

Self-buckling at the nanoscale

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Keywords: self-buckling, buckling, nanoscale, nanotubes, fullerenes, peapods

Abstract

In this paper the self-buckling of nanostructures, such as nanotubes, fullerenes and peapods, is analytically treated; this surprising phenomenon is due to the interaction among the nanostructures caused by the surface energy; it is peculiar of the nanoscale and has not a macroscopic counterpart. The influence of the surrounding nanostructures on one of them in a crystal is nearly identical to that of a liquid having surface tension equal to the surface energy of the solid. For the beneficial implications of the self-buckling on the overall mechanical strength see Pugno (2010; The design of self-collapsed super-strong nanotube bundles, *Journal of the Mechanics and Physics of Solids*, Available Online).

Introduction

The elastic buckling under pressure, and even without pressure, i.e. the self-buckling of nanotubes in a bundle, was firstly investigated by atomistic simulations in [1]. These authors have performed molecular dynamics simulations to confirm that carbon nanotubes undergo a discontinuous collapse transition under hydrostatic pressure. They predicted also a critical diameter for the self-collapse (at atmospheric pressure), lying between 4.2 and 6.9 nm with the considered force field. In addition, there was good agreement between their simulations, simply calibrated with X-ray compression data for graphite, and the experimentally observed transition pressures for laser-grown nanotubes. This level of agreement raised confidence that the simple and computationally inexpensive force field used in [1] may be suitable for examining the nanomechanics of nanotubes.

Moreover, the self-buckling of nanotubes in a bundle has been experimentally observed [2]. These authors have introduced a method for the direct spinning of pure carbon nanotube fibres from an aerogel formed during chemical vapour deposition. The continuous withdrawal of product from the gas phase as a fibre imparts high commercial potential to the process, including the possibility of in-line post-spin treatments for further product optimisation. Also, they have shown that the mechanical properties of the fibres are directly related to the type of nanotubes present (i.e., multiwall or single wall, diameters, etc.), which in turn, can be, at least ideally, controlled by the careful adjustment of process parameters. In particular, they obtained high performance fibers from dog-bone, i.e. self-collapsed, carbon nanotubes.

Only very recently, the theoretical explanation of the self-buckling has been given, including its beneficial implication on the overall mechanical strength [3] in the case of sliding failure. Roughly, the self-collapse enlarges the interface surface area between the nanotubes and thus also the strength of the junctions between nanotubes and finally the overall fracture strength of the bundle, in case of sliding failure. For the prediction of the complimentary intrinsic fracture see [4-11].

The present paper is focused on the self-buckling of nanotube/fullerene crystals.

2. Theory

We treat the crystal as a liquid-like material with surface tension $\gamma_t = \gamma$, as imposed by the energy equivalence (the surface tension has the thermodynamic significance of work spent to create the unit surface, as the surface energy), thus deducing a pressure γ/R acting on a single nanotube of radius R within a bundle, as evinced by the Laplace's equation. In other words, considering a cylindrical cavity/nanotube of size R under a pressure p in a liquid/nanotube bundle having surface tension/energy γ , the free energy (per unit length) of the system can be written as $E = -p(\pi R^2) + \gamma(2\pi R) + const$ and has to be minimal at the equilibrium; thus posing $dE = 0$, we find $p = \gamma/R$. Note that for a crystal composed by fullerenes of radius R , the pressure $p = 2\gamma/R$ on a fullerene could be deduced from $E = -p\left(\frac{4}{3}\pi R^3\right) + \gamma(4\pi R^2) + const$ posing $dE = 0$, again in agreement with the prediction of the Laplace's equation. Mixed systems, such as peapods, are also considered.

2.1 Nanotubes

The critical pressure p_c can be accordingly derived as:

$$p_c = \frac{3N^\alpha D}{R^3} - \frac{\gamma}{R} \quad (1)$$

where N is the number of walls and $1 \leq \alpha \leq 3$: assuming perfect bonding between the walls would correspond to $\alpha = 3$, whereas for independent walls $\alpha = 1$; D is the bending stiffness of graphene; however, note that in the equations appears always the group $N^\alpha D$, that is the total bending stiffness.

The first term in eq. (1) is that governing the buckling of a perfectly elastic cylindrical long thin shell (of bending stiffness $N^\alpha D$), whereas the second term is the pressure imposed by the surrounding nanotubes, significant only at the nanoscale.

Treating the atomistic simulations results for single walled nanotubes [1], excluding the two smallest nanotubes for which the buckling pressure was not accurately determined, a relevant agreement with eq. (1) is observed (coefficient of correlation $R^2=0.97$), fitting a plausible value of $D_{fit} \approx 0.2 \text{ nN} \cdot \text{nm}$.

From eq. (1) we derive the following condition for the self-collapse, i.e. collapse under zero pressure, of a nanotube in a bundle:

$$R \geq R_c^{(N)} = \sqrt{\frac{3N^\alpha D}{\gamma}} = \sqrt{6}R_0^{(N)} \quad (2)$$

Taking $D = 0.1 \text{ nN} \cdot \text{nm}$ and $\gamma = 0.18 \text{ N/m}$ we find $2R_c^{(1)} \approx 2.7 \text{ nm}$. Considering an intermediate coupling between the walls with $\alpha \approx 2$, the critical diameters for double and triple walled nanotubes are $2R_c^{(2)} \approx 5.4 \text{ nm}$ and $2R_c^{(3)} \approx 8.1 \text{ nm}$. Note that for self-similar structures ($t/R = const$)

the minimum thickness Nt ($D \propto t^3$) required for the self-buckling is very small, thus the self-collapse is peculiar of the nanoscale and does not have a macroscopic counterpart.

In [2], 17 experimental observations on the self-collapse of nanotubes in a bundle have been reported, see Table 1. A number of 5 single walled nanotubes with diameters in the range 4.6-5.7nm were all observed as collapsed; moreover, while the 3 double walled nanotubes observed with internal diameters in the range 4.2-4.7nm (the effective diameters are larger by a factor of $\sim 0.34/2\text{nm}$) had not collapsed, the observed 8 double walled nanotubes with internal diameters in the range 6.2-8.4nm had collapsed. Finally, a triple walled nanotube of 14nm internal diameter (the effective diameter is $\sim 14.34\text{nm}$) was observed as collapsed too. All these 17 observations are in agreement with our theoretical predictions of eq. (2), supporting our conjecture of liquid-like nanotube bundles.

Nanotube number	Number N of walls	Diameter of the internal wall [nm]	Collapsed (Y/N) Exp. & Theo.
1	1	4.6	Y
2	1	4.7	Y
3	1	4.8	Y
4	1	5.2	Y
5	1	5.7	Y
6	2	4.2	N
7	2	4.6	N
8	2	4.7	N
9	2	6.2	Y
10	2	6.5	Y
11	2	6.8	Y
12	2	6.8	Y
13	2	7.9	Y
14	2	8.3	Y
15	2	8.3	Y
16	2	8.4	Y
17	3	14.0	Y

Table 1: Self-collapse of nanotubes in a bundle: our theory exactly fits the experimental observations [2].

2.2 Fullerenes

Similarly, the critical pressure of fullerenes in a fullerite crystal is:

$$p_c = \frac{2}{\sqrt{3(1-\nu^2)}} \frac{N^\alpha E t^2}{R^2} - \frac{2\gamma}{R} \quad (3)$$

where $1 \leq \alpha \leq 2$ describes the interaction between the walls, E is the Young modulus and t is the monolayer thickness ($\sim 0.34\text{nm}$); the first term is that posed by elasticity (that considers $\alpha = 2$; see for instance [12]), whereas the second one models the fullerene interaction, as previously discussed. Note that the factor $(t/R)^2$ for fullerenes, appearing instead of $(t/R)^3$ for nanotubes, shows that the critical pressure for fullerenes is much higher than that for nanotubes, at least for $t/R \ll 1$.

From eq. (3) we derive the following condition for the self-buckling:

$$R_C^{(N)} = \frac{1}{\sqrt{3(1-\nu^2)}} \frac{N^\alpha E t^2}{\gamma} \quad (4)$$

Note that for $\nu = 0$, $N = 1$, $E = 1\text{TPa}$, $t = 0.34\text{nm}$, $\gamma = 0.2\text{N/m}$, we find $R_C^{(1)} \approx 334\text{nm}$, showing that fullerenes are highly stable and thus that peapods with high fullerene concentrations are ideal solution against nanotube buckling. Note that for self-similar structures ($t/R = \text{const}$) the minimum thickness Nt required for the self-buckling is very small, thus the self-collapse is peculiar of the nanoscale and does not have a macroscopic counterpart.

2.3 Peapods

In the case of peapods, the collapse pressure is increased as a consequence of the presence inside the nanotube of the fullerenes; since the critical pressure of fullerenes is much higher than that of a nanotube, we treat the peapod as a nanotube of finite length L , equal to the (centre-centre) distance between two adjacent fullerenes. Note that the classical buckling formula of cylindrical shells assumes infinite length.

According to elasticity [13] for a long cylinder the buckling pressure is:

$$p_c = \frac{3N^\alpha D}{R^3}, \quad L \gg L_c \quad (5a)$$

whereas for short cylinders [13]:

$$p_c = \frac{4\pi^2 N^\alpha D}{RL^2}, \quad L \ll L_c \quad (5b)$$

The critical length governing the transition can be calculated equating eqs. (5a) and (5b):

$$L_c = \frac{2\pi}{\sqrt{3}} R \quad (6)$$

For intermediate lengths, elasticity poses [13]:

$$p_c = \frac{\pi^2 \sqrt{\sqrt{1-\nu^2}} N^\alpha D}{RL\sqrt{Rt}}, \quad L \sim L_c \quad (5c)$$

Revisiting the previous elastic results, we thus expect for the buckling of peapods the following regimes:

$$p_c = \frac{3N^\alpha D}{R^3} - \frac{\gamma + \gamma_t}{R}, \quad L \gg L_c \quad (6a)$$

$$p_c = \frac{\pi^2 \sqrt{\sqrt{1-\nu^2}} N^\alpha D}{RL\sqrt{Rt}} - \frac{\gamma + \gamma_t}{R}, \quad L \sim L_c \quad (6b)$$

$$p_c = \frac{4\pi^2 N^\alpha D}{RL^2} - \frac{\gamma + \gamma_t}{R}, \quad L \ll L_c \quad (6c)$$

Let us introduce the fullerene content as:

$$f = \frac{2R}{L} \tag{7}$$

the previous equation become:

$$p_c = \frac{3N^\alpha D}{R^3} - \frac{\gamma + \gamma_t}{R}, \quad f \ll f_c = \frac{\sqrt{3}}{\pi} \tag{7a}$$

$$p_c = \frac{\pi^2 \sqrt{\sqrt{1-v^2}} N^\alpha D}{2R^2 \sqrt{Rt}} f - \frac{\gamma + \gamma_t}{R}, \quad f \sim f_c \tag{7b}$$

$$p_c = \frac{\pi^2 N^\alpha D}{R^3} f^2 - \frac{\gamma + \gamma_t}{R}, \quad f \gg f_c \tag{7c}$$

These stiffening three regimes are summarized in Figure 1.

We can estimate the ratio q between the buckling pressures for $f=0$ and $f=1$, as:

$$q = \frac{p_c(f=1)}{p_c(f=0)} = \frac{\pi^2 - \frac{(\gamma + \gamma_t)R^2}{N^\alpha D}}{3 - \frac{(\gamma + \gamma_t)R^2}{N^\alpha D}} \tag{8}$$

Noting that in the treated case $\frac{\gamma R^2}{N^\alpha D} \ll 1$, we expect $q \approx \pi^2/3$ (as confirmed by atomistic simulations, J. Elliot, private communication).

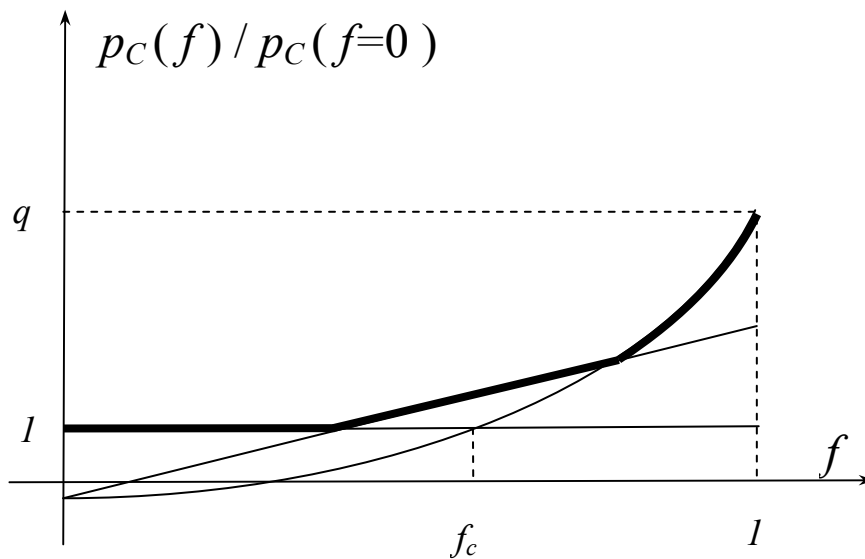


Figure 1: Theoretical dependence of the buckling pressure versus fullerene content.

From eqs. (6) we derive the following conditions for the self-buckling:

$$R_C^{(N)} = \sqrt{3} \sqrt{N^\alpha} \sqrt{\frac{D}{\gamma + \gamma_t}}, \quad L \gg L_c \quad (9a)$$

$$R_C^{(N)} L_C^{(N)2} = \frac{\pi^4 D^2 \sqrt{1 - \nu^2}}{(\gamma + \gamma_t)^2 t}, \quad L \sim L_c \quad (9b)$$

$$L_C^{(N)} = \sqrt{2\pi} \sqrt{N^\alpha} \sqrt{\frac{D}{\gamma + \gamma_t}}, \quad L \ll L_c \quad (9c)$$

Note that for small fullerene content the self-collapse is dictated by a critical radius, as for empty nanotubes, whereas for large fullerene content the self-collapse is dictated by a critical distance between two adjacent fullerenes (in the intermediate case, length and radius are comparable).

3. Conclusions

New formulas to control the self-buckling or nanotube/fullerene crystals are provided, and could have interesting applications for producing smart actuators and super-strong materials [3].

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