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Thermal stability of a free nanotube from single-layer black phosphorus

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Abstract
Similar to a carbon nanotube fabricated from a graphene sheet, a black phosphorus nanotube (BPNT) can also be theoretically produced by curling rectangular single-layer black phosphorus (SLBP). In the present study, the effect of the thermal vibration of atoms on the failure of a BPNT is investigated using molecular dynamics simulations. Two types of double-shell BPNTs obtained by curling the SLBP along its armchair/pucker and zigzag directions respectively are involved in simulation. At finite temperature, a bond on the outer shell of the tube is under tension due to both the curvature of the tube and the serious thermal vibration of the atoms. As the length of a bond with such elongation approaches its critical value, i.e. 0.279 nm, or the smallest distance between two nonbonding phosphorus atoms is over 0.389 nm caused by a great variation of the bond angle, the tube fails quickly. The critical stable states of either an armchair or a zigzag BPNT at finite temperature are calculated and compared. To achieve a stable BPNT with high robustness, the tube should have a higher radius or should work at a lower temperature. Only when the BPNT has structural stability does it have the potential application as a nanowire in a future nano electro-mechanical system.

Keywords: black phosphorus, nanotube, temperature effect, critical curvature, stability

1. Introduction
Phosphorus is the 15th element in group 5A of the periodic table. Black phosphorus (BP), which is the most stable structure among the phosphorus allotropes [1–4], is a semiconductor material formed with sp³ hybridized bonds. During the past few years [5–11], the single layer of black phosphorous (SLBP), as a new two-dimensional (2D) material, has attracted much attention due to its unique electronic properties, e.g. over 10⁴ of drain current modulation, a high charge-carrier mobility (up to 10⁴ cm² V⁻¹ s⁻¹), etc.

When used as a component in a nano device, the structural configuration of an SLBP should be stable for the mechanical stability of the device, which has invoked the understanding of the mechanical properties of SLBP. Using dispersion-corrected density functional theory, Appalakondaiah et al [12] investigated the van der Waals (vdW) interactions among the atoms in the orthorhombic BP, and presented elastic properties of multi-layer BP. Jiang and Park [13] studied the mechanical parameters of SLBP under uniaxial tension by ab initio calculations. Their results showed that the SLBP is an orthotropic material during elastic deformation. The elastic modulus along the pucker direction, ~106.4 GPa, is about 2.5 times of that along the (in-plane) vertical direction. Due to the fact that a 3sp³ bonding strength is weaker than that of a 2sp², the modulus of SLBP is far less than that of single layer graphene (~1 TPa). In particular, Jiang and Park [8] found that the Poisson’s ratio of SLBP in the out-of-plane direction was negative when an SLBP is under uniaxial tension along the pucker direction. Also using first principles calculations, Hu et al [7] investigated the mechanical and electronic properties of both the SLBP and bilayer BP under either isotropic or...
uniaxial strain, and found that the band gap varies with the deformation. Wei and Peng [14] studied the ideal tensile strength and critical strain of SLBP and proposed a general formulation to calculate the Young’s moduli for such a 2D structure based on continuum mechanics. Kou et al [15] studied the ripple deformation in an SLBP induced by compression along the pucker direction. Using density functional tight binding calculations, Sorkin and Zhang [16] studied the edge stress and moduli of phosphorene and examined the structure and stability of the phosphorene edges with such stress. Recently, Jiang [17] set up a set of parameters for the Stillinger–Weber (SW) potential from the valence force field model. The accuracy of using these parameters was checked by comparing the phonon spectrum obtained from ab initio calculations. In his work, the stress-strain curves of an SLBP under uniaxial tension were given at different temperatures. Sha et al [18] investigated the moduli and fracture limits of SLBP under either uniaxial or bi-axial loading using the SW potential. Yang et al [19] researched the mechanical behavior of SLBP under shear loading at finite temperature.

In the above studies, the nanotube from SLBP is not considered. As a carbon nanotube can be obtained by curling a graphene sheet, similarly, a BP nanotube (BPNT) might also be obtained by curling an SLBP. Up to now, only a few works have introduced BPNT. To find new nano-structured materials with new properties, Seifert and Hernández [20] once gave a discussion on the fabrication of a stable nanotube from such an element as phosphorus rather than carbon. In their work, a 2D honeycomb was firstly formed from a BP sheet. Then, a 2D honeycomb sheet was obtained by removing atoms from the BP sheet. Finally, a tube was fabricated by curling the 2D honeycomb sheet. Guo et al [21] reported the electronic properties of phosphorene based nanostructures, including BPNTs. In their report, two types of BPNTs (figures 1(e) and (f)) were involved. Obviously, mechanical deformation of few-layer BP is significant for its electronic properties. However, the strength of the 3sp bond in SLBP is much lower than that between the 2sp2 carbon atoms in graphene. When the radius of a BPNT is too small, the P–P bonds on the outer shell of the tube are easily broken. Especially, at finite temperature, thermal vibration of atoms on a BPNT will reduce the strength of the tube further. Without the stability of BPNT, the other physical properties of such nano structures are meaningless. When curling a SLBP to form a BPNT, both of the curling directions and the radius of the curved neutral layer determines its geometric configurations. In this paper, we will present the study of the stability of BPNT with respect to the critical curvature of the BPNTs shown in figures 1(e) and (f), and the minimum number of periodic cells along the circular direction of a BPNT at finite temperatures.

2. Computational models

Figure 1 gives two types of BPNTs by curling a rectangular SLBP along different directions. For an armchair BPNT (A-BPNT), the whole tube is adopted in simulation. The system is kept at a canonical NVT ensemble and the temperature increases from 4.3 K to a specified temperature, e.g. 150 or 300 K, after 1 million time steps. After arriving at the temperature, 10 million more time steps of relaxation are carried out. For a zigzag BPNT, we only choose an arch segment from the tube for simulation. The segment will be relaxed for 10 million time steps at a canonical NVT ensemble with a constant temperature. During molecular dynamics (MD) simulation, near each straight side, only one layer of top atoms and one layer of adjacent bottom atoms are fixed.

To have perfect computation efficiency with reasonable accuracy for nonlinear behavior of a BP nanoscale structure, the SW potential developed by Jiang [17] is chosen to describe the interaction among atoms in the structure [22]. In the present study, we choose LAMMPS [23] for the following simulations. In the time integration, the time step is 0.1 fs.

The two models of BPNTs shown in figure 1 are obtained by ideal geometrical mapping of the SLBP. During mapping, the inner layer (colored green) becomes shorter as compared with its original length, and the outer layer (colored purple) becomes longer. Hence, the bonds on the outer layer are under tension. If the tensile deformation of the outer layer is too high, the P–P bonds break. Besides, in a practical application, the nano structure should work at a finite environmental temperature. Hence, the tube becomes more fragile when thermal vibration of the atoms on the tube is involved. To find a stable BPNT, in the present study, a BPNT obtained by geometrical mapping of SLBP is relaxed in thermal environments. When the tube remains undamaged during relaxation, it is stable. When the number of periodic cells along the circular direction of the tube reaches a minimum, the critical radius of the tube is obtained.

3. Results and discussions

3.1. Critical curvature of a BPNT at different temperatures

After a series of tests, we find that the minimum number of periodic cells along the circular direction of an A-BPNT is only 6 at 4.3 K (see the top layer in figure 2(a)). The minimum number increases to 9 at 150 K or 16 at 300 K. When the number of periodic cells is less than the minimum number, the tube collapses within a few ps. For example, at 4.3 K, the A-BPNT with chirality of (6, 7, 360°) is stable, however, the A-BPNT (5, 7, 360°) becomes a triangular prism (see the second inserted snapshot in figure 2(a)). Why does it happen? It is known that the inner layer of the tube becomes shorter after geometrical mapping, and the distances between the atom on the inner layer and its neighbor atoms is reduced. The shorter distances between the non-bonded atoms on the inner layer result in the stronger attraction (vdW interaction); simultaneously, the P–P bonds on the outer tube are under tension due to the curving of the tube. The tube fails to keep a stable configuration under such conditions. As there are only six periodic cells along the circular direction of the A-BPNT (6, 7, 360°) at 4.3 K, the critical value of the curved angle per
Figure 1. Geometric configurations of nano shells from SLBP: (a) top view of SLBP; (b) zigzag view of SLBP; (c) armchair view of SLBP; (d) unit cell with bond lengths of \( L_{12} = L_{13} = L_{45} = L_{46} = 0.2224 \text{ nm} \); \( L_{14} = 0.2244 \text{ nm} \); bond angles of \( \alpha = 96.36 \text{ degree} \) and \( \beta = 102.09 \text{ degree} \); (e) armchair BPNT (A-BPNT), which is formed by curling the armchair sides of SLBP within the red rectangle in (a); (f) zigzag BPNT (Z-BPNT), which is formed by curling the zigzag sides of SLBP within the blue rectangle in (a). \( R \) is the radius of the curved neutral layer (dash curve in (f)). For simplicity, using \((N_A, N_Z, \theta)\) labels the chirality of a BPNT where \( N_A \) and \( N_Z \) are the numbers of the periodic cells along the armchair and zigzag directions within the rectangle, respectively, \( \theta \) is the curved angle. For example, the A-BPNT in (e) is represented as \((N_A, N_Z, \theta) = (12, 8, 360^\circ)\), and the Z-BPNT in (f) is of \((12, 8, 240^\circ)\). \( R \) is the radius of the curved neutral layer (dash line in (f)) of the curved shell.

Figure 2. Variation histories of the potential energy of curved SLBPs along different directions at different environmental temperatures, e.g. 4.3, 150 and 300 K: (a) along the armchair direction, the A-BPNTs are formed with a chirality of \((N_A, 7, 360^\circ)\); (b) along the zigzag direction, the Z-BPNTs are formed with a partial chirality of \((6, 15, \theta/\text{sita})\) at 4.3 K or \((6, 31, \theta)\) at 150 and 300 K. The snapshots of related (axial view) models at 800 ps are inserted.
periodic cell (CAPPC) can be defined as

$$\theta^\text{crit}_A = \theta / N_A = 360^\circ / 6 = 60^\circ$$

(1)

At 150 K, the A-BPNT with a chirality of (9, 7, 360°) is stable but not for A-BPNT (8, 7, 360°). Clearly, the critical value of the CAPPC (along the armchair direction) is 40° at 150 K. Hence, the curvature of A-BPNT (8, 7, 360°) is lower than that of A-BPNT (6, 7, 360°) which is stable at 4.3 K. If the environmental temperature is 300 K, even the configuration of A-BPNT (15, 7, 360°) is unstable. The critical value of the CAPPC is 22.5°. It is concluded that the thermal vibration of atoms on the tube is the second major reason for tube destruction as compared with curvature related deformation.

To find the critical curvature angle of a Z-BPNT (e.g. figure 1(f)) at finite temperature, we curl the same rectangular SLBP along the zigzag direction with different curved angles. Figure 2(b) gives three critical states of the Z-BPNTs. At 4.3 K, the critical value of $\theta$ is 224° because the arch structure (Z-BPNT (6, 15, $\theta$)) is broken if $\theta$ is slightly higher than 224° (see the second insert snapshot in figure 2(b)). Hence, the critical value of the CAPPC (along the zigzag direction) can be calculated by equation (2), i.e.:

$$\theta^\text{crit}_Z = \theta / N_Z = 224^\circ / 15 \approx 14.9^\circ$$

(2)

When the temperature is high, e.g. 150 K, the critical value of $\theta$ is 265° for the arch structure of Z-BPNT (6, 31, $\theta$). Correspondingly, the critical value of the CAPPC is ~8.5°, which is far less than 14.9° at 4.3 K. At 300 K, the CAPPC is ~6.9°. Comparing the three failure models shown in figure 2(b), we also find that the damage area is nearby the center of the arch structure at a low temperature, e.g. 4.3 or 150 K. However, at 300 K, the damage area (shown in the 6th snapshot in figure 2(b)) is close to the lower fixed end. The reason is that the drastic thermal vibration of phosphorus atoms on the arch structure leads to a random initial damage on the structure.

From above, one concludes that the critical curvature of either a stable A-type or Z-type BPNT is higher at a lower temperature.

3.2. Failure mechanism of Z-BPNTs

From above, we also find that the critical value of the CAPPC of an A-BPNT is much higher than that of a Z-BPNT at the same temperature. Hence, the stability of a Z-BPNT is lower than an A-BPNT at the same temperature. To demonstrate the failure of a Z-BPNT due to local damage on the outer layer at finite temperature, the arch structure of Z-BPNT (6, 15, $\theta$) is chosen and the bond lengths and bond angles on the outer layer nearby the initial fracture area (see figure 3) are calculated because the bonds are under tension during deformation.

Figure 2(b) implies that the Z-BPNT (6, 15, $\theta$) at 4.3 K is in the critical stable state when $\theta = 224°$. It is known that the temperature effect, i.e. the thermal vibration of the atoms, is negligible for the arch structure at such a low temperature. Hence, the failure of the arch structure is mainly caused by tensile deformation if the value of $\theta$ increases slightly, e.g. $\theta = 225°$. To reveal the initial damage source of the arch structure, the variations of the bond lengths and bond angles nearby the failure area (figure 3) are calculated. Figure 4 shows the histories of the ten bond lengths and four angles on the outer layer of the arch structure at either the stable state ($\theta = 224°$) or the failure state ($\theta = 225°$).

When $\theta = 225°$, all of the ten bonds have very small variation and are less than 0.25 nm (figures 4(a) and (c)), which is less than the maximal bond length (0.279 nm). Among the six bond angles, $\alpha_1$, which is at the center of the outer layer of the arch structure, has the highest variation. Meanwhile, the variation of the bond angle is lower when the distance between the center atom and atom $c$ (the center atom of $\alpha_1$) is higher (figures 4(b) and (d)). When $\theta = 225°$, $L_{bc}$, the length of bond $b$–$c$ (between atoms b and c; similar to other bonds), jumps up suddenly after 2750 fs. It reaches the maximum bond length, i.e. 0.279 nm, at 2820 fs. After that, bond $b$–$c$ breaks and the local fracture keeps developing. Simultaneously, the lengths of the rest of the bonds, e.g. $L_{ab}$, $L_{cd}$, decrease. The reason is that the area nearby the broken bond $b$–$c$ becomes a new free boundary, and the initial tensile deformation of the rest of the bonds nearby the new boundary drops (figures 4(a) and (c)). Comparing the variation of $\alpha_1$, $\alpha_5$ and $\alpha_6$ (figure 4(b)), we find that the bond angles along the axial-direction vary similarly to those in the structure with $\theta = 224°$. However, along the circular-direction, the values of $\alpha_2$, $\alpha_3$ and $\alpha_4$ drop sharply when bond $b$–$c$ breaks. It is also attributed to the appearance of the new boundary nearby the broken bond $b$–$c$.

In the SW potential for BP, the distance between two non-bonded atoms, e.g. $L_{abc}$ also has a maximum, i.e. 0.389 nm [17]. In the above analysis, we only find the difference between the variation histories of bond lengths and bond angles nearby the center of the outer layer of the arch structure, and only the critical curvature of the arch structure is obtained. The reason for the fracture of bond $b$–$c$ is not given yet. In figure 5, we provide the histories of $L_{bc}$ and $\alpha_1$ during [2500, 3000] fs. The curves indicate that $\alpha_1$ approaches maximum (1.9657 rad at peak 1 in the upper layer of figure 5) at 2710 fs when $\theta = 224°$. Meanwhile, $L_{bc} = 0.2422$ nm, $L_{cd} = 0.2389$ nm, and $L_{bd}$, i.e. the distance between atoms b and d, can be obtained by the formulation

$$L_{bd} = \sqrt{L_{bc}^2 + L_{cd}^2 - 2L_{bc}L_{cd} \cos(\alpha_1)}.$$  

(3)

$L_{bd}$ is 0.4003 nm, which is greater than its maximum value (0.389 nm). Fortunately, the value of $\alpha_1$ drops from then on and the bond lengths, i.e. $L_{bc}$ and $L_{cd}$, are much lower than their maximal value (0.279 nm). Hence, the structure remains undamaged.

For the case of $\theta = 225°$, at 2710 fs, $\alpha_1 = 1.976$ rad, $L_{bc} = 0.2469$ nm (< 0.279 nm), $L_{cd} = 0.2373$ nm (< 0.279 nm) and $L_{bd} = 0.4043$ nm > 0.389 nm. However, $\alpha_1$ keeps increasing before 2798 fs (at peak 2 in the upper layer of figure 5). Especially, $L_{bc}$ increases continuously before 3000 fs. At 2820 fs, $L_{bd}$ reaches its maximal value and bond...
b–c is broken. It implies that the local stability of the arch structure is lost due to $L_{bd} > 0.379 \text{ nm}$ when $\theta$ is over $224^\circ$, rather than to the thermal vibration of atoms.

### 3.3. Temperature effect on the failure of BPNTs

Figure 2 indicates that the critical CAPPC of the same BPNT is lower at a higher temperature. In the above discussion, the effect of the thermal vibration of atoms on the failure of BPNT at 4.3 K is neglected. Now, we want to know the relationship between the critical CAPPC of a Z-BPNT and the environmental temperature. With the understanding of this relationship, one can design a stable BPNT in a nano device.

The relationship is analyzed via the following steps.

1. **Pure thermal deformation of a P–P bond**

   From the three fractured structures shown in figure 2(b), we know that the initial damage of the tube is as random as the temperature is high. It implies that the first breakage of the bond is caused by the highest thermal vibration of the atoms on the bond. Hence, the maximal thermal vibration induced by the elongation of the P–P bonds on SLBP at finite temperature should be obtained. To find the maximal elongation at a specified temperature, we fix one pucker side of a rectangular BP sheet with a size of 10.4 nm by 10.6 nm, and in statistics the bonds are more than 2.0 nm far away from the four sides of the sheet during 200 ps of relaxation at a NVT ensemble.

   Figure 6 indicates that the thermal vibration induced bond elongation increases with the increasing temperature. The engineering strain of a P–P bond is over 10% when the environmental temperature is over 200 K. Hence, the serious variation of bond length due to temperature influences the mechanical stability of BPNTs.

   From the fitting function listed in figure 6 or equation (4), one can obtain the amplitude of the thermal vibration of the P–P bond at finite temperature ($T$).

   $\Delta L_{45}^{\text{Temp}} = \Delta L_{46}^{\text{Temp}} = X$

   $= (-f_2 + \sqrt{f_2^2 - 4f_3(f_1 - T)})/(2f_1), \quad (4)$

   where $f_1$, $f_2$ and $f_3$ are fitting parameters given in figure 6.

2. **Pure tensile deformation**

   The curvature induced tensile deformation of the outer layer, for example, of a BPNT (figure 7), can be calculated. It is known that the arc length between atoms b and d on a Z-BPNT (figure 7(c)) is higher than their distance ($L_{bd}$) on the free SLBP sheet at 0 K. The difference can be calculated from equation (5), i.e.

   $\Delta L_{56}^{\text{Tensile}} = \Delta L_{bd}^{\text{Tensile}} = \frac{1}{2} L_{bd} \cdot \cos \beta \cdot \theta_{z}^{\text{crit}}, \quad (5)$

   where $L_{56}$ and $\beta$ are introduced in the caption of figure 1. As the length variation of $L_{56}$ is mainly due to the variation of angle $\alpha 1$, it can be calculated from

   $\Delta \alpha 1 = \arcsin(\Delta L_{56}^{\text{Tensile}} \cdot \cos(0.5\alpha)/L_{45})$

   $= \arcsin(\cos(0.5\alpha) \cdot L_{bd} \cdot \cos \beta \cdot \theta_{z}^{\text{crit}} / (2L_{45})) \quad (6)$

3. **Conditions for a stable BPNT**

   To maintain the stability of a BPNT, the three conditions in equation (7) should be satisfied, simultaneously,

   $L_{45} = L_{45} + \Delta L_{45}^{\text{Tensile}} + \Delta L_{45}^{\text{Temp}} < 0.279 \text{ nm}$

   $L_{46} = L_{46} + \Delta L_{46}^{\text{Tensile}} + \Delta L_{46}^{\text{Temp}} < 0.279 \text{ nm}$

   $L_{56} = \sqrt{L_{45}^2 + L_{46}^2} - 2L_{45}L_{46} \cos(\alpha + \Delta \alpha 1) < 0.389 \text{ nm} \quad (7)$

   The first two inequations imply that no bond on the BPNT is broken at finite temperature. The third one
demonstrates that the variation of $\alpha_1$ should be low when the two bonds 4–5 and 4–6 are under tension.

In equation (7), $L_{45}$ and $L_{46}$ are constants. Hence, one can find that a BPNT at a higher temperature will bear lower tensile deformation. That is the reason that the critical value of CAPPC of a BPNT decreases with the increasing of environmental temperature. From equation (7) one can obtain the coupling effect of the temperature effect and curvature of a stable BPNT.

Figure 4. Histories of bond angles and bond lengths in the Z-BPNTs of (6, 15, $\theta$) at 4.3 K with a different curved angle, i.e. $\theta = 224^\circ$ and $\theta = 225^\circ$. $L_{xy} = L_{yz}$ ($x, y = a, b, c, d, e, f, g, h, i, j, k, l, m$). (a) Bond lengths comparison along the axial direction; (b) bond angles comparison along the axial direction; (c) bond lengths comparison along the circular direction; (d) bond angles comparison along the circular direction.

(4) Robustness design of a stable BPNT

For a BPNT used in a practical application, the tube should be far away from its critical stable state. The above results demonstrate that both the environmental temperature and curvature have significant influence on the stable state. Therefore, the robustness of a stable BPNT can be expressed by the capacity of the tube when temperature becomes higher as it is working. For example, if a BPNT is stable at temperature $T$, it still undamaged at $T + \Delta T$. The positive
increment, $\Delta T$, indicates the robustness of the tube. In comparison, if the environmental temperature is well controlled, the number of periodic cells on the cross section (i.e. along the circular direction) of the tube should be greater than the minimal number of periodic cells of the tube at the temperature (figure 8). The difference between the two numbers also demonstrates the robustness of the BPNT.

4. Conclusions

To find the effect of temperature on the failure of a BPNT at a canonical NVT ensemble, a series of MD simulations are presented. In the simulation, two types of BPNTs are obtained by curling the rectangular SLBP sheet along different directions. From the results, some concluding remarks are drawn.
1. Bond elongation due to thermal vibration increases with the increasing of temperature. The critical curvature of either an A-type or a Z-type BPNT is higher at lower temperature.

2. The failure of a Z-BPNT at a specified temperature is mainly due to the buckling of angle \( \alpha_1 \), which locates in the middle part of the tube. For a A-BPNT, the failure of the tube is caused by both the breakage of P–P bonds on the outer layer of the tube and the strong attraction of the atoms on the inner layer.

3. For a stable BPNT at finite temperature, all the bond lengths should be less than 0.279 nm, and the smallest distance between non-bonded atoms should be less than its maximal value, i.e. 0.389 nm, simultaneously.

From an application point of view, a BPNT should have a lower curvature than its critical value at the same temperature. A BPNT with a higher radius or at a lower temperature will have higher robustness in acting as a component in a nano device. If one does not require a cylindrical BPNT, he/she can fabricate a BPNT with several pieces of SLBP nanoribbon [24].

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