Ordering in boron and nitrogen functionalized graphene layers

Agnieszka Jamróz [1], **Michał Łopuszyński** [2] **and Jacek A. Majewski** [1]

[1] *Faculty of Physics, University of Warsaw, ul. Hoża 69, 00-681 Warszawa, Poland*
[2] *Interdisciplinary Centre for Mathematical and Computational Modelling, University of Warsaw, ul. Prosta 69, 02-106 Warszawa, Poland*

For a long time carbon nanotubes (CNTs) and in recent decade graphene layers (GL) have been considered as the promising materials for future nanoelectronics. One of the interesting features of the graphene layers is opportunity to engineer their properties by suitable functionalization. The functionalization with boron and nitrogen plays an important role, since B and N are natural dopants for carbon systems (*p*- and *n*-type, respectively) and both atoms built stable molecules with C. The probability of obtaining stable C-B and C-N alloys is very high even for B and N concentrations exceeding 50%. It has been confirmed in our *ab initio* calculations in the framework of the density functional theory [1] employing supercell calculations and considering certain distributions of B and N atoms over the graphene lattice. However, such type of calculations cannot make complete search over the configurational alloy space to establish the distribution patterns of dopant species in the host matrix. This issue is crucial, since the alloy morphology influences the electronic properties of the doped materials.

In these studies, we determine the degree of structural ordering in B and/or N doped CNTs and GLs, and analyze short-range and long-range ordering, as quantified by the Warren-Cowley short-range order and the Bragg-Williams long-range order parameter, respectively, employing the formalism successfully applied for nitride ternary and quaternary alloys [2]. This comprehensive analysis covers relevant range of dopant concentrations and temperatures and is based on Monte Carlo calculations within the NVT ensemble employing Valence Force Field (VFF) approach of the fine tuned Keating-like model [3], essentially in the form of Perebeinos and Tersoff [4], for the calculation of total energies of the doped system. Unknown up to now parameters of the VFF model for C-B, C-N, B-B, N-N, and N-B bonds have been determined to reproduce the results of *ab initio* calculations in the framework of density functional theory employing the SIESTA (and sometimes VASP) code for various ordered structures containing B and N dopants.

The employed computational scheme allows one to find the equilibrium distribution of dopants over the graphene lattice for the whole range B and N concentrations as a function of temperature. Further, we determine ordering effects in in the studied alloys. We address also the important issue how the elastic properties of doped systems are influenced by doping, and calculate phonon spectra in the C-B and C-N alloys.

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