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The asymptotic properties of strength and compliance of single-walled carbon nanotubes containing random defects

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ABSTRACT: Mechanical response of deformable bodies is often concerned with either the sum or the extreme of an underlying random process. This paper investigates the asymptotic statistical properties of ultimate strength (σ_u) and compliance (C) of single-walled nanotubes (SWNTs) containing random defects using the technique of atomistic simulation (AS). Under a weak dependence condition among the segment strengths (that decay to zero with increasing distance between the segments), consistent with the non-local nature of atomic interactions, formalized here in the form of strong mixing, the asymptotic properties of σ_u (as the extreme of the strong mixing sequence) and C (as the sum of a related strong mixing sequence) are studied with increasing tube length, l. The extremal index, measuring the stochastic dependence in the strength field, is estimated. These results appear to validate the strong mixing property of the strength field.

1 INTRODUCTION

1.1 *Statistics of material response*

All real materials have defects. Depending on the scale, such defects may have significant effects on mechanical properties. A large class of problems in mechanical behavior of materials can be modeled by assuming a body, Ω, to consist of a two-phase material – say, the matrix and defects. The defects are distributed randomly in the matrix according a spatial point process, Π. Depending on the process in which the material is manufactured or loaded, this point process is not necessarily homogeneous.

In the special case when the numbers of defects in non-overlapping regions are independent, the process Π can be modeled as a spatial Poisson process in state space $\mathbb{R}^3$ with mean measure,$\mu(B) = \int_B \lambda\left(\underline{z}\right) d\underline{z}$, where B is a bounded set in $\mathbb{R}^3$ and $\lambda(\underline{z})$ is the intensity of the process. The Poisson assumption is clearly violated, however, when factors such as finite size of defects, coalescence of several defects into one defect, or the disintegration of one defect into several etc. are considered.

At the initial time t_0 the domain Ω and every region within it are in thermodynamic equilibrium. Now consider the properties of the defects. A defect at location $\underline{z}$ may be characterized at time t by a set of properties (i.e., marks), $\underline{\Theta}(\underline{z}, t)$, that, depending on the application of interest, could variously include its volume, surface area, density, orientation, elastic modulus, ultimate strength, damage state, nearest-neighbor distance, etc. In general, $\underline{\Theta}(\underline{z}, t)$ is random in nature.

Independence between marks at two different locations and between the marks and the point process, as often considered, is too restrictive. It is more reasonable to suppose that the influence decreases with increasing separation in space and time.

Let us now focus on some important property, $R(\underline{z}, t)$, of the defects. Let the randomness in the matrix be negligible compared to that of R so that the randomness in material response is governed by R.. Let us concentrate on a volume elementΔV around $\underline{z}$ in Ω and time t such that it contains $N(\Delta V(\underline{z}))$defects. Let R_i be the response of the i th defect located at $\underline{z}_i$.

Stochastic modeling of material response quite often involves looking at either sums (or, equivalently, averages) or extremes of the process $R(\underline{z}, t)$ over ΔV (Lu and Bhattacharya 2006). The former leads to bulk or globally averaged properties such as stiffness, while the latter leads to strength properties sensitive to local features such as fracture strength.

1.2 *Scope of this work*

In this paper, we investigate the asymptotic properties including dependence of the extremum and the

sum of processes related to R at the *atomistic* scale and how they affect material response and failure. The subject structure is the single walled carbon nanotube (SWNT) with finite sized Stone-Wales defects. The "sum" in question is tube compliance, and the "extreme" refers to the the tube's strength. A nanotube 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. The strength, $W_{(n)}$, of the tube is the minimum of the sequence $\{W_n\}$ of individual segment strengths, and the compliance, $C_{(n)}$, of the tube is the sum of the sequence of individual compliances, $\{C_n\}$. The two sequences $\{W_n\}$ and $\{C_n\}$ are related.

We assume that the strength random field in the tube is stationary and statistically dependent (owing to the non-local nature of atomic interactions) such that the dependence falls off with increasing separation among the segments. The *extremal index*, measuring the amount of statistical dependence in a random sequence,is determined for the SWNT random strength field. The mechanical behaviour of the SWNTs are studied with atomistic simulations.

1.3 *Carbon nanotubes and their defects*

Carbon nanotubes (CNTs) are one or more layers of helical carbon microtubules, in which each layer can be described as rolling a single sp^2 graphene sheet into a cylinder along a vector called the chiral vector (m, n).

The study of carbon nanotubes has been motivated largely due to their extraordinary electronic, mechanical and optical 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.

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.

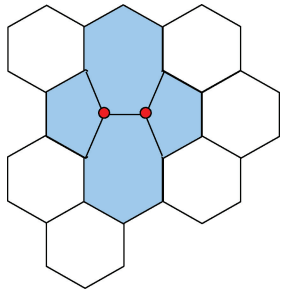


Figure 1. An SW defect showing bond rotation.

2 INCORPORATING RANDOM STONE-WALES DEFECTS IN SWNT MECHANICS

The Stone-Wales (SW) defect is composed of two pentagon-heptagon pairs, and can be formed by rotating an sp^2 bond by 90 degrees (Figure 1). SW defects are stable and often 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. Lu and Bhattacharya (2004) investigated the role of one SW defect (located at the midsection of an armchair SWNT) on tensile properties over a range of loading speeds, and found that the presence of the defect significantly affects ultimate strength as well as ultimate strain at all loading speeds; the effect of the defect on stiffness is much less. 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.

Song et al. (2006) have claimed that formation of SW defects is a precursor to fracture of SWNTs. The SW rotation occurs before the bond breakage occurs as it is energetically favoured, but beyond a certain point, the bond breakage becomes favorable, and a bond in the vicinity the defect will break. Importantly the rotated bond itself does not break.

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%.

There is not enough information in the experimental literature to provide a clear picture of statistics of SW defects (e.g., location, density, clustering tendency etc.), 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 (Lu and Bhattacharya 2005). However, we also need to account for 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. 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 $\lambda_h A_t$. Details about the defect field on the finite SWNT may be found in Lu (2005).

With the equilibrium sp^2 C-C bond length being 1.42 Å, the major axis diameter of a Stone-Wales defect is about 7.1 Å. Based on this, we conservatively fix the minimum-neighbor distance h of the Matern process at 8.0 Å.

Once the location of the SW defect is generated, the sp^2 bond closest to the defect point is found, and then the bond is rotated by 90° to form an SW defect. Randomly occurring SW defects can thus be located on a graphene sheet, which in turn, can be wrapped to produce the corresponding SWNT (Figure 2).

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).

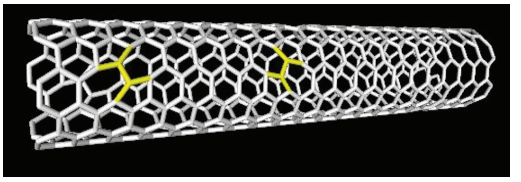


Figure 2. A (6,6) SWNT, two SW defects are highlighted.

It corresponds with the Brenner potential for strains below 10% (Belytschko, Xiao et al. 2002).

We adopt the cutoff distance (r_c) as well as the critical inter-atomic separation (r_f) as: $r_f = r_c = 1.77$ Å in this paper. 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 $d = a_0\sqrt{3}(m^2 + n^2 + mn)/\pi$.

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 (300 K in this example). The mechanical loading is applied through moving the atoms at both ends away from each other at constant speed without relaxing until fracture occurs.

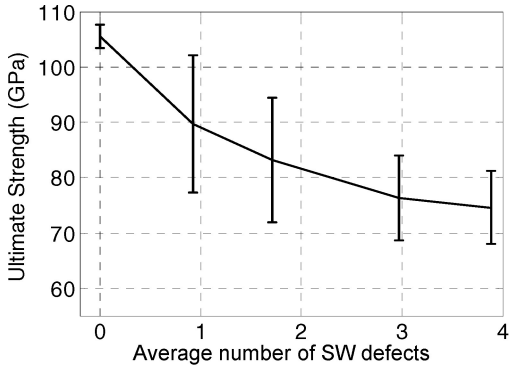
In order to study the asymptotic behavior of strength and compliance, we start with a single-walled nanotube (SWNT) in (6,6) armchair configuration. The tube diameter is 8.14Å. The length, l, of the tube is 49.2 Å. The total number of atoms in the simulation is 480. A typical time history of tensile loading to fracture generated for such a tube can be found in Bhattacharya and Lu (2006).

Benchmarking studies investigating the tensile and fracture behavior of such simulations have already been reported in the literature (Lu and Bhattacharya 2004; Lu and Bhattacharya 2005; Lu and Bhattacharya 2005; Lu and Bhattacharya 2006).

Figure 3 shows the first two moments of SWNT ultimate strength as a function of the average number of SW defects on the tube. For each average number of defects, 33 SWNTs were analyzed. The average number of defects in Figure 3 range from 0 to 3.9. Zero average defects imply a defect-free tube. The next higher value of 0.9 is arrived at thus: We start with $\lambda = 0.8 \times 10^{-3}/\text{Å}^2$ as the rate of the underlying Poisson field; this value of λ produces an average of 1 Poisson point on the tube, and after the Matern thinning imposed by $h = 8.0$ Å, leaves an average of 0.9 SW defects on the same tube. The value of 3.9 average defects correspond to $\lambda = 4.8 \times 10^{-3}/\text{Å}^2$.

The strength variability in the absence of any defect (zero average defects) in Figure 3 arises solely from thermal fluctuations.

The ultimate strength is calculated at the maximum force point, $\sigma_u = F_{max}/A_0$, where F is the maximum axial force, A_0 is the cross section area assuming the thickness of tube wall is 0.34 nm. The tube compliance is determined as the reciprocal of the initial stiffness, E. The initial stiffness is determined by first fitting a quadratic curve between the initial portion of the potential energy, P, vs. axial deformation, x (up to the point corresponding to 3.48% axial strain), as $P = ax^2$. The initial stiffness is linearly related to the parameter a through the initial geometry of the tube.



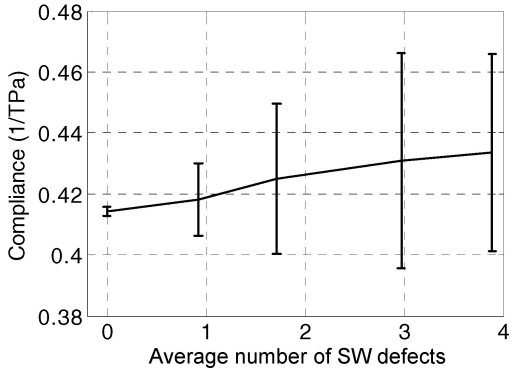


Figure 3. Statistics of SWNT ultimate strength and compliance as a function of average number of defects on the tube (dashed line = mean, vertical bar = mean +/− one standard deviation).

3 ASYMPTOTIC MECHANICAL BEHAVIOR OF SWNTS WITH INCREASING TUBE LENGTH

3.1 *Increasing length and its effect on strength*

Recall that 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, $W_{(n)}$:

$$W_{(n)} = \min\{W_1, W_2, ..., W_n\} \tag{1}$$

where W_i is the strength of the *ith* segment. Owing to the presence of random defects and random velocities of the atoms, each W_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 W_i has the same marginal cumulative distribution function (CDF), F_W.

If the W_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 theory (Galambos 1987) shows that the probability distribution of the minimum, $W_{(n,iid)}$, under appropriate normalization, $v_n(z) = c_n + d_n z$, converges as $n \to \infty$to:

$$v_n(z) = c_n + d_n z \text{ , converges as } n \to \infty \text{ to:}$$

$$P\left[W_{(n,\text{iid})} \le v_n\right] = L_{(n)}(v_n) \to L_c(z) = 1 - \exp\left[-(1-cz)^{-1/c}\right],\ 1 - cz > 0 \tag{2}$$

where L_c is one of the three classical asymptotic extreme value distributions and depends on the parameter, c.

The i.i.d. assumption on strength of the tube segments appears unrealistic, since there is likely to be dependence among strengths of neighboring segments due to the non-local nature of atomic interactions. 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 decaying dependence can be formalized by a strong mixing condition applied to minima of stationary sequences. The strong mixing condition on a strictly stationary sequence of random variables $\{W_n\}$ ensures that the sigma-algebras, $\mathfrak{A}$ and $\mathfrak{B}$ generated, respectively, by the sub-sequences $\{W_1, \ldots, W_p\}$ and $\{W_{p+k}, W_{p+k+1}, \ldots\}$, become asymptotically independent as the distance between them (i.e., k) becomes large (Leadbetter et al. 1983).

We now introduce two conditions, $D(u_n)$ and $D'(u_n)$, that help establish limiting distributions of extrema from dependent stationary sequences. The former ensures that there is no long-term memory effect in the sequence, while the latter ensures that there is no clustering of very low values.

Condition $D(u_n)$ is a much weakened version of (and implied by) strong mixing and apply, not to the entire sigma-algebras generated by the subsequences, but only to certain sequence of events of the type $\{W_i > u_n\}$. The strong mixing requirement above is not essential for the asymptotic distribution of minima to exist – the much weaker Condition $D(u_n)$ along with $D'(u_n)$ would suffice, but strong mixing is required for the central limit theorem to hold for partial sums of the sequence and the asymptotic independence between minima and the partial sums of the sequence demonstrated later in the paper.

The importance of conditions $D(u_n)$ and $D'(u_n)$ is that under them, the asymptotic distribution of the minima of the dependent sequence is still one of three classical types – Weibull, Gumbel or Frechet (Eq. (2)), although the convergence is slower than that in the i.i.d. case:

$$P\left[W_{(n)} \le v_n\right] \to \hat{L}_c(z) = 1 - \exp\left[-\theta\left(1-cz\right)^{-1/c}\right] \qquad (3)$$

where $1 - cz > 0, 0 < \theta \le 1$. The rate of convergence is governed by the *extremal index*, θ, of the sequence and is discussed in Section 3.2.

Let us now investigate how the distribution of nanotube strength approaches its limiting form as the tube length increases. Of the three limiting distributions, we focus on the Weibull model only since the Weibull model is widely adopted for the "weakest link" type strength variables for materials and systems across spatial scales and materials. Of course, there are other types of "size effects" besides the statistical type being considered here ...(Bazant 2000), but those are outside the scope of this paper and will be taken up elsewhere.

We continue with the (6,6) armchair SWNT configuration and increase its length, l, while keeping the average rate of occurrence of SW defects per unit tube surface area constant ($\lambda = 1.59 \times 10^{-3}/\text{Å}^2, h = 8\text{Å}$). We start with the smallest length $l_0 = 49.2\text{Å}$, and analyze tubes up to 492 Å long in steps of $l_0, 2l_0, 3l_0, 4l_0, 5l_0, 6l_0$ and $10l_0$. The corresponding loading rates are 2.5, 5.0, 7.5, 10.0, 12.5, 15.0 and 25.0 nm/ns such that the strain rate is constant. 33 samples are generated for each value of l. Since the tube is prismatic, the cross-sectional area of each segment is equal (denoted by A_0) and all discussion pertaining to tube strength above applies equally well when it is normalized by A_0. We thus adopt the more common stress-based description of mechanical strength here (rather than force-based) and present the results in terms of ultimate strength, σ_u , of the nanotubes.

Table 1 shows the statistics and Weibull goodness-of-fit of the 33 samples of the ultimate strength of SWNTs with Stone-Wales defects as the tube length increases from l_0 to $10l_0$.The mean and variance were estimated from each set of 33 samples first, following which the two Weibull parameters were determined. The goodness-of-fit test was based on these estimated parameters.

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

				Weibull parameters		Weibull goodness of fit	
n	Tube length, l (Å)	μ (Gpa)	V(%)	ω (Gpa)	k	χ^2 statistic	level of significance
1	49.19	87.30	12.4	91.9	9.73	20.3	1.49×10^{-4}
2	98.38	86.04	6.98	88.7	17.7	11.3	0.2004
3	147.6	84.68	5.74	86.8	21.7	3.18	0.3644
4	196.8	82.89	4.03	84.4	31.1	6.82	0.0779
5	246.0	79.38	5.97	81.5	20.8	3.91	0.2714
6	295.2	78.64	6.95	81.0	17.8	1.73	0.6309
10	492.0	76.63	5.96	78.6	20.8	3.55	0.3149

Based on 33 samples for each l, μ = mean, V = coefficient of variation (s.d./mean), ω = Weibull scale parameter, k = Weibull shape parameter.

It is clear that the distribution shifts to the left (i.e., mean decreases) and becomes narrower (i.e., c.o.v. decreases) with increasing l: this is consistent with the behavior of extremes from a stationary population. The quality of Weibull fit (judged from the level of significance of the Chi-squared test) among this set of data is found to generally improve with increasing l, and is best when $l = 6l_0$.

3.2 *The extremal index of the strength field*

We now investigate the degree of dependence in the strength field in terms of its extremal index. The extremal index, θ, is a positive fraction between zero and one. The value of $\theta = 1$ corresponds to the i.i.d. case while the case of $\theta = 0$ is degenerate and implies long-range dependence. 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. This interpretation will be formalized later in obtaining numerical estimates of the extremal index for the carbon nanotubes.

The extremal index also helps underline the degree of conservatism in making the i.i.d. hypothesis when predicting the distribution of the minima from a random sequence. Eqs. (2) and (3) clearly show that L_c (obtained from the i.i.d. assumption) and $\hat{L}_c$ (the actual CDF) are not only of the same type for any given value of c, but also for any value of z, we always get $L_c > \hat{L}_c$. In other words, the distribution with the i.i.d. assumption is always to the left of the actual (that considers dependence) and thus underpredicts the strength.

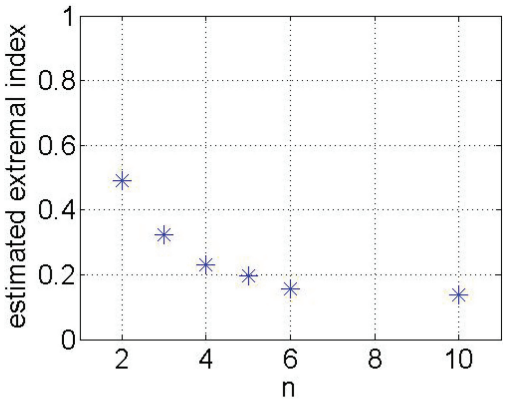


Figure 4. Limiting extremal index as a function of tube length.

We can estimate the extremal index if we have the statistics of nanotube strength for known values of n:

$$\hat{\theta} \approx \frac{1}{n} \frac{\ln G_{W(n)}(x)}{\ln G_{W(1)}(x)} \tag{4}$$

where $G_{W(n)}$ is the complementary distribution function of a nanotube of length nl_0. It is apparent from Eq. (4) that the *estimated* extremal index depends on the threshold x, although what we are ultimately interested in is its limiting value as $x \to 0$. Based on results from maxima of a stationary dependent sequence ..(Hsing 1993), we propose the following threshold dependent form for the extremal index:

$$P\left[M_{2,r} > x \middle| W_1 \le x \right] = \theta + R\left(F_W(x)\right) \tag{5}$$

where r is an integer denoting "run length". This form is regardless of the type of limiting distribution for the sequence (Eq. (3)). The quantity $M_{p,q} = \min\left\{W_p, \ldots, W_q\right\}$ and the residual $R\left(F_W(x)\right) \to 0 as x \to x_0 = \inf(x : F_W(x) > 0)$. From this representation, the limiting value $\hat{\theta}_0$, at $x = 0$, may be estimated (Lu and Bhattacharya 2006).

Figure 4 plots the limiting value $\hat{\theta}_0$ as function of tube length. A strong dependence in the strength field is suggested in Figure 4, the extremal index is seen to approach the numerical value of around 0.16. Costly atomistic simulations will no longer be required for predicting the strength distribution of longer tubes, the extremal index can be used in conjunction with Eq. (4) to estimate at least the left tail for any value of n. The estimate of θ can also be instrumental in deciphering the underlying correlation structure in the random strength field, although it is outside the scope of this work.

3.3 *Compliance statistics and its asymptotic independence from strength*

We continue with the above formulation of a nanotube being composed of n segments of equal length, cross-sectional area A_0 and random strength W_i with marginal distribution F (independent of i). The compliance of the entire tube, $C_{(n)}$, as a function of n, can be given as the sum of the individual segment compliances, C_i:

$$C_{(n)} = C_0 + \sum_{i=1}^{n} C_i \tag{6}$$

where C_0 is the contribution from inertial effects. We now make use of the fundamental description of mechanical failure that we have used in atomistic simulation for solids above, namely, fracture of solids is displacement based. An atomic bond is regarded as broken if the inter-atomic separation exceeds the critical value r_f. If the tube segments are small enough, and the static force-displacement behavior of each segment can be assumed to be linear up to failure, then compliance of each segment may be approximated as:

$$C_i = \frac{A_0}{l_0} \frac{\alpha r_f}{W_i} \tag{7}$$

where α is constant for given tube chirality and l_0. The compliance of the entire tube can then be given by:

$$C_{(n)} = C_0 + \frac{A_0}{l_0} \alpha r_f \sum_{i=1}^{n} \frac{1}{W_i} \tag{8}$$

If the stationary sequence $\{W_n\}$ is strongly mixing, so is $\{1/W_n\}$. It is known that (i) sums of stationary and strong mixing sequences are asymptotically normal; further, (ii) these sums are asymptotically independent of the extrema of the sequences (Anderson and Turkman 1991; Hsing 1995). It will be instructive to determine how well our results support these two important properties of strong mixing sequences.

Table 2 shows the statistics of the compliance of SWNTs with Stone-Wales defects as a function of tube length, l. The distribution shifts slowly to the right and narrows slightly with increasing l : this is consistent with the behavior of partial sums from a stationary sequence (Eq. (8)). We also investigate the goodness of Normal fit on the SWNT compliance data as the tube length increases from l_0 to $10l_0$. 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. It is clear from Table 2 that the accuracy of the Normal hypothesis improves as l increases.

Finally, Figure 5 shows the correlation coefficient between the compliance and the ultimate strength of the tube as the tube length increases.

Table 2. Statistics of SWNT compliance as a function of tube length.

				Normal goodness of fit	
n	Tube length, l (Å)	μ (1/TPa)	V	χ^2 statistic	Level of significance
1	49.2	0.3682	2.61%	8.27	0.0407
2	98.4	0.4267	5.20%	33.7	2.26e-07
3	147.6	0.4316	4.81%	30.1	1.32e-06
4	196.8	0.4281	1.19%	2.45	0.484
5	246.0	0.4309	0.83%	1.73	0.631
6	295.2	0.4561	1.12%	1.00	0.801
10	492.0	0.4660	0.78%	1.00	0.803

Based on 33 samples for each n, μ = mean, V = coefficient of variation (s.d./mean)

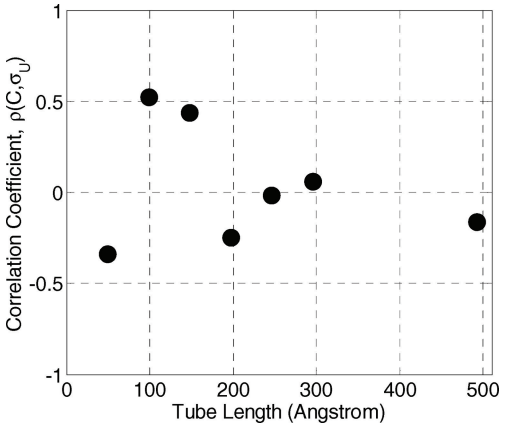


Figure 5. Asymptotic independence of tube strength and compliance.

If the strong mixing property holds, the sum and extremum form a sequence should become asymptotically independent. Figure 5, which shows the diminishing correlation coefficient between the compliance and the ultimate strength as $l$increases, indeed suggests that the strong mixing assumption holds for SWNTs.

4 SUMMARY AND CONCLUSIONS

Defects are commonly present in materials and they occur/evolve randomly in space and time. These defects may have significant effects on the material properties. Material properties governed by sums (or averages) of some underlying stochastic phenomena can be shown to diverge from and become independent of properties governed by extremes arising of the same phenomena. In this paper we considered random Stone-Wales (SW) defects in carbon nanotubes (CNTs) and, through the technique of atomistic simulation, quantified their effect on the asymptotic behavior of ultimate strength and compliance as the tube length increases.

The existence of dependence in the ultimate strength random field of the nanotube (that decreases with increasing separation), consistent with the nonlocal nature of atomic interactions, was considered, – a strong mixing condition was assumed for the field to formalize the dependence structure. Limiting expressions for the distribution of strength as tube length became large was developed. The extremal index, which can be used to characterize the strength of said dependence was estimated. It can help avoid costly numerical simulations for predicting the strength distribution of longer tubes.

The conservatism introduced by the commonly made i.i.d. (independent and identically distributed) assumption was also discussed. The distribution of ultimate strength, σ_u, and compliance, C, 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. Seven values of l spanning an order of magnitude were considered (from 49 to 490 Angstroms) 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. The distribution of C as the scaled sum of the reciprocal of the strong mixing strength sequence was studied with increasing tube length as well. The compliance of the tube increased with increasing length and became asymptotically Normal. Finally, the compliance and strength of the tube were found to be asymptotically uncorrelated. These results appeared to validate the strong mixing property of the strength field. These findings can be used in future studies to better model the random mechanical behavior of nanotubes and nanotube based devices.

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