Appendix F The "hydrated solute model"

In this Appendix the "hydrated solute model" introduced in section 5.8 is discussed in more detail.

F.1 Basic equations and definitions

Together with its hydration shell, an mCD molecule can be considered as a new entity, here denoted as mCD-HYD. The rotational structure factors of mCD-HYD, $A_{l(\text{mCD-HYD})}(Q)$ are given by [109]:

$$A_{l(\text{mCD-HYD})}(Q)=\sum_{\mu=1}^{n+3\times N_{\text{HYD}}}\sum_{\nu=1}^{n+3\times N_{\text{HYD}}}[<b_\mu><b_\nu>+\frac{\sigma_{\mu\,\text{INC}}\delta_{\mu\nu}}{4\pi}]j_l(Qr_\mu)j_l(Qr_\nu)P_l(\cos\theta_{\mu\nu}) \quad (F1)$$

where $(n+3\times N_{\text{HYD}})$ is the total number of atoms in "mCD-HYD". The number of atoms in the mCD molecule is n, the number of D_2O molecules in hydration shell is N_{HYD}, rendering the number of the atoms in D_2O molecules equal to $3\times N_{\text{HYD}}$. The vectors r_μ and r_ν give positions of the μth and νth atoms, respectively, in the coordinate system of the center of mass (c.m.) of the mCD molecule; $\theta_{\mu\nu}$ is an angle between r_μ and r_ν. P_l is the Legendre polynomial of degree l, j_l is the spherical Bessel function of order l. $<b_\mu>$ and $\sigma_{\mu\,\text{INC}}$ are the coherent scattering length and the incoherent scattering cross section of the μth atom, respectively.

$A_{l(\text{mCD-HYD})}(Q)$ can be decomposed as follows:

$$A_{l(\text{mCD-HYD})}(Q) = A_{l(\text{mCD})}(Q) + A_{l(\text{mCD-W})}(Q) + A_{l(\text{W-W})}(Q) \quad (F2)$$

The structure factors $A_{l(\text{mCD})}(Q)$ are given by the "standard solute model", see section 5.5. The expression for $A_{l(\text{mCD-W})}(Q)$ reads:

$$A_{l(\text{mCD-W})}(Q)=2\sum_{\mu=1}^{n}\sum_{j=1}^{N_{\text{HYD}}}\sum_{\nu=1}^{3}<b_\mu><b_{j\nu}>j_l(Qr_\mu)j_l(Qr_{j\nu})P_l(\cos\theta_{\mu-j\nu}) \quad (F3)$$

where $r_{j\nu}$ and r_μ are the vectors from the c.m. of the solute molecule to the νth atom of the jth water molecule and the μth atom in the mCD molecule, respectively; $\theta_{\mu-j\nu}$ is the angle between the vectors r_μ and $r_{j\nu}$.

The expression for $A_{l(\text{mW-W})}(Q)$ is given by:

$$A_{l(\text{W-W})}(Q)=\sum_{i=1}^{N_{\text{HYD}}}\sum_{\mu=1}^{3}\sum_{j=1}^{N_{\text{HYD}}}\sum_{\nu=1}^{3}[<b_{i\mu}><b_{j\nu}>+\frac{\sigma_{i\mu\text{INC}}\delta_{i\mu-j\nu}}{4\pi}]j_l(Qr_{i\mu})j_l(Qr_{j\nu})P_l(\cos\theta_{i\mu-j\nu}) \quad (F4)$$

where $r_{j\nu}$ is the vector from the c.m. of the solute molecule to the νth atom of the jth water molecule ($r_{i\mu}$ is defined in the same way), and $\theta_{i\mu-j\nu}$ is the angle between the vectors $r_{i\mu}$ and $r_{j\nu}$. In addition, $\delta_{i\mu-j\nu} = 1$ if $i=j$ and $\nu=\mu$ and 0 otherwise.

One way to evaluate the structure factors $A_{l(\text{mCD-W})}(Q)$ and $A_{l(\text{mW-W})}(Q)$ consists in the tentative assignment of the positions of water molecules around the solute molecule (here: mCD molecule). The basis for such an assignment can be crystal structures of mCD hydrates.

Alternatively, water molecules could be placed around a mCD molecule wherever the hydrogen bond water-mCD can be formed. The simplest way is to approximate water molecules by spheres and align these spheres around the solute molecule. In any case, the knowledge of so obtained coordinates of atoms of water molecules will allow the evaluation of $A_{l(\text{mCD-W})}(Q)$ and $A_{l(\text{mW-W})}(Q)$ from eqs. (F3, F4).

F.2 An approach leading to the derivation of eqs. (5.33) and (5.34)

Because the positions (and orientations) of the hydration water molecules are *not generally known*, the procedure described in section 5.8 represents a convenient way for the evaluation of $A_{l(\text{mCD-W})}(Q)$ and $A_{l(\text{mW-W})}(Q)$. The following assumption is made: the probability to find a center-of-mass of a hydration water molecule is uniformly distributed over the whole volume of the hydration shell (for the definition of the hydration shell see section 5.8). The number density, p, of molecules in the hydration shell of volume V_{SHELL} is

$$p = N_{\text{HYD}}/V_{\text{SHELL}} \tag{F5}$$

so that the probability to find the c.m. of a water molecule in the volume element $d\mathbf{r}$ is $p d\mathbf{r}$. The rotational structure factors $A_{l(\text{mCD-W})}(Q)$ and $A_{l(\text{mW-W})}(Q)$ are evaluated from eq. (5.33) and eqs. (5.34,5.35), respectively. Below, these equations will be derived with the simultaneous discussion of underlying assumptions.

The general expression for the function $v(\mathbf{Q}, t)$ (see section 2.3) reads:

$$v(\mathbf{Q}, t) = \sum_{\mu, \nu = 1}^{m, m} \left[<b_\mu><b_\nu> + \frac{\sigma_{\mu\,\text{INC}}\delta_{\mu\nu}}{4\pi} \right] \chi_{\mu\nu}(\mathbf{Q}, t) \tag{F6}$$

where m is the number of atoms in the molecule and $\chi_{\mu\nu}(\mathbf{Q}, t)$ is given by:

$$\chi_{\mu\nu}(\mathbf{Q}, t) = \left\langle \exp\left[-i\mathbf{Q}.(\mathbf{r}_\mu(0) - \mathbf{r}_\nu(t)) \right] \right\rangle \tag{F7}$$

For isotropic rotational diffusion $v(\mathbf{Q}, t)$ is given by eq. (2.26):

$$v(\mathbf{Q}, t) = \sum_{l=0}^{\infty} (2l+1) A_l(Q) F_l(t) \tag{F8}$$

with $A_l(Q)$:

$$A_l(Q) = \sum_{\mu, \nu = 1}^{m, m} \left[<b_\mu><b_\nu> + \frac{\sigma_{\mu\text{INC}}\delta_{\mu\nu}}{4\pi} \right] j_l(Qr_\mu) j_l(Qr_\nu) P_l(\cos\theta_{\mu\nu}) \tag{F9}$$

For a "hydrated solute molecule", $m = n + 3 \times N_{\text{HYD}}$, so that eq. (F6) can be re-written as:

$$v_{\text{mCD-HYD}}(\mathbf{Q}, t) = \sum_{\mu, \nu = 1}^{n+3\times N_{\text{HYD}}, n+3\times N_{\text{HYD}}} \left[<b_\mu><b_\nu> + \frac{\sigma_{\mu\,\text{INC}}\delta_{\mu\nu}}{4\pi} \right] \chi_{\mu\nu}(\mathbf{Q}, t) \tag{F10}$$

The function $v_{\text{mCD-HYD}}(\mathbf{Q}, t)$ can be split into three parts:

$$v_{\text{mCD-HYD}}(\mathbf{Q}, t) = v_{\text{mCD}}(\mathbf{Q}, t) + v_{\text{mCD-W}}(\mathbf{Q}, t) + v_{\text{W-W}}(\mathbf{Q}, t) \tag{F11}$$

As seen from eq. (F8), $v_{\text{mCD}}(\mathbf{Q}, t)$ contains the rotational structure factors of the mCD molecule,

$A_{l(mCD)}(Q)$. In the following two sections, the expressions for $A_{l(mCD-W)}(Q)$ and $A_{l(W-W)}(Q)$ will be obtained.

F.3 Derivation of equation (5.33)

The expression for $v_{mCD-W}(\boldsymbol{Q}, t)$, analogously to eq. (F6), taking that $\chi_{\mu\nu}(\boldsymbol{Q}, t) = \chi_{\nu\mu}(\boldsymbol{Q}, t)$, reads:

$$v_{\text{mCD-W}}(\boldsymbol{Q},t)=2\sum_{\mu=1}^{n}\sum_{\nu=1}^{3\times N_{\text{HYD}}}<b_{\mu}><b_{\nu}>\chi_{\mu\nu}(\boldsymbol{Q},t) \tag{F12}$$

where the factor "2" accounts for the fact that, while in eq. (F6) the summations over μ and ν are both performed over *all* atoms (i.e. atoms belonging to the mCD *and* hydration D_2O molecules), the summations in eq. (F12) are performed only over the atoms belonging to the mCD molecule ($\mu = 1 .. n$) in the first sum and over those in D_2O molecules ($\nu = 1 .. 3 \times N_{\text{HYD}}$) in the second sum. Eq. (F12) can be rewritten using eq. (F7) as:

$$v_{\text{mCD-W}}(\boldsymbol{Q},t)=2\sum_{\mu=1}^{n}\sum_{j=1}^{N_{\text{HYD}}}\sum_{\nu=1}^{3}<b_{\mu}><b_{j\nu}>\langle\exp[-i\boldsymbol{Q}.(\boldsymbol{r}_{\mu}(0)-\boldsymbol{r}_{j\nu}(t))]\rangle \tag{F13}$$

with $\boldsymbol{r}_{j\nu}$ being the vector from the c.m. of the solute molecule to the νth atom of the jth water molecule; $\boldsymbol{r}_{j\nu} = \boldsymbol{R}_j + \boldsymbol{a}_{j\nu}$, where $\boldsymbol{R}_j$ is the vector giving the position of the c.m. of the hydration water molecule. The vector $\boldsymbol{a}_{j\nu}$ gives the position of the νth atom in the jth water molecule in the coordinate system of the c.m. of the jth water molecule. It follows from eq. (F7), assuming that $\boldsymbol{R}_j$ and $\boldsymbol{a}_{j\nu}$ are uncorrelated:

$$\chi_{\mu-j\nu}(\boldsymbol{Q},t)=\langle\exp[-i\boldsymbol{Q}.(\boldsymbol{r}_{\mu}(0)-\boldsymbol{R}_{j}(t))]\rangle\langle\exp[i\boldsymbol{Q}.\boldsymbol{a}_{j\nu}(t)]\rangle \tag{F14}$$

Thus, eq. (F13) can be rewritten as (with $\boldsymbol{a}_{j\nu}$ instead of $\boldsymbol{a}_{j\nu}(t)$ because $\boldsymbol{a}_{j\nu}(t)$ doesn't depend on the position of the water molecule relative to the mCD molecule and all $\boldsymbol{a}_{j\nu}(t)$ are equally probable):

$$v_{\text{mCD-W}}(\boldsymbol{Q},t)=2\sum_{\mu=1}^{n}<b_{\mu}>\sum_{j=1}^{N_{\text{HYD}}}\langle\exp[-i\boldsymbol{Q}.(\boldsymbol{r}_{\mu}(0)-\boldsymbol{R}_{j}(t))]\rangle\sum_{\nu=1}^{3}<b_{j\nu}>\langle\exp[i\boldsymbol{Q}.\boldsymbol{a}_{j\nu}]\rangle \tag{F15}$$

Averaging over the orientation of $\boldsymbol{Q}$ relative to $\boldsymbol{a}_{j\nu}$ yields:

$$\sum_{\nu=1}^{3}<b_{\nu}>\langle\exp[i\boldsymbol{Q}.\boldsymbol{a}_{\nu}]\rangle=\sum_{\nu=1}^{3}<b_{\nu}>\frac{\sin Qa_{\nu}}{Qa_{\nu}}=b_{\text{EFF W}}(Q) \tag{F16}$$

where a_{ν} is the distance of the νth atom to the c.m. of water molecule. The index j was dropped in eq. (F16), because the orientation of the jth water molecule is independent of $\boldsymbol{R}_j$. From eq. (F15) it follows:

$$v_{\text{mCD-W}}(\boldsymbol{Q},t)=2\,b_{\text{EFF W}}(Q)\sum_{\mu=1}^{n}<b_{\mu}>\sum_{j=1}^{N_{\text{HYD}}}\langle\exp[-i\boldsymbol{Q}.(\boldsymbol{r}_{\mu}(0)-\boldsymbol{R}_{j}(t))]\rangle \tag{F17}$$

From eqs. (F6-F9) it follows that $A_{l(mCD-W)}(Q)$ is given by:

$$A_{l(\text{mCD-W})}(Q)=2\,b_{\text{EFF W}}(Q)\sum_{\mu=1}^{n}\sum_{j=1}^{N_{\text{HYD}}}<b_\mu>j_l(Qr_\mu)\,j_l(QR_j)\,P_l(\cos\theta_{\mu-j}) \qquad \text{(F18)}$$

where $\boldsymbol{R}_j$ is the position of the c.m. of the hydration water molecule and $\theta_{\mu-j}$ is the angle between $\boldsymbol{r}_\mu$ (the vector giving the position of the μth atom in the mCD molecule) and $\boldsymbol{R}_j$.

Because the water molecule can be found in every volume $d\boldsymbol{R}$ with probability $p\,d\boldsymbol{R}$, eq. (F18) can be written as an integral, rendering eq. (5.33):

$$A_{l(\text{mCD-W})}(Q)=2\,p \times b_{\text{EFF W}}(Q)\times\sum_{\mu=1}^{n}\langle b_\mu\rangle\,j_l(Qr_\mu)\int_{V_{SHELL}}j_l(QR_j)P_l(\cos\theta_{\mu-j})\,d\,\boldsymbol{R}_j \quad \text{(F19)}$$

It is important to note that $A_{l(\text{mCD-W})}(Q)$ doesn't contain the incoherent scattering cross sections, because the function $v_{\text{mCD-W}}(\boldsymbol{Q}, t)$ depends on the correlations between the positions of two different groups of atoms.

F.4 Derivation of equation (5.34)

In similar fashion, as was shown above for $v_{\text{mCD-W}}(\boldsymbol{Q}, t)$, it follows from eqs. (F10, F11):

$$v_{\text{W-W}}(\boldsymbol{Q},t)=\sum_{\mu=1}^{3\times N_{\text{HYD}}}\sum_{\nu=1}^{3\times N_{\text{HYD}}}\left[<b_\mu><b_\nu>+\frac{\sigma_{\mu\,\text{INC}}\delta_{\mu\nu}}{4\pi}\right]\chi_{\mu\nu}(\boldsymbol{Q},t) \qquad \text{(F20)}$$

Using eq. (F7), which provides $\chi_{\mu\nu}(\boldsymbol{Q}, t)$, eq. (F20) can be rewritten as:

$$v_{\text{W-W}}(\boldsymbol{Q},t)=\sum_{i=1}^{N_{\text{HYD}}}\sum_{\mu=1}^{3}\sum_{j=1}^{N_{\text{HYD}}}\sum_{\nu=1}^{3}\left\{\left[<b_{i\mu}><b_{j\nu}>+\frac{\sigma_{i\mu\,\text{INC}}\delta_{i\mu j\nu}}{4\pi}\right]*\right.$$
$$\left.\langle\exp[-i\boldsymbol{Q}.(\boldsymbol{R}_i(0)+\boldsymbol{a}_{i\mu}(0)-\boldsymbol{R}_j(t)-\boldsymbol{a}_{j\nu}(t))]\rangle\right\} \qquad \text{(F21)}$$

For convenience, $v_{\text{W-W}}(\boldsymbol{Q}, t)$ will be split into two terms:

$$v_{\text{W-W}}(\boldsymbol{Q},t)=v_{\text{W-W DIST}}(\boldsymbol{Q},t)+v_{\text{W-W SELF}}(\boldsymbol{Q},t) \qquad \text{(F22)}$$

Assuming that: a) the orientation of the hydration water molecule relative to the solute molecule is not correlated with the position of the c.m. of this water molecule; b) that the relative orientations of two distinct hydration water molecules are uncorrelated; it follows from eqs. (F21, F22):

$$v_{\text{W-W DIST}}(\boldsymbol{Q},t)=\sum_{i=1}^{N_{\text{HYD}}}\sum_{\mu=1}^{3}\sum_{j\neq i=1}^{N_{\text{HYD}}}\sum_{\nu=1}^{3}\left\{<b_{i\mu}><b_{j\nu}>*\right.$$
$$\left.\langle\exp[-i\boldsymbol{Q}.(\boldsymbol{R}_i(0)-\boldsymbol{R}_j(t))]\rangle\langle\exp[-i\boldsymbol{Q}.\boldsymbol{a}_{i\mu}(0)]\rangle\langle\exp[i\boldsymbol{Q}.\boldsymbol{a}_{j\nu}(t)]\rangle\right\} \qquad \text{(F23)}$$

$$v_{\text{W-W SELF}}(\boldsymbol{Q},t)=\sum_{i=1}^{N_{\text{HYD}}}\sum_{\mu=1}^{3}\sum_{\nu=1}^{3}\left\{\left[<b_{i\mu}><b_{i\nu}>+\frac{\sigma_{i\mu\,\text{INC}}\delta_{\mu\nu}}{4\pi}\right]*\right.$$
$$\left.\langle\exp[-i\boldsymbol{Q}.(\boldsymbol{R}_i(0)-\boldsymbol{R}_i(t))]\rangle\langle\exp[-i\boldsymbol{Q}.(\boldsymbol{a}_{i\mu}(0)-\boldsymbol{a}_{i\nu}(t))]\rangle\right\} \qquad \text{(F24)}$$

One can rewrite eq. (F23) noticing that (see eqs. (F14-F16)):

$$b_{\text{EFF W}}^2(Q)=\sum_{\mu=1}^{3}\sum_{\nu=1}^{3}<b_\mu><b_\nu>\langle\exp[-i\boldsymbol{Q}.\boldsymbol{a}_\mu(0)]\rangle\langle\exp[i\boldsymbol{Q}.\boldsymbol{a}_\nu(t)]\rangle \qquad \text{(F25)}$$

as:

$$v_{\text{W-W DIST}}(\boldsymbol{Q},t)=b_{\text{EFF W}}^2\left(\sum_{i=1}^{N_{\text{HYD}}}\sum_{j\neq i=1}^{N_{\text{HYD}}}\langle\exp[-i\,\boldsymbol{Q}.(\boldsymbol{R}_i(0)-\boldsymbol{R}_j(t))]\rangle\right) \qquad \text{(F26)}$$

Eq. (F24) can be rewritten as:

$$v_{\text{W-W SELF}}(\boldsymbol{Q},t)=b_{\text{SELF W}}(Q)\times\sum_{i=1}^{N_{\text{HYD}}}\langle\exp[-i\,\boldsymbol{Q}.(\boldsymbol{R}_i(0)-\boldsymbol{R}_i(t))]\rangle \qquad \text{(F27)}$$

with $b_{\text{SELF W}}(Q)$ given by (see also eq. (2.39)):

$$b_{\text{SELF W}}(Q)=\sum_{\mu=1}^{3}\sum_{\nu=1}^{3}[<b_\mu><b_\nu>+\frac{\sigma_{\mu\,\text{INC}}\delta_{\mu\nu}}{4\pi}]\,j_0(Q\,r_{\mu\nu}) \qquad \text{(F28)}$$

with $r_{\mu\nu}=r_\mu - r_\nu$. Here, in writing eqs. (F27, F28), it was tacitly assumed that the hydration water molecule doesn't change its orientation relative to the solute molecule, i.e. that $a_\nu(t)=a_\nu(0)$.

Thus, one can now combine $v_{\text{W-W DIST}}(\boldsymbol{Q}, t)$ and $v_{\text{W-W SELF}}(\boldsymbol{Q}, t)$ into an expression for $v_{\text{W-W}}(\boldsymbol{Q}, t)$:

$$v_{\text{W-W}}(\boldsymbol{Q},t)=\sum_{i=1}^{N_{\text{HYD}}}\sum_{j=1}^{N_{\text{HYD}}}g_{W\,ij}(Q)\langle\exp[-i\,\boldsymbol{Q}.(\boldsymbol{R}_i(0)-\boldsymbol{R}_j(t))]\rangle \qquad \text{(F29)}$$

with $g_{W\,ij}(Q)$:

$$i\neq j \quad : \quad g_{W\,ij}(Q)=b_{\text{EFF W}}^2(Q)$$
$$i=j \quad : \quad g_{W\,ij}(Q)=b_{\text{SELF W}}(Q)=\sum_{\mu=1,\nu=1}^{3,3}[\langle b_\mu\rangle\langle b_\nu\rangle+\frac{\sigma_{\mu\,\text{INC}}\delta_{\mu\nu}}{4\pi}]\,j_0(Q\,r_{\mu\nu}) \qquad \text{(F30)}$$

From eq. (F29) and eqs. (F6-F9) one readily obtains $A_{l(\text{W-W})}(Q)$ as:

$$A_{l(\text{W-W})}(Q)=\sum_{i=1}^{N_{\text{HYD}}}\sum_{j=1}^{N_{\text{HYD}}}g_{W\,ij}(Q)\,j_l(QR_i)\,j_l(QR_j)\,P_l(\cos\theta_{i-j}) \qquad \text{(F31)}$$

Since the c.m. of the hydration water molecule can be in every volume element d$\boldsymbol{R}$ of the hydration shell with the probability pd$\boldsymbol{R}$, the sum can be written as an integral, rendering eq. (5.34):

$$A_{l(\text{W-W})}(Q)=p^2\times\int_{V_{\text{SHELL}}}\int_{V_{\text{SHELL}}}g_{W\,ij}(Q)\,j_l(QR_i)\,j_l(QR_j)\,P_l(\cos\theta_{i-j})\,d\,\boldsymbol{R}_i\,d\,\boldsymbol{R}_j \qquad \text{(F32)}$$

with $g_{W\,ij}(Q)$ defined as:

$$\boldsymbol{R}_i\neq\boldsymbol{R}_j \quad : \quad g_{W\,ij}(Q)=b_{\text{EFF W}}^2(Q)$$
$$\boldsymbol{R}_i=\boldsymbol{R}_j \quad : \quad g_{W\,ij}(Q)=b_{\text{SELF W}}(Q)=\sum_{\mu=1,\nu=1}^{3,3}[\langle b_\mu\rangle\langle b_\nu\rangle+\frac{\sigma_{\mu\,\text{INC}}\delta_{\mu\nu}}{4\pi}]\,j_0(Q\,r_{\mu\nu}) \qquad \text{(F33)}$$

F.5 The extended "hydrated solute model"

In writing eqs. (F27, F28), it was assumed that the hydration water molecule doesn't rotate. This assumption is most probably not fulfilled in reality; therefore, the model based on such an assumption may be inadequate under certain circumstances. The expression for the scattering function of the hydrated solute, $S_{\text{mCD-HYD}}(Q, \omega)$, with the reorientational motion of the

water molecules in the hydration shell taken into account, is derived below.

At first, eq. (F24) can be rewritten as:

$$v_{\text{W-W SELF}}(\boldsymbol{Q},t) = v_{\text{SELF W}}(\boldsymbol{Q},t) \times \sum_{i=1}^{N_{\text{HYD}}} \langle \exp[-i\boldsymbol{Q}.(\boldsymbol{R}_i(0) - \boldsymbol{R}_i(t))] \rangle \tag{F34}$$

where the expression for $v_{\text{SELF W}}(\boldsymbol{Q}, t)$ reads:

$$v_{\text{SELF W}}(\boldsymbol{Q},t) = \sum_{\mu,\nu=1}^{3,3} [<b_\mu><b_\nu> + \frac{\sigma_{\mu\,\text{INC}}\delta_{\mu\nu}}{4\pi}] \langle \exp[-i\boldsymbol{Q}.(\boldsymbol{a}_\mu(0) - \boldsymbol{a}_\nu(t))] \rangle \tag{F35}$$

Combining of $v_{\text{W-W DIST}}(\boldsymbol{Q}, t)$ (given by eq. (F26)) and $v_{\text{W-W SELF}}(\boldsymbol{Q}, t)$ leads to $v_{\text{W-W}}(\boldsymbol{Q}, t)$:

$$v_{\text{W-W}}(\boldsymbol{Q},t) = \sum_{i=1}^{N_{\text{HYD}}} \sum_{j=1}^{N_{\text{HYD}}} g_{W\,ij}(Q,t) \langle \exp[-i\boldsymbol{Q}.(\boldsymbol{R}_i(0) - \boldsymbol{R}_j(t))] \rangle \tag{F36}$$

with $g_{W\,ij}(Q, t)$ given by:

$$\begin{aligned} i \neq j &: g_{W\,ij}(Q,t) = b_{\text{EFF W}}^2(Q) \\ i = j &: g_{W\,ij}(Q,t) = v_{\text{SELF W}}(\boldsymbol{Q},t) \end{aligned} \tag{F37}$$

Note that eqs. (F27-F30) are obtained from eqs. (F34-F37) by setting $\boldsymbol{a}_\nu(t) = \boldsymbol{a}_\nu(0)$.
Similarly to eq. (F31), the expression for $A_{l(\text{W-W})}(Q, t)$ reads:

$$A_{l(\text{W-W})}(Q,t) = \sum_{i=1}^{N_{\text{HYD}}} \sum_{j=1}^{N_{\text{HYD}}} g_{W\,ij}(Q,t)\, j_l(QR_i)\, j_l(QR_j)\, P_l(\cos\theta_{i-j}) \tag{F38}$$

For convenience, $A_{l(\text{W-W})}(Q, t)$ will be split into two parts:

$$A_{l(\text{W-W})}(Q,t) = A_{l(\text{W-W DIST})}(Q) + A_{l(\text{W-W SELF})}(Q,t) \tag{F39}$$

with the distinct (and time-independent) part $A_{l(\text{W-W DIST})}(Q)$ given by:

$$A_{l(\text{W-W DIST})}(Q) = b_{\text{EFF W}}^2(Q) \sum_{i=1}^{N_{\text{HYD}}} \sum_{j\neq i=1}^{N_{\text{HYD}}} j_l(QR_i)\, j_l(QR_j)\, P_l(\cos\theta_{i-j}) \tag{F40}$$

and the self part $A_{l(\text{W-W SELF})}(Q, t)$ (making use of the fact that for $i=j$, $P_l(\cos\theta_{i\text{-}j}) = 1$) is:

$$A_{l(\text{W-W SELF})}(Q,t) = v_{\text{SELF}}(Q,t) \sum_{i=1}^{N_{\text{HYD}}} j_l^2(QR_i) \tag{F41}$$

To recall: $v_{\text{mCD-HYD}}(\boldsymbol{Q}, t)$ is the sum of $v_{\text{mCD}}(\boldsymbol{Q}, t)$ (given by eq. (F6) with $m=n$), $v_{\text{mCD-W}}(\boldsymbol{Q}, t)$ (eq. (F17)), $v_{\text{W-W}}(\boldsymbol{Q}, t)$ (eq. (F36)). Then, eq. (F8) can be rewritten as:

$$v_{\text{mCD-HYD}}(\boldsymbol{Q},t) = \sum_{l=0}^{\infty} (2l+1) F_l(t)[A_{l(\text{mCD})}(Q) + A_{l(\text{mCD-W})}(Q) + A_{l(\text{W-W})}(Q,t)] \tag{F42}$$

with $F_l(t) = \exp(-D_r l(l+1)t)$.
As follows from eq. (2.30):

$$I_{\text{ROT mCD-HYD}}(\boldsymbol{Q}, t) = \gamma(\boldsymbol{Q})_{\text{CM mCD-HYD}} \times u_{\text{mCD-HYD}}(\boldsymbol{Q}) + v_{\text{mCD-HYD}}(\boldsymbol{Q}, t) \tag{F43}$$

The function $S_{\text{ROT mCD-HYD}}(Q, \omega)$ is the time-Fourier transform of $I_{\text{ROT mCD-HYD}}(\boldsymbol{Q}, t)$ and reads:

$$S_{\text{ROT mCD-HYD}}(Q,\omega) = \sum_{l=0}^{\infty} S_{\text{ROT mCD-HYD}}^l(Q,\omega) \tag{F44}$$

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with:

$$S^{0}_{\text{ROT mCD-HYD}}(Q, \omega) = \delta(\omega) \times \{b^2_{\text{EFF mCD-HYD}}(Q) \times \gamma_{\text{CM mCD-HYD}}(Q) + A_{0(\text{mCD})}(Q) + A_{0(\text{mCD-W})}(Q)$$

$$+ A_{0(\text{W-W DIST})}(Q)\} + A_{0(\text{W-W SELF})}(Q) \times S_{\text{HYDW}}(Q, \omega) \tag{F45}$$

$$S^{l}_{\text{ROT mCD-HYD}}(Q, \omega) = (2l + 1) \times \{[A_{l(\text{mCD})}(Q) + A_{l(\text{mCD-W})}(Q) + A_{l(\text{W-W DIST})}(Q)] \times \text{Lor}(l(l+1)D_{\text{r}}, \omega)$$

$$+ A_{l(\text{W-W SELF})}(Q) \times \text{Lor}(l(l+1)D_{\text{r}}, \omega) \otimes S_{\text{HYDW}}(Q, \omega) \tag{F46}$$

The expression for $b_{\text{EFF mCD-HYD}}(Q)$ reads:

$$b_{\text{EFF mCD-HYD}}(Q) = \sum_{\mu=1}^{n+3 \times N_{\text{HYD}}} <b_\mu><\exp[-i\boldsymbol{Q}.\boldsymbol{r_\mu}]>_{\Omega} = \sum_{\mu=1}^{n+3 \times N_{\text{HYD}}} <b_\mu> \frac{\sin Qr_\mu}{Qr_\mu} \tag{F47}$$

where the subscript Ω stands for the averaging over all relative orientations of $\boldsymbol{Q}$ and $\boldsymbol{r_\mu}$. Clearly, $b_{\text{EFF mCD-HYD}}(Q) = b_{\text{EFF mCD}}(Q) + b_{\text{EFF HYD}}(Q)$; the function $b_{\text{EFF mCD}}(Q)$ is readily evaluated from the coordinates of mCD atoms. The expression for $b_{\text{EFF HYD}}(Q)$ reads:

$$b_{\text{EFF HYD}}(Q) = \sum_{\mu=1}^{3 \times N_{\text{HYD}}} <b_\mu><\exp[-i\boldsymbol{Q}.(\boldsymbol{R_i}+\boldsymbol{a_{i\mu}})]>_{\Omega} =$$

$$= \sum_{i=1}^{N_{\text{HYD}}} \langle \exp[-i\boldsymbol{Q}.\boldsymbol{R_i}]\rangle \sum_{\mu=1}^{3} <b_\mu><\exp[-i\boldsymbol{Q}.\boldsymbol{a_\mu}]> \tag{F48}$$

where $\boldsymbol{R_i}$ and $\boldsymbol{a_{i\mu}}$ have the same meaning as defined in the text after eq. (F13). If follows then:

$$b_{\text{EFF HYD}}(Q) = b_{\text{EFF W}}(Q) \sum_{i=1}^{N_{\text{HYD}}} \frac{\sin QR_i}{QR_i} \tag{F49}$$

Finally, eq. (F49) can be written in the same fashion as eqs. (F19, F32):

$$b_{\text{EFF HYD}}(Q) = p \times b_{\text{EFF W}}(Q) \times \int_{V_{\text{SHELL}}} j_0(QR_i) d\boldsymbol{R_i} \tag{F50}$$

The function $v_{\text{SELF W}}(Q, t)$ depends on the nature of the reorientational motion of the hydration water molecule. Assuming, for example, the case of the isotropic rotation, it follows (see eqs. (2.26-2.28)):

$$v_{\text{SELF W}}(\boldsymbol{Q}, t) = \sum_{l=0}^{\infty} (2l+1) A_{l(\text{HYDW})}(Q) F_{l(\text{HYDW})}(t) \tag{F51}$$

$$A_{l(\text{HYDW})}(Q) = \sum_{\mu,\nu=1}^{3,3} [<b_\mu><b_\nu> + \frac{\sigma_{\mu\text{INC}}\delta_{\mu\nu}}{4\pi}] j_l(Qr_\mu) j_l(Qr_\nu) P_l(\cos\theta_{\mu\nu}) \tag{F52}$$

The function $S_{\text{HYDW}}(Q, \omega)$ is the time-Fourier transform of $v_{\text{SELF W}}(Q, t)$ and given by:

$$S_{\text{HYDW}}(Q, \omega) = \sum_{l=0}^{\infty} S^{l}_{\text{HYDW}}(Q, \omega) \tag{F53}$$

$$S^{0}_{\text{HYDW}}(Q, \omega) = A_{0(\text{HYDW})}(Q) \times \delta(\omega); \quad S^{l}_{\text{HYDW}}(Q, \omega) = (2l+1) \times A_{l(\text{HYDW})}(Q) \times \text{Lor}(l(l+1)D_{\text{r HYDW}}, \omega) \tag{F54}$$

where $D_{\text{r HYDW}}$ is the rotational diffusion coefficient of the water molecule in the hydration shell. Of course, functions $A_{l(\text{HYDW})}(Q)$ are the same as for bulk water.

Setting $D_{\text{r HYDW}} = 0$ results in the function $S^{l}_{\text{ROT mCD-HYD}}(Q, \omega)$, which would be obtained

assuming $a_v(t) = a_v(0)$. For water, the functions $A_{l(\text{HYDW})}(Q)$ for $l \neq 0$ are negligible for $Q < 0.5$ Å^{-1}. Therefore, in fitting of the "hydrated solute model" no error was introduced by setting $a_v(t) = a_v(0)$ and employing $A_{l(\text{mCD-W})}(Q)$ and $A_{l(\text{mCD-W})}(Q)$ derived as described in sections F3 and F4, respectively.

Finally, $S_{\text{mCD-HYD}}(Q, \omega)$ is just a convolution of $S_{\text{ROT mCD-HYD}}(Q, \omega)$ from eq. (F44) with the translational scattering function $S_{\text{TR mCD-HYD}}(Q, \omega)$. The latter is the same as the translational scattering function for the solute molecule, given for the "standard solute model" by eq. (5.12).

F.6 Concluding remarks

In section F1 it was suggested that the structure factors $A_{l(\text{mCD-W})}(Q)$ and $A_{l(\text{W-W})}(Q)$ could be evaluated by taking water molecules to be spheres, and aligning these spheres on the surface of the solute molecule. One option is to specify the coordinates of every sphere, and additionally, the orientation of a water molecule relative to the solute molecule. In this way, coordinates of all atoms belonging to all hydration water molecules are known and $A_{l(\text{mCD-W})}(Q)$ and $A_{l(\text{W-W})}(Q)$ are found straightforwardly from eqs. (F3) and (F4), respectively. This approach will be referred to as the method of atom coordinates.

Alternatively, it is reasonable to assume that the precise orientation of the water molecules won't influence $A_{l(\text{mCD-W})}(Q)$ and $A_{l(\text{W-W})}(Q)$ very much for $Q < 2.5$ Å^{-1} (because the resolution in the "real space" is of the order $2\pi/Q$). It is also reasonable to make a simplifying assumption (made in sections F3 and F4), namely that the orientation of the hydration water molecule relative to the solute molecule is not correlated with the position of the center of mass of this water molecule. Then, $A_{l(\text{mCD-W})}(Q)$ and $A_{l(\text{W-W})}(Q)$ can be evaluated from eqs. (F18) and (F31), respectively. This approach, the method of c.m. coordinates, has an advantage: one needs only coordinates of the centers of spheres (i.e. c.m. of hydration water molecules).

The methods of atom coordinates and c.m. coordinates were both used to evaluate $A_{l(\text{mCD-W})}(Q)$ and $A_{l(\text{W-W})}(Q)$ for the case of the complete monomolecular coverage of the surface of the mCD molecule by D_2O molecules. Both methods yielded very similar results.

In addition, the functions $A_{l(\text{mCD-W})}(Q)$ and $A_{l(\text{W-W})}(Q)$ evaluated from eqs. (F19, F32) were qualitatively the same, as $A_{l(\text{mCD-W})}(Q)$ and $A_{l(\text{W-W})}(Q)$ found by the method of c.m. coordinates.

The structure factors $A_{l(\text{mCD-W})}(Q)$ and $A_{l(\text{W-W})}(Q)$, as seen from eqs. (F18, F31), depend on $b_{\text{EFF W}}(Q)$ and $b_{\text{SELF W}}(Q)$. For D_2O, $b^2_{\text{EFF W}}(Q=0) \approx 3.67$ barn, whereas for H_2O $b^2_{\text{EFF W}}(Q=0) \approx 0.03$ barn, see Tab. 2.1 (and at $Q < 1$ Å^{-1}, $b^2_{\text{EFF W}}(Q) > 3.0$ barn for D_2O and $b^2_{\text{EFF W}}(Q) < 0.04$ barn for H_2O). In addition, the term $b_{\text{SELF W}}(Q)$ for H_2O is dominated by the incoherent cross section and practically Q-independent. Thus, the Q dependence of the QENS scattering intensity due to

the presence of the hydration shell is virtually absent for H_2O solutions (because $A_{l(mCD-W)}(Q) \approx 0$ and $A_{l(W-W)}(Q)$ is nearly Q-independent).

In sections 5.8 and F2 the assumption was made that the probability to find a center-of-mass of a hydration water molecule (p) is uniformly distributed over the whole volume of the hydration shell. This assumption *is not necessary*; generally, one can have p as a function of R, (i.e. as a function of position of the c.m. of water molecule relative to the solute molecule) so that p will come into the integrand expression in eqs. (F19, F32). Thus, even complex assumptions about the distribution of water molecules in the hydration shell can directly give $A_{l(mCD-W)}(Q)$ and $A_{l(W-W)}(Q)$.

Finally, it is clear that the present implementation of the "hydrated solute model" can be used for the analysis of QENS spectra of any solution, where the phenomenon of solvation or adsorption of small particles on relatively large particles takes place.