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A continuous mixture of two different dimers in liquid water[†]

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It is hitherto thought that liquid water is composed of tetrahedrally coordinated molecules with an asymmetric interaction of the central molecule with neighboring molecules. Kühne *et al., Nat. Commun.*, 2013, **4**, 1450 suggested that this asymmetry, energetic rather than geometric, is the cornerstone to reconcile the homogeneous and inhomogeneous viewpoints of liquid water. In order to investigate the geometric origin of that asymmetry, we have scrutinized Molecular Dynamics (MD) simulations of water through a careful analysis of the five-dimensional probability distribution function of Euler angles in which the relative positions and orientations of water molecules are obtained. We demonstrate that, beyond the ubiquitous tetrahedral structure with well-defined molecular dimers, there is a series of possible molecular orientations that define the structure. These orientations are generated by rotating the neighboring molecule around the O-H axis that is involved in the Hydrogen bond scheme. Two of the possible orientations have a higher probability, giving rise to two kinds of dimers: one close to the lowest energy of a water dimer in vacuum with an almost perpendicular alignment of the dipole moment, and another one with a parallel orientation of the dipole moment which is less tightly bound. These two different dimers have an effect on the orientation of further water dipole moments up to a distance of ≈6Å. Liquid water can therefore be described as a continuous mixture of two kinds of dimers where the Hydrogen bonds have the same geometry but the interaction energies are different due to a different mutual orientation of the dipoles of the participating water molecules.

1 Introduction

The local structure of liquid water is still a controversial subject. In contradiction to the classical picture of a symmetric tetrahedral local order of neighboring water molecules around a central one[1–4], two main alternative descriptions have been proposed: a local order with only one acceptor and one donor that would lead to a chain and ring structure of liquid water[5] and a two-state model that would imply an inhomogeneous picture of the water structure[6–8]. Kühne *et al.* proposed recently[1] a way to reconcile the classical picture of the short range order of water with its counterparts by means of an asymmetry of the electronic interaction between molecular contacts. This asymmetry was found in the interaction between the two strongest hydrogen bond donors and acceptors. Recently Kühne *et al.* have also found a difference in the geometry of these hydrogen bonds[9]. In the present contribution, we will perform a careful analysis of molecular dynamics simulations to show that, beyond the differences on H-bond geometries, there is also a difference in the relative orientation of two water molecules that go together with a difference in the contact energy.

Many approaches have been used to characterize the configurations of molecules in a liquid phase[5,11–21]. In the present work, the local arrangement of water molecules will be described with the distribution function $g(d_{\mathrm{OO}}, \omega_{\mathrm{OO}}, \omega_{\mathrm{ori}})$[22] which denotes the probability to find a water molecule at a distance d_{OO} from a central one (measured from the oxygen atom of one water molecule to the oxygen atom of the other molecule) where the position and orientation of the water molecules in space are ω_{OO} and ω_{ori} respectively. The *position* of the second water molecule with respect to the first one will be described by the relative position of the second oxygen in polar coordinates d_{OO}, θ_{OO}, ϕ_{OO} where θ_{OO} denotes the latitude and ϕ_{OO} the longitude. The *orientation* of

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the second water molecule with respect to the first is described by the three Euler angles ϕ_{ori}, θ_{ori}, and ψ_{ori} using the *zyz* convention. For details confer to the Supporting Information.

In order to determine the distance d_{OO} and relative position/orientation $\omega_{\mathrm{OO}}, \omega_{\mathrm{ori}}$ of two water molecules, it is necessary to define a coordinate system on each molecule. For the choice how to attach the coordinate system to the molecule it is important to note that the Euler angles ϕ_{ori} and ψ_{ori} become degenerate at the poles. In order to avoid regions of interest to be situated at the poles, two definitions of orthonormal axes sets were used in this study: To study the relative *position* of two molecules, the z axis was defined along the dipole of the water molecule, x perpendicular to the H-O-H plane and y in the H-O-H plane (see inset of figure 1). As for the relative *orientation*, however, a different set of coordinate axes was chosen with z perpendicular to the H-O-H plane, x parallel to the H-O-H plane and y along the molecular dipole.

After determining the relative positions and orientations of all water molecules in this manner, different subsets of pairs were selected so that the properties of different groups could be studied. The first discrimination between molecules was based on their distance. Instead of a hard cut-off distance range criterion, molecules were grouped by counting the first four molecules that were closest to the central one.

In order to do the analysis of the molecular arrangement of liquid water we have used three models TIP4P/2005, its flexible version TIP4P/2005f and the SPC/E model. The results given by the three are qualitatively the same therefore we will only show the results for the TIP4P/2005 model.

2 Positional ordering in the first hydration shell

The first quantity that describes the short range order of the molecules is their positional arrangement around a central molecule. It is the nature of a liquid that these positions change continuously but there are nevertheless some preferred locations. These preferred locations can be visualized with the distribution function $g(\cos(\theta_{\mathrm{OO}}), \phi_{\mathrm{OO}})$ which is shown for the first four neighbors surrounding a central molecule in figure 1. Hydrogen bond acceptors are located in the northern hemisphere ($\cos(\theta_{\mathrm{OO}}) > 0$) and donors in the southern hemisphere ($\cos(\theta_{\mathrm{OO}}) < 0$). The highest probabilities to find a neighbouring molecule are at $\theta_{\mathrm{OO}} = 52.28°$ which is half the H-O-H angle of the TIP4P/2005 water molecule and very close to the tetrahedral angle of $\theta_t/2 = 54.7°$. The distribution of donors is more disordered than the one of the acceptors, in agreement with previous studies using a variety of water models and simulation methods[15,18,19]. The fact that donors are more disordered might be related to the capability of classical force-fields to encode the different distribution of acceptor and donor electrons, the so-called negativity track between the lone pairs of a water molecule[9]. It is possible to quantify this difference between donor and acceptor distributions by an information theoretical approach (see supplementary information †). As one would expected, the difference is maximal for the first four neighbours and decreases rapidly until the fifth neighbour. Astonishingly enough, the asymmetry then increases again until the eighth neighbour and fades out continuously until it is negligible from the neighbour number twenty on.

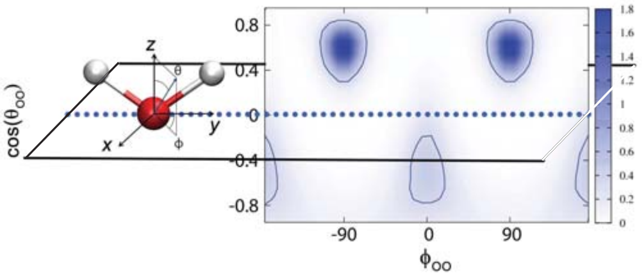

Fig. 1 (color online). Position distribution function $g(\cos(\theta_{\mathrm{OO}}), \phi_{\mathrm{OO}})$ describing the probability of finding a molecule in a certain region of space in spherical coordinates. The contour for $g(\cos(\theta_{\mathrm{OO}}), \phi_{\mathrm{OO}}) = 0.3$ is shown. The axes chosen to study the position are shown in the inset of the figure.

3 Orientational ordering in the first hydration shell

The orientation of neighbouring molecules is encoded in the three-dimensional function $g(\cos(\theta_{\mathrm{ori}}), \phi_{\mathrm{ori}}, \psi_{\mathrm{ori}})$ which shows the distribution of orientations of the neighbouring molecules at a given position (see supplementary information for more details†). By selecting the position as mentioned above, the orientation of neighbouring Hydrogen bond donors and acceptors with respect to a central water molecule can be evaluated separately. For the following analysis, two groups were made: one contains the two closest neighbouring donors and the other the two closest acceptors.

Both, donor and acceptor orientational distributions

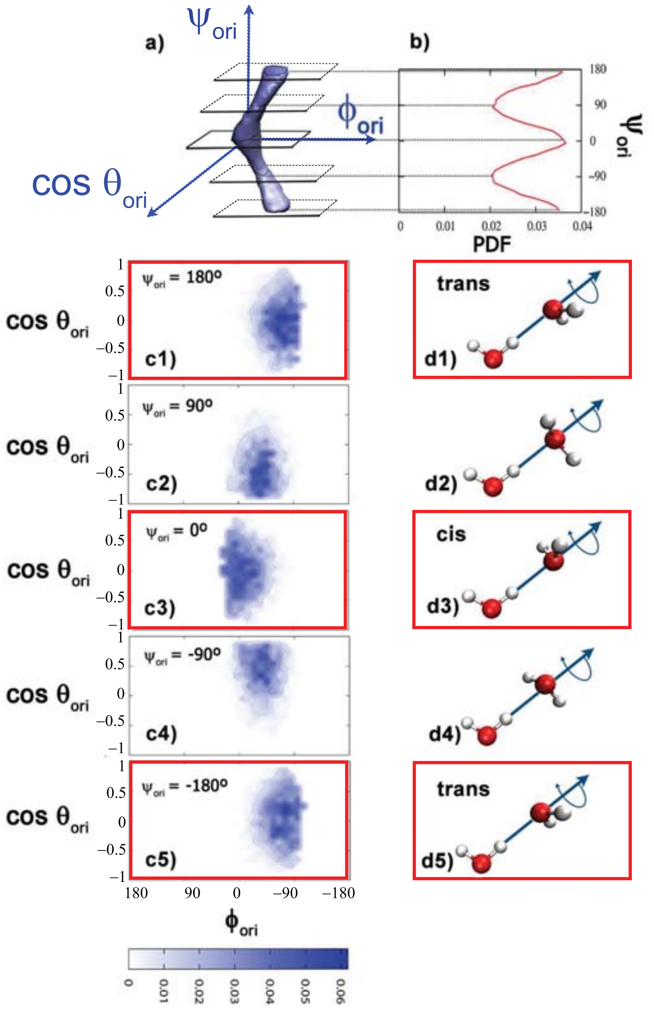

Fig. 2 (color online). (a) Three dimensional probability distribution $g\left(\cos(\theta_{\mathrm{ori}}), \phi_{\mathrm{ori}}, \psi_{\mathrm{ori}}\right)$ describing the orientation of a water acceptor molecule. (b) Probability of successive cuts of $g\left(\cos(\theta_{\mathrm{ori}}), \phi_{\mathrm{ori}}, \psi_{\mathrm{ori}}\right)$ along planes perpendicular to the ψ_{ori} axis. We show in panel (c) $g\left(\cos(\theta_{\mathrm{ori}}), \phi_{\mathrm{ori}}\right)$ for successive cuts of the probability distribution of panel (a) at different values of ψ_{ori}. In panel (d) we show the orientations obtained from the maximum of $g\left(\cos(\theta_{\mathrm{ori}}), \phi_{\mathrm{ori}}\right)$.

can be visualized as 3D isocontour surfaces. The isocontour surface for hydrogen bond acceptors is shown in figure 2, the one for donors is virtually the same. In both cases the surface resembles a spiral winding around the z axis. Inside the isocontour surface, there is a continuum of possible molecular orientations. The part of orientational space which is not inside the isocontour surface is explored less frequently by the molecules and there are even orientations that were never observed in the presented simulations. Since the spirals enclose a continuous volume, it is possible to transform each probable orientation into another one continuously along a path within the spiral, i. e. there is a certain sequence of orientations through which the molecules pass when they change the orientation. The question that will be studied in the following is: Which are the most probable orientations for a Hydrogen bond acceptor (or donor) to be in?

To answer this question, i. e. to find the most probable orientation of the molecules, 2D slices were cut through the orientational distributions in figure 2 to allow a view inside the isocontour surfaces. These slices were in both cases cuts along horizontal xy planes of the 3D distributions shown in figure 2a at several heights, i. e. several values of z. In the case of Hydrogen bond acceptors, this corresponds to a series of $g(\cos(\theta_{\mathrm{ori}}), \phi_{\mathrm{ori}})$ at several ψ_{ori} values (see figure 2b). Exemplary cuts are shown below their corresponding 3D isocontour surfaces in figure 2b. As it can be seen in the figure, successive slices correspond to a rotation of the molecule around the O-H axis of the central molecule. In panel b we show the probability for each slice, which defines the probability for a particular orientation. Those with maximum probability are highlighted in the same figure and correspond to the orientations: $\psi_{\mathrm{ori}} = \pm 180^\circ$ and $\psi_{\mathrm{ori}} = 0^\circ$.

The two most likely orientations for both dimers – formed by a central molecule and either an acceptor or a donor – are therefore two possible configurations: one with a parallel dipole alignment and another one with an angle of about $\Phi_{\text{dip-dip}} \approx 110^\circ$ between dipoles. In analogy to the classification of conformations in hexagonal ice[27], the parallel dipole alignment will be referred to as *cis* while the one with a $\Phi_{\text{dip-dip}} \approx 110^\circ$ angle between them will be called *trans*, cf. figure 2d. We note in passing that the *trans* configuration is very close to the most stable water dimer in vacuum[28]. Both, donors and acceptors, were found with equal probability in a *cis* or *trans* configuration so that the *cis*:*trans* ratio was in either case 50:50 (in hexagonal ice, the proportion of *trans* pairs is higher with a *cis*:*trans* ratio of about 40:60[27]).

Both dimers were characterized by measuring the correlations between conformations and interaction energies as well as the their correlation with dipole moment orien-

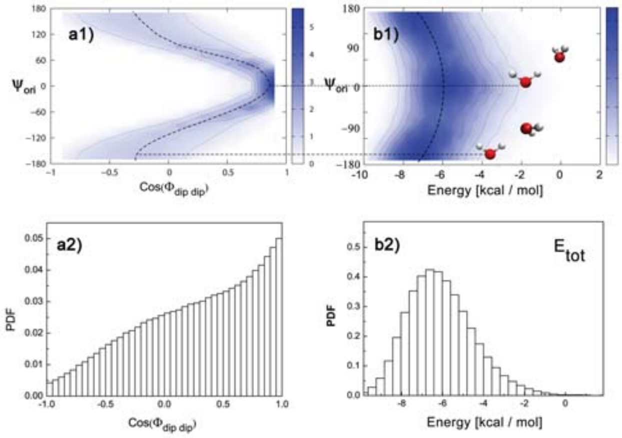

Fig. 3 (color online). Two dimensional probability maps for the relative dipole orientation $\Phi_{\text{dip-dip}}$ (a1) and energy (b1) of an acceptor as a function of the Euler angle ψ_{ori}. Panels a2 and b2 show the projection of the data in figures a1 and b2 onto the x axis, i. e. the probability density functions of $\Phi_{\text{dip-dip}}$ and of the energy of a dimer involving a neighbouring acceptor molecule.

tations.It must be pointed out that the calculation of the energy between two water molecules is done using a pairwise additive potential. If a polarizable model were used, the effect of the surrounding molecules within the first hydration shell would explicitly be taken into account and would probably lead to a stronger correlation between the orientation of the deemed molecules. The 2D probability distribution functions of the energy and relative dipole orientation $\cos(\Phi_{\text{dip-dip}})$ of the dimer with the angle ψ_{ori} is shown in figure 3. The 1D probability distributions of these quantities integrated over all angles ψ_{ori} are shown in the same figure (for one acceptor, similar results were obtained for the donors). From figure 3 it is clear that the relative dipole orientation of two molecules can be understood as the combination of a broad peak associated with the *trans* conformation where dipoles are approximately in a perpendicular orientation together with a narrower peak associated to *cis* dimers where dipoles are parallel. Such a bimodal distribution is not visible on first sight in the 1D probability distribution of the energy. Only if plotted as a function of angle ψ_{ori} it becomes clear that the total energy for an acceptor consists of tightly linked dimers in *trans* conformation with almost perpendicular dipoles and more loosely linked dimers in *cis* conformation with almost parallel dipoles. The difference in energy between the *cis* and *trans* dimers calculated between the maxima of the two 2D distribution $P\left(E, \psi_{\text{ori}}\right)$ for both dimers is 1.3 kcal/mol.

Kühne *et al.* also found an asymmetry between the contacts of water molecules (in that case the energy difference was about 2.5 kcal/mol) which was associated to an electronic criterion and recently to a different geometry of the hydrogen bond[9]. In our work we also find that the differences in energy have an electronic origin, they result from different dipole-dipole interactions between molecules which in turn have a clear geometric origin with the relative orientation of the two molecules. However it has to be considered that these two asymmetries might arise from different physical origins since our simulation is purely classical.

4 Correlations beyond the dimers

We have investigated if, beyond the evident difference in molecular orientation, the existence of two different dimers causes any differences in the ordering of the molecules around them, both within the first hydration shell and beyond.

The first question is whether the presence of any of the two different dimers has any effect on the position or orientation of the other molecules in the first hydration shell. To answer it, one acceptor (donor) involved in a *cis* or *trans* dimer was chosen and the previous analysis was repeated for the other three molecules: no appreciable differences have been found. This means that if a neighbouring water molecule is in a certain configuration, it does not impose any restriction to the relative orientation of the other Hydrogen bonded molecules.

The second question is whether different dimers affect the *positional* short range order at a length scale greater than approx. one molecular length scale. This was studied through two methods: (a) the partial radial distribution functions, (b) the 2D positional maps like the one in Figure 1. Concerning (a), three partial radial distributions were compared: the g_{OO} of all water molecules, the g_{OO} of water dimers with a *cis* acceptor, and the g_{OO} of water dimers with a *trans* acceptor. There is no appreciable difference between these cases. This means that the two dimers cannot create differences in the microscopic molecular density, and it is therefore unlikely that they are responsible for high/low density liquid water ordering. Concerning (b), three 2D positional maps $g(\cos(\theta_{\text{OO}}), \phi_{\text{OO}})$ for molecules beyond the first hydration shell were compared using the same groups as above. Again there was no appreciable difference, with the agreement being slightly less good at distances associated to the first minimum in the g_{OO} radial distribution function where the probability to find a water molecules is low (these analysis are included in the supplementary information†).

The third question is finally whether different dimers

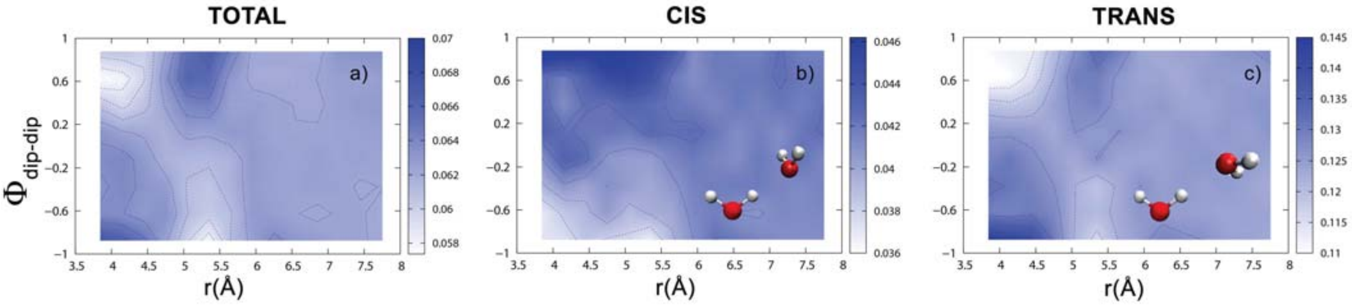

Fig. 4 (color online). Probability map of the relative dipole orientation of a neighbour molecule with respect to the central one ($\Phi_{\text{dip-dip}}$) as a function of the distance, for molecules beyond the first hydration shell. In panel a we show the results for any water molecule and in panels b and c we restrict the calculations for molecules having an acceptor in *cis* or *trans* configuration respectively.

affect the *orientational* short range order at a length scale greater than one molecular length scale. It is rather challenging to compare the orientational 3D probability distributions of Euler angles which depend on the molecular position and on the distance from the central molecule. For this reason we have chosen to study the dipole moment orientation with respect to that of the central molecule ($\Phi_{\text{dip-dip}}$) as a characteristic molecular direction. This choice is also supported by the fact that, as we have demonstrated, differences in energies are caused by different dipole orientations. Although different dimers seem to have no effect on the position of water molecules and on the orientation in the first hydration shell, we find a different scenario for the orientation of molecules beyond the length scale of one molecule. Figure 4 shows the probability distribution of $\Phi_{\text{dip-dip}}$ as a function of the distance, starting from the first minimum of the g_{OO} partial radial distribution function, i. e. beyond the first hydration shell. Again, these calculations were performed for the three groups: all water molecules, the water dimers with a *cis* acceptor, and the water dimers with a *trans* acceptor. Figure 4 reveals that the dipole orientation distribution for molecules is different up to distances of about 6 Å in the three cases. In particular, molecules in *cis* configuration (a parallel dipole moment) influence next neighbours so that they also align parallel up to a distance of about 6 Å, forming some kind of chain of dipoles. On the other hand molecules in a *trans* configuration alternate the dipole orientation also up to a distance of 6 Å.

The structure of liquid water is therefore the result of a continuous mixture of molecules participating in one of two dimers with different energies that result from a different dipole orientation: on the one hand *trans* dimers that have almost perpendicular dipole moments and a low energy and on the other hand *cis* dimers that have parallel dipole moments and are less tightly bonded. We therefore have found as in the work of Kühne *et al.* an asymmetry in the energy of water molecule contacts (whether it is the same as in that case must be further investigated). Nevertheless, we demonstrate a clear difference of the geometry of these contacts thanks to a careful analysis of the local structure of liquid water. In our opinion further analysis of the local structure of water must take this asymmetry into account which is not due to differences in the Hydrogen bonding geometry but rather to different dipole orientations.

5 Methods

5.1 Molecular Dynamics simulation

Molecular Dynamics (MD) simulations were performed using a system of 512 water molecules at T=298 K and ρ=0.9979 g/cm^3. The analysis presented here were extracted from a simulation with the TIP4P/2005 water model[24]. This is a rigid non-polarizable model which reproduces many properties of liquid water and ice[25,26]. The same analysis was also performed on simulations of the widely used SPC/E water model[29] and the flexible TIP4P/2005f water model[30] which gave qualitatively the same results. Long-range electrostatic interactions were calculated with the Ewald summation technique. The time step was set to 2 fs in the case of the rigid water models and 0.1 fs in the case of the flexible water model. The simulations consisted of an equilibration run of 100 ps followed by a production run of 1000 ps. During the production run, the configurations were stored every 500 time steps for further analysis.

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