Boron-doped derivatives of graphene have been intensely investigated because of their electronic and catalytic properties. The maximum experimentally observed concentration of boron atoms in graphite was 2.35% at 2350 K. By employing quantum chemistry coupled with molecular dynamics, we identified the theoretical doping limit for single-layer graphene at different temperatures, demonstrating that it is possible to achieve much higher boron doping concentrations. According to the calculations, 33.3 mol% of boron does not significantly undermine thermal stability, whereas 50 mol% of boron results in critical backbone deformations, which occur when three or more boron atoms enter the same six-member ring. Even though boron is less electro-negative than carbon, it tends to act as an electron acceptor in the vicinity of C–B bonds. The dipole moment of B-doped graphene depends strongly on the distribution of dopant atoms within the sheet. Compared with N-doped graphene, the dopant–dopant bonds are less destructive in the present system. The reported results motivate efforts to synthesize highly B-doped graphene for semiconductor and catalytic applications. The theoretical predictions can be validated through direct chemical synthesis.

Introduction

Graphene is a well-known allotrope of carbon. A two-dimensional, single-atom-thick, honeycomb layer of graphite, graphene exhibits unusual properties and promises vibrant applications.1–21 Doping, co-doping and supporting graphene-based nanostructures have been vigorously investigated both experimentally and theoretically with the goal of tuning electronic and catalytic properties, carrier mobility, thermal conductivity, etc.22–29 The researchers’ interest is fostered by a number of important fundamental and technological applications of doped graphenes.30–36 The existing chemical doping techniques offer relatively straightforward approaches to substitute carbon atoms with selected non-metal heteroatoms, while preserving the original hexagonal arrangement. Doping with nitrogen, sulfur and boron has been demonstrated. Certain combinations of these atoms result in stable nanostructures.

The total number of valence electrons in the dopant atom is responsible for the type of doping. That is, addition of boron results in p-type doping, whereas the addition of nitrogen or sulfur results in n-type doping. Boron- and nitrogen-doped graphenes exhibit interesting electrocatalytic activity and higher electrical conductivity compared to pristine graphene. Purpose-specific covalent doping gives rise to hydrogen and energy storage applications for graphene37 and graphene-based heterostructures.38

Substitutional doping introduces significant chemical disorder, since the boron–carbon covalent bond is longer than the carbon–carbon bond in the pristine graphene lattice. Additional disorder is expected from thermal motion and the newly introduced oscillation frequencies of the boron–carbon bonds. The maximum reported solubility of boron in graphite is 2.35% at 2350 K.39 Boron-doped graphene is of fundamental interest because high boron concentrations give rise to quantum interference effects while at the same time preserving the remarkable transport properties of graphene.40

The existence of a fullerene-like molecule consisting entirely of boron atoms was recently recorded by the photoelectron spectroscopy experiments of Zhai and coworkers.41 In contrast to the buckyball, the all-boron fullerene surface, which is bonded uniformly via delocalized σ and π bonds, is not perfectly smooth and exhibits unusual heptagonal faces. The stability of such a system greatly enriches the chemistry of boron and promotes efforts to obtain new boron-rich and boron-based nanomaterials. Therefore, it is both natural and important to consider various C$_x$B$_y$ nanostructures.
The current work determined the maximum boron concentration in the B-doped graphene that would preserve thermal stability. In particular, our calculations demonstrate that it is possible to achieve far higher doping concentrations compared to the current experimental record. Using molecular dynamics simulations based on a reliable and efficient electronic-structure method, we consider a range of C:B ratios, starting from a single dopant atom per hexagonal ring and finishing with triple boron–boron–boron chains. Various arrangements of boron atoms within the sheet were analyzed, and the results give a detailed interpretation of the boron chemistry context. A broad span of temperatures was considered. The conclusions were validated by several independent criteria, including formation energies, structure functions, and visual inspection of the trajectories. The properties of boron-doped graphene were found to be quite different from those of nitrogen-doped graphene. The simulation results can be verified directly by chemical synthesis.

Methodology

PM7-MD simulations were used to record 100 ps long trajectories at 300, 500, and 1000 K. Additionally, the duration of the simulation on the “B–B” system was extended to 1 ns to test convergence. A constant temperature was maintained by the Anderson temperature coupling procedure with a relaxation constant of 50 fs.\textsuperscript{42} The equations-of-motion were propagated with the 0.5 fs time-step. At every step of the molecular dynamics, the self-consistent field (SCF) was achieved at the PM7 semi-empirical level of theory\textsuperscript{43} and a specifically tuned, computationally efficient Slater-type basis set. The resulting forces acting on every atom in the system, including hydrogens, were used to obtain accelerations and forces for the velocity Verlet algorithm. The energy convergence criterion for the SCF procedure was set to $5 \times 10^{-6}$ Hartree. Prior to simulating finite-temperature dynamics, the geometry of each system was optimized to remove all forces exceeding 10 kJ mol$^{-1}$ nm$^{-1}$.

PM7 is a last-generation, semi-empirical method\textsuperscript{43–45} that originates from the Hartree–Fock (HF) formalism. A number of integrals were substituted with empirical data, resulting in a huge increase in the computational efficiency and a competitive accuracy. Empirical data allows one to include electron-correlation effects implicitly. Therefore, PM7 is free of systematic faults produced by \textit{ab initio} HF. PM7 benefits from purpose-specific corrections for hydrogen bonding, weak van der Waals attraction, and peptide bonds to accurately represent proteins, etc.\textsuperscript{46,47} \textit{Ab initio} and experimental data for more than 9000 compounds were used for the parametrization.\textsuperscript{47} PM7 employs effective-core potentials to represent non-valence electrons. Diminishing the number of explicit electrons greatly increases the speed of the wave function convergence. Employing PM7-MD in the present work made it possible to observe up to 2 000 000 consequent single-point calculations of relatively large graphene quantum dots, whose proper sampling is currently not feasible with density functional theory methods.

We used the Gabedit (ver. 2) software\textsuperscript{48} to build and functionalize the B-doped graphene nanostructures, the VMD (ver. 1.9) software\textsuperscript{49} to visualize trajectories and prepare artwork, and the MOPAC2012 code (openmopac.net)\textsuperscript{43} to obtain immediate energy gradients. The PM7-MD simulations reproduce the system’s dynamics in real-time following an energy gradient and accounting for thermal motion at a given temperature. Observation of a chemical reaction (e.g. decomposition) is possible provided that the reaction’s rate constant is commensurate with the trajectory length. The PM7-MD method was successfully applied before to problems in chemistry such as competitive solvation of ions,\textsuperscript{50} global minimum search for precious metal nanostructures,\textsuperscript{51} aminated graphene stability,\textsuperscript{52} gas capture,\textsuperscript{53} etc.

Results and discussion

The systems for the PM7-MD simulations were constructed to account for both the concentration of the boron atoms and their distribution within the sheet. We compared systems with one, two and three dopant atoms per hexagonal ring, with $–$B–B$–$, $–$B–B–$–$ and $–$C–B– covalent bonds in the starting configuration (Table 1). These positions for the dopant atoms were found to be the most stable based on preliminary estimations of formation enthalpies. Only carbon atoms, which are two bonds away from the sheet edge, were substituted by boron atoms. This condition was met to decrease undesirable

<table>
<thead>
<tr>
<th>Nickname</th>
<th>n(C)</th>
<th>n(B)</th>
<th>n(H)</th>
<th># Electrons</th>
<th>Comments</th>
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<td>Two B per ring, in \textit{para} position</td>
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</tr>
<tr>
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<td>12</td>
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<td>398</td>
<td>One B–B bond per ring</td>
</tr>
<tr>
<td>“3B”</td>
<td>74</td>
<td>22</td>
<td>26</td>
<td>388</td>
<td>3 B per ring with one B–B bond</td>
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<tr>
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<td>26</td>
<td>386</td>
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<tr>
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<td>16</td>
<td>36</td>
<td>732</td>
<td>Larger system; 2 B in \textit{para}-position</td>
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<td>40</td>
<td>442</td>
<td>“B–B” interacting with $B_{10}H_{14}$</td>
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<td>12</td>
<td>26</td>
<td>478</td>
<td>“B–B” interacting with $C_{20}$</td>
</tr>
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</table>
finite-size effects and to extrapolate the obtained results to an infinite graphene sheet. Two sizes of graphene sheets were compared (Table 1). In both cases, the edge carbon atoms were terminated by hydrogen atoms. All simulated systems were in their singlet states, and the corresponding electronic-structure calculations were based on the restricted HF method. Since stability of B-doped graphene can depend on interactions with boron and carbon containing particles in the environment, we additionally simulated a boron hydride cluster \( \text{B}_{10}\text{H}_{14} \) and a small fullerene \( \text{C}_{20} \) in direct contact with the B-doped graphene (Table 1). Both fullerene, \( \text{C}_{20} \), and decaborane, \( \text{B}_{10}\text{H}_{14} \), are reactive compounds.

Fig. 1 depicts equilibrated configurations of the B-doped graphene systems at 1000 K. Visual inspection of these snapshots allows for characterization of the systems thermal stabilities. Whereas the “1B”, “para”, and “B–B” systems remain perfectly stable with minor shape violations, the “meta”, “3B”, and “B–B–B” systems exhibit significant deformations. Interestingly, B–B bonds in the starting configuration, per se, do not undermine stability. However, the presence of three or more boron atoms within a single six-member ring leads to significant deformations. The boron–boron bond length is equal to 1.56 Å, as derived from simulations at 300–1000 K. It is 10% longer than the C–C bond, 1.41 Å. Thus, certain perturbations of the honeycomb lattice of graphene are inevitable. It is, therefore, important in which positions the dopant atoms are located, since higher symmetry of the nanostructure is able to compensate for perturbations. In turn, the C–B bond length in the “B–B” system is 1.52 Å. Since the difference in electronegativity between carbon, 2.55, and boron, 2.04, is relatively small, the discussed bonds are expected to be weakly polar. By analogy with principles of organoboron chemistry, these compounds must be stable, although susceptible to oxidation processes. The computed B–B bond length (the “B–B” system) in B-doped graphene is smaller than that in boranes, 1.924(3) Å, obtained experimentally.\(^5\) Note that the C–C bond length is not modified upon doping. It ranges from 1.38 to 1.42 Å depending on the system and temperature. One could anticipate that the longer B–B bonds strain the C–C bonds. Hence, the hexagonal ring is expected to be significantly strained. A strained ring implies an elevated reactivity of the compound.

The heat of formation, \( H \), denotes a change in enthalpy during the formation of one mole of the compound from its constituent elements (simple substances). The PM7 Hamiltonian was specifically parametrized to provide highly accurate \( H \) values for multiple molecules and crystals. Fig. 2 and 3 compare \( H \) for different doping sites at 300–1000 K. Higher temperatures significantly increase \( H \). This increase is a convenient energetic measure of lowering the thermodynamic stability. Surprisingly, the “1B” system exhibits a higher \( H = 1.933 \text{ MJ mol}^{-1} \) at 300 K than the “para” system, \( H = 1.665 \text{ MJ mol}^{-1} \) at 300 K, despite featuring a smaller boron concentration per ring. Boron atoms in the para positions clearly stabilize one another. In turn, the “meta” system appears much more unstable, \( H = 2.902 \text{ MJ mol}^{-1} \) at 300 K. The instability increases up to \( H = 4.022 \text{ MJ mol}^{-1} \) at 1000 K. The corresponding structure deformations, including the effect of thermal motion, are shown in Fig. 1.

The systems with one or more B–B covalent bonds (Fig. 3) exhibit similar heats of formation, wherein higher concen-
Concentrations of boron and more B–B bonds are less favorable: $H(B\text{-}B) < H(3B) < H(B\text{-}B\text{-}B)$. Importantly, the $-B\text{-}B\text{-}C\text{-}C\text{-}C$ pattern is more thermodynamically stable than the $-C\text{-}B\text{-}C\text{-}B\text{-}C\text{-}B$ pattern, 2.567 vs. 2.902 MJ mol$^{-1}$. This observation is drastically different from the case of N-doped graphene, for which we recently showed N–N bonds to be a critical defect.$^{55}$

Although all computed $H$ values are above zero, this does not mean that the B-doped graphene structures cannot be synthesized. Although they cannot be obtained by self-assembly starting from the corresponding simple compounds directly, more sophisticated experimental techniques can be employed.

The radial distribution functions (RDFs) for C–C, B–B, and C–B distances within the B-doped graphene sheet, system "1B", are given in Fig. 4 at 300–1000 K. These atom-atom peaks constitute an aid for deciphering X-ray diffraction experiments and analyzing the high-temperature behavior of these nanostructures. The RDFs for all the simulated systems are given in Fig. S1–S5.$^\dagger$ The peak heights decrease with increasing temperature and distance. Narrower and taller peaks suggest higher stabilities at the designated temperature. Fig. 4, S1–S5$^\dagger$ confirm the visual analysis of Fig. 1 by indicating the poor, long-range order for all systems with three boron atoms per ring: "meta", "3B", and "B–B–B". In turn, very sharp, long-range orders are observed in the "1B" and "para" systems. The "B–B" system exhibits intermediate features. To test the

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**Fig. 2** Heats of formation of systems (a) "1B", (b) "para", (c) "meta" versus simulated time at 300 (blue dash-dotted line), 500 (green dashed line), and 1000 K (red solid line).

**Fig. 3** Heats of formation of systems (a) "B–B", (b) "3B", (c) "B–B–B" versus simulated time at 300 (blue dash-dotted line), 500 (green dashed line), and 1000 K (red solid line).

**Fig. 4** Radial distribution functions for carbon–carbon (red solid line), boron–boron (green dashed line), and carbon–boron (blue dash-dotted line) distances computed from the 100 ps long trajectory (system "1B").
validity of our results with respect to the simulation time, we performed a ten times longer, 1 ns simulation for the “B–B” system at 300, 500 and 1000 K. We observed no differences between the data averaged over the 0.1 ns and 1 ns trajectories. Note that the results of the RDF analysis are in excellent agreement with the heats of formation, discussed above.

The C–C covalent bonds and the C–C non-covalent distances (Table 2) characterize the graphene backbone. The “meta” system exhibits the most differences from the other simulated systems. It has a fourth peak at a higher distance, 4.40 Å, which means that the expected peak at ca. 3.80 Å is absent. The peak height provides another straightforward measure of structure stability. For instance, the least stable systems generally have lower peaks. Note that the locations of the first two peaks, but not heights, are quite similar in all the systems. The computed values are also in agreement with the experimental lengths of the C–C bonds in the aromatic compounds.

The average Coulson charges computed at 1000 K amount to \(-0.29 \pm 0.02\) (“1B”), \(+0.07 \pm 0.00\) (“para”), \(-0.16 \pm 0.01\) (“meta”), \(-0.04 \pm 0.00\) (“B–B”), \(+0.04 \pm 0.00\) (“3B”), and \(+0.01 \pm 0.00\) (“B–B–B”). The averaging and standard error calculations were performed over all the boron atoms in the sheet and over the simulated time. In most systems, the charge is sufficiently close to zero. The largest deviations are observed in the “1B” and “meta”. By intercalating into the graphene sheet, the boron atom affects three covalent bonds, including B–B bonds in some configurations. Fig. S6† shows that the doped boron atoms contain 2.5 p-electrons and only 0.63 s-electrons. These values were averaged over the “1B” and “meta” structures at 0 K. The averages computed separately for “1B” and “meta” were identical. The carbon atoms of graphene are sp² hybridized, and donate one p-electron into the π-electron system.

Table 2 Most probable carbon–carbon distances and RDF peaks in the B-doped graphene. \(R_{1} - R_{2}\) are the positions of the first four peaks, whereas \(h_{1} - h_{4}\) are the dimensionless heights of the first four peaks

<table>
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<th>System</th>
<th>(R_{1} ) Å</th>
<th>(h_{1} )</th>
<th>(R_{2} ) Å</th>
<th>(h_{2} )</th>
<th>(R_{3} ) Å</th>
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<tr>
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<td>2.90</td>
<td>2.5</td>
<td>3.80</td>
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<td>2.48</td>
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<td>2.92</td>
<td>2.3</td>
<td>3.82</td>
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<td>1.5</td>
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<td>3.78</td>
<td>1.9</td>
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<td>28.1</td>
<td>2.48</td>
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<td>3.1</td>
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<tr>
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<td>1.38</td>
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<td>2.48</td>
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<td>2.8</td>
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Each of the s, pₓ, pᵧ and p₂ orbitals contain one electron. Boron has one less electron than carbon. Half of the missing electrons de-occupy the s-orbital, and the other half come from a p-orbital. Despite its lower electronegativity, according to the Pauling scale, boron pulls a certain amount of electron density from carbon. This is because boron requires an additional electron to achieve the half-filled shell configuration, which is more energetically favorable. For instance, most boron atoms in the “1B” system acquire slightly negative charges (Fig. 5a). Thermal fluctuations of the charge on the selected boron atom at 1000 K are modest (Fig. 5b, note the 0.1 e⁻ scale on the y-axis). Fig. S6† shows that the doped boron atoms contain 2.5 p-electrons and only 0.63 s-electrons. The carbon atoms, located near the edge of the sheet and terminated by hydrogen, obtain some s-electron density from the hydrogens, which are less electronegative.

The results for the systems containing 2 boron atoms per ring are in agreement with the basic principles of electrophilic substitution. An electron withdrawing group decreases the electron density in the ortho- and para-positions, but not in the meta. Indeed, the charge on boron is negligible in both the “para” and “B–B” systems, whereas the charge is mostly negative in the “meta” system.

The dipole moment of the entire sheet greatly depends on the distribution of the B atoms (Fig. 6). The smallest dipole moments are observed in the “para” (2.27 D) and “3B” (2.33 D) systems. Both molecules contain boron atoms in the para-positions: 1, 4 and 1, 2, 4, respectively. The boron atoms in the para-positions compensate each other to a certain extent. In comparison, the dipole moment is up to four times larger in systems without such compensation, including the “1B”,

![Fig. 5](image-url) (a) Coulson charges averaged along the 100 ps trajectory and their standard deviations on different boron atoms of the B-doped graphene (system “1B”); (b) typical fluctuations of the charge on a B atom due to thermal motion at 1000 K.
“meta” and “B–B” systems (Fig. 6). A single boron atom per ring, system “1B”, already produced a large dipole moment of 8.55 D. The value of the dipole moment characterizes the nanostructure’s response to an external electric field. For instance, sensor applications should be sensitive to the B-doping pattern.

The simulation of the “B–B” system in direct contact with fullerene C_{20} and decaborane B_{10}H_{14} allowed us to study the effect of the interaction of B-doped graphene with boron and carbon containing particles available in the environment. We did not observe any chemical changes during a 1000 ps long PM7-MD trajectory at 500 K. The boron–carbon covalent interactions in the B-doped graphene are stronger than the intermolecular interactions between these elements in the considered compounds. Both fullerene C_{20} and decaborane B_{10}H_{14} are reactive compounds. The simulation demonstrates that the B-doped graphene is stable to chemical transformations with reactive boron and carbon structures.

The chemical integrity of the graphene derivatives was maintained over the 0.1–1 ns times used in our investigation. Sampling of macroscopic times is beyond the reach of our methodology, as well as other computational methods that account for the quantum-chemical nature of the simulated entities. Stability of the simulated systems over the simulated times suggests stability over larger time scales, since the simulations sample a significant number of bond oscillations, angle deformations, etc. It should be noted that rare events, which can possibly initiate decomposition of the entire structure, could not be accounted for.

The presented results are based on a relatively small graphene sheet, and one may wonder whether the structure and stability depend on the system size. Fig. S7 and Table S1† compare the “para” system to the “big” system that also represents the para arrangement of two borons per ring (Table 1). While all peak positions were found to be very similar, on average, the peaks are higher for the “para” system. This is likely explained by the higher flexibility in larger structures. Note that this effect is pronounced for the B–B and C–B peaks, but it is not clear for the C–C peaks, since the C–C peaks are closer together and are harder to resolve. The fourth C–C peak is positioned only at 3.82 Å, while the fourth B–B peak is positioned at 5.78 Å.

Conclusions
We have demonstrated theoretically that it is possible to achieve a high boron doping concentration in graphene, far exceeding the concentrations currently obtained in experiments. Using molecular dynamics simulations based on a reliable and computationally efficient electronic-structure method, we have investigated the stability of B-doped graphene over a range of temperatures as a function of boron concentration and dopant atoms distribution. One and two boron atoms per hexagonal ring were found to provide stable heteroatomic nanostructures. Therefore, 100/6 and 100/3 mol% of boron in graphene are theoretically stable, even at high temperatures. Higher boron concentrations, involving three dopant atoms per hexagonal ring, result in significant structure perturbations upon thermal motion. Out of those systems, the one containing only a single B–B bond per ring is the most sustainable. The results were validated using several criteria, including heats of formation, RDFs, and geometry inspection. Although the systems under investigation did not decompose into monomolecular constituents during the simulation, we expect many of them to be highly reactive in a real chemical environment, containing oxidants, hydrogen sources and other reagents. Unlike the case of the N-doped graphene,† the dopant–dopant bonds do not undermine the system stability. This conclusion agrees well with the previous knowledge about boron compounds with multiple boron–boron covalent bonds, e.g. boranes and boron fullerene B_{80}, in which the B–B bonds are stable. The theoretical predictions can be verified by direct chemical synthesis.

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References
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