

Dihedral-angle-corrected registry-dependent interlayer potential for multilayer graphene structures

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The structural relaxation of multilayer graphene is essential in describing the interesting electronic properties induced by intentional misalignment of successive layers, including the recently reported superconductivity in twisted bilayer graphene. This is difficult to accomplish without an accurate interatomic potential. Here, we present a new, registry-dependent Kolmogorov-Crespi-type interatomic potential to model interlayer interactions in multilayer graphene structures. It consists of two parts, representing attractive interaction due to dispersion and repulsive interaction due to anisotropic overlap of electronic orbitals. An important new feature is a dihedral-angle-dependent term that is added to the repulsive part to describe correctly several distinct stacking states that the original Kolmogorov-Crespi potential cannot distinguish. We refer to the new model as the dihedral-angle-corrected registry-dependent interlayer potential (DRIP). Computations for several test problems show that DRIP correctly reproduces the binding, sliding, and twisting energies and forces obtained from *ab initio* total-energy calculations based on density-functional theory. We use the new potential to study the structural properties of a twisted graphene bilayer and the exfoliation of graphene from graphite. Our potential is available through the OpenKIM interatomic potential repository at <https://openkim.org>.

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I. INTRODUCTION

Since the discovery of graphene [1], two-dimensional (2D) materials have been shown to possess remarkable electronic, mechanical, thermal, and optical properties with great potential for nanotechnology applications, such as semiconductors, ultrasensitive sensors, and medical devices [2–5]. Stacked 2D materials (or “heterostructures”) have even more unusual and novel properties that their monolayer and 3D counterparts do not possess [6,7]. For example, the electronic band gap of a graphene bilayer can be tuned by applying a variable external electric field, which allows great flexibility in the design and optimization of semiconductor devices such as p-n junctions and transistors [8]. A different manifestation of interesting behavior not found in the bulk is the recently reported superconductivity in intentionally misaligned (by a relative twist of $\sim 1.1^\circ$) graphene bilayers [9]. As a prototype of a stacked 2D material, multilayer graphene (“graphitic structure” hereafter) exhibits strong *sp*² covalent bonds within layers and weak van der Waals (vdW) and orbital repulsion interactions between layers. Although weak, it is the interlayer interaction that defines the function of nanodevices such as nanobearings, nanomotors, and nanoresonators [10].

To simulate the mechanical behavior of graphitic structures, it is necessary to model the interactions between the electrons and the ions, which produce the forces governing atomic motion and deformation. First-principles approaches that involve solving the Schrödinger equation are most

accurate, but due to hardware and algorithmic limitations these methods are typically limited to studying small molecular systems and crystalline materials characterized by compact unit cells with an upper limit on the number of atoms in the range of $\sim 10^3$. Empirical interatomic potentials are computationally far less costly than first-principles methods and can therefore be used to compute static and dynamic properties that are inaccessible to quantum calculations, such as dynamical tribological properties of large-scale graphene interfaces [11–13].

There have been many efforts to produce an interatomic potential that would adequately describe the properties of graphitic structures, in particular the interactions between layers. However, as we argue in detail in this paper, the existing potentials fall short of capturing key elements of the graphitic structures of interest. Therefore, there is a pressing need to construct an accurate interlayer potential that will elucidate many of the important structural properties of these structures.

The paper is structured as follows. In Sec. II, we briefly review the nature of existing interatomic potentials that might be applied to graphitic structures, explain their shortcomings, and elaborate on the need for constructing a new potential. In Sec. III, the functional form of the new model is presented, together with a description of the fitting process that determines the values of all the parameters that appear in it. In Sec. IV, the predictions of the new model for several canonical properties of interest are compared with other potentials and results from *ab initio* total-energy calculations based on density-functional theory (DFT). Large-scale applications of the new model are discussed in Sec. V. The paper is summarized in Sec. VI.

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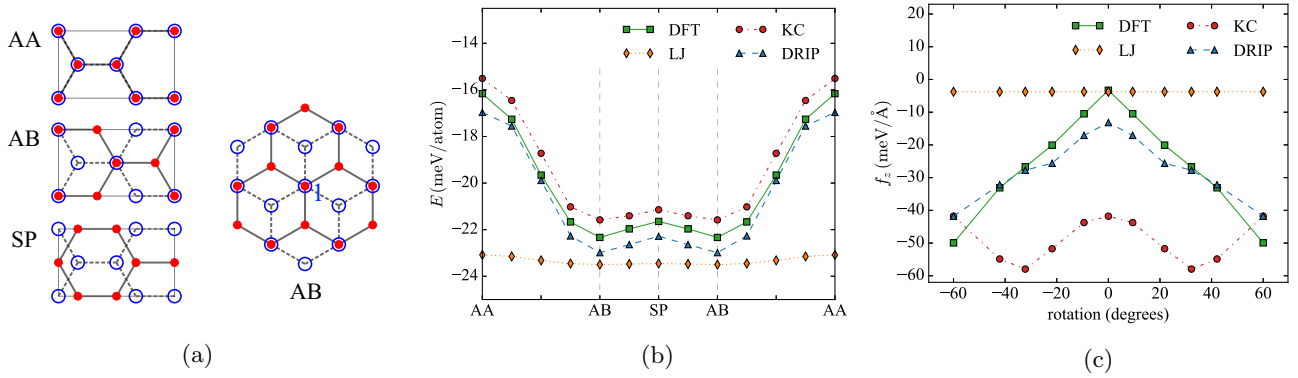


FIG. 1. Energy and force variations when sliding and twisting a graphene bilayer. (a) Schematic representation of high-symmetry graphene bilayer configurations: AA, AB, and saddle point (SP) stackings. (b) Energy variation of sliding one layer relative to the other along the armchair direction. (c) Out-of-plane component of the force on the atom at the rotation center [blue circle labeled 1 in the bottom layer in panel (a)]. Rotation by 0° corresponds to AB stacking, and rotation by $\pm 60^\circ$ corresponds to AA stacking. In both sliding and twisting, periodic boundary conditions are applied and the layer spacing is fixed at 3.4 \AA . Details are provided in Sec. IV.

II. NEED FOR NEW GRAPHITIC POTENTIAL

A large number of interatomic potentials have been developed to model the strong covalent bonds in carbon systems. Among these are bond-order potentials, such as the Tersoff [14,15] and REBO [16,17] potentials, which allow for bond breaking and formation depending on the local atomic environments. Such models have been shown to be accurate for many problems and are widely used, but are not suitable for layered 2D materials since they do not include long-range weak interactions. To address this, the AIREBO [18] potential (based on REBO) added a 6–12 form of the Lennard-Jones (LJ) potential [19] to model vdW interactions. For graphitic structures, the LJ potential works well in describing the overall binding characteristics between graphene layers. For example, the LJ parametrization used in AIREBO predicts an equilibrium layer spacing of 3.357 \AA and a c -axis elastic modulus of 37.78 GPa for graphite, in good agreement with first-principles and experimental results. The isotropic nature of LJ—that is, the fact that it depends only on distance between atoms and not orientation—makes it too smooth to distinguish energy variations for different relative alignments of layers [20]. Figure 1(b) shows the energy variation obtained by sliding one layer relative to the other along the armchair direction of a graphene bilayer. The energy remains nearly constant with a maximal difference of 0.41 meV/atom between the AA and AB stackings, a small fraction (6.6%) of the DFT result (also shown in the figure).

The reason that the LJ potential fails to capture the energy variations due to interlayer sliding is that in addition to vdW, the interlayer interactions include short-range Pauli repulsion between overlapping π orbitals of adjacent layers. These repulsive interactions are not well described by a simple pair potential like LJ [10,12,13]. To account for this registry effect (relative alignment of layers), Kolmogorov and Crespi (KC) developed a registry-dependent interlayer potential for graphitic structures [10]. In the KC potential, the dispersive (vdW) attraction between layers is described using the same theoretically motivated r^{-6} term as in LJ, and π orbital overlap is modeled by a Morse-type [21] exponential multiplied by a registry-dependent modifier that depends on the transverse

distance between atom pairs. The KC potential has been modified and reparameterized to better fit the energy variations between different stacking states predicted by DFT-D (DFT with dispersion corrections) [22]. It has also been adapted for other 2D materials such as h-BN [12] and graphene/h-BN [13,23] heterostructures.

The energy corrugation obtained by the KC potential is in agreement with DFT as shown in Fig. 1(b). However, the forces obtained from the KC potential deviate significantly from the DFT results. This implies that equilibrium structures associated with energy minima will differ as well. To illustrate this point, consider a graphene bilayer where one layer is rigidly rotated relative to the other. Figure 1(c) shows the force in the z direction (perpendicular to the layers) acting on the bottom atom on the rotation axis [atom 1 in the bottom layer in Fig. 1(a)] as a function of rotation angle. The force predicted by the KC potential decreases and then increases from AA ($\pm 60^\circ$) to AB (0°), whereas DFT predicts a monotonic increase from AA to AB. In particular, the KC potential yields the same z force for the AA and AB stackings,¹ which indicates that the KC potential cannot distinguish the overlapping atoms at the rotation center in these states. This is intrinsic to the KC potential. The force on the central atom in the AA and AB states is identical, regardless of the choice of KC parameters. The modified KC potential [22] has the same problem. The LJ potential does even worse [Fig. 1(c)], predicting a constant force on the central atom that is independent of the rotation angle.

In the present paper, a new registry-dependent interlayer potential for graphitic structures is developed that addresses the limitations of the KC potential described above. A dihedral-angle-dependent term is introduced into the registry modifier of the repulsive part that makes it possible to distinguish forces in AA and AB states. We refer to this potential as the dihedral-angle-corrected registry-dependent interlayer potential (DRIP). DRIP is validated by showing that it correctly

¹Note that the x and y components of the force are zero at AA and AB due to symmetry.

reproduces the DFT energy and forces for different sliding and rotated states as well as structural and elastic properties. It is then applied to study structural relaxation in twisted graphene bilayers and exfoliation of graphene from graphite; these representative example are large-scale applications that cannot be studied using DFT. The potential has been implemented as a KIM Model Driver [24] and the parametrization in this paper has been implemented as a KIM Model [25] at OpenKIM [26,27]. (See details in Appendix.)

III. DEFINITION OF NEW MODEL

The DRIP functional form is

$$\mathcal{V} = \frac{1}{2} \sum_{i \in \text{layer 1}} \sum_{j \in \text{layer 2}} (\phi_{ij} + \phi_{ji}), \quad (1)$$

where the pairwise interaction is based on the KC form with dihedral modifications:

$$\phi_{ij} = f_c(x_r) \left[e^{-\lambda(r_{ij}-z_0)} [C + f(\rho_{ij}) + g(\rho_{ij}, \{\alpha_{ij}^{(m)}\})] - A \left(\frac{z_0}{r_{ij}} \right)^6 \right], \quad m = 1, 2, 3. \quad (2)$$

The cutoff function $f_c(x)$ is the same as that used in the ReaxFF potential [28] and the interlayer potential for h-BN [12,13]:

$$f_c(x) = 20x^7 - 70x^6 + 84x^5 - 35x^4 + 1 \quad (3)$$

for $0 \leq x \leq 1$ and vanishes for $x > 1$, while it has zero first and second derivatives at $x = 1$; in the expressions where this function appears, its argument is always nonnegative. The variable x_r in Eq. (2) is the scaled pair distance $x_r = r_{ij}/r_{\text{cut}}$. The use of $f_c(x_r)$ ensures that DRIP is smooth at the cutoff r_{cut} (set to 12 Å), a feature that the KC model does not possess.

The term with r_{ij}^{-6} dependence in Eq. (2) models attractive vdW interactions (as in LJ), while the repulsive interactions due to orbital overlap are modeled by the exponential term multiplied by a registry-dependent modifier. The transverse distance function $f(\rho)$ has the same form as in KC:

$$f(\rho) = e^{-y^2} [C_0 + C_2 y^2 + C_4 y^4], \quad y = \frac{\rho}{\delta}, \quad (4)$$

with its argument in Eq. (2) given by the expression

$$\rho_{ij}^2 = r_{ij}^2 - (\mathbf{n}_i \cdot \mathbf{r}_{ij})^2, \quad (5)$$

in which \mathbf{r}_{ij} is the vector connecting atoms i and j , r_{ij} is the corresponding pair distance, and \mathbf{n}_i is the layer normal at atom i . For example, as shown in Fig. 2, \mathbf{n}_i can be defined as the normal to the plane determined by the three nearest-neighbors of atom i : k_1 , k_2 , and k_3 :

$$\mathbf{n}_i = \frac{\mathbf{r}_{k_1 k_2} \times \mathbf{r}_{k_1 k_3}}{\|\mathbf{r}_{k_1 k_2} \times \mathbf{r}_{k_1 k_3}\|}. \quad (6)$$

Note that, in general, $\rho_{ij} \neq \rho_{ji}$ because the normals \mathbf{n}_i and \mathbf{n}_j depend on their local environments.

The dihedral angle function is given by

$$g(\rho, \{\alpha_{ij}^{(m)}\}) = B f_c(x_\rho) \sum_{m=1}^3 e^{-\eta \alpha_{ij}^{(m)}}, \quad (7)$$

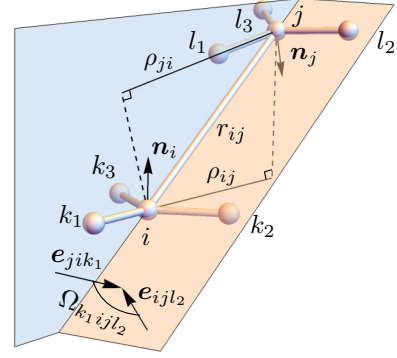


FIG. 2. Schematic representation of an atomic geometry that defines the normal vectors \mathbf{n}_i and \mathbf{n}_j and the dihedral angle $\Omega_{k_1ijl_2}$.

where $\alpha_{ij}^{(m)}$ is the product of the three cosines of the dihedral angles formed by atom i (in layer 1), its m th nearest-neighbor k_m , atom j (in layer 2), and its three nearest-neighbors l_1 , l_2 , and l_3 :

$$\alpha_{ij}^{(m)} = \cos \Omega_{k_m i j l_1} \cos \Omega_{k_m i j l_2} \cos \Omega_{k_m i j l_3}, \quad (8)$$

$$\cos \Omega_{kijl} = \mathbf{e}_{jik} \cdot \mathbf{e}_{ijl}, \quad (9)$$

$$\mathbf{e}_{jik} = \frac{\mathbf{r}_{ik} \times \mathbf{r}_{ji}}{\|\mathbf{r}_{ik} \times \mathbf{r}_{ji}\|}, \quad \mathbf{e}_{ijl} = \frac{\mathbf{r}_{jl} \times \mathbf{r}_{ij}}{\|\mathbf{r}_{jl} \times \mathbf{r}_{ij}\|}. \quad (10)$$

To understand the physical origin of the terms defined in Eqs. (8)–(10), recall that a dihedral angle Ω is the angle between two planes defined by four points that intersect at a line defined by two of them as shown in Fig. 2. Here, the intersection line is defined by atoms i and j . The two planes are then defined by atoms (j, i, k_1) and (i, j, l_2) . The normals to these planes are \mathbf{e}_{jik_1} and \mathbf{e}_{ijl_2} , respectively, defined in Eq. (10), with the corresponding dihedral angle given by Eq. (9). The dihedral product $\alpha_{ij}^{(m)}$ monotonically decreases when twisting a graphene bilayer from AB to AA stacking, and consequently can be utilized to construct a potential function that distinguishes AB and AA stacking and the intermediate stacking states. The cutoff function $f_c(x_\rho)$ in Eq. (7) is the same as that in Eq. (3), and $x_\rho = \rho/\rho_{\text{cut}}$, where we set $\rho_{\text{cut}} = 1.562 \text{ \AA}$ to include only a few of the computationally expensive four-body dihedral angle interactions. The potential has a total of ten parameters, C_0 , C_2 , C_4 , C , δ , λ , B , η , A , and z_0 , and two cutoffs r_{cut} and ρ_{cut} .

To determine the values of all the parameters that appear in the DRIP potential, we constructed a training set of energies and forces for graphene bilayers at different separation, sliding, and twisting states. The training set is generated from DFT calculations using the VIENNA AB INITIO SIMULATION PACKAGE (VASP) [29,30]. The exchange-correlation energy of the electrons is treated within the generalized gradient approximated (GGA) functional of Perdew, Burke, and Ernzerhof (PBE) [31].

Standard density functionals such as the local density approximation (LDA) and GGA accurately represent Pauli repulsion in interlayer interactions, but fail to capture vdW forces that result from dynamical correlations

TABLE I. Properties obtained from various DFT vdW corrections compared with ACFDT-RPA and experimental results. Also included are results from various empirical potentials. The properties include equilibrium layer spacings of bilayer graphene in AB stacking, d_{AB} , bilayer graphene in AA stacking, d_{AA} , and graphite, d_{graphite} ; optimal interlayer binding energies for bilayer graphene (binding energy at the equilibrium spacing in AB stacking), E_{AB} , and graphite, E_{graphite} ; energy differences between AA-stacked and AB-stacked bilayers, ΔE_{AA-AB} , and SP and AB stackings, ΔE_{SP-AB} , at a layer spacing of $d = 3.4 \text{ \AA}$; and the elastic modulus along the c axis for graphite, C_{33} . All properties are computed using the in-plane lattice constant $a = 2.46 \text{ \AA}$.

	d_{AB} (\AA)	d_{AA} (\AA)	d_{graphite} (\AA)	E_{AB} (meV/atom)	E_{graphite} (meV/atom)	ΔE_{AA-AB} (meV/atom)	ΔE_{SP-AB} (meV/atom)	C_{33} (GPa)
PBE+D2	3.248	3.527	3.218	24.84	55.20	10.35	1.16	39.12
PBE+D3	3.527	3.713	3.483	21.40	47.09	3.80	0.42	35.04
PBE+TS	3.357	3.511	3.329	36.36	82.33	7.97	1.01	68.31
PBE+TSIHP	3.379	3.529	3.350	35.73	80.42	7.48	1.22	64.73
PBE+MBD	3.423	3.638	3.398	22.63	48.96	6.17	0.69	31.64
PBE+dDsC	3.447	3.639	3.410	28.04	63.00	5.53	0.74	38.43
ACFDT-RPA	3.39 ^a		3.34 ^b		48 ^b			36 ^b
Experiment			3.34 ^c		$43 \pm 5^d, 35 \pm 10^e, 52 \pm 5^f$	7.7 ^g	0.86 ^g	36.5 ^{h}, 38.7ⁱ}
AIREBO	3.391	3.418	3.357	22.85	48.86	0.41	0.04	37.78
LCBOP	3.346	3.365	3.346	12.51	25.03	0.47	0.01	29.77
KC	3.374	3.602	3.337	21.60	47.44	6.07	0.44	34.45
DRIP	3.439	3.612	3.415	23.05	47.38	6.02	0.71	32.00

^aReference [38].

^bReference [39].

^cReference [40].

^dReference [41].

^eReference [42].

^fReference [43].

^gReference [44]. Values inferred from experimental data on shear mode frequencies.

^hReference [45].

ⁱReference [46].

between fluctuating charge distributions.² To address this limitation, various approximate corrections have been proposed including the D2 method [32], the D3 method [33], the Tkatchenko and Scheffler (TS) method [34], the TS method with iterative Hirshfeld partitioning (TSIHP) method [35], the many-body dispersion (MBD) method [36], and the dDsC dispersion correction method [37]. To select a correction for the DRIP training set, we used these dispersion correction methods to compute a number of structural, energetic, and elastic properties. The results are shown in Table I, along with experimental values and more accurate adiabatic-connection fluctuation-dissipation-theory-based random-phase-approximation (ACFDT-RPA) computations that have been shown to provide a very accurate description of vdW interactions [38,39]. The conclusion from these comparisons is that D2 and D3 provide inaccurate estimates for the layer spacing of AB graphene and graphite (d_{AB} and d_{graphite}), and TS, TSIHP, and dDsC significantly overestimate the graphite binding energy E_{graphite} . MBD provides the best overall accuracy for all considered properties and is therefore the vdW correction used in this work together with the PBE functional.

²GGA predicts no binding at all at physically meaningful spacings for graphite. LDA gives the correct interlayer spacing for AB stacking; however, it underestimates the exfoliation energy by a factor of two and overestimates the compressibility [10].

Each monolayer of the graphene bilayer is modeled as a slab with in-plane lattice constant $a = 2.46 \text{ \AA}$, and the supercell size in the direction perpendicular to the slab is set to 30 \AA to minimize the interaction between periodic images. The sampling grid in reciprocal space is $20 \times 20 \times 1$, with an energy cutoff of 500 eV. A primitive unit cell of a graphene bilayer consists of four basis atoms. To generate a graphene bilayer with different translational registry, the two atoms in the bottom layer are fixed at fractional positions $\mathbf{b}_1 = (0, 0, 0)$ and $\mathbf{b}_2 = (\frac{1}{3}, \frac{1}{3}, 0)$ relative to the graphene lattice vectors $\mathbf{a}_1, \mathbf{a}_2$, and \mathbf{c} , where \mathbf{c} is perpendicular to the plane defined by \mathbf{a}_1 and \mathbf{a}_2 with length equal to the interlayer distance d . The other two atoms are located at $\mathbf{r}_1 = (p, q, 1)$ and $\mathbf{r}_2 = (p + \frac{1}{3}, q + \frac{1}{3}, 1)$. The two parameters $p \in [0, 1]$ and $q \in [0, 1]$ determine the translational registry. For example, the graphene bilayer is in AA stacking [Fig. 3(a)] when $p = 0$ and $q = 0$, and in AB stacking [Fig. 3(b)] when $p = \frac{1}{3}$ and $q = \frac{1}{3}$. Due to the symmetry of the honeycomb lattice, only 1/12 of

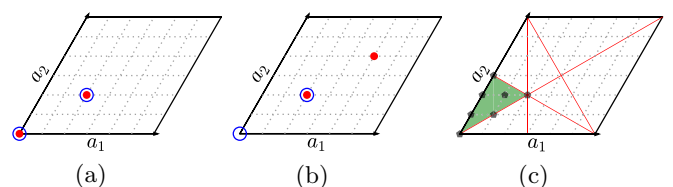


FIG. 3. Primitive unit cell of a graphene bilayer: (a) AA stacking, (b) AB stacking, and (c) unique sampling region and sampling points.

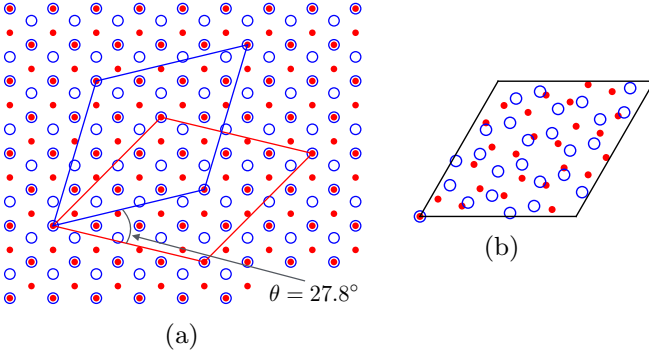


FIG. 4. Example of commensuration of a graphene bilayer. (a) The two layers are commensurate when rotated relative to each other by $\cos^{-1}(\frac{23}{26}) = 27.8^\circ$, which corresponds to $m = 3, n = 7$ according to the condition in Eq. (11). (b) The resulting supercell after rotation, with 26 atoms in each layer.

the area defined by \mathbf{a}_1 and \mathbf{a}_2 needs to be sampled to fully explore all translational registry states [see the shaded region in Fig. 3(c)]. The DRIP training set comprised the seven states indicated in the shaded region of Fig. 3(c), specifically $(p, q) = (0, 0), (0, \frac{1}{6}), (0, \frac{2}{6}), (0, \frac{3}{6}), (\frac{1}{6}, \frac{1}{6}), (\frac{1}{6}, \frac{2}{6}), (\frac{2}{6}, \frac{2}{6})$. These states include all the high-symmetry states of interest, including the AA, AB, and saddle point (SP) stackings ($p = 0, q = \frac{3}{6}$). The seven translational registry states are sampled at different layer spacings d , varying from 2.7 Å to 4.5 Å with a step size of 0.1 Å. For layer spacings larger than 4.5 Å but smaller than the cutoff $r_{\text{cut}} = 12$ Å, only bilayer graphene in AB stacking is included since the difference between the stacking states in this range is negligible (see discussion in Sec. IV). Thus, $7 \times 19 + 75 = 208$ translation configurations are included in the training set.

In addition to translation configurations, a set of twisted bilayer configurations are included in the training set. It is possible to construct a commensurate supercell arbitrarily close to any twisting angle according to the commensuration condition [20,47,48]

$$\theta = \cos^{-1} \left(\frac{3n^2 - m^2}{3n^2 + m^2} \right), \quad (11)$$

where m and n are any two integers satisfying $0 < m < n$. As an example, considering the AB-stacked bilayer in Fig. 4(a), a commensurate bilayer can be obtained by rotating one of the layers by $\theta = 27.8^\circ$ ($m = 3, n = 7$) with the supercell shown in Fig. 4(b). Four types of twisted bilayers with rotation angles $9.43^\circ, 21.79^\circ, 32.30^\circ$, and 42.10° (corresponding to $(m, n) = (1, 7), (1, 3), (1, 2)$, and $(2, 3)$) are included in the training set. The twisted configurations were evaluated at layer spacings from 3.0 Å to 4.0 Å with a step size of 0.1 Å. Thus $4 \times 11 = 44$ twisted configurations are included in the training set. This does not include rotations for $\theta = 0^\circ$ and $\theta = \pm 60^\circ$ corresponding to the AB and AA stacking states, respectively, which are already included in the training set.

The parameters of the potential are optimized by minimizing a loss function that quantifies the difference between the interatomic potential predictions and the training set. The training set includes M configurations with concatenated coordinates \mathbf{r}_m for $m \in [1, M]$, such that $\mathbf{r}_m \in \mathbb{R}^{3N_m}$, where N_m

TABLE II. DRIP parameters obtained by minimizing the loss function $L(\xi)$ defined in Eq. (12) and preset cutoffs.

Parameter	Value	Parameter	Value
C_0 (meV)	11.598	B (meV)	7.6799
C_2 (meV)	12.981	η (1/Å)	1.1432
C_4 (meV)	32.515	A (meV)	22.216
C (meV)	7.8151	z_0 (Å)	3.3400
δ (Å)	0.83679	r_{cut} (Å)	12
λ (1/Å)	2.7158	ρ_{cut} (Å)	1.562

is the number of atoms in configuration m . The loss function is

$$L(\xi) = \sum_{m=1}^M \frac{1}{2} w_m^e [E_m(\mathbf{r}_m; \xi) - E_m^{\text{DFT}}]^2 + \sum_{m=1}^M \frac{1}{2} w_m^f \|\mathbf{f}(\mathbf{r}_m; \xi) - \mathbf{f}_m^{\text{DFT}}\|^2, \quad (12)$$

where ξ is the set of potential parameters, E_m and $\mathbf{f}(\mathbf{r}_m; \xi) = -(\partial \mathcal{V} / \partial \mathbf{r})|_{\mathbf{r}_m} \in \mathbb{R}^{3N_m}$ are the DRIP potential energy and concatenated forces in configuration m , and w_m^e and w_m^f are the weights associated with the energy and forces of configuration m . For energy in units of eV and forces in units of eV/Å, these weights have units of eV^{-2} and $(\text{eV}/\text{Å})^{-2}$, respectively.

The DFT energy and forces used in the loss function, Eq. (12), E_m^{DFT} and $\mathbf{f}_m^{\text{DFT}}$, require explanation. Since DFT provides only the total energy and forces on atoms due to both intralayer and interlayer interactions, it is necessary to separate out the interlayer contributions when constructing the training set. This is accomplished as follows. For configuration m , first the total energy and forces of the bilayer are obtained from DFT: $E_m^{\text{DFT, bilayer}}, \mathbf{f}_m^{\text{DFT, bilayer}}$. Then each monolayer is computed separately by removing all atoms from the other monolayer. Thus, there will be two energies, $E_m^{\text{DFT, layer 1}}$ and $E_m^{\text{DFT, layer 2}}$, and two forces, $\mathbf{f}_m^{\text{DFT, layer 1}}$ and $\mathbf{f}_m^{\text{DFT, layer 2}}$ (although each force vector will only contain nonzero components for the atoms belonging to its monolayer). The DFT interlayer energy and forces appearing in Eq. (12) are then defined as

$$E_m^{\text{DFT}} = E_m^{\text{DFT, bilayer}} - E_m^{\text{DFT, layer 1}} - E_m^{\text{DFT, layer 2}}, \quad (13)$$

$$\mathbf{f}_m^{\text{DFT}} = \mathbf{f}_m^{\text{DFT, bilayer}} - \mathbf{f}_m^{\text{DFT, layer 1}} - \mathbf{f}_m^{\text{DFT, layer 2}}. \quad (14)$$

In the present case, the training set includes $M = 252$ configurations. Both the energy weight w_m^e and force weight w_m^f ($m = 1, \dots, 252$) are set to 1. The optimization was carried out using the KIM-based Learning-Integrated Fitting Framework (KLIF) [49] with a geodesic Levenberg-Marquardt minimization algorithm [50–52]. The objective is to find the set of parameters ξ that minimizes $L(\xi)$. The optimal parameter set identified by this process and preset cutoffs are listed in Table II.

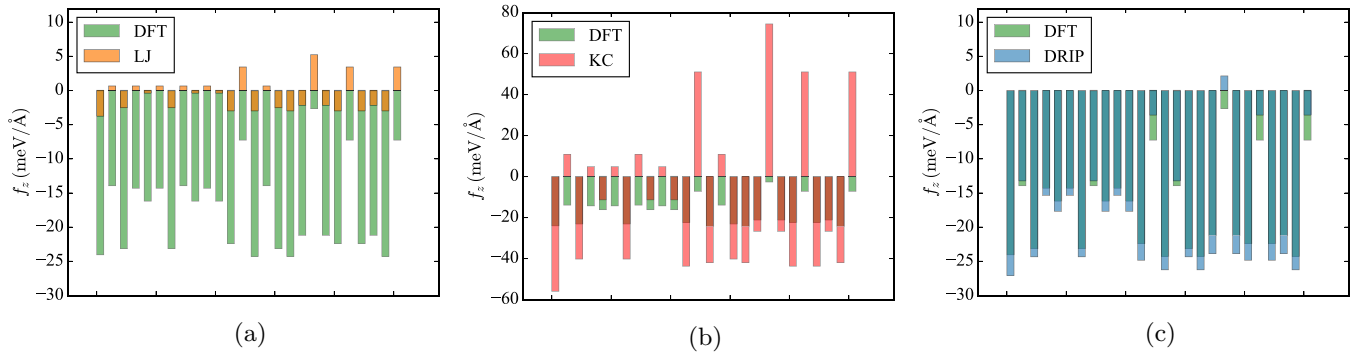


FIG. 5. Out-of-plane component of the forces on the 26 atoms in the bottom layer of the twisted bilayer shown in Fig. 4 (each represented as a bar) computed from DFT and the (a) LJ potential, (b) KC potential, and (c) DRIP model. The layer spacing is 3.4 \AA .

IV. TESTING OF THE NEW POTENTIAL

We performed an extensive set of calculations to test the ability of DRIP to reproduce its training set (described in Sec. III), and test its transferability to configurations outside the training set. The calculations using the potential were performed with LAMMPS [53,54] and DFT calculations with VASP [29,30]. Periodic boundary conditions are applied in both in-plane directions, and the in-plane lattice constant is fixed at $a = 2.46 \text{ \AA}$. The setup for the DFT computations is the same as that used for generating the training set in Sec. III.

Figure 5 shows the unrelaxed forces on the atoms in the bottom layer of the twisted bilayer shown in Fig. 4 with a layer spacing of $d = 3.4 \text{ \AA}$. There are 26 atoms in the bottom layer. For each, the out-of-plane force (z component) is displayed as a bar. The plot compares the results of LJ, KC, and DRIP with DFT. For the LJ potential, the parametrization in the AIREBO potential is used. The DRIP forces are in very good agreement with DFT, whereas the LJ potential yields almost zero forces, and the KC potential greatly overestimates the forces. (Note that the force ranges in the three panels are different). The force on the central atom when twisting a bilayer obtained from DRIP [denoted as 1 in Fig. 1(a)] is displayed in Fig. 1(c) as a function of rotation. The results are in agreement with DFT, indicating that the dihedral modification in DRIP successfully addresses the deficiency of the KC potential discussed in Sec. II.

To investigate the accuracy of the potentials in a dynamical setting, trajectories are generated at a temperature of 300 K using *ab initio* molecular dynamics (AIMD) for bilayers in AA and AB stackings and the twisted bilayer shown in Fig. 4. For each configuration along the trajectories, the DFT forces due to interlayer interactions are computed using the procedure defined in Eq. (14) and explained above. Next, LAMMPS is used to compute the LJ, KC, and DRIP interlayer forces for the AIMD configurations. The error in the potential forces is shown in Fig. 6. Each dot in the plot represents one atom pulled from one of the configurations along the AIMD trajectories. The horizontal coordinate in the plot is the magnitude of the in-plane component (left panels) and out-of-plane component (right panels) of the DFT interlayer force acting on the atom. The force is separated in this way because the in-plane component is significantly smaller than the out-of-plane component. (Note that this is

only the force due to interlayer interactions. The force due to intralayer bonding is not included.) The vertical coordinate is the magnitude of the difference between the potential and DFT force vectors for that atom. We see that the in-plane force error for LJ aligns with the diagonal, i.e., the error equals the DFT force, which means that LJ predicts an in-plane force close to zero. This is because LJ provides a poor model for

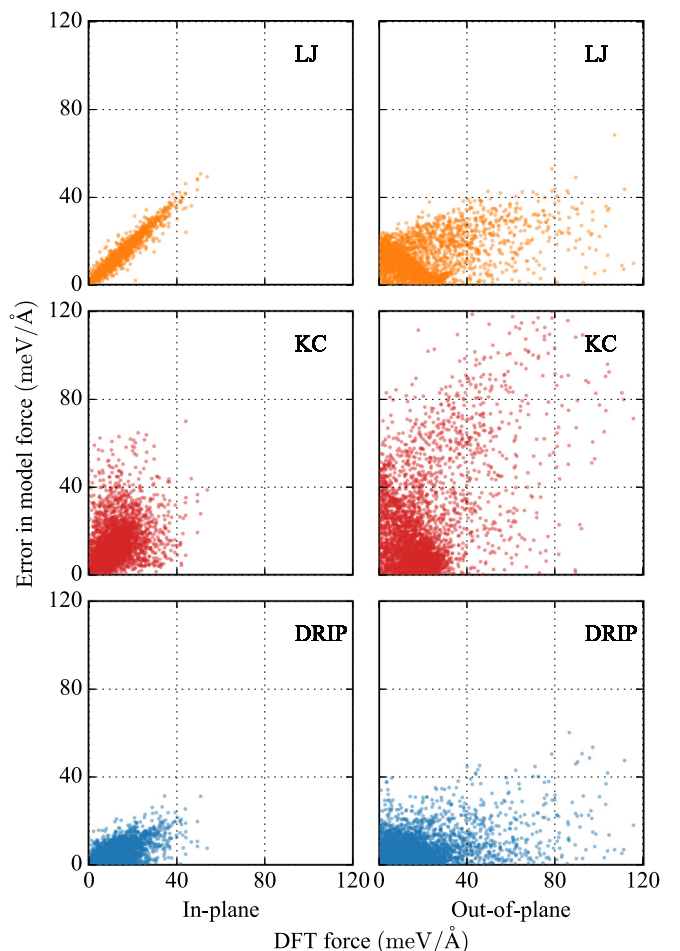


FIG. 6. Deviation of potential forces from DFT results due to interlayer interactions. The configurations are taken from three AIMD trajectories at 300 K.

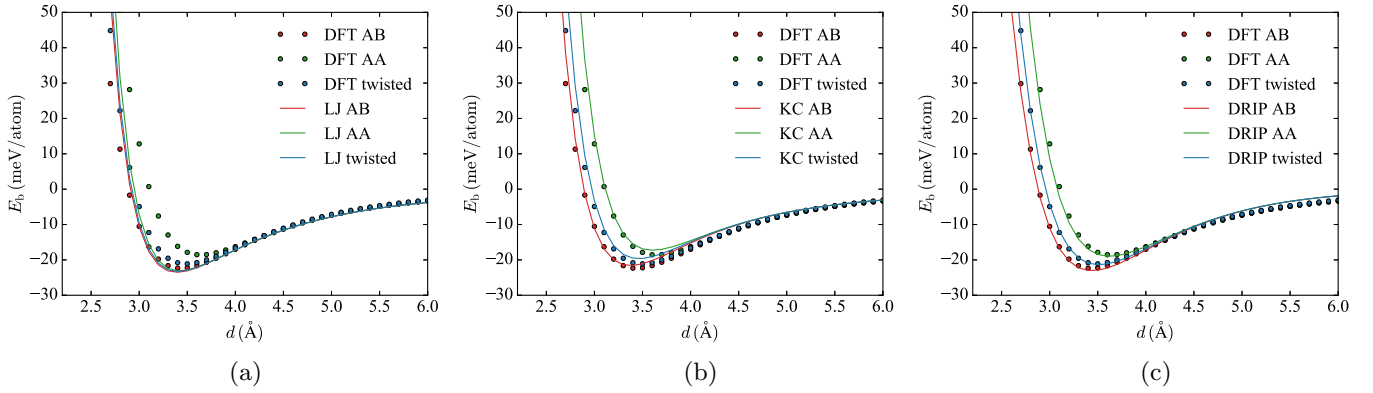


FIG. 7. Interlayer binding energy E_b of a graphene bilayer versus layer spacing d for AA stacking, AB stacking, and a twisted bilayer with rotation angle $\theta = 27.8^\circ$ (see Fig. 4) using (a) LJ potential, (b) KC potential, and (c) DRIP model, compared to DFT results.

the anisotropic overlap of electronic orbitals between adjacent layers and thus has almost no barrier for relative sliding. The KC model performs better in the sense that it predicts resistance to sliding, however the overall accuracy in forces is poor (see Sec. II for a discussion of the limitations of the KC model). In contrast, DRIP provides consistently accurate in-plane forces across the range of DFT forces with errors less than 20 meV/\AA . For the out-of-plane component, both LJ and DRIP perform comparably providing good accuracy across the range of DFT forces, whereas the KC model again shows poor accuracy with very large errors in some cases.

Next, we consider energetics. The interlayer binding energy E_b of a graphene bilayer as a function of layer spacing d is shown in Fig. 7 for AB and AA stackings and the twisted configuration shown in Fig. 4. The LJ potential [Fig. 7(a)] cannot distinguish these states and gives nearly identical binding energy versus layer spacing curves for all three. Both KC [Fig. 7(b)] and DRIP [Fig. 7(c)] correctly capture the energy differences between the three stacking states. For all three potentials, the twisted bilayer curve lies between the other two, which is expected since the AB and AA stackings are minimum and maximum energy states. Also notable is that at large layer spacing, the curves for all three stacking states merge since registry effects due to π -orbital overlap become negligible and interactions are dominated by vdW attraction, which are the same for all three states and captured equally well by all three potentials.

A more complete view of the interlayer energetics is obtained by considering the generalized stacking fault energy (GSFE) surface obtained by sliding one layer relative to the other while keeping the layer spacing fixed. Figure 8 shows the results for a layer spacing of $d = 3.4 \text{ \AA}$ calculated using DRIP and DFT. DRIP is in quantitative agreement with DFT results. The KC GSFE has a similar appearance and the LJ GSFE is nearly flat. The KC and LJ results are not included for brevity, but the energies of the three potentials along the dashed line in the left panel of Fig. 8 are displayed in Fig. 1(b).

As a final test, Table I shows the predictions of DRIP for a number of structural, energetic, and elastic properties. The table also includes results for the LCBOP [55] and AIREBO [18] potentials, as well as DFT and experimental results as described in Sec. III. The LCBOP potential uses two Morse-type [21] terms to model long-range interactions, and

LJ [19] is used in the AIREBO potential as discussed in Sec. I. The properties of the DRIP model are in good agreement with the PBE+MBD DFT computations with which the training set was generated.

V. APPLICATIONS

To further compare the predictions of the KC potential and DRIP, we carried out two large-scale simulations, beyond the capability of DFT: (1) structural relaxation in a twisted graphene bilayer and (2) exfoliation of a graphene layer off graphite. In these simulations, the interlayer interactions are modeled using either KC or DRIP, and the REBO [17] potential is used to model the intralayer interactions.

A. Structural relaxation of a twisted graphene bilayer

The electronic properties of stacked 2D materials can be manipulated by controlling the relative rotation between the layers, which in turn leads to different structural relaxation. A prototypical problem is the twisting of a graphene bilayer. The bilayer is created by rotating one layer relative to the other by $\theta = 0.82^\circ$, setting $(m, n) = (1, 81)$ as discussed in Sec. III. The out-of-plane relaxation δ of an atom is obtained by subtracting the mean out-of-plane coordinates of all atoms

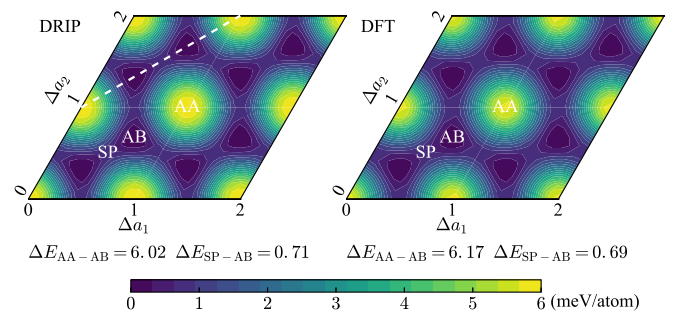


FIG. 8. The GSFE obtained by sliding one layer relative to the other at a fixed layer spacing of $d = 3.4 \text{ \AA}$. The energy is relative to the AB state, which is -22.98 meV/atom for DRIP (on the left) and -22.33 meV/atom for DFT (on the right). The sliding parameters Δa_1 and Δa_2 are in units of in-plane lattice constant $a = 2.46 \text{ \AA}$.

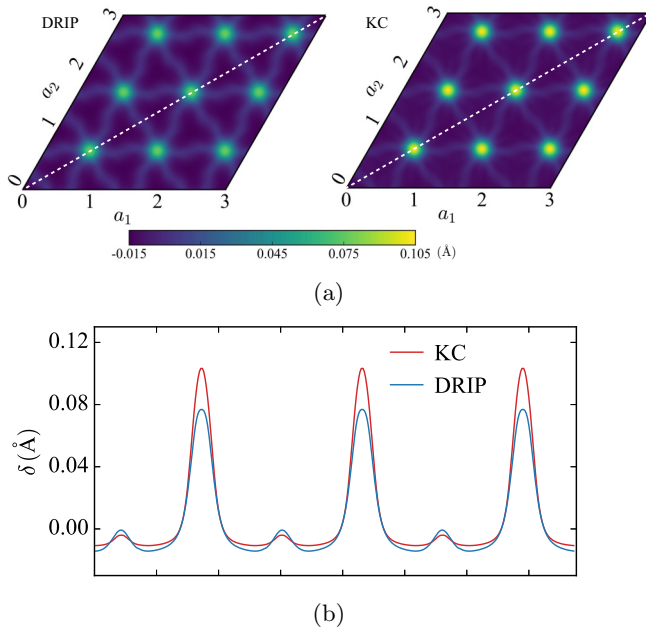


FIG. 9. Out-of-plane relaxation in a twisted bilayer with a relative rotation of $\theta = 0.82^\circ$. (a) Contour plot obtained from the DRIP model and the KC potential, and (b) relaxation along the diagonal indicated by the dashed line in panel (a). The bilayers shown in the figure corresponds to 3×3 supercells used in the computation, i.e., a_1 and a_2 are in units of in-plane lattice constant $a = 2.46 \text{ \AA}$.

in the top layer from the out-of-plane coordinate of that atom:

$$\delta_i = z_i - \frac{1}{N} \sum_{j=1}^N z_j, \quad (15)$$

where z_i is the out-of-plane coordinate of atom i in the top layer and $N = 9842$ is the number of atoms in the top layer.³

The out-of-plane relaxation of the twisted bilayer is plotted in Fig. 9. The results of the DRIP and KC models are qualitatively similar. The bright spots correspond to high-energy AA stacking, the long narrow ribbons correspond to SP stacking, and the triangular regions correspond to alternating AB and BA stackings. It has been shown that the formation of this structure is due to local rotation at AA domains [56]. Quantitatively, however, the two potentials give different out-of-plane relaxation, especially at the peaks as seen in Fig. 9(b). The peak value predicted by DRIP is 0.076 \AA , which is 26% smaller than the KC potential value of 0.103 \AA . This difference at the peaks could lead to significant differences in electronic properties because twisted graphene bilayers develop highly localized states around AA-stacked regions for small twist angles [57].

B. Exfoliation of graphene from graphite

Graphene can be prepared by exfoliating graphite. In this process, the vdW attraction between layers is overcome by peeling a single layer off a graphite crystal. A method as

³Using the atoms in the bottom layer will yield the same results because the relaxed structure of the bottom layer and the top layer are identical.

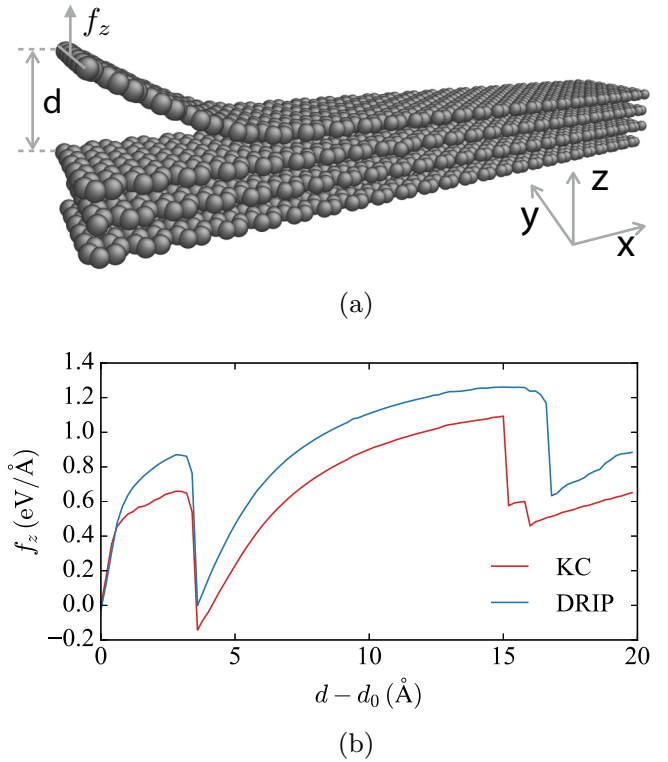


FIG. 10. (a) Schematic demonstrating the process of peeling a graphene layer off graphite and (b) the normal force, f_z , needed to peel the top layer as a function of the displacement at the left end of the top layer, $d - d_0$. The armchair direction of graphite is aligned with the x axis. The initial layer spacing is $d_0 = 3.35 \text{ \AA}$.

simple as sticking Scotch tape to graphite and applying an upward force can be used [1]. To simulate this process, one edge of the top layer of a graphite crystal is pulled up under displacement control conditions as illustrated in Fig. 10(a). The atoms at the left end of the top layer are displaced in the z direction according to $d = d_0 + 0.2k$, where $d_0 = 3.35 \text{ \AA}$ is the initial layer spacing, and $k = 0, 1, \dots, 99$ is the step number. At each step k , once the displacement is applied to the left atoms, the remaining atoms in the top layer are relaxed. The substrate (bottom three layers) is kept rigid during this process. The system contains 600 atoms in each layer of size 105.83 \AA and 14.76 \AA in the x and y directions, respectively. The system is periodic in the y direction and nonperiodic the other two directions.

The normal force, f_z , needed to pull the left end of the top layer is plotted in Fig. 10(b). Both the KC and DRIP models give qualitatively similar results. The force first increases as the left end is pulled up and then exhibits a sudden drop at about 3 \AA . The normal force has two contributions: (1) inter-layer interactions with atoms in the substrate and (2) covalent-bonded interactions with other atoms in the top layer. The former is almost unchanged before and after the load drop, therefore the drop is mainly due to the in-plane interactions in the top layer. Before the load drop, the right-end of the top layer is trapped in a local minimum created by the substrate (similar to the one denoted as AB in Fig. 8, although there we only consider a graphene bilayer) and, consequently, as the left end is pulled up, the top layer experiences an increasing

axial strain. At about 3 Å, the right-end of the top layer snaps into an adjacent local minimum by moving in the negative x direction. (A movie showing the snap-throughs associated with the load drops is provided in the Supplemental Material [58].) As a result, the axial strain in the top layer is released and the load is reduced. The same explanation applies to the load drop at a displacement of about 15 Å, and it is expected to continue to occur periodically with continued pulling.

As for the results in Sec. V A, KC and DRIP are in qualitative agreement, but there are quantitative differences. The KC potential predicts an initial peeling load of about 0.65 eV/Å, which is about 75% of the 0.87 eV/Å value predicted by DRIP. The second snap-through occurs at a displacement of 16.6 Å for DRIP, and at 15.0 Å for KC.

VI. SUMMARY

The interlayer interactions in stacked 2D materials play an important role in determining the functionality of many nanodevices. For graphitic structures, the two-body pairwise LJ potential is too smooth to model the energy corrugation in different stacking states. The registry-dependent KC potential improves on this and correctly captures the energy variation, but fails to yield reasonable forces. In particular, the KC model does not distinguish forces on atoms in the AA and AB stacking states that are different in DFT calculations. The KC model is also discontinuous at the cutoff, which can lead to difficulties in energy minimization and loss of energy conservation in dynamic applications.

To address these limitations, we developed a new potential for graphitic structures based on the KC model. The DRIP model has a smooth cutoff and includes a dihedral-angle-dependent term to distinguish different stacking states and obtain accurate forces. The potential parameters were determined by training on a set of energies and forces for a graphene bilayer at different layer spacing, sliding and twisting, computed using GGA-DFT calculations, augmented with the MBD dispersion correction to account for the long-range vdW interactions.

To test the quality of the potential, we employed it to compute energetics, forces, and structural and elastic properties for a graphene bilayer in different states and graphite. The validation tests show that compared with first-principles results:

- (1) DRIP correctly predicts the equilibrium layer spacing, interlayer binding energy, and GSFE of a graphene bilayer, as well as the equilibrium layer spacing of graphite.
- (2) DRIP underestimates the c -axis elastic modulus C_{33} of graphite by about 10% relative to ACFDT-RPA and experiments, but this result is in good agreement with PBE+MBD to which DRIP was fit.
- (3) DRIP provides more accurate forces than the KC model across the entire range of bilayer rotations and in particular distinguishes the forces in the AA and AB states that the KC potential cannot.

In two large-scale applications, not amenable to DFT calculations, we showed that DRIP and the KC potential agree qualitatively, but differ quantitatively by 26% in the out-of-plane relaxation of a twisted graphene bilayer, and by 23%

in the normal force required to peel one graphene layer off graphite.

The added four-body dihedral-angle-dependent correction in DRIP is very short ranged ($\rho_{\text{cut}} = 1.562$ Å) and therefore the computational overhead relative to KC is small. In fact, for the large-scale applications (bilayer relaxation and peeling) described in Sec. V, DRIP was actually faster than the KC potential in terms of the overall computation time due to improved convergence.

Although DRIP was parameterized against a training set consisting of graphene bilayers, it can be used to describe interlayer interactions for other systems such as graphite and multiwalled carbon nanotubes where the carbon atoms are arranged in layers. This potential only provides a description of the interlayer interactions, and therefore must be used together with a companion model that provides the intralayer interactions, such as the Tersoff [14,15] or REBO [16,17] potentials. The DRIP functional form and associated carbon parametrization are archived in the OpenKIM repository [24–26]. They can be used with any KIM-compliant molecular simulation code, see Appendix for details.

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APPENDIX: USING THE OPEN KNOWLEDGEBASE OF INTERATOMIC MODELS (OpenKIM)

The Open Knowledgebase of Interatomic Models (OpenKIM) is an open-source, publicly accessible repository of classical interatomic potentials, as well as their predictions for material properties that can be visualized and compared with first-principles data. Interatomic potentials stored in OpenKIM that are compatible with the KIM application programming interface (API) are called KIM Models. KIM Models will work seamlessly with a variety of major simulation codes that are compatible with this standard including LAMMPS [53,54], ASE [59,60], DL_POLY [61], and GULP [62,63].

As an example, we describe how a KIM Model would be used with LAMMPS. In LAMMPS, reactive interatomic potentials are specified using the `pair_style` command. LAMMPS has a `pair_style kim` option for using KIM Models. To use KIM Models with LAMMPS, perform the following steps:

- (1) Install the KIM API (see instructions at [64]).
- (2) Download and install the desired potential from [24,25] (see instructions that come with the API).
- (3) Enable KIM Models in LAMMPS by typing: `make yes-kim` and then compiling LAMMPS.

In a LAMMPS input script, a KIM Model is then selected in the same way as other LAMMPS potentials. For example, the potential developed in this paper can be used with the following two commands:

```
pair_style kim DRIP_WenTadmor_2018_C__MO_070247075036_000
pair_coeff * * C
```

To use it together with another potential for the intralayer interactions, such as Tersoff [14,15] or REBO [16,17], use the LAMMPS “pair_style hybrid/overlay” command (see the LAMMPS manual for details).

The advantage of releasing a potential as a KIM Model (as opposed to just a file compatible with LAMMPS or another code), is that it will work with not just LAMMPS, but other major codes as noted above. In addition, a KIM Model has a KIM ID and a DOI that can be cited in publications. The KIM ID provides a unique permanent link to the archived content and includes a three-digit version number to track changes. For example, a modification to the model parameters would lead to a version upgrade (or a new forked model if appropriate). Citing a KIM ID in a publication makes it possible for the reader to download the exact potential used in the reported simulation and to reproduce the results.

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