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On the Impossibility of Separating Nanotubes in a Bundle by Longitudinal Tension

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Nanotubes in a bundle tend to bunch as a consequence of van der Waals attraction and their extremely high surface to volume ratio. In this article we demonstrate that they cannot be separated by applying an arbitrary large longitudinal tension. Thus, cooperation between nanotubes in a bundle is guaranteed, even under large tension. Such a finding could have an important role in designing self-assembled macroscopic nanotube-based cables.

Keywords: Adhesion; Bunching; Bundle; Cable; Fracture; Nanotube; Tension

INTRODUCTION

Since their discovery [1,2] carbon nanotubes have stimulated intense study. In particular, unique and extraordinary mechanical properties were predicted [3–8], such as an extremely high Young's modulus ($\sim 1\,\mathrm{TPa}$), ultimate strength ($\sim 100\,\mathrm{GPa}$), and consequently failure strain (~ 0.1), similar to those of graphite in-plane [9]. Such properties have experimentally been confirmed by direct measurements [10,11], developing a nanotensile testing apparatus and using two opposite atomic force microscope tips. Furthermore, the low carbon density ($\sim 1300\,\mathrm{Kg/m^3}$) suggests that carbon nanotubes have promising high-strength and light-weight structural applications, *e.g.*, for innovative nano-electromechanical systems [12–14] or macro- [15] and even mega- [16] cables. Nanotubes in bundles tend to bunch as a consequence of the van der Waals attraction. This beneficial cooperation could be of interest if it is

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not lost by increasing the applied tension. The aim of this paper is the demonstration of the cooperation existence, under arbitrary large applied tension (the nanotubes would break prior to their separation).

MATHEMATICAL MODEL

The equilibrium contact width, w, of two identical compact circular cylinders having diameter D (not subject to forces or constraints and in parallel) can be determined using the well-known JKR theory of adhesion, as demonstrated in [17], finding $w = 4\left(\frac{D^2\gamma(1-\upsilon^2)}{\pi E}\right)^{1/3}$; E, υ are the cylinder Young's modulus and Poisson's ratio, respectively, and γ is the surface energy. Due to deformation near the contact region of size $w \times x$, there is an accompanying stored elastic energy Φ_b in the cylinders (of length x) that must satisfy the energy balance $\mathrm{d}\Phi_b = 2\gamma x \mathrm{d}w$; thus, by integration, $\Phi_b = \frac{\pi E D^2_+ x}{128(1-\upsilon^2)}\left(\frac{w}{D}\right)^4$ [18].

Let us consider the system shown in Figure 1, composed of two parallel stretched multiwalled (with vanishing internal diameter) nanotubes of length L and placed at a distance p (separation distance). We are going to apply classical concepts of structural mechanics, see [19]. The nanotubes, if sufficiently close, will tend to bunch due to van der Waals surface attraction. Indicating with $A = \pi D^2/4$ the nanotube cross-sectional area, with $2l$ the non-contact length, along the direction θ, and with x the contact length (along the vertical direction $\theta = 0$), the elastic energy stored in the system due to the applied longitudinal (along the nanotube/bundle axis) stress σ can be written as $\Phi_s = \sigma^2 A\left(2l/\cos^2\theta + x\right)/E$. On the other hand, the external work is $W = 2\sigma A(2u + u_0)$, where u denotes the vertical displacement due to the stretching of the non-contact portion (*i.e.*, due to $\Delta l = l\sigma/(E\cos\theta)$), whereas $u_0 = \Delta x = x\sigma/E$ is the vertical displacement due to the stretching of the contact length. Since $p/2 = l\sin\theta = (l + \Delta l)\sin(\theta + \Delta\theta)$ and $u = (l + \Delta l)\cos(\theta + \Delta\theta) - l\cos\theta$, we deduce $u = l\sqrt{(1 + \Delta l/l)^2 - \sin^2(\theta)} - l\cos\theta$. Both l and θ (and $\Delta l/l$) are functions of $x : l = (L - x)/2$, where L is the nanotube length, and $\sin\theta = p/(L - x)$. Thus, the total potential energy of the system is $\Pi(x) = \Phi_b(x) + \Phi_s(x) - W(x)$. The classical approximation of small displacements ($u/l \to 0$; which implies small deformations) cannot be applied in this context; however, we note that small deformations ($\Delta l/l \to 0$) imply in our system small displacements. In the limit of small deformations/displacements we have verified the validity of

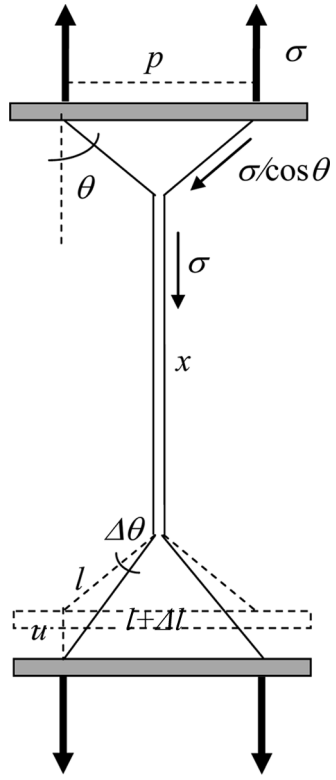

FIGURE 1 Bunching between two nanotubes in a bundle: energy balance.

Clapeyron's theorem [$W(x) = 2\Phi_b(x)$]. The anti-bunching stress (*i.e.*, the stress required to separate the nanotubes) can be derived by the following energy balance: $\mathrm{d}\Pi(x)/\mathrm{d}x = 2\gamma w$. Since we find $\mathrm{d}\Phi_b(x)/\mathrm{d}x = \gamma w/2$, the condition for separating the nanotubes becomes $\mathrm{d}\Pi^*(x)/\mathrm{d}x = \mathrm{d}\Phi_s(x)/\mathrm{d}x - \mathrm{d}W(x)/\mathrm{d}x = 3/2(\gamma w)$, where Π^* is the reduced potential energy. Introducing the dimensionless variables $\eta = p/(L - x)$ and $\varepsilon = \sigma/E$, we calculate:

$$\frac{1}{EA}\frac{\mathrm{d}\Phi_s}{\mathrm{d}x} = \left[1 - \frac{3}{1-\eta^2} + \frac{2}{(1-\eta^2)^2}\right]\varepsilon^2 \tag{1}$$

$$\frac{1}{EA}\frac{\mathrm{d}W}{\mathrm{d}x} = 2\varepsilon\left(2\frac{\mathrm{d}u}{\mathrm{d}x} + \varepsilon\right) \tag{2a}$$

$$2\frac{\mathrm{d}u}{\mathrm{d}x} = \left[\left(1+\frac{\varepsilon}{\sqrt{1-\eta^2}}\right)^2 - \eta^2\right]^{-\frac{1}{2}}\left[\frac{\varepsilon}{1-\eta^2}\left(1+\frac{\varepsilon}{\sqrt{1-\eta^2}}\right)\frac{\eta^2}{\sqrt{1-\eta^2}} - \eta^2\right] + \frac{\eta^2}{\sqrt{1-\eta^2}} + \sqrt{1-\eta^2} - \sqrt{\left(1+\frac{\varepsilon}{\sqrt{1-\eta^2}}\right)^2 - \eta^2}. \quad (2b)$$

In the limit of $\varepsilon \to 0$ [in which we consistently have $\mathrm{d}W(x)/\mathrm{d}x = 2(\mathrm{d}\Phi_b(x)/\mathrm{d}x)$] we deduce $1/EA(\mathrm{d}\Pi^*/\mathrm{d}x)\big|_{\varepsilon\to 0} = (-\eta^2+\eta^4)/(1-\eta^2)^2\varepsilon^2$. A negative value of the reduced potential energy variation clearly shows that in this limit the anti-bunching cannot be reached by applying an arbitrary large finite tension, but a large tension is out of the validity of the previous formula. Noting that $0 \le p/L \le \eta \le 1$ we make an expansion for both $\eta \to 0$ or $\eta \to 1$, preserving the hypothesis of large displacements/deformations. The results are: $1/EA(\mathrm{d}\Pi^*/\mathrm{d}x)\big|_{\eta\to 0} = -\varepsilon^2\eta^2/(1+\varepsilon)$ or $1/EA(\mathrm{d}\Pi^*/\mathrm{d}x)\big|_{\eta\to 1} = 2\varepsilon^2/(1-\eta^2)^2$. An always negative value for $\eta \to 0$ suggests that long bunched nanotubes cannot be fully separated by applying a longitudinal tension, even if a short delamination at the ends of the bundle ($x = L - p$, $\eta = 1$) is expected as soon as a small tension is applied; this can be evinced from the positive singularity of $1-\eta^2$ in the reduced potential energy for $\eta \to 1$. In particular, under a strain ε, we predict at the ends of the bundle a separation of extension:

$$l = \frac{p}{2\eta} = \frac{p}{2\sqrt{1-2\sqrt{\varepsilon^2 EA/(3\gamma w)}}}. \quad (3)$$

The calculation is valid for realistic values of $p \ll L$.

Note that, for vanishing surface energy, the required anti-bunching strain (or force) is always zero, *i.e.*, the nanotubes are obviously not bunched if the surface energy is zero. This can be easily evinced by the fact that the reduced potential energy is proportional to the square of the strain, and that the anti-bunching condition implies a proportionality between this reduced potential energy and the surface energy.

Regarding the limitations of our approach we have to note that it is based on fracture mechanics and, thus, (i) on the energy balance during crack growth and (ii) on small strains or better on a linear constitutive law. (i) For short adhesion(/crack) length a force(/stress) equilibrium would be more appropriate. Following [20], the maximum applied stress is predicted to be limited (Fig. 2) and equal to $\sigma_{\max} \approx F_C L/(2Ap)$ ($p \ll L$), where F_C is the critical force existing between the two nanotubes just before separation. Thus, the force is

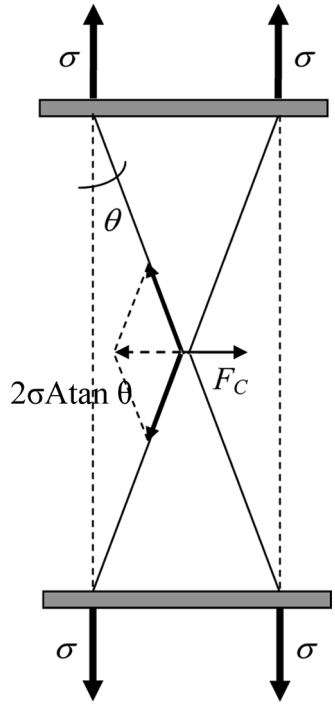

FIGURE 2 Bunching between two nanotubes in a bundle: force equilibrium.

expected to be larger than the nanotube intrinsic strength only for realistic slender bundles. (ii) If the nonlinear material behaviour is relevant our analysis cannot be applied; this is not the case of carbon nanotubes, showing a nearly linear regime up to fracture.

CONCLUSIONS

We conclude that cooperation due to bunching between nanotubes in a bundle is guaranteed even under large longitudinal tensions. Such a finding could have interesting applications for designing macroscopic self-assembled nanotube-based cables (see, for instance, suspended and cable stayed bridges [21]).

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