Elastic properties of single-walled carbon nanotubes in transverse directions

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The elastic deformation of single-walled carbon nanotubes under hydrostatic pressure has been modeled using the molecular structural mechanics method. The computational results indicate that the radial direction elastic modulus deceases with the increase in tube diameter. The circumferential direction elastic modulus is insensitive to tube diameter, and roughly equal to the axial direction modulus. The hydrostatic pressure for tube buckling also deceases with increasing tube diameter and is in the range of 1.5–11 GPa for single-walled carbon nanotubes with diameters of 0.6–2.0 nm; this prediction is in good agreement with existing experimental results. The tube chirality has minor effect on the radial modulus and buckling strength.

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Since the discovery of carbon nanotubes in 1991, considerable efforts have been made for studying the physical and mechanical properties of this novel material. Among the many potential applications, carbon nanotube-reinforced polymer and ceramic matrix composites have been explored.[1] Their high stiffness, extraordinary strength, ability to sustain large elastic strain, as well as high respect ratio and low density made carbon nanotubes the ideal reinforcement material. It has been theoretically and experimentally confirmed that the axial Young's modulus of carbon nanotubes is about 1.0 TPa[2–8] and the axial tensile strength is as high as 63 GPa.[9,10] Since the previous studies of carbon nanotubes have mainly focused on the axial properties, their behavior transverse to the axial direction, i.e., radial or circumferential, is not well understood. The knowledge of nanotube transverse elastic properties is essential in the study of the interfacial residual stresses, and the failure mechanism of nanocomposites, as well as the mechanical performance of nanowire templates, hydrogen containers, and nanogears based on carbon nanotubes.

The radial deformability of multiwalled carbon nanotubes was first examined by Ruoff *et al.*[11] Their experiments showed that van der Waals forces between adjacent nanotubes can deform them substantially, destroying the cylindrical symmetry. Hertel *et al.*[12] also observed a shape change of nanotube cross section, from circular to elliptical, at the point of overlap between two contacting nanotubes. Lordi and Yao[13] studied the response of carbon nanotubes to asymmetrical radial compressive forces by experiments and computer simulations. They concluded that the elasticity and resilience of nanotubes depend on the tube radius and the number of tube layers under compression. Shen *et al.*[14] characterized the mechanical properties of multiwalled nanotubes in radial direction using nanoindentation tests with a scanning probe microscope. They reported that the radial modulus increased from 9.7 to 80.0 GPa with increasing compressive stress, and the compressive strength was estimated to be higher than 5.3 GPa. Yu *et al.*[15] also conducted nanoindentation tests on multiwalled carbon nanotubes using a tapping-mode atomic force microscope, and reported the effective radial elastic modulus range of 0.3–4 GPa.

Single-walled carbon nanotubes were reported to be more deformable in the radial direction than multiwalled carbon nanotubes.[16] However, there is still a lack of quantitative measurement of the radial modulus of single-walled carbon nanotubes. Tang *et al.*[17] reported the deformation of single-walled carbon nanotubes under hydrostatic pressure using a diamond anvil cell and *in situ* x-ray diffraction. It was shown that single-walled carbon nanotubes maintain linear elasticity under hydrostatic pressure up to 1.5 GPa. But they did not give the value of radial elastic modulus. To date, the only report of the radial modulus of a single-walled carbon nanotube is from Reich *et al.*[18] using an *ab initio* calculation for the nanotube diameter of 0.8 nm.

This letter reports a modeling of the elastic deformation of single-walled carbon nanotubes under hydrostatic pressure using the molecular structural mechanics method.[8,19,20] The variations of radial and circumferential Young's modulus with nanotube diameter and chirality are reported. Also, the maximum hydrostatic pressure that a single-walled carbon nanotube can withstand without collapsing has been determined.

For simulating the elastic deformation of carbon nanotubes in transverse directions, hydrostatic pressure provides a convenient loading condition, where the radial and circumferential deformations occurred simultaneously and the stress and strain fields are uniform. For a single-walled carbon nanotube with tube diameter D and wall thickness t, the radial (r) and circumferential (θ) stresses under external pressure P can be approximated using the concept of continuum mechanics:

$$\sigma_r = P, \quad \sigma_\theta = PD/2t, \tag{1}$$

respectively. If the effect of Poisson's ratio is ignored, the radial (E_r) and circumferential (E_θ) elastic moduli can be expressed as

$$E_r = \sigma_r/\varepsilon_r, \quad E_\theta = \sigma_\theta/\varepsilon_\theta, \tag{2}$$

where ε_r and ε_θ are the strains in the radial and circumferential directions, respectively.

For determining ε_r and ε_θ of a nanotube subject to hydrostatic pressure, the molecular structural mechanics approach proposed by the authors[8] is applied. The concept of this approach originated from the observation of geometric similarities between nanoscopic fullerenes and macroscopic

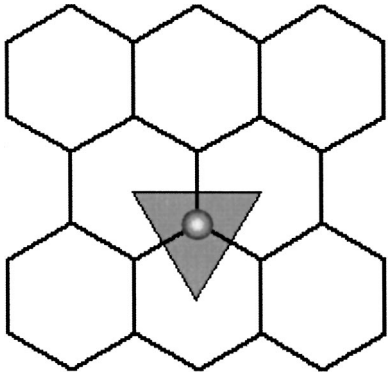

FIG. 1. A surface area contributing the resultant force acting on an atom.

space frame structures. In a carbon nanotube, each atom is bonded covalently with three nearest neighbors. When a nanotube is subjected to external forces, the displacements of atomic nuclei are constrained by the covalent bonds. If a nanotube is viewed as a space frame with ''beams'' connecting the carbon atoms, its deformation can be simulated by the technique of structural mechanics. In essence, we assume that the covalent bond between two neighboring carbon atoms can be simulated as an equivalent structural beam with a circular cross section. Then, following the concept of structural mechanics, only three stiffness parameters, i.e., the tensile resistance *EA*, the flexural rigidity *EI*, and the torsional stiffness *GJ*, need to be determined for deformation analysis of the equivalent beam. Here, *E*, *G*, *A*, and *J* are, respectively, the Young's modulus, shear modulus, cross-sectional area, and polar inertia of the beam. Based on the energy equivalence between local potential energies in computational chemistry and elemental strain energies in structural mechanics, a direct relationship between the structural mechanics parameters and the molecular mechanics force field constants is established. Once these virtual beams are assembled to form a nanotube, the computationally efficient structural mechanics technique can be readily utilized to solve the resulting atomistic deformation problem for a nanotube subjected to various loading conditions.

In the calculation of the radial deformation of a nanotube, the nanotube aspect ratio is selected to be 10. In order to eliminate the end effects, the radial displacement used for calculating the radial and circumferential strains is taken as the average of atomic displacements around the middle cross section of the nanotube. The number of atoms involved in the calculations is in the range of 240–3500, depending on the nanotube diameter. Under the loading condition of hydrostatic pressure, we assume the resultant force from the pressure acting on a triangular surface area around an atom is concentrated on the atom (Fig. 1). Figure 2 shows the results of radial displacement as a linear function of hydrostatic pressure for an armchair and a zigzag nanotube. The radial and circumferential strains are calculated by

$$\varepsilon_r = \varepsilon_\theta = u_r / R, \tag{3}$$

where u_r stands for the radial displacement and R denotes the radius of the nanotube. Then, from Eq. (2), the radial and

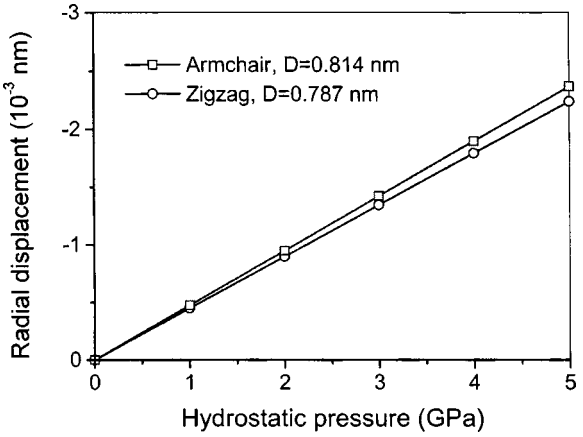

FIG. 2. Radial displacement of nanotube under hydrostatic pressure.

circumferential modulus can be obtained.

Figure 3 shows the variation of transverse Young's modulus of single-walled carbon nanotubes with tube diameter. It can be seen that E_θ is almost independent of the nanotube diameter and the tube chirality has a very minor effect. The magnitude of E_θ is about 1.0 TPa, which is the commonly accepted value for carbon nanotube axial Young's modulus. This result is consistent with the in-plane isotropic elastic nature of a graphene sheet. The insensitivity of carbon nanotube axial Young's modulus to tube chirality has been reported in Refs. 4, 5, and 8.

Figure 3 also shows that the radial Young's modulus is highly dependent on the tube diameter and it deceases rather rapidly with increasing tube diameter. This is due to the increase of radial strain with increasing tube diameter at a given external pressure (Fig. 4). Similar to the case of circumferential Young's modulus, the tube chirality also has no effect on the radial Young's modulus when the tube diameter is greater than 1.2 nm.

For comparison, Fig. 3 also shows the *ab initio* result reported by Reich *et al.*,[18] and obtained by using the local-density approximation of density-functional theory. Due to the formidable computational task involved in the *ab initio* calculation, only the radial modulus of a single-walled carbon nanotube with a diameter of 0.8 nm was given and its value is 650 GPa.

Because of their hollow nature, nanotubes may collapse under critical hydrostatic pressure. Chesnokov *et al.*[21] ob-

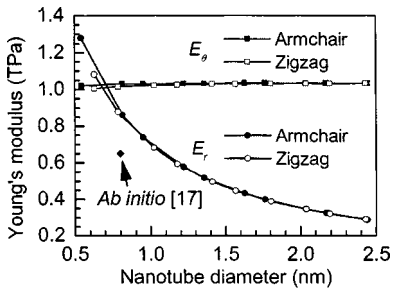

FIG. 3. Young's modulus of single-walled carbon nanotubes in transverse directions.

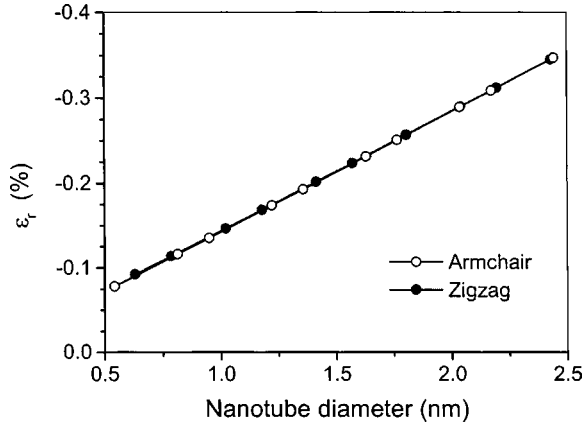

FIG. 4. Radial strain vs nanotube diameter under constant hydrostatic pressure (1.0 GPa).

served in their high pressure experiment that single-walled carbon nanotubes with a diameter distribution peaked around 1.36 nm undergo reversible deformation up to 2.9 GPa. Tang *et al.*[17] found that the radial deformation of nanotubes with a diameter of 1.4 nm is reversible up to 4 GPa, but the lattice structure seems to be destroyed when the pressure is higher than 5 GPa.

By using the molecular structural mechanics approach, the buckling pressure for single-walled carbon nanotubes can be treated as an eigenvalue problem. The minimum loading factor $\lambda_{\min}$ can be solved from[22]

$$(\mathbf{K}_E + \lambda \mathbf{K}_G)\mathbf{U} = 0, \tag{4}$$

where $\mathbf{K}_E$, $\mathbf{K}_G$ are the elastic matrix and geometrically nonlinear matrix, respectively. **U** is the displacement vector. Figure 5 displays the buckling pressure of single-walled carbon nanotubes versus tube diameter. It is shown that the buckling

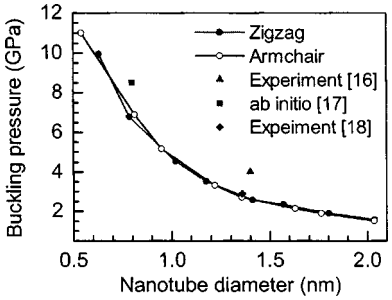

FIG. 5. Buckling pressure of single-walled carbon nanotubes.

pressure deceases with the increase of tube diameter and the results are in good agreement with the available experimental and *ab initio* findings.

In summary, this paper predicts the radial stiffness and buckling strength of single-walled carbon nanotubes. The molecular structural mechanics method is applied for modeling the elastic response of nanotubes subjected to hydrostatic pressure. The computational results indicated that the radial modulus deceases with increasing tube diameter. The circumferential modulus is insensitive to tube diameter, and roughly equal to the axial modulus. The hydrostatic pressure for nanotube buckling also deceases with the increase of tube diameter and is in the range of 1.5–11 GPa for single-walled carbon nanotubes with diameters of 0.6–2.0 nm. The tube chirality has minor effect on the radial modulus and buckling strength.

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