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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 C82@(10,10) or C60@(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 nanovectors for drug delivery.

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 el 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 C82@(10,10) system finding huge thermomechanical stresses, in the gigapascal range. A C60@(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 nanovectors 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

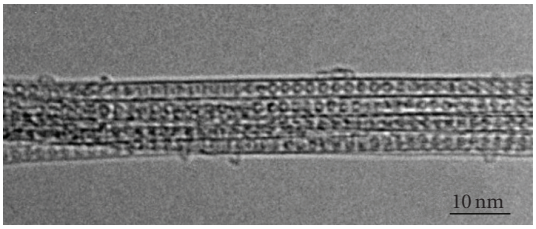

Figure 1: Example of fullerenes at nanotubes (Courtesy of Chiu Po-Wen).

p and q, respectively. The radial σ_r and circumferential σ_ϑ stressesat a generic radius $a < r < b$ are [13]

$$\sigma_r = \frac{1}{b^3 - a^3}\left(-b^3 q + a^3 p + \frac{a^3 b^3}{r^3}(q-p)\right),$$
$$\sigma_\vartheta = \frac{1}{b^3 - a^3}\left(-b^3 q + a^3 p - \frac{a^3 b^3}{2r^3}(q-p)\right). \quad (1)$$

Linear elastic isotropic laws for spherical symmetry become

$$\varepsilon_r \equiv \frac{\mathrm{d}u}{\mathrm{d}r} = \frac{\sigma_r}{E} - \frac{2\nu}{E}\sigma_\vartheta, \qquad \varepsilon_\vartheta \equiv \frac{u}{r} = \frac{\sigma_\vartheta}{E} - \frac{\nu}{E}(\sigma_\vartheta + \sigma_r), \quad (2)$$

where E and ν are the Young modulus and Poisson ratio of the material and u is the radial elastic displacement (along r). We will apply (1) and (2) to fullerenes, thus considering them as elastic spheres.

Analogously, let us consider a linear elastic isotropic cylinder (of length L) of inner and outer radii a and b subjected to inner and outer pressures p and q, respectively. The radial and circumferential stresses at a generic radius $a < r < b$ are [13]

$$\sigma_r = \frac{1}{b^2 - a^2}\left(-b^2 q + a^2 p + \frac{a^2 b^2}{r^2}(q-p)\right),$$
$$\sigma_\vartheta = \frac{1}{b^2 - a^2}\left(-b^2 q + a^2 p - \frac{a^2 b^2}{r^2}(q-p)\right). \quad (3)$$

Linear elastic isotropic laws for cylindrical symmetry become

$$\varepsilon_r \equiv \frac{\mathrm{d}u}{\mathrm{d}r} = \frac{\sigma_r}{E'} - \frac{\nu'}{E'}\sigma_\vartheta, \qquad \varepsilon_\vartheta \equiv \frac{u}{r} = \frac{\sigma_\vartheta}{E'} - \frac{\nu'}{E'}\sigma_r,$$
$$E' = E, \quad \nu' = \nu \text{ for plane stress;} \quad (4)$$
$$E' = \frac{E}{1-\nu^2}, \quad \nu' = \frac{\nu}{1-\nu} \text{ for plane strain.}$$

We can assume plain stress condition (i.e., $\sigma_z = 0$) or plane strain condition (i.e., $\varepsilon_z = 0$, for which in addition $\sigma_z = \nu(\sigma_r + \sigma_\vartheta)$). Assuming a nanotube with free ends, the first case is the most realistic, whereas the second case better describes fixed ends; thus we will treat nanotubes as elastic cylinders, by (3) and (4).

Consider a single fullerene at temperature T as a linear elastic isotropic sphere (elastic properties with subscript "f") having inner and outer radii r_i and r_o, respectively. The confinement from the nanotube is described by the external pressure p. According to (1) and (2)

$$\sigma_r(r) = -\frac{1 - r_i^3/r^3}{1 - r_i^3/r_o^3}p,$$
$$\sigma_\vartheta(r) = -\frac{1 + r_i^3/2r^3}{1 - r_i^3/r_o^3}p, \quad (5)$$
$$u_{\text{tot}}(r) = u(r) + \alpha_f(T)\Delta T r$$
$$= \left[\frac{\sigma_\vartheta(r)}{E_f} - \frac{\nu_f}{E_f}(\sigma_\vartheta(r) + \sigma_r(r)) + \alpha_f(T)\Delta T\right]r,$$

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

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

$$r_o^* = r_o + u_{\text{tot}}(r = r_o). \quad (6)$$

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):

$$\sigma_r(r) = \frac{R_i^2/R_o^2 - R_i^2/r^2}{1 - R_i^2/R_o^2}p, \qquad \sigma_\vartheta(r) = \frac{R_i^2/R_o^2 + R_i^2/r^2}{1 - R_i^2/R_o^2}p, \quad (7)$$

$$u_{\text{tot}}(r) = u(r) + \alpha_n(T)\Delta T r = \left[\frac{\sigma_\vartheta(r)}{E_n'} - \frac{\nu_n'}{E_n'}\sigma_r(r) + \alpha_n(T)\Delta T\right]r. \quad (8)$$

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

$$R_i^* = R_i + u_{\text{tot}}(r = R_i). \quad (9)$$

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

$$r_o^*(p, \Delta T) = R_i^*(p, \Delta T). \quad (10)$$

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 $r_i^*(p^*, \Delta T) = r_o^*(p^*, \Delta T) - tR_o^*(p^*, \Delta T) = R_i^*(p^*, \Delta T) + t$, where t is the shell thickness (0.34 nm); moreover, $r_0^*(p^*, \Delta T) = R_i^*(p^*, \Delta T)$ can be derived from (9). From the computed

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

T [K]	α_f [K^{-1}]	α_n [K^{-1}]	$r_o^{/}$ [nm]	$R_i^{/}$ [nm]	r_o^* [nm]	R_i^* [nm]
290	0.000006	−0.000009	0.500000	0.530000	0.500000	0.530000
280	0.000005	−0.000008	0.499973	0.530045	0.499973	0.530045
270	0.000005	−0.000008	0.499950	0.530086	0.499950	0.530086
260	0.000005	−0.000008	0.499931	0.530124	0.499931	0.530124
250	0.000004	−0.000008	0.499917	0.530159	0.499917	0.530159
240	0.000004	−0.000007	0.499906	0.530191	0.499906	0.530191
230	0.000003	−0.000007	0.499900	0.530219	0.499900	0.530219
220	0.000003	−0.000007	0.499898	0.530245	0.499898	0.530245
210	0.000003	−0.000006	0.499900	0.530267	0.499900	0.530267
200	0.000002	−0.000006	0.499906	0.530286	0.499906	0.530286
190	0.000002	−0.000006	0.499917	0.530302	0.499917	0.530302
180	0.000001	−0.000005	0.499931	0.530315	0.499931	0.530315
170	0.000001	−0.000005	0.499950	0.530324	0.499950	0.530324
160	0.000000	−0.000005	0.499973	0.530331	0.499973	0.530331
150	0.000000	−0.000005	0.500000	0.530334	0.500000	0.530334
140	0.000000	−0.000004	0.500031	0.530334	0.500031	0.530334
130	−0.000001	−0.000004	0.500067	0.530331	0.500067	0.530331
120	−0.000001	−0.000004	0.500106	0.530324	0.500106	0.530324
110	−0.000002	−0.000003	0.500150	0.530315	0.500150	0.530315
100	−0.000002	−0.000003	0.500198	0.530302	0.500198	0.530302
90	−0.000003	−0.000003	0.500250	0.530286	0.500250	0.530286
80	−0.000003	−0.000002	0.500306	0.530267	0.500306	0.530267
70	−0.000003	−0.000002	0.500367	0.530245	0.500367	0.530245
60	−0.000003	−0.000002	0.500329	0.530219	0.500329	0.530219
50	−0.000002	−0.000002	0.500286	0.530191	0.500286	0.530191
40	−0.000002	−0.000001	0.500238	0.530159	0.500238	0.530159
30	−0.000001	−0.000001	0.500186	0.530124	0.500186	0.530124
20	−0.000001	−0.000001	0.500129	0.530086	0.500129	0.530086
10	0.000000	0.000000	0.500067	0.530045	0.500067	0.530045

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 $E_f = E_n = E \approx 1\,\text{TPa}$, $\nu_f = \nu_n = \nu \approx 0$ (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

$$R_n = \frac{R_o + R_i}{2} \approx 0.0392\sqrt{n^2 + m^2 + nm}\ \text{nm},$$
$$R_f = r = \frac{r_o + r_i}{2} \approx 0.0458\sqrt{l}\ \text{nm}, \tag{11}$$

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 β_f of carbon fullerenes is [15]

$$\beta_f \approx 3\alpha_f(T) \approx \begin{cases} -1 \times 10^{-5}\dfrac{T}{70} & T < 70\,\text{K}, \\ 1 \times 10^{-5}\dfrac{T - 150}{80} & 70\,\text{K} \le T < 400\,\text{K}, \end{cases} \tag{12}$$

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:

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

Table 2: Computed values for C82@(10,10), thermomechanical stresses are in the gigapascal range.

T [K]	$r_o^{/}$ [nm]	$R_i^{/}$ [nm]	p [MPa]	σ_{rf}, σ_{rn} [MPa]	$\sigma_{\vartheta f}$ [MPa]	$\sigma_{\vartheta n}$ [MPa]	r_o^* [nm]	R_i^* [nm]
290	0.56000	0.53000	18939.39	−18939.39	−12941.92	42929.29	0.55469	0.55919
280	0.55997	0.53004	18892.14	−18892.14	−12909.63	42822.18	0.55468	0.55916
270	0.55994	0.53009	18849.84	−18849.84	−12880.72	42726.29	0.55466	0.55914
260	0.55992	0.53012	18812.49	−18812.49	−12855.20	42641.64	0.55465	0.55912
250	0.55991	0.53016	18780.09	−18780.09	−12833.06	42568.21	0.55465	0.55911
240	0.55990	0.53019	18752.65	−18752.65	−12814.31	42506.01	0.55464	0.55909
230	0.55989	0.53022	18730.16	−18730.16	−12798.95	42455.04	0.55464	0.55909
220	0.55989	0.53024	18712.63	−18712.63	−12786.96	42415.30	0.55464	0.55909
210	0.55989	0.53027	18700.05	−18700.05	−12778.37	42386.78	0.55465	0.55909
200	0.55990	0.53029	18692.42	−18692.42	−12773.16	42369.49	0.55466	0.55910
190	0.55991	0.53030	18689.75	−18689.75	−12771.33	42363.44	0.55467	0.55911
180	0.55992	0.53031	18692.03	−18692.03	−12772.89	42368.61	0.55469	0.55913
170	0.55994	0.53032	18699.27	−18699.27	−12777.83	42385.01	0.55471	0.55915
160	0.55997	0.53033	18711.46	−18711.46	−12786.16	42412.63	0.55473	0.55917
150	0.56000	0.53033	18728.60	−18728.60	−12797.88	42451.49	0.55475	0.55920
140	0.56004	0.53033	18750.69	−18750.69	−12812.97	42501.57	0.55478	0.55923
130	0.56007	0.53033	18777.74	−18777.74	−12831.46	42562.89	0.55481	0.55927
120	0.56012	0.53032	18809.75	−18809.75	−12853.33	42635.43	0.55485	0.55932
110	0.56017	0.53031	18846.70	−18846.70	−12878.58	42719.20	0.55489	0.55936
100	0.56022	0.53030	18888.62	−18888.62	−12907.22	42814.19	0.55493	0.55942
90	0.56028	0.53029	18935.48	−18935.48	−12939.24	42920.42	0.55497	0.55947
80	0.56034	0.53027	18987.30	−18987.30	−12974.65	43037.88	0.55502	0.55953
70	0.56041	0.53024	19044.07	−19044.07	−13013.45	43166.56	0.55508	0.55960
60	0.56037	0.53022	19033.19	−19033.19	−13006.02	43141.91	0.55504	0.55956
50	0.56032	0.53019	19020.96	−19020.96	−12997.66	43114.18	0.55499	0.55951
40	0.56027	0.53016	19007.37	−19007.37	−12988.37	43083.36	0.55494	0.55946
30	0.56021	0.53012	18992.41	−18992.41	−12978.15	43049.47	0.55489	0.55940
20	0.56014	0.53009	18976.10	−18976.10	−12967.00	43012.49	0.55483	0.55933
10	0.56007	0.53004	18958.43	−18958.43	−12954.92	42972.43	0.55476	0.55927

Thus, according to these numerical solutions, following the analysis reported in Section 2, we derive

$$p = p^* = \begin{cases} E\dfrac{(R_f+t/2)(1+\alpha_f\Delta T)-(R_n-t/2)(1+\alpha_n\Delta T)}{R_n/t(R_n-t/2)+R_f/(2t)(R_f+t/2)} = \chi & \text{if } \chi > 0 \text{ (contact)}, \\ 0 & \text{if } \chi \le 0 \text{ (no contact)}, \end{cases}$$

$$\sigma_{rf,n}^{(\max)} = -p, \quad \sigma_{\vartheta f} = -\frac{R_f}{2t}p, \quad \sigma_{\vartheta n} = \frac{R_n}{t}p,$$
$$R_{f,n}^* = R_{f,n}\left(1 + \frac{\sigma_{\vartheta f,n}}{E} + \alpha_{f,n}\Delta T\right),$$
$$R_{f,n}^{/} = R_{f,n}(1 + \alpha_{f,n}\Delta T), \tag{14}$$

where $\sigma_r^{(\max)}$ is the maximum radial stress, thus evaluated at r_o and R_i (at r_i and R_o 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 ($R_n \approx 0.68$ nm) coupled with C60 ($R_f \approx 0.35$ nm) or C82 ($R_f \approx 0.41$ 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 gigapascale 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, ν) 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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