On the bending of rectangular atomic monolayers along different directions: an ab initio study

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Abstract

We study the bending of rectangular atomic monolayers along different directions from first principles. Specifically, choosing the phosphorene, GeS, TiS$_3$, and As$_2$S$_3$ monolayers as representative examples, we perform Kohn–Sham density functional theory calculations to determine the variation in transverse flexoelectric coefficient and bending modulus with the direction of bending. We find that while the flexoelectric coefficient is nearly isotropic, there is significant and complex anisotropy in bending modulus that also differs between the monolayers, with extremal values not necessarily occurring along the principal directions. In particular, the commonly adopted orthotropic continuum plate model with uniform thickness fails to describe the observed variations in bending modulus for GeS, TiS$_3$, and As$_2$S$_3$. We determine the direction-dependent effective thickness for use in such continuum models. We also show that the anisotropy in bending modulus is not associated with the rehybridization of atomic orbitals.

Supplementary material for this article is available online

Keywords: mechanical deformation, rectangular atomic monolayers, density functional theory, bending modulus, transverse flexoelectric coefficient

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

1. Introduction

Over the past two decades, crystalline atomic monolayers—dozens have now been synthesized [1,2] and thousands have been predicted to be stable from first principles Kohn–Sham density functional theory (DFT) calculations [3,4]—have been the subject of intense research [5–7]. This is due to their interesting and exotic mechanical [8], electronic [9], and optical properties [10], which are typically muted or non-existent in their bulk counterparts. The most common lattice structures among these 2D materials are honeycomb and rectangular. While the properties of honeycomb monolayers are generally found to be isotropic [11–14], i.e., independent of in-plane direction, significant anisotropy is common in rectangular monolayers [15–18].

The responses/properties of atomic monolayers under mechanical deformations are important in several technological applications, including flexible electronics [19,20], nanoelectromechanical devices [21,22], nanocomposites [23,24], wearable mechanical sensors [25,26], and single-photon emitters [27,28]. This has motivated a number of studies on the mechanical properties of atomic monolayers, both experimental [8,29–31] and theoretical/DFT [8,29] as well as on their response to mechanical deformations, both experimental [32,33] and theoretical/DFT [32–34]. These efforts have generally focused on tensile deformations, since bending requires sophisticated experiments with high accuracy in measurements [8] and ab initio DFT simulations are computationally intensive, scaling cubically with system size, which makes them nonviable at practically relevant bending curvatures [35]. Indeed, such studies can be performed using computationally cheaper alternatives such as tight binding [36–38] and classical force fields [39–47]. However, these methods typically lack the resolution required to study nanoscale systems such as monolayers, as is evident by the significant scatter in the reported bending moduli values for even elemental monolayers, e.g., 0.8 to 2.7 eV for graphene [39,46], and 0.4 to 38 eV for silicene [43,47].
In recent work, cyclic-helical symmetry-adapted DFT calculations [48,49] have been used to compute the bending moduli for forty-four atomic monolayers [35] as well as the transversal flexoelectric coefficient—measures the rate of change of the out-of-plane dipole moment with curvature, which arises due to the bending-induced strain gradient across the thickness [50]—for fifty-four atomic monolayers [51], along their principal directions. It has been found that atomic monolayers with honeycomb lattice, i.e., group IV monolayers, transition metal dichalcogenides (TMDs), group III monochalcogenides, and group IV dichalcogenides, have bending modulus and flexoelectric coefficient values that do not vary between the principal directions, whereas those with rectangular lattice, i.e., group V monolayers, group IV monochalcogenides, transition metal trichalcogenides (TMTs), and group V chalcogenides, have significantly different bending modulus but nearly same flexoelectric coefficient values along the principal directions. These and previous ab initio studies have however not considered the bending of monolayers along directions that are different from the two principal directions, which provides the motivation for the current work.

In this work, we study the bending of rectangular atomic monolayers along different directions using Kohn–Sham DFT. Specifically, choosing the phosphorene, GeS, TiS₂, and As₂S₃ monolayers as representative examples—each has been synthesized, and belongs to a notable monolayer group that has a rectangular lattice structure—we investigate the variation in transverse flexoelectric coefficient and bending modulus with the bending direction. We find that while the flexoelectric coefficient is nearly isotropic, there is significant and complex anisotropy in the bending modulus that also differs between the monolayers. For each of the monolayers, we determine the direction-dependent effective thickness to be used in orthotropic continuum plate models. We also study the correlation between the underlying electronic structure and the direction-dependent bending modulus.

2. Methods

We perform Kohn–Sham DFT calculations using the real-space electronic structure code SPARC [52–54], which employs the systematically improvable finite-difference method. Specifically, we simulate the bending of the selected atomic monolayers using the Cyclix-DFT feature [48], which has been well tested in a number of physical applications [35,48,50,51,55–58]. In particular, edge-related effects are removed by considering the nanotube obtained by rolling the monolayer along a certain direction, with the nanotube’s radius chosen to be equal to the desired bending radius of curvature [48,49,59]. The cyclic and helical symmetry of the resulting nanotube is then exploited to reduce the computations to the fundamental domain—possesses same number of atoms as the monolayer’s periodic unit cell—thereby significantly accelerating the calculations [48], enabling efficient simulations in the practically relevant low-curvature limit. See figure 1 for an illustration of the bending of the phosphorene monolayer along an arbitrary direction, with the resulting chiral nanotube having only four atoms in its fundamental domain.

For a given bending direction, we calculate the transversal flexoelectric coefficient μ₁ using the relation [50,51]:

$$\mu_1 = \frac{\partial}{\partial R} \left( \frac{1}{A} \int_{\Omega} (r - R_{eff}) \rho(x) \, dx \right),$$

where 1/κ is the radius of the nanotube, A is the nanotube’s cross-sectional area within the fundamental domain Ω, r is the radial coordinate at x, R_{eff} is the radial ionic centroid, and ρ(x) is the ground state electron density. In particular, the flexoelectric coefficient is computed by employing a numerical approximation to the derivative in equation (1), i.e., the quantity in brackets—referred to as the radial polarization—is evaluated at multiple curvatures near the curvature at which the flexoelectric coefficient needs to be computed, and the corresponding curve-fit is used to approximate the derivative.

For a given bending direction, we calculate the bending modulus D by fitting data to the expression:

$$\varepsilon(\kappa) = \varepsilon_0 + \frac{DA\kappa^2}{2},$$

where ε(κ) is the ground state energy of the nanotube with radius 1/κ.

In all simulations, we employ the Perdew–Burke–Ernzerhof (PBE) [62] exchange-correlation functional, and ONCV [63] pseudopotentials from the SPMS [64] collection. The computed lattice constants for the monolayers (Supplementary Material) are in good agreement with both experimental [65–68] and theoretical studies [3,4], verifying the accuracy of the chosen exchange-correlation functional and pseudopotentials. We consider ten bending directions for each of the selected atomic monolayers: phosphorene, GeS, TiS₂, and As₂S₃. In order to simulate mildly bent sheets, i.e., calculate quantities corresponding to the low curvature limit, we choose bending curvatures: 0.15 ≤ κ ≤ 0.25 nm⁻¹, commensurate with experimental studies for bending [69]. All numerical parameters in Cyclix-DFT, including the real-space and Brillouin zone grid spacings, vacuum in the radial direction, and relaxation tolerances for cell/atom are chosen such that the computed flexoelectric coefficient and bending modulus values are accurate to within 0.01e and 1%, respectively. In practice, this requires the computed ground state energy to be converged to within 10⁻⁵ Ha/atom, which is necessary to capture the extremely small differences, particularly those arising during the computation of the bending modulus.

We note that without the use of the cyclic-helical symmetry-adapted framework [48], many of the simulations needed here would have been tremendously expensive, if not impossible, e.g., the As₂S₃ system with κ = 0.15 nm⁻¹ and
bending along $\theta = 61.2$ degrees has a total of 583, 520 electrons in the unit cell for periodic boundary conditions, which is well beyond the reach of traditional DFT formulations/implementations. This reduces to only 56 electrons in the symmetry-adapted framework, which is identical to the number in standard periodic unit cell calculations for the monolayer.

3. Results and discussion

We now present results of the aforedescribed Kohn–Sham DFT bending simulations for the phosphorene, GeS, TiS$_3$, and As$_2$S$_3$ atomic monolayers. Additional details regarding the simulation data and results presented/discussed here can be found in the Supplementary Material.

In figure 2, we present the variation in the values of the transversal flexoelectric coefficient $\mu_T$ and bending modulus $D$ with the direction of bending. On the one hand, we observe that the flexoelectric coefficient is nearly independent of direction, indicating that it is isotropic for the chosen monolayers. On the other hand, the bending modulus is noticeably affected by the bending direction, resulting in significant and complex variation that also differs between the different monolayers (likely due to the different underlying lattice and electronic structures), indicating that it is highly anisotropic. In particular, the ratio of maximum to minimum bending modulus for the phosphorene, GeS, TiS$_3$, and As$_2$S$_3$ monolayers is 5.3, 3.1, 2.3, and 3.3, respectively, with the maximum and minimum values not occurring along the principle directions for the GeS, TiS$_3$, and As$_2$S$_3$ monolayers, i.e., all monolayers but phosphorene. Interestingly, the variation in phosphorene’s bending modulus is squarely opposite to its anisotropy in longitudinal acoustic phonons [70], and unlike the bending modulus/longitudinal acoustic phonons, the maximum and minimum values of the group velocity for transverse acoustic phonons do not occur along the principal directions [70].

The values of the flexoelectric coefficient and bending modulus along the principle directions are in excellent agreement with those reported in [35,51], which also employ DFT calculations with the same exchange-correlation functional, i.e., PBE. Comparisons for other directions cannot be made due to the unavailability of experimental/DFT studies in literature, as also noted in the introduction. In the case of phosphorene, there has been a recent study on its direction-dependent bending modulus using the tight binding approximation [36]. While there is reasonable agreement in the qualitative features between [36] and the current work, there are significant quantitative differences, with values deviating by as much as 2 eV. These differences can be attributed to the approximate nature of tight binding methods, particularly when compared to Kohn–Sham DFT, further highlighting the need for ab initio calculations in such studies.

It is common to employ an orthotropic continuum plate model for the higher-scale analyses of atomic monolayers, e.g., vibrations and instabilities [17,37,71–76]. In this model, the out-of-plane bending modulus is related to the in-plane Young’s modulus $Y$ and Poisson’s ratio $\nu$ through the relation [77]:

$$D(\theta) = \frac{Y(\theta)t^3}{12(1-\nu(\theta))\nu(\theta+\pi/2)}, \quad (3)$$

where $t$ is the thickness of the plate. To check the validity of this model in the current context, given that the thickness of monolayers is not well-established [78–80], we first calculate their direction-dependent Young’s modulus and Poisson’s ratio in the flat configuration, again using the SPARC...
electronic structure code [52–54]. Next, we substitute the computed bending modulus, Young’s modulus, and Poisson’s ratio into equation (3) to determine the effective thickness as a function of direction, i.e., \( t(\theta) \), the results for which are presented in figure 3. We observe that while the effective thickness is nearly independent of direction for phosphorene, there is significant anisotropy for the other monolayers, suggesting the failure of the continuum model when using a constant thickness for these systems. In particular, the direction-dependent effective thickness determined here can be used in such continuum models for higher-scale analyses. Note that the effective thickness for phosphorene reported by [36] is significantly more anisotropic than the one here, again a likely consequence of [36] using the more approximate tight binding methods.

To get further insight into the observed anisotropy in the bending modulus, we calculate the atomic orbital projected density of states (PDOS) for the flat and bent monolayers, i.e.,
nanotubes. In figure 4, we plot the PDOS so obtained for the flat sheet as well as directions along which the monolayer has the largest and smallest bending modulus. We observe that while there are significant differences at the level of the magnetic quantum number resolved PDOS (Supplementary Material), the curves at the level of the angular quantum number (i.e., summed over the magnetic quantum number, for each principal and angular quantum number) are similar in all cases. Given that we are considering small bending curvatures that do not significantly change the relative orientation of the atoms from the flat sheet configuration, the PDOS results suggest that bending does not cause rehybridization of orbitals relative to the flat sheet, and the anisotropy in the bending modulus is not a consequence of the rehybridization of orbitals, but rather due to the structure-dependent directional weakening of bonds, i.e., the change in strength of the bonding.
different bonds is determined mainly by the orientation of the bending direction relative to the lattice configuration.

4. Concluding remarks

In this work, we have studied the bending of four rectangular atomic monolayers: phosphorene, GeS, TiS₃, and As₂S₃, along different directions, from first principles. In particular, we have performed Kohn–Sham DFT calculations to determine the variation in transverse flexoelectric coefficient and bending modulus with bending direction. We have found that the flexoelectric coefficient is nearly isotropic, whereas the bending modulus has significant and complex anisotropy that also differs between the monolayers, with the maximum and minimum values not necessarily occurring along the principal directions. In particular, the orthotropic continuum plate model—commonly employed in literature for atomic monolayers—fails to describe the observed variations in bending modulus for GeS, TiS₃, and As₂S₃. We have determined the direction-dependent effective thickness that can be used in such continuum models, which has applications in higher-scale vibrational and instability analyses. We have also found that the anisotropy in bending modulus is not a consequence of the rehybridization of atomic orbitals, but rather due to the structure-dependent directional weakening of bonds. The bending of bilayers/multilayers and heterostructures presents itself as a worthy subject of future research.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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