Poisson’s Ratio of Layered Two-dimensional Crystals

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Abstract

We present first-principles calculations of elastic properties of multilayered two-dimensional crystals such as graphene, $h$-BN and $2H$-MoS$_2$ which shows that their Poisson’s ratios along out-of-plane direction are negative, near zero and positive, respectively, spanning all possibilities for sign of the ratios. While the in-plane Poisson’s ratios are all positive regardless of their disparate electronic and structural properties, the characteristic interlayer interactions as well as layer stacking structures are shown to determine the sign of their out-of-plane ratios. Thorough investigation of elastic properties as a function of the number of layers for each system is also provided, highlighting their intertwined nature between elastic and electronic properties.

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Under uniaxial stress, Poisson’s ratio defined by the ratio of the strain in the transverse direction ($\varepsilon_t$) to that of the longitudinal direction ($\varepsilon_l$), $\nu = -\varepsilon_t/\varepsilon_l$, measures the fundamental mechanical responses of solids against external loads [1–5]. It has strong correlation with atomic packing density, atomic connectivity [2] and structural phase transition [3–5]. The theory of elasticity allows values of Poisson’s ratio of an isotropic material ranging from $-1$ to 0.5, i.e., from extremely compressible to incompressible materials [1, 5]. Thus, when a solid is subjected to a uniaxial compression, it expands ($\nu > 0$), remains to be the same ($\nu = 0$), and shrinks ($\nu < 0$) in the transverse direction depending on the sign of Poisson’s ratio. Typically, different Poisson’s ratio or its sign indicates dramatic variations in mechanical properties. For example, when isothermal modulus is extremely larger than shear modulus, the material reaches its incompressible limit as shown in most liquids or rubber ($\nu \sim 0.5$) and in the opposite case, re-entrant foams and related structures show the negative $\nu$ or auxetic property [3–9]. The Poisson’s ratio of common solid state crystals usually falls in the range of $0 < \nu < 0.5$ while gases and cork have $\nu \simeq 0$ [3,9].

Anisotropic materials with directional elastic properties often show more dramatic variations in their Poisson’s ratios such as the directional auxetic property [5]. In this regard, the experimental realization of graphene [10, 11], the thinnest and the strongest material [12–15], now offers a new platform to understand electronic and elastic properties of well-defined anisotropic materials and their heterostructures. Even though the Young’s modulus and Poisson’s ratio of graphene have been studied quite thoroughly [12–21], those along the out-of-plane direction for its few-layered forms have barely been known. Neither do for all the other available two-dimensional crystals. Since electronic properties of layered two-dimensional crystals vary a lot depending on their chemical composition as well as the number of layers [22–24], their corresponding elastic properties, especially for few layered structures, are anticipated to change accordingly. Motivated by recent rapid progress in manipulating various two-dimensional crystals and their stacking structures [23–25], we have calculated fundamental mechanical properties of three representative van der Waals (vdW) crystals along all crystallographic directions of their few-layered structures.

In this work, we present a theoretical study using a first-principles approach on the elastic properties of layered two-dimensional crystals, including graphene, $h$-BN and $2H$-MoS$_2$, in which the vdW energy is one of the governing interactions between their layers while they exhibit very different electronic properties. We find that the Poisson’s ratios
of graphene, h-BN and 2H-MoS$_2$ along out-of-plane direction are negative, near zero and positive, respectively, whereas their in-plane Poisson’s ratios are all positive. The diverseness of out-of-plane Poisson’s ratio is attributed to their disparate electronic properties as well as stacking structures. Thorough investigation on their elastic properties while varying the number of layers are also reported.

We first consider graphene with AB stacking, h-BN and 2H-MoS$_2$ with AA’ stacking. All the three have C$_{3v}$ symmetry. Generally, for a material with C$_{3v}$ symmetry, the stiffness tensor without shear part can be written with four independent parameters,

$$
\begin{pmatrix}
\sigma_x \\
\sigma_y \\
\sigma_z
\end{pmatrix} =
\begin{pmatrix}
A & B & C \\
B & A & C \\
C & C & D
\end{pmatrix}
\begin{pmatrix}
\epsilon_x \\
\epsilon_y \\
\epsilon_z
\end{pmatrix} ,
$$

(1)

with the choice of z as the axis for the three-fold rotational symmetry [1]. Here, $\sigma_i$ and $\epsilon_i$ are the stress and strain respectively along the $i$-th axis. The components of stiffness tensor can be obtained by differentiating the total energy $E_{\text{tot}}$ in terms of strain; $A = \partial^2 E_{\text{tot}}/\partial \epsilon_x^2 = \partial^2 E_{\text{tot}}/\partial \epsilon_y^2$, $B = \partial^2 E_{\text{tot}}/\partial \epsilon_x \partial \epsilon_y$, $C = \partial^2 E_{\text{tot}}/\partial \epsilon_x \partial \epsilon_z$, and $D = \partial^2 E_{\text{tot}}/\partial \epsilon_z^2$. By taking the inverse of the stiffness tensor, one can get the compliance tensor,

$$
\begin{pmatrix}
\epsilon_x \\
\epsilon_y \\
\epsilon_z
\end{pmatrix} =
\begin{pmatrix}
1/E_i & -\nu_i/E_i & -\tilde{\nu}_o/E_o \\
-\nu_i/E_i & 1/E_i & -\tilde{\nu}_o/E_o \\
-\nu_o/E_i & -\nu_o/E_i & 1/E_o
\end{pmatrix}
\begin{pmatrix}
\sigma_x \\
\sigma_y \\
\sigma_z
\end{pmatrix} .
$$

(2)

The subscripts $i$ and $o$ represent in-plane and out-of-plane respectively. $E_i$ and $E_o$ are the Young’s moduli along the $x(y)$ and $z$ axis respectively. There are two out-of-plane Poisson’s ratios; $\nu_o$ is the Poisson’s ratio along the $z$ axis when the stress is applied along the $x$ or $y$ directions while $\tilde{\nu}_o = \nu_0 E_0/E_i$ is the Poisson’s ratio along the $x$ or $y$ direction when the stress is applied along the $z$ direction. $\nu_i$ is the in-plane Poisson’s ratio along the $x(y)$ axis when the stress is applied along the $y(x)$ axis.

Using a first-principles approach based on density-functional theory with plane wave basis set [26], we calculate total energies, $E_{\text{tot}}(\epsilon_x, \epsilon_y, \epsilon_z)$, of all systems at $5 \times 5 \times 5$ grid points in the strain space of $(\epsilon_x, \epsilon_y, \epsilon_z)$. To obtain the accurate binding energy and interlayer distance including the vdW energy, we have used the revised version [27] of the nonlocal correlation functional method developed by Vydrov and van Voorhis [28] that is successful for reproducing both values following results from more accurate methods [29]. In order to
FIG. 1: Lattice structures of (a) AB-stacked graphene (b) AA'-stacked h-BN and (c) 2H-MoS$_2$. The parameter $d$ is the interlayer distance of each structure. In 2H-MoS$_2$, $d$ is the vertical distance between Mo atoms in adjacent layers and $d_1$ is the vertical intralayer sulfur-to-sulfur distance. 

reduce spurious interaction between neighbouring supercells, a large vacuum over 68 Å is introduced and relatively high energy cut-off above 100 Rydberg as well as dense k-point grids up to $29 \times 29$ are used to converge the results.

For the total energy calculations with tensile strain on all systems in which the layers are stacked along the $z$ axis, a primitive cell with unit vectors, $u_1 = (a, b, 0)$, $u_2 = (-a, b, 0)$, $u_3 = (0, 0, c)$ are used [Fig. 1]. Strain along $x$ and $y$ axis is defined by $\epsilon_x = (a - a_0)/a_0$ and $\epsilon_y = (b - b_0)/b_0$, where $a_0$ and $b_0$ are the lattice parameters of the equilibrium structure. Strain across the layers along the $z$ axis is defined by $\epsilon_z = (d - d_0)/d_0$ where $d$ and $d_0$ are the interlayer distance and that of the equilibrium structure, respectively. The calculated lattice parameters of $a_0$ and $d_0$ for infinitely stacked bulk systems are 2.47 Å, 2.52 Å, 3.22 Å and 6.72 Å, 6.61 Å, 12.42 Å for graphite, h-BN, and 2H-MoS$_2$, respectively, which are in excellent agreements with previous studies [30–33]. The slight variation of $a_0$, $b_0$ and $d_0$ depending on the number of layers are reflected in our calculations. $A$, $B$, $C$ and $D$ in Eq. (1) are calculated by interpolating $E_{\text{tot}}$ on the strain space and Young’s modulus and Poisson’s ratio from compliance tensor in Eq. (2).

Figure 2 shows Young’s moduli and Poisson’s ratios for the three materials with various number of layers. In-plane elastic constants, $E_i$ and $\nu_i$, are barely dependent on the
FIG. 2: Elasticity constants of graphene (empty rectangle), h-BN (filled rectangle) and $2H$-MoS$_2$ (cross) as a function of number of layers up to ten layers, in-plane (a) Young’s modulus and (b) Poisson’s ratio and out-of-plane (c) Young’s modulus and (d) Poisson’s ratio.

number of layers [Figs. 2(a) and (b)]. Under in-plane tensile stress, the hexagonal network of atoms is deformed for graphene and h-BN while, for $2H$-MoS$_2$, sulfur-to-sulfur distance across the plane along the $z$ axis within one layer can also be deformed. Furthermore, the hexagonal structure of graphene and h-BN with rigid $\sigma$ bond supported by $\pi$ bond is stiffer than that of $2H$-MoS$_2$. This makes $2H$-MoS$_2$ more flexible to applied stress resulting in lower in-plane Young’s modulus [Fig. 2(a)] and larger in-plane Poisson’s ratio [Fig. 2(b)].
Young’s moduli across layers, $E_o$, increase for all of the three materials with the increase of the number of layers reflecting the accumulation of long-range interlayer van der Waals interaction [Fig. 2(c)].

Contrary to similar behaviours between in-plane elastic properties of the three materials, out-of-plane elastic properties between those differ qualitatively [Fig. 2(d)]. The most notable one is that multilayered graphene structures have out-of-plane Poisson’s ratio as negative as $\nu = -0.09$ [Fig. 2(d)] with slight dependence on the layer number variations. Materials with axial negative Poisson’s ratio have been reported during the last few decades such as foams with re-entrant atomic structures [5–9] and those with non-axial one are shown in some simple cubic metals [34, 35]. The present case is for the axial negative ratio in a layered material where the vdW interaction governs the binding between layers without re-entrant structure. More interestingly, $h$-BN shows very small out-of-plane Poisson’s ratio near zero crossing from negative to positive values as number of layers increases whereas $2H$-MoS$_2$ has positive Poisson’s ratio as shown in Fig. 2(d). So, the three layered crystals have qualitatively different Poisson’s ratios spanning all possibilities of their signs.

To understand the qualitative difference in out-of-plane Poisson’s ratios of the three layered systems, we first decompose the binding energy of bilayer systems into repulsive and attractive parts. Figure 3(a) shows the binding energy curve between two layers of graphene, $E_{\text{bind}}(d) \equiv \frac{1}{2} \left[ E_{\text{b}}^b(d) - 2E_{\text{s}}^s \right]$ where $E_{\text{b}}^b(s)$ is the total energy of bilayer (single layer) graphene. $E_{\text{bind}}(d)$ is shown as solid (no strain) and open (8.1% equibiaxial nominal strain) circles as a function of the distance, $d$, between the layers. The calculated binding energy within $d = 4 \sim 9$ Å is well described by $E_{\text{bind}}(d) \sim d^{-4}$. The fitting curves of $d^{-4}$, which reflect asymptotic vdW interaction, are drawn in as a solid (dashed) line without (with) strain. The difference between the total energy and vdW energy for each case is also plotted in the same plot, two curves on top, representing purely repulsive characteristics called Pauli repulsion [36, 37]. It does not fit to any single power of $d^{-\alpha}$ but is well fit by an exponentially decaying function, $E_{\text{bind}}(d) \sim \left[ \exp(d^2/\sigma^2) - 1 \right]^{-1}$, with $\sigma = 1.37$ Å for the case without strain. We note that the $d^{-3}$ dependence of vdW energy of bilayer graphene, which was recently reported [38] is valid only at a distance larger than 9 Å [39] therefore not relevant near equilibrium distance considered here.

Figure 3(a) indicates that both vdW attraction and Pauli repulsion on bilayer graphene are enhanced under tensile strain. However, noting that the Pauli repulsion energy showing
exponential increase with $d$ is much stiffer than attractive vdW energy, equilibrium interlayer distance is critically sensitive to the change of the former than the latter. Thus, the equilibrium interlayer distance under the strain is mainly determined not by the strain-enhanced vdW attraction \cite{40} but by the enhancement of the repulsion. In graphene, electronic states pointing away from the layers are composed of linear combinations of $p_z$ orbitals of atoms called $\pi$ orbitals and form the $\pi$ band \cite{41}. Since the occupied electrons of $\pi$ orbitals in adjacent layers expel each other from their overlap region \cite{42}, the enhanced repulsion with external strain shown in Fig. 3 (a) may indicate the strain-induced spatial variation of $\pi$ electrons pushing the two layers away while the vdW interaction still keeps their binding.

We find that the in-plane strain indeed elongates the spatial distribution of electron density away from the layer making the Pauli repulsion increase over the vdW attraction. We calculate the spatial distribution of density of $\pi$ band along the $z$ axis in a single layer graphene: $\rho_{\pi}(z) \equiv \int_{E_F}^{\infty} dE \int dxdy \rho_E(x,y,z)$. Here, $\rho_E(x,y,z)$ is the local density of state for

FIG. 3: Binding energy as a function of interlayer distance, $d$, for bilayer (a) graphene and (b) $h$-BN. The fitting curves for attractive and repulsive parts are drawn in for unstrained case (solid line) and $\varepsilon_x = \varepsilon_y = 0.08$ equibiaxial strain case (dashed line). The insets show magnified views near equilibrium.
the $\pi$ band only and is summed over the in-plane unit cell ($x$ and $y$ axis). Graphene is located at $z = 0$ and the Fermi energy of the neutral system is denoted by $\varepsilon_F$. Our \textit{ab initio} calculation result for the maximum of $\rho_\pi(z)$ decreases with tensile strain while its tail increases implying that $\pi$ orbital spreads out along the $z$ axis with strain. Quantitatively, we calculate the density-weighted length of $\pi$ orbital along the $z$ axis using \( \langle \pi(z) \rangle = \int dz |z|\rho_\pi(z)/\int dz \rho_\pi(z) \) that gives $L_\pi = 0.673 \text{ Å}$ without strain. We find that the value of $L_\pi$ indeed increases by 0.6 \% as the equibiaxial strain increases by 2 \%, thereby explaining the value of the negative Poisson’s ratio near $-0.1$ along out-of-plane direction. This elongation can be understood simply by considering overlaps between neighbourig atomic orbitals. For a charge neutral graphene, the spatial distribution of $\pi$ orbitals along the perpendicular direction to the layer is contracted compared to $p_z$ orbitals of an isolated carbon atom because of overlap between nearby $p_z$ orbitals. In-plain tensile strain returns the carbon atoms in graphene back to isolated one so that the $\pi$ orbitals should be elongated.

A simple tight-binding (TB) picture can corroborate the elongation of spatial distribution of $\pi$ orbitals under strain. Consider the Bloch wave function within the TB approximation, \( \phi_{A(B)}(\vec{k}, \vec{r}) = N^{-1/2} \sum \bar{R}_{A(B)} e^{i\vec{k} \cdot \vec{R}_{A(B)}} \varphi_{A(B)}(\vec{r} - \vec{R}_{A(B)}) \), where subscript $A(B)$ represents the sublattice index, $\varphi_{A(B)}(\vec{r} - \vec{R}_{A(B)})$ is the normalized $p_z$ orbital of the carbon atom at $\vec{R}_{A(B)}$, while $\bar{R}_{A(B)}$ runs the positions of atoms in the $A(B)$ sublattice [41]. With the nearest neighbor hopping, $t$, and the overlap, $s = \langle \varphi_A(\vec{r} - \vec{R}_A) | \varphi_B(\vec{r} - \vec{R}_A - \vec{\delta}_j) \rangle$, the $\pi$-orbital is given by $\psi_{\pi}(\vec{k}, \vec{r}) = \frac{f(\vec{k})}{|f(\vec{k})|} \phi_A(\vec{k}, \vec{r}) + \phi_B(\vec{k}, \vec{r})$ where $f(\vec{k}) = \sum_{j=1}^3 e^{i\vec{k} \cdot \vec{\delta}_j}$ and $\vec{\delta}_j$ points to the three nearest neighbors. Considering $s \ll 1$, \( L_\pi = \frac{1}{S_{BZ}} \int_{BZ} d^2k \ l_\pi(\vec{k}) \), where $l_\pi(\vec{k}) \equiv \frac{\langle \psi_{\pi}(\vec{k}) \rangle^2 |\psi_{\pi}(\vec{k})\rangle^2}{\langle \psi_{\pi}(\vec{k}) \rangle^2 |\psi_{\pi}(\vec{k})\rangle^2} \approx l_{p_z} - |f(\vec{k})|(l_{p_z}s - l_\delta)$ is the density-weighted length of the $\pi$ orbital at $\vec{k}$ and $S_{BZ}$ is the area of the first Brillouin zone (BZ). Here, \( l_{p_z} = \int d^3r \ |z| \varphi_A(\vec{r})^2 \) is the length of an isolated $p_z$ orbital and \( l_\delta = \int d^3r \ \varphi_A^*(\vec{r} - \vec{R}_A)|z|\varphi_B(\vec{r} - \vec{R}_A - \vec{\delta}_1) \). If the maximum overlap between nearest neighbor $p_z$ orbitals is at $|z| = z_0$ and $\varphi_A^*(\vec{r} - \vec{R}_A)\varphi_B(\vec{r} - \vec{R}_A - \vec{\delta}_1)$ is trivial elsewhere, then \( l_\delta \approx z_0s \) so that $l_\pi(\vec{k}) \approx l_{p_z} - |f(\vec{k})|(l_{p_z} - z_0)s$ and that $L_\pi \approx l_{p_z} - l_h(\vec{\delta}_1)$ where $l_h \equiv \frac{(l_{p_z} - z_0)s}{S_{BZ}} \int_{BZ} d^2k |f(\vec{k})|$. It is straightforward to find that $l_h > 0$ and $\partial l_h/\partial |\vec{\delta}_1| < 0$. Therefore, the above simple formulation for $L_\pi$ implies that the out-of-plane distance of $\pi$-orbital is shorter than that of bare $p_z$ orbital and that the applied tensile strain can increase its distance.

Now, let us compare elastic properties of multilayered $h$-BN with graphene. A previous study [43] shows that the ionic interaction energy in the $h$-BN is negligible in determining
the electrostatic repulsion as well as dispersion forces so that the interlayer distance is very similar to graphite regardless of apparent difference in the static polarizability between the two layered materials. Our analysis, however, shows the elastic properties can be quite different; amplitude of out-of-plane Poisson’s ratio of h-BN is nowhere close to that of multilayer graphene but order of magnitude smaller [Fig. 2(d)]. Figure 3(b) shows that under tensile strain, vdW interaction increases as in graphene while the Pauli repulsion barely changes. For a bilayer graphene with $AB$ stacking, half of the carbon atoms of one layer are right on top of the carbon atoms of the other layer so that the tails of $p_z$ orbitals from two layers directly overlap with each other. For a bilayer h-BN with $AA'$ stacking, however, fully-filled $p_z$ orbital of nitrogen atom from one layer is on top of the empty $p_z$ orbital of boron from the other layer so that the interlayer Pauli repulsion is not as sensitive to the slight change of the length of $p_z$ orbitals as in the case of graphene.

The length of $p_z$ orbital of a single-layer h-BN, in fact, does change due to the strain in the same manner as that of graphene. Therefore, a negative interlayer Poisson’s ratio should appear in h-BN as multilayer graphene if the interlayer alignment of $p_z$ orbitals follows that of graphene. This can be realized by changing the stacking structure of h-BN from $AA'$ to $AA$. We have computed the elastic properties for this artificial bilayer structure and found that the out-of-plane Poisson ratio is $-0.12$, thus confirming our theory. On the other hand, the out-of-plane Poisson’s ratio of bilayer $2H$-MoS$_2$ is mainly determined by the flattening of each layer under tensile strain that gives positive value. Our calculation shows that the change of interlayer distance, $d$, of $2H$-MoS$_2$ in Fig. 1(c) in response to a given in-plane tensile stress mainly comes from the change of $d_1$; $\Delta d_1 \approx (3/4)\Delta d$.

In conclusion, we have studied the elastic properties of multilayered two-dimensional crystals including graphene, h-BN, and $2H$-MoS$_2$, with interlayer van der Waals interaction properly taken into account. In-plane elastic properties are found to be barely dependent on the number of layers for all three materials. Our analysis reveals that graphene is a very peculiar axial auxetic material when in-plain strain is applied. The mechanism is attributed to quantum mechanical origin rather than to structural one such as re-entrant foam. In contrast, the Poisson’s ratio of h-BN with $AA'$ stacking is found to be nearly zero and that of MoS$_2$ is positive.

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