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DFT based Neural Network Force Fields from Energy Decompositions

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ABSTRACT

In order to develop force fields (FF) for molecular dynamics simulations that retain the accuracy of *ab initio* density functional theory (DFT), we developed a machine learning (ML) protocol based on an energy decomposition scheme that extracts atomic energies from DFT calculations. Our DFT to FF (DFT2FF) approach provides almost hundreds of times more data for the DFT energies, which dramatically improves accuracy with less DFT calculations. In addition, we use piecewise cosine basis functions to systematically construct symmetry invariant features into the neural network model. We illustrate this DFT2FF approach for amorphous silicon where only 800 DFT configurations are sufficient to achieve an accuracy of 1meV/atom for energy and 0.1eV/A for forces. We then use the resulting FF model to calculate the thermal conductivity of amorphous Si based on long molecular dynamics simulations. The dramatic speedup in training

in our DFT2FF protocol allows the adoption of a new simulation paradigm where an accurate and problem specific FF for a given physics phenomenon is trained on-the-spot through a quick DFT pre-calculation and FF training.

1. Introduction

Machine learning methods have been rapidly developed to solve scientific problems in biology, chemistry, physics and engineering [1-6] in recent years. In the field of atomic and molecular studies, one of the major applications of machine learning is to obtain the quantitative structure-activity relationships (QSAR) [7-9]. In molecular simulations, the relationship between the total energy of a system and its atomic or molecular structure is one of the most important properties because derivatives of the total energy with respect to atomic positions give rise to forces, which can be used to perform molecular dynamic simulations [10, 11]. Such a relationship is described by the potential energy surface (PES) of the system. The PES is difficult to obtain in experiment; rather, it is typically sampled by solving the Schrodinger equation. In practice, density functional theory (DFT) approximation to the Schrodinger Hamiltonian is used. Once the information about the system is calculated using DFT, machine learning models can be applied to fit the PES.

Many PES machine learning models have been developed over the last decade, including the high dimensional neural network potential (HDNNP) model [12], Bag of Bonds (BoB) model [13], Gaussian Approximation potentials (GAP) [14], deep tensor neural networks (DTNN) [15]. In particular, two types of machine learning models have been widely used. One is based on neural network, like the HDNNP, another is based on Gaussian process regression, like the GAP,

which is a direct high dimensional interpolation scheme. Both models use features calculated from atomic structures as their inputs. Various types of atom-centered symmetry functions [16] have been used to collectively map the chemical environment of individual atoms to a set of descriptors (also known as features). These features are typically translationally, rotationally and permutationally invariant. In the current study, we will use the neural network model. In such a model, the generated features are fed into a multilayer neural network to yield the total energy of the system. However, the mapping of the atomic environment to descriptors is not unique, and many choices of symmetry functions have been reported in the literature. [16-20]

Compared with the conventional classical molecular force fields, the neural network force field (NNFF) can be more accurate in the atomic configuration space where it is fully trained, but it can fail catastrophically in regions where it is not exposed[21]. One way to make a proper use of this feature of NNFF is to train the NNFF, if not on-the-flight, but at least on-the-spot. For each target physical phenomenon, one can first carry out an *ab initio* DFT simulation on a smaller system for a shorter time, while at the same time ensuring that the DFT simulation covers all the possible local atomic configurations essential to the physical phenomena to be studied. This will be followed by a standard and quick NNFF training, and the resulting NNFF can then be used to simulate a much larger system for a much longer time. To make this procedure practical, one has to satisfy the following requirements: (1) a quick generation of large amount of DFT data; (2) a universal NNFF model; (3) a corresponding quick training procedure of this model; (4) finally, the ability to yield accurate NNFF results compared to DFT data within the desired configurational region.

In this work, we present a new model to fit NNFF which satisfies the above requirements by using atomic energies decomposed from a DFT calculation and piecewise cosines for systematic symmetry features. The model is implemented in TensorFlow® to utilize directed acyclic graph (DAG) to accelerate computation. The resulting NNFF for a test amorphous silicon system has an accuracy of 1.0 meV/atom in energy and 0.1eV/A for the forces. We also show how the resulting NNFF can be used to calculate material properties which could be too expensive to calculate directly using DFT.

Our work follows closely to the HDNNP model [12]. However, in the current HDNNP approach, typically, $\sim 10,000$ DFT trajectory steps will be used to fit the HDNNP models [12, 22]. These can take many days for the DFT calculation. A major advance in the current study is to decompose the DFT total energy of a given system into atomic energies belonging to each atom. Importantly, such atomic energy only depends on the positions of the nearby atoms. As a result, a unified single atom neural network potential (SANNP) model can be used taking into account the data from all atoms. In comparison, in HDNNP, only the total energy of the system is used in the training set although the atomic energies are implicitly assumed in the model. Due to the increase of the data set, we found that ~ 1000 molecular dynamics (MD) steps is sufficient to train an accurate SANNP. This makes it practical to carry DFT calculation and SANNP training overnight, making it possible for an on-the-spot SANNP development. Another type of machine learning force field is based on Gaussian process aggregation [14]. Our energy decomposition method can be equally applicable for such approaches.

Combining the energy decomposition method with the piecewise cosine functions model, we show that the training of the SANNP using TensorFlow running on a GPU workstation only takes a few hours (requirement 3) and the resulting SANNP has an accuracy of $\sim 1\text{meV/atom}$ for the energy (of a 256 atom system) and 0.1eV/\AA for the forces (requirement 4). As an example, we have performed MD simulations to calculate the thermal conductivity of amorphous Si (a-Si), which is difficult to obtain using direct DFT calculations [23]. Although we have calculated Si in different temperatures, from low to melt liquid temperature, and found the procedure equally applicable, in the current study, we will focus on the results of the amorphous Si (a-Si) structure. The a-Si structures can be generated from the random bond switching model [24], followed by DFT MD simulations at different temperatures. It is also worth to note that the current SANNP can be easily extended to systems with M_e type of atoms. In such cases, each type of center atoms will have its own SANNP model, and for a given SANNP model, the number of atom pair features increases by a factor of M_e , while the number of three atom feature increases by a factor of M_e^2 . The extension of SANNP to such systems (an ongoing project) further exemplifies the importance of more DFT data, which can be provided by our energy decomposition scheme.

2. Method

2.1 High Dimensional Neural Network Potential (HDNNP)

The HDNNP is a machine learning model developed by Behler et al. [12] In this model, the total energy of a given system is assumed to be the simple sum of the atomic energies $E_{tot} = \sum_i E_i$. However, the DFT values of E_i are not known, and only E_{tot} is obtained for a given system. Nevertheless, such an assumption allows the construction of a HDNNP model as shown in Fig.1(a), where each horizontal bar is a small multilayer (typically 2 hidden layer) neural

network, and the edge weights on the last step connecting E_i to E_{tot} are fixed at 1. More importantly, the neural network parameters for each small network (horizon bar) are the same, such that the whole network consists N identical smaller networks (for single specie systems), where N is the number of atoms in the system.

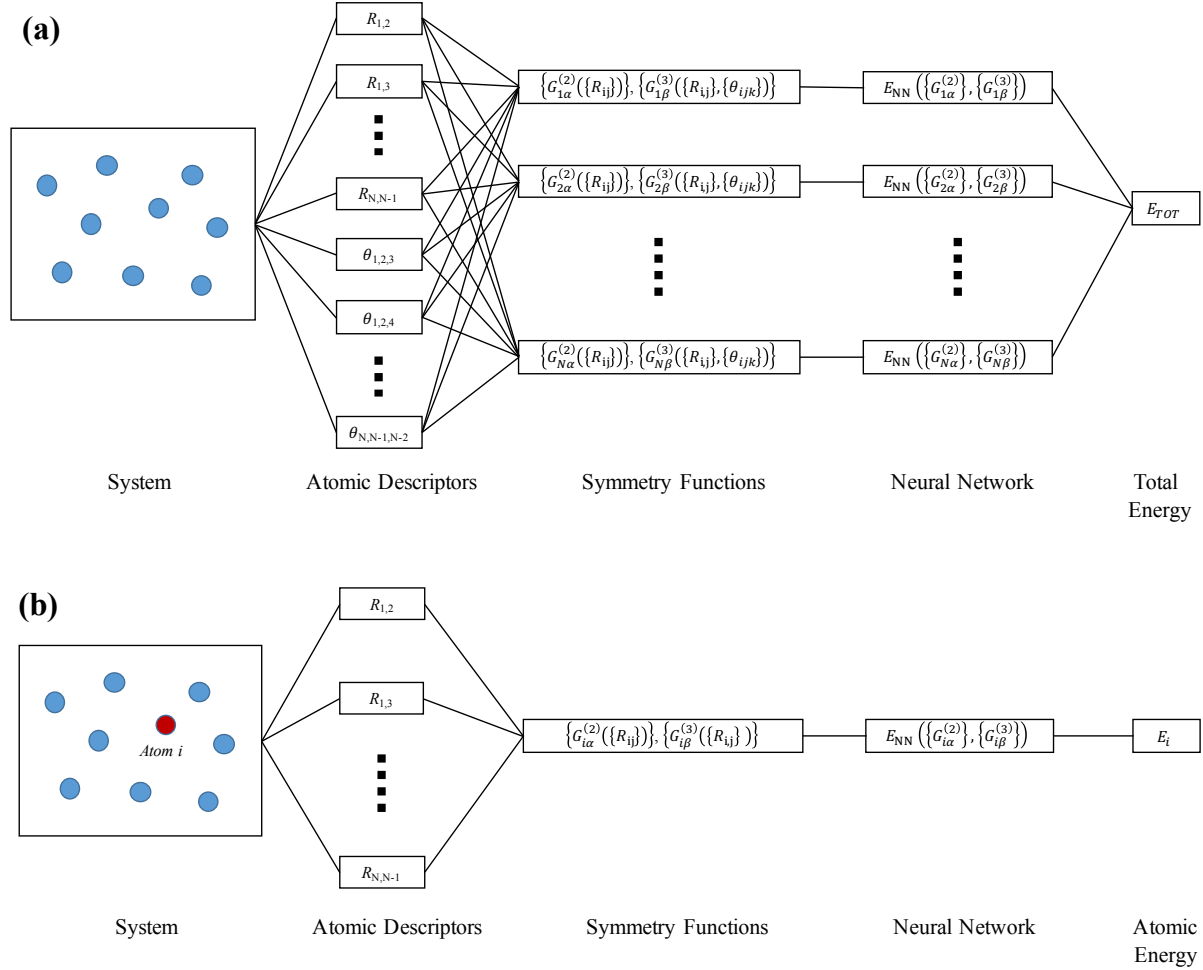


Figure 1. Schematics of the neural network models. (a) High dimensional neural network potential (HDNNP), (b) single atom neural network potential (SANNP). The leftmost box is the simulation system, the second column represents the atomic descriptors including interatomic distances, and three-body angles, the third column represents the symmetry functions, the fourth

column represents the neural network for the model, and the fifth column represents the energy term(s) to be trained for.

Mathematically, let $\{\mathbf{p}_{ij}, \mathbf{q}_{ijk}\}$ be a set of structural descriptors including the interatomic distances (R_{ij}) and angles (θ_{ijk}) between atom j and atom k about atom i , $\phi_\alpha^{(2)}$ and $\phi_\beta^{(3)}$ be the α^{th} 2-body symmetry function and β^{th} 3-body symmetry function, and $E_{NN}(\{G_{i\alpha}\}; \mathbf{w}, \mathbf{b})$ be the multilayer neural network model with descriptors $\{G_{i\alpha}^{(2)}, G_{i\beta}^{(3)}\}$ as its input, and weight parameters \mathbf{w} and bias parameters \mathbf{b} being its fitted model parameters. Then the general mathematical form of the original HDNNP is:

$$G_{i\alpha}^{(2)} = \sum_j \phi_\alpha^{(2)}(\mathbf{p}_{ij}); \quad G_{i\beta}^{(3)} = \sum_{jk} \phi_\beta^{(3)}(\mathbf{p}_{ij}, \mathbf{q}_{ijk}) \quad (1)$$

$$E_i = E_{NN}(\{G_{i\alpha}^{(2)}, G_{i\beta}^{(3)}\}; \mathbf{w}, \mathbf{b}) \quad (2)$$

$$E_{\text{tot}} = \sum_i E_i \quad (3)$$

As shown in Equation (1), the summation over atomic index j and j,k enforces permutation invariant, while the proper constructions of $\phi_\alpha^{(2)}$ and $\phi_\beta^{(3)}$ ensure the translational and rotational invariance of the descriptors $G_{i\alpha}^{(2)}$ and $G_{i\beta}^{(3)}$.

2.2 Atomic Energies

As an improvement to energy fitting using the total energy, we propose a way to actually calculate E_i from the DFT calculations. As a result, our network is simplified and consists with

only one small network (one bar in Fig.1), thus the dataset is increased by N fold, where N is the number of atoms in the DFT system, which is typically around 100-200.

To expand the dataset for training, the DFT total energy is partitioned into atomic energies outlined in Kang and Wang [23]. The critical point is to rewrite the DFT energy terms (kinetic, electrostatic) as the spatial integration of their respective energy densities [25], such that a Hirshfeld style spatial decomposition can be used to decompose the energy into atomic contributions. More specifically we have:

$$U^{DFT} = \sum_i \left[U_i^{DFT} + E_i^{(NL)} - E_{\text{self}} \right] + \sum_{i \neq j} V^P(|\mathbf{R}_{ij}|)$$

With

$$U_i^{DFT} = \int d\mathbf{r} [t_0(\mathbf{r}) + e_{\text{xc}}(\mathbf{r}) + e_{\text{CC}}(\mathbf{r})] \frac{w_i(|\mathbf{r}-\mathbf{R}_i|)}{\sum_j w_i(|\mathbf{r}-\mathbf{R}_j|)} \quad (4)$$

Where $w_i(\mathbf{r})$ is the radial charge density function [26] of the neutral atom at site i, $t_0(\mathbf{r})$ is the electronic kinetic energy density, $e_{\text{xc}}(\mathbf{r})$ is the exchange-correction energy density, $e_{\text{CC}}(\mathbf{r})$ is the Hartree energy density, $E_i^{(NL)}$ is the nonlocal contribution from the pseudopotential for atom i, E_{self} is an onsite energy integral constant, and $V^P(|\mathbf{R}_{ij}|)$ is the Coulomb interaction between ion pairs. Summarizing, individual atomic energy E_i has the following expression:

$$E_i^{DFT} = U_i^{DFT} + E_i^{(NL)} - E_{\text{self}} + 1/2 \sum_{j \neq i} V^P(|\mathbf{R}_{ij}|) \quad (5)$$

It is noted that the above energy decomposition is not unique. But for our SANNP development, this is not critical, as long as the sum of E_i agrees with the whole system total

energy, and E_i is a local property that only depends on the atomic configuration near atom i . It is known that there are remaining challenges for NNFF when long range Coulomb interaction is strong. In such cases, atomic charges might need to be fitted [27] and the corresponding energy contribution needs to be subtracted before applying the above decomposition scheme. As shown in S1 of Supplemental Materials [39], for non-polarized systems like amorphous Si, the atomic energy E_i is indeed a local property of its atomic configuration. For our current test system of amorphous silicon, there are not many obvious dramatically different choices (we have used the Hirshfeld partitioning scheme). This is particularly true since we have only one atom type (Si), so any reasonable partitioning will yield similar results. If there are two different atom types (say Ga and As), then there could be more room to tune the partitioning parameter.

2.3 Piecewise cosine symmetry functions

In order to use an artificial neural network to fit the atomic or total energies, the surrounding chemical environment of each atom has to be mapped to a set of descriptors using symmetry functions. To capture the complicated correlation within such an environment, permutation, translation and rotation invariant functions involving two body pairs and three atom triplets are typically used, as in Equation (1). In addition to the Gaussian-like symmetry functions, other approaches have been developed, including Zernike [18], Bispectrum [19] and Chebyshev radial distributions [20] and smooth overlap of atomic position (SOAP) [17]. Different descriptors might have different meaning, some in real space, some in spectrum space. Since artificial neural network is capable of learning the complicated relationships between the input and the target property, we feel it is straightforward to map the structural descriptors using simple local descriptions and allow the neural network to find the best fitting.

One example of local representations in numerical calculation is the piecewise linear functions in finite element analysis. These piecewise linear functions are defined on a set of nodes, such that any continuous function defined on this domain can be approximated as linear combinations of these local functions. For our purpose, in order to calculate the force, the derivative of the piecewise function with respect to the atomic position is needed. As a result, the piecewise linear shape functions are modified to differentiable piecewise cosine functions for our neural network model. The shapes of these piecewise cosine functions are shown in Figure 2 (a).

Using the piecewise cosine functions, the symmetry functions can be constructed in simple forms as follows:

$$R_{\alpha}^k = R_{inner} + (\alpha - 1)h_k \quad \text{where } \alpha = 1, 2, \dots, M_k$$

$$\varphi_{\alpha}^{(k)}(R_{ml}) = \begin{cases} \frac{1}{2} \cos\left(\frac{R_{ml} - R_{\alpha}^k}{h_k} \pi\right) + \frac{1}{2}, & |R_{ml} - R_{\alpha}^k| < h_k \\ 0, & \text{Otherwise} \end{cases} \quad (6)$$

$$G_{\alpha,l}^{(2)} = \sum_m \varphi_{\alpha}^{(2)}(R_{ml}) \quad (7)$$

$$G_{\alpha\beta\gamma,l}^{(3)} = \sum_{m,n} \varphi_{\alpha}^{(3)}(R_{ml}) \varphi_{\beta}^{(3)}(R_{nl}) \varphi_{\gamma}^{(3)}(R_{mn}) \quad (8)$$

where:

- $k=2,3$ specifies the 2-body and 3-body terms respectively,
- $h_k = (R_{outer} - R_{inner})/M_k$ is the width of the piecewise cosine function, with M_2 being the number of piecewise cosine basis functions for the 2-body term, and M_3 being the number of basis functions for each side of the 3-body term,
- $R_{ml} = |R_l - R_m|$ are the interatomic distance between atom l and atom m , and

- Σ_m and $\Sigma_{m,n}$ are sums over all atoms within the R_{outer} cutoff of atom l .

Once the inner and outer cutoff radii are determined, the two-body symmetry functions are completely determined by a single number M_2 . However, it is not practical to set $M_3=M_2$ for the number of three-body cosine basis functions because the number of three body symmetry functions will scale as $O(M_3^3)$. Therefore, we have used a balanced set of symmetry functions characterized by a single number M , where $M_2 = M^2$ and $M_3 = M$.

Our symmetry functions have similar forms as the Gaussian symmetry functions used in HDNNP [12] for the 2-body term, but with important simplifications. First, we no longer need to multiply the symmetry function by an arbitrary decay function to ensure that the symmetry function goes to 0 smoothly at R_{outer} (and also at R_{inner} if it is not 0 already), because these symmetry functions are local and the rightmost function is already decaying to 0 at R_{outer} . In a way these functions are more local than the Gaussian functions since they go to zero outside their perspective ranges. Moreover, in the three-body term, all three sides of each atomic triplet are treated equally and an arbitrary cosine term is no longer needed to describe the angle dependence. These piecewise cosine functions are shown in Figure 2(a). Physically, the values of the $G_{\alpha,l}^{(2)}$ simply represent the pair correlation function for the atom l with α being the distance from the center atom l . This is shown in Fig.2(b). Note, if we have infinitely large number of M_2 and M_3 (infinitely localized functions), one can show that, if all the $G_{\alpha,l}^{(2)}$ and $G_{\alpha\beta\gamma,l}^{(3)}$ are determined, the local atomic positions within R_{outer} will be completely determined (up to the translation, rotation and permutation degree of freedoms). Thus $G_{\alpha,l}^{(2)}$ and $G_{\alpha\beta\gamma,l}^{(3)}$ can uniquely

determine the atomic structures (upon translation, rotation, and permutation invariance) when the number of α , β , and γ approaches infinity. Should there be different atom types, the α , β , γ index should also include the information of atom types, besides the distance $h_{(\alpha,\beta,\gamma)}$.

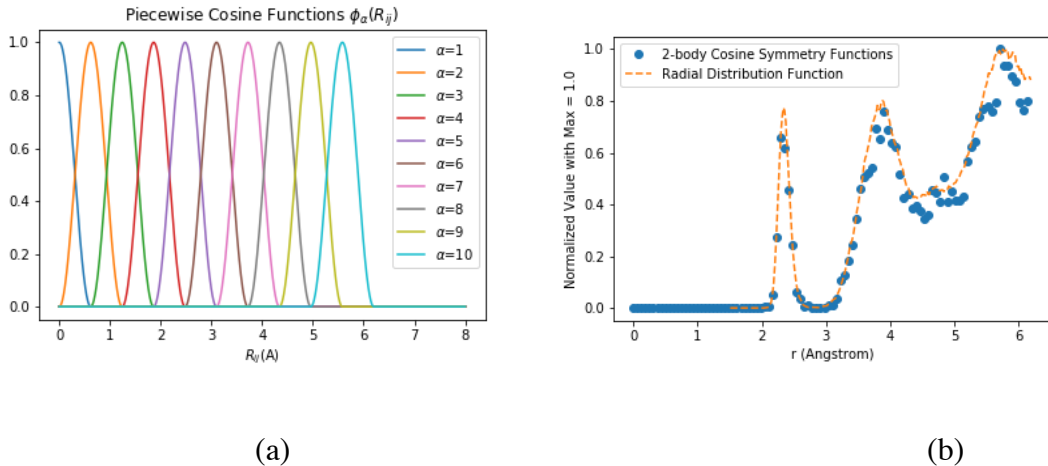


Figure 2. Piecewise cosine functions as basis functions to construct the symmetry functions. (a) graphical representation of the piecewise cosine functions when $M=12$ basis functions are used. (b) comparison of the radial distribution and the normalized values of the two-body piecewise cosine features with their respective nodes with $M=100$.

In summary, the original HDNNP formulation is modified in two major ways. First, since the total energy is decomposed to atomic energies, the neural network will be trained against the individual atomic energies directly. Second, the piecewise cosine functions are used as basis functions constructing symmetry functions to obtain the descriptors of the chemical environment.

2.4 Training procedure

In traditional classical force fields, although the functional form of the energy contributions or forces are known, the number of corresponding parameters is small and they are difficult to train because different force fields are based on different functional forms. Thus, classical force fields are usually trained with chemical and physical intuition on carefully selected quantum mechanical trajectories. On the other hand, neural network based machine learning models have many more parameters to flexibly fit any configurations, and the fitting is made possible by the back-propagation procedure[28].

First, we define a loss function that includes both atomic energies and atomic forces as $L = \text{MSE}(\{E_i\}) + \alpha \times \text{MSE}(\{\mathbf{F}_i\})$, where the SANNP forces on each atom is obtained by analytical differentiation of the total neural network energy with respect to the atomic coordinates, and $\text{MSE}()$ is the mean squared error. The training using L with respect to the neural network parameters \mathbf{w} and \mathbf{b} can be carried out using the TensorFlow® library. For this study, a two hidden layer neural network model with 500 nodes in each layer is used. The Adam optimizer [29] with a learning rate of 0.0001 is used to minimize the MSE loss function. To perform MD simulations at a certain temperature T_o , the neural network training must be supplemented with a higher temperature simulation data to cover a larger area of the configurational space. Thus, after training the neural network with DFT trajectories from the target temperature, higher temperature DFT trajectories are included to train for another 100 iterations for the combined training set.

The above model is implemented in our publicly accessible custom code, S2 of the Supplemental Materials [39]. Similar to quantum mechanical calculations in which near

complete basis sets are used when comparing different methods, a large two-layer neural network with 500 nodes each is used here to avoid the finite size effects of the neural network on the SANNP method. As shown in S3 of the Supplemental Materials [39], the neural network potential is well converged using 500 nodes, and the error is comparable to the case with only 40 nodes. The training set has 800 DFT configurations, each with 256 silicon atoms. The piecewise cosine functions with $M=10$, or equivalently 550 features in which $M_2 = M^2$ and $M_3 = M$, is used. The calculations are performed on an NVIDIA Titan X GPU. Each training iteration through the whole training set takes about 4.5 minutes when both atomic energies and forces are used. The forces converge to 0.1eV/A in the validation set after 150 training iterations, which takes about 11.4 GPU hours. When $M=5$, or equivalently 100 features, is used, it takes 2.4 minutes per training iteration. The forces converge to 0.13 eV/A in 200 iterations, which corresponds to about 8.1 hours.

To compare the accuracy and training speed between the SANNP and the HDNNP approaches, we construct an HDNNP model with the same set of features as our SANNP model and train them with the same data, but with HDNNP training on the total energies, E_{tot} , and with SANNP training on atomic energies, E_i . After training for 250 iterations using forces, the HDNNP results in an error of 0.168 eV/A, and the SANNP results in an error of 0.094 eV/A. As shown in Figure 3, the errors in SANNP decrease much faster than HDNNP with respect to training iterations. Other has reported similar slow convergence using HDNNP where a 30-atom system with about 1500 geometries in the training set slowly converges to 0.182eV/A after 2000 iterations [38].

It is not trivial to identify the reason for the improved performance in training from HDNNP to SANNP when both force and energies are used. One possible reason is that, the force is a derivative of the local energy, and it is the atomic energy, not the force, that explicitly appears in both SANNP and HDNNP. Having this atomic energy itself should be thus more straightforward and more reliable than having its derivative (and only infer the energy from the derivative). One can also analyze this problem based on the dependence of the atomic energy and atomic force to the environment as represented by the model. The forces of atom i involve the summation of neural network energies E_j of atom j in the neighborhood of atom i , as shown in the following equation:

$$\vec{F}_i = -\frac{dE_{tot}}{d\vec{R}_i} = -\sum_{j \in \text{Nb}(i), \alpha} \frac{\partial E_j}{\partial G_{j\alpha}} \frac{dG_{j\alpha}}{d\vec{R}_i}$$

Where atom j is in the neighborhood of atom i , and α is the descriptor index. Because the maximum distance between i and j is R_{cutoff} and E_j depends on all the atoms within R_{cutoff} of j , the effective cutoff radius for the force \vec{F}_i is $2R_{\text{cutoff}}$ [21]. At least according to the HDNNP and the SANNP models, the atomic force dependence is much wider than the atomic energy dependence. This will make the force-only fitting (with the total energy) much more difficult.

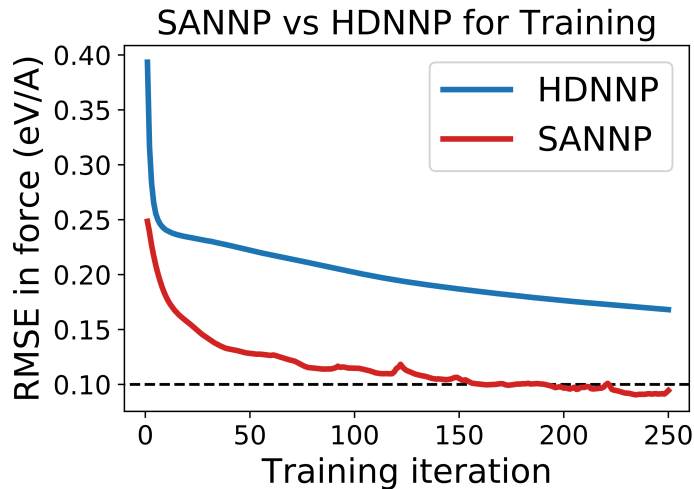
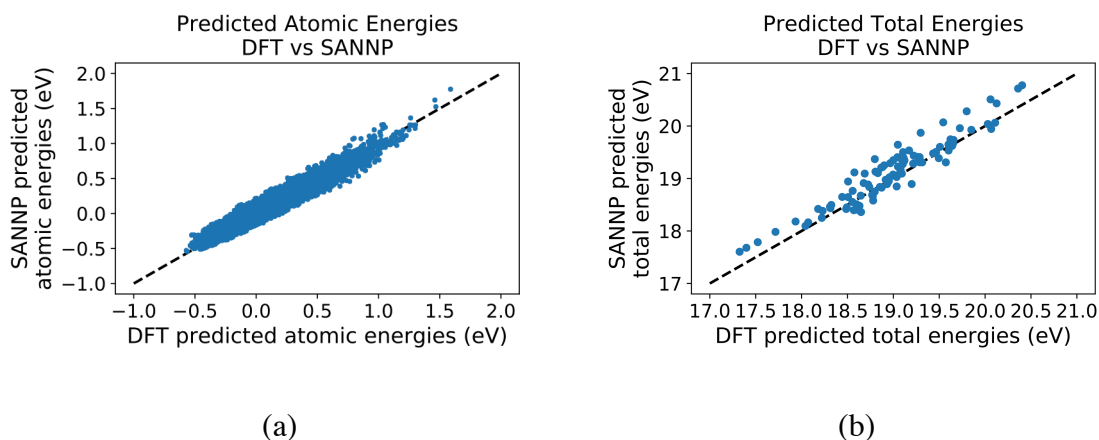


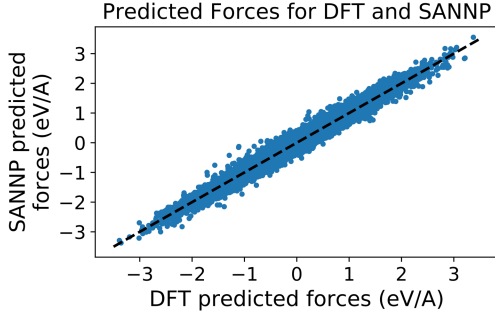
Figure 3. Training curves for SANNP and HDNNP. The errors reported are calculated from the test set. Similar results are obtained for the validation set. After 250 iterations, the errors for SANNP and HDNNP are 0.094eV/A and 0.168eV/A, respectively.

3. Results

3.1 Comparison between DFT and neural network potential

To validate our SANNP model using energy decomposition, piecewise cosine symmetry functions, and the proposed training procedure, we train the corresponding neural network for a periodic system of amorphous silicon, which is initially generated with a random covalent band switching model [24]. As shown in S4 of the Supplemental Materials, a set of 1000 DFT configuration is obtained from an *ab initio* molecular dynamics simulation of a periodic box with 256 silicon atoms, such that 800 points are used for training, 100 points are used for validation, and 100 points are used for testing. By decomposing the total energy into individual energies, the training set contains 204,800 atomic energies and 614,400 atomic forces. After training with the procedure described above, the test set errors in atomic energies, total energies, and forces are shown in Figure 4.





(c)

Figure 4. Comparison between the fitted SANNP model and DFT for the test set with 100 configurations. (a) comparison of SANNP atomic energies and DFT atomic energies in the test set. (b) comparison of the SANNP total energies and DFT total energies in the test set. (c) comparison of the SANNP forces and DFT forces in the test set. Note, none of the test set data is used in training the SANNP model.

Overall, the neural network potential is in good agreement with the DFT results, with the RMSE's in $\{E_i\}$, E_{tot} and $\{\mathbf{F}_i\}$ being around 50meV, 1.0meV/atom, and 0.10eV/A respectively in the test set. Although the neural network was not trained directly against E_{tot} , an extremely small E_{tot} RMSE of 1.0meV/atom is recovered. The reason is that the square of the error in the total energy is related to the error in atomic energies by $\Delta E_{\text{tot}}^2 = \sum \Delta E_i^2$ (assuming atomic energies for i and j are not correlated). Then the RMSE of the total energy is $\sqrt{\langle \Delta E_{\text{tot}}^2 \rangle} / N = \sqrt{N \langle \Delta E_i^2 \rangle} / N \sim \sqrt{\langle \Delta E_i^2 \rangle} / \sqrt{N}$. As the result, the RMSE of the total energy per atom is a factor of $1/\sqrt{N}$ smaller than the average RMSE of each individual atom. For our system, we have $N=256$, thus it is 16 times smaller, which leads to 1-3 meV/atom RMSE total energy error per atom. Note that, this is the error most papers cited for their NNP models. The reported

accuracies in $\{E_i\}$, E_{tot} and $\{F_i\}$ indicate that our new approach using atomic energies E_i can achieve high accuracy with a small number of DFT trajectories.

3.2 Application of the cosine-based symmetry functions

To evaluate the effectiveness of the piecewise cosine localization model, we have compared our model with the Gaussian-like symmetry functions used in the original HDNNP model. Except the change from the cosine like function to Gaussian function, all the other procedures are the same (however, only E_i are used in the training, atomic force F_i is not used in this test). As shown in Table 1, when training against the atomic energies, the piecewise functions with $M=4$ (or a total of 56 feature functions $M_2 = M^2$ and $M_3 = M$) achieve a similar accuracy as the case with more than 100 Gaussian-like symmetry functions. When more piecewise cosine functions with $M=5$ or a total of 100 functions are used, the energies can be fitted even better.

Basis sets (Total number of functions)	RMSE of E_i on the test set	MAE of E_i on the test set
Gaussian (110)	54.8 meV	43.5 meV
$M=4$ cosine (56)	57.7 meV	45.7 meV
$M=5$ cosine (100)	45.9 meV	36.1 meV

Table 1. Comparison of the symmetry functions for the training atomic energy E_i .

In fact, the quality of the piecewise cosine functions can be systematically improved by adjusting one parameter, M , with the number of two-body symmetry functions is $M_2 = M^2$, and the number of three-body symmetry functions is $(M^2+M^3)/2$. As shown in Figure 5, both the energies and forces are converging towards certain limits as M increases. In addition, the quality of the basis set can also be adjusted by changing the inner cutoff distance. In the case of

amorphous silicon, the interatomic distance between any two Si atoms is rarely less than 1.9Å. By increasing this inner cutoff, the piecewise cosine functions are more concentrated in the region of interest, thus allowing a better description and resulting in a more accurate model. As shown in Figure 5, the neural network potential with an inner cutoff of 1.9Å is consistently better than inner cutoff of 0Å. In summary, the piecewise cosine functions can be adjusted by tuning the number of functions (M) and the range of interatomic distances, which are both intuitive parameters to be adjusted in practice.

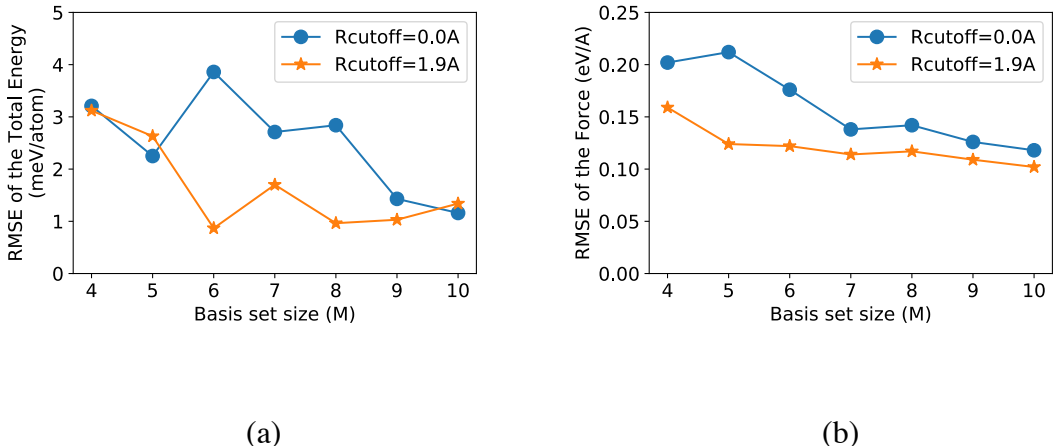


Figure 5. Errors in (a) total energies and (b) forces as functions of the size M of the piecewise cosine functions. Inner cutoff of $R_{\text{inner}}=0.0\text{\AA}$ (or no cutoff) and $R_{\text{inner}}=1.9\text{\AA}$ are also compared.

3.3 Comparison of DFT and NN for MD

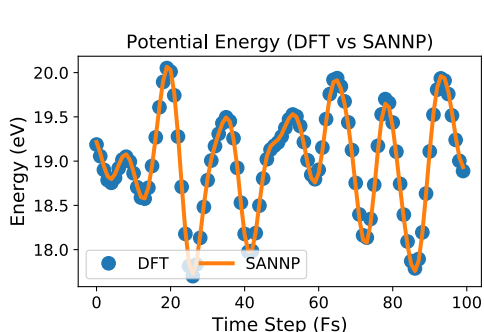
One of our main goals is to use the SANNP to perform molecular dynamic simulation. In addition to have small errors in energies and forces in the test set, an accurate neural network potential must also be able to reproduce similar quantities along its MD trajectory. In particular, the smoothness of the potential as well as the atomic forces are important. For this test, we have

performed an NVE molecular dynamics simulations on another amorphous silicon structure (not in the training set) using DFT for 1ps, and a random trajectory interval of 100 fs is chosen to compare the energies and forces between DFT and the previously trained SANNP. As shown in Figure 6(a), along the AIMD trajectories, the energies between DFT and SANNP match almost perfectly, with an RMSE of total energy of 1.1meV/atom, which is only slightly higher than that of the test set. Since the forces at each trajectory include all components of all atoms, to compare the DFT forces and the SANNP forces, we have projected the forces along the MD trajectory directions, as shown in Figure 6(b), and have also calculated the unit vector dot product between the DFT and SANNP forces, as shown in Figure 6(c). Overall, the projected forces agree well between DFT and SANNP with an RMSE of 0.13eV/A, and the scaled dot product indicates that the SANNP forces recover almost 99% of the DFT forces throughout the trajectory. Such a near unity dot-product means the forces for almost all atoms are in the same directions between SANNP and DFT.

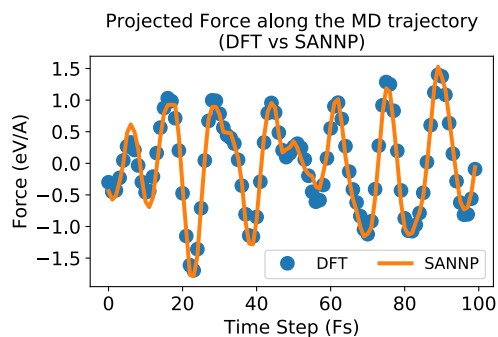
Since silicon is an important material, many empirical force fields have been developed. The energies for these classical force fields can also be calculated along the above AIMD trajectories. As shown in Figure 6(d), energies obtained for all methods have the same overall trend and local extrema, but the variation in energy at each trajectory is quite large for different force fields, as well as to the DFT energies. This indicates a much superior SANNP accuracy compared to other classical force fields, if the DFT energy is used as the reference.

The SANNP can also be compared with DFT with different practical parameters (pseudopotentials and exchange-correlation functionals). As shown in Figure 6(e), the energies

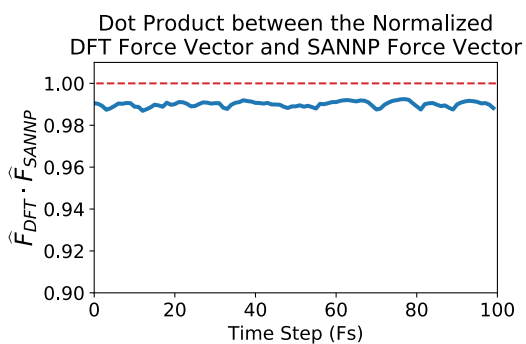
for different DFT are calculated along the same AIMD trajectories, and they are relatively close to each other. By zooming in onto the first 10 time steps of the trajectories, the differences between different DFT runs can be shown more clearly. As shown in Figure 6(f), the SANNP follows the original DFT results very closely, while different levels of DFT give much bigger errors. This indicates that the SANNP is already within the errors between different choices of DFT.



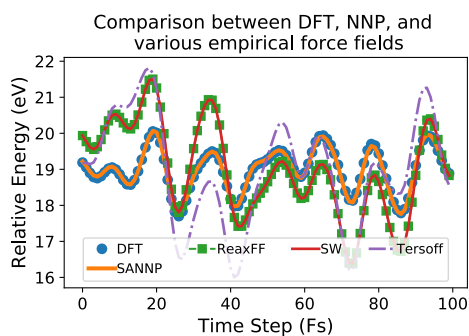
(a)



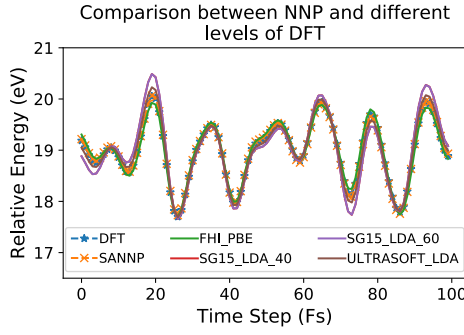
(b)



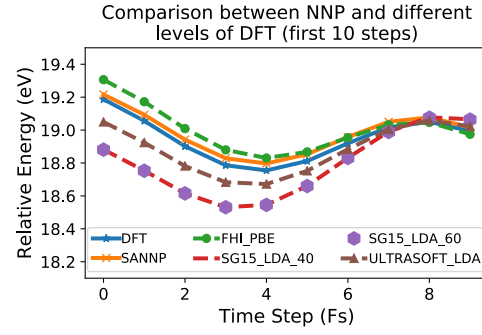
(c)



(d)



(e)



(f)

Figure 6. Comparison of DFT, neural network potential, and empirical force fields along a sequence of AIMD trajectories. (a) total energies between DFT and NNP (b) projected forces between DFT and neural network forces (c) scaled dot product between DFT and neural network forces (d) total energies between DFT, NNP, and classical force fields (with constant shifts for force field energies); (e) total energies between the neural network potential and various levels of DFT over 100fs (e) total energies between the neural network potential and various levels of DFT over 10fs

Although the neural network fits the DFT trajectory well, it is still necessary to compare the dynamics between DFT and SANNP to ensure that similar structural properties are generated. Starting from the same structure and initial velocities, NVE simulations are performed using DFT and SANNP independently. After 1ps, the radial distribution function and the normalized angular distribution are compared. The radial distribution is obtained from the total bond distribution normalized by r^2 , the angular distribution is normalized by $\sin(\theta)$. As shown in Figure 7, both distributions are almost indistinguishable between DFT and SANNP, confirming that the SANNP is capable of reproducing the DFT results through MD simulations.

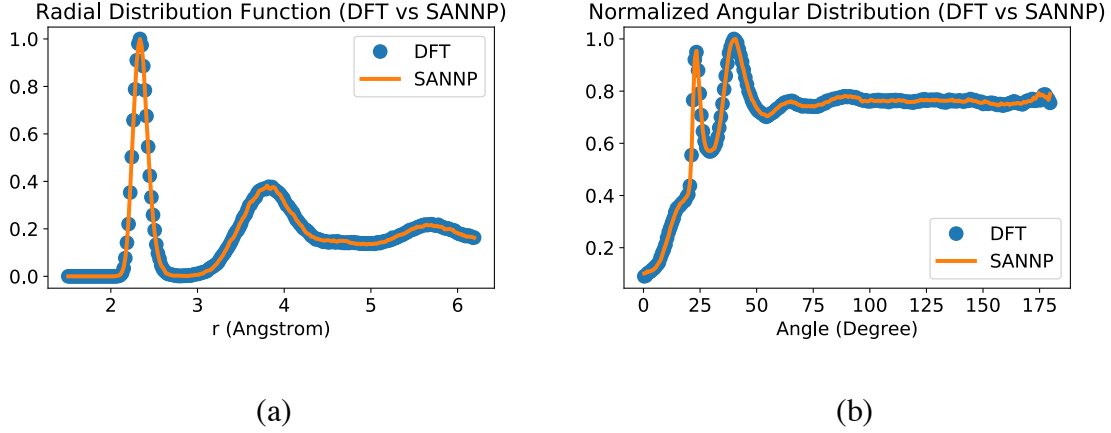


Figure 7. Comparison of (a) radial distributions and (b) angular distributions between DFT (blue) and single atom neural network potential, SANNP (orange).

3.4 Application of the NNP to thermal conductivity calculations

As shown in the previous sections, the SANNP is capable of performing MD simulations with DFT level of accuracy. Since the SANNP is significantly less computationally intensive than DFT, long time and large scale simulations can be performed. One class of problems that is difficult to be calculated with DFT level of accuracy is the classical transport properties, e.g., the thermal conductivity of amorphous silicon. By employing the SANNP to perform molecular dynamics simulations over a long time scale, the heat current auto-correlation function (HCACF), $\langle \mathbf{J}(t)\mathbf{J}(0) \rangle$, can be obtained. Using the Green-Kubo formulation, the thermal conductivity equals the integration of the HCACF,

$$\kappa = \int^t \langle \mathbf{J}(t)\mathbf{J}(0) \rangle dt \quad (9)$$

Although there is no unique spatial origin of \mathbf{R}_i to calculate the heat current $\mathbf{J}(t) = \frac{d}{dt} \sum_i \mathbf{R}_i E_i$, an alternative formulation [30] can be used to avoid this non-uniqueness as long as the atomic energies are explicitly represented as a function of the atomic coordinates, as in the SANNP. For this, we have:

$$\mathbf{J}(t) = \sum_i \mathbf{v}_i \left(\frac{1}{2} m_i v_i^2 + E_i \right) + \sum_i \sum_{j \neq i} \mathbf{R}_{ij} \nabla_i E_j \cdot \mathbf{v}_i \quad (10)$$

Where E_i is the atomic energy from the SANNP.

To obtain the HCACF by taking ensemble average of the heat current in Equation (10), we first shift the temperature of the system to the target temperature using the Andersen thermostat such that the canonical ensemble is correctly sampled. After the system is further stabilized at the target temperature for another 1ps, an NVE simulation is performed to sample the dynamics and obtain $\mathbf{J}(t)$.

The HCACF for amorphous silicon at 300K is shown in Figure 8(a), in which most of the correlation is within the first few hundred femtoseconds, and it quickly decays to zero. By integrating over the HCACF, the corresponding thermal conductivity κ is integrated to be 1.59 ± 0.1 W/m·K, as shown in Figure 8(b). This can be compared with the direct DFT calculated value of 1.4 ± 0.3 W/m·K [23] at the same temperature, as well as the experimental range of 1 to 2 W/m·K [31-33]. We have also calculated the temperature dependence of κ as shown in Figure 8(c). We see that κ decreases in a power law rate as temperature increases, the same trend as found in crystal Si structure [34]. However, the rate of decreasing is much slower in our case, a

result of the randomness in the amorphous Si, where the phonon scattering is caused mostly by the structure randomness instead of by the temperature dependent nonharmonic scattering. As a result, the temperature dependence is much smaller.

The accurate computation of the thermal conductivity using the SANNP implies that the heat current $\mathbf{J}(t) = \frac{d}{dt} \sum_i \mathbf{R}_i E_i$, and thus the local atomic energies, are properly obtained using our atomic energy decomposition scheme and accurately trained using our neural network model.

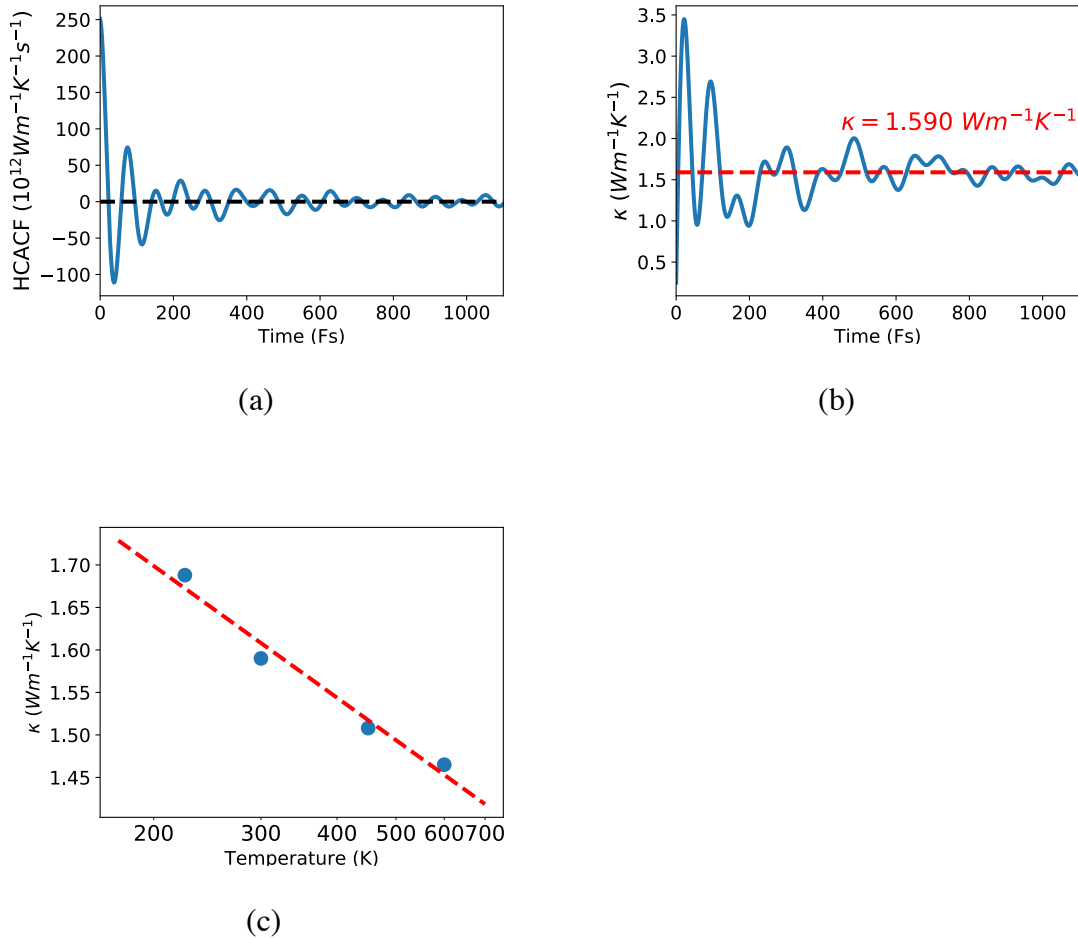


Figure 8. (a) The time evolution of the heat current auto-correlation function (HCACF), $\langle J_x(t)J_x(0) \rangle$, for amorphous silicon at 300K; (b) The time integration of the HCACF using

Equation (9) at 300K; (c) The temperature dependence of the thermal conductivity from 150K to 600K

4. Conclusion

In this study, we developed a Machine learned based scheme to partition the DFT total energy into atomic energies that depend only on the atoms nearby to a given atom. This leads to a unified single atom neural network potential (SANNP) model that uses the data for all atoms in training this SANNP. Compared to the traditional HDNNP method using only the total energy of the system, SANNP acquires hundreds of times more energy information from the same DFT. As a result, we found that only 1000 MD steps (which takes about half day to finish using GPU by the PWmat code [35-37]) is sufficient to train an accurate SANNP, which dramatically reduces the training time while dramatically increasing the accuracy.

In addition, we have deployed a new universal set of symmetry invariant feature functions using local piecewise cosine basis. We show that using piecewise cosine functions to construct the symmetry features provides a systematic and mathematically efficient way to represent the atomic configuration of nearby atoms for a given central atom. This provides a universal model applicable to any systems. Combining the energy decomposition method with the piecewise cosine functions model, we show that the training of the SANNP using TensorFlow running on GPU workstation takes 1/10 the time of standard methods while attaining total energy accuracy of $\sim 1\text{meV/atom}$ (of a 256 atom system) and force accuracy of 0.1eV/\AA . This accuracy is comparable, or even higher, than the uncertainties from using different pseudopotentials in DFT calculations. We anticipate that the dramatic reduction in the number of DFT pre-calculations

(with smaller number of steps) with the dramatic decrease in NN training time, plus the high accuracy and systematics of the SANNP model will enable DFT accuracy for large scale simulations.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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