

Size and Quality of Quantum Mechanical Data Set for Training Neural Network Force Fields for Liquid Water

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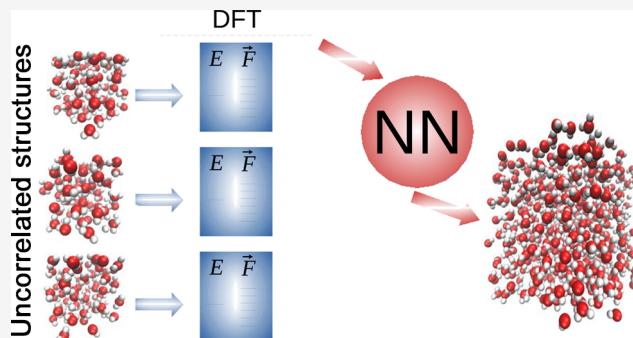
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ABSTRACT: Molecular dynamics simulations have been used in different scientific fields to investigate a broad range of physical systems. However, the accuracy of calculation is based on the model considered to describe the atomic interactions. In particular, *ab initio* molecular dynamics (AIMD) has the accuracy of density functional theory (DFT) and thus is limited to small systems and a relatively short simulation time. In this scenario, Neural Network Force Fields (NNFFs) have an important role, since they provide a way to circumvent these caveats. In this work, we investigate NNFFs designed at the level of DFT to describe liquid water, focusing on the size and quality of the training data set considered. We show that structural properties are less dependent on the size of the training data set compared to dynamical ones (such as the diffusion coefficient), and a good sampling (selecting data reference for the training process) can lead to a small sample with good precision.



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INTRODUCTION

Molecular dynamics simulations have been used in different scientific fields to investigate a broad range of physical systems, such as thermodynamic properties of liquids and physico-chemical aspects of interfaces and biomolecules.^{1–3} Its success relies on a number of factors, for example, the functional form assigned to describe inter- and intra-atomic interactions, the parametrization procedure (obtaining the potential parameters), and the quality of data employed - experimental or *ab initio* one.^{4,5,7–10} Most of the classical potentials are physically and/or chemically motivated, in which a simple analytical functional form is usually considered such as the Lennard-Jones potential.¹¹ As a consequence, transferability and accuracy are a common issue in this area of research.^{5,7,12}

In the particular case of water, many classical empirical models have been proposed to describe its properties. Although some classical models, such as the MB-Pol, provide fairly good results for water,^{13–15} there is no single water model capable of exactly reproducing all experimental results.¹⁶ In fact, over the last decades, there has been an advance in the understanding of the properties of water both by theory/simulations as well as experimentally. However, there are still some of its properties which are not yet fully understood, for example, the microscopic origin of the water anomalies.¹⁷ From a microscopic point of view, the quantum nature of the hydrogen bond network, the interplay between short- and long-range interactions, and nuclear quantum effects make the liquid water intrinsically difficult to be modeled. In this way, based on the nature of the phenomena that governs the

physical and chemical properties of liquid water, first-principles simulations seem to be the most appropriate choice, since they have, by construction, an accurate predictive potential. These types of simulations have the advantage of forgoing the requirement for a model or the parametrization of any experimental data. In particular, *ab initio* molecular dynamics (AIMD) allows one to obtain the energy/forces on-the-fly by a quantum mechanical method such as density functional theory (DFT)¹⁸ at each time step. The caveat is the limitation to small system sizes and short simulations time.⁵ Furthermore, the quality of the AIMD simulations is closely determined by the chosen exchange-correlation (xc) functional.^{19–21}

In this scenario, machine learning (ML) potentials - also known as ML force fields¹² - have introduced a paradigm change as one can now combine the quantum accuracy of AIMD with computational efficiency of empirical interatomic models. This allows one to simulate large systems for a long time with *ab initio* accuracy. These methods have been recognized as promising alternatives to underline new physical phenomena and aid in materials-discovery processes.^{6,12,22–30} In particular, the microscopic comprehension of bulk water can

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benefit from computer simulations based on ML potentials.^{26,31–34}

Many different ML methods have been used to construct these ML-based potentials, for example, artificial neural networks,^{4,6,8,35–40} kernel-based methods,^{30,41} Gaussian approximation potentials,^{42,43} and atomic cluster expansion.⁴⁴ In particular, deep Neural Network (NN) approaches have been shown to be a versatile tool able to produce accurate Force Fields (FFs) trained with DFT calculations.^{6,7,26} The successful/accuracy of ML potentials is directly related to the quality and size of the training data set employed.^{12,45,46} Usually, deep NN approaches require a large amount of data but typically provide a high accuracy.^{4,23,47} Therefore, having a deep NN potential trained with less DFT data reference is a very important issue,^{4,48} since the DFT calculation of the reference data set is highly computational demanding.

In this work, we investigate deep NNFFs designed at the level of DFT to describe liquid water, focusing on the size and quality of the training data set considered. Here, we chose to investigate the *ab initio* training data set based on the SCAN functional,⁴⁹ since it has shown some promising results for water.^{26,31,50–56} We show that correctly sampling the data set (selecting reference data for the training process) is a crucial step, and devising a method to efficiently obtain uncorrelated structures that provide a good distribution over the phase space allows one to significantly reduce the amount of data and the size of the NN required to have accurate NNFFs. As a result, we also show that the structural properties are less dependent on the size of the training data set compared to dynamical ones (e.g., the diffusion coefficient.)

METHODS

Computational Details. A crucial step in the development of the NN force field was to carefully select the bulk water configurations, which included configurations with long and short OH bonds before computing the DFT energies and forces used in the training process. The protocol to obtain those configuration was as follows: (i) the selected configurations were obtained considering nuclear quantum effects (NQEs) in classical MD simulations by carrying out partially adiabatic centroid molecular dynamics (PACMD)⁵⁷ simulations using a flexible water model (q-TIP4P/F force field⁵⁸) for a system composed of 64 water molecules; (ii) good phase space sampling was obtained by performing simulations with different temperatures ($T = 300$ and 600 K) and densities ($\rho = 0.88$, 1.0 , and 1.2 g/cm 3) and (iii) selecting uncorrelated configurations (i.e., geometrical structures) through radial distribution functions, choosing those that maximized the Jensen-Shannon distance.⁵⁹ In this way, a broad range of intra- and intermolecular geometric configurations were present in the training set.²⁶

For each set of PACMD simulations (different T and ρ), the geometries were collected every 100 fs from a total simulation time of 1 ns (10^4 configurations). After geometric selection criteria, the number of configurations was 5000 (1000) for $T = 300$ K (600 K), which resulted in 18×10^3 snapshots. Then, for each configuration, we performed a single point DFT calculation to obtain the total energies and forces. In our particular case, the reference data were obtained using the Vienna *Ab initio* Simulation Package (VASP)⁶⁰ and SCAN functional.⁴⁹ The plane wave basis was set up to an energy cutoff of 1600 eV (118 Ry), and the core–valence interaction was treated by the projected augmented wave (PAW)

method.⁶¹ Note that all DFT calculations are completely independent from each other and thus can be performed separately.

Training Process. A crucial point in the design of neural network-trained force fields is to determine the minimum size of the training set to obtain *ab initio* quality results. In this way, we trained our NNFFs using a randomly selected subset of the training data set ranging from 10% to 100% of the total data set.

We first selected 90% of the configurations as the training set and 10% as the testing set for assessment, which means 16200 (training) and 1800 (testing) structures. It is important to emphasize that the data used in the training is $n_{\text{data}} = n_{\text{energy}} + n_{\text{force}}$. We have one energy value per configuration (64 H₂O), $n_{\text{energy}} = 16200$. Whereas for force, there are three components, $\{f_x, f_y, f_z\}$, for each atom, i.e. $n_{\text{force}} = 16200 \times 3 \times 192$. Therefore, we have $n_{\text{data}} = 9347400$ training data.

On the other hand, in order to avoid overfitting (when the model performs worse on the testing data than on their training set), the number of fitted parameters, n_{parm} , cannot be larger than the number of training data points. In this work, we chose $n_{\text{data}}/n_{\text{parm}}$ to be at least 8. Note that in order to avoid overfitting one can either increase the size of the training set or reduce the number of layers and/or the number of neurons of each layer.^{6,8,62}

Therefore, we scaled down the neural network in order to keep the total number of fitted parameters in the same proportion. For example, for the NN topology, the number of hidden layers is 4, and the number of neurons in each layer is set to (32, 16, 4, 2) and (320, 160, 32, 16) for the 10% and 100% cases, respectively.

We used the current version of the DeePMD-kit code⁸ to generate deep neural network potentials for bulk water based on the SCAN functional. In particular, we use the Deep Potential-Smooth Edition descriptor, where the full relative coordinates are used to build the descriptor.^{6,63} The number of hidden layers is kept fixed, and the hyperbolic tangent was used as an activation function in the hidden layers. The loss function was minimized with the Adam stochastic gradient descent method,⁶⁴ composed by the mean squared errors of the energies and forces with a starting and stopping learning rate equal to 10^{-3} and 3.51×10^{-8} , respectively. The training process undergoes 2×10^6 steps in total. Further computational details can be found in the Supporting Information (SI).

Deep NN Molecular Dynamics. After we have obtained different deep NNFFs for liquid water trained with subsets of our DFT training data set, we can then perform deep NN Molecular Dynamics (NN MD) using the LAMMPS simulation package⁶⁵ and the DeepMD plugin.⁸ In this way, we can investigate the effects of the training data set size on the convergence of physical properties of water.

Simulations of water at different temperatures T and pressures P were performed to investigate the density convergence as a function of the training set size. These systems were first equilibrated over 50 ps by performing isothermal–isobaric (NPT) simulations (using the Nose–Hoover thermostat and barostat⁶⁵). The equilibrium densities were then obtained averaging over 2 ns.

We also carried out NVT simulations of bulk water (512 molecules), controlling the temperature via a stochastic velocity rescaling thermostat.⁶⁶ These large systems were equilibrated over 150 ps, and then additionally, 2 ns simulations were carried out at the production stage.

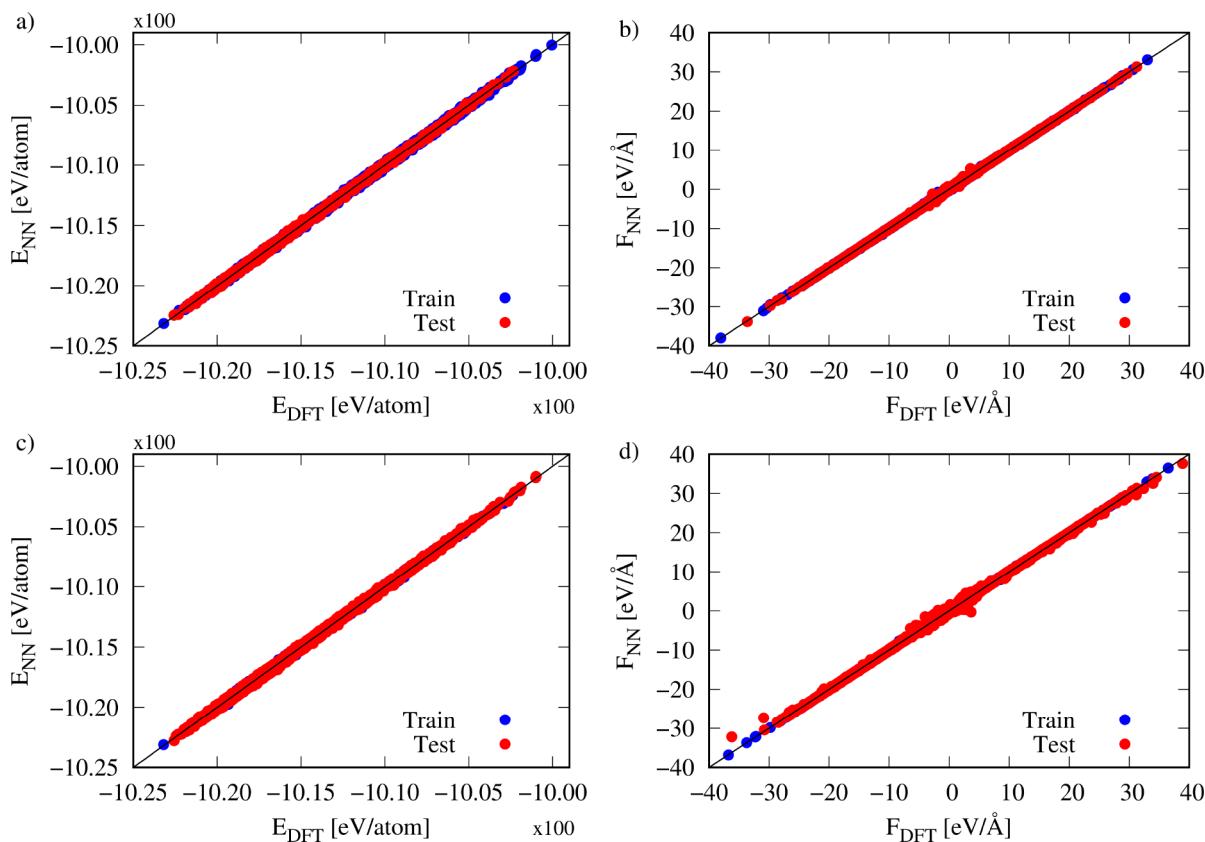


Figure 1. Parity graphs for energy and forces evaluated on the training and test data sets, where a) and b) refer to the 100% case while c) and d) refer to the case of 10%. The E_{NN} and F_{NN} are the NN predicted energy and force, respectively. The DFT data reference are represented by E_{DFT} and F_{DFT} .

RESULTS AND DISCUSSION

In order to illustrate the performance of our deep NN potential, we show in Figure 1 the parity graphs for the (a) energy and (b) force components. In this particular case, we tested our model on the test set (10% of DFT data reference) and also on the training set itself (90% of DFT data reference), which shows that the NN operates well on both data sets with roughly similar errors, that is a good feature to indicate that the fitted NN is neither underfitting nor overfitting.⁸

In particular, we find that the RMSEs (Root Mean Squared Errors) on the test set are ~ 46 meV/ Å (force) and ~ 0.53 meV/atom (energy). As recently pointed out by Wen and collaborators,⁶ the RMSE for forces and energy for a good (high accuracy) deep potential should be of the order of < 50 meV/ Å and ~ 1 meV/atom, respectively.

We performed a K-fold cross-validation procedure (see the SI for technical details), where our DFT reference data (18,000 snapshots) were separated into 10 subsets of equal size. We then trained/tested different models with different training subsets, while keeping the proportion of 90% for training and 10% for testing. We show in the SI the RMSEs obtained (Table 1-SI). We find that the testing errors do not change considerably with different training subsets, and the average of RMSE errors for energy and forces is equal to 0.533 meV/ atom and 46.6 meV/ Å, respectively. The deviations are on the order of 0.002% (energy) and 0.12% (force), which represents that the DFT reference data are uncorrelated.

In other words, the cross-validation tells us that the trained NNFF does not depend on a particular partition of the DFT data set. Thus, we can train different NNs using a randomly

selected subset of the training data set. To exemplify it, we show in Figure 1c) and d) the parity graphs for the 10% case (1620 randomly selected snapshots used to train a deep NNFF), which shows that this NNFF also performs well on both the testing and training data sets. In this way, we show in Figure 2 the RMSE and MAE (Mean Absolute Error) for energy (top panel) and force (bottom panel) as a function of the training data set size.

As we can see in Figure 2, the four curves show an initial decrease in error values, and after the size of the data set has reached 20%, they become essentially constant. However, it should be mentioned that even the 10% case is within the accuracy reported in the literature.⁶

Nonetheless, the observation only based on the errors evaluated on test data sets is not enough to affirm that the NNFF will work for a long MD simulation. For example, we considered a different case, where the NNFF was built with correlated data obtained from a 330 K NVT AIMD simulation with the van der Waals exchange–correlation functional (vdW-BH⁶⁷). In this case, the training data set has a size similar to the 50% uncorrelated case presented in Figure 2. Although we found the RMSE errors on the test data set smaller than those presented in Figure 2, we cannot simulate bulk water for a long time. The energy is only conserved up to ~ 20 ps; after that, the system makes nonphysical bonds between the atoms, and the energy is no longer conserved. See the SI for further details.

On the other hand, the deep NNFF trained with only uncorrelated 1620 frames (10% case) allows one to simulate water systems for long times, which shows that correct phase sampling is more important than just the amount of data used

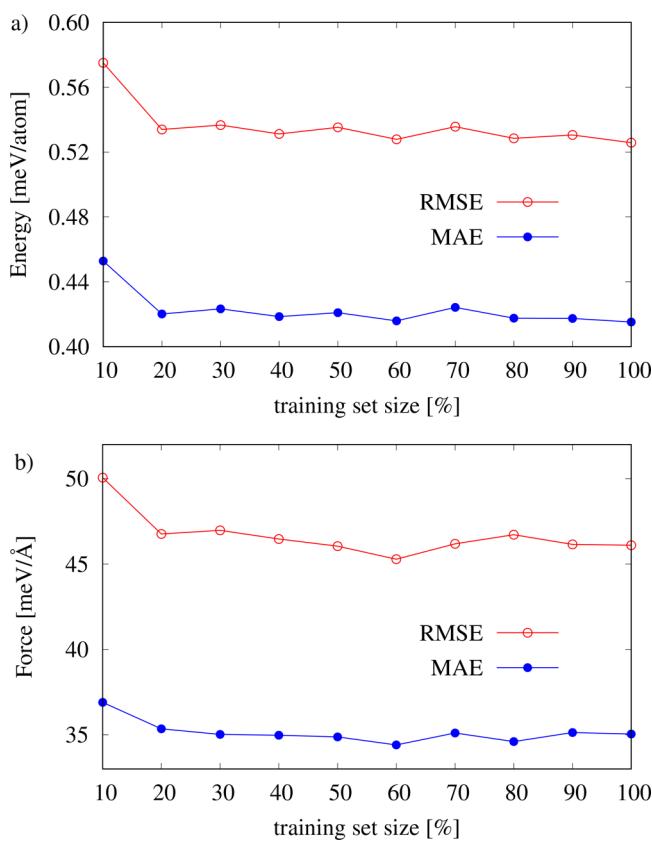


Figure 2. RMSE and MAE for energy (top panel) and forces (bottom panel) as a function of the training set size.

in the training process. For example in Table 1, we show the equilibrium water densities, ρ_{eq} , obtained at different temper-

Table 1. Equilibrium Densities, ρ_{eq} , for Liquid Water with 128 H₂O at Pressure Equal to 1 Bar and Temperature Equal to 300 and 350 K^a

	10% ρ_{eq} [g/cm ³]	100% ρ_{eq} [g/cm ³]
water: $T = 300$ K	1.015	1.013
water: $T = 350$ K	1.020	1.024
ice I _h : $T = 273$ K	0.957	0.961

^aWe also show the density result for ice I_h with 96 H₂O at $T = 273$ K and $P = 1$ bar.

atures and at fixed ambient pressure for the 10% and 100% cases. We also show the result for the hexagonal ice I_h with 96 H₂O at $T = 273$ K and $P = 1$ bar.

It is worth mentioning that for liquid water both NNFFs result in densities with the same precision although one was trained with 1620 samples and another one was trained with ten times more data points. Moreover, it also captures the ice I_h density in reasonable agreement with other SCAN results under similar thermodynamic conditions (AIMD:⁵⁰ 0.964 ± 0.023 ; SCAN DFT⁵⁵ 0.957 ± 0.004 ; NNFF⁵⁵ 0.949 ± 0.001).

Another interesting point is that although our DFT data reference was obtained for liquid water at different temperatures and densities, the NNFFs were able to estimate the ice density. In fact, the capability of an ML potential trained on liquid water alone predicting the properties of the ice phases was also recently reported by Monserrat et al.³²

In Figure 3, we show the pair correlation functions for oxygen–oxygen (g_{OO}), oxygen–hydrogen (g_{OH}), and hydro-

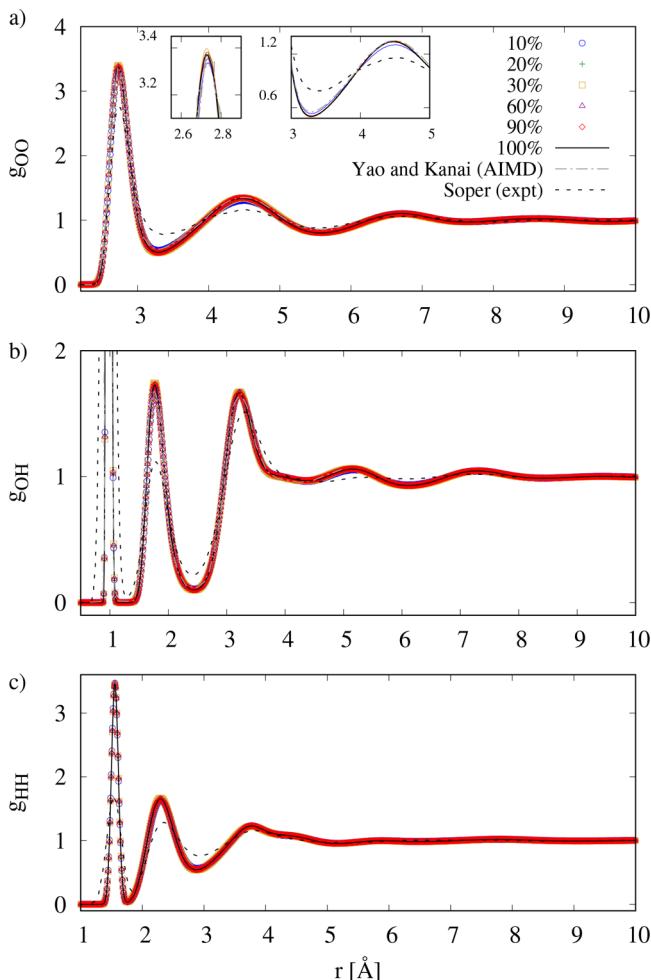


Figure 3. Radial distribution function for (a) O–O, (b) O–H, and (c) H–H pairs obtained via NNMD. Each percentage presented refers to the fraction of the original data set used for training. The g_{OO} and g_{OH} results⁵³ obtained from AIMD based on the SCAN functional for 55 water molecules at $T = 300$ K are represented by dashed lines. The experimental results from Soper⁶⁸ are also shown.

gen–hydrogen (g_{HH}), which are the main structural descriptors for water.^{68–70} These results were obtained for liquid water composed by 512 molecules at fixed density ($\rho = 0.997$ g/cm³) and temperature ($T = 300$ K). We also show the AIMD results for the SCAN functional for 55 water molecules at the same temperature recently presented by Yao and Kanai.⁵³ As it can be seen, all results are very similar.

For a better comparison between the NNFFs, we measured the relative error between the radial oxygen–oxygen distribution function for each trained NNFF with respect to the hundred percent case, as it is shown in Figure 4. Note that the errors are roughly the same, fluctuating around zero (approximately 2% of error). The only exception is the 10% case that presents errors of $\sim 6\%$ in the range of $3 < r < 5$ Å.

Furthermore, we also analyzed the vibrational spectra obtained from different molecular dynamics simulations (deep NNFFs trained with 10% and 100% of the training data set). All of them have approximately the same pattern,

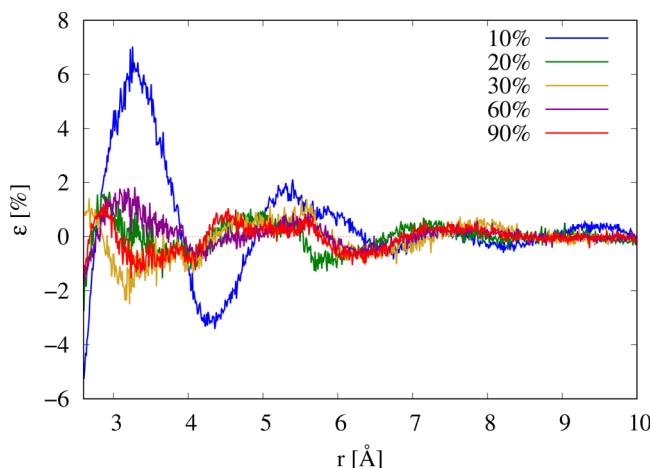


Figure 4. Relative error of the O–O radial distribution function for different data set sizes, as a function of the distance, r , in angstrom.

which means that the results for the structural and vibrational properties of bulk water are mostly independent of the size of the training data set employed to build deep NNFFs for liquid water, as long as they have been well chosen.

More importantly, since MD simulations can now be performed for a long time scale, we can investigate the dynamical properties as a function of time. An important feature of bulk water that is not usually well described by AIMD is its self-diffusion coefficient.²⁶ In fact, the self-diffusion coefficient can depend on many factors even when obtained from a classical MD simulation.^{16,71} In Figure 5, we show the

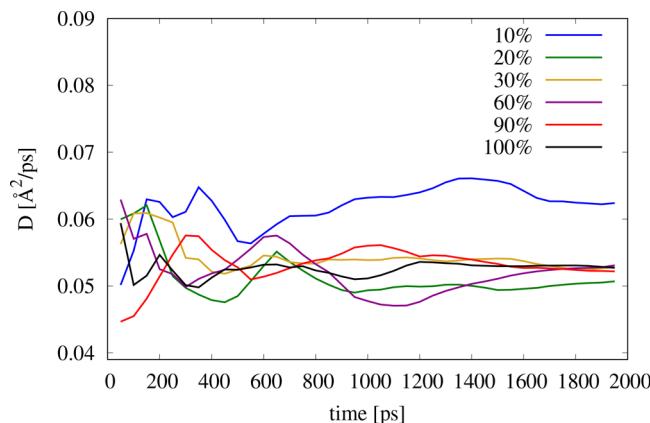


Figure 5. Self-diffusion coefficient as a function of simulation time, for 512 water molecules at $T = 300$ K and $\rho = 0.997$ g/cm³.

self-diffusion coefficient as a function of simulation time, where it was obtained from the Einstein equation of the mean square displacements of the center of mass of water molecules. For further technical details, see ref 26. As it can be seen, as the time increases, the fluctuations are reduced, and the value of D converges. As already shown, this only occurs after 2 ns, way above conventional AIMD capabilities. At a final time (2000 ps), the 10% case is the only one that presents a higher deviation with respect to the 100%.

It should be mentioned that in earlier works,^{5,8} the training data set used to build the ML force fields typically came from AIMD simulations. For example, the data obtained for a short simulation time (~ 20 ps), resulted in a total of 40×10^3 correlated configurations.⁸ On the other hand, more recently

active learning procedures have allowed for the construction of a ML potential with fewer training data points.⁷ In the work of Malosso et al., for example, the ML potential for liquid water was trained with 4000 configurations,⁵⁶ which is in agreement with the size of the training data set required for the convergence of the self-diffusion coefficient present in Figure 5. Thus, it is possible that by combining uncorrelated snapshots and active learning the size of the data set could be reduced even further.

CONCLUSIONS

In this work, we analyzed deep neural network potentials for liquid water/ice I_h based on the SCAN xc-functional.⁴⁹ We show that the structural properties such as the equilibrium densities at different temperature and pressures for water are quite independent of the size of the training data set considered, as the minimum amount employed here was the energy and forces of 1620 structures (64 H₂O). This quantity is much smaller than what is typically used in the training of other NN. This can be attributed to the method of selecting the snapshots for training, which provide a breadth of structures that best samples the phase space. In this way, we have found that the density, vibrational spectra, and the radial distribution function of water are less dependent on the size of the training data set compared to dynamical ones (e.g., the diffusion coefficient.) Finally, we envision that the uncorrelated physical inspired training data set procedure proposed here (sets that include a broad range of short and long OH bonds) together with active learning can be a way to produce reliable ML potentials constructed with fewer DFT training data points.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcb.2c09059>.

Training details, cross-validation, molecular dynamics results, and correlated data (PDF)

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Notes

The authors declare no competing financial interest.

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