

Highly efficient path-integral molecular dynamics simulations with GPUMD using neuroevolution potentials: Case studies on thermal properties of materials

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Path-integral molecular dynamics (PIMD) simulations are crucial for accurately capturing nuclear quantum effects in materials. However, their computational intensity and reliance on multiple software packages often limit their applicability at large scales. Here, we present an integration of PIMD methods, including thermostatted ring-polymer molecular dynamics (TRPMD), into the open-source GPUMD package, combined with highly accurate and efficient machine-learned neuroevolution potential (NEP) models. This approach achieves almost the accuracy of first-principles calculations with the computational efficiency of empirical potentials, enabling large-scale atomistic simulations that incorporate nuclear quantum effects. We demonstrate the efficacy of the combined NEP-PIMD approach by examining various thermal properties of diverse materials, including lithium hydride (LiH), three porous metal-organic frameworks (MOFs), liquid water, and elemental aluminum. For LiH, our NEP-PIMD simulations successfully capture the isotope effect, reproducing the experimentally observed dependence of the lattice parameter on the reduced mass. For MOFs, our results reveal that achieving good agreement with experimental data requires consideration of both nuclear quantum effects and dispersive interactions. For water, our PIMD simulations capture the significant impact of nuclear quantum effects on its microscopic structure. For aluminum, the TRPMD method effectively captures thermal expansion and phonon properties, aligning well with quantum mechanical predictions. This efficient NEP-PIMD approach opens new avenues for exploring complex material properties influenced by nuclear quantum effects, with potential applications across a broad range of materials.

I. INTRODUCTION

Since Rahman’s pioneering work in 1964 [1], molecular dynamics (MD) simulations have been playing a central role in modeling physical and chemical properties of matter. Two essential components of MD simulations are the interatomic potential and the integrator, both of which can be treated classically or quantum-mechanically. When it comes to describing the interatomic interactions, classical empirical models usually lack the required accuracy, while first-principles methods such as quantum-mechanical density functional theory (DFT) calculations have been the standard when the ac-

curacy in force calculations is crucial, despite being computationally very demanding. In recent years, the situation has improved with the advent of machine-learned potentials (MLPs) or force fields [2] that can achieve nearly quantum-mechanical accuracy with orders of magnitude enhancement on the computational efficiency over DFT calculations. With respect to integrators, there are classical ones based on classical statistical mechanics, leading to classical MD, as well as quantum-mechanical ones based on path-integral statistical mechanics [3], leading to path integral molecular dynamics (PIMD) [4]. PIMD can account for nuclear quantum effects (NQEs) [5] by employing multiple replicas for each atom, which substantially increases computational cost.

Due to the improved computational efficiency of MLPs over DFT calculations, MLP-PIMD simulations have gained popularity for studying materials with notable NQEs, particularly in water [6–14]. These previous studies often used separate packages for force calculation and integration, typically combining the LAMMPS package [15]

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with a MLP model for forces and the I-PI package [16–18] for PIMD integration and sampling. Although this modular approach is flexible, it can lead to suboptimal computational performance due to the overhead of interfacing different software packages.

In this study, we implement and benchmark an integrated MLP-PIMD approach within the GPUMD package [19], leveraging the highly efficient neuroevolution potential (NEP) approach [20–23]. NEP models have demonstrated extremely high computational efficiency comparable to typical empirical force fields [24–26] and have been employed to study physical properties that require extensive spatiotemporal sampling, such as fracture [27, 28], thermal transport [24, 25, 29–33], and phase transitions [34–37] as well as nucleation processes [38], among others [13, 26, 39, 40]. By integrating PIMD methods directly into the GPUMD package, we introduce the NEP-PIMD approach, a highly efficient computational tool capable of capturing both accurate interatomic forces and NQEs.

To demonstrate the effectiveness of the NEP-PIMD approach, we investigate thermal expansion and related properties in materials with strong NQEs, including crystalline lithium hydride (LiH), three different metal-organic frameworks (MOFs), liquid water, and elemental aluminum. LiH is ideal for exploring the isotope effect [41, 42], with experimental data available for isotope-dependent lattice parameters [43, 44]. For MOFs, experimental studies [45–53] show complex thermal expansion behavior, with both positive and negative coefficients. To our knowledge, theoretical investigations of MOFs thermal expansion using PIMD are limited, with only one study [54] based on an empirical force field. Water is a prototypical material for studying NQEs on the microscopic structure of a condensed system in the liquid phase. Aluminum is particularly well-suited for investigating quantum dynamics in the form of phonon properties, as it can be accurately described using low-order perturbation theory at low temperatures, providing a suitable reference for results obtained through thermostatted ring-polymer molecular dynamics (TRPMD). Leveraging our highly efficient NEP-PIMD approach, we systematically investigate the convergence of results with respect to the number of replicas in large-scale PIMD simulations, which effectively capture NQEs. Our approach paves the way for accurate and efficient large-scale modeling of materials with NQEs using PIMD.

II. METHODS AND MODELS

A. Path-integral molecular dynamics implemented in GPUMD

1. PIMD integration algorithms

PIMD is an MD method based on the path-integral formulation of quantum mechanics [3], as first proposed

by Parrinello and Rahman [4]. The crucial observation for deriving PIMD is that the quantum partition function for N particles can be approximately cast to a classical partition function of NP ($P \rightarrow \infty$) particles with the following Hamiltonian:

$$H_P = H_P^0 + U_P,$$

where

$$H_P^0 = \sum_{i=1}^N \sum_{j=1}^P \left[\frac{m_i \omega_P^2 (\mathbf{r}_j^{(i)} - \mathbf{r}_{j+1}^{(i)})^2}{2} + \frac{[\mathbf{p}_j^{(i)}]^2}{2m_i'} \right] \quad (1)$$

and

$$U_P = \sum_{j=1}^P U(\mathbf{r}_j^{(1)}, \mathbf{r}_j^{(2)}, \dots, \mathbf{r}_j^{(N)}). \quad (2)$$

That is, each quantum (physical) particle (indexed by i) is represented as a collection of P classical particles (replicas, indexed by j). For each i we have $\mathbf{r}_1^{(i)} = \mathbf{r}_{P+1}^{(i)}$, and the relevant interaction terms in Eq. (1) represent a ring of replicas connected by springs with frequency $\omega_P = k_B T P / \hbar$. Therefore, each physical particle is approximated by a “ring polymer” with P “beads”. Each of the P replicas of the N physical particles is still governed by the potential function U of the system, as can be seen from Eq. (2). While the mass m_i' in the kinetic energy terms is not necessarily the physical mass m_i , we follow the convention [4] of taking them to be equal.

From the Hamiltonian, one can derive equations of motion and derive integration algorithms. For simplicity, we follow the work of Cerriotti *et al.* [55] to present the algorithms in terms of a single one-dimensional physical particle, with mass m , position q , and momentum p . First, we consider the free ring polymer consisting of P beads with the Hamiltonian:

$$H_P^0 = \sum_{j=1}^P \left(\frac{p_j^2}{2m} + \frac{1}{2} m \omega_P^2 (q_j - q_{j+1})^2 \right).$$

Next, we define the following transform ($k = 0$ to $P-1$): [55]

$$\tilde{q}_k = \sum_{j=1}^P q_j C_{jk}, \quad (3)$$

$$\tilde{p}_k = \sum_{j=1}^P p_j C_{jk}, \quad (4)$$

where

$$C_{jk} = \begin{cases} \frac{1}{\sqrt{P}} & (k = 0) \\ \sqrt{2/P} \cos(2\pi jk/P) & (1 \leq k \leq P/2 - 1) \\ \frac{1}{\sqrt{P}} (-1)^j & (k = P/2) \\ \sqrt{2/P} \sin(2\pi jk/P) & (P/2 + 1 \leq k \leq P - 1). \end{cases}$$

This leads to a representation of the free ring-polymer Hamiltonian in terms of uncoupled harmonic oscillators:

$$H_P^0 = \sum_{k=0}^{P-1} \left(\frac{\tilde{p}_k^2}{2m} + \frac{1}{2} m \omega_k^2 \tilde{q}_k^2 \right),$$

where

$$\omega_k = 2\omega_P \sin(k\pi/P).$$

This set of equations of motion can be integrated for one time step Δt as follows [55]:

$$\begin{aligned} \tilde{p}_k &\leftarrow \cos(\omega_k \Delta t) \tilde{p}_k - m \omega_k \sin(\omega_k \Delta t) \tilde{q}_k, \\ \tilde{q}_k &\leftarrow \frac{1}{m \omega_k} \sin(\omega_k \Delta t) \tilde{p}_k + \cos(\omega_k \Delta t) \tilde{q}_k. \end{aligned}$$

Korol *et al.* [56] applied the Cayley transform to construct a more robust algorithm:

$$\tilde{p}_k \leftarrow \frac{1 - (\omega_k \Delta t / 2)^2}{1 + (\omega_k \Delta t / 2)^2} \tilde{p}_k - m \omega_k \frac{\omega_k \Delta t}{1 + (\omega_k \Delta t / 2)^2} \tilde{q}_k, \quad (5)$$

$$\tilde{q}_k \leftarrow \frac{1}{m \omega_k} \frac{\omega_k \Delta t}{1 + (\omega_k \Delta t / 2)^2} \tilde{p}_k + \frac{1 - (\omega_k \Delta t / 2)^2}{1 + (\omega_k \Delta t / 2)^2} \tilde{q}_k. \quad (6)$$

After integration, we can change the normal mode variables back to the original ones:

$$q_j = \sum_{k=0}^{P-1} \tilde{q}_k C_{kj}, \quad (7)$$

$$p_j = \sum_{k=0}^{P-1} \tilde{p}_k C_{kj}. \quad (8)$$

The above integration algorithm is for free ring polymers. To enable extension to interacting systems, the bead momenta need to be updated before and after the above set of operations, as follows:

$$p_j \leftarrow p_j - \frac{\partial U}{\partial q_j} \frac{\Delta t}{2}. \quad (9)$$

To thermostat the beads, both the Langevin-type thermostat [55] and the massive Nosé-Hoover chain thermostat [57] have been used. When using the Langevin-type thermostat, the integration over the bead momenta should be applied before and after the non-thermostatted operations as follows:

$$\tilde{p}_k \leftarrow \sum_{j=1}^P p_j C_{jk}, \quad (10)$$

$$\tilde{p}_k \leftarrow c_{1k} \tilde{p}_k + \sqrt{\frac{m}{\beta P}} c_{2k} \xi_k, \quad (11)$$

$$p_j \leftarrow \sum_{k=0}^{P-1} C_{jk} \tilde{p}_k. \quad (12)$$

Here ξ_k are normally distributed random numbers with zero mean and unit variance, $c_{1k} = e^{-(\Delta t/2)\gamma_k}$, $c_{2k} = \sqrt{1 - (c_{1k})^2}$, $\gamma_0 = 1/\tau_T$, and $\gamma_k = \omega_k$ ($k > 0$).

The time parameter τ_T is an input chosen for the centroid ($k = 0$) mode. When all the bead modes are thermostatted, the algorithm is known as PIMD. Without thermostating, the algorithm is known as ring-polymer molecular dynamics (RPMD), which has been proposed as a method for approximating time-correlation functions [58, 59]. If only the internal bead modes ($k > 0$) are thermostatted, the algorithm is known as TRPMD [60].

The above algorithms can be easily extended to multi-particle systems in three dimensions. The potential energy of the system can be evaluated by averaging over the replicas, while the kinetic energy can be more conveniently calculated using the virial estimate [57]:

$$K = \frac{3}{2} N k_B T - \frac{1}{2} \sum_{i=1}^N \frac{1}{P} \sum_{j=1}^P \left(\mathbf{r}_j^{(i)} - \mathbf{r}_c^{(i)} \right) \cdot \mathbf{F}_j^{(i)}.$$

Here,

$$\mathbf{r}_c^{(i)} = \frac{1}{P} \sum_{j=1}^P \mathbf{r}_j^{(i)}$$

is the centroid position of atom i , for which periodic boundary conditions should be taken into account. The force $\mathbf{F}_j^{(i)}$ is defined as

$$\mathbf{F}_j^{(i)} = - \frac{\partial}{\partial \mathbf{r}_j^{(i)}} U \left(\mathbf{r}_j^{(1)}, \mathbf{r}_j^{(2)}, \dots, \mathbf{r}_j^{(N)} \right).$$

The rank-2 virial tensor is calculated in a similar manner:

$$\mathbf{W} = - \sum_{i=1}^N \frac{1}{P} \sum_{j=1}^P \left(\mathbf{r}_j^{(i)} - \mathbf{r}_c^{(i)} \right) \otimes \mathbf{F}_j^{(i)} + \sum_{i=1}^N \frac{1}{P} \sum_{j=1}^P \mathbf{W}_k^{(i)}.$$

Here, $\mathbf{W}_k^{(i)}$ is the per-atom virial tensor for the k -th replica of the i -th atom as calculated from the potential, which has been derived explicitly for NEP [20, 22]. The pressure tensor is then calculated as

$$\mathbf{P} = \frac{N k_B T + \mathbf{W}}{V}, \quad (13)$$

where V is the volume of the system.

The algorithms presented above have been implemented into the open-source GPUMD package [19] during the course of this study. The implementation is fully on graphics processing units (GPU) using CUDA programming, with minimal data transfer between GPU and the host. The overall computational workflow of our implementation is as follows.

1. Preparation.

- (a) Allocate GPU memory for the bead variables, such as position, velocity, potential energy, force, and virial. There are P sets of these variables.

- (b) Pre-compute the transformation matrix C_{jk} and store the data in GPU memory.
- (c) Initialize the pseudo random number generator and the seeds based on the cuRAND library in CUDA.

2. Iterate the integration loop.

- (a) In the case of PIMD and TRPMD, apply the Langevin thermostat according to Eqs. (10) to (12). In TRPMD, only the non-centroid modes (internal bead modes) are thermostated.
- (b) Update velocities according to Eq. (9), for half time step $\Delta t/2$.
- (c) Update positions and velocities for the free ring-polymer system.
 - i. Transform to normal modes according to Eqs. (3) and (4).
 - ii. Perform the time stepping for the normal mode variables according to Eqs. (5) and (6).
 - iii. Transform back from normal modes according to Eqs. (7) and (8).
- (d) Calculate forces according to the updated bead positions.
- (e) Update velocities according to Eq. (9), for the half time step $\Delta t/2$.
- (f) When required, control the pressure using a Berendsen-like algorithm [61], with the instant pressure calculated according to Eq. (13). Although this algorithm does not lead to a true isothermal-isobaric ensemble, it is sufficient for accurately determining the average simulation cell dimensions.

B. Phonon properties from TRPMD

To showcase the application of the implemented TRPMD method, we examine the variations in phonon frequencies and phonon damping parameters in aluminum as a function of temperature. Phonon properties are derived from atomic velocities sampled during TRPMD simulations. Specifically, the velocities are used to compute the phonon spectral energy density (SED) with the Python package DYNASOR [62]. The SED is a measure of how the kinetic energy of the system is distributed over the different phonon modes making it closely related to the phonon dispersion. It can be obtained by defining $q_j^{\mu\alpha}(\mathbf{q}, t)$ as the contribution to the j -th normal coordinate coming from the displacement $u_{n\mu}^\alpha$ of the μ -th atom in Cartesian direction α , i.e.,

$$q_j^{\mu\alpha}(\mathbf{q}, t) = \frac{1}{\sqrt{N}} \sum_n \sqrt{m_\mu} u_{n\mu}^\alpha(\mathbf{q}, t) A_{\mu j}^{\alpha*}(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{R}_n^0}.$$

Here, n ranges from 1 to N , where N is the total number of unit cells in the crystal, m_μ represents the mass of the μ -th atom, $A_{\mu j}^{\alpha*}(\mathbf{q})$ is the complex conjugate of the vibrational eigenvector, and \mathbf{R}_n^0 denotes the position of the n -th unit cell relative to the origin.

The average kinetic energy of phonon mode j can be expressed as a time average in terms of $q_j^{\mu\alpha}(\mathbf{q}, t)$ [63]

$$\begin{aligned} \bar{\mathcal{T}}_j &= \sum_{\mu\alpha} \lim_{\tau_0 \rightarrow \infty} \frac{1}{\tau_0} \int_0^{\tau_0} \frac{1}{2} \dot{q}_j^{\mu\alpha*}(\mathbf{q}, t) \dot{q}_j^{\mu\alpha}(\mathbf{q}, t) dt \\ &= \lim_{\tau_0 \rightarrow \infty} \frac{1}{2\tau_0} \int_0^{\tau_0} \sum_{\mu\alpha} |\dot{q}_j^{\mu\alpha}(\mathbf{q}, t)|^2 dt. \end{aligned}$$

Through the use of Parseval's theorem the average kinetic energy may be expressed in the frequency domain as

$$\bar{\mathcal{T}}_j = \int_0^\infty \sum_{\mu\alpha} \lim_{\tau_0 \rightarrow \infty} \frac{1}{2\tau_0} |\dot{q}_j^{\mu\alpha}(\mathbf{q}, \omega)|^2 d\omega.$$

The SED is simply defined as the integrand

$$\Phi(\mathbf{q}, \omega) = \sum_{\mu\alpha} \lim_{\tau_0 \rightarrow \infty} \frac{1}{2\tau_0} |\dot{q}_j^{\mu\alpha}(\mathbf{q}, \omega)|^2.$$

By applying the convolution theorem and the fact that the conjugate of a Fourier transformed function $x(t)$ is equal to the Fourier transform of $x^*(-t)$, $|\dot{q}_j^{\mu\alpha}(\mathbf{q}, \omega)|^2$ can be simplified and the SED becomes

$$\Phi(\mathbf{q}, \omega) = \frac{1}{4\pi} \sum_{\mu\alpha} \int_0^\infty C_{\dot{q}\dot{q}}(\tau) e^{-i\omega\tau} d\tau.$$

Here $C_{\dot{q}\dot{q}}(\tau)$ is the auto correlation function of the time derivative of $q_j^{\mu\alpha}(\mathbf{q}, t)$ and is defined as

$$C_{\dot{q}\dot{q}}(\tau) \equiv \lim_{\tau_0 \rightarrow \infty} \frac{1}{\tau_0} \int_0^{\tau_0} \dot{q}_j^{\mu\alpha*}(\mathbf{q}, t - \tau) \dot{q}_j^{\mu\alpha}(\mathbf{q}, t) dt.$$

Phonon frequencies and damping parameters are determined by fitting the velocity correlation function for a damped harmonic oscillator, expressed in the frequency domain, to the peaks of the calculated SED. The equation of the velocity correlation function for a damped harmonic oscillator is given by

$$b(\omega) = B \frac{2\Gamma\omega^2}{(\omega^2 - \omega_0^2)^2 + (\Gamma\omega)^2},$$

where ω_0 is the phonon frequency of the mode, Γ is the damping parameter, related to the phonon lifetime as $\Gamma = 2/\tau_{ph}$, and B is the amplitude. The phonon frequencies correspond to the centroid frequencies of the peaks, while the damping parameters represent the full width at half maximum (FWHM) of the peaks.

C. NEP machine-learned potential models

1. NEP formalism

To construct accurate potential models driving the PIMD simulations, we use the NEP approach [20–22]. This is a neural-network-based MLP trained using the separable natural evolution strategy (SNES) [64] algorithm. Similar to many other MLPs, such as the Behler-Parrinello neural network potential [65], the total potential energy U of a system of N atoms is expressed as the sum of N site energies, $U = \sum_i U_i$, and each site energy U_i is modeled as a function of set of descriptors, $U_i = U_i(\{q_\nu^i\})$. Each descriptor q_ν^i depends on the atomic positions and is invariant under translation, rotation and permutation of atoms of the same species. The explicit forms of the descriptor in NEP are detailed in Ref. 22. As for the machine-learning model representing the function $U_i = U_i(\{q_\nu^i\})$, a feedforward neural network with a single hidden layer is used. For multi-species systems, we utilize the NEP4 version, which was recently introduced for many-species metals and their alloys [23].

2. NEP for LiH

For LiH, we use an iterative method to train the NEP model to accurately fit the potential energy surface [33]. A total of 603 structures were sampled, including the MD simulations at various temperatures (100 K to 1000 K), and with random strain perturbations (in the range of $\pm 1.5\%$ and $\pm 3\%$). Each structure contains 250 atoms. The Vienna Ab initio Simulation Package (VASP) with the projector-augmented wave method [66, 67] is used to obtain the energy, forces, and virial of each structure. In the DFT calculations, the Perdew-Zunger functional [68] with the local density approximation (LDA) is used to describe the exchange-correlation of electrons. The cutoff energy and the energy convergence threshold were chosen as 600 eV and 1×10^{-8} eV, respectively. The \mathbf{k} -point mesh was set to $2 \times 2 \times 2$. Then, 447 and 156 structures were randomly selected to form the training and testing datasets, respectively.

During the training processes, the cutoff radii for the radial and angular descriptor components were both set to 5 Å. The parity plots and accuracy metrics are shown in Fig. S1 of the Supplemental Material (SM). The root mean square error (RMSE) values of the total energy, atomic forces, and virial for the training dataset are 0.1 meV/atom, 9.5 meV/Å, and 0.8 meV/atom, respectively. In the testing dataset, the corresponding RMSE values are 0.1 meV/atom, 9.4 meV/Å, and 0.8 meV/atom. To further validate the MLP accuracy, we computed the phonon dispersion using the finite-difference method. As shown in Fig. S2 of the SM, our trained MLP accurately describes the lattice dynamics and can be reliably used to simulate the thermal expansion of LiH.

3. NEP for MOFs

Using three MOFs —MOF-5, HKUST-1, and ZIF-8— as examples of soft porous crystals, we explore the NQEs on their thermal expansion behavior through PIMD simulations powered by MLPs. For this purpose, we utilized three machine-learned NEP models, one for each MOF, previously developed and validated against DFT calculations at the Perdew-Burke-Ernzerhof (PBE) level [25]. Before investigating the thermal expansion behavior of these three MOFs, we assessed the reliability of the NEP models in PIMD simulations, given that spring interactions between beads might generate configurations not encompassed by the dataset of the previously developed NEP models [25]. While the original NEP models [25] were trained using PBE reference calculations that did not include long-range dispersion interactions, incorporating these interactions is crucial for accurately modeling the thermodynamic behavior of MOF crystals [69–71]. Here, we therefore used a newly developed NEP-D3 approach [71] to perform PIMD simulations, integrating the original NEP models with dispersion interactions using the DFT-D3 method with the Becke-Johnson damping function [72]. Specifically, the cutoff radius for the D3 potential and the calculation of coordination numbers are set to 12 Å and 6 Å, respectively, to balance accuracy and efficiency [71].

To validate this approach, PIMD simulations driven by the NEP-D3 models were conducted on the primitive cells of MOF-5, HKUST-1, and ZIF-8 using a ring polymer comprising 64 beads, gradually heating from 100 K to 500 K over 1 ns. During these simulations, all six cell components were independently adjusted to maintain zero pressure. For each MOF, 50 snapshots were uniformly selected from the trajectory, and static DFT calculations were performed on these snapshots. The static DFT calculation setup was identical to that used for the previous reference dataset [25]. As shown in Fig. S3 of the SM, the NEP-D3 and PBE-D3 approaches yield consistent results for total energy, forces, and virials, with energy, force, and virial RMSE values of 0.4 meV/atom, 53.1 meV/Å, and 7.7 meV/atom, respectively, demonstrating the reliability of the NEP-D3 model for modeling thermal expansion behavior in PIMD simulations.

4. NEP for liquid water

For liquid water, the NEP model from Ref. 73 is employed, which was trained on a data set containing 1888 structures [74] calculated based on the strongly constrained and appropriately normed (SCAN) functional [75]. For more details on the training of this model, see Ref. 73.

5. NEP for elemental aluminum

For elemental aluminum, bootstrapping and active learning were utilized for constructing the training dataset, up to three iterations. The training data included: (1) rattled structures based on the face-centered cubic (FCC) and hexagonal close packed (HCP) phases; (2) structures from energy-volume curves for the FCC, HCP, diamond, and body-centered cubic (BCC) phases; (3) structures generated via simulations of heating under pressures ranging from -5 to 10 GPa, including molten configurations; (4) configurations of (111), (110), and (100) surfaces, as well as vacancy configurations (rattled). In total, the reference dataset contains 1050 configurations and 52 187 atoms. Reference data were generated using DFT calculations as implemented in VASP and the van-der-Waals density functional method with consistent exchange [76, 77].

In the NEP model, the cutoff radii for radial and angular descriptor parts were set to 6 Å and 4 Å, respectively. For three-body terms, l_{\max} , was set to 4. The neural network has 40 neurons in the hidden layer. The ensemble model contains 5 submodels, created through bagging. The NEP model for aluminum was validated against various physical properties, including bulk phases, surface properties, melting behavior, and phonon spectra. The RMSE values obtained by averaging over the ensemble models are 1.2 meV/atom, 30 meV/Å, 14 meV/atom for energies, forces, and virials, respectively.

D. NEP-PIMD simulation details

In this work, we study LiH, water, aluminum, and three typical MOFs, including MOF-5 [78], HKUST-1 [79], and ZIF-8 [80]. For LiH, we used a $10 \times 10 \times 10$ cubic supercell with 8000 atoms. For the MOFs, we employed orthogonal $4 \times 4 \times 4$ supercells, containing 27 136 atoms for MOF-5, 39 936 atoms for HKUST-1, and 17 664 atoms for ZIF-8, respectively. In Fig. S4 of the SM, we illustrate the supercells of LiH and the three MOFs used in the MD simulations. The liquid water simulations were conducted using a cubic cell with 41 472 atoms. For aluminum, we used a $12 \times 12 \times 12$ cubic supercell with 6912 atoms for the bead convergence test and a $24 \times 24 \times 24$ triclinic supercell with 13 824 atoms for the TRPMD simulations.

We used a time step of 1 fs for LiH and aluminum, and 0.5 fs for MOFs and water. It might be safe to use a time step of 1 fs for MOFs as well, but we decided to follow the previous work [25], which used a time step of 0.5 fs in classical MD simulations of heat transport. To study thermal expansion, we control the isotropic pressure with a target value of 0 GPa in the PIMD simulations. For LiH, the total simulation time for each temperature was 50 ps, and the last 25 ps were used to calculate the cell dimensions. For the MOFs, the total simulation time for each temperature was 30 ps, and the last 10 ps were

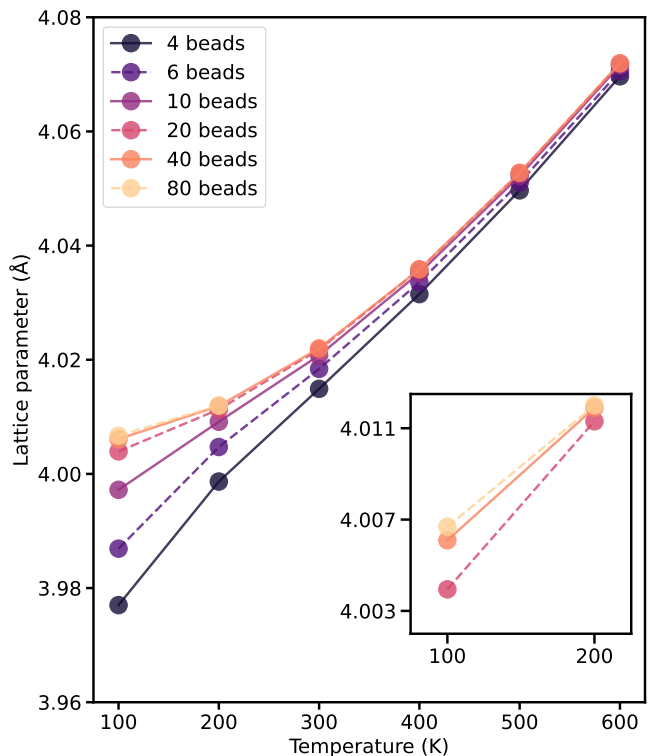


FIG. 1. Convergence of NEP-PIMD simulations with respect to the number of beads for the lattice parameter of LiH at various temperatures. The inset shows a zoomed-in view of the PIMD results at 100 K and 200 K.

used to calculate the cell dimensions. The total simulation time for water was 30 ps for each temperature, of which the last 20 ps were used to compute the radial distribution functions (RDFs). For aluminum, the total simulation time for each temperature was 510 ps, and the last 500 ps were used to calculate the cell dimensions and evaluate the phonon properties.

From the above simulation details, we see that our implementation of the NEP-PIMD approach in the GPUMD package achieves state-of-the-art efficiency, allowing for extensive simulations on nanosecond timescales for systems containing tens of thousand atoms using a large number of beads, sufficient to converge the ring polymer, i.e., approach the $P \rightarrow \infty$ limit in Eq. (1).

III. RESULTS AND DISCUSSION

A. LiH

Here, we first consider the natural isotopic abundance with 7.6% ^7Li and 92.4% ^6Li , while H is practically pure ^1H (99.99%). There is a balance between computational accuracy and efficiency with respect to the number of beads. The NQEs are expected to become more dominant at lower temperatures.

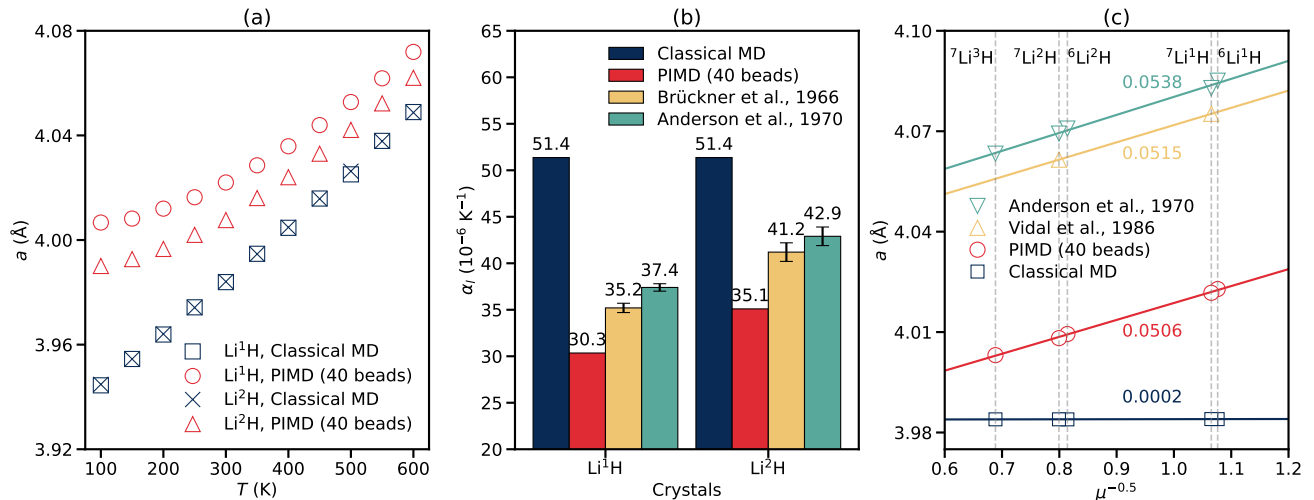


FIG. 2. Isotope effects on the thermal expansion of LiH. (a) Lattice parameters of Li^1H and Li^2H as a function of temperature. (b) Calculated room-temperature linear thermal expansion coefficients of Li^1H and Li^2H . Experimental data is from Refs. 81 and 44. (c) Room-temperature lattice parameters as a function of the reduced mass μ . For direct comparison, the simulation temperature for panel (c) is chosen as 298.15 K, matching the temperature at which data was acquired in Ref. 44. The data in Ref. 43 was obtained at 300 K.

Indeed, as shown in Figure 1, one can see that we need at least 40 beads to achieve full convergence for temperatures of 200 K and below. Considering the heavier atomic mass and thus weaker NQEs in other isotopic systems of LiH, 40 beads should be sufficient and are employed in all simulations of LiH.

Subsequently, we investigate the thermal expansion and the isotope-dependent lattice parameters of LiH. We first present the temperature-dependent lattice parameters (a) of Li^1H and Li^2H in Figure 2a. In our calculations, the lattice parameters of Li^1H and Li^2H from classical MD simulations are nearly identical, and both show a linear temperature dependence. This is in contrast to previous experimental observations [43, 44]. Upon inclusion of the NQEs, the correct trend and the isotope-induced differences are captured, particularly at low temperatures. We define the linear thermal expansion coefficient as:

$$\alpha_l = \frac{\partial \ln(a)}{\partial T}.$$

The discrete temperature-dependent a values are utilized to estimate α_l and the temperature step is set to 50 K. Figure 2b shows the room-temperature linear thermal expansion coefficients of Li^1H and Li^2H calculated using both PIMD and classical MD simulations. Our PIMD results for both Li^1H and Li^2H are in good agreement with earlier experimental measurements.

We further vary the atomic masses of Li and H to investigate whether the isotope effect on the lattice parameters are captured in NEP-PIMD simulations. Considering the experimental values measured by Anderson *et al.* [44], the simulations are performed at 298.15 K and five isotopic compositions are studied, including ${}^6\text{Li}^1\text{H}$,

${}^7\text{Li}^1\text{H}$, ${}^6\text{Li}^2\text{H}$, ${}^7\text{Li}^2\text{H}$, and ${}^7\text{Li}^3\text{H}$. The experimental studies revealed that the lattice parameters of isotopically engineered LiH can be evaluated using the formula $a = A\mu^{-1/2} + B$ [44], where μ is the reduced mass defined as $1/(m_{\text{Li}}^{-1} + m_{\text{H}}^{-1})$, and A and B are two coefficients. In Figure 2c, we plot the room-temperature lattice parameters as a function of the reduced mass μ . The calculated a values are about 1.5% smaller than the measured data. This is acceptable since DFT calculations based on the local density approximation (LDA) tend to underestimate the lattice parameter. Considering the isotope mass effect, the fitting coefficient A is $0.051 \text{ \AA} \sqrt{\text{g}}/\sqrt{\text{mol}}$, which is in excellent agreement with the experimental value of about $0.054 \text{ \AA} \sqrt{\text{g}}/\sqrt{\text{mol}}$ [44]. In contrast, the classical MD simulations predict a substantially weaker dependence. These findings demonstrate that our NEP-PIMD simulations yield a high accuracy in modeling the thermal expansion of LiH and its isotope effects.

B. MOFs

Figure 3a–c shows the energy profile as a function of temperature using different numbers of beads. In contrast to classical MD simulations, PIMD simulations predict a higher energy for all three MOFs due to zero-point energy contributions. Additionally, the energies tend to converge at bead numbers larger than 32 for all temperatures, leading to a significantly lower heat capacity when compared to classical MD. For the temperature-dependent volume as shown in Figure 3d–f, the PIMD simulations predict larger volumes than classical MD, particularly at lower temperatures where NQEs are more pronounced. The number of beads required to reach con-

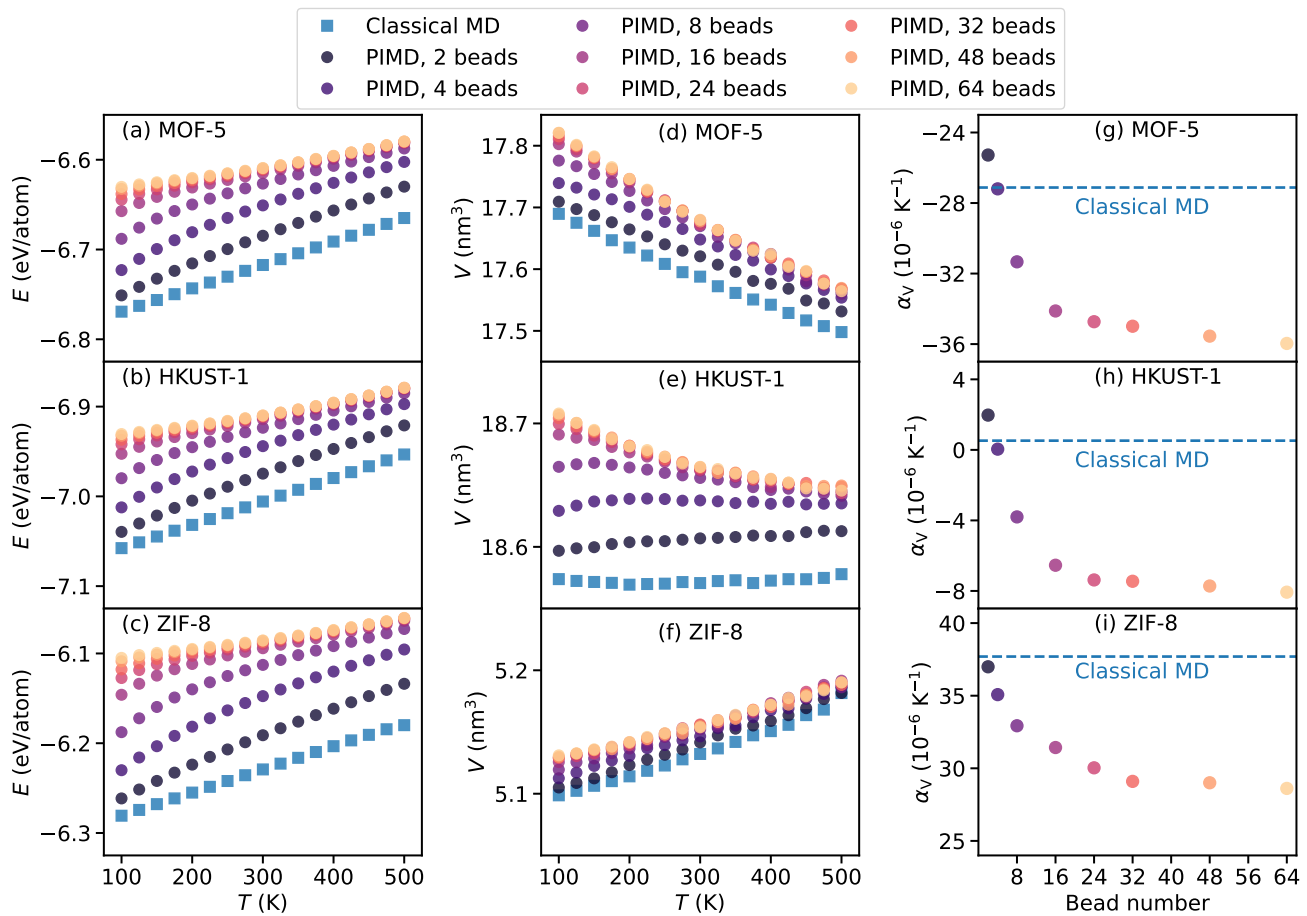


FIG. 3. The evolution of (a–c) energy (E) and (d–f) volume (V) as a function of temperature T using different bead numbers in PIMD simulations for MOF-5 (top), HKUST-1 (middle), and ZIF-8 (bottom). In panels (g–i), the volumetric TEC (α_V) are obtained by fitting the $V(T)$ results using Eq. (14). The classical MD results (blue squares or dashed lines) are also provided for comparison.

vergence is consistent with those observed for the energy.

Based on the $V(T)$ results, the temperature-independent volumetric TEC at zero pressure can be estimated as

$$\alpha_V = \frac{\partial \ln(V)}{\partial T}. \quad (14)$$

Figure 3g–i shows the estimated α_V , fitted using the above equation from PIMD simulation, as a function of the number of beads. For all MOFs, α_V decreases as the number of beads increases and reaches convergence at around 48 beads. The relative difference in the predicted α_V between 48 and 64 beads is less than 1.5% for MOF-5 and ZIF-8, and 4.5% for HKUST-1. Therefore, in the subsequent discussion, all PIMD results are based on simulations using 64 beads.

To quantify the impact of NQEs and long-range dispersion interactions on the TEC of MOFs, we estimated the $V(T)$ (see Fig. S5 of the SM) and corresponding α_V (see Figure 4) from four different sets of MD simulations. These sets include classical MD and PIMD, each driven

by either NEP or NEP-D3 models. It is evident that both dispersion interactions and NQEs are crucial for accurately estimating α_V , as the NEP-D3 with PIMD approach aligns most closely with previous experimental measurements (see Table S1 of the SM) [45–53]. For HKUST-1, excluding NQEs, the classical MD simulations predict a near-zero (NEP-D3) or even positive (NEP) α_V , resulting in a qualitatively incorrect prediction.

C. Water

While we in the previous sections studied the effect of NQEs on the *macroscopic* structure, we now examine its impact on the *microscopic* structure. Here, this is exemplified by the partial RDFs of water (Figure 5), which are significantly affected by NQEs because of the high hydrogen content of water.

The NQEs are particularly apparent in the first nearest-neighbor peak in both the oxygen–hydrogen (Figure 5a) and hydrogen–hydrogen (Figure 5b) RDFs, which

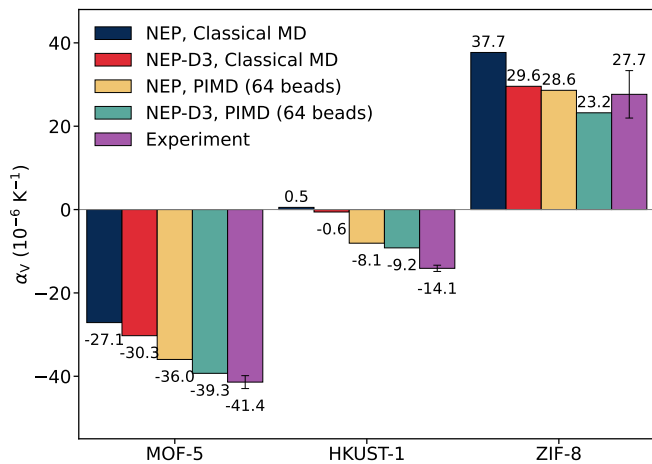


FIG. 4. Comparison of volumetric TEC of three MOFs predicted by classical MD and PIMD (64 beads) simulations with experimental data. For each MD approach, both NEP and NEP-D3 results are provided to examine the long-range dispersion effects. The presented experimental results for each MOF are obtained by averaging several previous studies [45–53], with the corresponding error bar denoting the standard error of the mean as detailed in Table S1 of the SM.

are significantly broadened compared to the classical limit. To converge these calculations one requires at least 32 beads in the temperature range of 280 to 320 K considered here, as illustrated by the FWHM of the first nearest-neighbor coordination peaks (Figure 6).

We once again observe that the effect of NQEs is more substantial at lower temperatures. This can be seen, e.g., by noting that the peak height difference between the second peak of the hydrogen–hydrogen RDF from classical MD and PIMD simulations is larger at 280 K than at 320 K (Figure 5b; see also Figure S6k–o, and Figure S7). The same effect is also observed in the first peak of the oxygen–oxygen RDF (Figure S6a–e; also see Figure S7). Overall the impact of NQEs on the O–O RDF is, however, much smaller than for the H–H and O–H RDFs due to the larger mass of O. All of these results agree well with experiment and previous PIMD simulations [6–8, 85–87].

The case of water also allows us to compare the computational efficiency of NEP with other MLPs (Figure 7). For the latter we resort to data from Ref. 18 for the BPNN [82], DeePMD [83], and MACE [84] models. We consider the timing for a classical simulation (equivalent to one bead) for consistency with Ref. 18.

The results demonstrate that for the system sizes considered here the NEP model is at least about one order of magnitude faster than the next efficient models (BPNN and DeePMD). This applies even though the latter were run on many hundred CPU cores (BPNN) and 8 GPUs (DeePMD), respectively, while the NEP data were obtained using a single A100 GPU. We also note that the performance of the latter diminishes only slightly when running on consumer GPUs as illustrated here by a RTX3080Ti card.

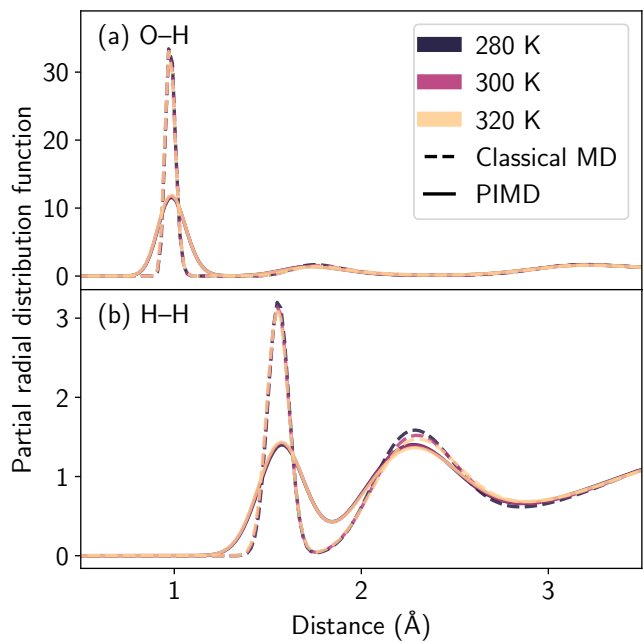


FIG. 5. Partial oxygen–hydrogen (a) and hydrogen–hydrogen (b) radial distribution functions from classical MD (dashed line) and 64-bead PIMD (solid line) simulations, for three different temperatures 280 K (dark color), 300 K (intermediate color), and 320 K (light color).

It is also noteworthy that the overhead associated with the driver-force evaluator approach is almost negligible for BPNN, DeePMD, and MACE thanks to a very efficient implementation of the interface in *i*-PI [18]. For those MLPs the cost of a force evaluation in their present implementations is at least on the order of 10 ms, which is larger than the typical overhead per step in *i*-PI [18]. In contrast, for NEP models, a typical force evaluation is approximately on the order of 1 ms (Figure 7; see also Figure S8 for a comparison of other NEP models used in this work). The cost per step would therefore be significantly affected by the communication overhead. The direct combination of PIMD with NEP in GPUMD avoids this extra cost, providing a much more efficient approach.

D. Aluminum

Figure 8 shows the convergence test of the lattice parameter of aluminum at various temperatures, obtained from PIMD simulations. Similar to the convergence tests for LiH, the NQEs dominate at lower temperatures. The results indicate that 64 beads are sufficient to achieve convergence even for the lowest temperatures considered here. Additionally, the lattice parameter has been determined using the QHA method as implemented in PHONOPY [88, 89]. At low temperatures, the PIMD and QHA lattice parameters exhibit similar temperature dependence, as expected. At higher temperatures, the

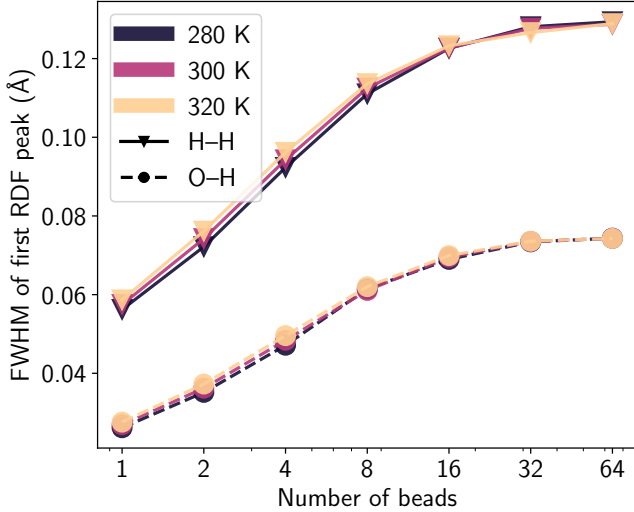


FIG. 6. FWHM of the first nearest-neighbor peak in the hydrogen–hydrogen (solid triangles) and oxygen–hydrogen (dashed circles) RDFs as a function of the number of PIMD beads for three different temperatures, revealing similar convergence behavior of the FWHM with number of beads, irrespective of temperature.

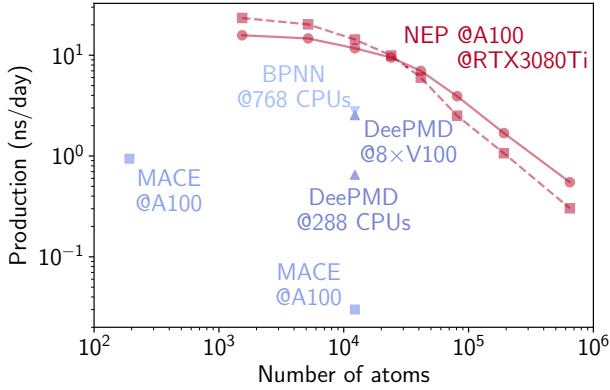


FIG. 7. Computational efficiency of different MLPs for water measured in terms of the ns that can be simulated per day of wall-clock time. The timing is given assuming a classical simulation (equivalent to one bead) in line with Table III in Ref. [18], which is also the source of the timings shown for BPNN [82], DeePMD [83], and MACE [84] models (all using the same time step of 0.5 fs). For NEP timing is shown for both A100 (solid) and RTX3080Ti (dashed) cards.

QHA results diverge from those obtained through PIMD simulations due to the incomplete treatment of anharmonicity in the former. The simulations of Al described from here on were performed using 16 beads, except for temperatures under 50 K, where 64 beads were employed to ensure convergence.

Next, we analyze the phonon properties of aluminum using TRPMD to demonstrate that the implemented

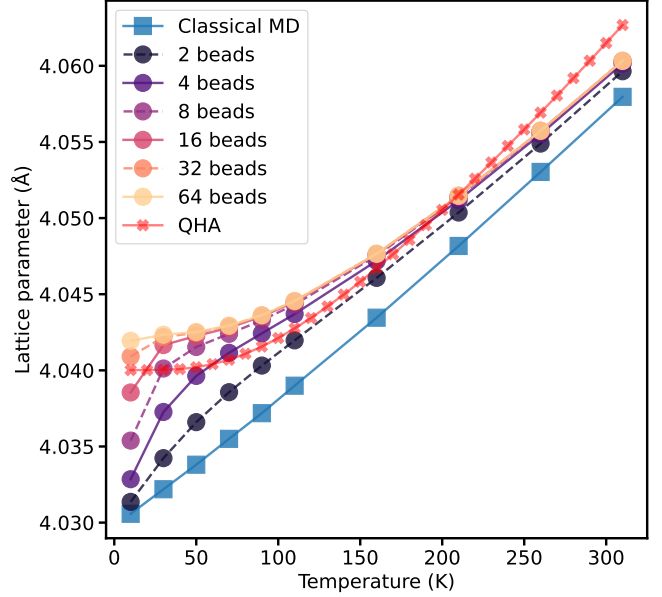


FIG. 8. Temperature dependence of the lattice parameter of aluminum obtained from QHA, classical MD, and PIMD simulations with different numbers of beads.

method can yield quantum dynamical properties. For this analysis, the lattice parameter is kept fixed at 4.05 Å to make sure the NQEs we observe actually originate from the dynamics rather than thermal expansion. Figure 9a–d shows the phonon frequency shift as a function of temperature for the transversal and longitudinal X and L -modes, where X and L are the reciprocal points $(1/2, 0, 1/2)$ and $(1/2, 1/2, 1/2)$, respectively. The frequency shift is determined by subtracting the zero-temperature frequency, obtained with PHONOPY from the frequency observed at each respective temperature. Additionally, for comparison, the phonon frequency shift is determined through self-consistent phonons, both classically and quantum mechanically. The HIPHIVE package [90] is used for this analysis. Examining the frequency shift obtained from classical MD and classical self-consistent phonons, we observe that it approaches zero as the temperature approaches absolute zero for all four modes. This behavior is expected since the zero-temperature frequency is calculated with small atomic displacements. In the classical scenario, there is no zero-point energy, and atomic displacements diminish and approach zero as the temperature decreases to absolute zero. However, in the quantum mechanical case, the frequency shift is not expected to reach zero due to quantum fluctuations. Observing the frequency shifts obtained from TRPMD and quantum mechanical self-consistent phonons, we see that this holds true, as these shifts are finite even at low temperatures. This demonstrates that TRPMD simulations account for NQEs, while classical MD simulations do not. The discrepancy between the self-consistent phonons results and the TRPMD simulations can be attributed to the incomplete inclusion of

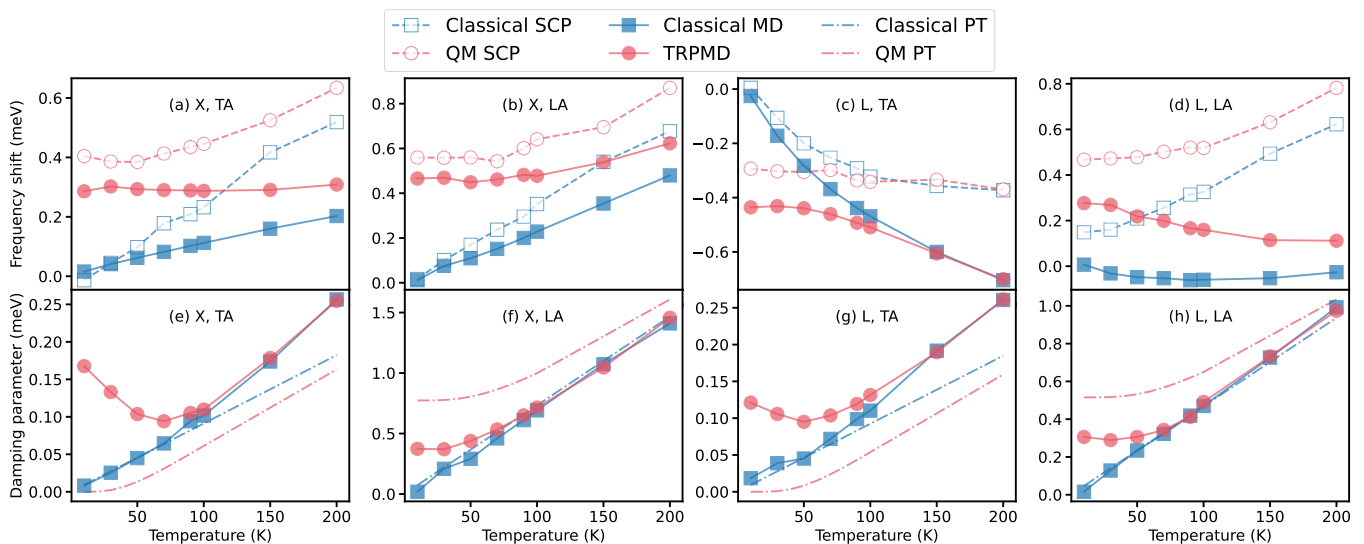


FIG. 9. Phonon frequency shift (a–d) and phonon damping parameters (e–h) of the transversal acoustic (TA) and longitudinal acoustic (LA) X and L -modes in elemental aluminum as a function of temperature. For comparison, the frequency shift and damping parameters have been calculated using self-consistent phonons (SCP) and perturbation theory (PT), respectively. These calculations have been performed using both classical and quantum mechanical (QM) approaches.

anharmonicity in the former. We note that a similar overestimation has also been observed for other materials [91].

Along with the phonon frequency shift, we also highlight the critical role of NQEs in calculating phonon lifetimes. Our study demonstrates how TRPMD enables the incorporation of these effects into simulations. Figure 9e–h shows the temperature dependence of the damping parameter Γ , which is inversely proportional to the phonon lifetime τ_{ph}

$$\Gamma = \frac{2}{\tau_{\text{ph}}}.$$

For comparison the damping has also been obtained with perturbation calculations conducted with KALDO [92].

It is evident that the damping obtained through classical MD approaches zero, meaning phonon lifetimes tend toward infinity, as the temperature goes to zero. This characteristic makes damping a more convenient quantity for analysis compared to the lifetimes. By contrast, due to the inclusion of NQEs, the TRPMD damping remains finite as the temperature approaches zero. When comparing the damping obtained through TRPMD simulations to that calculated using quantum mechanical perturbation theory, a similar temperature dependence is observed, reinforcing the conclusion that TRPMD effectively captures the quantum dynamical behavior of the damping. For the two transversal modes, the damping obtained through TRPMD increases when the temperature falls below 70 K and 50 K, respectively. This increase is also observed in the longitudinal L -mode, though it is less pronounced. This behavior is likely due to the coupling between the dynamics of the beads and the

ring-polymer centroid dynamics [60]. While TRPMD dampens this coupling, it does not entirely eliminate it. By contrast, the damping of the transversal modes predicted by quantum mechanical perturbation theory tends to zero as the temperature nears absolute zero. This is likely due to the absence of higher-order anharmonic terms, as KALDO only incorporates force constants up to the third order.

IV. CONCLUSIONS

In summary, we have integrated the PIMD method with machine-learned NEP models into the GPUMD package, enabling efficient and accurate MD simulations that account for NQEs. The effectiveness of the NEP-PIMD approach is demonstrated by studying thermal properties of four different types of materials: ionic LiH, three porous MOFs, liquid water, and elemental aluminum.

Our results show that including the NQEs is crucial for accurately modeling the thermal expansion of LiH, MOFs and aluminum, achievable with NEP-PIMD simulations. Specifically, the isotope effect on the lattice parameter of LiH predicted by NEP-PIMD simulations exhibits a dependence on the reduced mass, in good agreement with the experimental observations, whereas classical MD simulations predict a negligible isotope dependence. For the porous MOFs, our results indicate that incorporating dispersive interactions into the NEP models, along with NQEs via PIMD, brings the simulated values closer to experimental data. Furthermore, accounting for NQEs in liquid water significantly affects the microscopic structure, which is crucial for obtaining simulated

structural properties that align more closely with experimental results. In the case of elemental aluminum, incorporating NQEs is essential for accurately capturing thermal expansion and phonon properties. While classical MD simulations show both the phonon frequency shift and damping parameter approaching zero as the temperature decreases, TRPMD simulations, which include NQEs, predict finite values that align well with quantum mechanical perturbation theory.

The integration of the NEP-PIMD into the GPUMD package opens new pathways for investigating the properties of a wide range of materials affected by NQEs, enabling large-scale PIMD simulations with high fidelity and efficiency. Notably, during the preparation of our manuscript, this implementation of the NEP-PIMD approach into the open-source GPUMD package has already been utilized to study some static and dynamic properties in liquid water [93], crystalline silicon [94], and $\text{Cs}_3\text{Bi}_2\text{I}_6\text{Cl}_3$ [95].

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Conflict of Interest

The authors have no conflicts to disclose.

Data availability

The source code and documentation for GPUMD are available at <https://github.com/brucefan1983/GPUMD> and <https://gpumd.org>, respectively. Representative input and output files for thermal expansion calculations of MOFs and LiH are freely available at <https://github.com/hityingph/supporting-info>. The training datasets and the trained NEP models for MOFs and LiH are freely available at <https://gitlab.com/brucefan1983/nep-data>, the NEP model and data for water are available at <https://doi.org/10.5281/zenodo.10257363>, and the NEP model for aluminum along with the DFT reference data used for its construction are available at <https://doi.org/10.5281/zenodo.13712924>.

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Supplemental Material:

Highly efficient path-integral molecular dynamics simulations with GPUMD using neuroevolution potentials: Case studies on thermal properties of materials

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Supplemental Tables

Table S1: Volumetric thermal expansion coefficients of three MOFs obtained from previous experimental measurements.

Material	α_V (10^{-6} K $^{-1}$)	Temperature range (K)	Approach	Reference
MOF-5	-45.9	30–293	single-crystal X-ray diffraction	[1]
	-42.0	4–600	neutron powder diffraction	[2]
	-39.3	80–500	powder X-ray diffraction	[3]
	-43.8	100–425	powder X-ray diffraction	[4]
	-36.0	20–400	powder neutron diffraction	[4]
HKUST-1	-12.3	80–500	powder X-ray diffraction	[5]
	-14.7	100–300	neutron powder diffraction	[6]
	-15.3	100–300	powder X-ray diffraction	[7]
ZIF-8	35.7	100–300	powder X-ray diffraction	[8]
	19.6	280–380	powder X-ray diffraction	[9]

Supplemental Figures

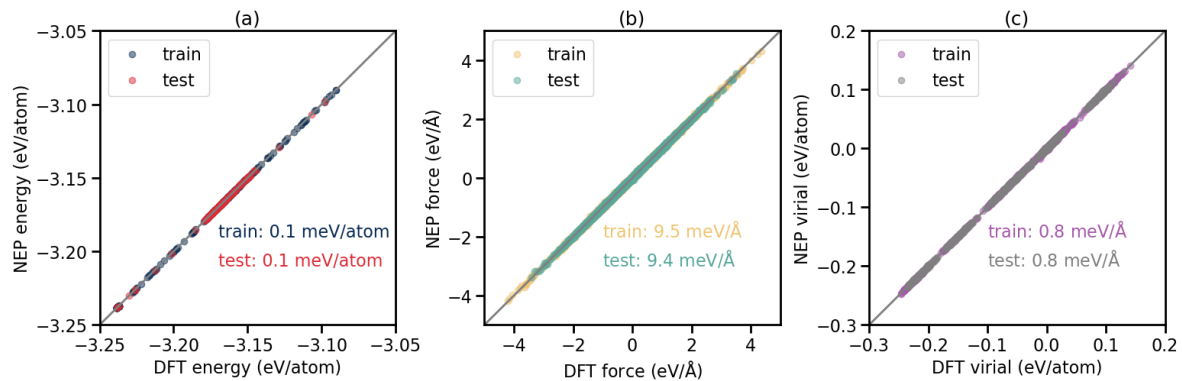


Figure S1: The partial plots of (a) total energy, (b) atomic forces, (c) virial for LiH. The insets show the RMSE of the training and testing datasets.

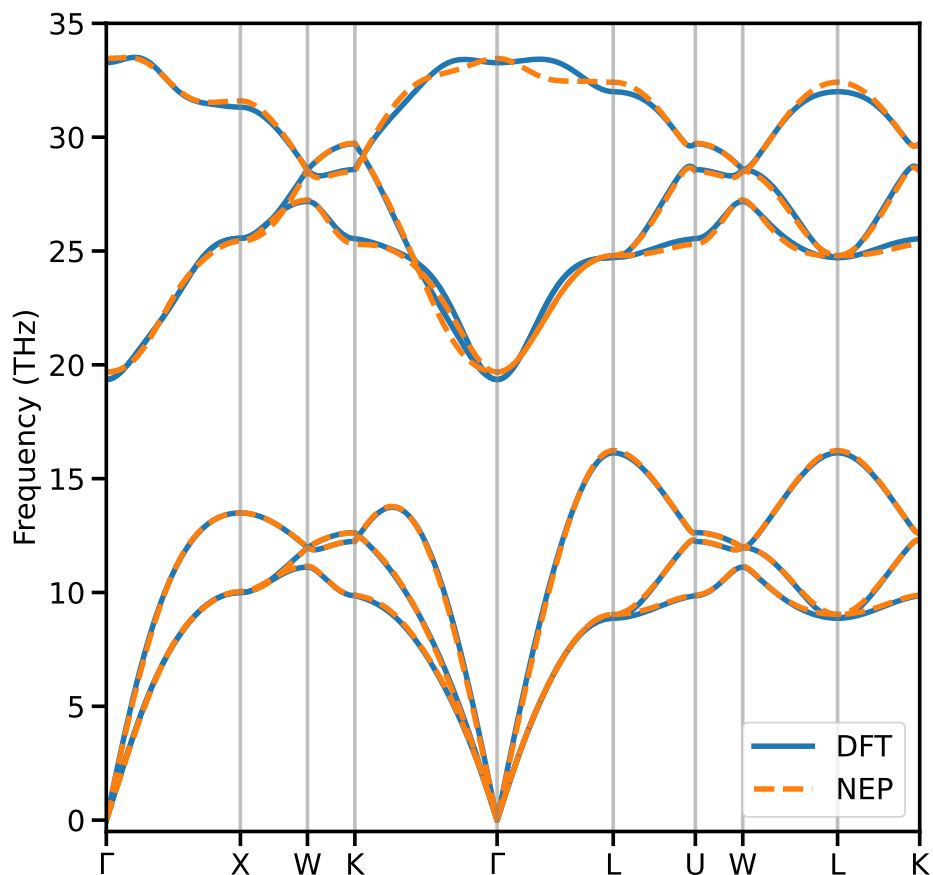


Figure S2: Phonon dispersion relations for LiH. The blue and orange lines are calculated using DFT and NEP based finite-difference (FD) method.

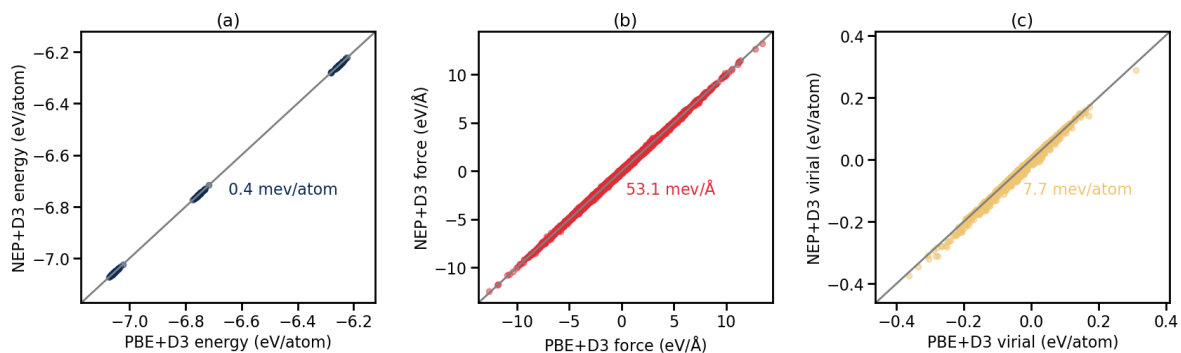


Figure S3: The partial plots of (a) total energy, (b) atomic forces, (c) virial as predicted by the NEP-D3 approach, are compared against PBE-D3 calculations for snapshots extracted from PIMD simulations of three MOFs.

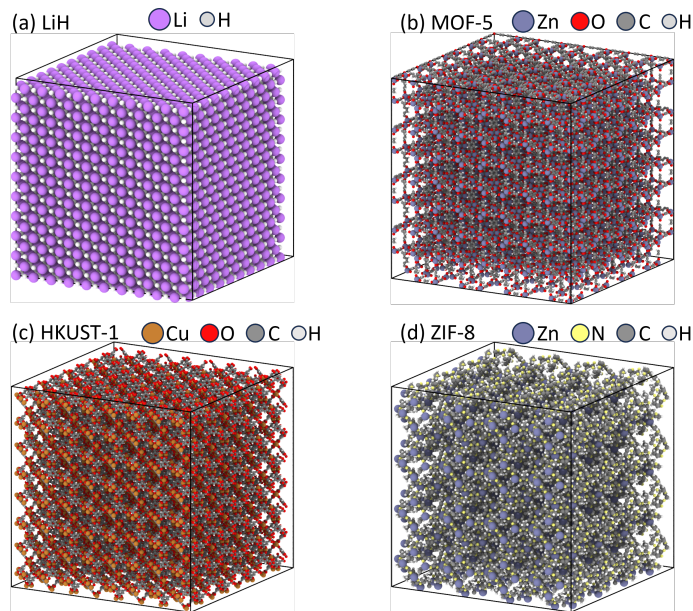


Figure S4: The atomic supercells investigated in this work: (a) $10 \times 10 \times 10$ cubic supercell of LiH (8000 atoms), $4 \times 4 \times 4$ supercells of (b) MOF-5 (27136 atoms), (c) HKUST-1 (39936 atoms), and (d) ZIF-8 (17664 atoms).

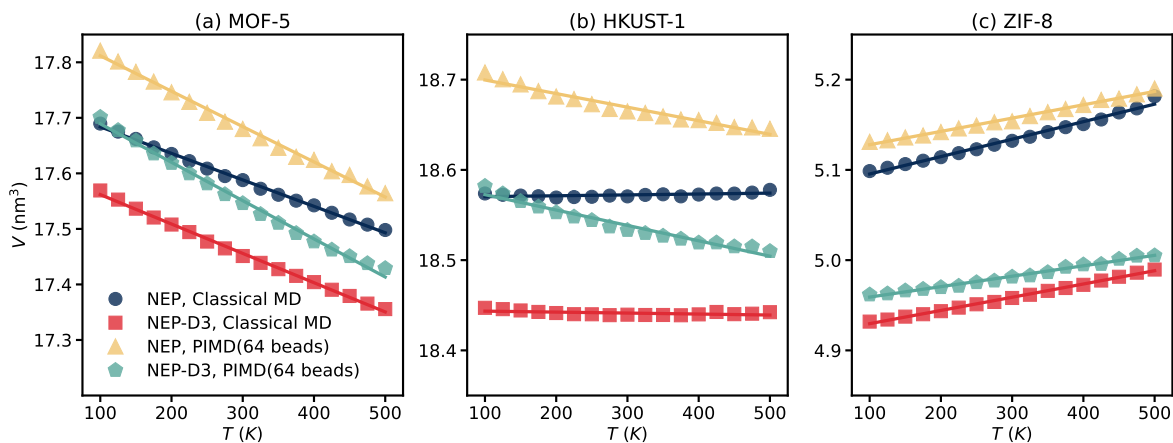


Figure S5: The volume of (a) MOF-5, (b) HKUST-1, and (c) ZIF-8 as a function of temperature, obtained from classical MD simulations driven by NEP (blue circles) or NEP-D3 (red squares), along with PIMD simulations using 64 beads, driven by NEP (orange triangles) or NEP-D3 (green pentagons). For each $V(T)$ result, a solid line is fitted using Eq. (14) of main text.

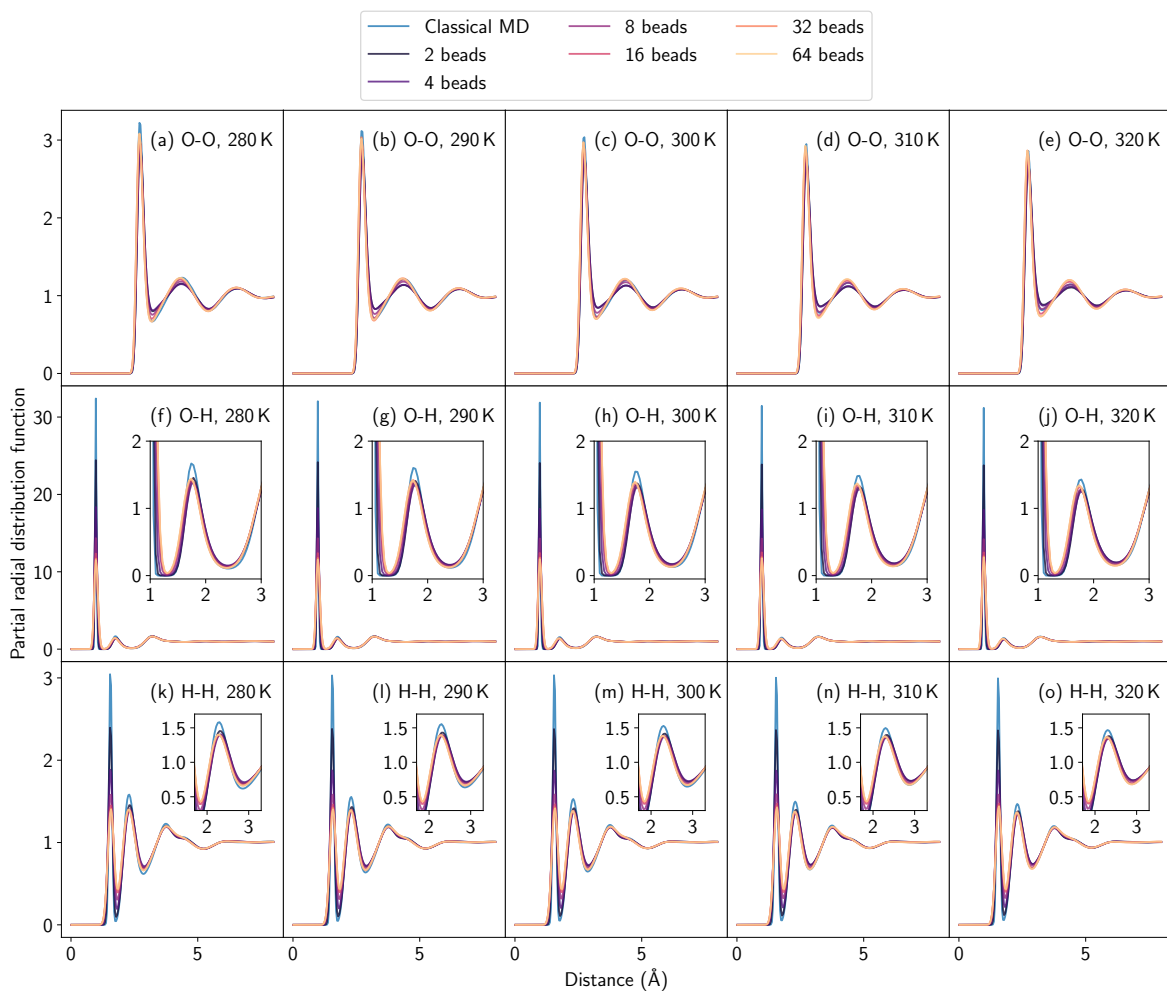


Figure S6: Partial oxygen–oxygen (a–e), oxygen–hydrogen (f–j) and hydrogen–hydrogen (k–o) radial distribution functions from classical MD and PIMD simulations with different numbers of beads, each for five different temperatures: 280 K (a,f,k), 290 K (b,g,l), 300 K (c,h,m), 310 K (d,i,n), and 320 K (e,j,o). The insets show a zoomed-in view of the second peaks of the O–H and H–H RDFs at each temperature.

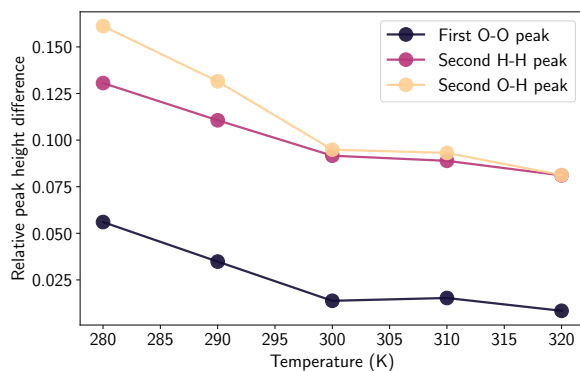


Figure S7: Relative peak height difference between classical MD and 64-bead PIMD for the first nearest-neighbor peak in the oxygen–oxygen (dark color), second peak of the hydrogen–hydrogen (intermediate color) and second peak of the oxygen–hydrogen (light color) RDFs. Note the peak height difference increasing when the temperature decreases.

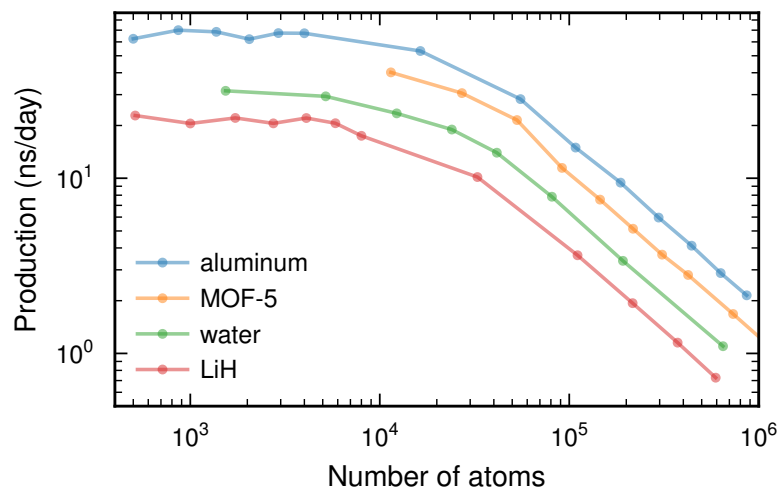


Figure S8: Computational efficiency on a single A100 GPU of the NEP models for aluminum, MOF-5, water, and LiH. The efficiency is measured in terms of simulated ns per day of wall-clock time, assuming a classical simulation (equivalent to one bead) and using a time step of 2 fs for aluminum and 0.5 fs for MOF-5, water and LiH.

Supplemental References

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