ATOMISTIC SIMULATION FOR STUDYING THE ASYMPTOTIC BEHAVIOR OF ULTIMATE STRENGTH OF CARBON NANOTUBES WITH RANDOMLY OCCURRING DEFECTS

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Abstract

While CNTs are found to have ultra-high stiffness and strength, an enormous scatter is also observed in available laboratory results. This paper studies the effects of randomly distributed Stone-Wales (SW or 5-7-7-5) defects on the mechanical properties of single-walled nanotubes (SWNTs) using the technique of atomistic simulation. A Matern hard-core random field applied on a finite cylindrical surface is used to describe the spatial distribution of the SW 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 24.2. A modified Morse potential is adopted to model the interatomic forces. Ultimate strength is calculated from the simulated force time histories. The asymptotic behavior of the ultimate strength of SWNT with defects as tube length, l, increases is discussed. The distribution shifts to the left and becomes narrower with increasing l and appears to fit the Weibull distribution rather well.

Introduction

The study of carbon nanotube (CNT) has been motivated largely due to its extraordinary electronic and mechanical properties. CNT is found to be among the most robust materials: it has high elastic modulus (order of 1 TPa), high strength (up to 150 GPa), good ductility (up to 15% max strain), flexibility to bending and buckling and robustness under high pressure. CNTs are now used as fibers in composites, scanning probe tips, field emission sources, actuators, sensors, lithium ion and hydrogen storage etc.

A survey of recent studies on the elastic modulus and strength of single-walled and multi-walled carbon nanotube (SWNT and MWNT), detailed in Lu and Bhattacharya (2004) shows: (i) the Young's modulus of SWNT is found to range from 0.31~1.25TPa, the Young's modulus of MWNT ranges from 0.1 to 1.6 TPa; (ii) the strength varies from about 5GPa to 150Gpa; and (iii) these mechanical properties reported from experiments and analysis show *significant variation*. A substantial part of the random effect is believed to occur from random defects and/or local energy fluctuations.

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 (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. Studies have shown that defects have significant influence on the formation as well as on the electronic and mechanical properties of CNTs (Charlier 2002).

The Stone-Wales (SW) defect is composed two pentagon-heptagon pairs, and can be formed by rotating a sp^2 bond by 90 degrees (SW rotation). It has been found that under certain condition, SWNTs respond to the mechanical stimuli via the spontaneous formation of SW defect beyond a certain value of applied strain around 5%~6% . These SW defects are formed when bond rotation in a graphitic network transforms four hexagons into two pentagons and two heptagons which is accompanied by elongation of the tube structure along the axis connecting the pentagons, and shrinking along the perpendicular direction. 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 necking. This whole response is plastic, with necking and growth of a “line defect” (Yakobson 1998) The nucleation of SW defects has been found to depend on the tube chiralities, diameters and temperature.

In spite of defects being inevitably present in CNTs and the knowledge that these defects may have significant effects on the mechanical and other properties of CNTs, surprisingly little work has been directed in the available literature toward studying the randomness in these defects and the influence of such randomness on CNT mechanical properties in a systematic and probabilistic way. In this study, we try to build toward this missing link by focusing on the role of randomly occurring SW defects in the ultimate strength of SWNTs.

Simulation of SWNTs with defects

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. 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, 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 for the defect field. Let X denote the underlying homogeneous Poisson point process on $\mathbb{R}^2$ with intensity λ. The points of X are marked by iid random numbers, $m(\xi_i)$, uniformly distributed in (0,1) and independent of the field X. The thinning deletes the i^{th} point of X (with mark $m(\xi_i)$) if the sphere $b(\xi_i,h)$ of diameter h around ξ_i contains any points of X with marks smaller than $m(\xi_i)$.

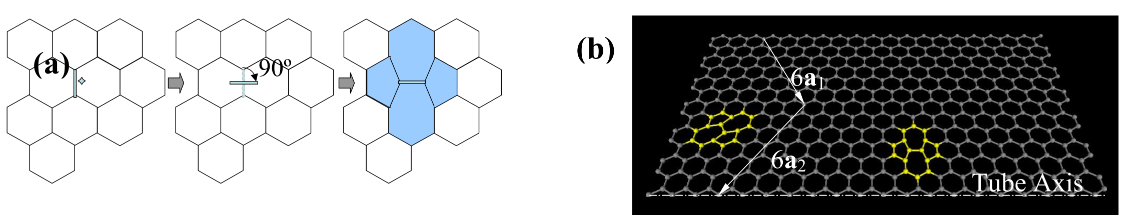

Figure 1 (a) Rotation of carbon bonds to form SW defects (b) graphene sheet with 2 random defects (a_1 and a_2 are unit vectors and (*m*,*n*) is the tube charility)

In this study, we fix h at 8.0 Å. Once the location of the SW defect is generated, we find the sp^2 bond closest to the defect point, and then rotate the bond by 90º to form a SW defect, as shown in Figure 1(a). An example of a graphene sheet with two SW defects generated is shown in Figure 1(b).

The probability that there is no point (*void probability*) in an area C around the point ξ_i given that its mark is t is simply $P(\xi_i \in X_h \mid m(\xi_i) = t) = e^{-\lambda t C}$. The area C depends on the location, y_i of the point:

$$C(y_i;h) = \begin{cases} h^2\left(\pi/2+\theta+\sin 2\theta/2\right), \theta = \arcsin y_i/h, & y_i < h \\ \pi h^2 & h < y_i < b-h \\ h^2\left(\pi/2+\theta+\sin 2\theta/2\right), \theta = \arcsin(b-y_i)/h, & h < y_i < b-h \end{cases} \quad (1)$$

Since the marks are uniformly distributed, i.e., $f_{m(\xi_i)}(t)$ =1 in $0 < t < 1$, y is uniformly distributed in [0, b] being coordinate of a Poisson process, and since $m(\cdot)$ and y are independent, the unconditional survival probability for a Poisson point on a finite tube of length b is, the probability, p_h:

$$p_h = P(\xi_i \in X_h) = \frac{1}{b}\int_0^b \frac{1-e^{-\lambda C(y;h)}}{\lambda C(y;h)}dy \quad (2)$$

Because the thinning is independent of the original Poisson process, the intensity of Matern hard-core process is $\lambda_h = p_h\lambda$. The average number of SW defects on an area A_t is $\lambda_h A_t$.

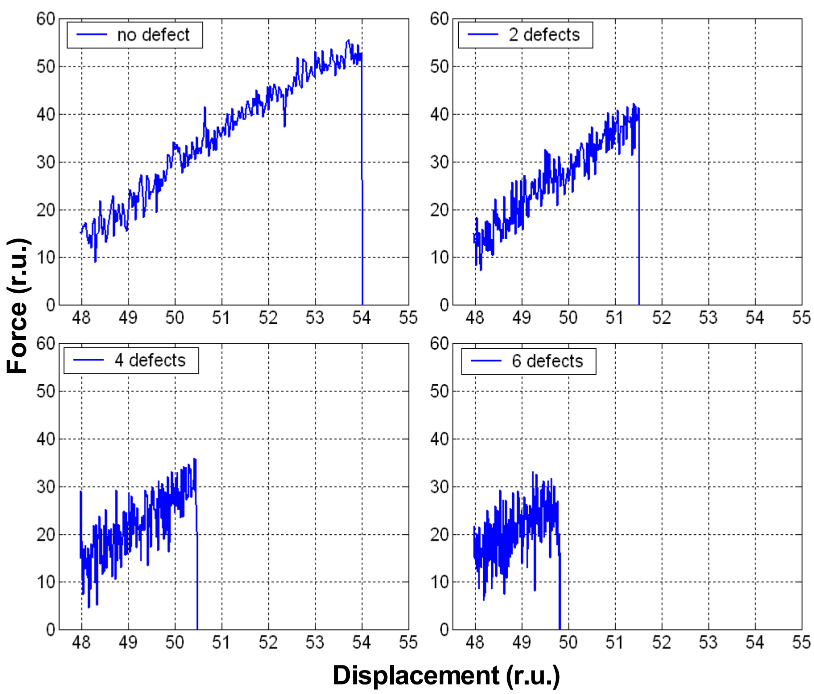

Figure 2 Force-displacement curves of nanotubes with various number of defects

We adopt the (6,6) armchair configuration having diameter 8.14Å for simulation of ultimate strength. The lengths of the tubes varied between 49.2 Å and 196.8Å as detailed subsequently. The total number of atoms in the simulation varies between 480 and 1920.

The load deformation behavior of the SWNTs with defects are studied using atomistic simulation. A modified Morse potential model for describing the interaction among carbon atoms (Belytschko et al. 2002) is adopted. The initial atomic positions are obtained by wrapping a graphene sheet (Figure 1) into a cylinder along the chiral vector $\mathbf{C}_n = m\mathbf{a}_1 + n\mathbf{a}_2$. 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 tube diameter is $d = a_0\sqrt{3(m^2+n^2+mn)}\big/\pi$. The initial atomic velocities are randomly chosen from a uniform distribution (between the limits −0.5 and 0.5) and then rescaled to match the initial temperature of 300K. No temperature control is implemented. The mechanical loading is applied through moving the atoms at both ends away from each other at constant speed without relaxing until fracture occurs. The ultimate strength is calculated as, $\sigma_u = F_{max}/A$, where F_{max} is the maximum force in the loading time history, and A is the original cross-sectional area assuming tube thickness as 0.34 nm. Figure 2 shows the force-displacement relations of a 49.2 Å long (6,6) SWNT with 0, 2, 4 and 6 SW defects respectively, each with the same initial velocity distribution. The displacement controlled loading rate is 10 m/s. Further details may be found in Lu and Bhattacharya (2004).

Asymptotic behavior of strength of SWNT with defects

A tube may be considered to be partitioned into n segments of length Δ_i for i = 1, …, n. The length of the tube, $l_n = \sum_{i=1}^{n} \Delta_i$, depends on n, as does the strength of the tube, $W_{(n)} = \min\{X_1, X_2, ..., X_n\}$ 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. If the X_i 's are iid (independent and identically distributed) with marginal distribution F and possess some very general properties that are satisfied by all common distribution functions, extreme value analysis (Leadbetter et al. 1983) shows that the probability distribution of $W_{(n)}$, under appropriate normalization, $v_n(w) = c_n + d_n w$, converges to $P\left[W_{(n)} \le v_n\right] = L_{(n)}\left(v_n\right) \to L(w) \quad \text{as } n \to \infty$ where L is one of the three classical asymptotic extreme value distributions of the same type as, $L_c(z) = 1 - \exp\left[-\left(1-cz\right)^{-1/c}\right], \quad 1 - cz > 0$ and depends on the parameter, c. With c = 0, L_c is interpreted in the limit as Gumbel distribution for minima (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 iid 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 (condition $D(u_n)$) and there is no clustering of very low values (condition $D'(u_n)$) (Leadbetter et al. 1983). In such cases, it can be shown that the asymptotic distribution is still one of three classical ones, although the convergence is slower than that in the iid case as described below.

Let $\{\hat{X}_i\}$ be a stationary dependent sequence with the same marginal distribution F as above. The sequence 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) $P\left[\hat{W}_{(n)} \geq v_n(\tau)\right] \to \exp(-\theta\tau)$ where $\hat{W}_{(n)} = \min\{\hat{X}_1, \hat{X}_2, ..., \hat{X}_n\}$.

The extremal index defined above is a positive fraction between zero and one: $0 < \theta \leq 1$ (Hsing 1993). It can be shown that the asymptotic distribution of the minimum in the dependent stationary case, $\hat{L}_c$, can be given in terms of the extremal index as:

$$\hat{L}_c(z) = 1 - \exp\left[-(1-cz)^{-\theta/c}\right], \quad 1-cz > 0,\ 0 < \theta \leq 1 \tag{3}$$

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 $\theta = 1$ implies the iid case while the case of $\theta = 0$ is degenerate and implies long-range dependence.

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 (GPa)	k	χ^2 statistic	level of significance
49.19	87.30	12.35%	87.71	8.83	26.09	9×10^{-6}
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

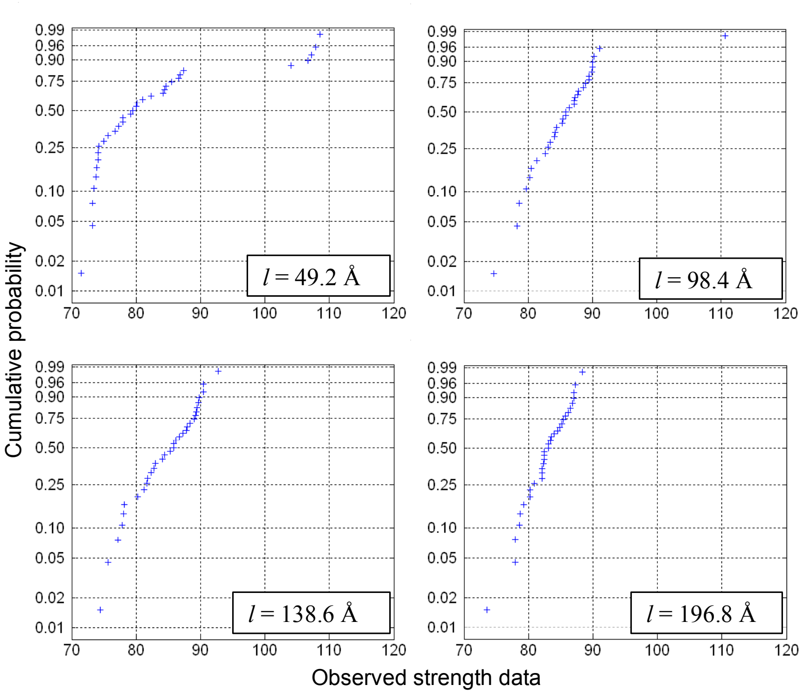

Figure 3 Goodness of Weibull fit for SWNT ultimate strength with increasing tube length (33 samples each)

We therefore 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 ($\lambda = 1.59\times10^{-3}$/sq Å, h = 8Å in Eq (2)). Four values of l are considered: l_0 = 49.2 Å, $2l_0$ $3l_0$ and $4l_0$. The corresponding loading rates are 2.5, 5.0, 7.5 and 10.0 m/s such that the strain rate is constant. 33 samples are generated for each value of l.

Table 1 shows the statistics of the ultimate strength of SWNTs with Stone-Wales defects as a function of tube length, *l*. 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, we investigate the goodness of Weibull fit on the strength data as the tube length increases from *l* to 4*l*. 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). The quality of Weibull fit using the Chi-squared test is found to be the best when $l = 3\ l_0$. From a graphical analysis on Weibull probability paper, however, the quality of fit appears to monotonically increase with increasing *l* (Figure 3).

Summary and Conclusions

Defects are almost invariably present in CNTs, and these defects may have significant effects on the mechanical and other properties of CNTs. An accurate understanding of the stochastic nature of the formation and evolution of these defects is necessary for a wide adoption of CNTs in practical applications. In this paper we considered the random nature of Stone-Wales defects in SWNTs and, through the technique of atomistic simulation, quantified the effect of such randomness on the ultimate strength of SWNTs and the asymptotic behavior of ultimate strength as the tube length increases. Our findings qualitatively agree with the limited experimental observations available in the literature. Consideration of random energy fluctuations at the atomic scale, a more accurate interatomic potential, a more realistic spatial description of defects and inclusion of cyclic loading are expected to provide further insights into the problem.

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