# Thermomechanical properties of two-dimensional covalent organic frameworks studied by machine-learning molecular dynamics

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## Abstract:

Two-dimensional (2D) covalent organic frameworks (COFs) are promising emerging 2D polymeric materials with broad applications such as adsorption, energy storage, and catalysis. However, their mechanical properties have not been systematically studied yet. Here, the machine-learned neuroevolution potential (NEP) was developed to study the elastic properties of representative 2D COFs, e.g., COF-1 and COF-5. The trained NEP enables one to study the mechanical properties of 2D COFs in realistic situations (e.g., finite size and temperature) and enjoys greatly improved computational efficiency as compared with density functional theory calculations. With the aid of the obtained NEP, molecular dynamics (MD) simulations together with the strain fluctuation method were employed to evaluate the elastic constants of the considered 2D COFs at different temperatures. The elastic constants of COF-1 and COF-5 monolayers are found to decrease with growing temperature, though they are almost isotropic, irrespective of the temperature. The thermally induced softening of 2D COFs below a critical temperature is majorly attributed to their inherent ripple configurations at finite temperatures, while, above the critical temperature, the damping effect of anharmonic vibrations becomes the dominant factor. Based on the proposed mechanisms, analytical models were developed for capturing the temperature dependence of the elastic constants, which were found to agree with MD simulation results well. This work provides an in-depth insight into the thermomechanical properties of 2D COFs, which guides the development of COF materials with tailored mechanical behaviors for enhancing their performance in various applications.

## Introduction

In recent years, covalent organic frameworks (COFs) have emerged as a highly promising class of crystalline porous polymers, which possess unique structures composed of a network of dynamic covalent bonds.<sup>1</sup> Owing their unique structures, COFs possess a large void space and a high surface area, which render them have the capacity to be used in capturing and separating hydrogen, carbon dioxide, methane and other gases.<sup>2-4</sup> Besides, COFs are promising catalytic platforms because of their abundant uniform and open channels as well as the excellent insolubility nature and high stability, which are crucial to the mass transfer process in catalysis.<sup>5,6</sup> The highly efficient size selectivity of COFs due to their uniform pores also renders them can be employed as highly efficient and size-selective catalysts.<sup>7</sup> Meanwhile, COFs have been designed as potential Li ion solid-state conductors as well as the flexible electronics, since most of them are flexible and have the high conductivities among the reported crystalline porous materials.<sup>8,9</sup>

Among different types of COFs, two-dimensional (2D) COFs are currently receiving much attention due to their unique structural properties. Each individual layer in 2D COFs maintains its in-plane stability through the strong covalent bonds, while neighboring layer components are connected with each other via the weak interlamellar interaction. The inherent structure of 2D COFs allows the precise manipulation and customization of their pores at the nanoscale level.<sup>10</sup> As a result, 2D COFs can be designed with multi-level porosity, which makes them possibly exhibit the excellent performance in the applications of adsorption, catalysis and manufacture of micro/nano devices.<sup>11,12</sup> The aforementioned practical applications of 2D COFs could be affected by their mechanical properties, because previous studies on various other 2D materials indicate that their physical and chemical properties can be significantly affected by mechanical stimuli.<sup>13</sup> For example, by applying a strain to 2D materials, the rate of diffusion of adsorbed guest materials in them can be controlled.<sup>14</sup> The strain engineering is also an effective method to modify the size of pores of 2D materials, allowing the separation of different gas mixtures at a specific pore size<sup>15</sup> and the change of the water permeability for 2D materials.<sup>16,17</sup> In the thermal catalysis applications of 2D materials such as 2D MXenes, the operational conditions typically encompass elevated temperatures and pressures. The catalytic

efficacy is notably contingent upon the thermodynamic and mechanical robustness of 2D MXenes.<sup>18</sup> When used in the manufacture and application of nanosensors, the stable mechanical performance of the component 2D films is crucial to the production and reusability of these devices.<sup>19</sup> Although the mechanical property of 2D COFs is a fundamental intrinsic feature relevant to most of their applications, there are relatively few reports on their mechanical behaviors.

In spite of two very recent experimental reports on the tensile properties of multilayer COFs,<sup>20,21</sup> the atomistic simulations including density functional theory (DFT) calculations and molecular dynamics (MD) simulations are generally employed to investigate the mechanical properties of 2D COFs. By using DFT calculations, Kapri et al.<sup>22</sup> very recently calculated the elastic tensor of some 2D COFs. Although the DFT approach is of high accuracy, it is computationally expensive, which is thus difficult to be employed for studying the COFs with large pores or complex structures. Moreover, it is usually difficult to consider the effects of crystal size and finite temperature in DFT calculations. To overcome the limitations of DFT calculations, MD simulations are usually treated as a more effective method in theoretically studying the mechanical behaviors of 2D COFs. By exploiting MD simulations, Zhang<sup>23</sup> reported a phase transition occurring in 2D COFs due to compression, which was found to have an effect on the elastic constants, band gap and thermal conductivity of 2D COFs. Li and Brédas<sup>24</sup> reported that the existence of structural defects will significantly reduce the stiffness of 2D COFs. Very recently, Hao et al.<sup>25</sup> revealed that 2D COFs possess a superior impactresistant capability under the high-velocity impact. Although these initial results reveal some fundamental mechanical characters of 2D COFs, there still exist some limitations in these MD studies. For example, these studies were based on some empirical potentials (OPLS all-atom force field potentials,<sup>26</sup> AIREBO potential,<sup>27</sup> and ReaxFF potential<sup>28</sup>) specifically developed for other materials rather than COFs.<sup>24,29,30</sup> Thus, the accuracy of these existing empirical potentials in describing 2D COFs becomes questionable. Recently, the machine-learned potential (MLP) trained by the quantum DFT data has shown to be a promising on-demand approach in investigating the mechanical properties of 2D materials,<sup>31</sup> which thus could be further extended to study the mechanical behaviors of 2D COFs.

Motivated by these ideas, in this work we developed the neuroevolution potential (NEP)

framework-based MLPs<sup>32,33</sup> for two representative 2D COFs, i.e., COF-1 and COF-5.<sup>1</sup> Compared with other MLPs, the present NEP approach is more computationally efficient but can achieve a high accuracy.<sup>33</sup> The obtained NEP was further applied to investigate the elastic properties of the considered monolayer COFs at different temperatures by using the extensive MD simulations together with the strain-fluctuation method.<sup>34,35</sup> The temperature is found to generally have a softening effect on the elasticity of 2D COFs, though the temperature sensitivity of elastic constants is different when below and above a critical temperature. Specifically, the larger softening effect observed below the critical temperature is ascribed to the thermal rippling of 2D COFs, while the suppression of the increased nonharmonic forces above the critical temperature. Based on the proposed mechanisms, analytical models were also developed to better capturing the temperature dependence of elastic constants of 2D COFs.

#### **Simulation Models and Methods**

#### Simulation models

In this study, we focused on two typical monolayer COFs, i.e., COF-1 and COF-5, which are assembled through reactions between organic precursors, resulting in the strong covalent bonds to afford porous, stable and crystalline materials. Specifically, as shown in Figure 1a, COF-1 is composed of the building blocks of benzene-1,3,5-tricarboxylic acid (BTC) and 1,3,5-tris (4-aminophenyl) benzene (TAPB), while COF-5 contains the building blocks of 1,4-benzenedicarboxylic acid (BDC) and 1,2-bis (4-pyridyl) ethylene (BPE). Here, MD simulations were employed to study the mechanical behaviors of aforementioned monolayer COF materials. It is known that the mechanical properties especially the elastic moduli rely on the size of the structures considered in MD simulations. The elastic modulus could be underestimated if the selected size is too small.<sup>36</sup> Thus, to ensure the accuracy of the simulation results, we chose a simulation size of 24.4 nm  $\times$  26.6 nm for COF-1 that consisted of 12,852 atoms and a size of 26.1 nm  $\times$  24.1 nm for COF-5, which contained 7,680 atoms. The free boundary condition was used in the out-of-plane direction to avoid image-image interactions, while periodic boundaries were employed in the in-plane directions.



**Figure 1.** The workflow of training the NEP model for 2D COFs. (a) Primitive cells of COF-1 and COF-5. (b) Construction of training and testing data sets. (c) Schematic of the NEP frameworks. (d) Supercells of monolayer COF-1 and COF-5 used to evaluate their elastic properties. The OVITO package was used here for visualization.<sup>37</sup>

#### Acquisition of dataset from first-principles calculations

As illustrated in Figure 1b, totally 2400 structures were constructed for training and testing the NEP model, which were equally comprised of structures of COF-1 and COF-5. Moreover, 2000 structures were extracted from *ab-initio* molecular dynamics (AIMD) simulations, while the other 400 structures were obtained by manual perturbations. All structures in the reference dataset were based on primitive cells of COF-1 and COF-5. In AIMD simulations, the structural sampling was performed under NVT ensemble with Nosé-Hoover heat bath,<sup>38</sup> in which the system temperature was linearly raised from 1 K to 1000 K within 10 ps. Here, the time step was set as 1 fs. The perturbated structures were obtained by randomly adding 5% perturbations to the lattice constants and changing the atomic coordinates with a distance less than 0.2 Å. With the structures of COF-1 and COF-5 established through the aforementioned process, we calculated their energy, virial, and atomic force using single-point DFT calculations. All DFT calculations and AIMD simulations were implemented by the VASP package<sup>38,40</sup> with Perdew-Burke-Ernzerhof functional.<sup>41</sup> The electronic self-consistent loop was set as a 2 × 2 × 1.

#### Training of the NEP framework for monolayer COFs

The MLP model based on the third generation of NEP framework<sup>42</sup> was trained by using the GPUMD package with a workflow briefly shown in Figure 1c.<sup>42</sup> Here, we randomly divided the total dataset into a training dataset and a testing dataset in a ratio of 4:1. In order to train the NEP potential for the considered monolayer 2D COFs, several hyperparameters are needed to be set. The hyperparameters used for testing can be found in Supporting Information (Table S1). The impact of various hyperparameters on the accuracy of the NEP model has been thoroughly evaluated. Specifically, the cutoff radii for the radial and angular descriptor components were  $r_c^R = 10$  Å and  $r_c^A = 4$  Å, respectively. The Chebyshev polynomial expansion orders for the radial and angular descriptor components were  $n_{\text{max}}^{\text{R}} = 6$  and  $n_{\text{max}}^{\text{A}} = 6$ 4. The suitability of the selected hyperparameters was confirmed by the results shown in Figure S1. Moreover, the Legendre polynomial expansion order for the angular descriptor components was  $l_{\text{max}} = 4$ . Besides, we employed 100 neurons in the hidden layer of the neural network. The default setting was used for the normalized factors of  $\lambda_1$ ,  $\lambda_2$ ,  $\lambda_e$ ,  $\lambda_f$  and  $\lambda_v$ , which were 0.1, 0.1, 1.0, 1.0, and 0.1, respectively. The population size and the number of generations in the algorithm were  $N_{\rm pop}$  = 50 and  $N_{\rm gen}$  = 5 × 10<sup>6</sup>, respectively. After determining the aforementioned hyperparameters, we can finally get an NEP function for both COF-1 and COF-5.

#### **Strain-fluctuation methods**

The NEP model obtained above can be employed in MD simulations for further evaluating the elastic properties of monolayer COF-1 and COF-5 at the finite temperature, which was implemented by the strain-fluctuation method.<sup>34,35</sup> In doing this, all COF structures were relaxed for 1000 ps at 0 GPa in the NPT ensemble by using the stochastic cell rescaling method,<sup>43</sup> which makes the structures reach their equilibrium at a certain temperature. In all simulations, the strain  $\varepsilon_{ij}$  was determined from the following equation:<sup>34,35</sup>

$$\varepsilon_{ij} = \frac{1}{2} \left[ \langle h \rangle_{ik}^{-T} h_{kl}^{T} h_{lm} \langle h \rangle_{mj}^{-1} - \delta_{ij} \right].$$
(1)

Here,  $h_{ij} = {\mathbf{a}, \mathbf{b}, \mathbf{c}}_{ij}$  is a matrix with components of principal axes ( $\mathbf{a}, \mathbf{b}$  and  $\mathbf{c}$ ) of the simulation box, which can be extracted from MD simulations and also has the ability to describe the size and shape of the simulation box. The matrix  $\langle h \rangle_{ij}$  describes the average shape of the system as the reference state.  $\langle h \rangle_{ij}^{-T}$  is the inverse of the transpose of  $\langle h \rangle_{ij}$ .  $\delta_{ij}$  is the Kronecker tensor. The full second-order compliance tensor **S** at the temperature *T* and pressure *P* was then obtained as:<sup>44</sup>

$$S_{\alpha\beta\gamma\kappa} = \frac{\langle V \rangle}{k_{\rm B}T} \operatorname{cov}(\varepsilon_{\alpha\beta}(t), \varepsilon_{\gamma\kappa}(t)) = \frac{\langle V \rangle}{k_{\rm B}T} \langle (\varepsilon_{\alpha\beta}(t) - \langle \varepsilon_{\alpha\beta} \rangle) (\varepsilon_{\gamma\kappa}(t) - \langle \varepsilon_{\gamma\kappa} \rangle) \rangle, \qquad (2)$$

where  $k_{\rm B}$  is the Boltzmann constant,  $\varepsilon_{\alpha\beta}(t)$  [or  $\varepsilon_{\gamma\kappa}(t)$ ] is the strain at the time of *t*, and  $\langle V \rangle$  describes the average of volume. Here, the layer thickness was set as 3.34 Å in the calculation of the volumes of monolayer COFs, which equals to their van der Waals distances.<sup>45,46</sup> Based on the compliance tensor **S** extracted above, we can finally calculate the second-order stiffness tensor **C** by inversing the matrix **S**, i.e.,  $\mathbf{C} = \mathbf{S}^{-1}$ .

The result in Figure S2 shows the evolution of the elastic constants with respect to the simulation time, which indicates a convergency of elastic stiffness tensors after the simulation with 1000 ps. Thus, the unit cell vector was output in another successive simulation with 500 ps, which was further divided into five groups. The average of compliance tensors of these five groups was treated as the final result, while the standard error of five groups of data was regarded as the calculation error.

#### **Results and Discussion**

## Validation of the NEP model for COF-1 and COF-5

In Figure 2a and 2b, we show the evolution of loss functions for the training dataset of the considered 2D COFs with respect to generations. All loss functions are found to become completely converged when the training is performed after 10<sup>6</sup> generations. The corresponding energy, force and virial of 2D COFs predicted by NEP are also compared against the corresponding DFT results in Figure 2. Here, extremely small values of root-mean square (RMS) error of energy, force and virial 2 indicate that the NEP model trained here is capable of accurately predicting the energy, force and virial properties of monolayer COFs considered here.



**Figure 2.** The evolution of various loss functions for the training and testing dataset with respect to the generation together with the corresponding energy, force and virial obtained from NEP compared to the values obtained from DFT calculations for both the training and testing datasets of COF-1 and COF-5.

To assess the accuracy of the trained NEP model in describing the structures of considered 2D COFs in MD simulations, in Figure 3 we compared the radial distribution function (RDF) of COF-1 and COF-5 extracted from NEP-based MD and AIMD simulations at 300 K. A good agreement is observed between these two methods, indicating that the NEP model faithfully captures the structural characteristics of monolayer COF-1 and COF-5.

To further validate the precision of the NEP in evaluating the mechanical properties of COF-1 and COF-5, we applied the finite uniaxial and biaxial strain perturbations to monolayer COFs by altering their lattice constants at absolute zero, which were subsequently relaxed by using the NEP to minimize their energy. As a result, equations of state representing the energy evolution of structures with the changed lattice constants can be obtained. As shown in Figure 4, equations of state obtained from DFT calculations are identical to the results calculated by NEP models. We further employed the energy-strain method to calculate the elastic constants of COFs, which was implemented by VASPKIT.<sup>45</sup> In this method, the elastic stiffness tensor is derived from the second-order derivative of the energy change with respect to the applied

strain.<sup>48</sup> Since COF-1 and COF-5 considered here possess a 2D hexagonal structure, only three independent elastic constants, i.e.,  $C_{11}$ ,  $C_{12}$  and  $C_{66}$  were calculated. All components of the elastic stiffness tensor calculated from NEP models are summarized in Table 1, in comparison with the corresponding DFT results. As for all elastic constants of COF-1 and COF-5, the error between NEP and DFT results is within 2.6%. This good agreement demonstrates the accuracy of the trained NEP model in evaluating the elastic properties of considered 2D COFs.



**Figure 3.** RDFs of (a) COF-1 and (b) COF-5 calculated by using classical MD simulations at 300 K driven by DFT (solid lines) and NEP (dashed lines).



**Figure 4.** Energy changes of the primitive cell of (a) COF-1 and (b) COF-5 due to the uniaxial and biaxial strains, which were obtained by using both DFT and NEP calculations. The insets illustrate the corresponding loading conditions.

Elastic constant (GPa) –	COF-1		COF-5	
	NEP	DFT	NEP	DFT
$C_{11}$ –	88.3	90.2	57.2	57.4
$C_{12}$	71.9	73.4	49.6	50.9
$C_{66}$	8.2	8.4	3.8	3.8

**Table 1.** Elastic constants of COF-1 and COF-5 monolayers obtained from NEP models and DFT calculations.

#### Thermomechanical properties of monolayer COFs

Apart from the high computational cost, DFT calculations usually are only available for calculating the elastic constants of a material at the zero-temperature ground state, since the lattice structure of the material is considered to be in its most stable configuration at zero temperature and the influence of thermal fluctuations thus becomes ignorable. Nevertheless, as the temperature increases, atoms in a material vibrate more vigorously, resulting in the thermal expansion and changes in the mechanical properties of materials. Therefore, when studying the elastic properties of a material at finite temperatures, it becomes necessary to take some additional factors such as thermal effect and anharmonic contributions into account.<sup>49,50</sup>

In this study, we employed the strain-fluctuation method to calculate the elastic constants of COF-1 and COF-5 over a temperature range from 10 K to 500 K. Here, the interval is 10 K for the temperature increasing from 10 to 100 K, while it is 50 K for the temperature largely growing from 100 to 500 K. Figure 5 illustrates the variation in the elastic constants of  $C_{11}$ ,  $C_{12}$  and  $C_{66}$  with respect to the temperature. For COF-1, at temperatures below 70 K, a sharp decrease is observed in both  $C_{11}$  and  $C_{12}$  with growing temperature. Now,  $C_{11}$  and  $C_{12}$  of COF-1 decline from 88.3 to 14.1 GPa and 71.9 to 1.6 GPa, respectively, as the temperature increases from 0 to 70 K. In contrast, an extremely small change is observed in  $C_{66}$ , which only decreases from 8.2 to 6.1 GPa in this process. However, when the temperature becomes larger than 70 K, the elastic constants decrease slightly comparing to those at the temperature under 70 K. As shown in Figure 5a, when the temperature increases from 70 to 500 K,  $C_{11}$  and  $C_{12}$  of COF-1 changed from 14.1 to 5.0 GPa and from 1.6 to 1.48 GPa, respectively.

The similar trend is observed in the elastic constants of COF-5 at different temperatures.

As shown in Figure 5b,  $C_{11}$  and  $C_{12}$  of COF-5 decrease from 57.2 to 9.3 GPa and from 49.6 to 2.8 GPa, respectively, when the temperature increases from 0 to 40 K. In this process,  $C_{66}$  of COF-5 slightly decreases from 5.3 to 3.8 GPa. When the temperature further grows from 40 to 500 K, a decrease with much smaller rate is observed in  $C_{11}$ ,  $C_{12}$  and  $C_{66}$  of COF-5, which, specifically, decrease from 9.3 to 5.9 GPa, from 2.8 to 2.4 GPa and from 3.8 to 1.6 GPa, respectively. Based on the above findings, we come to the conclusion that the elastic constants of both COF-1 and COF-5 decrease as the temperature grows, but the sensitivity of the elastic constants to the temperature change is very different at the temperatures smaller or larger than a threshold, i.e., 70 K for COF-1 and 4 0K for COF-5. This result indicates there may exist different mechanisms for the thermally induced softening of 2D COFs at small and large temperatures, which will be explained in details later.



**Figure 5.** Elastic constants of (a) COF-1 and (b) COF-5 at different temperatures ranging from 0 to 500 K. Here, the hollow circles denote the results at 0 K extracted from DFT calculations.

Based on the obtained elastic constants, we can further calculate the Young's modulus E of monolayer COFs through the following formula:<sup>51</sup>

$$\frac{1}{E(\vec{a})} = \sum_{i,j,k,l=x,y} a_i a_j a_k a_l S_{ijkl}, \quad \vec{a} = \begin{pmatrix} \cos(\varphi) \\ \sin(\varphi) \\ 0 \end{pmatrix} \quad 0 \le \varphi \le 2\pi , \quad (3)$$

where  $S_{ijkl}$  is the full second-order compliance tensor as defined above,  $\vec{a}$  is the direction vector, and  $\varphi$  is the orientation angle in the plane.

It is worth noting that, like some other 2D materials with the similar hexagonal structures such as graphene, hexagonal-boron nitride (h-BN) and transition metal-dichalcogenide, the

present 2D COFs also possess two principal directions, i.e., zigzag and armchair directions as shown in Figure 1d. In order to study the dependence of the Young's modulus on the crystalline orientation, we specifically evaluated here E at zigzag and armchair directions by setting  $\varphi$  in Equation 3 as 0 and  $\pi/2$ , respectively. As for both COFs, the values of their E in zigzag and armchair directions almost coincide with each other, irrespective of the temperature (see Figure 6). This result, to some extent, indicates the elastic isotropy of the monolayer COFs considered here. Moreover, Figure 6 also indicates that the Young's modulus of COF-1 is generally much larger than that of COF-5, since COF-1 is much denser. In terms of the thermal effect, its effect on the Young's modulus is exactly similar to that on the above elastic constants. Specifically, when the temperature is smaller than the critical value (70 K for COF-1 and 40 K for COF-5), the Young's moduli of COF-1 and COF-5 decrease from 29.7 GPa and 16.0 GPa to 11.0 GPa and 8.4 GPa, respectively. However, when the temperature is larger than the critical values, the Young's modulus becomes less sensitive to the temperature change though it similarly decreases as the temperature grows. For instance, as the temperature further increases from the critical temperatures (70 K for COF-1 and 40 K for COF-5) to 500 K, the Young's moduli of COF-1 and COF-5 are reduced by only 35.5% and 40.0%, respectively.

A comparison of the Young's modulus of the present 2D COFs to the values of some other representative 2D materials with the similar planar structure such as graphene<sup>36</sup> and h-BN<sup>52</sup> is illustrated in Table 2. In line with the method employed here, the Young's moduli of monolayer graphene and h-BN shown here were similarly extracted from the strain-fluctuation method. As shown in Table 2, whether at the ground state (0 K) or at the room temperature (300 K), the Young's modulus of 2D COFs is much lower than that of graphene and h-BN, denoting the high flexibility of the present 2D COFs.



**Figure 6.** Young's moduli in the armchair and zigzag directions of (a) COF-1 and (b) COF-5 at different temperatures ranging from 0 to 500 K.

**Table 2.** A comparison of the Young's modulus of the present 2D COFs to the values of some other 2D materials including graphene<sup>36</sup> and h-BN.<sup>52</sup>

Matarial	Young's modulus (GPa)			
	0 K	300 K		
Graphene <sup>36</sup>	939	424		
h-BN <sup>52</sup>	723	180		
COF-1 (present)	30	16		
COF-5 (present)	16	8		

#### Mechanism of the thermomechanical behaviors

Since the elastic properties of 2D materials are usually related to their configurations, taking COF-1 monolayer as an example, we illustrate their structures at two representative temperatures i.e., 10 K and 200 K to explain the significant thermomechanical behaviors observed in 2D COFs below a critical temperature (70 K for COF-1). It can be seen from Figure 7a and 7b that the serious thermal rippling exists in COF-1 at the temperature of 200 K, while COF-1 at the temperature of 10 K almost retains its original flatness configuration. Thus, as sketched in Figure 7c, the elongation of monolayer COFs at relatively low temperatures is equivalently resisted by the in-plane tensile stiffness, since it exhibits the planner configuration. However, as the temperature becomes larger, the de-rippling of the thermally rippled COFs by bending dominates their elongation now (Figure 7d). As a monolayer material with atomic

thickness, monolayer COFs usually possess extremely small bending stiffnesses. Thus, the thermally induced serious thermal rippling at a relatively large temperature is responsible for the reduction in the elastic constants of monolayer COFs at high temperatures. Actually, many previous MD simulation studies have pointed out that the out-of-plane thermal rippling in 2D materials exerts a notable influence on their elastic moduli.<sup>36,53</sup>



**Figure 7.** Configurations of COF-1 at the temperatures of (a) 10 K and (b) 200 K. Here, the contour illustrates the out-of-plane deformation. (c, d) Corresponding equivalent mechanical models of COF-1 at the temperatures of 10 K and 200 K. The planner COF is represented by an extension spring with the stiffness of  $K_1$ , while the rippled COF is represented by a torsion spring with the stiffness of  $K_2$ .

To better quantitatively measure the out-of-plane displacement of monolayer COFs caused by the thermal rippling at different temperatures, we calculated the time-averaged RMS displacement  $\bar{h}$  by using the following equation:

$$\overline{h} = \sqrt{\left(\sum_{i=1}^{N} \frac{w_i^2}{N}\right)_t},\tag{4}$$

where *N* is the total number of atoms and  $w_i$  is the out-of-plane displacement of the *i*-th atom. The RMS displacement together with the corresponding configurations of both COF-1 and COF-5 at temperatures of 10, 50 and 200 K are shown in Figure 8. The results of the structures at some other temperatures are presented in Figures S3 and S4. The results illustrate that as the temperature increases, both monolayer COF materials exhibit the similarly noticeable increase in the out-of-plane fluctuations. To further compare and analyze the out-of-plane fluctuations of COF-1 and COF-5, Figure 9 offers a detailed depiction of their RMS displacements over a temperature range from 10 K to 500 K. The results consistently demonstrate that the degree of thermal rippling also correspondingly increases as the temperature rises within the temperature range considered in our MD simulations. Moreover, when the temperature is lower than 100 K, the RMS displacement of COF-1 is smaller than that of COF-5. As the temperature increases larger than 100 K, the RMS displacement of COF-1 turns to inversely become larger than that of COF-5.



**Figure 8.** Configurations of (a) COF-1 and (b) COF-5 at different temperatures. Here, the contour illustrates the out-of-plane deformation of COFs.



**Figure 9.** RMS amplitudes of the thermal rippling of COF-1 and COF-5 at different temperatures ranging from 10 to 500 K. Here, the lines correspond to the results fitted by the model developed by the statistical mechanics and thermodynamics.

For a better understanding of the thermal rippling, we simplified the monolayer COF as a continuum 2D membrane. At a finite temperature, the membrane without any external forces can be fluctuated with both in-plane and out-of-plane modes. The RMS amplitude of the out-of-plane fluctuation  $\overline{h}$  of COFs below the critical temperature can be calculated according to the statistical mechanical analysis, which has the following expression:<sup>53</sup>

$$\overline{h} = \sqrt{\frac{L_0^2 k_{\rm B} T \gamma_n}{16 \pi^4 D}} \quad , \tag{5}$$

where  $L_0$  represents the size of monolayer COFs, D denotes the bending stiffness and  $\gamma_n$  is a dimensionless coefficient. We employed the above formula to fit the RMS displacements extracted from MD simulations. As illustrated by the solid lines in Figure 9, the theoretical model can well fit the MD simulation results below the critical temperature (40 K for COF-5 and 70 K for COF-1), which, to some extent, confirms that the rippling of monolayer COFs is indeed induced by the thermal fluctuation. Specifically, the fitting formula is  $\bar{h} = 0.22\sqrt{T}$  for COF-1 and  $\bar{h} = 0.29\sqrt{T}$  for COF-5. It is noted that the difference of fitting coefficients of COF-1 and COF-5 is due to their different bending stiffnesses, since both COFs considered in MD simulations have the similar dimension. Theoretically, COF-1 monolayer is expected to have a higher bending stiffness compared to COF-5 monolayer, since COF-1 monolayer possesses a

much denser structure.

We further extended the above theories to explain the thermally induced softening of the Young's modulus of 2D COFs below the critical temperature, since the out-of-plane fluctuation now plays a dominant role in determining the elastic behaviors of 2D COFs.<sup>53,54</sup> According to the statistical mechanics and thermodynamics, the Young's modulus of monolayer COFs below the critical temperature can be expressed by the following formula:

$$E = E^* - \frac{E^* k_{\rm B} T}{16\pi D} \left( \frac{4\pi^2 D}{E^* L_0^2} + \varepsilon_0 \right)^{-1}, \qquad (6)$$

where  $E^*$  is the Young's modulus at the ground state and  $\varepsilon_0$  represents the residual strain. In our calculations, the moduli in two principal directions were averaged for the Young's modulus of both COF materials. As depicted in Figure 6, the dependence of the Young's modulus on the temperature below the critical temperature can be well fitted by the theoretical model of Equation 6 for both 2D COFs. Remarkably, values of  $E^*$  extracted from the curve fitting agree well with the results directly obtained from MD simulations.

Based on the analyses presented herein, the reduction in the elastic modulus of 2D COFs at relatively lower temperatures can be attributed to the synergistic interplay of the thermal rippling phenomenon and the well-established harmonic vibrations. The earlier theoretical investigation focusing on the flexible membranes beyond the harmonic approximation has elucidated the noteworthy influence arising from the anharmonic coupling between bending and stretching modes. This coupling effectively mitigates the impact of out-of-plane thermal fluctuations on the elastic modulus, thereby attenuating the observed softening effect.<sup>53,55</sup> In the current study, we conducted a parallel analysis to assess the impact of anharmonic forces across different temperature regimes. Specifically, we computed the Grüneisen parameter for COF-1 and COF-5, a parameter that furnishes insights into their underlying anharmonic interactions.<sup>56</sup> The Grüneisen parameter can be mathematically expressed as:<sup>57,58</sup>

$$\gamma = \frac{3\alpha B V_{\rm m}}{C_{\rm v}},\tag{7}$$

where  $\alpha$  is the linear thermal expansion coefficient, *B* is the bulk modulus,  $V_{\rm m}$  is the molar volume, and  $C_{\rm v}$  is the isometric heat capacity. Based on the values of  $\alpha$ , *B* and  $C_{\rm v}$  evaluated from NEP-based MD simulations, in Figure 10 we display the Grüneisen parameters for COF-

1 and COF-5 at different temperatures. It is found that at a relatively small temperature below the critical value, the Grüneisen parameter of 2D COFs is negative with a large magnitude. Usually, the negative Grüneisen parameter of ZA modes is due to the membrane effect.<sup>59</sup> At low temperatures, only low-frequency out-of-plane acoustic modes will be excited, while the high frequency optic modes with positive Grüneisen parameters are frozen. Thus, the out-of-plane thermal fluctuations should have the dominant effect on the thermomechanical behaviors of 2D COFs below the critical temperature. As the temperature increases, the magnitude of the Grüneisen parameters is found to significantly decrease and tend to a stable value close to zero, indicating that other high-frequency modes are get excited and dominate the thermomechanical behaviors now. Thus, above the critical temperature, the relationship between the Young's modulus and the temperature can be described by the well-known Wachtman relationship:<sup>55,59</sup>

$$E = E_0 - BT \exp\left(\frac{-T_0}{T}\right),\tag{8}$$

where  $E_0$  is the Young's modulus at absolute zero when the effect of out-of-plane fluctuations is excluded, B and  $T_0$  are arbitrary constants. As shown in Figure 6, the relationship between the Young's moduli of both 2D COFs and the temperature indeed can be well fitted by the Wachtman's equation above the critical temperatures. Moreover, after the curve fitting,  $T_0$  was found to be approximately 0.1 K. Thus, considering  $T >> T_0$ , Equation 7 can be simplified into  $E = E_0 + BT_0 - BT$ , which further proves a linear relationship between the Young's modulus and the temperature above the critical temperature as observed in MD simulations.



Figure 10. Calculated temperature-dependent Grüneisen parameter for COF-1 and COF-5.

#### **Summary and Conclusions**

In summary, we have developed an NEP model-based MLP for accurately evaluating the mechanical properties of two classical 2D COFs (monolayer COF-1 and COF-5). Through comparing with the results obtained from DFT calculations, the MLP trained here was proven to have the capability to enable one to study the elastic behaviors of monolayer COFs with the greatly improved computational efficiency and high accuracy. Thus, the trained MLP was further employed in MD simulations to calculate the elastic constants of monolayer COFs with relatively large sizes and at high temperatures, implemented by the strain-fluctuation method. An elastic isotropy was observed in both COF-1 and COF-5, irrespective of the temperature. However, the elastic constants of both COF monolayers are significantly dependent on the temperature, which are found to decrease as the temperature grows. Moreover, the temperature sensitivity of elastic constants is found to decrease after a critical temperature, e.g., ~70 K for COF-1 and ~40 K for COF-5, as different thermomechanical mechanisms dominate before and after the critical temperature. Specifically, the thermomechanical behaviors are ascribed to the thermal rippling effect before the critical temperature, while they are mainly dominated by the damping effect of anharmonic vibrations after the critical temperature. Based on these mechanisms, two analytical models were also proposed for the temperature dependence of elastic constants before and after the critical temperature, which were found to fit the MD simulation results well. The present study not only offers a precise potential for describing the thermomechanical behaviors of monolayer COFs but also provides valuable insights into the elastic properties of 2D COFs in realistic situations.

## ASSOCIATED CONTENT

The source code and documentation for gpumd are available at https://github.com/brucefan1983/GPUMD, respectively. The training and testing results for the NEP models are freely available at https://github.com/bing93wang/COF-NEP/.

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