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Published in:
Chemical Communications

DOI:
10.1039/c8cc04855j

Published: 01/01/2018

Document Version
Early version, also known as pre-print

Please cite the original version:
On the Exfoliation and Anisotropic Thermal Expansion of Black Phosphorus.†

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Black Phosphorus is a bulk solid allotrope of elemental phosphorus, that can be seen as an infinite stacking of phosphorene sheets. It is interesting from a technological point of view as well as from an electronic structure perspective due to the importance of electron correlation effects. In a recent paper [J. Phys. Chem. Lett. 8, 1290 (2017)] a highly accurate exfoliation energy has been computed. Building upon these results we carefully benchmark various dispersion-corrected density functional approximations. The choice of the range-separating function that suppress London dispersion at short interatomic distances apparently has a substantial influence on the results. Having chosen the suitable functional, we have computed the thermal expansion coefficients of black phosphorus via a quasi-harmonic approximation. The computed coefficients manifest a strong anisotropy between the two in-plane directions. Our calculations, however, do not support existence of negative thermal expansion in black Phosphorus, reported in some theoretical studies.

Black phosphorus (black-P) is, among the many allotropes of elemental solid phosphorus, the one which has attracted substantial interest in the last decades. This is on the one hand due to its peculiar features as a bulk solid such as high mobility and its relevance in electronic and optoelectronics. On the other hand, its structure is composed of an infinite stacking of phosphorene layers and the possibility to exfoliate it to obtain the 2D phosphorene sheets is intriguing.

From the computational point of view, black-P demonstrated to be an extremely challenging system. Its key properties appear to be regulated by a delicate equilibrium of covalent interactions and both middle- and long-ranged dispersive forces, which is quite difficult to describe properly at the quantum mechanical level by using traditional density functional theory (DFT) techniques.

Recently, high-level many-body electronic structure methods have been used to compute the exfoliation energy (E\text{ex f}) of black-P. In 2015, the work by Shulenburger et al. reported the Quantum Monte Carlo (QMC) value of E\text{ex f} ≈ -151 meV/atom. Almost simultaneously, some of us applied the periodic local MP2 approach using orbital-specific virtuals combined with fragment local CCSD(T) corrections. This led to an estimate of E\text{ex f} = -151 meV/atom, which was also supported by our PBE0-D3 results. We later revised our estimate of E\text{ex f}, by employing the periodic Local-direct ring CCD method rather than LMP2 as the low-level model, corrected then to the LCSD(T) level with finite clusters. The new value for E\text{ex f} = -92 meV/atom, was much closer to the QMC result. The reason of the failure of MP2 or spin-component-scaled-MP2 even as a low-level model in the correction scheme for black-P was found to be the gross overestimation of the long-range part of binding by these methods due to their inability to capture the Coulomb screening effects, apparently very strong in this narrow gap system.

The objective of this work is (i) by using these benchmark values as references, to find a modestly computationally demanding model that provides an appreciable accuracy for black-P, and (ii) to apply this model within the quasi-harmonic approximation to compute the thermal expansion coefficients for this system. In a material kept together by relatively weak interactions like black-P, comparison with realistic experimental settings has to include thermal effects, both in the energetics and in the structure of the crystal. The above mentioned studies only describe a static 0 K picture of the black-P properties. For modelling the temperature dependent thermodynamic properties, the quasi-harmonic
approximation (QHA) has been shown to be quite efficient. It is substantially less costly than molecular dynamics simulations conducted at a comparable level of theory, while still being able to capture thermal expansion to reasonable accuracy. In recent years, QHA has been applied to molecular crystals dominated by van der Waals interactions using classical force fields, and the QHA has been applied to molecular crystals dominated by van der Waals interactions using classical force fields, and the QHA has been applied to molecular crystals dominated by van der Waals interactions using classical force fields, and the QHA has been applied to molecular crystals dominated by van der Waals interactions using classical force fields, and the QHA has been applied to molecular crystals dominated by van der Waals interactions using classical force fields, and the QHA has been applied to molecular crystals dominated by van der Waals interactions using classical force fields, and the QHA has been applied to molecular crystals dominated by van der Waals interactions using classical force fields, and the QHA has been applied to molecular crystals dominated by van der Waals interactions using classical force fields, and the QHA has been applied to molecular crystals dominated by van der Waals interactions using classical force fields.

To benchmark the ability of density functional approximations (DFA) in describing the exfoliation energy of black-P, we include a widely used generalized gradient approximation (GGA) functional PBE its hybrid variant PBE0 as well as the strongly constrained and appropriately normed (SCAN) meta-GGA functional that has been shown to yield excellent properties for molecules, bulk solids, as well as layered materials.

The exfoliation energies and the cell volumes, computed with different DFAs, are given in Figure 2 together with the reference values. Let us first focus on exfoliation energies (abscissa axis); The references here are taken from Ref. 19 (Diffusion Monte Carlo (DMC)) and Ref. 18 (LDRCCD+ALCCSD(T)). The long-range dispersion contribution clearly has a substantial impact on the exfoliation energy (see Figure 2 and Table S1). Both the type of correction scheme and the form of the damping function seem to have a significant effect on the computed binding energy. While there is nearly no interlayer binding with plain PBE, results close to the reference can be computed by PBE-D3 (2d, atm) and PBE-MBD, which are the methods with most promising statistical evaluations on benchmark sets of molecular crystals and small molecule adsorptions. Still, the dependence on the damping function is unusually strong as demonstrated by the combination of PBE0 with D3 in both its rational damping (bj) and its zero-damping (zd) flavors but also add other approaches, such as TS and MBD. The effect of three-body Axilrod-Teller-Muto (aT) term is also tested.

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All the employed DFT-D methods consist of a semi-local exchange correlation part combined with corrections for missing long-range London dispersion interactions:

$$E_{DFT-P} = E_{DFA}^{\text{semi-local}} + E_{\text{disp}}^{\text{local}}$$

While the wavefunction methods seamlessly describe electron correlation at all length scales, DFT-D methods use a range-separation function (or damping function) to cut off the unphysical dispersion correction for small interatomic distances. These damping functions are parameterized (one to three fitted parameters) to reproduce the reference interaction energy on sets of small molecular dimers, e.g. S22 set and extensions. The main focus in this work is on the D3-type London dispersion corrections – both in the Becke-Johnson (bj) damping or zero-damping (zd) flavors – but also add other approaches, such as TS and MBD. The effect of three-body Axilrod-Teller-Muto (aT) term is also tested.

For comparison with other DFAs, specifically testing different strategies to include London dispersion interactions, the VASP5.4 software suite with a projector-augmented plane wave orbital expansion (PAW) has been employed for evaluating exfoliation energies. PAW and Crystal calculations yield E_ref that are in agreement within 5 meV/atom (using a PBE functional, see SI, Table S1).
accuracy”, further investigations, e.g. by many-body electronic structure methods, are strongly recommended.

In order to enable this test with the low-cost ’3c’ methods, we parametrized the zero-damping function of D3 using the standard least-square optimization on small molecular dimers (S66x8 set). The results confirm the strong dependence on the medium-range regime. At the same time, this reparamaterization makes ’3c’ methods deliver reasonably accurate exfoliation energies, just slightly worse compared to PBE0-D3(zd). The three-body Axilrod-Teller-Muto type term is small, but improves the agreement with the reference by about 10 meV/atom. Comparing PBE-D3(zd,atm) with its hybrid variant PBE0-D3(zd,atm) shows that the inclusion of non-local Fock exchange improves both interaction energy and the equilibrium geometry slightly.

In addition to the exfoliation energy, the equilibrium geometry of black-P is a fundamental property that should be reproduced accurately in order to allow a faithful prediction of its thermal properties. X-ray measurements provided a unit cell volume estimate of 19 Å$^3$ per atom, back-corrected for the zero-point and thermal expansion to 18.8 Å$^3$ per atom.

![Fig. 2 Exfoliation energy and cell volume of black-P computed with different DFAs vs the reference values. The reference exfoliation energies are taken from the high-level calculations.](image)

The reference value for the volume is the experimental estimate of 19 Å$^3$ per atom, back-corrected for the zero-point and thermal expansion to 18.8 Å$^3$ per atom.

![Fig. 3 Thermal expansion of the unit cell volume $V$ and individual lattice parameters $x$ computed with the PBE0-D3(zd,atm) method with increasing phonon sampling, the crystallographic directions are defined in Fig. 1.](image)

The inset shows the used supercells compared to the crystallographic cell drawn in red. 2x2x2 (32 atoms) and 3x3x3 (108 atoms) are supercells of the 4-atom primitive cell. 3x1x2-conv (48 atoms) is a supercell of the centered crystallographic cell.

and in the volume. However, for some of the minimal-basis 3c-methods (in particular HF-3c) the volume is very much off despite an accurate prediction of the exfoliation energy. Interestingly, a proper choice of the damping function is sufficient to correct this pathological behavior in a sense that the errors in both quantities become consistent.

![Fig. 3](image)

One of the DFAs, that perform very well also for both the volume and exfoliation energy, is PBE0-D3(zd, atm) and we will therefore employ this method for the study of the thermal expansion.

In the top panel of Fig. 2 we report the dependence of the unit cell volume expansion as a function of temperature. The effect of the QHA approximation is already quite significant at 0 K. The zero-point expansion of 0.6% is similar in size to the thermal expansion up to 400 K. The results obtained with the three supercells do not differ significantly in the range up to 300 K, while differences up to 20% are seen at higher temperatures (>600 K).

Here, the shape of the supercell seems to have a more substantial impact on results than its size. At the room temperature, the computed thermal expansion coefficient $\alpha$ is $20 \times 10^{-6}$ K$^{-1}$, which compares very well with the value of $22 \times 10^{-6}$ K$^{-1}$ reported by...
Riedner and coworkers.  

Finally we consider the thermal expansion of black-P along the individual crystallographic directions $a$, $b$ and $c$, which is presented in the bottom panel of Fig. 3. The calculations reveal a very high anisotropy for this quantity. Results of the different supercell models deviate slightly, but the ratio between the corresponding expansion coefficients and thus the anisotropy remains nearly independent from the size of the supercell. Furthermore, it is quite remarkable that the expansion along the in-plane direction $c$ is small, it was found positive for all of the considered temperatures. Hence our calculations do not support existence of a negative thermal expansion regime in black-P, reported in the theoretical study of Ref. 23.

From the linear parts of the curves in Fig. 3 corresponding to the largest supercell, we obtain the following thermal expansion coefficients: $\alpha_a = 1$ K$^{-1}$, $\alpha_b = 11$ K$^{-1}$, $\alpha_c = 8$ K$^{-1}$. They agree appreciably well with the experimental values reported in Ref. 23 $\alpha_a = 8$ K$^{-1}$, $\alpha_b = 11$ K$^{-1}$, $\alpha_c = 5$ K$^{-1}$. We note that the anisotropy revealed in our calculations is noticeably higher than that in the reported experimental data. At the same time, we highlight the large variation in the experimental datasets reported in that work – e.g. values of $\alpha_a = 22$ K$^{-1}$, $\alpha_b = 38$ K$^{-1}$, $\alpha_c = 39$ K$^{-1}$ are reported from Keyes et al. – and the preliminary character of some of them. Therefore, in the light of the present findings, new experimental efforts to refine the thermal coefficients for black-P would be desirable.

To conclude, we have complemented our earlier works on the high-level quantum-mechanical treatment of black phosphorus by taking into account thermal effects at the DFT level. The appropriate DFT functional (PBE0-D3 with zero-damping and three body corrections) was chosen as it accurately reproduces both the semi-experimental cell volume and the computed high-level excitation energy. Our quasi-harmonic calculations reveal a strong anisotropy in the thermal expansion, but give no indication of a previously claimed negative thermal expansion. Our results agree appreciably well with measured thermal expansion coefficients. However, since the experimental data, which is yet very scarce, does not demonstrate a strong anisotropy of the thermal expansion coefficients, the presented results call for new experimental efforts. This work also sets methodological guidelines for tackling other quantities related to the thermal properties of black phosphorus, such as, for example, its highly anisotropic thermal conductivity.

## Conflicts of interest

There are no conflicts to declare.

## Notes and references