Keywords: Self-correlation function, Jump-length probability, Elastic incoherent structure factor (EISF), Fickian diffusion, Jump rotation

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This is the self-correlation function, $G_s(r, t + \tau) = \int G_s(r - l, t)P(l, \tau)dl$, at $r, t + \tau$ and is equal to function at $r - l, t$ with a jump it is coming to r with a probability $P(l, \tau)$ of jump length l with a timescale τ, which is the residence time at the site.

So, physical it is easy to understand, if the particle is sitting at a site, it can jump from here to another site. So, this jump length if it is l, then from $r - l$ it comes to r in a time $t + \tau$ when $P(l, \tau)$ is the jump length probability for the residence time of τ. So, it sits here, after some time it jumps, after some time it again jumps, and so on. So, there is a residence time and there is a jump length.

So, jump length probability given by $P(l, \tau)$, dependence also includes the residence time τ. These are small quantities, since we are talking about a medium in which a particle is diffusing through short jumps and in short timescales. I can do a Taylor expansion of this correlation function $G_s(r, t + \tau)$ in time (t) and in space (r). So, this is in time, on the right-hand side this is in space.

Now, here $G_s(r,t)$ can be taken outside in this expression, because there is no $P(l,\tau)$ involved in this term. Once I take it out, and we know that $P(l,\tau)$, once we integrate over all jump lengths, it has to be equal to 1. At least the particle jumps with some length, so, $\int P(l,\tau)dl = 1$.

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So, I can write down, with Taylor expansion in time:

$$G_s(r,t+\tau) = G_s(r,t) + \tau \frac{\partial G_s(r,t)}{\partial t} + \frac{\tau^2}{2}\frac{\partial^2 G_s(r,t)}{\partial t^2} + \cdots$$

I can do Taylor expansion of r.h.s. in space (r).

$$\int G_s(r-l,t)P(l,\tau)dl = \int P(l,\tau)dl \times \left[G_s(r,t) - l\nabla G_s + \frac{1}{2}\sum_{i=1}^{3}\sum_{j=1}^{3} l_i l_j \frac{\partial^2 G_s}{\partial x_i \partial x_j} + \cdots \right]$$

. Now, l has equal chance of being positive or negative. So, when I do integration over the entire space, (shown here just for dx) and same true for dy and dz. If I do this integration, it should give me 0 being first order in l. And then l_x, l_y, l_z can be positive and negative with equal probability they will sum up over to become 0. That means this term $l\nabla G_s(r,t)$, integrating over space goes to zero. I wrote $\frac{\partial G_s}{\partial x}$, but now, there will be $l_x \frac{\partial G_s}{\partial x}$, $l_y \frac{\partial G_s}{\partial y}$ terms also. And then there is a second order term. The first order term goes to 0 because l is isotropic.

So, integral of $P(l,\tau)$ over space is unity and the first term on both the sides are equal and cancel each other. I get this equation here.

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$$\tau\frac{\partial G_s(r,t)}{\partial t} = \frac{1}{2}\int \sum_{i=1}^{3} l_i^2 \frac{\partial^2 G_s(r,t)}{\partial x_i^2}P(l,\tau)dl$$

So, after neglecting the higher order terms we get this equation. And then because, as I said that $P(l,\tau)$ is isotropic, so,

$$\int l_i^2 P(l,\tau)dl = \frac{1}{3}\langle l_i^2(\tau)\rangle$$

Here, l_i indicates the components l_x, l_y, or l_z. Because they are isotropic this gives me average l_i^2 which is $l_x^2 + l_y^2 + l_z^2$ the average and $1/3^{\text{rd}}$ of that.

All three components are equally possible and I get this equation.

$$\frac{\partial G_s(r,t)}{\partial t} = \frac{\langle l_i^2(\tau) \rangle}{6\tau} \nabla^2 G_s(r,t)$$

This equation is the equation for diffusive motion that is dictated by this self-correlation function of a particle. If I write it actually in slightly simpler form in one dimension,

$$\frac{\partial G_s(x,t)}{\partial t} = D \frac{\partial^2 G_s(x,t)}{\partial x^2}$$

Where D takes up constant terms. For a 1D Fickian diffusion the equation can be written as

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

So, the concentration C and G_s are identical. I can use a solution of Fick's diffusion equation and use it here for $G_s(r,t)$.

Neglecting the higher order terms

$$\tau \frac{\partial G_s(r,t)}{\partial t} = \frac{1}{2}\int \sum_{i=1}^{3} l_i^2 \frac{\partial^2 G_s(r,t)}{\partial x_i^2} P(l,\tau)dl$$

Because $P(l,\tau)$ is isotropic

$$\int l_i^2 P(l,\tau)dl = \frac{1}{3}\langle l^2(\tau)\rangle$$

Therefore,

$$\frac{\partial G_s(r,t)}{\partial t} = \frac{\langle l^2(\tau)\rangle}{6\tau} \nabla^2 G_s(r,t)$$

Fick's law $\qquad \frac{\partial G_s(r,t)}{\partial t} = D\nabla^2 G_s(r,t)$

The solution of the Fick's law must satisfy the following initial condition,

$$G_s(r,0) = \delta(r)$$

and

$$\int G_s(r,t)dr = 1$$

Now, the solution of the Fick's law also must satisfy some very basic conditions. One is that at $t = 0$, the self-correlation function, $G_s(r,0) = \delta(r)$ because we know that at $t = 0$ it is starting from some point which I am calling as origin. This origin is not fixed. It can be anywhere in the medium, but this is a delta function for this particular particle. Another is that if I integrate $G_s(r,t)$ at any time over the whole space, it is equal to 1. Physical significance of this is that the particle has to be somewhere at that time t and that is why $G_s(r,t)$ integral over all the space is equal to 1. So, these are the conditions which the Fick's law must satisfy in its solution.

And the solution is,

$$G_s(r,t) = (4\pi Dt)^{-3/2} \exp\left(-\frac{r^2}{4Dt}\right).$$

This is a Gaussian and the Gaussian has a width at any time, which is $4Dt$ here. So, if the particle starts from the origin at time $t = 0$, as time goes on its position (probability) widens like a Gaussian with a width of $4Dt$. That means, if I can measure at some time the width then I can find out D and if I go to infinity, then this Gaussian becomes broader and broader, and ultimately, the particle is uniformly distributed all over the space.

This is the significance of this solution of Fick's equation which also I am using as $G_s(r, t)$ By taking a Fourier transform over space of this function, I can get the intermediate scattering law. And which goes as $e^{-DQ^2 t}$.

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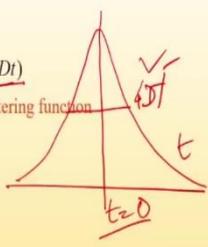
So, now that I mentioned you, it is easy to do a Fourier transform of this and then the Fourier transform of this over variable r gives me e^{-DQ^2t} in 'Q' space.

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And once more if I do the Fourier transform of this exponential function $e^{-DQ^2 t}$ over time 't' then what I get is a Lorentzian in 'ω' space. So, this is the Lorentzian which I have mentioned again and again when I showed that the due to diffusion, the particle has a Lorentzian distribution in ω. This is a Lorentzian I am talking about. This Lorentzian with the width DQ^2 can be used to determine the diffusion constant D given that we know the Q value for the experiment.

This is a Lorentzian which we will be measuring in our experiments. And if the particle is diffusing in an infinite medium, then we only have this Lorentzian. But if it is diffusing in a finite medium, then I will also have a $+\delta(\omega)A(\omega)$ term, an elastic incoherent structure factor (EISF), which tells me the geometry of the space in which the particle is diffusing. So, this is for an infinite medium and this is for a finite medium, and I will show you how to derive $A(Q)$ for a finite medium.

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This is what I stated just now, the scattering exhibits the shape of a Lorentzian function whose half width at half maxima (HWHM) increases with the momentum transfer Q according to a DQ^2 law. This is also often written as $1/\tau$ where τ is the residence time. I can quickly do a dimension analysis; you can see D is given in cm^2/sec and Q is cm^{-1}, so, DQ^2 has dimension 1/sec, which is time inverse.

And here, I can also write the whole thing as $\left(1/\tau\right)^2$, where τ is given as a residence time. We will be talking interchangeably about DQ^2 and $1/\tau$ and these two are equivalent unit wise and physically also, because DQ^2 dictates how fast it is diffusing which will also depend if there is a residence time at every site.

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And the solution is

$$G_s(r,t) = (4\pi Dt)^{-3/2} \exp(-r^2/4Dt)$$

Fourier transformation in space lead to intermediate scattering function

$$I_{inc}(Q,t) = \exp(-DQ^2 t)$$

Fourier transformation in time leads to incoherent scattering law

$$S_{inc}(Q,\omega) = \frac{1}{\pi} \frac{DQ^2}{\omega^2 + (DQ^2)^2}$$

So the scattering law exhibits the shape of a Lorentzian function whose half-width at half maxima (HWHM) increases with the momentum transfer according to a DQ^2 law and provides a direct method of determining the diffusion constant.

But the takeaway from this expression is that if I do the experiment, I can measure the width of the energy transfer peak, which is a Lorentzian, then from there, I can find out the diffusion constant, which is a very important factor or an important physical quantity for understanding dynamics of particles, especially self-dynamics in various media.

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$S_{inc}(Q,\omega)$ for different localized motions

Example: 2-fold Jump Rotation

$p(r_1,t)$ and $p(r_2,t)$ are probability of finding the particle at time t at site r_1 and r_2

$$\frac{dP(r_1,t)}{dt} = -\frac{1}{\tau}P(r_1,t) + \frac{1}{\tau}P(r_2,t) \qquad \frac{dP(r_2,t)}{dt} = -\frac{1}{\tau}P(r_2,t) + \frac{1}{\tau}P(r_1,t)$$

$$\frac{P(r_1,t)}{dt} + \frac{dP(r_2,t)}{dt} = 0 \quad \Longrightarrow \quad P(r_1,t) + P(r_2,t) = Constant$$

Let me give you an example. I just talked about Fick's diffusion. But now, let me take an example which is a 2-fold jump rotation. Suppose there are two sites, so it can be an H_2 molecule which may be rotating in a medium with two allowed positions for the two 'H' atoms, but not allowed translation. So, it is just rotation or rotational jump between two sites I am talking about.

This hydrogen goes from site 1 to site 2, site 2 to site 1. So, basically, in brief, I am talking about a 2-fold jump rotation. For H_2 of course, it is not exactly right, because there are two particles and I am talking about a single particle and there are two sites. The particle will go from one site to another site by jumping.

So, if I write down the residence time as τ at a site, then I can write a very simple loss and gain equation. Let us say I started with the site, let me call this site r_1 and there is another site r_2. So, the change in probability of being at site r_1. This is like radioactive decay equation. If the residence time is τ then it is a statistical fact that probability $-P(r_1, t)$ divided by τ will tell me after τ time, what is the probability that it has leaked out or gone to the other site. And this is a loss term and the gain term is if the particle was at second site, what is the probability that it has leaked into this site. So, basically, it is gain minus loss, gives me the probability that particle at r_1, t and its rate of change with time probabilistically.

Similarly, I can write the same thing for the second site r_2, t where the loss term now is that the particle is lost from second site to first site and there is a gain term, which is coming from to first site to second site.

If I add up these three equations, we get a very obvious result that $P(r_1, t) + P(r_2, t) = Const.$, actually this constant should be 1. Because it should be either here or there at a time t and together, they should be 1. Here from these two equations when we add up, $\frac{dP(r_1,t)}{dt} + \frac{dP(r_2,t)}{dt} = 0$, gives me a constant value.

I can solve it; this is a very simple first order equation. But I just give you the solutions. So, basically two constants A and B have to be determined for the solution and this is the time variable and how the probabilities are changing with time. This I can straightaway plug-in into the solutions. At $t = 0$, $P(r_1, t) = A + B$ and $P(r_2, t) = A - B$.

The $A + B$ can be equal to 1 if the particle starts from site 1 and then $A - B$ should be equal to 0 putting $t = 0$. At time $t = 0$, if I solve these two, I get the solutions $P_1^{(1)}$ and $P_1^{(2)}$, these are the two probabilities, one is that it was at site 1 at time $t = 0$, what is probability it continues. Same for the other site.

Now, using these probabilities I can write down this intermediate scattering function which has got a time-dependent part and a time-independent part. This is the EISF part. Because here the jump between the sites is stochastic and the time variation is given by this part.

But the fact is that because there is a finite size diffusion, we also have something called the elastic incoherent structure factor, which has got a Q dependence like this. I have specifically written down Q dependence for $A_0(Q)$ and $A_1(Q)$. This $[A_1(Q)]$ is the pre factor of the time dependent part. And this $[A_0(Q)]$ is the pre factor [time-independent], if I want, I can put a $\delta(\omega)$ here. So, when I take a Fourier transform, this will give me the elastic line broadened by the instrumental resolution, and this will give me the Lorentzian line broadened by the instrumental resolution and the pre factor $A_1(Q)$.

$$P(r_1, t) = A + Be^{-\frac{2t}{\tau}} \checkmark \qquad P(r_2, t) = A - Be^{-\frac{2t}{\tau}} \checkmark \qquad \begin{array}{l} A + B = 1 \\ A - B = 0 \end{array}$$

$$P(r_1, t; r_1, 0) = \frac{1}{2}\left[1 + e^{-\frac{2t}{\tau}}\right] = P_1^{(1)}(t) \qquad P(r_2, t; r_1, 0) = \frac{1}{2}\left[1 - e^{-\frac{2t}{\tau}}\right] = P_1^{(2)}(t)$$

$$I(Q, t) = \langle e^{iQ.r(t)} e^{-iQ.r(0)} \rangle$$

$$I(Q, t) = A_0(Q) + A_1(Q)e^{-\frac{2t}{\tau}}$$

$$A_0(Q) = \frac{1}{2}[1 + \cos Q.(r_1 - r_2)]$$

$$A_1(Q) = \frac{1}{2}[1 - \cos Q.(r_1 - r_2)]$$

Time Fourier transform

$$(Q)\delta(\omega) + A_1(Q)\frac{1}{\pi}\frac{2\tau}{4 + \omega^2\tau^2} \qquad (D\,Q^2)^{\sim}$$

This is true for a jump diffusion between 2 sites and often that happens in many of our problems. As I said, $I(Q, t)$ gives us $A_0(Q)$ which is this the Q dependence for the elastic incoherent structure factor and the other part gives me a Lorentzian or if you see the previous expression, I wrote $(DQ^2)^2$ and here it is $\omega^2\tau^2$. So, they are very, very similar in nature. This is a Lorentzian distribution. This Lorentzian time distribution can give me the jump times τ, but this part, $A_0(Q)$ and its variation with Q tells me what is the geometry of the jump. Here, it is 2-fold, it can be even three points or a three-fold jump. So, the particle may be jumping between these points or it can be even a 6-fold jump, where the particle is jumping between 6 sites or the particle may be continuously diffusing over a circle. For all these, we can make similar equations, which is very simple. In case of 3 points, I will have 3 terms and two of them will be the gain terms and one will be the loss term when the particle starts from any of the three points. And one can easily solve the probability equation. I have derived one example. I will give the results for other cases.

Now, let us just write down it for a powder sample. So far, I have kept calculating $S(Q,\omega)$. The only difference in case of powder sample, we have to take all possible orientations of Q (vector) and that is you can see that it is $\sin\theta\,d\theta\,d\varphi$. integration over $\sin\theta\,d\theta\,d\varphi$ will give one the orientational average of $S(Q,\omega)$.

And then what we get is this. This is the elastic incoherent structure factor and there is the natural Lorentzian. The Q dependent pre factor of the EISF, which comes from the geometry of rotation is given by these expressions, these are Bessel functions of zeroth order, which are basically $\frac{\sin x}{x}$: zeroth order spherical Bessel functions.

So, with these expressions, once we do an experiment, we can measure the Lorentzian and we can also measure $A_0(Q)$ or $A_0'(Q)$ for a powder sample as a function of Q and get the kind of rotational geometry that is there in the system.

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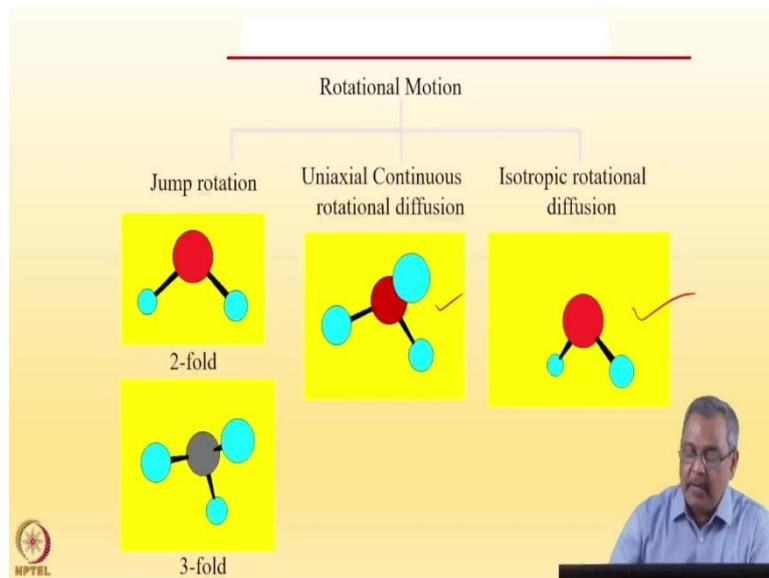
A pictorial demonstration that we can have 2-fold jump rotation, 3-fold jump diffusion or uniaxial continuous rotational diffusion. we can have. An isotropic rotational diffusion means this axis is not fixed. This axis can have any orientation and the particle can have a rotational diffusion over a sphere. Here it will be over a circle, here it will be over a sphere. So, these are some possible situations about the possible physical constraints over which a molecule can diffuse.

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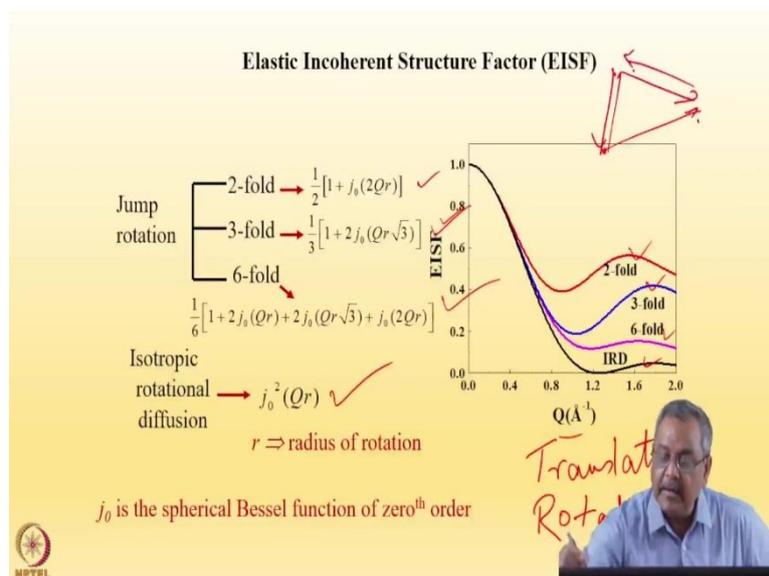
Let me just give you the expression for elastic incoherent structure factors, for various jump rotation models. As I mentioned to you earlier about 2-fold, 3-fold, 6-fold jump models and isotropic rotational diffusion on a circle. These are the expressions for the corresponding EISFs.

For isotropic, rotational diffusion, the EISF is $j_0^2(Qr)$, where r is the radius of rotation and j_0 is a spherical Bessel function of zeroth order. This schematic shows you that what will be the variation of EISF with respect to Q for a 2-fold, 3-fold, 6-fold and continuous jump rotational diffusion and by measurement of EISF we can select or we can guess which one of these models is valid for a molecule for example, some organic molecule, which is undergoing a rotational diffusion.

So, we are not only talking about translational diffusion, but we are also talking about rotation and we are introducing a term called rotational diffusion. If there are three sites, just like translational diffusion, the particle can come from one site to another, go back there, i.e. jump from one site to another. So, they can undergo jump diffusion between these three sites.