Mechanical properties of nanosheets and nanotubes investigated using a new geometry independent volume definition

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Abstract
Cross-sectional area and volume become difficult to define as material dimensions approach the atomic scale. This limits the transferability of macroscopic concepts such as Young’s modulus. We propose a new volume definition where the enclosed nanosheet or nanotube average electron density matches that of the parent layered bulk material. We calculate the Young’s moduli for various nanosheets (including graphene, BN and MoS\(_2\)) and nanotubes. Further implications of this new volume definition such as a Fermi level dependent Young’s modulus and out-of-plane Poisson’s ratio are shown.

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1. Introduction

While mechanical reinforcement with single-wall carbon nanotubes (SWCNTs) has been a hot topic since the 1990s [1], recently interest is also growing in individual-layer or few-layer based nanomaterials such as graphene, BN and MoS\(_2\) [2–5]. Bulk mechanical properties are commonly specified using well-defined parameters such as Young’s modulus \(E\) (see also (1) and\(^4\)). When making the transition to nanoobjects this leads to complications, since the object boundaries and hence volume and cross-section have no general and transferable definition. Thus while elastic tensors remain unambiguously defined at these scales, the conversion of both experimental and theoretical strains and forces into mechanical constants such as Young’s modulus require a definition of mechanically active volume.

To date no such generalized and transferable volume definition exists. A common approach is to use geometric ‘macroscopic’ volume models such as a rectangular slab for flat graphene or an empty cylinder for SWCNTs. However literature values chosen for the thickness \(t\) of the graphene slab or SWCNT cylinder range from \(t = 0.6–3.4\ \text{Å}\) [6, 7], leading to wildly different volumes or cross-sections. The result is a wide scatter in reported values of the in-plane Young’s modulus for graphene and the axial Young’s modulus for SWCNTs, between 0.5 and 5.0 TPa [6, 7]. Currently the most common approach for graphene is to consider it as a uniform slab with thickness of the inter-layer spacing of graphite (3.35 Å). When both theory and experiment adopt this same value, the result is reasonably matching values of the in-plane Young’s modulus between theory 0.86 [8] –1.11 TPa [9] and experiment 1.0 [10] –1.02 TPa [11]. Simply transferring
the graphite inter-layer distance to the cylinder thickness for SWCNTs provokes questions about the influence of curvature on the volume [12, 13], especially for narrow nanotubes. To date all such geometric approaches have in common the lack of a conceptual framework required for its generalization to other related structures.

Volume can alternatively be defined based on a sum of spherical overlapping atomic radii, such as covalent or Van der Waals radii [14–17]. However by drawing on a library of pre-existing small molecules rather than considering the precise system in hand, such definitions once again suffer from a lack in transferability. Notably π-bond systems are very poorly represented via Van der Waals radii [18]. Thus to date there is no general method to describe mechanically active nanoobject volume, capable of describing different kinds of structures without introducing various empirical or experimental parameters.

In this paper we present a new geometry independent, parameter free and transferable volume definition based on the electron density distribution in the material, accessible from general density functional (DFT) calculations. We apply this to calculations of Young’s modulus and Poisson’s ratio of nanosheets and single-wall carbon nanotubes. This new definition provides a robust, reliable, quantitative basis for future mechanical studies of nanomaterials.

2. Method

In the following study we use DFT calculations under the local density approximation, implemented in the AIMPRO code [19–21]. Relativistic pseudopotentials are included via the Hartwigsen–Goedecker–Hutter scheme [22]. The basis consists of Gaussian function sets multiplied by polynomial functions including all angular momenta up to maxima $p$ ($l = 0, 1$) and $d$ ($l = 0, 1, 2$) [23]. For example, for carbon a $pd^dp$ basis set was used, resulting in 38 independent functions. Periodic boundary conditions are used, with system-dependent plane wave energy cutoffs up to 175 Ha (Ha: Hartree energy), and a non-zero electron temperature of $kT = 0.04$ eV to create electronic level occupation. The $k$-point grids were sufficiently fine to give energies converged to better than $10^{-5}$ Ha. Atomic positions and lattice parameters were geometrically optimized until the maximum atomic position change in a given iteration dropped below $10^{-6} a_0$ (a$_0$: Bohr radius). To avoid interaction, supercell sizes were chosen such that the distance between structures was larger than 22.7 $a_0$ (12 Å). For Young’s modulus calculations we apply small strains $\epsilon$ ($\pm0.5, \pm1.0, \pm2.0\%$) staying in the harmonic regime, leading to

$$E = \left. \frac{1}{V_0} \frac{\partial^2 U}{\partial \epsilon^2} \right|_{\epsilon=0},$$

as an expression of the Young’s modulus $E$. $V_0$ defines the volume at equilibrium and $U$ the total energy. A detailed description of the Young’s modulus calculations is given in (see footnote 1).

3. Volume definition based on the electron density

In order to define nanoobject volume, we start with the average electron density $\rho$ of a bulk material. This can always be defined as $\rho_{\text{bulk}} = Q_{\text{total}}/V_0$, where $Q_{\text{total}}$ gives the total number of electrons in a cell of volume $V_0$, e.g. the conventional unit cell. For any system the local electron density $n(\vec{r}_i)$ ($i = 1..N$) can be generated in real space at every point $\vec{r}_i$ in a fine uniform 3D mesh of $N$ points in a supercell. Many DFT codes such as AIMPRO already define a real-space 3D mesh to describe the system electron density, and thus for computational efficiency we use the pre-generated mesh in the following analysis. The grid mesh density is sufficiently fine that the final calculated volume is converged to less than 1% variation (see footnote 1).

The total number of electrons in the supercell (SC) with known volume $V_{\text{SC}}$ is fixed, and can be expressed as the sum of the electron density over all points multiplied by the fractional volume associated with every point,

$$Q_{\text{total}} = \frac{V_{\text{SC}}}{N} \cdot \sum_{i=1}^{N} n(\vec{r}_i).$$

This definition is independent of the type of structure or supercell, for example a bulk calculation or a single-layer nanosheet surrounded by vacuum. In order to define nanoobject volume we now introduce an electron density cut-off $c$. We can find all the points $N_{n>c}$ with electron density $n(\vec{r}_i) > c$. This leads to the number of electrons $Q(c)$ and volume $V(c)$, knowing $V_{\text{SC}}$ and the number of grid points $N$,

$$Q(c) = \frac{V_{\text{SC}}}{N} \cdot \sum_{i=1}^{N_{n>c}} n(\vec{r}_i),$$

$$V(c) = \frac{N_{n>c}}{N} \cdot V_{\text{SC}}.$$ We propose to choose this electron density cut-off such that the resultant nanoobject volume (here nanosheet or nanotube volume) has the same average electron density as the parent (layered) bulk material:

$$\rho_{\text{bulk}} = \left( \frac{Q(c)}{V(c)} \right)_{\text{nanoobject}} = \rho(c)_{\text{nanoobject}}.$$ This leads to a new expression for the volume $V(c) = Q(c)/\rho_{\text{bulk}}$, where $c$ corresponds to the crossing point of the average electron densities for nanosheet or nanotube and parent layered bulk material, as indicated with an arrow in figure 1 for single- (SL), bi- (BL), tri-layer (TL) graphene with graphite. In all systems examined here these volumes enclose more than 99.35% of the total electrons in the supercell (see table 1 and 2 and footnote 1). The Young’s modulus $E$ can now be expressed using volume $V_0(c)$, which is only dependent on the electron distribution and thus takes directly into account the geometry of the structure,

$$E(c) = \left. \frac{1}{V_0(c)} \frac{\partial^2 U}{\partial \epsilon^2} \right|_{\epsilon=0}.$$
4. Young’s modulus of nanosheets and nanotubes

Calculated Young’s moduli using the new volume definition for single-, bi- and tri-layer graphene are in good agreement with experimental values of ≈1 TPa [11] (see table 1). Since these experimental values assume slabs with graphite inter-layer thickness of 3.35 Å, we converted our volumes into equivalent slab thicknesses for comparison. Although we note that the enclosed volumes are in reality not uniform slabs but show surface undulation reflecting the electron distribution in the underlying lattice. The equivalent layer thickness we obtain varies with the number of layers, from 3.31 Å for SL-graphene converging towards our calculated graphite layer spacing of 3.32(3) Å with increasing layer number. This shorter layer distance is close to the inter-layer spacing of graphite, this suggests that a 3.35 Å thick geometric slab is a reasonable approximation to determine pristine graphene volume. However, there are many situations for which the geometric slab model is no longer applicable (for example defective systems such as vacancy-containing graphene), where the new electron density based volume approach proposed here can still be applied.

Table 2. Axial Young’s modulus E calculated for different SWCNTs. t indicates the hypothetical cylinder thickness (brackets indicate completely filled tubes) centred around the SWCNT atom positions, with equivalent volume to that defined by the electron density cut-off c. \( N_Q = Q(c)/Q_{\text{total}} \) gives the ratio of enclosed electrons and e the evaluated electron density cut-off.

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| SWCNT | \( E(c) \) (TPa) | c (\( e^−/a_0^3 \)) | t(Å) | \( N_Q \) (%) |
|-------|-----------------|-----------------|-----|------------|
| (armchair) | (2, 2) | 0.642 | 0.00272 | 3.04 | 99.45 |
| (3, 3) | 1.049 | 0.00255 | 3.21 | 99.60 |
| (4, 4) | 0.995 | 0.00246 | 3.25 | 99.61 |
| (5, 5) | 1.018 | 0.00243 | 3.27 | 99.62 |
| (8, 8) | 1.057 | 0.00240 | 3.30 | 99.63 |
| (10, 10) | 1.063 | 0.00238 | 3.31 | 99.64 |
| (zigzag) | (3, 0) | 0.885 | 0.00295 | 3.00 | 99.36 |
| (4, 0) | 0.969 | 0.00255 | 3.12 | 99.53 |
| (5, 0) | 0.969 | 0.00252 | 3.20 | 99.61 |
| (6, 0) | 1.010 | 0.00247 | 3.23 | 99.61 |
| (9, 0) | 1.005 | 0.00240 | 3.29 | 99.63 |
| (12, 0) | 1.028 | 0.00240 | 3.30 | 99.63 |
| (17, 0) | 1.054 | 0.00236 | 3.31 | 99.64 |
| (chiral) | (4, 1) | 1.001 | 0.00244 | 3.17 | 99.60 |
| (8, 2) | 1.019 | 0.00241 | 3.27 | 99.63 |
| (8, 4) | 1.046 | 0.00240 | 3.29 | 99.63 |
| (12, 6) | 1.054 | 0.00239 | 3.30 | 99.63 |

Exp. \( E \approx 1 \) TPa [27, 28]

slightly smaller inter-layer distance for graphite results from the chosen pseudopotentials and the LDA-DFT approach.
Young’s modulus

The system and hence the modulus by depopulating bonding states or populating example, varying the Fermi level can change the Young’s electron density has further conceptual implications. For Defining volume via a well-defined cut-off in the system electron density in equilibrium, the enclosed volume models.

5. Fermi level dependent Young’s modulus and Poisson’s ratio of graphene

Defining volume via a well-defined cut-off in the system electron density has further conceptual implications. For example, varying the Fermi level can change the Young’s modulus by depopulating bonding states or populating anti-bonding states, softening the bond spring constants of the system and hence the $\frac{\partial^2 U}{\partial \epsilon^2}$ term of (6). However since volume is now defined in terms of a cut-off defined for the first time in the literature. Figure 2 shows the calculated effect of varying the Fermi level on the Young’s modulus of graphene. Over moderate doping levels ($\pm 0.0625 e^-$/atom), a classical fixed volume model would suggest a gradual drop in Young’s modulus as the system becomes more positive ($E(V = \text{const.})$). However this modulus trend is actually inverted once the corresponding volume decrease is included. Such complex doping-dependence of mechanical properties is not accessible with classical geometrical slab or sphere volume models.

This new volume definition also enables access to other mechanical properties such as the out-of-plane Poisson’s ratio for surface dominated nanoobjects, since it is possible to calculate the volume and hence an equivalent thickness change as the sample is strained. The Poisson’s ratio is constant for small strains, and we have taken the average for six strained/compressed cases (see footnote 1). For graphene we find the in-plane Poisson’s ratio to be $\nu_{12} = 0.20$ and for the first time we also calculate the out-of-plane value to be $\nu_{13} = 0.015$, using the graphene electron density cut-off $c = 0.0024 e^-/a^0_0$ (see footnote 1). Our calculated Poisson’s ratios for graphite ($\nu_{12} = 0.21$, $\nu_{13} = 0.00$) and $V$ for graphene are in good agreement with literature values [7]. We note that for carbon based ‘all surface’ systems such as single-layer graphene or SWCNTs an electron density cut-off around 0.0024 $e^-/a^0_0$ delivers an accurate mechanical volume description with a very stable and very high ratio of enclosed electrons of more than 99.5% (see also footnote 1). To apply such a universal material cut-off value to a broader range of structures such as nanoribbons and organic molecules would significantly extend the utility of this volume definition, and will be the subject of a future publication.

6. Conclusion

To summarize, we propose a new definition of mechanically active volume applicable to nanoobjects derived from layered bulk materials, using a volume chosen such that the average electron density of the nanoobject matches that of the parent bulk material. This definition is geometry independent, transferable, invokes no empirical parameters and can be implemented in all standard DFT approaches. It correctly extrapolates between individual nanoobjects and bulk systems. Since both experimental and theoretical derivation of Young’s modulus require a volume definition, the same calculated volumes can be applied to both. Based on this one general volume definition, for the first time consistent and comparable values for Young’s moduli of various new nanosheets and single-wall carbon nanotubes have been calculated. All values show good agreement with the parent bulk in-plane Young’s modulus. This can be really stated for the first time, as the calculations are based on a transferable underlying method. In addition this new approach allows study of systems whose volume varies, for example by shifting the Fermi level. It can be easily applied to nanostructures containing defects such as vacancies, which will locally modify the electron density distribution and hence volume. This volume definition could also be applied in other systems where nanoscale volume is needed such as the definition of internal porosity for metal-oxide frameworks.

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