Interlayer breathing and shear modes in few-layer black phosphorus

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2016 J. Phys.: Condens. Matter 28 165401
(http://iopscience.iop.org/0953-8984/28/16/165401)

View the table of contents for this issue, or go to the journal homepage for more

Download details:

IP Address: 168.122.67.92
This content was downloaded on 18/03/2016 at 11:16

Please note that terms and conditions apply.
Interlayer breathing and shear modes in few-layer black phosphorus

Jin-Wu Jiang¹, Bing-Shen Wang² and Harold S Park³

¹ Shanghai Institute of Applied Mathematics and Mechanics, Shanghai Key Laboratory of Mechanics in Energy Engineering, Shanghai University, Shanghai 200072, People’s Republic of China
² State Key Laboratory of Semiconductor Superlattice and Microstructure and Institute of Semiconductor, Chinese Academy of Sciences, Beijing 100083, People’s Republic of China
³ Department of Mechanical Engineering, Boston University, Boston, MA 02215, USA

E-mail: jwjiang5918@hotmail.com

Received 8 December 2015, revised 25 February 2016
Accepted for publication 26 February 2016
Published 18 March 2016

Abstract

The interlayer breathing and shear modes in few-layer black phosphorus are investigated for their symmetry and lattice dynamical properties. The symmetry groups for the even-layer and odd-layer few-layer black phosphorus are utilized to determine the irreducible representation and the infrared and Raman activity for the interlayer modes. The valence force field model is applied to calculate the eigenvectors and frequencies for the interlayer breathing and shear modes, which are explained using the atomic chain model. The anisotropic puckered configuration for black phosphorus leads to a highly anisotropic frequency for the two interlayer shear modes. More specifically, the frequency for the shear mode in the direction perpendicular to the pucker is less than half of the shear mode in the direction parallel with the pucker. We also report a set of specular interlayer modes having the same frequency for all few-layer black phosphorus with layer numbers \( N \) being a multiple of 3, because these modes manifest themselves as collective vibrations of atoms in specific layers. The optical activity of the collective modes enables possible experimental identification for these modes.

Keywords: breathing mode, shear mode, few-layer black phosphorus, group symmetry

(Some figures may appear in colour only in the online journal)

1. Introduction

Heterostructures are a sequential stacking of two different two-dimensional (2D) layered materials [1], which are coupled together via interlayer van der Waals interactions. Characterization of the interlayer coupling in the heterostructures can be done using a lattice dynamical analysis. Specifically, the interlayer breathing (B) mode and shear (C) mode directly represent the interlayer coupling properties in the layered materials. The frequency for the B mode is depending on the number of layers, so this mode can be used to determine the number of layers of the heterostructure, while the C mode gives insight into the friction between two neighboring 2D layers.

The C mode in few-layer graphene was examined experimentally by Tan et al in 2012 [2]. The frequency for the highest-frequency C mode depends on the layer number \( (N) \) as \( \sqrt{1 + \cos(\pi/N)} \), which was explained by the chain model, and is around \( 30 \text{ cm}^{-1} \) in few-layer graphene. Due to its low frequency, the C mode can be excited easily, so it is sensitive to the near-Dirac point quasi-particles [2]. In particular, the C mode is easily excited during cross-plane thermal transport in the layered materials, due to its low frequency. The scattering between the C mode and the acoustic modes may play an important role for the cross-plane thermal transport in the layered materials. More recently, two experiments found that the signal of the C mode can be enhanced by folding the graphene layers [3, 4]. The B mode in few-layer graphene has also been studied by several groups [5, 6].

As another important 2D layered material, few-layer MoS2 has also attracted significant attention for its interlayer modes. Several experiments have measured the \( N \) dependence for
the frequency of the interlayer B mode and C mode in few-layer MoS$_2$ [7–10]. The frequency of the interlayer B mode decreases with increasing layer number, while the C mode exhibits the opposite behavior.

Few-layer black phosphorus (FLBP) is another emerging 2D layered material with that shows an $N$-dependent band gap [11, 12]. However, few works have been performed for the phonon modes in black phosphorus. The phonon dispersion for bulk black phosphorus was measured [13, 14] in 1980s. The experiment was explained by Kaneta et al using the valence force field model (VFFM) [15, 16] or the adiabatic bond charge model [17]. While the layer number dependence for the interlayer B and C modes in FLBP is studied by Ribeiro-Soares et al [18], there have not been any studies on the layer number dependence for the interlayer C mode and not been any studies on the layer number dependence for the interlayer B and C modes in FLBP, in which an important and interesting effect to quantity is that of the frequency of the interlayer C mode and not been any studies on the layer number dependence for the interlayer C mode.

In this paper, we study the symmetry and the lattice dynamical properties for the interlayer B mode and C mode in FLBP. The symmetry groups for the FLBP with even or odd layer numbers are compared. Using these symmetry groups, we analyze the symmetry for the interlayer B and C modes, including their irreducible representations and their infrared (IR) and Raman activity. The VFFM is utilized to compute the eigenvectors and frequencies for the interlayer B and C modes, while the calculated results are explained by the linear chain model. As a result of the intrinsic geometric anisotropy in the puckered configuration of BP, the two interlayer C modes have very different frequencies. Furthermore, we present a set of collective interlayer modes in FLBP with layer number $N = 3i$ with integer $i$. The frequencies for these collective modes are independent of the layer number and these modes are optically active, so they should be experimentally measurable.

2. Symmetry analysis for BP structure

2.1. Bulk BP

There are eight atoms in the orthorhombic cell for bulk BP. The bases for the orthorhombic cell are as follows,

$$\bar{A}_1 = a\hat{e}_x,$$

$$\bar{A}_2 = b\hat{e}_y,$$

$$\bar{A}_3 = c\hat{e}_z,$$  

where $\hat{e}_x$, $\hat{e}_y$, and $\hat{e}_z$ are unit vectors in the three cartesian directions. The lattice constants $a = 4.1766$ Å and $b = 3.2197$ Å are computed from the Stillinger–Weber potential [19]. The VFFM used for the interlayer interaction is linear, so it cannot be used to optimize the interlayer structure. We thus take the value of the lattice constant $c = 10.587$ Å from [12].

The primitive unit cell for the bulk BP contains four atoms [20]. The bases for the primitive unit cell are,

$$\bar{a}_1 = \bar{A}_1,$$

$$\bar{a}_2 = \frac{1}{2}(\bar{A}_2 - \bar{A}_3),$$

$$\bar{a}_3 = \frac{1}{2}(\bar{A}_2 + \bar{A}_3).$$

Each unit cell can be labelled by a lattice vector $\bar{R}_{hk0} = l\bar{a}_1 + m\bar{a}_2 + n\bar{a}_3$, with $l_1$, $l_2$, and $l_3$ as three integers. The lattice vector corresponds to a translation symmetry operation, $\bar{T}_{hk0}$, which translates the bulk BP by a lattice vector $\bar{R}_{hk0}$.

The point group for the bulk BP is $D_{3h} = \{E, C_{3z}, C_{2x}, C_{2y}, i, \sigma_{xz}, \sigma_{yz}, \sigma_{zx}\}$. $C_{3z}$ is the rotation for $\pi$ around the $z$-axis, $i$ is the inversion symmetry and $\sigma_{xy}$ is the reflection with respect to the $z = 0$ plane. Four of these eight symmetry operations, $C_{3z}$, $C_{2x}$, $\sigma_{xy}$, and $\sigma_{zx}$, are accompanied by the following nonprimitive translations,

$$\bar{r}_b = \frac{1}{2}(\bar{A}_1 + \bar{A}_3).$$  

The transnational symmetry and the point group together construct the space group ($D_{3h}^{3}$) of bulk BP; i.e. $D_{3h}^{3} = \bar{T}_{hk0} \otimes D_{3h}$.

The reciprocal vectors are determined by the bases for the primitive unit cell through the relation

$$\bar{b}_i \cdot \bar{a}_j = 2\pi\delta_{ij},$$

which gives,

$$\bar{b}_1 = \frac{2\pi}{a} \hat{e}_x,$$

$$\bar{b}_2 = \frac{2\pi}{b} \hat{e}_y - \frac{2\pi}{c} \hat{e}_z,$$

$$\bar{b}_3 = \frac{2\pi}{b} \hat{e}_y + \frac{2\pi}{c} \hat{e}_z.$$  

$\bar{b}_1$ is in $x$-direction, while $\bar{b}_2$ and $\bar{b}_3$ lie in the $yz$ plane. The first Brillouin zone for bulk BP is shown in figure 1.

The $Z$ point in the first Brillouin zone plays an important role in the present work. The wave vector for the $B$ mode and $C$ mode in the bulk BP is located at the $Z$ point of the first Brillouin zone, and not at the $\Gamma$ point of the first Brillouin zone. This can be demonstrated as follows. The wave vector for the $Z$ point is,

$$\bar{k}_z = \frac{1}{2}(-\bar{b}_2 + \bar{b}_3).$$

We shall treat the unit cell containing the four atoms (1, 2, 3, 4) in figure 2 as the (0, 0, 0) unit cell. The lattice vector for this unit cell is $\bar{R}_{000} = 0$. This unit cell (0, 0, 0) is in the same plane as the unit cell containing atoms (5, 6, 7, 8). The lattice vector for the latter unit cell is $R_{001} = A_2 = \bar{a}_2 + \bar{a}_3$, so its phase factor in the Bloch theory is $k_z \cdot \bar{R}_{001} = 0$, which means that the phase factors for the unit cells in the same BP plane are the same. The lattice vector for the unit cell
The first Brillouin zone for bulk BP. Top is the projection of the first Brillouin zone onto the \(yz\) plane. Bottom is the three-dimensional first Brillouin zone for bulk BP.

There are twelve phonon modes at the \(\Gamma\) point or \(Z\) point for bulk BP, corresponding to the four atoms in the primitive unit cell. The symmetry for these phonon modes can be analyzed according to the point group \(D_{2h}\) of bulk BP. Table 1 lists the eight irreducible representations for the point group \(D_{2h}\). There are two symbols for each irreducible representation in the first column of table 1. The first symbol is for phonon modes at the \(\Gamma\) point, while the second symbol is for the phonon modes at the \(Z\) point in the first Brillouin zone.

Table 2 shows the symmetry analysis for phonon modes at the \(\Gamma\) point or the \(Z\) point in the first Brillouin zone. \(\Gamma^{\text{vib}} = \Gamma^{\text{as}} \oplus \Gamma^{\text{vec}}\) is the vibrational representation, with \(\Gamma^{\text{as}}\) as the permutation representation and \(\Gamma^{\text{vec}}\) as the vector representation. The decomposition of the vibrational representation gives the irreducible representation for each phonon mode at the \(Z\) point in the first Brillouin zone. The vibrational representation can be decomposed as follows, using the character table method,

\[
\Gamma^{\text{vib}} = 2\Gamma_{1}^{\text{Z}} \oplus \Gamma_{3}^{\text{Z}} \oplus 2\Gamma_{1}^{\text{Z}} \oplus \Gamma_{4}^{\text{Z}} \oplus \Gamma_{2}^{\text{Z}} \oplus \Gamma_{3}^{\text{Z}} \oplus \Gamma_{1}^{\text{Z}} \oplus 2\Gamma_{4}^{\text{Z}}.
\]

The twelve phonon modes at the \(Z\) point in the first Brillouin zone belong to these 12 irreducible representations on the right-hand side of equation (13). From the eigenvector, it can be determined that the \(B\) mode in bulk BP belongs to the \(Z_{1}^{\text{Z}}\) irreducible representation, the \(C_{z}\) mode belongs to the \(Z_{3}^{\text{Z}}\) irreducible representation, and the \(C_{x}\) mode belongs to the \(Z_{2}^{\text{Z}}\) irreducible representation. These results are shown in the second line of table 3.

The IR activity for each phonon mode can be analyzed by decomposing the vector representation in the following,

\[
\Gamma^{\text{vec}} = \Gamma_{1}^{\text{Z}} \oplus \Gamma_{3}^{\text{Z}} \oplus \Gamma_{4}^{\text{Z}}.
\]

The vector representation is three-dimensional, so there are three one-dimensional irreducible representations in the resulting decomposition. This result predicts that phonon modes corresponding to these three irreducible representations will be IR-active in the optical scattering process. According to this result, the \(B\) mode \(Z_{1}^{\text{Z}}\) and \(C_{z}\) mode \(Z_{3}^{\text{Z}}\) in bulk BP are IR-active, while the \(C_{x}\) mode \(Z_{2}^{\text{Z}}\) is IR inactive.

The Raman activity for each phonon mode can be determined by decomposing the six-dimensional tensor representation.
The bases for the tensor representation, $\Gamma^{xy}$. The bases for the tensor representation are $x^2 + y^2$, $z^2$, $x^2 - y^2$, $xy$, $xz$, and $yz$. The tensor representation is decomposed as follows,

$$
\Gamma^{xy} = 3Z_2^2 \oplus Z_3^2 \oplus Z_1^4 \oplus Z_4^4.
$$

According to this decomposition result, none of the three interlayer modes is Raman active in bulk BP.

The above decomposition results for phonon modes at the Z point in bulk BP are shown in the third line of table 2. The symmetry analysis for phonon modes at the $\Gamma$ point in the first Brillouin zone of bulk BP are shown in the second line of table 2. The symmetry for the three interlayer modes for bulk BP are shown in the second line of table 3.

### 2.2. Few-layer BP

The FLBP studied in the present work has the same stacking order as the bulk BP as shown in figure 2, which can be regarded as the AB stacking, while the group symmetry for the AA stacking FLBP was analyzed in a previous work [18]. There is no translational symmetry in the z-direction for FLBP. Hence, the orthorhombic cell for the FLBP is the primitive unit cell in this structure. The bases are $\tilde{A}_1$ and $\tilde{A}_2$. There are $4N$ atoms in the primitive unit cell of the FLBP. These eight point group symmetry operations in the bulk BP are still symmetry operations in the FLBP, but accompanied by different nonprimitive translations.

For even-layer FLBP, the point group for the FLBP with even $N$ is $D_{2h}$. Two of these eight symmetry operations, $C_{2z}$ and $\sigma_{yz}$, are accompanied by the following nonprimitive translations,

$$
\tau_{E1} = \frac{1}{2}(\tilde{A}_1 + \tilde{A}_2).
$$

Another two symmetry operations, $C_{\bar{z}}$, and $\sigma_{xy}$, are accompanied by the following nonprimitive translations,

$$
\tau_{E2} = \frac{1}{2} \tilde{A}_y.
$$

The irreducible representation for each phonon mode at the $\Gamma$ point is found by decomposing the vibrational representation for the FLBP with even $N$. The symmetry analysis results are shown in the fourth line of table 2.

### Table 2. Symmetry analysis for phonon modes in bulk BP (Γ point and Z point) and FLBP (Γ point).

<table>
<thead>
<tr>
<th>Point group</th>
<th>Mode number</th>
<th>$\Gamma^{vib}$</th>
<th>$\Gamma^{IR}$</th>
<th>$\Gamma^{R}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk at Γ point</td>
<td>$D_{2h}$</td>
<td>12</td>
<td>$2A_g \oplus B_{1g} \oplus 2B_{2g} \oplus B_{3g}$</td>
<td>$B_{1u} \oplus B_{2u} \oplus B_{3u}$</td>
</tr>
<tr>
<td>Bulk at Z point</td>
<td>$D_{2h}$</td>
<td>12</td>
<td>$2Z_2^2 \oplus Z_3^2 \oplus 2Z_4^2 \oplus Z_1^4$</td>
<td>$Z_4^4$</td>
</tr>
<tr>
<td>FLBP, even N</td>
<td>$D_{2h}$</td>
<td>12$N$</td>
<td>$2N_{A1} \oplus N_{B1} \oplus 2N_{B2} \oplus N_{B3}$</td>
<td>$B_{1u} \oplus B_{2u} \oplus B_{3u}$</td>
</tr>
<tr>
<td>FLBP, odd N</td>
<td>$D_{2h}$</td>
<td>12$N$</td>
<td>$2N_{A1} \oplus N_{B1} \oplus 2N_{B2} \oplus N_{B3}$</td>
<td>$B_{1u} \oplus B_{2u} \oplus B_{3u}$</td>
</tr>
</tbody>
</table>

Note: The total number of phonons is listed in the third column. Phonon modes are classified by the irreducible representations of $\Gamma^{vib}$ in the fourth column. The irreducible representations of the IR and Raman-active modes are listed in the fifth and sixth columns, respectively. $N$ is the layer number.

### Table 3. The irreducible representation for the $B$ mode and $C$ modes.

<table>
<thead>
<tr>
<th>Mode</th>
<th>$B_1$ mode</th>
<th>$C_1$ mode</th>
<th>$C_2$ mode</th>
<th>$B_2$ mode</th>
<th>$C_3$ mode</th>
<th>$C_4$ mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>$Z_1$ (IR)</td>
<td>$Z_1$ (IR)</td>
<td>$Z_1$ (No)</td>
<td>$B_2$ (IR)</td>
<td>$B_2$ (IR)</td>
<td>$B_2$ (IR)</td>
</tr>
<tr>
<td>FLBP, even N</td>
<td>$A_1$ (IR)</td>
<td>$B_2$ (IR)</td>
<td>$B_2$ (IR)</td>
<td>$B_2$ (IR)</td>
<td>$B_2$ (IR)</td>
<td>$B_2$ (IR)</td>
</tr>
<tr>
<td>FLBP, odd N</td>
<td>$A_1$ (IR)</td>
<td>$B_{2a}$ (IR)</td>
<td>$B_{2u}$ (IR)</td>
<td>$B_{2u}$ (IR)</td>
<td>$B_{2u}$ (IR)</td>
<td>$B_{2u}$ (IR)</td>
</tr>
<tr>
<td>Layer dependence</td>
<td>$\sqrt{1 - \cos \frac{\pi}{N}}$</td>
<td>$\sqrt{1 + \cos \frac{\pi}{N}}$</td>
<td>$\sqrt{1 - \cos \frac{\pi}{N}}$</td>
<td>$\sqrt{1 + \cos \frac{\pi}{N}}$</td>
<td>$\sqrt{1 + \cos \frac{\pi}{N}}$</td>
<td>$\sqrt{1 + \cos \frac{\pi}{N}}$</td>
</tr>
</tbody>
</table>

Note: IR or Raman-activity is listed in the parentheses, where ‘No’ indicates optically inactive. $N$ is the layer number.

### Table 4. VFFM parameters.

<table>
<thead>
<tr>
<th>$\alpha_1$</th>
<th>$\alpha_2$</th>
<th>$\alpha_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference [16]</td>
<td>0.321</td>
<td>-0.01</td>
</tr>
<tr>
<td>Present work</td>
<td>0.281</td>
<td>-0.067</td>
</tr>
</tbody>
</table>

Note: The original parameters from [16] are listed in the second line. The third line lists optimized parameters used in the present work. All parameters are in the unit of eV Å$^{-2}$. The corresponding potential is $V = \frac{1}{2}t \begin{pmatrix} \mathbf{i} & -\mathbf{i} \end{pmatrix} \cdot \mathbf{\hat{r}}_j \mathbf{\hat{r}}_i$, where $\mathbf{i}$ is the displacement for atom $j$ and $\mathbf{\hat{r}}_j$ is the unit vector from atom $i$ to atom $j$.

### Table 5. Frequency (in cm$^{-1}$) for the $B$ mode, $C_1$ mode, and $C_2$ mode in bulk BP.

<table>
<thead>
<tr>
<th>Mode</th>
<th>$B_1$</th>
<th>$C_1$</th>
<th>$C_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp</td>
<td>87.1</td>
<td>19.4</td>
<td>51.6</td>
</tr>
<tr>
<td>Reference [16]</td>
<td>92.8 (↑ 6.5%)</td>
<td>21.1 (↑ 8.8%)</td>
<td>53.5 (↑ 3.7%)</td>
</tr>
<tr>
<td>Present work</td>
<td>87.1 (0%)</td>
<td>20.0 (↑ 3.1%)</td>
<td>51.7 (↑ 0.2%)</td>
</tr>
</tbody>
</table>

Note: Theoretical results from [16] (3rd line) and the present work (4th line) are compared with experiments (2nd line). The values in parentheses (3rd line and 4th line) are the relative difference between the theoretical prediction and the experiment.
For the $B$ mode, we are interested in the first lowest-frequency $B\,(B_1)$ mode and the second lowest-frequency $B\,(B_2)$ mode in FLBP. The eigenvectors for these two $B$ modes are shown in figure 4. For the $C$ mode, we are interested in the first highest-frequency $C$ mode ($C_{1\alpha}$ or $C_{1\beta}$) and the second highest-frequency $C\,(C_{2\alpha}$ or $C_{2\beta}$) mode. The eigenvectors for these $C$ modes are shown in figures 5 and 6. The third line of table 3 shows the symmetry for these modes in the FLBP with even $N$.

For odd-layer FLBP, the point group is also $D_{2h}$. Four of these eight symmetry operations, $C_{2\alpha}$, $C_{2\beta}$, $\sigma_{xy}$, and $\sigma_{yz}$, are accompanied by the following nonprimitive translations,

$$\bar{\gamma}_0 = \frac{1}{2}(\hat{\mathbf{a}}_1 + \hat{\mathbf{a}}_2).$$  \hfill (17)

The symmetry analysis for phonon modes at $\Gamma$ point in the odd-layer FLBP are shown in the fifth line of table 2. The symmetry for the interlayer modes are shown in the fourth line of table 3. The IR-activity and Raman-activity are also shown in the table.

3. Interaction potential

The intralayer interaction is described by a recently developed Stillinger–Weber potential [19]. We apply the VFFM for the interlayer coupling between two adjacent BP layers [16]. This VFFM contains the following bond stretching interaction,

$$V = \frac{1}{2} \alpha [(\hat{u}_i - \hat{u}_j) \cdot \hat{e}_j]^{2},$$  \hfill (18)

where $\hat{u}_j$ is the displacement for atom $j$, $\hat{e}_j$ is the unit vector from atom $i$ to atom $j$, $\alpha = \alpha_1$, $\alpha_2$, and $\alpha_3$ are the parameters for the first-, second-, and third-nearest-neighbor interactions, respectively. Figure 2 shows the configuration for bulk BP. The interlayer first-nearest-neighbor distance is the distance between atoms 9 and 2, i.e. $d_1 = 3.7311$ Å. The interlayer second-nearest-neighbor distance is the distance between atoms 9 and 3, i.e. $d_2 = 3.8520$ Å. The interlayer third-nearest-neighbor distance is the distance between atoms 9 and 7, i.e. $d_3 = 4.9612$ Å.

The original VFFM parameters from [16] are listed in the second column in table 4. These parameters are further optimized in the present work by fitting the frequencies of interlayer phonon modes in bulk phosphorus, and are also listed in table 4. After optimization, frequencies for the interlayer $B$ mode and $C$ mode in bulk BP agree well with the experimental results as shown in table 5.

The phonon modes are calculated using GULP [21]. Table 5 lists the frequency for the $B$ mode and two $C$ modes in bulk BP. Due to the intrinsic geometric anisotropy due to the puckered configuration, the frequency for the interlayer shear mode in the $x$-direction ($C_{1\pi}$) is quite different from the frequency of the interlayer shear mode in the $y$-direction ($C_{1\pi}$). The frequencies of the interlayer modes from the optimized VFFM parameters agree quite well with the experiment, with a maximum error of about 3% for the $C_{1\pi}$ mode. The eigenvectors for the interlayer modes in the bulk BP are shown in figure 3. The figure is produced using XCRYSDEN [22]. Table 4 shows that $\alpha_{2\beta}$ is negative in both the original VFFM parameter set and the optimized parameter set. A negative VFFM parameter implies that BP becomes unstable under high pressure. This pressure induced structure instability was investigated experimentally by Yamada et al [14].

4. Numerical results

For the interlayer mode in the layered structure, each layer can be regarded as a single atom. The entire layered structure can thus be considered as a single atomic chain with free boundary conditions at the two ends. This atomic chain model has been successfully applied to simulate the interlayer modes in few-layer graphene [2] and few-layer MoS$_2$ [9]. It can be assumed that each atom in the chain only interacts with its nearest-neighbor atoms. The eigenvector for the phonon mode $\tau$ in the chain model is,

$$u_j^{\tau} \propto \cos \left[ \frac{(\tau - 1)(2j - 1)\pi}{2N} \right],$$  \hfill (19)

where $\tau$ is the mode index, $N$ is the total atom number and $j$ is the site index for each atom. The first mode ($\tau = 1$) is the acoustic mode. The frequency for mode $\tau$ is

$$\omega_\tau = \sqrt{\frac{\beta}{2\mu c^2}} \left[ 1 - \cos \left( \frac{(\tau - 1)\pi}{N} \right) \right].$$  \hfill (20)

$\mu = 1.53 \times 10^{-26}$ kgÅ$^{-2}$ is the mass per unit area of the single-layer BP, $c$ is the speed of light in cm s$^{-1}$ and $\beta$ is the force constant per unit area.

Figure 3. Eigenvectors for the three interlayer modes in bulk BP. (a) $B$ mode. (b) $C_{1\alpha}$ mode. (c) $C_{1\beta}$ mode. The arrow on top of each atom represents the vibrational amplitude of the eigenvector.
We discuss four sets of interlayer phonon modes for FLBP in this section. The eigenvectors for these modes are shown in figures 4–8. The layer number dependence for the frequency are shown in figures 9 and 10.

The first set is the two \( B \) modes, i.e. \( B_1 \) mode and \( B_2 \) mode. The \( B_1 \) mode corresponds to the phonon mode with \( \tau = 2 \) in the chain model. Figure 4 shows that the eigenvector of the \( B_1 \) mode indeed follows the prediction of the chain model, i.e. 
\[
\sigma = \pi u \cos \left( \frac{\pi j N}{2} \right)
\]

The \( N \)-dependence for the frequency of the \( B_1 \) mode is shown in figure 9, where the black solid line illustrates a perfect fitting of the frequency for the \( B_1 \) mode to the function
\[
\omega = \frac{\beta_B}{2 \pi c^2} \left( 1 - \cos \left( \frac{\pi}{N} \right) \right).
\]
The fitting parameter \( \beta_B = 9.8 \times 10^{10} \text{Nm}^{-3} \) is exactly the same as that obtained from the \( B_1 \) mode. This agreement further confirms the success of the chain model in the description of the layered structure.

The second set of phonon modes are the interlayer \( C_x \) modes in FLBP, including the first highest-frequency \( C_x \) mode and the second highest-frequency \( C_x \) mode. This mode can also be described by the chain model. The \( C_x \) mode corresponds to the phonon mode with \( \tau = N \) in the chain model. The eigenvector of the \( C_x \) mode is shown in figure 5. This eigenvector follows the function \( u_x \propto \cos \left( \frac{(2j - 1)x}{2N} \right) \). The fitting parameter \( \beta_{C_x} = 5.5 \times 10^{10} \text{Nm}^{-3} \) is the force constant for the transverse motion in the \( x \)-direction for the chain model.

Insert Figure 4 here.
Figure 5. Eigenvectors and frequencies for two \( C_x \) modes. Bottom is the highest-frequency \( C_x \) mode. Top is the second-highest-frequency \( C_x \) mode.

Figure 6. Eigenvectors and frequencies for two \( C_y \) modes. Bottom is the highest-frequency \( C_y \) mode. Top is the second-highest-frequency \( C_y \) mode.
The $N$-dependence of the frequency is also consistent with the chain model prediction by equation (20) with $\tau = N - 1$.

The third set of phonon modes are two interlayer Cy modes in FLBP; i.e. the first highest frequency Cy$_1$ mode and the second highest-frequency Cy$_2$ mode. These modes can also be described by the chain model. Cy$_1$ mode corresponds to the phonon mode with $\tau = N$ in the chain model, while the Cy$_2$ mode corresponds to the phonon mode with $\tau = N - 1$ in the chain model. The eigenvectors of these two modes are shown in figure 6. They agree with the chain model prediction in equation (19). The frequencies of these two modes are shown in figures 9 and 10. They can be fitted by the frequency in the chain model in equation (20). The fitted parameter $\beta = \times 3.6 \times 10^{19} \text{Nm}^{-3}$ is the force constant for the $y$-directional transverse motion for the chain model. The transverse force constant is about $\times 1.28 \times 10^{19} \text{Nm}^{-3}$ for the few-layer graphene [2] and $\times 2.7 \times 10^{19} \text{Nm}^{-3}$ in the few-layer MoS$_2$ [9]. These values are sandwiched between the two transverse force constants $\beta_{Cy}$ and $\beta_{Cy}$ in FLBP.

The fourth set of phonon modes are the collective vibration modes corresponding to the mode index $\tau = N + 1$ in the chain model. According to equation (19), the eigenvector for this set of vibration modes is $u_j \propto \cos\left(\frac{2j - 1}{N} \pi\right)$. Hence, we have $u_j = 0$ for $j = 2, 5, 8, ..., 3i + 2$ with integer $i$; $u_j \propto \cos(\pi/6)$ for $j = 1, 4, 7, ..., 3i + 1; u_j \propto -\cos(\pi/6)$ for $j = 3, 6, 9, ..., 3i$. The frequency for this set of vibration modes is independent of layer number $N$, i.e. $\omega_{\tau} = \sqrt{\frac{\beta}{4\mu N^2 v^2}}$. For instance, figure 7 shows the collective $B$ mode in FLBP with $N = 3, 6, 9$ (from left to right). The eigenvector can be regarded as the collective vibration of the small segments (dotted rectangles).

![Figure 7](image)

Figure 7. Interlayer collective $B$ modes with the same frequency for FLBP with $N = 3, 6, 9$ (from left to right). The eigenvector can be regarded as the collective vibration of the small segments (dotted rectangles).

The frequency for this set of vibration modes is independent of layer number $N$, i.e. $\omega_{\tau} = \sqrt{\frac{\beta}{4\mu N^2 v^2}}$. For instance, figure 7 shows the collective $B$ mode in FLBP with $N = 3, 6, 9$ (from left to right). The eigenvector can be regarded as the collective vibration of the small segments (dotted rectangles).

![Figure 8](image)

Figure 8. Interlayer collective $C$ modes with the same frequency for FLBP with $N = 3, 6, 9$. Bottom is the $C_x$ mode, and top is the $C_y$ mode.
so this set of collective modes are a general feature for all layered structures, including few-layer graphene, few-layer MoS$_2$, and few-layer BP.

We note that our manuscript was put publicly on arXiv in December 2014 [23]. During the submission process of the present manuscript, there have been several experiments measuring the frequency of the interlayer $B$ and $C$ modes in the FLBP [24–30]. The frequency of the $B_1$ mode in bilayer BP is about 62.7 cm$^{-1}$ by Ling et al [24], or 67.5 by Dong et al [25], which are quite close with 60.4 cm$^{-1}$ in the present work. The frequency of the $B_1$ mode in four-layer BP is about 35 cm$^{-1}$ by Luo et al [26], which is quite close to 32.3 cm$^{-1}$ in the present work. Some theoretical studies also emerge on the layer number dependence of the interlayer $B$ and $C$ modes very recently [31, 32].

5. conclusion

To summarize, we have analyzed the lattice dynamical properties for the interlayer $B$ and $C$ modes in FLBP. The symmetry group for the FLBP with even layer numbers is compared with the FLBP with odd layer numbers. The symmetry properties for the interlayer modes are determined based on the symmetry groups. The IR and Raman activity for the phonon modes is also determined. We applied the VFFM to compute the eigenvectors and frequencies for the interlayer modes, which can be successfully explained by the chain model. The two $C$ modes have very different frequencies, due to the anisotropic puckered configuration for the BP layer. We found a particular set of collective phonon modes with the same frequency in the FLBP with layer number $N = 3i$ ($i$ integer). These collective phonon modes have a constant frequency with respect to the layer number.

Acknowledgments

The work is supported by the Recruitment Program of Global Youth Experts of China, the National Natural Science Foundation of China (NSFC) under Grant No. 11504225, and the start-up funding from Shanghai University. HSP acknowledges the support of the Mechanical Engineering department at Boston University.

References

[28] Late D J 2015 ACS Appl. Mater. Interfaces 7 5857