

Notes on ionic water

Davide Tisi*

SISSA

*This line break forced with *

(Dated: February 28, 2020)

The following are some notes on the results of ionic water with NN

I. INTRODUCTION

We used some data of partial dissociated water (PDL) to fit a NN potential with DeepMD code [1, 2]. Before to analyse the statical, dynamical and conduction properties we show in Table I the thermodynamic conditions of the two simulations.

	ρ g/cm ³	T K	P GPa
<i>ab initio</i>	2.04	1970 ± 60	33 ± 1
DeepMD	2.03	2013 ± 60	30.0 ± 1.3

TABLE I. Summary of the thermodynamical conditions of the two simulations *ab initio* and with NN potential

The NN simulation has a average temperature a bit higher but the pressure is slightly lower (**not compatible**). In the following sections we can compare the different staticala and dynamical properties: the radial distribution function (gofr), the vibrational density of state (VDOS), the electrical and thermal conductivity.

II. GOFR

The first and easiest property to check is the radial distribution function, both *ab initio* and NN results are obtained from a 100 ps trajectory. The static properties are very well reproduced, in fact Fig. 1 shows the gofr computed from the *ab initio* and NN trajectory, the results are in good agreement and are compatible for any r .

III. VDOS

The second properties we can analyse is the vibrational density of states (VDOS), a dynamical properties which gives us the self-diffusion coefficient, or diffusivity, for $\omega = 0$:

$$\text{VDOS}_\alpha(\omega) = \frac{1}{3N_\alpha} \sum_{i=0}^{N_\alpha} \int_{-\infty}^{\infty} \langle \mathbf{v}_i(0)\mathbf{v}_i(t) \rangle_{\text{eq}} e^{i\omega t} dt \quad (1)$$

$$D_\alpha = \frac{1}{2} \text{VDOS}_\alpha(\omega = 0), \quad (2)$$

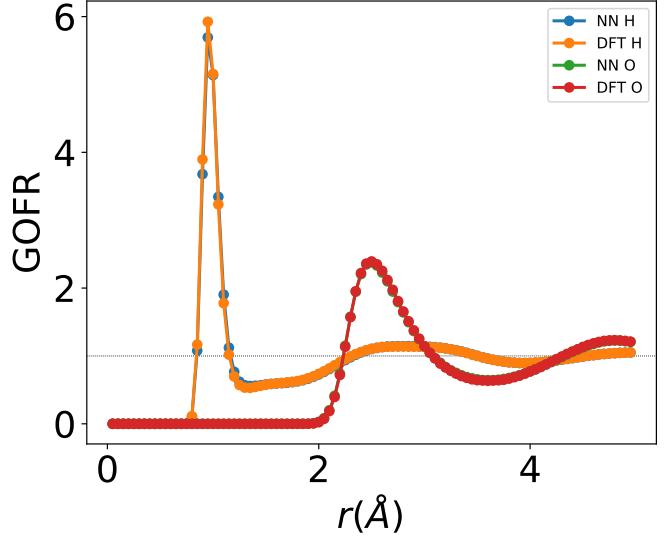


FIG. 1. Comparison between gofr computed from the *ab initio* (blue lines) and DeepMD (red lines) trajectories, both 100 ps long. The results are compatible for all the distances.

where N_α is the total number of atoms of the species α .

Fig. 2 shows $\bar{D}(\omega) = \frac{1}{2} \text{VDOS}(\omega)$ computed with the *ab initio* and DeepMD trajectory, while for oxygens the results are quite compatible, for hydrogens the two spectra have slightly different features, in particular at zero the spectra are not consistent, leading to different values of self-diffusivity: $\bar{D}_H^{\text{AIMD}} = 3.10 \pm 0.10$, $\bar{D}_H^{\text{NN}} = 3.55 \pm 0.15$, $\bar{D}_O^{\text{AIMD}} = 0.92 \pm 0.04$ and $\bar{D}_O^{\text{NN}} = 1.06 \pm 0.05$.

IV. ELECTRICAL CONDUCTIVITY

The electrical conductivity σ is computed as the zero-frequency value of the power spectrum of the following charge flux:

$$\mathbf{J}_Z = q_H \sum_{i \in H} \mathbf{v}_i + q_O \sum_{i \in O} \mathbf{v}_i, \quad (3)$$

where \mathbf{v}_i is the atomic velocity of i -th atom, while the atomic charges are equal to the integer oxidation numbers $q_H = +1$ and $q_O = -2$.

The estimates and uncertainties of σ are obtained via cepstral analysis. Fig. 3 shows the dependence of σ from the corrector factor, c , (left panel) and F^* (right panel). For $c > 1$ all the values of σ are consistent with each

* dtisi@sissa.it

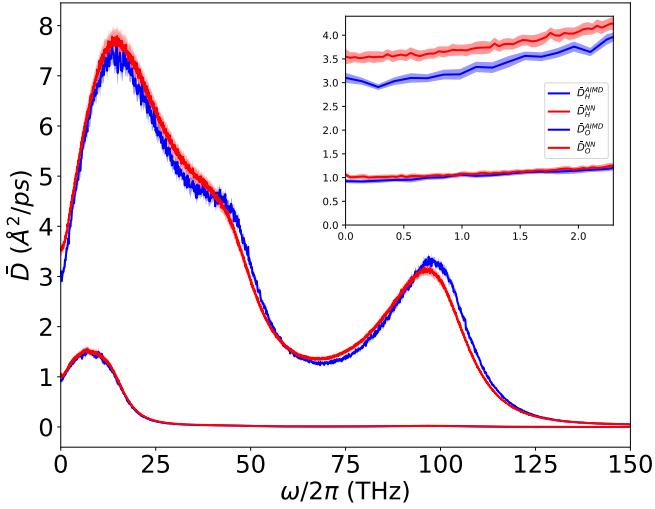


FIG. 2. $\bar{D}(\omega) = \frac{1}{2}\text{VDOS}(\omega)$ for both *ab initio* (blue lines) and DeepMD (red lines) trajectories, respectively 100 ps and 900 ps long. The self-diffusivity, $\bar{D}_\alpha(\omega = 0)$ are not consistent and the NN gives always an higher diffusivity.

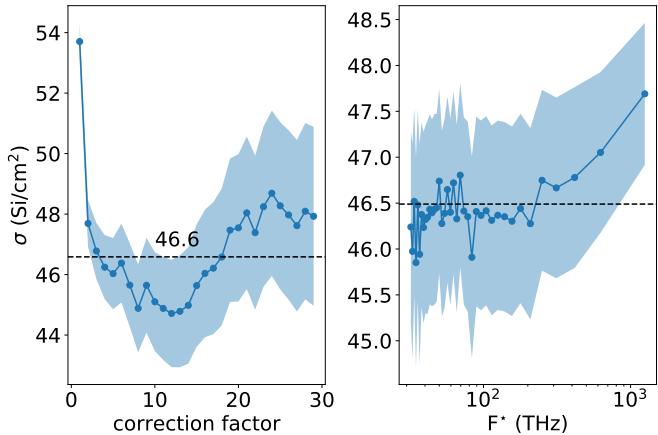


FIG. 3. Dependence of σ from the corrector factor, c , to the AIC criterion (left panel) and from F^* (right panel). The black dotted lines are the mean values. All the results of the right panel are obtained with $c = 2$, which is the one that, in the right panel, has the smallest number of P^* between those which give σ consistent with the average.

other, so for the F^* analysis we employed $c = 2$, which gives us the smallest number of P^* . From the right panel of Fig. 3 we can see that σ do not depend on F^* and so we can decide an "optimal" value of F^* : $\sigma^{NN}(F^* = 50) = 46.7 \pm 1.0$ S/cm consistent with the *ab initio* value $\sigma^{AIMD} = 45 \pm 5$ S/cm

V. THERMAL CONDUCTIVITY

The thermal conductivity is computed as the zero-frequency value of the heat flux:

$$\mathbf{J} = \frac{1}{\Omega} \left[\sum_i \varepsilon_i \mathbf{v}_i + \sum_{i,j} (r_i - r_j) \frac{\partial u_i}{\partial r_j} v_j \right] \quad (4)$$

where ε_i are the atomic contribution to the total energies $\sum_i \varepsilon_i = E = K + U$ and $\sum_i u_i = U$. Fig. 4 shows the behaviour of κ as function of F^* for many values of c , for $c > 1$ all the results are consistent with each other so, in order to minimize the error we can chose $c = 2$ and then $F^* = 57$, that leads us to: $\kappa^{NN} = 4.09 \pm 0.09$ W/(mK) consistent with the *ab initio* value $\kappa^{AIMD} = 4.2 \pm 0.3$ W/(mK)

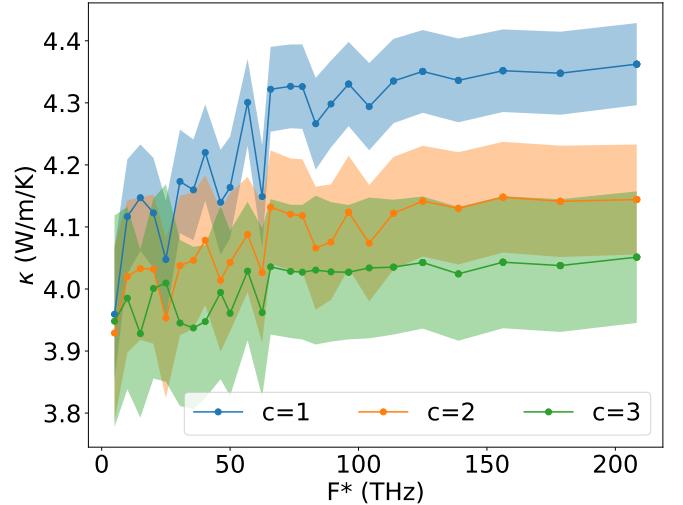


FIG. 4. Value of κ as function of F^* for different values of c .

VI. CONCLUSION

Table II summarizes and compares the results for the *ab initio* and DeepMD simulation.

	κ W/(mK)	σ S/cm	$D_{H(O)}$ $\text{\AA}^2 / \text{ps}$	ρ g/cm ³	T K	P GPa
<i>ab initio</i>	4.2 ± 0.3	45 ± 5	3.10 ± 0.10 0.92 ± 0.04	2.04	1970 ± 60	33 ± 1
DeepMD	$4.09 + 0.09$	46.7 ± 1.0	3.55 ± 0.15 1.06 ± 0.05	2.03	2013 ± 60	30.0 ± 1.3

TABLE II. Summary of the results of the two simulations *ab initio* and with NN potential

VII. SECOND SIMULATION

We trained a new model with a different number of parameters, a fitting network with 4 layers with 300, 250, 200, 100 neurons respectively. After performing a simulation with the new potential we can compare the three results: from AIMD, from the first NN (which will be labeled NN_0) and from the second NN (which will be labeled NN_1). In the beginning we can compare again the thermodynamic conditions:

	ρ g/cm ³	T K	P GPa
<i>ab initio</i>	2.04	1970 ± 60	33 ± 1
NN_0	2.03	2013 ± 60	30.0 ± 1.3
NN_1	2.03	$1967 + / - 58$	$22.8 + / - 1.3$

TABLE III. Summary of the thermodynamical conditions of the three simulations: *ab initio*, with NN_0 and with NN_1 potential.

Again all the thermodynamic parameters are compatible except the pression that is quite low. Figs. 5 and 6 show the result for the gofr and the VDOS, respectively. The latter is similar in all the cases but at zero they gives a different value of the diffusivity, in particular for NN_1 (black line): $\bar{D}_H^{NN_1} = 3.36 \pm 0.18$ and $\bar{D}_O^{NN_1} = 0.97 \pm 0.04$.

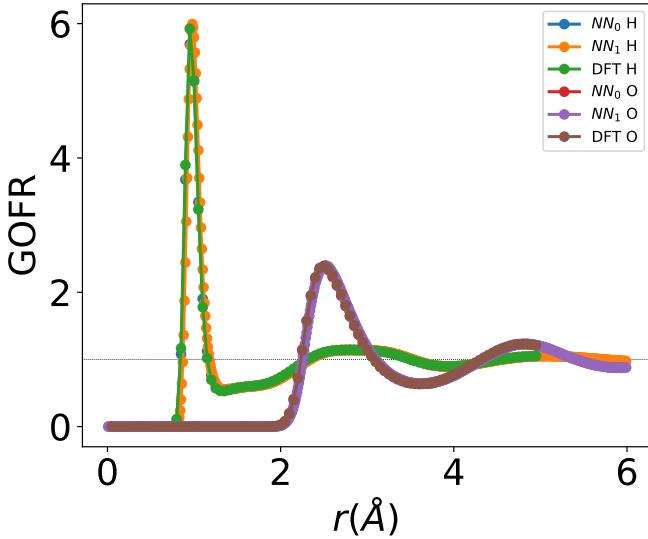


FIG. 5. Comparison between gofr computed from the *ab initio* (blue lines), NN_0 (red lines), NN_1 (black line) trajectories, both 100 ps long. The results are compatible for all the distances.

The analysis of the charge properties are the same of

section Section IV, so we will report only the result in the final table. Now we pass to the thermal transport properties, again we analyse κ as function of c and F^* (Fig. 7). We choose $c = 2$ and $F^* = 55$, thus $\kappa^{NN_1} = 3.35 \pm 0.09$, not consistent with the value obtained from

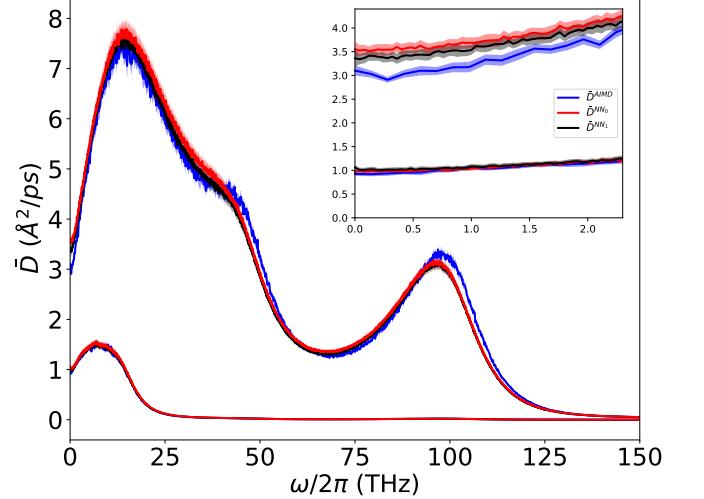


FIG. 6. $\bar{D}(\omega) = \frac{1}{2} \text{VDOS}(\omega)$ for *ab initio* (blue lines), NN_0 (red lines), NN_1 (black lines) trajectories, respectively 100 ps, 900 ps and 900 ps long. The self-diffusivity, $\bar{D}_\alpha(\omega = 0)$ are not consistent and the NN gives always an higher diffusivity.

both *ab initio* and NN_0 . Fig. 8 shows the power spectrum for simulation NN_0 (orange) and NN_1 , we can see that even for window-filtered spectra (shadow regions) NN_0 is higher than NN_1 .

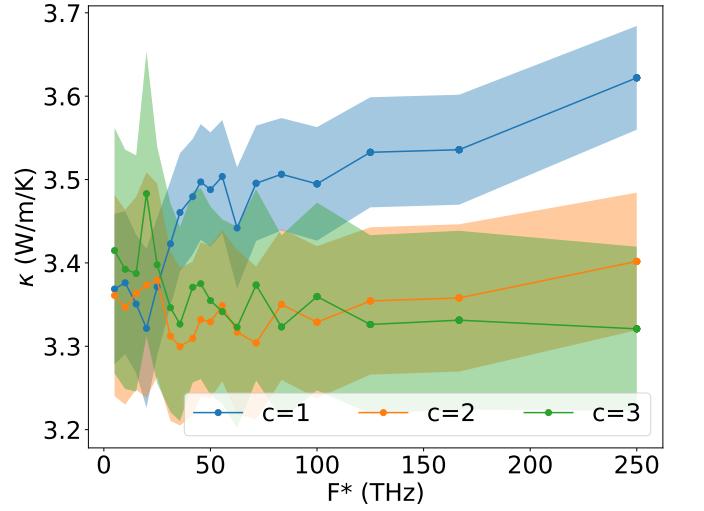


FIG. 7. Value of κ as function of F^* for different values of c .

[1] L. Zhang, J. Han, H. Wang, R. Car, and E. Weinan, Deep Potential Molecular Dynamics: A Scalable Model with the

Accuracy of Quantum Mechanics, *Physical Review Letters*

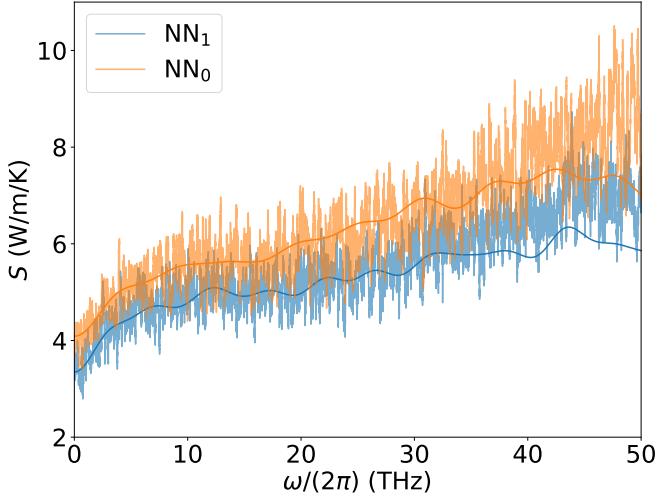


FIG. 8. Heat spectrum for the NN₀ (orange lines), NN₁ (blue lines) trajectories. The shadowed area represent the width filter, with width equal to 0.1 THz, of the true spectrum while the continuous line is the cepstral-filtered spectrum. κ is estimate as the zero values of the cepstrum.

- 120**, 143001 (2018), arXiv:arXiv:1707.09571v1.
[2] H. Wang, L. Zhang, J. Han, and W. E, DeePMD-kit: A deep learning package for many-body potential energy representation and molecular dynamics, Computer Physics Communications **228**, 178 (2017), arXiv:1712.03641.