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Relationship between local buckling and atomic elastic stiffness in multi-walled carbon nanotubes under compression and bending deformations

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ABSTRACT

This paper discusses unified criteria for the local buckling of multi-walled carbon nanotubes in both compression and bending deformations from a standpoint of atomic simulations. Defective and non-defective five-walled carbon nanotubes are subjected to compression and bending deformation by the molecular dynamics method using the adaptive intermolecular reactive empirical bond order potential. The atomic elastic stiffness of each atom, B_{ij}^{α}, is then evaluated during the deformations to discuss the onset of local buckling. The B_{ij}^{α} corresponds to the second-order derivatives of the atomic energy, *i.e.*, the gradient of the local stress–strain surfaces in six-dimensional strain space. If B_{ij}^{α} has a negative eigenvalue, a local unstable path will exist in the direction of the strain. Under compression, the smallest eigenvalues, $\lambda_{(1)}^{\alpha}$, of the B_{ij}^{α} for all atoms changes to a negative value long before buckling occurs, while the second-smallest eigenvalues, $\lambda_{(2)}^{\alpha}$, of the B_{ij}^{α} of some atoms change to a negative value just prior to buckling. Under bending deformation, the change in the positivity of $\lambda_{(2)}^{\alpha}$ corresponds to a rippling deformation on the side of compressive bending stresses. A variation in the location of defects in the carbon nanotubes affects the peak stresses under compression and the peak moments under a bending deformation. However, for all models, local buckling occurs from the dense region of atoms whose $\lambda_{(2)}^{\alpha} < 0$ in some outer layers. This suggests that the atomic elastic stiffness is capable of acting as an evaluation criterion for local buckling in multi-walled carbon nanotubes.

1. Introduction

Since their discovery [1], carbon nanotubes (CNTs) have been researched extensively in several scientific fields to understand their mechanical, electrical and thermal properties. They have been found to possess a high axial stiffness and exhibit very high strength under axial tension. On the other hand, buckling of the CNTs occurs easily under axial compressive loads. This unstable behavior of CNTs has been studied using atomic simulations and continuum mechanics because experimental measurements of axial compression are difficult to perform owing to the small scale and high aspect ratio of CNTs. The mechanical properties, including the buckling behavior in CNTs, have been reviewed by Rafiee et al. [2] and Yengejeh et al. [3]. Buehler et al. [4] have investigated single-walled CNTs (SWCNTs) under axial compression using the molecular dynamics (MD) method. While the buckling behavior could be estimated with thin-shell models for SWCNTs possessing small aspect ratios, it changes to a rod-like buckling mode in SWCNTs with large aspect ratios, analogous to the Euler theory in continuum mechanics. Effects of atomic-scale defects observed by an experimental study [5,6] on buckling behavior has been discussed using MD methods [7] and continuum-shell models [8]. Under a bending deformation, local buckling behavior is also observed on the side of compressive stresses [9,10]. The buckling behavior of SWCNTs under compression and bending deformations has been systematically investigated using atomic simulations and continuum mechanics [11–13]. In addition, Garg et al. [14] have observed the onset of local buckling and the post-buckling under compression and bending in multi-walled CNTs (MWCNTs) using the finite element-based nested structural shell representation model. However, there is limited research reporting unified criteria for local buckling under compression and bending in MWCNTs using atomic simulations.

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We performed compression and bending simulations of defective and non-defective MWCNTs using the MD method, and evaluated the atomic elastic stiffness of each atom, B_{ij}^{α}, to discuss the onset of local buckling. The B_{ij}^{α} corresponds to the second-order derivatives of the atomic energy, or the gradient of the local stress–strain surfaces in the six-dimensional strain space. If B_{ij}^{α} has a negative eigenvalue, a local unstable path will exist in the strain direction. Some studies have discussed the buckling behavior of SWCNTs under compression using the positivity of the Hessian of the energy in the whole system [15,16]. Kinoshita et al. investigated the buckling limits of non-defective and defective SWCNTs using molecular mechanics simulations, and checked the positivity of the system Hessian against all of the degrees of freedom. The buckling point is defined by the change of the minimum eigenvalue from positive to negative, and the global buckling mode, such as Euler buckling, is detected as the eigenvector corresponding to the minimum eigenvalue. In contrast, the eigenvalue analysis of B_{ij}^{α} in this study is used to easily comprehend the disappearance of the local stiffness at each atom position rather than discuss the unstable mode for the whole system. In our previous study [17], the $\det(B_{ij}^{\alpha})$ of all atoms were found to change to a negative value long before buckling occurred, while the second-smallest eigenvalues of B_{ij}^{α} of some atoms changed to a negative value just prior to buckling. The existence of dense regions of atoms that possess two negative eigenvalues of B_{ij}^{α} was found to correspond with the onset points of local buckling under compression. In the present study, we further examined the B_{ij}^{α} in MWCNTs under bending deformations and discussed the relationships between local buckling and eigenvalues of B_{ij}^{α} to clarify the criteria for local buckling in MWCNTs under compression and bending deformations.

2. Computational model

2.1. Atomic elastic stiffness

The elastic stiffness or stress–strain coefficients are written as [18]

$$B_{ijkl} \equiv \left(\frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}}\right) = C_{ijkl} + \frac{1}{2}(\sigma_{il}\delta_{jk} + \sigma_{jl}\delta_{ik} + \sigma_{ik}\delta_{jl} + \sigma_{jk}\delta_{il} - 2\sigma_{ij}\delta_{kl}), \quad (1)$$

where δ_{ij} is the Kronecker delta. With an isothermal process, the stress, σ_{ij}, and the elastic coefficients, C_{ijkl}, are defined as

$$\sigma_{ij} = \frac{1}{V}\left(\frac{\partial F}{\partial \eta_{ij}}\right), \quad C_{ijkl} = \frac{1}{V}\left(\frac{\partial^2 F}{\partial \eta_{ij}\partial \eta_{kl}}\right). \quad (2)$$

Here, F is the Helmholtz free energy and V is the system volume at equilibrium. Note that the differentiation in Eq. (2) is for the infinitesimal virtual strain, η_{ij}, at equilibrium under an external load. In the linear elasticity region, B_{ijkl} is identical to C_{ijkl}, but they are not equivalent in the nonlinear elasticity region or the finite strain region. That is, B_{ijkl} represents the gradient at the stress–strain surface in six-dimensional strain space, whether the system is linearly or nonlinearly elastic. Wang et al. has proposed a method for evaluating the lattice stability at a finite strain and temperature on the basis of the positive definiteness of the elastic stiffness coefficients [19,20]. In this method, the symmetric part of the tensor in Eq. (1), $B_{ijkl}^{\mathrm{sym}} \equiv (B_{ijkl} + B_{lkji})/2$, dominates the lattice stability. Namely, the symmetric tensor B_{ijkl}^{sym} is represented by the 6×6 matrix B_{ij} $(i,j = 1\text{–}6)$, in the Voigt notation [18]. If any eigenvalues of B_{ij} become negative, the crystal loses resistance to the strain that corresponds to the eigenvector for the negative eigenvalue. Thus, the instability criterion can be written as $\det(B_{ij}) < 0$.

We next apply this criterion to the local domain, and we discuss the local deformation behavior using the atomic elastic stiffness, B_{ij}^{α} [17,21,22], where α is an arbitrary atom for which we can define B_{ij}^{α}. The B_{ij}^{α} is numerically evaluated using the change in atomic stress, σ_i^{α}, that occurs owing to a local strain perturbation applied to the atomic structure under compression and bending simulations,

$$B_{ij}^{\alpha} = \frac{\Delta \sigma_i^{\alpha}}{\Delta \varepsilon_j} = \frac{\Delta \sigma_i^{\alpha}(\mathbf{X}) - \Delta \sigma_i^{\alpha}(\mathbf{x})}{\Delta \varepsilon_j}. \quad (3)$$

The local strain perturbation, $\Delta\varepsilon_i$, is set to 0.001, and corresponds to the deformation present between the different equilibria **x** and **X**.

2.2. Simulation procedure

MWCNTs with many layers should be investigated to observe the universal behavior, because it is difficult to separate the effect of the innermost or outermost layer in MWCNTs with a small number of layers, such as double- and triple-walled CNTs. Thus, the MWCNT model used in this work was composed of five layers (*i.e.*, five walls, denoted 5WCNT), with each subsequent concentric layer possessing a chirality [23] of (7,7), (12,12), (17,17), (22,22) and (27,27), respectively. The non-defective 5WCNT is made using a MD calculation for 50 ps at 0.1 K using a periodic boundary condition in the longitudinal direction (z axis) only. During the calculation, a normal stress in the longitudinal direction is held to be zero by expansion or contraction of the tube length. Interatomic interactions are evaluated using the adaptive intermolecular reactive empirical bond order (AIREBO) potential [24]. The potentials are developed by Stuart et al. from the second-generation REBO potential [25] and can describe transitions between covalent bonding interactions and non-bonding ones owing to the chemical environment changes. The time increment for the MD calculation was set to 1 fs, the total number of atoms was 27,200, and the cell length in the longitudinal direction was 19.36 nm after relaxation. The average interlayer distance after relaxation is 0.3335 nm, which is close to the interlayer distance of graphite of 0.3354 nm using the AIREBO potential [24]. This suggests that the effect of interlayer interactions on the initial structural instability is smaller than in other chirality models. Various defects are observed in CNTs and graphene sheets, such as one carbon atom vacancies, two neighboring vacancies, and pentagon–octagon–pentagon defects [5,6]. In this study, a vacancy-type (VT) defect (*i.e.*, a one carbon atom vacancy) was inserted by removing an atom from each layer of the non-defective 5WCNT to investigate the effect of the location of the defect. A 5WCNT with a VT defect on the innermost layer is labeled in this work as a VT1 model. In this way, five defective 5WCNT models with a VT defect in each of the five subsequent concentric 5WCNT layers are produced, and are respectively labeled the VT1, VT2, VT3, VT4 and VT5 models.

Next, each defective and non-defective 5WCNT was subjected to uniaxial compression under a periodic boundary condition in the longitudinal direction. The compressive strain was provided by a uniform contraction of each atom position to avoid the occurrence of elastic waves, and the strain rate was held constant at $-2.0 \times 10^8\ \mathrm{s}^{-1}$. In a previous study [17], we have reported results for the compression of 5WCNTs, but the relaxation durations before compression in that study were as short as 15 ps. Thus, the results found in the present study are slightly different from those previous results.

In addition, each defective and non-defective 5WCNT was subjected to a bending deformation wherein the atomic structures