1   Sanity check

The static structure factor is the Fourier transform of the radial distribution function $g_2(r)$.

$$S(\vec{q}) = 1 + \rho \int_V d\vec{r}\, e^{-i\vec{q}\cdot\vec{r}} g_2(r) \tag{1}$$

r is the distance between two water molecules and $\vec{r}$ is the vector connecting them. To compute the integral directly from MD simulation of water, I have to do the following modifications: for each frame k from the simulation, find all unique combination of pairs of molecules within distance R and sum up their contributions to the Fourier transform. R has to be chosen since the size of the simulation box is finite. Hence an estimate of $S(\vec{q})$ from on simulation frame is:

$$S(\vec{q}) \approx \frac{1}{N} \sum_{i,j,=1}^{N} e^{-i\vec{q}\cdot(\vec{r_i}-\vec{r_j})} \Delta_{ij} \tag{2}$$

where $\Delta_{ij} = 1$ if $\left|\vec{r_i} - \vec{r_j}\right| \leq R$ and is 0 otherwise.

Since liquid water is isotopic, intuition tells us that the pointing $(\vec{r_i} - \vec{r_j})$ shouldn't matter and only its length should. Debye's formula formalizes this and the above summation is equivalent to:

$$S(Q) \approx \frac{1}{N} \sum_{i,j,=1}^{N} \frac{\sin(Qr_{ij})}{Qr_{ij}} \Delta_{ij} \tag{3}$$

where $r_{ij} = \vec{r_i} - \vec{r_j}$ and Q is the magnitude of $\vec{q}$.

Averaging over many independent simulation frames gives an estimate from the simulation of $S(Q)$. There is also a finite-size effect introduced by the simulation box. See the two Salcuse papers in the notes for details. The finite-size effect is implemented in the code.

I have done some checking to make sure that the explicit Fourier transform makes sense with my simulation data. So far I have checked that it produces a small imaginary part, and also seems to be only dependent on the magnitude of $\vec{q}$ but not its pointing. Also, equations 2 and 3 give the same answer when I use them to compute $S(Q)$ from averaging over independent frames from the simulations. This makes me think that I have been doing the explicit Fourier transform correctly for the radial distribution.

2   Direct calculation of the correlator from simulation

The intensity from scattering from a pair of water molecules is:

$$I(\vec{q},\omega) = \left| \sum_{i}^{2} f(q) e^{-i\vec{q}\cdot(R_\omega \vec{r_i})} \right|^2 \tag{4}$$

where R_ω is the rotation operator by angle ω and $f(q)$ is the atomic form factor for oxygen. I am ignoring hydrogen for now since it does not scatter x-ray strongly. If we just expand equation 4 explicitly, we have

$$I(\vec{q}, \omega) = 2\left|f(q)\right|^2 (1 + \cos \vec{q} \cdot (R_\omega \vec{r_{12}})). \tag{5}$$

We want to compute, from the simulation data, the correlator between two pairs of water molecule, i.e. a single 4-point ensemble. The correlator is the following integral:

$$C(\vec{q_1}, \vec{q_2}) = \int_\omega I(\vec{q_1}, \omega) I(\vec{q_2}, \omega) d\omega. \tag{6}$$

Assuming our water box simulation is an good approximation of the statistical behavior of real water, we can estimate $C(\vec{q_1}, \vec{q_2})$ by summing over all possible 4-point ensemble in the simulations. Specifically,

$$C(\vec{q_1}, \vec{q_2}) \propto \frac{4\left|f(q)\right|^4}{M} \sum_{m=1}^{M} \sum_{i,j,k,l}^{N} (1 + \cos \vec{q_1} \cdot (R_\omega \vec{r_{ij,m}}))(1 + \cos \vec{q_2} \cdot (R_\omega \vec{r_{kl,m}})) \tag{7}$$

where N is the total number of water molecules in the simulation, the index m denotes the m-th frame in the simulation. We are averaging over M statistically independent frames. The summation over indices i, j, k, and l are over all unique 4-point ensembles.

The atomic form factor for oxygen is approximately the sum of some gaussian functions. With $0 < q < 25 \text{Å}^{-1}$, $f(q)$ is

$$f(q) = \sum_{i}^{4} a_i \exp{\left(-b_i(\frac{q}{4\pi})^2\right)} + c \tag{8}$$

and the a_i's and b_i's are constants summarized in the table below.

a_1	b_1	a_2	b_2	a_3	b_3	a_4	b_4	c
3.0485	13.2771	2.2868	5.7011	1.5463	0.3239	0.867	32.9089	0.2508

3 Protocol of computation