

Mechanics of Carbon Nanotubes: A Continuum Theory Based on Interatomic Potentials

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Abstract. It is commonly believed that continuum mechanics theories may not be applied at the nanoscale due to the discrete nature of atoms. We developed a nanoscale continuum theory based on interatomic potentials for nanostructured materials. The interatomic potential is directly incorporated into the continuum theory through the constitutive models. The nanoscale continuum theory is then applied to study the mechanical deformation and thermal properties of carbon nanotubes, including (1) pre-deformation energy; (2) linear elastic modulus; (3) fracture nucleation; (4) defect nucleation; (5) electrical property change due to mechanical deformation; (6) specific heat; and (7) coefficient of thermal expansion. The nanoscale continuum theory agrees very well with the experiments and atomistic simulations without any parameter fitting, and therefore has the potential to be utilized to complex nanoscale material systems (e.g., nanocomposites) and devices (e.g., nanoelectronics).

1. Introduction

There has been extensive research on carbon nanotubes (CNTs) since their first discovery [1,2] and the establishment of effective synthesis techniques [3]. A single-wall carbon nanotube (SWNT) is a cylinder of graphene with a single layer of carbon atoms, and its diameter is on the order of 1 nm. There are also multi-wall carbon nanotubes (MWNTs) that consist of multi-layers of graphene rolled in to themselves to form a cylindrical tube, and the diameters of MWNTs are much larger (e.g., 50 nm). The lengths of carbon nanotubes range from a few nanometers to 100 microns or even higher. Depending on their chiralities, carbon nanotubes have either metallic (m) or semiconducting (s) electronic structures. The m-nanotubes have the potential to serve as the interconnects in nanoelectronics, while the s-nanotubes can be switched on and off as field-effect transistors that are 500 times smaller than current devices. Collins et al. [4] developed a novel technique to convert MWNTs into either metallic or semiconducting conductors and to fabricate arrays of field-effect transistors from SWNT. This represents a major step in the development of nanotube-based electronics.

Electrical property of carbon nanotubes can be changed by mechanical deformation. Using the tip of an atomic force microscope (AFM) to deflect a suspended SWNT with both ends clamped to two metal electrodes, Tomblor et al. [5] observed that the electrical conductance of an SWNT is reduced by two orders of magnitude, i.e., a metal-like SWNT becomes a semiconducting nanotube upon mechanical deformation. Moreover, the deformation and associated change of electrical conductivity are completely reversible upon unloading of the AFM. This unique electromechanical behavior makes carbon nanotubes a potential candidate for nanoscale sensors, but also has major implications on the reliability of nanotube-based electronics.

Carbon nanotubes also display superior mechanical and thermal properties and may be used as

reinforcements in composite materials. Experimental studies have repeatedly shown that carbon nanotubes have high Young's modulus on the order of 1 TPa, can sustain more than 4% strain without permanent deformation and 10% strain without fracture. These observations have also been confirmed by extensive atomistic simulations. The existing atomistic simulations, however, have limitations concerning both time and length scales, and have difficulty for complex systems involving multiple carbon nanotubes as in nanotube-based electronics and nanotube-enforcing composites. It is therefore desirable to establish a nanoscale continuum theory for carbon nanotubes as well as for general nanostructured materials.

A nano-continuum theory is established in this paper based on atomistic models. The interatomic potential for carbon [6] is incorporated in the continuum theory through the constitutive model of solids. The continuum strain energy density is obtained by averaging energy in atomic bonds over orientations and distribution. We begin with a brief description of the interatomic potential for carbon in section 2. The nanoscale continuum theory for carbon nanotubes is established in section 3. Several examples are briefly shown in section 4 to demonstrate that this nanoscale continuum theory agrees very well with experiments and molecular dynamics simulations without any additional parameters fitting beyond what appear in the underlying atomistic potential.

2. An Interatomic Potential for Carbon

Brenner [6] established an interatomic potential for carbon as

$$V(r_{ij})=V_R(r_{ij})-B_{ij}V_A(r_{ij}), \quad (1)$$

where r_{ij} is the distance between atoms i and j , V_R and V_A are the repulsive and attractive pair terms (i.e., depending only on r_{ij}), and B_{ij} represents a multi-body coupling between the bond $i-j$ and the local environment of atom i , i.e., depending on atoms outside the pair $i-j$. It is important to point out that all parameters in Brenner's interatomic potential have been determined to fit the binding energy and lattice constants of graphite, diamond, simple cubic and face-centered-cubic structures for pure carbon, as well as the vacancy formation energy for diamond and graphite. The analytical expressions of V_R , V_A and B_{ij} are given by Brenner, and are not repeated here.

The equilibrium bond length determined from Brenner's interatomic potential is $r_0=0.145\text{nm}$, which agrees well with the well-known bond length of graphite (0.144nm).

3. A Nanoscale Continuum Theory for Carbon Nanotubes

Unlike molecular dynamics simulations that keep track of every atom, the proposed nanoscale continuum theory represents the collective behavior of a few atoms based on the modified Cauchy-Born rule. The Cauchy-Born rule states that all atoms are subject to a homogeneous deformation move according to a single mapping from the undeformed to the deformed configurations. For a centrosymmetric atomic structure with pair of bonds in the opposite directions around each atom, the Cauchy-Born rule ensures the equilibrium of atoms because forces are in the opposite direction and can be cancelled. However, the Cauchy-Born rule must be modified for a carbon nanotube since its hexagonal lattice structure does not possess centrosymmetry such that the corresponding atomic motion cannot ensure the equilibrium of each atom [7-9]. Here we provide a brief description of the modification of the Cauchy-Born rule for the hexagonal lattice structure. Details of this approach are given by Zhang et al [7,9] and Jiang et al [8].

A non-centrosymmetric, hexagonal lattice structure can be decomposed into two triangular sub-lattices. Each sub-lattice has the centrosymmetry and therefore follows the Cauchy-Born rule. However, the two sub-lattices may undergo a relative translation \mathbf{X} to release the energy due to the assumption of single mapping. This relative translation \mathbf{X} represents an internal degree of freedom for the hexagonal lattice structure and remains to be determined by enforcing the equilibrium of atoms.

The following steps are performed to establish the constitutive model in the continuum theory based on the interatomic potential:

(1) For a given Green strain \mathbf{E} , the bond length r of a stretched atomic bond is related to the unstretched bond length r_0 by

$$r^2 = r_0^2 (n_i + x_i) (\delta_{ij} + 2E_{ij}) (n_j + x_j), \quad (2)$$

where δ_{ij} is the Kronecker delta, \mathbf{n} is the unit vector along the bond in the undeformed configuration, and the vector \mathbf{x} is related to the translation \mathbf{X} and the deformation gradient \mathbf{F} by $x_i = F_{ij}^{-1} X_j / r_0$;

(2) The energy stored in the atomic bond between carbon atoms i and j is given by Brenner's multi-body interatomic potential discussed in section 2;

(3) For the hexagonal lattice structure, each atom i has three neighboring atoms j such that the strain energy density W on the continuum level can be obtained from the energy stored in the atomic bonds by $W = \Sigma V(r_{ij}) / (2\Omega)$, where the summation Σ is over three nearest-neighbor interactions with atom i , V is Brenner's interatomic potential for carbon, the factor $\frac{1}{2}$ represents the equipartition of bond energy between two atoms in each pair, and Ω is the average area per atom within the tube surface;

(4) The vector \mathbf{x} is determined by minimizing the strain energy density W with respect to \mathbf{x} , which is equivalent to the equilibrium of each atom in the hexagonal lattice structure possessing no centrosymmetry;

(5) The second Piola-Kirchhoff stress \mathbf{S} is obtained from the derivative of strain energy density W with respect to the Green strain \mathbf{E} , while the incremental modulus tensor \mathbf{C} is the second order derivative of W with respect to \mathbf{E} .

We should emphasize one important point here. Although the basis of this nanoscale continuum theory, Cauchy-Born rule assumes that the lattice deforms homogeneously, we only use this theory for constitutive relations of unit cell, and the constitutive relations are versatile for macroscopic uniform and non-uniform deformation. Specifically, if the deformation is relatively uniform, the unit cell can contain large number of atoms; if the deformation is relatively non-uniform, the unit cell has to be small enough to characterize the non-uniform deformation field.

The equilibrium equation and traction boundary conditions are the same as those in classical continuum theories. A similar approach based on the Cauchy-Born rule was formulated recently for bulk materials by Tadmor et al [10,11].

4. Examples: Mechanical and Thermal Properties of Carbon Nanotubes

We studied the mechanical and thermal properties of carbon nanotubes using nanoscale continuum theory and compare the results with experiments and the atomistic simulations. We skip some details of the analysis and present the results only. It is emphasized that *the proposed nanoscale continuum theory involves no fitting parameters beyond those used to define the interatomic potential*.

4.1 Pre-deformation energy. Jiang et al. [8] studied the energy stored in a carbon nanotube with finite diameter without any deformation. If the energy state for a graphene (i.e., a single, flat layer) of carbon atoms is taken as zero, figure 1 shows the pre-deformation energy (per atom) versus the tube radius R . The solid line was obtained by Robertson et al. [12] using molecular dynamics simulations based on Brenner's interatomic potential. It displays an inverse square dependence of the pre-deformation energy on R , i.e., R^{-2} . The dots are the results for the nanoscale continuum theory based on the same interatomic potential. It is observed that, *without any parameter fitting, the pre-deformation energy predicted by the nanoscale continuum theory agrees very well with the molecular dynamics simulations*. Even for tube radius as small as 0.2 nm, which corresponds to a carbon nanotube with only 6 atoms in the circumferential direction, the nanoscale continuum theory still agrees well with molecular dynamics studies.

The continuum analysis also provides a simple explanation of the R^{-2} dependence of the pre-deformation energy. This is because that both strain and stress in the tube are proportional to the curvature $1/R$ at small deformation.

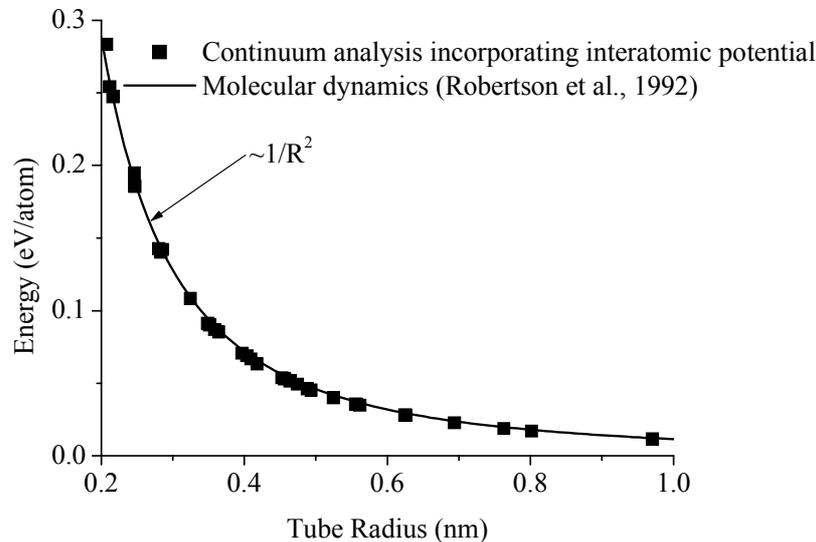


Figure 1. The pre-deformation energy versus the carbon nanotube radius.

4.2 Linear elastic modulus. Zhang et al. [7] obtained the linear elastic Young's modulus for an SWNT as 0.70 TPa. This is obtained from the linear elastic stiffness of 236 N/m calculated by the nanoscale continuum theory, and the commonly used tube thickness of 0.335 nm, which is the interlayer distance of graphite. *Without any parameter fitting, the Young's modulus predicted by the nanoscale continuum theory agrees well with Cornwell and Wille's [13] molecular dynamics simulations based on the same interatomic potential.* Jiang et al. [8] studied the Young's modulus of an SWNT with diameter dependence. Figure 2 presents the Young's modulus of an SWNT, normalized by that of graphene, versus the CNT diameter for armchair CNTs. *It is observed that the nanoscale continuum theory agrees well with the tight-binding simulations [14] over a wide range of CNT diameter without any parameter fitting.*

4.3 Fracture nucleation. Yakobson et al. [15] used molecular dynamics simulations to study a carbon nanotube under tension, and observed that the break strain ranges from 25% to 55%, depending on temperature and aspect ratio of CNTs. Prior to the breaking strain, the nanotube undergoes uniform deformation. One or few atomic bonds break once the breaking strain is reached.

The nanoscale continuum theory does not keep track of every atom and therefore cannot be applied directly to study this bond breaking process. Zhang et al. [9] modeled this problem as bifurcation instability as CNT becomes unstable with respect to nonuniform, localized deformation at the breaking strain. Using the nanoscale continuum theory, Zhang et al. [9] conducted a nonlinear bifurcation analysis for a CNT under tension, and determined the bifurcation strain to be 35% to 42% for different sets of CNTs with different aspect ratio. Thus, *without any parameter fitting, the bifurcation strain predicted by the nanoscale continuum theory agrees reasonably well with the breaking strain observed in molecular dynamic simulations based on the same interatomic potential.*

4.4 Defect nucleation: Stone-Wales transformation. Nardelli et al. [16,17] and Yakobson et al. [18] studied defect nucleation in an SWNT under tension using molecular dynamics simulations. They observed that, when the tensile strain reaches a critical value around 5%, a carbon bond that was perpendicular to the tensile loading direction suddenly rotated 90 degrees. A dislocation dipole was nucleated, and the local hexagonal lattices became pentagons and heptagons. This 90-degree rotation of an atomic bond is called Stone-Wales transformation.

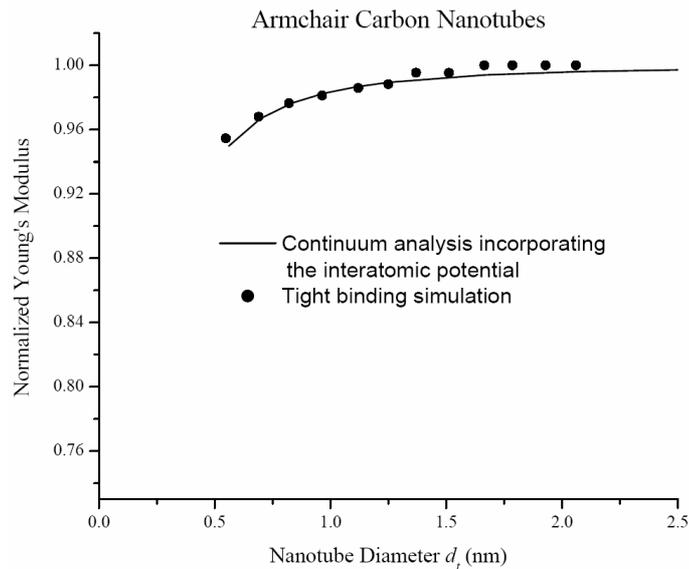


Figure 2. The Young's modulus of carbon nanotubes (CNTs) normalized by that of graphene, versus the CNT diameter d_t for armchair carbon nanotubes.

Jiang et al. [19] and Song et al. [20] have used the nanoscale continuum theory to investigate the defect nucleation in an SWNT. Figure 3 shows the strain energy in an SWNT (10,10) versus the axial strain for a perfect, hexagonal lattice (marked by 6-6) as well as for a defected lattice that undergoes the Stone-Wales transformation (marked by 57-75) locally. It is observed that a perfect lattice (6-6) has lower energy than that for a defected lattice (57-75) at the small strain. However, the trend reverses at the larger strain, indicating that a defected lattice has lower energy and is therefore more stable. The two curves intercept at a strain of 4.95%, which agrees very well with molecular dynamics simulations. *Without any parameter fitting, the critical strain for defect nucleation (Stone-Wales transformation) predicted by the nanoscale continuum theory agrees well with the molecular dynamics simulations [16-18].*

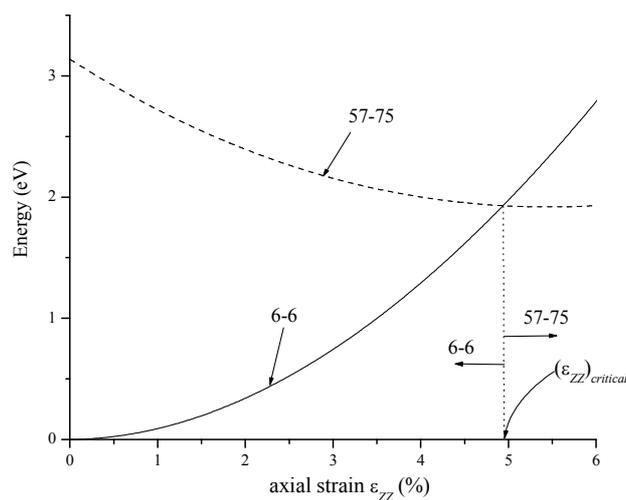


Figure 3. Strain energy versus the axial strain for a carbon nanotube under tension; the solid line is for a perfect (6-6) lattice; the dashed line is for a defected lattice (57-75).

4.5 Electrical property change due to mechanical deformation. Liu et al. [21] have used the nanoscale continuum theory together with an empirical k -space tight-binding method to investigate the electrical property change of an SWNT upon mechanical deformation. This is motivated by the experiment performed by Tombler et al's [5], which showed that the electrical conductance of a CNT may change by two orders of magnitude due to mechanical deformation, i.e., a metallic-like CNT may become a semiconducting one once the deformation is imposed. We use the nanoscale continuum theory to determine the positions of atoms in the deformed CNT and then use the k -space tight-binding method (e.g., a direct diagonalization approach exploiting the symmetry of the nanotube) to calculate the band gap energy. If the nanotube has zero or very small band gap energy, it is metallic with finite conductance, and electrons are free to move along its length. If there is a finite energy gap, electrons will have to overcome this energy barrier in order to move in the carbon nanotube and the tube may behave like a semiconducting one.

Liu et al. [21] have studied several sets of carbon nanotube under tension/torsion. Figure 4 shows the energy gap versus the twist κ (angle of rotation per unit length) for an armchair (5,5) SWNT. The energy gap is zero for the undeformed carbon nanotube (i.e., $\kappa=0$), which indicates that the (5,5) armchair carbon nanotube is like a metallic tube. However, as the twist κ becomes non-zero, the energy gap increases quickly, which creates a significant energy barrier for electrons to move in the carbon nanotube such that the tube behaves like a semiconducting one. *This is consistent with Tombler et al's [5] conclusion that the mechanical deformation has a significant effect on the electrical properties of carbon nanotubes.*

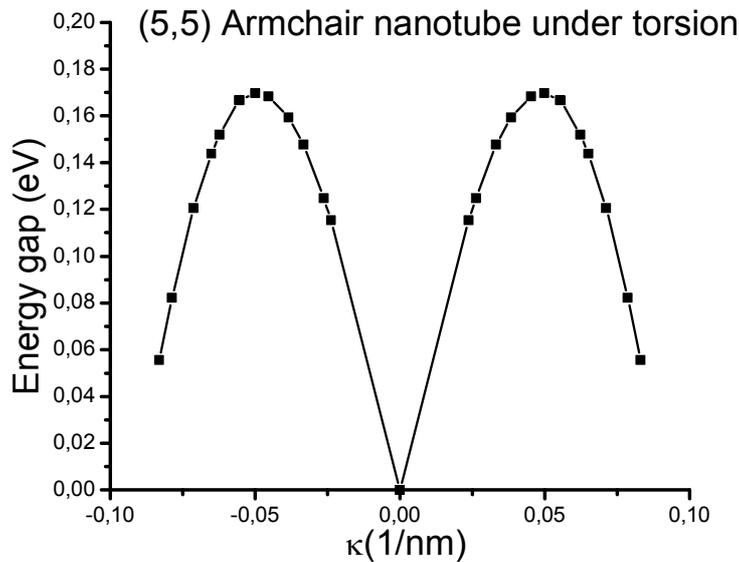


Figure 4. The energy gap versus the twist (rotation angle per unit length) for a (5,5) armchair carbon nanotube under torsion.

4.6 Specific heat. Many nanoscale material systems (e.g., nanocomposites) and devices (nanoelectronics) are intended to operate at the room or high temperature. The nanoscale continuum theory described in section 3 has no finite temperature effect since the interatomic potential does not depend on temperature. In order to account for this important effect, Jiang et al. [22,23] developed a finite-temperature continuum theory based on interatomic potential. At finite temperature, the potential energy $\sum V(r_{ij})$ in section 3 is replaced by the Helmholtz free energy $A = \sum V(r_{ij}) - TS$, where T is the temperature, S is the entropy, and the summation \sum is for all atomic bonds.

Jiang et al. [22,23] used local harmonic model [24] to approximate the energy S by

$$S = -k_B \sum_{i=1}^N \sum_{\kappa=1}^3 \ln \left[2 \sinh \left(\frac{h\omega_{i\kappa}}{4\pi k_B T} \right) \right], \quad (3)$$

where k_B is the Boltzmann constant, h is the Planck's constant, $\omega_{i\kappa}$ are the vibrational frequencies of atom i , which can be calculated from the diagonalization of a 3×3 matrix

$$\left| \omega_{i\kappa}^2 \mathbf{I}_{3 \times 3} - \frac{1}{m} \frac{\partial \sum V(r)}{\partial x_i \partial x_i} \right| = 0. \quad (4)$$

Jiang et al. [23] calculated the specific heat C_V using nanoscale continuum theory with finite temperature effect. The specific heat is defined as the heat energy required per unit volume of solid per degree of temperature change, and depends on the vibrational frequencies of atom i . Therefore, the specific heat becomes

$$C_V = \frac{6.022 \times 10^{23} h^2}{16\pi^2 k_B T} \sum_{\kappa=1}^3 \frac{\left(\frac{1}{T} - \frac{1}{\omega_{\kappa}} \frac{d\omega_{\kappa}}{dT} \right) \omega_{\kappa}^2}{\sinh^2 \left(\frac{h\omega_{\kappa}}{4\pi k_B T} \right)}. \quad (5)$$

Figure 5 shows the specific heat (per mole of atoms) versus temperature. For comparison, the experimental data for graphite [25] is also shown in Fig. 5. *Without any parameter fitting, the specific heat predicted by the nanoscale continuum theory with finite temperature effect agrees very well with the experimental data for graphite over the entire range of temperature.*

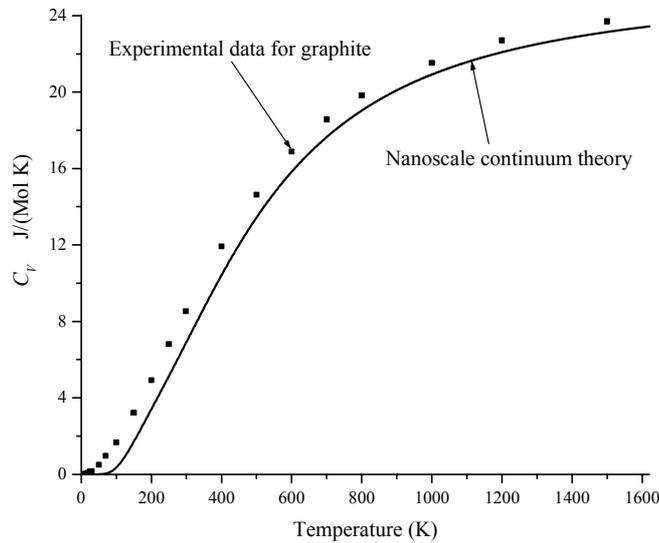


Figure 5. Temperature dependence of the specific heat for carbon nanotubes.

4.7 Coefficient of thermal expansion. Jiang et al. [23] studied the coefficient of thermal expansion (CTE) of SWNT by the nanoscale continuum theory with finite-temperature effect. At a given temperature, the Helmholtz free energy is minimized to provide the new bond length. The CTE is the fractional change in the linear dimension of solid per degree of temperature change. Figure 6 shows the CTE of CNT versus temperature and the experimental data for graphite α -axis [25]. *Without any*

parameter fitting, the CTE predicted by the nanoscale continuum theory for CNT agrees reasonably well with the experimental data for graphite. It is observed that the CTE of CNT is negative for temperature $T < 456\text{K}$, in other words, CNT shrinks when the temperature rises. The experimental data for graphite also show negative α -axis CTE for a large range of temperature.

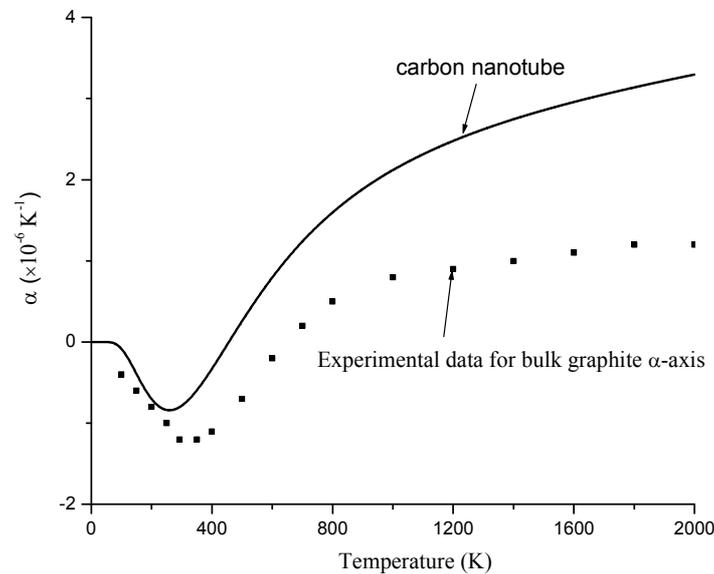


Figure 6. Temperature dependence of the coefficient of thermal expansion for carbon nanotubes.

5. Concluding Remarks

We have proposed a nanoscale continuum theory that incorporates the interatomic potential into the constitutive models of continuum mechanics, and have applied the theory to study the mechanical and thermal properties of carbon nanotubes. The theory is similar to the previously developed Virtual-Internal-Bond model for cohesive modeling of fracture [26-27], but has significantly extended the modeling capability in the directions of electromechanical coupling, atomistic defects, and thermal effects. The nanoscale continuum theory links the constitutive model of solids at the continuum level to the interatomic potential at the atomic level. For the hexagonal lattice structure of carbon nanotubes, the Cauchy-Born rule is modified in order to ensure the equilibrium of atoms. This modification is based on the introduction of an internal degree of freedom and the energy minimization. We have applied the nanoscale continuum theory to study several important mechanical deformation modes, including the dependence of the pre-deformation energy on the nanotube radius, linear elastic modulus, the critical strain for fracture nucleation, defect nucleation in the form of Stone-Wales transformation, electrical property change due to torsion of a carbon nanotube, specific heat, and coefficient of thermal expansion. The results obtained by the nanoscale continuum theory agree very well with experiments and atomistic simulations without any parameter fitting. The proposed approach to link continuum analysis to atomistic models can also be applied to other nano-structured materials

5. Concluding Remarks

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