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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 MoS₂) 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.

 Online supplementary data available from stacks.iop.org/JPhysCM/25/155302/mmedia

(Some figures may appear in colour only in the online journal)

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 MoS₂ [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 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

⁴ Supplemental materials available at stacks.iop.org/JPhysCM/25/155302/mmedia for additional information and theoretical details.

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 *pdddp* 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^{-7} 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 ϵ ($\pm 0.5, \pm 1.0, \pm 2.0\%$) staying in the harmonic regime, leading to

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

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 ρ of a bulk material. This can always be defined as $\rho_{\text{bulk}} = Q_{\text{total}}/V_0$, where Q_{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_{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,

$$Q_{\text{total}} = \frac{V_{\text{SC}}}{N} \cdot \sum_{i=1}^N n(\vec{r}_i). \quad (2)$$

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_{SC} and the number of grid points N ,

$$Q(c) = \frac{V_{\text{SC}}}{N} \cdot \sum_{i=1}^{N_{n>c}} n(\vec{r}_i), \quad (3)$$

$$V(c) = \frac{N_{n>c}}{N} \cdot V_{\text{SC}}. \quad (4)$$

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:*

$$\rho_{\text{bulk}} = \left(\frac{Q(c)}{V(c)} \right)_{\text{nanoobject}} = \rho(c)_{\text{nanoobject}}. \quad (5)$$

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,

$$E(c) = \frac{1}{V_0(c)} \left. \frac{\partial^2 U}{\partial \epsilon^2} \right|_{\epsilon=0}. \quad (6)$$

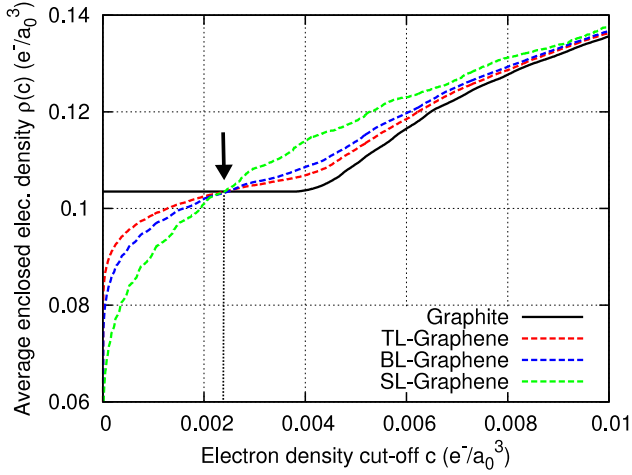


Figure 1. Average enclosed electron density $\rho(c) = Q(c)/V(c)$ as a function of the electron density cut-off c for single-layer (SL), bi-layer (BL), tri-layer (TL) graphene and graphite. The arrow indicates the cut-off given by (5), values shown in table 1.

Table 1. Calculated in-plane Young’s modulus E for different nanosheets and their parent bulk materials. t indicates the single-layer thickness of a slab 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 compared to the total number of electrons in the supercell.

Sheets	$E(c)$ (TPa)	c (e^-/a_0^3)	t (Å)	N_Q (%)
SL-graphene	1.059	0.002 40	3.31	99.64
BL-graphene	1.059	0.002 47	3.32	99.81
TL-graphene	1.058	0.002 37	3.32	99.88
4L-graphene	1.055	0.002 26	3.32	99.91
Graphite (bulk)	1.055	—	3.32	100.0
SL-BN	0.898	0.002 68	3.19	99.60
BL-BN	0.891	0.002 88	3.19	99.78
TL-BN	0.886	0.002 77	3.19	99.86
h-BN (bulk)	0.880	—	3.19	100.0
SL-WS ₂	0.251	0.002 90	6.14	99.89
WS ₂ (bulk)	0.242	—	6.17	100.0
SL-MoS ₂	0.222	0.002 93	6.12	99.85
MoS ₂ (bulk)	0.219	—	6.14	100.0
SL-MoSe ₂	0.188	0.003 35	6.35	99.87
MoSe ₂ (bulk)	0.188	—	6.36	100.0
SL-MoTe ₂	0.132	0.003 29	6.87	99.87
MoTe ₂ (bulk)	0.132	—	6.91	100.0

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

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 c the evaluated electron density cut-off.

	SWCNT	$E(c)$ (TPa)	c (e^-/a_0^3)	t (Å)	N_Q (%)
(armchair)	(2, 2)	0.642	0.002 72	(3.04)	99.45
	(3, 3)	1.049	0.002 55	(3.21)	99.60
	(4, 4)	0.995	0.002 46	3.25	99.61
	(5, 5)	1.018	0.002 43	3.27	99.62
	(8, 8)	1.057	0.002 40	3.30	99.63
(10, 10)	(10, 10)	1.063	0.002 38	3.31	99.64
	(zigzag)	(3, 0)	0.885	0.002 95	(3.00)
(zigzag)	(4, 0)	0.969	0.002 55	(3.12)	99.53
	(5, 0)	0.969	0.002 52	(3.20)	99.61
	(6, 0)	1.010	0.002 47	3.23	99.61
	(9, 0)	1.005	0.002 40	3.29	99.63
	(12, 0)	1.028	0.002 40	3.30	99.63
	(17, 0)	1.054	0.002 36	3.31	99.64
	(chiral)	(4, 1)	1.001	0.002 44	(3.17)
(8, 2)		1.019	0.002 41	3.27	99.63
(8, 4)		1.046	0.002 40	3.29	99.63
(12, 6)		1.054	0.002 39	3.30	99.63
Exp. E		≈ 1 TPa [27, 28]			

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

We have further calculated the Young’s modulus of recently isolated nanosheets [3] using the new volume definition (table 1). In general single-layer average thicknesses are only slightly smaller than the bulk inter-layer distance, due to the absence of extremely weak inter-layer electron delocalization effects [24]. We obtain good agreement for MoS₂ with experiment, the only one of these to be experimentally determined to date to the best of our knowledge (0.27 ± 0.1 TPa [25], 0.33 ± 0.07 TPa [26] compared to our value of 0.222 TPa).

In general the in-plane Young’s moduli for nanosheets are similar to their parent bulk material: the in-plane force constants are similar, the out-of-plane interactions are weak, and the single-layer volume is close to that of one bulk layer. This observation makes prediction of nanosheet mechanical properties easier when the Young’s modulus of the bulk materials are known.

Since our calculated averaged graphene layer thickness 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.

Next the Young’s moduli of different SWCNTs have been calculated. In the literature different methods have been applied but all have in common an estimated wall thickness. Using the new volume definition with equal average electron density $\rho(c)$ to graphite, the axial Young’s moduli for a range of armchair, zigzag and chiral SWCNTs are summarized in

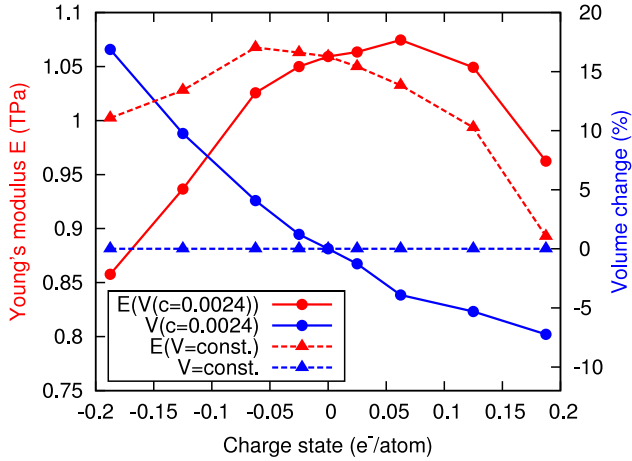


Figure 2. Young's modulus $E(V(c = 0.0024))$ and volume $V(c = 0.0024)$ for graphene as a function of doping level/charge state, with volume defined using the graphene electron density cut-off of $c = 0.0024 e^-/a_0^3$. The effective Young's modulus $E(V = \text{const.})$ fixing the volume at the charge neutral value shows the modulus variation with charge state due purely to changes in bond strength.

table 2 (for detailed comparison with other theoretical studies see footnote 1). The in-plane Young's moduli converge to that of graphite and graphene for larger diameters, and thus lower curvature. The enclosed electron ratio N_Q similarly converges to the graphene value. However the equivalent wall thickness now varies, and in particular for CNTs with diameters below around 4.7 \AA the CNTs are completely filled (independent of the chirality) (see footnote 1). This agrees with the lower diameter limit for the filling of SWCNTs with water [29].

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 $\partial^2 U / \partial \epsilon^2$ term of (6). However since volume is now defined in terms of a cut-off defined for the system electron density in equilibrium, the enclosed volume will now also be Fermi level dependent. This means that changes in $1/V_0(c)$ in (6) can also modify the Young's modulus. The current approach includes both of these effects 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 ($\pm 0.0625 e^-/\text{atom}$), 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 $c = 0.0024 e^-/a_0^3$ (see footnote 1). Our calculated Poisson's ratios for graphite ($\nu_{12} = 0.21$, $\nu_{13} = 0.00$) and ν_{12} 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 $0.0024 e^-/a_0^3$ 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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