Molecular dynamics study on radial deformation of armchair single-walled boron nitride nanotubes

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Radial deformation of boron nitride nanotubes (BNNTs) plays a significant role in the performances of BNNT-based applications. By performing molecular dynamics simulations, the radial deformation of armchair single-walled BNNTs was investigated. The deformation energy barrier was found to follow a decreasing trend with increasing tube diameter. Two threshold diameters were identified that demarcate three stability regimes for the deformed single-walled BNNTs. Whereas the van der Waals interaction was simply favorable for radial deformation, the electrostatic interaction had a complex effect; it prevented deformation from the initial cylindrical shape but promoted collapse when the opposing tube wall came into proximity.

Boron nitride nanotubes (BNNTs), which are structural analogues of carbon nanotubes (CNTs) composed of alternating boron and nitrogen atoms, have been considered a boon to the present nanotechnology era owing to their extraordinary mechanical properties, thermal conductivity, and chemical stability. BNNTs possess an axial Young’s modulus as high as 1.3 TPa and a thermal conductivity of over 3000 W·m⁻¹·K⁻¹, which are comparable to those of their carbon counterparts. However, in contrast to CNTs, BNNTs exhibit high oxidation stability, a large chirality-independent band gap, and significant ionicity. These characteristics position BNNTs as promising candidates for various applications in high-performance fiber assemblies, composite reinforcements, electrical insulators, and hydrogen storage.

Despite their high axial stiffness, like CNTs, BNNTs are rather flexible in the radial direction, and their cross sections possess circular, peanut-like, or dumbbell-like shapes under various degrees of radial deformation. Such radial deformation has been found to markedly influence not only the intrinsic properties of BNNTs but also the performance of BNNT-based materials. Both experiments and theoretical modeling have demonstrated that radial compression can greatly reduce the resistance and band gap of BNNTs, changing them from insulators to semiconductors. The hydrogen storage capacity of BNNTs was found experimentally to increase remarkably upon deformation to the dumbbell-like shape or collapsed state, and a first-principles study also indicated that radial deformation could be used to modulate the hydrogen adsorption site on BNNTs. Moreover, radial deformation of BNNTs is also critical to their structural configuration in BNNT bundles and their assemblies. Radial collapse of BNNTs results in a greater contact area between neighboring tubes and enhances the intertube load transfer efficiency, ultimately determining the mechanical strength of BNNT fibers and BNNT-reinforced composites. As a result, radial deformation is an important issue for obtaining a complete understanding of the structural properties of BNNTs, as well as their applications.

Experimental efforts have already been made to investigate the radial mechanical properties of BNNTs. By using atomic force microscopy, Zheng et al. showed that the radial elastic moduli of single-walled BNNTs (SWBNNTs) follow a decreasing trend with increasing tube diameter and are lower than those of SWCNTs of the same size. Subsequent studies of multiwalled BNNTs then identified correlations between the radial moduli and both the diameter and number of tube layers. Nevertheless, a comprehensive understanding of the radial deformation and collapse of nanotubes requires not only experimental observations but also theoretical simulations to uncover the underlying mechanisms. Theoretical studies focused on radially deformed SWCNTs have already been successful in evaluating the effects of van der Waals (vdW) interactions on prediction of two threshold diameters (D_{meta} and D_{abs}). For SWCNTs with diameter $D < D_{abs}$, both the cylindrical and collapsed configurations can be in the equilibrium state, although the former is energetically favorable, whereas the latter is only metastable. For $D > D_{abs}$, the collapsed configuration becomes energetically favorable, whereas the cylindrical configuration is in the metastable state. Compared to CNTs, the different atom types and partially ionic nature of BNNTs make understanding their radial deformation more challenging, as both electrostatic and vdw interactions exist in the BN system. However, in contrast to the extensive studies on CNTs, to date few efforts have been made to investigate the radial mechanical properties of BNNTs and the underlying mechanisms by theoretical methods, and this represents an obstacle on the path to optimizing the performance of BNNT-based assemblies and materials. Herein, we focus on the radial deformation and stability of SWBNNTs to provide useful information for potential applications of BNNTs.

Molecular dynamics (MD) simulations were performed in this study by using the LAMMPS code with the adoption of the reactive force field (ReaxFF), which considers both the vdw and electrostatic interactions reliably by performing charge equilibration calculations. A series of armchair SWBNNTs [(11, 11) and (5n,5n), $n = 3–8$] with radii ranging from 0.76 to 2.77 nm were investigated. Periodic boundary conditions in the axial direction were used in all of the calculations. The cylindrical and collapsed minimum...
configurations were first obtained using the damped dynamics geometry optimization algorithm. An initial estimate for the collapsed SWBNNT configuration was acquired in the same way as in previous studies on collapsed SWCNTs.\textsuperscript{21)} By performing nudged elastic band (NEB) calculations with the optimized cylindrical and collapsed configurations of SWBNNTs, the minimum energy pathway (MEP) between the two local energy minima was identified. In this method, the elastic band is discretized into replicas that connect the two end states, and the spring constants at each replica are carefully chosen to eliminate the sliding-down problem. The energies as well as a detailed view of the collapse process can thus be obtained for further analysis.

The energy profiles along the collapse MEP of (25, 25) SWBNNTs are shown in Fig. 1 (the energy variations of the other tubes are not shown here for clarity). It is expected that the total energy increases in the initial stage of radial deformation and begins to decrease in the transition state, which was also observed in the deformation of SWCNTs.\textsuperscript{1,20,21)} To clarify the effects of vdW and electrostatic interactions, their energy profiles are illustrated in Fig. 1, as well as the bending energy arising from bending deformation of the cross section from the cylindrical shape. It was found that the bending energy always increases and represents the absolute majority of the total energy before the transition state, suggesting that the radial rigidity of SWBNNTs comes mainly from bending of the tube walls. Although the long-range vdW and electrostatic interactions play a minor role in deformation from the initial state to the transition state, it is interesting to note that they make opposite contributions to the total energy; the vdW interaction decreases, whereas the electrostatic interaction increases. In other words, the electrostatic interaction strengthens the radial rigidity of the SWBNNT, whereas the vdW interaction has the opposite effect. The reason for the differences between the vdW and electrostatic interactions will be further discussed in the following part. When radial deformation continues after the transition state, the energies of both the vdW and electrostatic interactions decrease because the opposing walls come into close proximity and attract each other to stick together.

To investigate the effect of the radius on the deformation properties of SWBNNTs, the energy barrier \( E_b \) and the energy difference between the initial cylindrical and final collapsed states \( E_d \) were recorded and are shown in Figs. 2 and 3, respectively. The inset in Fig. 2 graphically illustrates the definitions of \( E_b \) and \( E_d \). It was found that \( E_b \) decreased with increasing SWBNNT radius, as shown in Fig. 2. This implies that a SWBNNT with a larger radius collapses more easily, which is consistent with the experimental result that the rigidity of SWBNNTs follows a decreasing trend with increasing tube radius.\textsuperscript{18)} The relationship between the energy barrier \( E_b \) and the SWBNNT radius \( R \) can be fitted by the equation \( E_b = 8.36R^{1.77} \). This fitting equation was obtained from the continuum model in our previous study.\textsuperscript{20)} The equation provides an explicit formula for predicting the deformation barrier that needs to be overcome to obtain a collapsed SWBNNT from the initial cylindrical configuration. Moreover, because the collapse process induced by hydrostatic pressure of a reasonable magnitude closely resembles the passage along the MEP,\textsuperscript{21)} the calculated energy barriers here are also sufficient to estimate the magnitude of hydrostatic pressure necessary to initiate the collapse of SWBNNTs.

As mentioned above, there exist two critical threshold diameters for SWCNTs, which should also be expected to exist for radially deformed SWBNNTs. To obtain the values of \( D_{\text{meta}} \) and \( D_{\text{hub}} \) for SWBNNTs, the collapsed configurations of SWBNNTs with different radii were further investigated. As shown in the inset in Fig. 3, the collapsed SWBNNTs exhibit a dumbbell-like cross section composed of a flat contact zone and two bulbs at the ends. The distance
between the flattened faces, \(d \approx 0.31 \text{ nm}\), is approximately 10% smaller than the vdW equilibrium distance (0.34 nm), indicating that the electrostatic interaction contributes additional attractive forces to the vdW interaction in the contact zone. The parameter \(L_f\) corresponds to the length of the flat contact zone. The circular dots in Fig. 3 illustrate the relationship between \(L_1\) and the SWBNNT radius; it is clear that \(L_f\) increases linearly with increasing SWBNNT radius. By assuming that the circumference remains unchanged in the course of radial transformation, \(L_f\) can be expressed in the form \(L_f = \pi R - a\).\(^{20}\) Fitting of our simulation results gave a relationship of \(L_f = \pi R - 2.29\), indicating a critical point of \(R_c1 = 0.73 \text{ nm}\). The calculation for a tube with a radius smaller than 0.73 nm results in a negative value of \(L_f\), which is obviously physically unreasonable, indicating that a collapsed configuration does not exist for SWBNNTs with a diameter \(D < D_{meta} = 2R_c1 = 1.46 \text{ nm}\).

After the value of \(D_{meta}\) was determined, the value of \(D_{abs}\) was then considered by evaluating the dependence of \(E_d\) on the SWBNNT radius, as shown by the squares in Fig. 3. It was found that for SWBNNTs with small radii, such as (11,11) and (15,15), \(E_d\) is positive, which means that the collapsed state is a metastable state. When the SWBNNT radius exceeds a critical value denoted as \(R_{c2}\), for example, in the (35,35) and (40,40) SWBNNTs, \(E_d\) becomes negative, and the collapsed configuration is energetically more stable than the cylindrical state. To explicitly determine the value of \(D_{abs} (= 2R_{c2})\), the relationship between the energy difference \(E_d\) and the radius \(R\) was also fitted to give \(E_d = -7.46 - (1.87R - 16.20/R)\) on the basis of the continuum model in the previous study.\(^{20}\) By assigning \(E_d\) the value of zero, \(D_{abs}\) was then determined to be 3.12 nm.

It is interesting to note that the calculated values of \(D_{meta}\) (1.46 nm) and \(D_{abs}\) (3.12 nm) for SWBNNTs are both smaller than those for SWCNTs, which were reported as 2.2–2.7 and 4.1–6.0 nm, respectively, in various previous studies.\(^{11,20,21}\) This difference between SWBNNTs and SWCNTs found in our simulation is in line with the experiments of Zheng et al., which revealed that the radial elastic moduli of SWBNNTs are lower than those of SWCNTs with the same diameters.\(^{18}\)

To evaluate their contributions to the collapse of SWBNNTs, the vdW and electrostatic interaction energy differences (\(E_d^{vdW}\) and \(E_d^{ele}\)) were calculated, and they are shown in Fig. 4. It can be seen that both \(E_d^{vdW}\) and \(E_d^{ele}\) decrease with increasing SWBNNT radius. However, there are two major differences between \(E_d^{vdW}\) and \(E_d^{ele}\). First, the magnitude of \(E_d^{vdW}\) is much greater than that of \(E_d^{ele}\). Taking the (40,40) SWBNNT with a radius of 2.77 nm as an example, the value of \(E_d^{vdW}\) is \(-11.02\text{ meV/atom}\), whereas \(E_d^{ele}\) is only \(-1.75\text{ meV}\). This should be attributed to the different properties of the vdW and electrostatic interactions. For the collapsed SWBNNTs, the atoms in one of the two flattened faces, whose separation distance is 0.31 nm, attract all of the atoms in the other one through the vdW interaction. In contrast, both attractive and repulsive forces are simultaneously present for atoms between the two flattened faces through the electrostatic interaction, as the boron and nitrogen atoms are alternately arranged, which greatly reduces the overall interaction strength between the two flattened faces. It should be pointed out that the overall electrostatic interaction in the flattened contact zone is still attractive, which could be expected because the separation distance of 0.31 nm is smaller than the vdW equilibrium distance (0.34 nm), and the \(E_d^{ele}\) value for SWBNNTs with radii greater than 1.38 nm is negative.

For the SWBNNTs with radii under 1.38 nm, another difference can be found between the vdW and electrostatic interactions; the value of \(E_d^{vdW}\) remains negative, whereas \(E_d^{ele}\) is positive. As both the vdW and electrostatic interactions are favorable for contact of the flattened faces in a collapsed SWBNNT, it is thus necessary to clarify the underlying mechanism of the change of \(E_d^{ele}\) from positive to negative with increasing radius. The positive electrostatic interaction arises from interaction between atoms with the same type of charge, the strength of which is determined mainly by the interaction distances in this study, because the magnitudes of the charges are found to be almost constant during the deformation process. To investigate the difference in the repulsive electrostatic interaction before and after the collapse, the radial distribution function \([g(r)]\) of the boron atoms in the (20,20) SWBNNT, whose \(E_d^{ele}\) is around zero, was then calculated, as shown in Fig. 5. The \(g(r)\) value for the nitrogen atoms is the same. The radial distribution function was plotted for radial distances smaller than 0.50 nm because the strength of the electrostatic interaction decays rapidly with increasing interaction distance. As shown in Fig. 5, there are two peaks located at 0.25 and 0.44 nm for the cylindrical state, which correspond to the distances between a boron atom and its nearest and next-nearest neighboring boron atoms within the tube wall, respectively.
However, there are also two additional peaks located at 0.34 and 0.42 nm for the collapsed SWBNNT. It was found that the 0.34 nm peak represents the nearest distance between boron atoms within the two flattened faces in the contact zone, whereas the 0.42 nm peak is related to the next-nearest distance at the two bulb ends, as shown by the inset in Fig. 5.

For the flattened atoms in one of the two flattened faces, their nearest nitrogen atoms within the other face are located at a distance of 0.31 nm, resulting in an attractive force to offset the repulsive interaction between the boron atoms. Thus, there exists an overall negative electrostatic interaction in the flattened contact zone of a collapsed SWBNNT. However, for the boron atoms in the bulb ends, their repulsive electrostatic interaction cannot be offset because the attractive distances in the end zone are about 0.54 nm, leading to an overall positive electrostatic energy. As a result, when the flattened part of a collapsed SWBNNT is small, the value of $E_{\text{ff}}^{d}$ is positive and decreases continuously with increasing length of the flattened contact zone or SWBNNT radius. Considering the positive effect of the electrostatic interaction on the radial rigidity of an SWBNNT, it is now clear that the electrostatic interaction plays two opposing roles in radial deformation of an SWBNNT. The electrostatic interaction prevents deformation of the SWBNNT from its equilibrium cylindrical shape but promotes its collapse when the opposing tube wall comes into close proximity.

Finally, the radial deformation of a zigzag SWBNNT (70, 0) and a chiral SWBNNT (50, 30) with diameters nearly the same as that of the armchair SWBNNT (40, 40) were also studied to reveal the effects of chirality. The energy profiles along the collapse pathway of the three tubes are shown in Supplementary Fig. S1. It was found that the energy barriers $E_{b}$ of all three SWBNNTs are almost identical at 1.34 meV/atom, suggesting that $E_{b}$ is insensitive to the chirality. Nevertheless, the chiral SWBNNT has a smaller energy difference $E_{\text{ff}}^{d}$ than the other two SWBNNTs, whose $E_{b}$ values are almost the same. Because $E_{b}$ is closely related to the interlayer properties in the flattened contact zone, as mentioned above, the atomic arrangements and corresponding interlayer interaction of the three collapsed SWBNNTs were then investigated. It was found that atoms in the flattened part of the collapsed armchair and zigzag SWBNNTs stay uniformly in the AA’ and AB stacking modes, respectively, whereas the stacking of the collapsed chiral tube is random (insets in Fig. S1 in the online supplementary data http://stacks.iop.org/APEX/10/105001/mmedia). The AA’ and AB stacking arrangements are nearly the same in terms of energetics because their calculated binding energy difference is within 1%, leading to similar $E_{b}$ values. Nevertheless, as shown in Fig. S2 in the online supplementary data http://stacks.iop.org/APEX/10/105001/mmedia, the binding energies of randomly stacked tube walls are higher than those of tubes with AA’ and AB stacking. Therefore, it is not surprising that the magnitude of the $E_{b}$ value of the chiral SWBNNT is smaller than those of the armchair and zigzag tubes.

In summary, by using the NEB algorithm in the framework of MD, we identified three stability regimes for armchair SWBNNTs under radial deformation. The regimes are divided by two threshold diameters, $D_{\text{meta}}$ and $D_{\text{pbo}}$, which are 1.46 and 3.12 nm, respectively. For SWBNNTs with diameters smaller than 1.46 nm, only cylindrical configurations are stable; for SWBNNTs with diameters between 1.46 and 3.12 nm, the collapsed configurations are metastable, but the cylindrical configurations are energetically favorable; and for SWBNNTs with diameters larger than 3.12 nm, the fully collapsed configurations become energetically stable, whereas the cylindrical configurations are metastable. The transition state barriers were found to decrease with increasing tube radius, and this relationship can be represented by a simple formula. The effects of the vdW and electrostatic interactions on radial deformation of SWBNNTs were also investigated. Both interactions introduce attractive forces that cause the opposing flattened walls in a collapsed SWBNNT to stick together, although the vdW interaction makes the major contribution to the interaction strength. Nevertheless, the electrostatic interaction also prevents deformation of the SWBNNT from its cylindrical shape and strengthens the radial rigidity. The results and discussion in this study are useful not only for understanding the radial mechanical properties of SWBNNTs observed in previous experiments but also for optimizing the performance of BNNT-based materials and assemblies, such as load transfer in BNNT fibers and BNNT-reinforced composites.

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