Interfacial Properties of Carbon Nanotube Arrays

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ABSTRACT

The present study springs from the investigation of Salvetat *et al.*[4] in which the ratio of flexural deformation to applied load of carbon nanotube arrays was used to determine effective Young's and shearing modulii. Results showed both modulii to decrease with increasing array size. The present study [2,3,5] describes a model that accounts for the dependence of the flexural compliance on the shearing tractions between the individual CNT that occur due to van der Waals forces. The magnitude of the shearing traction is determined by matching the model prediction of stiffness to experimental results.

Independently, the vibrational properties of single walled carbon nanotube arrays have been measured recently [1] and a linear relationship between first natural frequency and D/L^2 was postulated. Using the model described above, the authors show that this relationship is highly non-linear especially for large values of the parameter, D/L^2.

Keywords: carbon nanotube arrays, flexural stiffness, shearing traction, stress transfer, van der Waals interactions.

1 INTRODUCTION

The study of load transfer between carbon nanotubes (CNT) has been the subject of considerable recent research, focusing on their effectiveness as reinforcing elements in composite materials. Among the less known quantities is the shearing cohesiveness between SWNT, which is governed by van der Waals interactions and determines the load transfer between SWNT in an array (also called rope). By analogy with graphite, we expect the elastic constants related to van der Waals forces to be of the same order of magnitude as C_{44}, the shearing stiffness elastic constant [6]. However there has been only modest success in establishing the magnitude of the relevant elastic constant by either measurement or simulation. It is thus necessary to measure and quantify these effects to have an overall understanding of mechanical behavior of SWNT arrays and derived materials. The present study considers only identical SWNT and perfect hexagonal close-packed array geometries in order to quantify the shearing tractions.

The experimental investigation of Salvetat *et al.* [4] reported flexural deformation to applied load for a series of SWNT arrays. Calculated effective Young's and shearing modulii were found to decrease with increasing array size (diameter) and this decrease was attributed to shearing deformation in classical Euler beam theory. In the present study, the authors describe a mechanism that accounts for the dependence of the flexural compliance of the array on the shearing tractions between the individual CNT that are expected to occur due to van der Waals forces. In this approach, the difference between the sum of the flexural stiffnesses of non-bonded CNT in the array and the experimentally observed flexural rigidity is attributed to an unknown shearing traction. The magnitude of the shearing traction is determined by matching the model prediction of stiffness to the experimental results. Two extreme situations bound the values of the shearing stress; perfect bonding, corresponding to the value obtained for the interior of a solid body and perfect sliding corresponding to no interfacial stress. It is possible to define a parameter *k* (shear transfer efficiency) that varies between 0 and 1 as the array changes from unbonded to fully bonded. Correspondingly, a fractional value of *k* determines the magnitude of the interlayer shearing tractions.

Measurements of the first natural frequency of carbon nanotube cantilever arrays have been analyzed in terms of the classical Euler-Bernoulli beam theory [11] to obtain values of the flexural stiffness:

$$f_i = \frac{\beta_i^2 D}{8\pi L^2}\sqrt{\frac{E}{\rho}} \tag{1}$$

Where β_i is a function of the support conditions and the diameter and length of the beam are *D* and *L*, respectively, while the ratio E/ρ in equation (1) is the ratio of the Young's modulus to mass density of the vibrating array. Jaroenapibal *et al.* [1] plotted frequency vs. D/L^2, extracting a surprisingly low value for the array flexural modulus from the slope. It was suggested that the observed low flexural modulii were due to "…weak tube-tube interactions within the bundle…," [1] but no quantitative explanation was provided. Furthermore, the effective Young's modulus of the array was found to be constant for all examined array diameters. The model developed for flexural compliance is readily extended to explore the effects of interactions between adjacent CNT upon array vibrational characteristics. The size dependence of effective Young's modulus leads to a non linear relationship in Eq. (1), and an asymptotic limit in the maximum frequency of vibration attainable from a given array size.

2 MODEL DEVELOPMENT

In order to construct analyses of the CNT hexagonal arrays, it is convenient to develop equivalent layered structures that possess identical flexural properties. To do so, the total moment of inertia of the equivalent rectangular cross-section layers are equated to the total moment of inertia of the rows of cylinders by appropriately choosing the widths and thicknesses of each rectangular layer. For example, for a seven element array, the following values are obtained:

$$h_i = \frac{\sqrt{3}}{2} D_{na} \tag{2}$$

$$b_1 = \frac{\pi}{\sqrt{3}} D_{na} \qquad b_2 = \frac{\pi\sqrt{3}}{2} D_{na} \tag{3}$$

Both geometries are presented in Figure 1.

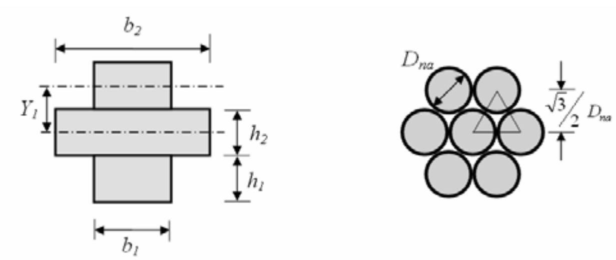

Fig. 1. Equivalent three-layer structure for a seven element array

Elastic properties of SWNT are determined following an approach described elsewhere [7], where the thin cylinder of a single graphene sheet is replaced by a solid circular cylinder with equivalent elastic stiffness.

In order to determine the effective density and flexural stiffness of the individual (10,10) CNT, the flexural stiffness of a solid cylinder of diameter equal to 1.36+0.317 nm is equated to that of the hollow cylinder of equal diameter as illustrated in Figure 2. The hollow cylinder wall thickness is taken equal to the stand-off distance of 0.317 nm for the (10,10) CNT in a hexagonal array [8]. These calculations yield an effective flexural modulus of the individual (10,10) CNT equal to 876 GPa.

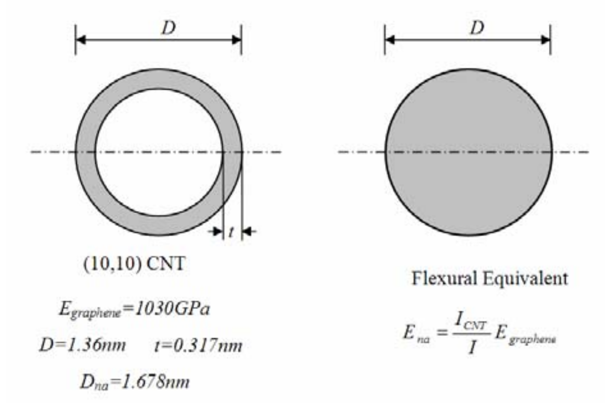

Fig. 2. Equivalent flexural modulus of a SWNT

The model equations are presented for a simple three layer system but are readily extended to any number of layers. Consider the free body diagrams for every layer of the cantilever geometry and for a given value of shear transfer as shown in Figure 3.

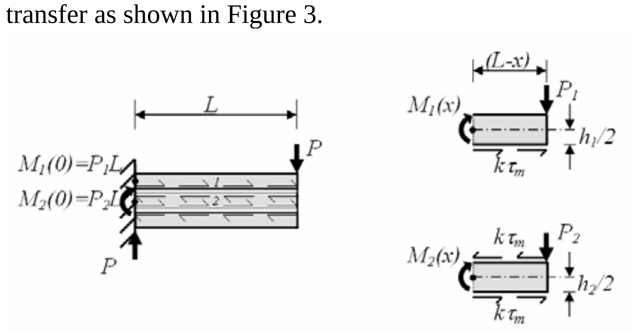

Fig. 3. Free body diagram for the equivalent layered structure under cantilever conditions

The moment distributions can be calculated as a function of the (yet unknown) shearing tractions:

$$EI_1 \frac{d^2 y_1}{dx^2} = M_1(x) = \left(P_1 - \frac{k\tau_m b_1 h_1}{2}\right)(L - x) \tag{4a}$$

$$EI_2 \frac{d^2 y_2}{dx^2} = M_2(x) = (P_2 - k\tau_m b_1 h_2)(L - x) \tag{4b}$$

The deflections can be calculated from integration of the previous equations. They must be equal to the overall deflection if the interface is perfectly bonded (*k*=1). In addition, the total external load must be conserved:

$$\frac{PL^3}{3EI_T} = \frac{L^3}{3EI_2}(P_2 - k\tau_m b_1 h_2) = \frac{L^3}{3EI_1}\left(P_1 - \frac{k\tau_m b_1 h_1}{2}\right) \tag{5}$$

$$2P_1 + P_2 = P \tag{6}$$

Solving the system above it is possible to calculate the maximum values of the shearing tractions, and the load splitting among the different layers.

By allowing the shear transfer efficiency, *k* to vary between zero and one it is possible to adjust the compliance to match the values determined experimentally. The compliance of the three-layer cantilever can then be expressed as:

$$\frac{\delta}{P} = \frac{L^3}{3E_{eff} I_T} \tag{7}$$

For different support conditions, like fixed-fixed the procedure can repeated to obtain:

$$\frac{\delta}{P} = \frac{L^3}{192E_{eff} I_T} \tag{8}$$

The effective flexural Young's modulus of the CNT array can be expressed in terms of the flexural modulus of the CNT, E_{na}, the geometric properties of the effective laminate and the shearing transfer efficiency, k ($0 \le k \le 1.0$), as described in detail earlier [2]:

$$E_{eff} = \frac{E_{na} \dfrac{\sum_i I_i}{I_T}}{1 - k\left(1 - \dfrac{\sum_i I_i}{I_T}\right)} \tag{9}$$

The summation is done over all layers. The total moment of inertia I_T differs from the sum of individual moments of inertia for each layer because they are located at certain distance from the neutral axis.

3 APPLICATIONS

The predictions of equations (8) and (9) may be compared to the experimental data obtained independently by Jaroenapibal *et al*.[1] and Salvetat *et al*.[4] for a large range of array diameters (4.5 to 68 nm) as shown in Figure 3. The value of the adjustable parameter (shear transfer efficiency) has been kept constant at 0.93. These results show that the array effective flexural modulus exhibits a dramatic decrease in magnitude over a range of array diameter from 4.5 to 20 nm, reaching a value of approximately 10 GPa for diameters near 60 nm. While the chirality of the single walled CNT in the arrays examined by Salvetat *et al*. (18,0) differed from that of the Jaroenapibal *et al*. work, (10,10), the difference is small: 876 versus 865 GPa (1% difference). If the range of diameter of interest is restricted to D > 20 nm, variation in array flexural modulus is significantly reduced. Correspondingly, if the diameter of the harmonic oscillator of interest is less that 15 nm, a constant value of array flexural modulus cannot allow for accurate prediction of the first natural frequency of the oscillator.

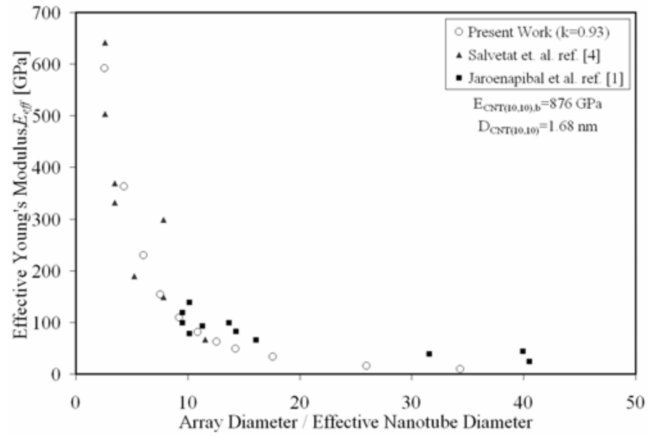

Fig. 3. Effective Young's modulus vs. array size

The flexural modulii reported by Salvetat *et al*. [4] for diameter, D = 3.0 nm, (not shown in Figure 3) differ significantly from predictions of equation (9). However, given that the flexural modulus for the (18,0) CNT is 865 GPa, it is unlikely that array modulii can exceed the stiffness of the CNT making up the array. Reported values of 1310 and 899 GPa (not shown) must therefore be considered the result of experimental inaccuracies.

Jaroenapibal *et al*. [1] plot the first natural frequency of the array versus D/L^2, for a variety of arrays. They calculated a constant Young's modulus of 76±4 GPa. The linearity of their results suggests that the array flexural modulus, *E* is independent of diameter. This result is in clear contradiction to the prediction of Equation (9) and the experimental data presented.

If the natural frequencies are calculated for the minimum and maximum reported values of array aspect ratio, D/L =67 and 143, and then compared to experimental data, the nonlinearity of the relationship becomes apparent. Each contour in Figure 4 corresponds to a constant array aspect ratio and the dimensions of extreme points on each contour illustrate the range of array diameter. It is evident that the natural frequencies for the extreme points differ significantly from the linear relationship proposed [1].

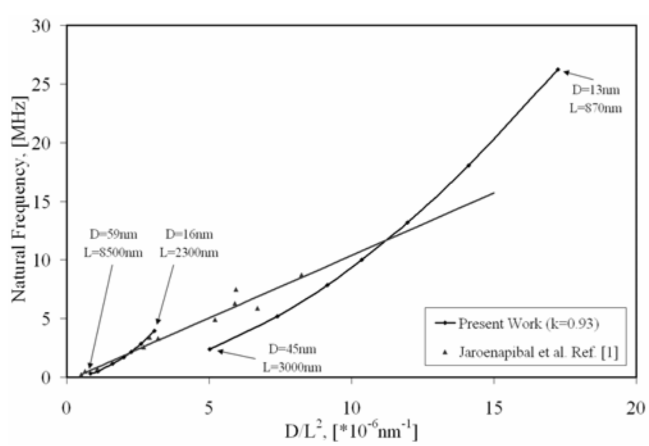

Fig. 4. First natural vibrational frequency for several arrays (diameters from 13 to 59nm)

Figure 5 presents vibrational frequencies for arrays of constant length of 1 μm. It is clear that the natural frequency approaches a maximum value of approximately 22 MHz as array diameter, D is increased beyond 20 nm. A more detailed analysis of the design space for oscillators based on CNT arrays is presented elsewhere [5].

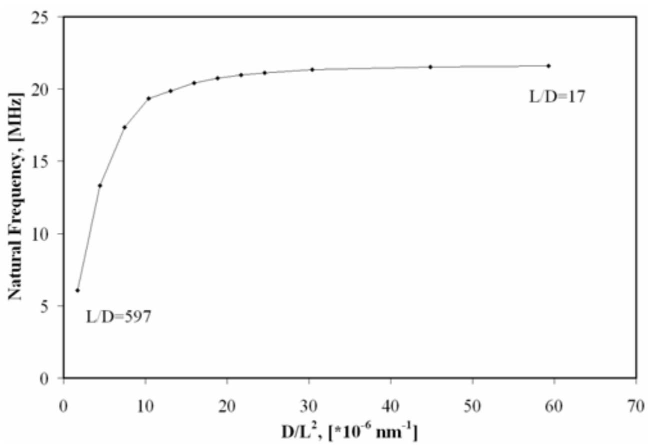

Fig. 5. First natural vibrational frequency for equal length (1μm)

4 CONCLUSIONS

A methodology is developed to analyze the elastic response of carbon nanotube arrays undergoing flexure. The only adjustable parameter is the shear transfer efficiency that quantifies the effectiveness of stress transfer across the interfaces of different layers. The shear transfer efficiency can be directly correlated to the compliance of the structure, providing an effective means to calculate its value from available experimental data.

The model can be readily extended to consider different support conditions such as cantilever, or different nanotube diameters. Without modification of the adjustable parameters it predicts variations in effective bending modulus over a wide range of array diameters (4.5 to 65 nm), that compare favorably with experimental data obtained for a common deformation mode (flexure) under two different boundary conditions (fixed-fixed and cantilever), by two independent research groups.

Contrary to the expected behavior (frequency grows unlimited with diameter), the presented model predicts a maximum limit for the attainable frequency for fixed array length, and above a specific diameter, the frequency remains almost constant. This last observation has important implications in the design of harmonic devices based on carbon nanotubes [9], since the precise size control of the bundle dimensions becomes less and less important for larger arrays.

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