Interatomic potential suitable for the modeling of penta-graphene: Molecular statics/molecular dynamics studies

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Szymon Winczewski [a, *], Mohamad Yousef Shaheen [b], Jarosław Rybicki [a, c]

[a] Faculty of Applied Physics and Mathematics, Gdansk University of Technology, Narutowicza 11/12, 80-233, Gdańsk, Poland
[b] Faculty of Engineering Technology, University of Twente, Drienerlolaan 5, 7522 NB, Enschede, The Netherlands
[c] TASK Computer Centre, Gdansk University of Technology, Narutowicza 11/12, 80-233, Gdańsk, Poland

ABSTRACT

We test the potentials available for elemental carbon, with the scope to choose the potential suitable for the modeling of penta-graphene, the latest two dimensional carbon allotrope. By using molecular statics and molecular dynamics simulations we show that there is only one potential — namely the Tersoff-type potential proposed by Erhart and Albe in 2005 — which is able to correctly describe all the important features of penta-graphene. We show that this potential gives structural, mechanical and energetic parameters which are in accordance with the previously reported ab initio results.

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1. Introduction

The synthesis of carbon nanotubes in 1992 [1,2] and the discovery of graphene in 2004 [3,4] have opened a completely new area of search for new carbon allotropes. Based on theoretical considerations many new carbon forms have been proposed since then, and as a result, the set of known carbon forms has been enriched by several low-dimensional [5—11] and bulk [12—16] structures. Despite the fact that many of these structures have not been synthesized yet, this new trend has shown the importance of theoretical studies — especially ab initio quantum mechanical calculations — for the search for new materials of designed properties, often unique.

The fact that most of the carbon allotropes have a structure consisting of hexagons as its main feature, has motivated the search for a new carbon allotrope which would have a structure completely composed of pentagons. As a result a new two-dimensional carbon allotrope, called penta-graphene, was proposed by Zhang et al. in 2014 [9], as an, exfoliated equivalent" of the T12-carbon [12], the existence of which was also predicted based on the ab initio calculations.

Penta-graphene (PG) can be seen as a layer of pentagons constructed from a mixture of sp^2- and sp^3-bonded carbon atoms. Zhang et al. reported that due to its unusual atomic structure —

closely resembling the well-known Cairo pentagonal tiling — PG possesses many unique properties. It was found to be mechanically, dynamically and thermally stable, and able to withstand temperatures as high as $T = 1000$ K. It was also reported that PG displays ultra-high mechanical strength, with the strain at maximum stress being as high as 21%. The stiffness of PG was also found to be very high, with the corresponding (in-plane) Young's modulus being as high as $E = 263$ GPa nm, which is more than two-thirds of that of graphene ($E = 345$ GPa nm). PG was also found to exhibit auxetic behavior, that is the anomalous property of becoming wider rather than thinner when stretched. Zhang et al. also reported that PG exhibits an intrinsic (and indirect) band gap, as large as $E_g = 3.25$ eV. This feature renders PG as a better material — than graphene — for two-dimensional transistors, which require the presence of a large band gap to obtain a good switch-off.

1.1. State of the art

Since its discovery PG has been studied intensively by several groups [11,17—29]. The stability of PG and its experimental reachability was questioned by Ewels et al. in Ref. [17]. Based on the ab initio calculations they concluded that PG should be difficult to isolate, also pointing out that PG should rapidly restructure toward graphene in the presence of even a few catalytic impurities. A similar observation about the potential instability of PG was made by Cranford [18], who studied finite, hydrogen-terminated sheets of PG. By using the MD simulation he concluded that bond breaking should be observed even at relatively small deformations (ca. 5%),

leading to transformations of pentagons into hexagons and heptagons. According to his work, a similar effect should be observed at elevated temperatures (*ca.* 600 K), resulting in transformation of PG into (defective) graphene.

Sun et al. [11] presented the results of extensive studies on the mechanical properties of PG. By combining DFT calculations with the fourth order continuum elasticity theory they calculated a complete set of (fifteen) anisotropic nonlinear elastic constants of monolayer PG, showing that the applied continuum formalism (originally proposed by Wei et al. for graphene [30]) is able to accurately describe the non-linear elastic behavior of PG in a wide range of strains, even as large as 30%. Sun et al. also investigated the fracture of PG. They concluded that due to longer bond length and lower charge density the sp^3 bonds are more vulnerable to failure than the sp^2 bonds. Sun et al. also studied the mechanism of PG deformation, demonstrating that the negative Poisson's ratio of PG originate from de-wrinkling of different atomic planes.

The influence of doping and functionalization on the properties of PG has been also investigated. Berdiyorov et al. [19] found that electronic properties of PG can be fine-tuned, by substituting C atoms with Si, B and N. They showed that the band gap size can be significantly reduced, even to 0.2 eV. According to them the strongest reduction of the band gap is obtained for Si substitutions on the top (or bottom) plane of PG. They also showed that surface termination with fluorine and hydroxyl groups results in an increase in the band gap. The functionalization of PG sheets was also investigated by Li et al. [20], who found that hydrogenation and fluorination can effectively tune the electronic and mechanical properties of PG, changing the Poisson's ratio from negative to positive, and reducing the Young's modulus.

The thermal conductivity of PG has been also studied. Using classical equilibrium molecular dynamics (MD), Xu et al. [21] found that the thermal conductivity of PG at the room temperature is about 170 W/(m K), which is much lower than that of graphene, which is 2000—4000 W/(m K) [31]. They also identified the main mechanism of thermal conduction. By analyzing phonon frequencies and phonon mean free paths they found out that the acoustic phonons make a contribution of about 90% to the thermal conductivity, also showing that phonons with mean free paths larger than 100 nm make a contribution over 50%. They have also demonstrated that the remarkably lower thermal conductivity of PG (compared with graphene) results from the lower phonon group velocities and fewer collective phonon excitations.

The influence of functionalization on the thermal properties of PG has been also studied. Using DFT calculations combined with an iterative solution of the phonon Boltzmann transport equation, Wu et al. [22] found that hydrogenation of PG leads to large (76% increase) improvement in thermal conductivity.

Other spatial forms of PG have been also investigated. Yu and Zhang studied the electronic properties of layered PG [23]. They showed that there is no direct-to-indirect band gap transition in PG by varying strain, layer number, and stacking misalignment. Owing to its characteristics, few-layer PG was recognized by Yu and Zhang [23] as a very promising material for optoelectronic and photovoltaic applications. Recently, Rajbanshi et al. [24] by using DFT studied penta-graphene nanoribbons (PGNRs), concluding that PGNRs are thermodynamically meta-stable with respect to graphene nanoribbons. They also found that on application of uniaxial strain the band gap of PGNRs decreases continuously, yielding a strain-tunable optoelectronic material.

Another potential application of PG has been recently highlighted by Xiao et al. [25]. By using DFT calculations they found that PG provides very high ion storage capacity and fast ion diffusivity, and therefore is a promising anode material for the Li/Na-ion batteries.

1.2. Problem statement

The above presented analysis of the current state of knowledge shows how significant the future role of PG may be. At the same time, it illustrates the increasing importance of atomistic modeling techniques. So far, the DFT methods have been mainly used in studies on PG and − to the best of our knowledge − there are only three papers, which have reported the application of empirical potentials to model PG [18,21,26].

In the first article Cranford [18] has employed the reactive force field [32] (REAX) to study the mechanical properties and the chemical stability of PG, while in the second Ebrahimi [26] has used the reactive empirical bond order (REBO) potential [33] to study the effect of hydrogen coverage on the buckling of PG. It is important to note that no preliminary validation of the chosen description method has been carried out in both of the aforementioned works.

Contrary to this, Xu et al. [21] performed such validation by testing four different interatomic potentials: the original Tersoff potential [34,35], the optimized Tersoff potential [36,37], the REBO potential [33] and the environment-dependent interatomic potential [38] (EDIP). By comparing the calculated structural and mechanical parameters with the results of the *ab initio* calculations they concluded that among the tested interaction models the original Tersoff potential most closely reproduces the properties of PG. Therefore, it was used in Ref. [21] to study the transport phenomena in PG. However, it must be noted that the Poisson's ratio of PG calculated with the use of the original Tersoff potential was found in Ref. [21] to be equal to −0.174, which strongly (more than 2.5-times) differs from the *ab initio* result of Zhang et al. [9], which is −0.068. Such a significant difference suggests that the original Tersoff potential may not be the best choice when modeling PG at the empirical level.

It is well known that the credibility of the results obtained from any atomistic simulation depends first and foremost on the quality of the model employed to describe interatomic interactions. The last three decades have brought significant advances in the development of empirical potentials. This is especially true in the case of carbon. Due to the significance of this element for the nanotechnology revolution, many new potentials have been proposed for carbon [32—52], in order to describe its various − and often very different − forms. Since all potentials for carbon have been parameterized without accounting for the properties of PG − which was unknown when the potentials were developed − before starting modeling PG at the empirical level it is important to first test how well, or whether at all, the existing potentials reproduce the properties of this new − and very exotic − form of carbon.

It must be stressed that the unusual structure of PG makes this system somehow challenging for the empirical potentials. This originates from the fact that there are two types of bonding schemes present in PG, with the entire structure being a, mixture" of sp^2- and sp^3-hybridized atoms. This is a reason why the basic building blocks in PG differ significantly from their counterparts seen in diamond and graphite/graphene (*e.g.* the carbon-carbon bond lengths characteristic for diamond and graphite/graphene are 1.54 Å and 1.42 Å, respectively, the corresponding bonds in PG have the lengths of 1.55 Å and 1.34 Å, respectively, also the valence angles typical for PG − *i.e.* 98.6, 112.2, 113.5 and 134.4° − differ significantly from those typical for diamond − 109.5° — and graphite/graphene − 120°). Therefore, it is not clear if even the potentials, which are known as being able to (simultaneously) describe purely sp^2- and purely sp^3-systems, will be able to correctly capture the characteristics of PG.

The above observations led us to start the studies the results of which are presented in this paper. We considered 14 different empirical potentials available for carbon and based on molecular