

Module III, Lecture 02: Correlation Functions and Spectral Densities

The only part of Bloch-Redfield-Wangsness spin relaxation theory that we could say nothing about in the previous lecture were the correlation functions. They are, in general, unknown, but the simple and popular cases of isotropic and anisotropic rotational diffusion will be treated in this lecture.

Correlation functions – isotropic rotational diffusion

It was demonstrated in the previous lectures that, in the case of rotationally modulated spin interactions in rigid molecules, the anisotropic part of the spin Hamiltonian always has the following form:

$$\hat{H}(t) = \sum_{k,m=-2}^2 \mathfrak{D}_{km}^{(2)}(t) \hat{Q}_{km} \quad (1)$$

where $\mathfrak{D}_{km}^{(2)}(t)$ are second-rank Wigner functions that depend on molecular orientation (and therefore time) and \hat{Q}_{km} are rotational basis operators. Under the assumption that the noise in the system is stationary, the most general form of a correlation function between two Wigner functions is:

$$G_{kmpq}(\tau) = \langle \mathfrak{D}_{km}^{(2)}(t) \mathfrak{D}_{pq}^{(2)*}(t+\tau) \rangle = \langle \mathfrak{D}_{km}^{(2)}(0) \mathfrak{D}_{pq}^{(2)*}(\tau) \rangle \quad (2)$$

where the angular brackets denote the ensemble average, *e.g.* the average over all the differently oriented molecules in a liquid sample. Such ensemble averages may be recast in terms of probability distributions, for example:

$$\langle x \rangle = \int_{-\infty}^{\infty} xp(x) dx \quad (3)$$

where $p(x)$ is the ensemble probability density function for the values of x . In this way, the ensemble average of the product of differently timed Wigner functions in Equation (2) can be written in terms of integrals of probabilities of encountering systems in a particular orientation:

$$G_{kmpq}(\tau) = \langle \mathfrak{D}_{km}^{(2)}(0) \mathfrak{D}_{pq}^{(2)*}(\tau) \rangle = \iint \mathfrak{D}_{km}^{(2)}(\Omega_0) \mathfrak{D}_{pq}^{(2)*}(\Omega) P(\Omega_0) P(\Omega, \tau | \Omega_0, 0) d\Omega_0 d\Omega \quad (4)$$

where $P(\Omega_0)$ is the probability density of initial orientations and $P(\Omega, \tau | \Omega_0, 0)$ is the probability density of molecules having an orientation Ω at time τ , having had an orientation Ω_0 at time zero. Probability densities $P(\Omega_0)$ and $P(\Omega, \tau | \Omega_0, 0)$ may be thought of as fractional concentrations – they give the “concentration” of molecules in a particular location in the orientation space.

We will assume in this section that the molecules in our sample are spherical particles undergoing isotropic rotational diffusion. That means that the initial probability distribution $P(\Omega_0)$ is uniform, meaning that $P(\Omega_0) = 1/8\pi^2$, and so the integral simplifies to:

$$G_{kmpq}(\tau) = \frac{1}{8\pi^2} \iint \mathfrak{D}_{km}^{(2)}(\Omega_0) \mathfrak{D}_{pq}^{(2)*}(\Omega) P(\Omega, \tau | \Omega_0, 0) d\Omega_0 d\Omega \quad (5)$$

There will be diffusion from one orientation into another, and we will assume that P obeys the isotropic rotational diffusion equation:

$$\frac{\partial}{\partial \tau} P(\Omega, \tau | \Omega_0, 0) = -D(\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2) P(\Omega, \tau | \Omega_0, 0) = -D\hat{L}^2 P(\Omega, \tau | \Omega_0, 0) \quad (6)$$

where D is the rotational diffusion constant and $\{\hat{L}_x, \hat{L}_y, \hat{L}_z\}$ are the angular momentum operators. Because Wigner functions are eigenfunctions of the total momentum operator \hat{L}^2 :

$$\hat{L}^2 \mathfrak{D}_{km}^{(l)}(\Omega) = l(l+1) \mathfrak{D}_{km}^{(l)}(\Omega) \quad (7)$$

it is reasonable to seek a solution to Equation (6) in terms of Wigner functions:

$$P(\Omega, \tau | \Omega_0, 0) = \sum_{l=0}^{\infty} \sum_{k,m=-l}^l A_{km}^{(l)}(\tau | \Omega_0, 0) \mathfrak{D}_{km}^{(l)}(\Omega) \quad (8)$$

If we substitute this solution back into Equation (6), we get the expression for the time-dependent coefficients $A_{km}^{(l)}(\tau | \Omega_0, 0)$:

$$\begin{aligned} \sum_{l=0}^{\infty} \sum_{k,m=-l}^l \frac{\partial}{\partial \tau} A_{km}^{(l)}(\tau | \Omega_0, 0) \mathfrak{D}_{km}^{(l)}(\Omega) &= -D \sum_{l=0}^{\infty} \sum_{k,m=-l}^l l(l+1) A_{km}^{(l)}(\tau | \Omega_0, 0) \mathfrak{D}_{km}^{(l)}(\Omega) \\ \frac{\partial}{\partial \tau} A_{km}^{(l)}(\tau | \Omega_0, 0) &= -Dl(l+1) A_{km}^{(l)}(\tau | \Omega_0, 0) \quad \Rightarrow \quad A_{km}^{(l)}(\tau | \Omega_0, 0) = e^{-Dl(l+1)\tau} A_{km}^{(l)}(0) \end{aligned} \quad (9)$$

The general solution therefore acquires the form:

$$P(\Omega, \tau | \Omega_0, 0) = \sum_{l=0}^{\infty} \sum_{k,m=-l}^l C_{km}^{(l)} \mathfrak{D}_{km}^{(l)}(\Omega) e^{-Dl(l+1)\tau} \quad (10)$$

where $C_{km}^{(l)}$ are the coefficients determined by the initial condition. The completeness condition for Wigner functions of integer rank is:

$$\sum_{l=0}^{\infty} \sum_{k,m=-l}^l \frac{2l+1}{8\pi^2} \mathfrak{D}_{km}^{(l)*}(\Omega_0) \mathfrak{D}_{km}^{(l)}(\Omega) = \delta(\Omega - \Omega_0) \quad (11)$$

and therefore the initial condition (all systems pointing at Ω_0 at time zero) yields:

$$\begin{aligned} \sum_{l=0}^{\infty} \sum_{k,m=-l}^l C_{km}^{(l)} \mathfrak{D}_{km}^{(l)}(\Omega) &= \delta(\Omega - \Omega_0) \quad \Rightarrow \quad C_{km}^{(l)} = \frac{2l+1}{8\pi^2} \mathfrak{D}_{km}^{(l)*}(\Omega_0) \\ P(\Omega, \tau | \Omega_0, 0) &= \sum_{l=0}^{\infty} \frac{2l+1}{8\pi^2} \sum_{k,m=-l}^l \mathfrak{D}_{km}^{(l)*}(\Omega_0) \mathfrak{D}_{km}^{(l)}(\Omega) e^{-Dl(l+1)\tau} \end{aligned} \quad (12)$$

We can now use the orthogonality condition for Wigner functions:

$$\int \mathfrak{D}_{k_1 m_1}^{(l_1)*}(\Omega) \mathfrak{D}_{k_2 m_2}^{(l_2)}(\Omega) d\Omega = \frac{8\pi^2}{2l_1+1} \delta_{l_1, l_2} \delta_{k_1, k_2} \delta_{m_1, m_2} \quad (13)$$

to compute the integral in Equation (5):

$$\begin{aligned} G_{abcd}(\tau) &= \frac{1}{8\pi^2} \iint \mathfrak{D}_{ab}^{(2)}(\Omega_0) \mathfrak{D}_{cd}^{(2)*}(\Omega) P(\Omega, \tau | \Omega_0, 0) d\Omega_0 d\Omega = \\ &= \frac{1}{8\pi^2} \sum_{l=0}^{\infty} \frac{2l+1}{8\pi^2} e^{-Dl(l+1)\tau} \sum_{k,m=-l}^l \iint \mathfrak{D}_{ab}^{(2)}(\Omega_0) \mathfrak{D}_{cd}^{(2)*}(\Omega) \mathfrak{D}_{km}^{(l)*}(\Omega_0) \mathfrak{D}_{km}^{(l)}(\Omega) d\Omega_0 d\Omega = \\ &= \frac{1}{8\pi^2} \sum_{l=0}^{\infty} \frac{2l+1}{8\pi^2} e^{-Dl(l+1)\tau} \sum_{k,m=-l}^l \left[\int \mathfrak{D}_{km}^{(l)*}(\Omega_0) \mathfrak{D}_{ab}^{(2)}(\Omega_0) d\Omega_0 \right] \left[\int \mathfrak{D}_{cd}^{(2)*}(\Omega) \mathfrak{D}_{km}^{(l)}(\Omega) d\Omega \right] = \\ &= \frac{1}{8\pi^2} \sum_{l=0}^{\infty} \frac{2l+1}{8\pi^2} e^{-Dl(l+1)\tau} \sum_{k,m=-l}^l \left[\frac{8\pi^2}{2l+1} \delta_{l,2} \delta_{k,a} \delta_{m,b} \right] \left[\frac{8\pi^2}{2l+1} \delta_{l,2} \delta_{k,c} \delta_{m,d} \right] = \frac{\delta_{a,c} \delta_{b,d}}{5} e^{-6D\tau} \end{aligned} \quad (14)$$

And so the final expression for the correlation function in the case of isotropic rotational diffusion is:

$$G_{abcd}(\tau) = \langle \mathcal{D}_{ab}^{(2)}(0) \mathcal{D}_{cd}^{(2)*}(\tau) \rangle = \frac{\delta_{a,c} \delta_{b,d}}{5} e^{-6D\tau} = \frac{\delta_{a,c} \delta_{b,d}}{5} e^{-\frac{\tau}{\tau_c}} \quad (15)$$

$$D = \frac{kT}{8\pi\eta r^3} \quad \Rightarrow \quad \tau_c = \frac{1}{6D} = \frac{4\pi\eta r^3}{3kT}$$

where τ_c is known as the *rotational correlation time*, η is the *dynamic viscosity* of the solvent and r is the *hydrodynamic radius* of the molecule, which is assumed to be spherical. The equation connecting the rotational diffusion constant to the particle radius, solvent viscosity and temperature is derived from the Stokes' law. Equation (15) is the most common rotational correlation function in current use.

Correlation functions – rotational diffusion of a symmetric top

For a symmetric top molecule, the rotational diffusion equation acquires the following form:

$$\frac{\partial}{\partial \tau} P(\Omega, \tau | \Omega_0, 0) = - \left[D_{\parallel} \hat{L}_Z^2 + D_{\perp} (\hat{L}_X^2 + \hat{L}_Y^2) \right] P(\Omega, \tau | \Omega_0, 0) \quad (16)$$

where D_{\parallel} and D_{\perp} are the axial and equatorial rotational diffusion constants of what is now assumed to be an ellipsoidal particle, and $\{\hat{L}_X, \hat{L}_Y, \hat{L}_Z\}$ are the same angular momentum operators as above. Wigner functions are still a convenient choice, because they are also eigenfunctions of the diffusion operator in the square brackets in Equation (16):

$$\begin{aligned} - \left[D_{\parallel} \hat{L}_Z^2 + D_{\perp} (\hat{L}_X^2 + \hat{L}_Y^2) \right] \mathcal{D}_{km}^{(l)}(\Omega) &= - \left[(D_{\parallel} - D_{\perp}) \hat{L}_Z^2 + D_{\perp} (\hat{L}_X^2 + \hat{L}_Y^2 + \hat{L}_Z^2) \right] \mathcal{D}_{km}^{(l)}(\Omega) = \\ &= -\lambda_m^{(l)} \mathcal{D}_{km}^{(l)}(\Omega), \quad \lambda_m^{(l)} = \left[l(l+1) D_{\perp} + m^2 (D_{\parallel} - D_{\perp}) \right] \end{aligned} \quad (17)$$

This being the only difference from the entire derivation given above (everything else flows through identically), we can conclude that in the case of the axially anisotropic rotational diffusion:

$$G_{abcd}(\tau) = \langle \mathcal{D}_{ab}^{(2)}(0) \mathcal{D}_{cd}^{(2)*}(\tau) \rangle = \frac{\delta_{a,c} \delta_{b,d}}{5} e^{-[6D_{\perp} + b^2(D_{\parallel} - D_{\perp})]\tau} \quad (18)$$

where the rotational diffusion constants are related to the two radii of the ellipsoid in a way that directly follows from Equation (15):

$$D_{\parallel} = \frac{kT}{8\pi\eta r_{\parallel}^3}, \quad D_{\perp} = \frac{kT}{8\pi\eta r_{\perp}^3} \quad (19)$$

Importantly, Equation (16) implicitly assumes the molecular frame of reference to be the eigenframe of the rotational diffusion tensor – this condition must be observed during the spin system setup for the relaxation theory calculations.

Correlation functions – anisotropic rotational diffusion

In the fully anisotropic case we have:

$$\frac{\partial}{\partial \tau} P(\Omega, \tau | \Omega_0, 0) = - \left[D_{XX} \hat{L}_X^2 + D_{YY} \hat{L}_Y^2 + D_{ZZ} \hat{L}_Z^2 \right] P(\Omega, \tau | \Omega_0, 0) \quad (20)$$

in which $\{D_{XX}, D_{YY}, D_{ZZ}\}$ are now the three (assumed different) eigenvalues of the rotational diffusion tensor. The Wigner functions are no longer the eigenfunctions of the differential operator in the square brackets, but they are not very far from them, because:

$$\hat{L}_Z \mathfrak{D}_{km}^{(l)}(\Omega) = m \mathfrak{D}_{km}^{(l)}(\Omega) \quad (21)$$

$$\hat{L}_\pm \mathfrak{D}_{km}^{(l)}(\Omega) = (\hat{L}_X \pm i \hat{L}_Y) \mathfrak{D}_{km}^{(l)}(\Omega) = \sqrt{l(l+1) - m(m \pm 1)} \mathfrak{D}_{k, m \pm 1}^{(l)}(\Omega)$$

With some effort (verifiable by back substitution followed by application of Equations (21)), we can obtain the second rank eigenfunctions of the fully anisotropic rotational diffusion operator in the basis of second rank Wigner functions:

m	$\lambda_{km}^{(2)}$	$\Psi_{km}^{(2)}(\Omega)$
1	$4D_{XX} + D_{YY} + D_{ZZ}$	$(\sqrt{2})^{-1} [\mathfrak{D}_{k,1}^{(2)}(\Omega) + \mathfrak{D}_{k,-1}^{(2)}(\Omega)]$
2	$D_{XX} + 4D_{YY} + D_{ZZ}$	$(\sqrt{2})^{-1} [\mathfrak{D}_{k,1}^{(2)}(\Omega) - \mathfrak{D}_{k,-1}^{(2)}(\Omega)]$
3	$D_{XX} + D_{YY} + 4D_{ZZ}$	$(\sqrt{2})^{-1} [\mathfrak{D}_{k,2}^{(2)}(\Omega) - \mathfrak{D}_{k,-2}^{(2)}(\Omega)]$
4	$2D_{XX} + 2D_{YY} + 2D_{ZZ} - 2\Delta_D$	$(\sqrt{2 + (\Lambda_D^-)^2})^{-1} [\mathfrak{D}_{k,2}^{(2)}(\Omega) + \Lambda_D^- \mathfrak{D}_{k,0}^{(2)}(\Omega) + \mathfrak{D}_{k,-2}^{(2)}(\Omega)]$
5	$2D_{XX} + 2D_{YY} + 2D_{ZZ} + 2\Delta_D$	$(\sqrt{2 + (\Lambda_D^+)^2})^{-1} [\mathfrak{D}_{k,2}^{(2)}(\Omega) + \Lambda_D^+ \mathfrak{D}_{k,0}^{(2)}(\Omega) + \mathfrak{D}_{k,-2}^{(2)}(\Omega)]$

where the m index now runs plainly from 1 to 5 – projection ranks have been mixed in the new eigenfunctions, and therefore $m \in [-2, 2]$ indexing is no longer appropriate. The new shorthand symbols are defined as follows:

$$\Delta_D = \sqrt{D_{XX}^2 + D_{YY}^2 + D_{ZZ}^2 - D_{XX}D_{YY} - D_{XX}D_{ZZ} - D_{YY}D_{ZZ}}$$

$$\Lambda_D^\pm = \sqrt{\frac{2}{3} \frac{D_{XX} + D_{YY} - 2D_{ZZ} \pm 2\Delta_D}{D_{XX} - D_{YY}}}$$

Other l ranks will make an appearance in the equations below, but would not eventually be necessary. Similarly to the treatment before, the general solution to Equation (20) is:

$$P(\Omega, \tau | \Omega_0, 0) = \sum_{l=0}^{\infty} \sum_{m=-l}^l \sum_{k=1}^{2l+1} C_{km}^{(l)} \Psi_{km}^{(l)}(\Omega) e^{-\lambda_{km} \tau} \quad (22)$$

Because the eigenfunctions in the table above have been normalized, the completeness relation remains the same as Equation (11) and for the case where all systems are initially pointed at Ω_0 we get:

$$P(\Omega, \tau | \Omega_0, 0) = \sum_{l=0}^{\infty} \frac{2l+1}{8\pi^2} \sum_{m=-l}^l \sum_{k=1}^{2l+1} \Psi_{km}^{(l)*}(\Omega_0) \Psi_{km}^{(l)}(\Omega) e^{-\lambda_{km}^{(l)} \tau} \quad (23)$$

Keeping in mind the Wigner function orthogonality relations in Equation (13), we can now take the integral in Equation (5):

$$\begin{aligned}
G_{abcd}(\tau) &= \frac{1}{8\pi^2} \sum_{l=0}^{\infty} \frac{2l+1}{8\pi^2} \sum_{k=-l}^l \sum_{m=1}^{2l+1} e^{-\lambda_{km}^{(l)}\tau} \iint \mathfrak{D}_{ab}^{(2)}(\Omega_0) \mathfrak{D}_{cd}^{(2)*}(\Omega) \Psi_{km}^{(l)*}(\Omega_0) \Psi_{km}^{(l)}(\Omega) d\Omega_0 d\Omega = \\
&= \frac{1}{8\pi^2} \sum_{l=0}^{\infty} \frac{2l+1}{8\pi^2} \sum_{k=-l}^l \sum_{m=1}^{2l+1} e^{-\lambda_{km}^{(l)}\tau} \left[\int \Psi_{km}^{(l)*}(\Omega_0) \mathfrak{D}_{ab}^{(2)}(\Omega_0) d\Omega_0 \right] \left[\int \Psi_{km}^{(l)*}(\Omega) \mathfrak{D}_{cd}^{(2)}(\Omega) d\Omega \right]^* = \quad (24) \\
&= \frac{1}{8\pi^2} \sum_{l=0}^{\infty} \frac{2l+1}{8\pi^2} \sum_{k=-l}^l \sum_{m=1}^{2l+1} e^{-\lambda_{km}^{(l)}\tau} \left[\frac{8\pi^2}{2l+1} \delta_{l,2} \delta_{ka} h_{mb} \right] \left[\frac{8\pi^2}{2l+1} \delta_{l,2} \delta_{kc} h_{md}^* \right] = \sum_{k=1}^5 \frac{\delta_{ac} h_{mb} h_{md}^*}{5} e^{-\lambda_{km}^{(2)}\tau}
\end{aligned}$$

where the m index on the eigenvalues has been dropped (they did not depend on it anyway) and the superscript indicating second rank has been omitted because it is no longer algebraically relevant. The new constants h_{mb} may be computed by brute force and depend on their indices in the following way:

$m \setminus b$	-2	-1	0	1	2
1	0	$(\sqrt{2})^{-1}$	0	$(\sqrt{2})^{-1}$	0
2	0	$-(\sqrt{2})^{-1}$	0	$(\sqrt{2})^{-1}$	0
3	$-(\sqrt{2})^{-1}$	0	0	0	$(\sqrt{2})^{-1}$
4	$\left(\sqrt{2+(\Lambda_D^-)^2}\right)^{-1}$	0	$\Lambda_D^- \left(\sqrt{2+(\Lambda_D^-)^2}\right)^{-1}$	0	$\left(\sqrt{2+(\Lambda_D^-)^2}\right)^{-1}$
5	$\left(\sqrt{2+(\Lambda_D^+)^2}\right)^{-1}$	0	$\Lambda_D^+ \left(\sqrt{2+(\Lambda_D^+)^2}\right)^{-1}$	0	$\left(\sqrt{2+(\Lambda_D^+)^2}\right)^{-1}$

Spectral density functions

Let us now look at a specific element of the relaxation superoperator in Hilbert space in a representation where the static Hamiltonian is diagonal (this is a significant assumption – it is not always feasible, for purely numerical reasons, to diagonalize a Hamiltonian):

$$\langle \hat{\rho}_a | \hat{R}_{ab} | \hat{\rho}_b \rangle = \sum_{kmpq} \int_0^{\infty} G_{kmpq}(\tau) \text{Tr} \left(\hat{\rho}_a^\dagger [\hat{Q}_{km}, [e^{i\hat{H}_0\tau} \hat{Q}_{pq}^\dagger e^{-i\hat{H}_0\tau}, \hat{\rho}_b]] \right) d\tau \quad (25)$$

Using the cyclic permutation rule, we can reorder the commutators under the trace:

$$\begin{aligned}
\text{Tr} \left(\hat{\rho}_a^\dagger [\hat{Q}_{k,m}, [e^{i\hat{H}_0\tau} \hat{Q}_{pq}^\dagger e^{-i\hat{H}_0\tau}, \hat{\rho}_b]] \right) &= \text{Tr} \left(e^{i\hat{H}_0\tau} \hat{Q}_{pq}^\dagger e^{-i\hat{H}_0\tau} [\hat{\rho}_a, [\hat{\rho}_b, \hat{Q}_{km}]] \right) = \\
&= \text{Tr} \left(e^{i\hat{H}_0\tau} \hat{Q}_{pq}^\dagger e^{-i\hat{H}_0\tau} \hat{P}_{km}^{(a,b)} \right), \quad \hat{P}_{k,m}^{(a,b)} = [\hat{\rho}_a, [\hat{\rho}_b, \hat{Q}_{km}]]
\end{aligned} \quad (26)$$

The trace of a product of four matrices can be computed explicitly in the indexed notation:

$$\begin{aligned}
\text{Tr} \left(e^{i\hat{H}_0\tau} \hat{Q}_{pq}^\dagger e^{-i\hat{H}_0\tau} \hat{P}_{km}^{(a,b)} \right) &= \sum_{irsj} \left[e^{i\hat{H}_0\tau} \right]_{ir} \left[\hat{Q}_{pq}^\dagger \right]_{rs} \left[e^{-i\hat{H}_0\tau} \right]_{sj} \left[\hat{P}_{km}^{(a,b)} \right]_{ji} = \\
&= \sum_{ij} e^{i\omega_j\tau} \left[\hat{Q}_{pq}^\dagger \right]_{ij} e^{-i\omega_j\tau} \left[\hat{P}_{km}^{(a,b)} \right]_{ji} = \sum_{ij} e^{i(\omega_i - \omega_j)\tau} \left[\hat{Q}_{pq}^\dagger \right]_{ij} \left[\hat{P}_{km}^{(a,b)} \right]_{ji} = \sum_{ij} e^{i\omega_{ij}\tau} \left[\hat{Q}_{pq}^\dagger \right]_{ij} \left[\hat{P}_{km}^{(a,b)} \right]_{ji}
\end{aligned} \quad (27)$$

and the integral becomes a collection of Fourier transforms:

$$\langle \hat{\rho}_a | \hat{R}_{ab} | \hat{\rho}_b \rangle = - \sum_{ijkmpq} [\hat{Q}_{pq}^\dagger]_{ij} [\hat{P}_{km}^{(a,b)}]_{ji} \int_0^\infty G_{kmpq}(\tau) e^{i\omega_j \tau} d\tau = - \sum_{ijkmpq} [\hat{Q}_{pq}^\dagger]_{ij} [\hat{P}_{km}^{(a,b)}]_{ji} J_{kmpq}(\omega_{ij}) \quad (28)$$

$$J_{kmpq}(\omega) = \int_0^\infty G_{kmpq}(\tau) e^{i\omega \tau} d\tau, \quad \omega_{ij} = \omega_i - \omega_j$$

The Fourier transform of the correlation function is called the *spectral density function*. It has a physical meaning of energy density of the stochastic perturbation at a given frequency. In the isotropic tumbling approximation we have:

$$J(\omega) = \int_0^\infty e^{-\tau/\tau_c} e^{i\omega \tau} d\tau = \frac{1}{1/\tau_c + i\omega} = \frac{\tau_c}{1 + \omega^2 \tau_c^2} - \frac{i\omega \tau_c^2}{1 + \omega^2 \tau_c^2} \quad (29)$$

The real part of this function is a Lorentzian curve. It determines the relaxation rate (it would acquire a minus when it appears in the Liouville – von Neumann equation). The (usually much smaller) imaginary part contributes to the frequency part of the LvN equation and for that reason is known as *dynamic frequency shift*. The DFS is usually ignored in practical simulations.

Spectral densities in non-rigid molecules: the Lipari-Szabo model

Analytical simplicity is a rare virtue in relaxation theory, and it is probably the only virtue of the Lipari-Szabo restricted local motion model. We can observe that, in a spherical molecule where the overall rotational diffusion is independent from the restricted local diffusion of a particular group, the correlation function can be factored as

$$G(\tau) = G_{\text{global}}(\tau) G_{\text{local}}(\tau) \quad (30)$$

Lipari-Szabo approximation assumes that both functions are exponential and the resulting spectral density function therefore is:

$$J(\omega) = \frac{S^2 \tau_c}{1 + \omega^2 \tau_c^2} + \frac{(1 - S^2) \tau}{1 + \omega^2 \tau^2}, \quad \tau = \left(\frac{1}{\tau_c} + \frac{1}{\tau_{\text{int}}} \right)^{-1} \quad (31)$$

where S^2 is called *order parameter*. It can be interpreted as a fraction of the full body angle that is spanned by the restriction cone of the internal motion. This form for the spectral density function is widely used in protein NMR spectroscopy.

Translational diffusion

The relaxation theory derived in the previous lecture specifically assumed rotationally modulated interactions because a complete and elegant relaxation theory is only available for the rotationally modulated case. Special cases for translationally modulated interactions are also analytical and we will consider a simple case of a translationally modulated scalar interaction in this section.

Consider a correlation function of the amplitude multiplier $f(t)$ of a distance-dependent interaction taken at two different times in a system governed by isotropic translational diffusion:

$$G(\tau) = \langle f(t) f(t + \tau) \rangle = \langle f(0) f(\tau) \rangle \quad (32)$$

From the same probability argument as we used for the rotational diffusion in Equation (4), we get:

$$G(\tau) = \iint f(\vec{r}_0) f(\vec{r}) P(\vec{r}_0) P(\vec{r}, \tau | \vec{r}_0, 0) d^3 \vec{r}_0 d^3 \vec{r} \quad (33)$$

where $P(\vec{r}_0)$ is the probability density of distances and $P(\vec{r}, \tau | \vec{r}_0, 0)$ is the probability density of a system having a distance \vec{r} at time τ , having had a distance \vec{r}_0 at time zero. We will assume that the probability distribution $P(\Omega_0)$ is uniform, and so the integral simplifies to

$$G(\tau) = \frac{1}{V} \iint f(\vec{r}_0) f(\vec{r}) P(\vec{r}, \tau | \vec{r}_0, 0) d^3\vec{r}_0 d^3\vec{r} \quad (34)$$

where V is the sample volume. The probability density $P(\vec{r}, \tau | \vec{r}_0, 0)$ may be thought of as fractional concentration – it gives the “concentration” of systems with a particular value of the distance. There will be diffusion from one distance into another, and we will assume that P obeys the diffusion equation:

$$\frac{\partial}{\partial \tau} P(\vec{r}, \tau | \vec{r}_0, 0) = -D \nabla^2 P(\vec{r}, \tau | \vec{r}_0, 0), \quad P(\vec{r}, 0 | \vec{r}_0, 0) = \delta(\vec{r} - \vec{r}_0) \quad (35)$$

where D is the relative diffusion constant and the hard sphere boundary condition:

$$\left. \frac{\partial P}{\partial r} \right|_{r=d} = 0 \quad (36)$$

where d is the distance of closest approach. There are no simple analytical solutions for the correlation function in Equation (34), but various limits and approximations are available in the literature.