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Supplementary Information

PAW mediated *ab initio* simulations on linear response phonon dynamics of anisotropic black phosphorous monolayer for thermoelectric applications

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1. Convergence of Thermal Conductivity value

It is clear that harmonic and anharmonic force constants are acting as input in predicting thermal conductivity value from lattice dynamics. This lattice dynamics is solved via linearized Boltzmann transport equation (BTE) for phonons using ShengBTE code. The BTE is being explained for lattice thermal conductivity value using the Fourier's rule, as follow;

$$k_l = \sum_i C_{phonon,i} \zeta^2_{g,l,i} \eta_{l,i}$$

The summation given in the above equation is over all the phonon modes in the first Brillouin zone of the reciprocal space. The mode index (i) computes phonon wave vector (k) and polarization (ζ). Besides, $C_{phonon,i}$ is the volumetric specific heat and $\zeta_{g,l,i}$ is the l-component of the phonon group velocity vector ($\mathbf{v}_{g,i}$). $\eta_{l,i}$ is the phonon lifetime. As a result, the phonon mean free path can be written as $|(\mathbf{v}_{g,i})|\eta_{l,i}$. The specific heat can be obtained using Bose Einstein statistics. The group velocity vector in the calculation is correlated to the mode frequency of the phonon. The phonon

frequencies are obtained via diagonalizing the dynamical matrix iterative solution of the linearized BTE for phonons [1].

These harmonic and anharmonic force constants have been obtained from *ab initio* DFPT calculations. The calculation of lattice thermal conductivity from the DFPT force constants requires detailed specification of the supercell size, the force interaction cut-offs and nearest-neighbors for the MLBP like 2D material. Here, we show the convergence of the lattice thermal conductivity of MLBP with these calculation parameters.

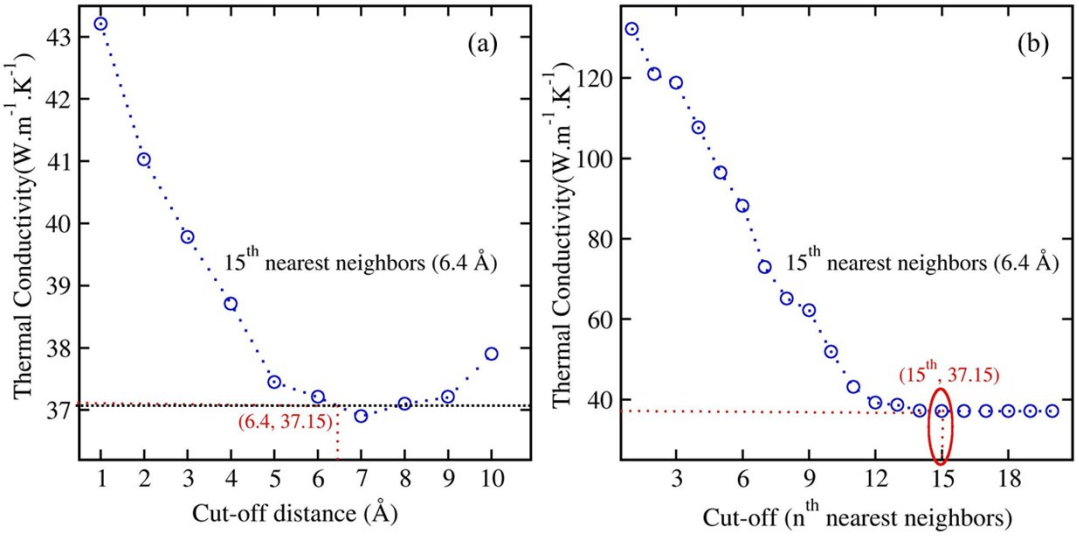

Fig. S1: Variation in thermal conductivity value with respect to (a) cut-off interaction distance in Å and (b) nearest neighbors for MLBP with the cubic force constant at 300 K. The red color ellipse shows the convergence of thermal conductivity at 15th nearest neighbors within 5 % with a cut-off radius of 6.4 Å by solving the linearized phonon BTE.

Here, Fig. S1 shows the variation of lattice thermal conductivity value of MLBP as a function of the cubic force-constant interaction cut-off and nearest neighbor atoms at a temperature of 300 K. The cubic force constants are obtained using 128 atom supercells with 12 Å vacuum for MLBP system along *z*-direction. It is noticed (Fig. S1 (a)) that the lattice thermal conductivity value changes abruptly with respect to cut-off interaction distance and reached a dip (called as

equilibrium converged value) around 6.4 Å, after that it follows a diverging trend. Thus, 6.4 Å is taken as converged cut-off interaction radius for further converge test as a function of nearest neighbors. Similarly, it is observed (Fig. S1 (b)) that the values of lattice thermal conductivity are more or less converge after 15th nearest neighbors with the same interaction cut-off value 6.4 Å. The cubic force constants gained here using finite differences of the Hellman-Feynman forces satisfying crystal symmetries and translational invariance (i.e., the acoustic sum rule) due to certain errors in the simulation [2].

2. Inclusion of van der Waals interaction

The *van der Waals* (*vdW*) interactions affect the structural and physical properties of 2D sheet like structures, i.e. MLBP due to its directional anisotropy. These interactions are considered in our present calculations and compared the results with excluding the same. From the value of lattice thermal conductivity (shown in Fig. 6 (b) of the main manuscript), the *vdW* interactions have significant effects on the result of lattice thermal conductivity. We have tested the convergence of thermal conductivity with respect to cut-off interactions and nearest neighbors (Fig. S1) where, we fixed the convergence test within 5% with cut-off interactions of 6.4 Å up to 15th nearest neighbors in the cubic anharmonic interatomic force constants (IFCs) calculation. Based on the comparison of the thermal conductivity results between with vdW-DF and non-vdW interactions, we notice that the vdW interactions are critical for precisely taking the behaviour of interatomic interactions in MLBP, and should be considered for better accuracy in the results in case of linear response lattice dynamics of MLBP.

References

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2 W. Li, L. Lindsay, D. A. Broido, D. A. Stewart and N. Mingo, *Phys. Rev. B*, 2012, **86**, 174307.