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# Lifetime distribution of clusters in binary mixtures involving hydrogen bonding liquids

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## ABSTRACT

Hydrogen bonded liquids are associated liquids and tend to exhibit local inhomogeneity in the form of clusters and segregated sub-nano domains. It is an open question as to whether Hbonded clusters in pure water have common features with the water segregated pockets observed in various aqueous binary mixtures, such as water-alcohol mixtures, for example. In the present study, we demonstrate through classical molecular dynamics studies of the lifetime distributions of the hydrogen bonds in different types of binary mixtures, that these lifetimes exhibit the same universal features in the case of the pure liquids, independently of the species concentrations. The same types of three distinct lifetimes are observed, all of them in the sub-picosecond regime. The primary lifetime concerns that of Hbonded dimers, and strongly depends on Hbonding criteria such as the bonding distance. The two others are independent of bonding criteria. The secondary lifetime concerns Hbonded cluster lifetimes, while the tertiary lifetime concerns the topology of these clusters, such as chains or globules, for example. This surprising separation in three distinct lifetimes suggests the existence of associated three distinct kinetic mechanisms in the very short sub-picosecond time scales.

## Introduction

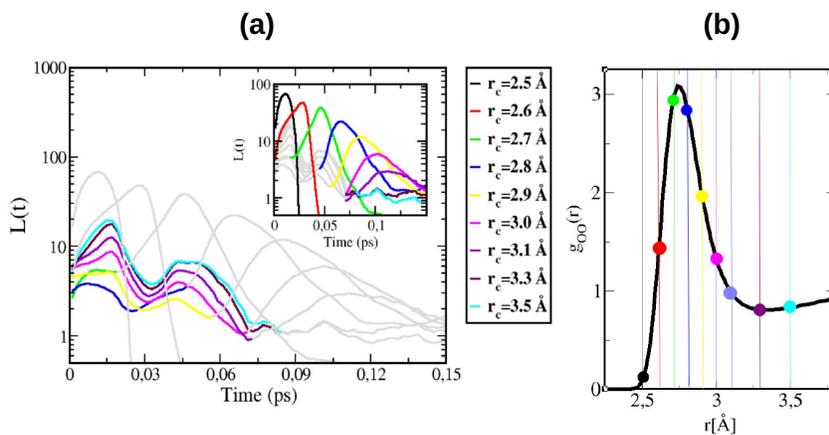
Hydrogen bonding is an important physical process, occurring in many different contexts, ranging from chemical systems CITE to pharmaceutical CITE and biological systems CITE. It links proton donor and proton acceptor molecules through a quantum mechanical process CITE, creating a labile molecular entity, which is both fragile and robust to the surrounding thermal disruptive agitation. It is robust enough to allow newly formed labile molecules to play an important role in the system, and fragile enough so that this role is only temporary. In that, it permits the appearance and destruction of transient molecular entities, but also specific architectures such as DNA, for example. Hence, the lifetime of such labile transient structure is an important physical parameter. If  $h_{ij}(t)$  represents the Hbond event, which is 1 when two molecules  $i$  and  $j$  make an Hbond, and 0 if not, then  $h_{ij}(t)$  is a random variable in the system, and its statistics can be studied conveniently, for example by computer simulations. Quantities such as the average, or the auto-correlation of this variable, can be computed. Interestingly, only the correlations has been the focus of previous studies CITE. In a recent work CITE, based on a classical description of Hbonding through Coulomb charge association, we have examined the lifetime of the Hbond, which is related to the average of  $h_{ij}(t)$ , for several Hbonding molecules, such as water, alcohol and amine. We have uncovered an unexpected interesting universality in the lifetime distribution across these very different molecules, which appears at very short times in the sub-picosecond regime. We have provided arguments which support the fact that cluster formation is the reason for this universality, all clusters being built by assembling pairs of bonded molecules into larger entities. Additionally, we have shown that the long time kinetics were system specific, in contrast to the very short time behaviour. This is a non-intuitive behaviour, since it is generally believed that it is the long time kinetics which should have universal features since one reaches the macroscopic limit CITE CHANDLER-LUZAR. The fact that the study of Hbond links to the existence of cluster formation is an interesting reductionism, in the sense that it brings an important problem in physical chemistry into the realm of clustering and aggregate formation, which is well known in associating liquids and mixtures.

In the present work, this study is extended to the cases of mixtures, both for the case of two associated liquids, and those with a non-associating solute partner. Typically, we will consider aqueous alcohol and aqueous-amine mixture for the first case, aqueous DMSO, alcohol acetone and alcohol alkane for the second type. All such mixtures are typical examples of molecular emulsions CITE, and are known to present sub-nano scale inhomogeneity. While one would expect marked concentration dependence between neat liquids and various mixtures, precisely because of the local segregation of the species, our results suggest a surprising similarity between the three types of cluster lifetimes. More specifically, if  $L_{ab}(t, x, r_c)$  designates the

lifetimes distributions of clusters between species  $a$  and  $b$  for a given concentration  $x$  of species  $a$ , and for cutoff we find that, while the curve shapes of the three species-species combinations differ markedly, the  $x$ -dependence is nearly the same show marked differences

## Results

Fig.1 is an introductory reminder of the features reported in Ref.CITE-hblife, which should serve as a guidance to study the various mixtures studied herein.



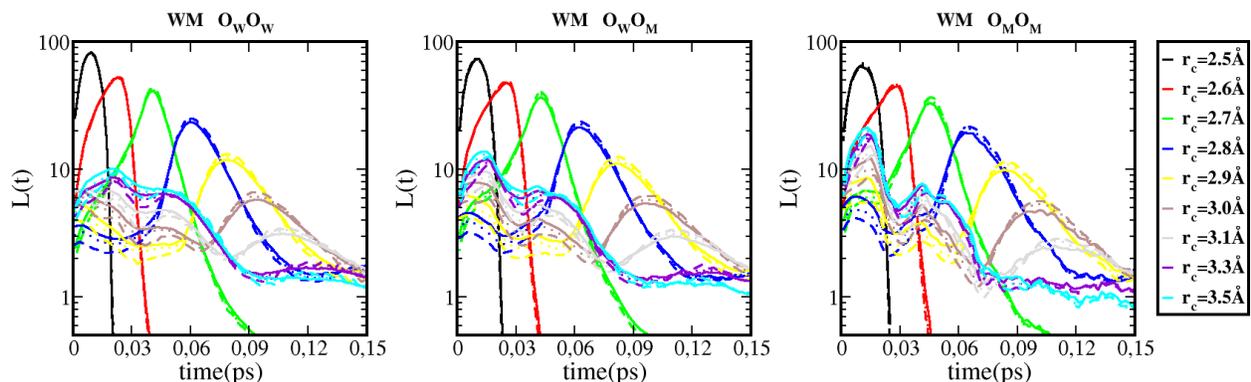
**Figure 1.** (a) H-bond life time distributions  $L(t)$  for pure water (SPC/E model) for different bonding distances  $r_c$ . (b) The first peak of the water oxygen-oxygen radial distribution function  $g_{OO}(r)$ , where the different  $r_c$  values are reported with the color codes corresponding to Fig.1a. Refer to the text for additional explanations.

Fig.1 shows the oxygen-oxygen contact lifetimes curves in the left panel, for the OPLS methanol model, and for various distance  $r_c$  cutoff values taken along the first maximum of oxygen-oxygen pair distribution curve shown in the right panel. Typical points are depicted in specific colors corresponding to the curves shown in the left panel. We immediately note the strong dependence in  $r_c$ , but there are more subtle features. First of all, we note that the strongest dependence comes from the first maximum, as shown in the inset. The lifetimes corresponding to the  $r_c$  dependent maximum increase with these  $r_c$  values. As the cutoff value passes over the first maximum, we see that the lifetime curves develop 2 secondary maximum, which are highlighted in the main part of the left panel (while the first maximum shown in the inset are now colored in grey in order to enhance their existence). What we observe is that these 2 secondary and tertiary maximum are now nearly insensitive to  $r_c$ , in contrast to the first maximum of the inset, suggesting that the typical lifetimes corresponding to these maximum, do not depend on  $r_c$ . In Ref-CITE, we have attributed the first maxima to oxygen dimer lifetimes, while the secondary and tertiary  $r_c$  independent maximum were attributed respectively to larger clusters and to their shape dependence. We have provided several evidences to support this interpretation. The existence of the secondary and tertiary peak is highly non-intuitive. Indeed, Hbonding concerns essentially dimers, hence only the behaviour of the first peak can be rationalized as follows. For small bonding distances only dimers exist and they do not last very long. As this distance is increased, the possibility that a dimer exist within a cluster is more probably, hence its lifetime is increased through cluster cooperativity. Apparently, this cooperativity is so important that clusters have their own lifetime peak, namely the secondary peak as witnessed in Fig.1a. All clusters appear to have the same mean-lifetime, as witnessed by the similarity of positions of these secondary peaks. Moreover, clusters of different shape appear to last differently, to the extent that this give rise to an autonomous tertiary peak related to the shape induced persistence. These two last features are as outstanding as they are totally non-intuitive. Finally, for a given large  $r_c$ , both these secondary clusters live shorter times than the dimers. This may be related to the feeble number of isolated dimers, but also to the fact that clusters live shorter times than the dimers they contain. Finally, there are no more distinct peak features beyond 0.2ps and  $L(t)$  decays algebraically CITE CHANDLER.

What happens to such peaks in mixing conditions? It important to note that, although we found a universality of curve shapes and lifetimes, the curves reported in Fig.1 differ for different species. The results we show below indicate that these 3 features are preserved, even for the cross species bonding patterns.

## Water-methanol mixtures

Fig.2 shows the lifetimes for the water-methanol (WM) mixtures, and for several  $r_c$  values corresponding for different color codes. Three typical concentrations of methanol are depicted (with different line styles), and for the 3 Hbonding possibilities, which are those involving the oxygens of water ( $O_W-O_W$ ) in Fig.2a, the cross oxygen bonds ( $O_W-O_M$ ) in Fig.2b, and those between methanol oxygens ( $O_M-O_M$  in Fig.2c). The pure water and pure methanol curves are shown in full lines in Fig.1a and Fig.1c, respectively. The first striking feature is that all curves look very similar in all 3 panels. This is possibly due to the fact that Hbonding occurs for all oxygen atoms, whether they belong to water or methanol. The second striking feature is that there is a very small concentration dependance of the lifetimes  $L(t)$ . As explained in Ref.CITE, but also in the introductory part to this section, the various curves shown in each panel show 2 typical features. A series of high peaks dominate the figures, whose maximum is seen to move to larger times with increasing  $r_c$  values, as well as decreasing in amplitude. In addition, from  $r_c$  values corresponding to crossing the maximum of the  $g_{OO}(r)$  (see Fig.1 ), each curve is seen to develop additional peaks at times smaller than the first peak and also having larger amplitudes. These peaks come in two, and we named them secondary and tertiary peaks. It is these peaks which correspond to the cluster modes. The secondary peak corresponds to clusters, while the tertiary peak would correspond to topology of these clusters (chain-like or globular-like, for example). For the present case of mixtures, it is seen that the first peaks show very little concentration dependance, with, however, an increase of dependance with larger  $r_c$  values. The secondary and tertiary peaks show a somewhat stronger concentration dependance, in fact quite similar to that corresponding to the fact that they are for larger  $r_c$  values. Let us try to rationalise the various trends observed in Fig.1a-c.



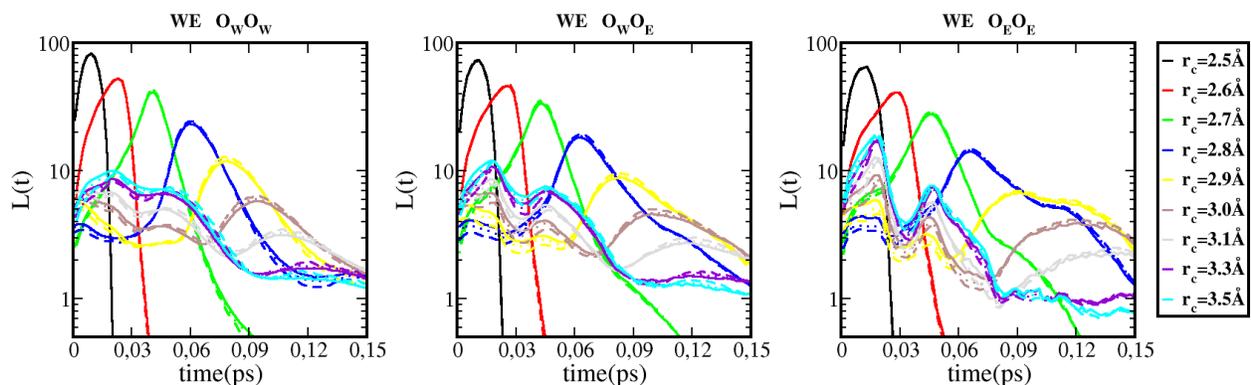
**Figure 2.** H-bond life time distributions  $L(t)$  for water-methanol (WM) mixtures, for (a) water-water clusters, (b) for water-methanol clusters, and (c) for methanol-methanol clusters. The full lines are for pure water (a) and pure methanol (c), The dotted lines for  $x_M = 0.2$ , the small dashes for  $x_M = 0.5$  and large dashes for  $x_M = 0.8$ .

We first note that the disposal of the concentration dependance of the primary peaks for water-water clusters (a) is opposite of that for methanol-methanol clusters (b). Namely, in Fig.1a, these curves shows an increase of magnitude with decreasing water concentration. It is the inverse in Fig.1c: the magnitude increases with increasing methanol concentration. This behaviour is in fact exactly that of the first peak of the respective  $g_{OO}(r)$ . When water concentration decreases, water dimers gain strength. This can be witnessed by the fact that the first peak of  $g_{O_W O_W}(r)$  increases when water concentration increases. Similarly, methanol first peak of  $g_{O_M O_M}(r)$  is seen to decrease when methanol content decreases. This observation confirms that these primary peaks correspond indeed to water-dimers. Next, we observe that the secondary and tertiary peaks behave in opposite manner of their respective primary peaks. Indeed, in Fig.1a, the peaks are seen to decrease with water concentration, while in Fig.1c, they are seen to increase with decreasing methanol concentration. This indicates that water clusters become more loose with increasing methanol concentration, while methanol clusters become stronger when methanol is minority. This is similar to surfactant self-aggregating in water. Fig.1b shows that, from the primary peaks, water-methanol dimers increase in strength with increasing methanol content, but from secondary and tertiary peaks, that larger clusters decrease in strength with the increase of methanol content.

## Water-ethanol mixtures

Next, we examine water-ethanol mixtures. We expect here to see how the extention of the alky tail influences the data observed in Fig.2 for methanol. Fig.3 show trends very similar to Fig.2, indicating that there are very little lifetime distribution differences

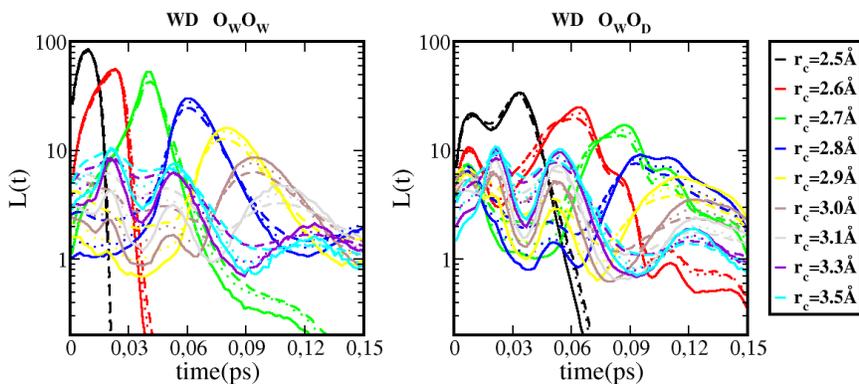
in trends, if we except the differences between methanol and ethanol in the shape of the distributions. It tends to further confirm the idea of universal features introduced for pure liquids.



**Figure 3.** H-bond life time distributions  $L(t)$  for water-ethanol (WE) mixtures, for (a) water-water clusters, (b) for water-ethanol clusters, and (c) for ethanol-ethanol clusters. The full lines are for pure water (a) and pure ethanol (c), The dotted lines for  $x_E = 0.2$ , the small dashes for  $x_E = 0.5$  and large dashes for  $x_E = 0.8$ .

### Water-DMSO mixtures

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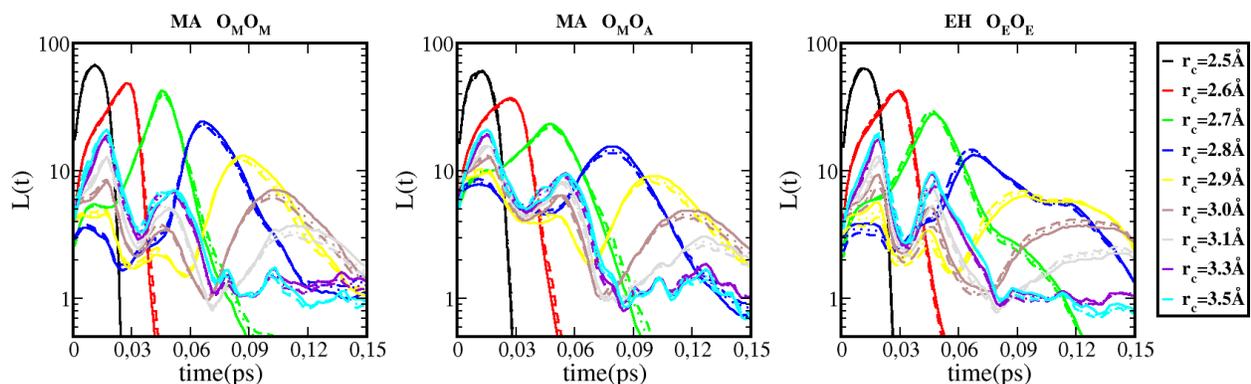


**Figure 4.** H-bond life time distributions  $L(t)$  for water-DMSO.

### Alcohol-solute mixtures

We examine now the case of mixing alcohols with polar and non-polar solute. Fig.4 shows the lifetimes of the oxygen-oxygen Hbonding for the methanol-acetone mixture, while Fig.5 shows the data for ethanol-hexane mixtures.

In the case of methanol acetone, both Hbonds between methanol molecules, and those between methanol and acetone can be calculated, since acetone is only an acceptor of Hbonds. However, for the ethanol-hexane mixtures, ethanol is the only Hbonding species, as depicted in Fig.3c. Once again, all three panels of Fig.3 show the same 3 peak characteristics observed for the 2 previous mixtures, and the single component liquids in Ref.CITE. However, it is interesting to compare methanol and ethanol self-bonding in presence of water and the solutes. Comparison of Fig.1c and Fig.3a show both the striking similarities in curve shapes for each  $r_c$ , but also the small inversion of peak behaviour with alcohol concentration. However, we note that in Fig.3a, there is very little concentration dependance, even for the secondary and tertiary peaks. This observation is corroborated by our previous studies of methanol-acetone, where we observed that methanol tended to form same types of clusters as in pure liquid. Similarly, we observe in Fig.3b that methanol and acetone Hbonding distribution is equally nearly concentration

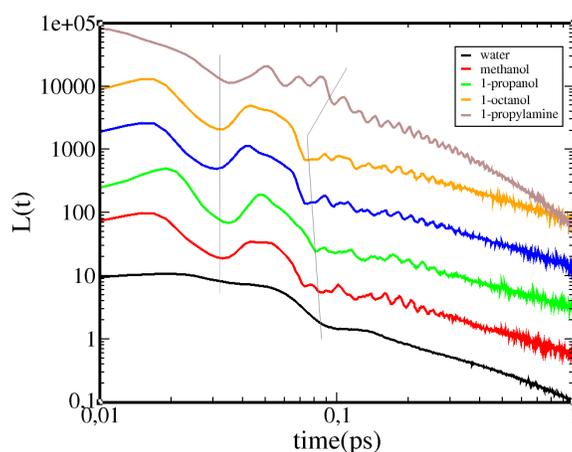


**Figure 5.** H-bond life time distributions  $L(t)$  for methanol-acetone (MA) mixtures, for (a) methanol-methanol clusters, (b) for methanol-acetone clusters in methanol-acetone mixtures, and (c) for ethanol-ethanol clusters in ethanol-hexane mixtures. The full lines are for pure methanol (a) and pure ethanol (c), The dotted lines for  $x_A = 0.2$ , the small dashes for  $x_A = 0.5$  and large dashes for  $x_A = 0.8$ , where  $x_A$  is the alcohol mole fraction.

independent. But the most important point here is that, even the Hbonding between an associating and non-associating species obeys the universality of time distribution. This finding confirms once more that these distributions are really about clusters, which are a permanent feature of the mixtures examined here. Finally, we note that ethanol Hbond lifetime distribution in hexane is nearly the same in water as in hexane, despite the very different properties of these two latter liquids. In addition, there appear to be no inversion of curves with concentration dependence.

### On the tertiary topology peak

The various plots of  $L(t)$  in the figures shown above, but also those for single component liquids in Ref.CITE, very clearly show that the primary peak vanishes when  $r_c$  is close to the first minimum of the pair distribution function (see Fig.1, for example). In that case, only the secondary and tertiary cluster peaks remain, and these can be compared across different systems. This was done in Ref.CITE in Fig.9, and it clearly showed that the differences between the tertiary peaks across different Hbonding liquids were more marked than that from secondary peaks, hence witnessing that these liquids were forming different typology of clusters (chain, branched, globule, etc...).



**Figure 6.** xxxx

In Fig.5, we compared, for  $r_c = 3.5\text{Å}$ , the secondary and tertiary peaks for each pairs of oxygen-oxygen correlations in the mixtures studied above.

## Discussion

The present study underlines the fact that the Hbond based clustering has very similar basis across different Hbonding species and atoms. This is particularly important in mixtures, despite the fact that Hbonding differences in interactions imposes a micro-segregation of the species CITE. Both in single component or mixtures, the elementary unit is the pair of Hbonding molecules. The present study confirms the universal character of this Hbonding, since it is essentially based on Coulomb pairing at the level of the description in computer simulations. The fact that simulations based on classical force fields are able to reproduce satisfactorily thermo-physical, dynamical and scattering properties of many systems, is a strong support to the validity of the findings of the present study. The secondary and tertiary peak features of the lifetime are based on the pair representation. The present study shows that these larger clusters obey very similar patterns even in mixing conditions. This is important for understanding and interpreting molecular binding properties in realistic systems, particularly at the short time scales where chemical reactions occur usually, which is the case with mixtures. This is why the present study may be important in confirming what was already found in the case of pure liquids.

## Methods

The main physical quantity introduced and examined in our previous work [CITE] was lifetime distribution of hydrogen bonds in different types of pure associative liquids. In the present work we extend our research to the mixtures listed in the Introduction. Again, purely geometric criteria has been used in order to detect a hydrogen bond in the system, meaning that a random pair of molecules  $i$  and  $j$  is considered to be hydrogen bonded if the distance  $r_{ij}$  between the corresponding donor and acceptor atoms ( $A_i$  and  $B_j$ ) satisfies  $r_{ij} \leq r_C$  and if the angle  $\theta_{ij} = \angle B_j A_i H$  obeys  $\theta_{ij} \leq \theta_C$ . The critical values  $r_C$  and  $\theta_C$  are equal to 3.5 Å and 30° respectively. The probability distribution of hydrogen bonds  $L(t)$  is properly defined in our previous work [CITE] and the same definition is used here.  $L(t)$  has been calculated using module *gmx hbond* (with *-life* option) which is available in GROMACS package [CITE].

We used SPC/E [CITE] and TIP4P\_2005 [CITE] forcefields to simulate water and OPLS-UA [CITE] and TraPPE-UA [CITE] forcefields to simulate alcohols. Propylamine was simulated using OPLS-AA forcefield [CITE].

Furthermore, we used leap-frog integrator with the timestep of 2 fs. PME method was used when taking electrostatic interactions into account and LINCS algorithm was used to constraint the length of intramolecular bonds. The temperature was held fixed at T=300 K by using a Nose-Hoover thermostat with the time constant of 0.1 ps and the pressure was kept at p=1 bar with Parrinello-Rahman barostat with the time constant of 1 ps.

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## Author contributions statement

All authors equally participated to this work.

## Additional information

**Competing interests** There are no competing interests to signal.