BIGDML: Towards Exact Machine Learning Force Fields for Materials

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Machine-learning force fields (MLFF) should be accurate, computationally and data efficient, and applicable to molecules, materials, and interfaces thereof. Currently, MLFFs often introduce tradeoffs that restrict their practical applicability to small subsets of chemical space or require exhaustive datasets for training. Here, we introduce the Bravais-Inspired Gradient-Domain Machine Learning (BIGDML) approach and demonstrate its ability to construct reliable force fields using a training set with just 10–200 geometries for materials including pristine and defect-containing 2D and 3D semiconductors and metals, as well as chemisorbed and physisorbed atomic and molecular adsorbates on surfaces. The BIGDML model employs the full relevant symmetry group for a given material, does not assume artificial atom types or localization of atomic interactions and exhibits high data efficiency and state-of-the-art energy accuracies (errors substantially below 1 meV per atom) for an extended set of materials. Extensive path-integral molecular dynamics carried out with BIGDML models demonstrate the counterintuitive localization of benzene–graphene dynamics induced by nuclear quantum effects and allow to rationalize the Arrhenius behavior of hydrogen diffusion coefficient in a Pd crystal for a wide range of temperatures.

I. INTRODUCTION

The development and implementation of accurate and efficient machine learning force fields (MLFF) is transforming atomistic simulations throughout the fields of physics [1–5], chemistry [6–13], biology [14, 15], and materials science [16–21]. The application of MLFFs has enabled a wealth of novel discoveries and quantum-mechanical insights into atomic-scale mechanisms in molecules [3, 6, 21–24] and materials [2, 4, 25–27].

A major hurdle in the development of MLFFs is to optimize the conflicting requirements of ab initio accuracy, computational speed and data efficiency, as well as universal applicability to increasingly larger chemical spaces [28]. In practice, all existing MLFFs introduce tradeoffs that restrict their accuracy, efficiency, or applicability. In the domain of materials modeling, all MLFFs known to the authors employ the so-called locality approximation, i.e. the global problem of predicting the total energy of a many-body condensed-matter system is approximated by its partitioning into localized atomic contributions. The locality approximation has been rather successful for capturing local chemical degrees of freedom as demonstrated in a wide number of applications [29–33]. However, we emphasize that the locality assumption disregards non-local interactions and its validity can only be truly assessed by comparison to experimental observables or explicit ab initio dynamics. This fact restricts truly predictive MLFF simulations of realistic materials, whose properties are often determined by a complex interplay between local chemical bonds and a multitude of non-local interactions.

The chemical space of materials is exceedingly diverse if we count all possible compositions and configurations of a given number of chemical elements. For example, an accurate MLFF reconstruction of the potential-energy surface (PES) of elemental bulk materials to meV/atom accuracy often requires many thousands of configurations for training [20, 29, 34–37]. The MLFF errors also increase at least by an order of magnitude when including defects or surfaces [31, 34]. Heterotomonic materials and interfaces between molecules and materials would require substantially more training data for creating predictive MLFFs and accuracies much better than 1 meV/atom, eventually making the modeling of such materials intractable. In addition, there is a strong desire to go beyond traditional density-functional theory (DFT) reference data in the field of atomistic materials modeling [38–40]. Beyond-DFT methods can only be realistically applied to compute dozens or hundreds of geometries, mak-
ing the construction of beyond-DFT MLFFs impractical.

To address these challenges, in this work we introduce a Bravais-Inspired Gradient Domain Machine Learning (BIGDML) model for periodic materials that is accurate, data efficient, and computationally inexpensive at the same time. The BIGDML model extends the applicability domain of the Symmetric Gradient-Domain Machine Learning (sGDML) framework [22, 41, 42] to include periodic systems with unit cells containing up to roughly hundred atoms. The BIGDML model employs a global representation of the full system, i.e. treating the supercell as a whole instead of a collection of atoms. This avoids the uncontrollable locality approximation, but also restricts the maximum number of atoms in the unit cell. To extend the applicability of BIGDML to much larger unit cells will require the development of a global multiscale representation, which will be the topic of our future work. An additional advantage of a global representation is that cross-correlations between forces on different atomic species are dealt with rigorously, at variance with existing atomic representations. Similarly to the sGDML model, another key advantage of the BIGDML model is the usage of physical constraints (energy conservation) and all relevant physical symmetries of periodic systems, including the full translation and Bravais symmetry groups. As a consequence, BIGDML models achieve meV/atom accuracy already for 10-200 training points, surpassing state-of-the-art atom-based models by 1-2 orders of magnitude. This result underlines once again the importance of including prior knowledge, including physical laws and symmetries, into ML models. Clearly, what is known does not need to be learned from data — in effect the data manifold has been reduced in its complexity (see e.g. [22, 23, 33, 43–46]).

Altogether, the BIGDML framework opens the possibility to accurately reconstruct the PES of complex periodic materials with unprecedented accuracy at very low computational cost. In addition, the BIGDML model can be straightforwardly implemented as an ML engine in any periodic DFT code, and used as a molecular dynamics driver after being trained on just a handful of geometries.

II. RESULTS

The BIGDML framework relies on two advances: (i) a global atomistic representation with periodic boundary conditions (PBC), (ii) the use of the full translation and Bravais symmetry group for a given material.

A. PBC-preserving Representation

To avoid localization of interatomic interactions and artificial (from the electronic perspective) atom-type assignment, we use an efficient global representation with PBC. Following the sGDML approach for molecules [22, 41], we take the atomistic Coulomb matrix (CM) [47] as a starting representation. When used with sGDML, the CM has been proven to be a robust, accurate, and efficient representation [22, 41, 48].

Here, we introduce a generalization of the molecular CM descriptor to represent periodic materials, $D^{(PBC)}$. In order to construct the Coulomb matrix for extended systems, we first enforce the PBC using the minimal-image convention (MIC) [49, 50]:

$$P_{ij}^{(PBC)} = \begin{cases} \frac{1}{|r_{ij} - A \mod(A^{-1}r_{ij})|} & \text{if } i \neq j \\ 0 & \text{if } i = j \end{cases}$$

where $r_{ij} = r_i - r_j$ is the difference between two atomic coordinates $i$ and $j$, and $A$ is the matrix defined by the supercell translation vectors as columns. Fig. 1-A-left shows the Coulomb matrix descriptor when considering only the supercell structure with no PBC, which means that the ML model considers the system as a finite “molecule”. The right side of Fig. 1-A shows the descriptor with the PBC enforced (Eq. 1), having now the correct periodic structure. Many widely used periodic global representations already exist, for example CM-inspired global descriptors such as the Ewald-sum, or extended Coulomb-like and sine matrices [51]. In the cases of the extended Coulomb-like and Ewald matrices, these representations account the contribution of the same atom iteratively by considering its multiple periodic images, which is computationally demanding and algebraically involved. From these global periodic representations [51], only the sine matrix avoids using redundant information, since it just depends on the atomic positions in a single unit cell. Our choice of CM with PBC enforced using MIC is the simplest and most efficient choice, which also turns out to be exceptionally accurate and data-efficient, as will be shown below.

As an alternative to the global approach, many local materials’ representations have been developed. Among those representations, there are numerous descriptors based on atomic local environments, for example atom-density representations [52–55], partial radial-distribution functions [56], FCHL descriptor [57], rotationally-invariant internal representation [58], many-body vector interaction [59] and moment tensor potentials [17]. In all these cases, the PBC can be naturally incorporated by using the MIC, as it has been done for mechanistic force fields. These local representations in principle aim at the construction of transferable interatomic MLFFs, as done by GAP/SOAP framework [54] which is the basis of a series of high quality chemical bonding potentials for phosphorus [31], carbon [34], and silicon [20]. However, the intrinsic cutoff radius in these descriptors limits the extent of atomic environments, neglecting the ubiquitous long-range interactions and correlations between different atomic species. Here, by using a $D^{(PBC)}$ global descriptor we avoid the need of fine-tuning representation hyperparameters while preserving
FIG. 1. Description of the main components of BIGDML models. A) Coulomb Matrix representation for non-periodic (left) and periodic (right) supercell (2×2×3L) of Pd$_1$/MgO (100). B) Description of the local symmetries (i.e. Bravais group $G$ or point group of the unit cell) and the translation symmetries of the unit cell $T$. C) Analytical form of the sGDML predictor where the explicit usage of the full symmetry group of the supercell $F$ (in blue) and the Coulomb matrix PBC descriptor (in red). D) Systematic symmetrization of the PES. The axis in the PES are the $x$ and $y$ coordinates of the Pd atom in units of the lattice constant of MgO. Models: i) Pure GDML, ii) GDML+$D^{(PBC)}$, iii) sGDML+$D^{(PBC)}(s=G)$, iv) sGDML+$D^{(PBC)}(s=T)$, and v) BIGDML. Panel vi) displays the incremental accuracy upon addition of each symmetry for the Pd$_1$/MgO (100) system. All models used for this comparison were trained on 50 data samples.
high accuracy in the description of the many possible configuration states of a material.

B. Translation Symmetries and the Bravais’ Group

The full symmetry group $F$ of a crystal is given by the semidirect product of translation symmetries $T$ and the rotation and reflection symmetries of the Bravais lattice $G$ (Bravais’ group): $F = T \otimes G$ [60] (See Fig. 1-B). This is a general result, meaning that it applies to any periodic system of dimension $d$, $F^{(d)} = T^{(d)} \otimes G^{(d)}$. In practice, the translation group $F$ is constructed by the set of translations of the Bravais cell that span the supercell using the primitive translation vectors as a basis, while the Bravais’ group $G$ is the symmetry point group of the unit cell. In order to illustrate these concepts, as an example let us consider a graphene (2D) supercell of size $5 \times 5$. Its full symmetry group is $T_{5 \times 5}^{(2)} \otimes G^{(2)} = T_{5 \times 5}^{(2)} \otimes D_{6h}$ and contains 300 symmetry elements. Further important materials with ample symmetries are surfaces and interfaces. Analogous to molecules possessing internal rotors, molecules interacting with a surface are another case of a fluxional system. For example, benzene adsorbed on graphene has a full fluxional symmetry group defined by the direct product of graphene’s full symmetry group and benzene’s molecular point group, $[T_{5 \times 5}^{(2)} \otimes D_{6h}]_{\text{graphene}} \otimes [D_{6h}]_{\text{benzene}}$, which contains 3600 symmetry elements. Such a large number of symmetries reduces considerably the region of configuration space needed to be sampled to reconstruct the full PES and consequently generate MLFF models with high data efficiency. The presented arguments generalize to other materials, such as molecular crystals, rigid bulk materials, porous materials, and hybrid organic-inorganic materials, i.e. perovskites.

C. The BIGDML model

The construction of a BIGDML model consists in combining a global PBC-descriptor and the full symmetry group of the system in the gradient-domain machine learning framework (See Fig. 1), which leads to a robust and highly data efficient MLFF, capable of reaching state-of-the-art accuracy using only a few dozens of training points. We would like to stress here that such unprecedented data efficiency opens up many opportunities to study advanced materials using high levels of electronic-structure theory, such as sophisticated DFT approximations or even coupled-cluster theory [61].

In a nutshell, the periodic global supercell descriptor and symmetries presented in the previous sections are combined with the sGDML framework to create the BIGDML predictor displayed in Fig. 1-C. To illustrate the effects of the symmetries in the PES reconstruction process for the atom–surface Pd$_1$/MgO system, Fig. 1-D presents a diagram where the different core elements of the BIGDML model are systematically included and the resulting (learned) PES displayed. In this figure, the shown PES corresponds to the energy surface experienced by a Pd atom. The panel i) displays the reconstructed energy surface with no symmetries, where the training samples are the purple squares and represent the position of the Pd atom. In panel ii) the PBC are enforced by the periodic descriptor (eq. 1), and then this is combined with the use of the point group of the unit cell in panel iii) and with translation symmetries in panel iv). From the last two panels, we can see the characteristic contribution of each symmetry group, $G$ symmetrizes the local PES by adding effective training samples (shown as grey circles) while $T$ delocalises the effective sampling over the whole supercell. Then, by considering the full symmetry group $F$, in panel v) we arrive to the PES reconstructed by the BIGDML model where the effective training data symmetrically span the whole supercell. The panels i) to v) show the increasing symmetrization of the PES, but also illustrate the accuracy gain at each stage. The prediction accuracy plot shown in panel vi) clearly shows the important impact of each symmetry group in generating accurate and robust BIGDML models.

D. Prediction performance of BIGDML for different materials

The BIGDML model can be applied to accurately reproduce atomic forces and total energy of bulk materials, surfaces, and interfaces. To illustrate the applicability of BIGDML, in this section we have selected representative systems that cover the broad spectrum of materials, and study the prediction accuracy of our MLFFs as judged by the learning curves (test error as a function of the number of data points used for training). The considered systems include bulk materials (graphene as a representative 2D material, 3D metallic and semiconducting solids), surfaces (Pd adsorbed on MgO surface), and van der Waals bonded molecules on surfaces (benzene adsorbed on graphene), as well as a bulk material with interstitial defects (hydrogen in palladium). For a detailed description of the database generation and the levels of theory, as well as the parameters of the simulations and software packages employed, we refer the reader to the Methods section.

1. Bulk materials

Graphene as a representative 2D material. Graphene is a well characterized layered material that continues to exhibit many remarkable properties despite being thoroughly studied [35, 62, 63]. Hence, developing accurate and widely applicable force fields for graphene and its derivatives is an active research area. Recently,
Rowe et al. [35] presented a comprehensive comparison of existing hand-crafted force fields and a Gaussian-process approximated potential (GAP) using the Smooth Overlap of Atomic Positions (SOAP) local descriptor. The GAP/SOAP approach was shown to generalize much better than mechanistic carbon FFs. In Fig. 2 we show the learning curves of the BIGDML model for 5×5 supercell of graphene, showing that only 10 geometries (data samples) are needed to match the best-performing method to date (≈25 meV Å⁻¹ in force RMSE) [35]. The performance and data efficiency of BIGDML is remarkable, given that it uses less than 1% of the amount of data employed by atom-based local descriptors. More importantly, by increasing the number of data samples used for training to 100, we reach a generalization error of ≈1 meV (0.02 meV/atom) in energies and ≈6 meV Å⁻¹ for forces. To our knowledge, such accuracies have not been obtained in the field of MLFFs for extended materials. In order to put our results into context of state-of-the-art MLFFs, in Fig. 3 we show the learning curves comparing GAP/SOAP and BIGDML for graphene (See Supplementary Figure 2 for an extended comparison using different materials). Given the same data for training, BIGDML achieves an improvement of a factor of 10 to 30 in accuracy, both for the total energy and atomic forces. The same conclusions hold for other systems studied in this work, as shown in the Supporting Information.

3D materials: The case of cubic crystals. In the case of 3D materials, we apply our model to monoatomic metallic materials covering common cubic crystal structures: Pd[FCC], Au[FCC] and Na[BCC]. Figure 2 shows the learning curve for these three structures with a supercell of 3×3×3 and symmetry groups $T_{\text{3×3×3} \times O_h}^3$. An accuracy of ≈10 meV Å⁻¹ for a monoatomic metal material can be achieved using approximately 70 samples in the case of Pd (only 10,000 atomic forces), which is only a fraction of the data (less than 1%) required by other models to obtain the same accuracy [37].

2. Surfaces

One of the main challenges of constructing MLFFs on local atomic environments is that such representations can fail to capture subtle local changes with global implications. For example, when describing a surface or an interface, atoms of the same element are described by the same atomic embedding function which in order to en-
code the many possible neighbourhoods (atoms in deeper layers, atoms close to the surface of the material) requires large amounts of training data. This eventually leads to degradation of MLFF performance, a problem that could become practically intractable for local MLFFs when dealing with molecule-surface interactions. These limitations can be addressed in local models but at the cost of higher complexity models and manual tuning of hyperparameters, hence losing the key advantages of MLFFs. In this section we show that the BIGDML method does not have such limitations by studying two representative systems: chemisorbed Pd/MgO-surface and physisorbed benzene/graphene.

**Atom chemisorbed at a surface: Pd\textsubscript{1}/MgO.** In recent years, it has been shown that single-atom catalysts (SACs) can offer superior catalytic performance compared to clusters and nanoparticles [64–66]. These heterogeneous catalysts consist of isolated metal atoms supported on a range of substrates, such as metal oxides, metal surfaces or carbon-based materials. As a showcase, here we use a single Pd atom supported on a pristine MgO (100) surface. The considered supercell consists of a 2×2 slab of MgO(100) with 3 layers, where the lowest layer is kept fixed, and a single Pd atom is deposited on the surface.

The full symmetry group for this system is \( T^{(2)}_{2 \times 2} \otimes C_{4v} \) with 64 elements. The learning curve (see Fig. 2) shows that only 200 samples are needed to reach energy and force accuracy values of \( \approx 34 \text{ meV} \) (\( \approx 0.7 \text{ meV/atom} \)) and \( \approx 30 \text{ meV Å}^{-1} \), respectively. Similarly as in the case of learning force fields for molecules in the gas phase, the target error is always relative to the relevant dynamics of the system and its energetics [22, 41, 42]. In this context, the Pd atom is chemisorbed at an oxygen site and the lowest energetic barrier that the Pd atom experiences is of 450 meV, thus our error is \( \approx 6\% \) of this value. In Fig. 4 we show the minimum-energy barrier (MEB) of Pd atom displacing from one minimum to another on the MgO surface computed by the nudged elastic band (NEB) method (See Methods section for details). It must be noted that the Pd atom never crossed this barrier during the MD simulation used to generate the reference dataset, as displayed by the purple lines in Fig. 4 indicating the distribution of the Pd atom location in the training dataset. Hence, even though the model did not have information regarding the saddle point, the energetic barrier was nevertheless correctly modeled by BIGDML by incorporating translational and Bravais symmetries.

**Molecule physisorbed at a surface: Benzene/graphene.** A highly active field of research in materials science concerns the interaction between molecules and surfaces, due to its fundamental and technological relevance. From the modeling point of view, describing non-covalent interactions within the framework of DFT remains a competitive research area given its intricacies which has led to very accurate dispersion interaction methods [67–71]. Nevertheless, most of the studies about these systems focus on global optimizations or short MD simulations. Here, we demonstrate the applicability of BIGDML by learning the molecular force field of the benzene molecule interacting with graphene.

The full symmetry group of the benzene/graphene system is \( T^{(2)}_{5 \times 5} \otimes C_{6v}^{\text{Graphene}} \otimes C_{6v}^{\text{Benzene}} \), which has a total of 3600 elements. This large number of symmetries greatly reduces the configurational space sampling requirements to reconstruct its PES, as can be seen from the learning curve shown in Fig. 2 where the energy error quickly drops below \( \approx 43 \text{ meV} \) (1 kcal mol\(^{-1}\)) training only on 10 datapoints and \( \approx 21 \text{ meV} \) with 30 training datapoints. For this system, the energy generalisation accuracy starts to saturate at 0.18 meV/atom when training on 100 configurations. Achieving such high generalization accuracy using only a handful of training datapoints for such a complex system convincingly illustrates the high potential of the BIGDML model, since it suddenly opens the possibility of performing predictive simulations for a wide variety of systems where only static DFT calculations are available so far.

The systems discussed in this section offer a general picture of the broad diversity of extended materials that the BIGDML model can describe with high data efficiency and unprecedented accuracy.

### E. Validation of BIGDML models for materials properties

In the previous section we demonstrated the prediction capabilities of the BIGDML method using statistical accuracy measures. Now, we assess the predictive power of BIGDML models in terms of predicting physical properties of materials. In this section we first perform a thorough test for ML models by assessing the phonon spectra of 2D graphene and 3D bulk materials. Then, we proceed to test the performance beyond the harmonic
FIG. 5. Phonon spectra (left) and vibrational densities of states (right) for (a) graphene, (b) bulk sodium, and (c) bulk palladium along the high-symmetry paths in their respective Brillouin zones. The dashed line represents BIGDML and the continuous line the reference DFT-PBE level of theory. The differences between DFT and BIGDML are visually imperceptible.

approximation by carrying out molecular dynamics simulations and comparing observables against explicit DFT calculations. All simulations performed in this section were done using the best trained models displayed in the learning curves (See Fig. 2 and Methods section).

2. Molecular dynamics simulations

Graphene. Simulations of graphene at finite temperature using an accurate description of the interatomic forces is a highly relevant topic given the plethora of

| Bands | DFT-PBE | BIGDML |
|-------|---------|---------|
| DOS   |         |         |
applications of this material. In particular, a necessary contribution to its realistic description is the inclusion of nuclear quantum effects (NQE). For example, the experimental free energy barrier for the permeability of graphene-based membranes to thermal protons can only be correctly described by including the NQE of the carbon atoms [76, 77]. In order to corroborate that our graphene BIGDML model is giving the correct physical delocalization of the nuclei, we performed path-integral molecular dynamics (PIMD) simulations at 300 K for a \(5 \times 5\) supercell. In Fig. 6 we compare the distribution of first neighbor interatomic distance \(r_{CC}\) between classical MD (blue) and PIMD (orange), results showing that the fluctuations in \(r_{CC}\) double its value when considering NQE. These findings are in excellent agreement with explicit first-principles PIMD simulations in the literature [77].

As an additional robustness test, we have performed extended classical MD simulations at various temperatures using the EAM force field [78] and a BIGDML model trained on this level of theory, obtaining a perfect match between these two different methods. This further validates the predictive power of our methodology even at long time scales. These results are shown in the Supporting Information.

Up to this point, we have performed simulations to validate our models under different conditions. In the next section we perform predictive simulations, which highlight the potential of BIGDML for novel applications, including unexpected NQE-driven localization of benzene/graphene dynamics and the diffusion of interstitial hydrogen in bulk palladium.

F. Validation of BIGDML in dynamical simulations of materials

1. Benzene/graphene

The interaction between different molecules and graphene has been extensively studied given the potential applications of molecule/graphene systems as electrical and optical materials and even as candidates for drug delivery systems [79–89]. Of particular interest is the understanding of the effective binding strength and structural fluctuations of adsorbed molecules at finite temperature, which requires long time-scale molecular dynamics simulations, unaffordable when using explicit \textit{ab initio} calculations. Here we will demonstrate that BIGDML models can be used for studying explicit long-time dynamics of a realistic systems such as benzene (Bz) adsorbed on graphene with accurate and converged quantum treatment of both electrons and nuclei (See Fig. 7-A). The Bz/graphene system has three minima that resemble those of the benzene dimer: the \(\pi-\pi\) stacking (parallel-displaced) structure as global minimum and two local minima corresponding to parallel and T-shaped configurations, as displayed in Fig. 7-B [3] along with the corresponding structural parameters and adsorption energies computed at the PBE+MBD level of theory [68, 69, 90]. The calculated adsorption energy for the global minimum is in a very good agreement with experimental measurements of 500±80 meV [91].

An extensive amount of studies exist on the implica-
tions of NQE on properties of molecules and materials at finite temperature [92, 93], however much less is known about the implications of NQE for non-covalent van der Waals (vdW) interactions [3, 94]. In the particular case of Bz/graphene, considering the translational symmetries of the PES experienced by the Bz molecule as well as thermal fluctuations and its many degrees of freedom, it is to be expected that the Bz dynamics will be highly delocalized. Nonetheless, it was recently reported that the inclusion of NQE in a molecular dimer can considerably enhance intermolecular vdW interactions [3]. However, the adsorption/binding energy ratio between Bz/graphene and Bz/Bz system is \( E_{ads}^{Bz/\text{graphene}}/E_{int}^{Bz/Bz} \approx 4 \), therefore it is not clear how NQEs will affect such strongly interacting vdW systems.

In order to assess the role of temperature and NQE for Bz/graphene, in Fig. 7-C we present the results obtained from classical MD and PIMD simulations at 300K using a BIGDML FF trained at the PBE+MBD level of theory. At this temperature, the benzene molecule tends to mostly populate configurations at an angle of \( \approx 10^\circ \) relative to the graphene normal vector in both cases (see Fig. 7-A). Nevertheless, classical MD simulations explore substantially wider regions of the PES, reaching angles of up to \( 80^\circ \), close to the T-site. In contrast, PIMD simulations yield a localized sampling of \( \theta \) with a maximum angle of \( \approx 30^\circ \). To understand the origin of this localization, we have systematically increased the “quantumness” of the system by raising the number of beads in the PIMD simulations to converge towards the exact treatment of NQE. This approach provides concrete evidence of the progressive localization of the benzene normal orientation as the NQE increase (see Supporting Information). The physical origin of this phenomenon is the NQE-induced interatomic bond dilation, where the zero-point energy generated by NQE drive the system beyond the harmonic oscillation regime. The intramolecular de-localization produces effective molecular volume dilation and increases the average polarizability of benzene and graphene rings, akin to a recent analysis of non-covalent interactions between molecular dimers upon constraining their center of mass [3]. In contrast, in this work no constraints were imposed on the Bz/graphene system, suggesting that the Bz molecule localization on graphene should be observable in experiments. In order to further rationalize the NQE-induced stabilization of vdW interactions, we have computed the vdW interaction energy as a function of compression/dilation of the Bz molecule on graphene and found a linear dependence between dilation and vdW interaction (see Supporting Information). This analysis fully supports our hypothesis of NQE-induced stabilization and dynamical localization.

The rather fundamental nature of the underlying physical phenomenon of NQE-induced stabilization suggests that many polarizable molecules interacting with surfaces will exhibit a similar dynamical localization effect. It is worth mentioning that a thorough analysis of the Bz/graphene system demands extensive simulations which are now made accessible due to the computational efficiency and accuracy of the BIGDML model. Our modeling could also be applied to larger molecules with peculiar behavior under applied external forces [95].

2. Hydrogen interstitial in bulk palladium

Hydrogen has become a promising alternative to fossil fuels as a cleaner energy source. Nevertheless, finding a safe, economical and high-energy-density hydrogen storage medium remains a challenge [96]. One of the proposed methods is to store hydrogen in interstitial sites of the crystal lattices of bulk metals [96–98]. Among these metals, palladium has been widely researched as a candidate, since it can absorb large quantities of hydrogen in a reversible manner [97].

Characterizing the diffusion of hydrogen in the crystal lattices at different temperatures is crucial to assess their performance as storage materials. Hence, in this section we study a system consisting of a hydrogen atom interstitial in bulk palladium with a cubic supercell containing 32 Pd atoms with full symmetry group \( T^{(3)}_{2 \times 2 \times 2} \otimes O_h \), and described at the DFT-PBE level of theory (See Methods section for more details). The BIGDML learning curve for this system in presented in Fig. 2. Within the FCC lattice there are two possible cavities for hydrogen atoms storage: the octahedral (O-sites) and the tetrahedral (T-sites) cavities (See Fig. 8-A-top), where the O-site is the global minimum [97] and it is separated from the T-site by an energetic barrier of \( \approx 160 \text{ meV} \) as shown in Fig. 8-A-bottom. Additionally, from this figure we can see the excellent agreement between BIGDML model and the reference DFT calculations.

Given the height of the energetic barrier between the two minima, it is to be expected that the NQE-induced delocalization of the hydrogen atom would be insufficient to promote H-atom tunneling at temperature close to room temperature, while at higher temperatures classical thermal effects should dominate the dynamics. In contrast, Kimizuka et al. [97] reported a study based on transition state theory (TST) suggesting that not only the inclusion of the NQE has indeed a strong effect on the H-atom diffusion, but also they reported that NQE hinder the migration from O-site to T-site. In order to elucidate realistic dynamics of the H atom in the metal lattice and the impact of the NQE without relying on approximations such as TST, we performed direct classical MD and PIMD simulations at different temperatures (from 100 K to 1000 K) (see Methods for more details). We first studied the NQE-induced statistical sampling of the hydrogen atom in each cavity as shown in Fig. 8-B (See supporting material for an animated version of this figure). This helps us to visualize hydrogen dynamics in the temperature range from 100 K to 300 K and to determine the shape of the cavity, which transforms from a cube to a much larger truncated octahedron as the temperature increases.
FIG. 8. A) (Top) Minima of the trajectory used to calculate the minimum-energy path (MEP) for the diffusion of H in FCC Pd. (Bottom) MEP as calculated using BIGDML (continuous line) and DFT-PBE (circles) between adjacent O- and T-sites. B) Three-dimensional plots of the probability distribution of the H atom in the O-site at different temperatures. C) Transition rates from O-sites to T-sites of an H atom in bulk Pd as function of the temperature. The green circles and yellow squares represent the values calculated using classical MD and PIMD using the BIGDML model, respectively. The dotted lines are the Arrhenius fit to the data from BIGDML@MD (green) and the classical transition state theory (TST) by Kimizuka et al. [97] (blue), and the red diamonds are TST-PIMD by Kimizuka et al. too.

Then, from the generated (classical and quantum) trajectories we have estimated the diffusivity of the hydrogen atom as a function of the temperature, which are shown in Fig. 8-C along with TST results. From these results we observe the usual Arrhenius temperature dependence in the classical MD case, but more interestingly the quantum dynamics lead to essentially the same diffusion coefficients. In fact, it is to be expected that NQE do not play a major role in diffusivity in this particular case at room temperature given that the thermal energy is \( \approx 26 \text{ meV} \) while the energetic barrier between the O and T sites is 160 meV (Fig. 8-A). Hence, the NQE do not provide the excess of energy required to promote proton tunneling. Furthermore, as the temperature increases the NQE become less important and the classical thermal effects dominate the dynamics, hence the hydrogen diffusion remains Arrhenius-like. Comparing our explicit MD simulations with previous approximate TST results [97] we see that there are pronounced differences. The TST prediction of the classical frequency transition rate considerably overestimates the actual value obtained from our more robust simulations. The deviations observed in TST are due to the neglect of anharmonicities in this approximate theory, which are in contrast fully treated in our MD/PIMD simulations. The results presented in this section demonstrate how BIGDML enables long PIMD simulations to obtain novel insights into dynamical behavior of intricate materials containing vacancies or interstitial atoms.

III. DISCUSSION

In this work, we introduced the BIGDML approach — a MLFF for materials that is accurate, straightforward to construct, efficient in terms of learning on reference \textit{ab initio} data, and computationally inexpensive to evaluate. The accuracy and efficiency of the BIGDML method stems from extending the sGDML framework for finite systems [22, 41] by employing a global periodic descriptor and making usage of translational and Bravais symmetry groups for materials. The BIGDML approach enables carrying out extended dynamical simulations of materials, while correctly describing all relevant chemical and physical (long-range) interactions in periodic systems contained within the reference data. In principle, the BIGDML method would allow to execute exact dynamics of materials once high-level electronic structure force calculations for periodic systems (with CCSD(T) or Quantum Monte Carlo methods) become a reality [38–40]. We remark that the molecular sGDML approach has already fulfilled this long-standing goal for molecules with up to a few dozen atoms [3, 22].

We have demonstrated the applicability and robustness of the BIGDML method by studying a wide variety of relevant materials and their static and dynamical properties, for example successfully assessing the performance of BIGDML models for physical observables in the har-
monic and anharmonic regimes in the form of phonon bands and molecular dynamics. Furthermore, we carried out predictive simulations on interstitial hydrogen diffusion in bulk Pd, as well as accurately capturing intricate van der Waals forces and the dynamics of the interface formed by molecular benzene and 2D graphene layer.

From the practical perspective, the BIGDML approach represents an advantageous framework beyond its accuracy and data efficiency, given that the model generation is a straightforward process starting from the simplicity of database generation and its out-of-the-box training procedure [42]. Given the very few data samples needed to generate a relatively accurate BIGDML model (see Fig. 2), our model can be coupled with any DFT code to substantially accelerate DFT-based dynamics with minimal human effort invested in constructing the initial dataset. To illustrate the gain in computational speed, we remark that for benzene/graphene we gain a factor of 50,000 for computing atomic forces with BIGDML when compared to the PBE+MBD level of electronic-structure theory. This gain would further increase when using a higher level of quantum-mechanical methods for generating reference data.

Many powerful MLFFs for materials have been proposed and some are already widely used for materials modeling [53, 99]. In order to embed the BIGDML model into the current context of MLFFs for materials, it is convenient to address some of the limitations that current methodologies face, as well as to discuss goals to pursue with the next generation of MLFFs in materials science.

All current MLFFs for materials known to the authors employ the locality approximation, i.e. they build a model for an energy of an atom in a certain chemical environment, which is defined by a cutoff function. The typical employed cutoffs are of 3-8 Å, being of a rather short range. Increasing the cutoff does not necessarily lead to a better model, because electronic interactions exhibit hard-to-learn multiscale structure [9]. In addition, different interaction scales are mutually coupled. An attractive feature of the locality approximation is that in principle the short-range interactions are transferable to different systems. However, in practice this is not a general finding. For example, it was shown that a general-purpose GAP/SOAP MLFF for carbon [34] yields errors an order of magnitude higher in graphene compared to the same methodology trained specifically on graphene data [35]. In addition, local MLFFs typically decouple interaction potentials of different atoms by assigning atom types. For example, carbon in benzene and carbon in graphene could be treated as different atom types. Obviously, such decoupling makes the learning problem harder because more data is necessary to “restore the coupling” between different atomic species.

BIGDML solves both problems of localization in a robust way by using a global descriptor with periodic boundary conditions. Any type of interaction can be captured by BIGDML and all atoms are mutually coupled by construction. The disadvantage of such an approach is that a BIGDML model is system-specific and, hence, not transferable between different systems or even between different supercell sizes for the same system. Despite this slight drawback, it is clear that having an access to a MLFF that can robustly represent all possible interactions in extended materials is a substantial achievement. In addition, we should stress that BIGDML has a superior learning capacity compared to local MLFFs, since it can reach generalization accuracies of up to two orders of magnitude better than localized MLFFs (see Fig. 3).

Another crucial aspect of MLFFs is their data efficiency and ability to correctly capture all relevant symmetries for a given system. Symmetries play a crucial role when studying nuclear displacements (phonons, thermal conductivities, etc.). BIGDML solves both of these challenges at the same time. The symmetries are obtained from the periodic cell and the reference geometries in a data-driven way. Symmetries are known to effectively reduce the complexity of the learning problem and we have convincingly demonstrated this fact for finite molecular systems [22]. Periodic systems have even more symmetries than molecules, making the force field re- construction effectively a lower-dimensional task. While this qualitative outcome could have been expected prior to the formulation of BIGDML, the enormous practical advantage of incorporating crystalline symmetries is remarkable. Even a few dozen samples (atomic forces for a few unitcell geometries) already yield BIGDML models that can be used in practical applications of molecular dynamics.

We would like to remark further that while BIGDML is a kernel-based approach, elegantly able to formally include symmetries and prior physical information, it will be an interesting and important challenge to transfer the learning machinery established here also to deep learning approaches (such as convolutive neural networks, graph neural networks or even generative adversarial models) ideally by incorporating symmetries, prior physical knowledge and equivariance constructions into their architecture (see Refs. [23, 33, 100, 101] for some first steps in this direction).

With the advent of new advanced materials such as high performance perovskite solar cells, topological insulators and van der Waals materials, it is crucial to construct reliable MLFFs capable of dynamical simulations at the highest level of accuracy given by electronic-structure theories while maintaining relatively low computational cost. While local MLFFs and BIGDML are complementary approaches, we would like to emphasize that global representations and symmetries could also be readily incorporated in other MLFF models. The challenge of developing accurate, efficient, scalable, and transferable MLFFs valid for molecules, materials, and interfaces thereof suggests the need for many further developments aiming towards universally applicable MLFF models.
IV. METHODS

1. Data generation and DFT calculations

Given the different types of calculations and materials in this work, we present the details of the data generation, model training and simulations organized per system. All the databases were generated using molecular dynamics simulations using the NVT thermostat.

Graphene. Here we used a 5×5 supercell at the DFT level of theory at the generalized gradient approximation (GGA) level of theory with the Perdew-Burke-Ernzerhof (PBE) [90] exchange-correlation functional. We performed the calculation in the Quantum Espresso [102, 103] software suite, using plane-waves with ultrasoft pseudopotentials and scalar-relativistic corrections. We used an energy cutoff of 40 Ry. A uniform 3×3×1 Monkhorst-Pack grid of k-points was used to integrate over the Brillouin zone. The ab initio MD (AIMD) used to generate the database was ran at 500 K during 10,000 time steps using an integration step of 0.5 fs. The results displayed in Fig. 6 were performed using PIMD simulations with 32 beads and we ran the simulation for 300 ps using an integration step of 0.5 fs.

Pd/MgO. In this case, we used a 2×2 supercell with 3 atomic layers to model the MgO (100) surface. The calculations were performed in Quantum Espresso, using an energy cutoff of 50 Ry and integrating over the Brillouin zone at the Γ-point only. For this system, we ran an AIMD at 500 K with an integration step of 1.0 fs during 10,000 integration steps to generate the material’s database.

Benzene/graphene. For this particular example we have used the same graphene supercell mentioned above and placed a benzene molecule on top. In order to include the correct non-covalent interactions between the benzene molecule and the graphene layer, we have used an all-electrons DFT/PBE level of theory with the many body dispersion (MBD) [68, 69] treatment of the van der Waals interaction using the FHI-aims [104] code. The AIMD simulation for the system’s database constructions was performed at 500 K using an integration step of 1.0 fs during 15,000 steps. The results displayed in Fig. 7 were performed using PIMD simulations using 1, 8, 16 and 32 beads (in order to guarantee that we have achieved converged NQE) and we ran the simulation for 200 ps using an integration step of 0.5 fs.

Bulk metals. In this case we were interested in a variety of materials and their different interactions. Then, we have considered Pd[FCC] and Na[BCC] described at the DFT/PBE level of theory using the Quantum Espresso software. The databases were created by running AIMD simulations at 500 K and 1000 K for Pd, and 300 K for Na using a time steps of 1.0 fs for all the simulations. Monkhorst-Pack grids of 3×3×3 k-points were used to integrate over the Brillouin zone for all materials. All calculations for the bulk metals were spin-polarized.

2. The sGDML framework

A data efficient reconstruction of accurate force fields with ML hinges on including the right inductive biases in the model to compensate for finite reference dataset sizes. The Symmetric Gradient-Domain Machine Learning (sGDML) achieves this through constraints derived from exact physical laws [22, 41, 42]. In additional to the basic roto-translational invariance of energy, sGDML implements energy conservation, a fundamental property of closed classical and quantum mechanical systems. The key idea behind sGDML is to define a Gaussian Process (GP) using a kernel \( k(x, x') = \nabla_x k_E(x, x') \nabla_{x'} \) that models any force field \( f_E \) as a transformation of some unknown potential energy surface \( f_E \) such that

\[
    f_E = -\nabla f_E \sim \mathcal{GP} \left[ -\nabla \mu_E(x), \nabla x k_E(x, x') \nabla_{x'} \right].
\]

Here, \( \mu_E : \mathbb{R}^d \rightarrow \mathbb{R} \) and \( k_E : \mathbb{R}^d \times \mathbb{R}^d \rightarrow \mathbb{R} \) are the prior mean and prior covariance functions of the latent energy GP-predictor, respectively.

The sGDML model also incorporates all relevant rigid space group symmetries, as well as dynamic non-rigid symmetries of the system at hand into the same kernel, to further improve its efficiency. Those symmetries are automatically recovered as atom-permutations via multi-partite matching of all geometries in the training dataset [22]. BIGDML extends sGDML to periodic systems, which posses unique permutational symmetries that were previously not considered.

3. Coulomb matrix PBC implementation

The periodic boundary conditions were implemented using the minimum image convention. Under this convention, we take the distance between two atoms to be the shortest distance between their periodic images. We start by expressing the distance vectors \( d_{ij} = r_i - r_j \) in
the basis of the simulation supercell lattice vectors as

$$d_{ij} = A c_{ij}, \quad (3)$$

where $A$ is a $3 \times 3$ matrix which contains the lattice (supercell) vectors as columns, and $c_{ij}$ are the distance vectors in the new basis. We then confine the original distance vectors to the simulation cell,

$$d_{ij}^{(PBC)} = d_{ij} - A \text{int}(c_{ij}), \quad (4)$$

where $\text{int}(x)$ is the nearest integer function. By replacing the ordinary distance vectors $d_{ij}$ with $d_{ij}^{(PBC)}$ in the Coulomb matrix descriptor, it becomes

$$D_{ij}^{(PBC)} = \begin{cases} 1 & \text{if } i \neq j \\ \frac{1}{|d_{ij}^{(PBC)}|} & \text{if } i = j \end{cases} \quad (5)$$

In practice, only the $d_{ij}^{(PBC)}$ upper triangular matrix is used.

4. Software: Interface with i-PI

For this work, a highly optimised interface of BIGDML has been implemented in the i-PI molecular dynamics package [105]. The main features of this implementation are: (1) it allows the use of periodic boundary conditions and stress tensor calculation, (2) parallel querying of all beads at once in PIMD simulations and (3) it uses the highly optimized sGDML GPU implementation in PyTorch to parallelise beads calculations, dramatically increasing the simulation efficiency.

5. Software: Interface with Phonopy for phonons

An ASE calculator is already provided by the sGDML package, this allows to use all its simulation options. In particular, the phonon analysis for materials is easy computed in this package using Phonopy [106]. An example of the scripts used to compute the phonons in this paper is provided in the Supporting Information.

V. SOFTWARE AVAILABILITY

Our code, documentation and datasets are available at http://sgdml.org.

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