

# Supporting Information for Universal features in lifetime distribution of clusters in hydrogen bonding liquids

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## 1 Angular distribution of Hbonds

The water SPC/E model and OPLS ethanol model are used below to show the hydrogen bond distribution in terms of the hydrogen donor-acceptor angle, and for various Hbonding distances  $r_c$ .

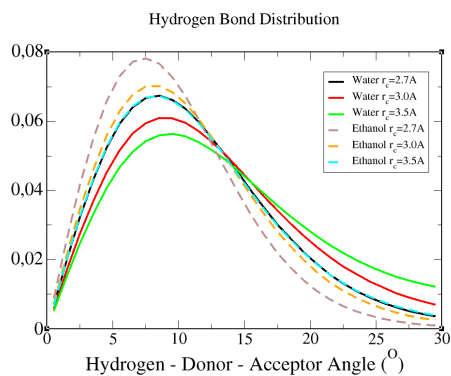


Fig.SI- 1. Hbond distribution for SPC/E water (full lines) and OPLS ethanol (dashed lines), as a function of the O-H-O angle, and with different Hbonding distance  $r_c$ .

A comparison with Fig.2 in the main paper shows very similar features, namely that the maximum, indicating the most probable angle is quite similar

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between water and alcohols, and for different bonding distances sample around the first peak of  $g_{OO}(r)$  depicted in Fig.1.

## 2 Cluster distribution

The cluster distribution probability  $P(s)$  as a function of cluster size  $s$  is shown below for the SPC/E water model (black line and symbols), OPLS methanol (green) and ethanol (blue) models, together with typical clusters snapshots. The oxygen atoms are shown in red, hydrogen atoms in white and methyl/methylene groups in cyan. For the ethanol cluster, the methyl/methylene groups are shadowed in order to better visualize the hydroxyl group chaining pattern.

This figure helps appreciate that behind various cluster shapes (branched, loop, chains), the universal pattern related to the underlying chaining of the hydroxyl groups.

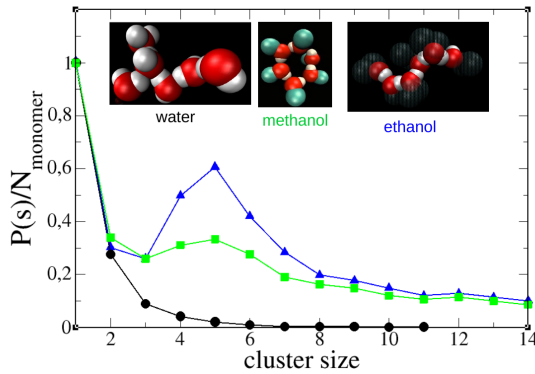


Fig.SI- 2. Cluster size distribution  $P(s)$  as function of the cluster size  $s$ , for SPC/E water (black line and symbols), OPLS methanol (green) and OPLS ethanol (blue). Typical cluster shapes for each species are shown in the insets (see text).

## 3 Comparison of $L_{HB}(t)$ for different force field models

### 3.1 Water

The equivalent of Fig.3 for the SPC/E water model is reported below in Fig. 3 for the TIP4P 2005 model [1] and in Fig. 4 for the TIP5P model [2].

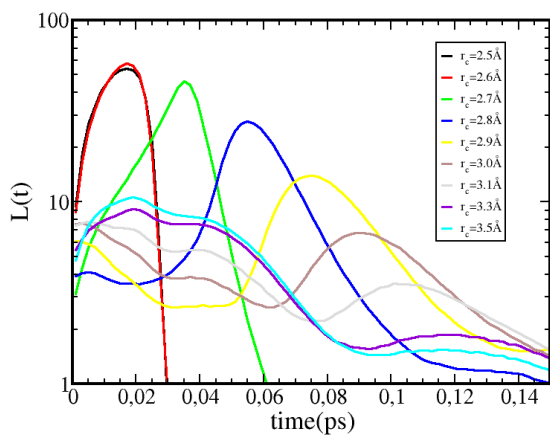


Fig.SI- 3. Hbond life time distribution for the TIP4P 2005 water model, with different Hbonding distance  $r_c$ .

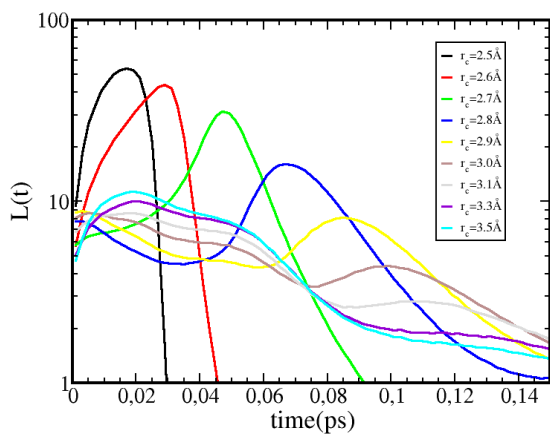


Fig.SI- 4. Hbond life time distribution for the TIP5P water model, with different Hbonding distance  $r_c$

## 3.2 Alcohols

### 3.2.1 Methanol

The equivalent of Fig.5 for the OPLS methanol model is reported below in Fig. 5 for the TraPPE model [3].

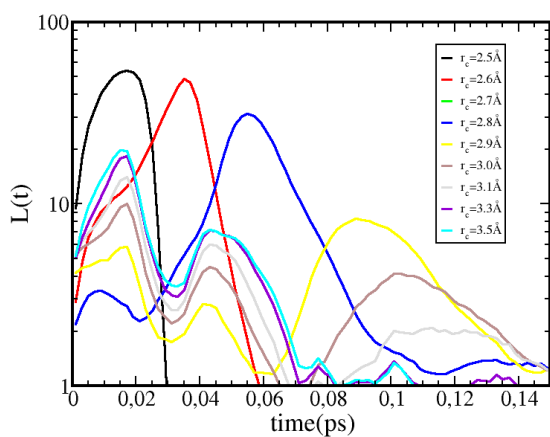


Fig.SI- 5. Hbond life time distribution for the TraPPE model for methanol

### 3.2.2 Ethanol

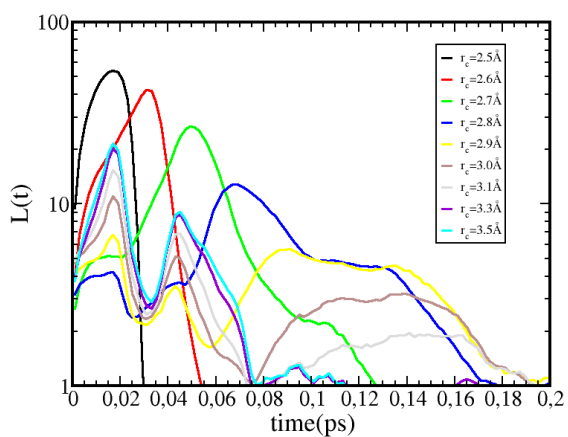


Fig.SI- 6. Hbond life time distribution for the TraPPE model for ethanol

### 3.2.3 1-propanol

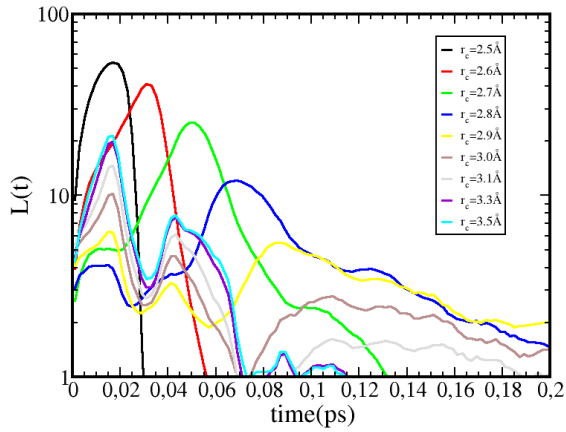


Fig.SI- 7. Hbond life time distribution for the TraPPE model for 1-propanol

## 4 Lifetimes distribution for other models

Below we report the lifetime distributions for the two other models discussed in the text, namely 1-octanol in Fig. 8 and 1-propylamine in Fig. 9.

### 4.1 1-octanol

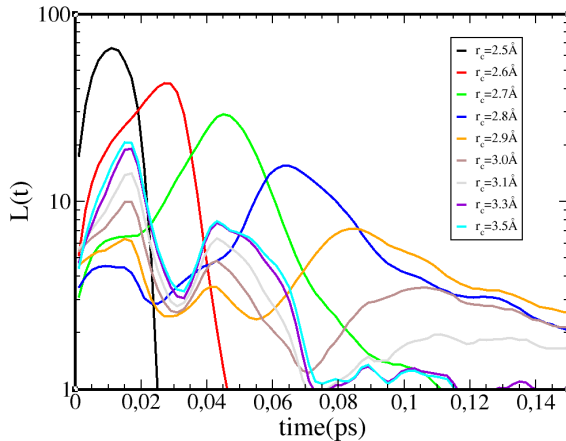


Fig.SI- 8. Hbond life time distribution for the OPLS model [4] for 1-octanol.

### 4.2 1-propylamine

The lifetime distribution for 1-propylamine is somewhat different from that reported previously for various water and monool models, since it concern the amine group  $\text{NH}_2$  Hbonding mechanism. This difference is seen only in the

third peak and the tail, as discussed in the main paper in Fig.9. Here, we report the  $r_c$  cutoff dependance in details in the figure below 9.

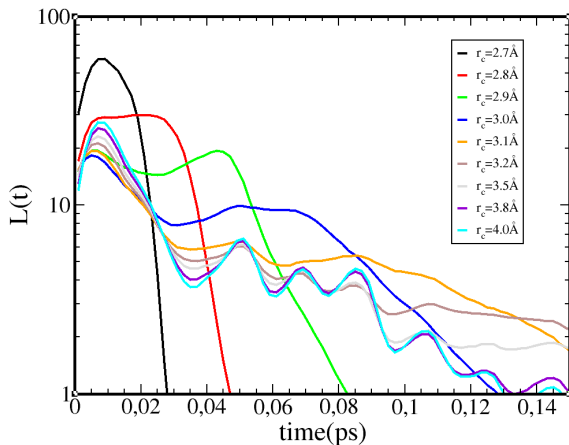


Fig.SI- 9. Hbond life time distribution for the GROMOS model for 1-propylamine

We observe that this 3rd peak is not so well differentiated as for the OH bonding species. It is essentially made of sub-oscillatory patterns, which appear to decay almost continuously for higher times. We hypothesize that these secondary oscillations come from the alkyl tail “bath” which affects more the  $\text{NH}_2$  clusters than it does for the alcohols. This hypothesis is rationalized by our previous computer simulations studies of 1-propylamine[5, 6], which has a very different clustering pattern than its alcohol counterpart 1-propanol. While 1-propanol has quite clearly visible chain-like clusters of the OH head groups, 1-propylamine has much less well defined pattern. This is seen experimentally through the smaller pre-peak in the Xray scattering intensities of 1-propylamine [6], compared with that of 1-propanol[7]. Consequently, the alkyl tail entropic constraint exerted on the head group cluster is larger for 1-propylamine, and this results in the biting of this influence into the 3rd peak of the lifetime distributions.

## References

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