Multiscale-failure criteria of carbon nanotube systems under biaxial tension–torsion

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Abstract

The failure criteria for carbon nanotube system fracture under biaxial tensile–torsional loads are developed based on a multiscale approach that adopts continuum mechanics models to describe atomistic predictions of failure from molecular dynamics simulations. The failure strength or envelope of carbon nanotube systems under this type of loading is significantly different from what occurs under uniaxial tensile loading and, importantly, is different from the predictions of failure criteria for macroscopic objects. The failure criteria developed here can be used to design carbon nanotube-based devices and materials, such as nanoelectromechanical systems and nanocomposites, which undergo biaxial tensile–torsional loading.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The unique electrical and mechanical properties of carbon nanotubes (CNTs) have attracted considerable interest and sparked discussion of their potential use in applications such as nanoelectromechanical systems (NEMS) \cite{1} and nanotube composite materials \cite{2}. In these and similar applications, biaxial tensile and torsional loads on the CNTs are widely expected to occur. For instance, CNTs may be used as drive shafts \cite{3}, torsion bar springs \cite{4}, and torsional actuators \cite{5} that can experience torsion as well as tension. Thus, understanding the mechanical responses of CNTs undergoing this type of loading is important in optimizing their use in new materials and devices. While numerous studies have examined some aspect of the mechanical responses of CNTs, such as their strength \cite{6–9}, buckling instability \cite{10, 11}, elastic modulus \cite{12, 13}, and twist induced by tension \cite{14} under uniaxial loading conditions, there is much that is still unknown about other aspects of the mechanical responses of CNTs in biaxial tensile and torsional loading, especially concerning the details of failure responses or failure criteria.

When stress is applied to a part in a uniaxial manner, stress and strength can be compared directly to estimate whether or not the part will fail. This comparison is relatively simple because there is only one value of stress and strength. However, the problem becomes more complex when the stress state is multiaxial. In such cases, there are a multitude of stresses but only one significant value for strength, and this requires that failure be characterized using multiaxial strength (or failure) criteria \cite{15}. Under multiaxial loading conditions, the details of failure at the micromechanical and nanomechanical levels are so incomplete that the failure process cannot be followed analytically \cite{15}. Thus, failure criteria for macroscopic objects have evolved from attempts to develop analytical or empirical macromechanical models to describe experimental observations of failure under multiaxial loading \cite{15}. Such failure criteria use the concept of ‘a failure surface’ or ‘a failure envelope’ generated by plotting principal stress components in principal material axes \cite{15}.
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Gall K, Diao J K and Dunn M L 2004 Nano Lett. 4 2431
Atomistic and multiscale analyses of brittle fracture in crystal lattices

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Applicability of the Griffith criterion [A. A. Griffith, Philos. Trans. R. Soc. London, Ser. 221, 163 (1920); S. Zhang, S. L. Melilke, R. Khare, D. Troya, R. S. Ruoff, G. C. Schatz, and T. Belytschko, Phys. Rev. B 71, 115403 (2005)] for predicting the onset of crack extension in crystal lattices is systematically evaluated using atomistic and multiscale simulations with a focus on the effects of crack size and lattice discreteness. An atomistic scheme is developed to determine the true Griffith load defined by the thermodynamic energy balance of crack extension for both finite-sized and semi-infinite crack models. For a model monolayer lattice, we identify a characteristic crack length (about ten lattice spacings) below which the Griffith fracture stress markedly overestimates the true Griffith load. Through a stability analysis of crack-tip bond separation, the athermal (nonthermally activated) loads of instantaneous fracture are determined, thereby yielding the estimated lattice trapping range. Our simulations show that the strength of lattice trapping depends on the interaction range of the interatomic force fields. Using the reaction pathway exploration method, we determine the minimum energy paths of bond breaking and healing at a crack tip, giving a more precise estimate of the lattice trapping range. The activation energy barriers governing the rate of kinetic crack extension are extracted from the minimum energy paths. Implications concerning the distinction between the athermal and Griffith fracture loads are discussed. Based on these results, a general criterion is established to predict the onset of crack growth in crystal lattices. In addition to taking into account the lattice trapping effect, this criterion is applicable to a large spectrum of crack sizes.

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I. INTRODUCTION

Predicting the failure strength of nanostructured materials often involves quantum mechanical calculations or atomistic models with empirical force fields. While these numerical methods have been useful to elucidate the failure mechanisms at the atomic level, their prohibitive computational cost becomes a major concern for specimens of realistic size. In contrast, the fracture criteria established within the framework of continuum fracture mechanics have been widely used to predict the critical conditions for the onset of crack extension in continua. If such continuum-based fracture criteria were applicable to nanostructured materials, the aforementioned computational burden could often be avoided. Thus, it is both fundamentally and practically critical to evaluate the applicability of these fracture criteria to crystal lattices with the consideration of flaw size and lattice discreteness.

The fundamental fracture criterion for brittle continua is the energy-balance criterion by Griffith,1,3 which holds when there is no generation or motion of dislocations or other dissipation mechanisms, such as void nucleation. The Griffith criterion states that a crack meets the critical growth condition when the net change in the total energy of the system $\Delta E$ vanishes upon crack extension by an infinitesimal distance $\Delta a$:

$$\Delta E = (G - 2\gamma_s)\Delta a = 0, \quad (1)$$

where $G$ is the elastic energy release rate and $\gamma_s$ is the surface energy density which measures the fracture resistance of the material. For a model system with a central crack of length $2a$ embedded in an infinitely large, linear elastic medium, subject to remotely applied uniform tension, the energy-balance criterion yields a critical stress

$$\sigma_c' = \sqrt{2Y\gamma_s/\pi a} \quad (2)$$

for plane-stress condition, where $Y$ denotes Young’s modulus. To distinguish the critical stress given by Eq. (2) from the true Griffith load given by the energy-balance criterion of Eq. (1), the critical stress determined by Eq. (2) is hereafter referred to as the Griffith fracture stress.

The Griffith fracture stress has been widely used to predict the onset of crack extension in continua, yet it suffers deficiencies when applied to specimens with nanosized cracks. For extremely short cracks ($a \rightarrow 0$), the Griffith fracture stress may exceed the theoretical strength $\sigma_{th}$ of the perfect lattice, which, of course, is nonphysical. In addressing this issue, Gao et al.5 suggested that a characteristic crack length can be identified as $a^* \approx Y\gamma_s/\sigma_{th}^2$, below which the Griffith fracture stress overestimates the true fracture stress and the material becomes flaw insensitive. Pugno and Ruoff5 developed a quantized fracture mechanics (QFM) theory, where the classical stress intensity factor is redefined by considering an infinitesimal crack extension at the crack tip. With a predetermined geometric parameter, the QFM theory predicts satisfactory results on the fracture strengths of nanostructured materials. Recently, Mattoni et al.5 proposed a modified Griffith condition, where Young’s modulus and surface energy density are taken to be strain dependent. Despite yielding an improved agreement between the predicted Griffith fracture stress and the failure load, these
computational schemes developed in this work are general and can be applied to study the energetics and kinetics of ductile fracture involving dislocation nucleation or motion at a crack tip. Brittle fracture by bond breaking generally prevails at low temperatures. There exists a critical temperature at which ductile fracture by dislocation motions prevails and brittle-to-ductile transition occurs. A study of such phenomena in systems of flat monolayer lattices and curved monolayers of single-walled carbon nanotubes is currently under way.

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The effects of extensive pitting on the mechanical properties of carbon nanotubes

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Abstract

As previously demonstrated, a single hole is sufficient to markedly reduce the fracture strength of a carbon nanotube (CNT). Herein we present calculations exploring the effects of multiple holes on the modulus, fracture strength, and fracture strain of CNTs. The modulus decreases sharply and approximately linearly as a function of the pitting density. A few holes cause a decrease in the failure strain but extensive pitting leads to higher failure strains. These results suggest that the unusually low modulus measurements and high failure strains reported in the experiments of Yu et al. [Science 287 (2000) 637] were a consequence of purification induced oxidative pitting.

1. Introduction

Quantum mechanical (QM) calculations [1–6] predict that defect-free carbon nanotubes (CNTs) have Young’s modulus values of ~1 TPa, fracture strengths of ~100 GPa, and failure strains of ~20–30% depending on their chirality, with generally good agreement existing between the predictions of tight binding [1,2,5], semiempirical [3,4,6], and density functional theory [5,6] methods. A number of experimental studies [7–12] have been conducted for CNT fracture, but agreement both between the experimental results and between theory and experiment is limited. Some of the experiments [8–10] involved multiwalled CNTs (MWCNTs) for which more than one shell is load bearing, and this complicates experimental–theoretical comparisons. Two experiments [7,11] reported fracture studies of arc-discharge-grown MWCNTs, and only the outermost shell was load bearing for those samples. The experiment of Yu et al. [7] reported 19 fracture strength measurements ranging from 11 to 63 GPa (with a mean value of 28 GPa), four modulus measurements of 950, 470, 335, and 274 GPa, and four failure strain measurements, one below 3% and three between 11% and 13%. The later experiment of Ding et al. [11] reported data for 14 MWCNTs with fracture strengths ranging from 10 to 66 GPa (with a mean value of 24 GPa), modulus measurements ranging from 620 to 1200 GPa (with a mean value of 955 GPa), and failure strains ranging from 1.0% to 6.3% (with a mean value of 2.6%).

The discrepancy between theory and experiment for the fracture strengths has received the most attention, and early theories [13] focused on stress-induced Stone–Wales defects [14] as the likely cause of the low strength measurements. It was eventually realized that even though Stone–Wales defects become energetically favorable at higher strains, the transformation barriers remain sufficiently high [4,15] that such processes could not explain fracture measurements at room temperature. It was subsequently observed [6,16,17] that the MWCNTs used in the
the CNT fracture measurements of Yu et al. [7]. In fact, plausible pitting densities of 0.1–0.2 lead to the range of failure stresses of 10–30 GPa, which corresponds to the failure stresses most commonly observed in the experiments. Alternative theories involving stress-induced Stone–Wales defects [13] cannot explain the modulus measurements and are not consistent with the much lower failure strains reported in the Ding et al. [11] measurements of unpurified CNTs.

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References

The role of defects in the design of space elevator cable: From nanotube to megatube

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Abstract

Researchers are claiming that the feasibility of space elevator cable is now realistic, thanks to carbon nanotube technology, proposing its realization within a decade. However, the current view of basing the design of the megacable on the theoretical strength of a single carbon nanotube is naïve, as has recently been emphasized. In this paper the role of thermodynamically unavoidable atomistic defects with different size and shape is quantified on brittle fracture, fatigue and elasticity, for nanotubes and nanotube bundles. Nonasymptotic regimes, elastic plasticity, rough cracks, finite domains and size effects are also discussed. The results are compared with atomistic simulations and nanotensile tests of carbon nanotubes. Key simple formulas for the design of a flaw-tolerant space elevator megacable are reported, suggesting that it would need a taper ratio (for uniform stress) of about two orders of magnitude larger than currently proposed.

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1. Introduction

A space elevator basically consists of a cable attached to the Earth’s surface for carrying payloads into space [1]. If the cable is long enough, i.e. around 150 Mm (a value that can be reduced by a counterweight), the centrifugal forces exceed the gravity of the cable that will work under tension [2]. The elevator would stay fixed geosynchronously; once sent far enough, climbers would be accelerated by the Earth’s rotational energy. A space elevator would revolutionize the methodology for carrying payloads into space at low cost, but its design is very challenging. The most critical component in the space elevator design is undoubtedly the cable [3], which requires a material with very high strength and low density.

If we consider a cable with constant cross-section and a vanishing tension at the planet surface, the maximum stress–density ratio for the Earth, reached at the geosynchronous orbit, is 63 GPa/(1300 kg m$^{-3}$), corresponding to 63 GPa if low carbon density is assumed for the cable. It is only recently, after the discovery of carbon nanotubes [4], that such large failure stresses have been measured experimentally, during tensile tests on ropes composed of single-walled [5] or multiwalled [6–8] carbon nanotubes, both of which were expected to have an ideal strength of 100 GPa. Note that for steel (density 7900 kg m$^{-3}$, maximum strength 5 GPa) the maximum stress expected in the cable would be 383 GPa, whereas for Kevlar (density 1440 kg m$^{-3}$, strength 3.6 GPa) it would be 70 GPa, both much higher than their respective strengths [3].

However, an optimized cable design must consider a uniform tensile stress profile rather than a constant cross-sectional area [2]. Accordingly, the cable could be built from any material simply by using a sufficiently large taper ratio, i.e., the ratio of the maximum (at the geosynchronous orbit) to the minimum (at the Earth’s surface) cross-sectional area. For example, for steel and Kevlar huge and unrealistic taper ratios of $10^{33}$ and $2.6 \times 10^{8}$, respectively, would be required, whereas for carbon nanotubes...
Ab initio calculation of ideal strength and phonon instability of graphene under tension

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Graphene-based sp²-carbon nanostructures such as carbon nanotubes and nanofibers can fail near their ideal strengths due to their exceedingly small dimensions. We have calculated the phonon spectra of graphene as a function of uniaxial tension by density functional perturbation theory to assess the first occurrence of phonon instability on the strain path, which controls the strength of a defect-free crystal at 0 K. Uniaxial tensile strain is applied in the x (nearest-neighbor) and y (second nearest-neighbor) directions, related to tensile deformation of zigzag and armchair nanotubes, respectively. The Young’s modulus \( E=1050 \text{ GPa} \) and Poisson’s ratio \( \nu =0.186 \) from our small-strain results are in good agreement with previous calculations. We find that in both x and y uniaxial tensions, phonon instabilities occur near the center of the Brillouin zone, at \( (\epsilon_{xx},\epsilon_{yy})=0.016 \) and \( (\epsilon_{xx},\epsilon_{yy})=0.194,\epsilon_{yy}=0.266,\epsilon_{yy}=121 \text{ GPa},\epsilon_{yy}=-0.027 \), respectively. Both soft phonons are longitudinal elastic waves in the pulling direction, suggesting that brittle cleavage fracture may be an inherent behavior of graphene and carbon nanotubes at low temperatures. We also predict that a phonon band gap will appear in highly stretched graphene, which could be a useful spectroscopic signature for highly stressed carbon nanotubes.

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I. MOTIVATION

The ideal strength is the highest achievable strength of a defect-free crystal at 0 K. Even though a conventional material deforms or fractures at macroscopic stresses far below its ideal strength, the ideal strength is nonetheless a crucial theoretical parameter, because it fundamentally characterizes the nature of chemical bonding in that crystal. The Peierls-Nabarro model of dislocation, for instance, relies on the Frenkel model of ideal strength, because defects such as cracks and dislocations work like levers, amplifying the far-field stress to near ideal strength levels inside the defect core in order to move. It is thus not surprising that the study of ideal strength can tell us a lot about why some materials (such as diamond) are intrinsically brittle, while others (such as copper) are intrinsically ductile.

The ideal strength becomes even more important with the progress of nanotechnology. Recent experiments on nanocrystals, nanoporous materials, and nanoindentation have revealed a host of ultrastrength phenomena, defined by internal stress levels broadly and persistently rising up to a significant fraction of the ideal strength. Ultrastrength materials typically have geometric features around or less than \( L_e \approx 10^2 \text{ nm} \). To put this in perspective, computers one can buy off the shelf now have chips with 65 nm strained silicon features. At such material length scales, the population dynamics of defects is fundamentally different from that in the macroscale material, leading to size-dependent mechanical behavior at \( L > L_e \), which, however, starts to level off at \( L < L_e \) due to the intrinsic upper bound, the ideal strength.

Carbon nanotube is an ultimate example of small-size, ultrastrength material. By bending multiwalled carbon nanotubes (MWCNTs) inside an atomic force microscope, Falvo et al. estimated that 16% tensile strain can be achieved in local regions of some MWCNTs without breaking them. Yu et al. measured the tensile response of single-walled carbon nanotube (SWCNT) ropes and inferred a mean breaking strength of 30 GPa, 3% of their mean Young’s modulus of 1002 GPa. Ding et al. measured the fracture strengths and moduli of arc-grown MWCNTs. The outer-shell fracture strength was estimated to range from 10 to 66 GPa, and the Young’s modulus from 620 to 1200 GPa. Demczyk et al. conducted room-temperature pulling and bending tests on MWCNT of diameter of 12.5 nm and measured an astonishing 150 GPa failure strength, which is 17% of its Young’s modulus, \( E=900 \text{ GPa} \). The authors noted there is no narrowing of the nanotubes immediately before failure (the deformation was elastic and reversible), and the nanotubes fail “as essentially defect-free materials.” The 150 GPa strength value, however, seems to be inconsistent with their reported 5% strain prior to failure. Barber et al. measured the tensile strength of MWCNTs produced by chemical vapor deposition and fitted the data to the Weibull-Poisson distribution. A characteristic strength value of 109 GPa was obtained. Márquez-Lucero et al. reported similar high strengths in carbon nanotubes and nanofibers. These recent experiments indicate that ultratensile strength can indeed be achieved in an important component of nanotechnology.

It is reasonable to speculate that graphene-based carbon nanotubes, nanofibers, etc., hold record or near-record ideal tensile strength among all materials. It is well known that the electronic structure and mechanical properties of carbon nanotubes are similar to those of flat graphene, aside from quantum confinement effect. For this reason, in this paper...
Tight-binding molecular dynamics study of the role of defects on carbon nanotube moduli and failure

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We performed tight-binding molecular dynamics on single-walled carbon nanotubes with and without a variety of defects to study their effect on the nanotube modulus and failure through bond rupture. For a pristine (5,5) nanotube, Young’s modulus was calculated to be ~1.1 TPa, and brittle rupture occurred at a strain of 17% under quasistatic loading. The predicted modulus is consistent with values from experimentally derived thermal vibration and pull test measurements. The defects studied consist of moving or removing one or two carbon atoms, and correspond to a 1.4% defect density. The occurrence of a Stone-Wales defect does not significantly affect Young’s modulus, but failure occurs at 15% strain. The occurrence of a pair of separated vacancy defects lowers Young’s modulus by ~160 GPa and the critical or rupture strain to 13%. These defects apparently act independently, since one of these defects alone was independently determined to lower Young’s modulus by ~90 GPa, also with a critical strain of 13%. When the pair of vacancy defects adjacent, however, Young’s modulus is lowered by only ~100 GPa, but with a lower critical strain of 11%. In all cases, there is noticeable strain softening, for instance, leading to an ~250 GPa drop in the apparent secant modulus at 10% strain. When a chiral (10,5) nanotube with a vacancy defect was subjected to tensile strain, failure occurred through a continuous spiral-tearing mechanism that maintained a high level of stress (2.5 GPa) even as the nanotube unraveled. Since the statistical likelihood of defects occurring near each other increases with nanotube length, these studies may have important implications for interpreting the experimental distribution of moduli and critical strains. © 2007 American Institute of Physics. [DOI: 10.1063/1.2756832]

I. INTRODUCTION

Pristine carbon nanotubes (CNT’s) offer tremendous potential improvements in tensile strength over that of conventional materials for structures. With a tensile strength many times that of even very high strength (1.4 GPa) steels, but at only 1/6–1/3 the density, CNTs could be used for a broad variety of applications in which strength-to-weight ratios are important, such as for lightweight, quickly erectable infrastructure; airframes; bridges; and armor. But before these practical uses can be realized, macromaterials will need to be fabricated from CNT’s. These macromaterials will involve macroscale quantities of CNT’s, often adjoined with other materials. In these nanocomposite materials, individual CNT’s could represent a strain relief mechanism or a load-carrying member. The prediction and characterization of CNT failure modes are therefore of fundamental importance in the design of structures and composite materials using CNT’s. A major factor that can affect CNT failure is the presence of defects that result from production or fabrication, the environment they have been exposed to, or prior stress. Furthermore, the functionalization of CNT’s (Ref. 2) to promote intertube and matrix bonding will alter the mechanical properties of individual tubes in a manner roughly analogous to defects.1,3

The prediction of CNT failure modes is an important issue for both experimental and simulation work. Experimental measurements of mechanical properties of individual CNT’s have a large variance because of the inherent difficulty in manipulating, characterizing, and measuring the behavior of objects at the nanometer scale (see reviews by Qian et al.4 and Yu5). In contrast, the simulation of individual CNT mechanical properties is less demanding than experimental determination as relatively few atoms are involved. The simulation results can be used to verify and further understand experimental results; see, for example, results from Kaplan-Ashiri et al.6,7 on Young’s modulus.

Different groups have used numerical simulations to predict Young’s modulus of CNT’s with generally good agreement between independent studies and available experimental data. Sears and Batra8 found that the values of Young’s modulus reported by ten different research groups between 1992 and 2002 varied between 0.94 and 1.24 TPa. Note that the value of Young’s modulus depends on the value taken for the tube wall thickness, which is not a well-defined quantity (see, for example, the discussion by Srivastava et al.9). Sears

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Atomistic simulations of the mechanical properties of ‘super’ carbon nanotubes

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Abstract
The mechanical properties of the so-called ‘super’ carbon nanotubes (STs) are investigated using classical molecular dynamics simulations. The STs are built from single-walled carbon nanotubes (SWCNTs) connected by Y-like junctions forming an ordered carbon nanotube network that is then rolled into a seamless cylinder. We observed that the ST behaviour under tensile tests is similar to the one presented by fishing nets. This interesting behaviour provides a way to vary the accessible channels to the inner parts of STs by applying an external mechanical load. The Young’s modulus is dependent on the ST chirality and it inversely varies with the ST radius. Smaller reduction of breaking strain values due to temperature increase is predicted for zigzag STs compared to SWCNTs. The results show that, for STs with radius ~5 nm, the junctions between the constituent SWCNTs play an important role in the fracture process. The Young’s modulus and tensile strength were estimated for hierarchical higher-order STs using scaling laws related to the ST fractal dimension. The obtained mechanical properties suggest that STs may be used in the development of new porous, flexible, and high-strength materials.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Many attempts have been made in order to develop procedures to controllably assemble a large number of single-walled carbon nanotubes (SWCNTs) in terms of position and orientation [1–6]. The achievement of such procedures would allow the fabrication of ordered SWCNT networks representing a breakthrough in the ‘bottom-up’ manufacturing approach. These ordered networks would open possibilities to design new materials with desirable electronic and mechanical properties.

Recently, the structure of the so-called ‘super’ carbon nanotubes (STs) was proposed [7] (figure 1). This structure can be generated from an ordered carbon network based on the honeycomb symmetry, generically named super-graphene, which is heuristically constructed by replacing the carbon–carbon bonds of the graphene architecture by single-walled carbon nanotubes (SWCNTs) and the carbon atoms by Y-like junctions. The associated STs can be then generated by rolling up super-graphene sheets. Similarly to a (n, m) SWCNT [8], [N, M] STs with different chiralities can be constructed. The STs are represented as [N, M]@(n, m) and are characterized by the (n, m) SWCNT used to form them, the necessary junctions to join consecutive SWCNTs, and the distance between these junctions. The ST construction is not limited to carbon nanotubes and to the honeycomb...
[33] Chand S J 2000 J. Mater. Sci. 35 1303
Atomic geometry and energetics of carbon nanotube necking

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Molecular mechanics simulations were performed to probe the incipient plastic deformation in carbon nanotubes (CNTs), which involves nucleation of Stone–Wales (SW) defects and spiral glide of 5/7 dislocation dipoles that lead to quantized necking through a stepwise reduction in tube diameter. Quantification of the strain-dependent energetics of dislocation glide reveals that such dislocation motions are energetically favoured at high tensile strain. Pre-existing dislocations critically affect subsequent nucleation and separation of SW defects, as manifested by the competing deformation modes of symmetric versus asymmetric necking. The results provide a quantitative basis for the dislocation dynamics simulations of superplastically deformed CNTs.

1. Introduction

The promising applications of carbon nanotubes (CNTs) as ultra-stiff, high-flexibility fibres in nanocomposites have directed considerable efforts to the study of the mechanics of CNTs both experimentally [1–5] and theoretically [6–24]. At high loads, the deformation of CNTs may take two distinct routes [7]: cleavage brittle fracture [9–11, 13, 15, 21, 22] or plastic flow [7, 8, 11, 12, 16], with active mechanisms mediated by temperature. At low temperatures, brittle fracture via bond breaking prevails and often involves stress-mediated formation of large open-ring structures [9, 10, 15, 21], whereas at elevated temperatures, plastic deformation dominates and proceeds by nucleation and motion of Stone–Wales (SW) defects [8, 11, 12, 16, 19, 23], which can be viewed as a 5/7–7/5 dislocation dipole formed by rotating a C–C bond by 90°. Extensive experiments [1–3] and numerical simulations, ranging from first-principles calculations [6, 9, 10, 12, 13, 15], empirical atomistic simulations [10 11, 17, 21, 22, 24], to Cauchy–Born rule [25] based continuum modelling, have been performed to study the brittle fracture of CNTs. In contrast, the deformation mechanisms of CNTs at high temperatures have received much less attention until the recent discovery of superplastic CNTs [4, 5] in which single-walled carbon nanotube (SWCNT) underwent 280% elongation and 15-fold radial reduction with marked kink formation at about 2000°C. Whereas in-situ experiments have

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defects in CNTs; these processes can lead to quantized necking through a stepwise reduction in the tube diameter. Specifically, we have identified two competing modes of atomic-scale necking, i.e. symmetric versus asymmetric neck formation and propagation in CNTs. We have further studied the mechanics governing this competing process based on the elastic interactions between dislocations on a cylindrical surface of curved CNTs. These results can guide the formulation of continuum constitutive model, and also provide a quantitative basis for the dislocation dynamics simulations of superplastically deformed CNT.

We conclude by commenting that the present study focuses on the thermodynamic driving forces of the formation and glide of dislocations. For a complete description of dislocation activities in CNTs, it is also necessary to evaluate the activation energy barriers of dislocation nucleation and motion that control the kinetic rate of plastic flow. Also note that the plastic deformation in CNTs may proceed by dislocation climb [4]. Such a process will compete against dislocation spiral glide to sustain the plastic flow of CNTs at high temperatures. Activation energy barriers between consecutive slip steps of 5/7 dislocations in bent CNTs have recently been calculated by Mori et al. [29], where only one dislocation dipole was considered. In order to obtain a full understanding of the large plastic flow in CNTs, work is currently underway to compute the activation energy barriers of sequential dislocation nucleation and motion (both slip and climb) in CNTs using the atomic configurations obtained from the present study.

Acknowledgements

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References

Molecular mechanics modeling of carbon nanotube fracture

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Abstract

The fracture of carbon nanotubes (CNTs) is studied in this paper. Molecular mechanics models that incorporate the modified Morse potential and reactive empirical bond-order potential are developed to envisage the fracture behavior of perfect CNTs. The tensile strength, fracture strain, and fracture angle under tension are discussed, and special attention is paid to the effects of tube chirality. Explicit expressions for the fracture solutions for achiral carbon nanotubes are presented, but only numerical results are available for chiral carbon nanotubes. The predicted results of the present model are in good agreement with existing data and those of molecular mechanics simulations via the Materials Studio software package, which indicates the effectiveness of the developed models.

1. Introduction

Carbon nanotubes (CNTs), which were discovered by Iijima [1], are carbon macromolecules in a periodic hexagonal arrangement with a cylindrical shell shape. As the strength of CNTs is of great interest, the atomic mechanisms of CNT failure have been extensively investigated both experimentally and theoretically [2–7].

In experiments, atomic force microscopy (AFM) or transmission electron microscopy (TEM) is usually employed to measure the breaking strain and observe the fracture patterns of CNTs [8–12]. The reported experimental values of the breaking strain are quite diverse, and range from 13% [8], 17% [9], 30% [10], and 50% [11] to 280% [12] due to the variability of the samples and measurement conditions. There are two major perspectives on such a scattered range of experimental data. Belytschko et al. [13] suggested that the fracture strain, which ranged from 2% to 13% [8], can be attributed to defects in CNTs, because these values are lower than those for pristine CNTs that are generated by molecular mechanics simulations. There are different types of defects in CNTs, such as Stone-Wales transformation [14,15], “lattice-trapped” states [16], single vacancy [17–19], and its derivative point defects [20]. These defects can significantly reduce the strength of CNTs. However, based on the classical molecular dynamics simulations, tight-binding, and ab initio calculations, Yakobson et al. [21] concluded that the strength of CNTs is highly dependent on their strain level, strain rate, temperature, and chirality. The fracture strain appears to range from 30% to 40% at room temperature. At high temperatures, CNTs can sustain extensive elongation with a very high strain rate [16], up to 280%, which was reported by Huang et al. [12], due to the possibility of plastic yield. With a decrease in temperature, the tensile strength with brittle fracture will increase and has no perceptible dependence on the strain rate. Despite these insights, some challenging questions still remain, such as the dependence of the fracture modes on the chirality of CNTs.

In their analysis of the tensile strength and strain of CNTs, Yakobson et al. [21] pointed out that the continuum elasticity theory cannot predict any special features, because under tension, the CNT remains structurally stable, and preserves a straight cylinder geometry. However, extensive molecular dynamics simulations are inapplicable to a system on a larger scale because of the expensive


The effect of Stone–Wales defect on the tensile behavior and fracture of single-walled carbon nanotubes

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Abstract

The effectiveness of carbon nanotubes as reinforcements in the next generation of composites is designated by their mechanical behavior as standalone units. One of the most commonly present topological defects, whose effect on the mechanical behavior of carbon nanotubes needs to be clarified, is the Stone–Wales (SW) defect. In this paper, the effect of SW defect on the tensile behavior and fracture of armchair, zigzag and chiral single-walled carbon nanotubes (SWCNTs) was studied using an atomistic-based progressive fracture model. The model uses the finite element method for analyzing the structure of SWCNTs and the modified Morse interatomic potential for describing the nonlinear force-field of the C–C bonds. In all cases examined, the SW defect serves as nucleation site for fracture. Its effect on the tensile behavior of the SWCNTs depends solely on nanotube chirality. In armchair SWCNTs, contrary to zigzag ones, a significant reduction in failure stress and failure strain was predicted; ranging from 18% to 25% and from 30% to 41%, respectively. In chiral SWCNTs, the effect of the defect is between those of the armchair and zigzag SWCNTs, depending on chiral angle. The stiffness of the nanotubes was not affected. The nanotube size was found to play a minimal role in the tensile behavior of SW-defected SWCNTs; only in cases of very small nanotube diameters, where the fraction of defect area to the nanotube area is high, was a larger decrease in the failure stress predicted.

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Keywords: Carbon nanotubes; Finite element analysis; Interatomic potential; Progressive fracture analysis; Stone–Wales defect

1. Introduction

Due to their extraordinary mechanical properties, carbon nanotubes (CNTs) are being considered as the ideal reinforcing material for the next generation of composites. In this role, CNTs' performance is designated by their mechanical behavior as stand alone units. So far, in the majority of studies, CNTs have been treated as defect-free materials. However, experimental observations [1] have revealed that topological defects, such as the Stone–Wales (SW) defect, and vacancy defects, are commonly present. The presence of defects in CNTs is consolidated by the recent findings of Mielke et al. [2] who predicted that the presence of vacancy defects significantly reduces the failure stress and failure strain of CNTs providing an explanation for the extant theoretical–experimental discrepancies.

The SW defect is the most important defective structure in CNTs. Investigations have shown that besides the effect that may have on the mechanical behavior of CNTs, SW defect also affects their electronic, magnetic and hybridization characteristics. Because of its multiple effect, the SW defect demonstrates several utilities. For example, the transition in the Y junction, contemplated in CNT based molecular electronics, is achieved through the incorporation of many SW defects either by design or otherwise [3]. Similarly, a transition of nanotubes from one diameter to another can be achieved by locating a few SW defects strategically in the transition region. In addition, when nanotubes are used as fibers in nanocomposites, interfacial
6. Conclusions

In the present paper, a study was accomplished on the effect of SW defect on the tensile behavior and fracture of SWCNTs. It was found that the SW defect serves as nucleation site for fracture. Its effect on the tensile behavior of SWCNTs concerns the failure stress and failure strain and depends solely on nanotube chirality. In armchair SWCNTs, there is a significant reduction in failure stress and failure strain ranging from 18% to 25% and from 30% to 41.4%, respectively. On the other hand, in zigzag SWCNTs, the SW defect formed by the 90° rotation of a longitudinal bond does not affect their tensile behavior at all, while the defect formed by the 90° rotation of a diagonal bond reduces the failure stress and failure strain of the nanotubes by about 3% and 15%, respectively. The effect of a SW defect in chiral SWCNTs is between those of the armchair and zigzag SWCNTs according to the chiral angle. For the SW-defected (16,8) tube considered in this work, a 15.18% reduction was predicted in the failure stress and a 32.4% in failure strain. The stiffness of the SWCNTs was not affected by the presence of SW defects. The nanotube size was found to play a minimal role on the tensile behavior of SW-defected SWCNTs; only in cases of small nanotube diameters, where the fraction of defect area to the nanotube area is high, was a larger decrease in the failure stress predicted.

Additionally to the fulfillment of the basic scope described in the previous paragraph, this paper intends also to give support to the belief that continuum mechanics methods combined to the appropriate physics can be an efficient computational tool for modeling the structure of CNTs and predicting their mechanical behavior. The PFM used to accomplish the current study treats CNTs as space-frame structures in order to enable use of finite elements for modeling their response to mechanical loading. The FE method has lent the PFM the ability to model nanotube systems with a very large number of atoms subjected to complex mechanical loading conditions in small CPU times. For example, the analysis of the (18,18) tube (1200 atoms, 120 load steps) took about 120 s on a Pentium® 4 CPU 3.20 GHz, 1.0 GB RAM personal computer. This ability is the main advantage of atomistic-based continuum mechanics approaches over the classical atomistic modeling approaches, such as MD simulations.

The modified Morse interatomic potential used to describe the nonlinear force-field of the C–C bonds, may not be appropriate for describing fracture evolution, since it does not take into account many-body interactions as well as reconfiguration of bonds, but gives correct predictions for the fracture initiation and the behavior of the nanotube prior to fracture. Besides, the specific potential has been extensively used in the literature for predicting the mechanical properties and behavior of CNTs with success. Nevertheless, it is in the authors’ interests to incorporate many-body potentials in the PFM and compare their performance in various cases against the pairwise modified Morse potential.

References

Hydrogen sorption in defective hexagonal BN sheets and BN nanotubes

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We perform ab initio simulations on the interaction of molecular hydrogen with the native and substitutional defects of single hexagonal boron-nitride sheets and small-diameter (8,0) nanotubes. We find that the adsorption of molecular hydrogen on both types of structure is endothermic with respect to dissociation, with the small-diameter nanotube possessing the smaller barrier. Although chemisorption along the tube axis is energetically preferred, the barrier for dissociation is lower for chemisorption across the tube axis, implying that chemisorbed hydrogen can be kinetically trapped in a higher energy state. Dopants that maximize the localization of the highest occupied molecular orbital and lowest unoccupied molecular orbital states maximize hydrogen binding energies. Carbon dopants do not enhance H₂ binding in contrast to the literature, whereas silicon dopants for nitrogen provide H₂ binding energies of 0.8 eV, at the upper end of the range required to meet DOE targets for hydrogen storage. The formation energy of most defects is reduced with increasing curvature except for the carbon substitutionals. Vacancies reduce the barriers for H₂ dissociation for the planar sheets but not for strongly curved nanotubes. The surface stress induced by nanotube curvature boosts the hydrogen storage capabilities of vacancies compared to the sheet, with the nitrogen vacancy chemisorbing 4H and allowing a H₂ molecule to enter the interior of the tube. The hydrogen binding properties of boron-nitride systems are strongly dependent on the defects and dopants present. Pretreating of these systems so as to partially remove nitrogen should enhance H₂ adsorption properties.

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I. INTRODUCTION

Energy is a major issue for the world today. Energy consumption is intimately linked with CO₂ emission, a major human contributor to undesirable climate change. Several energy solutions are available, including large increases in energy efficiency, energy generation by renewable sources, and increasing usage of nuclear power. However, fossil fuels with a high-energy density will still be a dominant feature in the energy economy in the near future. If CO₂ emission is to be rapidly reduced, there should be a switchover to a clean energy carrier, of which hydrogen is particularly powerful.1,2 One of the main problems limiting the use of hydrogen for energy applications is the difficulty of storing it safely.1–4 A promising series of hydrogen storage materials are systems that possess a fullerene structural motif, such as carbon or boron-nitride nanotubes. Hydrogen adsorption on these systems can be modified via external pressure5,6 or transition metal doping.7–9

Boron-nitride nanotubes are particularly attractive because, as opposed to carbon nanotubes, their electronic properties are independent of helicity, diameter, and number of walls, and as well they have a strong tendency to form zigzag nanotubes.10,11 The hydrogen storage capacity of multiwall BN nanotubes has been measured to be 1.8–2.6 wt %,12 at a pressure of 10 MPa at room temperature, with 70% of the hydrogen chemisorbed to the nanotube and the rest physisorbed. Compared to carbon systems, boron nitride can store hydrogen at elevated temperatures.12,13 The addition of metal nanoparticles such as platinum causes the creation of voids and other point defects in the tubes that boost hydrogen storage capacity to approximately 4.2 wt %,14 close to the US DOE targets for vehicular hydrogen storage for 2007.

Boron nitride can exist in a hexagonal graphitelike structure (h-BN) that can be rolled up to form a boron-nitride nanotube (BNT), analogous to carbon nanotubes. Unfortunately, in these systems, the binding of molecular hydrogen to the boron-nitride substrate is very weak, about −0.09 eV/H₂.15 For practical vehicular hydrogen storage applications, the molecular binding energy should be of order −0.2 to −0.7 eV/H₂.

There are several papers that discuss the simulation of hydrogen storage mechanisms in BN nanosystems. Mårild et al.16 performed density functional theory local density approximation (DFT-LDA) simulations on the adsorption of atomic hydrogen and fluorine on a h-BN cluster. They found that adsorption on boron atoms causes a local sp² to sp³ transformation but that adsorption on nitrogen does not occur. Wu et al.17 considered the chemisorption of isolated hydrogen atoms on an (8,0) BNT with DFT-LDA, finding that hydrogen prefers to chemisorb along the tube axis, implying that hydrogen atom adsorption, finding that increasing deformation increases the adsorption energy of H atoms on N. Jhi and Kwon20 found from DFT-PBE simulation that H₂ physisorbs weakly onto h-BN and BNTs and does not dissociate, with a molecular binding energy larger than for the equivalent adsorption on graphite or carbon nanotubes. The addition of carbon dopants or Stone-Wales defects increased the H₂ binding energy. Modifications of the sp³ binding induced by these types of defects were determined to be responsible for the increase in binding strength. Wu et al.21 performed DFT-PW-91 simulations on the effects of several native defects on hydrogen dissociation, using the nudged elastic band (NEB) method to determine the minimum energy path (MEP) of H₂ dissociation. They found that the barrier for hydrogen disso-
reducing the energetic penalty for atoms surrounding the vacancy to adopt a locally $sp^3$ structure allowing the twofold atoms bordering the vacancy to adsorb more hydrogen and catalyzing spillover hydrogen storage.

In conclusion, we have shown via detailed simulation that the hydrogen binding properties of nanostructured boron-nitride systems are strongly dependent on the defects and dopants present, with both covalent and noncovalent binding behaviors observed. This variation has important consequences for the usage of these materials for hydrogen storage and other applications such as nanoscale electronics.

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Atomistic-continuum and \textit{ab initio} estimation of the elastic moduli of single-walled carbon nanotubes

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Abstract


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Keywords: Quasicontinuum; Atomistic-continuum; Cauchy–Born rule; Membrane; Nonlinear elasticity; \textit{Ab initio} calculations

1. Introduction

Carbon nanotubes are known to possess a remarkable ability to sustain large elastic deformations without developing lattice defects, in spite of some experimental observa-

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Failure strength of brittle materials containing nanovoids

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By means of atomistic simulations, we investigate the failure strength in plane strain conditions of a brittle solid containing nanosized stress concentrators, i.e., a straight crack, a cylindrical hole, or a spherical hole. We find that the failure strength of the defected solid strongly depends on the defect size, in contrast with the predictions of standard elasticity theory. A high strength reduction due to voids as large as few atoms is observed. Such results have been included in two analytical failure criteria, namely, the average stress criterion and the point stress criterion. Both models introduce a length scale typical of the system, tailored at describing the process zone near the nanovoids. We provide a numerical estimate for this length scale, which is found to be specific for any defect, and we reconcile atomistic results to continuum into a coherent picture.

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I. INTRODUCTION

Defects such as cracks and voids affect the mechanical behavior of brittle solids since they modify the overall strength of the material. Sometimes such defects are unavoidable because they form during materials synthesis and processing such as, e.g., ceramic sintering. On the other side, voids may be introduced into the material by design in order to obtain specific properties. This is the case of porous materials where pores at a suitable concentration are used to control the thermal or acoustic isolation, the impact energy absorption, and many other properties.1 In any case, such inhomogeneities are of great relevance on the mechanical response of the system, since they enhance the local stress and they possibly may initiate failure. In addition, as the technological demand for extremely high strength materials increases (as well as the development of nanoscale devices or machines), defects as small as a few nanometers cannot be neglected. As an example, it has been recently found that even one- or two-atom vacancy defect can reduce the failure strength of carbon nanotubes by an amount of 26%.2,3 We will show that sizable strength reduction due to voids as large as few atoms are observed in bulk β-SiC as well.

The strength of materials containing cracks and voids is traditionally described according to stress intensification or stress concentration arguments, respectively.4,5 The need of different approaches is motivated, according to linear elastic fracture mechanics (LEFM), by the mathematical divergence of the stress field near the crack tip. Following LEFM, loading produces a 1/√x singularity at the crack tip (where x is the distance from the crack tip along the plane of the crack) and a critical stress equal to zero is expected. As a consequence, a straightforward prediction of failure stress as uniquely based on local stress criteria cannot be applied. The critical stress of the cracked body is therefore calculated by analyzing the stress singularity at the crack tip: the failure takes place when the stress intensity factor K is equal to the material fracture toughness Kc.6,7 This criterion relies on the energy balance of the Griffith theory.8 In contrast, elasticity theory predicts that the failure from a void (as it is the case of cylindrical or spherical holes) takes place when the maximum local stress equals the ideal material strength σth.9 Both alternative continuum approaches (for cracks and voids) are based on linear elasticity and they unlikely work at the nanoscale. Their possible weaknesses could, in principle, be due to the failure of at least one of the three underlying (constitutive) hypotheses they rely on: either continuum mechanics, elasticity, or linearity.

In order to improve classical continuum models, modern theories of fracture are generally formulated so as to incorporate into their formalism a suitable material length scale λ: this key quantity is aimed at describing a process zone close to the crack tip where at least one of the above constitutive hypotheses fails. The characteristic length scale is typically given by

$$\lambda \sim \frac{2K_c^2}{\pi \sigma_{th}^2}. \quad (1)$$

The interpretation of the length λ is not unique and it could be related to the existence of either a plastic zone (i.e., the mechanical response is beyond pure elasticity), a cohesive zone (linearity is lost), or a discrete unit for crack advancement (continuum hypothesis is no longer applicable).

In the framework of brittle fracture formalism, the characteristic length λ has been incorporated in four different models. The point stress criterion9,10 (PSC) assumes that the failure occurs if the stress becomes equal to σth at a suitable distance l from the notch, corresponding to $l \sim \lambda/4$. An alternative approach is the average stress criterion9,10 (ASC) according to which the failure occurs if the mean value of the stress along a line (or a surface, or a volume) starting at the notch root is equal to $\sigma_{th}$; the length l of such a line is in this case as large as λ. Furthermore, the equivalent linear elastic fracture mechanics (equivalent LEFM)8 assumes the existence of a crack at the root of the notch (i.e., the effective crack length is longer than its original size): the failure is predicted to occur when this effective crack reaches the criti-
thermic length actually depends on the defect type. Its value is estimated to be 0.60 nm for cracks, 0.66 nm for cylindrical holes, and 0.79 nm for spherical voids. The larger process zones associated with holes are interpreted as an evidence of a higher flaw-tolerance regime for holes and/or voids than for cracks.

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Modeling of fracture of carbon nanotubes with vacancy defect

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The fracture of achiral carbon nanotubes (CNTs) with one atomic vacancy is studied. Nonuniform variation of the fracture strain is observed from molecular mechanics simulations, and an elastic shell model is developed to describe the research findings. Hardening and softening domains near the edges of the tubes are specifically positioned. The effectiveness of the continuum mechanics model is further verified by molecular mechanics simulations via the MATERIALS STUDIO software package. In addition, the dependence of hardening or softening domains on the length and diameter of the CNTs is investigated. The rupture progress of defected carbon nanotubes with the vacancy at different locations is observed from molecular mechanics simulations, and adequate physical interpretations of the block-tearing fracture mode are provided.

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Carbon nanotubes (CNTs) can be viewed as one (or more) graphite sheet(s) rolled into a seamless tube. The way the graphite sheet is wrapped is represented by a pair of indices \((n,m)\) that is called the chirality. When the indices are set as \(n=m=0\), the nanotubes are called “armchair” and “zigzag,” respectively, or simply achiral CNTs. Existing studies have shown that CNTs exhibit superior mechanical properties over other known materials and hold substantial promise as fibers in composites and other devices, since properties over other known materials and hold substantial promise as fibers in composites and other devices.

Defects in CNTs can be initiated at the stage of CNT growth and purification, or during device or composite production by chemical treatment or by irradiation. There are different types of defects in CNTs, such as Stone-Wales defects, bond-breaking defects, and single vacancies and their derivative point defects. Among these types of defects, the effect of atomic vacancies has been studied extensively. A single atomic vacancy in a CNT can be simulated by removing a single atom and the three associated bonds. The configuration of the single vacancy is referred to as a nonreconstructed defect. This configuration is metastable but can survive for macroscopic times at low temperatures. On the other hand, the removal of carbon atoms from the hexagonal network of the CNT creates a number of carbon atoms with unsaturated valence orbitals. The excess energy arising from the unsaturated valence orbitals promotes reconstructions local to the vacancy. The effects of both the nonreconstructed and reconstructed atomic vacancy defects on mechanical properties of CNTs, especially the fracture of defected CNTs, have been investigated. Sammalkorpi et al. studied how the Young’s modulus and tensile strength of CNTs with vacancy defects depend on the defect characteristics by employing molecular mechanics simulations and a simple elastic rod theory. Their results showed that the tensile strength and fracture strain of a single-walled CNT decrease by nearly a factor of 2 if a nonreconstructed vacancy is present. Although the available fracture strain for defected CNTs was found to decrease to some extent in all molecular mechanics simulations, findings on the nonuniform variation of the fracture strain with respect to the location of the vacancy have seldom appeared; we have observed this from molecular mechanics (MM) simulations. Such an interesting and significant phenomenon needs to be investigated through an effective model. In addition, a study of the rupture progress of CNTs is also indispensable to enable a thorough understanding of the fracture of vacancy-defected CNTs.

In this Rapid Communication, an elastic shell model is developed to investigate the variation of the fracture strain of vacancy-defected CNTs with respect to the location of the defect. The prediction of the fracture strain from the continuum mechanics model is verified by MM simulations. The observation of a distinct rupture progress of the defected CNTs is also reported and interpreted via continuum mechanics.

In our MM simulations, the force field used to model the interatomic interactions in MATERIALS STUDIO is a condensed-phase optimized molecular potential for atomistic simulation studies (COMPASS) force field, which is the first ab initio force field that was parametrized and validated using condensed-phase properties, and has been proved to be applicable in describing the mechanical properties of CNTs. In MM calculations, the configurations are optimized at zero temperature to avoid thermal effects. Our MM simulations show that the fracture strains \(e_{\text{pristine}}\) for a pristine armchair (10,10) and zigzag (15,0) CNT are 41% and 34%, respectively. The fracture strains are in good agreement with the predictions by Yakobson et al. and Mięlik et al., which are 42% for a (11,3) CNT and 30% for a (5,5) CNT. Figure 1 shows the strain energy per atom versus the strain using the potential function for (15,0) and (10,10) CNTs with single vacancies at the centers of the tubes and the length to diameter ratio \(L/d=10\) that are subjected to an axial tensile loading and fixed at the two boundaries. In the simulations of defected CNTs, the single vacancy is located at the center of the tubes to avoid edge effects. The bond breaking can be determined from the drop of the strain energy due to the release of energy at the corresponding fracture. Hence, the occurrence of the first bond breaking can be observed at a...
leading to the fracture mode of a block-tearing configuration initiated at the edge propagates toward the defect location, sectional breaking during the rupture process, the occurrence of bond breaking at the edge is observed. The bond breaking initiated at the edge propagates toward the defect location, leading to the fracture mode of a block-tearing configuration seen in Fig. 4(b). Such a fracture mode, different from the one shown in Fig. 4(a) when the defect is at the center of the tube, due to force redistribution and defect-location effects. From elastic beam theory, the force on the tube will redistribute at the partially broken cross section, leading to an induced moment in the direction of the defect. The induced moment will thus stimulate a tensile stress on the edge at the position opposite to the defect. In addition to the induced tensile stress on the edge, the bending rigidity of the beam element under tension becomes smaller when the defect location is toward the edge. As such, the induced tensile stress undergoes a larger redistribution on the edge when the defect is closer to the edge. Thus, the edge block-tearing phenomenon is observed only when the defect is very close to the edge as shown in Fig. 4(b). The special fracture mode is of significance as knowledge of the simultaneous fracture at the defect location and the edge of CNTs will enable more understanding of the mechanical behavior of the materials, especially the fracture of the edge portion of a CNT when interacting with another substrate.

In summary, an elastic shell model is developed to study the fracture of achiral CNTs with one atomic vacancy. With the developed model, hardening and softening effects are found and the corresponding effective domains are observed. MM simulations are conducted to verify the effectiveness of the developed model. In addition, the dependence of the hardening or softening domains on the length and diameter of CNTs is investigated. A block-tearing fracture mode is observed via MM simulations when the defect is close to the edge of the tubes. A physical interpretation of the phenomenon is provided.

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A bridging domain and strain computation method for coupled atomistic–continuum modelling of solids

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SUMMARY

We present a multiscale method that couples atomistic models with continuum mechanics. The method is based on an overlapping domain-decomposition scheme. Constraints are imposed by a Lagrange multiplier method to enforce displacement compatibility in the overlapping subdomain in which atomistic and continuum representations overlap. An efficient version of the method is developed for cases where the continuum can be modelled as a linear elastic material. An iterative scheme is utilized to optimize the coupled configuration. Conditions for the regularity of the constrained matrices are determined. A method for computing strain in atomistic models and handshake domains is formulated based on a moving least-square approximation which includes both extensional and angle-bending terms. It is shown that this method exactly computes the linear strain field. Applications to the fracture of defected single-layer atomic sheets and nanotubes are given. Copyright © 2006 John Wiley & Sons, Ltd.

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KEY WORDS: bridging domain; graphene sheets; moving least square; molecular mechanics

1. INTRODUCTION

Modelling of material failure often involves phenomena simultaneously occurring at multiple length scales. On the one hand, such behaviour cannot be described by continuum mechanics without...


A molecular-mechanics based finite element model for strength prediction of single wall carbon nanotubes

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Abstract

The aim of this work was to develop a finite element model based on molecular mechanics to predict the ultimate strength and strain of single wall carbon nanotubes (SWCNT). The interactions between atoms was modelled by combining the use of non-linear elastic and torsional elastic spring. In particular, with this approach, it was tried to combine the molecular mechanics approach with finite element method without providing any not-physical data on the interactions between the carbon atoms, i.e. the CC-bond inertia moment or Young’s modulus definition. Mechanical properties as Young’s modulus, ultimate strength and strain for several CNTs were calculated. Further, a stress–strain curve for large deformation (up to 70%) is reported for a nanotube Zig-Zag (9,0). The results showed that good agreement with the experimental and numerical results of several authors was obtained.

A comparison of the mechanical properties of nanotubes with same diameter and different chirality was carried out. Finally, the influence of the presence of defects on the strength and strain of a SWNT was also evaluated. In particular, the stress–strain curve a nanotube with one-vacancy defect was evaluated and compared with the curve of a pristine one, showing a reduction of the ultimate strength and strain for the defected nanotube.

The FE model proposed demonstrate to be a reliable tool to simulate mechanical behaviour of carbon nanotubes both in the linear elastic field and the non-linear elastic field.

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Keywords: Carbon nanotubes; Molecular mechanics; Young’s modulus; Mechanical properties; Finite element analysis

1. Introduction

Since their discovery carbon nanotubes [1] have attracted considerable attention in scientific communities. This is partly due to their remarkable mechanical, electrical and thermal properties. In particular, material composites such as carbon nanotube, nanoparticle-reinforced polymers and metals have shown potentially wide application.

Specifically to mechanical properties, single wall nanotubes (SWNTs) have the highest Young’s modulus about 1 TPa, if normalized to their diameter, and this is one of the main reason why carbon nanotubes (CNTs) have attracted much interest for low weight structural composites [2].

A detailed summary of CNT’s mechanical properties can be found in [3]. A Young’s modulus for SWNTs and multi wall nanotubes (MWNTs) was reported to be 1.25 TPa, while a Poisson ratio around 0.14–0.28 was reported depending on the approach and the energy potential used. Further, experimental data of 15 SWNT bundles under tensile load showed that, the Young’s modulus ranged from 0.32 up to 1.47 TPa with an average of 1.02 TPa. The tensile strength ranged from 13 to 53 GPa [4]. In the case of MWNTs a Young’s modulus of 0.9 TPa was estimated by conducting pulling and bending tests [5].

Computational simulation for predicting mechanical properties of CNTs has been recognised to be a powerful tool to overcome the difficulties arising from the measurements of nanoscale dimensions. Several approaches can be used to evaluate the mechanical properties of SWNT and MWNT [6]. Xiao et al. [8] found a tensile strength for Armchair (126.2 GPa) and Zig-Zag (94.5 GPa) with a maximum strain of 23.1% and 15.6–17.5%, respectively. Natsuki and Endo [12], predicted the maximum stress to be around 70 GPa at 11% of strain for the Zig-Zag nanotube and 88 GPa at 15% for Armchair. Sun [13] found a tensile strength from 77 GPa (Zig-Zag) up to 101 GPa (Armchair). Further, an independence of the tensile strength from nanotube diameter was found.
Using theory and computation to model nanoscale properties

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This paper is designed to provide an overview of the use of theoretical methods to describe nanoscience problems. A number of examples are provided where theory has been used for nanoscale problems, and I hope to use these examples to illustrate some of the possibilities for getting theory to work, and also some of the existing challenges. This is a field where no one type of theory can be used in all cases, and where the marriage of theories associated with different length scales is still somewhat rocky. Thus, some of the problems will be addressed by pushing traditional atomistic theories, such as electronic structure theory, to systems that are much larger than they have been traditionally calibrated for, and for which serious approximations need to be introduced to calculate useful numbers. In other areas, one tries to push continuum theories down to smaller length scales than they were originally developed for, and again one needs to introduce approximations to make these produce useful results. Another approach involves multiscale theories, in which the atomistic and continuum scales are matched together. Alternatively, one can use course-grained models, in which one attempts to describe the effective properties of small groups of atoms that are contained within a larger nanoscale structure.

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Abbreviations: PA, peptide amphiphile; AFM, atomic force microscopy; QM, quantum mechanics; MM, molecular mechanics; CM, continuum mechanics; UNCD, ultrananocrystalline diamond; SERS, surface-enhanced Raman spectroscopy.

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Size effect in the tensile fracture of single-walled carbon nanotubes with defects

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Abstract
Molecular simulation is used to determine the fracture strength of single-walled carbon nanotubes (SWNT) containing different concentrations of randomly distributed point defects. The results are analysed using Weibull statistics, and the dependence of the statistical distribution of fracture strengths on defect concentration is established. Arguments from extreme order statistics are then used to formulate a relationship between the length of SWNT and their fracture strength. The results of this investigation help to explain the large differences between SWNT fracture strengths measured in experiments (13–52 GPa) and those obtained from theoretical calculations assuming defect-free nanotubes (∼185 GPa).

1. Introduction
Most of the studies on carbon nanotubes regard them as ‘ideal’ defect-free structures. However, since the discovery of carbon nanotubes [1], people have found out that defects on carbon nanotubes are very common and have significant influence on their properties, especially mechanical properties [2–6]. Several kinds of defects may occur on carbon nanotubes. In the present investigation, we focus on three kinds of localized (point-like) defects: functionalization defects caused by chemical functionalization [7–9], Stone–Wales type topological defects (5-7-7-5 defects) [3, 10, 11] and structural defects (vacancies) [12] as shown in figure 1. We use molecular mechanics to calculate the fracture strength of comparatively ‘short’ SWNT containing such defects in varying concentrations ranging from 0 to 7.5% for vacancies and functionalization defects, and from 0 to 2.5% for Stone–Wales defects (for these, we use lower defect concentrations since one topological defect changes the structure of four adjacent hexagons). We then use statistical arguments to address the size dependence of fracture strength and extrapolate our results to nanotube lengths used in experiments.

Computation techniques including quantum mechanics, molecular mechanics and continuum shell modelling have been used to evaluate mechanical properties of carbon nanotubes [13–20]. Among these techniques, molecular mechanics based on Brenner’s potential is generally considered accurate in simulating the mechanical properties of carbon nanotubes during quasi-static deformation and at not too high temperatures [21, 22]. (Given the high binding energies, thermal energies are negligibly small at ambient temperature where most deformation experiments have been carried out.) This potential is characterized by the quantum-mechanical concept of bond order formalism, and is particularly useful in modelling graphite and carbon nanotube structures when changes in bonding may occur. The fracture strength of defected carbon nanotubes observed in simulations with Brenner’s potential shows reasonable agreement with results obtained from quantum mechanics computations [23].

2. Methodology
To simulate SWNT under tensile load, we carry out a sequence of small elongation steps. In every step, we move the atoms at both ends of a carbon nanotube by a small amount (0.01 Å per step) in the axial direction from the centre of the SWNT as shown in figure 2. Then we relax the deformed SWNT by energy minimization, using Brenner’s code to evaluate the SWNT potential energy. A rigid restraint is applied which fixes the atoms at the ends to prevent the SWNT from restoring its initial structure (lowest-energy structure at zero load).


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Studies of nanotube-based resonant oscillators through multiscale modeling and simulation

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We propose a multiscale method to study nanotube-based resonant oscillators. In the multiscale model, nanotubes are modeled via molecular dynamics, while the metal paddle is modeled as a rigid body. The molecular and continuum models are attached to each other through the interfaces on which carbon atoms are located. We employ the concepts of “virtual” atoms and bonds to effectively couple the molecular and continuum models. Using the proposed multiscale method, we investigate both linear and nonlinear characteristics of resonant oscillators. Effects of vacancy and temperature on mechanisms of oscillators are discussed.

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I. INTRODUCTION

Since carbon nanotubes have extraordinary mechanical and electrical properties, they have been utilized as essential components in the design of novel nanoscale materials and devices. Tremendous molecular-dynamics simulations have been conducted to study the physical phenomena of nanotube-based composites and devices. Xiao and Hou studied the mechanics of nanocomposites in which defect-free carbon nanotubes were embedded through molecular-dynamics simulations. Srivastava employed molecular dynamics to discuss and test a phenomenological model for the rotational dynamics of a single laser-powered molecular motor that powered carbon nanotube-based gears. Molecular dynamics also assist researchers to investigate the temperature-related energy dissipation of nanoscale devices. Recently, a new nanoscale device in which an individual carbon nanotube serves as a torsional spring and mechanical support has been successfully fabricated. However, numerical modeling and studies of this device have not been reported.

Williams et al. reported the fabrication of nanoscale mechanical devices incorporating multiwalled carbon nanotubes (MWNTs) as the torsional spring elements. They utilized electron-beam lithography to pattern a device element directly onto an individual MWNT on a silicon dioxide substrate. Consequently, the device consisted of a suspended lever, i.e., the “paddle,” connected by an MWNT as a torsion beam. Papadakis et al. used similar techniques to synthesize asymmetric oscillators that were also called resonant oscillators. The metal paddles in their experiments were not centered on the MWNTs, and the MWNTs were strained primarily in torsion. Once the paddle was given an electrostatic force, the oscillation was observed and the measured resonance frequencies were in the range of 1–9 MHz. Such oscillators can be used as sensors and clocks for high-frequency electronics. For example, with these nanoscale resonant oscillators, the clocks can be achieved with a single-stage device. More recently, Meyer et al. built a torsional pendulum with an individual single-walled carbon nanotube (SWNT), which was also used as a torsional spring and mechanical support for the metal paddle. They reported that this SWNT-based pendulum could be reproducibly turned to any position between 0° and almost 180°. All of the fabricated resonant oscillators described above had a paddle with a volume of about 0.04 μm³ and a nanotube with a length of around 500 nm. Therefore, a molecular-dynamics model of such an oscillator may contain up to trillions of atoms and become infeasible for current computer resources.

Since molecular dynamics has limitations in simulating large nanosystems, multiscale methods are attractive to scientists and engineers. Recently developed multiscale modeling techniques have shown promise in treating phenomena at both nano- and larger scales. Multiscale methods can be divided into two classes: hierarchical multiscale methods and concurrent multiscale methods. Most hierarchical models contain a continuum approximation based on the properties of a subscale model, such as a molecular-dynamics (MD) model. The intrinsic properties of the material are determined at the atomic level and embedded in the continuum model according to a homogenization procedure. However, the effects of defects cannot be considered with nanoscale continuum approximation. Concurrent multiscale methods employ an appropriate model in which different methodologies are employed in each spatial scale simultaneously. The typical concurrent multiscale methods include the macroatomistic \textit{ab initio} dynamics (MAAD) method and the bridging domain coupling method. They mainly coupled a continuum model (finite element methods) with a molecular model (molecular dynamics). Consequently, large models can be simulated without losing physical phenomenon details at the nanoscale.

In this paper, we develop a multiscale method that couples a continuum model and a molecular model to study the mechanical behavior of nanotube-based resonant oscillators. In the proposed multiscale model, the nanotube is modeled with molecular dynamics, while the metal paddle is modeled as a continuum. The edge-to-edge coupling technique is employed in this multiscale method to efficiently attach the continuum model and the molecular model. Without losing accuracy, the metal paddle is treated as a rigid body since it has only small deformation during the torsional oscillation.

The outline of this paper is as follows. A multiscale modeling of nanotube-based resonant oscillators is proposed in Sec. II. The coupling of molecular dynamics and rigid body kinetics is introduced. In Sec. III, we discuss oscillation mechanisms of resonant oscillators that are linear oscillator
had lower energy dissipate rates, i.e., higher quality factors. The issue of energy dissipation should be considered when designing nanoelectromechanical systems utilizing nanotube-based resonant oscillators.

It should be noted that it was possible to simulate half of the resonant oscillator systems since the systems simulated in this paper were symmetric. However, if the metal paddle does not attach to the center of the carbon nanotube, the whole system must be modeled. On the other hand, we only consider SWNTs in this paper. The MWNT-based resonant oscillators can also be simulated via the proposed multiscale method. Such modeling and simulation will be our future research.

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Coupled quantum mechanical/molecular mechanical modeling of the fracture of defective carbon nanotubes and graphene sheets

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Coupled quantum mechanical/molecular mechanical (QM/MM) calculations were used to study the effects of large defects and cracks on the mechanical properties of carbon nanotubes and graphene sheets. The semi-empirical method PM3 was used to treat the QM subdomains and a Tersoff-Brenner potential was used for the molecular mechanics; some of the QM calculations were also done using density functional theory (DFT). Scaling of the Tersoff-Brenner potential so that the modulus and overall stress-strain behavior of the QM and MM models matched quite closely was essential for obtaining meaningful coupled calculations of the mechanical properties. The numerical results show that at the nanoscale, the weakening effects of holes, slits, and cracks vary only moderately with the shape of the defect, and instead depend primarily on the cross section of the defect perpendicular to the loading direction and the structure near the fracture initiation point. The fracture stresses for defective graphene sheets are in surprisingly good agreement with the Griffith formula for defects as small as 10 Å, which calls into question the notion of nanoscale flaw tolerance. The energy release rate at the point of crack extension in graphene was calculated by the J-integral method and exceeds twice the surface energy density by 10% for the QM(DFT)/MM results, which indicates a modest lattice trapping effect.

I. INTRODUCTION

Due to their favorable mechanical properties, carbon nanotubes (CNTs) and exfoliated graphene sheets have attracted considerable interest as nanoreinforcements for polymer composites. Electronic structure calculations1–7 of the mechanical behavior of pristine CNTs predict fracture strengths in the range of 75–135 GPa and ultimate strains of as much as 30%. However, manufacture of mass-quantities of perfect CNTs or graphene sheets may prove challenging; in practice, mechanical properties will often be limited by the presence of defects—in many cases of substantial size. Oxidative purification treatments8–10 are commonly used in the production of CNTs and we have suggested6,11 that these can result in pitting, which provides a plausible explanation for the deviations between the CNT strength measurements of Yu et al.12 and theoretical predictions. One route for the exfoliation of graphene sheets involves thermal exfoliation of graphite oxide.13 During this process approximately 30% of the carbon atoms are lost as CO2; thus, the resulting sheets are expected to be highly defected. A detailed understanding of the consequences of such defects may be crucial to the effective utilization of these materials.

Previous electronic structure calculations of defected CNTs were limited to small defects because of the high computational cost of QM calculations. Therefore, the studies6,14 of larger defects were restricted to MM calculations. However, the modified15,16 second generation17 Tersoff-Brenner (MTB-G2) potential employed in those calculations tends to systematically underestimate the strength of both pristine and defected CNTs as compared to QM calculations, and has been shown3 to predict qualitatively different mechanisms for the fracture of defected CNTs. Thus, a better understanding of the role of defects in CNTs necessitates electronic structure calculations.

One way to treat a system of large molecules is to adopt linear scaling QM methods, which reduce the order of computation to O(N), where N is the total number of orbitals. Another approach to treating large systems is to couple a QM method to an MM method so that the important regions of the system are treated quantum mechanically and MM interactions are used elsewhere. In fracture studies, only part of the system, such as the vicinity of defects, requires an accurate treatment of bond breaking; for such systems QM methods can be used for these regions and MM methods can be applied to the rest of the system. Although the MM potential does not need to be able to model bond fracture accurately, it must still predict stiffnesses and strengths that are consistent with the QM results; in the following we will present a simple scaling scheme to improve the compatibility of the QM and MM mechanical properties.

Here we describe a set of coupled quantum mechanical/ molecular mechanical (QM/MM) calculations of the fracture of CNTs with large defects and the fracture of graphene sheets. We also consider the effect of lattice trapping18–21 by calculating the energy release rate of a crack in a QM/MM model of a graphene sheet using the J-integral22 method.

The rest of the paper is organized as follows. Section II gives an overview of the coupling method and its implementation. In Sec. III the results of fracture in the presence of defects such as one- and two-atom vacancy defects as well as nanosized holes and slits are presented. Section IV describes the results for lattice trapping in graphene sheets. Conclusions are given in Sec. V.
nanoscale (5–20 nm) defects: for any defect, the strength is below the theoretical strength, as would be expected.

Crack-like defects, which we called slits, were constructed by removing four rows of carbon atoms in the zigzag CNTs and by removing three rows of carbon atoms in the armchair CNTs. The resulting dangling bonds were capped with hydrogen atoms. This is to be contrasted with crack models based on omitting bonds between adjacent atoms in MM calculations, which are pervasive in the literature. Such defects cannot exist in electronic structure models because interactions between nearby atom pairs cannot simply be neglected at moderate distances. Thus, the ability of such schemes to accurately model crack behavior is questionable. Crack-like defects can be formed by displacing a lattice according to the asymptotic near-field of elastic fracture mechanics, as we reported in Sec. IV. However, such cracks will not exist in a solid in a stress-free state.

To ascertain the magnitude of lattice trapping in graphene, we computed the energy release rate using a discrete J-integral and compared it to twice the surface energy density, $2\gamma$. These results indicate a modest amount of lattice trapping; the energy release rate calculated by DFT for a graphene sheet at fracture exceeds $2\gamma$ by 10%.

The coupled QM/MM calculations were performed with the ONIOM methodology. We checked the accuracy of the method by performing a series of calculations for small defects with QM fragments of increasing size. The resulting stress-strain curves agreed closely over most of the range even for relatively small QM fragments. The fracture stresses and strains also appear to converge, but are more sensitive to the QM fragment size and even for the largest two fragments studied, the fracture stresses and strains differed from the pure QM results by 4% and 8%, respectively, for a [10,0] CNT with a two-atom vacancy defect. Thus, the absolute accuracy of the coupled QM/MM calculations for the failure stress is probably only a few percent and the results are more useful for comparing defects of various sizes than in obtaining quantitative values of failure stresses.

We introduced a simple scaling scheme to improve the compatibility of the MM and QM models. If the MM interaction potential is used unscaled, mismatches between the stiffness and strength of the MM and QM subdomains result in highly spurious behavior. Comparisons of the QM/MM calculations with MM calculations using the scaled potential show good agreement for the failure stresses and stress-strain curves. In most cases, the differences were less than 15%, and the qualitative pattern of dependence on defect size agreed well. It should be noted that this good agreement is only achieved for the scaled MM potential. The details of the fracture processes predicted by the QM/MM method and the MM method differ significantly. For example, QM/MM calculations show significantly more elongation of the bond at the crack tip.

The results provide further credence to the hypothesis that large defects such as holes are the reason behind the low CNT fracture strengths observed in some experiments. Although the QM/MM models predict failure stresses that are about 40% higher than unscaled MM results modeled previously, they are still in the range observed in the Yu et al. experiments.

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Modulus, Fracture Strength, and Brittle vs. Plastic Response of the Outer Shell of Arc-grown Multi-walled Carbon Nanotubes

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Abstract The fracture strengths and elastic moduli of arc-grown multi-walled carbon nanotubes (MWCNTs) were measured by tensile loading inside of a scanning electron microscope (SEM). Eighteen tensile tests were performed on 14 MWCNTs with three of them being tested multiple times (3×C23, 2×C2, and 2×C2, respectively). All the MWCNTs fractured in the “sword-in-sheath” mode. The diameters of the MWCNTs were measured in a transmission electron microscope (TEM), and the outer diameter with an assumed 0.34 nm shell thickness was used to convert measured load-displacement data to stress and strain values. An unusual yielding before fracture was observed in two tensile loading experiments. The 18 outer shell fracture strength values ranged from 10 to 66 GPa, and the 18 Young’s modulus values, obtained from a linear fit of the stress–strain data, ranged from 620 to 1,200 GPa, with a mean of 940 GPa. The possible influence of stress concentration at the clamps is discussed.

Keywords Nanotube · Fracture · Yield · Modulus · Strength

Introduction

The experimental discovery of multi-walled carbon nanotubes (MWCNTs) in 1991 [1] and single-walled carbon nanotubes (SWCNTs) in 1993, [2, 3] has spawned considerable interest in carbon nanotubes. Theoretical studies have predicted that defect-free CNTs should have a Young’s modulus of ~1 TPa, [4–6] similar to the in-plane modulus of graphite (if a shell thickness of 0.34 nm is used). Among numerous examples, MWCNTs have been studied in nanoscale devices, [7–9] and as filler in composites [10–12]. The mechanical properties of CNTs are clearly of both intrinsic and practical importance.

Several techniques have been developed for exploring the mechanical properties of individual CNTs. For example, the elastic moduli of cantilevered MWCNTs were obtained from mechanical resonance observed inside a TEM [13–16]. The elastic moduli of MWCNTs deposited across pores on an alumina nanopore membrane were obtained from bending tests carried out with an AFM, [17] and the same approach was used to obtain the elastic and shear moduli of SWCNT ropes [18]. The fracture strengths and elastic moduli of MWCNTs [19] and SWCNT ropes [20] have been obtained by tensile testing inside a SEM.

We present a detailed study of the mechanical properties of arc-grown MWCNTs by tensile loading inside an SEM. Individual MWCNTs were tensile loaded until fracture by using a piezo-actuated nano-manipulator [21]. The fracture strengths, failure strains and elastic moduli of the MWCNTs were obtained from the measured geometry, the load at failure, and the load-displacement (which with the measured geometry is converted to stress–strain) data. No


Optimized adhesives for strong, lightweight, damage-resistant, nanocomposite materials: new insights from natural materials

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Abstract
From our investigations of natural composite materials such as abalone shell and bone we have learned the following. (1) Nature is frugal with resources: it uses just a few per cent glue, by weight, to glue together composite materials. (2) Nature does not avoid voids. (3) Nature makes optimized glues with sacrificial bonds and hidden length. We discuss how optimized adhesives combined with high specific stiffness/strength structures such as carbon nanotubes or graphene sheets could yield remarkably strong, lightweight, and damage-resistant materials.

1. Introduction

The abalone shell, a composite of calcium carbonate plates sandwiched between organic material, is 3000 times more fracture resistant than a single crystal of the pure mineral [1]. The organic component, comprising just a few per cent of the composite by weight, working together with the structural geometry [2, 3], is thought to hold the key to nacre’s fracture toughness [4].

In addition to the details of the structural geometry, one of the main mechanisms that lets a few per cent of ‘glue’ make such an enormous difference in fracture toughness is the sacrificial bond and hidden length mechanism [4, 5]. By ‘glue’ in this context we mean polymer adhesive molecules that hold together the hard elements in a composite structure. In the case of biological structures these glues tend to be composed of proteins, proteoglycans, and glycoproteins. The study of such glues is just in its infancy, but so far it appears that one of the key factors is the presence of charged side groups on the biological polymer adhesive molecules that can form sacrificial bonds with other charged groups on the polymers and on the hard elements—sometimes with the help of ions in solution. For example, Ca\textsuperscript{2+} ions can help form sacrificial bonds between negatively charged side groups such as phosphate groups.

Sacrificial bonds and hidden length in structural molecules and composites have been found to greatly increase the fracture toughness of biomaterials by providing a reversible, molecular-scale energy-dissipation mechanism. This mechanism relies on the energy, of order 100 eV, needed to reduce entropy and increase enthalpy as molecular segments are stretched after being released by the breaking of weak bonds, called sacrificial bonds. This energy is relatively large compared to the energy needed to break the polymer backbone, of order a few eV. In many biological cases, the breaking of sacrificial bonds has been found to be reversible, thereby additionally providing a ‘self-healing’ property to the material. Due to the nanoscopic nature of this mechanism, single molecule force spectroscopy [6–8] using an atomic force microscope has been a useful tool to investigate this mechanism [4, 5].

Bone consists of mineralized collagen fibrils and a non-fibrillar organic matrix, which acts as a ‘glue’ that holds the mineralized fibrils together [9]. Here again the glue is just a few per cent by weight. This glue may resist the separation of mineralized collagen fibrils. As in the case of the abalone shell, in addition to the details of the structural geometry, one of the main mechanisms that lets a few per cent of glue make such an enormous difference in fracture toughness is the sacrificial bond and hidden length mechanism [4, 10]. This mechanism is also used in spider silk [11] and some diatoms, which are...
needs to consider the statistical nature of defects that results in a decrease of strength with length or size for conventional materials; this can perhaps be mitigated, and perhaps even eliminated, by future developments in fabrication techniques for the nanotubes. One must however appreciate the challenge of synthesizing carbon nanotubes that are completely defect free, and there is no evidence that such defect free CNTs have been produced to date. If one accepts that the CNTs will have some defects that reduce their strength, then a real optimized adhesive must be chosen as a compromise between the benefits of longer strong elements, such as a lower percentage of the weaker glue, with the disadvantage that longer strong elements may themselves be weaker! It is thus of interest to consider the types of defects that have the largest impact on strength of CNTs—namely point defects or clusters of missing atoms (in short, holes) [27–29, 32, 33]. Indeed, even a few missing atoms and thus small holes in the tube structure can cause a significant reduction in strength, as is discussed in detail elsewhere [27]. In this regard, it is possible that graphene sheets, if extracted from ‘high quality’ graphite, might contain both smaller, and also fewer, critical defects. On the other hand, synthetic approaches which yield essentially perfect (defect-free) carbon nanotubes may yet be found.

3. Summary

The concept of an optimized adhesive is based on using only enough adhesive to fully transfer the desired load to the strong elements in a composite material. This full transfer will require a fixed number of adhesive molecules—indeed, independent of the length of the strong element. Thus, the longer the strong elements, the less the fractional weight of the glue in the composite material. Fractional weights as small as a few per cent are found in natural materials such as abalone shells and bone.

Making synthetic composite materials with just a few per cent of glue remains a challenge for the future. Nature gives us some hints to help. For example, it is not important to avoid microscopic voids. In fact it is better to have microscopic voids than to fill them with excess glue molecules because these can actually weaken the material. Moreover, it is useful to use entropic elasticity or friction to dissipate energy in the glue molecules rather than in breaking strong bonds if we want a tough material. Finally, it is useful to focus on having the only bonds that are broken during energy dissipation be weak bonds that can be reformed, such as Coulomb or van der Waals or hydrogen bonds if we want a self-healing material.

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Parallel replica dynamics for driven systems: Derivation and application to strained nanotubes

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We show that parallel replica dynamics can be extended to driven systems (e.g., systems with time-dependent boundary conditions). Each processor simulates a replica at a driving rate that is $M$ times faster than the desired rate, where $M$ is the number of processors. As in regular parallel replica dynamics, when a transition to a new state is detected on any processor, the times are summed and every processor is restarted in the new state. The state-to-state dynamics are shown to be correct if the processors run at the same speed and the system is driven slowly enough (on each processor) so that the escape rates do not depend on the time history of the drive. We demonstrate the algorithm by stretching a carbon nanotube with a preexisting vacancy, noting a significant dependence of the nature of nanotube yield on the strain rate. In particular, we are able to achieve strain rates slow enough such that the time scale for vacancy diffusion is faster than that for mechanical yield at a temperature of 2000 K. We thus observe vacancy-induced morphological changes in the nanotube structure, providing some insight into previously unexplained experimental features.

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I. INTRODUCTION

The molecular-dynamics (MD) simulation method has proven marvelously powerful in a large variety of studies in physics, chemistry, materials science, and biochemistry. It provides a view of system behavior with full atomic detail, requiring only a form for the interatomic forces and the assumption that the dynamics are well described by classical mechanics. An important limitation, however, is the fact that MD simulation times are limited to at most microseconds—while technologically important and scientifically interesting processes typically take place over longer times. For many systems, the evolution on these longer time scales consists of extended periods of uninteresting excursions within a single state of the system (e.g., thermal vibrations within a local energy basin), punctuated by occasional fluctuation-based events that take the system to a new state. For this type of system, it has not been obvious that AMD methods can be directly applied, as the state-to-state rate constants are in general changing with time.

In this paper, we show that parallel replica dynamics can in fact be generalized to treat this type of driven-system case. We derive the relevant equations in the presence of time-dependent rate constants and discuss the additional requirements on the system and on the implementation for the approach to be valid. We then demonstrate the method by stretching (to yield) a carbon nanotube with a preexisting vacancy at strain rates inaccessible to direct MD. For different strain rates, we see significant differences in both how the nanotube yields and in the details of atomic motion leading up to yield. We also see the formation of features that are the result of morphological changes caused by the motion of the preexisting vacancy. Such features have been previously observed in experiment in which nanotubes suspended on a substrate were irradiated with electrons, though their origin was unknown.

II. PARALLEL REPLICA DYNAMICS

The complete derivation of parallel replica dynamics has been given previously; we summarize it here. The parallel replica method assumes only that, once a correlation time has passed since the system entered the present state, the probability distribution function for the time to the next escape is exponential,

$$p_{\text{escape}}(t)dt = k \exp(-kt)dt.$$  

This applies to a typical MD simulation performed on a single processor. Here, $k$ is the total escape rate to leave that state, i.e., the sum of the rates for all the individual escape paths. This exponential condition holds for any chaotic, er-
Vacancy defects and the formation of local haecckelite structures in graphene from tight-binding molecular dynamics

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The dynamics of multivacancy defects in a graphene layer is investigated by tight-binding molecular dynamics simulations and by first principles calculation. The simulations show that four single vacancies in the graphene layer first coalesce into two double vacancies, each consisting of a pentagon-heptagon-pentagon (5-8-5) defective structure. While one of the 5-8-5 defects further reconstructs into a 555-777 defect, which is composed of three pentagonal rings and three heptagonal rings, another 5-8-5 defect diffuses toward the reconstructed 555-777 defect. During the 5-8-5 defect diffusion process, three interesting mechanisms, i.e., “dimer diffusion,” “chain diffusion,” and “single atom diffusion,” are observed. Finally, the four single vacancies reconstruct into two adjacent 555-777 defects, which is a local haecckelite structure.

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I. INTRODUCTION

Vacancy is one of the most common defects in crystalline solids and affects profoundly the physical properties of the solids. Low concentration of vacancy defects present in graphite1 during defective growth or as part of the thermal equilibrium process. These defects are much more prevalent in electron or ion irradiated materials and are believed to be the predominant defects on irradiated graphite surfaces.2 Since graphite is commonly used as a substrate in various microscopy techniques,3 characterization of surface defect in graphite at the atomic scale is an important research drive. Point defects induced by irradiation damage in graphite is also a subject of great scientific and technological interest because of the application of graphite as moderators in thermal nuclear reactors.4 Furthermore, the emerging field of carbon nanoscience5 shares a lot of useful information from graphitic systems including defect structure and energetics. Various carbon nanostructures such as carbon nanotube branched junctions6–8 have been produced through generation and recombination of vacancy defects in single-walled carbon nanotubes.

Vacancy in graphitic systems has attracted considerable experimental and theoretical studies for many years. Various advanced experimental techniques such as scanning tunneling microscope (STM),2 positron annihilation spectroscopy,9 and transmission electron microscope10 have been used to investigate the structure and properties of vacancies in graphite and carbon nanotubes. At the same time, a number of theoretical calculations have also been performed to study the vacancy in graphite.11–15 However, most of the previous theoretical studies focused only on the structure of single vacancy. Much less is known for the dynamics of the vacancy as well as the structure and dynamics of multivacancies. In order to gain more information about the structures of multivacancies, the dynamical behavior of vacancies, and the effects of vacancies on the structure and stability of the graphene layer, atomistic simulation studies of multivacancies in a graphene layer will be very useful and highly desirable.

Since classical molecular dynamics simulations are not reliable for studying such complex systems as vacancy defects in graphite or carbon nanotube and ab initio molecular dynamics is too expensive for long time dynamical simulation of large systems, we chose to perform the quantum molecular dynamics simulation for these systems using the tight-binding molecular dynamics (TBMD) method. Recently, we have modified the environment-dependent tight-binding (TB) carbon potential by Tang et al.16 We have also used this modified TB potential to investigate the structure and energetics of vacancy and adatoms in a graphene layer and carbon nanotube and performed TBMD simulations to study the dynamics of vacancy in a graphene layer. In this paper, TBMD simulation studies of the structure and dynamics of multivacancies in a graphene layer will be reported. In particular, the collective behavior of the vacancies and the diffusion of a double vacancy observed from the TBMD simulations will be discussed in detail.

II. CALCULATIONAL METHOD

The TBMD simulations are performed using the recently modified environment dependent tight-binding (EDTB) carbon potential. We note that the original EDTB carbon potential by Tang et al. is not sufficient to describe the angle dependence of the bonds because the effective interatomic distance is scaled only by the coordination number which is not angular sensitive.16 In our modified potential, the angle dependence of bonds is taken into account by redefining the...
VACANCY DEFECTS AND THE FORMATION OF LOCAL…

The simulated STM image of local haeckelite structure shows that the carbon atoms in pentagonal rings contribute to the bright spots.

IV. SUMMARY

We have performed TBMD simulation for a graphene layer with four scattered single vacancies. In the simulation, the single vacancies first coalesce into double vacancies of 5-8-5 defect structure and then further reconstruct into a local haeckelite structure consisting of two neighboring 555-777 defects. During the reconstruction process, we also observed three interesting mechanisms for the diffusion of a 5-8-5 vacancy. These mechanisms are “dimer diffusion,” “chain diffusion,” and “single atom diffusion” mechanisms. The simulated STM image of local haeckelite structure shows that the carbon atoms in pentagonal rings contribute to the bright spots.

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ACKNOWLEDGMENTS

18. http://cms.mpi.univie.ac.at/vasp/
Abstract

The fracture strain of carbon nanotubes (CNTs) obtained by molecular dynamics is about 30%, which is much higher than the experimental results (10–13%). The present study shows that this difference results mainly from defects in CNTs. As the tensile strain reaches a few percent, defects are nucleated in the form of Stone–Wales transformation (90° rotation of a bond). A bond in the vicinity of rotated bond breaks as the tensile strain reaches about 13%, which agrees well with the experimental results. Therefore, the Stone–Wales transformation is the precursor of CNT fracture.

Keywords: Stone–Wales transformation; Bond breakage; Fracture; Carbon nanotube

1. Introduction

Carbon nanotubes (CNTs) possess superior properties and have many potential applications such as nanoelectronics, nanoscale electromechanical systems (NEMS), and nanocomposites. The mass density of CNTs is only one-sixth of that for steel, but their Young’s modulus is six times higher than steel and is of the order 1 TPa; the strength of CNTs is of the order 50 GPa, which is two orders of magnitude higher than that of steel (e.g., see the review articles, [1–5]).

The atomistic studies have shown that CNTs have large tensile fracture strain around 30% [6–8] or even higher [9]. The continuum theory of Zhang et al. [10] and Jiang et al. [11] based on interatomic potentials for carbon [12,13] also predicts the fracture strain in the same range [14,15]. However, the experimental studies of Yu et al. [16] for multiwall CNTs found the tensile failure strain of CNTs between 10% and 13%, which is much lower than the aforementioned atomistic simulations or atomistic-based continuum studies. Most multiwall CNTs fail in a sheath-like pattern with only the outer nanotube failing. Since the van der Waals interactions between CNT walls are weak, this failure is essentially the same as that for single-wall CNTs. Yu et al. [17] also measured the failure strain of single-wall CNT bundles, and found even lower failure strains around 5–6%. Belytschko et al. [18] and Dumitrica et al. [19] showed that this discrepancy between the atomistic and experimental studies of failure strains can be attributed to the nonphysical cutoff function introduced in Brenner’s [12] interatomic potential. They used a modified Morse potential to fit the Brenner potential for strain up to 10%, and predicted the failure strain between 10% and 16%, which agrees with most of Yu et al.’s [16] experimental results.

Belytschko et al. [18] introduced a weak bond in the CNT to serve as the site for bond breakage in their atomistic simulations of CNT fracture. The strength of the weak bond was 10% lower than others. The weak bond broke first upon loading, and bond breakage rapidly propagated to neighbor bonds, leading to brittle fracture of the CNT. It is unclear, however, whether the fracture strain of CNTs depends on this imperfection. It is also unclear how fracture starts in a perfect CNT without any preexisting defects.

The purpose of this paper is to study the failure of single-wall CNTs without introducing any initial imperfections.
shown in Fig. 7(b) gives the lowest strain for bond breakage in the vicinity of rotated bond. The critical strain (9.8%) for Stone–Wales transformation in zigzag (10,0) CNT is much higher than its counterpart (5.5%) for (5,5) armchair CNT, but the strains for bond breakage are rather close (12.7% versus 13.3%), and both agree well with the fracture strain reported in Yu et al.’s [16] experiments.

4. Concluding remarks

We have used a hybrid atomistic/continuum model to study the Stone–Wales transformation and bond breakage in carbon nanotubes (CNTs) subject to tension. It is shown that bond breakage occurs after the Stone–Wales transformation, and the failure strain is about 13%, which is much smaller than the fracture strain (around 30%) reported in molecular dynamics studies, but it agrees well with the experimental results. Therefore, the Stone–Wales transformation is the precursor of CNT fracture. In other words, bond breakage does not occur directly in a perfect CNT which requires 30% strain. Instead, it follows Stone–Wales transformation and occurs at only 13% strain.

Acknowledgments

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A comparison of different methods of Young’s modulus determination for single-wall carbon nanotubes (SWCNT) using molecular dynamics (MD) simulations

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Abstract

The computed values of Young’s modulus (Y) of single-wall carbon nanotubes given by four common methods based on (i) the determination of stress for a fixed value of strain, (ii) the determination of strain energy for a fixed value of strain, (iii) the longitudinal vibrations, and (iv) the transverse vibrations, and a new method (v) based on the determination of strain for a fixed value of stress have been compared to check the consistency of different methods. The computed values of Y are found to be in agreement with each other with the exception that results of the transverse vibration method differ from those given by other methods when the aspect ratio, namely, the ratio of length to the radius of the tube, is small; the results of the transverse vibration method for the tubes of small diameter are also found to differ from those given by other methods when the commonly used value of thickness of the tube, 3.4 Å, is assumed. The solutions of these problems are discussed in terms of an appropriate consideration for the value of thickness and diameter dependent end-correction in the length of the tube. Effect of defects in the form of vacancies, van der Waals (VDW) interactions, chirality, and diameter of the carbon nanotubes on Y has also been investigated. Y is found to be sensitive to the number of vacancies. Y is found to decrease by ~1% when VDW interactions between carbon atoms are ignored. Y is also found to be lower for an armchair tube compared to a zigzag tube of the same diameter. As regards the dependence of Y on diameter, we found that as the diameter increases from ~7 Å to ~25 Å, Young’s modulus drops by 4% and 8%, respectively, for armchair and zigzag tubes. These results are discussed and compared with other experimental and computed results reported in the literature.

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Keywords: Carbon nanotubes; Young’s modulus; MD simulations

1. Introduction

Since the discovery of carbon nanotubes (CNTs) in 1991 by Iijima [1], much attention has been focused on the exploration and application of their extraordinary physical properties. Qian et al. [2] have shown that an addition of just 1 wt.% CNTs results in a 25% increase in the tensile strength of polystyrene-based composite film. With the rapid progress towards the synthesis of large quantity and high quality CNTs in recent years, carbon nanotubes have been used as nanofillers to enhance the mechanical strength of polymeric matrices [3–6]. Among the mechanical properties of nanotubes, the axial Young’s modulus (Y) shows an extraordinary feature in that its value is exceptionally high.

The determination of Young’s modulus for CNTs has been a subject of considerable interest [7]. The computation of Y of CNTs may be classified into two categories. One is molecular dynamics (MD) simulation using a potential

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References


Mechanical properties of ultrananocrystalline diamond prepared in a nitrogen-rich plasma: A theoretical study

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We examine the mechanical properties of ultrananocrystalline diamond (UNCD) produced by plasma-enhanced chemical vapor deposition, with a focus on thin films created with high levels of nitrogen in the plasma. A model with several of the attributes of the corresponding experimental UNCD is developed and its properties explored. Simulations are performed using semiempirical quantum mechanics and density functional theory. Our results predict a Young’s modulus of 0.69 TPa, failure strain of 0.13, and a tensile fracture stress of 61 GPa which are 66%, 100%, and 61%, respectively, of those predicted for UNCD produced in the absence of nitrogen. As in the case of UNCD produced without nitrogen in the plasma deposition, the fracture stress ($\sigma_f = 61$ GPa) is very large compared to that observed experimentally; these indicate that the experimental specimens contain large defects and some estimates are made of the size of these defects using the Griffith formula with the surface energy computed here. The effect of nitrogen on the mechanical properties of atom-wide UNCD grain boundaries is also investigated. Throughout, the accuracy of the various simulation methods is compared and evaluated.

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I. INTRODUCTION

Plasma-enhanced chemical vapor deposition techniques can be used to make thin diamond films composed of extremely small (3–5 nm) diamond grains and atom-wide grain boundaries (~0.2–0.4 nm wide).1–4 The material, which is called ultrananocrystalline diamond (UNCD), has very impressive mechanical properties (hardness, fracture stress, smoothness).5–8 Adding nitrogen to the plasma used to make these films has a dramatic effect on their electrical conductivity.9–14 Because of these properties, UNCD is an excellent candidate for use in the production of microelectromechanical and nanoelectromechanical systems.15,16

Low-level plasma-nitrogen films have morphologies which are similar to those produced in the absence of nitrogen. However, the structure of UNCD changes significantly as the level of nitrogen in the plasma is increased above 5%.10 Grain boundaries (GB’s) become significantly wider, and the average single-crystal diamond (SCD) grain size increases. For example, films produced using 20% plasma nitrogen have GB’s which are ~2 nm wide and average grain sizes of 16 nm.13

Increased plasma-nitrogen levels also result in an increased GB volume fraction. This fraction can be estimated using17

$$V_{GB} = \frac{3\Delta(d - \Delta)^2}{d^3},$$

where $\Delta$ is the GB thickness and $d$ the average grain diameter. For UNCD produced without nitrogen in the plasma, $\Delta \sim 0.3$ nm and $d \sim 4$ nm, which suggests a $V_{GB} = 0.19$, and 20% plasma-nitrogen films have a $\Delta \sim 2$ nm and $d \sim 16$ nm, so $V_{GB} = 0.29$.

The differences in volume fraction and average grain size suggest that whereas for films produced in the absence of plasma nitrogen one can envision a material in which grains essentially butt up against each other, high-level plasma-nitrogen films are better envisioned as diamond grains embedded in large amounts of GB material.

The GB’s are composed of a mix of $sp^2$- and $sp^3$-hybridized carbon.13 Near-edge x-ray-absorption fine-structure spectroscopy suggests that 13.5% of the carbon in films produced with 20% plasma nitrogen is $sp^2$ hybridized.13 Assuming that all of the $sp^2$ carbon is confined to the GB’s, this 13.5% value suggests that 0.135/0.287 or 47% of GB carbon atoms are $sp^2$ hybridized.

Some nitrogen is incorporated into UNCD films produced with nitrogen in the plasma. High-resolution secondary-ion-mass spectroscopy indicates that the level of nitrogen in the films is a maximum when they are grown with 18% plasma nitrogen.13 At this nitrogen level, the nitrogen concentration in the resulting films is $2.2 \times 10^{20}$ cm$^{-3}$ (1–2 nitrogen atoms per 1000 carbon atoms). The nitrogen is thought to be present at the GB’s rather than being within the SCD grains.18

The presence of SCD grains cemented to each other by wide GB layers (which have widths which are on the same length scale as the grain radii) makes nitrogen-rich plasma UNCD films a kind of composite material. These films are different than most composites in that the distinct materials are, in this case, both made of carbon atoms, whereas in most others, each component has a higher level of chemical distinctness. Nevertheless, this UNCD is composed of grains which are SCD like and of GB’s which exhibit, because of their high level of $sp^2$ hybridization, some properties which are not exhibited by other diamond thin films.

There appears to be excellent connectivity between the two phases, resulting in a material that is extremely stiff and strong. For example, UNCD has a Young’s modulus18 $E = 0.850$ TPa and a tensile fracture stress19 $\sigma_f = 2–3$ GPa. Both of these values approach those of natural diamond20–22 ($E \sim 1$ TPa and $\sigma_f \sim 4$ GPa).
A progressive fracture model for carbon nanotubes

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Abstract

An atomistic-based progressive fracture model for simulating the mechanical performance of carbon nanotubes by taking into account initial topological and vacancy defects is proposed. The concept of the model is based on the assumption that carbon nanotubes, when loaded, behave like space-frame structures. The finite element method is used to analyze the nanotube structure and the modified Morse interatomic potential to simulate the non-linear force field of the C–C bonds. The model has been applied to defected single-walled zigzag, armchair and chiral nanotubes subjected to axial tension. The defects considered were: 10% weakening of a single bond and one missing atom at the middle of the nanotube. The predicted fracture evolution, failure stresses and failure strains of the nanotubes correlate very well with molecular mechanics simulations from the literature.

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Keywords: A. Nanostructures; B. Fracture; C. Finite Element Analysis (FEA); Carbon nanotubes

1. Introduction

Carbon nanotubes (CNTs), due to their extraordinary mechanical properties, have stimulated great interest and extensive research with regard to the measurement of their exact mechanical properties and search for potential structural applications ever since their discovery by Iijima [1]. Specific characteristics, such as the exceptionally high stiffness and strength, which are in the range of TPa, the extreme resilience, the ability to sustain large elastic strain as well as the high aspect ratio and low density make CNTs the ideal reinforcing material for a new class of superstrong nano-composites [2]. Besides the use of CNTs as conventional carbon fibers for reinforcing polymer matrix, several potential applications have been lately explored. Amongst them, is the use of CNTs for improving the out-of-plane and interlaminar properties of currently used advanced composites as well as their alignment perpendicular to cracks in order to slow down the crack growth by bridging up the crack faces [3,4].

The effective use of CNTs in structural applications depends on their mechanical performance as stand alone units. Experimental observations have revealed that topological defects, such as the Stone–Wales defect and vacancy defects, are commonly present in CNTs [5]. Defects degrade the mechanical performance of CNTs, since they alter not only their inelastic properties but also the elastic, such as the Young’s modulus and Poisson’s ratio. The longitudinal and transverse stiffnesses as well as the flexural rigidity in tension, torsion and bending are, consequently, being altered. For example, Chandra et al. [6] have shown that the presence of Stone–Wales defect reduces the stiffness of the defected area by about 30–50% resulting in reduction of the nanotube Young’s modulus.

Mechanical properties and deformation of CNTs have been extensively studied during the last few years both experimentally and theoretically. From the viewpoint of


On the strength of the carbon nanotube-based space elevator cable: from nanomechanics to megamechanics

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Abstract

In this paper various deterministic and statistical models, based on new quantized theories proposed by the author, are presented for estimating the strength of a real, and thus defective, space elevator cable. The cable, ~100 000 km in length, is composed of carbon nanotubes, ~100 nm long: thus, its design involves nanomechanics and megamechanics. The predicted strengths are extensively compared with the experimental and atomistic simulation results for carbon nanotubes available in the literature. All these approaches unequivocally suggest that the megacable strength will be reduced by a factor at least of ~70% with respect to the theoretical nanotube strength, today (erroneously) assumed in the cable design. The reason is the unavoidable presence of defects in so huge a cable. Preliminary in-silicon tensile experiments confirm the same finding. The deduced strength reduction is sufficient to place in doubt the effective realization of the space elevator, that if built as designed today will certainly break (in the author’s opinion). The mechanics of the cable is also revised and possible damage sources discussed.

(Some figures in this article are in colour only in the electronic version)

Invited paper presented at Nanoscience and Nanotechnology 2005

1. Introduction

A space elevator (figure 1) basically consists of a cable attached to the Earth’s surface for carrying payloads into space (Artsutanov 1960). If the cable is long enough, i.e., around 150 000 km (reducible by a counterweight), the centrifugal forces exceed the gravity of the cable, that will work under tension (Pearson 1975). The elevator would stay fixed geosynchronously. Once sent far enough, climbers would be accelerated by the Earth’s
On the strength of the carbon nanotube-based space elevator cable S1989

to be reduced by a factor of at least ~70% with respect to the theoretical strength of a carbon nanotube, assumed in the current design. Such a reduction is sufficient to cast doubt on the effective realization of the space elevator. It is the author’s opinion that the cable, if realized as designed today (see Edwards and Westling 2003), will break.

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Ozonization at the Vacancy Defect Site of the Single-Walled Carbon Nanotube

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The ozonization at the vacancy defect site of the single-walled carbon nanotube has been studied by static quantum mechanics and atom-centered density matrix propagation based ab initio molecular dynamics within a two-layered ONIOM approach. Among five different reaction pathways at the vacancy defect, the reaction involving the unsaturated active carbon atom is the most probable pathway, where ozone undergoes fast dissociation at the active carbon atom at 300 K. Complementary to the experiments, our work provides a microscopic understanding of the ozonization at the vacancy defect site of the single-walled carbon nanotube.

1. Introduction

Single-walled carbon nanotubes (SWCNTs) have been intensively studied during the past decade since the discoveries of Iijima in the early 1990s. A lot of potential applications of the SWCNTs have been proposed due to their unique properties: high Young’s modulus, high thermal conductivity, and high aspect ratio structure, etc. Over the years, applications of the SWCNTs have been successfully realized as chemical sensors, hydrogen storage materials, and vacuum electronic devices. Access to the interior of the SWCNTs is essential for most of these applications.

Unfortunately, most of the SWCNTs are synthesized with closed hemispherical fullerene-like end-caps, which prevent internal adsorption of chemical reagents. It is thus often necessary to open the capped ends via chemical means, which take advantage of the higher reactivity of the end-caps. Such a higher reactivity is a result of the fact that the pyramidalization angles of any hemispherical fullerene-like end-caps are bigger than those of the sidewalls of the nanotubes. Gas-phase ozone oxidation is one of the well-developed end-opening methods. The oxidation process removes the caps and introduces or enlarges vacancy defects on the sidewall, producing two kinds of functional groups, esters and quinones, at the ends or at the defective sites of the sidewall. After high-temperature thermal treatment, these two functional groups will decompose and emit a large amount of CO and CO2. Olefin ozonolysis can be understood through the standard Criegee’s mechanism (Scheme 1). As an 18-valence-electron, 1,3-dipolar molecule, ozone reacts with an olefin via the 1,3-dipolar cycloaddition (1,3-DC) to the σ bond of the olefin and forms the primary ozonide, which has an unstable five-membered ring. The C–C single bond and one of the O–O bonds of the primary ozonide then break to produce a carbonyl compound and a carbonyl oxide in a zwitterion form. These two compounds will recombine to form an ozonide. Recently, a similar Criegee’s mechanism has been proposed in the reactions of ozone with C60 and the SWCNTs.

Several theoretical studies have been carried out to understand the ozonization of the perfect SWCNTs and the SWCNTs with Stone-Wales defects. To the best of our knowledge, there has been no reported theoretical studies on the chemical reaction of ozone with the vacancy defect sites of the SWCNTs. Vacancy defects can either occur as native defects or be induced by ion or electron irradiation of the SWCNTs. The structures, mechanical and electronic properties, and potential applications of the SWCNTs with vacancy defects have been recently predicted theoretically. Direct observations of the vacancy defects on graphite and double-walled carbon nanotubes have been reported recently by Iijima and co-workers using in situ high-resolution transmission electron microscopy technique. In our previous studies, we have shown that the vacancy defect introduces localized electronic states at the defect site, which leads to regioselectivity on the sidewall and further facilitates the selective functionalization of the SWCNTs. Such reactivity of the vacancy defect was utilized to cut the SWCNTs in a well-controlled oxidative way by Smalley and co-workers.

In this work, we present our theoretical studies of the ozonization at the single vacancy defect site on the sidewall of the (5,5) SWCNT to further understand the chemical properties of the vacancy defect site. We anticipate a similar reactivity of the vacancy defects on the outermost layer of the multiwalled carbon nanotubues (CNTs), because the large interlayer distance makes the chemical effect of the inner CNTs on the outermost CNT unlikely. Moreover, the chirality of the SWCNT should have a more important effect on the reactivity of the vacancy defect than the diameter of the SWCNT, since the chirality of the SWCNT can readily modify the structure of the vacancy defect. It is our hope that our studies will make the first step toward the comprehensive understanding of the chemistry of the vacancy defect site of CNTs of various forms.

2. Computational Methods

We first built a fragment of the (5,5) SWCNT of 120 carbon atoms with 20 end-capping hydrogen atoms, C120H20. The hydrogen atoms are used to saturate the carbon atoms with dangling bonds at the two ends. We then removed one carbon atom from the middle of the sidewall of C120H20, producing an ideal single vacancy, which contains three carbon atoms with dangling bonds (Figure 1a). Due to the large system size, we first employed the semiempirical AM1 method to optimize the geometry. We further refined the AM1 optimized geometry with density functional theory (DFT) at the B3LYP/6-31G(d)
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Dynamic quantized fracture mechanics

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Abstract A new quantum action-based theory, dynamic quantized fracture mechanics (DQFM), is presented that modifies continuum-based dynamic fracture mechanics (DFM). The crack propagation is assumed as quantized in both space and time. The static limit case corresponds to quantized fracture mechanics (QFM), that we have recently developed to predict the strength of nanostructures. DQFM predicts the well-known forbidden strength and crack speed bands—observed in atomistic simulations—which are unexplained by continuum-based approaches. In contrast to DFM and linear elastic fracture mechanics (LEFM), that are shown to be limiting cases of DQFM and which can treat only large (with respect to the “fracture quantum”) and sharp cracks under moderate loading speed, DQFM has no restrictions on treating defect size and shape, or loading rate. Simple examples are discussed: (i) strengths predicted by DQFM for static loads are compared with experimental and numerical results on carbon nanotubes containing nanoscale defects; (ii) the dynamic fracture initiation toughness predicted by DQFM is compared with experimental results on microsecond range impact failures of 2024-T3 aircraft aluminum alloy. Since LEFM has been successfully applied also at the geophysics size-scale, it is conceivable that DQFM theory can treat objects that span at least 15 orders of magnitude in size.

Keywords Dynamic fracture · Quantized fracture · Finite fracture · Nanostructures · Nanotubes · Strength · Impacts

1 Introduction

Two classic treatments of linear elastic fracture mechanics (LEFM) are Griffith’s criterion (1920), an energy-based method, and a method based on the stress-intensity factor developed by Westergaard (1939). These have been shown to be equivalent, as in the correlation between (static) energy release rate and stress-intensity factors formulated by Irwin (1957). An extension towards dynamic fracture mechanics (DFM) was proposed by Mott (1948), which included in Griffith’s energy balance the contribution of the kinetic energy. Dynamic stress-intensity factors were then also proposed, as well as the dynamic generalization of Irwin’s correlation, see the Freund’s book (1990). Since LEFM and DFM can be applied only to large and sharp cracks under moderate loading rates, we choose to modify them by accounting for the dis-
References


The asymptotic properties of random strength and compliance of single-walled carbon nanotubes using atomistic simulation

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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 ($\sigma_u$) and compliance ($C$) of single-walled nanotubes (SWNTs) containing random defects using the technique of atomistic simulation (AS). The defects considered are of the Stone–Wales (SW) kind and a Matern hard-core random field applied on a finite cylindrical surface is used to describe the spatial distribution of the SW defects. A nanotube can be viewed as consisting of nominally identical segments of equal length possessing a stationary distribution of ultimate strength, $\sigma_u$. 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 $\sigma_u$ (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. We simulate a set of displacement controlled tensile loading up to fracture of (6, 6) SWNTs with length between 49 and 492 Å. With increasing $l$, the distribution of $\sigma_u$ is found to shift to the left and become narrower and appears to fit the Weibull distribution rather well; the compliance of the tube increases with increasing $l$ and becomes asymptotically normal. The compliance...
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 Å) 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 behaviour of nanotubes and nanotube based devices.

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A small set of preliminary results from this work was presented at the Ninth International Conference on Structural Safety and Reliability held in Rome, Italy, in June 2005.

References


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Deep levels in the band gap of the carbon nanotube with vacancy-related defects

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We study the modification in the electronic structure of the carbon nanotube induced by vacancy-related defects using the first-principles calculation. Three defect configurations which are likely to occur in semiconducting carbon nanotubes are considered. A vacancy-adatom complex is found to bring about a pair of localized states deep inside the energy gap. A pentagon-octagon-pentagon topological defect produced by the divacancy is structurally stable and gives rise to an unoccupied localized state in the gap. We also discuss the character of partially occupied localized state produced by a substitutional impurity plus a monovacancy.

As excellent conductors\textsuperscript{1,2} with long mean free path and remarkably high mobility, carbon nanotubes (CNTs) have diverse potential applications in nanoelectronics. Though the properties of the atomically perfect CNT have been understood relatively well, experimental and theoretical reports on the defects such as vacancy and impurity substitution are limited. Recently, Gómez-Navarro \textit{et al}. showed that even a low concentration of vacancies in single-walled carbon nanotubes (SWNTs) can produce a large decrease in their electrical conductance.\textsuperscript{3} Through a sequence of high resolution transmission electron microscopy images recorded \textit{in situ} on one of the SWNTs; on the other hand, Hashimoto \textit{et al}. showed that the adatoms appear mostly in the vicinity of the vacancies.\textsuperscript{4} In the scanning tunneling microscopy (STM) experiment on a semiconducting CNT, localized gap states were observed in semiconducting SWNTs.\textsuperscript{5,6} In particular, a pair of gap states was found far from the band gap edge forming deep levels in the STM measurement.

In this letter, we report the electronic structure of CNTs with various vacancy-related defects. The first-principles pseudopotential calculations are carried out based on the density functional theory\textsuperscript{7} within the local density approximation\textsuperscript{8} with spin polarization for the exchange-correlation functional. The ionic potential is described with the norm-conserving Troullier-Martins pseudopotential.\textsuperscript{9} Wave functions are expanded in a double-$\zeta$ basis set with an energy cutoff of 80 Ry implemented in the SIESTA code.\textsuperscript{10,11} As a model system, we choose the (17,0) zigzag CNT of $\sim$13.4 Å in diameter and $\sim$0.5 eV in the band gap. The supercell size in the lateral direction is 25 Å to avoid the interaction between neighboring CNTs and that in the axial direction is 22 Å. The atomic position is relaxed until the forces on the atoms are reduced to within 0.02 eV/Å.

First, we have tested many different geometries with vacancies to reproduce experimentally observed two unoccupied deep levels in a semiconducting nanotube.\textsuperscript{5,6} A simple model of a vacancy-adatom complex is presented in Fig. 1(a). If a single atom is removed from the nanotube, two of three carbon atoms around the vacancy rebond (bond length of 1.57 Å) by the Jahn-Teller distortion. The third atom has the dangling bond even after the relaxation.\textsuperscript{12,14} The monovacancy alone does not reproduce the experimental spectra of a pair of deep levels.\textsuperscript{5,6} The adatom may be mobile because it has a lower diffusion barrier ($\sim$0.47 eV) (Ref. 15) than that for vacancy migration ($\sim$1.7 eV).\textsuperscript{16} Here the bond length between the adsorbed C atom and the atom on the tube is 1.34 Å. It is a typical C–C double bond and indicates that the adatom has two unpaired electrons. The binding energy of the adsorbed C atom in the model system is about 5.6 eV. It is comparable with the bonding energy of the C–C double bond ($\sim$6.3 eV). Thus we conclude that our model structure is energetically stable.

When a vacancy-adatom complex like our model structure is introduced, two unoccupied flat levels appear within the semiconducting gap, as plotted in Fig. 1(b). Since they exist far from the band edges of the (17,0) CNT, they can be called deep levels. In many cases, a deep level in the semiconductor acts as a recombination center and decreases...
junctions with complex topological defects reveal common features in electronic properties of the localized states. However, the wave functions may not have the mirror symmetry in general. Vacuum-related defects produce localized levels near the Fermi level even in the metallic CNT. The difference from the semiconducting CNT is that, since there exists a finite density of states at all energies in metallic CNTs, the localized states are actually in resonance with the extended states with finite broadening.

In summary, relatively deep localized gap states caused by various vacancy-related defects are found in the semiconducting SWNT in ab initio pseudopotential calculations. Because of the periodic boundary condition in the supercell method, our systems correspond to the case where defects are arranged in order. Band structures show weak band dispersions due to weakly interacting gap states in the intrinsic band gap of the semiconducting CNT. In the realistic case of the random distribution of defects, there would be slightly broadened density of states in the gap produced by nearly degenerate localized gap states. The broadening will be enhanced as the defect density increases. These states can be have as recombination centers of electron and hole carriers. As in bulk semiconductors such as silicon and gallium arsenide, these levels can significantly affect the transport and optical properties of the semiconducting CNTs.

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Symmetry-, time-, and temperature-dependent strength of carbon nanotubes

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Although the strength of carbon nanotubes has been of great interest, their ideal value has remained elusive both experimentally and theoretically. Here, we present a comprehensive analysis of underlying atomic mechanisms and evaluate the yield strain for arbitrary nanotubes at realistic conditions. For this purpose, we combine detailed quantum mechanical computations of failure nucleation and transition-state barriers with the probabilistic approach of the rate theory. The numerical results are then summarized in a concise set of equations for the breaking strain. We reveal a competition between two alternative routes of brittle bond breaking and plastic relaxation, determine the domains of their dominance, and map the nanotube strength as a function of chiral symmetry, tensile test time, and temperature.

T
he highest strengths of solids are obtained from specimens of utmost uniformity and perfection. Even a single defect can cause drastic loss of strength. Thin solid filaments (whiskers) have long been viewed as material structures that can sustain the greatest mechanical tension (1, 2). Small cross sections permit little room for defects in their bulk, and the only heterogeneity is caused by inevitable presence of the surface and the interfacet edges. Discovery (3) of carbon nanotubes (CNTs) offered, at least in principle, the next level of perfection, when in a cylindrical network all atoms are equivalently tied to the neighbors, and no “weak spot” is apparent. This intrinsic uniformity, together with the known strength of carbon bonds, must lead to extreme resistance to mechanical tension, as has been anticipated all along (4, 5). On the other hand, establishing the quantitative level of breaking strain and identifying the details of atomic-scale rearrangements responsible for initial yield turned out to be elusive both experimentally and theoretically.

In recent years, much progress has been made in elucidating the atomic mechanisms of CNT failure. In experiment, refined loading techniques often based on atomic force microscopy and combined with electron microscopic imaging allowed one to measure the breaking-strain level and observe the overall failure patterns (6–10). The reported experimental values of breaking strain ranged within 2–19% because of variability of the samples and measurement conditions (6–8). In theory, bond rotation [that is a concerted movement of two atoms, known in chemistry as Stone-Wales isomerization (SW) (11)] has been recognized as a key step in mechanical relaxation (12–14). It leads to the lowest energy defect, a cluster of two pentagons and heptagons, 5/7/7/5. In the lattice of hexagons (the nanotube body) it represents a dislocation dipole, which explains its formation under high tension. This particular relaxation step is most favorable thermodynamically, but because of the high barrier of SW (15–17) it requires thermal activation. In contrast, another mechanism recently analyzed (18) needs no thermal activation but occurs at higher tension as a sequence of direct brittle bond-breaking steps, when a series of “lattice-trapped” states (19) can be identified. Further work has also begun (20, 21) in computing how the defects can reduce the CNT strength.

Despite these insights, the questions at what strain an ideal tube begins to yield and which primary atomic rearrangement is actually dominant remained unanswered. In this article, we present a simultaneous study of the two mechanisms, combining molecular dynamics (MD) simulations, careful quantum mechanical evaluation of the energy characteristics for the key configurations, and reaction rate theory (22) for the probability of yield event. This approach allows one to calculate breaking-strain values for nanotubes of different symmetry and diameter at different temperatures and load rates. Such a comprehensive view, inaccessible with direct MD, results in a strength map relating the load level, its duration, temperature, and chirality of the sample. The results of these calculations indicate that both ductile-type bond flip and the brittle bond-breaking mechanisms coexist and either can play the dominant role in failure in a particular test.

Results and Discussion

It is important to remember that even for a well defined flawless nanotube the tensile failure process depends considerably on a number of parameters, such as sample type (diameter $d$ and chiral symmetry, i.e., the angle $0° \leq \chi \leq 30°$ between the roll-up vector and the zigzag roll-up vector), applied strain $\varepsilon$, test duration $t$ (or similarly, the strain rate $d\varepsilon/dt \approx \varepsilon/t$), and temperature $T$. Searching such a multidimensional parameter space in direct MD is impractical, even with the least taxing classical interatomic force field. However, MD remains a good tool for performing a preliminary hands-off search to identify the primary failure modes, which should then further be explored in detail. We have performed such simulations with quantum [nonorthogonal tight-binding approximation (23)] MD. We specifically considered different lattice temperatures and different applied tension (fixed degree of elongation). Different CNT types were considered with the test duration in subnanosecond range, well shorter than any experimental test. Fig. 1 illustrates, through selected representative configurations, the two main possibilities that emerge in the course of extensive simulations. Under high tension, the load is transferred differently to the bonds according to their orientations relative to the axis (color-coded in Fig. 1a). Further, the type of first lattice transformation depends qualitatively on temperature. At low $T$, thermal fluctuations appear insignificant and the yield event is purely “mechanical.” In this mode, one of the highly elongated bonds (marked blue in Fig. 1, for this “cold” mechanism) breaks and the crack-like configurations emerge (Fig. 1b). As discussed later, careful minimization with constraint (maintaining the tensile strain) shows (18) these states to be metastable, shallow energy minima, corresponding to the distinguishable n broken bonds ($n = 1, 2$, and 6 in the examples of Fig. 1b–d), a nucleating brittle crack.

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Abbreviations: CNT, carbon nanotube; SW, Stone-Wales isomerization; MD, molecular dynamics; DFT, density functional theory.$^1$

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Perforated organometallic nanotubes prepared from a Rh N-heterocyclic carbene using a porous alumina membrane

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Fabrication of perforated organometallic nanotubes using a di-rhodium bis(N-heterocyclic carbene) complex by a simple nanoporous template wetting technique is described along with characterization data from scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDS), proton NMR and Mass spectroscopy.

Many groups world-wide are involved in the development of nanotubes. The ubiquitous carbon nanotubes receive much attention. The fabrication of nanotubes from polymers via a templating methodology has been reported recently. Nanotubes have been demonstrated to have potential application for hydrogen storage and fuel cell technology. Despite these large scale synthetic efforts very few examples of organometallic nanotubes have been reported. We report the preparation of nanotubes from an organometallic material based on the porous alumina membrane templating methodology. Furthermore, the organometallic nanotubes contain semi-regular perforations (pores) along the main axis of the tube. This highly desirable property opens the possibility of controlled drug delivery with biocompatible metals and many other applications.

The construction of nanotubes, especially single-walled carbon nanotubes (SWNTs), has focused on solid walled materials. In part this is driven by the applications that have been envisaged and the available methodologies. Much has been reported concerning defects (holes) in the walls of SWCNTs and their spherical counterpart C60. Solid-walled nanotubes are the microscopic counterparts to rigid PVC pipe. An alternative macroscopic model is perforated pipe, which has regularly spaced pores that serve many functions.

The orange, crystalline di-Rh bis(N-heterocyclic) carbene (NHC) complex I depicted below was recently reported by two of us. The potential for crosslinking the Rh centers into a polymeric array made them interesting potential starting materials for nanotube synthesis. The nanotubes were fabricated by wetting a porous alumina membrane template with a toluene solution of I and allowing the solution to permeate the membrane until it was saturated. The solvent was allowed to evaporate under ambient conditions. The excess precipitate was removed from the surface of the membrane, and the alumina was dissolved with 3 N NaOH followed by centrifugation. The aqueous supernatant was discarded and a yellow solid was isolated. This material was rinsed with water and dried at room temperature.

Preliminary identification of the morphology was conducted by optical microscopy after dissolving the template but before re-suspension and washing (Fig. 1). Bunches of aligned strands or fibers were noted as may be seen in Fig. 1. The alignment of the nanotubes is a simple consequence of the structure of the porous alumina membrane. Individual nanotubes appeared to be about 20 μm in length.

The structure and constitution of these nanotubes were addressed first. Samples for scanning electron microscopy (SEM) were prepared and immediately imaged for morphological information and for quantitative length and diameter measurements (Fig. 2). No gold coating was used for the SEM sample preparation and yet the imaging was free from any charge build-up. This fact is indirect evidence that the nanotubes may be conductive. Fig. 2 shows images of these tubes with pores at regular intervals. The regularity is so astonishing that it causes doubt that these are due to the surface profile of the alumina template. Many groups around the world have used porous alumina membranes for the fabrication of nanomaterials but there are no similar reports in the literature that indicate perforation features on the nanotubes such as those observed in our case. Therefore, we suggest that the pores are due to the nature of the

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Fig. 1 Optical images at 1000 × magnification illustrating the nature of and alignment of the fibers obtained initially.
by liquid secondary ion mass spectroscopy (LSIMS). An identical observation was made for the starting material 1.10

These observations make even more intriguing the question of the nature of the molecular forces or non-covalent interactions holding the perforated organometallic nanotube together. There are several possible explanations. It could be intermolecular van der Waals attractions between butyl groups with or without concomitant π-stacking of the aromatic rings.13 Alternatively, the porous alumina membrane may catalyze a ligand exchange process whereby Rh–I–Rh and/or Rh-cyclooctadiene–Rh bridges are formed.14,15 The ready dissolution of the nanotubes in chloroform and the spectroscopic data (vide supra) seem to preclude the formation of μ-oxo (Rh–O–Rh) or μ-hydroxo (Rh–OH–Rh) bridges during treatment with NaOH.16,17 The suggested explanations account for the ready solubility in chloroform and account for recovery of 1.

In conclusion, we have fabricated nanotubes from a di-Rh N-heterocyclic carbene complex by a facile technique. These organometallic nanotubes seem to have good electrical conductive properties and show promise as nanowires. In addition, the presence of perforations (nanopores) at regular intervals in the nanotubes opens the possibility of numerous other applications. In the case of our nanotubes, the perforations around their sidewalls would make it easier for material to diffuse in and out of the tubes. Work is underway to ascertain the chemical structure of the tubes, to determine the molecular or non-covalent forces holding the tubes together, to insert objects into the tubes and to gain insight into the source of the perforations (nanopores), which will enhance our ability to control them.

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Notes and references

† Experimental: The 25 mm alumina disc templates with pore size of 200 nm were procured from Whatman Inc. The alumina template was sonicated for 10 min in deionised water to clean the pores and allowed to dry. Air and moisture stable di-Rh I (9.98 mg) was dissolved in toluene (5 mL). An aliquot of the solution was applied to the top of a template by microsyringe and the solvent allowed to evaporate overnight under a lamp in air. The excess solid was removed from the top of the template with a toluene dampened Kimwipe®. The template was dissolved with 3N NaOH (2 mL), the solid was centrifuged, and the supernatant was decanted. The nanotubes were washed twice by suspension in distilled H2O followed by centrifugation and decantation. They were suspended in water and drop-cast onto a Si substrate and dried before analysis. Optical microscopy images were collected from a Nikon Eclipse E600. A Leo Supra 55 was used to collect the SEM images and a Philips CM300 was used to collect the TEM images and the EDS data. High resolution proton NMR data were recorded on a Varian Inova 500 MHz instrument.


Analysis of localized failure of single-wall carbon nanotubes

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Abstract

A method is developed to determine the conditions for the onset of localized failure of carbon nanotubes. Examples of failure modes include ductile necking under tension or localized crushing under compression. A nanoscale continuum theory for carbon nanotube is adapted. The onset of localized failure is identified by the singularity point of the acoustic tensor derived from continuum energy function based on Tersoff–Brenner potential. The analysis predicts 35–44% of breaking strains for tension and 18–25% compressive strain for plastic collapse. The results are in agreement with molecular dynamics simulations and experimental estimations reported in the literature.

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Keywords: Carbon nanotube; Strain localization; Material failure; Acoustic tensor

1. Introduction

Carbon nanotubes (CNT) have been found to have exceptional mechanical and electronic properties. Applications of CNTs as building blocks for high-strength material or nanodevice have been proposed and investigated in many studies. The mechanical characteristics of nanotube reinforced material or nanodevices with nanotube as building blocks depend on the intrinsic mechanical properties of CNTs. These include not only the elastic modulus of CNTs, which describes the elastic property at small strains, but also the stability and failure of CNTs at large strains.

Early studies show that CNTs can be subject to very large strain without causing failure or defect formation. Yakobson et al. [30,31] investigated the buckling behavior of CNTs under large deformation using molecular dynamics (MD). It has been showed that under axial compression, nanotubes exhibit structural instabilities resulting in sideways buckling at as early as 5% of compressive strain. Large diameter tubes may buckle earlier by way of wall rippling. Torsion of a tube above a critical value results in ribbon-like flatten shapes. When bended beyond a buckling point, multiple kinks develop on the compressive side of the wall. These simulations agree with the experimental findings by Iijima et al. [13]. Arroyo and Belytschko [3,4] replicated these buckling patterns using finite element formulation based on crystal elasticity derived from bond-order potentials, and predicted a family of buckling patterns and post-buckling motions.

In these deformations, the CNT remains in the elastic limit, and restores its original geometry once the load is removed. Another category of instability, which we characterize as localized failure in a sense to be made clear later, has also been observed and reported in the literature. Yakobson et al. [31] and recently Marques et al. [17], studied the failure of CNT under tension at large strains. The initial response appears homogeneous; the hexagon bonds extend as the tube is stretched. At a certain critical level, one of few C–C bonds break almost instantaneously, and the resulting “hole” in a tube wall
Appendix A. Comparison with buckling analysis

This appendix provides a brief comparison with the buckling analysis in [33] and the current work for the special case of armchair tube under uniaxial tension. Starting from a relation between elasticity tensors $\mathbf{\mathcal{A}}$ and $\mathcal{D}$

$$\mathcal{A}_{i\alpha\beta} = S_{ij} \delta_{ij} + F_{\alpha\beta} F_{ij} \mathcal{D}_{i\alpha\beta},$$  \hspace{1cm} (A.1)

where $\mathbf{S}$ is the second Piola–Kirchhoff stress and $\mathcal{D}$ is the referential elasticity tensor, the acoustic tensor can be written as

$$Q_{ij} = S_{ij} N a N_{\beta} \delta_{ij} + F_{\mu} F_{\mu} \mathcal{D}_{i\alpha\beta} N a N_{\beta}.$$ \hspace{1cm} (A.2)

For the uniaxial tension specified in (29), the non-zero terms are axial stress $S_{11}$, the axial stretch $\lambda_{Z}$ and hoop stretch $\lambda_{T}$. Setting $\mathbf{N} = \mathbf{E}_{Z}$, the nonzero entries of $Q$ are

$$Q_{11} = S_{11} + \lambda_{Z}^{2} D_{ZZZZ},$$
$$Q_{22} = S_{11} + \lambda_{T}^{2} D_{OZTZ},$$
$$Q_{12} = \lambda_{Z} \lambda_{T} D_{ZZT}. $$ \hspace{1cm} (A.3)

The condition $\text{det} Q = 0$ reduces to

$$\left( D_{ZZZZ} + \frac{S_{11}}{\lambda_{Z}^{2}} \right) \left( D_{OZT} + \frac{S_{11}}{\lambda_{T}^{2}} \right) - D_{ZZT} = 0.$$ \hspace{1cm} (A.4)

Assuming that $B(\cos \theta_{ij}, \cos \theta_{ik})$ in T–B potential is constant and that $\eta = 0$, as in Ref. [33], the tangent modulus takes the form

$$\mathcal{D} = \frac{A_{0}}{} \sum_{i=1}^{3} \left( \frac{\nu_{i}}{r_{i}^{2}} - \frac{V_{i}}{r_{i}} \right) \mathbf{A}_{i} \otimes \mathbf{A}_{i} \otimes \mathbf{A}_{i} \otimes \mathbf{A}_{i},$$ \hspace{1cm} (A.5)

where $V_{i} = V_{i}(r_{i}) = V_{R}(r_{i}) - B V_{A}(r_{i})$. In this case, $D_{OZT} = D_{OZT} = D_{OZZZ} = D_{ZZZT} = 0$ holds regardless of chirality angle. The jump condition reduces to

$$S_{22} + \lambda_{2}^{2} D_{ZZZZ} = 0 \quad \text{or} \quad S_{11} + \lambda_{T}^{2} D_{OZTZ} = 0,$$ \hspace{1cm} (A.6)

whichever reaches first. In tension, actual computation shows that $S_{22} + \lambda_{2}^{2} D_{ZZZZ} \neq 0$ within the range of stretch considered, therefore the critical state is characterized by $S_{22} + \lambda_{2}^{2} D_{ZZZZ} = 0$.

The criterion deduced by Huang’s group (Eq. (32) of [33]) states that

$$\left( D_{ZZZZ} + \frac{S_{11}}{\lambda_{Z}^{2}} \right) \left( D_{OZT} + \frac{S_{11}}{\lambda_{T}^{2}} \left( \frac{m n R}{L} \right) \right) = D_{OZT}^{2}.$$ \hspace{1cm} (A.7)

where $R$ is the tube radius and $L$ is the tube length. Now, if $R \to \infty$, to make the right-hand side finite, the first factor should be diminishingly small, which yields the same condition. In [35], Huang et al. further showed that for axisymmetric buckling, the critical strain for an armchair is almost insensitive to tube geometry.

References

Fracture of vacancy-defected carbon nanotubes and their embedded nanocomposites

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In this paper, we investigate effects of vacancy defects on fracture of carbon nanotubes and carbon nanotube/aluminum composites. Our studies show that even a one-atom vacancy defect can dramatically reduce the failure stresses and strains of carbon nanotubes. Consequently, nanocomposites, in which vacancy-defected nanotubes are embedded, exhibit different characteristics from those in which pristine nanotubes are embedded. It has been found that defected nanotubes with a small volume fraction cannot reinforce but instead weaken nanocomposite materials. Although a large volume fraction of defected nanotubes can slightly increase the failure stresses of nanocomposites, the failure strains of nanocomposites are always decreased.

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I. INTRODUCTION

It is known that carbon nanotubes (CNTs) have large tensile modulus and high thermal conductivity. The Young’s moduli of CNTs are around 1 Tpa and their thermal conductivity can be 6600 W/m K. On the other hand, CNTs are expected to have high strength. Previous theoretical analyses and numerical simulations predicted failure strengths of up to 300 Gpa for CNTs. Consequently, they have been proposed as ideal fibers for the manufacture of the next generation of composite materials with mechanical and thermal management applications. However, low failure stresses, which are in the range of 21–63 Gpa, were observed in the experiments. Such observation conflicted with theoretical and numerical analyses outcomes.

Some researchers have pointed out the significant effects of defects on nanotube fracture. Defects in CNTs can arise from various causes. Chemical defects consist of atoms/groups covalently attached to the carbon lattice of the tubes such as oxidized carbon sites or chemical vapor deposition. Topological defects correspond to the presence of rings other than hexagons, mainly studied as pentagon/heptagon pairs. Incomplete bonding defects like vacancies may be caused through impact with high-energy electrons in the transmission electron microscopy environment, see Banhart, or defects in the original outer nanotube shell.

Chemical defects usually occur during functionalizing CNTs so that chemical bonds can be formed between CNTs and the matrix material in nanocomposites. Consequently, the mechanical properties of nanocomposites can be significantly enhanced because of the strong interfacial load transfer. However, we do not think that functionalization will have significant effects on the nanotube fracture itself. dislocation, also called Stone-Wales dislocation, results in high failure strengths in comparison with the experimental results. Incomplete bonding, especially vacancy, will form nanoscale cracks or holes that can have large variations in size. Such an initial mechanism can dramatically reduce the strength of CNTs. Belytschko et al. obtained reasonable results that can account for the fractures in the experiments with an n-atom defect model (vacancy due to n atoms missing). However, since the bonds along the hypothetical crack were not reconstructed, the physical plausibility of these defects remains in question. In research performed in collaboration with Belytschko, Car, Ruoff, Schatz, etc., the role of vacancy defects and holes in the fracture of CNTs was studied. Both quantum mechanical and molecular mechanics calculations indicated that the holes due to one- and two-atom vacancy defects could reduce failure stresses by as much as ∼26%. In their studies, nanotubes were assumed at zero temperature.

Since high strengths of CNTs were predicted, it was assumed that the toughness of their embedded composite materials could be significantly increased. Generally, three types of materials can be used as the matrix: polymers, ceramics, and metal. Because polymers have low density and are easy to shape, they are the first choice as the matrix of fiber reinforced composites. As a structural material, ceramics present many advantages over polymers, such as high rigidity and hardness, even at high temperature, and low sensitivity to corrosion. However, they are brittle. Such weakness can be made up by reinforcing the composites with CNTs. Lately, there has been more interest in using metal as the matrix material for composites. It has been found that the fracture toughness of a metal matrix composite with nanotubes can be increased by up to 200%.

In this paper, we will first study the failure mechanism of vacancy-defected CNTs using molecular dynamics. As a difference from previous research work, vacancy defects are modeled by taking out atoms and then reconstructing bonds. Various temperatures will be considered to investigate temperature effects on the fracture of CNTs. We also study size effects of vacancy defects on a nanotube fracture at room temperature, i.e., T=300 K. Then, nanotube-embedded aluminum (CNT/Al) composites are considered to investigate effects of vacancy defects on fracture of nanocomposites. In this paper, only nonbonded interatomic interaction, i.e., van der Waals energy, is considered at the CNT/Al interface, since no chemical reactions were observed during processing of CNT/Al composites in the experimentation.
the vacancy. We also found that temperature effects on the strength of vacancy-defected nanotubes are not as significant as those on the strength of pristine nanotubes. In addition, we employed CNT/Al nanocomposites to demonstrate whether vacancy-defected nanotubes can reinforce composite materials or not. Due to experimental observation, no chemical bonds exist at the CNT/Al interface. Several interesting phenomena were observed for defected CNT/Al composites other than pristine CNT/Al composites. At first, a critical volume fraction should be reached for vacancy-defected nanotubes to reinforce composite materials. For example, a large volume fraction defected nanotubes can increase the failure stress, i.e., strength, of nanocomposites, the defected nanotubes reduce the failure strain of CNT/Al composites. We should point out that only the weak CNT/matrix interface is considered in this paper. Strong load transfer at the CNT/matrix interface may be achievable through functionalization of nanotubes. This will be our future research topic.

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Interwall interaction and elastic properties of carbon nanotubes

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The physical properties of a wide range of nonchiral single-walled carbon nanotubes (SWNT) and double-walled carbon nanotubes (DWNT) with nonchiral commensurate walls are studied. Equilibrium structures of SWNT and DWNT, as well as the interwall interaction energies of DWNT, are computed using a local density approximation within density functional theory with periodic boundary conditions and Gaussian-type orbitals. Based on ab initio structural characteristics, elastic properties of SWNT and DWNT are calculated. Relative motion of the walls of DWNT with different radii and chiralities is explored using ab initio results for the interwall interaction energies. Relative positions of nonchiral commensurate walls of DWNT which correspond to extrema of the interwall interaction energy are derived. For DWNT with incompatible rotational symmetries of the walls, the possibility of orientational melting is predicted. Ab initio values of barriers to relative rotation and sliding of the walls of DWNT are used to calculate threshold forces. For nonreversible telescopic extension of the walls, maximum overlap of the walls for which threshold forces are greater than capillary forces is estimated. A method for selecting pairs of nonchiral commensurate walls in multiwalled carbon nanotubes (MWNT) is proposed.

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I. INTRODUCTION

Carbon nanotubes are promising material for potential components of future nanoelectronic and nanomechanical devices.1-4 Weak interwall interactions within MWNT provide perfect bearing for possible novel nanodevices based on relative sliding, rotation, or screwlike motion of the walls.5-10 Theoretical study of the interwall interaction and relative motion of the walls in carbon nanotubes holds the key to success of these applications.

Neglecting their structure at the ends, which can be either open or closed, carbon nanotubes are single or multiple layers of a cylinder rolled up from graphene sheets. Only one parameter is needed to fully determine the structure of the middle section of a SWNT: the chirality index \((n, m)\) which corresponds to a two-dimensional lattice vector \(\mathbf{c} = n\mathbf{a}_1 + m\mathbf{a}_2\), where \(\mathbf{a}_1\) and \(\mathbf{a}_2\) are equivalent lattice vectors of graphene.11 A segment defined by the vector \(\mathbf{c}\) becomes the circumference of cylindrical surface of a nanotube wall which can be well modeled by an infinite tube, where periodic boundary conditions are applicable.12 Two types of SWNT characterized by the chirality index of \((n, n)\) and \((n, 0)\) have a simple translational symmetry, and these are referred to as armchair and zigzag nanotubes forming different pattern of hexagons in circumference. DWNT consist of two coaxially arranged SWNT with the interwall distance close to the graphite interlayer distance of 3.35 Å.13

The walls of DWNT are commensurate if the ratio of the lengths of their unit cells is a rational fraction. In this case, a DWNT is a quasi-one-dimensional crystal with the length of unit cell equal to the lowest common factor of the lengths of unit cells of constituent SWNT. Lack of commensurability between the neighboring nested SWNT implies a dramatic weakening of the corrugation in the interwall interaction potential.14 Barriers to the relative motion of the commensurate walls of sufficiently long DWNT are proportional to the nanotube length: \(\Delta U = \Delta U_c N_c\), where \(\Delta U_c\) is the barrier per unit cell and \(N_c\) is the number of unit cells in the nanotube. Conceivably, there is a possibility of fabrication of DWNT with commensurate walls with a custom-ordered value of barriers to relative motion of the walls. Therefore, these DWNT can be considered as potential components in nanodevices for which a precise control of motion of the walls is required. In contrast to the commensurate case, barriers to relative motion of incommensurate walls of DWNT do not increase with the nanotube length, but fluctuate near the average value.5,6,15 Such incommensurate systems, even if they contain thousands of carbon atoms, have barriers to the relative motion of the walls comparable to those of a single unit cell.

The most commonly used convention employs the term “commensurate walls” for the walls which are commensurate with their structures obtained by graphene plane mapping on a cylindrical surface with the bond lengths kept constant (see, for example, Refs. 14, 15, and 17–20). Otherwise, the walls are defined as incommensurate. However, the bond lengths of the walls of nanotubes slightly differ from those in graphite, and for this reason the lengths of unit cells of isolated commensurate walls are also slightly different. Interwall interactions in DWNT lead to the contraction (or expan-
INTERWALL INTERACTION AND ELASTIC…

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Equilibrium configuration and continuum elastic properties of finite sized graphene

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Abstract
This paper presents a continuum mechanics approach to modelling the elastic deformation of finite graphene sheets based on Brenner’s potential. The potential energy of the graphene sheet is minimized for determining the equilibrium configuration. The four edges of the initially rectangular graphene sheet become curved at the equilibrium configuration. The curving of the sides is attributed to smaller coordination number for the atoms at the edges compared to that of the interior atoms. Considering two graphene models, with only two or all four edges constrained to be straight, the continuum Young’s moduli of graphene are computed applying the Cauchy–Born rule. The computed elastic constants of the graphene sheet are found to conform to orthotropic material behaviour. The computed constants differ considerably depending on whether a minimized or unminimized configuration is used for computation.

1. Introduction

Since the discovery of carbon nanotubes by Iijima et al [1] in 1991, the prospects of this new material have motivated widespread research towards several potential applications. Graphene is a term that refers to a single layer of carbon atoms which are densely packed into a hexagonal ring structure, and is widely used to describe the properties of carbon based materials including graphite, large fullerenes, nanotubes etc. The discovery of the single-walled carbon nanotube (SWNT) was first reported in 1993 [2, 3]. The diameters of SWNTs range from 0.4 to 2–3 nm and the lengths are usually of micrometre order. Usually SWNTs come in the form of bundles which are hexagonally arranged to form a crystal-like structure [4].

Extremely small size, outstanding physical properties and unique atomic arrangement of carbon nanotubes are some of the attractive features that have triggered intensive research in a wide variety of fields, i.e., chemistry, physics, material science, medicine, and engineering. Many researchers have reported in the literature theoretical and experimental results showing as high an elastic modulus as 1 TPa, that exceeds those of any previously existing materials. Because of the very high elastic modulus and tensile strength (approximately 10–100 times more than the hardest steel [5]) and low weight, carbon nanotubes have found potential applications in the areas of space as well as material reinforcement in composite technologies [6]. Carbon nanotubes (CNTs) behave like a semiconductor or metal, depending on the orientation of carbon atoms, and find wide range of potential applications in the field of electronic industry. CNTs have very high current carrying capacities (approximately 1000 times as that of copper wires [7]) and have high thermal stability up to 2800°C in vacuum, so they find wide applications in the electrical industry.

Many researchers have reported analysis of carbon nanotubes by theoretical modelling. There are mainly two bonding potentials used in theoretical modelling, namely, direct bonding potential and indirect bond potential (interlayer potential) to compute the mechanical properties. The bonding potentials can be further categorized in terms of three models, i.e., force field model, bond order model and semi-empirical model. The molecular mechanics force field (MM2, MM3) was introduced by Allinger and co-workers [8, 9]. A generic force field was proposed by Mayo et al [10]. The bond order model was proposed by Abell [11], and extension to the carbon...
vertical direction (to simulate lateral contraction) by assuming a variable value of Poisson’s ratio. This becomes necessary as the lateral contraction is not automatic because potential minimization is not done to obtain equilibrium configuration. Figure 8 shows the plot of Young’s modulus against the assumed Poisson’s ratio values. The minimum point gives us the second set of values (1 TPa, 0.25).

The first set of values is expected to be more accurate because the values have been computed allowing for local adjustments of atomic positions to reach the equilibrium configurations.

5. Summary and conclusions

The elastic constants of finite graphene sheet have been determined by modelling it as a continuum. It has been observed that the equilibrium adjustments of atoms have much influence on the computed elastic constants. Computations considering equilibrium adjustments lead to Young’s modulus and Poisson’s ratio values around 0.7 TPa and 0.4, respectively, whereas computations ignoring equilibrium adjustments yield 1 TPa and 0.25, respectively. Nevertheless, papers reporting the elastic constant values often do not mention whether equilibrium adjustments have been considered in their computations. This may be one of the reasons for the wide scatter in the elastic properties found in the literature.

The variation of bond lengths caused by equilibrium adjustments of atoms during the potential minimization process has also been studied. The elastic constants $Y_1$, $Y_2$, $v_{12}$, $v_{13}$ and $G_{12}$ have been computed for two graphene models, namely, with two straight edges and four straight edges. The study of inter-relationship between these constants seems to suggest that graphene behaves like an orthotropic material.

References

Nanoscale Weibull statistics

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In this paper a modification of the classical Weibull statistics is developed for nanoscale applications. It is called nanoscale Weibull statistics. A comparison between nanoscale and classical Weibull statistics applied to experimental results on fracture strength of carbon nanotubes clearly shows the effectiveness of the proposed modification. A Weibull’s modulus of \(-3 \leq m \leq 3\) is deduced for nanotubes. The approach can treat (also) a small number of structural defects, as required for nearly defect-free structures (e.g., nanotubes) as well as a quantized crack propagation (e.g., as a consequence of the discrete nature of matter), allowing to remove the paradoxes caused by the presence of stress intensifications. © 2006 American Institute of Physics. [DOI: 10.1063/1.2158491]

I. INTRODUCTION

Weibull statistics\(^1\) for strength (or time to failure, fatigue life, etc.) of solids and deterministic linear elastic fracture mechanics\(^2\) (LEFM) do not apply properly at the nanoscale. Weibull statistics assumes that the number of critical flaws is proportional to the volume or to the surface area of the structure, whereas single-crystal nanostructures are anticipated to be either defect-free or to have a small number of (critical) defects. Recently LEFM, which assumes infinite ideal strength of solids, as well as large (with respect to the so-called “plastic zone”) and perfectly sharp cracks, has been modified and a theory, quantized fracture mechanics\(^3\) (QFM), has been presented that quantizes the crack advancement. QFM is intended for treating defects of any size and shape (e.g., atomic vacancies and nanoholes). In this paper we present a modification of the Weibull statistics for describing the strength of solids (also) at the nanoscale. We apply this statistical treatment to the largest collection of carbon nanotube strengths available.\(^4\) The Weibull modulus for nanotubes is obtained as \(-3 \leq m \leq 3\); furthermore, the statistical data analysis suggests that a small number of defects were critical for such nanotubes. An application to different types of whiskers is also discussed. The proposed approach, coupled with quantized fracture mechanics, can treat stress distribution also if dominant stress intensifications are present, thus removing the classical paradoxes related to the nonconvergence of the Weibull integrals.

II. CLASSICAL WEIBULL STATISTICS

Classical Weibull statistics\(^1\) assumes the probability of failure \(P_f\) for a specimen of volume \(V\) under uniaxial stress \(\sigma(P)\) (a function of the considered point \(P\) in the volume \(V\)) as

\[
P_f = 1 - \exp\left(-\frac{\sigma(P)}{\sigma_{0V}}\right)^m \int_V dV,
\]

or equivalently,

\[
P_f = 1 - \exp\left(-V\left(\frac{\sigma}{\sigma_{0V}}\right)^m\right),
\]

where \(\sigma_{0V}\) and \(m\) are Weibull’s scale (with anomalous physical dimension) and shape (dimensionless) parameters, respectively, and \(V\) is an “equivalent” volume that refers to a specimen,\(^5\) e.g., the maximum stress \(\sigma(P)\) and \(V = V\).

The surface-flaw-based Weibull distribution simply replaces the volume \(V\) in Eqs. (1) with the surface area \(S\) of the specimen (and \(\sigma_{0S}\) with a new constant \(\sigma_{0S}\)),

\[
P_f = 1 - \exp\left(-\frac{\sigma(P)}{\sigma_{0S}}\right)^m \int_S dS,
\]

or

\[
P_f = 1 - \exp\left(-S\left(\frac{\sigma}{\sigma_{0S}}\right)^m\right).
\]

Note that \(\sigma_{0V}\) or \(\sigma_{0S}\) have the anomalous physical dimensions of a stress times a volume or a surface raised to \(1/m\), so that the exponents in Eqs. (1) and (2) are evidently dimensionless.

The cumulative probability \(P_f(\sigma)\) can be obtained experimentally as\(^6\)

\[
P_f(\sigma) = \frac{i - 1/2}{N},
\]

where \(N\) is the total number of tests and the observed strengths \(\sigma_1, \ldots, \sigma_N\) are ranked in ascending order.

The volume- and surface-based approaches become identical for the case of fracture of the external wall of nanotubes under (nearly) uniform tension, such as for the 19
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Theoretical study of the stability of defects in single-walled carbon nanotubes as a function of their distance from the nanotube end

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Point defects, including atom vacancies, adatom, and Stone-Wale defects, close to a (5,5) single-walled carbon nanotube (SWNT) open end were studied by density functional theory (DFT), semiempirical PM3 methods, and the empirical Brenner potential. It is found that defect stability increases as they become closer to the SWNT open end. Based on these results, a model for removing defects in a growing SWNT is proposed, where the defects diffuse to the SWNT end. Furthermore, the calculations show that the semiempirical PM3 method compares well with DFT results, and is accurate enough for studying defect formation in SWNTs. In contrast, the empirical Brenner potential yields large errors and is sometimes not even qualitatively correct.

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I. INTRODUCTION

As the most important nanomaterial, carbon nanotubes (CNTs), including single-walled carbon nanotubes (SWNTs) and multiwalled carbon nanotubes (MWNTs), have been studied extensively since their discovery in 1991 and 1993. A comparison with other nanomaterials, such as semiconducting nanowires and nanobelts, CNTs distinguish themselves by their extremely small diameters (e.g., the diameter of the smallest SWNT is 0.4 nm [Ref. 5]), ultralong lengths (e.g., isolated SWNTs up to several centimeters and decimeter long SWNT bundles have been produced in experiments), high chemical stability, outstanding mechanical properties (such as tensile strengths of up to 150 GPa, which are more than 300 times that of steel), and excellent electronic properties. All of these favorable physical, chemical, and mechanical properties make CNTs the most likely candidate for a diverse range of applications, such as very small electronic devices, ultralarge scale integrated circuits, high density memories, chemical sensors, superhard and superstrong materials, hydrogen storage, and nanomachines.

Although much progress has been made to produce CNTs in a controlled way, it is still not sufficiently well controlled to allow for industrial applications. The growth mechanism is not well understood. One important problem that is related to the growth mechanism is how CNT defects are fixed during the nucleation process, especially when CNTs grow at relatively low temperatures. For example, typical temperatures for catalytic chemical vapor deposition (CCVD) CNT growth are 800–1500 K, which is several times lower than the melting point of graphite, about 4100 K. Certainly, thermal annealing at these low temperatures cannot fix a high density of defects in condensed carbon structures to form the perfect graphitic layers that are needed to nucleate CNT walls. In the experimental production of CNTs, a lot of amorphous carbon is often formed as the main byproduct. In contrast, carbon atoms near catalyst particles form high quality graphitic layers, which implies that the catalyst plays a crucial role in healing defects in nucleated carbon structures at low temperatures.

Recent molecular dynamics (MD) simulations also show that, when free carbon atoms incorporate into the open end of a SWNT on a catalyst particle surface, various defects (e.g., pentagons, heptagons, adatoms, and vacancies) are readily formed. A scooter mechanism has been proposed to explain how a catalyst atom fixes these defects. The catalyst atom stays on the open end of the SWNT and, when a defect is formed, the catalyst atom “scoots” to the defect position and fixes it. If all defects are fixed by the scooter mechanism, the SWNT maintains an open end during the nucleation process. Such a mechanism can explain the healing of defects on the open end of a growing SWNT only. If some defects are not healed at the CNT end during nucleation, they will not be healed by the scooter mechanism and, in the absence of a second healing mechanism, will remain in the CNT wall. That is, if the scooter mechanism were the only way to heal defects, the working efficiency of the catalyst atom must be extremely high to grow pristine SWNTs. For example, the defect density on a high quality SWNT may be as low as one defect per micron, and if we assume one defect is formed for every 10 added carbon atoms on the tube end then the catalyst atom must fix about 99.99% of the defects. This must be done in a very short time scale since the growth rate of SWNTs is very high (e.g., it has been reported that SWNT growth rates are as large as 20 μm/s in CCVD experiments at 1173 K, which means each defect is exposed to the catalyst for just 10−3 s). Such high catalytic efficiency is not probable. Hence in order to understand the growth mechanism of high quality CNTs, one should consider more mechanisms for healing the defects, especially for healing the defects in CNT walls.

In this contribution we consider a mechanism where defects in SWNT walls diffuse to the open end of the growing SWNT, where they can be healed by, for example, the scooter mechanism. The position dependence stability of various point defects close to the SWNT open end was studied by density functional theory (DFT), the semiempirical PM3 method, and the empirical Brenner potential.

II. METHOD OF THE THEORETICAL STUDY

There are three kinds of point defects in CNTs: vacancy, add-atom (AA), and Stone-Wale (SW) defects, which can
CCVD. In addition, CNTs produced in high temperature CCVD often have a higher quality than those produced by low temperature CCVD.

IV. CONCLUSION

In conclusion, studies based on DFT, PM3, and the Brenner potential show that the stability of point defects in SWNTs increases as they become nearer to the open end of the nanotube. Based on these results, we propose that defects in SWNTs can be healed by their diffusing to the nanotube end, where they are removed by the catalyst particle. It is also found that the PM3 method, which is computationally cheaper than the DFT method, is sufficiently accurate to study defect formation energies and structures. On the other hand, the Brenner potential is only qualitatively correct.

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Modeling of carbon nanotube clamping in tensile tests

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Abstract

In this paper, the stress distributions in carbon nanotube clamps such as those formed by the electron beam induced deposition (EBID) technique are analyzed and the contributing factors, including nanotube position, stiffness of clamp material, and thickness of the clamping pad between the AFM tip and the nanotube are examined for the case of tensile loading of the nanotube. The nanotube is modeled at the atomistic scale by the molecular structural mechanics approach and is assumed to be defect free. The clamp material is analyzed by the continuum finite element method. The nanotube and the clamp are assumed to be bonded perfectly to each other. This bonding condition sets the upper limit of clamping capacity. The simulation results indicate that the location and intensity of stress concentration are sensitive to the nanotube orientation. Misaligned nanotubes are likely to break near the edge of the clamp. The clamp material with a lower stiffness (for the stiffness range studied) and a thicker clamping pad between the nanotube and the AFM tip reduce the magnitude of stress concentrations in the clamp.

Keywords: Carbon nanotube; Clamping; Nanocomposites; Multiscale modeling; Tensile testing

1. Introduction

The term ‘clamping’ here refers to the secure fastening of an already positioned specimen. The sound clamping of a specimen is critical to producing reliable test results of mechanical properties, such as elastic modulus, tensile strength, hardness and fracture toughness. At the macroscopic scale, traditional methods for specimen fastening utilize mechanical, pneumatic or hydraulic clamping [1]. At the microscopic scale, electrostatic and magnetic clamping techniques, for instance, are commonly used for precision machining operations [2,3]. More recently, the development of nanotechnology requires the characterization of properties of nanostructured materials and, hence, the research of nanoscale ultra-precision clamping of specimens [4]. One of the interesting challenges in this regard is the clamping of carbon nanotubes for tensile tests.

Since their discovery, carbon nanotubes offer tremendous opportunity for nanotechnology applications. Examples of their potential applications include as reinforcements for composites [5,6], components of nanoelectromechanical systems [7–9], and storage for hydrogen fuel [10]. Intensive research has been focused on the mechanical and physical properties of carbon nanotubes. Theoretical and experimental studies have confirmed that carbon nanotubes possess extraordinary axial stiffness and tensile strength [11–15]. In these experiments, the appropriate clamping of carbon nanotubes is critical.

There are several suitable methods for attaching a nanotube to a substrate. These include using adhesives such as acrylates, methacrylates or epoxies, employing electrostatic forces, exploiting the chemical affinity between the substrate and the nanotube, and synthesizing...
tensile testing. In this paper, we analyze the stress distribution of nanotube clamps formed by the EBID technique and examine the contributing factors, including nanotube position, stiffness of clamp material, and thickness of the clamping pad between the AFM tip and the nanotube. The numerical analysis is performed by a multiscale modeling technique. The nanotube is modeled at the atomistic scale by the molecular structural mechanics approach, and the clamp material is analyzed by the continuum finite element method. The nanotube and the clamp material are assumed to be perfectly bonded. The simulation results indicate that the location and intensity of stress concentration are sensitive to the nanotube orientation. The clamp material with a relatively lower stiffness reduces the magnitude of stress concentration. Also, the increase of the thickness of the clamping pad between a nanotube and the AFM tip reduces the tensile stress concentration. The misalignment between the applied tensile force and the nanotube orientation results in bending and torsional loads on the nanotube and, hence, additional interfacial shear stress concentrations in the clamp material. Also, the misalignment is in part responsible for having caused failure of carbon nanotubes near the edge of the clamp.

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Stochastic strength of nanotubes: An appraisal of available data

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Abstract

This paper summarizes and discusses the limited statistically significant, currently available, experimental data for the tensile strength of individual nanotubes of any sort. Only three such data sets currently exist: two for multi-wall carbon nanotubes and one for multi-wall WS₂ nanotubes. It is shown here that Weibull–Poisson statistics accurately fits all strength data sets and thus seems to apply at the nano-scale as well as it does at the micro- and macro-scales. The significance and trends of the Weibull shape and scale parameters, and their relation to the specific structural features of the different nanotubes, are discussed in each case. More recent fracture analyses are also discussed and, in that context, the role of defects in quasi-perfect structures in relation to the theoretical strength is examined.© 2005 Elsevier Ltd. All rights reserved.

Keywords: Nanotubes; Nanoscale; Weibull; Biocomposites

1. Introduction

The strength of any material is inherently governed by the statistical distribution of defects in its microstructure, and by specimen shape and volume. In fibrous materials, the comparatively small fiber diameter represents an upper bound for critical defect size. It is commonly assumed that, in strong micro-scale fibers such as carbon and glass, the severity of the flaws follows a Poisson distribution and the strength of a fiber is then determined by the most severe flaw, so that the fiber fails when the weakest point in the fiber fails. This behavior may conveniently be modeled by a Weibull two-parameter distribution. If $\sigma_l$ is the failure strength of the nanotube, the cumulative distribution function $F(\sigma_l)$ for the two-parameter Weibull distribution is given by

$$F(\sigma_l) = 1 - \exp \left[ -\left(\frac{\sigma_l}{\alpha}\right)^\beta \right],$$

(1)

$F(\sigma_l)$ is often simply termed the probability of failure (denoted by $P_f$), $\alpha$ is the scale parameter (it has dimensions of stress and is smaller for longer or thicker fibers), and $\beta$ is the shape parameter (no dimensions). And indeed, most fibers used in composite materials (carbon/graphite, Kevlar, glass) do follow quite accurately the Weibull–Poisson statistical model.

Going down in scale by 2–3 orders of magnitude (from a 10-μm diameter fiber down to a 10–100 nm nanotube), questions may be asked as to the validity of this classical model: is the defect population still describable by the random Poisson model? Would not the criticality of individual defects in nanometer-scale objects be expected to be more severe than in micron- or macro-sized specimens, because of the closeness in scale between defects and structures? Can the stochastic strength still be fitted to a Weibull model and is this model still appropriate at the nanoscale? What is the role of single defects in a nanotube with an almost perfect structure?

As a matter of fact, the mechanical strength of carbon nanotubes is found to be noticeably higher – by one to two orders of magnitude – than that of
at the same time, causes more variability in strength. Such a strength-enhancing mechanism by wall-to-wall interactions may possibly be observed in future research with other multi-tubular structures. The novel QFM scheme shows promises to model the strength of nanotubes as well, despite the presence of a free parameter.

Acknowledgements

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References

Continuum Mechanics Modeling and Simulation of Carbon Nanotubes

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Abstract. The understanding of the mechanics of atomistic systems greatly benefits from continuum mechanics. One appealing approach aims at deductively constructing continuum theories starting from models of the interatomic interactions. This viewpoint has become extremely popular with the quasicontinuum method. The application of these ideas to carbon nanotubes presents a peculiarity with respect to usual crystalline materials: their structure relies on a two-dimensional curved lattice. This renders the cornerstone of crystal elasticity, the Cauchy–Born rule, insufficient to describe the effect of curvature. We discuss the application of a theory which corrects this deficiency to the mechanics of carbon nanotubes (CNTs). We review recent developments of this theory, which include the study of the convergence characteristics of the proposed continuum models to the parent atomistic models, as well as large scale simulations based on this theory. The latter have unveiled the complex nonlinear elastic response of thick multiwalled carbon nanotubes (MWCNTs), with an anomalous elastic regime following an almost absent harmonic range.

Key words: Continuum mechanics, Carbon nanotubes, Finite elasticity, Atomistic models, Nanotube-based devices.

1. Introduction

Carbon nanotubes (CNTs) can be viewed as graphene sheets (a two-dimensional hexagonal lattice of carbon atoms) wrapped into cylinders one atom thick of specific chirality and diameter. Although irradiation or the synthesis process can produce defects into the crystal structure, these nanostructures are remarkably perfect. Since their discovery in 1991 [18], CNTs have attracted much attention due to their unique structure and mechanical, chemical and electronic properties [11]. These properties have made of CNTs the central element in an array of nanostructured materials, as well as nanosensors and devices. Mechanics plays a central role in nanotube-based nanotechnology. On the one hand, the exceptional mechanical properties (a nominal Young’s modulus of 1 TPa, ideal strength of over 100 MPa) has prompted intense research in nanostructured materials such as nanotube-based nanocomposites. On the other hand, the strong function of other properties such as electrical conductance [37]
Large chunks of very strong steel

H. K. D. H. Bhadeshia*

Most new materials are introduced by selectively comparing their properties against those of steels. Steels set this standard because iron and its alloys have so much potential that new concepts are discovered and implemented with notorious regularity. In this 52nd Hatfield Memorial Lecture, I describe a remarkably beautiful microstructure consisting of slender crystals of ferrite, whose controlling scale compares well with that of carbon nanotubes. The crystals are generated by the partial transformation of austenite, resulting in an extraordinary combination of strength, hardness and toughness. All this is in bulk steel without the use of expensive alloying elements. We now have a strong alloy of iron, which can be used for making items that are large in all three dimensions, which can be made without the need for mechanical processing or rapid cooling and is cheap to produce and apply.

Keywords: Nanotubes, Strong steel, Bainite, Space elevator, Entropy defects

Introduction

It is possible to think of many ways of creating extremely strong materials. Polycrystalline metals can be strengthened by reducing the scale of the microstructure whereas single crystals benefit from perfection. Carbon based materials can in principle become incredibly strong if the only mode of deformation involves stretching of carbon–carbon covalent bonds. These and many other mechanisms of strengthening unfortunately have limitations. In particular, it is difficult to make strong, isotropic materials which can be used to manufacture large components of arbitrary shape, while maintaining an attractive combination of properties at a reasonable cost. Such a material would be commercially viable over a broad range of applications.

Imagine in this context, an exceedingly strong steel that can be made in large chunks, one that is easy to manufacture and has an affordable cost. Before describing this novel material, it is important to review the meaning of strength because there are many promises in the modern scientific and popular literature of materials which possess strength beyond our dreams. I shall attempt in this lecture to make appropriate comparisons to show how steels feature in this scenario.

Theoretical strength

The strength of crystals increases sharply as they are made smaller.1–7 This is because the chances of avoiding defects become greater as the volume of the specimen decreases. In the case of metals, imperfections in the form of dislocations are able to facilitate shearing at much lower stresses than would be the case if whole planes of atoms had to collectively slide across each other.8,9 Because defects are very difficult to avoid, the strength in the absence of defects is said to be that of an ideal crystal.

In an ideal crystal, the tensile strength is \( \sigma_t \approx 0.1E \), where \( E \) is the Young’s modulus. The corresponding ideal shear strength is \( \sigma_s \approx \mu/2n \), where \( \mu \) is the shear modulus, \( n \) a repeat period along the displacement direction and \( a \) the spacing of the slip planes.8 For ferritic iron, \( \mu = 80–65 \text{ GPa} \) and \( E \approx 208–2 \text{ GPa} \).10 It follows that the ideal values of tensile and shear strength should be \( \sim 21 \) and \( \sim 11 \text{ GPa} \), respectively. In fact, tensile strengths approaching the theoretical values were achieved by Brenner as long ago as 1956 during testing whiskers of iron of \( \sim 2 \mu \text{m} \) diameter (Fig. 1a).5,7 It is interesting that these stress levels fall out of the regime where Hooke’s law applies (Fig. 1b).

The strength decreased sharply as the dimensions of the whiskers increased (Fig. 1a), because of ‘defects which are distributed statistically in a rather complex manner’.5,7 Therefore, it was recognised many decades ago that it is not wise to rely on perfection as a method of designing strong materials, although it remains the case that incredible strength can be achieved by reducing dimensions, in the case of iron, to a micrometre scale. It is in this context that we now proceed to examine claims that large scale engineering structures can be designed using long carbon nanotubes.11,12

Gigatubes

The existence of single walled carbon tubes was pointed out in 1976,13 but the subject seems to have become prominent after the discovery of \( C_{60} \) in 198514 and the identification of nanotubes by Iijima in 1991.15 These tubes can be imagined to be constructed from sheets of
Statement 5: the bainite, obtained by transformation at very low temperatures, is the hardest ever, has considerable ductility (almost all of it uniform), does not require mechanical processing, and does not require rapid cooling. Therefore, the steel after heat treatment does not have long range residual stresses. It is very cheap to produce and has uniform properties in very large sections. In effect, the hard bainite has achieved all of the essential objectives of structural nanomaterials which are the subject of so much research... BUT IN LARGE CHUNKS!

As is always the case, there remain many parameters that have yet to be characterised, for example the fatigue and stress corrosion properties.

Acknowledgements

The author is grateful to M. Endo for providing the images of the graphene and the schematic illustration of the graphene to nanotube transition. It is an especial pleasure to acknowledge Francisca Garcia Caballero for the original work on hard bainite. I would also like to thank Carlos Garcia Mateo, Mathew Peet, Kazu Hase, Suresh Babu, Mike Miller, Peter Brown, David Crowther and others who continue to contribute to the subject.

References

The mechanical properties of single-crystal and ultrananocrystalline diamond: A theoretical study

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Abstract

We examine the mechanical properties of single-crystal and ultrananocrystalline diamond (UNCD) by simulating their fracture using semiempirical quantum mechanics and density functional theory. Our results predict a failure strain of 0.13 and a fracture stress of 100 GPa for UNCD, which are 37% and 43%, respectively, that of single-crystal diamond. The Young’s modulus of UNCD is \( E = 1.05 \) TPa which is only slightly smaller than that of single-crystal diamond (\( E = 1.09 \) TPa). The UNCD fracture stress value (\( \sigma_f = 100 \) GPa) is very large compared to that observed experimentally (\( \sigma_f < 5 \) GPa). We use Griffith theory to show that this difference is due to defects in UNCD.

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1. Introduction

Thin diamond films composed of extremely small (3–5 nm) diamond grains and atom-wide grain boundaries (~0.2 nm wide) can now be produced using plasma-enhanced chemical vapor deposition techniques [1–4]. The material, which is called ultrananocrystalline diamond (UNCD), is very strong with mechanical properties (Vickers hardness, \( H_V = 88 \) GPa [5], and Young’s modulus, \( E = 950 \) GPa [6]) similar to those of single-crystal diamond (\( H_V = 100 \) GPa [7], and \( E = 1050 \) GPa [8,9]). The films are also smooth, with a mean surface roughness of ~20–40 nm [10,11]. Nitrogen-doping of the plasma can be used to make these films conduct significant amounts of electric current [12–17]. These properties combine to make UNCD an excellent candidate for use in the development of microelectromechanical systems [5,18].

We are interested in examining the strain-to-fracture behavior of these UNCD films using semiempirical quantum mechanics and density functional theory. Strain is applied to the diamond cluster, and the positions of the atoms are adjusted to minimize its energy, subject to the constraint provided by the strain.

The structure of UNCD films makes a complete examination of their fracture properties difficult. In addition to the grain boundaries which form between adjacent 3–5 nm diamond grains, these films contain other types of defects. Groups of diamond grains tend to form structures which are ~100 nm in size. Interfaces form between adjacent groups of diamond grains, producing grain boundaries with structures which are not well understood.

In this work, our primary focus will be on the mechanical properties of atom-wide grain boundaries which form between adjacent 3–5 nm diamond grains. References to the term ‘grain boundary’ in the remainder of the Letter are meant to refer to these grain boundaries. The effect of defects larger than these grain boundary structures will, however, also be discussed.
energy of the clusters as they were strained to failure. In the second, MSINDO was used to calculate structures as a function of strain, and PBE used to calculate energies of the structures. In the third approach, PBE was used, as MSINDO was in the first approach, to calculate both energies and structures as a function of strain. The third approach is the most accurate but is very computationally time-consuming. The second approach is only modestly more computationally expensive than the first but predicts Young’s modulus, failure strain and fracture stress values which are within 8%, 6% and 6%, respectively, of the full-strain PBE values for single-crystal diamond, and 9%, 23% and 16%, respectively, for UNCD. MSINDO alone was much less accurate.

Experimentally observed fracture stress values for single-crystal diamond and UNCD are approximately 1/50th of the corresponding theoretical values. We have shown that simple grain boundaries cannot be responsible for this decrease in strength and that Griffith theory, based on the calculated surface energy, suggests defects on the scale of 500 nm; defects of this scale have been observed experimentally.

Acknowledgments

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References

Stability of carbon nanotubes under electron irradiation: Role of tube diameter and chirality

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As recent experiments demonstrate, the inner shells of multiwalled carbon nanotubes are more sensitive to electron irradiation than the outer shells. To understand the origin of such counterintuitive behavior, we employ a density-functional-theory based tight-binding method and calculate the displacement threshold energies for carbon atoms in single-walled nanotubes with different diameters and chiralities. We show that the displacement energy and the defect production rate strongly depend on the diameter of the nanotube and its chirality, with the displacement energy being lower, but saturating towards the value for graphite when the tube diameter increases. This implies that the threshold electron energies to produce damage in nanotubes with diameters smaller than 1 nm are less than the commonly accepted value for graphitic nanoparticles. We also calculate the displacement energies for carbon atoms near defects and show that if a single vacancy is formed, it will likely be transformed to a double vacancy, as the nanotube atomic network with double vacancies has no energetically unfavorable undercoordinated atoms.

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I. INTRODUCTION

Electron irradiation of carbon nanotubes has proved to be an outstanding example of nanoengineering. In modern electron microscopes with field emission guns, the electron beam can be focused onto areas of several Å. This allows one to selectively modify nanostructures on an atomic scale by displacing or removing atoms from pre-defined regions. Carbon nanotubes are particularly suited for beam-induced nanomanipulation since the graphitic network has a high tendency to re-arrange after the formation of point defects. For example, welding1 and coalescence2 of carbon nanotubes by the electron beam have been demonstrated, which opens a different way for making a network of connected nanotubes for material reinforcement and use in nanoelectronics. The mechanical properties of nanotube bundles,3 and in principle macroscopic nanotube samples,4 can be improved due to intertube links produced by electron irradiation.

The irradiation-induced structural transformations in single-walled and multiwalled nanotubes (SWNTs/MWNTs) are due to the defects, mostly vacancies and interstitials, created by the impacts of energetic electrons followed by saturation of highly reactive dangling bonds at undercoordinated carbon atoms. Thus knowing the defect production mechanism and how the defect production rate is related to the beam characteristics is extremely important for controlling the transformations. Moreover, as carbon nanotubes are routinely characterized nowadays in the transmission electron microscope (TEM), the complete understanding of the interaction of energetic electrons with nanotubes should also minimize the amount of damage when it is an undesirable side effect.

Several TEM studies on irradiation-induced defects in carbon nanotubes have already been carried out.5–13 Early experiments5 showed that SWNTs exposed to focused electron irradiation were locally deformed and developed neck-like features due to removal of carbon atoms by knock-on displacements. Uniform irradiation of SWNTs (Ref. 9) resulted in surface reconstructions and drastic dimensional changes, as a corollary of which the apparent diameter of the nanotubes decreased from 1.4 to 0.4 nm. Experimental and theoretical studies also demonstrated that the electron beam creates defects nonuniformly: carbon atoms are most rapidly removed from surfaces lying normal to the beam direction.6,10

Very recently, it has been shown experimentally13 that MWNTs subjected to electron irradiation are destroyed from inside and that it is the inner shell which collapses first. Concurrently with these experiments, qualitatively similar results12 were obtained for double-walled nanotubes at different temperatures.

It has been demonstrated13 that a lower stability of the inner shells is due to a combination of two effects: a higher defect production rate in the inner shells and fast migration of carbon interstitials via the inner hollow in the axial direction. The defect production rate is related to the tube diameter, as the displacement threshold is lower for thin nanotubes with highly curved atomic network.

In this work, we theoretically study the relationship between the tube diameter and displacement rate in more detail. We also address the role of chirality. Finally, to better understand the evolution of nanotubes under high-dose irradiation, we calculate the displacement energies for carbon atoms near defects which can exist in nanotubes or appear due to interaction with the electron beam.

II. EVOLUTION OF MWNTS UNDER HIGH-DOSE ELECTRON IRRADIATION: TEM EXPERIMENTS

Similar to recent experiments,13 MWNTs were exposed to an intense focused electron beam in a TEM (FEI Tecnai F-30) with field emission electron gun operating at 300 kV. To prevent the agglomeration of interstitial atoms,8 the speci-
Biological structures mitigate catastrophic fracture through various strategies

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Abstract. Gao et al. (PNAS, 100, 5597–5600 (2003)) have argued that load-bearing mineralized hard tissues, including bones, shells, and teeth, are nanocomposites, in which the mineral phase has nanoscale dimensions that ensure optimum strength and flaw tolerance. In particular, it has been claimed that the thickness of these brittle building blocks, being smaller than a critical size, $h^*$, of the order of tens of nanometers, renders them insensitive to the presence of crack-like flaws and enables them to achieve near-theoretical strength, which is why Nature employs nanoscale features in mineralized biological composites. We find this point of view, which Gao et al. and others have quoted in subsequent publications and presentations, unpersuasive and present several counterexamples which show that biological structures, as a result of being comprised of relatively fragile constituents that fracture at stress levels several orders of magnitude smaller than the theoretical strength, adopt various strategies to develop mechanical responses that enable them to mitigate catastrophic failure. Nanoscale structural features are not a result of an innate resistance to very high stresses.

Key words: Biological structures, crack bridging, flaw-intolerance, flaw-tolerance, nanoscale structures, toughening.

1. Cracks always weaken brittle solids

It has been realized since the seminal work of Griffith in (1921) that cracks or flaws always weaken brittle solids, and that increasing strength with decreasing specimen dimensions is not a question of flaw tolerance but of the decreasing probability that a “strength-defining” (Griffith) flaw is present in the area or volume being loaded. The argument of Gao et al. that nanoscale components in mineralized hard tissue could (and for toughness and strength of the overall structure are required to) attain (near) theoretical strength and flaw tolerance must therefore be rigorously examined. We will first present a classical elementary atomistic model that shows that a brittle structure containing a crack tens of nanometers long cannot achieve its theoretical strength, contrary to the argument of Gao et al.; this atomistic model is relevant to all brittle solids containing nanoscale defects, including mineralized hard tissues. We conclude that it is unlikely that if Nature’s design were optimized, it would be
Biological structures mitigate catastrophic fracture


Predicting the elastic properties of single-walled carbon nanotubes

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Abstract

Advances in the prediction of the mechanical properties of single-walled carbon nanotubes (SWNTs) are reviewed in this paper. Based on the classical Cauchy-Born rule, a new computational method for the prediction of Young’s modulus of SWNTs is investigated. Compared with the existing approaches, the developed method circumvents the difficulties of high computational efforts by taking into consideration of the microstructure of nanotube and the atomic potential of hydrocarbons. Numerical results of Young’s modulus and its variation with respect to the deformation gradient tensor are given and discussed. The results obtained are in good agreement with those obtained by laboratory experiments and other numerical methods.

Keywords: Carbon nanotube; Cauchy-Born rule; Atomic potential function; Young’s modulus

1. Introduction

Since Iijima (1991) found multi-walled carbon nanotubes (MWNTs) in the soot produced by the arc discharge technique, carbon nanotubes (CNTs) have attracted much attention due to their superior mechanical, thermal and electrical properties...


Effect of randomly occurring Stone–Wales defects on mechanical properties of carbon nanotubes using atomistic simulation

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Abstract

The remarkable mechanical properties of carbon nanotubes (CNTs) have generated a lot of interest in recent years. While CNTs are found to have ultra-high stiffness and strength, an enormous scatter is also observed in available laboratory results. This randomness is partly due to the presence of nanoscale defects, heterogeneities etc, and 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 (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 loadings up to fracture of SWNTs with (6, 6) armchair and (10, 0) zigzag configurations and aspect ratio around six. A modified Morse potential is adopted to model the interatomic forces. We find that fracture invariably initiates from a defect if one is present; for a defect-free tube the crack initiates at quite random locations. The force–displacement curve typically behaves almost linearly up to about half way, although there is no obvious yield point. Three mechanical properties—stiffness, ultimate strength and ultimate strain—are calculated from the simulated force and displacement time histories. The randomness in mechanical behaviour resulting only from initial velocity distribution was found to be insignificant at room temperature. The mean values of stiffness, ultimate strength and ultimate strain of the tube decrease as the average number of defects increases, although the coefficients of variation do not show such a monotonic trend. The introduction of an additional defect has the most pronounced effect on the randomness in mechanical properties when the tube is originally defect free. We also find that, for a given mean number of defects in the tube, the zigzag configuration has less strength and less ultimate strain on average, but more uncertainty in its stiffness and ultimate strain, compared with the armchair tube.

(Some figures in this article are in colour only in the electronic version)
Effect of randomly occurring Stone–Wales defects on mechanical properties of carbon nanotubes using atomistic simulation

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Mechanics of defects in carbon nanotubes: Atomistic and multiscale simulations

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Molecular mechanics (MM) calculations together with coupling methods bridging MM and finite crystal elasticity are employed to simulate the fracture of defected carbon nanotubes (CNTs) and to compare with the available experimental results. The modified second generation Brenner potential (MTB-G2) is adopted in the calculations. Our MM calculations show fair agreement with quantum mechanical (QM) benchmarks, and indicate that one- and two-atom vacancies reduce the fracture strength of CNTs by 20%–33% (whereas the QM calculations predict 14%–27%), but these fracture strengths are still much higher than the experimental data. We then demonstrate that this experimental and theoretical discrepancy can be attributed to the presence of large-scale defects, such as those that may arise from oxidative purification processes. Simulations on multiwalled CNTs and tubes twisted prior to tensile loading show negligible effects on the fracture strength, which indicates that these are not the causes of low experimental values. The effects of chirality and tube diameter on fracture strengths are also investigated.

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I. INTRODUCTION

Predicting the strength of carbon nanotubes (CNTs) is an interesting challenge from both the scientific and engineering viewpoints. From a scientific viewpoint, a CNT ostensibly offers a clean model for the study of fracture, since the fracture of a single molecule should involve only chemical bond breaking at the atomic scale without other complications such as grain boundaries. From an engineering viewpoint, a thorough understanding of CNT fracture is needed for the design of CNT-reinforced composites. So far, comparisons of experimental data and theoretical calculations have manifested large discrepancies. According to the experimental measurements of Yu et al.,1 the fracture strengths of 19 multiwalled CNTs (MWCNTs) ranged from 11 to 63 GPa with a mean value of 27.8 GPa (see Fig. 1). However, recent quantum mechanical (QM) calculations2–7 for pristine tubes agree reasonably well with each other and indicate that the fracture of nanotubes is brittle at room temperature with a fracture stress in the range of 75–135 GPa depending on tube chirality. It is thus of interest to examine whether plausible defects or other possible effects stemming from the differences between the experiments and the numerical models could explain these discrepancies.

The cause of defects and their effects on the physical properties of CNTs have attracted considerable attention. One of the most intensively studied defects is the 5-7-7-5 dislocation formed by a Stone-Wales (SW) transformation.8 It has been shown by QM calculations that the SW transformation is energetically favored above a tensile strain of about ~5%–6% for armchair tubes9,10 and ~12% for zigzag tubes.10 Aggregation of SW defects has been hypothesized to lead to crack initiation;11 however, QM analysis6 indicates that aggregations of SW defects do not markedly reduce the fracture strength of CNTs—at least at moderate temperatures where brittle failure mechanisms prevail. It was also noted8 that empirical bond-order potentials12 incorrectly predict such weakening, which suggests that these potentials must be used with caution when treating defected CNTs. Irradiation with energetic ions or electrons can knock carbon atoms out of the hexagonal lattice, producing single-atom or multiatom vacancies in CNTs.13–15 Density functional theory (DFT) calculations showed that vacancy defects can form links between adjacent graphite layers,16 providing a mechanism for improved intershell or intertube mechanical coupling.17,18 In a recent study on the fracture of CNTs,7 it was argued that large defects could be introduced in MWCNTs by oxidative purification processes.19,20

Due to the small size of CNTs, fracture experiments are extremely challenging, and measurements of the tensile failure strength of individual tubes are fairly limited.1,21 QM calculations2–7 have therefore been used to elucidate the fracture of CNTs; however, the computational cost limits QM studies to CNTs with relatively small dimensions. Molecular

FIG. 1. Distribution of fracture stresses in the experiment of Yu et al. (Ref. 1).
TABLE IV. Size effects on the fracture strength of DWCNTs.

<table>
<thead>
<tr>
<th>CNTs</th>
<th>$D_{\text{outer}}$ (Å)</th>
<th>$\sigma_{\text{cr}}$ (GPa)</th>
<th>$\Delta R_{\text{outer}}$ (Å)</th>
<th>$\Delta R_{\text{inner}}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[50, 0][24, 24]</td>
<td>39.15</td>
<td>68.7(67.8)</td>
<td>0.07(0.12)</td>
<td>0.03</td>
</tr>
<tr>
<td>[71, 0][36, 36]</td>
<td>55.59</td>
<td>68.6(68.3)</td>
<td>0.10(0.13)</td>
<td>0.07</td>
</tr>
<tr>
<td>[116, 0][62, 62]</td>
<td>90.83</td>
<td>69.3(68.8)</td>
<td>0.17(0.24)</td>
<td>0.14</td>
</tr>
<tr>
<td>[220, 0][122, 122]</td>
<td>172.26</td>
<td>69.6(69.1)</td>
<td>0.32(0.42)</td>
<td>0.26</td>
</tr>
<tr>
<td>[388, 0][219, 219]</td>
<td>303.80</td>
<td>70.1(69.4)</td>
<td>0.50(0.78)</td>
<td>0.43</td>
</tr>
</tbody>
</table>

V. CONCLUDING REMARKS

Motivated by discrepancies between theoretical and experimental fracture strengths of CNTs, we studied the effects of vacancy defects, holes, and slits on fracture strength using MM and coupled MM/CM techniques. Where possible, these results are compared to available quantum mechanical calculations and fair agreement is observed. The MM calculations show that one- and two-atom vacancy defects weaken CNTs by 20%–33%, whereas MM calculations have shown 14%–27% reductions in strengths of these defects. The computed fracture strengths are slightly greater than the highest experimental values of Yu et al. and substantially greater than the average measured fracture strength. Holes (which may readily be introduced by oxidative purification processes) and slits (which are less likely to be experimentally relevant, but which have formal interest due to their resemblance to cracks) lower the fracture strength more significantly, falling in the upper range of the experimental observations. Slits and holes with a comparable cross section were observed to weaken tubes to a similar degree. The effect of tube chirality on fracture was explored; fracture strength increased monotonically with increasing chiral angle and armchair tubes were most resistant to the weakening effects of holes.

In addition to the MM calculations, calculations using a coupling method that bridges MM and finite crystal elasticity were presented. This coupling method enables the study of large-diameter SWCNTs and MWCNTs. Our simulations show that the presence of inner tubes only slightly increases the fracture strength of the CNTs considered, indicating small intershell mechanical coupling. Simulations of DWCNTs with two-atom vacancy defects in the outer shell show that the fracture strength is size dependent, but the variation is only a few GPa for the range of tube diameters considered. Twisting the tube prior to loading and other load imperfections were observed to negligibly affect the fracture strength of MWCNTs, but reduced the fracture strength of SWCNTs by as much as ~4% at a twisting angle of 15°. Therefore, imperfections in the loading are not a likely source of the low experimental fracture strengths.

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Fracture paths and ultrananocrystalline diamond

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Abstract

We use the simulated fracture of ultrananocrystalline diamond (UNCD) to illustrate how different fracture paths can result in different predictions of system properties. At zero temperature, the system is unable to explore the potential energy surface far from the fracture path being investigated. This can result in misleading predictions for the mechanical properties of UNCD. In non-zero temperature simulations, the system can explore more of the potential energy surface, but these are computationally intense simulations. We show how lower bounds to the energy path during fracture can be determined in pure and nitrogen-doped UNCD without doing finite temperature simulations.

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1. Introduction

Using plasma-enhanced chemical vapor deposition techniques, it is now possible to make thin diamond films containing extremely small (3–5 nm) diamond grains and atom-wide grain boundaries (~0.2 nm wide) [1–4]. This material, called ultrananocrystalline diamond (UNCD), has very impressive mechanical properties (~97 GPa hardness and 967 GPa Young’s modulus, which are similar to single-crystal diamond) [5,6]. These films can be doped with nitrogen to produce diamond films with significant electrical conduction [7–13]. These properties combined with the fact that the films are smooth (mean surface roughness = 20–40 nm) [14,15], makes them an excellent candidate for use in the development of microelectromechanical systems [16,17].

We are interested in examining the strain-to-fracture behavior of these UNCD films using semiempirical quantum mechanics. A complete examination of diamond fracture would necessarily involve some consideration of the effect of temperature, T. The quantum mechanical simulations we describe in this work are performed at T = 0. Strain is applied to the diamond structure, and the atoms adjust their positions in an attempt to minimize the energy of the cluster, subject to the constraint provided by the strain. In this minimization, only the local potential energy surface (PES) is explored. A more global exploration of the PES is possible when thermal effects are included. In the latter case atoms are vibrating about their lattice positions as strain is applied. Such an exploration can dramatically effect the reaction path taken on the way to diamond fracture. These thermal effects are important, as physically realistic fracture paths tend to be those which require the minimum amount of energy necessary for a given process [18]. However, the sampling of thermal paths is a very time-consuming process when electronic structure calculations are used to determine energies.

A partial solution to this problem is to examine more than one, or several fracture paths at T = 0. In this scheme the various paths explore different regions of the PES. The examination of many such paths should allow for a thorough exploration of the PES. In real systems thermal effects would allow the system to find its way between some of the paths. As a result, an
same is true for the pure UNCD crystal although the two grain boundaries in that case are not sufficiently different to produce a significant difference in asymptotic energy, as shown in Fig. 2.

4. Conclusions

Presented here is a theoretical investigation of different fracture paths leading to UNCD fracture. Both pure and nitrogen-doped UNCD were investigated. Because the diamond cluster size required for meaningful simulations means thermal effects are difficult to fully incorporate in quantum-mechanical studies, an investigation of multiple fracture paths was made. Results from the different fracture paths were examined, and a better approximation to the real fracture energy path provided. This makes it possible to locate lower bounds to the energy path during fracture without doing thermal sampling or simulated annealing.

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References

Mechanical properties of carbon nanotubes with vacancies and related defects

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Although as-grown carbon nanotubes have relatively few defects, defects can appear at the purification stage or be deliberately introduced by irradiation with energetic particles or by chemical treatment when aiming at the desired functionality. The defects, especially vacancies, give also rise to a deleterious effect—deterioration of axial mechanical properties of nanotubes. By employing molecular dynamics simulations and continuum theory we study how the Young’s modulus and tensile strength of nanotubes with vacancy-related defects depend on the concentration of defects and defect characteristics. We derive an analytical expression, with coefficients parametrized from atomistic computer simulations, which relates the Young’s modulus and defect density in carbon nanotubes. We further show that the tensile strength and critical strain of single-walled nanotubes decrease by nearly a factor of 2 if an unreconstructed vacancy is present. However, this deterioration in the mechanical characteristics is partly alleviated by the ability of nanotubes to heal vacancies in the atomic network by saturating dangling bonds.

I. INTRODUCTION

Carbon nanotubes (CNTs) have extremely high axial Young’s modulus of about 1 TPa (Refs.1–6) and tensile strength approaching 60 GPa.1,7 These exceptional mechanical properties along with low weight of CNTs and recent improvements in their synthesis and purification techniques make CNTs ideal candidates for reinforcement of various materials, e.g., polymers.8–10 High stiffness and the tensile strength of CNTs should also provide the mechanical stability for electric nano-circuits formed by CNTs with covalent inter-tube junctions.11

These outstanding mechanical characteristics hold for nearly perfect CNTs. However, if CNTs have defects in the atomic network, one can expect that due to their quasi-one-dimensional atomic structure even a small number of defects will result in some degradation12 of their characteristics. The defects can appear at the stage of CNT growth and purification,13,14 or later on during device or composite production. Moreover, defects in CNTs can deliberately be created by chemical treatment15 or by irradiation11,16–18 to achieve the desired functionality.

As an example of this, defects are expected to increase CNT adhesion to a polymer matrix,18,19 which should result in improvements of the composite mechanical characteristics. Likewise, defects may enhance the overall characteristics of bundles of single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). In these structures the interactions between intact nanotubes are governed by weak van der Waals forces, so that the axial mechanical load is carried only by the SWNTs at the rope perimeter20 or by the outermost shell in MWNTs. Thus, creating strong defect-mediated covalent bonds between SWNTs in bundles16,17,21–24 or between shells of MWNTs25 by, for example, irradiation should provide load transfer to the inner tubes (shells). On the other hand, irradiation will create not only covalent bonds between the tubes but also defects in the atomic network.

Very recent experiments24 on electron irradiation of carbon nanotube bundles followed by mechanical testing of the bundle bending modulus (which is proportional to the Young’s modulus) indicate that small dose irradiation gives rise to a very large improvement in the mechanical properties of irradiated bundles. This result was understood in terms of irradiation-induced inter-tube links which provided load transfer and correspondingly enhanced the shear modulus inside the bundle. However, high-dose irradiation resulted in deterioration of mechanical characteristics due to accumulation of the irradiation-induced damage, and specifically vacancies, in the nanotube atomic network.

In addition to linking the nanotubes by covalent bonds, irradiation has experimentally been demonstrated to give rise to complete welding11 and coalescence26 of nanotubes thus opening new ways for electron/ion beam-assisted engineering of nano-circuits. The driving force for these structural transformations was found to be the formation of vacancies with chemically reactive dangling bonds followed by annealing of the damage in which the bonds were saturated. However, even spatially-localized irradiation will create defects not only in the junction region, but also in the rest of the system due to, e.g., sputtered carbon atoms. This will inevitably result in deterioration of the mechanical stability of the system.

Therefore, to understand the role of defects in mechanical strength and to fully exploit the advantages potentially provided by the irradiation techniques, one should know how vacancy-related defects influence the mechanical characteristics of CNTs.

Although continuum methods27–29 work well for perfect materials, they cannot directly be applied to nanotubes with defects, as these methods assume the material to be perfect. However, a combination of these methods and atomistic simulations can be used for evaluating elastic properties of nanotubes with defects, while only atomistic methods can be employed for simulating the plastic behavior. In this paper, by employing atomistic computer simulations and analytical
Quantized fracture mechanics

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Abstract

A new energy-based theory, quantized fracture mechanics (QFM), is presented that modifies continuum-based fracture mechanics; stress- and strain-based QFM analogs are also proposed. The differentials in Griffith’s criterion are substituted with finite differences; the implications are remarkable. Fracture of tiny systems with a given geometry and type of loading occurs at ‘quantized’ stresses that are well predicted by QFM: strengths predicted by QFM are compared with experimental results on carbon nanotubes, β-SiC nanorods, α-Si3N4 whiskers, and polysilicon thin films; and also with molecular mechanics/dynamics simulation of fracture of carbon nanotubes and graphene with cracks and holes, and statistical mechanics-based simulations on fracture of two-dimensional spring networks. QFM is self-consistent, agreeing to first-order with linear elastic fracture mechanics (LEFM), and to second-order with non-linear fracture mechanics (NLFM). For vanishing crack length QFM predicts a finite ideal strength in agreement with Orowan’s prediction. In contrast to LEFM, QFM has no restrictions on treating defect size and shape. The different fracture Modes (opening I, sliding II and tearing III), and the stability of the fracture propagations, are treated in a simple way.

§ 1. Introduction

The phenomenon of fracture is of great interest. Two classic treatments are Griffith’s criterion (1920), an energy-based method, and a method based on the stress-intensity factor (Westergaard 1939); these present a well-known paradox. For a linear elastic structural element containing a crack of infinitesimal length, both these methods of continuum-based linear elastic fracture mechanics (LEFM), shown to be equivalent (Irwin 1957), incorrectly predict an infinite load at failure. Conversely from elasticity, a singularity in the stress field at the crack tip (Westergaard 1939) is derived also for infinitesimal crack length; combined with the classical assumption that failure occurs when the maximum stress equals or exceeds the material strength, failure must occur at the physically unreasonable zero load. We choose to modify

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corresponding predictions for the strength of nanotubes with short cracks of length \(2l \approx 2a, 4a, 6a, 8a\) are reported in table 2 and compared with QFM and MM simulations.

§A5. Circular holes

The stress near a hole of radius \(\rho\) (center at \(x, y = 0\)) in an infinite plate subjected to a remote stress field \(\sigma\) is (Kirsch 1898; see Carpinteri 1997)

\[
\sigma_r = \frac{\sigma}{2} \left( 1 - \frac{\rho^2}{r^2} \right), \quad \sigma_\theta = \frac{\sigma}{2} \left( 1 + \frac{\rho^2}{r^2} \right)
\]

(cos \(2\theta\)) (the shearing stress does not affect our predictions). Assuming isotropic linear elastic constitutive laws and applying equation (3b) by integration, we obtain the result of equation (7) if \(\nu = 0\). Assuming \(\nu = \theta = 0\), three limit cases are interesting: (i) for \(\rho^* \rightarrow 0\), \(\sigma/\sigma_C \rightarrow 1\); (ii) for \(\rho^* \rightarrow \infty, \sigma/\sigma_C \rightarrow 1/3\) (case of elasticity and classical tensile criterion, that assumes the continuum hypothesis, i.e., \(a \rightarrow 0\)); for \(\rho^* \rightarrow 1/2\) (one vacancy in an ideal two-dimensional lattice), \(\sigma/\sigma_C \rightarrow 0.71\).

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Density functional calculations of response of single-walled armchair carbon nanotubes to axial tension

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Abstract

The response of single-walled armchair carbon nanotubes (SWACNTs) to axial tension was studied using density functional calculations. A new response causing an abrupt change in nanotube structure at specific strains was detected. Atom rearrangement results in a lower energy than expected. The geometry of armchair nanotube plays an important role in the observed response, with the effect of curvature being important. There is a meaningful relationship between rearrangement strain and nanotube diameter. Rearrangement can be explained using the Poisson effect, which increases with the lateral displacement and is inversely proportional to nanotube index number.

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Keywords: Armchair nanotube; Rearrangement; Tension; Response mechanism; Circumferential pressure; DFT

1. Introduction

Strength of materials emerges from strength of chemical bonds. Not only the strength of chemical bonds plays an important role in mechanical ability of materials but arrangement of bonds is also important. For instance, though the strength of C–C single (or double) bond is approximately equal in different substances, known allotropes of carbon (namely diamond, graphite, and fullerene) have entirely different physical properties. Carbon nanotubes (CNTs) are very important members of fullerenes. In a cylindrical network of CNTs all atoms are equivalently tied to the neighbors, and no “weak spot” is apparent. This intrinsic uniformity, together with the known strength of carbon bonds, must lead to extreme resistance to mechanical tension [1]. The strong in-plane graphitic C–C bonds make free defect CNTs that are strong and stiff against axial strains and very flexible against non-axial strains [2]. CNTs combine high stiffness with resilience and the ability to buckle and collapse in a reversible manner [3–5]. Despite the very large strain, any bond breaking or switching did not occur in nanotubes. Excellent mechanical response to severe deformation and strain is the main cause of attracting much experimental [5–14] and theoretical [1,3,4,15–27] investigations to them since their discovery in 1991. It was demonstrated that carbon nanotubes have exceptional mechanical properties. Their excellent flexibility during bending has been observed by experiment and simulated by theory [3–5]. Loading techniques, often based on atomic force microscopy that combined with electron microscopic imaging, allow one to measure the breaking-strain level and Young modulus, and to observe the overall failure patterns experimentally [1]. At first, the elastic modulus in multi-walled carbon nanotubes (MWCNTs) has experimentally been determined by Treacy and co-workers [5]. It has been determined equal to 1.8 ± 0.9 TPa by measuring thermal vibrations using TEM. Wong et al. [10] obtained the lower value 1.28 ± 0.59 TPa using the
armchair tubes directly exert a structural pressure on circumferential bonds during tension due to Poisson effect. At specific strains, structural pressure increases enough to overcome resistant forces and rearrange the structure. Physically, the pathway that the structure moves along depends on strain rate, temperature, etc., which by the way is not the subject of this work. It is deduced from Table 1 that the structural effect is in the reverse proportion to the nanotube index. On the other hand, rearrangement strain defer to the higher values by the increase of nanotube diameter. It is well-known that in armchair nanotubes the Poisson ratio decreases by the increase of diameter [37].

Another evident of reverse proportionality of tube index with structural effect is obtained by comparison between the results of Mielke et al. [20] and Ogata and Shibutani [38]. As can be seen in Fig. 4b, the deformed hexagon undergoes the transverse tension; L corresponds to lateral displacement. Obviously, the escalation of strain increases the lateral displacement. As a criterion for a comparison between the rate of this effect and the diameter of nanotube, we established a simple formula:

$$P \propto \frac{L}{n}$$  \hspace{1cm} (1)

where $P$ is Poisson effect, $L$ is lateral displacement and $n$ is nanotube index number. Our formula implies that (3,3) armchair nanotube is the first one to reach to adequate strain, (4,4), (5,5), (6,6) and (8,8) armchair nanotubes are the latter ones, respectively. As can be seen in Table 1 and Fig. 1, there is a good agreement between qualitative prediction of formula and calculations.

4. Conclusions

A new response mechanism was detected along tension of single-walled armchair carbon nanotubes by density functional calculation using B3LYP method. Structural changes are not topological, but help nanotube to bear more strain. In this mechanism, an important factor is the changes of bond lengths that are precisely aligned with circumference. These bonds are physically in correlation with longitudinal bonds. This behavior can obviously be seen at a specific strain. In relationship with Poisson effect, a structural effect is also attended which is called circumferential pressure. This mechanism can be explained by this concept. The effect of tube diameter has also been examined. The results show that the rearrangement strain refers to higher values by the increase in the diameter of CNT. Qualitatively, we introduced a formula for circumferential pressure that can successfully predict the delay in rearrangement strain.

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Fig. 4. (a) The situation of transverse tension in graphene. (b) A hexagon of graphene sheet and deformed structure undergoes transverse tension; L is the magnitude of lateral displacement.
Ultrastrong, Stiff, and Lightweight Carbon-Nanotube Fibers**

By Xiefei Zhang, Qingwen Li, Terry G. Holesinger, Paul N. Arendt, Jianyu Huang, P. Douglas Kirven, Timothy G. Clapp, Raymond F. DePaula, Xiazhou Liao, Yonghao Zhao, Lianxi Zheng, Dean E. Peterson, and Yuntian Zhu*

From the stone ages to modern history, new materials have often been the enablers of revolutionary technologies.[1] For a wide variety of envisioned applications in space exploration, energy-efficient aircraft, and armor, materials must be significantly stronger, stiffer, and lighter than what is currently available. Carbon nanotubes (CNTs) have extremely high strength,[2–5] very high stiffness,[6,7] low density, good chemical stability, and high thermal and electrical conductivities.[8] These superior properties make CNTs very attractive for many structural applications and technologies. Here we report CNT fibers that are many times stronger and stiffer per weight than the best existing engineering fibers and over twenty times better than other reported CNT fibers. Additionally, our CNT fibers are nonbrittle and tough, making them far superior to existing materials for preventing catastrophic failure. These new CNT fibers will not only make tens of thousands of products stronger, lighter, safer, and more energy efficient, but they will also bring to fruition many envisioned technologies that have been to date unavailable because of material restrictions.

Strong, stiff, and lightweight are critical property requirements for materials that are used in the construction of space shuttles, airplanes, and space structures. These properties are assessed by a material’s specific strength and specific stiffness, which are defined as the strength or stiffness (Young’s modulus) of a material divided by its density.[9] The combination of high strength, high stiffness, and low density affords CNTs with extremely high values for specific strength and specific stiffness. The most effective way to utilize these properties is to assemble CNTs into fibers. However, despite extensive worldwide efforts to date, the specific strength and specific stiffness of CNT fibers that have been reported by various research groups are much lower than currently available commercial fibers.[10–22] In early studies, researchers attempted to reinforce polymer fibers with short CNTs, but the reinforcement was limited by several issues, including poor dispersion, poor alignment, poor load transfer, and a low CNT volume fraction.[10–15] Recently, pure CNT fibers (also called yarns) were reported with and without twisting.[16–22] For example, Zhang et al.[20] demonstrated that spinning from aligned CNT arrays could significantly improve the strength of CNT fibers by twisting them. However, to date no breakthrough has been reported in the specific strength and specific stiffness of CNT fibers.

Here we report CNT fibers with values for specific strength and specific stiffness that are much higher than values reported for any current engineering fibers as well as previously reported CNT fibers. As shown in Figure 1, the specific strength...


