A FINITE ELEMENT MODEL FOR THERMAL DILATATION OF CARBON NANOTUBES

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Abstract. The paper presents a finite element model that can be used for modelling of a nanotube thermal contraction with temperature increase. Since carbon nanotubes exhibit anisotropic thermal contraction, the ordinary structural mechanics approach based on the beam finite elements acting as interatomic bonds cannot be directly applied. To circumvent this problem, a set of additional rod elements is introduced into the model. If different coefficients of thermal expansion are used for the beam and rod elements, anisotropic thermal contraction can be modelled. An exact calculation procedure for these thermal expansion coefficients is presented. The proposed model is tested on one carbon nanotube and results are compared to the data available in literature. Influence of the stiffness of additional rod elements on the obtained results is not noticed.

1. INTRODUCTION

Most materials expand with temperature increase. However, in some rare cases materials contract with temperature rise, like some sorts of rubber, polyethylene, oxides NaTi$_2$P$_3$O$_{12}$, ZrW$_2$O$_8$, boron nitride and for this research most interesting – layered graphite. Obviously, it would be very useful to have a material that does not change dimensions with temperature variations. Although it is not realistic to expect to find such materials in nature, perhaps these can be fabricated as a some sort of composite material. Since the layered graphite is based on the same type of sp$^2$ carbon bonds as carbon nanotubes, it is not surprising that some researchers turned their attention to the thermal dilatation of carbon nanotubes. Among the first results in that direction are documented in works by Yosida [1] and Maniva et al. [2]. Using x-ray diffraction of single-walled carbon nanotubes (SWCNT), a negative coefficient of thermal expansion was observed. A number of numerical studies followed [3,4]. Almost exclusively based on the molecular dynamics simulations, those managed to repeat the behaviour experimentally noticed by Yosida. In one case [3], a finite element shell model was used to model thermal contraction. Molecular dynamics simulation in the latter paper pinpointed the cause of thermal contraction to the vibration effects. In particular, temperature increase leads toward increase in the bond length, but on the other side the entropy also increases. Higher structural and vibrational entropy leads to the nanotube vibration, what results in actual decrease of the nanotube dimensions as a consequence of different vibration modes. As an additional result, it was noticed that the coefficient of thermal expansion (CTE) differs in longitudinal and radial direction. Even some analytical approaches were noticed. Research [5] found out that the thermal contraction disappears at high temperatures. Also, as the initial radius of nanotube is decreased, the range of negative CTE shrinks.
On the numerical side of the mechanical nanotube modelling in the last few years, several attempts were noticed to substitute computationally expensive molecular dynamic simulations with alternative solutions. Perhaps the most successful approach is the one based on the frame-like finite element model [6-12], named as the structural mechanics approach. The approach employs beam finite elements that model interatomic bonds, while nodes are positioned at the atom positions. It was successfully applied to both SWCNT and multi-walled carbon nanotubes (MWCNT) in isothermal and nonisothermal [9] environments.

This research starts from above beam finite element model of a carbon nanotube. A principal goal was to offer a reliable tool for the simulation of carbon nanotube contraction by such finite element method. To the best of authors' knowledge, there isn’t a single suitable technique of this type proposed in the literature. If the CTE of carbon nanotube is the same in all direction, the solution would be straightforward. However, different CTE in the radial and longitudinal direction complicates procedure. Standard beam finite elements do not offer the possibility to model such behaviour. Therefore, a simple procedure is offered to circumvent such problem. Sets of rod elements with adjusted material properties are added to the frame-like carbon nanotube structure effectively enabling anisotropic contraction. The model is tested and compared to the results obtained by other authors that used molecular dynamics approach.

2. NUMERICAL MODEL OF A CARBON NANOTUBE

2.1. Model of interatomic interactions

The molecular mechanics considers a nanotube as a large molecule consisting of atoms. In molecular dynamics simulations, these atoms are treated as material points and their motion is modelled by the appropriate equations. Electron – nucleus and nucleus – nucleus interactions are generating forces that drive such motion. Obviously, these forces should be defined in some manner. The usual approach is to use the steric potential energy in its general form [6]:

\[ U = \sum U_r + \sum U_b + \sum U_\theta + \sum U_\phi + U_{vdw}, \]

where potential \( U_r \) describes bond-stretching, \( U_b \) bond angle bending, \( U_\theta \) dihedral angle torsion, \( U_\phi \) out-of-plane torsion and \( U_{vdw} \) is potential due to van der Waals interaction. These potentials are defined only by the relative positions of atoms:

\[ U_r = 0.5k_r(\Delta r)^2 \quad U_b = 0.5k_b(\Delta \theta)^2 \]

\[ U_\phi = 0.5k_\phi(\Delta \phi)^2, \]

where \( k_r, k_b, k_\phi \) are material constants describing bond stretching forces, bond angle bending and torsional resistance, respectively. Increments \( \Delta r, \Delta \theta, \Delta \phi \) describe the change in the distance between two atoms, bond angle and bond twisting angle, respectively. Contribution from van der Waals interaction is usually neglected.

Similar relationships are used in the structural mechanics. The energy related to the axial, bending and torque loading of a beam is defined by:

\[ U_{ax} = \frac{1}{2} \int \frac{N^2}{EA} \, dL = \frac{EA(\Delta L)^2}{2L}; \]

\[ U_{b} = \frac{1}{2} \int \frac{M^2}{EI} \, dL = \frac{EI(\Delta \alpha)^2}{2L}; \]

\[ U_{t} = \frac{1}{2} \int \frac{T^2}{GJ} \, dL = \frac{GJ(\Delta \beta)^2}{2L}. \]

If increments in Eqs. (2) \( \Delta (\bullet) \) are compared to those in Eqs. (3), the following relations follow:

\[ k_r = EA/L; \quad k_b = EI/L; \quad k_\phi = GJ/L. \]

In that way, interatomic interactions can be substituted by the beam finite elements with properties defined by the Eqs. (4). Nodes are placed on the atom positions with beam elements representing bonds. Beam parameters \( E, A, I \) and \( J \) should be selected to match known constants \( k_r, k_b, k_\phi \).

2.2. A finite element model for the thermal contraction of nanotube

The main issue that should be solved in the finite element modelling of the thermal contraction of a nanotube is the difference in the longitudinal \( \alpha_L \) and the radial \( \alpha_R \) CTEs [3,4]. Standard beam finite elements cannot handle anisotropy in CTE so an alternative way to define different behaviour in the radial and longitudinal direction should be envisaged. Consequently, a set of rod elements is introduced to the each repetitive section of a nanotube, Fig. 1. At each section of nanotube, a central node is added and connected with a rod element to the each nanotube node of the corresponding section.
Corrected CTEs of beams used to model bonds $\alpha_{corr}^L$ and additional rod elements $\alpha_{corr}^R$ can be determined in order to match experimentally noticed behaviour.

Actual values of $\alpha_L$ and $\alpha_R$ are treated as given. To obtain these experimentally consistent contractions, $\alpha_{corr}^L$ and $\alpha_{corr}^R$ can be calculated employing the standard strength of materials techniques. Therefore, the thermal dilatation of the nanotube beam elements will be described by the $\alpha_{corr}^L$ while the additional rod elements will be described by $\alpha_{corr}^R$.

If the radial movement of one atom of nanotube is considered, then its radial movement due to the temperature change equals $\alpha_{corr}^L \Delta TR$ and due to the mechanical force arising from the attached rod element is described as $k_{tube} R_F = F_{tube}/AE$. Radial stiffness of the nanotube $k_{tube}$ cannot be calculated directly in a closed form, at least not in a simple manner. However, it can be easily evaluated by the finite element simulation, by loading the nanotube with unit forces in the radial direction and taking radial displacement as the nanotube stiffness. Thermal dilatation and mechanical dilatation defined above should match actual radial dilatation of the nanotube $\alpha_{rad} \Delta TR$:

$$\alpha_{rad} \Delta TR + \frac{F_{tube}}{k_{tube}} - \alpha_{corr}^L \Delta TR = 0.$$  \hfill (5)

Additionally, if one rod element of a repetitive ring section of a nanotube is isolated, Fig. 2, then its thermal dilatation $\alpha_{corr}^R \Delta TR$ and the mechanical dilatation due to the force arising from the influence of nanotube $F_{rod} = F_{rod} / AE$ should give the experimentally noticed radius change $\alpha_{rad} \Delta TR$:

$$\alpha_{rad} \Delta TR + \frac{F_{rod} R}{AE} - \alpha_{corr}^R \Delta TR = 0.$$  \hfill (6)

Since the force in rod element $F_{rod}$ is equal in magnitude but opposite in direction to the forces acting on nanotube $F_{rod}$, the latter equation can be rewritten as:

$$\alpha_{rad} \Delta TR + \frac{F_{rod} R}{AE} - \alpha_{corr}^R \Delta TR = 0.$$  \hfill (7)

Finally, the longitudinal dilatation of a nanotube should be considered. The nanotube with the corrected CTE $\alpha_{corr}^L$ will have thermal dilatation $\alpha_{corr}^L \Delta TL$. It will also change length due to the mechanical loads arising from rod forces for some $\Delta Lf$. This again have to coincide with the actual value of thermal contraction $\alpha_{rad} \Delta TL$:

$$\alpha_{rad} \Delta TL + \Delta Lf - \alpha_{corr}^L \Delta TL = 0.$$  \hfill (8)

The mechanical dilatation $\Delta Lf$ can be evaluated by the introduction of Poisson' ratio:

$$\nu = \frac{\Delta Lf}{\Delta Rf / R} \Rightarrow \Delta Lf = \frac{\nu \Delta Rf L}{R} = \frac{\nu F_{tube} L}{R k_{tube}}.$$  \hfill (9)

Poisson' ratio is determined from the same model that is used for determination of nanotube radial stiffness $k_{nano}$. With Eq. (9), Eq. (8) is rephrased into:

$$\alpha_{rad} \Delta TL + \frac{\nu F_{tube} L}{R k_{tube}} - \alpha_{corr}^L \Delta TL = 0.$$  \hfill (10)

The linear system of three Eqs. (5), (7), and (10) should be solved for three unknowns $\alpha_{corr}^L$, $\alpha_{corr}^R$, and $F_{rod}$. Of interest are only corrected CTEs, obtained as follows:

$$\alpha_{corr}^L = \frac{1}{1 - \nu} \left[ \frac{R_{k_{tube}}} {AE} \alpha_L + \alpha_R \left( 1 + \frac{R_{k_{tube}}} {AE} (\alpha_L - \alpha_R) \right) \right];$$

$$\alpha_{corr}^R = \alpha_L + \frac{AE}{R_{k_{tube}}} (\alpha_L - \alpha_R).$$  \hfill (11)
It should be noted that the axial stiffness $AE$ of the rod elements should be small compared to the beam stiffness. Otherwise, the rod elements will provide unacceptable additional stiffness to the nanotube.

3. EXAMPLE – MODELLING OF THE THERMAL CONTRACTION OF AN ARMCHAIR SINGLE WALLLED CARBON NANOTUBE

To test proposed model, a carbon nanotube with the armchair configuration is selected. Length of nanotube is 24.4155 nm with diameter 0.68 nm, Fig. 3. The same type of nanotube was used in [3].

Coefficients in Eqs. (7) are taken from [6] based on the experience with graphite sheets and their values are: $k_r = 938$ kcal/molÅ$^2 = 651.72$ nN/nm, $k_{rr} = 126$ kcal/molrad$^2 = 0.875$ nNnm/rad$^2$, $k_4 = 40$ kcal/molÅ$^2 = 0.2778$ nNnm/rad$^2$. Using these values, the structural mechanics parameters of the beam element can be calculated from Eqs. (4). Cross-area properties of rod elements are taken to be the same as for beam elements. However, Young modulus was smaller by a factor of 1000 compared to the beam elements. Influence of such decreased stiffness can be neglected in mechanical analysis.

To obtain correct value of rod CTE, radial stiffness of the nanotube section $k_{tub}$ should be evaluated as mentioned earlier. Procedure described in Section 2 was employed, and loading of a nanotube finite element model with unit forces resulted in the stiffness $k_{tub} = 52.4$ nN/nm. Furthermore, Possion’ ratio defined by Eq. (9) is calculated from the same model as $v = 0.21$. Data for the longitudinal and radial CTEs of a nanotube was taken from [3] and for the purpose of completeness are presented in Fig. 4. The values in research [3] were obtained by the simulation of thermal vibrations by the molecular dynamics. CTEs can be, of course, obtained by experimental research as well.

With all data at hand, for each temperature $T = 100, 200, \ldots 800$K finite element calculations were performed and thermal contractions were obtained and compared to the results given in [3]. Results are summarized in Table 1. Therefore, $\alpha_{corr}$ take positive values in all cases except for 100K. $\alpha_{corr}$ remain negative and differ only slightly from actual values $\alpha$. An excellent agreement can be noticed.

To evaluate influence of additional rod elements, nanotube was analyzed in basic loading cases of the bending and the axial deformation. Obtained results were compared to the nanotube model without rod elements.

In the first analysis, nanotube was loaded by the forces acting in nodes at the one end of a nanotube, while the motion of nodes at the other end was constrained. The resultant force was 0.01 nN. Obtained displacements in both cases were 0.428 nm. As expected, influence of additional stiffness cannot be noticed.

The both models were loaded axially by a resultant force of 1nN. In the both cases results were the same with the axial displacement 0.01001 nm. Again, rod elements do not have any influence on the results.

4. CONCLUSIONS

The paper presented a simple technique for the modelling of anisotropic contraction of a carbon nanotube in thermally variable environment by the structural mechanics approach. Procedure can be used for simulation of any kind of nanotube if the actual values of thermal contractions are known either from experiments or molecular dynamics simulations. The proposed model offers various possibilities of modelling nanotube composites by finite element method. For example, simulations can be carried out to find the optimal distribution of nanotubes in a matrix in order to obtain composites that does not significantly change dimensions with temperature variations.
Table 1. Results and corrected CTEs for beam ($\alpha_\text{L}^\text{corr}$) and rod elements ($\alpha_\text{R}^\text{corr}$).

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>100</th>
<th>200</th>
<th>300</th>
<th>400</th>
<th>500</th>
<th>600</th>
<th>700</th>
<th>800</th>
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<tbody>
<tr>
<td>$\Delta D / D$ (MD)</td>
<td>-9.0E-5</td>
<td>-1.4E-4</td>
<td>-1.92E-4</td>
<td>-2.40E-4</td>
<td>-3.00E-4</td>
<td>-3.30E-4</td>
<td>-3.92E-4</td>
<td>4.52E-4</td>
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<tr>
<td>$\Delta D / D$ (FEM)</td>
<td>-8.998E-5</td>
<td>-1.401E-4</td>
<td>-1.920E-4</td>
<td>-2.402E-4</td>
<td>-3.003E-4</td>
<td>-3.304E-4</td>
<td>-3.915E-4</td>
<td>-4.546E-4</td>
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<tr>
<td>Diff. between</td>
<td>-0.0253</td>
<td>0.0464</td>
<td>0.0136</td>
<td>0.0778</td>
<td>0.0886</td>
<td>0.1081</td>
<td>-0.1167</td>
<td>0.5752</td>
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<tr>
<td>$\Delta D / D$ [%]</td>
<td>-7.227E-7</td>
<td>-7.886E-7</td>
<td>-8.173E-7</td>
<td>-8.685E-7</td>
<td>-8.786E-7</td>
<td>-9.806E-7</td>
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<td>-1.078E-6</td>
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<tr>
<td>$\alpha_\text{L}^\text{corr}$ [1/K]</td>
<td>-7.600E-5</td>
<td>-1.540E-4</td>
<td>-2.340E-4</td>
<td>-3.248E-4</td>
<td>-4.100E-4</td>
<td>-5.340E-4</td>
<td>-6.475E-4</td>
<td>-7.760E-4</td>
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<tr>
<td>$\Delta L / L$ (MD)</td>
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<td>-1.541E-4</td>
<td>-2.339E-4</td>
<td>-3.250E-4</td>
<td>-4.102E-4</td>
<td>-5.343E-4</td>
<td>-6.459E-4</td>
<td>-7.777E-4</td>
</tr>
<tr>
<td>$\Delta L / L$ (FEM)</td>
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<td>-1.541E-4</td>
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</tr>
<tr>
<td>Diff. between</td>
<td>0.0335</td>
<td>0.0455</td>
<td>-0.0390</td>
<td>0.0623</td>
<td>0.0464</td>
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<td>0.2137</td>
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<tr>
<td>$\alpha_\text{R}^\text{corr}$ [1/K]</td>
<td></td>
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