

Mechanical and Tribological Properties of Layered Materials under High Pressure: Assessing the Importance of Many-Body Dispersion Effects

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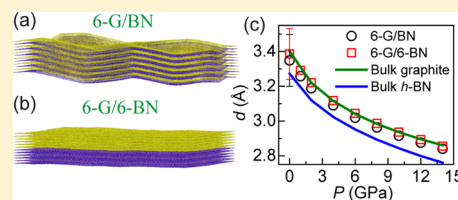
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S Supporting Information

ABSTRACT: The importance of many-body dispersion effects in layered materials subjected to high external loads is evaluated. State-of-the-art many-body dispersion density functional theory calculations performed for graphite, hexagonal boron nitride, and their heterostructures were used to fit the parameters of a classical registry-dependent interlayer potential. Using the latter, we performed extensive equilibrium molecular dynamics simulations and studied the mechanical response of homogeneous and heterogeneous bulk models under hydrostatic pressures up to 30 GPa. Comparison with experimental data demonstrates that the reliability of the many-body dispersion model extends deep into the subequilibrium regime. Friction simulations demonstrate the importance of many-body dispersion effects for the accurate description of the tribological properties of layered material interfaces under high pressure.



1. INTRODUCTION

Accurate modeling of the interlayer interactions in layered materials is of paramount importance for obtaining a quantitative description of their unique mechanical and tribological properties. Recently, a new generation of van der Waals (vdW) dispersion models was proposed within the framework of density functional theory (DFT) and their accuracy in predicting the binding energy (BE) and interlayer distance of two-dimensional materials was assessed^{1–4} against higher level methods such as the random phase approximation (RPA)^{5,6} and quantum Monte Carlo (QMC),⁷ as well as against experiment.^{8–11} Specifically, for layered materials that are not highly polarizable or ionic (e.g., graphene and hexagonal boron nitride (*h*-BN)), the Tkatchenko-Scheffler (TS) approach¹² and the many-body dispersion (MBD) method,^{13,14} in combination with the Heyd–Scuseria–Ernzerhof (HSE) hybrid density functional approximation,^{15–17} were found to predict reliable equilibrium distances, binding energies,^{1–3,18} and elastic constants.^{2,3} So far, however, the accuracy of these vdW dispersion models has been tested mainly near the equilibrium configuration of model bilayers. In this work, we assess the accuracy of the TS and MBD vdW dispersion models at the equilibrium and subequilibrium interlayer distance regimes by combining state-of-the-art DFT calculations with classical molecular dynamics (MD) simulations.

As test cases, which are relevant in view of many practical applications,^{2,19–24} we consider bulk graphite, bulk hexagonal boron nitride (*h*-BN), and their heterostructures. We first performed DFT calculations of binding energy (BE) curves and sliding potential energy surfaces (PES) for graphite, bulk *h*-BN, and their alternating heterostructures adopting two different methods: HSE + TS and HSE + MBD. From these two sets of reference data, we obtained two distinct parametrizations of our classical registry-dependent interlayer potential (ILP),^{25–28} which is able to accurately capture both BE curves and PES of these layered materials. Finally, we performed extensive equilibrium MD simulations under hydrostatic pressure ranging between 0 and 30 GPa, from which we extracted the interlayer distance as a function of the applied pressure (*c*–*P* curve).

We find that the *c*–*P* curves generated by the ILP parameters fitted against the HSE + MBD reference data compare well with experimental measurements,^{29–35} for both graphite and bulk *h*-BN, over the entire range of pressures investigated. The bulk modulus extracted from the pressure–volume (*P*–*V*) curves also agrees well with experimental data. However, results obtained by adopting the ILP parameters fitted against the HSE + TS reference data deviate from

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experimental results, especially for graphite. Results of sliding friction simulations under high pressure further demonstrate the importance of an accurate description of the interlayer interactions in the subequilibrium regime for obtaining qualitatively and quantitatively correct results.

2. METHODS

2.1. DFT Calculations. We used the MBD and TS augmented HSE functional, as implemented in the FHI-AIMS code,³⁶ with the tier-2 basis-set,³⁷ using tight convergence settings, including all grid divisions and a denser outer grid. For the two-dimensional (2D) systems, a vacuum of 50 Å was used with a k -grid of $19 \times 19 \times 1$ points. For the MBD calculations, a large cutoff value of 1300 Å was used for integrating the dipole field, as required for low-dimensional systems, together with a supercell cutoff of 45 Å. With these settings the MBD energy is converged to the level of 10^{-4} eV/atom. For the three-dimensional (3D) systems, a k -grid of $19 \times 19 \times 7$ points was used. The MBD convergence rate as a function of the cutoff parameters in the 3D calculations was faster compared with the 2D case. A smaller cutoff value of 300 Å and a supercell cutoff value of 30 Å were used. The MBD energy with this setting was estimated to be converged to 10^{-4} eV/atom, as well. At the high-pressure regime, the supercell cutoff radius had to be lowered from 30 to 25 Å to accelerate the calculations; however, at that scale, the effect of this reduction on the results was found to be negligible. In all cases, the HSE + TS energy was converged to 10^{-6} eV.

2.2. Equilibrium MD Simulation Protocol. To calculate the c - P curves of graphite and bulk h -BN, we adopted supercell models consisting of 12 roughly square layers ($5 \text{ nm} \times 5 \text{ nm}$), each containing 880 carbon atoms or 440 boron + 440 nitrogen atoms, respectively. The layers in graphite are arranged in an alternating AB stacking, with a period c initially set equal to the experimental value of 6.70 Å.³⁰ The layers in bulk h -BN are arranged in an alternating AA' stacking (boron atop nitrogen), with a period c initially set equal to the experimental value of 6.66 Å.³² Intralayer interactions within each graphene and h -BN layer are modeled via the second-generation REBO potential³⁸ and the Tersoff potential,³⁹ respectively.

Interlayer interactions are modeled using the ILP or the Kolmogorov–Crespi (KC) potentials (for graphite), the construction of which is explained in detail in refs 25–27, 40, 41, reparametrized herein to better describe the subequilibrium regime, as described below. All MD simulations were performed with the LAMMPS simulation package.⁴² The velocity-Verlet integrator with a time step of 1 fs was used to solve the equations of motion while enforcing periodic boundary conditions in all directions. A Nosé–Hoover thermostat with a time constant of 0.25 ps was used for constant temperature simulations. To maintain a specified hydrostatic pressure, the three translational vectors of the simulation cell were adjusted independently by a Nosé–Hoover barostat with a time constant of 1.0 ps.^{43,44} To generate the c - P curves, we first equilibrated the systems in the NPT ensemble at a temperature of $T = 300 \text{ K}$ and a fixed target pressure for 100 ps. After equilibration, the c lattice parameter was computed by averaging over a subsequent simulation period of 100 ps. The same procedure was repeated for different pressures ranging from 0 to 30 GPa, and the c - P curve was constructed. Tests with longer equilibration and averaging runs (200 ps + 200 ps) gave similar results.

2.3. Definition of the Interlayer Distance for Highly Deformed Surfaces.

For the alternating graphene/ h -BN heterostructures, the out-of-plane deformation is large due to their intrinsic intralayer lattice vector mismatch. To calculate the c - P curves of this system, a new definition of the interlayer distance is required since the difference between the center of mass (COM) of the neighboring layers along c axis is no longer a good measure. In the present study, to evaluate the interlayer distance for highly curved surfaces, we first found for each atom, i , on a given layer its nearest neighbor, j , on the adjacent layer. Then, we projected the vector connecting the pair along the local normal directions at the two atomic positions (see ref 40 for the definition of the normal vectors). The average between the two values is defined as the local distance between the layers. Further averaging over all positions i provides the value of the interlayer distance for a given configuration. At finite temperature, we also average over time to take into account thermal fluctuations. We note that for planar interfaces this definition matches the above-mentioned COM definition.

2.4. Friction Simulations. To study the effects of external load on friction, we built 4-layer graphene and 4-layer h -BN homogeneous rectangular models with optimal stacking. The lateral dimensions of each model were $5 \text{ nm} \times 5 \text{ nm}$, and periodic boundary conditions were applied in both lateral directions. The rigid top layer (slider) was attached to a spring ($K_{\text{dr}} = 10 \text{ N/m}$) moving at a constant velocity ($v_{\text{dr}} = 5 \text{ m/s}$) along the zigzag direction, and the bottom layer (substrate) was kept at rest. The force-fields used here were the same as those described above for the static calculations. A Langevin thermostat was added to the two internal layers and the damping coefficients used were $\eta_x = \eta_y = \eta_z = 1 \text{ ps}^{-1}$. The systems were first equilibrated at 300 K for 400 ps with a time step of 1 fs, in absence of the pulling force, following which the friction simulations commenced. The static friction force is defined as the maximum force recorded across the entire force-trace, and the kinetic friction force is calculated as $\langle F_{\text{kinetic}} \rangle = \langle K_{\text{dr}}(v_{\text{dr}}t - x_{\text{slider}}) \rangle$, where t is the simulation time, x_{slider} is the position of center-of-mass of the slider along sliding direction, and $\langle \bullet \rangle$ denotes a steady-state time average. The statistical errors have been estimated using 10 different datasets, each calculated over a time interval of 300 ps.

3. FORCE-FIELD PARAMETERIZATION

The study of the properties of bulk graphite and h -BN under high pressure requires an interlayer potential (ILP) flexible enough to allow an accurate description of interactions in both equilibrium and subequilibrium regimes and, most important, to be able to describe the strongly anisotropic character of the layered materials under study. We chose our recently developed ILP,²⁷ for which we previously provided two sets of parameters for homogeneous and heterogeneous systems based on graphene and h -BN.^{25,26} We stress here that these sets of parameters were fitted manually against HSE + MBD reference data focusing on achieving good agreement only in the near-equilibrium and long-range interaction regime. More recently,²⁸ we have provided a refined set of parameters fitted using an automatic interior-point technique^{45,46} that allowed us to improve the agreement with the reference HSE + MBD data. Furthermore, in ref 28, we also provided a set of refined parameters for the KC potential⁴⁰ for graphene based systems. We note that all above parametrizations have been benchmarked against DFT reference data calculated in a

bilayer geometry, considering interlayer distances ranging from 2.5 to 15 Å.

3.1. Binding Energy Curves. Here, due to the importance of the subequilibrium interlayer distance regime for the tribological properties of layered materials, we perform new benchmark HSE + TS and HSE + MBD calculations for bulk graphite, *h*-BN, and their alternating heterostructures, considering interlayer distances in the range of 2–10 Å with increased resolution. Figure 1 presents binding energy curves

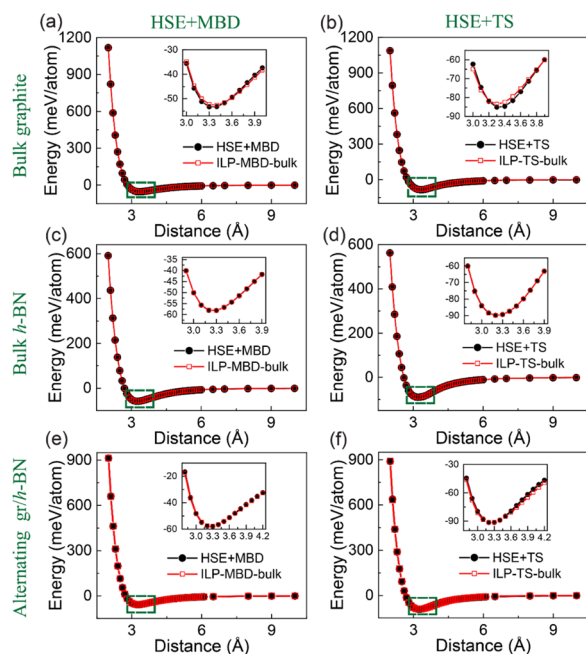


Figure 1. Binding energy curves of the fully periodic structures of bulk graphite (upper row), bulk *h*-BN (middle row), and C-stacked alternating graphene/*h*-BN heterojunctions (bottom row), calculated using HSE + MBD (left column, full black circles) and HSE + TS (right column, full black circles), along with the corresponding ILP fits (open red squares). The reported energies are measured relative to the value obtained for infinitely separated layers and are normalized by the total number of atoms in the unit cell. The insets provide a zoom-in on the equilibrium interlayer distance region.

calculated for the fully periodic structures of bulk graphite (first row), bulk *h*-BN (second row), and C-stacked²⁶ alternating graphene/*h*-BN heterojunctions (third row) using HSE + MBD (left column, full black circles) and HSE + TS (right column, full black circles). The corresponding ILP fits are marked in red open squares. As may be expected, the HSE + TS approach provides deeper potential energy wells than HSE + MBD with similar equilibrium interlayer distances (see a detailed analysis in the Benchmark Tests section below). Notably, the ILP can be well fitted (using the procedure described in ref 28) against both the pair-wise HSE + TS results and the many-body reference data throughout the entire interlayer distance range considered, which extends deep into the subequilibrium regime.

3.2. Sliding Potential Energy Surfaces. The upper rows of Figures 2 and 3 show the sliding PES of the three fully periodic structures considered, calculated at their equilibrium interlayer distances using HSE + MBD and HSE + TS, respectively. The corresponding ILP data appear in the middle row of both figures and the differences between the reference DFT data and the ILP results are presented in the lower

panels. For all three systems, the HSE + MBD approach predicts somewhat lower PES corrugation than the HSE + TS method. The ILP fitting is in good qualitative and quantitative agreement with the DFT reference data. Specifically, for the HSE + MBD results, the maximal deviation between the DFT reference and ILP results for bulk graphite is 4.7% of the overall PES corrugation. The corresponding differences for bulk *h*-BN and the heterogeneous structures are 0.25% and 4.2%, respectively.

Notably, while the ILP with its present parameterizations captures well all main symmetries of the full sliding energy surface corrugation, it cannot generally be expected to capture the symmetry of the dispersive component alone [see Section 5 of the Supporting Information (SI)]. This is because the sliding energy corrugation associated with this component is found to be typically lower than 2 meV/atom, which is below the expected accuracy of the ILP for these systems (see lower panels of Figures 2 and 3). In cases where Pauli repulsions dominate the sliding energy surface, such as those used as reference for the present ILP parameterization, this has a negligible effect. However, in scenarios where the sliding energy corrugation is dominated by the dispersive component, this may have an important effect. Such scenarios can be encountered in large moiré superstructures characterized by high surface undulations that result in large interlayer separations, which may require dedicated parameterization of the ILP.

3.3. Parameters. All fitting parameters can be found in Section 1 of the SI. We mark the new ILP parameterizations presented herein as ILP-TS-bulk and ILP-MBD-bulk. For clarity, we name the original ILP parameters of refs 25, 26, and the refined parameters of ref 28, both fitted against bilayer calculations, as ILP-MBD-bilayer-original and ILP-MBD-bilayer-refined, respectively. Finally, we name the original parameters of the KC potential of ref 40 and the refined ones of ref 28 as KC-original and KC-MBD-bilayer-refined, respectively. The sensitivity test of the ILP parameters is provided in Section 2 of the SI.

4. BENCHMARK TESTS

4.1. Compressibility. The simulation results for graphite and bulk *h*-BN under hydrostatic pressure are presented in Figure 4, along with the experimental *c*–*P* curves. We note that the slope of the normalized *c*–*P* curve for graphite, akin to the compressibility $\sim \partial[(c(P) - c_0)/c_0]/\partial P$, predicted by the ILP-TS-bulk parametrization (green stars in panel a) deviates from the experimental one at loads $\gtrsim 4$ GPa, systematically overestimating the experimental values obtained under hydrostatic pressure (up- and down-oriented violet triangles, cyan pentagons, black circles). A similar behavior is observed also for the case of *h*-BN. The *c*–*P* curves obtained from the ILP-MBD-bulk parametrization (open diamonds in panels a and b) somewhat deviate from the experimental data only at considerably high pressures, $\gtrsim 20$ and $\gtrsim 8$ GPa, respectively, for graphite and *h*-BN. Notably, the ILP parameterizations performed against bilayer (ILP-MBD-bilayer-refined, open circles in panel a) and bulk graphite (open diamonds) reference data provide comparably good agreement with the experimental data, indicating that interactions between non-adjacent graphene layers are negligible. Somewhat larger differences are observed for the case of *h*-BN (see open circles and open diamonds in panel b). We further observe that if the ILP is not well parameterized in the subequilibrium regime, the

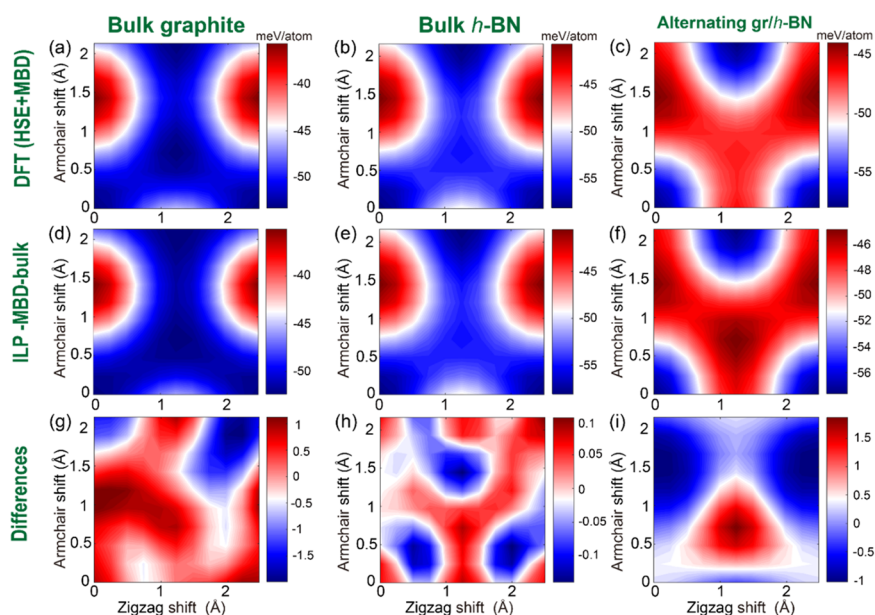


Figure 2. Sliding energy surfaces of the periodic structures considered, calculated at an interlayer distance of 3.3 Å. The first and second rows present the sliding energy surface of bulk graphite (left panels), bulk *h*-BN (middle panels), and alternating graphene/*h*-BN (right panels) systems, calculated using HSE + MBD and ILP-MBD-bulk parameterization, respectively. The third row presents their differences. The parameters of Table S1 in the SI are used for the ILP calculations. The reported energies are measured relative to the value obtained for the infinitely separated layers and are normalized by the total number of atoms in the unit cell.

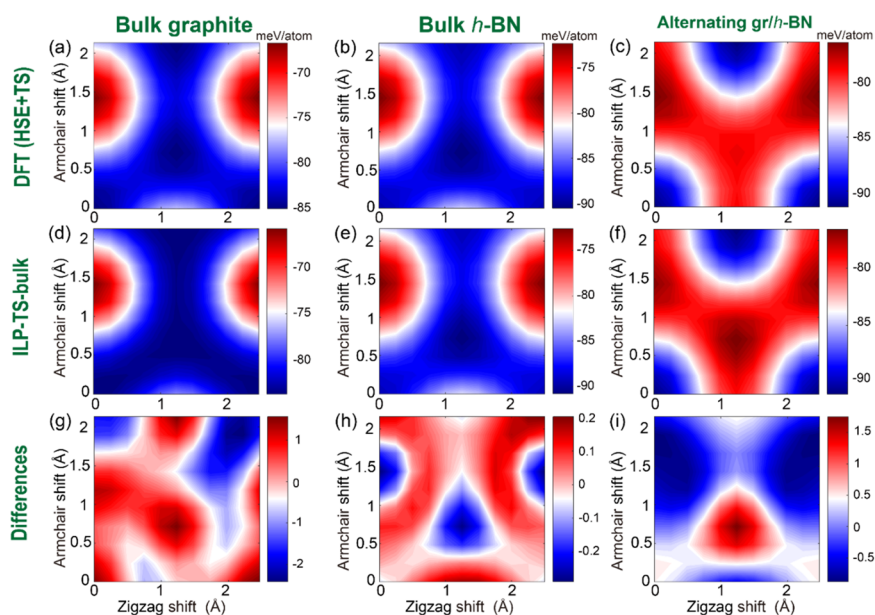


Figure 3. Sliding energy surfaces of the periodic structures considered, calculated at an interlayer distance of 3.3 Å. The first and second rows present the sliding energy surface of bulk graphite (left panels), bulk *h*-BN (middle panels), and alternating graphene/*h*-BN (right panels) systems, calculated using HSE + TS and ILP-TS-bulk parameterization, respectively. The third row presents their differences. The parameters of Table S2 in the SI are used for the ILP calculations. The reported energies are measured relative to the value obtained for the infinitely separated layers and are normalized by the total number of atoms in the unit cell.

obtained *c*–*P* curves deviate significantly from the experimental data. See, for example, the deviation of the ILP-MBD-bilayer-original results for bulk *h*-BN (open brown squares) from the experimental values, in the right panel of Figure 4. We note that the ILP-MBD-bilayer-original parameterization provides a relatively good fit for bilayer graphene down to 2.8 Å and thus the *c*–*P* curves calculated for graphite are in good agreement with the experimental data in the presented pressure range. Finally, while the original KC interlayer

potential for graphite (brown triangles in panel a) loses accuracy at high pressures (≥ 4 GPa), our new KC potential parameterization (blue triangles) yields results in agreement with the ILP-MBD-bulk parameterization.

The main conclusion that can be drawn from the above results is that the new MBD ILP parameterization, which extends down to an interlayer distance of 2 Å, performs very well across the entire pressure range investigated. This indicates that the DFT reference data are reliable even in the

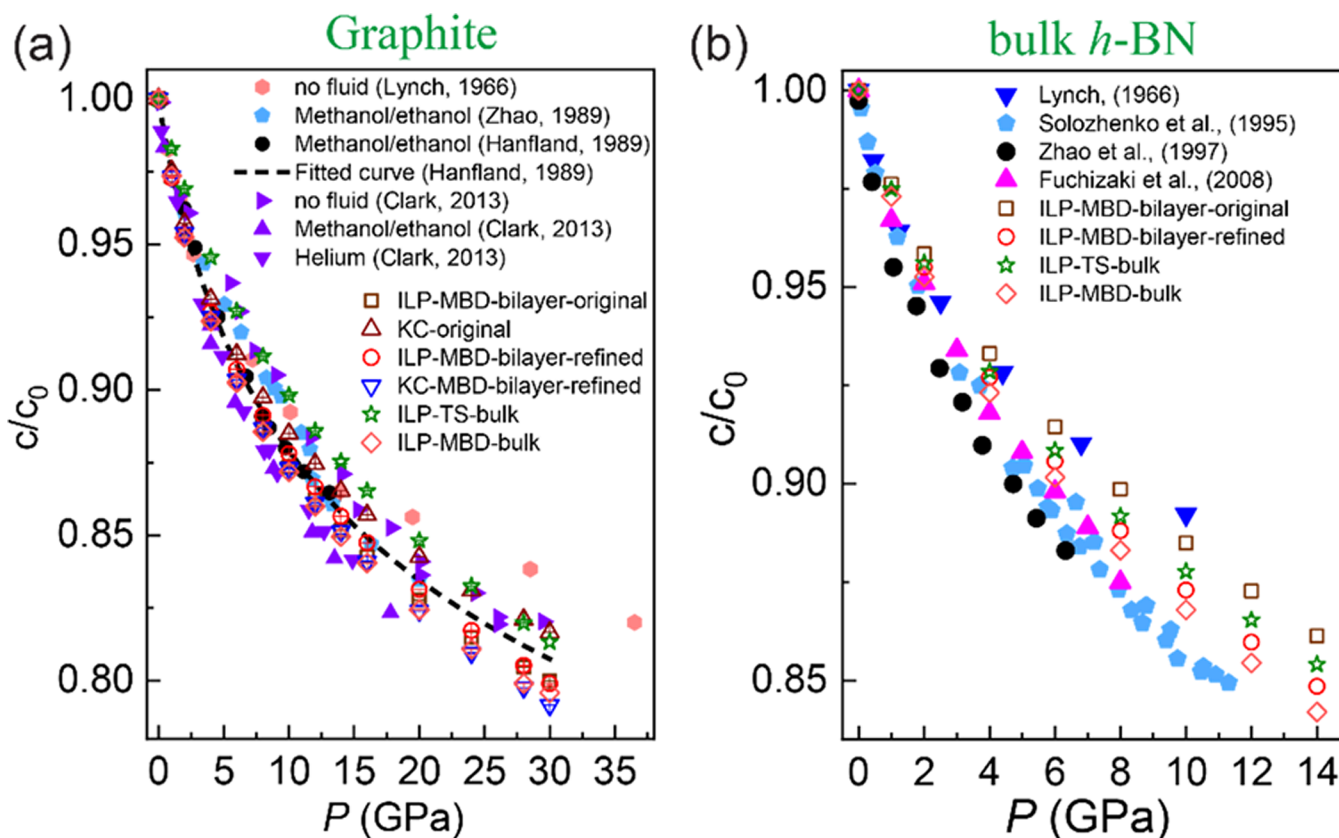


Figure 4. Measured and computed pressure dependence of the c lattice parameter of (a) bulk graphite and (b) bulk h -BN. Each result is normalized by the zero pressure value, c_0 , corresponding to the same measurement or computation. Full symbols represent experimental results and open points represent NPT simulation results for different parameterizations of the ILP and KC potentials, as specified in the corresponding set labels. Error bars for the simulated data, obtained from the temporal standard deviation of the interlayer distance thermal fluctuations at equilibrium, are smaller than the symbol width.

deep subequilibrium regime, where bulk graphite and h -BN are compressed down to 0.6 of their equilibrium interlayer distance.

4.2. Bulk Moduli. To verify that the HSE + MBD ILP parameterization, including the high-pressure regime, does not harm its ability to predict low-pressure bulk properties, we calculate the bulk moduli of bulk graphite and h -BN and compare against experimental values. The computed bulk moduli are obtained by fitting our simulation data across the entire pressure range considered to the Murnaghan equation of state (EOS):^{30,47}

$$V(P)/V_0 = [1 + (B'_V/B_V^0)P]^{-1/B'_V} \quad (1)$$

Here, V_0 and $V(P)$ are the unit-cell volumes in the absence and presence of an external hydrostatic pressure, P , and B_V^0 and B'_V are the bulk modulus and its pressure derivative at zero pressure, respectively. The corresponding Murnaghan fits for the various ILP and KC parameterization results can be found in Section 3 of the SI. Figure 5 shows experimental $V(P)$ curves, along with those obtained by the various ILP parameterizations considered above and the corresponding fits of the ILP-TS-bulk and ILP-MBD-bulk results to eq 1. While high-pressure experimental volumetric data is less abundant than interplane lattice constant information, especially for graphite, we find that the MBD parameterized ILP results are overall in better agreement with the most recent experimental data, across the pressure range considered. The extracted bulk moduli for bulk graphite and h -BN, along with

their zero pressure derivatives, binding energies, and lattice constants are compared in Table 1.

As can be seen in Table 1, the values of bulk modulus predicted for graphite by the MD simulations, using any of the MBD ILP parameterizations agree well with the experimental data (ranging between 30.8 and 33.8 GPa). They are also in good agreement with previous PBE + MBD@rsSCS calculations, predicting a bulk modulus of 29 GPa.³ Furthermore, both the original, empirically fitted KC potential, and our MBD parameterization of it provide reasonable agreement with a slight overestimation of the experimental bulk modulus. Comparing the MBD results to other first-principles methods, we obtain the commonly observed behavior, where the local density approximation (LDA) provides reasonable prediction of the bulk modulus of graphite (but not necessarily for the right reasons) while the Perdew–Burke–Ernzerhof (PBE) gradient-corrected exchange correlation density functional approximation strongly underestimates it. RPA calculations overestimate the experimental values by $\sim 10\%$, the empirical Grimme D2 pairwise dispersion correction overestimates the modulus by $\sim 15\%$, and all TS-based calculations (including our TS parameterized ILP) overestimate the bulk modulus of graphite by up to 80%. Considering the bulk modulus derivative with respect to the external pressure, we find that all MBD force-field parameterizations, as well as the empirically fitted KC potential, provide good agreement with the lower experimental value of 8.9 ± 0.1 . The only outlier within our test set is the TS-

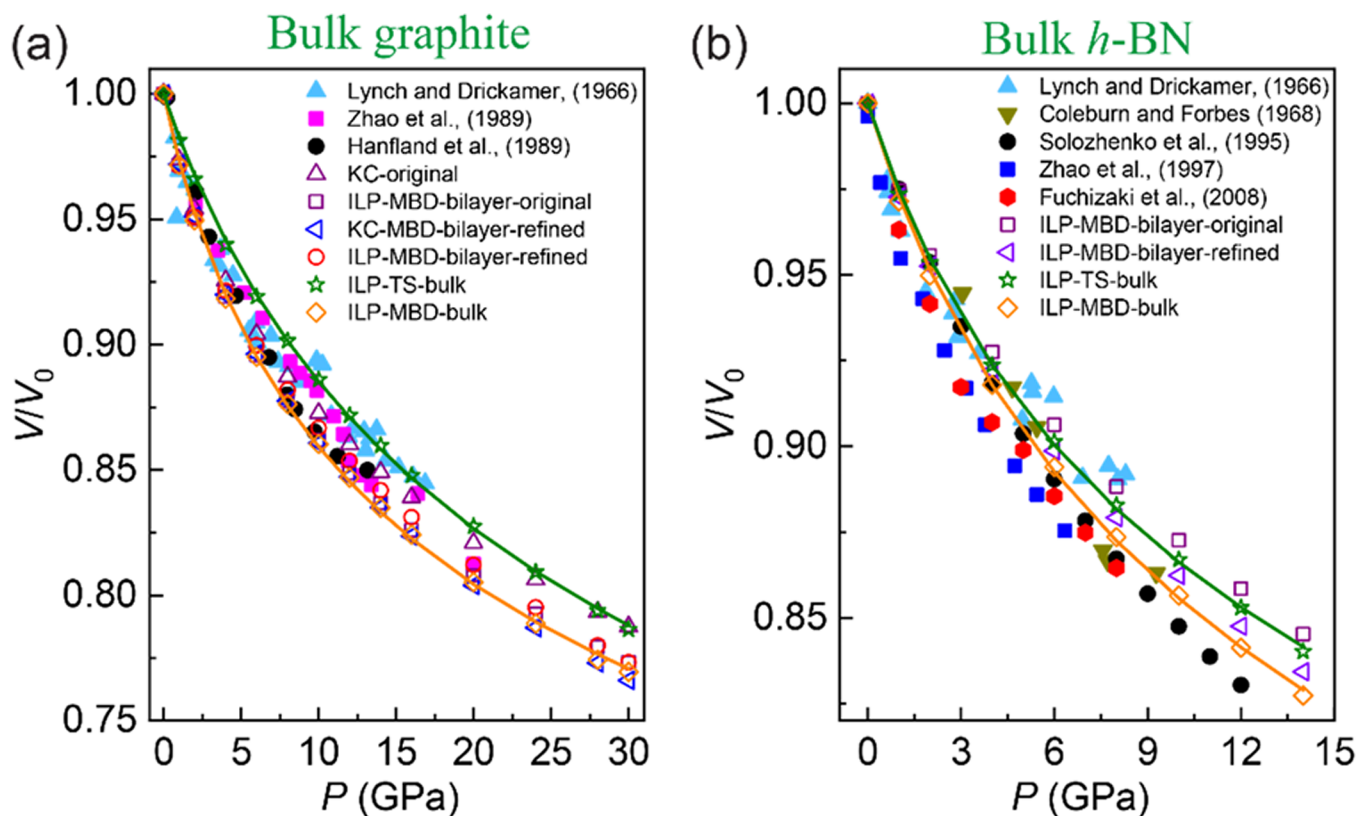


Figure 5. Murnaghan plot for (a) bulk graphite and (b) bulk *h*-BN. Full points denote experimental results with different measurement methods and open symbols denote NPT simulations results for different parameterizations of the ILP and KC potentials, as specified in the corresponding set labels. For clarity of presentation, we also show Murnaghan fitting curves of our simulation results obtained with the ILP-MBD-bulk (orange line) and ILP-TS-bulk (green line) parameterizations.

Table 1. Bulk Modulus (B_V^0) and Its Zero Pressure Derivative (B_V'), Intra- (a_0) and Inter- (c_0) Layer Lattice Constants and Binding Energy (E_{bind}) of Bulk Graphite, Calculated Using the Various Force-Field Parameterizations and Compared with Experimental and First-Principles Values

	Method	B_V^0 (GPa)	B_V'	a_0 (Å)	c_0 (Å)	E_{bind} (meV/atom)
Experiments	X-ray diffraction, ref 29	32 ± 2^a	12.3 ± 0.7^a	2.4612	6.7078	
	X-ray diffraction, ref 30	33.8 ± 0.3	8.9 ± 0.1	2.603(4)	6.706(3)	
	X-ray diffraction, ref 31	30.8 ± 2		2.462	6.707	
First-principles	LDA + PAW/US, ref 48	30.30/28.98		2.46	6.78	
	LDA, LCGTO-FF, ref 49	50.9, ^b 38.3 ^c				
	PBE, ref 50	1		2.47	8.84	1
	PBE + D2, ref 50	38		2.46	6.45	55
	RPA, ref 51	36			6.68	48
	QMC, ref 7			2.4595	6.85(7)	56(5)
	PBE + TS, ref 52	56		2.46	6.65	
	PBE + TS, ref 53	59		2.46	6.68	82
	PBE + TS/SCS, ref 53	43		2.46	6.75	55
	PBE + TS/HI, ref 1	57		2.46	6.74	81
	PBE + MBD@rsSCS, ref 3	29		2.46	6.82	48
	HSE + TS, this paper			2.462	6.60	85.12
	HSE + MBD, this paper			2.462	6.60	53.29
MD simulations ^d	ILP-MBD-bulk	34 ± 2	8.1 ± 0.3	2.46031(2)	6.8036(6)	51.51(1)
	ILP-TS-bulk	55 ± 2	6.2 ± 0.3	2.45934(4)	6.6605(7)	81.97(2)
	ILP-MBD-bilayer-refined, ref 28	34 ± 3	8.1 ± 0.6	2.46027(5)	6.742(2)	50.73(3)
	ILP-MBD-bilayer-original, ref 25	33 ± 1	8.5 ± 0.3	2.46026(4)	6.768(1)	50.58(2)
	KC-MBD-bilayer-refined, ref 28	35 ± 2	7.7 ± 0.4	2.46029(3)	6.788(1)	51.21(3)
	original KC, ref 40	37 ± 2	8.9 ± 0.4	2.46036(5)	6.752(2)	46.18(3)

^aFit with eq 1. ^bEOS fit. ^cCubic fit. ^dThe MD simulations were performed at 300 K.

Table 2. Bulk modulus (B_V^0) and Its Zero Pressure Derivative (B_V'), Intra- (a_0) and Inter- (c_0) Layer Lattice Constants and Binding Energy (E_{bind}) of Bulk *h*-BN, Calculated Using the Various Force-Field Parameterizations and Compared to Experimental and First-Principles Values

	methods	B_V^0 (GPa)	B_V'	a_0 (Å)	c_0 (Å)	E_{bind} (meV/atom)
Experiments	X-ray diffraction, ref 54			2.50399(5)	6.6612(5)	
	X-ray diffraction, ref 29	22 ± 4^a	18 ± 3^a	2.5040	6.6612	
	X-ray diffraction, ref 32	36.7 ± 0.5	5.6 ± 0.2	2.504(2)	6.660(8)	
	X-ray diffraction, ref 33	17.6 ± 0.8	19.5 ± 3.4	2.5043(1)	6.6566(6)	
	X-ray diffraction, ref 55	27.6 ± 0.5	10.5 ± 0.5	2.504(4)	6.659(2)	
	X-ray scattering, ref 56	25.6 ± 0.8		2.506	6.657	
	X-ray diffraction, ref 34	21	16	2.50(5)	6.66(3)	
First-principles	theory, ⁵⁷	27.7 ± 0.2	9.0 ± 0.1			
	LDA, ref 58	30.1	10.1	2.496	6.4896	57
	RPA, ref 59				6.60	39
	PBE + D2, ref 50	56		2.51	6.17	77
	PBE + TS, ref 52	37		2.51	6.71	
	PBE + TS, ref 53	36		2.50	6.64	87
	PBE + TS/SCS, ref 53	34		2.50	6.67	73
	PBE + TS/HI, ref 1	23		2.51	6.78	62
	PBE + MBD@rsSCS, ref 3	30		2.50	6.59	59
	HSE + TS, this paper			2.500	6.40	89.85
	HSE + MBD, this paper			2.500	6.60	58.17
MD simulation ^b	ILP-MBD-bulk	33 ± 2	7.8 ± 0.6	2.4959(1)	6.6035(2)	56.33(3)
	ILP-TS-bulk	35 ± 2	8.7 ± 0.6	2.49334(6)	6.5111(7)	88.24(2)
	ILP-MBD-bilayer-refined, ref 28	35 ± 2	8.0 ± 0.6	2.49513(5)	6.5461(2)	57.38(3)
	ILP-MBD-bilayer-original, ref 25	38 ± 3	8.7 ± 0.9	2.49561(5)	6.5817(7)	56.32(1)

^aFit with eq 1. ^bThe MD simulations were performed at 300 K.

parameterized ILP, which underestimates the bulk modulus pressure derivative by nearly 30%.

All DFT and force-field parameterizations appearing in Table 1 provide good agreement with the experimental values of the intra- and interlayer lattice constants. The accuracy of both first-principles and force-field predictions of the intralayer lattice constant is found to be ~ 0.01 Å, whereas the accuracy of the interlayer lattice constant is within ~ 0.1 Å, apart from PBE and PBE + D2 that overestimate and underestimate the interlayer lattice constant, respectively. Finally, all MBD calculations and force-field parameterizations provide bulk graphite binding energies within 10% of both RPA and QMC results. Nonetheless, all TS calculations overestimate the binding energy by nearly 50%.

The experimental values of the bulk modulus and its pressure derivative for bulk *h*-BN are more scattered than those for graphite, ranging from 17.6 to 36.7 GPa and 5.6 to 19.5, respectively. Therefore, it is difficult to draw a definite conclusion regarding the method that provides the best results. Nevertheless, all methods listed in Table 2, apart from PBE + D2, yield values within the experimentally measured range.

Similar to the case of graphite, all DFT and force-field parameterizations appearing in Table 2 provide good agreement with the experimental values of the intra- and interlayer lattice constants. The accuracy of both first-principles and force-field predictions of the intralayer lattice constant is found to be ~ 0.01 Å, whereas the accuracy of the interlayer lattice constant is within ~ 0.1 Å, apart from the PBE + D2 value that underestimates the interlayer lattice constant by ~ 0.5 Å. Finally, all MBD calculations and force-field parameterizations provide bulk *h*-BN binding energies that are $\sim 44\%$ above the RPA results and the corresponding TS calculations overestimate the binding energy by more than a factor of 2. We

note, however, that these deviations may result in part from the approximate nature of the RPA calculation itself. We further note that the experimental values listed in Tables 1 and 2 were obtained by adopting different approximations for the EOS (see Section 3 of the SI for details). In Table S3 of Section 3 of the SI, we provide the elastic moduli obtained by fitting our P – V curves using three different versions of the EOS. We found that all EOS yielded consistent values of the bulk modulus. This suggests that the differences between the various experimental values of the bulk modulus arise from the different methods adopted to collect the data, rather than from the choice of the EOS used for their fitting, in contrast with the observation reported in ref 60.

Overall, we find that even when parameterized against extremely high pressure HSE + MBD reference data, the ILP provides good agreement with the experimental data for all bulk parameters considered. The fact that the corresponding TS-parameterized ILP fails to predict several bulk parameters indicates the importance of including MBD effects in the calculation and validates the reliability of the HSE + MBD method for describing graphitic and *h*-BN-based systems at both low and high external pressures.

4.3. Phonon Spectra. To further demonstrate the ability of the newly parameterized HSE + MBD ILP to predict low-pressure properties, we computed the phonon dispersion curves of graphite and bulk *h*-BN at zero pressure and temperature and compared them with the experimental data reported in refs 61 and 62, respectively. The results reported in Figure 6a,b show that the dispersion of the low-energy out-of-plane (ZA) branches, which are related to the soft flexural modes of the layers, is well described for both bulk graphite and bulk *h*-BN (see Figure 6c,d). The larger deviations from the experimental data, observed for the high energy transverse (TO) and longitudinal (LO) optical modes, are mainly caused

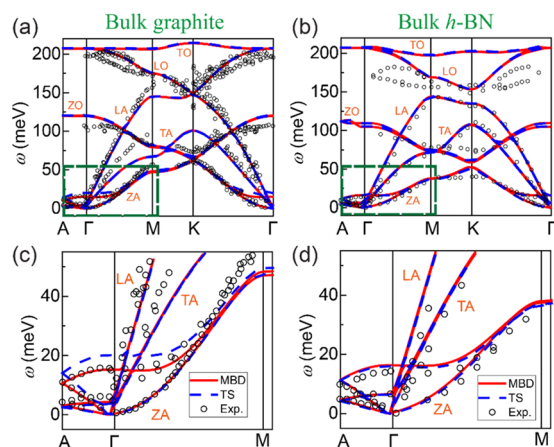


Figure 6. Phonon spectra of (a) bulk graphite and (b) bulk *h*-BN. Red solid lines and blue dashed lines are dispersion curves calculated using the ILP with parameters listed in Table S1 (ILP-MBD-bulk) and Table S2 (ILP-TS-bulk) in the SI, respectively. Experimental results of bulk graphite⁶¹ and bulk *h*-BN⁶² are given by open black circles. Panels (c) and (d) show a zoom-in of the low-energy phonon modes around the Γ -point (green rectangles in panels a and b) for graphite and *h*-BN, respectively.

by the intralayer potential used in our simulations. More details can be found in ref 63. In contrast, while the HSE + TS parameterized ILP provides a good description of the low-frequency phonon spectrum of bulk *h*-BN, large deviations from the low-energy experimental ZA branches are obtained for bulk graphite.

5. APPLICATIONS

5.1. Heterogeneous Graphene/*h*-BN Stacks under High Pressure. In the previous sections, we have analyzed the performance of MBD-based ILP parameterizations for predicting the mechanical properties of homogeneous graphene and *h*-BN-based structures under high pressure. Using the same protocol, here we predict the behavior of two bulk heterogeneous structures formed between graphene and *h*-BN. The first one consists of 12 alternating layers of graphene and *h*-BN with aligned lattice vectors. We will refer to this model as 6-G/BN (see Figure 7a). The second model is constructed by stacking a six-layer graphite slab with AB stacking atop a six-layer *h*-BN slab with AA' stacking, in an aligned configuration. We name this model 6-G/6-BN (see Figure 7b). For both systems, periodic boundary conditions are applied in all three directions. Due to their in-plane lattice mismatch of $\sim 1.8\%$, graphene and *h*-BN form an incommensurate interface. To satisfy lateral periodic boundary conditions while preserving the experimental lattice mismatch, we followed the method outlined in ref 24 and built large rectangular supercells, where each graphene and *h*-BN layer contains 12 544 and 12 120 atoms, respectively. For both heterojunctions, we performed simulations using the ILP-MBD-bulk parameterization.

Figure 7a,b reports snapshots of the 6-G/BN and 6-G/6-BN models at 300 K and zero pressure. In contrast to the nearly flat (maximal corrugation of ~ 0.8 Å) homogeneous junctions, the heterogeneous systems exhibit large out-of-plane deformations. In particular, the alternating stack exhibits vertical distortions of the order of ~ 10 Å and the 6-G/6-BN model displays deformations of ~ 3 Å. These large deformations result from the delicate interplay between the intralayer elastic energy contribution and the long-range interlayer dispersion inter-

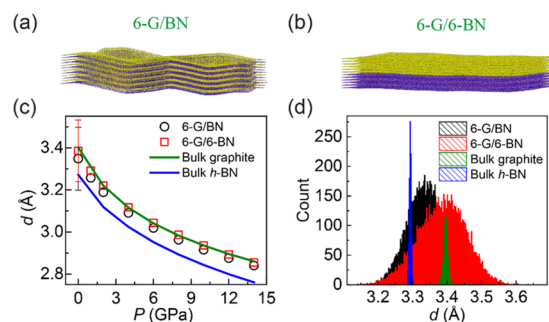


Figure 7. Snapshots of the (a) 6-G/BN and (b) 6-G/6-BN systems at zero pressure and 300 K. Individual graphene and *h*-BN layers are colored in yellow and blue, respectively. (c) Pressure dependence of the interlayer spacing, d , of 6-G/BN and 6-G/6-BN. ILP-MBD-bulk results for the homogeneous bulk graphene (full green line) and bulk *h*-BN (full blue line) systems are presented for comparison. (d) Distribution of the interlayer distance (averaged over time) of 6-G/BN (black) and 6-G/6-BN (red) at 300 K and zero external pressure. Corresponding results for the homogeneous bulk graphene (green) and bulk *h*-BN (blue) are presented for comparison. The standard deviation of the distribution in panel d defines the error bars in panel c.

actions within the incommensurate junction.^{26,64} The difference in the out-of-plane deformations of the two heterojunctions results from the fact that the bending rigidity of a 6-layer stack of graphene or *h*-BN is higher than the bending rigidity of the individual layers.

Figure 7c shows the pressure dependence of the average graphene/*h*-BN interlayer spacing of the two heterojunctions (see Methods section for our definition of the interlayer spacing in corrugated structures). The corresponding results for bulk graphite and bulk *h*-BN are also plotted for comparison purposes. We find that the average interlayer distances of both heterostructures are consistently larger than that of bulk *h*-BN and similar to that of graphite. Furthermore, on average, the interlayer distance of the 6-G/6-BN junctions is slightly larger than that of the 6-G/BN system.

Beyond thermal fluctuations, the inherently corrugated heterostructures exhibit a distribution of interlayer distances; the error bars in panel c illustrate the standard deviation of the distribution at zero pressure, which remains nearly constant for finite pressures (not shown for clarity). Notably, for both heterostructures, these distributions are considerably wider than the thermally broadened interlayer distance distributions of the homogeneous counterparts (see Figure 7d). The bulk modulus and its pressure derivatives obtained by fitting the results to the Murnaghan $V(P)$ equation produce similar values for both materials (see Table 3), which are comparable also to those of the corresponding homogeneous bulk structures.

As illustrated in panels e and f in Figure 1, the zero temperature equilibrium interlayer distances and binding energies predicted by HSE + MBD for the aligned bulk alternating C-stacked graphene/*h*-BN heterojunction are comparable to those of the homogeneous bulk values, giving

Table 3. Bulk Modulus of Heterogeneous Structures Calculated Using the ILP-MBD-Bulk Parameterization

structure	B_V^0 (GPa)	B_V'
6-G/BN	31 ± 1	9.0 ± 0.4
6-G/6-BN	32 ± 1	8.4 ± 0.4

3.3 Å and 58.0 meV/atom, respectively. As may be expected, due to thermal fluctuations, the corresponding room temperature average interlayer distance is somewhat larger (3.348 ± 0.004 Å, with the small uncertainty reflecting the negligible effect of thermal fluctuations in this case) and the binding energy is lower (52.59 ± 0.04 meV/atom). Similarly, for the 6-G/6-BN heterostructure, the room-temperature MBD simulations predicted equilibrium interlayer distance and binding energy of 3.386 ± 0.005 Å and 53.28 ± 0.02 meV/atom, respectively.

5.2. Normal Load Dependence of Friction. To evaluate the effects of the accuracy of the ILP in the subequilibrium regime for a practical dynamical application, we calculated the normal load dependence of friction in homogeneous graphene and *h*-BN sliding interfaces. We adopted three sets of ILP parameterizations: the original bilayer parameterization of refs 25 and 26, the refined bilayer parameterization of ref 28, and the MBD bulk parameterization presented herein. Details of the simulation setup are given in the Methods section.

As can be clearly seen in Figure 8, for the four-layer graphene model, the original bilayer parameterization predicts

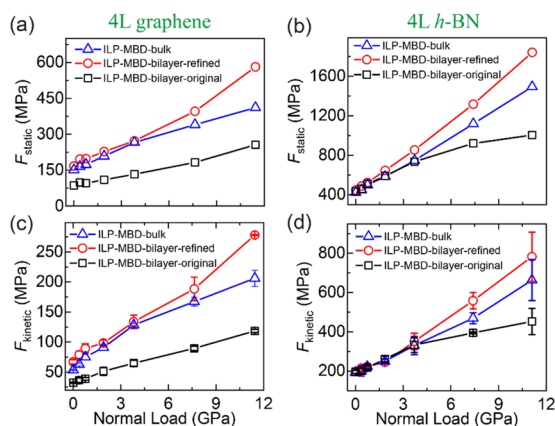


Figure 8. Normal load dependence of the static friction (top row) and kinetic friction (bottom row) for bulk graphite (left column) and bulk *h*-BN (right column). The simulations are performed at a temperature of 300 K using the MBD-bulk (open blue triangles), MBD-bilayer-refined (open red circles), and MBD-bilayer-original (open black squares) ILP parameterizations. See Section 2.4 of the Methods section for the error evaluation procedure.

consistently lower static and kinetic friction forces compared to the refined bilayer parameterization, across the entire load range considered, with increasing deviations at the higher load regime. This results from the fact that the two parameterizations provide similar agreement with the reference DFT binding data near the equilibrium interlayer distance but deviate at the subequilibrium regime. There, the automatic fitting procedure utilized in the refined parameterization provides better agreement with the reference data. As the same automatic fitting procedure is utilized also in the new MBD bulk parameterization, it is found to be in good agreement with the refined bilayer parameterization results at the lower pressure regime. With increasing pressure, the overall interlayer distance decreases and next-nearest neighboring layers interactions in the bulk configuration become more important. This is reflected by the fact that in this regime, the bulk parameterization provides somewhat lower friction force values than the refined bilayer ILP. A very similar behavior is found for the

four-layer *h*-BN system but with better agreement between the three ILP parameterization up to an external pressure of ~ 3 GPa. This is consistent with the differences between the sliding PES and sliding energy barriers obtained by the various parameterizations for the studied junctions (see Sections 4 and 6 of the SI).

Notably, for the case of *h*-BN, the original ILP parameterization predicts a sub-linear variation of the friction forces with pressure, whereas the new parameterization exhibits a linear behavior. This difference in qualitative behavior of the frictional properties stands in contrast with the compressibility results presented above, which were found to be less sensitive to the choice of ILP parameterization. This, in turn, further emphasizes the importance of an accurate description of the interlayer interactions in the sub-equilibrium regime in order to obtain reliable qualitative and quantitative predictions of the tribological response of layered materials interfaces under high external loads. Specifically, the fact that the ILP-MBD-bulk parameterization provides a better fit to the reference DFT data across the entire interlayer distance regime suggests that a linear friction dependence on pressure should be expected for this system.

6. CONCLUSIONS

In summary, we studied the reliability of HSE + TS and HSE + MBD DFT calculations for the description of the interlayer interactions in graphite and *h*-BN at subequilibrium interlayer distances. This was achieved by parameterizing our anisotropic ILP against the dispersion-corrected DFT reference data, across a wide interlayer distance range. The ILPs were then used to perform fully atomistic MD simulations of bulk systems subjected to external pressure. By comparing the simulation results to experimental compressibility data of graphite and *h*-BN we found that the MBD-parameterized ILP provides better and satisfactory agreement with experiment up to pressures of 30 and 14 GPa for graphite and *h*-BN, respectively. The bulk modulus of graphite, extracted from a Murnaghan plot obtained from the HSE + MBD parameterized ILP, was also found to be in good agreement with experimental data. Corresponding reference data for *h*-BN are too scattered. The agreement of calculated and experimental phonon spectra indicates that extending the applicability of our ILP to the deep subequilibrium interlayer distance regime does not sacrifice its ability to describe material properties at low external loads. Using the MBD parameterization, we were able to predict some structural and mechanical properties of two graphene/*h*-BN based heterostructures. We found that despite the highly corrugated superstructure formed, their load-dependent interlayer distance is very similar to that of graphite and somewhat larger than in *h*-BN. The extracted bulk moduli of both heterogeneous structures were found to be comparable to those of the two homogeneous bulk systems investigated. Finally, dynamic friction simulations of the homogeneous systems suggest that the results strongly depend both qualitatively and quantitatively on the type of ILP parameterization. This demonstrates the importance of carefully choosing the DFT reference dataset for predicting the tribological properties of layered materials. The analysis performed in the present work suggests that the ILP-MBD-bulk parameterization provides a better description of the interlayer interactions in homogeneous and heterogeneous junctions of graphene and *h*-BN at a wide range of external loads. We are currently extending the investigation to include

transition-metal dichalcogenides such as MoS₂, MoSe₂, WS₂, and WSe₂. This will allow us to draw general conclusions regarding the applicability of the HSE + TS and HSE + MBD approximations and the corresponding ILPs for modeling layered materials subject to high external pressure.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jctc.9b00908>.

Interlayer potential (ILP) fitting parameters; sensitivity test of the ILP parameters; bulk modulus of graphite and hexagonal boron nitride; sliding potential energy surfaces for bilayer configurations at subequilibrium interlayer distances; dispersive component of the sliding energy surfaces; and sliding energy barriers under different normal loads (PDF)

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Notes

The authors declare no competing financial interest.

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