VERIFICATION OF THE ACCURACY OF ANALYTICAL MODELS OF HYDROSTATICALLY PRESSURIZED BUCKLING OF SINGLE- AND MULTI-WALLED CARBON NANOTUBES

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Abstract- This study focuses on the analysis of cross-sectional deformations of single- and multi-walled carbon nanotubes through molecular dynamics (MD) simulations. Shell theory is valid only within the linear elastic region, and cannot be considered to deal with large deformation behaviours beyond elastic approximation. Against this backdrop, we performed molecular dynamics simulations to explore buckling behaviour of carbon nanotubes under high pressure. We confirmed various large-amplitude deformation modes, in which the stable mode is strongly dependent on the diameter of the innermost tube and the number of concentric walls. In corrugation patterns, the cylindrical symmetry of the innermost tube is maintained even under high external pressure, while cylindrical symmetry is lost as deformation progresses. In addition, we quantitatively compared the critical pressure from MD simulations and continuum elastic approximation.

Keywords- Carbon Nanotube, Molecular Dynamics Simulation, Thin Shell Theory Analysis, Cross-Sectional Buckling, Radial Corrugation.

II. INTRODUCTION

A carbon nanotube (CNT) consists of a graphene sheet (two-dimensional hexagonal lattices of carbon atoms) rolled up into a cylinder. CNTs are one of the most promising nanomaterials and have excellent mechanical properties such as extremely high elastic modulus and tensile strength. For example, the Young's modulus of nanotubes is estimated to be on the order of terapascals (i.e., several times stiffer than steel) and the tensile strength is as high as tens of gigapascals. On the other hand, carbon nanotubes are known to have remarkable flexibility when subjected to external hydrostatic pressure and bending force. Hence, CNTs have applications in many devices such as sport products, IC chips, and nanofibres.

Therefore, precise knowledge of the deformation mechanism and available geometry of CNTs is crucial for understanding the precise physics and developing nanotube-based applications. Shima and Sato carried out simulations based on the thin cylindrical shell theory to predict the occurrence of wavy carbon nanotubes [1]. However, shell theory is valid only within the linear elastic region, and cannot be applied for discussing large deformation behaviours that are beyond elastic approximation.

In this study, we carried out atomistic modelling analyses to investigate the behaviour of corrugating deformation in relatively small multi-walled carbon nanotubes (MWCNTs) for which the continuum approximations may break down. We performed molecular dynamics (MD) simulations earlier to explore the buckling behaviour in the cross-section of carbon nanotubes under high pressure. In this work, we demonstrated a novel radial deformation, called the radial corrugation [2] , of MWCNTs numerous concentric walls under hydrostatic pressure. We confirmed various large-amplitude deformation modes in which the stable mode depended strongly on the tube diameter D and the number of concentric walls N.
In addition, we determined the critical pressure for the MD simulation and continuum elastic approximation by varying the innermost tube diameter and the number of walls, N = 1–3 while keeping the innermost tube diameter fixed. We quantitatively compared.
the critical pressure for the MD simulation and continuum elastic approximation. The results provide useful information for developing nanofluidic or nanoelectrochemical devices whose performances depend crucially on the geometry of the inner hollow cavity of the nanotubes.

II. ANALYTICAL MODEL

The stable cross-sectional shape of single-walled carbon nanotubes (SWCNTs) and MWCNTs under hydrostatic pressure P can be evaluated precisely through MD simulations of cylindrical walls. In this study, we dealt with CNTs with concentric zigzag-type tubes; each wall of a CNT was represented by a chiral vector of (m, 0). The CNTs were arranged with the tube axis parallel to the z axis. The dimension of the simulation box along the z axis was unit length along the tube axis (4.26 Å), and periodic boundary condition was imposed only in the z direction.

2.1. Buckling Behaviour through MD Simulations for MWCNTs

Figures 1, 2, and 3 show the cross-sectional view, side view, and overhead view of the chiral vector (m, 0) = (9,0)/(18,0)/(27,0)/(36,0). We performed MD simulations to explore the buckling behaviour in the cross section of CNTs under hydrostatic pressure.

2.2. Quantitative Comparison of Critical Pressure in the Innermost Tube of Fixed Diameter

Table 1 lists the chiral vectors and cross-sectional views of the analytical models. We compared the critical pressure for MD simulations and continuum elastic approximation quantitatively for N = 1–3 with constant innermost tube diameter.

III. FORMULATION

MD simulation is an atomistic simulation method that evaluates material characteristics by means of the position and velocity data of moving atoms. In MD simulations, atoms are considered as particles that follows Newtonian mechanics. Equation (1) is the kinematic equation of each of the N atoms. These atoms move under the influence of forces exerted by others. Thus, the radial deformation and more accurate critical pressure can be determined than that possible by the continuum elastic approximation.

$$\frac{d^2 r_i}{dt^2} = \frac{F_i}{m_i} \quad i = 1,2...,N \qquad (1)$$

Equation (1) represents the simultaneous second order ordinary differential equation in a three-dimensional space.

The structural relaxation of the MWCNTs under hydrostatic pressure was simulated by the MD calculation scheme; that is, the Newtonian equation of motion of atoms was numerically solved using the Verlet method.

$$r_i(t+\Delta t) = 2r_i(t) - r_i(t-\Delta t) + (\Delta t)^2 \frac{F_i(t)}{m_i} \qquad (2)$$

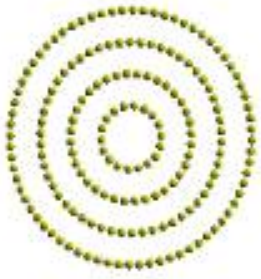


Fig.1. Cross-sectional view of (m, 0) = (9,0)/(18,0)/(27,0)/(36,0)

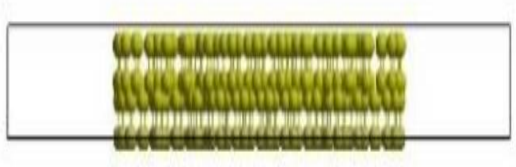


Fig.2. Side view of (m, 0) = (9,0)/(18,0)/(27,0)/(36,0)

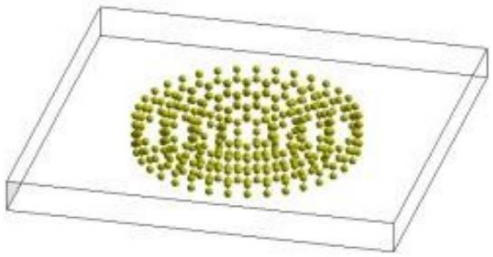
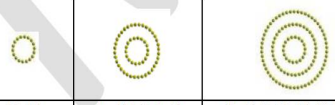
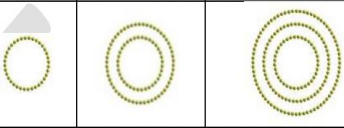
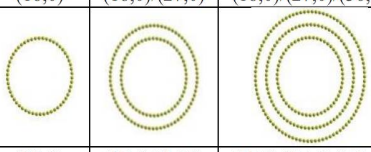


Fig.3. Overhead view of (m, 0) = (9,0)/(18,0)/(27,0)/(36,0)

Table 1: Chiral vectors and cross-sectional views of analytical models

Innermost tube diameter: D (nm)	Number of concentric walls: N		
	1	2	3
0.694			
	(9,0)	(9,0)/(18,0)	(9,0)/(18,0)/(27,0)
1.409			
	(18,0)	(18,0)/(27,0)	(18,0)/(27,0)/(36,0)
2.110			
	(27,0)	(27,0)/(36,0)	(27,0)/(36,0)/(45,0)

$$v_i(t) = \frac{1}{2\Delta t}\{r_i(t+\Delta t) - r_i(t-\Delta t)\} \qquad (3)$$

For atom i, the position vector is represented by ri, and the velocity by vi.

where Δt is the time step.

The positions and velocities of particles were determined using equations (2) and (3). In this study, we considered Brenner potential as the interatomic potential for SWCNTs and AIREBO (adaptive intermolecular reactive empirical bond order) potential for the MWCNTs [3−4]. AIREBO potential accommodates covalent and non-covalent bonds.

IV. RESULTS AND DISCUSSION

4.1. Buckling Behaviour through MD Simulations for MWCNTs

Figure 4 shows a cross-sectional view of the buckling behaviour of (m, 0) = (9,0)/(18,0)/(27,0)/(36,0). The mode index n indicates the wave number of the deformation mode along the circumference. The outer walls show significant radial corrugation (n = 4) along the circumference, while innermost tube maintains its cylindrical symmetry (Fig. 4 (b)). The cylindrical symmetry of the innermost tube is maintained even under high pressure that causes buckling of the CNTs, but it is disrupted as deformation progresses. We attribute large deformations (drop shape: Fig. 4 (d)) to the concentration of deformed parts after buckling.

Figure. 5 shows a phase diagram of the radial deformation modes observed above Pcr on N = 1–4 with the innermost diameter D = 0.694–2.110nm. In this figure, larger D and smaller N values tend to correspond to elliptic modes (n = 2). This also indicates that smaller D and larger N values yield higher corrugation models (n>3). Various corrugation modes were obtained depending on the values of D and N. Our results were consistent with the predictions of the continuum elastic approximation model in that the number of corrugation modes tends to decrease with decreasing D and N. A quantitative examination of the present results through sophisticated atomistic simulations may provide a better understanding of the corrugation properties of MWCNTs.

4.2. Quantitative Comparison of Critical Pressure in the Innermost Tube of Fixed Diameter

Figure. 6 shows Pcr as a function of N for various D values. The solid line corresponds to MD simulation results, and the dotted line, the results of the continuum elastic approximation. The critical pressure decreases as the innermost tube diameter increases in both MD simulation and continuum elastic approximation. Further, the critical pressure obtained from MD simulation and continuum elastic approximation agree well with each other for N = 2 and 3.

CONCLUSIONS

Multiple radial corrugations peculiar to MWCNTs under hydrostatic pressures were studied, and the main conclusions are as follows:

1. In terms of corrugation patterns, the cylindrical symmetry of the innermost tube was maintained even under high pressure that caused buckling of CNTs, but the symmetry was broken as deformation progressed.
2. A phase diagram was plotted to obtain the requisite values of N and D for a desired corrugation mode.
3. The critical pressure values obtained by MD simulations and continuum elastic approximation agreed well for N = 2 and 3.
4. The critical pressure decreased as the innermost tube diameter increased in MD simulation and continuum elastic approximation.

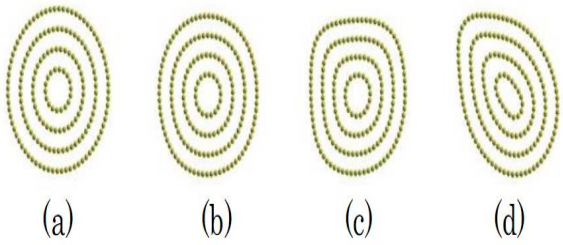


Fig.4. Buckling behaviour of (m, 0) = (9,0)/(18,0)/(27,0)/(36,0)

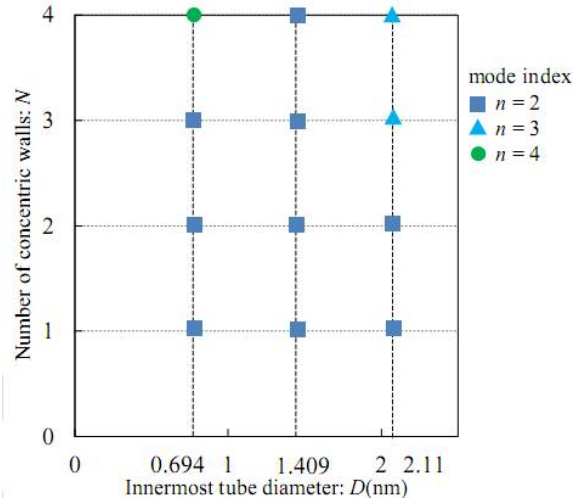


Fig.5. Phase Diagram

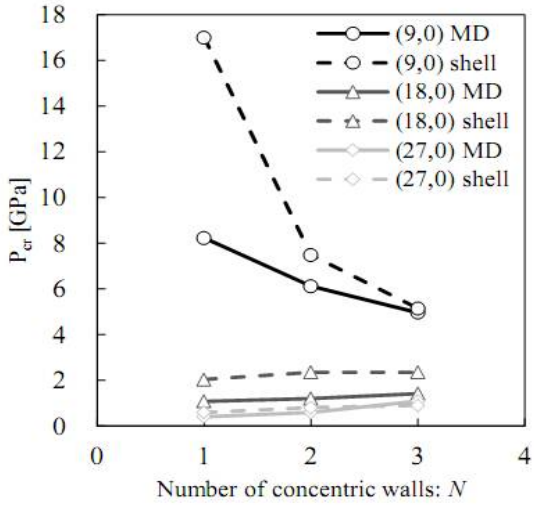


Fig.6. Critical Pressure

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