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First-principles finite-temperature study of polyethylene using stochastic self consistent harmonic approximation

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1. Background

Understanding finite-temperature properties of materials from first-principles is essential for predicting their structural, vibrational, and thermodynamic behavior.¹⁾ While density functional theory (DFT) has become a powerful tool for describing materials at the atomic scale, accurate treatment of finite-temperature effects remains challenging because thermal fluctuations and anharmonic interactions are often beyond the harmonic approximation. The quasi-harmonic approximation (QHA) provides a practical approach by incorporating volume-dependent phonon contributions to the free energy;²⁾ however, it neglects explicit anharmonic effects arising from the interaction between vibrational modes.

The stochastic self-consistent harmonic approximation (SSCHA) provides a framework to include anharmonic effects in finite-temperature simulations by optimizing a temperature-dependent auxiliary force-constant.³⁾ Unlike QHA, SSCHA accounts for anharmonic renormalization of vibrational modes and allows the exploration of temperature-dependent potential energy landscapes. Recent developments have demonstrated the capability of SSCHA to describe complex anharmonic phenomena, including phonon renormalization, thermal expansion, and structural instabilities. However, the computational cost of SSCHA remains significant because it requires extensive sampling of atomic configurations and evaluation of forces and energies for many displaced structures.

Machine-learning interatomic potentials (MLPs) provide an efficient solution to this

limitation by reproducing the accuracy of first-principles calculations while enabling large-scale sampling of the potential energy surface. By combining MLPs with advanced electronic-structure methods, it becomes possible to perform finite-temperature simulations with near first-principles accuracy at a computational cost suitable for extensive thermodynamic calculations.

In this work, we demonstrate the application of SSCHA for investigating the finite-temperature properties of crystalline polyethylene (PE) using a MLP trained on the meta-generalized gradient approximation Strongly Constrained and Appropriately Normed (r²SCAN) functional. Polyethylene provides an ideal test system because its structural and vibrational properties are strongly influenced by weak intermolecular interactions and anharmonic effects. We examine the temperature-dependent free-energy landscape and vibrational properties obtained from SSCHA simulations.

2. Computational methods

The MLP used in this work is based on the message passing neural network interatomic potential implemented in NequIP.⁴⁾ It was trained with r²SCAN energy and atomic forces of 2500 configurations. Evaluated on an independent test data, the model give

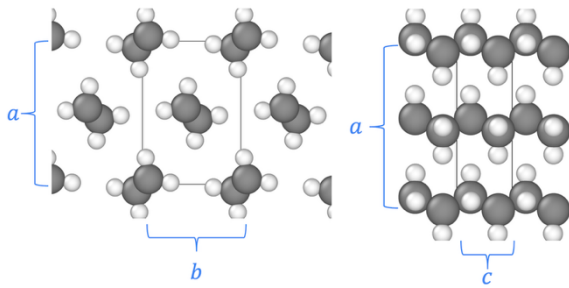


Figure 1 PE crystal structure.

a generalization error of 0.22 eV/atom and 25 meV/Å which are sufficiently small compared to the range of energy and forces sampling during SSCHA calculations.

The SSCHA calculations were performed using the Python-SSCHA package. We have used $2 \times 2 \times 4$ PE supercell throughout our simulations. The SSCHA free energy calculation was performed at 0, 100, 200, and 300 K using 1000 configurations. We have used Vinet equation of state to get the equilibrium PE lattice parameters.

3. Result and discussion

3.1. Free energy profile

Crystalline polyethylene adopts an orthorhombic structure, as illustrated in Figure 1. The crystal is characterized by three lattice parameters, a , b , and c where the c -axis is parallel to the polymer chains, while the a - and b -axes describe the intermolecular packing perpendicular to the chain direction.⁵⁾ Owing to the anisotropic nature of the crystal, the intermolecular interactions along the a and b directions are considerably weaker than the covalent bonding along the polymer backbone. Consequently, the temperature dependence of the free energy and vibrational properties is expected to differ among the three lattice directions.

Figure 2 shows the PE free energy profile at different temperature for a , b , and c lattice. The equilibrium structure at each temperature was determined from the minimum of the free-energy curve. At 0 K, the free-energy profiles exhibit well-

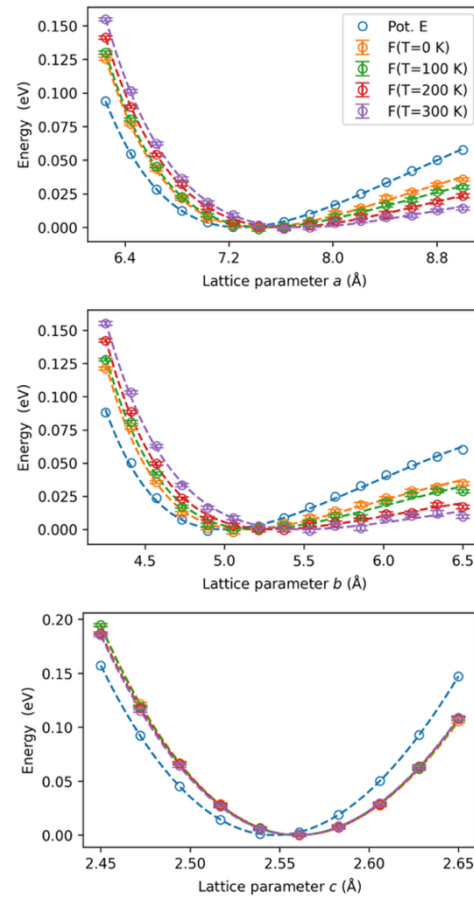


Figure 2: PE free energy profile along a , b , and c lattice.

The dashed lines show the equation of state interpolation. The error bars of free energy show the SSCHA statistical error.

defined minima along all three lattice directions, corresponding to the stable equilibrium structure of polyethylene. The positions of these minima are slightly different from those obtained from the static potential energy surface, demonstrating that vibrational contributions play an important role even at low temperatures.

Compared with the potential energy curves, the free-energy profiles show a smoother dependence on the lattice parameters. This behavior originates from the vibrational contribution to the free energy, which incorporates the effects of atomic fluctuations around the equilibrium structure. As temperature increases, the vibrational contribution becomes increasingly significant and modifies the shape of the free-energy landscape. In particular, the minima become broader

and the curvature around the equilibrium position decreases, indicating a softer free-energy surface at elevated temperatures.

The temperature-induced shift of the free-energy minimum directly reflects thermal expansion. As the temperature increases, the equilibrium lattice parameters move toward larger values because the balance between the static energy and vibrational free-energy contributions changes. Therefore, the thermal expansion behavior can be understood as a consequence of the temperature-dependent evolution of the free-energy landscape.⁶⁾

At higher temperatures, the reduced curvature around the minimum indicates increased structural flexibility and enhanced thermal fluctuations. Such flattening of the free-energy landscape is expected to become increasingly important when approaching structural transformations or melting, where the stability of the crystalline phase is reduced. Although the present analysis focuses on the crystalline phase and does not directly determine the melting transition, the temperature-dependent free-energy landscape provides important insight into the changing stability of the structure under thermal excitation.

The smooth free-energy profiles obtained from the MLP potential demonstrate its capability to reproduce the first-principles-level energy landscape while enabling extensive finite-temperature sampling. These results establish a foundation for further investigation of thermal expansion, vibrational properties, and anharmonic effects in polyethylene using the SSCHA framework.

3.2. Temperature-dependent vibration

Figure 3 compares the SSCHA phonon dispersions of crystalline polyethylene at 0 and 300 K. The overall topology of the phonon spectrum is preserved upon heating, and no imaginary phonon frequencies are observed throughout the Brillouin zone. This confirms that the crystalline phase remains dynamically stable

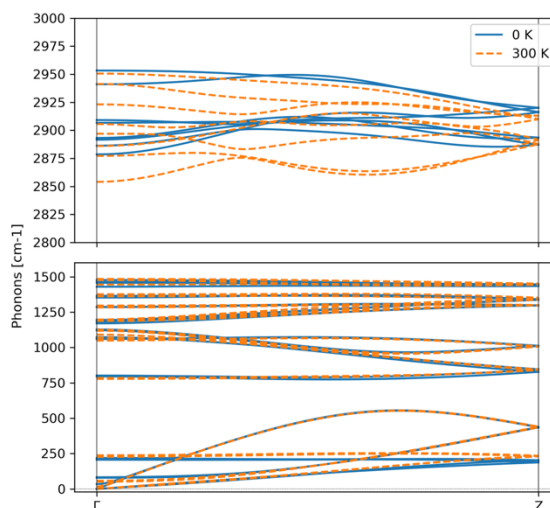


Figure 3: SSCHA auxiliary phonon dispersion of PE at 0 and 300 K.

at 300 K, while finite-temperature effects primarily manifest as the renormalization of phonon frequencies rather than qualitative changes in the vibrational spectrum.⁷⁾

The most pronounced temperature dependence is found in the low-frequency region below approximately 250 cm^{-1} . Several acoustic and low-energy optical branches exhibit appreciable frequency shifts together with changes in their dispersion. These modes correspond predominantly to collective molecular motions governed by relatively weak intermolecular van der Waals interactions. Consequently, they are particularly sensitive to thermal expansion and anharmonic lattice vibrations, making them the primary contributors to the temperature dependence of the vibrational free energy.

Noticeable phonon renormalization is also observed in the high-frequency C—H stretching region between approximately 2850 and 2950 cm^{-1} . Several stretching branches soften with increasing temperature, while their overall dispersion is preserved. The observed shifts originate from the anharmonicity of the C—H stretching potential and the coupling between intramolecular vibrations and thermally expanded crystal structures. Although the covalent C—H bonds remain intact, finite-temperature anharmonic effects

produce measurable changes in their vibrational frequencies.

In comparison, the intermediate-frequency modes between approximately 800 and 1500 cm^{-1} exhibit relatively smaller temperature-induced changes. These modes, which are mainly associated with C—C skeletal vibrations together with CH_2 bending, wagging, and twisting motions, retain nearly the same dispersion throughout the Brillouin zone. The smaller renormalization indicates that these intramolecular vibrations are less sensitive to thermal fluctuations than the low-frequency intermolecular modes.

The mode-dependent phonon renormalization illustrates the importance of explicitly including anharmonic effects in finite-temperature vibrational calculations. While the overall vibrational spectrum remains qualitatively unchanged, the selective shifts of both the low-frequency intermolecular modes and the high-frequency C—H stretching modes contribute to the temperature-dependent vibrational free energy. These results demonstrate that the SSCHA framework captures finite-temperature phonon renormalization while maintaining the dynamical stability of crystalline polyethylene.

4. Conclusion

In this work, we demonstrated the application of the SSCHA for investigating the finite-temperature properties of crystalline polyethylene using a machine-learning interatomic potential trained on the $r^2\text{SCAN}$ functional. The calculated free-energy profiles provide a direct description of the temperature-dependent equilibrium structure and illustrate the origin of thermal expansion through the evolution of the free-energy landscape. Furthermore, the temperature-dependent phonon dispersions reveal mode-selective anharmonic renormalization while confirming the dynamical stability of the crystal up to 300 K. These results demonstrate that the combination of SSCHA and machine-learning potentials provides an efficient

and accurate framework for first-principles finite-temperature simulations of molecular crystals, enabling large-scale anharmonic calculations that would otherwise be computationally prohibitive.

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