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Regular Article

Machine Learning Force Fields for Predicting Thermodynamic Properties of PA6T/6I Copolymers

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Abstract: This study employed molecular dynamics (MD) simulations, utilizing both a machine learning force field (MACE-OFF) and a traditional force field (PCFF), to predict the thermal properties of poly(hexamethylene terephthalamide-co-isophthalamide) (PA6T/6I) copolymers. The simulations are benchmarked against experimental data to assess the predictive accuracy of these two methodologies for the thermal properties of PA6T/6I copolymers. Our findings reveal that the MACE-OFF force field, after calibration for the PA6T/6I copolymer, offers significant precision in modeling π-π and hydrogen-bonding interactions, closely mirroring the results from M06 functional simulations. The MD simulations underscore the MACE-OFF model's ability to deliver more stable thermal properties, including the glass transition temperature (T_g) and density, for copolymer systems with varying PA6T content, aligning well with experimental observations. Furthermore, a comprehensive analysis of dynamic properties, such as mean squared displacement and free volume, within the PA6T/6I copolymers was performed to decipher the mechanisms underlying the temperature-dependent changes in thermal properties observed throughout the simulation process. A thorough examination of the fluctuations in inter-chain and intra-chain hydrogen bonding within the copolymer systems has unveiled the correlation between the molecular packing arrangement and thermal properties. This research establishes that the MACE-OFF model accurately simulates the thermal dynamical behavior of PA6T/6I copolymers, a capability that could be extended to other polyamide systems.

Key words: machine learning, force field, molecular dynamics simulations, Poly(hexamethylene terephthalamide-co-isophthalamide) (PA6T/6I) copolymers, thermal properties

1. Introduction

Simulating the thermal properties of polymers necessitates an understanding of their microstructures, which is challenging due to the intricate conformations of polymers and the time-consuming nature of such predictions. Hence, selecting an appropriate method for polymer dynamics simulations is crucial for accurately predicting polymer properties. Although ab initio molecular dynamics (AIMD) methods [1,2], which employ density functional theory (DFT) [3], offer highly accurate depictions of the electronic structure and enable precise capturing of intermolecular interactions, they are restricted to small systems with relatively short timescales and are computationally intensive. Consequently, their application to complex systems like polymers is problematic [4,5]. As a result, classical molecular dynamics (MD) simulations are frequently utilized for large-scale polymer computations.[6] However, traditional MD simulations depend on empirically derived potential functions, which can compromise the accuracy of the simulations [7]. Therefore, there is a pressing need to develop efficient methods that balance precision and computational efficiency in polymer dynamics simulations.

In recent years, the advent of machine learning techniques, particularly machine learning force fields (MLFF) [8-12], has presented a promising solution for the precise study of polymer MD. Machine learning potentials learn nonlinear functional relationships from extensive datasets of structural samples and their corresponding property outputs, akin to an effective set of quantum mechanical potential rules [13], thus circumventing the need to directly solve the complex and elusive physical relationships between sample structures and their properties. One of the early algorithms associated with machine learning is the feedforward neural network [14]. However, this approach lacks a clear feature selection mechanism and is limited in its capacity to represent complex molecular structures and interactions. For instance, Teso-Fz-Betoño et al. encountered issues such as vanishing gradients and contradictory gradient directions when training with feedforward networks [15]. The Behler-Parrinello neural network (BPNN) method [16] can handle the spatial positions of all atoms in a system, thereby predicting the total energy and forces. Vassilev-Galindo et al. applied the BPNN model to predict the thermal isomerization process of azobenzene and found that BPNN is overly reliant on local descriptors, which hinders its ability to effectively capture long-range interactions [17]. This limitation leads to suboptimal performance when dealing with larger or more complex flexible molecules [17]. The message passing neural network (MPNN) [18,19] is a neural network architecture designed for graph-structured data, learning the representation of the graph through a message-passing mechanism between nodes and edges. Xue et al. combined MPNN with ReaxFF, using MPNN to compute bond order and bond energy, thereby enhancing the performance in calculating the potential energy surface, reaction energies, and equation of state.[20] However, most MPNN-based interatomic potentials use message passing that only considers two-body interactions, which may pose challenges to the generalizability of the model [21].

Due to the issues mentioned above, finding a suitable model framework for MD simulations is particularly important. The MACE model [22], based on an equivariant graph neural network architecture, is characterized by its use of a high-order many-body message passing mechanism, which enables high-precision predictions with very few message passing iterations. Grunert et al. were able to accurately predict properties such as activation energy in MD processes and significantly improve accuracy through simple fine-tuning [23]. The model trained with MACE demonstrated high accuracy in bond dissociation predictions and exhibited strong extrapolation capabilities, enabling predictions for non-equilibrium structures [24]. In summary, the MACE model has demonstrated high accuracy and excellent extrapolation capability on several datasets [25,26], performing exceptionally well even under high-temperature conditions [23].

Owing to these benefits, MACE has been extensively utilized in MD simulations, with our particular emphasis on its application within polymer systems. Poly(hexamethylene terephthalamide-co-isophthalamide) (noted as PA6T/6I) is a semi-aromatic polyamide known for its combination of the superior processing flowability characteristic of aliphatic polyamides, along with low water absorption, exceptional heat resistance, and notably enhanced mechanical properties [27,28]. The processing of PA6T/6I enables the development of a range of high-performance plastics and fibers. Consequently, conducting MD simulations on PA6T/6I to explore its thermodynamic properties is of considerable importance.

In this study, we compared the glass transition temperature (T_g) results obtained from simulations using the PCFF and the machine learning force field (MACE-OFF) against experimental values, thereby validating the precision of the MACE-OFF simulations. Moreover, we employed both methodologies to scrutinize the impact of varying PA6T contents and temperatures on the free volume, mean square displacement, and hydrogen bond numbers within the copolymer system. Ultimately, we delved into the correlation between the stacking pattern of the benzene rings and the number of hydrogen bonds. This research underscores the viability of employing MACE-based models in polymer dynamics simulations and illustrates that machine learning force fields can precisely elucidate the interplay between the structure and properties of materials.

2. Simulation models and computational details

2.1 Machine learning force fields

We utilized the MACE-OFF model, a short-range, transferable force field specifically designed for organic molecules and constructed on the foundation of the MACE model architecture [29]. This model is developed from first-principles reference data, which are generated using cutting-edge machine learning techniques [29]. It is parameterized for key chemical elements that are prevalent in organic chemistry, a feature that empowers the MACE-OFF model to precisely simulate neutral molecular systems, including drug molecules and biopolymers. MPNNs [30,31] represent a category of graph neural networks (GNNs) [32-35] that map a labeled graph to a target space, which can be either a graph or a vector space. The MPNN operates through a message passing mechanism between nodes, where, at each layer, a node's feature information is integrated with the features of its neighboring nodes. This process enables the model to learn a comprehensive representation of both the individual nodes and the graph as a whole.

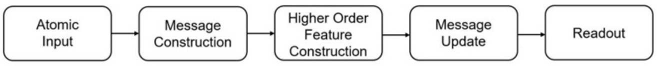

Figure 1. Workflow of the MACE model.

The workflow of the MACE model is illustrated in Figure 1. MACE [22] is a machine learning architecture that takes the positions and chemical elements of atoms as input and learns to predict the potential energy of atomic systems. The total energy is decomposed into atomic site energies, enabling linear scaling with system size:

$$\mathrm{E_{total}} = \sum_{\mathrm{i}} \mathrm{E_i} \tag{1}$$

Each atom and its environment are represented as a graph, where nodes correspond to atoms, and edges are defined for neighboring atoms within a cutoff distance $\mathrm{r_{cut}}$. The initial node features are learnable embeddings of the atomic numbers:

$$\mathrm{h^{(0)}_{i,k00}} = \sum_{\mathrm{z}} \mathrm{W_{kz}}\, \delta_{\mathrm{zz_i}} \tag{2}$$

These features are updated through a message-passing process, which iteratively incorporates information from neighboring atoms and their geometric arrangement. At each layer t, atomic features are updated as:

$$\mathrm{h^{(t+1)}_{i,kLM}} = \sum_{\bar{\mathrm{k}}} \mathrm{W^{(t)}_{kL,\bar{k}}}\, \mathrm{m^{(t)}_{i,\bar{k}LM}} + \sum_{\bar{\mathrm{k}}} \mathrm{W^{(t)}_{kz_iL,\bar{k}}}\, \mathrm{h^{(t)}_{i,\bar{k}LM}} \tag{3}$$

where $\mathrm{m^{(t)}_{I,\bar{k}LM}}$ are messages constructed from equivariant many-body features of the local environment. In the first layer ($t = 0$), only the first term is present. After two iterations (layers), the site energy of each atom is obtained via read-out functions applied to the updated features: