INTERFACIAL STRESS TRANSFER IN CARBON NANOTUBE SYSTEMS

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ABSTRACT: Stress transfer is of paramount importance in composite materials, since load must be transferred from the matrix to the reinforcement element as efficiently as possible in order to fully realize the potential of the latter. In addition, the benefits obtained from a given reinforcement are conventionally measured in terms of its volume fraction, so efficient usage of the occupied volume places another requirement on a successful reinforcement.
Understanding load transfer is key in Multiwalled carbon nanotubes, for which it is known that the intershell interactions are orders of magnitude weaker than those along the principal axis. Traditionally stress transfer in composites has been analyzed through shear lag load models, which prescribe an interfacial shear stress as a function of the local deformation. The present work assumes the validity of continuum mechanics at the scales of interest and introduces a different concept called shear transfer efficiency that quantifies the ability of a given interface to withstand the shear stress necessary to transfer load. The two approaches are demonstrated to be equal for a two-shell structure and for larger structures the much simpler shear transfer model is able to reproduce numerical solutions of the shear lag model, with reasonable accuracy. The length dependence of the effective elastic properties typical of shear lag models is not present in the corresponding shear transfer model.
The models developed based on the shear transfer efficiency are capable of capturing the experimentally observed decrease in stiffness as the size of the carbon nanotube structure is increased, under a variety of deformation modes. Interestingly, experiments performed independently by two research groups are brought into agreement without adjustment of parameters.

INTRODUCTION

The interaction between shells in a multi-walled carbon nanotube (MWNT) structure is of paramount importance in composite materials applications because the effective reinforcement capabilities of a given structure depend strongly on how efficiently it is able to transfer the load from the matrix to its interior. This issue remains the subject of significant research for theoreticians as well as experimentalists[1-4]. Uncertainties arise primarily from the difficulties in calculating the atomic interactions within the material for sliding[1]. A conventional Lennard-Jones potential[5] cannot be directly applied to this situation since the separation between layers remains constant.
We utilize continuum mechanics at the scales of interest and define a parameter that while varying from zero to one, spans between frictionless sliding and perfect bonding among individual graphene layers[6,7]. Individual graphene sheets making up the nanotube are considered as isotropic hollow cylinders with thickness equal to that of the

equilibrium separation between layers. The central idea of this analysis is the description of the interface bonding properties through a single parameter termed the shear transfer efficiency, k.

Two loading conditions are of interest: extension and twisting. For both conditions, the load is introduced only to the outermost layer, and is transferred to the inner shells through interlayer shear transfer. An implicit assumption is that only shearing stresses are responsible for load transfer between shells. Normal stress transfer due to Poisson's effects and to the kinematics of the deformation are deemed to be second order due to the low value of Poisson's ratio for graphene and are neglected in the present analysis.

A comparison with a conventional shear lag model is described based on an approach developed elsewhere[8,9], and found to be equivalent to the shear transfer model described here for a double-walled carbon nanotube (DWNT). For a larger number of walls, shear lag analytical solutions[10] are very complicated or not possible at all, so numerical solutions were generated and compared to the simpler shear transfer model. Excellent agreement is found by varying one adjustable parameter which is determined from a series of numerical solutions. The length dependence of the effective elastic properties typical of shear lag models is not present in the corresponding shear transfer model.

MODEL PARAMETERS

The separation between individual layers of graphene in a multiwall carbon nanotube is assumed to be constant. The structure is determined by specifying either the outer or the inner diameter and the number of layers. It is assumed that the layers are commensurate to immediate neighbor layers (their chiral vectors are parallel), thereby providing optimum conditions for shear transfer[2]. The family of commensurate carbon nanotubes described by *(5n, 5n), n = 1,2,3,…,* will be employed as a model system. With this restriction, some of the conclusions may not be exact for other chiralities.

The elastic constants of graphite are taken as estimates of the properties of MWNT layers. The geometry is approximated as depicted in Figure 1.

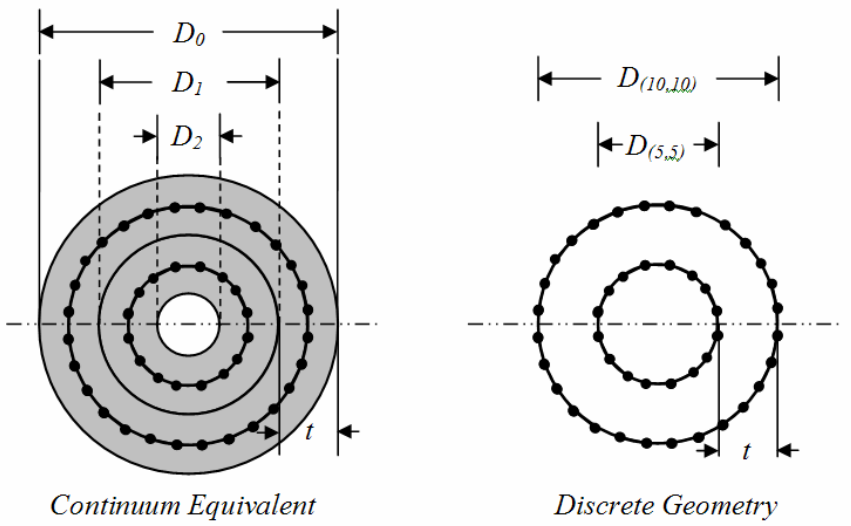

Fig. 1. Equivalent Continuum Geometry

EXTENSIONAL DEFORMATION – SHEAR TRANSFER

The shear transfer model (STM) assumes there is an unknown shear traction acting over each interface between concentric cylinders. The maximum value of the unknown traction is calculated for the condition of uniform deformation corresponding to perfect bonding at the interface, and scaled linearly through a parameter k, the shear transfer efficiency. The geometry is defined in Fig. 2.

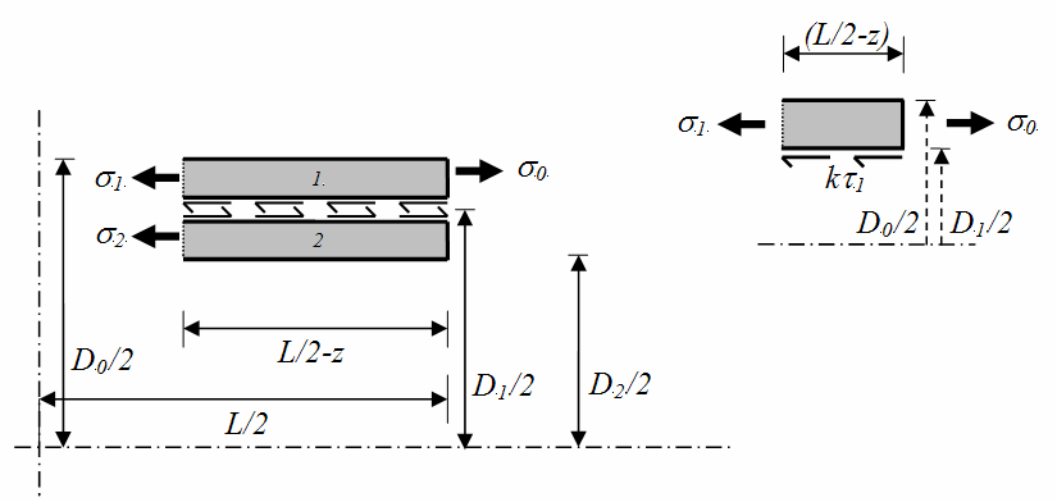

Fig. 2. Shear Transfer Model for DWNT

The distribution of shear stresses is not relevant, only its integrated effect is. The solution is obtained in terms of geometrical parameters and the applied external stress, allowing easy extension to cases with variable intershell separation:

$$\int_0^{L/2}\left[\int_z^{L/2}\tau_{im}(z)dz\right]dz=\frac{\sigma_0 A_1 L}{2\pi D_i}\left(1-\frac{\sum_{l=1}^{i}A_l}{A_T}\right) \qquad (1)$$

Finally, it is possible to calculate an effective Young's modulus for the MWNT structure by dividing the applied external stress, σ_0 by the deformation calculated for the outermost shell. The result follows:

$$E_{eff}=\frac{\frac{A_1}{(A_T+A_0)}Y}{\left[1-k\left(1-\frac{A_1}{A_T}\right)\right]} \qquad (2)$$

where Y is the Young's modulus graphene and taken as equal for all shells. This result is remarkably simple and it allows direct calculation of k if the geometry and the effective Young's modulus of the MWNT system are measured under pure extension.

Note the definition of the total area AT and the area of the central annulus, A_0, are not explicit in the previous derivation. The limiting cases corresponding to perfect bonding (k=1) and no shear transfer (k=0) lead the following equations for effective Young's Modulus:

$$\overline{E}_{k=1} = \frac{A_T Y}{\left(A_T + A_0\right)} \qquad \overline{E}_{k=0} = \frac{A_1 Y}{\left(A_T + A_0\right)} \tag{3}$$

where A_1 is the area of the outermost shell.

Extensional Deformation – Shear Lag Model

A shear lag model is presented based on the MWNT geometry shown in Figure 2. At any location z, a differential element *dz*, as shown in Figure 3, can be considered to be under static equilibrium yielding a relationship between the axial stress in each tube and the shear stress acting between tubes. This model assumes a radius-independent value for the elastic constants (Young's modulus is constant for all shells) and the inter-wall interaction coefficients are taken as those of graphite[18].

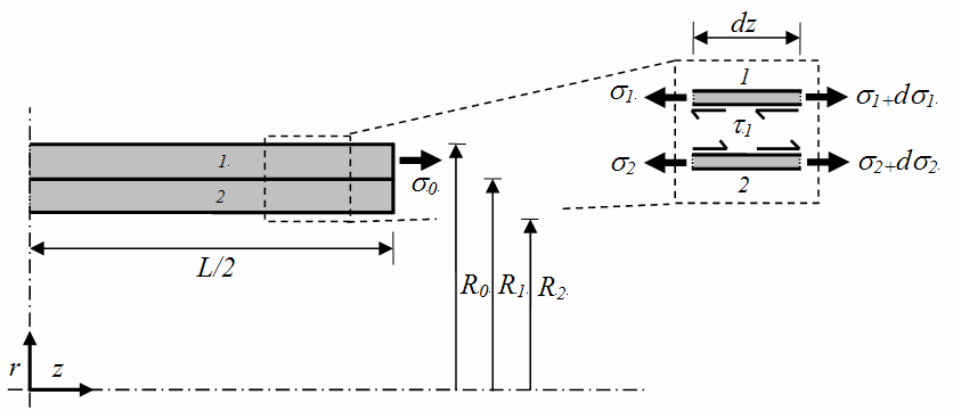

Fig. 3. Shear Lag Model for DWNT

The development of an analytical solution from a shear lag-type model begins with the general equilibrium equations for the following physical situation. Consider the equilibrium of a differential element within the two shells of length *dz*:

$$\frac{d\sigma_1}{dz} = \frac{2\pi R_1}{A_1}\tau_1 \qquad \frac{d\sigma_2}{dz} = -\frac{2\pi R_1}{A_2}\tau_1 \tag{4}$$

A linear shear stiffness relationship is assumed to govern the tangential sliding between layers. Note that only one component of shear stress is accounted for here.

$$\tau_1 = G_1\gamma_1 = G_1\left(\frac{u_1 - u_2}{h_1}\right) \tag{5}$$

Where u_1 and u_2 are axial deformations of shells 1 and 2, G is the effective shear modulus and h_1 is the separation distance between the shells. Taking the derivative of equation (5), and combining it with equations (4) yields the relationships:

$$\frac{A_1}{2\pi R_1}\frac{d^2\sigma_1}{dz^2} = \frac{G_1}{h_1}\left(\frac{\sigma_1}{Y} - \frac{\sigma_2}{Y}\right) \tag{6}$$

$$\frac{A_2}{2\pi R_1}\frac{d^2\sigma_2}{dz^2} = \frac{G_1}{h_1}\left(\frac{\sigma_2}{Y} - \frac{\sigma_1}{Y}\right) \tag{7}$$

where the first derivatives of deformation are recognized as the axial strains in each tube. These have been expressed in terms of stress for a linear elastic material. Global force equilibrium applied at any location z allows σ_2 to be expressed as a function of σ_1.

Boundary conditions are the applied axial stress σ_0 at z=L/2 and symmetry of the solution at the center of the tube (z=0):

$$\sigma_1\left(\frac{L}{2}\right) = \sigma_0 \qquad \sigma_2\left(\frac{L}{2}\right) = 0 \tag{8}$$

$$\frac{d\sigma_1}{dz}(0) = 0 \qquad \frac{d\sigma_2}{dz}(0) = 0 \tag{9}$$

The governing equations (6-7) for σ_1 and σ_2 can be solved by standard techniques defining the following parameters:

$$\lambda^2 = \frac{2\pi R_1 G_1}{Y h_1}\left(\frac{1}{A_1} + \frac{1}{A_2}\right) \tag{10}$$

Shear stress between the tubes can be computed using equations (4):

$$\tau_1(z) = \frac{\sigma_0}{2\pi R_1}\left(\lambda \frac{Sinh(\lambda z)}{Cosh\left(\lambda \frac{L}{2}\right)}\right)\frac{A_1 A_2}{A_1 + A_2} \tag{11}$$

The interlayer shear stresses are presented in Figure 4 for a (5,5)/(10,10) DWNT, using the standard separation between planar graphite (0.34nm), the shearing modulus for graphite (4.5 GPa), and a half MWNT length of 50 nm.

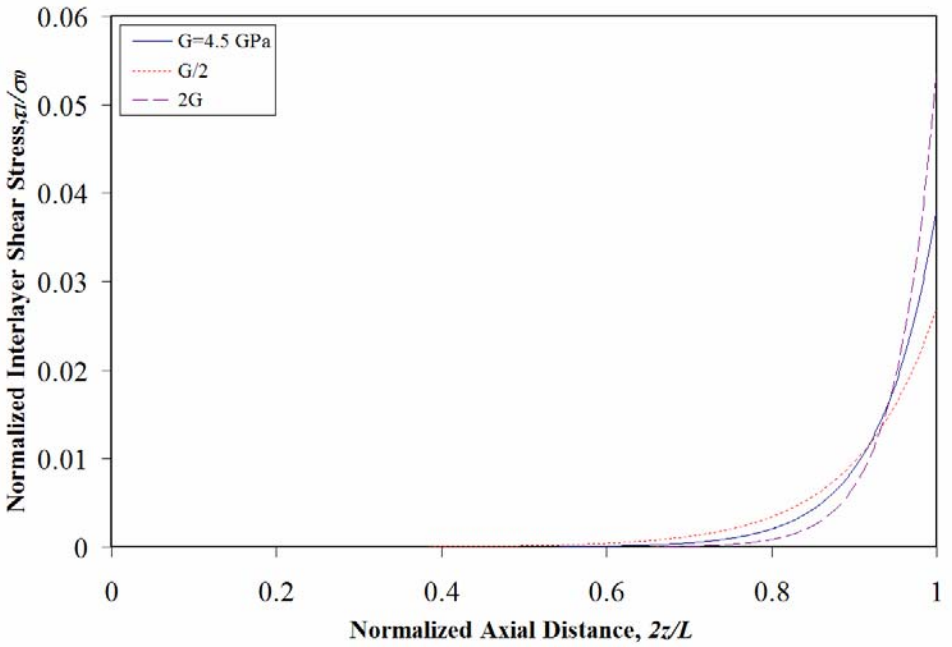

Fig. 4. Interlayer Shear Stress for DNWT for several values of G

The effective modulus of the DWNT can be calculated from the total displacement of the outermost layer, $u_1(L/2)$, as follows:

$$E_{eff} = \frac{\sigma_0 L}{2u_1(L/2)} \frac{A_1}{A_0 + A_1 + A_2} \tag{12}$$

$$u_1\left(\frac{L}{2}\right) = \frac{\sigma_0}{Y}\left[\frac{A_1}{A_1 + A_2}\frac{L}{2} + \frac{A_2}{A_1 + A_2}\frac{Tanh\left(\lambda\frac{L}{2}\right)}{\lambda}\right] \tag{13}$$

The resulting expression for effective Young's Modulus is:

$$E_{eff} = \frac{YA_1}{A_0 + A_1 + A_2}\left(\frac{A_1 + A_2}{A_1 + A_2 B}\right) \tag{14}$$

$$B = \frac{Tanh\left(\lambda\frac{L}{2}\right)}{\lambda\frac{L}{2}} \tag{15}$$

The previous derivations in equations (14)-(15) can be extended to consider a pair of hollow CNT. The resulting expression for effective modulus is:

$$E_{eff} = \frac{Y \dfrac{A_T}{(A_T + A_0)}}{1 - B\left(1 - \dfrac{A_T}{A_1}\right)} \tag{16}$$

Expressions (2) and (16) are of the same form, keeping in mind that the parameters B and k span the same physical limits in opposite directions:

$$k = 0 \qquad B = 1 \qquad L = 0 \tag{17}$$

$$k = 1 \qquad B = 0 \qquad L \to \infty \tag{18}$$

The shear transfer model does not exhibit dependence of k upon L, whereas such length dependence is inherent to the shear lag model. The dependence of effective Young's modulus on B and k is presented in Figure 5 for a standard set of parameters.

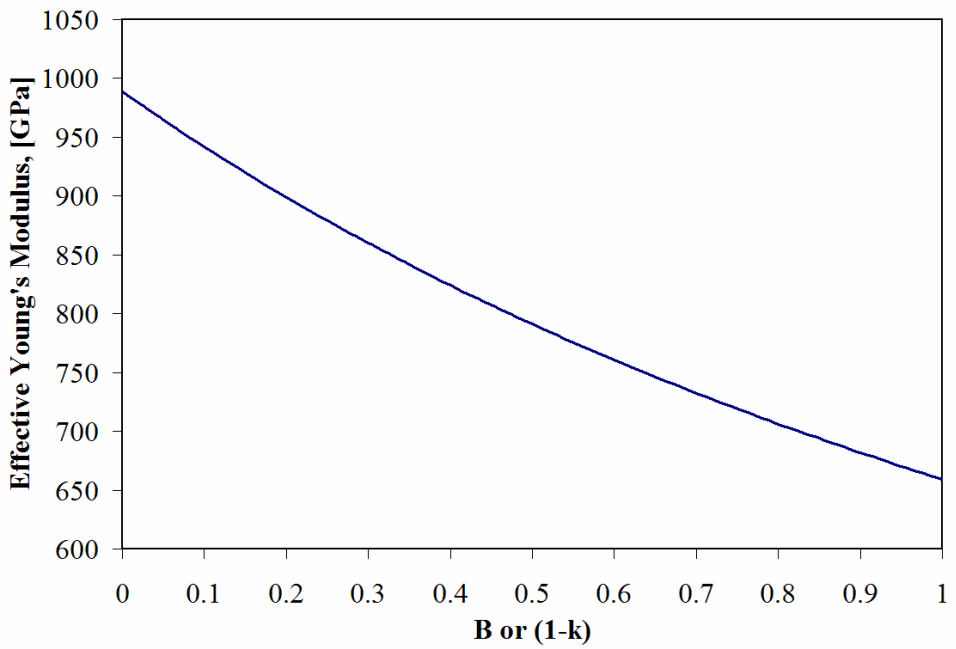

Fig. 5. Effective Young's Modulus of DWNT as a Function of Shear Transfer Efficiency

The influence of length on effective modulus can be illustrated by using equation (15) to relate B to L, as shown in Figure 6. The dependence of modulus upon length is only reflected in the shear lag model. However, it is possible to reflect the length dependence within the shear transfer model by equating $k=1-B$.

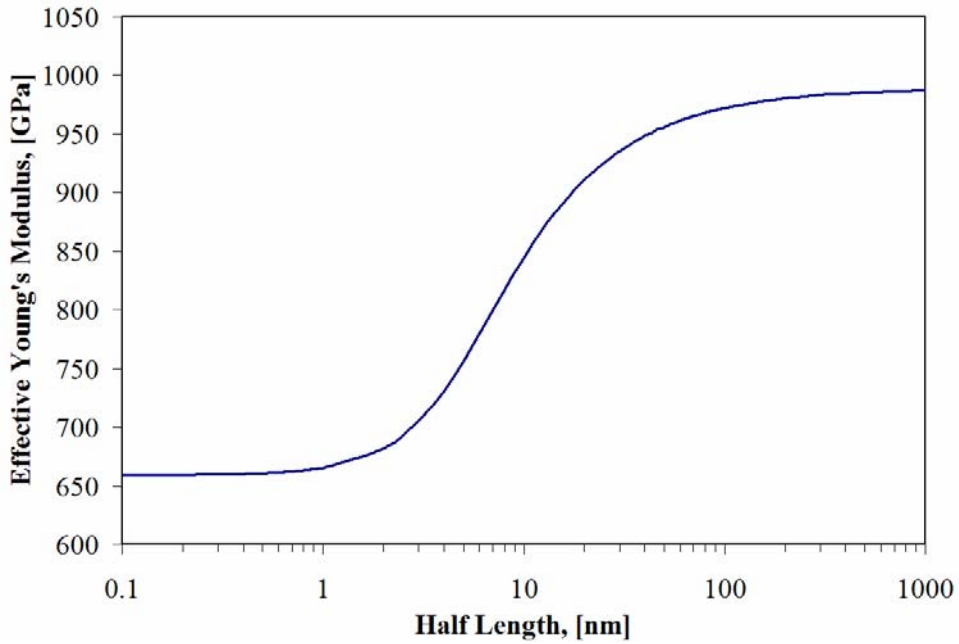

Fig. 6. Effective Young's Modulus of DWNT as a Function of Length

Model Comparison for MWNT

Analytical solutions for the shear lag model are not easily obtained beyond two concentric cylinders, so numerical solutions must be generated and compared to the corresponding equations for the shear transfer model.

Figure 7 presents the maximum shear stress profiles for 2, 3, 4, 5 and 6 layers, keeping all other parameters constant, and normalized by the external applied stress. In addition the maximum interlayer shear stress is approximately 5 percent of the external stress. The profile dependence on the number of layers becomes weaker as the number grows, but the overall stiffness of the system is affected by the number of layers dramatically.

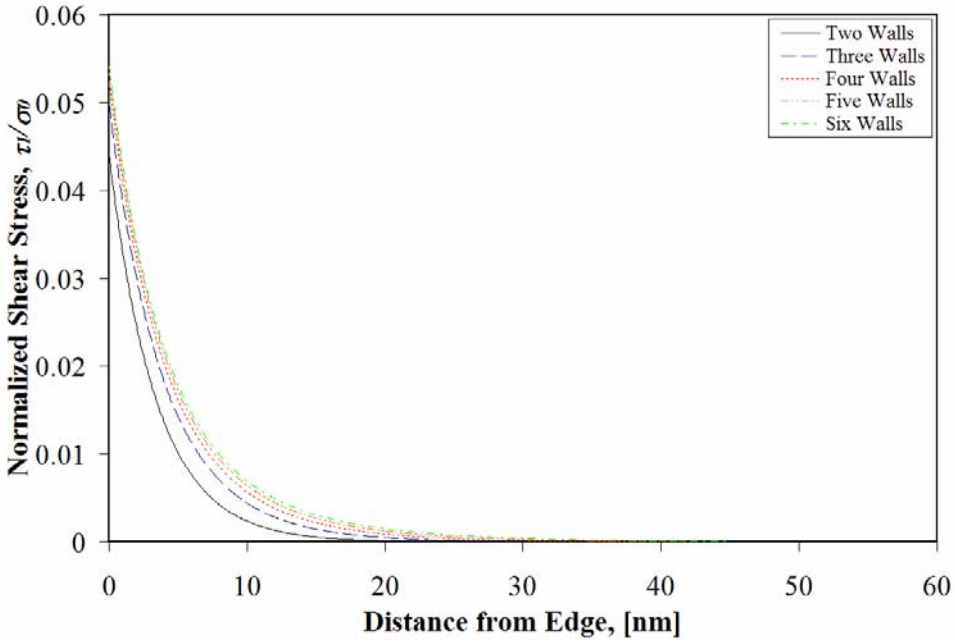

Fig. 7. Shear Stress profiles for MWNT – Numerical Solutions

As stated by Li and coworkers[15] and our previous work[11,12], the limiting cases for load transfer are always the same: either the load is shared proportionally among all constituent nanotubes or only the outer shell carries it all (*k=0* and *k=1*). Figure 8 presents the effective modulus as a function of length for 2,3,4,5 and 6 walls, normalized by the maximum possible value for each case as given by equation (2) setting *k=1*.

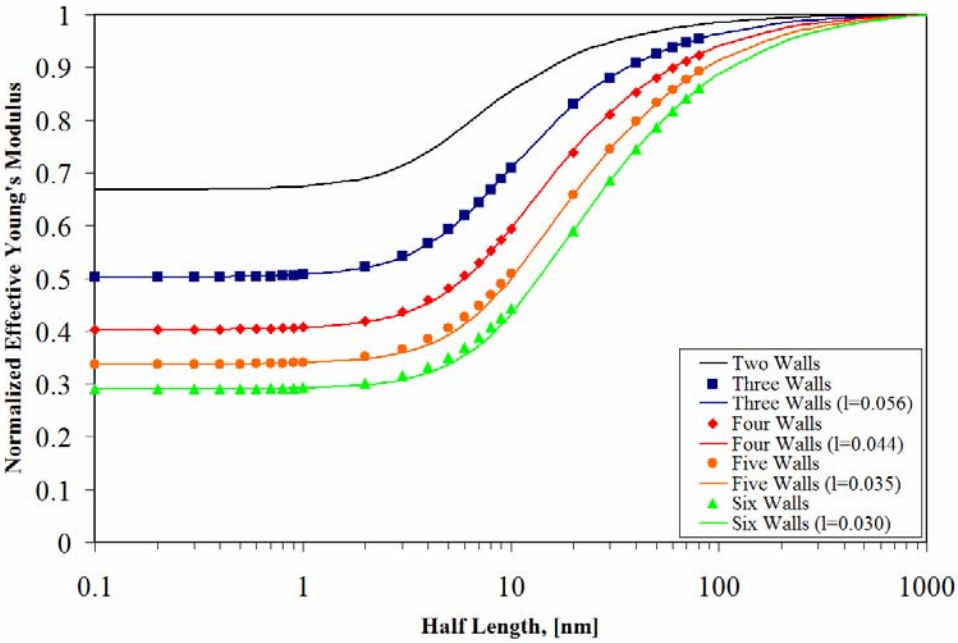

Fig. 8. Effective Young's Modulus for MWNT – Numerical Solutions

The length dependence for effective Young's modulus increases as the number of layers is increased. For the number of layers typically reported by experimenters[3,19,20] and the accepted values for the elastic constants of graphite[18] that have been used in this work, the lengths for which stress transfer limitations become irrelevant are on the order of microns. This observation is not in agreement with the low values of Young's modulus measured. The reduction of modulus due to length would require test samples of 100 nm or less. Yet the length required for modulus tests likely exceeds 1 μm, where there is no length dependence.

The numerical solutions can be approximated using equations (2) and (16). A standard minimization procedure is followed to calculate the optimum value of the parameter λ that reproduces the analytical solution best for each number of walls (the values for up to six walls are listed on the legend of Figure 8). The following empirical expression is proposed for any number of layers:

$$\lambda = 0.1617 n^{-0.9432} \qquad (19)$$

The previous expression has been derived from a simple regression based on numerical solutions for up to ten-shell MWNT. Its most important limitation is the fact that it is based on a specific set of MWNT: *(5m,5m)*. For a different MWNT family, the determination of an effective fitting parameter would require the repetition of numerical solutions for the new geometry in order to obtain the constants in Equation (19).

Given the fact that both solutions have been demonstrated to be equal for the DWNT, the key issue to be noticed is that the much simpler fully analytical solution of the shear transfer model is able to approximate the much more complicated numerical solution of the shear lag model for any number of layers. However the accuracy of the fit decreases as the number of layers increases. This fact is not surprising since the analytical solutions for more than two layers involve several eigenvalues as opposed to our single parameter approximation.

Conclusions

For extensional deformations, the shear transfer model for MWNT has been compared to a shear lag approach similar to that developed by Li and coworkers[15,16] and an exact equivalence has been found for double-walled nanotubes. Due to the fact that the shear transfer model is independent of the distribution of shearing stresses and only takes into consideration its integrated effect, the two approaches are not identical. However, a simple relationship between the shear transfer efficiency and the effective modulus has been established.

For more than two walls the simple shear transfer model can reasonably approximate the numerical solution obtained from the shear lag model, but there is no general way to estimate the fitting parameter for a large number of layers usually found in experiments. An empirical equation based on numerical solutions for up to ten shells has been presented.

The length dependence of the effective elastic properties of MWNT is an inherent feature of the shear lag model and is not explicitly present in the shear transfer model. A critical literature review[3,19-21] was conducted with the goal of identifying trends suggesting length dependence of modulus, but experimental data is scarce and errors are too large to arrive at meaningful conclusions[22]. Our predictions show that in order to observe changes in modulus due to length would require test samples of approximately 100 nm. However, typical lengths found in experiments exceed several microns, where it is predicted that there is no length dependence. Careful experimental studies aimed at determining length dependence on the effective modulus for the systems studied are both important and problematic.

References

1. M. Huhtala, A.V. Krasheninnikov, J. Aittoniemi, S. Stuart, K. Nordlund, and K. Kaski, Improved mechanical load transfer between shells of multiwalled carbon nanotubes, *Phys. Rev. B.*, 70, 045404, (2004).

2. A.N. Kolmogorov and V.H. Crespi, Smoothest Bearings: Interlayer Sliding in Multiwalled Carbon Nanotubes, *Phys. Rev. Lett.* 85, 4727 (2000)

3. M.F. Yu, O. Lourie, M.J. Dyer, K. Moloni, T.F. Kelly and R.S. Ruoff, *Science* **287**, 637 (2000).

4. J. Cummings, and A. Zettl Low-Friction Nanoscale Linear Bearing Realized from Multiwall Carbon Nanotubes, *Science*, **289**, 602 (2000).

5. L.A. Girifalco, M. Hodak and R.S. Lee, Carbon Nanotubes, Buckyballs, Ropes, and a Universal Graphitic Potential, *Phys. Rev. B.*, Vol. **62**(19), 13104, (2000).

6. M.R. Falvo, J. Steele, R.M. Taylor II and R. Superfine, Gearlike rolling motion mediated by commensurate contact: Carbon nanotubes on HOPG, *Phys. Rev. B*, **62**(16), R10665, (2000)

7. M. Dienwiebel, G.S. Verhoeven, N.Pradeep, J.W.M. Frenken, J.A. Heimberg and H.W. Zandbergen, Superlubricity of Graphite, *Phys. Rev. Lett*. **92**, 126101, (2004).

8. A. Kolmogorov, V.H. Crespi, M.H. Schleier-Smith and J C. Ellenbogen, Nanotube-Substrate Interactions: Distinguishing Carbon Nanotubes by the Helical Angle, Phys. Rev. Lett. 92, 085503, (2004).

9. A. Kolmogorov and V.H. Crespi, A registry-dependent interlayer potential for graphitic systems, Phys. Rev. B, 71, 235415, (2005).

10. A. Buldum and J.P. Lu, Atomic Scale Sliding and Rolling of Carbon Nanotubes, *Phys. Rev. Lett*. **83**, 5050, (1999).

11. R.B. Pipes and L. Zalamea, Energetics of Imperfectly Bonded Carbon Nanotubes in Flexure, in press, *Composites Science and Technology*, (2006).

12. R.B. Pipes, J.P. Salvetat, P. Hubert, and L. Zalamea, Flexural Deflection as a Measure of van der Waals Interaction Forces in the CNT Array, *Composites Science and Technology*, 66(9), 1122, (2006).

13. J.P. Salvetat, G.A.D. Briggs, J.M. Bonard, R.R. Bacsa, A.J. Kulik, T. Stockli, N.A. Burnham and L. Forro, Elastic and Shear Moduli of Single-Walled Carbon Nanotube Ropes, *Phys. Rev. Lett.*, **82**(5), 944, (1999).

14. Jaroenapibal, D.E. Luzzi, S. Evoy, and S. Arepalli, Transmission Electron Microscopic studies of mechanical properties of single-walled carbon nanotube bundles, *Appl. Phys. Lett.*, **85**, 4328, (2004).

15. L. Shen and J. Li, Transversely isotropic elastic properties of multiwalled carbon nanotubes, *Phys. Rev. B* **71**, 035412, (2005).

16. L. Shen and J. Li, Transversely isotropic elastic properties of single-walled carbon nanotubes, *Phys. Rev. B* **69**, 045414, (2004).

17. J. A. Nairn, On the Use of Shear-Lag Methods for Analysis of Stress Transfer in Unidirectional Composites, *Mechanics of Materials*, **26**, 63, (1997).

18. Dresselhaus, M.S., Dresselhaus, G., Sugihara, K. , Spain, I.L. and Golberg, H.A., Graphite Fibers and Filaments, Springer-Verlag, p. **87**, (1988).

19. M.F. Yu, B.I., Yakobson and R.S. Ruoff, *J. Phys. Chem. B*. 104(37), 8764, (2000).

20. P.A. Williams, S.J. Papadakis, A.M. Patel, M.R. Falvo, S. Washburn, and R. Superfine, *Phys. Rev. Lett.*, **89**, 255502, (2002)

21. J.P. Salvetat, A.J. Kulik, J.M. Bonard, G.A.D. Briggs, T. Stöckli, K. Méténier, S. Bonnamy, F. Béguin, N.A. Burnham and L. Forró, Elastic Modulus of Ordered and Disordered Multiwalled Carbon Nanotubes, *Advanced Materials*, **11**(2), 161, (1999).

22. L. Zalamea and R.B. Pipes, Analysis of Experimental Data on Mechanics of MWNT, *to be presented at IMECE 2006*.