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On the Nanoindentation of the Carbon Nanotubes

A new inverse approach is proposed in this paper, which combines elements of nonlocal theory and molecular mechanics, based on the experimental results available in the nanoindentation literature. The effect of the inlayer van der Waals atomistic interactions for carbon nanotubes with multiple walls (MWCNT) is included by means of the Brenner -Tersoff potential and experimental results. The neighboring walls of MWCNT are coupled through van der Waals interactions, and the shell buckling would initiate in the outermost shell, when nanotubes are short. The nanoindentation technique is simulated for the axially compressed of individual nanotubes, in order to evaluate the load-unloaded-displacement, the curve critical buckling and the appropriate values for local Lamé constants.

Keywords: *Nanoindentation, carbon nanotubes, buckling, Brenner-Tersoff potential, van der Waals force, kink.*

1. Introduction

Indentation is a testing method which received considerable recent interest in the mechanical characterisation of materials [1]-[4]. The goal of such testing is to extract elastic modulus and hardness of the specimen material from readings of indenter load and depth of penetration. The forces involved are usually in the millinewtons (10^{-3} N) range and are measured with a resolution of nanonewtons (10^{-9} N). The depths of penetration are on the order of microns with a resolution of less than a nanometre (10^{-9} N). The size dependence of nanoindentation is still an open problem [5]. At the micron or nanometer scale, the size effect of deformation is inherent [6], [7], and similarly indentation at the nano/microscale also displays a strong size effect. The spreading of intershell distances and the inlayer van der Waals interactions in MWCNTs depend on the tube size [8]. With

different dimensions and geometries of MWCNTs, the mechanical properties are also size dependent [9], [10].

There are many works reported in the CNTs modeling which are extensively reviewed by Srivastava and Atluri [11]. The long-range nanoindentation response of MWCNTs was studied by a new method combining features of nonlocal theory and molecular mechanics by Munteanu and Chiroiu [12]. An inverse problem in the theory of shell buckling of MWCNTs is proposed in this paper based on [12] and [13]-[15] with the emphasis on the simulation of the nanoindentation technique.

2. Theory

Advances in multi-scale computational methods for nanostructures are made by coupling the continuum-models with more-realistic details at quantum and atomistic scales [16]. The model we propose in this paper directly couples a region described with full atomistic detail to a surrounding region modelled using continuum concepts. Current parallel supercomputer simulations can manipulate about 10^9 atoms using a simple empirical potential, amounting to a volume of less than 1 cubic micron. But attaining the scale needed for typical polycrystals, at least 10^6 cubic microns, is very difficult to be realized. Atomistic methods must be used in conjunction with larger scale methods through multi-scale modelling methods. In the atomistic-continuum coupling a very important item is determination of the total potential energy of a system as a function of the degrees of freedom, which can be atom positions.

Continuum mechanics assumes that, for a material, there exists a strain energy density functional W, and the energy in a volume $\mathrm{d}V$ around point X is $W(X)\mathrm{d}V$. The overall potential energy of the material is then an integral over the volume Ω of the body

$$E^c = \int_{\Omega} W(X)\mathrm{d}V \,. \tag{1}$$

If X is a point in the undeformed state of the body, by some applied forces or imposed displacements on the body, the point X moves to the point x. The displacement referenced to the original state of the body $u(X) = x - X$. The difference $\mathrm{d}x - \mathrm{d}X$ describes the local de-formation with reference to X. The deformation gradient is

$$F(X) = \frac{\mathrm{d}x}{\mathrm{d}X} = I + \nabla u(X)\,, \tag{2}$$

where ∇ is the gradient with reference to X. The Lagrangian strain is given by

$$E = (F^T F - I)/2\,, \tag{3}$$

which becomes $\varepsilon = (\nabla u + (\nabla u)^T)/2$, for the infinitesimal deformations.

To determine the equilibrium strain field for applied forces and displacements in the body, the energy E^c must be minimized. The locality of $W(X)$ implies that the strain energy density at X is equal to the strain energy per unit volume of an infinite perfect crystal deformed according to a homogeneous deformation gradient $F(X)$.

The locality of $W(X)$ is a key assumption for constructing the coupled methods, because the real atomistic energy is nonlocal. When ∇F is large, the nonlocality plays an important role and the local $W(X)$ cannot describe this nonlocality.

3. Inverse problem

The coupling between the atomistic region and the continuum one is realized by an inverse problem which models the transition between these regions. The inverse problem of the coupled atomistic-continuum method contains two very important assumptions. The first assumption refers to the expression of $W(X)$ for the carbon nanotube. The $W(X)$ is derived by using the assumption that the potential functional Σ

$$\Sigma = \Sigma_0 + \int_{V-\sigma} \left[\frac{1}{2} \lambda'(|\mathbf{x}' - \mathbf{x}|) e_{kk}(\mathbf{x}) e'_{ll}(\mathbf{x}') + \right. \\ \left. + \mu'(|\mathbf{x}' - \mathbf{x}|) e_{kl}(\mathbf{x}) e'_{kl}(\mathbf{x}') \right] \mathrm{d}v'(\mathbf{x}'), \tag{4}$$

is identified with the Brenner-Tersoff potential [17], [18]. In (4), λ, μ are the classical Lamé elastic constants, and λ' and μ' are the nonlocal Lamé elastic functions which depend on $|\mathbf{x}' - \mathbf{x}|$, Σ is the potential functional over all argument functions of $\mathbf{x}'$ covering the entire body, defined by $\rho_0 \psi = \Sigma(\mathbf{x}', \mathbf{x}'_{,k})$, with $\psi = \varepsilon - \theta\eta$ the free energy functional, Σ_0 refers to the value in the natural state, and ρ_0 the density in the natural state, δ_{kl} is the Kronecher delta, e_{kl} is the strain tensor of the linear theory $2e_{kl} = u_{k,l} + u_{l,k}$ and u_k the components of the displacement vector.

The nonlocal Lamé elastic functions $\lambda'(|\mathbf{x}' - \mathbf{x}|)$ and $\mu'(|\mathbf{x}' - \mathbf{x}|)$ are influence functions, which are positive decreasing functions of $|\mathbf{x}' - \mathbf{x}|$,

$$\lambda'(|\mathbf{x}' - \mathbf{x}|) = \alpha(|\mathbf{x}' - \mathbf{x}|)\lambda \ , \\ \mu \ (|\mathbf{x}' - \mathbf{x}|) = \alpha(|\mathbf{x}' - \mathbf{x}|)\mu \ , \tag{5}$$

The potential functional Σ is expressed in terms of the repulsive potential $V_R(|\mathbf{x}'-\mathbf{x}|)$, the attractive potential $V_A(|\mathbf{x}'-\mathbf{x}|)$ and the Lennard-Jones potential $V_{dvw}(|\mathbf{x}'-\mathbf{x}|)$

$$\Sigma = \Sigma_0 + \gamma \int_{V-\sigma} [V_R - \beta V_A + V_{vdw}] dv'(\mathbf{x}'), \tag{6}$$

with γ and β, the coupling factors, and

$$V_R(|\mathbf{x}'-\mathbf{x}|) = \frac{D_e f_c(|\mathbf{x}'-\mathbf{x}|)}{S-1} \exp\left(-A_1(|\mathbf{x}'-\mathbf{x}|)\right),$$

$$V_A(|\mathbf{x}'-\mathbf{x}|) = \frac{SD_e f_c(|\mathbf{x}'-\mathbf{x}|)}{S-1} \exp\left(-A_2 |\mathbf{x}'-\mathbf{x}|)\right)$$

$$V_{vdw} = 4\tilde{\varepsilon}\left[\left(\frac{r_0}{(|\mathbf{x}'-\mathbf{x}|)}\right)^{12} - \left(\frac{r_0}{(|\mathbf{x}'-\mathbf{x}|)}\right)^{6}\right],$$

$$2 f_c = (1+\cos\left(\frac{\pi(|\mathbf{x}'-\mathbf{x}|-R_1)}{R_2-R_1}\right),$$

$$f_c(|\mathbf{x}'-\mathbf{x}|) = \begin{cases} 1, & |\mathbf{x}'-\mathbf{x}| < R_1, \\ f_{0c}, & R_1 < |\mathbf{x}'-\mathbf{x}| < R_2, \\ 0, & |\mathbf{x}'-\mathbf{x}| > R_2, \end{cases}$$

where $D_e = 6.32\text{eV}$, $S = 1.29$, $\tilde{\varepsilon}$ the energy at the minimum in V_{vdw}, and r_0 is the distance between two atoms at which $V_{vdw} = 0$. For carbon atoms, $\varepsilon_0 = 0.0556$ kcal/mol, $r_0 =$ 3.4 Å. The function $f_c(|\mathbf{x}'-\mathbf{x}|)$ is an optional *cut-off* function and it may be used to smoothly limit the interactions in (6) within a predefined range of neighboring atoms, effectively defined by radii $R_1 = 1.70$ Å and $R_2 = 2.00$ Å [19].

The second assumption of the inverse problem is the simulation of the nanoindentation test used in [20] with referring to a commercial nanoindenter with extremely fine force and displacement resolution ($\approx$300nm and $\approx$1 nm, respectively). A Berkovich three-sided py-ramidal tip was used in the current investigation, with a nominal tip radius of 100 nm. The study case is an axially compressed MWCN of diameter $d = 50$nm, length $L = 100$nm. The nanotubes used in this study has 15 walls, the outer radius is $R_{outer} = 25$ nm, and inner radius is $R_{inner} = 20$ nm. The projected contact area for a conical indenter

is $A = \pi h^2 \tan^2 \theta$, where h is the maximum indentation depth, and θ is the half angle of the indenter. For a Berkovich indenter, $A = 24.56h^2$, and for a Vickers indenter, $A = 24.50h^2$. For both Berkovich and Vickers indenters, $\theta = 70.3^\circ$. Let us note by V the volume of the structure and by S the surface between the indenter and the sample.

The total volume of MWCNT can be defined as the product of the cross-sectional area A_{mw} and the length L [21]

$$A_{mw} = \pi[(R_{outer} + 0.17)^2 - (R_{inner} - 0.17)^2], \quad (7)$$

where 0.17 is a half layered thickness of nanotube.

The inverse problem is solved by a genetic algorithm. The experimental results [20] are used to calculate the load-unloaded-displacement curve, as shown in fig.1. As the experiments report, the loading portion consists of three stages: an initial linear increase, then a sudden drop in the slope and the curve becoming flat, and a third stage comprising and increasing load. The sudden decrease in the slope is the signature MWCNT shell buckling, which indicates the collapse process. After buckling, neighboring nanotubes come into contact with the indenter tip, which results in an increase in load, as seen in figure 1 in the third stage. The position of zero displacement corresponds to a nonzero load. Applying our theory, the critical buckling experiments is calculated, 2.18μN, very closed with the experimental result (between 2 and 2.5μN).

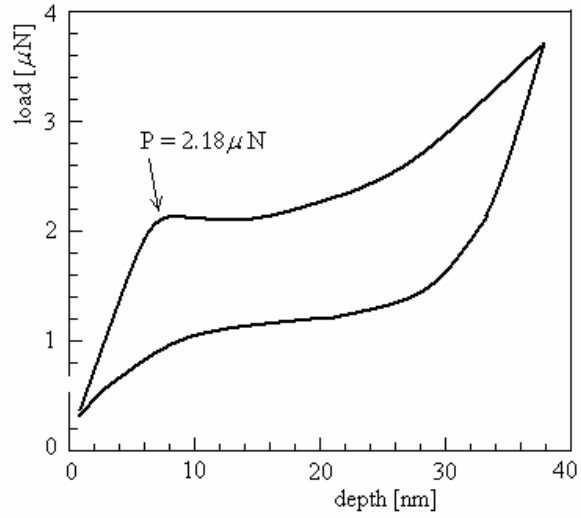

Figure 1. Scheme of the load-unloaded-displacement curve.

4. Results

The deformation is analysed with respect to the bending angle θ. Two points of local buckling are observed in the nanotube at $\theta = 25.58^{\circ}$. When θ increases, the axial compression in the tube increases too, and when the compressive stress reaches a critical value, the tube will locally buckle. The buckling mechanism can be described by localized functions with no change in shape, known as solitons or kinks [22], [23]. The value of ζ at the point of local buckling is around 0.14. With the increase in θ, the top and bottom parts of the kink get closer to each other, and at a certain stage, the distance between them reaches the critical equilibrium distance. Upon additional loading, this distance remains unchanged because there are no external normal loads applied on the walls to prevail over the repulsive van der Waals forces.

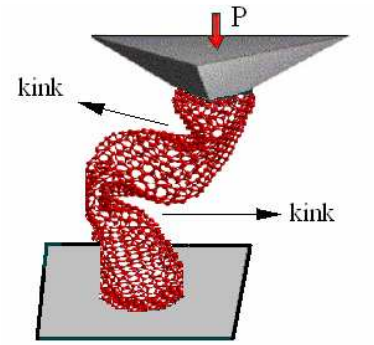

Figure 2. Two points of local buckling.

For $\theta > 25.58^{\circ}$, two regions in which a kink mechanism of deformation appears. This region is represented in figure 2. In according to experiments and molecular dynamics simulations, the pattern of the deformation resembles the kink mechanism similar to that of a macrotube.

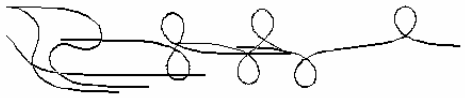

Figure 3. The generation of kink deformations.

A portion of the wall flattens and forms a domain that rotates about a central hinge line. This portion is treated by the molecular dynamic.

Once the kink mechanism starts, the nanotube becomes a mechanical mechanism. The remaining part of the tube remains circular although it flattens and decreases its curvature.

The generation of the kink deformations is presented in figure 3. Figure 4 shows the cross section of the nanotube for different values of $\zeta = \frac{R - R_c}{R}$, where R and R_c, are the radius before and after deformation. A consequence of the kink deformation mechanism is the rippling configuration of the nanotube. Figure 5 presents the rippling configuration.

Figure 6 represents the variation of the dimensionaless curvature C with respect cu θ. The sinusoidal shape of this curve is another consequence of the kink deformation mechanism.

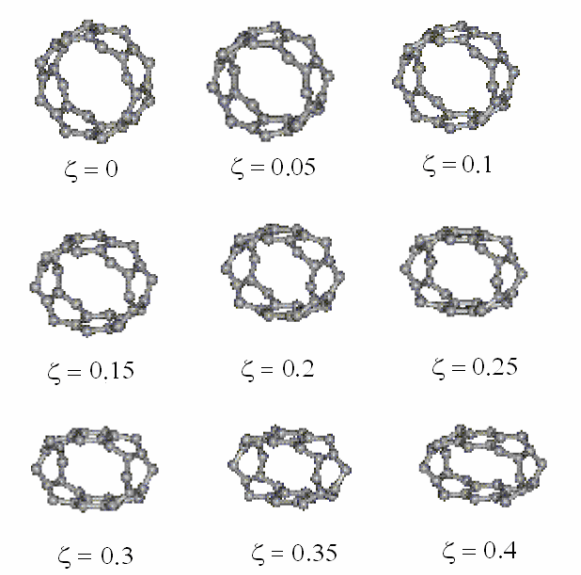

Figure 4. Cross section of the nanotube for different values of ζ.

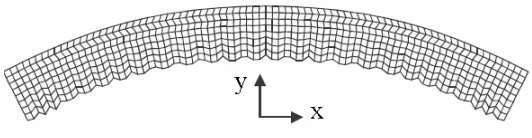

Figure 5. The rippling configuration of a CNT.

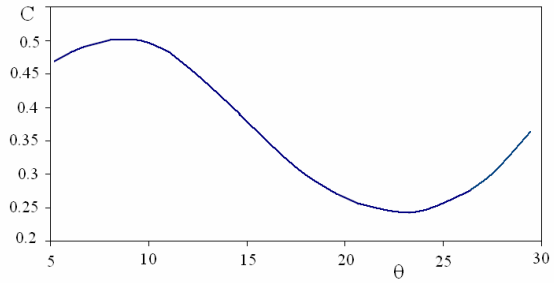

Figure 6. The variation of dimensionless curvature with respect to θ.

5. Conclusions

An inverse problem is proposed in this paper to describe the shell buckling mechanism of MWCNT by combining elements of nonlocal theory and molecular mechanics. The effect of the inlayer van der Waals atomistic interactions for MWCNTs included by means of the Brenner-Tersoff potential. The neighboring walls of a multiwalled nanotube are coupled through van der Waals interactions, and the buckling would initiate in the outermost shell, when nanotubes are short $L/d \approx 1-20$.

The nanotube will locally buckle at $\theta = 25.58^{\circ}$, where θ is the bending angle. For $\theta > 25.58^{\circ}$, a kink deformation mechanism is starting and a portion of the nanotube becomes to rotate about a central hinge line. For large distances, the van der Waals force is attractive, but when the separation between the atoms is below the equilibrium distance of 3.42Å, it becomes strongly repulsive. Upon complete unloading from angles below 110° the nanotube completely recovers. At a very large bending angle of 120°, atomic bonds break and the deformation of the nanotube becomes irreversible.

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