Research Article
Thermomechanical Stresses in Fullerenes at Nanotube

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The thermomechanical stresses acting between a nanotube and fullerenes encapsulated on it are computed. After a general formulation, based on elasticity, we have applied the analysis to C\textsubscript{82}@\textsubscript{(10,10)} or C\textsubscript{60}@\textsubscript{(10,10)} peapods finding stresses in the gigapascal range or vanishing, respectively. The analysis suggests that a thermal control could be used to produce smart fullerenes at nanotube systems, for example, as two-stage nanovehicles for drug delivery.

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1. INTRODUCTION

The Royal Swedish Academy of Sciences awarded the 1996 Nobel Prize in Chemistry jointly to Curl, Kroto, and Smalley for their discovery in 1985, together with Heath and O’Brien [1], of fullerenes. It is common belief that the discovery of carbon nanotubes (CNTs) took place in 1991 thanks to Iijima [2], who reported in Nature the observation of multiwalled CNTs. In 1993, in the same issue of Nature, two independent groups, again Iijima with Ichihashi [3] and Bethune et al. [4], reported the observation of single-walled CNTs. The impact of these papers on the scientific community has been unquestionably tremendous. In spite of this, the first direct observation of a multiwalled CNT (by force subsequent to the production of the transmission electron microscope) was previously reported in 1952 in the Journal of Physical Chemistry of Russia by Radushkevich and Lukyanovich [5], whereas an image, even if controversial, of a single- (or possibly double-) walled CNT was reported in 1976 by Oberlin et al. in the Journal of Crystal Growth [6].

Two editorials, appearing in Carbon in 1997 [7] and 2006 [8], support these pioneering observations.

Aside from the controversy surrounding the discovery of nanotubes, fullerenes and nanotubes have introduced humanity to the new nanoera. In particular, the giant strength and Young’s modulus of carbon fullerenes and nanotubes, combined with a low density, promise to revolutionize materials science, as required in the design of super-strong space elevator megacables [9] or super-adhesive Spiderman suits [10]. Combining the two nanostructures even more intriguing systems could be realized.

In this paper, we analyze the thermomechanical stresses acting between a nanotube and encapsulated fullerenes (e.g., see [11, 12]). We have solved the problem treating the fullerenes as a fluid inside an elastic channel (nanotube). We have applied the analysis to a C\textsubscript{82}@\textsubscript{(10,10)} system finding huge thermomechanical stresses, in the gigapascal range. A C\textsubscript{60}@\textsubscript{(10,10)} system is also considered for comparison and is found free of stresses. Thus the analysis suggests that a thermal control could be used to produce smart fullerenes at nanotube systems, for example, as two-stage nanovehicles for drug delivery.

2. THE THERMOMECHANICAL ELASTIC MODEL

Consider a nanotube filled by fullerenes (Figure 1). After a temperature variation, the nanotube diameter will change, interacting with the fullerenes. We treat the nanotube as an elastic cylindrical shell and the fullerenes as elastic spheres. We assume a constant pressure distribution between nanotube and fullerenes, due to the small spacing between fullerenes (0.34 nm), so that their action on the nanotube can be considered as a distributed pressure, for example, as a fluid inside an elastic channel.

Let us consider a linear elastic isotropic sphere of inner and outer radii \(a\) and \(b\) subjected to inner and outer pressures...
confinement from the nanotube is described by the external pressure \( p \). According to (1) and (2)

\[
\begin{align*}
\sigma_r(r) & = -\frac{1 - r_i^2/r_o^3}{1 - r_i^2/r_o^3} p, \\
\sigma_\theta(r) & = -\frac{1 + r_i^2/2r_o^3}{1 - r_i^2/r_o^3} p, \\
u_{tot}(r) & = u(r) + \alpha_f(T)\Delta Tr
\end{align*}
\]

where \( u_{tot} \) is the total (elastic + thermal) radial displacement, \( \alpha_f \) is the thermal expansion coefficient for fullerene (in general a function of the temperature, see Section 3), and \( \Delta T \) is the temperature variation.

Thus the fullerene elastic outer radius \( r_o^* \) (\( r_o \) if unstrained) is

\[
r_o^* = r_o + u_{tot}(r = r_o).
\]

Now consider a nanotube at temperature \( T \) as a linear elastic isotropic cylinder (elastic properties with subscript "n") having inner and outer radii \( R_i \) and \( R_o \), respectively. The confinement from the fullerenes is described by the internal pressure \( p \). According to (3) and (4):

\[
\begin{align*}
\sigma_r(r) & = \frac{R_i^2/R_o^2 - R_i^2/r_r^2}{1 - R_i^2/R_o^2} p, \\
\sigma_\theta(r) & = \frac{R_i^2/R_o^2 + R_i^2/r_r^2}{1 - R_i^2/R_o^2} p, \\
u_{tot}(r) & = u(r) + \alpha_n(T)\Delta Tr
\end{align*}
\]

Thus the nanotube elastic inner radius \( R_i^* \) (\( R_i \) if unstrained) is

\[
R_i^* = R_i + u_{tot}(r = R_i).
\]

The compatibility of the displacements (elastic contact between nanotube and fullerenes) implies

\[
r_o^*(p, \Delta T) = R_o^*(p, \Delta T).
\]

The solution of (10) gives the effective internal pressure \( p^* \); the fullerenes/nanotube internal/external radius as a function of temperature are simply given by \( r_r^*(p^*, \Delta T) = R_i^*(p^*, \Delta T) - tR_o^*(p^*, \Delta T) = R_o^*(p^*, \Delta T) + t \), where \( t \) is the shell thickness (0.34 nm); moreover, \( r_o^*(p^*, \Delta T) = R_o^*(p^*, \Delta T) \) can be derived from (9). From the computed
value of the pressure $p^*$, the thermomechanical stresses and strains in the fullerenes and nanotubes can be calculated via (1)–(4).

### 3. APPLICATION TO THE C82(10,10) OR C60(10,10) PEAPODS

According to the previous analysis, we consider nanotube or fullerenes as elastic cylindrical or spherical thin shells; we assume a constant thickness $t$ and plane stress condition and both nanotube and fullerenes composed by the same material, for which we assume $E_f = E_n = E \approx 1$ TPa, $\nu_f = \nu_n = \nu \approx 0$ (carbon). For an $(n,m)$ nanotube and for Cl fullerenes, the mean radii (at room temperature, i.e., at 290 K) are respectively given by

$$R_n = \frac{R_o + R_i}{2} \approx 0.0392\sqrt{n^2 + m^2 + nm} \text{ nm},$$

$$R_f = r = \frac{r_o + r_i}{2} \approx 0.0458\sqrt{l} \text{ nm},$$

so that $R_i = R_n + t/2$ and $r_o = R_f + t/2$ with $t = 0.3$ nm (close to the van der Waals spacing [14]). For $r_o > R_i$ mechanical stresses will be present.

In addition, the thermal volumetric expansion coefficient $\beta_f$ of carbon fullerenes is [15]

$$\beta_f \approx 3\alpha_f(T) \approx \begin{cases} 
-1 \times 10^{-5} \frac{T}{70} & T < 70 \text{ K}, \\
1 \times 10^{-5} \frac{T - 150}{80} & 70 \text{ K} \leq T < 400 \text{ K}, 
\end{cases}$$

(12)

which thus changes sign around 70 K, whereas the thermal expansion coefficient of a carbon nanotube, according to [15], is always negative in the considered temperature range:

$$\alpha_n \approx -1.2 \times 10^{-5} \frac{T}{400} \quad T < 400 \text{ K}. \quad (13)$$

### Table 1: Computed values for C60(10,10), thermomechanical stresses are vanishing.

<table>
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<tr>
<th>$T$ [K]</th>
<th>$\alpha_f$ [K$^{-1}$]</th>
<th>$\alpha_n$ [K$^{-1}$]</th>
<th>$r_o$ [nm]</th>
<th>$R_i$ [nm]</th>
<th>$r_o$ [nm]</th>
<th>$R_i$ [nm]</th>
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</table>
Thus, according to these numerical solutions, following the analysis reported in Section 2, we derive

\[ p = p^* + \left[ \frac{E (R_f + t/2)(1 + \alpha_f \Delta T) - (R_n - t/2)(1 + \alpha_n \Delta T)}{R_n - t/2 + R_f/(2t)(R_f + t/2)} \right] \]

\[ = \left\{ \begin{array}{ll}
0 & \text{if } \chi > 0 \text{ (contact)}, \\
\chi & \text{if } \chi \leq 0 \text{ (no contact)}
\end{array} \right. \]

\[ \sigma_{rf,n}^{(\max)} = -p, \quad \sigma_{nf} = -\frac{R_f}{2t} p, \quad \sigma_{nn} = \frac{R_n}{t} p, \]

\[ R_{f,n}^* = R_{f,n} \left( 1 + \frac{\sigma_{nf,n}^{(\max)}}{E} + \alpha_f,\Delta T \right), \]

\[ R_{f,n}' = R_{f,n}' \left( 1 + \alpha_f,\Delta T \right), \]

(14)

where \( \sigma_{rf,n}^{(\max)} \) is the maximum radial stress, thus evaluated at \( r_o \) and \( R_i \) (at \( r_o \) and \( R_i \) we have \( \sigma_r = 0 \)) and \( R_{f,n}' \) are the radii of the nanotube and fullerenes if assumed to be not interacting.

The cases of a (10,10) nanotube \( (R_n \approx 0.68 \text{ nm}) \) coupled with C60 \( (R_f \approx 0.35 \text{ nm}) \) or C82 \( (R_f \approx 0.41 \text{ nm}) \) fullerenes cooled from 290 K to 10 K are reported in Tables 1 and 2, respectively. Note that the diameter variation is very small, but stresses are huge for C82@(10,10), in the gigapascal range, but are vanishing for the C60@(10,10) peapod. Note the maximum circumferential tensile stress in the nanotube around 70 K of 43 GPa, whereas the circumferential compression in the fullerenes is of 13 GPa; the calculated contact pressure is of 19 GPa.

Considering different elastic constants \((E, \nu)\) would correspond to slightly different values, whereas the thermal expansion coefficients and in general the radii, unfortunately not fully defined for an atomistic object (see (8) and (11)), play a dramatic role on the computed thermomechanical stresses. Thus the analysis is accurate in the procedure but the deduced thermal stresses must be viewed just as an example of calculation. Slightly changing the definition of the radii (e.g., considering a different value for \( t \)) we have found an intermediate behaviour in which the interaction fullerenes-nanotube vanishes only in a given temperature range. This suggests that fullerenes (other types of nanoparticles can
be envisioned too) could be released from the nanotube by thermal activation, a perhaps useful concept for producing innovative two-stage nanovectors capable of smartly delivering the fullerenes/drugs by a remote thermal control.

4. CONCLUSIONS

According to our analysis, the thermomechanical stresses of a fullerenes at nanotube peapod can be tuned by varying the temperature in a controllable way. Tunable stiffness and band structure (metallic, semiconductor) of a nanotube could thus be achieved by embedding fullerenes on it and by controlling the temperature. The analysis suggests that smart fullerenes at nanotube peapods, such as two-stage nanovectors for drug delivery, could in principle be realized by remote thermal activation.

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REFERENCES

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