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The asymptotic distribution of ultimate strength of single-walled carbon nanotubes using atomistic simulation

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ABSTRACT: This paper models the effects of randomly distributed Stone-Wales (SW) defects on the asymptotic distribution of ultimate strength of single-walled nanotubes (SWNTs) using the technique of atomistic simulation (AS). A Matern hard-core random field applied on a finite cylindrical surface is used to describe the spatial distribution of the Stone-Wales defects. We simulate a set of displacement controlled tensile loading up to fracture of SWNTs with (6,6) armchair configuration and aspect ratios between 6.05 and 36.3. A modified Morse potential is adopted to model the interatomic forces. SWNT ultimate strength is calculated from the simulated force and displacement time histories. The asymptotic distribution of the ultimate strength is found to shift to the left and become narrower with increasing tube length, l, and appears to fit the Weibull distribution rather well. The extremal index, measuring the stochastic dependence in the strength field, is estimated. The stiffness and strength of the tube are found to be asymptotically uncorrelated.

1 INTRODUCTION

The study of carbon nanotubes (CNTs) has been motivated largely due to their extraordinary electronic and mechanical properties (Salvetat et al. 1999; Yakobson and Avouris 2001; Bernholc et al. 2002). The combination of high stiffness, high strength and good ductility with unique electronic properties (e.g., CNTs can be metallic or semiconducting depending on chirality) make the carbon nanotube a potentially very useful material. CNTs are now used as fibers in composites, scanning probe tips, field emission sources, electronic actuators, sensors, Lithium ion and hydrogen storage and other electronic devices. Also, CNTs can be coated or doped to alter their properties for further applications.

A survey of recent results on the elastic modulus and strength of single-walled and multi-walled carbon nanotube (SWNT and MWNT) has been reported in Lu and Bhattacharya (2005). The collected data clearly show the strength to vary between 5GPa and 150Gpa; elastic modulus and failure strain also show significant variation. Such variation has also been noticed by a few recent studies (Chandra et al. 2004; Sears and Batra 2004). An analytical understanding of these variations, their sources and how they can be controlled is essential before CNTs and CNT-based products can be considered for widespread use across industries.

Defects such as vacancies, metastable atoms, pentagons, heptagons, Stone-Wales (SW or 5-7-7-5) defects, heterogeneous atoms, discontinuities of walls, distortion in the packing configuration of CNT bundles, etc. are widely observed in CNTs (Iijima et al. 1992; Zhou et al. 1994; Charlier 2002). Such defects can be the result of the manufacturing process itself: according to an STM observation of the SWNTs structure, about 10% of the samples were found to exhibit stable defect features under extended scanning (Ouyang et al. 2001). Defects can also be introduced by mechanical loading and electron irradiation.

The Stone-Wales (SW) defect, which is the focus of this paper, is composed two pentagon-heptagon pairs, and can be formed by rotating a sp^2 bond by 90 degrees (SW rotation). SW defects are stable and commonly present in carbon nanotubes, and are believed to play important roles in the mechanical, electronic, chemical, and other properties of carbon nanotubes. For example, Chandra et al. (2004) found that the SW defect significantly reduced the

Elastic modulus of single-walled nanotubes. Mielke et al. (2004) compared the role of various defects (vacancies, holes and SW defects) in fracture of carbon nanotubes, and found that various one- and two-atom vacancies can reduce the failure stresses by 14~26%. The SW defects were also found to reduce the strength and failure strain, although their influence was less significant than vacancies and holes.

It has been found that SWNTs, under certain conditions, respond to the mechanical stimuli via the spontaneous formation of SW defect beyond a certain value of applied strain around 5%~6% (Nardelli et al. 1998). More interestingly, the SW defect can introduce successive SW rotations of different C-C bonds, which lead to gradual increase of tube length and shrinkage of tube diameter, resembling the necking phenomenon in tensile tests at macro scale. This process also gradually changes in chirality of the CNT, from armchair to zigzag direction. This whole response is plastic, with necking and growth of a "line defect", resembling the dislocation nucleation and moving in plastic deformation of crystal in many ways. Yakobson (1998) thus applied dislocation theory and compared the brittle and ductile failure path after the nucleation of the SW defect.

The formation of SW defects due to mechanical strains has also been reported by other groups of researchers. In their atomistic simulation study, Liew et al. (2004) showed that SW defects formed at 20~25% tensile strain for single-walled and multi-walled nanotubes with chirality ranging from (5,5) to (20,20). The formation of SW defects explained the plastic behavior of stress-strain curve. They also predicted failure strains of those tubes to be about 25.6%. A hybrid continuum/atomistic study by Jiang et al. (2004) reported the nucleation of SW defects both under tension and torsion. The reported SW transformation critical tensile strain is 4.95%, and critical shear strain is 12%. The activation energy and formation energy of the SW defects formation are also studied and related to the strength of the nanotube (Samsonidze et al. 2002; Zhao et al. 2002; Zhou and Shi 2003). The nucleation of SW defects was found to depend on the tube chiralities, diameters and external conditions such as temperature.

Nevertheless, surprisingly little work has been directed in the available literature toward studying the randomness in defects and the influence of such randomness on CNT mechanical properties in a systematic and probabilistic way. Here in this paper, we investigate the effect of randomly occurring Stone-Wales defect in SWNTs as a potentially significant case study. We make reasonable assumptions on the random nature of the SW defects and, through the technique of atomistic simulation, quantify the effect of such randomness on the asymptotic behavior of ultimate strength as the tube length increases. Details of the atomistic simulation procedure have been given in Lu (2005).

2 EFFECT OF RANDOM DEFECTS ON SWNT MECHANICAL PROPERTIES

To our knowledge, there are few published works to date that study the effects of random defects, especially of the Stone-Wales kind, on the mechanical properties of CNTs. The study by Saether (2003) investigated the transverse mechanical properties of CNT bundles subject to random distortions in their packing configuration. This distortion, quantified by a vector describing the transverse displacement of the CNTs, may be caused by packing faults or inclusions. The magnitude and direction of the vector were both uniform random variables. The transverse moduli of CNT bundles were found to be highly sensitive to small distortions in the packing configuration. In another instance, Belavin et al (2004) studied the effect of random atomic vacancies on the electronic properties of CNTs.

Since there is not enough information in the experimental literature to provide a clear picture of statistical properties of the defects, it is reasonable to start with the assumption that the defects occur in a completely random manner, which implies an underlying homogeneous Poisson spatial process. We also acknowledge the fact that the SW defect is not a point defect but has a finite area and there should be no overlap between neighboring defects. Therefore, we adopt a Matern hard-core point process (Matern 1960) for the defect field. We emphasize that the Matern process has the property that any two points are at least h apart. The intensity of Matern hard-core process is $\lambda_h = p_h\lambda$ where λ is intensity of the underlying homogeneous Poisson point process and p_h is the probability that an arbitrary point from the underlying Poisson process will survive the Matern thinning. Thus, the average number of SW defects on an area A_t is $\lambda_h A_t$.

For a finite tube of length b, the probability p_h can be computed as:

$$p_h = \frac{1}{b}\int_0^b \frac{1-e^{-\lambda A(y)}}{\lambda C(y;h)}dy \tag{1}$$

where C is the area over which a Poisson point at (x_0, y_0) searches for its neighbors:

$$C(y_0;h) = \begin{cases} C'(y_0;h) & y_0 < h \\ \pi h^2 & h < y_0 < b-h \\ C''(y_0;h) & h < y_0 < b-h \end{cases} \qquad (2)$$

with $C'(y_0;h) = h^2\left(\frac{\pi}{2} + \theta + \frac{1}{2}\sin 2\theta\right), 0 < y_0 < h$ where $\theta = \arcsin y_0 / h$. $C''(y_0;h)$ in Eq. (2) can be given simply by replacing $\theta = \arcsin(b - y_0)/h$ in the expression for C'.

In this study, we fix h at 8.0 Å, and use a set of reasonable values for λ, the rate of the underlying Poisson field. The detailed procedure of generating SW defects has been provided in Lu (2005). Once the location of the SW defect is selected, the sp^2 bond closest to the defect point is found, and then the bond is rotated by 90º to form a SW defect.

In order to study the effects of Stone-Wales defects on mechanical properties and the fracture process of carbon nanotubes, we adopt a single-walled nanotube (SWNT) in (6,6) armchair configuration. The tube diameter is 8.14Å. The lengths of the tube was made to vary between 49.2 Å and 295.2 Å. The total number of atoms in the simulation varied between 480 (for the 49.2 Å long tube) and 2880 (for the 295.2 Å long tube).

For the atomistic simulation part of this study, a modified Morse potential model for describing the interaction among carbon atoms (Belytschko et al. 2002) is applied. This potential model does not have some of the shortcomings of the bond order potential models (Dumitrica et al. 2003; Troya et al. 2003). We adopt the cutoff distance (r_c) and the critical inter-atomic separation (r_f) as: $r_f = r_c = 1.77$ Å in this example. The distance between neighboring carbon atoms on the graphene sheet, a_0, is 1.42 Å, which is the C-C sp^2 bond length in equilibrium. The initial atomic positions are obtained by wrapping a graphene sheet into a cylinder along the chiral vector $\mathbf{C}_n = m\mathbf{a}_1 + n\mathbf{a}_2$ such that the origin (0,0) coincides with the point (m, n). The tube diameter is thus obtained as $d = a_0\sqrt{3(m^2+n^2+mn)}\big/\pi$.

The initial atomic velocities are randomly chosen according to a uniform distribution (between the limits −0.5 and 0.5) and then rescaled to match the initial temperature (300K in this example). The mechanical loading is applied through moving the atoms at both ends away from each other at constant speed (2.5 m/s to 10m/s depending on tube length) without relaxing until fracture occurs. The ultimate strength is calculated at the maximum force point, $\sigma_u = F_{max}/A$, where F is the maximum axial force, A is the cross section area, assuming the thickness of tube wall is 0.34 nm. Figure 1 shows the first two moments of SWNT ultimate strength as a function of the average number of SW defects on the tube. The strength variability in the absence of any defect (zero average defects) is interesting: it arises solely from thermal fluctuations.

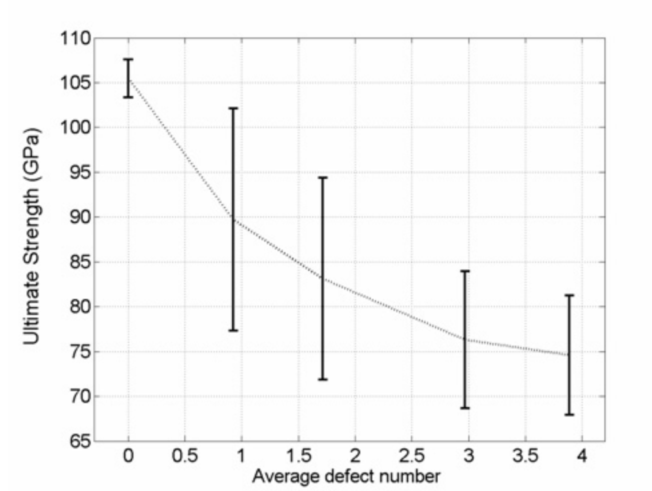

Figure 1: SWNT ultimate strength as a function of average number of defects on the tube (dashed line = mean, vertical bar= mean +/- one standard deviation)

3 ASYMPTOTIC BEHAVIOR OF ULTIMATE STRENGTH OF SWNTS

The asymptotic behavior of the ultimate strength of SWNT with defects as tube length increases is considered next. A tube may be considered to be composed of n segments of length Δ_i for $i = 1, \ldots, n$. The length of the tube, $l_n = \sum_{i=1}^{n} \Delta_i$, depends on n, as does the strength of the tube, $W_{(n)}$:

$$W_{(n)} = \min\{X_1, X_2, \ldots, X_n\} \qquad (3)$$

where X_i is the strength of the i^{th} segment. Owing to the presence of random defects and random velocities of the atoms, each X_i is random in nature; consequently $W_{(n)}$ is random as well. It is reasonable to assume that the strength field is statistically homogeneous, hence, if $\Delta_i = l_0$ for each i, then each X_i has the same marginal distribution function, F.

It is well known that if the X_i 's are i.i.d. (independent and identically distributed) and possess some very general properties that are satisfied by all common distribution functions, extreme value analysis (Galambos 1987) shows that the probability

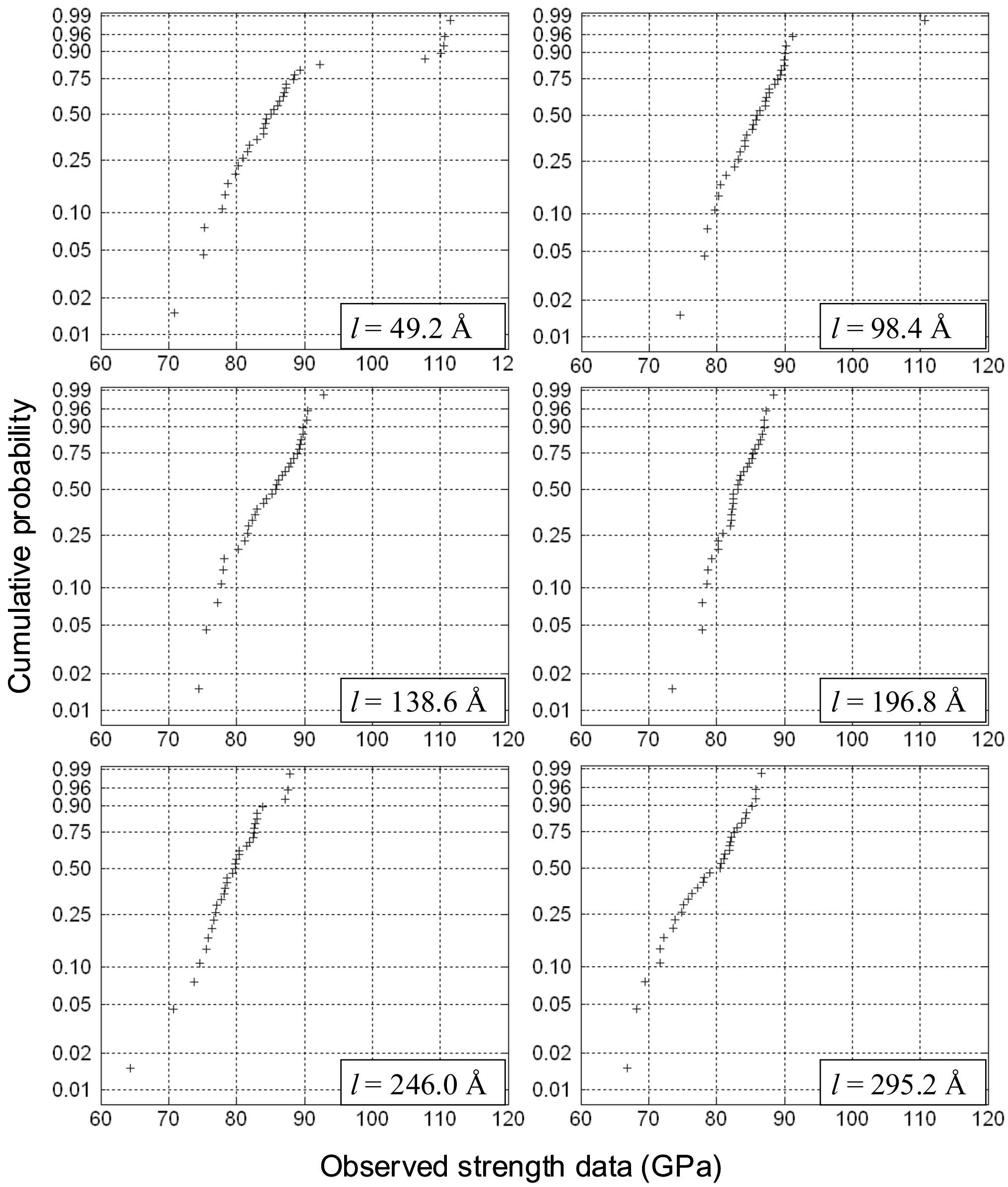

Figure 2: Weibull probability plot for SWNT ultimate strength with increasing tube length (33 samples each)

distribution of the minimum, $W_{(n,\text{iid})}$, under appropriate normalization, $v_n(z) = c_n + d_n z$, converges as $n \to \infty$ to:

$$P\left[W_{(n,\text{iid})} \le v_n\right] = L_{(n)}\left(v_n\right) \to L_c(z) = \\ 1-\exp\left[-\left(1-cz\right)^{-1/c}\right],\ 1-cz>0 \qquad (4)$$

where L_c is one of the three classical asymptotic extreme value distributions and depends on the parameter, c. With $c = 0$, L_c is interpreted in the limit as Gumbel distribution for minima ($L_G(z)=1-\exp(-\exp z)$) ; with $c < 0$, L_c is the Weibull distribution for minima; and with $c > 0$, L_c is the Frechet distribution for minima.

The i.i.d. assumption on strengths of the tube segments appears unrealistic, since there is likely to be dependence at least among strengths of neighboring segments. Fortunately, the above classical results can be extended to the dependent stationary case as well, as long as the dependence reduces with increasing separation i.e., there is no long-range memory effect and there is no clustering of very low values. This can be formalized by Conditions $D(u_n)$ and $D'(u_n)$ (Leadbetter et al. 1983) applied to minima of stationary sequences. In such cases, the asymptotic distribution is still one of three classical ones, although the convergence is slower than that in the i.i.d. case as described subsequently.

We investigate the distribution of ultimate strength, σ_u, with increasing tube length, l, of (6,6) armchair SWNTs while keeping the average rate of occurrence of SW defects per unit tube surface area constant ($\lambda = 1.59\times10^{-3}$/Å^2, h = 8 Å). Six values of l are considered: l_0 = 49.2A, $2l_0$, …, $6l_0$. The corresponding loading rates are 2.5, 5.0, 7.5, 10.0, 12.5 and 15.0 m/s such that the strain rate is constant. 33 samples are generated for each value of l. Figure 2 shows the distribution of the 33 samples for each l as drawn on Weibull probability paper. The quality of Weibull fit appears to improve with increasing tube length.

Table 1 shows the statistics of the ultimate strength of SWNTs with Stone-Wales defects as a function of tube length, l. It is clear that the distribution shifts to the left and becomes narrower with increasing l : this is consistent with the behavior of extremes from a stationary population. Since the Weibull model is widely adopted for the "weakest link" type strength variables for materials and systems across spatial scales and industries, we investigate the goodness of Weibull fit on the SWNT strength data as the tube length increases from l_0 to $6l_0$. Using the first two moments calculated from the 33 data points, a Chi-squared goodness of fit is performed in each case with 6 equi-probable intervals, i.e., 3 degrees of freedom.

Table 1: Statistics of SWNT ultimate strength as a function of tube length

Tube Length, l (Å)	μ (GPa)	V	Weibull parameters		Weibull goodness of fit	
			ω	K	χ^2 statistic	level of significance
49.19	87.30	12.35%	91.88	9.73	20.27	1.49×10^{-4}
98.38	86.04	6.98%	88.66	17.70	11.34	0.2004
147.57	84.68	5.74%	86.81	21.66	3.18	0.3644
196.76	82.89	4.03%	84.37	31.09	6.82	0.0779
246.0	79.38	5.97%	81.46	20.78	3.91	0.2714
295.2	78.64	6.95%	81.03	17.76	1.73	0.6309
Based on 33 samples for each l						

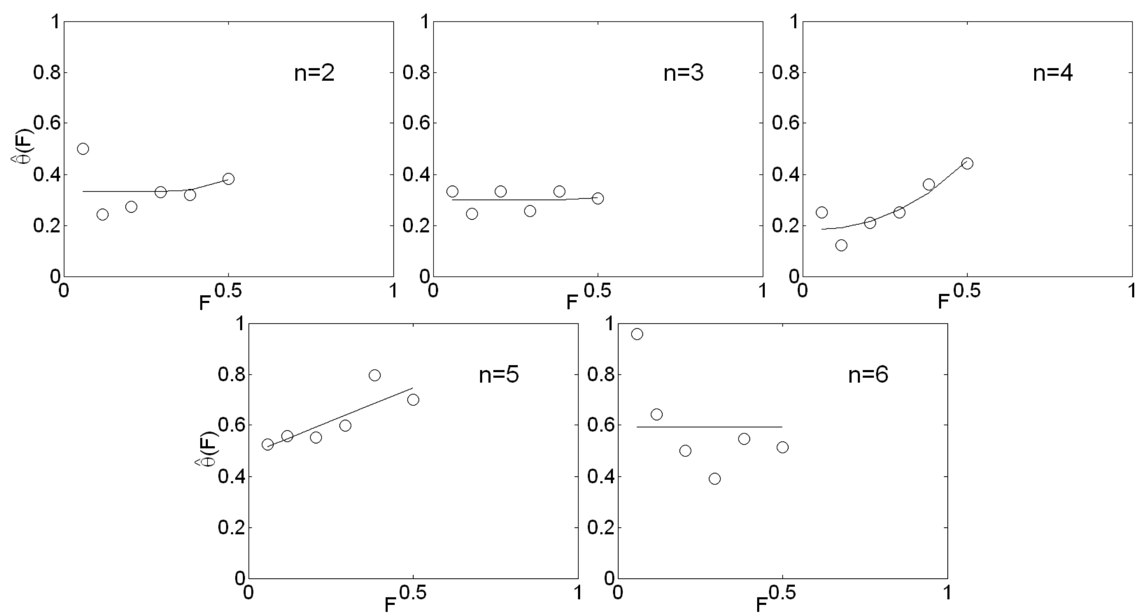

Figure 3: Estimated extremal index as a function of non-exceedance probability for various tube lengths (circle = observed value, solid line = fit of Eq. (8))

The quality of Weibull fit among this set of data using the Chi-squared test is found to be the best when $l = 6l_0$ although the improvement is not monotonic.

We now investigate the degree of dependence in the strength field mentioned above. The stationary dependent sequence $\{X_i\}$ with marginal distribution F has extremal index θ, if for each $\tau > 0$, as $n \to \infty$, (i) there exists a sequence $v_n(\tau)$ such that $nF(v_n(\tau)) \to \tau$, and (ii) $P\left[W_{(n)} \geq v_n(\tau)\right] \to \exp(-\theta\tau)$ where $W_{(n)}$ is given by Eq. (3). The extremal index is a positive fraction between zero and one: $0 < \theta \leq 1$ (Hsing 1993; Smith and Weissman 1994). It can be shown that the asymptotic distribution of the minimum, $W_{(n)}$, in the dependent stationary case converges to $\hat{L}_c$ which can be given in terms of the extremal index as:

$$P\left[W_{(n)} \leq v_n\right] \to \hat{L}_c(z) = 1 - \exp\left[-\theta\left(1 - cz\right)^{-1/c}\right] \quad (5)$$

where $1 - cz > 0,\ 0 < \theta \leq 1$.

In the context of characterizing the minima of a stationary sequence, the extremal index may be interpreted as the reciprocal of the limiting mean cluster size below a low threshold. The case of $\theta = 1$ corresponds to the i.i.d. case while the case of $\theta = 0$ is degenerate and implies long-range dependence. Clearly, L_c and $\hat{L}_c$ are of the same type for any given value of c. The significance of this result is that the distribution of the minimum $W_{(n)}$ of a stationary dependent sequence, provided it converges (which can be guaranteed by Conditions $D(u_n)$ and $D'(u_n)$), may be estimated, at least in the left tail, simply with the help of the marginal distribution F and the extremal index θ of the underlying process, as

$$P\left[W_{(n)} \geq u_n\right] \approx G^{n\theta}(u_n) \quad (6)$$

for sufficiently high u_n and large n where $G = 1 - F$ is the complementary distribution function of each X_i (i.e., the strength of a tube of length l_0). We can then estimate the extremal index if we have the statistics of nanotube strength for known values of n :

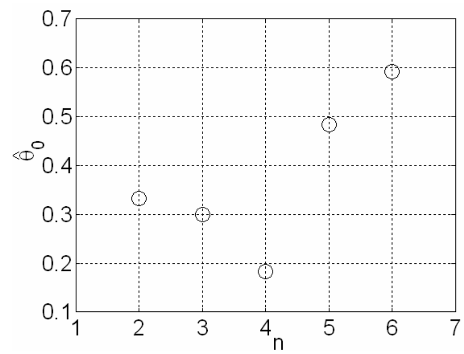

Figure 4: Limiting extremal index as a function of tube length

$$\hat{\theta} \approx \frac{1}{n}\frac{\ln G_{(n)}(x)}{\ln G(x)} \quad (7)$$

where $G_{(n)}$ is the complementary distribution function of a nanotube of length nl_0. It is apparent from Eq. (7) that the estimated extremal index depends on the threshold x. The error between the estimate at some arbitrary threshold $x > 0$ and the estimate, $\hat{\theta}_0$, at zero has been suggested (Hsing 1993) to have a log-linear relation with $F(x)$:

$$\hat{\theta}(x) = \hat{\theta}_0 + \beta_1 F(x)^{\beta_2},\quad \beta_1 \neq 0,\ \beta_2 > 0,\quad \text{as } F(x) \to 0 \quad (8)$$

Figure 3 shows the estimated extremal index $\hat{\theta}$ as a function of non-exceedance probability (i.e., F) for tubes of different lengths. It is clear that there is a substantial amount of dependence in the strength field, and strengths of the individual segments are clearly not i.i.d. Figure 4 plots the limiting value of each of these plots as function of tube length. Although a strong dependence in the strength field is again suggested in Figure 4, the extremal index is seen to fluctuate significantly, presumably due to the small values of n. It is expected that with increasing computational power, stable estimates of θ can be obtained which, in turn, will be instrumental in deciphering the underlying correlation structure in the random strength field.

Finally, the stiffness and strength of the tube are found to become asymptotically uncorrelated with increasing tube length as shown in Figure 5. This property presumably arises from the asymptotic independence of bulk and extremal properties of materials as discussed in (Bhattacharya 2002).

4 SUMMARY AND CONCLUSIONS

Defects are commonly present in CNTs, and these defects may have significant effects on the mechanical and other properties of CNTs. A wide scatter has been reported in the mechanical properties of carbon nanotubes. In this paper we considered the random nature of Stone-Wales (SW) defects in CNTs and, through the technique of atomistic simulation, quantify the effect of such randomness on the asymptotic behavior of ultimate strength as the tube length increases.

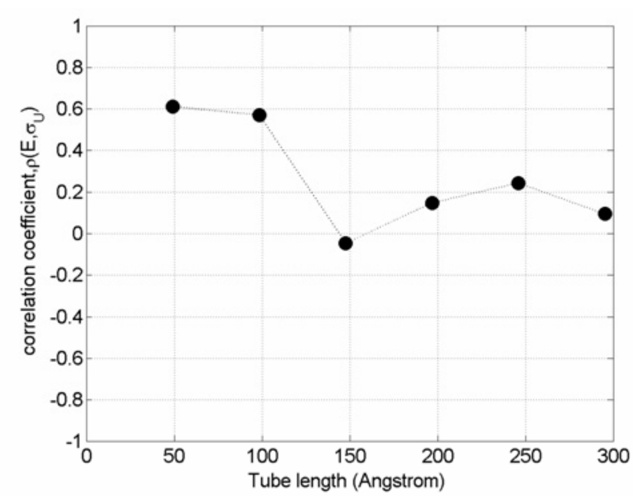

Figure 5: Asymptotic independence of tube strength and stiffness

The distribution of ultimate strength, σ_u, with increasing tube length, l, of (6,6) armchair SWNTs was investigated. The average rate of occurrence of SW defects per unit tube surface area was kept constant. Six values of l were considered and the loading was adjusted such that the strain rate was the same for each tube length. The strength distribution was found to shift to the left and become narrower with increasing l, and also appeared to fit the Weibull distribution rather well, consistent with the behavior of extremes arising from a stationary population. The existence of correlation in the ultimate strength random field of the nanotube was considered, and limiting expressions for the distribution function was developed. The extremal index, which can be used to characterize the said dependence was estimated. Stable estimates of the extremal index will be instrumental in deciphering the underlying correlation structure in the random strength field.

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