## You may also like

# Equilibrium configuration and continuum elastic properties of finite sized graphene 

To cite this article: C D Reddy et al 2006 Nanotechnology 17864

View the article online for updates and enhancements.

Electrical transport and photovoltaic effects of core-shell $\mathrm{CuO} / \mathrm{C}_{60}$ nanowire heterostructure
Qiaoliang Bao, Chang Ming Li, Lei Liao et al.

- A dual-colored bio-marker made of doped ZnO nanocrystals Y L Wu, S Fu, A I Y Tok et al.
- The Design of High Precision Arbitrary Waveform Generator Based on DDS Technology and FPGA Li-Min Ren, Xiao Xue and Yang-Bing Zheng



# Equilibrium configuration and continuum elastic properties of finite sized graphene 

C D Reddy ${ }^{1,2}$, S Rajendran ${ }^{1}$ and K M Liew ${ }^{1,2}$<br>${ }^{1}$ School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore<br>${ }^{2}$ Nanyang Centre for Supercomputing and Visualisation, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore<br>E-mail: MSRajendran@ntu.edu.sg

Received 15 July 2005, in final form 12 October 2005
Published 16 January 2006
Online at stacks.iop.org/Nano/17/864


#### 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 $2-3 \mathrm{~nm}$ 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 $2800^{\circ} \mathrm{C}$ 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
system was made by Tersoff [12]. Brenner [13] introduced the bond order function to describe the effect of formation and breakage of carbon-carbon bonds. Many researchers have used Brenner's potential to explore the formation of fullerenes and their properties [14, 15], indentation and friction at nanoscale [16, 17], and energetics of nanotubes [18]. Recently, a second-generation potential energy function has been developed by Brenner et al [19] based on empirical bond order formalism for solid carbon and hydrocarbon molecules. This revised potential has provided a powerful method for modelling complex chemistry involving large-scale atoms. The semi-empirical model, proposed by Pettifor and Oleinik [20], is derived based on the tight-binding approach. The LennardJones potential energy has been widely used to compute the energy between the inter-atomic layers [21].

Researchers have reported widely varying Young's modulus values for CNT in the range $0.5-5.5 \mathrm{TPa}$. The large scatter of these values is apparently due to different measurement techniques, simulation methods, and dimensions (diameter, thickness and configuration) of SWNTs. The concept of in-plane stiffness is often considered to reduce the major ambiguity due to the thickness assumption. The diameter and configuration of SWNTs do not have much effect on Young's modulus. Very few researchers have reported the elastic properties of graphene. The Young's modulus and Poisson's ratio of graphene have been computed using an ab initio method by Kudin et al [22] as 1.02 TPa and 0.149 respectively, while Van Lier et al [23] reported Young's modulus for graphene sheet as 1.11 TPa . Arrayo et al [24] calculated the Young's modulus and Poisson's ratio of graphene based on Brenner potentials (1990) [13] and modified Brenner potentials (2002) [19] as $0.694 \mathrm{TPa}, 0.412$ and $0.714 \mathrm{TPa}, 0.397$, respectively.

Very recently, researchers [25] have succeeded in extracting individual planes of carbon atoms from graphite crystals, which results in the production of a few atomic layers of graphene including single-layer graphene to fabricate devices from them. However, studies on the elastic properties of graphene are scarce, hence the motivation for the present work.

In the present paper, the effect of using a minimized or unminimized configuration for the determination of elastic constants is studied. The spatial variations of equilibrium bond length are also studied for these configurations. The influence of the size of the graphene sheet on the computed Young's modulus values is studied. Two models, i.e., with only two or all four edges constrained to be straight, are considered for the analysis. The possible orthotropicity of the material behaviour is explored. Finally, the reason for the large scatter in the Young's modulus reported in the literature is explored.

## 2. Interatomic potential for carbon

The Tersoff-Brenner potential, $V_{\mathrm{B}}$, for hydrocarbons [13] is considered for the present work and it follows the bond-order formalism of the atomic system [26]. This potential has been widely used for the simulation of carbon nanotubes, and it expresses the binding energy in terms of bond lengths and angles, as a sum over bonds:

$$
\begin{equation*}
V_{\mathrm{B}}\left(r_{i j}\right)=\sum_{i} \sum_{j(>i)}\left[V_{\mathrm{R}}\left(r_{i j}\right)-\overline{B_{i j}} V_{\mathrm{A}}\left(r_{i j}\right)\right] \tag{1}
\end{equation*}
$$

where $r_{i j}$ is the distance between atoms $i$ and $j . V_{\mathrm{R}}$ and $V_{\mathrm{A}}$ are the repulsive and attractive pairs of energy terms given by

$$
\begin{align*}
V_{\mathrm{R}}\left(r_{i j}\right) & =\frac{D^{(e)}}{S-1} \mathrm{e}^{-\sqrt{2 S} \beta\left(r_{i j}-R^{(e)}\right)} f_{c}\left(r_{i j}\right)  \tag{2}\\
V_{\mathrm{A}}\left(r_{i j}\right) & =\frac{D^{(e)} S}{S-1} \mathrm{e}^{-\sqrt{2 / S} \beta\left(r_{i j}-R^{(e)}\right)} f_{c}\left(r_{i j}\right) . \tag{3}
\end{align*}
$$

The second set of Brenner's potential parameters, i.e., $D^{(e)}=6.0 \mathrm{eV}, S=1.22, \beta=21 \mathrm{~nm}^{-1}$ and $R^{(e)}=$ 0.1390 nm , used here are the ones determined from the known physical properties of carbon, graphite and diamond [13]. The smooth continuous cut-off function $f_{c}\left(r_{i j}\right)$ is used to limit the range of potential:

$$
f_{c}\left(r_{i j}\right)=\left\{\begin{array}{l}
1 \quad r_{i j}<R^{(1)}  \tag{4}\\
\frac{1}{2}\left\{1+\cos \left[\frac{\pi\left(r_{i j}-R^{(1)}\right)}{R^{(2)}-R^{(1)}}\right]\right\}, \\
R^{(1)}<r_{i j}<R^{(2)} \\
0 \quad r_{i j}>R^{(2)}
\end{array}\right.
$$

where the cut-off constants $R^{(1)}=0.17 \mathrm{~nm}$ and $R^{(2)}=$ 0.2 nm . The multi-body coupling parameter in equation (1) of the bond between atoms $i$ and $j$ is given by $\overline{B_{i j}}=\left(B_{i j}+\right.$ $\left.B_{j i}\right) / 2$, where

$$
\begin{equation*}
B_{i j}=\left[1+\sum_{k(\neq i, j)} G\left(\theta_{i j k}\right) f_{c}\left(r_{i k}\right)\right]^{-\delta} \tag{5}
\end{equation*}
$$

where $k$ represents atoms other than $i$ and $j, r_{i k}$ is the distance between atoms $i$ and $k, \delta=0.5$ is a constant and $\theta_{i j k}$ is the angle between the bonds $i-j$ and $i-k$. The function $G$ is given by

$$
\begin{equation*}
G\left(\theta_{i j k}\right)=a_{0}\left[1+\frac{c_{0}^{2}}{d_{0}^{2}}-\frac{c_{0}^{2}}{d_{0}^{2}+\left(1+\cos \left(\theta_{i j k}\right)\right)^{2}}\right] \tag{6}
\end{equation*}
$$

where the parameter values $a_{0}, c_{0}$ and $d_{0}$ are $0.00020813,330$ and 3.5 , respectively.

## 3. Determination of elastic properties

In continuum mechanics, the constitutive relations between load and deformation have been established prior to solving a specific problem. If the material is homogeneous and isotropic, the material can be represented by two independent constants, namely, Young's modulus $Y$ and Poisson's ratio $v$. For a material undergoing a uni-axial deformation, $Y$ is defined as

$$
\begin{equation*}
Y=\frac{1}{V_{0}}\left(\frac{\partial^{2} V_{\mathrm{B}}}{\partial \varepsilon^{2}}\right)_{\varepsilon=0} \tag{7}
\end{equation*}
$$

where $V_{0}$ is the volume corresponding to the initial equilibrium configuration of graphene, $V_{\mathrm{B}}$ the total strain energy under tensile deformation and $\varepsilon$ is the tensile strain. However, different thickness values have been hypothesized [27] for SWNT or graphene, and therefore the volume $V_{0}$ is not properly defined. Hence, the in-plane stiffness $C$, which is independent of the thickness of graphene, is defined as an alternative measure in place of Young's modulus:

$$
\begin{equation*}
C=\frac{1}{A_{0}}\left(\frac{\partial^{2} V_{\mathrm{B}}}{\partial \varepsilon^{2}}\right)_{\varepsilon=0} \tag{8}
\end{equation*}
$$



Figure 1. Initial configuration of graphene.
where $A_{0}$ is the equilibrium surface area of graphene sheet. If thickness $h$ is defined for a graphene sheet, then the volume can be defined as $V_{0}=A_{0} h$, and the Young's modulus is $Y=C / h$. The thickness is usually taken to be 0.34 nm . The Poisson's ratio can be defined as

$$
\begin{equation*}
v=-\frac{\Delta w}{w} / \frac{\Delta L}{L} \tag{9}
\end{equation*}
$$

where $w$ is the width of the graphene sheet, $L$ is the length, and $\Delta w$ and $\Delta L$ are the changes in the width and length, respectively. For a material undergoing a shear deformation, $G$ is similarly defined as

$$
\begin{equation*}
G=\frac{1}{V_{0}}\left(\frac{\partial^{2} V_{\mathrm{B}}}{\partial \phi^{2}}\right)_{\phi=0} . \tag{10}
\end{equation*}
$$

## 4. Results and discussions

### 4.1. Equilibrium configuration and bond length

To determine the equilibrium configuration and the bond length, we consider a graphene sheet made of 120 atoms fitting into a rectangular envelope as shown in figure 1. The Brenner potential of the rectangular graphene sheet is minimized with the rigid body modes (i.e., two translational modes and one rotational mode) restrained. The final envelope of graphene sheet after minimization is no longer a rectangle. The initially straight edges of the rectangular envelope deform to curved edges as shown in figure 2. This is attributed to the nonuniform extension/contraction of the lattice caused by the variation in the coordination numbers of individual carbon atoms. The coordination number is a measure of the number of neighbouring atoms. For a graphene sheet, the coordination number for boundary atoms is two while that of inner atoms is three. Due to the variation in coordination


Figure 2. Equilibrium configuration (dotted line) and initial configuration (continuous line). Alphabetical characters marked represent various equilibrium bond lengths (see table 1).

Table 1. Bond length variation in equilibrium configuration of graphene.

| Alphabet | Bond length <br> $(\mathrm{nm})$ | Alphabet | Bond length <br> $(\mathrm{nm})$ |
| :--- | :--- | :--- | :--- |
| A | 0.139 | E | 0.145 |
| B | 0.141 | F | 0.146 |
| C | 0.143 | G | 0.147 |
| D | 0.144 |  |  |

number, the equilibrium bond length of carbon-carbon is not uniform everywhere in the finite graphene. The bond lengths can be arranged into seven groups and are labelled by letters A-G in figure 2 and listed in table 1. The letter A refers to the minimum bond length of 0.139 nm , which occurs in the central region of the top and bottom edges. The maximum bond length labelled by letter G is 0.147 nm , and it occurs near the four corners. The average bond length of the graphene has been computed as 0.144 nm , which agrees well with that of equilibrium bond length reported by Arroyo et al [24] and Zhang et al [28]. A careful study of figure 2 reveals that the net influence of the atoms surrounding a $\mathrm{C}-\mathrm{C}$ bond is to increase the length of the bond as compared with a single $\mathrm{C}-\mathrm{C}$ equilibrium bond length.

The study of bond length variation is then extended to graphene sheets with 66, 276 and 496 carbon atoms. Here again, a similar trend is observed, i.e., the bond lengths of interior bonds are found to be around 0.145 nm (accurate to three decimal places), which is same as the bond length of finite graphene obtained by Arroyo et al [24] using periodic boundary conditions. This suggests that the bond length of interior bonds in the finite graphene is already close to that of infinite graphene.

The computed elastic properties are presented in sections 4.2-4.5. These properties are computed based on



Figure 3. Different widths considered for Poisson's ratio calculations.
prescribed displacement loading on the edges of the graphene model. The curved nature of the edges poses difficulties in applying the displacement loading and boundary conditions. For the present work, two models are considered. In model 1 the left and right edges or the top and bottom edges of the envelope are constrained to remain straight, and in model 2 all four edges are constrained to remain straight. With these constraints applied, the equilibrium configuration is first obtained by minimizing the potential before applying the displacement loading. For the present work, the minimization is done using an optimization code. The elastic properties are computed using the relations in equations (7)-(10). The orthotropicity of the computed elastic properties is then checked using the well known relations of the orthotropic material model.

### 4.2. Model 1: two straight edges

The Cauchy-Born rule, referred to as a method of the homogeneous deformations, is a fundamental kinematic rule that links the deformation of lattice vectors to that of the continuous medium, and is recently proven rigorously to hold under certain conditions [29]. By means of the CauchyBorn rule, the continuum elastic potential can be obtained by equating the deformation energy of the graphene to that of an equivalent volume of the continuum. The resulting continuum constitutive graphene model depends only on the interatomic interactions.

Constraint equations are applied to left and right edges of the graphene sheet to make the edges straight. Appropriate displacements are applied on these edges for uni-axial tensile and compressive loading, and the corresponding equilibrium potential energy is computed for a series of loadings. Figure 4 shows the plot of equilibrium potential energy versus engineering strain, $\varepsilon$. By using polynomial curve fitting, the potential is expressed in terms of $\varepsilon$ as

$$
\begin{equation*}
V_{\mathrm{B}}=a_{0}+a_{1} \varepsilon+a_{2} \varepsilon^{2}+a_{3} \varepsilon^{3}+a_{4} \varepsilon^{4}+\cdots . \tag{11}
\end{equation*}
$$



Figure 4. Potential versus strain for uni-axial tensile deformation.

If the potential computations are correct, then $a_{1}$ in equation (11) must reduce to zero or a negligible number. When equilibrium configurations are used for the computation, this happens. Using equations (7) and (11), the Young's modulus, $Y_{1}$, is computed as 0.669 TPa . (The Young's modulus $Y_{1}$ computed without minimization of potential is 1.012 TPa , which agrees well with the Young's modulus of graphene [23] and SWNT [30]. The procedure is described in section 4.5.) A comparison of Young's modulus and Poisson's ratio of graphene sheet computed by several authors from different methods is shown in table 2. The equilibrium potential versus shear strain graph is similar to that of tensile loading (figure 4), and hence is not shown. Following a similar approach to that discussed above, the shear modulus is computed using equation (10) as 0.179 TPa . Van Lier [23] computed the Young's modulus as 1.11 TPa , by considering only the two middle carbon atoms from the set of ten atoms to eliminate the side-effects caused by graphitic sheet termination.

The potential minimization of graphene simulation is computationally intensive. Hence, only a limited number of finite graphene sheets with $66,120,276$ and 496 carbon atoms have been considered to study the variation of Young's modulus with size of graphene and the results are shown in table 3. From this table, the variation of Young's modulus with size is seen to be very small. Hence, for further computations, the graphene sheet with 120 carbon atoms has been considered as a trade-off between accuracy and computational time. The computed elastic constants of graphene with 120 carbon atoms are summarized in table 6. The present Young's modulus of 0.669 TPa for graphene is close to that of the graphene Young's modulus reported by Arroyo et al [24] and the Young's modulus of SWNT reported by Zhang et al [28].

From the uni-axial tensile loading, the Poisson's ratio is computed using equation (9). The Poisson's ratios computed at the midsection of graphene considering three widths, namely between $1-1$ and $1^{\prime}-1^{\prime}$ layers, $2-2$ and $2^{\prime}-2^{\prime}$ layers and $3-3$ and $3^{\prime}-3^{\prime}$ layers (figure 3 ), are shown as dots, squares and circles, respectively, in figure 5. The extrapolated Poisson's ratio values for zero percentage elongation (figure 5) corresponding to these three cases are $0.416,0.371$ and 0.367 , respectively, for the case of two straight edges. The computed Poisson's ratio

Table 2. Young's modulus and Poisson's ratio values reported by several authors.

| Reported by | Young's modulus (TPa) | Poisson's ratio | Remarks |
| :---: | :---: | :---: | :---: |
| Present with minimization of potential | 0.669 | 0.416 | Graphene (Brenner) |
| Arroyo et al [24] | 0.694 | 0.412 | Graphene (Brenner) |
| Kudin et al [22] | 1.02 | 0.149 | Graphene (ab initio) |
| Reddy et al [31] | 1.11 | 0.45 | Graphene (Truss element model) |
| Lier et al [23] | 1.11 | - | Graphene (ab initio) |
| Present without minimization of potential | 1.012 | 0.245 | Graphene (Brenner) |
| Shen et al [32] | 0.213-2.08 | 0.16 | SWNT (MM) |
| Yu et al [33] | 0.32-1.47 | - | SWNT (Experiments) |
| Zhang et al [28] | 0.694 | - | SWNT (Brenner) |
| Sammalkorpi et al [34] | 0.7 | - | SWNT (MD) |
| Lu [30] | 0.97 | 0.28 | SWNT (Empirical force constant model) |
| Yoon et al [35] | 1 | 0.25 | DWNT (Vibrations) |



Figure 5. Poisson's ratio for the graphene model with two straight edges (unconnected symbols) and for four straight edges (connected symbols).

Table 3. Young's modulus variation with size of graphene sheet.

| No. of <br> atoms | Young's modulus <br> (TPa) | No. of <br> atoms | Young's modulus <br> (TPa) |
| :---: | :--- | :--- | :--- |
| 66 | 0.659 | 276 | 0.677 |
| 120 | 0.669 | 496 | 0.682 |

Table 4. Poisson's ratio $v_{12}$ for the case of two straight edges and four straight edges.

| Between layers <br> (figure 3) | Two straight <br> edges | Four straight <br> edges |
| :--- | :--- | :--- |
| $1-1$ and $1^{\prime}-1^{\prime}$ | 0.416 | 0.428 |
| $2-2$ and $2^{\prime}-2^{\prime}$ | 0.371 | 0.389 |
| $3-3$ and $3^{\prime}-3^{\prime}$ | 0.367 | 0.384 |

of 0.416 agrees well with that of Arroyo et al [24], namely 0.412 . The Poisson's ratio computed without minimization of potential is around 0.25 , which agrees well with that of Poisson's ratio of SWNT [30]. The results are summarized in table 4.

Table 5. Orthotropicity measurement.

| Model | Orthotropicity measure: $\left(\frac{Y_{1}}{Y_{2}} \frac{v_{21}}{v_{12}}\right)$ |
| :--- | :--- |
| Model 1: two straight edges | 0.9205 |
| Model 2: four straight edges | 0.9991 |

### 4.3. Model 2: four straight edges

The same study is extended to the four-straight-edge graphene model. Constraint equations have been applied to all the four edges to make them remain straight during the minimization to obtain equilibrium configuration. Using equations (7), (10) and (11), the Young's modulus and shear modulus have been computed and tabulated in table 6 . If the graphene sheet is looked upon as a two-dimensional continuum made of orthotropic material, then the elastic constants must satisfy the following conditions:

$$
\begin{gather*}
Y_{1}, Y_{2}, G_{12}>0  \tag{12}\\
\frac{\nu_{12}}{Y_{1}}=\frac{\nu_{21}}{Y_{2}}  \tag{13}\\
\left|\nu_{12}\right|<\left(\frac{Y_{1}}{Y_{2}}\right)^{\frac{1}{2}}, \quad\left|\nu_{21}\right|<\left(\frac{Y_{2}}{Y_{1}}\right)^{\frac{1}{2}}  \tag{14}\\
v_{21}<\frac{1-v_{21}^{2}\left(\frac{Y_{1}}{Y_{2}}\right)}{2}<\frac{1}{2} \tag{15}
\end{gather*}
$$

where $\left(Y_{1}, v_{12}\right)$ and $\left(Y_{2}, \nu_{21}\right)$ are the sets of Young's modulus and Poisson's ratio in longitudinal and lateral directions, respectively. $G_{12}$ is the shear modulus of the graphene sheet. The elastic constants determined using the four-straight-edge model satisfy all the orthotropic conditions, equations (12)(15). However, the elastic constants determined using the two-straight-edge model do not satisfy equation (13). From equation (13), we may define the quantity ( $\frac{Y_{1}}{Y_{2}} \frac{v_{21}}{v_{12}}$ ) as a measure of orthotropicity, and its value is equal to unity if the material conforms to orthotropic material model. The computed values of this measure for the two models are listed in table 5 .

The elastic constants, being material properties, are expected to be independent of the size and boundary conditions. However, from the above studies, the computed elastic constants are observed to vary slightly with respect to


Figure 6. Potential versus strain plot before and after the rupture of bonds.

Table 6. Elastic constants for the graphene model with two straight edges and four straight edges.

| Elastic <br> constants | Two straight <br> edges | Four straight <br> edges |
| :--- | :--- | :--- |
| $Y_{1}$ | 0.669 TPa | 0.671 TPa |
| $\nu_{12}$ | 0.416 | 0.428 |
| $G_{12}$ | 0.179 TPa | 0.384 TPa |
| $Y_{2}$ | 0.812 TPa | 0.816 TPa |
| $\nu_{21}$ | 0.465 | 0.520 |

the size and boundary conditions. This suggests that finite sized graphene does not exactly behave like a continuum. Such dependence of Young's modulus on the radius of single-walled carbon nanotubes has been reported in the literature (e.g., see [32, 34, 36]).

### 4.4. Potential versus strain, and stress versus strain relationships

Figure 6 shows the plot of potential versus strain for a loading that continues even beyond the first rupture of a $\mathrm{C}-\mathrm{C}$ bond of graphene sheet. The first bond breaks around $33 \%$ elongation labelled by the letter B and the corresponding failure stress 0.123 TPa . These values agree well with the CNT failure strain/stress values, $30 \%$ and 0.11 TPa respectively, reported by Mielke et al [37] and $29.5 \%$ and 0.115 TPa respectively, reported by Ogata et al [38]. The first bond breakage occurs at a bond near a corner marked by the symbol $G$ in figure 2 . For loading beyond first rupture, the potential value drops and rises several times due to different bonds breaking at different locations and the resultant structural rearrangements of the lattice structure of the graphene. The potential equation is obtained from figure 6 using polynomial curve fitting until the first rupture point B and is expressed in the form of equation (11). By differentiating this expression with respect to the small strain measure, $\varepsilon$, the expression for the corresponding stress, $\sigma$, becomes

$$
\begin{equation*}
\sigma=\frac{\mathrm{d} V_{\mathrm{B}}}{\mathrm{~d} \varepsilon}=a_{1}+2 a_{2} \varepsilon+3 a_{3} \varepsilon^{2}+4 a_{4} \varepsilon^{3}+\cdots . \tag{16}
\end{equation*}
$$



Figure 7. Stress-strain curves: $\sigma$ versus $\varepsilon$ (dots) and $S$ versus $E$ (circles).

The relation between small strain, $\varepsilon$, and the Green strain, $E$, is written as

$$
\begin{equation*}
E=\frac{1}{2}\left(\varepsilon^{2}+2 \varepsilon\right) . \tag{17}
\end{equation*}
$$

Substituting equation (17) in (11), we get $V_{\mathrm{B}}$ in terms of $E$. By differentiating this expression with respect to $E$, we get the expression for the second Piola-Kirchoff stress:

$$
\begin{equation*}
S=\frac{\mathrm{d} V_{\mathrm{B}}}{\mathrm{~d} E}=\left(\frac{\mathrm{d} V_{\mathrm{B}}}{\mathrm{~d} \varepsilon}\right)\left(\frac{\mathrm{d} \varepsilon}{\mathrm{~d} E}\right)=\sigma \frac{\mathrm{d} \varepsilon}{\mathrm{~d} E} . \tag{18}
\end{equation*}
$$

The $\sigma$ and $S$ values are plotted against $\varepsilon$ and $E$, respectively, in figure 7. $(\sigma, \varepsilon)$ and $(S, E)$ are conjugate pairs such that the areas under these curves are the same. The stress-strain curve is almost linear in the range of $0-2.5 \%$ elongation and becomes nonlinear thereafter. In the linear range, it does not matter which of these two stress-strain plots is used for the analysis. However, in the nonlinear range, it is important to use an appropriate stress-strain curve depending on the stress/strain measure used. The $S$ versus $E$ curve is particularly useful for the total Lagrangian approach.

### 4.5. Different elastic property values reported in the literature

Although the Young's modulus and Poisson's ratio values reported in the literature have considerable scatter, a majority of values fit into two sets (refer table 2). A Young's modulus value of around 0.7 TPa and a Poisson's ratio value of around 0.4 belong to one set. The other set has values around 1 TPa and 0.25 , respectively. Our numerical experiments show that the first set of values often results when an equilibrium graphene configuration (i.e., the one with minimized potential) is used for the computation and the deformed configuration is obtained by potential minimization. The second set of values results when a non-equilibrium graphene configuration is employed and no potential minimization is carried out to obtain the deformed configuration. To illustrate this, the initial (unminimized) configuration of graphene sheet, figure 1, with 0.142 nm as the uniform bond length for all bonds is considered. A small tensile horizontal displacement is applied to all the atoms. All the atoms are also moved in the


Figure 8. Young's modulus versus Poisson's ratio of graphene.
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 ( $1 \mathrm{TPa}, 0.25$ ).

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 $Y_{1}, Y_{2}$, $\nu_{12}, \nu_{21}$ 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

[1] Iijima S 1991 Nature 35456
[2] Iijima S and Ichihashi T 1993 Nature 363603
[3] Bethune D S, Klang C H, de Vries M S, Gorman G, Savoy R, Vazquez J and Beyers R 1993 Nature 363605
[4] Thess A et al 1996 Science 273483
[5] Erik T T, Zhifeng R and Tsu-Wei C 2001 Compos. Sci. Technol. 611899
[6] Smitherman D V J 2000 Space Elevators An Advanced Earth-Space Infracture for the New Millennium NASA/cp-2000-210429
[7] Collins P G and Avouris P 2000 Sci. Am. 28362
[8] Allinger N L 1977 J. Am. Chem. Soc. 998127
[9] Allinger N L, Yuh Y H and Lii J H 1989 J. Am. Chem. Soc. 1118551
[10] Mayo S L, Olafson B D and Goddard W A 1990 J. Phys. Chem. 948897
[11] Abell G C 1985 Phys. Rev. B 316184
[12] Tersoff J 1988 Phys. Rev. Lett. 612879
[13] Brenner D W 1990 Phys. Rev. B 429458
[14] Brenner D W, Harrison J A, White C T and Colton R J 1991 Thin Solid Films 206220
[15] Robertson D H, Brenner D W and White C T 1992 J. Phys. Chem. 966133
[16] Harrison J A, White C T, Colton R J and Brenner D W 1992 Surf. Sci. 27157
[17] Tupper K J and Brenner D W 1994 Thin Solid Films 253185
[18] Robertson D H, Brenner D W and Mintmire J W 1992 Phys. Rev. B 4512592
[19] Brenner D W, Shenderova O A, Harrison J A, Stuart S J, Ni B and Sinnott S B 2002 J. Phys.: Condens. Matter 14783
[20] Pettifor D G and Oleinik I I 2000 Phys. Rev. Lett. 844124
[21] Girifalco L A, Hodak M and Lee R S 2000 Phys. Rev. B 6213104
[22] Kudin K N, Scuseria G E and Yakobson B I 2001 Phys. Rev. B 64235406
[23] Lier G V, Alsenoy C V, Doren V V and Greelings P 2000 Chem. Phys. Lett. 326181
[24] Arroyo M and Belytschko T 2004 Phys. Rev. B 69115415
[25] Novoselov K S, Giem A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 Science 306666
[26] Tersoff J 1988 Phys. Rev. B 376991
[27] Yakobson B I, Brabec C J and Bernholc J 1996 Phys. Rev. Lett. 762511
[28] Zhang P, Jiang H, Huang Y, Geubelle P H and Hwang K C 2002 Int. J. Solids Struct. 393893
[29] Friesecke G and Theil F 2002 J. Nonlinear Sci. 12445
[30] Lu J P 1997 Phys. Rev. Lett. 791297
[31] Reddy C D, Rajendran S and Liew K M 2005 Int. J. Nanosci. 4631
[32] Shen L and Li J 2004 Phys. Rev. B 69045414
[33] Yu M F, Files B S, Arepalli S and Ruoff R S 2000 Phys. Rev. Lett. 845552
[34] Sammalkorpi M, Krasheninnikov A, Kuronen A, Nordlund K and Kaski K 2004 Phys. Rev. B 70245416
[35] Yoon J, Ru C Q and Mioduchowski A 2005 Trans. ASME J. Appl. Mech. 7210
[36] Chang T and Gao H 2003 J. Mech. Phys. Solids 511059
[37] Mielke S L, Troya D, Zhang S, Li J, Xiao S, Car R, Ruoff R S, Schatz G C and Belytschko T 2004 Chem. Phys. Lett. 390413
[38] Ogata S and Shibutani Y 2003 Phys. Rev. B 68165409

