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A STUDY OF RANDOMNESS IN FRACTURE OF CARBON NANOTUBES USING ATOMISTIC SIMULATION

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ABSTRACT

The intense interest in carbon nanotubes (CNTs) in recent years owes in part to their extraordinary mechanical properties. Yet, enormous scatter is observed in their strength and stiffness properties. This scatter originates at least in part from the presence of nanoscale defects and the insufficient understanding and controlling of these defects by the interested community. This paper investigates the effect of randomness in atomic arrangements on the strength, stiffness and fracture properties of SWNTs (single wall carbon nanotubes) using the technique of atomistic simulation (AS). The focus is on the Stone-Wales (SW or 5-7-7-5) defects that either exist naturally or are introduced to improve performance. The core of any atomistic simulation is a deterministic set of rules governing the interaction among a large number of atoms and randomness needs to be introduced carefully. Nanotubes with (6,6) armchair configuration and aspect ratio 6.05 subjected to displacement controlled axial loading are simulated with the modified Morse potential. The distribution of SW defects is modeled with a Matern hard-core spatial process based on a homogeneous Poisson field. Effects of varying spatial distributions of the SW defects on the fracture process including elastic modulus, ultimate strength and ultimate strain are studied.

Keywords: Atomistic simulation, carbon nanotube, fracture, Stone-Wales defects, Matern random field

INTRODUCTION

CNTs and randomness in their properties

Increasing interests are focused on carbon nanotube (CNT) due to its extraordinary properties. An interesting statistics by Terrones (2003) has shown an exponential growth of the number of

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publications on CNTs. A substantial part of them are focused on the mechanical properties of CNTs. Based on these studies, it is believed that CNTs have high elastic modulus (order of 1 TPa), high strength (order of 100 GPa), good ductility (up to 15% max strain), flexibility to bending and buckling and robustness under high pressure (Terrones 2003; Bernholc et al. 2002; Yakobson and Avouris 2001; Ruoff and Lorents 1995; Salvetat et al. 1999).

Table 1 shows surveys of recent studies on the elastic modulus and strength of single-walled CNTs (a similar survey for multi-walled CNT can be found in (Lu and Bhattacharya 2004), from which a few general conclusions can be drawn: (i) the Young's modulus of SWNT is found to range from 0.31~1.25TPa; (ii) the Young's modulus may depend on chiralities; (iii) experiments roughly show a trend that Young's modulus drops quickly as the diameter of tubes increases; (iv) the strength varies a lot from about 5GPa to 150GPa. (v) last but not the least important, these mechanical properties (elastic modulus, strength and ductility) reported from experiments and analysis show *significant variation*.

Table 1 A survey of Young's Modulus of SWNTs

Ultimate strength (GPa)	Young's modulus (TPa)	Diameter (nm)	Length (nm)	Method/Comment
NA	1.25 -0.35 / +0.45	1.0 ~ 1.5	23.4 ~ 36.8	(Krishnan et al. 1998) Thermal vibration experiment
NA	0.97 ~ 1.20	0.4 ~ 3.4	10	(Yao and Lordi 1998) AS using EAM potential. Modulus increases significantly with decreasing diameter and increase slightly with decreasing helicity.
NA	0.8 ~ 1.22	0.8 ~ 2.0	NA	(Hernandez et al. 1998) Ab initio calculation. Modulus depends on chiralities.
NA	0.50 ~ 0.82	0.6 ~ 1.4	Infinite[a]	(Sanchez-Portal et al. 1999) Ab initio calculation. Very little dependence on diameters and chiralities.
≥45±7	NA	1.1 ~ 1.4	>4000	(Walters et al. 1999) AFM bending test on SWNT ropes. Maximum strain is measured as (5.8±0.9)%, strength is calculated by assuming E is 1.25 TPa
4.92	0.311	1.36	NA	(Dereli and Ozdogan 2003) Tight-binding simulation, maximum strain 22%. Poisson ratio 0.287. Modulus slightly depends on diameters.
40~50	1.0	0.4 ~ 2.2	6 ~ 1000	(Wei et al. 2003) Theoretical analysis based on AS. Modulus, yield strain and strength depend on loading rate. Yield strain depends on tube length.
[a]Simulating infinite long tube with periodic boundary condition				

The huge scatter in these properties are possibly due to the variation in tube sizes (diameter and length), chiralities, random defects distribution, local fluctuations, errors in measurements and even different ways in defining the cross-sectional area. Effects of sizes and chiralities of nanotubes on their mechanical properties have been studied (Wong et al. 1997; Poncharal et al. 1999; Li and Chou 2003), however, their roles are still not very clear. Studies also show that the elastic modulus measured from tubes with similar diameters varies quite significantly (Table 1). It is doubtful that measurement errors are fully responsible for the huge variation. The lack of consensus in defining the cross-sectional area (Hernandez et al. 1998; Sanchez-Portal et al. 1999) can be rectified with a simple multiplicative factor and is not a major source of the randomness.

Therefore, a substantial part of the random effect is believed to occur from random defects and/or local energy fluctuations. In this study, we focus on the role of randomly occurring defects, particularly Stone-Wales defects, in the mechanical properties and fracture of CNTs.

Role of defects in the mechanical properties CNTs

Defects such as vacancies, metastable atoms, pentagons, heptagons, Stone-Wales (SW or 5-7-7-5) defects, heterogeneous atoms, discontinuities of walls, 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 (Nardelli et al. 1998a, b; Lambin et al. 1995) and electron irradiation (Ajayan et al. 1998). It is reasonable to believe that these defects are randomly distributed in CNTs.

Studies have shown that defects have significant influence on the formation as well as on the electronic and mechanical properties of CNTs (Charlier 2002; Yakobson and Avouris 2001; Nardelli et al. 1998a). Pentagon and heptagon defects are believed to play key roles in the formation and deformation of CNTs. For example, with the help of pentagon and heptagons, one can build special structures based on the original hexagon lattice, such as capping, intramolecular junctions, variation in diameter or chirality, welding, coalescence, x-junction etc. (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 is 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% (Nardelli et al. 1998b). 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 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 nucleation of SW defects has been studied in many ways, and was found to depend on the tube chiralities, diameters and external conditions such as temperature. The activation energy and formation energy of the SW defects formation are also studied and related to the strength of the nanotube (Zhao et al. 2002; Samsonidze et al. 2002; Zhou and Shi 2003). As a result, fracture of CNTs, depending on the easiness to nucleate SW defects, exhibits brittle/ductile behaviors under different conditions.

It is thus clear that (i) defects are almost invariably present in CNTs, (ii) these defects may have significant effects on the mechanical and other properties of CNTs, and as summarized in Table 1, (iii) a wide scatter has been observed in the mechanical properties of carbon nanotubes. Yet, 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. To our knowledge, the only relevant example until now is the study of the effect of random vacancies on the electronic properties of CNTs recently done by

Belavin et al (2004). Here in this paper, we try to build toward this missing link by making reasonable assumptions on the random nature of SW defects in CNTs and, through the technique of atomistic simulation, quantify the effect of such randomness on (i) the fracture process of SWNTs at the atomic scale and (ii) three representative mechanical properties, namely, the elastic modulus, ultimate strength and ultimate strain of SWNTs.

ANALYSIS OF RANDOMNESS IN CNT MECHANICAL PROPERTIES

Modeling random defects

Ideally, modeling defects in CNTs would require a real 3-D space random field model. However, since each SW defect is a local rearrangement of carbon atoms on the tube wall, we can treat the SW defects as disks with a certain area that are randomly distributed on the 2D surface. This way, it is sufficient to consider two characteristics of the defects distribution: (i) The location of the points relative to the study area, and (ii) the location of points relative to each other.

Unfortunately, not enough information can be found in the literature that can provide a thorough 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. A similar model has been applied by Belavin et al. (2004) to generate randomly distributed vacancies on the walls of CNTs. Although the model they applied is simple and effective, it is not really 2D spatial and it cannot be extended to defects involving more than one atom such as a SW defect.

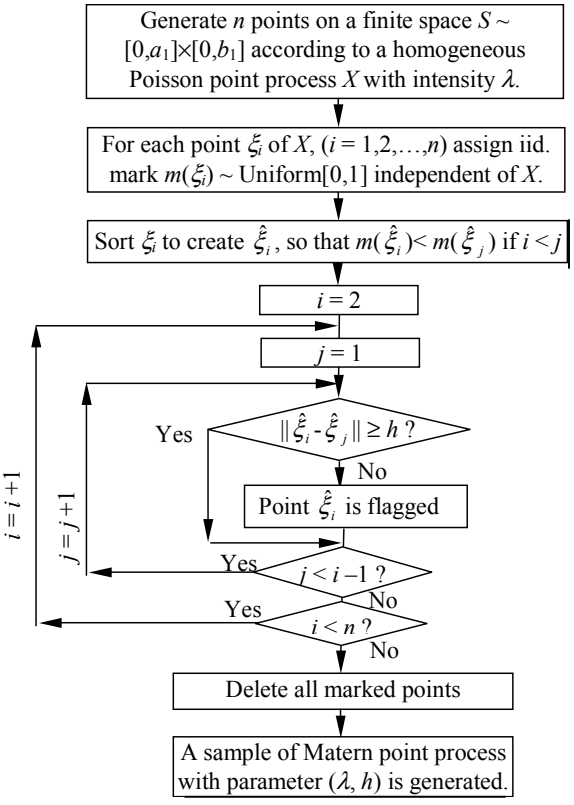

Figure 1 Generating Matern process

In our study, we 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 1986; Stoyan et al. 1987; Matern 1960) for the defect field. A Matern hard-core process is simply a thinned Poisson point process in which the constituent points are forbidden to lie closer than a minimum distance h. Let X denote the underlying homogeneous Poisson point process on $\mathbb{R}^2$ with intensity λ. Now let the points of X be marked by iid random numbers, $m(\xi_i)$, uniformly distributed in (0,1) and independent of the field X. The dependent thinning deletes the i^{th} point of X (with mark $m(\xi_i)$) if the sphere $b(\xi_i,h)$ contains any points of X with marks smaller than $m(\xi_i)$. Formally the thinned process, X_h, is given by:

$$X_h = \{\xi_i \in X : b(\xi_i, h) \cap X = \phi \text{, or for all } \xi_j \in b(\xi_i, h) \cap X,\ m(\xi_j) > m(\xi_i)\} \quad (1)$$

We emphasize that the process X_h has the property that any two points are at least h apart. In this study, we fix h at 8.0 Å, and use a set of reasonable values for λ. The detailed procedure of generating SW defects is illustrated in the flowchart in Figure 1. Once the location of the SW defect is selected, 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 2. An example of a graphene sheet with two SW defects generated with this approach is shown in Figure 3.

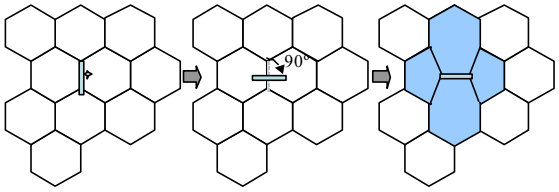

Figure 2 Rotation of carbon bonds to form SW defects

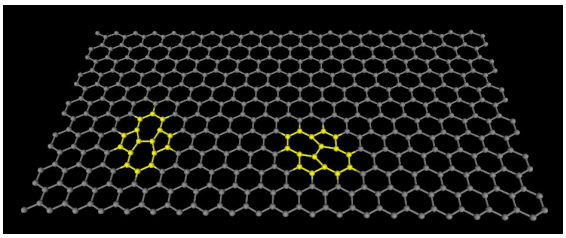

Figure 3 Graphene sheet with 2 random distributed defects

The intensity λ_h of X_h is given by, $\lambda_h = p_h \lambda$ in which $p_h = P(\xi_i \in X_h)$ is the probability that a point of the original X survives. The average number of SW defects on a tube of surface area A_t is $\lambda_h A_t$ We note that p_h is a function only of λ and h if the process is applied to an infinite plane. However, since the tube is finite in the axial direction (y) and has effectively a periodic boundary in the circumferential direction, the term p_h depends on the tube length, b:

$$p_h = \int_0^b \int_0^1 P(\xi_i \in X_h \mid m(\xi_i) = t,\ y = y_0) f_{m(\xi_i)}(t) dt \quad f_y(y_0) \quad dy_0 = \frac{1}{b} \int_0^b \frac{1 - e^{-\lambda A(y;h)}}{\lambda A(y;h)} dy \quad (2)$$

where $A(y;h)$ is the surrounding area in which a point searches for its neighbors.

Atomistic simulation of CNTs with defects

Atomistic simulation (AS) is used as a tool to conduct computational tensile loading experiment to investigate the behavior of perfect/defected nanotubes. By correctly defining the interactive potential functions of certain materials and setting other conditions, this method can simulate complex physical/chemical phenomena with acceptable accuracy, and provides more freedom to investigate small-scale world where experiments are very difficult to conduct. In this study, a modified Morse potential model for describing the interaction between carbon atoms (Belytschko et al. 2002) is applied. A (6,6) armchair single wall carbon nanotube (SWNT) with length 49.2Å and diameter 8.14Å is adopted for simulation. The mechanical loading is applied through moving the atoms at both ends away from each other at a constant speed of 10m/s without relaxing until fracture occurs. The initial velocities of atoms are assigned randomly and then rescaled to match the initial temperature, 300K. No temperature control is applied.

Figure 4 shows one realization each of the force-displacement relation of the SWNT for 0, 2, 4 and 6 SW defects, respectively. The initial velocity distribution is the same in each case. We can readily see that the force-displacement curves behave almost linearly up to about half way, although there is no obvious yield point. The compliance then begins to increase up to the

breaking point where an abrupt drop of force occurs. The Young's modulus is calculated as the initial slope of the curve. The ultimate strength is calculated at the maximum force point, $\sigma_u = F_{max}/A$, where A is the cross section area, assuming the thickness of tube wall is 0.34 nm (Iijima et al. 1992). The ultimate strain, which corresponds to the ultimate strength, is calculated as $\varepsilon_u = \Delta L_u/L$, where L is the original tube length. We clearly notice that nanotubes with more defects are likely to break at smaller strains and has less strength. The effect of defects on the Young's modulus, however, is much less pronounced.

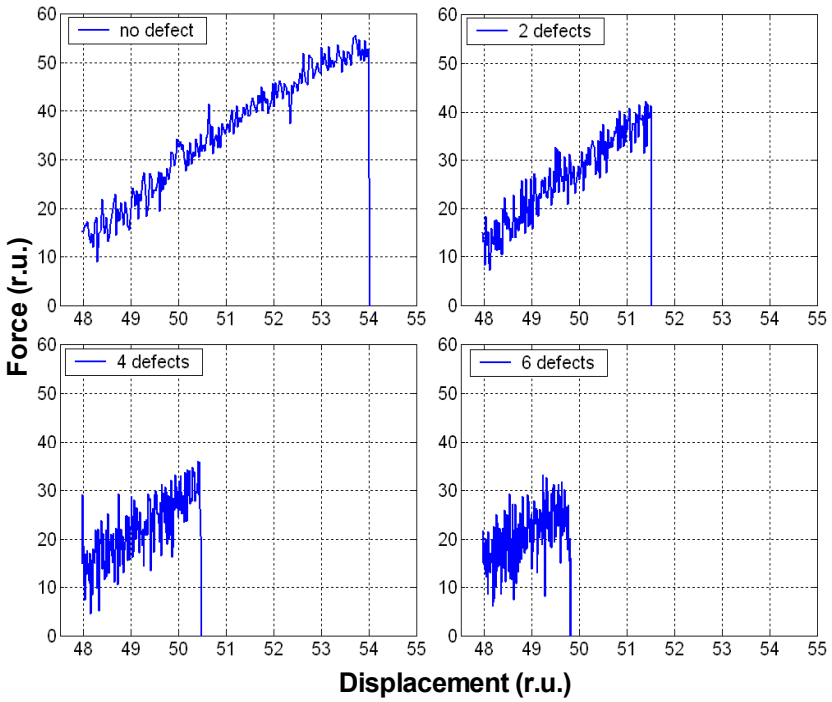

Figure 4 Force-displacement curves of nanotubes with various defect intensities

We now study the effects of randomness in the spatial distribution of SW defects. We start with the benchmark case of the defect-free SWNTs ($\lambda = 0$) and carry out 50 computational experiments leading to fracture. From these 50 sample functions we determine the statistics of the SWNT mechanical properties as shown in Table 2. The only source of randomness here is in the distribution of the initial atomic velocities. We then introduce randomly occurring SW defects according to a Matern hardcore process; four different mean field values are chosen ranging from 0.9 to 3.9 defects.

For each of these mean values, 50 realizations of the Matern field are generated and fracture is simulated in each case as before. In order to systematically study the effects of spatial randomness, the initial velocity distributions are kept identical to those in the respective 50 defect-free cases. Statistics of Young's modulus, ultimate strength and ultimate strain for the four cases are listed in Table 2. It is clear that the mean stiffness, mean strength as well as mean ductility of the tube decrease as the average number of defects increase. However, the uncertainty associated with each property (quantified by the c.o.v.) does not show such monotonic trend – it is rather interesting to note that the c.o.v.'s reach their respective maxima when the average number defects is in the range 1 – 3.

We didn't notice any dislocations generated from the SW defects as reported in some simulations (Nardelli et al. 1998a, b). This may be due to limitations in the potential model and/or the particular tensile loading mode used in our simulation: our tensile loading is continuous and monotonic at room temperature and we used a modified Morse potential, while Nardelli et al. used a Bond order potential model and allowed unloading and relaxation at high

temperature. Simulations of tensile loading of SWNTs can also give other important information such as the time histories of energies and bond angles, dependence of mechanical properties on diameter, chirality and loading rate, etc. (Lu and Bhattacharya 2004).

Table 2 Initial modulus, ultimate strength and ultimate strain of SWNTs with different SW defect intensities

Mean Poisson points λA_t	Mean Matern disks $\lambda_h A_t$	E* (TPa)		σ_u* (GPa)		ε_u*	
		μ	V	μ	V	μ	V
0	0	0.851	1.01%	105.48	2.01%	12.45%	4.93%
1.0	0.925	0.793	5.50%	89.71	13.80%	8.69%	33.91%
2.0	1.716	0.771	6.25%	83.11	13.52%	7.20%	36.05%
4.0	2.970	0.738	7.77%	76.29	10.02%	5.50%	29.56%
6.0	3.889	0.716	6.76%	74.56	8.93%	4.94%	31.61%
*based on statistics of 50 samples; μ = mean; V = coefficient of variation (c.o.v.), E = Young's modulus, σ_u = ultimate strength, ε_u = ultimate strain (strain at max force)							

CONCLUSIONS

The fracture process of carbon nanotubes was studied using atomistic simulation to determine the effects of randomly occurring Stone-Wales (5-7-7-5) defects on SWNT mechanical properties. The random field describing the SW defects was modeled as a Matern hard core process applied on a finite cylindrical surface. The modified Morse Potential was adopted for the atomistic simulation, no relaxation or temperature control was allowed, and constant rate displacement controlled tensile loading was applied at the tube ends. Force-displacement relations of (6,6) armchair SWNTs under tensile loading corresponding to various defect distributions were described. For each defect distribution, a set of 50 fracture simulations were performed: the Young's modulus, the ultimate strength and the ultimate strain were computed in each case and the statistical scatter was analyzed. The presence of defects was found to play an important role in mechanical properties of SWNTs. Mean stiffness, strength and ductility decreased as the average number of defects increased, however , the c.o.v.'s reached their respective maxima when the average number defects was in the range 1 – 3. Efforts to include energy fluctuations at the atomic scale and more realistic spatial modeling of defects are in progress.

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