Evaluation of Nonuniform Strain in Carbon Nanotube with Bend Junction*

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Abstract
Carbon nanotubes (CNTs) have been attracting attention because of their prominent mechanical and electronic properties. In this study, we investigate the deformation of single-walled carbon nanotubes (SWCNTs) with a bend junction using molecular dynamics in order to analyze strain concentration due to the tube shape (macroscopic effect) and the membered ring shape (microscopic effect). At first, we propose a method for evaluating the local strain at each membered ring. Then, we analyze the strain concentration at the bend junction due to the both of macroscopic and microscopic effects. The strain concentration caused by the microscopic effect is separated by a rough analysis; and it is about 1.5 times higher than that caused by the macroscopic effect.

Key words : Computational Mechanics, Molecular Dynamics, Tensile Properties, Carbon Nanotube, Bend Junction, Strain Concentration

1. Introduction

The carbon nanotube (CNT) has been attracting attention as a new material with nano-scale structures(1)-(4). The CNT is a hollow tube made by rolling up a graphene sheet, and consists of six-membered rings. The CNT has superior mechanical strength(5), high chemical stability and anomalous electric properties of different conductivity depending on its diameter and pitch angle. Furthermore, the properties change due to the deformation(6)-(7). Since the arrangements of five and seven-membered rings enable many structures, including a bend junction(8), the CNT has high applicability for nano components. Therefore, evaluation of its mechanical properties is important(9)-(12).

Since strain is a fundamental parameter in the evaluation of mechanical properties in macroscopic structures, there have been many attempts to evaluate the strain in atomic-scale structures in order to discuss their behavior(13)-(15). In particular, it is inevitable to study non-uniformity in the deformation of atomic-scale structures. This is because non-uniform parts exist in materials or structures in general and strain concentration causes fracture.

For macroscopic structures, analyses based on continuum mechanics have shown that the strain concentrates near junctions(16)-(20). In other words, the macroscopic structure (component shape) brings about non-uniform strain. On the other hand, CNTs not only have a macroscopic non-uniform structure but also a microscopic one, where atomic arrangements are different from other regions. Therefore, the strain concentration in atomic-scale structures is caused by both macroscopic and microscopic effects.

In this study, a single-walled CNT (SWCNT) with a bend junction was selected to analyze non-uniform strain caused by macroscopic and microscopic effects. We propose a method for evaluating the local strain, and we evaluate the non-uniform strain due to the macroscopic and microscopic non-uniform structures.
2. CNT with a bend junction

2.1. Basic structure of CNT

Figure 1 schematically shows a graphene sheet. The structure of a CNT, which is made by rolling up a graphene sheet, is uniquely represented by the chiral vector. The chiral vector \( C_v \) is defined as a vector connecting the starting and ending points of the circumference of the CNT, which is described in terms of the unit vectors \( a_1 \) and \( a_2 \) of the two-dimensional hexagonal lattice:

\[
C_v = m a_1 + n a_2 \equiv (m, n) \quad (1)
\]

where \( m \) and \( n \) are integers. The nanotube diameter \( d \) and chiral angle \( \theta \) are given by

\[
d = \frac{\sqrt{3} a \sqrt{m^2 + mn + n^2}}{\pi} \quad (2)
\]

\[
\theta = \tan^{-1} \frac{\sqrt{3} n}{2m + n} \quad (3)
\]

where \( a \) is the nearest interatomic distance. The armchair \((m = n, \theta = 30^\circ)\) and zigzag \((n = 0, \theta = 0^\circ)\) CNTs have a characteristic structure showing no helicity.

2.2. CNT with a bend junction

A CNT with a bend junction is produced by connecting two different nanotubes. The bend angle \( \phi \) can be related to the chiral angles of the two tubes \( \theta_1 \) and \( \theta_2 \) as:

\[
\phi = |\theta_1 + \theta_2| \quad (4)
\]

This indicates that a zigzag CNT and an armchair CNT always make a 30° bend. Figure 2 shows the simulation model used in this study. The model consists of an \((8,8)\) armchair CNT and a \((14,0)\) zigzag CNT because these two CNTs have almost the same diameter; 1.084 nm and 1.096 nm for the \((8,8)\) and \((14,0)\) CNTs, respectively. The former is arranged parallel to the \( z \)-axis and the latter is rotated 30° clockwise from the \( z \)-axis. Due to the geometric restriction, five and seven-membered rings are introduced at the inside and outside of the bend junction. Although there are many bend junction models formed by connecting other CNTs, the above is selected as a fundamental example because (i) the armchair and zigzag CNTs are simple and typical CNTs, and (ii) a bend junction can be stabilized naturally by few five and seven-membered rings. As shown in the figure, the length from the bend corner to the lower end is 4.047 nm and that from the bend corner to the upper end is 3.943 nm. The model contains 1068 carbon atoms. The nearest interatomic distance of the graphene sheet is set to 0.142 nm based on an experimental result, and the initial atomic positions of the model are determined by rolling up the sheet.
3. Simulation procedure

3.1. Tensile simulation

The atomic positions under a no external load condition are determined by structural relaxation using molecular dynamics. The Brenner potential, which is popular in the study of CNTs, is adopted in the simulations. After the temperature is controlled to be 5 K by the velocity scaling scheme for the initial 1200 steps, the simulation is continued for 228,000 steps removing kinetic energy every 5 steps. The verlet algorithm is used for the numerical integration under the time step of 1 fs. Then, as shown in Fig. 2, a load increment, $\Delta f = 0.2$ nN, is applied to 14 atoms at the upper end while the lower end is fixed, and it is relaxed by the molecular dynamics technique. During the structural relaxation of 50,000 steps under each load, the kinetic energy is removed when the temperature reaches 1 K. The tensile simulation is conducted up to the applied load of 1.0 nN by repeating the loading/relaxation process.

3.2. Evaluation method of local strain based on linear interpolation equations of displacements

Since the CNT mainly consists of six-membered rings and the deformation of the CNT can be assumed to be the accumulation of those of the rings, we analyze the strain of each ring.

In order to define the strain, the stable state under no external load is defined as the reference state ($\varepsilon = 0$) in this study.

Cylindrical coordinates are used because the CNT has cylindrical geometry. A loop composed of six-membered rings, shown in Fig. 3(a), is defined as a group. The centers of the membered rings in the group are determined (Fig. 3(a)), and the plane $\alpha$ where the centers are on is fixed by the least squares method (Fig. 3(b)). The axial direction is defined as the normal of the plane $\alpha$, and the radial and circumferential directions are determined by the circle passing through the centers of the membered rings (Fig. 3(c)).

As shown in Fig. 4, a membered ring is divided into triangular elements connecting the neighboring vertices, 123, 234, ..., and 612. Since the membered ring can be regarded to be an infinitely thin plate, the displacements in the element, $u_r$, $u_\theta$, and $u_z$, are expressed as a function of only $\theta$ and $z$. Therefore, we approximate the displacements at $(r, \theta, z)$ in each
triangular element using the following linear equations:

\[ u_r(\theta, z) = c_1 + c_2 \theta + c_3 z \]  
\[ u_\theta(\theta, z) = c_4 + c_5 \theta + c_6 z \]  
\[ u_z(\theta, z) = c_7 + c_8 \theta + c_9 z \]  

which are interpolation of displacement often used in an element of FEM (Finite Element Method) analysis. Here, \((r_0, \theta_0, z_0)\) and \((r, \theta, z)\) are the coordinates before and after the deformation, respectively. Taking the triangular element 123 as an example (Fig. 4), the constants \(c_1, \ldots, c_9\) are determined by substituting six coordinates of nodes, \(\theta_1, z_1, \ldots, \theta_3, z_3\), and nine displacements of nodes, \(u_{1r}, u_{1\theta}, u_{1z}, \ldots, u_{3z}\), into Eqs. (5)–(7). The displacements of the node are given by

\[ u_r = r - r_0 \]  
\[ u_\theta = r_0(\theta - \theta_0) \]  
\[ u_z = z - z_0 \]

The strain of each triangular element is determined by:

\[ \varepsilon_{ij} = \frac{1}{2}(u_{ij} + u_{ji} + u_{ik}u_{kj}) \]  

and Eq. (11) is expanded in the cylindrical coordinate system as follows:

\[ \varepsilon_r = \frac{\partial u_r}{\partial r} + \frac{1}{2}\left(\left(\frac{\partial u_r}{\partial r}\right)^2 + \left(\frac{\partial u_\theta}{\partial r}\right)^2 + \left(\frac{\partial u_z}{\partial r}\right)^2\right) \]  
\[ \varepsilon_\theta = \frac{1}{r}\left(\frac{u_r}{r} + \frac{\partial u_\theta}{\partial \theta}\right) + \frac{1}{r^2}\left(\frac{\partial u_r}{\partial \theta} - \frac{u_\theta}{\partial \theta}\right) + \frac{1}{r^2}\left(u_r^2 + u_\theta^2 + \frac{\partial u_r}{\partial \theta} + \frac{\partial u_\theta}{\partial \theta}\right) \]  
\[ \varepsilon_z = \frac{\partial u_z}{\partial z} + \frac{1}{2}\left(\left(\frac{\partial u_z}{\partial z}\right)^2 + \left(\frac{\partial u_\theta}{\partial z}\right)^2 + \left(\frac{\partial u_r}{\partial z}\right)^2\right) \]
Finally, the strain of each membered ring is evaluated as the average among the triangular elements in the ring. For example, the strain, $\varepsilon_z$, of a six-membered ring is expressed by the following equation:

$$
\varepsilon_z = \frac{1}{6} \left[ \varepsilon_{123}^{123} + \varepsilon_{234}^{234} + \varepsilon_{345}^{345} + \varepsilon_{456}^{456} + \varepsilon_{561}^{561} + \varepsilon_{612}^{612} \right]
$$

The above method is based on the continuum approximation in which the CNT consists of infinite thin plates. As the Brenner potential is a three-body one, the energy is described by the distance and angle between atoms within the cut-off radius $r_c (= 0.2 \text{ nm})$. Figure 5 shows the relationship between the cut-off and a six-membered ring of the CNT. Since the nearest
interatomic distance of the CNT is 0.142 nm, the bond length, $r_{\alpha\beta}$ and $r_{\alpha\gamma}$, and angle, $\beta_{\alpha\gamma}$, are the basic units for evaluating the energy of the CNT by the Brenner potential. This unit $a\beta\gamma$ corresponds to the triangular element in Fig. 4. Therefore, the above method implicitly includes the three-body effect of the bond length and angle. The strain evaluated by this method contains the macroscopic strain due to the whole shape (tension of the bent tube) and the microscopic one caused by the atomic positions (arrangement of membered rings). In the next section, we discuss the strain at the bend junction focusing on the macroscopic and microscopic effects.

4. Results and discussion

Figure 6 shows the change in the distribution of the axial strain, $\varepsilon_z$. The strain smoothly increases from the outside to the inside of the CNT. High tensile strain concentrates at the inside of the bend junction while the outside of the bend junction is highly compressed. These are caused by the macroscopic non-uniform structure (deformation of the bent tube). Note that two rings at the inside of the bend junction (seven-membered rings) show a higher strain compared to the neighboring rings. At the inside of the bend junction, a large deformation occurs around the seven-membered rings, and the high strain region disperses thorough the CNT with increasing applied load. Figure 7 magnifies the inside and outside of the bend junction shown in Fig. 6. The six-membered ring located between the seven-membered rings
at the inside of the bend junction has high strain as well as the seven-membered rings. This means that the microscopic non-uniform structure of the seven-membered ring affects the neighboring rings and causes strain concentration. On the other hand, at the outside of the bend junction, the strain at each ring is almost zero. The tensile load and bending moment act on the CNT (Fig. 2), and the bending moment compresses the outside of the bend junction and negates the tensile load. Thus, the strain at the outside of the bend junction becomes almost zero.

Figure 8 shows the change in the distribution of the circumferential strain, $\varepsilon_\theta$. Compressive strain concentrates at the inside of the bend junction with increasing applied load while a high tensile strain region is observed at the outside of the bend junction. Figure 9 magnifies the inside and outside of the bend junction shown in Fig. 8. At the inside of the bend junction, the strain at the seven membered rings increases with increasing applied load. On the other hand, at the outside of the bend junction, the seven-membered ring has the highest tensile strain, and five and six-membered rings located around the seven-membered ring also show high strain. This indicates that the circumferential strain, $\varepsilon_\theta$, also shows strain concentration due to the microscopic non-uniform structure.

Figure 10 shows the change in the distribution of the shear strain, $\varepsilon_r\theta$. The strain at the inside and outside of the bend junction is large while that at other regions is almost zero. Figure 11 magnifies the inside and outside of the bend junction shown in Fig. 10. At both the inside and outside of the bend junction, the strain increases with distance from the inside.
or outside. However, under the load of 0.4 nN or greater, the seven-membered rings and the six-membered rings located below them do not conform to this tendency and have high strain. This is due to the microscopic non-uniform structure.

A rough analysis was conducted to decide the macroscopic and microscopic effects. Figure 12 shows the axial strain along the inside of the CNT under the load of 0.2 nN. The dashed-line indicates the strain distribution evaluated by the method proposed in this study, which contains both the macroscopic effect (bent tube) and the microscopic effect (five and seven-membered rings). The solid line indicates the strain distribution calculated by a simple cantilever with a bend junction with a fixed end and a free end under load. As the cantilever has a similar shape to the CNT, the strain distribution shows only the macroscopic effect. Although more detailed analysis is possible by FEM, we use a simple analysis here because the continuum approximation near the bend junction is arbitrary. The dashed-line shows a much larger value compared to the solid-line near the bend junction ($z = 4.0$ nm), which is due to the microscopic effect of the five and seven-membered rings. Although the macroscopic effect is not exact, the microscopic effect is estimated to be 1.5 times larger than the macroscopic effect.

5. Conclusions

In this study, we have proposed a method for evaluating the local strain in a carbon nanotube (CNT) and have analyzed the strain concentration at a bend junction. The results are summarized as follows:

(1) A method for evaluating the local strain based on linear interpolation equations of displacements has been proposed, wherein five, six and seven-membered rings are divided into triangular elements. Then, the strain of each triangular element is obtained by the displacements of the nodes in the element. The strain of the membered ring is evaluated as the average among the triangular elements in the ring.

(2) A load is applied on an end of a CNT with a bend junction (8,8)/(14,0) while the other end is fixed. Strain concentration occurs at the bend junction due to the macroscopic non-uniform structure (whole shape) and the microscopic one (disarray of atoms).

(3) The axial strain, $\varepsilon_z$, concentrates at the inside and outside of the bend junction. $\varepsilon_z$ is high at two seven-membered rings at the inside of the bend junction and it is high even at the six-membered ring located between the seven-membered rings.

(4) The strain distribution of the CNT is due to both macroscopic and microscopic effects. A cantilever, which imitates the approximated shape of the CNT, gives the strain concentration due to the macroscopic effect. The comparison clarified that the strain concentration caused by the microscopic non-uniform structure is about 1.5 times larger than that by the
macroscopic one.

References