From Kam's work, we know that the autocorrelator is

$$C(q,\psi) =< I(\vec{q_1})I(\vec{q_2}) > - < I(\vec{q_1}) >< I(\vec{q_2}) > \tag{1}$$

where $\vec{q_1}$ and $\vec{q_2}$ have the same magnitude q. To compute this from MD simulation we have:

$$< I(\vec{q_1})I(\vec{q_2}) >= \frac{4\left|f(q)\right|^4}{N_{tthd}} \sum_{i,j,k,l}^{N} (1+\cos\vec{q_1}\cdot\vec{r}_{ij})(1+\cos\vec{q_2}\cdot\vec{r}_{kl}) \tag{2}$$

and

$$< I(\vec{q}) >= \frac{2\left|f(q)\right|^2}{N_{pair}} \sum_{i,j}^{N} (1+\cos\vec{q}\cdot\vec{r}_{ij}) \tag{3}$$

where i, j, k, l are indices representing the vertices of the nearest-neighbor tetrahedrons. I use a two-vector representation of a tetrahedron, i.e each is denoted by $\{\vec{r}_{ij},\vec{r}_{lk}\}$, $\vec{r}_{ij}=\vec{r}_i-\vec{r}_j$ etc. That means for each set of neighbors, there are three different two-vector presentations. I will deal with how this will impact the calculation of $C(q,\psi)$ later. The averages are over all the tetrahedrons/pairs.

I used simulation ran laster quarter (Fall 2015) and the results are plotted in figure **??**. I had a similar plot in the Fall 2015 notes that is just the $<$

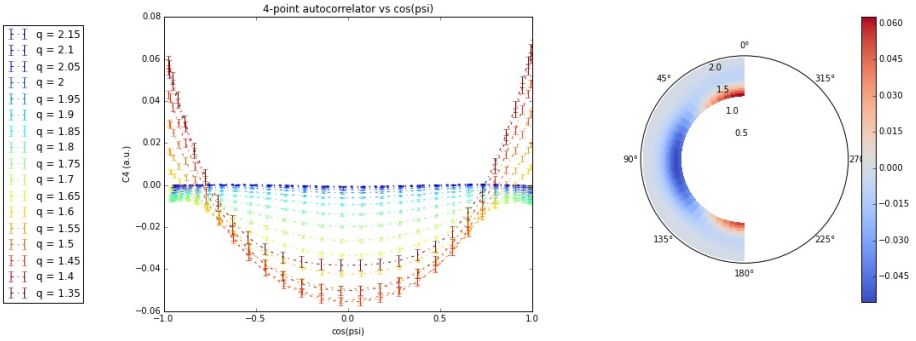

Figure 1: Autocorrelator $C(q,\cos\psi)$ computed from simulated water

$I(\vec{q_1})I(\vec{q_2}) >$ term. Subtracting the $< I(\vec{q_1}) >< I(\vec{q_2}) >$ "normalizes" the autocorrelator.

Examining the radial distribution function in figure **??** tells me the upper bound of q I might expect good sampling for tetrahedron configurations. The ref drops to zero at around 0.25 nm which translated into about 2.5 $\mathring{A}^{-1}$. I also know from finding nearest-neighbor tetrahedrons in MD simulations that $\left|\vec{r}_{ij}\right|$'s are no more than 0.5 nm. So the lower bound of q should be around 1.3 $\mathring{A}^{-1}$. So the range of q I have looked at are between 1.3 to 2.5 $\mathring{A}^{-1}$.

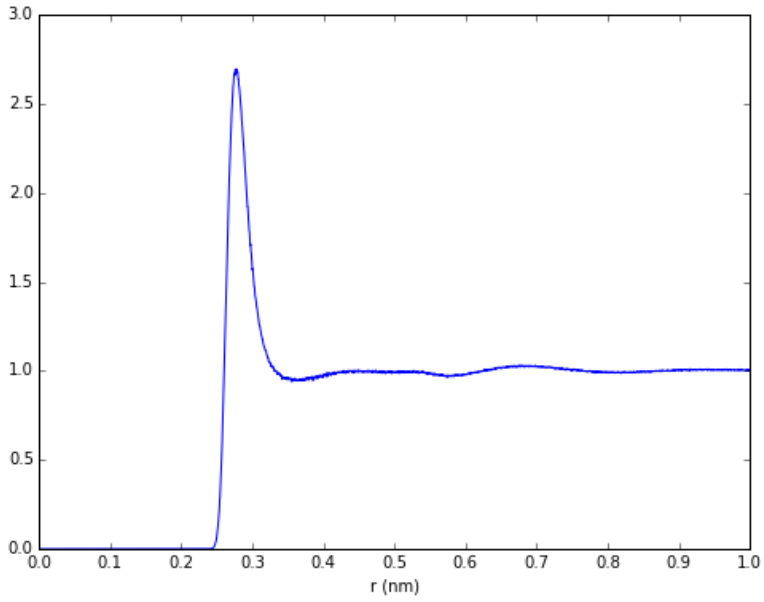

Figure 2: Radial distribution function of simulated water.

1 two-vector representation of tetrahedrons

One question to ask here is: does the two-vector representation $\{\vec{r}_{ij}, \vec{r}_{lk}\}$ affect the result of $C(q, \psi)$? If I have vertices labeled, 1, 2, 3, and 4, I can have three grouping if I am to divide them into two pairs, namely $\{(1,2),(3,4)\}$, $\{(1,3),(2,4)\}$, and $\{(1,4),(2,3)\}$. So every tetrahedron has three unique ways to scatter two photons (strictly speaking I think it have $3 \times 2 = 6$ way for two photons). The question is will $C(q, \psi)$ be dependent on which grouping I choose.

My understanding is it does not but the grouping allows me to get more configurations to average over. Figure **??** show that the curves computed using different groups converges to their average with one sigma.

2 Projection of C4 into Legendre polynomials

How am I going to compare the simulation to the CXS data? Ultimately, I am hoping that the CXS is good enough for me to distinguish between models for water out there (TIP3, TIP4, SPC, SPC/E, etc.).

Again, Kam's paper tells me that I can expand $C(q, \psi)$ in terms of the

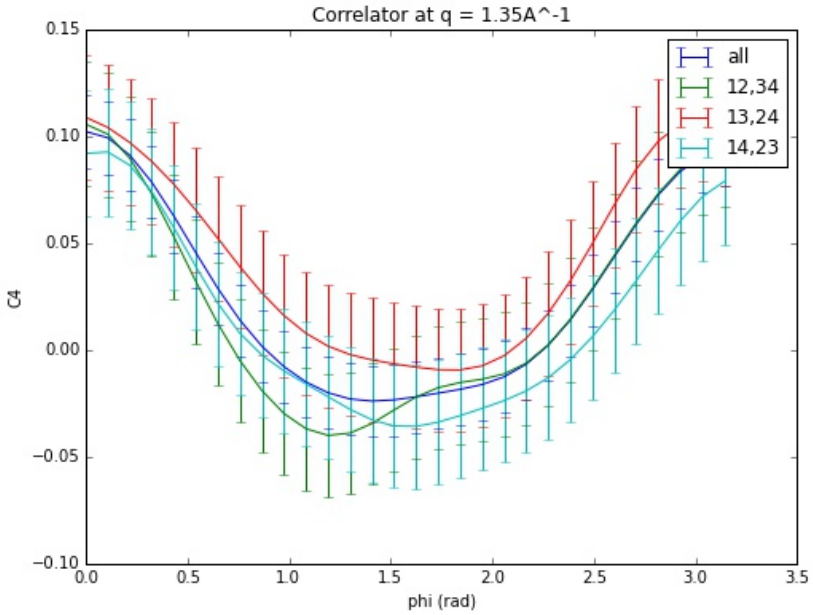

Figure 3: Comparing $C(q\psi)$ computed from different two-vector representations of the tetrahedron, $q = 1.35\mathring{A}^{-1}$.

Legendre polynomials $P_l(\cos\psi)$:

$$C(q,\psi) = \sum_l B_l(q) P_l(\cos\psi) \tag{4}$$

I need error bars on the coefficient plot. I need to estimate how much simulation do I need to do to be able to distinguish C amongst the different force fields/ models for water.