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Supplementary information

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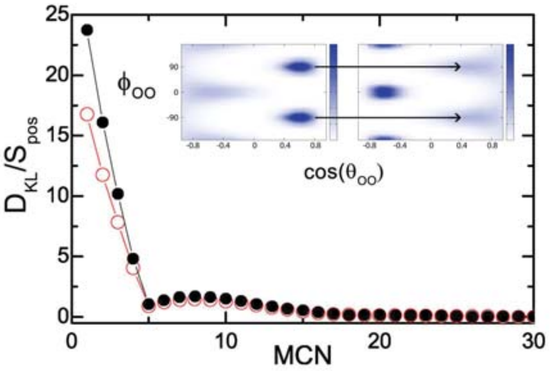

FIG. 1: (color online). The symmetrized Kullback-Leibler divergence between the distribution of donors and acceptors as a function of the Molecular Coordination Number. The inset shows the maps where alternatively donors and acceptors occupy the same spots of the 2D probability distribution $g(\cos(\theta_{OO}), \phi_{OO})$.

I. QUANTIFYING THE DONOR/ACCEPTOR DISTRIBUTION ASYMMETRY

Figure 1 of the main paper shows that there is a different distribution of oxygen atoms belonging to donors and acceptors around a central water molecule. This distribution is encoded in the 2D probability distribution function $g(\cos(\theta_{OO}), \phi_{OO})$ where in the north hemisphere we can find acceptors and in the southern hemisphere we can find donors. Since we are interested in quantifying the difference between the distribution of donors and acceptors, we are indeed searching a magnitude able to calculate how different are the distributions of northern and southern hemispheres. Information theory provides us with a tool to calculate the "distance" between two different probability distributions: the Kullback-Leibler divergence (D_{KL}) defined as:

$$D_{KL}\left(P||Q\right) = \sum_i P_i \ln \frac{P_i}{Q_i} \tag{1}$$

Although D_{KL} is not a real distance because it is not symmetric, i.e. $D_{KL}\left(P||Q\right) \neq D_{KL}\left(Q||P\right)$, it is possible to define a symmetrized version as $D_{KL}(P,Q) = 1/2\left(D_{KL}\left(P||Q\right) + D_{KL}\left(Q||P\right)\right)$. In the present case we have checked the three distances (the two non-symmetrized and the simmetrized one) getting approximately the same results, and exactly the same trends. In order to be able to calculate this distance we have chosen an alternative axis set to the one of figure 1 of main text so that donors are located in the position of the acceptors (see inset of figure 1). We show in figure 1 the results for the symmetrized D_{KL} as a function of the number of the Molecular Coordination Number, i.e. the number that results after ordering molecules by increasing distances. As expected, the first four neighbors have the maximum possible assymetry in the liquid. However after the fifth neghbour we see that the assymetry again increases having a maximum for molecule number eight to fade out for an $MCN > 20$. In order to rule out that this assymetry is a trivial effect due to an increasingly loose of correlation with distance, we have divided D_{KL} by the entropy associated to the maps ($S = \sum_i P_i \ln P_i$) obtaining again the same trend.

II. DETERMINING MOLECULAR ORIENTATION

In order to extract the orientational short range order of a liquid an axis set XYZ is attached to each molecule of the simulation box. We then calculate for each molecule, that will be called *central* for the sake of clarity, the projection of the $X'Y'Z'$ axes attached to *neighbor* molecules, on the XYZ frame of the central molecule. During the analysis all molecules will play the role of central molecule and that of neighbor molecules will be played by the ones that are selected by a distance criterion to the central one. In this way we obtain the Cartesian components of the neighbor axes set, using as a reference frame the axis set of the central molecule. Then, we calculate the relative orientation of the neighbor molecule with respect to the central one by calculating the Euler angles. These angles are defined as successive rotations around an arbitrary axis C, another rotation around a second arbitrary axis C' and a last rotation around the first axis C. Moreover rotations can be left or right handed. In this work we have chosen the ZYZ convention so that right handed rotations are done around Z, Y and Z axes. In figure 2 we show a water molecule arbitrarily rotated by the Euler angles convention used in this work.

In order to get the three Euler angles from a rotated frame it is necessary to calculate the full rotation matrix in three dimensions from the rotation matrices around each chosen axes. However, since the trigonometric functions sine and cosine are not able to distinguish between angles in all four quadrants it is necessary to add a function that allows the calculation of the sign of the angle. For this reason we use the following expressions to calculate the Euler angles from the rotated axes coordinates:

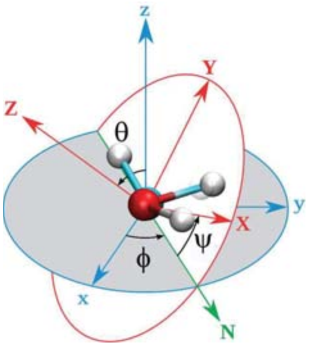

FIG. 2: (color online). Water molecule rotated arbitrarily using the Euler angles θ, ϕ, ψ defined as right handed rotations around Z Y and Z axes respectively.

$$\theta = Z_{Z'} \tag{2}$$

$$\phi = \frac{Z_{Y'}}{\|Z_{Y'}\|} \arccos \frac{Z_{X'}}{\sqrt{1 - Z_{Z'}^2}} \tag{3}$$

$$\psi = -\frac{Y_{Z'}}{\|Y_{Z'}\|} \arccos \frac{-X_{Z'}}{\sqrt{1 - Z_{Z'}^2}} \tag{4}$$

Where $\epsilon_{\epsilon'}$ with $\epsilon = x, y, z$, is the projection of the neighbor axes ϵ' in the central molecule axes set ϵ.

Once the Euler angles are obtained for all the selected pairs of molecules it is necessary to calculate the three-dimensional probability density function $g\left(\cos(\theta_{\text{ori}}), \phi_{\text{ori}}, \psi_{\text{ori}}\right)$. To do that it is important to ensure that all the 3D bins have the same size. If the bins are chosen to be equally sized for angle θ the probability density function for randomly oriented molecules would be that of a normalized cosine, having therefore a maximum for $\theta = 90^\circ$ and minima for $\theta = 0^\circ$ and $\theta = 180^\circ$.

In order to obtain equally sized 3D bins for $g\left(\cos(\theta_{\text{ori}}), \phi_{\text{ori}}, \psi_{\text{ori}}\right)$ the statistics must be performed using bins equidistributed in $\cos(\theta)$ instead of θ. In fact the statistics of any angle that is coming from the projection of one vector into another like the angle between two dipoles $\Phi_{dip-dip}$ in figure 4 of the main text must be done with a cosine-sized binning, otherwise there will be always a fake negligible probability to find two parallel or anti-parallel vectors.

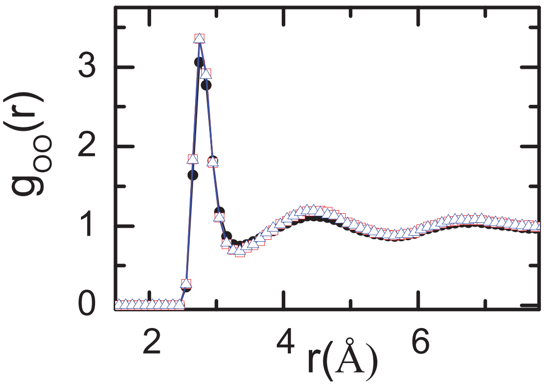

FIG. 3: (color online). Partial radial distribution function between two oxygen atoms around molecules having a first neighbor either in cis (squares), a trans (triangles) configuration. The total partial radial distribution Oxygen-Oxygen is represented in black full circles.

III. BEYOND THE FIRST NEIGHBOR

A series of tests has been carried out to see if the presence of different dimers alters the positional short range order of water molecules without finding any evidence for such an effect (see main text). First of all we have calculated the partial radial distribution functions between two oxygen atoms of water, participating the central molecule in a *trans* or *cis* dimer. As it can readily be seen in figure 3 there are no noticeable differences between oxygen distances for molecules forming a *cis* or *trans* dimer. Moreover, we compare those partial radial distribution functions with that of all oxygens without any restriction, obtaining the same result as for the segregated oxygens.

We have also performed a more detailed test to investigate if molecules forming either of the two dimers have a different 3D spatial distribution of oxygen atoms around them. To do that we show in figure 4 the positional maps $g(\cos(\theta_{OO}), \phi_{OO})$ as the ones in figure 1 of the main paper but for neighbors from 1 to 12. We have chosen the molecule located at $\cos(\theta) \approx 0.66$ and $\phi \approx 90°$ to be either in *cis* or *trans* configuration. From the figure we see that the position of molecules does not change around molecules forming a *cis* or *trans* dimer since the obtained maps are the same for the three cases: without dimer discrimination, *cis* or *trans*.

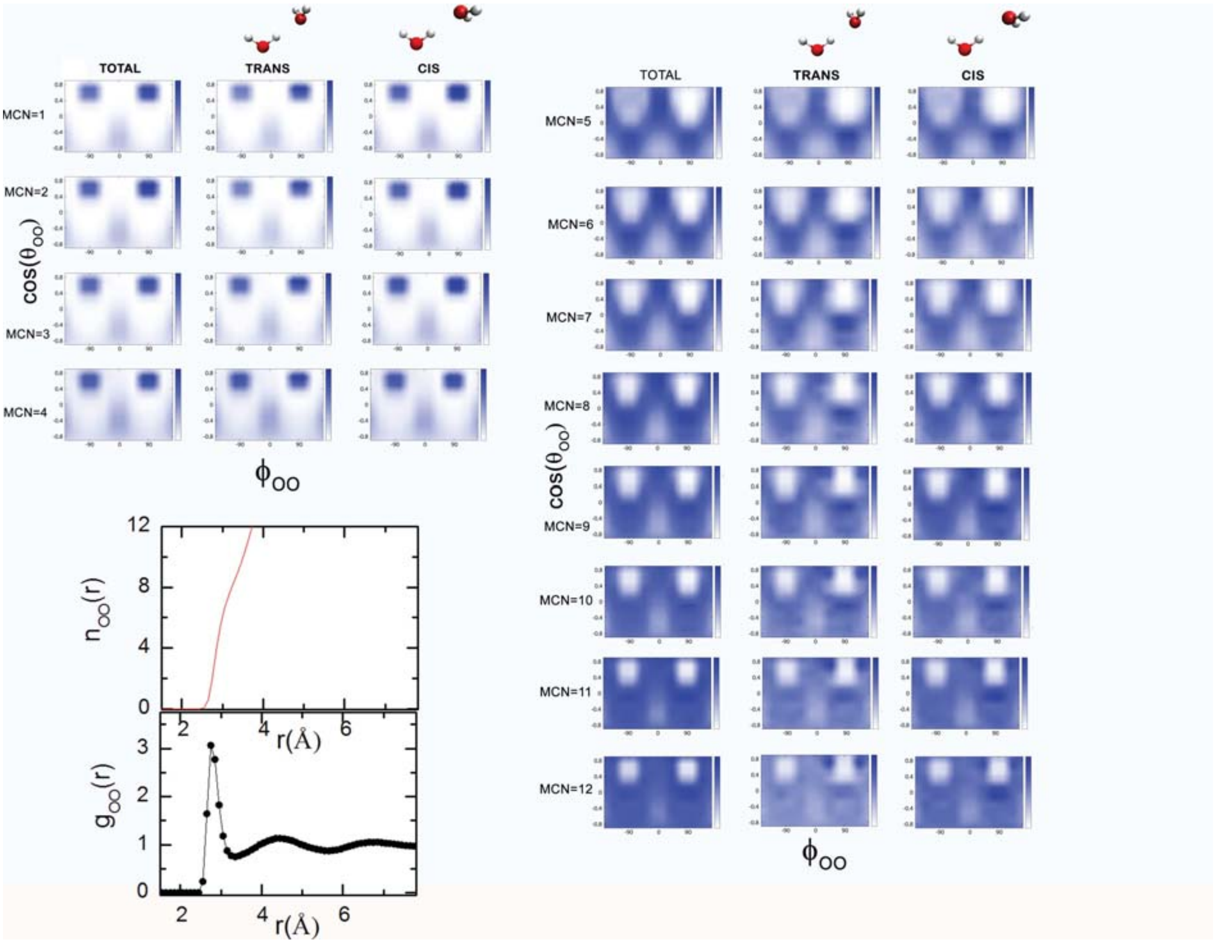

FIG. 4: (color online). Positional maps $g(\cos(\theta_{\rm OO}), \phi_{\rm OO})$ for three cases: without dimer discrimination and being the neighbor molecule at $(\cos(\theta) \approx 0.66, \phi \approx 90°)$ *cis* or *trans*. In the same figure we add the partial radial distribution function and the molecular coordination number for the sake of clarity.