

Research of feedforward neural network applicability in computer simulation of polymers

© D.V. Shein, D.V. Zav'yalov, V.I. Konchenkov

Volgograd State Technical University,
400005 Volgograd, Russia
e-mail: danil.shein2013@yandex.ru

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In this paper we investigate the adequacy of deep learning force field models for modeling amorphous bodies. A polymer with the studied physical properties, polyphenylene sulfide, was chosen as a test substance. The simulation results shows that the forces predicted by neural networks acting on polymer atoms are significantly different from the forces calculated by *ab initio* molecular dynamics methods. A qualitative comparison with the force field model of a simpler compound, black phosphorene, shows that feedforward neural networks are unsuitable for modeling complex amorphous substances.

Keywords: Molecular dynamics, feedforward neural networks, force fields, polyphenylene sulfide, black phosphorene.

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Introduction

In computer simulation, molecular dynamics (MD) methods are often used, which can be divided into two main categories: *ab initio* (first principles) MD methods and the classical MD method. Approaches from the first category include the simulation of electron dynamics according to the density functional theory (DFT) [1,2], which takes up most of the computational time in calculations. Due to its simplicity, the classical MD method requires much less computational resources, but it is often not possible to achieve the same accuracy, than during simulation with the first principles.

It is known that in the last decade, deep learning has been widely used in various fields of science, including physics. For example, attempts have been made [3,4] to introduce neural networks (NN) into the classical MD method to predict force fields and interatomic interaction potentials, which makes it possible to perform simulations at the speed of the classical MD method and with the accuracy of *ab initio* methods.

In this paper, we will consider the possibility of using NN with the DeePMD [3] method to simulate polymers using the example of a relatively simple compound — of polyphenylene sulfide (PPS) [5].

1. Methods

The force field model in the DeePMD method is built as a dependence of the total energy of the system on the positions of atoms relative to each other:

$$E = \sum_i E_i = \sum_i E_s(i)(R^i), \quad (1)$$

where R^i — is a matrix of relative coordinates — distances from an atom i to an atom j within some interaction radius r_c . The dependence of the energies $E_s(i)$ on the matrix of relative coordinates is built in two steps: first, a matrix of features D^i is constructed according to the matrix R^i in order to preserve the translational, rotational, and permutation symmetry of the system; then the NN is adjusted so that $E_s(i) = N_{s(i)}^f(D^i)$, it is called fitting (FNN). The descriptor D^i is also constructed through the NN $N_{s(i)}^e(R^i)$, called an embedding (ENN). An additional column vector can be used to form the descriptor. It is computed as a function of the type of atom (chemical element) through another neural network $N^i(A^i)$, which is called an atomic-type embedding (TENN).

All three networks, TENN, ENN, and FNN, are feedforward NNs containing multiple hidden layers.

The data for NN training are the simulation results *ab initio* methods. Of these, the two main ones are singled out: Born-Oppenheimer MD [6] and Car-Parrinello MD (CPMD) [7]. The latter approach is the most computationally efficient, and therefore we will carry out the simulation using the CPMD method in the free software package Quantum ESPRESSO.

2. Polyphenylene Sulfide Model

To prepare for the training of the PPS force field model, we first, as mentioned earlier, collect the Canonical Ensemble (NVT) CPMD simulation data from several simulations. They differ from each other in the different starting positions of the atoms (deviations from their initial positions). Besides that, each launch was no different: in the first 100,000 steps of the trajectory, the system was balanced with an initial temperature of 0 K and with a final temperature of 300 K.

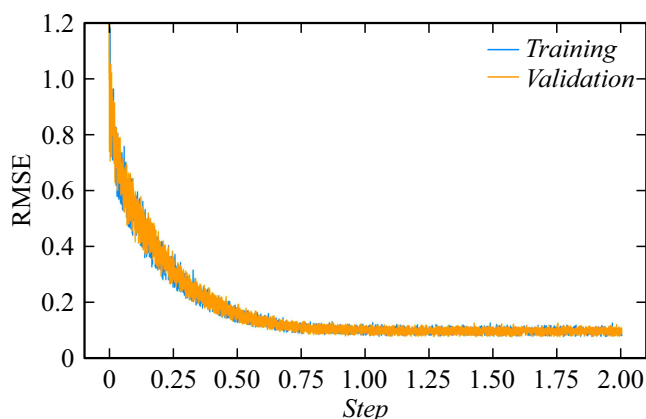


Figure 1. Loss functions in Training and Control.

At equilibrium, the next 50,000 steps are saved to be used as deep learning data. The temperature is controlled by a Nose-Hoover thermostat [8] with a frequency of 25 THz. The kinetic energy cut-off for the wave functions is chosen to be 80 Ry, and for the charge density and pseudopotentials — 320 Ry.

The unit cell is a configuration of 132 atoms.

A total of 140,000 frames were collected for the training data, 10,000 frames for the validation data, and 2,000 frames for testing.

The most stable computer model of polyphenylene sulfide is obtained after $2 \cdot 10^6$ training steps with the following neural networks parameters: TENN: {2, 4, 8, 16}; ENN: {20, 40, 80}; FNN: {200, 200, 200, 200, 200}. Here, separated by commas, is the number of neurons in the hidden layers in the NN. The test using the test command in DeePMD shows the following root mean square errors: energies — $9.8 \cdot 10^{-2}$ eV; energies per atom — $7.4 \cdot 10^{-4}$ eV; forces — 0.22 eV/Å; virial — 0.29 eV, virial per atom — $2.2 \cdot 10^{-3}$ eV.

Potential models trained with other NN parameters or the number of training steps led to rapid destabilization of the simulated substance. Here are some examples of models that have been tested:

1. TENN: {2, 4, 8}, ENN: {20, 40, 80}, FNN: {200, 200, 200, 200, 200};
2. TENN: {2, 4, 8, 16}, ENN: {60, 60, 60}, FNN: {200, 200, 200, 200, 200};
3. TENN: {2, 4, 8, 16}, ENN: {10, 20, 40, 80}, FNN: {200, 200, 200, 200, 200, 200}.

The first model had $2 \cdot 10^6$ steps, and the second and third — of $3 \cdot 10^6$ steps.

By model stability, we mean that, firstly, when simulating a material with classical MD in an NPT ensemble, its density remains approximately constant over time and close to experimental values, and secondly, the structure of monomer elements (phenylsulfide in the case of PPS) is preserved.

The training and control curves (Fig. 1) indicate that the model has been trained correctly.

3. Results and discussion

To test the stability of the model, we equilibrate a system of 4752 atoms in an NVE ensemble using a Berendsen thermostat [9] for 200 ps. The polyphenylene sulfide in the system is heated from 10 to 273 K. Then, at a constant temperature (273 K), the PPS passes into the NPT ensemble (a thermostat and a Nose-Hoover barostat are used).

Up to about 100 ps (or up to a temperature point of about 140 K), the distances between the atoms in one PPS benzene radical remained constant on average (Fig. 2). At the same time, the standard deviation (RMSD) of particles from the initial positions of the simulated PPS reaches a value of 0.1 Å. With increasing temperature, the molecular structure is disrupted more and more, at the time of transition to the NPT ensemble, the RMSD is equal to 3.3 Å. By the last point in the simulation time, the RMSD increased to 4.5 Å. The displacement of hydrogen atoms in the compound is especially noticeable.

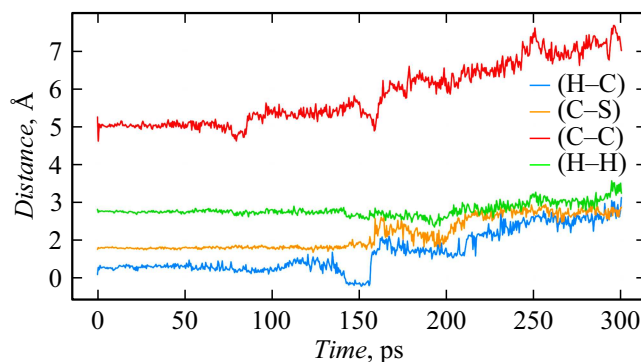


Figure 2. Change in particle distance in atomic pairs in a single PPS phenylsulfide.

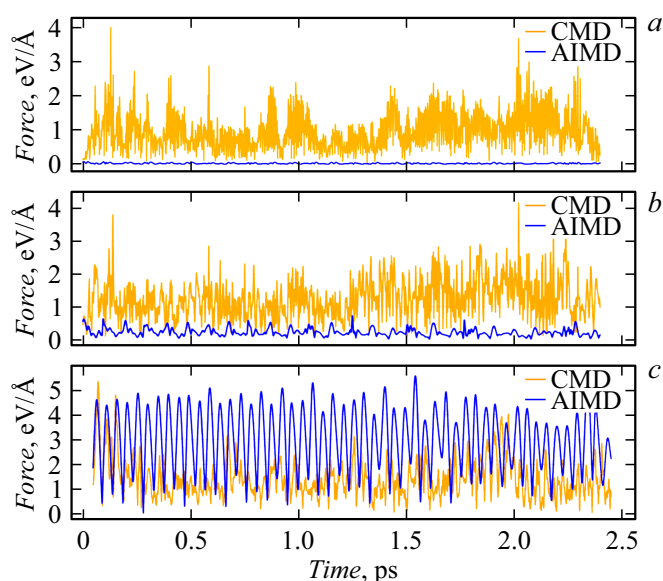


Figure 3. Forces acting on individual atoms in PPS in classical CMD and AIMD simulations: *a* — hydrogen, *b* — carbon, *c* — sulfur.

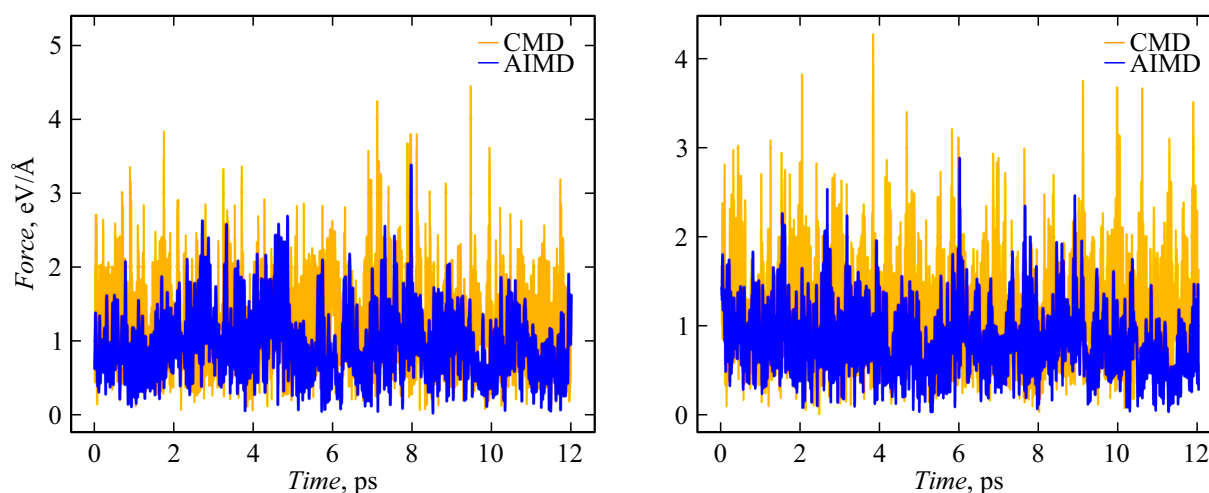


Figure 4. Forces acting on different individual phosphorus atoms in black phosphorene in classical CMD and AIMD simulations.

This result suggests that the force field model incorrectly predicts the potentials of interatomic interactions.

As a confirmation of this assumption, we run the PPS simulation using classical molecular dynamics in the same configuration (same starting positions, velocities, and number of particles) as in the system in the training set. We use a force field model with the same parameters of neural networks here. The simulation result (Fig. 3) shows that the forces acting on hydrogen atoms are significantly larger in the classical MD relative to *ab initio* MD. The forces acting on carbon atoms are also larger. The effect on sulfur atoms, however, is lowered by the force field model.

Let us build a computer model of black phosphorene [10] using the same strategy that we used to simulate PPS. The results of classical MD (Fig. 4) show an adequate agreement between the phosphorene predicted by the force field model and the data from *ab initio* MD.

The forces of both materials, PPS and black phosphorene, are compared in simulations with the same temperature (300 K) in the NVT ensemble.

Conclusion

Based on the work results it can be concluded that the feed-forward NNs of DeePMD method are apparently poorly suited for simulation of amorphous substances. This can be explained by the presence of a large number of degrees of freedom in polymer chains, which are not fully considered by simple NNs. On the contrary, for crystalline structures, as shown by the example of black phosphorene, such a network architecture is able to build an adequate force field model.

It should be noted that there is currently a number of studies that use feed-forward NNs as an auxiliary tool for determining the surface of potential energy in large organic molecules. In [11,12] it is proposed the following approach to the study of protein molecules, called by the

authors NN-TMFCC — neural network two-body molecular fractionalization with conjugate caps. The molecule is broken down into fragments corresponding to the amino acids in the protein, and the effect of broken bonds is compensated by the artificial introduction of functional groups — acetyl and methylamine groups. In each of these fragments, the position of the atoms is varied many times, and the energy and forces acting on the atoms are calculated by the methods of the density functional theory. From the data obtained, a dataset is formed, which serves to train the NN with a direct coupling, calculating the energies and forces acting on the atoms in the selected fragment of the protein molecule. Further, simulations are carried out using the method of classical molecular dynamics, which uses a protein-specific model of the force field, parameterizing the interaction of the above-mentioned protein fragments.

In the future, we plan to develop an approach to building the force field models with NNs, using graph, convolutional and transformer architectures. It is expected that with their help it will be possible to build adequate force field models of amorphous substances.

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Conflict of interest

The authors declare that they have no conflict of interest.

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