here is what is known as the Einstein relation.

So, Albert Einstein is of course more known for his principle of relativity but back in 1905 or 1906 he actually derived this particular relation for the diffusion coefficient that is known as the Einstein relation and that becomes one of the fundamental equations of the Brownian motion and for the diffusivity.

The physical approach is the following we know that diffusion ultimately is characterizes the mean square displacement that any particle undergo with time that is why it has a unit of meter square per second. It characterizes the mean square of displacement a particle can undergo in a given time and if I want to think of the mean square displacement we are talking about an autocorrelation function for the displacement and then we have already said that the autocorrelation function for displacement can be related to the autocorrelation function of the velocity and from Brownian dynamics equation I just described I have an equation for the velocity. So, what we do is we construct an equation for the autocorrelation function for the velocity, using that we get the autocorrelation function for the displacement and using that we can then get the diffusion coefficient D that is the approach that we are going to follow. So-

$$D \equiv \frac{m^2}{s} = \frac{\langle x^2 \rangle}{t}$$

$$\langle v(t) v(t') \rangle = \left\langle \int_{-\infty}^{t} dt_1 \frac{1}{m} e^{-\left(\frac{t-t_1}{\tau_v}\right)} F_r(t_1) \int_{-\infty}^{t'} dt_2 \frac{1}{m} e^{-\left(\frac{t'-t_2}{\tau_v}\right)} F_r(t_2) \right\rangle$$

$$¿ \frac{1}{m^2} \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t} dt_2 e^{-\left(\frac{t-t_1}{\tau_v}\right)} e^{-\left(\left(t-\frac{t_2}{\tau_v}\right)\right)} \langle F_r(t_1) F_r(t_2) \rangle$$

As we know –

$$\langle F_r(t_1) F_r(t_2) \rangle = 2\zeta k_B T \delta(t-t')$$

So for a case when t is less than t' we have-

$$\langle v(t) v(t') \rangle = \frac{1}{m^2} \int_{-\infty}^{t} dt_2 e^{-\left(\frac{t-t_1}{\tau_v}\right)} e^{-\left(\frac{t-t_1}{\tau_v}\right)} 2\zeta k_B T$$

Now we can write this as-

$$\langle v(t) v(t') \rangle = \frac{2\zeta k_B T}{m^2} \int_{-\infty}^{t} dt_1 e^{-\left(\frac{t+t'}{\tau_v}\right)} e^{\frac{2t_1}{\tau_v}}$$

$$¿\frac{2\zeta k_B T}{m^2} e^{-\left(\frac{t+t'}{\tau_v}\right)} \left[\frac{e^{\frac{2t_1}{\tau_v}}}{\frac{2}{\tau_v}}\right]_{-\infty}^{t}$$

$$¿\frac{2\zeta k_B T}{m^2} e^{-\left(\frac{t+t'}{\tau_v}\right)} \frac{e^{\frac{2t_1}{\tau_v}}}{\frac{2\zeta}{m}}$$

After cancellations we get the final equation as-

$$\langle v(t) v(t')\rangle = \frac{k_B T}{m} e^{\frac{t-t'}{\tau_v}}$$

So, now if you repeat the stuff for t higher than t' so if I do the case t higher than t' now just like I integrated with t_2 first in that in the case that we have discussed in this case we will do integration with t_1 first and then you can do the derivation yourself but the answer would simply be this now we have-

$$\langle v(t) v(t')\rangle = \frac{k_B T}{m} e^{\frac{t-t'}{\tau_v}}$$

It should be true because the autocorrelation function of the velocity must decay with time. So, if t is less than t' here the argument here is negative so long the higher the difference the lower the function would be it will decay as I increase the t – t' .

On the other hand when t is higher than t' I will simply fixed it with a minus sign of that that would also decay with time. So, the ultimate reason why we have chosen to do this in particular way because we want the autocorrelation function to decay with time and of course you can look into the math aspect of it but basically the idea is that we have to do these two cases separately because in both the cases the autocorrelation function must be decaying with as the time increases that is the time duration between the two things.

So, I can write these two things together in a simple notation so combining what I can now write is-

$$\langle v(t)v(t')\rangle = \frac{k_B T}{m} e^{-\left|\frac{t-t'}{\tau_v}\right|}$$

So, if t is higher than type tau prime in both the cases or whether t is higher than tau t prime or t is less than t prime in both the cases the mod value is positive but I put a minus sign here to ensure that the function always decreases as the gap between t and t' increases.

It also means that the function is even that is a function is same for positive time difference and negative time difference that is something we have established for an autocorrelation function. So, if I plot this I should get like this a function like this which is decreasing on both the sides actually symmetric around the difference is = 0. So, with that I want to stop here and in the next class I will take this further and derive the diffusion coefficient that we get from the Einstein relation.

Thank you.