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Density-functional description of polymer crystals: A comparative study of recent van der Waals functionals

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Due to the lack of treatment of long-range dispersion energies, density functional theory with local and semilocal approximations of exchange-correlation energy is known to fail in describing van der Waals complexes, including polymer crystals. This limitation can be overcome by using a different class of functionals, called van der Waals density functional (vdW-DF), originally developed by Dion *et al.* [Phys. Rev. Lett. **92**, 246401 (2004)]. In this work, we performed a systematic study of structural properties of polymeric crystals using the original vdW-DF functional by Dion *et al.* and its variants and refinements. Our study shows that this class of functional outperforms the conventional LDA or PBE functionals and gives results with similar accuracy to that of empirical dispersion-corrected schemes such as DFT-D. This study suggests the use of vdW-DF2 functional — a revised version of vdW-DF functional — to obtain a high-fidelity prediction of structural and other properties of polymeric materials. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4953170>]

I. INTRODUCTION

In recent years, density functional theory (DFT) has become the standard workhorse for simulations of materials at the atomic level. The theory is formally exact for ground-state properties, but approximations must be employed in practical calculations.^{1,2} Although local and semilocal approximations of the exchange-correlation (xc) functionals provide many spectacular successes for a variety of materials, they have been known to be deficient in describing certain classes of materials, including van der Waals bonded systems. Over the last ten years, many attempts have been made to overcome this shortcoming of DFT. These attempts mainly belong to two approaches. The first one is the so-called DFT-D approach where the interatomic dispersion-energy contributions to the DFT total energies are included as simple parametrized pairwise additive terms. This makes the method computationally as favorable as that of standard DFT with local/semilocal functionals, but at the price of being empirical as fitting parameters are employed in the construction of pairwise dispersion energies. Actually, the idea of the DFT-D approach was first used in quantum chemistry almost 40 years ago in the context of Hartree-Fock theory.^{3,4} A decade ago, the scheme has been adapted to DFT framework by Grimme,⁵ and later on the accuracy of DFT-D calculations has been much improved by including the environment-dependence of dispersion coefficients that are needed for the evaluation of dispersion energies.^{6,7} In

the second approach, a different class of exchange-correlation functionals where long-range dispersion energies are taken into account in the functional itself has been developed. The theoretical basis for the development is the adiabatic-connection fluctuation dissipation formalism in which an exact xc-energy expression is written in terms of interacting linear response functions at different coupling strengths of Coulomb interaction. Direct evaluation of exact-exchange and correlation energies within the random phase approximation (RPA), the so-called EXX/RPA scheme, has been used to successfully describe a wide range of molecular and crystalline van der Waals systems.^{8–10} However, application of the EXX/RPA method is still limited to relatively small systems due to its high computational demand. An approach that requires less computational expense was first developed by Dion *et al.* in Ref. 11 and was termed van der Waals density functional (vdW-DF). In this approach, an approximation of interacting response functions in terms of electronic density was developed to evaluate nonlocal correlation energy—the component of total energy responsible for long-range dispersion forces. Thus, similar to standard local or semilocal functionals, this nonlocal correlation energy can be expressed as a functional of charge density via a double integral where the charge density at two spatial points is correlated by a nonlocal kernel depending on the density and density gradient at those two points. In fact, vdW-DF by Dion *et al.* was constructed by combining the nonlocal correlation energy with the exchange and local-correlation energies treated in usual local-density and generalized-gradient approximations (GGAs). As a result, vdW-DF can be used just as other standard functionals in DFT electronic structure codes.

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Although vdW-DF has been proved to describe structural and energetic properties of various van der Waals complexes rather accurately, see, e.g., the review in Ref. 12, there remain two unsatisfactory issues, namely, the consistent overestimation of intermolecular distances, and the error in the binding energy (BE) which in many important circumstances is still outside the so-called “chemical accuracy” of 1 kcal/mol (~ 43 meV). The origin of these shortcomings was attributed to the inaccurate revised Perdew-Burke-Ernzerhof exchange functional¹³ (revPBE) incorporated within the vdW-DF. To improve the performance of vdW-DF, Cooper¹⁴ has developed a new enhancement factor for the generalized gradient approximation (GGA) of the exchange functional that reduces the short-range exchange repulsion in the limit of low reduced density gradient — defined as $s = |\nabla n|/(2k_F n)$, with $k_F = (3\pi^2 n)^{1/3}$ and n is the electronic density — and is an asymptote to that of the revPBE upper bound in the large s limit. The test on S22 dataset — the set of 22 weakly interacting dimers — showed that, when the revPBE exchange functional in vdW-DF was replaced by the one developed by Cooper, the binding energy (BE) was in better agreement with the CCSD(T) benchmark results and intermolecular distances were improved as well. Klimeš *et al.* took a somehow more empirical approach by tuning parameters of several GGA exchange functionals so as to make the calculated binding energies fit best with the CCSD(T) benchmarks.^{15,16} As a result, optimizing B88¹⁷ and B86b¹⁸ GGA exchange functionals originally developed by Becke leads to significantly reduced mean absolute deviations (MADs) of binding energies of S22 dataset (to about ~ 10 meV). These functionals are termed DF-optB88 and DF-optB86b in this work.

Recently two considerable elaborations of vdW-DF have been introduced. The first one was the second version of vdW-DF, named vdW-DF2, and was proposed by the main developers of the first vdW-DF.¹⁹ In this improved functional, a refitted version²⁰ of PW86 exchange functional²¹ was used instead of the revPBE exchange and the nonlocal kernel was also modified by using the large- N asymptote gradient correction. For the S22 dataset, the vdW-DF2 functional showed a considerable improvement over its precursor with a MAD of binding energies less than 50 meV and the MAD of equilibrium distances reduced from 0.23 to 0.13 Å. Hamada has showed that B86b GGA exchange functionals can also be revised and replaced PW86 in vdW-DF2 (termed revDF2 in this work) to make the functional more accurate.²² The second development was the VV10 functional²³ introduced by Vydrov and van Voorhis. Unlike vdW-DF and vdW-DF2 functionals, the nonlocal kernel in VV10 is approximated by a simple model. Consequently, there remains an arbitrary parameter for controlling the short range damping in the kernel. This parameter was fixed by fitting on binding energies of S22 dataset. Applications of the VV10 functional have shown remarkable improvements of binding energies and equilibrium intermolecular separations. We note that very recently the VV10 functional has been revised²⁴ to utilize a very efficient integration scheme of Román-Pérez and Soler²⁵ in a plane-wave implementation.

Polymeric crystals are an important class of materials with many applications not only in daily life products but also in low-cost electronic devices and in capacitors for electrostatic energy storage. Having both strong covalent interactions along the intrachain direction and weak van der Waals interactions between polymer chains, polymer crystals also form a stringent test case for any theoretical schemes dealing with van der Waals interactions. In a recent publication, Liu *et al.* have studied structural properties of 10 polymeric crystals with reliable crystallographic data using several DFT-D schemes.²⁶ The obtained results showed that overall the performance of these dispersion-corrected functionals is considerably improved when compared with that of (semi)local functionals and better accuracy is obtained for corrected schemes that take into account the environment-dependence of dispersion coefficients, i.e., DFT-D3 by Grimme *et al.*⁶ and DFT-TS by Tkatchenko and Scheffler.⁷ While van der Waals density functionals have been extensively applied to study vdW complexes such as molecular and layer systems, molecular crystals, and absorption of molecules on surfaces [see, e.g., the recent review by Berland *et al.* in Ref. 27], application to polymer crystals is still rather limited. Indeed, we are aware of only a few studies, namely, the polyethylene (PE) crystal structure by the original vdW-DF²⁸ and the recent applications of vdW density functionals in developing a dataset of polymers and related materials^{29,30} for designing, in particular but not limited to, high dielectric constant polymers, based on computation- and data-driven approaches. Thus, a thorough investigation of the performance of different vdW density functionals for polymer crystals is needed. In this paper, we systematically investigate the performance of the aforementioned state-of-the-art *ab initio* van der Waals density functionals for 10 polymeric crystals studied in Ref. 26, namely, polyethylene (PE), polyacetylene (PA), poly(glycolic acid) (PGA), poly(phenylene oxide) (PPO), poly(oxyethylene) (POM), poly(p-phenylene sulfide) (PPS), two forms of poly(vinylidene fluoride) (β -PVDF and α -PVDF), poly(tetrafluoroethylene) (PTFE), and poly(vinyl chloride) (PVC). The functionals employed in this study include vdW-DF by Dion *et al.*, DF-C09 by Cooper, DF-optB88 and DF-optB86b by Klimeš *et al.*, vdW-DF2 by Lee *et al.*, revDF2 by Hamada, and rVV10—a revised version of VV10 functional by Vydrov and van Voorhis.

II. COMPUTATIONAL DETAILS

All calculations in our study were performed using the PWSCF code of the QUANTUM ESPRESSO distribution³¹ in which several flavors of van der Waals density functionals are implemented in a plane-wave pseudopotential (PP) approach, including the self-consistent evaluation of the nonlocal potential.³² The calculation of forces and stress tensor³³ corresponding to the nonlocal correlation part was also made possible recently and this feature allows one to perform automated geometry optimizations. Since no pseudopotential generated with nonlocal correlation functionals is available to date, we employ pseudopotentials generated using the PBE xc-functional in the Vanderbilt’s ultrasoft framework as published in the GRBV pseudopotential library.³⁴ Although these PPs

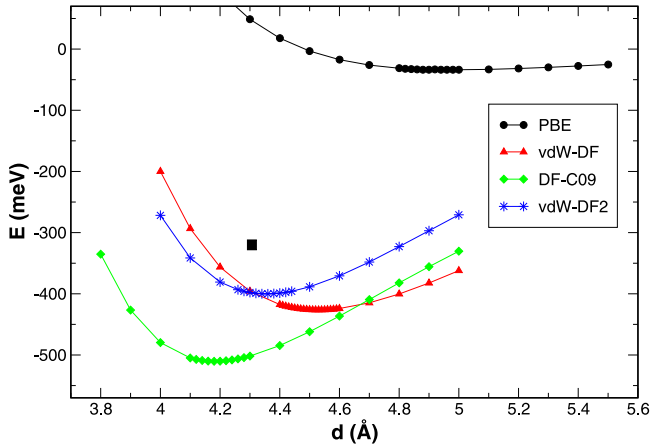


FIG. 1. Cohesive energy of PE crystal as a function of distance d between two polymer chains computed using PBE and several van der Waals density functionals. The black solid square indicates the experimental result.

were designed to be used with a relatively low plane-wave cutoff—40 Ry for the wave functions and a charge-density cutoff of 200 Ry, we used rather high cutoffs—70 Ry for the former and 700 Ry for the latter—to achieve good energy and stress³⁵ convergences. For each system, Brillouin zone sampling was carried out on a Monkhorst–Pack k -point grid generated with the same set of parameters reported in Ref. 26.

To determine the equilibrium structures of polymer crystals, we employed the standard procedure for geometry optimization where atomic and unit cell shape/size are relaxed so as to successively minimize forces and stresses. As pointed out by Liu *et al.*,²⁶ care must be taken when applying this approach to weakly bound systems such as polymer crystals. This is because potential energy surfaces (PESs) computed using certain functionals, notoriously with PBE and the like, can be very shallow. As a result, predefined convergence criteria for terminating geometry optimization procedures may be met for geometries far from the equilibrium configuration. However, these artifacts are less likely to happen when nonlocal correlations are treated correctly,

though approximately, in van der Waals density functionals. It is clearly seen in Fig. 1 that for PE crystal the PES computed from several arbitrarily selected vdW density functionals is much deeper than that of PBE functional. In our study, we used very tight convergence thresholds of 10^{-4} Ry/bohr for forces and 10^{-7} Ry for energies to ensure good convergence of structural optimizations. We explicitly verified for the case of PE that when vdW density functionals are used, lattice parameters obtained using a automated geometry optimization procedure are identical to those calculated in a more reliable but very time-intensive strategy adopted in Ref. 26 (where the complete PES is scanned by varying a and b while c is fixed at a value obtained from a calculation for a single polymer chain).

The fact that the internal structure of PE chain is relatively simple compared to other crystals studied in this work might question the reliability of the automated geometry optimization procedure when applied to study other complex systems. To reduce the uncertainty in the obtained results, we performed a further verification procedure namely that for each system, 5 different starting atomic configurations were constructed by randomly varying the lattice parameters within 10% of experimental values and automated geometry optimization was then performed using those configurations. We observed that the final results are in good agreement with each other for most of the cases. There are, however, a few cases with odd results indicating that the optimization procedure is trapped on a local minimum. We ensured that these cases can be adequately handled by using slightly tighter thresholds.

III. RESULTS AND DISCUSSION

A. Single polymer chain

Nonlocal vdW density functionals were developed specifically for describing weakly bonded systems. A successful vdW functional should, besides its ability to capture the essence of dispersion interactions, at least not degrade the

TABLE I. c -lattice constants (in Å) of 10 polymers obtained from calculations for a single isolated chain with different vdW density functionals. The results from PBE functionals and experimental values are also included for comparison. Mean deviations (MD), mean absolute deviations (MAD), and mean absolute relative deviations (MARD) are indicated in the last three lines.

Polymer	Expt.	PBE	vdW-DF	DF-C09	DF-optB88	DF-optB86b	vdW-DF2	revDF2	rVV10
PE	2.55	2.563	2.575	2.552	2.562	2.557	2.580	2.559	2.566
PA	2.46	2.477	2.481	2.473	2.474	2.474	2.484	2.475	2.479
PPO	9.72	9.833	9.819	9.709	9.730	9.730	9.849	9.752	9.805
POM	3.56	3.645	3.670	3.570	3.593	3.591	3.677	3.601	3.625
PPS	10.26	10.325	10.250	10.123	10.167	10.151	10.282	10.184	10.237
PGA	7.02	7.058	7.106	7.034	7.063	7.049	7.134	7.054	7.080
α -PVDF	4.62	4.665	4.685	4.620	4.635	4.630	4.680	4.640	4.645
β -PVDF	2.56	2.596	2.609	2.580	2.588	2.586	2.610	2.588	2.594
PTFE	2.62	2.663	2.674	2.637	2.647	2.645	2.672	2.647	2.654
PVC	5.08	5.112	5.138	5.087	5.105	5.098	5.147	5.101	5.116
MD (Å)		-0.049	-0.056	0.007	-0.011	-0.006	-0.067	-0.015	-0.035
MAD (Å)		0.049	0.058	0.023	0.030	0.028	0.067	0.030	0.040
MARD (%)		1.06	1.38	0.41	0.65	0.58	1.52	0.66	0.91

performance of traditional functionals for strong ionic-covalent interactions such as covalent bonds along the chain direction of polymers. We therefore investigate in this part the performance of vdW density functionals for single polymer chains. Table I presents *c*-lattice constants of 10 single polymer chains computed using different vdW functionals. The obtained results show that in general vdW density functionals give similar accuracy to PBE in describing the bond length along the polymer chains. The combination of C09 exchange by Cooper with the first generation of vdW-DF is most accurate with MAD as small as half of that of PBE, while both vdW-DF and vdW-DF2 are slightly worse than PBE.

B. Polymer crystals

Structural properties of ten polymer crystals considered in this work have been studied using different variants of van der Waals density functional. The results are shown in Table II in comparison with experimental values (if available). The cohesive energy, E_c , per unit cell has been computed as

$$E_c = N_{\text{chain}}E_{\text{chain}} - E_{\text{bulk}}, \quad (1)$$

where E_{bulk} is the total energy of bulk unit cell with N_{chain} single chains and E_{chain} is the total energy of the unit cell containing the single isolated chain. Bulk modulus at zero

TABLE II. Lattice parameters, densities, cohesive energies (E_c), and bulk moduli (B_0) for ten polymer crystals (PE, PA, PPO, POM, PPS, PGA, β -PVDF, α -PVDF, PTFE, PVC) calculated using different van der Waals density functionals. Available experimental values are also included for comparison.

Polymer	Method	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	Density (g/cm ³)	E_c (eV)	B_0 (GPa)	Polymer	Method	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	Density (g/cm ³)	E_c (eV)	B_0 (GPa)
PE	Expt.	7.12 ^a	4.85 ^a	2.55 ^a	0.997	0.32 ^b	6.4 ^c	PGA	Expt. ⁴¹	5.22	6.19	7.02	1.700		
	vdW-DF	7.34	5.19	2.58	0.948	0.43	7.8		vdW-DF	5.34	6.24	7.11	1.627	1.78	14.5
	DF-C09	6.84	4.76	2.55	1.122	0.51	12.2		DF-C09	5.13	5.80	7.03	1.843	2.03	20.5
	DF-optB88	6.93	4.85	2.56	1.083	0.49	11.8		DF-optB88	5.15	5.88	7.06	1.803	2.08	21.2
	DF-optB86b	6.95	4.86	2.56	1.077	0.50	10.2		DF-optB86b	5.17	5.88	7.05	1.799	2.02	19.3
	vdW-DF2	7.05	4.98	2.58	1.029	0.40	10.9		vdW-DF2	5.22	6.04	7.14	1.712	1.76	19.5
	revDF2	6.97	4.88	2.56	1.070	0.37	9.9		revDF2	5.19	5.90	7.05	1.786	1.62	18.1
	rVV10	6.90	4.77	2.56	1.106	0.45	13.6		rVV10	5.13	5.85	7.08	1.814	1.89	22.2
PA	Expt. ⁴²	4.24	7.32	2.46	1.130			β -PVDF	Expt. ⁴²	8.58	4.91	2.56	1.972		
	vdW-DF	4.24	7.70	2.48	1.068	0.50	8.2		vdW-DF	8.63	4.79	2.60	1.979	0.96	17.9
	DF-C09	3.91	7.17	2.47	1.249	0.60	13.2		DF-C09	8.26	4.57	2.57	2.192	1.00	21.8
	DF-optB88	3.99	7.29	2.47	1.204	0.59	12.9		DF-optB88	8.29	4.60	2.58	2.162	1.06	23.7
	DF-optB86b	3.99	7.29	2.47	1.204	0.59	11.8		DF-optB86b	8.33	4.62	2.58	2.142	1.02	21.7
	vdW-DF2	4.11	7.49	2.48	1.133	0.48	11.4		vdW-DF2	8.41	4.67	2.60	2.083	0.95	23.2
	revDF2	4.01	7.32	2.47	1.193	0.47	10.8		revDF2	8.35	4.64	2.58	2.127	0.83	20.1
	rVV10	3.96	7.23	2.47	1.223	0.54	14.1		rVV10	8.25	4.58	2.58	2.181	0.98	25.2
PPO	Expt. ⁴²	8.07	5.54	9.72	1.408		4.1	α -PVDF	Expt. ⁴²	9.64	4.96	4.62	1.925		
	vdW-DF	8.30	5.58	9.93	1.330	2.04	9.8		vdW-DF	9.63	4.98	4.70	1.887	1.36	15.7
	DF-C09	7.47	5.43	9.87	1.528	2.46	14.7		DF-C09	9.27	4.79	4.63	2.069	1.38	17.7
	DF-optB88	7.68	5.45	9.90	1.476	2.43	14.8		DF-optB88	9.28	4.81	4.66	2.045	1.49	20.2
	DF-optB86b	7.65	5.46	9.88	1.482	2.41	13.4		DF-optB86b	9.33	4.83	4.65	2.030	1.44	18.3
	vdW-DF2	7.96	5.54	9.98	1.390	1.89	12.5		vdW-DF2	9.39	4.87	4.70	1.979	1.26	20.3
	revDF2	7.66	5.52	9.90	1.461	1.83	12.2		revDF2	9.37	4.85	4.65	2.013	1.07	16.9
	rVV10	7.56	5.48	9.93	1.487	2.21	15.3		rVV10	9.20	4.79	4.66	2.071	1.33	21.6
POM	Expt. ⁴³	4.77	7.65	3.56	1.540			PTFE	Expt. ⁴⁴	8.73	5.69	2.62	2.552		
	vdW-DF	4.81	7.90	3.65	1.438	0.79	10.6		vdW-DF	8.54	5.94	2.67	2.452	0.71	17.9
	DF-C09	4.64	7.27	3.54	1.670	0.92	16.6		DF-C09	8.34	5.82	2.64	2.592	0.66	15.9
	DF-optB88	4.66	7.39	3.58	1.618	0.93	16.8		DF-optB88	8.39	5.79	2.64	2.590	0.72	20.9
	DF-optB86b	4.69	7.40	3.57	1.610	0.91	15.4		DF-optB86b	8.35	5.82	2.64	2.589	0.71	18.6
	vdW-DF2	4.68	7.65	3.65	1.526	0.76	15.3		vdW-DF2	8.38	5.84	2.67	2.542	0.56	20.5
	revDF2	4.69	7.44	3.57	1.601	0.69	14.4		revDF2	8.41	5.85	2.65	2.548	0.46	15.5
	rVV10	4.61	7.35	3.60	1.635	0.85	18.3		rVV10	8.28	5.77	2.65	2.624	0.58	19.9
PPS	Expt. ⁴²	8.67	5.61	10.26	1.440			PVC	Expt. ⁴²	10.24	5.24	5.08	1.523		6.0
	vdW-DF	8.78	5.77	10.47	1.354	2.27	8.8		vdW-DF	10.47	5.31	5.14	1.453	1.23	13.9
	DF-C09	7.96	5.50	10.39	1.579	2.81	13.7		DF-C09	9.70	5.08	5.09	1.655	1.39	13.5
	DF-optB88	8.17	5.56	10.43	1.516	2.75	13.4		DF-optB88	9.91	5.10	5.11	1.607	1.43	14.0
	DF-optB86b	8.16	5.56	10.41	1.521	2.72	12.5		DF-optB86b	9.90	5.12	5.10	1.606	1.39	12.6
	vdW-DF2	8.53	5.65	10.50	1.420	2.16	11.7		vdW-DF2	10.18	5.19	5.15	1.526	1.19	13.4
	revDF2	8.20	5.57	10.40	1.512	2.13	11.7		revDF2	9.92	5.14	5.10	1.596	1.08	11.9
	rVV10	8.08	5.54	10.47	1.533	2.57	14.8		rVV10	9.79	5.06	5.12	1.637	1.34	12.4

^aReference 45.

^bReference 36.

^cReference 40.

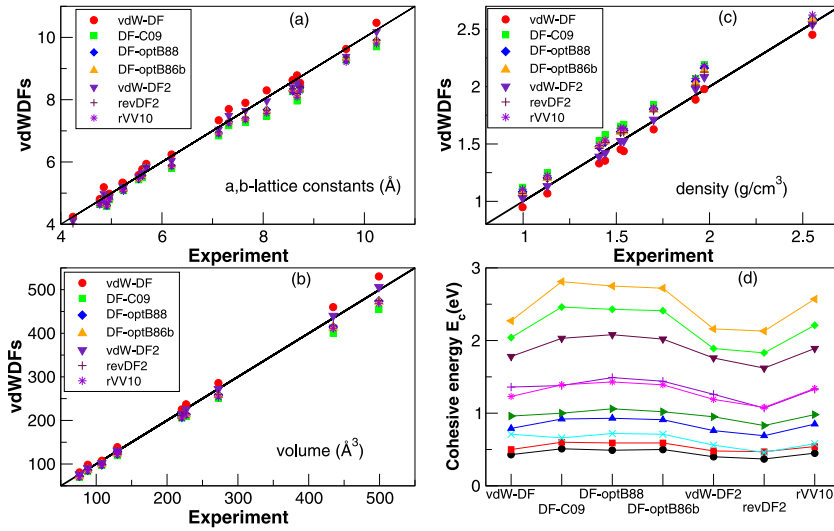


FIG. 2. ((a)–(c)) Equilibrium structural properties (a, b -lattice constants, volume, and density, respectively) of 10 polymer crystals as predicted by different *ab initio* van der Waals density functionals. (d) Cohesive energies (each curve is for a polymer; the solid lines are drawn as guide to the eyes).

pressure, B_0 , was obtained using a finite difference of the equation

$$B_0 = -V_0 \frac{dP}{dV}. \quad (2)$$

To this end, we performed two additional geometry optimizations where the unit cell parameters were relaxed under a small external pressure of $P_{\text{ext}} = \pm 0.1$ GPa.

It is anticipated that the presence of other polymer chains in bulk systems only has minor effect on the c -lattice constant of isolated chains because they interact via dispersion forces which are very small compared to strong covalent bonds along the chain. This is indeed the case as showed in Table II where relaxed c -lattice constants in bulk systems are only slightly changed when compared to the values in Table I. For a, b -lattice constants, unit cell volumes, and densities at equilibrium, the results predicted by all vdWDFs considered in this work are overall in good agreement with experimental values as can be seen in Figs. 2(a)–2(c). They are also closer to experiments than that of local/semi-local functionals. In particular, while the largest deviation from experiments for LDA and GGAs reported in Ref. 26 is 15%, it is reduced by a factor of 2 (to 8%) for the case of vdWDFs which is comparable to that of dispersion-corrected functionals. Fig. 2(a) also shows that in general vdW-DF and vdW-DF2 tend to overestimate the a, b -lattice constants which leads to an overestimation of unit cell volume (Fig. 2(b)) and underestimation of density (Fig. 2(c)). Other functionals show the opposite trend. This behavior of vdW-DF and vdW-DF2 is consistent with the fact that these two functionals also give overestimation of intermolecular distances.^{14,22}

To compare the results obtained using different levels of theory, we have computed mean deviations (MDs), mean absolute deviations (MADs), mean absolute relative deviations (MARDs), and root-mean-square errors (RMSEs) of a, b -lattice constants from our calculations, as well as the a, b -lattice constants reported by Liu *et al.* (obtained using local/semilocal and dispersion-corrected functionals), with respect to the available experimental values. The data are summarized in Table III and are also graphically represented in Fig. 3. It is observed that, among different vdW density

functionals considered, vdW-DF and vdW-DF2 give the most accurate results for a, b -lattice constants. The errors of energy-optimized functionals (DF-optB88, DF-optB86b) and revDF2 are similar and slightly larger than that of vdW-DF and vdW-DF2. The DF-C09 and rVV10 give largest errors. Compared to the results of dispersion-corrected functionals, the accuracy of vdW density functionals is similar. Overall, the vdW-DF2 gives the smallest error compared to other vdW functionals as well as the dispersion-corrected ones.

Experimental values for cohesive energy, E_c , and bulk modulus, B_0 , are only available for a few systems. Indeed, we are only aware of E_c for PE crystal and it was reported to be 0.32 ± 0.01 eV at zero temperature.³⁶ For PE crystal, both vdW and dispersion-corrected functionals predict E_c in the range between 0.4/0.5 eV, except for the case of revDF2 where E_c is 0.37 eV. This number compares well with the experimental value if one takes into account the zero-point energy correction which was estimated to be about 0.04 eV.²⁸

TABLE III. Mean deviations (MD), mean absolute deviations (MAD), mean absolute relative deviations (MARD), and root-mean-square errors of a, b -lattice constants predicted by using different levels of theory with respect to the experimental values. Values for local/semilocal and dispersion-corrected functionals were obtained using results reported by Liu and co-workers.²⁶

Functional	MD (Å)	MAD (Å)	MARD (%)	RMSE (Å)
LDA	-0.42	0.42	6.18	0.47
PBE	0.44	0.44	7.13	0.52
PW91	0.42	0.42	6.93	0.50
PBE-D2	-0.25	0.27	4.21	0.29
PBE-D3	-0.14	0.15	2.46	0.23
PBE-TS	-0.11	0.15	2.36	0.19
vdW-DF	0.11	0.14	2.19	0.18
DF-C09	-0.28	0.29	4.20	0.34
DF-optB88	-0.20	0.21	3.11	0.25
DF-optB86b	-0.19	0.21	3.01	0.25
vdW-DF2	-0.07	0.12	1.83	0.15
revDF2	-0.17	0.19	2.71	0.23
rVV10	-0.25	0.26	3.77	0.31

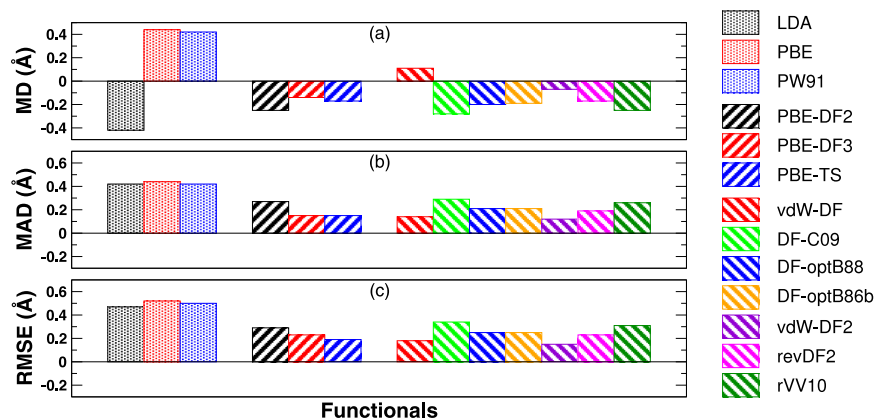


FIG. 3. Bar graphs of errors of a , b -lattice constants predicted by using different levels of theory with respect to the experimental values as indicated in Table III: (a) mean deviations (MD), (b) mean absolute deviations (MAD), and (c) root-mean-square errors (RMSE).

Overall, vdW density functionals overestimate the cohesive energy up to 150%. Similar trend was also observed for the case of molecular crystals.^{37,38} Although experimental cohesive energies for other polymers are not available to compare with, we plot in Fig. 2(d) the values of E_c for all polymers calculated using different vdW density functionals to see the trend. The figure shows the consistent behavior that vdW-DF, vdW-DF2, and revDF2 give smaller cohesive energies than other functionals do. It is worth to mention that for most molecular complexes in the S22 dataset the former functionals also underestimate the binding energies compared to the benchmark results from highly accurate CCSD(T) calculations.^{14,22} Apart from PE, experimental bulk moduli are also available for PPO and PVC. Similar to the behavior of dispersion-corrected functionals, bulk moduli predicted by vdW density functionals are consistently larger (by a factor ranging from 1.5 to 3) compared to experiments. It is known that the effect of temperature on bulk moduli can be significant. For instance, bulk modulus of benzene crystal decreases about 20% (from 5.72 to 4.60 GPa) when temperature increases over the range of 80 K (from 170 to 250 K).³⁹ For PE crystal, experimental bulk modulus was obtained at room temperature.⁴⁰ Thus, one can suspect that the large difference between calculated bulk moduli which were obtained from zero-temperature calculations and experiment is due to the temperature effect. Besides, the difference could also be partly caused by the amorphous nature of experimental samples and the imperfection of vdW density functionals in describing lattice constants.

IV. SUMMARY

In this work, we investigated the performance of state-of-the-art *ab initio* van der Waals functionals in describing structural properties for a variety of representative polymer crystals. The tested functionals are vdW-DF by Dion *et al.*, DF-C09 by Cooper, DF-optB88 and DF-optB86b by Klimeš *et al.*, vdW-DF2 by Lee *et al.*, revDF2 by Hamada, and a revised version of VV10 by Vydrov and van Voorhis as implemented in PWscf code. Our obtained results show that all vdW density functionals considered in this work can describe structural properties of polymer crystals reasonably well and among them vdW-DF2 gives the most accurate results compared to experiments. In general, the accuracy of these

ab initio van der Waals functionals is similar to that of dispersion-corrected functionals which is much better than conventional LDA/GGAs. Since *ab initio* van der Waals functionals have been implemented efficiently and they work in more or less the same manner as local/semilocal functionals, our study suggests that these vdWDFs should be used to study other properties, e.g., electronic or defect, of polymeric materials.

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