Reply to the 'Comment on "Universal features in the lifetime distribution of clusters in hydrogen-bonding liquids"' by J. Grelska, Phys. Chem. Chem. Phys. , 2024, 26 , https://doi.org/10.1039/D3CP05269A

Aurélien Perera, Bernarda Lovrinčević, Martina Požar

HAL Id: hal-04430334

https://hal.sorbonne-universite.fr/hal-04430334v1

Submitted on 31 Jan 2024

Reply to the 'Comment on "Universal features in the lifetime distribution of clusters in hydrogen-bonding liquids" ' by Joanna Grelska, Phys. Chem. Chem. Phys., D3CP05269A

Aurélien Perera[†][*], Bernarda Lovrinčević[‡] and Martina Požar[‡]

January 15, 2024

[†]Laboratoire de Physique Théorique de la Matière Condensée (UMR CNRS 7600), Sorbonne Université, 4 Place Jussieu, F75252, Paris cedex 05, France.

[‡]Department of Physics, Faculty of Sciences, University of Split, Ruđera Boškovića 37, 21000, Split, Croatia.

Abstract

In this reply, we discuss some aspects of the comments in Phys. Chem. Chem. Phys. D3CP05269A, by Grelska, about our work Phys. Chem. Chem. Phys. 2021, **23**, 19537. In this latter work, we have shown for the first time that, at short times below the picosecond range, the uninterrupted hydrogen lifetime probability $L(t)$ is composed of 3 peaks that are universal across many hydrogen bonding systems. By definition, $L(t)$ concerns pairs (dimers) of hydrogen bonded atoms, typically oxygen atoms. The first peak concerns the lifetime of strictly dimers, the second concerns the influence of chain clusters on dimers and the third the influence of their topology. The comment by Grelska contains a confirmation of our findings through similar calculations for other hydrogen bonding liquids. However, this author claims that it is the (first) dimer peak which concerns the topology of clusters, instead of the 3rd as we reported. Our response is that the 3rd peak reflects topology in the sense of branching, hence the presence of trimer bonding in the cluster, while the first peak shows clear species dependence at long times.

Hydrogen bonded entities differ from covalent constituents, since they are labile entities. It is therefore of paramount importance to know their lifetimes. The time dependence of probability distribution of uninterrupted hydrogen bonds $L(t)$ between two hydrogen bonded atoms can be directly computed in computer

---

[*]corresponding author (aup@lptmc.jussieu.fr)

simulations. Typically, these could be oxygen atoms, as in water or alcohols, or nitrogen atoms as in amines, for instance. In any case, $L(t)$ is about dimers, isolated or within larger clusters. In a seminal paper [1] , Luzar and Chandler showed that, for water $L(t)$ has a kinetic tail for long times, above 1ps. Although they mention small times features in $L(t)$, they call these "transient behaviour". In Ref.[2], we focused on this transient part, in the range less than 0.2ps, and found that the features were similar for several hydrogen bonding systems, such as water, lower mono-ols and amines. In addition, we showed that the long time kinetics were different across these different systems, contrary to the universality of the small time features. In a follow up paper [3], we showed that these features were equally preserved for mixture of hydrogen bonding liquids. Luzar and Chandler did not focus on the small time range because $L(t)$ depends in principle on several hydrogen bonding criteria, such as the distance r_c between the 2 bonding atoms and their mutual orientations θ_c. In contrast, the long time part of $L(t)$ describes the kinetics of the hydrogen bonding, albeit specific to a given system, and subsequently non-universal. As a consequence, the uncovering of an universal behaviour of the small time behaviour of $L(t)$, *despite* the dependence on r_c and θ_c, is a remarkable feat. The features in question consist of 3 peaks. The first peak depends strongly in r_c and θ_c, both in its position in time and its amplitude, hence changes with different r_c values, but this dependence is universal. The two others are characterized by time *independent* positions, about $\tau_1 \approx 20\text{fs}$ and $\tau_2 \approx 50\text{fs}$, respectively.

In order to clarify our previous approach to the explanation of the short time features of $L(t)$, we show in Fig.1 the equivalent of Fig.1 in [3] but for the case of 1-octanol, for which we have used the OPLS model [4].
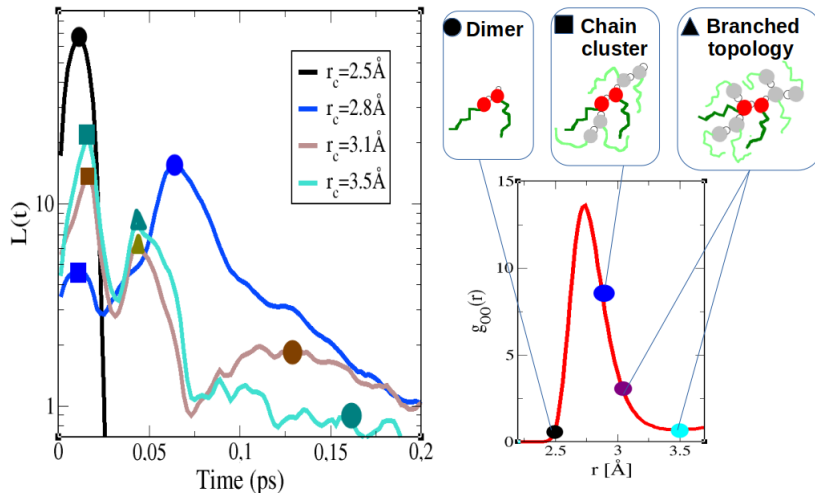
Figure 1: Illustration with 1-octanol (OPLS model) of the 3 peaks of $L(t)$ (left panel) and their correspondence with the position of hydrogen bonded atoms, as lone dimers or dimers within chain-like or branched clusters, along with the r_c dependance in the oxygen-oxygen pair correlation function $g_{OO}(r)$.

In Refs.[2, 3], we have argued that the first peak (dots in Fig.1) represents the lifetime of strictly dimers, hence depends on r_c and θ_c. The fact that this peak is seen to move to larger times with increasing r_c values is explained in the following way, in relation to the first peak of the bonding atoms (oxygen atom in Fig.1) pair correlation function $g_{OO}(r)$, which expresses the conditional probability of atom-atom contact. For very small r_c values (e.g. $r_c \approx 2.5\mathring{A}$), the contact probability is small, hence lifetime distribution is very narrow. However, since the underlying Coulomb interactions are higher at short distance, the lifetime probability is also highest. As r_c is increased, contact probabilities $g_{OO}(r)$ increase as well as Hbond life time. However, such bonds can now be broken by thermal agitation and the amplitude of $L(t)$ decreases, and its width also increases. However, as r_c increases, to the left of the widening of $L(t)$ one witnesses the appearance of a second peak at about $\tau_2 \approx 20$fs (blue square in Fig.1), a time smaller than the position of the corresponding first peak. Moreover, it is observed that the position of this second peak does not change as r_c is further increased, while its amplitude is seen to increase. When r_c is even further increased, this second peak is accompanied by a third peak (triangles in Fig.1) with smaller amplitude, positioned at about $\tau_3 \approx 50$fs, which is equally invariant with respect to r_c, while its amplitude increases, albeit with smaller trends that that of the second peak. This 3rd peak appears first when r_c is rather close to the first minimum of $g_{OO}(r)$, suggesting more complex libration modes.

3

These 2 secondary peaks are not easy to understand on the sole basis of a dimer of Hbonded atoms. If we consider that hydrogen bonding systems tend to produce larger aggregates than just dimers, then there is a difference between the lifetime of dimers in such cluster and that of isolated dimers. A cluster can only break and reform as dimers within break and reform. Therefore, the cluster lifetime in a strict sense is smaller than that of any dimers within. Since there is a measurable statistical quantity such as mean cluster lifetime, we believe that $\tau_2 \approx 20$fs is such a time, as related to that of the mean lifetime of any dimer within. In Ref.[2], we showed that this argument was consolidated by the study of $L(t)$ in our weak water models [5, 6] . Lifetime τ_1 must be independent of choice of r_c, since it is intrinsically related to the mean cluster lifetime, which is a physical observable under certain conditions [7], and this is exactly what we observe in Fig.1. In this context, what could be the origin of a third peak at $\tau_3 > \tau_2$? Our argument is that this situation is similar to the cluster size s_1 under the cluster distribution peak and the mean cluster size s_2. These two quantities need not be the same, and one has $s_1 < s_2$ as can be seen in our study of mono-ols [4]. We base our reasoning on the fact that τ_3 appears for r_c values greater than that for which τ_2 appears (see Fig.1). Allowing for larger r_c values is allowing for more dispersion of the cluster shapes. The fact that τ_3 exist in the calculations indicates that cluster shapes play a role, hence the name topology peak that we coined for τ_3. Herein, we would like to bring a new precision, that this 3rd peak might be related to the presence of branching in chain clusters, hence the presence of trimers (or higher). Indeed, branching becomes possible for r_c values close to the minimum of $g_{OO}(r)$, which means that when the entire first peak of the correlations are accounted for. It is important to note that both τ_2 and τ_3 are independent of the r_c values greater than the threshold values at which the corresponding peaks in $L(t)$ appear. This is not the case for τ_1, which is strongly dependent on the r_c cutoff value.

We come now to the comment by Grelska. We first note that, on the positive side, this author has recovered results identical to our, with similar τ_2 and τ_3 values, while using different force fields for the same alcohols as well as newer ones, and more importantly, while using Canonical ensemble simulations with constant NVT, in contrast to our isobaric ensemble simulations with constant NPT and ambient conditions. For finite N, the fluctuations in both ensembles are not the same[8, 9], and in addition it is not obvious that the average densities and pressures in both works are exactly the same. This demonstrates that our findings are relatively robust to simulation modeling conditions, suggesting that the 3 peaks might be genuine features of realistic systems, and not artifacts of simulations techniques and molecular models.

Grelska suggests that it is the first peak which represents the cluster shape and topology, instead of the third, as initially suggested by us. To support this argument, this author point to the fact that differences between mostly chain cluster forming alcohol and closed loop forming ones can be seen in the tail of $L(t)$. We observe that, in our first paper [2], similar differences can be observed between methanol (Fig.5 in Ref.[2]), ethanol and 1propanol (Fig.6), for instance in the blue ($r_c = 2.8\AA$) or the yellow ($r_c = 2.9\AA$) curves, in the

4

range $t > 0.08$ps. Such differences take the form of additional modulations in the tail of the first peak. We believe that such differences are attributable to molecular differences, and not topological differences, since all these 3 alcohols have very similar clustering tendencies [4]. Indeed, although being universal, each r_c dependent curve also depends on the system considered. We believe that it is these differences that the author has mistaken for information of topology in the sense as we mean it. In addition, we note that Grelska does not propose any alternative explanation for the appearance of the 3rd peak.

To conclude, in this reply to Grelska's comment, we have reminded the facts behind the universal features of the short time behaviour of $L(t)$, and we have explained our interpretations of the second and third peaks, in terms of differences between simple chains (clusters) and branched chains (topology). This version complements our original interpretation in terms of cluster and topology, since hydrogen binding liquids tends to form chain-like clusters with possibilities of branching which leads to richer topology. Finally, we recognize again that we do not provide any theoretical arguments to support these interpretations. Such a theory cannot be solely based on kinetic considerations, such as in Ref.[1], which ignore molecular details, and which are part of usual theoretical framework on the kinetics of clustering [10]. The requirement of having a theory which incorporates the microscopic kinetics through the dynamical van Hove correlation function $G_{OO}(r, t)$, with molecular details, is quite challenging [11, 12], and is currently being pursued.

Conflicts of interest

There are no conflicts of interest to declare

References

[1] A. Luzar and D. Chandler. Hydrogen-bond kinetics in liquid water. *Nature*, 379(6560):55–57, 1996.

[2] Ivo Jukić, Martina Požar, Bernarda Lovrinčević, and Aurélien Perera. Universal features in the lifetime distribution of clusters in hydrogen-bonding liquids. *Phys. Chem. Chem. Phys.*, 23:19537–19546, 2021.

[3] Ivo Jukić, Martina Požar, Bernarda Lovrinčević, and Aurélien Perera. Lifetime distribution of clusters in binary mixtures involving hydrogen bonding liquids. *Scientific Reports*, 12(1):9120, Jun 2022.

[4] Jennifer Bolle, S. Peter Bierwirth, Martina Požar, Aurélien Perera, Michael Paulus, Philipp Münzner, Christian Albers, Susanne Dogan, Mirko Elbers, Robin Sakrowski, Göran Surmeier, Roland Böhmer, Metin Tolan, and Christian Sternemann. Isomeric effects in structure formation and dielectric dynamics of different octanols. *Phys. Chem. Chem. Phys.*, 23:24211–24221, 2021.

[5] A. Perera, R. Mazighi, and B. Kežić. Fluctuations and micro-heterogeneity in aqueous mixtures. *The Journal of Chemical Physics*, 136(17):174516, 05 2012.

[6] B. Kežić, R. Mazighi, and A. Perera. A model for molecular emulsions: Water and weak water mixtures. *Physica A: Statistical Mechanics and its Applications*, 392(4):567–582, 2013.

[7] Takaya Satoh, Hiroyuki Ito, Hiroki Sakae, Toshio Ichihara, and Itsuo Katakuse. The lifetime distribution of cluster ions from sputtering ion source. *Journal of the Mass Spectrometry Society of Japan*, 51(2):354–358, 2003.

[8] Michael P. Allen and Dominic J. Tildesley. *Computer Simulation of Liquids.* Oxford University Press, 06 2017.

[9] Aurélien Perera, Martina Požar, and Bernarda Lovrinčević. Camel back shaped Kirkwood - Buff integrals. *The Journal of Chemical Physics*, 156(12):124503, 03 2022.

[10] Dietrich Stauffer. Kinetics of clusters in ising models. *Physica A: Statistical Mechanics and its Applications*, 186(1):197–209, 1992.

[11] Bernarda Lovrinčević, Martina Požar, Ivo Jukić, and Aurélien Perera. Role of charge ordering in the dynamics of cluster formation in associated liquids. *The Journal of Physical Chemistry B*, 127(25):5645–5654, Jun 2023.

[12] Bernarda Lovrinčević, Martina Požar, Ivo Jukić, David Perera, and Aurélien Perera. Dynamical correlations in simple disorder and complex disorder liquids. *Journal of Molecular Liquids*, 393:123421, 2024.