Calculation of order parameters

Mirco Zerbetto

October 14, 2008

In describing the interaction between the protein and the probe the ordering potential is assumed to be

$$\begin{aligned} U(\Omega) &= -c_0^2 D_{0,0}^2(\Omega) - c_2^2 \left[D_{0,2}^2(\Omega) + D_{0,-2}^2(\Omega) \right] - c_0^4 D_{0,0}^4(\Omega) + \\ & -c_2^4 \left[D_{0,2}^4(\Omega) + D_{0,-2}^4(\Omega) \right] - c_4^4 \left[D_{0,4}^4(\Omega) + D_{0,-4}^4(\Omega) \right] \end{aligned} \tag{1}$$

where $\Omega = (\alpha, \beta, \gamma)$ is the set of Euler angles that give the relative orientation between the protein and the probe and $D_{M,K}^L(\Omega)$ is a Wigner matrix.
Due to the general expression of Wigner matrices

$$D_{M,K}^L(\Omega) = e^{-iM\alpha} d_{M,K}^L(\beta) e^{-iK\gamma} \tag{2}$$

where $d_{M,K}^L(\beta)$ is the reduced Wigner matrix, the potential given in (1) is independent on the angle α. This implies that the orientational distribution over the α angle will be isotropic, i.e. a completely disordered distribution.
For what concerns β and γ angles, instead, the potential will impose some ordering. Of course, all informations about the "amount" of ordering are contained in the potential (in particular in the coefficients). However, looking the values of the coefficients is poorly intuitive and it would be better to have a single normalized coefficient to express order.
Basically, two order parameters are usually defined to quantify order in β angle and in γ angle; these are two numbers that range from 0 (complete disorder, isotropy) to 1 (complete ordering). Such order paramters are calculated as:

$$S_0^2 = \langle D_{0,0}^2(\Omega) \rangle \tag{3}$$

and

$$S_2^2 = \langle D_{0,2}^2(\Omega) + D_{0,-2}^2(\Omega) \rangle \tag{4}$$

where $\langle \ldots \rangle$ represents an avarage over Ω space.
Parameter S_0^2 gives informations about ordering along the director, while S_2^2 represents the ordering around the director.
At a first sight, the two integrals are in three dimensions, but a deeper analysis leads to more formally simple and computationally light expressions.

For what concerns the S_0^2 parameter, it is possible to write:

$$
\begin{aligned}
S_0^2 &= \mathcal{N}\int d\Omega D^2_{0,0}\left(\Omega\right)e^{-U(\Omega)} = \\
&= \mathcal{N}\int_0^{2\pi} d\alpha \int_0^{\pi} d\beta \sin\left(\beta\right)\int_0^{2\pi} d\gamma d^2_{0,0}\left(\beta\right)e^{u_0(\beta)+u_2(\beta)\cos\left(2\gamma\right)+u_4(\beta)\cos\left(4\gamma\right)} = \\
&= 2\pi\mathcal{N}\int_0^{\pi} d\beta \sin\left(\beta\right)d^2_{0,0}\left(\beta\right)e^{u_0(\beta)}\int_0^{2\pi} d\gamma e^{u_2(\beta)\cos\left(2\gamma\right)+u_4(\beta)\cos\left(4\gamma\right)} = \\
&= 2\pi\mathcal{N}\int_0^{\pi} d\beta \sin\left(\beta\right)d^2_{0,0}\left(\beta\right)e^{u_0(\beta)}f_0\left(\beta\right)
\end{aligned} \tag{5}
$$

where $\mathcal{N} = 1/\langle \exp\left[-U\left(\Omega\right)\right]\rangle$ and

$$
\begin{aligned}
u_0\left(\beta\right) &= c_0^2 d^2_{0,0}\left(\beta\right) + c_0^4 d^4_{0,0}\left(\beta\right) \\
u_2\left(\beta\right) &= 2\left[c_2^2 d^2_{0,2}\left(\beta\right) + c_2^4 d^4_{0,2}\left(\beta\right)\right] \\
u_4\left(\beta\right) &= 2c_4^4 d^4_{0,4}\left(\beta\right)
\end{aligned} \tag{6}
$$

Before inspecting the integral $f_0\left(\beta\right)$, it is useful to consider the calculation of the S_2^2 parameter. Starting from the observation that $D^2_{0,2}\left(\Omega\right) + D^2_{0,-2}\left(\Omega\right) = 2d^2_{0,2}\left(\beta\right)\cos\left(2\gamma\right)$, it is possible to write

$$
\begin{aligned}
S_2^2 &= 4\pi\mathcal{N}\int_0^{\pi} d\beta \sin\left(\beta\right)d^2_{0,2}\left(\beta\right)e^{u_0(\beta)}\int_0^{2\pi} d\gamma \cos\left(2\gamma\right)e^{u_2(\beta)\cos\left(2\gamma\right)+u_4(\beta)\cos\left(4\gamma\right)} = \\
&= 4\pi\mathcal{N}\int_0^{\pi} d\beta \sin\left(\beta\right)d^2_{0,2}\left(\beta\right)e^{u_0(\beta)}f_2\left(\beta\right)
\end{aligned} \tag{7}
$$

Finally, in an analogous way, its possible to write, for the integral in the normalization constant:

$$
\begin{aligned}
\langle e^{-U(\Omega)}\rangle &= \langle D^0_{0,0}\left(\Omega\right)e^{-U(\Omega)}\rangle = \\
&= 2\pi\int_0^{\pi} d\beta \sin\left(\beta\right)d^0_{0,0}\left(\beta\right)e^{u_0(\beta)}f_0\left(\beta\right)
\end{aligned} \tag{8}
$$

The above analysis shows that to calculate the order parameters it is necessary to calculate three integrals having the general expression:

$$
F_k^j = \int_0^{\pi} d\beta \sin\left(\beta\right)d^j_{0,k}\left(\beta\right)e^{u_0(\beta)}f_k\left(\beta\right) \tag{9}
$$

where

$$
f_k\left(\beta\right) = \int_0^{2\pi} \cos\left(k\gamma\right)e^{u_2(\beta)\cos\left(2\gamma\right)+u_4(\beta)\cos\left(4\gamma\right)} \tag{10}
$$

Now its time to make some considerations on the integral $f_k\left(\beta\right)$. Some properties have to be recalled in order to find an explicit formulation. First of all, let's remind the calculation of the following type of integrals:

$$
\begin{aligned}
A_n &= \int_0^{2\pi} d\gamma \cos\left(2n\gamma\right)e^{z\cos\left(2\gamma\right)} = \\
&= \frac{1}{2}\int_0^{4\pi} d\theta \cos\left(n\theta\right)e^{z\cos\left(\theta\right)} = \\
&= 2\int_0^{\pi} d\theta \cos\left(n\theta\right)e^{z\cos\left(\theta\right)} = \\
&= \left(-\right)^n 2\pi I_n\left(\left|z\right|\right)
\end{aligned} \tag{11}
$$

where $I_n(x)$ is a modified Bessel function of first kind; note that n must be integer in order to A_n to be different from zero.

In second place, these two properties are required

$$e^{z\cos(\theta)} = I_0(|z|) + 2\sum_{k=1}^{\infty}(-)^k I_k(|z|)\cos(k\theta) \tag{12}$$

$$\cos(\alpha)\cos(\beta) = \frac{\cos(\alpha-\beta)+\cos(\alpha+\beta)}{2} \tag{13}$$

The main idea is that of substituting, in the expression of f_k, the expansion in eq. (12) for the exponential $e^{u_4\cos(4\gamma)}$. In what follows, dependency on beta of the functions will be omitted in order to simplify the notation.

$$\begin{aligned}
f_k &= \int_0^{2\pi} d\gamma\cos(k\gamma)e^{u_2\cos(2\gamma)}e^{u_4\cos(4\gamma)} = \\
&= I_0(|u_4|)\int_0^{2\pi} d\gamma\cos(k\gamma)e^{u_2\cos(2\gamma)} + \\
&\quad +2\sum_{n=1}^{\infty}(-)^n I_n(|u_4|)\int_0^{2\pi} d\gamma\cos(4n\gamma)\cos(k\gamma)e^{u_2\cos(2\gamma)} = \\
&= (-)^{k/2}2\pi I_0(|u_4|)\, I_{k/2}(|u_2|) + \\
&\quad +2\sum_{n=1}^{\infty}(-)^n I_n(|u_4|)\int_0^{2\pi} d\gamma\left[\frac{\cos(2(\frac{k}{2}-2n)\gamma)+\cos(2(\frac{k}{2}+2n)\gamma)}{2}\right]e^{u_2\cos(2\gamma)} = \\
&= (-)^{k/2}2\pi I_0(|u_4|)\, I_{k/2}(|u_2|) + \\
&\quad +(-)^{k/2}2\pi\sum_{n=1}^{\infty}(-)^n I_n(|u_4|)\left[I_{k/2-2n}(|u_2|) + I_{k/2+2n}(|u_2|)\right] \\
&= (-)^{k/2}2\pi\left[I_0(|u_4|)\, I_{k/2}(|u_2|) + \Delta_{k/2}(|u_2|,|u_4|)\right]
\end{aligned} \tag{14}$$

Substitution of the above expression for $f_k(\beta)$ in the integral (9) reads

$$\begin{aligned}
F_k^j &= (-)^{k/2}2\pi\int_0^{\pi} d\beta\sin(\beta)d_{0,k}^j(\beta)\, e^{u_0(\beta)}I_{k/2}\left[|u_2(\beta)|\right] I_0\left[|u_4(\beta)|\right] \\
&\quad +(-)^{k/2}2\pi\int_0^{\pi} d\beta\sin(\beta)d_{0,k}^j(\beta)\, e^{u_0(\beta)}\Delta_{k/2}\left[|u_2(\beta)|,|u_4(\beta)|\right]
\end{aligned} \tag{15}$$

Some final considerations

- if $u_2 = u_4 = 0$, then the integral (9) has the simple shape

$$F_k^j = \delta_{k,0}2\pi\int_0^{\pi} d\beta\sin(\beta)d_{0,0}^j(\beta)\, e^{u_0(\beta)} \tag{16}$$

- if only $u_4 = 0$ then $\Delta_{k/2}(|u_2|,|u_4|) = 0$ and $I_0(|u_4|) = 1$, so

$$F_k^j = (-)^{k/2}2\pi\int_0^{\pi} d\beta\sin(\beta)d_{0,k}^j(\beta)\, e^{u_0(\beta)}I_{k/2}\left[|u_2(\beta)|\right] \tag{17}$$

- if only $u_2 = 0$ than f_k integral becomes

$$f_k(\beta) = 2\pi I_{k/4}(|u_4|) \tag{18}$$

which is different from zero only if $k/4$ is integer. The integral (9) becomes

$$F_k^j = 2\pi \int_0^\pi d\beta \sin(\beta) d_{0,k}^j(\beta)\, e^{u_0(\beta)} I_{k/4}\left[|u_4(\beta)|\right] \tag{19}$$

What has been found here is an explicit expression for the integral $f_k(\beta)$ which can be simply computed because there are many optimized libraries for the calculation of special functions, such as the $I_n(x)$ Bessel functions. Moreover, all the problem is reduced to the numerical calculation of an integral over a single variable, β. In terms of equation (9), the order parameters are obtained by

$$S_0^2 = F_0^2/F_0^0 \tag{20}$$
$$S_2^2 = 2F_2^2/F_0^0 \tag{21}$$

The two order parameters can be interpreted of the two spherical components of a symmetric order tensor $\boldsymbol{S}$ and sometimes it is useful to obtain the cartesian components:

$$S_{xx} = \sqrt{\frac{3}{8}} S_2^2 - \frac{1}{2} S_0^2 \tag{22}$$
$$S_{yy} = -\sqrt{\frac{3}{8}} S_2^2 - \frac{1}{2} S_0^2 \tag{23}$$
$$S_{zz} = S_0^2 \tag{24}$$