cphc.202100599: Response to Reviewers

Dear Editor,

Thank you for considering our paper "A machine learning model to classify dynamic processes in liquid water" for publication. We would like to thank the reviewers for their careful and detailed comments and suggestions, which significantly helped to improve the manuscript. We address their points individually below and indicate the changes we have made in response.

Yours sincerely

Prof. Shiben Li

Reviewer 1

Point 1.1: The authors devise a machine learning method to classify proton exchange events in liquid water in this well-written paper. The manuscript is very clear, the methods are original, and their description is accurate. In my opinion, the paper should be accepted for publication with minor corrections. The results are interesting.

Response: We sincerely thank the reviewer for the comment on our work. We address the questions in detail as follows.

Point 1.2: However, it would be beneficial to understand how a deep learning-based model like the one presented here can capture the complex H-bonded superstructures characteristic of liquid water (see Hassanali et al. PNAS 2013) and how interchange processes may display a concerted nature over a larger H-bonded networks of molecules.

Response: In PNAS, Hassanali et al. reported the mechanisms of proton transfer in liquid water by analyzing the H-bonded rings, which are represented as directed graphs. The directional correlations in H-bonded rings and the interconversion of different rings are studied in their work. Their inspiration of viewing water as a network composed of directed rings makes it possible to study the complex H-bonded superstructures characteristic of liquid water. In our work, we share the similarity of using a directed graph to represent the bulk water system, which did simplify our analysis. However, we have to admit that capturing the superstructures characteristic of liquid water is beyond the scope of this work. In this work, we just monitored one measure $\tilde{h}$ for one pair of water along the trajectory, because it is enough to detect interchange processes and translation defusions. However, the ability of neural networks is far beyond handing one measure. Therefore, extending the basic target from the H-bonded water pair to the water ring is possible using our workflow if we can find reasonable measures to represent the properties of H-bonded rings.

Let's illustrate the main idea of how to extend our model to H-bonded rings using a rough example. Hassanali et al. referred to the type of water molecule as DD, AA, and DA within the directed rings. Similarly, for any small size quasi ring i in liquid water, we can use a feature H_i to represent its connectivity state at time t as the following,

$$H_i(t) = \begin{cases} 1 & S_1 = 0 \\ 0 & \text{No ring formed} \\ -1 & S_1 > 0 \end{cases}$$

where S_1 is the number of DD-AA pairs in the ring. In this way, interchange processes would lead to the change of H. By analysing the time sequence of H, we may see the concerted property over H-bonded rings or networks.

We citeed the related works of Hassanali et al. in the Introduction and Summary, and explained the extensibility of our work at the end of the Summary.

Point 1.3: In their revision, it would be beneficial if the authors could comment on the ability of their method to detect the structure and dynamics of H-bonded rings of water molecules with a more efficient approach than the existing ones based on clustering and ad-hoc metrics.

Response: As you mentioned, there are some approaches in graph theory that can be used to help us to find the H-bonded rings and obtain the structure and dynamic properties. The graph representation for bulk water used in this work is served as a platform that allows us to use any approaches to explore more complex properties of H-bond networks. Using graphs to study H-bonded networks is a very interesting topic, and it would be much more exciting if we can obtain new dynamic properties of H-bonded networks with the help of machine learning. Therefore, we would like to include the content of H-bonded rings in the forthcoming study.

We gave comments in the Summary.

Reviewer 2

Point 2.1: In their manuscript, Huang et al. study the dynamic processes of bulk water using ab initio molecular dynamics and machine learning by using a recurrent neural network (RNN) classifier. A method is first used to label hydrogen bonds based on geometric criteria for each static snapshot to obtain the hydrogen bond population "h", and a RNN is then used to classify interchange or breakage based on a sequence of "h" over a time period. The authors then demonstrate this approach on an example studying the change in interchange and breakage as a function of temperature. This work is well-written with illustrative descriptions of the workflow, methodology and results. The methods are well described in the SI and its usage in this work appears to be reasonable. Overall, this is an excellent work on using machine learning to study H-bonding in water, and by using a clever approach with RNNs and graph-based description of the H-bonding networks. The topic is also timely and addresses important needs in the field for studying these dynamical processes. I would recommend publication of this work as is.

Response: We sincerely appreciate the reviewer for these positive comments on our work, which give us enough confidence to go further in this direction.