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Calculation of Strain Energy of Cantilevered Thick Multiwalled Carbon Nanotubes with Varying Forces at the Free End

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The expression of the strain energy of cantilevered thick multiwalled carbon nanotubes with varying forces, beyond the classical elastic limit, is derived. As a portion of these nanotubes exhibit severe bending with external forces, we have used a nonlinear relation between the bending moment and the bending curvature for this portion of the nanotubes. Our results satisfactorily explain the experimental results of Wong, Sheehan, and Lieber [*Science* 277, 1971 (1997)] and that of Poncharal, Wang, Ugarte, and de Heer [*Science* 283, 1513 (1999)].

Keywords: Carbon Nanotubes, Strain Energy, Mechanical Properties, Rippling Formation.

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1. INTRODUCTION

Since the discovery of carbon nanotubes (CNTs) by Ijima,[1] many experiments have been performed to study their mechanical properties like strength, stiffness, etc. which can be inferred from measuring the values of tensile strength and Young's modulus (E) respectively. The experimental measurements of mechanical properties of nanotubes involve the techniques such as transmission electron microscopy (TEM)[2–4] and atomic force microscopy (AFM).[5,6] From these experiments E was found to be of the order of 1 tera Pascal which is also confirmed by theory.[7–10] The value of the tensile strength of CNTs is found to be exceptionally high (∼giga Pascal).[11–13] This shows that CNTs are stiffer in tension and compression and stronger than any other known material. Further, under bending they show remarkable flexibility and large elastic deformation (up to 16%) without breaking.[14] When they are bent to high curvatures they exhibit wavelike distortion or ripple on their inner arc.[4]

In an experiment, Wong et al.[5] pinned one end of a multiwall carbon nanotube (MWCNT) and applied an external force, from the free end, at different locations along the nanotube to measure deflection versus the bending force using AFM. In this experiment, the strain energy showed a deviation from the usual quadratic behaviour. This behaviour cannot be explained by a linear elastic theory. In another experiment, Poncharal et al.[4] studied electrostatic and dynamic mechanical deflections in cantilevered MWCNTs using TEM. They observed a wavelike distortion on the inner arc of the bent thick nanotubes when the bending is severe. However, this phenomenon was not observed in bent thin nanotubes. The linear theory, which is valid only for very small bending deformations, cannot explain such phenomena. These force-deflection experiments of MWCNTs were set up mainly to determine the effective Young's modulus of MWCNTs.

In this paper we consider a thick MWCNT cantilevered at one end and subjected to a lateral force at the free end. The MWCNT is divided into two portions: the cantilevered end portion, where the bending is severe, shows the rippling mode and the free end portion exhibits the classical bending mode. In Section 2, we use a nonlinear relation between the bending moment (M) and the bending curvature (K) for the rippling mode portion and usual linear relation between M and K for the classical bending portion to derive the expression for the deflection. In Section 3, an expression of strain energy of a bent MWCNT is derived. These expressions, for illustration purposes, are used to calculate the normalized deflection and normalized strain energy in Section 4. Our results are an attempt to explain the rippling phenomenon. The normalized strain energy behaves reasonably well, with an empirical fit, as $(\text{deflection})^{1.502\pm0.007}$. This clearly demonstrates departure from the quadratic behaviour. The concluding remarks are given in Section 5.

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2. DERIVATION OF EXPRESSION FOR DEFLECTION OF A MWCNT

In the following steps we give the detailed theoretical derivation of our results. We consider a thick MWCNT, of length L, which is fixed at the $x = 0$ end and free at $x = L$. A lateral force P is applied at the free end so that there is bending in the MWCNT as shown in Figure 1. We are interested to derive expressions for the deflection and the strain energy as a function of P.

According to elastic beam theory, for static deflection, the bending moment $M(x)$ due to the force, P, at any point x is given by

$$M(x) = P(L - x) \tag{1}$$

where we have neglected weight of the MWCNT. $M(x)$ is constitutively related to the bending curvature $K(x)$ by the relation

$$M(x) = EIK(x) \tag{2}$$

where I is the moment of inertia of the cross section of MWCNT. From (1) and (2), we obtain

$$P(L - x) = EIK(x) \tag{3}$$

Let $y(x)$ be the beam deflection at x due to the force P. The curvature is given by

$$K(x) = \frac{d^2y(x)}{dx^2}\left\{1 + \left[\frac{dy(x)}{dx}\right]^2\right\}^{-3/2} \tag{4}$$

Then (3) becomes

$$P(L - x) = EI\frac{d^2y(x)}{dx^2}\left\{1 + \left[\frac{dy(x)}{dx}\right]^2\right\}^{-3/2} \tag{5}$$

Now we assume that when the force exceeds a critical value P_{cr}, the rippling mode emerges from the cantilevered end where the bending is severe. Let the transition point on the MWCNT be L_{cr}. So that the portion $0 < x < L_{cr}$ of the nanotube is in the rippling mode which needs the concept of nonlinear phenomena and the remaining portion of the nanotube $L_{cr} < x < L$ is in the classical bending mode which can be explained on the basis of linear elastic theory. Next we shall derive the expression for the deflection of the MWCNT for the two cases, viz., for $P \le P_{cr}$ and for $P > P_{cr}$. Then the expression for strain energy of the MWCNT for these two cases will be obtained.

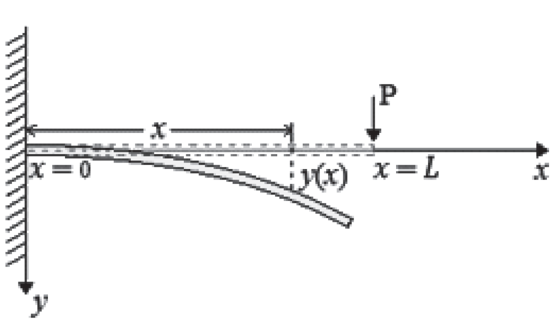

Fig. 1. A cantilevered thick MWCNT with a force at the free end.

2.1. Derivation of Deflection of the MWCNT for $P \le P_{cr}$

In this case, the deflection of the MWCNT is very small so that the entire nanotube is in the classical bending mode. Using linear theory of elasticity one can determine the value of deflection at the loading point, $x = L$, as

$$y(L) = \frac{PL^3}{3EI} \equiv \Delta_0, \quad \text{for } P \le P_{cr} \tag{6}$$

The deflection of the end of the beam increases as cube of the length as is the case in classical elastic theory.

2.2. Derivation of Deflection of the MWCNT for $P > P_{cr}$

When the applied force exceeds the critical value, $P > P_{cr}$, the bending in the portion $0 < x < L_{cr}$ is severe, so we use a nonlinear relation between M and K for this portion. On the other hand as the remaining portion $L_{cr} < x < L$ is in the classical bending mode,[15] a linear elastic theory will be able to explain the behaviour of the nanotube in this portion. We shall derive the expression of deflection separately for two portions of the nanotube. Let us denote the deflection of the MWCNT at distance x from the fixed end, for the portion $0 < x < L_{cr}$ by $y_1(x)$ and that for the portion $L_{cr} < x < L$ by $y_2(x)$.

(i) For the portion $0 < x < L_{cr}$

This portion of the MWCNT is in rippling mode. We use (5) with $y(x)$ replaced by $y_1(x)$. Thus

$$\frac{P(L - x)}{EI} = \frac{d^2y_1(x)}{dx^2}\left\{1 + \left[\frac{dy_1(x)}{dx}\right]^2\right\}^{-3/2} \quad \text{for } 0 < x < L_{cr} \tag{7}$$

Using the boundary conditions (deflection function and its first derivative both vanish at $x = 0$) $y_1(x)|_{x=0} = y_1'(x)|_{x=0} = 0$, we solve (7). This gives

$$\frac{dy_1(x)}{dx} = (ax - bx^2)[1 - (ax - bx^2)^2]^{-1/2} \quad \text{for } 0 < x < L_{cr} \tag{8}$$

where

$$a = \frac{PL}{EI} \quad \text{and} \quad b = \frac{P}{2EI} \tag{9}$$

Integrating (8), we obtain

$$y_1(x)|_{x=L_{cr}} = \int_0^{L_{cr}} (ax - bx^2)[1 - (ax - bx^2)^2]^{-1/2}\, dx \equiv \Delta_1 \quad \text{for } 0 < x < L_{cr} \tag{10}$$

In order to determine the value of L_{cr}, we solve (3). When $x = L_{cr}$, (3) becomes

$$L - L_{cr} = \frac{EI}{P} K(L_{cr}) = \frac{EI}{P} K_{cr}$$

where $K_{cr} \equiv K(L_{cr})$ is the critical curvature. Thus

$$1 - \frac{L_{cr}}{L} = \frac{EI}{PL} K_{cr} = \frac{P_{cr}}{P} \tag{11}$$

where $P_{cr} \equiv (EI/L)K_{cr}$. Let us define normalized force $p = P/P_{cr}$. Then (11) becomes

$$1 - \frac{L_{cr}}{L} = \frac{1}{p} \quad \text{or} \quad L_{cr} = L\left(1 - \frac{1}{p}\right) \tag{12}$$

This shows that L_{cr} depends on the normalized force. It is important to note from (12) that when $p = 1$, i.e., $P = P_{cr}$, $L_{cr} = 0$, implying that the whole MWCNT is in classical bending mode. Again when p is very large, i.e., $P \gg P_{cr}$, $L_{cr} \approx L$, showing that the entire tube is in rippling mode. Further, if the applied force is in between these values the MWCNT will exhibit mixed behaviour, i.e., a part of the tube will be in classical mode and the other part will be in rippling mode.

(ii) For the portion $L_{cr} < x < L$

As we have considered a thick MWCNT and this portion is in classical bending mode,[15] it is reasonable to consider the following equation for this portion of the tube

$$\frac{P(L-x)}{EI} = \frac{d^2 y_2(x)}{dx^2} \tag{13}$$

In order to solve the above equation we have to use additional boundary conditions, which require that $y(x)$ and $y'(x)$ are both continuous at the transition point $x = L_{cr}$. Thus the modified boundary conditions for the cantilevered beam are as follows:

$$y_1(x)|_{x=0} = y_1'(x)|_{x=0} = 0;$$
$$y_1(x)|_{x=L_{cr}} = y_2(x)|_{x=L_{cr}}$$

and

$$\left.\frac{dy_1(x)}{dx}\right|_{x=L_{cr}} = \left.\frac{dy_2(x)}{dx}\right|_{x=L_{cr}} \tag{14}$$

Using the above boundary conditions, we solve (13) and obtain the following result

$$y_2(x) = \frac{P}{EI}\left(\frac{Lx^2}{2} - \frac{x^3}{6}\right) + D_1 x + D_2 \tag{15}$$

where

$$D_1 \equiv \frac{P}{2EI} L_{cr} L\left(1 + \frac{1}{p}\right) \times \left(\left\{1 - \left[\frac{P}{2EI} L_{cr} L\left(1 + \frac{1}{p}\right)\right]^2\right\}^{-1/2} - 1\right) \tag{16a}$$

and

$$D_2 \equiv \Delta_1 - \frac{P}{2EI} L_{cr}^2 L\left(1 + \frac{1}{p}\right) \times \left\{1 - \left[\frac{P}{2EI} L_{cr} L\left(1 + \frac{1}{p}\right)\right]^2\right\}^{-1/2} + \frac{P}{3EI} L_{cr}^2 L\left(\frac{1}{2} + \frac{1}{p}\right) \tag{16b}$$

At $x = L$, the deflection of MWCNT is

$$y_2(L) = \Delta_0\left\{1 - \frac{3}{2}\left(1 - \frac{1}{p^2}\right) + \left(1 - \frac{1}{p}\right)^2 \times \left(\frac{1}{2} + \frac{1}{p}\right) + \frac{3}{2p}\left(1 - \frac{1}{p^2}\right) \times \left\{1 - \left[\frac{P}{2EI} L_{cr} L\left(1 + \frac{1}{p}\right)\right]^2\right\}^{-1/2} + \frac{3EI}{PL^3}\Delta_1\right\} \equiv \Delta_2 \tag{17}$$

We now introduce dimensionless quantities $\bar{x} = x/L$, $\bar{K}_{cr} = dK_{cr}/2$ and normalized deflection $\delta = \Delta_2/\Delta_{cr}$ where $\Delta_{cr} = P_{cr}L^3/(3EI)$ is the deflection corresponding to the critical force, P_{cr}, and d is the tube diameter. Then

$$\begin{aligned}\delta &= p \times \frac{\Delta_2}{\Delta_0} \\ &= p\left\{1 - \frac{3}{2}\left(1 - \frac{1}{p^2}\right) + \left(1 - \frac{1}{p}\right)^2\left(\frac{1}{2} + \frac{1}{p}\right) + \frac{3}{2p}\left(1 - \frac{1}{p^2}\right)\left\{1 - \left[\frac{P}{2EI} L_{cr} L\left(1 + \frac{1}{p}\right)\right]^2\right\}^{-1/2}\right. \\ &\quad \left. + \frac{3EI}{PL^3}\int_0^{L_{cr}} \frac{P}{2EI}(2Lx - x^2) \times \left\{1 - \left[\frac{P}{2EI}(2Lx - x^2)\right]^2\right\}^{-1/2} dx\right\}\end{aligned} \tag{18}$$

where we have used (10) along with (9) in writing (18). Thus,

$$\delta = \begin{cases} p, \quad \text{for } p \le 1, \\ \dfrac{1}{p^2} + \dfrac{3}{2}\left(1 - \dfrac{1}{p^2}\right)\left\{1 - \left[\bar{K}_{cr}\dfrac{L}{d}\left(p - \dfrac{1}{p}\right)\right]^2\right\}^{-1/2} \\ \quad + \dfrac{3}{2}\displaystyle\int_0^{(1-1/p)}\left\{1 - \left[\bar{K}_{cr}\dfrac{L}{d}p(2\bar{x} - \bar{x}^2)\right]^2\right\}^{-1/2} \\ \quad \times p(2\bar{x} - \bar{x}^2)\, d\bar{x}, \quad \text{for } p > 1 \end{cases} \tag{19}$$

3. DERIVATION OF STRAIN ENERGY OF A BENT MWCNT

As the MWCNT is bent, the nanotube is subjected to varying degrees of stresses and therefore possesses elastic strain energy. The strain energy can be calculated by finding work done by the external force. Thus the strain energy can be written as

$$U = \int_0^{\Delta} P(\Delta)\, d\Delta \tag{20}$$

where Δ is the deflection at the loading point. Now we shall derive the strain energy for two cases, i.e., for case (I) $P \le P_{cr}$ and for case (II) $P > P_{cr}$.

Case (I). For $P \le P_{cr}$

For this case the deflection at the loading point is Δ_0 as given in (6). So the strain energy will be

$$U = \int_0^{\Delta_0} P(\Delta)\, d\Delta \tag{21}$$

Integrating the above equation by parts, we obtain

$$U = P\Delta|_0^{\Delta_0} - \int_0^P \Delta_0\, dP = \frac{P^2L^3}{6EI} \equiv U_0, \quad \text{for } P \le P_{cr} \tag{22}$$

This is the standard strain energy in usual classical bending mode.

Case (II). For $P > P_{cr}$

The deflection at the loading point in this case is Δ_2 which is given in (17). The strain energy equation becomes

$$U = \int_0^{\Delta_2} P(\Delta)\, d\Delta \tag{23a}$$

Integrating the above equation by parts, we have

$$\begin{aligned} U &= P\Delta|_0^{\Delta_2} - \int_0^P \Delta\, dP = P\Delta_2 - \int_0^{P_{cr}} \Delta_0\, dP - \int_{P_{cr}}^P \Delta_2\, dP \\ &= P\Delta_2 - \frac{L^3P_{cr}^2}{6EI} - \int_{P_{cr}}^P \Delta_2\, dP \end{aligned} \tag{23b}$$

Now substituting the value of Δ_2 from (17) into (23b) and after straightforward algebraic simplifications we obtain

$$\begin{aligned} U = U_0\Bigg\{ & 4\frac{P_{cr}^3}{P^3} - 3\frac{P_{cr}^2}{P^2} + 3\frac{P_{cr}}{P}\left(1-\frac{P_{cr}^2}{P^2}\right) \\ & \times \left\{1-\left[\frac{P}{2EI}L_{cr}L\left(1+\frac{P_{cr}}{P}\right)\right]^2\right\}^{-1/2} \\ & + \frac{6EI}{PL^3}\Delta_1 - 3\frac{P_{cr}}{P_2}\int_{P_{cr}}^P\left(1-\frac{P_{cr}^2}{P^2}\right) \\ & \times \left\{1-\left[\frac{P}{2EI}L_{cr}L\left(1+\frac{P_{cr}}{P}\right)\right]^2\right\}^{-1/2} dP \\ & - \frac{6EI}{P^2L^3}\int_{P_{cr}}^P \Delta_1\, dP\Bigg\} \end{aligned} \tag{24}$$

We can rewrite (24) as follows

$$\begin{aligned} \frac{U}{U_0} = {} & \frac{4}{p^3} - \frac{3}{p^2} + \frac{3}{p}\left(1-\frac{1}{p^2}\right) \\ & \times \left\{1-\left[\frac{P}{2EI}L_{cr}L\left(1+\frac{P_{cr}}{P}\right)\right]^2\right\}^{-1/2} + \frac{6EI}{PL^3}\int_0^{L_{cr}}\frac{P}{2EI} \\ & \times (2Lx-x^2)\left\{1-\left[\frac{P}{2EI}(2Lx-x^2)\right]^2\right\}^{-1/2} dx \\ & - \frac{3}{p}\frac{1}{p}\int_{P_{cr}}^P\left(1-\frac{1}{p^2}\right) \\ & \times \left\{1-\left[\frac{P}{2EI}L_{cr}L\times\left(1+\frac{P_{cr}}{P}\right)\right]^2\right\}^{-1/2} dP \\ & - \frac{6EI}{P^2L^3}\int_{P_{cr}}^P\left\{\int_0^{L_{cr}}\frac{P}{2EI}(2Lx-x^2)\right. \\ & \left. \times \left\{1-\left[\frac{P}{2EI}(2Lx-x^2)\right]^2\right\}^{-1/2} dx\right\} dP \end{aligned} \tag{25}$$

Let us define normalized strain energy $U' = U/U_{cr}$ where $U_{cr} = P_{cr}^2L^3/(6EI)$ is the strain energy corresponding to the critical force P_{cr}. Now the expression for strain energy can be written in terms of dimensionless quantities as

$$U' = p^2 \times \frac{U}{U_0} \tag{26}$$

This has the value

$$U' = \begin{cases} p^2, \quad \text{for } p \le 1, \\ \frac{4}{p} - 3 + 3\left(p-\frac{1}{p}\right)\left\{1-\left[\bar{K}_{cr}\frac{L}{d}\left(p-\frac{1}{p}\right)\right]^2\right\}^{-1/2} \\ \quad +3p\int_0^{(1-1/p)}(2\bar{x}-\bar{x}^2)p \\ \quad \times\left\{1-\left[\bar{K}_{cr}\frac{L}{d}p(2\bar{x}-\bar{x}^2)\right]^2\right\}^{-1/2} d\bar{x} \\ \quad -3\int_1^p\left\{1-\left[\bar{K}_{cr}\frac{L}{d}\left(p-\frac{1}{p}\right)\right]^2\right\}^{-1/2}\left(1-\frac{1}{p^2}\right)dp \\ \quad -3\int_1^p dp\left\{\int_0^{(1-1/p)}p(2\bar{x}-\bar{x}^2)\right. \\ \quad \left.\times\left\{1-\left[\bar{K}_{cr}\frac{L}{d}p(2\bar{x}-\bar{x}^2)\right]^2\right\}^{-1/2} d\bar{x}\right\}, \\ \qquad \text{for } p > 1 \end{cases} \tag{27}$$

4. RESULTS AND DISCUSSION

For illustrative purposes, we consider a MWCNT of diameter, $d = 14.5$ nm and length, $L = 6.25 \times 10^3$ nm as used in the experiment of Poncharal et al.[4] and use the value of dimensionless transition curvature $\bar{K}_{cr} \approx 0.006$.[15] The expression (19) for normalized deflection δ at the load point and the expression (27) for normalized strain energy U' become as follows

$$\delta = \begin{cases} p, \quad \text{for } p \le 1, \\ \frac{1}{p^2} + \frac{3}{2}\left(1-\frac{1}{p^2}\right)\left\{1-\left[2.586\left(p-\frac{1}{p}\right)\right]^2\right\}^{-1/2} \\ \quad +\frac{3}{2}\int_0^{(1-1/p)}\{1-[2.586(2\bar{x}-\bar{x}^2)p]^2\}^{-1/2} \\ \quad \times p(2\bar{x}-\bar{x}^2)\, d\bar{x}, \quad \text{for } p > 1 \end{cases} \tag{28}$$

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and

$$U' = \begin{cases} p^2, \quad \text{for } p \le 1, \\ \dfrac{4}{p} - 3 + 3\left\{1 - \left[2.586\left(p - \dfrac{1}{p}\right)\right]^2\right\}^{-1/2}\left(p - \dfrac{1}{p}\right) \\ \quad + 3p\displaystyle\int_0^{(1-1/p)} (2\bar{x} - \bar{x}^2)p \\ \quad \times \{1 - [2.586(2\bar{x} - \bar{x}^2)p]^2\}^{-1/2}\, d\bar{x} \\ \quad - 3\displaystyle\int_1^p \left\{1 - \left[2.586\left(p - \dfrac{1}{p}\right)\right]^2\right\}^{-1/2} \\ \quad \times \left(1 - \dfrac{1}{p^2}\right) dp - 3\displaystyle\int_1^p \left\{\int_0^{(1-1/p)} p(2\bar{x} - \bar{x}^2) \right. \\ \qquad \left. \times \{1 - [2.586(2\bar{x} - \bar{x}^2)p]^2\}^{-1/2}\, d\bar{x}\right\} dp, \\ \quad \text{for } p > 1 \end{cases} \tag{29}$$

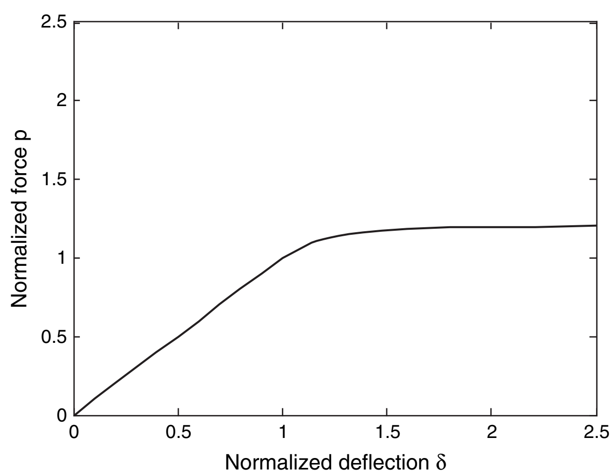

Fig. 2. Normalized force versus normalized deflection from (28) of the text.

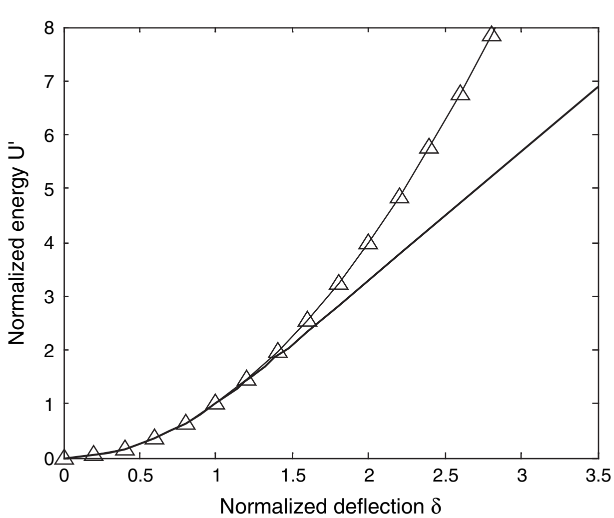

Fig. 3. Normalized energy versus normalized deflection. The -Δ- marks show quadratic dependence of energy on δ whereas the solid line shows behaviour of the energy by using (28) and (29) of the text.

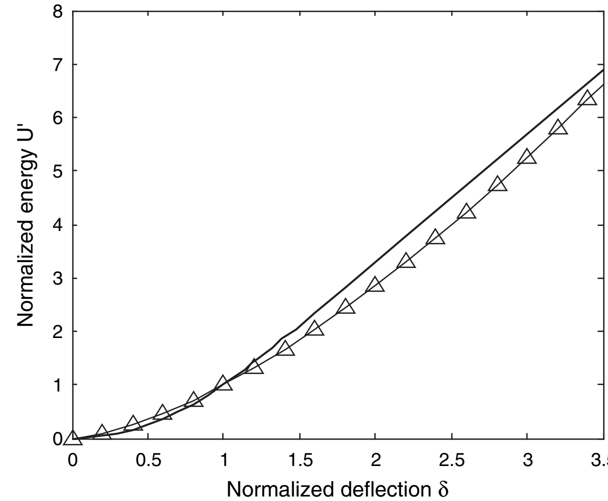

Fig. 4. An empirical fit of normalized energy versus normalized deflection. The empirical fit shows that normalized strain energy behaves as $U' = (\delta)^{1.502\pm0.007}$. The solid line represents the plot using (28) and (29) of the text whereas the -Δ- marks show the empirical fit.

From (28) and (29) one can see that both δ and U' depend only on the normalized force $p(=P/P_{cr})$. Using (28) we plot normalized force versus normalized deflection in Figure 2. A linear behaviour of δ can be observed up to the value of $p = 1$. After this value of p, nonlinear effects come into play and rippling mode emerges. Similarly, when we plot normalized strain energy U' versus normalized deflection δ in Figure 3, using (28) and (29), we observe quadratic dependence of U' on δ when $p \le 1$. For $p > 1$, normalized strain energy deviates substantially from quadratic behaviour (Fig. 3). We observe that this occurs due to nonlinear behaviour of carbon nanotubes when external forces exceed certain critical value. This behaviour is similar to the one observed by Wong et al.[5] In Figure 4, we demonstrate an empirical fit of normalized strain energy U' versus normalized deflection δ. This empirical fit agrees reasonably well with the relation $U' = (\delta)^{1.502\pm0.007}$ which clearly exhibits the departure of normalized strain energy from quadratic dependence with deflection.

5. CONCLUSION

We investigated behaviour of a cantilevered thick MWCNT subjected to a lateral force, greater than the critical value, at the free end. In our analysis we obtained non-quadratic nature of strain energy-deflection relationship. Our results try to explain the wavelike distortion as in Ref. [4] and deviation of strain energy from the quadratic behaviour with deflection of Ref. [5]. We would like to point out that Liu et al.[15] explained rippling phenomena observed in MWCNTs by using a bilinear bending moment-curvature relationship. From these results we would like to conclude that one should be careful in using linear theory while studying elastic properties of CNTs.

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