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Out-of-plane shear and out-of plane Young's modulus of double-layer graphene

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ABSTRACT

In this Letter we predict the out-of-plane Young's modulus (perpendicular to the basal plane) and the out-of-plane shear modulus of double-layer graphene using density functional theory calculations with periodic boundary conditions using the GAUSSIAN 09 program package. These values are discussed in the context of the corresponding values of graphite.

1. Introduction

Until the 1985, only two ordered forms of carbon were known to scientists, namely diamond, with its perfect crystal structure, and graphite, also crystalline but black and flaky and not at all transparent. Besides those ordered forms, also coal, coke, soot, lampblack, and the many kinds of charcoal were known. The graphite structure determines its properties, since it is made up of sheets of carbon atoms arranged in a hexagonal lattice, like a honeycomb of fused benzene rings, and with weak bonding between adjacent sheets. This means that graphite easily forms flakes where the sheets can slide over each other, providing use of graphite as a lubricant. In 2007, researchers in Manchester found a way to mechanically peel single two-dimensional sheets from three-dimensional graphite crystals [1]. Graphene is the name given to this flat monolayer of carbon atoms tightly packed into a two-dimensional honeycomb lattice.

Since the first experimental analysis [1], graphene has recently gained significant attention. In particular, its excellent mechanical properties are an important advantage for the practical applications of graphene [2]. These mechanical properties have been extensively investigated, and in particular, the most important elastic property, namely the (in-plane) Young's modulus has been studied using a wide range of experimental and theoretical approaches (see references in [3]). Recently we also investigated the in-plane Young's modulus and flexural moduli of double-layer graphene, including a short review about the currently available experimental and theoretical predictions of the (in-plane) Young's modulus and flexural modulus [3,4]. If one runs through the available experimental an theoretical results of in-plane Young's modulus, it is apparent that the results have a rather big deviation, ranging from 0.762 to 5.189 TPa (See references in [3]). The origin of these big differences lies in the different interpretation of the thickness of atomic platelets, which is not well defined and greatly influences the results. The in-plane shear modulus of single and multiple-layer graphenes have been measured to be 280 and 53 GPa, respectively [5–7]. The out-of-plane shear modulus has been theoretically determined to be in the range of 0.482–16.1 GPa using molecular structural mechanics and a mixed atomistic continuum finite element technique, respectively [8,9]. There are some experimental studies investigating the transverse elastic properties of suspended graphene sheets, but only the in-plane Young's modulus was extracted from the measurements [10]. According to our knowledge, up to now, no theoretical or experimental predictions exist for the out-of-plane Young's modulus of double layer graphene. The classical engineering definitions of these quantities are not unequivocally transferable to atomic scale materials, especially in the case of single-layer graphene, but it can be done in the case of multiple-layer graphene with no more complications than in the case of in-plane Young's modulus. The available theoretical results for the out-of-plane Young's modulus of graphite are in the range of 0.3–45.4 GPa [11–18], and the out-of-plane shear modulus of graphite is in the range of 3.9–5.0 GPa [13,16,18]. In the case of the out-of-plane Young's modulus the differences between the obtained results are rather big. If one analyses more deeply those results it turns out that the differences have a methodological origin, since many theoretical methods are not capable to describe correctly the interlayer interactions, and not a consequence of some fundamental difference as in the case of thickness definition for the in-plane Young's modulus. For multi-layered structures it is a rather good assumption that the weak interlayer interactions do not influence the in-plane Young's modulus. This assumption is not so evident in the cases of out-of-plane Young's and shear moduli, since the reacting forces are significantly lower, and most probably a weak interaction can be of influence much more than in the case of the in-plane Young's modulus.

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The goal of this Letter is to predict the out-of-plane Young's modulus and shear modulus of double-layer graphene, with special attention to the comparison with the corresponding values of graphite. The in-plane Young's modulus of double-layer graphene can be approximated through the in-plane Young's modulus of few-layer graphene and graphite; we investigate whether this approximation is especially valid in the case of the out-of-plane Young's modulus and the out-of-plane shear modulus.

2. Computational methods and theory

All quantum-chemical calculations have been performed using Density Functional Theory (DFT) using the pure LDA [19–23], and PBE [24,25], the short-range hybrid $HSE06_H$ [26–32] developed for solids (sometimes referred as HSEh1PBE), and the local M06L [33] functionals, in conjunction with 6-31G* [34] split-valence basis sets using Periodic Boundary Conditions (PBC) implemented in the GAUSSIAN 09 [35] program package. We used the smallest possible unit cells (2 carbons in graphite and 4 carbons in double-layer graphene) in our PBC calculations. Based on our experience, the mechanical properties of single- and double-layer graphene can be calculated accurately enough using the minimum unit cells [3]. To minimize errors arising from numerical instabilities, the convergence in the self consistent field procedure was set to 10^{-10} a.u. on the energy and 10^{-8} a.u. on the electron density, ultrafine integration grid (99 radial shells and 590 angular points per radial shells), and tight optimization criteria (15 μa.u. on maximum force, 10 μa.u. on RMS force, 60 μa.u. on predicted maximum displacement, and 40 μa.u. on RMS predicted displacement) were used.

The Young's modulus (E) was calculated according to [36]

$$E = \frac{\text{tensile stress}}{\text{tensile strain}} = \frac{\sigma}{\varepsilon} = \frac{\frac{F}{A}}{\frac{\Delta L}{L_0}} = \frac{FL_0}{A\Delta L}, \quad (1)$$

where F is the force, A is the area where the force is applied, L_0 is the relaxed length, and ΔL is the elongation/compression.

The shear modulus (G) was calculated according to

$$G = \frac{\text{tensile stress}}{\text{tensile strain}} = \frac{\tau}{\gamma} = \frac{\frac{F}{A}}{\frac{\Delta z}{l_0}} = \frac{Fl_0}{A\Delta z}, \quad (2)$$

where F is the force, A is the area where the force is applied, l_0 is the relaxed interlayer distance, and Δz is the transverse displacement. (See Figure 1)

We note that the methodology applied here is different from the one in Ref. [18], since we directly calculate forces from distorted structures, as we did in our previous studies [3,4,36]. We made use of the engineering approximation in the case of our Young's and shear moduli calculations, so the geometrical changes arising from the elongation/compression or distortion have been taken into account (in other words, the area in the Eqs. (1) and (2) always corresponds to the actual elongation/compression or distortion geometry, respectively, not the zero strain situation). It is also important to stress that in the case of the *in-plane* Young's modulus the thickness of the graphene sheet or the interlayer distance of graphite can greatly change the predicted value, meanwhile in the case of the *out-of-plane* Young's modulus the thickness of a (double or more) layer graphene or the interlayer distance of graphite has almost no influence. This difference is arising from the fact that the area where the force is acting in the case of the *out-of-plane* Young's modulus can always be pragmatically defined and can be determined with a relatively high precision (only the *in-plane* atomic distances are needed), while this is not the case for the *in-plane* Young modulus, because the area cannot always be defined pragmatically and the uncertainty of the determination is also higher (one needs the *out-of-plane* atomic distances, and/or one should define a platelet thickness of an atomic scale material). We have to emphasize that for the zero-strain point the equilibrium interlayer distance should always be used during the calculation of the out-of-plane Young's modulus from quantum-mechanical equations; otherwise the corresponding stress would not be zero. In all our calculations, the area in Eqs. (1) and (2) was calculated purely from the theoretical (optimized) geometries. In addition, in the case of the in-plane Young's modulus of graphite we also used the experimental interlayer distance (3.35 Å) [37] for comparative purposes. Finally we have to mention that our methodology, due to its nature, is not suitable to determine the out-of-plane Young's and shear moduli of single-layer graphene.

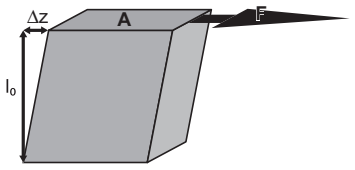

Figure 1. Definition of the quantities of relevance for the determination of the shear modulus.

During the out-of-plane Young's modulus calculations we defined two hypothetical planes (for the two layers of the double-layer graphene), and the carbon atoms were forced to remain in these planes. The out-of-plane Young's modulus was calculated using the average force acting on the atoms at 1.25%, 2.50%, and 3.75% elongation and 1.25% compression with respect to the equilibrium interlayer distance. The only further constraint was the increased or decreased distance of the two hypothetical layers, and the atoms were able to freely move within the two defined planes during the geometry optimizations of the elongated/compressed structures. In the case of the out-of-plane shear modulus calculations, two hypothetical planes were defined representing the two layers of the double-layer graphene and one atom of each layer was forced to be in the corresponding plane. Geometry optimizations were performed with the only further constraint being the distance between one of these clamped atoms and the projection of the other clamped atom on the same hypothetical plane (the transverse displacement). Therefore, the transverse movement corresponds to the minimum energy path. The shear modulus was calculated using the average force acting on atoms in ~0.07 Å steps in the transverse displacement. (In total 19 steps in between AA and AB stacking, using the minimum energy path). In the case of graphite the Young's modulus was calculated at 0.5% compression and elongation with respect to the corresponding crystallographic parameter; the atoms in the unit cell and the other crystallographic parameters (lengths and angles) were fully optimized. The corresponding forces were calculated on the elongated or compressed crystallographic parameter. The shear modulus was calculated similarly, but one of the crystallographic angles was fixed, and all the other parameters, including the atomic positions in the unit cell, were optimized. The corresponding shear stress was ~0.2% and ~0.6% (0.5% and 1.5% change in the interlayer-shift).

3. Results and discussion

In order to validate the quality of different functionals and the default parameters in our PBC calculations, we compare the calculated results of mechanical properties with accurate and widely accepted experimental results [38]. Unfortunately, mechanical properties determined by experiments are incomplete for graphene. As an alternative, we validated our methodology for graphite [38] The results are summarized in Table 1. The in-plane Young's